Synthetic and spectroscopic studies on some inorganic and organometallic compounds

D. Ridley

Summary

Part I: The low-frequency infrared spectra of some complex halides of zinc, cadmium, and mercury.

Metal-chlorine and -bromine infrared stretching frequencies are reported for a variety of complex halides of zinc, cadmium, and mercury, and for several alkyl- and aryl-mercury halides, including some perfluoro-derivatives. There is no clear relation between ν(M-X) and the type of ligand, but frequencies tend to be relatively high in complexes of chelating ligands. The frequency and intensity of the absorption bands due to ν(M-X) have been shown to be of value in predicting the co-ordination environment of the metal atom. Stretching frequencies involving bridging chlorine atoms are considered to be below 200 cm^{-1} and were not observed. Cadmium-chlorine are lower than mercury-chlorine stretching frequencies in analogous compounds and it is suggested that in several of the examined cadmium complexes, L_2CdCl_2, the metal has a distorted-octahedral rather than a tetrahedral enviroment. Some boronium salts are described which probably contain bridged $(M_2Cl_6)^{2-}$ anions (M=Zn or Cd).

Part II: Some alkoxy-, thio-, and amino-derivatives of methyl- and ethyl-zinc.

Phenol and some aliphatic alcohols react with dimethylzinc forming tetramers $(MeZnOR)_4$ and with 2-dimethylaminoethanol diethylzinc yields a trimer $(EtZnOCH_2CH_2NMe_2)_3$. Some thiols yield insoluble products

$(MeZnSR)_x$, but t-butylthiol gives pentamers $(MeZnSBu^t)_5$ and $(EtZnSBu^t)_5$ and iso-propylthiol yields a hexamer $(MeZnSPr^i)_6$. Dimethylamine forms insoluble $\left[(Me_2N)_2Zn\right]_x$ and no methylzinc compound but diphenylamine gives the dimer $(MeZnNPh_2)_2$. Methylzinc acetate and dimethylphosphinate are insoluble and involatile and are considered to be polymeric. All these products disproportionate when heated, evolving dimethylzinc, except $(MeZnOBu^t)_4$ which forms isobutene.

Reactions are described between many of these compounds and pyridine leading to the formation of monomeric and dimeric complexes containing four co-ordinate zinc.

Dimethylzinc does not react with benzophenone in toluene at 110° whereas diphenylzinc reacts smoothly to yield dimeric phenylzinc triphenylmethoxide. Under the same conditions diethylzinc affords trimeric ethylzinc diphenylmethoxide and ethylene. Diphenyl- and diethyl-zinc with phenylisocyanate in refluxing benzene yield tetrameric 1:1 adducts which afford benzanilide and propionanilide on hydrolysis. Possible structures for these 1:1 adducts and the above-mentioned compounds are discussed. Infrared data relating to methyl- and ethyl-zinc groups in the complexes are tabulated.

SYNTHETIC AND SPECTROSCOPIC STUDIES ON SOME INORGANIC AND ORGANOMETALLIC COMPOUNDS

-by-

D. RIDLEY.

A thesis submitted for the Degree of Doctor of Philosophy.

University of Durham.

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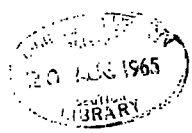

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The author is also indebted to the Science Research Council for a maintenance grant.

Memorandum

The work described in this thesis was carried out at the Science Laboratories of the University of Durham between October 1962 and May 1965, and has not been submitted for any other Degree. All the work described is the original work of the author, except that acknowledged by reference.

The work undertaken by the author consisted of two separate investigations, the results of which are incorporated in parts one and two of this thesis. Part of the work has been subject of two publications in the Journal of the Chemical Society (1964, p.166-173; 1965, p.1870-1877).

Summary

Part I: The low-frequency infrared spectra of some complex halides of zinc, cadmium, and mercury.

Metal-chlorine and -bromine infrared stretching frequencies are reported for a variety of complex halides of zinc, cadmium, and mercury, and for several alkyl- and aryl-mercury halides, including some perfluoro-derivatives. There is no clear relation between ν(M-X) and the type of ligand, but frequencies tend to be relatively high in complexes of chelating ligands. The frequency and intensity of the absorption bands due to ν(M-X) have been shown to be of value in predicting the co-ordination environment of the metal atom. Stretching frequencies involving bridging chlorine atoms are considered to be below 200 cm^{-1} and were not observed. Cadmium-chlorine are lower than mercury-chlorine stretching frequencies in analogous compounds and it is suggested that in several of the examined cadmium complexes, L_2CdCl_2, the metal has a distorted-octahedral rather than a tetrahedral enviroment. Some boronium salts are described which probably contain bridged $(M_2Cl_6)^{2-}$ anions (M=Zn or Cd).

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INTRODUCTION.

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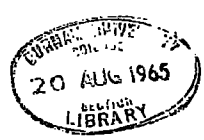
The work described in Part I of this thesis is concerned with the infra-red spectroscopic study of a number of complex halides of zinc, cadmium, and mercury. The metal-chlorine, and in some cases metal-bromine stretching frequencies have been observed, and have been shown to be of value in predicting the coordination environment of the metal atom. In this introduction the relevant data are reviewed, and some of the structural characteristics of Group IIB metal halide complexes are briefly discussed.

With the exception of metal-fluorine stretching frequencies, which have already received particular attention [1], metal-halogen stretching frequencies are known to occur in the 100-400 cm^{-1} region. A large amount of Raman data relating to complex metal-halogen anions are already available, although it is mainly confined to main Group elements. It is only comparitively recently [2] that complex halide anions of transition elements have been studied by means of Raman spectroscopy. The available infra-red data are not nearly as abundant, but it has recently increased rapidly with the increasing availability of grating spectrometers capable of scanning the infra-red region to a lower limit of 200 cm^{-1}.

The value of spectra in this region depends on the availability of data indicating the range of metal-halogen stretching frequencies,



and the extent of their dependance on the coordination environment of the metal atom. The metal-halogen stretching frequencies generally give rise to strong absorption bands, and the spectra in this region are relatively simple. Infra-red data for this region have therefore found application in coordination chemistry.

Metal-chlorine, and metal-bromine stretching frequencies have been reported for a series of tetrahedral complex anions of the type, MX_4^{2-}; (M = Mn,Fe,Co,Ni,Cu,Zn.)[3]. The former vibrations were reported to occur at approximately 380 cm^{-1}, and 290 cm^{-1} for M (III) and M (II) respectively. The corresponding metal-bromine vibrations occurred at 290 cm^{-1}, and 220 cm^{-1}. The higher frequencies indicate a higher degree of covalent bonding between the metal and halogen atoms; this is to be expected for anions in which the metal atom is more highly charged. The particular interest in these spectra was the structure of the band due to the higher of the two infra-red active vibrations, namely $\nu_3(f_2)$, assuming tetrahedral symmetry. As the vibration is triply degenerate in undistorted tetrahedral species, then any distortion due to antisymmetrical distribution of the non-bonding "d" electrons is reflected in a splitting of this particular band. Clearly, distortion could also be due to an unsymmetrical environment within the crystal, consequently infra-red data on crystalline compounds is not without ambiguity. It is somewhat surprising that a single band due to v(Cu-Cl), and v(Cu-Br) was observed for the complexes, $(Ph_3MeAs)_2^{+}(CuX_4)^{2-}$, as ligand field

theory predicts a highly distorted tetrahedral arrangement of ligands around the Cu^{2+} ion. The corresponding caesium complex Cs_2CuCl_4, which is known to have a distorted tetrahedral anion [4], shows a splitting of the ν_3 band of 28 cm^{-1}.

Adams et al [5] have published low frequency infra-red data for an extensive series of MX_4, MX_5, and MX_6 anions. Metal-chlorine stretching frequencies occurred in the range, 228-377 cm^{-1}, the lowest frequency being due to ν(Hg-Cl) in the complex $(Et_4N)_2^+ (HgCl_4)^{2-}$. The structure of the band due to $\nu_3(f_2)$ for the tetrachloro-mercurate anion indicated a highly distorted tetrahedral species, presumably due to the tendency of mercury to be linearly coordinated. The low value of the mercury-chlorine stretching frequency contrasts quite markedly with the Raman data. James and Janz [6] have assigned the four fundamentals due to the anion $HgCl_4^{2-}$, from a Raman study of solutions of mercuric chloride in molten potassium chloride. The $\nu_3(f_2)$ vibration is reported to occur at 276 cm^{-1}.

Low frequency infra-red studies have been applied to the coordination chemistry of some Group VIII and Group IV elements. Coates and Parkin [7], as well as assigning metal-halogen stretching frequencies for a large number of coordination complexes of gold, and some Group VIII elements, also found bands due to heavy metal-phosphorus, sulphur, and arsenic vibrations. Absorptions due to metal-halogen stretching

vibrations were used to distinguish between cis, and trans isomers of coordination complexes. The trans isomers gave rise to only one infrared active metal-halogen stretching vibration, while cis isomers, as expected, gave rise to two such vibrations. The observed values for trans-complexes were found to be in the range:-
403-408 cm^{-1} (Ni), 353-359 cm^{-1} (Pd), and 326-339 cm^{-1} (Pt(II)); while for cis-complexes the metal-chlorine stretching frequencies were considerably lower. The nickel-halogen vibrations in the neutral complexes occur at surprisingly high frequencies, v(Ni-Br) occurring at 340 cm^{-1}, and even v(Ni-I) was observed at 208 cm^{-1}. The absorption band due to v(Ni-Cl) in the complex $(Et_4N)^{+}_2 (NiCl_4)^{2-}$ occurs at 286 cm^{-1}, [5] which is considerably lower than 403-408 cm^{-1} in the neutral complexes. No such difference is observed for platinum, e.g. v(Pt-Cl) occurs at 320 cm^{-1} in the complex K_2PtCl_4.[8] This frequency is very close to the values found above for the trans complexes of Pt(II) halides.

In the univalent gold complexes, v(Au-Cl) was found to occur in the range, 311-329 cm^{-1}, and v(Au-Br) in the range 210-233 cm^{-1}. As expected the corresponding frequencies in the trivalent gold complexes are much higher; v(Au-Cl) and v(Au-Br) occurring in the ranges 371-302 cm^{-1}, and 264-213 cm^{-1} respectively. The isotopic splitting of the v(Au-Cl) band in the univalent gold complexes was particularly well observed, probably due to the facts that as well as there being only one stable isotope of gold, the vibration, being non-degenerate

would not be subject to splitting from effects within the crystal.

With a view to further elucidating the nature of the trans-effect, Adams et al [9] have examined the low frequency infra-red spectra of an extensive series of square planar complexes of the type, PtX_2L_2, (where X=Cl,Br; L=neutral ligand). The detector ligands were the halogen atoms and the platinum-halogen stretching frequencies were regarded as a measure of bond strength. For trans-complexes, the single infra-red active metal-halogen stretching frequency was found to be almost insensitive to the nature of the ligand; v(Pt-Cl) and v(Pt-Br) occurring at 339 ± 3 cm^{-1}, and 250 ± 9 cm^{-1} respectively. For cis-complexes however the two infra-red active stretching vibrations were found to be very dependant on the nature of the ligand, v(Pt-Cl) occurring in the ranges 343-302 cm^{-1}, and 328-281 cm^{-1}. The corresponding bromides were found to have v(Pt-Br) in the ranges 254-211 cm^{-1}, and 226-194 cm^{-1}. Satisfactory correlations of v(Pt-X) with electronegativity of the donor atom were obtained from data on the cis-complexes.

For a large number of octahedral transition metal complexes $(MD_2Cl_2)X$, where X is Cl^-, ClO_4^-, and D is the ligand diarsine, a trans-configuration has been established for all complexes except one form of (CoD_2Cl_2) ClO_4. [10] On the basis of infra-red spectral values, the latter complex has been assigned the cis-configuration, in agreement with the assignment from the ultraviolet and visible spectrum.

Stereochemical assignments have been made for a series of six-

coordinate adducts of tin (IV), and germanium (IV) halides [11]. The adducts were of the type MX_4L_2, where X=halogen, and L=tertiary base. The metal-halogen stretching frequencies were found to occur in much the same regions as the anions $(MCl_6)^{2-}$. For example, v(Sn-Cl) in the adducts were observed to fall within the range 324-275 cm^{-1}, while the higher of the two infra-red active vibrations for $(SnCl_6)^{2-}$ occurs at 310 cm^{-1}. Similarly v(Ge-Cl) was found to occur at 350-325 cm^{-1}, and 312 cm^{-1} for neutral adducts and the anion respectively. The above values are very considerably lower than those observed for the tetrahalides, v(Sn-Cl) being at 403 cm^{-1}, and v(Ge-Cl) at 453 cm^{-1}.

A low frequency infra-red study has recently been made on a series of adducts of organotin halides [12], represented by the formula, $(R_xSnX_{4-x}L_2)$, where X=halogen, R=alkyl, and L=some Lewis acid, usually a tertiary base. It is interesting to note that v(Sn-Cl) is greatly reduced as the hydrocarbon residue is increased, for example v(Sn-Cl) in $SnCl_4,Py_2$ occurs at 324 cm^{-1}, and in $MeSnCl_3$.bipy or $MeSnCl_3$.phenan; the frequencies fall to within the range 308-266 cm^{-1}. No frequency which could be attributable to v(Sn-Cl) was observed for the adducts Me_2SnCl_2bipy and Me_2SnCl_2 phenan; although the spectrometers employed were equipped with caesium bromide optics, and consequently had a lower limit of 250 cm^{-1}. Had caesium iodide optics been available the tin-chlorine frequencies in the latter adducts may well have been observed. If it is assumed that chlorine, being the most electronegative element in

the adducts is the recipient of any negative charge from the donating ligands, then the less the number of chlorine atoms in the adducts, the greater will be the effect on the Sn-Cl bond. The increasing ionic character of this bond is reflected in the considerable lowering of the stretching frequency. The 1:1 adduct of trimethyltin chloride and pyridine was found to have an extremely weak band due to the symmetrical stretching mode of the tin-carbon skeleton, and ν(Sn-Cl)was not observed. The authors concluded that in the molecule Me_3SnCl py, the tin atom was five-coordinate. This was later confirmed by Hulme [13], who showed by an X-ray structure analysis that the molecule existed in the solid state as a trigonal bipyramid having a planar SnC_3 group, with the chlorine atom and the pyridine molecule occupying axial positions.

Finally infra-red spectroscopy in the low frequency region referred to above, is becoming an increasingly important method for studying ionic melts [14]. Although special techniques are required for such high temperature studies, infra-red and Raman data provide a valuable tool for the study of nearest neighbour interactions and complex ion formation in molten salts.

Group IIB spectroscopic data.

When the present work started the available spectroscopic data for the complex halides of Group IIB elements were confined mainly to Raman studies of the tetrahedral anions MX_4^{2-}, which are present in aqueous solutions of the metal halide and excess alkali metal halide. A complete

comparison can only be obtained by referring to ν_1, the totally symmetric vibration, the frequencies of which are listed in Table I together with references.

TABLE I.

HALIDE	ZINC	CADMIUM	MERCURY	REFERENCES
MCl_4^{2-}	280 cm^{-1}	232 cm^{-1}	269 cm^{-1}	Zn.15,16;Cd.17;Hg,18
MBr_4^{2-}	172 cm^{-1}	166 cm^{-1}	166 cm^{-1}	Zn.16,19;Cd.18,19;Hg,18.
MI_4^{2-}	122 cm^{-1}	117 cm^{-1}	126 cm^{-1}	Zn.20,16;Cd.18,21;Hg,20.

The low value for the anion $CdCl_4^{2-}$ is doubtful, as only one very weak line was observed in the Raman spectrum of a solution of cadmium chloride in a large excess of potassium chloride. Later workers [18] have not confirmed the value. Apart from the above anomaly it can be seen that any effects due to increased mass of the central metal atom are practically negligible.

The infra-red active antisymmetrical stretching vibration ν_3, has been observed in the Raman spectra of certain of the above complex anions. As is generally the case, the reported frequencies are higher than for the totally symmetrical stretching vibration, for example ν_3 for $CdBr_4^{2-}$ [18], CdI_4^{2-} [20], and ZnI_4^{2-} [20] was found to occur at frequencies 185 cm^{-1} 145 cm^{-1}, and 170 cm^{-1} respectively. The anion $HgCl_4^{2-}$ which is present in solutions of mercuric chloride in molten potassium chloride has recently

been studied.[6] The symmetrical vibration ν_1, and antisymmetrical vibration ν_3, are reported to occur at frequencies of 267 cm^{-1} and 276 cm^{-1} respectively.

Apart from studies on the gaseous halides [22, 23] only the tetrahedral complex anions have been investigated by infra-red spectroscopy. For complexes containing $ZnCl_4^{2-}$ [3,5], ν(Zn-Cl) occurs in the range 271-292 cm^{-1}, while ν(Zn-Br) [3] was found to occur within the range 203-223 cm^{-1}. For complexes presumably containing the anions $CdCl_4^{2-}$ and $HgCl_4^{2-}$, ν(Cd-Cl) and ν(Hg-Cl) were found to occur at frequencies of 260 cm^{-1}, and 228 cm^{-1} respectively [5].

No spectroscopic data were available for neutral complexes of Group IIB metal halides, the present study being undertaken to provide such data, and attempt to correlate the metal-halogen stretching frequencies with the type of ligand and the coordination environment of the metal.

Some structural characteristics of Group IIB metal halides and their Complexes

The Group IIB elements, having an outer electronic configuration of $(n-1)\,d^{10}\,ns^2$ might be expected to have a tendency to expand their covalency from two to four, resulting in a tetrahedral distribution of ligands around the central metal atom. Suitable bonding is presumably accomplished by involving the use of sp^3-hybrid orbitals. This is generally true for zinc, but the increase in size in going from zinc to cadmium results in the latter very often being octahedrally coordinated.

Mercury, rather unexpectedly from the above considerations, very often exhibits digonal coordination. This is apparently due to the fact that the energy separation between the d^9s^1 and d^{10} s^o ground states are very much less for mercury than those of cadmium and zinc. The values given by Orgel [24] are, Zn^{2+}, 9·7 e.v.; Cd^{2+}, 10·0 e.v.; and Hg^{2+}, 5·3 e.v. This small energy separation is always associated with a strong tendency to linear coordination by d-s hybridisation.

Of the halides MX_2, only the difluorides crystallise as purely ionic lattices, zinc fluoride having the rutile structure, and both cadmium and mercury fluorides having fluorite structures. Zinc chloride is trimorphic, the α- and β- forms being built up of $ZnCl_4$ tetrahedra while the γ- form has a layer lattice similar to mercuric iodide. The metal atoms in the latter are tetrahedrally coordinated. Zinc bromide and zinc iodide have layer lattices similar to the cadmium halides in which the metal atom is octahedrally surrounded by halogen atoms.

Mercuric chloride, and mercuric bromide exist in the solid state as so called molecular crystals, in which the metal atom is octahedrally surrounded in a layer lattice, but two of the halogen atoms are very much closer to the mercury atom than the remaining four. Consequently, it is possible to identify molecules of HgX_2 within the crystal.

It has been well established from Raman studies that the halides, when dissolved in aqueous solutions of alkali metal halide, give rise to complex anions MX_4^{2-} which have tetrahedral symmetry. This is not always the case in the solid state. The complex chlorides $(Me_4N)_2ZnCl_4$ [25], Cs_2ZnCl_4 [26], and the complex bromide Cs_2ZnBr_4 [27], have all been the subject

of X-ray crystallographic analysis. In each case the zinc atom is tetrahedrally coordinated, although slightly distorted due to unsymmetrical siting of the cations. Occasionally zinc is octahedrally coordinated, e.g., in salts of the type K_4ZnCl_6 [28] which is isostructural with its cadmium analogue, and which contains discrete octahedral units. Octahedral coordination of zinc is also found in bis-hydrazine zinc chloride [29], $(N_2H_4)_2ZnCl_2$, the ZnN_4 being planar with the two chlorine atoms in axial positions. The two isostructural diammines $Zn(NH_3)_2Cl_2$, and $Zn(NH_3)_2Br_2$ contain discrete tetrahedral units. [30] An unusual stereochemistry occurs in the terpyridyl complex of zinc chloride, and its isostructural cadmium analogue. The metal atom is five-coordinate and the molecule is a distorted trigonal bipyramid. [31] More recently [32] bis (acetylacetonato) zinc (II) monohydrate has been shown to contain five-coordinate zinc, whereas in the anhydrous compound the zinc atom is tetrahedrally surrounded.

Although the salt $(Et_4N)_2\ CdCl_4$ has been prepared,[5] X-ray data are not available, although it probably contains tetrahedral anions. Usually however, complex chlorides of cadmium exhibit octahedral coordination, e.g., NH_4CdCl_3 [33] consists of chains of $CdCl_6$ octahedra condensed into layers and sharing edges. The diammine $Cd(NH_3)_2Cl_2$, is an octahedral complex although a tetrahedral distribution of ligands might perhaps be expected. The crystal contains infinite chains of $CdCl_6$ octahedra sharing edges. [34] The bis-pyridine complex py_2CdCl_2 has been reported [35]

to be isomorphous with the violet α-form of its cobalt analogue, and is therefore octahedrally coordinated through bridging chlorine atoms. The corresponding bromide [36] also has a chain structure with six-coordinate cadmium and bridging bromine atoms. A similar structure has been reported [37] for bis-biuret cadmium chloride, and its mercury analogue.

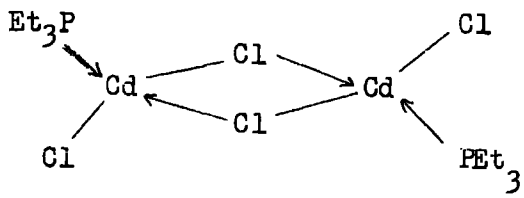
Numerous complexes of cadmium bromide and iodide with tertiary phosphines and arsines have been described [38], which are of three distinct types:-

a. $CdX_2 (PR_3)_2$

b. $(CdX_2 PR_3)_2$

c. $(CdX_2)(PR_3)_3$

Members of class a., are monomeric, and presumably are tetrahedral, whereas compounds belonging to class b., have been shown to be dimeric in benzene. The triethyl phosphine complex of cadmium bromide $(Et_3PCdBr_2)_2$ was shown by X-ray crystallographic analysis to be dimeric in the solid state, and to have a trans-halogen bridged structure:-



Tetrahedral coordination of the cadmium atoms is to be expected in

all compounds of this type.

The structure of the compounds of class c., have not been elucidated, and are not further considered.

The complex $(Et_4N)_2\ HgCl_4$, which apparently contains $HgCl_4^{2-}$ anions, has not been examined structurally, although the infra-red data [5] suggest that the mercury atom is in a highly distorted tetrahedral environment. Many complex chlorides of mercury are known, several of which have been examined by means of X-ray crystallography and their structures elucidated. The caesium complex $CsHgCl_3$ [39] has been shown to contain octahedrally surrounded mercury atoms, but two chlorine atoms are very much closer to the mercury atom than the remainder. The interatomic distances are reported to be; 2Hg-Cl at 2·29Å , and 4Hg-Cl at 2·70Å , and the complex may be considered as an aggragate of $HgCl_2$ molecules with Cs^+ and Cl^- ions. Similarly, the complex $K_2HgCl_4 \cdot H_2O$ has been shown by the same authors to be a crystal aggragate of $HgCl_2, K^+, Cl^-$, and molecules of water. The interatomic distances are; 2Hg-Cl at 2·29Å, 2Hg-Cl at 2·92Å , and 2Hg-Cl at 3·13Å. The individual molecules of mercuric chloride are non-linear, Cl-Hg-Cl being 173°.

Ammonium trichloromercurate, NH_4HgCl_3, [40] has been shown to consist of $HgCl_6$ octahedra linked together in such a way as to give layers of composition $(HgCl_3)_n^{n-}$, the layers being held together by NH_4^+ ions. Again, the distances between shared chlorine atoms and the mercury atoms

are so large that it is difficult to reconcile them with covalent bonding, and the structure is best described as a crystal aggragate. The inter atomic distances are given as; 4Hg-Cl at 2·96Å, and 2Hg-Cl at 2·34Å. The latter distance is somewhat larger than that of the $HgCl_2$ molecules in the above compounds, and appreciably larger than in crystalline mercuric chloride, the latter having an Hg-Cl distance of 2·25Å. [41] The diammine $Hg(NH_3)_2Cl_2$ and the isostructural bromide apparently contain the species, $(H_3N\text{-}Hg\text{-}NH_3)^{2+}$ randomly arranged in the crystal. [34]

In the complex $(Me_4N)\ HgBr_3$ [42], the mercury atom is trigonally coordinated in discrete $HgBr_3^-$ anions, in which Hg-Br bonds are nearly all the same length.

There is however interaction between anions, and the structure maybe regarded as being half-way between $HgBr_3^-$ anions, and a structure consisting of infinite chains of $(HgBr_3)_n^{n-}$.

An extensive series of complexes with tertiary phosphines and arsines has been described, [38] the compound types being classified as;-

a. $HgX_2(PR_3)_2$

b. $(HgX_2PR_3)_2$

c. $(HgX_2)_3\ (PR_3)_2$

d. $(HgX_2)_4\ (PR_3)_2$

Classes a., and b., have been shown to be structurally similar to the cadmium analogues, compounds of class b., being dimeric in benzene. A preliminary X-ray examination of the complex $(Et_3AsHgI_2)_2$ showed the mercury atom to be tetrahedrally coordinated, achieving four-colalency through bridged halogen atoms. As for the analogous cadmium compounds the halogen-bridged structure was found to have a trans-configuration.

Compounds belonging to class c., were shown to be a molecular aggragate in the solid state, of halogen-bridged dimers and free molecules of mercuric halide. A complete X-ray analysis was carried out on the complex, $(nBu_3As)_2\ (HgBr_2)_3$, which showed that the mercury atom in the individual molecules of mercuric bromide is octahedrally surrounded by six bromine atoms, there being slight interaction between the terminal and bridging bromine atoms of the dimer with the mercury atom of the free halide. The Hg-Br interatomic distance in the individual molecules of mercuric bromide is 2·25Å, which is in fact less than that in the crystalline halide, Hg-Br for the two closer bromine atoms being 2·48Å.

Finally the compounds of class d., have unknown structures and are not considered further in the present investigation.

E X P E R I M E N T A L.

In Part I of this thesis only, all of the analytical data are presented in the form usually adopted for the description of new compounds, although many of the compounds prepared during the present investigation have been described previously. Where described previously, the complexes are acknowledged by reference.

EXPERIMENTAL

Metal analyses

The complexes were all analysed for metal content using 'EDTA' methods. Preliminary oxidation of the complexes was by combustion in a closed oxygen-filled flask; the method has been previously described.[43]

Between 50-100 mgms. of complex were weighed into a small gelatin capsule and combusted in the usual way. Absorption of the oxidation products was accomplished by shaking with approximately 100 mls. of hydrochloric acid (1·0N) which had previously been placed in the 2-litre combustion flask. In the case of mercury it was necessary to reflux the oxidation products with concentrated nitric acid for several minutes, since the chloro-complexes yielded much mercurous chloride on combustion.

After diluting to a known volume, a suitable aliquot was taken and the pH adjusted to 4·5 using a known volume of 0·5N sodium hydroxide solution. The zinc solutions were further buffered to a pH of 5-6 using hexamethylenetetramine, and then titrated with 0·005M 'EDTA' solution using xylenol orange as an indicator. The end point was given by a sharp change from red colour, to pale yellow.

For the cadmium solutions it was found better to use a "back titration" technique. After adjusting the pH with hexamethylenetetramine an excess of 0·005M 'EDTA' solution was added, followed by several drops of 0·2% xylenol orange indicator. The solution was then titrated with 0·005M zinc acetate solution until the yellow colour changed sharply to deep red.

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PART I

THE LOW-FREQUENCY INFRARED SPECTRA OF SOME COMPLEX HALIDES OF ZINC, CADMIUM, AND MERCURY.

The mercury solutions were adjusted to pH6 by the addition of approximately 1ml. of pyridine, and the mixture titrated directly using a mixed indicator. The indicator consisted of BDH 4·5 indicator (three drops) and 0·2% xylenol orange (six drops). In the presence of mercuric ions a deep blue-violet colour was produced which progressively faded to pale grey on titration with 0·005M EDTA solution. The end point was given by a sharp change from pale grey to pink.

The complex halides with alkali metal or ammonium halides were not combusted, but dissolved in dilute acids before titration.

Infrared spectra.

Infrared spectra were measured with a Grubb-Parsons double-beam grating spectrometer (DB3/DM2), with a 200-line per cm. grating, swept with dry air. The calibration was checked against part of the rotational spectrum of water vapour, the instrument being used as a single beam one.[44] Specimens were mounted as Nujol mulls between caesium iodide discs, halogen exchange being avoided by placing thin Polythene sheets between the mulls and the caesium iodide.

Zinc complexes.

Many of the complexes examined in the present study have already been prepared by previous workers. These authors are referred to under the appropriate complex, but experimental details are not given in their entirety except where difficulties were encountered during their preparation.

Anhydrous zinc chloride.[45]

Finely powdered, slightly hydrated zinc chloride (20gms), and freshly distilled thionyl chloride (50mls.) were mixed in a round bottomed flask, and refluxed for two hours. After distilling off the excess thionyl chloride the remaining traces were removed under vaccuo, and the anhydrous zinc chloride transferred to a dry-box where it was stored for transferring samples for subsequent reactions.

Caesium tetrachlorozincate.[46] Cs_2ZnCl_4.

An aqueous solution containing zinc chloride, and caesium chloride in the molar ratio of 1:2 was allowed to evaporate at room temperature. The complex was obtained as large colourless crystals. (Found: Zn, 14·0%. Cs_2Cl_4Zn requires Zn, 13·8%.).

Dichlorobis(ammine)zinc.[47] $(NH_3)_2ZnCl_2$.

Anhydrous liquid ammonia was condensed onto anhydrous zinc chloride and the mixture allowed to remain at -80° for approximately one hour. The excess ammonia was removed under vaccuo, leaving the diammine as a white powder, m.pt. 210-240° (decomp.)(Lit.[47] 200°) (Found: Zn, 38·7%. $H_6Cl_2N_2Zn$ requires Zn, 38·4%.).

Dichlorobis(diethylamine)zinc[48] $(Et_2NH)_2ZnCl_2$.

Freshly distilled diethylamine was condensed onto anhydrous zinc chloride, and after approximately thirty minutes the excess diethylamine was removed under vaccuo, leaving the product as a white powder, m.pt.

54-55°. (No m.pt. quoted in literature). (Found: Zn, 31·6%. $C_8H_{22}Cl_2N_2Zn$ requires Zn, 31·2%.).

Dichlorobis(pyridine)zinc.[49] Py_2ZnCl_2

Pyridine and anhydrous zinc chloride were mixed in a molar ratio of 2:1 in hot ethanol. Large white crystals separated on cooling, and these were recrystallised from ethanol, m.pt. 204-206°. (No m.pt. quoted in literature). (Found: Zn, 22·2%. $C_{10}H_{10}Cl_2N_2Zn$ requires Zn, 22·2%.).

Dichloro(tetramethylethylenediamine)zinc. $(Me_2N\cdot CH_2-)_2ZnCl_2$

NNN′N′tetramethylethylenediamine and anhydrous zinc chloride were mixed in a molar ratio of 1:1 in a small amount of ethanol. On cooling the solution to 0°, long colourless needles slowly separated, m.pt. 177°. (Found: Zn, 25·7%. $C_6H_{16}Cl_2N_2Zn$ requires Zn, 25·9%.).

Dichloro(2,2′-bipyridyl)zinc.[50] Bipy $ZnCl_2$.

When hot ethanolic solutions of 2,2′-bipyridyl and anhydrous zinc chloride were mixed, a white solid precipitated immediately. The product was recrystallised from nitrobenzene, in which it was sparingly soluble, m.pt. >360°. (No m.pt. quoted in literature). (Found: Zn, 22·5%. $C_{10}H_8Cl_2N_2Zn$ requires Zn, 22·4%.).

Dichloro(1,10-Phenanthroline)zinc 1,10-phenan $ZnCl_2$.

The complex was precipitated when dilute ethanolic solutions of zinc chloride, and of o-phenanthroline were mixed together. Due to its low

solubility, the complex could not be recrystallised, but was washed with much ethanol, m.pt. >360°. (Found: Zn, 20·7%. $C_{12}H_8Cl_2N_2Zn$ requires Zn, 20·8%.).

Dichloro(2,2′,2″-tripyridyl) zinc.[51] Terpyridyl $ZnCl_2$

Anhydrous zinc chloride and 2,2′,2″-tripyridyl were mixed together in hot water. On cooling, the complex slowly crystallised as pale yellow needles, m.pt. >360°. (No m.pt. quoted in the literature.).

Dichlorobis(triethylphosphine) zinc[48] $(PEt_3)_2 ZnCl_2$.

Triethylphosphine was condensed onto anhydrous zinc chloride and the mixture allowed to warm to room temperature. The excess free base was removed under vaccuo leaving a white solid, m.pt. 97-98°. (no m.pt. quoted in literature.). (Found: Zn, 17·4%. $C_4H_{10}Cl_2P_2Zn$ requires Zn, 17·6%).

Dichlorobis(dimethylphenylphosphine) zinc. $(PMe_2Ph)_2ZnCl_2$

An ethanolic solution containing anhydrous zinc chloride and dimethylphenylphosphine in the ratio of 1:2, was cautiously diluted with water. After several hours, the complex separated as large white plates, m.pt. 118-119°. (Found: Zn, 15·9%. $C_{16}H_{22}Cl_2P_2$ Zn requires Zn, 15·9%.).

Dichlorobis(dimethyl-4-dimethylaminophenylphosphine) zinc. $(p\text{-}Me_2N\cdot C_6H_4 PMe_2)_2ZnCl_2$

Excess dimethyl-4-dimethylaminophenyl phosphine in anhydrous ether was added to an ethereal solution of anhydrous zinc chloride. A very fine suspension which quickly coagulated was produced, and the complex was

obtained by recrystallisation from dry methanol, m.pt. 152-153°. (lit.,[52] 151·5-152°)

Dichloro(1,2-bisdiphenylphosphino-ethane) zinc $(PPh_2 \cdot CH_2 -)_2 ZnCl_2$

An ethanolic solution of the chelating phosphine was added to a hot ethanol solution of anhydrous zinc chloride, and the complex crystallised on cooling, m.pt. 290-291°. (Found: Zn, 12·3%. $C_{26}H_{24}Cl_2P_2Zn$ requires Zn, 12·2%.).

Dichlorobis(triphenylphosphine) zinc [53]. $(PPh_3)_2ZnCl_2$

This complex has been described previously [53] but no preparative details have been given. Attempted preparation from ethanolic solution resulted in the isolation of unchanged triphenyl phosphine. Colourless crystals of a complex were obtained by allowing a mixture of an ethereal solution of anhydrous zinc chloride, and a dry benzene solution of triphenylphosphine to stand at room temperature for several hours, m.pt. 295°. (Lit.,[53] 209°). The discrepancy in m.pt. prompted a preparation of the complex by an alternative route, the method adopted being that used for the Ni(II) analogue. [54] Anhydrous zinc chloride (0·75g.) in glacial acetic acid (20mls.) was refluxed for two hours with triphenylphosphine (2·7g., 2 moles.) in butan-1-ol (20mls). The large colourless crystals which were obtained began to melt at 208°, finally giving a clear liquid at approximately 300° . (Found: Zn, 9·9%. $C_{36}H_{30}Cl_2P_2Zn$ requires Zn, 9.9%.).

Dichloro(1,2-diethylthioethane) zinc. $(EtS\cdot CH_2-)_2ZnCl_2$.

The chelating sulphide and an equimolar amount of anhydrous zinc chloride were refluxed in anhydrous ether for approximately two hours. After removing most of the ether by distillation, the remaining concentrated solution was cooled, and colourless crystals of the complex were obtained. Moisture was rigourously excluded throughout the preparation of the complex, m.pt. 95-96°. (Found: Zn, 23·1%. $C_6H_{14}Cl_2S_2$ Zn requires Zn, 22·8%.).

Bipyridylyldiphenylboronium trichlorozincate (bipy BPh_2)($ZnCl_3$).

To an ethanolic solution of anhydrous zinc chloride, was added an excess of 2,2′-bipyridylyldiphenylboronium chloride [57] dissolved in ethanol. The mixture was maintained at room temperature, and after several hours the complex chloride crystallised as colourless needles, m.pt. approx. 365°. (Found: Zn, 13·2%. $C_{22}H_{18}BCl_3N_2Zn$ requires Zn, 13·3%.). The use of a very large excess of boronium chloride did not result in crystallisation of a tetrachlorozincate.

Anhydrous zinc bromide.

Sufficiently anhydrous zinc bromide was obtained by dissolving "ANALAR" grade zinc oxide in hydrobromic acid, distilling of the excess acid, and finally heating the zinc bromide at 120° under vaccuo for several hours.

Caesium tetrabromozincate [27] Cs_2ZnBr_4

An aqueous solution containing caesium bromide, and zinc bromide in the molar-ratio of 2:1, was allowed to evaporate slowly at room temperature to yield large colourless crystals of the complex. (Found: Zn, 10·0%. Br_4Cs_2Zn requires Zn, 10·1%.).

Dibromobis(ammine) zinc [54a.] $(NH_3)_2ZnBr_2$.

Anhydrous liquid ammonia was condensed at -80°, onto anhydrous zinc bromide. An immediate reaction took place and after allowing to warm to room temperature, the excess ammonia was removed under vaccuo. The white solid obtained was found on analysis to be the tetrammine, $Zn(NH_3)_4Br_2$. (Found: Zn, 22·5%. $H_{12}Br_2N_4Zn$ requires Zn, 22·3%.).

The tetrammine was heated under vaccuo at 100-110° for fifteen minutes. Gas evolution was observed, and the remaining white solid was found to be the diammine, m.pt. 235-255° (decomp.). (Found: Zn, 25·1%. $H_6Br_2N_2Zn$ requires Zn, 25·2%.).

Dibromo(tetramethylethylenediamine) zinc. $(Me_2N\cdot CH_2-)_2ZnBr_2$

The complex crystallised slowly as glistening colourless plates m.pt. 178° , from an ethanolic solution containing the chelating amine and zinc bromide in equimolar quantities. (Found: Zn, 18·9%. $C_6H_{16}Br_2N_2Zn$ requires Zn, 19·2%.).

Dibromobis(pyridine) zinc. [55] Py_2ZnBr_2

On cooling an ethanolic solution containing zinc bromide, and an excess of pyridine, the complex crystallised as large colourless plates, m.pt. 220-222°. (No m.pt. quoted in literature.) (Found: Zn, 17·2%. $C_{10}H_{10}Br_2N_2Zn$ requires Zn, 17·1%.).

Dibromo(2,2′-bipyridyl) zinc. Bipy $ZnBr_2$

The complex was precipitated as a creamy white solid when ethanolic solutions of zinc bromide and 2,2′-bipyridyl were mixed. It was recrystallised from nitrobenzene in which it is sparingly soluble, m.pt. $>360°$. (Found: Zn, 17·1%. $C_{10}H_8Br_2N_2Zn$ requires Zn, 17·1%).

Dibromo(1,10-phenanthroline) zinc. 1,10-phenan $ZnBr_2$

The complex was prepared in a similar manner to that of the 2,2′-bipyridyl analogue, but was not recrystallised because of its very low solubility, m.pt. $>360°$. (Found Zn, 16·1%. $C_{12}H_8Br_2N_2Zn$ requires Zn, 16·1%.).

Dibromobis(triethylphosphine) zinc. $(Et_3P)_2ZnBr_2$.

An excess of triethylphosphine was added to a solution of anhydrous zinc bromide in ether. White crystals of the complex, m.pt. 130°, slowly formed. (Found:Zn, 14·1%. $C_{12}H_{30}Br_2P_2Zn$ requires Zn, 14·2%.).

Dibromobis(dimethylphenylphosphine) zinc. $(PMe_2Ph)_2ZnBr_2$.

An excess of dimethylphenylphosphine was added to a solution of zinc bromide in ethanol. The complex crystallised when the solution was

cooled to 0°, m.pt. 119°. (Found: Zn, 13·1%. $C_{16}H_{22}Br_2P_2Zn$ requires Zn, 13·0%.).

Dibromobis(dimethyl-4-dimethylaminophenylphosphine) zinc . $(p\text{-}Me_2N\cdot C_6H_4PMe_2)_2ZnBr_2$.

A dilute solution of the phosphine in ether was slowly added to a solution in ether of half an equivalent of anhydrous zinc bromide. The complex crystallised quickly as very small needles, m.pt. 143°. (Lit.,[52] 146°).

Dibromo(1,2-bisdiphenylphosphino-ethane) zinc. $(PPh_2\cdot CH_2-)_2ZnBr_2$.

When a hot propan-1-ol solution containing equimolar amounts of the chelating phosphine and zinc bromide was allowed to cool, crystals of the complex were deposited, m.pt. 287°. (Found: Zn, 10·5%. $C_{26}H_{24}Br_2P_2Zn$ requires Zn, 10·5%.).

Dibromobis(triphenylphosphine)zinc. $(PPh_3)_2ZnBr_2$.

Attempts to prepare the complex by allowing a mixture of an ethereal solution of zinc bromide, and a benzene solution of triphenylphosphine to slowly evaporate resulted only in the isolation of a mechanical mixture of halide and ligand. The method used for the zinc chloride analogue was therefore adopted. Anhydrous zinc bromide (1·2g) in glacial acetic acid (15mls.), was refluxed for one hour with triphenyl phosphine (2·6g.,2 moles.) in butan-1-ol (30mls). The complex crystallised on cooling, m.pt. 223°. (Lit.,[53] 220-221°).

Dibromo(1,2-diethylthioethane) zinc. $(EtS\cdot CH_2)_2ZnBr_2$.

White crystals of the complex slowly formed when an equimolar amount of the chelating sulphide was added to an ethereal solution of anhydrous zinc bromide. The complex, m.pt. 123° , was moisture sensitive though not to such an extent as the chloride analogue. (Found: Zn, 17·4%. $C_6H_{14}Br_2S_2Zn$ requires Zn, 17·4%.).

Bipyridylyldiphenylboronium tetrabromozincate. $(bipy\ BPh_2)_2ZnBr_4$.

An excess of 2,2'- bipyridylyldiphenylboronium bromide [57] dissolved in ethanol was added to an ethanolic solution of zinc bromide. The tetrabromozincate crystallised quickly as small colourless plates, m.pt. 260° . (Found: Zn, 6·49%. $C_{44}H_{36}BBr_4N_4Zn$ requires Zn, 6·37%.).

Bipyridylyldiphenylboronium tribromozincate. $(bipy\ BPh_2)ZnBr_3$.

The tribromozincate was prepared by recrystallising the tetrabromozincate from an ethanolic solution of anhydrous zinc bromide. The complex crystallised as colourless feathery needles, m.pt. 334-335°. (Found: Zn, 10·32%. $C_{22}H_{18}BBr_3N_2Zn$ requires Zn, 10·44%.).

Cadmium complexes.

Anhydrous cadmium chloride.

The method of preparation was the same as that used for the zinc analogue apart from the final stages. After removal of the thionyl chloride by vacuum distillation, the anhydrous halide was stored in a vacuum dessicator over solid potassium hydroxide for twenty-four hours

before using it to prepare complexes.

Potassium hexachlorocadmate.[28] K_4CdCl_6.

Water was caused to evaporate slowly from an aqueous solution of cadmium chloride and potassium chloride at approximately 90°. The cadmium chloride, and potassium chloride were in the molar ratio of 1:6, and the complex chloride was obtained as large opaque crystals. (Found: Cd, 23·5%. $CdCl_6K_4$ requires Cd, 23·3%.).

Ammonium hexachlorocadmate.[28] $(NH_4)_4CdCl_6$.

The complex was prepared by a method identical to that used for the potassium analogue. (Found: Cd, 28·2%. $H_{16}CdCl_6N_4$ requires Cd, 28·3%.).

Ammonium trichlorocadmate[33] NH_4CdCl_3.

An aqueous solution containing cadmium chloride, and ammonium chloride in the molar ratio of 1:1, was allowed to evaporate slowly at room temperature. The complex was obtained as transparent white needles. (Found: Cd, 47·6%. H_4CdCl_3N requires Cd, 47·5%.).

Dichlorobis(ammine) cadmium.[34] $(NH_3)_2CdCl_2$.

An ammoniacal aqueous solution of cadmium chloride was allowed to evaporate slowly at room temperature, and the complex was obtained as clusters of white needles. (Found: Cd, 51·9%. $H_6CdCl_2N_2$ requires Cd, 51·7%.).

Dichlorobis(pyridine) cadmium.[56] Py_2CdCl_2

A large excess of pyridine was added to a warm concentrated alcoholic solution of cadmium chloride. On cooling the solution, very small white needles were obtained, m.pt. 200° (decomp.). (No m.pt. quoted in literature). (Found: Cd, 33·2%. $C_{10}H_{10}CdCl_2N_2$ requires Cd, 33·0%.).

Dichloro(2,2′-bipyridyl)cadmium.[50] Bipy $CdCl_2$

On mixing ethanolic solutions of cadmium chloride, and 2,2′-bipyridyl, the immediate formation of a white suspension was observed. The suspension was filtered only with difficulty, but was sufficiently coagulated by refluxing and concentration of the solution. The white powder was insufficiently soluble to purify by recrystallisation and was washed with much ethanol, m.pt. $>360^\circ$ (No m.pt. quoted in literature.). (Found: Cd, 33·4%. $C_{10}H_8CdCl_2N_2$ requires Cd, 33·1%.).

Dichloro(1,10-phenanthroline) cadmium. 1,10-phenan $CdCl_2$.

The complex precipitated immediately as a white powder when ethanolic solutions of cadmium chloride, and o-phenanthroline were mixed. Due to its low solubility the complex was not recrystallised, but washed with much ethanol. m.pt. 360°. (Found: Cd, 31·1%. $C_{12}H_8CdCl_2N_2$ requires Cd, 30·9%.).

Dichloro(tetramethylethylenediamine) cadmium. $(Me_2N\cdot CH_2-)_2CdCl_2$.

A dry ethanolic solution of anhydrous cadmium chloride, and containing slightly greater than one molar equivalent of NNN′N′-

tetramethylethylenediamine, was allowed to stand at room temperature for one hour. The complex slowly crystallised as fine colourless needles, m.pt. 240° (decomp.). (Found: Cd, 37·4%. $C_6H_{16}CdCl_2N_2$ requires Cd, 37·6%.).

Dichloro(2,2′,2″,-tripyridyl) cadmium.[51] Terpyridyl $CdCl_2$.

A hot aqueous solution of cadmium chloride and one molar equivalent of 2,2′,2″-tripyridyl was allowed to cool slowly, giving the complex as small yellow crystals, m.pt.>360°. (No m.pt. quoted in literature).

Di-μ-chloro-dichlorobis(dimethylphenylphosphine) dicadmium. $\left[(PMe_2Ph)CdCl_2\right]_2$

A dilute solution of cadmium chloride, (0·5g), in ethanol (200mls), and containing one molar equivalent of dimethylphenylphosphine, was allowed to stand at room temperature. The complex slowly crystallised as colourless broad needles, m.pt. 254-259°. (Lit.,[52] 302-304° decomp.). (Found: Cd, 35·1%. $C_8H_{11}CdCl_2P$ requires 35·0%.).

Di-μ-chloro-dichlorobis(dimethyl-4-dimethylaminophenylphosphine) dicadmium. $\left[p\text{-}Me_2N\cdot C_6H_4PMe_2CdCl_2\right]_2$

The complex was obtained as colourless crystals from a solution of anhydrous cadmium chloride (0·5g.), in ethanol (200mls.), containing one molar equivalent of the phosphine. m.pt. 220-221°. (Lit.,[52] 215-217°).

Dichloro(1,2-bisdiphenylphosphinoethane)cadmium. $(PPh_2 \cdot CH_2-)_2CdCl_2$.

Anhydrous cadmium chloride (0·2g.) in hot ethanol (125mls.) was added to a solution of the phosphine (0·44g.) in hot propan-1-ol (20mls.). The complex crystallised as needles, m.pt. 265-266° ., on cooling the solution. (Found: Cd, 19·4%. $C_{26}H_{24}CdCl_2P_2$ requires Cd, 19·3%.).

Dichloro(1,2-diethylthioethane)cadmium. $(EtS \cdot CH_2-)_2CdCl_2$.

The sulphide was added in excess, to a solution of anhydrous cadmium chloride (0·2g.) in much dry ether. The complex was formed quickly as very small colourless crystals, m.pt. 140° (decomp.). (Found: Cd, 33·9%. $C_6H_{14}CdCl_2S_2$ requires Cd, 33·7%.).

Bipyridylyldiphenylboronium trichlorocadmate. (bipy BPh_2)$CdCl_3$

An excess of 2,2′-bipyridylyldiphenylboronium chloride in ethanol, was added to anethanolic solution of cadmium chloride. The trichlorocadmate crystallised as colourless plates, m.pt. 333° . (Found: Cd, 20·8%. $C_{22}H_{18}BCdCl_3N_2$ requires Cd, 20·8%.).

Dibromo(2,2′-bipyridyl)cadmium. Bipy $CdBr_2$.

When an ethanolic solution of cadmium bromide tetrahydrate was added to an ethanol solution of an equi-molar amount of 2,2′-bipyridyl, the complex was precipitated rapidly as a cream coloured powder, m.pt. 360°. The very low solubility of the complex prevented purification by recrystallisation, the complex being washed with much hot ethanol.

(Found: Cd, 26·5%. $C_{10}H_8Br_2CdN_2$ requires Cd, 26·3%.).

Dibromo(1,10-phenanthroline) cadmium. 1,10-phenan $CdBr_2$.

The complex precipitated rapidly from ethanolic solution, and like the 2,2′-bipyridyl complex it was insufficiently soluble to purify by recrystallisation. m.pt. >360°. (Found: Cd, 25·1%. $C_{12}H_8Br_2CdN_2$ requires Cd, 24·9%.).

Dibromo(tetramethylethylenediamine) cadmium. $(Me_2N\cdot CH_2-)_2CdBr_2$.

Addition of an equimolar amount of NNN′N′-tetramethylethylenediamine to a concentrated solution of cadmium bromide tetrahydrate in ethanol, caused the complex to crystallise as colourless needles, m.pt. 239°. (Found: Cd, 28·7%. $C_6H_{16}Br_2CdN_2$ requires Cd, 28·9%.).

Dibromo(1,2-bisdiphenylphosphinoethane) cadmium. $(PPh_2\cdot CH_2-)_2CdBr_2$.

The complex was obtained as a colourless powder, m.pt. 285-286°, by mixing solutions of cadmium bromide in ethanol, and the phosphine in hot propan-1-ol (Found: Cd, 16·9%. $C_{26}H_{24}Br_2CdP_2$ requires Cd, 16·8%.).

Di-μ-bromo-dibromobis(dimethylphenylphosphine) dicadmium $[(PMe_2Ph)CdBr_2]_2$

To a solution of cadmium bromide tetrahydrate (0·5g.), in ethanol (200mls.), was added dimethylphenylphosphine (0·2g). The solution was allowed to stand at room temperature, and the complex slowly crystallised. m.pt. 216-217°. (Lit.,[52] 180° decomp.). (Found: Cd, 27·3%. $C_8H_{11}Br_2CdP$ requires Cd, 27·4%.).

Di-μ-bromo-dibromobis(dimethyl-4-dimethylaminophenylphosphine)dicadmium. $[p\text{-}Me_2N\cdot C_6H_4PMe_2CdCl_2]_2$

Dimethyl-4-dimethylaminophenylphosphine (0·27g.), was added to a solution of cadmium bromide tetrahydrate (0·5g.), in ethanol (200mls.). The solution was maintained at room temperature, and the complex began to crystallise after several minutes, as colourless broad needles, m.pt. 223-224°. (Lit.,[52] 221-222°).

Bipyridylyldiphenylboronium tribromocadmate. $(bipy\ BPh_2)CdBr_3$

An excess of 2,2′-bipyridylyldiphenylboronium bromide [57] was added to a hot ethanolic solution of cadmium bromide tetrahydrate. The complex bromide crystallised quickly as small colourless plates, m.pt. 315-316°. (Found: Cd, 16·8%. $C_{22}H_{18}BBr_3CdN_2$ requires Cd, 16·8%.).

Mercury complexes.

The mercuric halides used to prepare the complexes were "ANALAR" grade, and were not further purified.

Caesium trichloromercurate. $CsHgCl_3$.

An aqueous solution of mercuric chloride and a large excess of caesium chloride, was allowed to evaporate slowly at room temperature. Small colourless crystals of the complex were formed after several days. (Found: Hg, 45·5%. Cl_3CsHg requires Hg, 45·6%).

Ammonium trichloromercurate.[58] NH_4HgCl_3.

Equimolar amounts of mercuric chloride and ammonium chloride were

fused together in a sealed tube. After approximately thirty minutes the melt was allowed to cool and the white opaque solid was not further purified.

Potassium tetrachloromercurate monohydrate.[59] $K_2HgCl_4 \cdot H_2O$.

The hydrated complex chloride was obtained as long opaque needles when a solution of mercuric chloride (9g.), and potassium chloride (10g.) in water (40mls.) was allowed to evaporate slowly at room temperature. (Found: Hg, 46·0%. $H_2Cl_4HgK_2O$ requires Hg, 45·8%.).

Trichloromercury oxonium chloride.[60] $(O(HgCl)_3)Cl$.

Large pieces of marble were stood in an aqueous solution of mercuric chloride for several weeks. The complex was obtained as small, very bright colourless crystals.

Dichloro(tetramethylethylenediamine) mercury. $(Me_2N \cdot CH_2-)_2HgCl_2$

A twofold excess of NNN′N′-tetramethylethylenediamine was added to a solution of mercuric chloride in ethanol. The mixture was allowed to stand at room temperature, and the complex very slowly crystallised as long colourless needles, m.pt. 164°. (Found: Hg 51·7%. $C_6H_{16}Cl_2HgN_2$ requires 51·8%.).

Dichlorobis(pyridine) mercury. Py_2HgCl_2

Crystalline mercuric chloride was dissolved in hot pyridine, and the solution allowed to cool. Long colourless needles of the complex

were obtained; m.pt. 108° (Lit.,[61] 108°).

Dichloro(2,2′-bipyridyl) mercury. Bipy $HgCl_2$.

The complex was obtained as a white insoluble powder, on mixing ethanolic solutions of mercuric chloride, and 2,2′-bipyridyl. The compound was washed with much hot ethanol. m.pt. 306-310° (decomp.). (Found: Hg, 47·3%. $C_{10}H_8Cl_2HgN_2$ requires Hg, 46·9%.).

Dichloro(1,10-phenanthroline) mercury. 1,10-phenan $HgCl_2$.

This complex, like the 2,2′-bipyridyl analogue was precipitated from ethanolic solution, and after filtration washed with much hot alcohol. m.pt. >360°. (Found: Hg, 44·8%. $C_{12}H_8Cl_2HgN_2$ requires Hg, 44·4%.).

Dichlorobis(triethylphosphine) mercury. $(Et_3P)_2HgCl_2$

To a stirred ethereal solution of mercuric chloride was slowly added two equivalents of triethylphosphine in ether solution. The complex crystallised rapidly as very small white needles, m.pt. 145-161° (decomp.), shrinking at 130°. (Found: Hg, 39·4%. $C_{12}H_{30}Cl_2HgP_2$ requires Hg, 39·6%.).

Di-μ-chloro-dichlorobis(dimethylphenylphosphine) dimercury. $\left[(PMe_2Ph)HgCl_2\right]_2$

An equimolar amount of dimethylphenylphosphine was added to a solution of mercuric chloride in hot ethanol, and the solution allowed to stand at room temperature. The colourless crystals which slowly formed were not recrystallised. m.pt. 179° (Lit.,[52] 168-169°)

(Found: Hg, 48·7%, $C_8H_{11}Cl_2HgP$ requires Hg, 48·9%.).

Di-μ-chloro-dichlorobis(dimethyl-4-dimethylaminophenylphosphine) dimercury. $[(p\text{-}Me_2N\cdot C_6H_4PMe_2)HgCl_2]_2$

To a hot ethanolic solution of mercuric chloride was added an equimolar amount of dimethyl-4-dimethylaminophenylphosphine. The complex slowly crystallised as the solution cooled to room temperature. m.pt. 235° (Lit.,[52] 233-235°).

Tetrachloro(1,2-bisdiphenylphosphinoethane) dimercury. $(PPh_2\cdot CH_2-)_2(HgCl_2)_2$.

Mercuric chloride (1·4g., 1 mole.) in hot acetone (50mls.), was added to a solution of the phosphine (2·0g., 1 mole) in hot acetone (50mls.). The complex crystallised as the solution cooled to room temperature. m.pt. 272-273° . (Found: C, 33·2%; H, 2·7%; Hg, 42·4%. $C_{26}H_{24}Cl_4Hg_2P_2$ requires C, 33·2%; H, 2·6%; Hg, 42·6%.).

Di-μ-chloro-dichlorobis(triphenylphosphine) dimercury.[38] $[(PPh_3)HgCl_2]_2$

The complex separated rapidly as glistening plates, m.pt. 308-312°., (Lit., [38] 206-209°), when an ethanolic solution of triphenylphosphine was added to an ethanol solution of an equimolar amount of mercuric chloride.

Di-μ-chloro-dichlorobis(triethylarsine) dimercury. $[(Et_3As)HgCl_2]_2$

Triethyl arsine was slowly added to a stirred solution of an equimolar amount of mercuric chloride in water. The flocculent white

precipitate was crystallised from methanol as colourless needles, m.pt. 163°. (Lit.,[38] 163°).

Hexachlorobis(triethylarsine)trimercury. $(Et_3As)_2(HgCl_2)_3$.

Triethyl arsine was slowly added to a stirred solution of a twofold excess of mercuric chloride in water. A flocculent white precipitate which was obtained, was filtered, and recrystallised from methanol as colourless needles, m.pt. 114°. (Found: Hg, 51.6%. $C_{12}H_{30}As_2Cl_6Hg_3$ requires Hg, 51.9%.).

Di-μ-chloro-dichlorobis(triphenylarsine)dimercury. $[(AsPh_3)HgCl_2]_2$

A solution of triphenylarsine in hot ethanol was added to an ethanolic solution containing one molar equivalent of mercuric chloride. The white crystalline complex separated rapidly, m.pt. 258°. (Lit.,[38] 251-253°).

Dichloro(1,2-diethylthioethane)mercury. $(EtS\cdot CH_2-)_2HgCl_2$.

The sulphide was added to a solution of one molar equivalent of mercuric chloride in hot ethanol, and the mixture allowed to cool slowly. The complex slowly crystallised as small white plates, m.pt. 97-98° (Lit.,[62] 99-100°).

Bipyridylyldiphenylboronium trichloromercurate. (bipy BPh_2)$HgCl_3$.

An ethanol solution of 2,2'-bipyridylyldiphenylboronium chloride[57] was added to a dilute ethanol solution containing one half a molar

equivalent of mercuric chloride. The trichloromercurate was precipitated immediately as a white powder, m.pt. 314°. The complex was not recrystallised, but washed with much ethanol. (Found: Hg, 31·8%. $C_{22}H_{18}BCl_3Hg$ requires Hg, 32·0%.).

Dibromo(tetramethylethylenediamine) mercury. $(Me_2N\cdot CH_2-)_2HgBr_2$

A two-fold excess of NNN′N′-tetramethylethylenediamine was added to a warm concentrated solution of mercuric bromide in ethanol. The mixture was allowed to cool to room temperature, and the complex crystallised very slowly as colourless rosettes, m.pt. 165°. (Found: Hg, 42·4%. $C_6H_{16}Br_2HgN_2$ requires Hg, 42·1%.).

Dibromo(2,2′-bipyridyl) mercury. Bipy $HgBr_2$.

The complex was immediately precipitated from a mixture of ethanolic solutions of mercuric bromide, and 2,2′-bipyridyl, as a cream coloured powder, m.pt. 286-290° (decomp.). (Found: Hg, 39·0%. $C_{10}H_8Br_2HgN_2$ requires Hg, 38·9%.).

Dibromo(1,10-phenanthroline) mercury. 1,10-phenan $HgBr_2$

On mixing ethanolic solutions of o-phenanthroline and mercuric bromide, the complex precipitated immediately as a cream-coloured powder, m.pt. 355-360°. (Found: Hg, 36·9%. $C_{12}H_8Br_2HgN_2$ requires Hg, 37·1%.).

Di-μ-bromo-dibromobis(dimethylphenylphosphine) dimercury. $[(PMe_2Ph)HgBr_2]_2$

Dimethylphenylphosphine was added to a dilute solution of an

equivalent amount of mercuric bromide in ethanol. The solution was maintained at room temperature, and the complex slowly crystallised, m.pt. 159-163° (Lit.,[52] 133-135°.) (Found: Hg, 39·9%. $C_8H_{11}Br_2HgP$ requires Hg, 40·2%.).

Di-μ-bromo-dibromobis(dimethyl-4-dimethylaminophenylphosphine) dimercury.[63] $[p\text{-}Me_2N\cdot C_6H_4\cdot PMe_2HgCl_2]_2$

Solutions of equimolar amounts of mercuric bromide, and the phosphine, in ethanol were mixed. A pale yellow precipitate was formed immediately, and after filtration was recrystallised from a large volume of acetone. m.pt. 200-202° (Lit.,[63] 201-204°).

Di-μ-bromo-dibromobis(triphenylphosphine) dimercury. $[PPh_3HgBr_2]_2$

A solution of triphenyl phosphine, in ethanol, was added to a hot ethanolic solution of an equimolar amount of mercuric bromide. The complex rapidly separated as glistening white plates, m.pt. 241-252°. (Lit.,[38] 240-250°).

Dibromobis(triphenylphosphine) mercury .[64] $(PPh_3)_2HgBr_2$.

On mixing ethanol solutions containing the phosphine, and halide in the stoicheiometric ratio of 2:1 the complex rapidly crystallised. m.pt. 263° . (Lit.,[64] 253-259°).

Dibromo(1,2-bisdiphenylphosphinoethane) mercury. $(PPh_2\cdot CH_2-)_2HgBr_2$

A solution of the chelating phosphine (2·0g.) in hot acetone was added to a solution of mercuric bromide (1·3g. 1 mole.), also in hot

acetone (50mls.). The complex crystallised as the solution cooled to room temperature. m.pt. 280-310° (decomp.) (Found: Hg, 26·0% $C_{26}H_{24}Br_2HgP_2$ requires Hg, 26·4%.).

Di-μ-bromo-dibromobis(triphenylarsine) dimercury. $[AsPh_3HgBr_2]_2$

Triphenylarsine, and an equimolar amount of mercuric bromide were dissolved in hot ethanol. On cooling, the complex separated as colourless plates, m.pt. 220-221° (Lit.,[38] 219°).

Dibromo(1,2-diethylthioethane) mercury. $(EtS\cdot CH_2-)_2HgBr_2$

The sulphide was added to an equimolar amount of mercuric bromide dissolved in hot ethanol. On cooling the solution, the complex quickly crystallised as colourless plates, m.pt. 110-111°. (Found: Hg, 39·0%. $C_6H_{14}Br_2HgS_2$ requires Hg, 39·3%.).

Bipyridylyldiphenylboronium tribromomercurate. (bipy BPh_2)$HgBr_3$.

To an ethanol solution of mercuric bromide, was added an excess of 2,2′-bipyridylyldiphenylboronium bromide, also dissolved in ethanol. The tribromomercurate precipitated immediately, and was insufficiently soluble to purify by recrystallisation. m.pt. 275°. (Found: Hg, 26·3%. $C_{22}H_{18}BBr_3HgN_2$ requires Hg, 26·3%.).

Organo-mercuric halides.

Several of the organo-mercuric halides which were studied, were already available in these laboratories, together with a number of

bis-organo mercury compounds which were used as starting materials for the halides.

Vinylmercuric chloride [65]

The method used was similar to that previously described,[65] except that tetravinyl tin was used as vinylating agent instead of n-butyl trivinyltin. A round bottomed flask (50ml.) containing ether (20mls.), and tetravinyltin (1·67g., 0·00736 mole.) was fitted with a sintered disc Soxhlet exctracter, on top of which was a reflux condenser. Mercuric chloride (2·0g., 0·00732 moles.) was placed on the sintered disc, and the ether mixture refluxed until all of the mercuric chloride was extracted. The mixture was refluxed for a further hour, and finally allowed to cool to room temperature. Vinyl mercuric chloride crystallised as large white plates, m.pt. 181°. (Lit.,[65] 185°).

Vinyl mercuric bromide.

The bromo analogue was similarly prepared. Mercuric bromide (2·0g., 0·0056 moles.) was extracted with a refluxing mixture of ether (20mls.) and tetravinyltin (1·26g., 0·0056 moles.). When all of the mercuric bromide dissolved, the mixture was refluxed for a further sixty minutes, and finally allowed to cool. Vinyl mercuric bromide crystallised as large white plates, m.pt. 169-170°. (Lit.,[65] 168-170°).

Phenyl mercuric chloride.

A solution of diphenylmercury (1·25g., 0·0035 moles.) in acetone

(25mls.) was quickly added to a stirred solution of mercuric chloride (1·0g., 0·0036 moles.) in the same solvent (25mls.). Phenyl mercuric chloride crystallised rapidly as very small white plates, m.pt. 262°. (Lit.,[66] 261-262°).

Phenylmercuric bromide.

A solution containing diphenyl mercury (1·0g., 0·0028 moles.) and mercuric bromide (3·0g., 0·0084 moles.) in ethanol (50mls.), was refluxed for thirty minutes, and finally allowed to cool to room temperature. Phenylmercury bromide crystallised as large white satin plates, m.pt. 277° (Lit.,[66] 276-277°).

p-Tolylmercuric chloride .

The method used was that of Whitmore et al [67]. A mixture of powdered mercuric chloride (30g., 0·111 moles.), and water (100mls), was heated in a large beaker, and a solution of sodium p-toluene sulphinate (25g., 0·140 moles), in boiling water (70mls.), carefully added to the hot solution. A heavy white precipitate was formed, and sulphur dioxide was evolved. When the effervescence had ceased, water (170mls.) was added, and the mixture boiled until evolution of sulphur dioxide had ceased. The hot mixture was filtered, and washed well with hot water, the residue being dried at 110°. The p-tolylmercuric chloride was recrystallised from boiling xylene as small white plates, m.pt. 243° . (Lit.,[68] 239°).

p-Tolylmercuric bromide.[69]

p-Bromotoluene (14·0g., 0.082 moles.) in ether (50mls.) was slowly added to a suspension of magnesium turnings (1·2g., 0·05 moles.) in ether (25mls.). The reaction mixture was continuously stirred and kept in an atmosphere of dry nitrogen. When reaction was complete, powdered mercuric bromide (30g., 0·083 moles.) in ether suspension was added, and the mixture refluxed for three hours. Hydrolysis of the reaction mixture with dilute hydrochloric acid, yielded a solid which was washed with alcohol and ether. Finally, p-tolyl mercuric bromide was recrystallised from benzene as fine, colourless needles, m.pt. 243-244°. (Lit.,[70] 234-235°).

p-Chlorophenyl mercuric chloride.

Bis-p-chlorophenyl mercury was refluxed in ethanol with a large excess of silver acetate, for several hours. Addition of conc. HCl yielded the chloride, which was recrystallised from ethanol. m.pt. 242°. (Lit.,[68] 240°).

Several attempts to prepare the bromide analogue resulted only in isolating the bis-organo mercury compound.

p-(Trifluormethyl)phenyl mercuric chloride .

The compound crystallised when a hot ethanolic solution containing the bis-organo mercurial, and a large excess of mercuric chloride, was allowed to cool. m.pt. 257°. (Found: Hg, 52·6%. $C_7H_4ClF_3Hg$ requires Hg, 52·7%.).

p-(Trifluoromethyl)phenyl mercuric bromide.

The bromide analogue was similary prepared, using a large excess of mercuric bromide. m.pt. 254°. (Found: Hg, 47·1%. $C_7H_4BrF_3Hg$ requires Hg, 47·0%.).

p-Dimethylaminophenyl mercuric chloride

A mixture of the bis-organo mercurial, and a large excess of mercuric chloride in boiling ethanol, was allowed to cool to room temperature. The organo mercury halide crystallised as cream-coloured plates. m.pt. 215-219°. (Found: Hg, 56·3%. $C_8H_{10}ClHgN$ requires Hg, 56·6%.).

p-Dimethylaminophenyl mercuric bromide.

The bromide analogue was similarly obtained as cream coloured plates. m.pt. 195-200° . (Found: Hg, 50·0%. $C_8H_{10}BrHgN$ requires Hg, 49·7%.).

Phenylethynylmercuric chloride.[66]

This was prepared by cleaving bis-phenylethynylmercury (10g. 0·025 mole.) with mercuric chloride (6·8g. 0·025 mole.) in tetrahydrofuran (125mls), which had previously been dried over lithium aluminium hydride. After standing overnight, the solvent was femoved, and benzene added. The pale yellow solid resulting was filtered off and recrystallised from 2:1 benzene-dioxane mixture. The compound was obtained as an off-white solid, m.pt. 270-272° . (Lit.,[71] 268-270°).

Trichloromethyl mercuric chloride.[72]

Dry mercuric chloride (8·7g., 0·0322 mole.) and anhydrous sodium trichloroacetate (5·9g., 0·0321 mole.) were refluxed with anhydrous monoglyme (50mls.) for approximately one hour, in a three necked flask fitted with stirrer and a condenser. During the first fifteen minutes much carbon dioxide was evolved. After reaction had ceased the mixture was poured into a large excess of water, and the heavy brown oil extracted with ether. After drying over anhydrous magnesium sulphate the ether was removed, and the solid product recrystallised from chloroform as fine white needles, m.pt. 187°. (Lit.,[72] 193°).

Trichloromethyl mercuric bromide.

The bromide was similarly prepared using mercuric bromide (12·0g., 0·033 mole.), and sodium trichloroacetate (6·2g., 0·033 mole.), in monoglyme (50mls.). The product was recrystallised from chloroform as small colourless plates, m.pt. 157-158° (Lit.,[72] 160-161°).

Pentafluorophenyl mercuric chloride.

Bispentafluorophenyl mercury was boiled with an equimolar amount of mercuric chloride in ethanol. After removal of the solvent under reduced pressure the residue was recrystallised from carbon tetrachloride as colourless plates, m.pt. 164-165°. (Found: Cl, 8·7; F, 23·8%. C_6ClF_5Hg requires Cl, 8·8; F, 23·6%.).

D I S C U S S I O N.

DISCUSSION

Zinc

Data for thirteen complexes containing the $ZnCl_2$ group, and eleven containing the $ZnBr_2$ group are given in Table I, together with data for Cs_2ZnCl_4, Cs_2ZnBr_4, and some boronium salts containing the anions $(ZnX_3)^-$, or $(Zn_2X_6)^{2-}$. For Cs_2ZnCl_4, ν(Zn-Cl) is at 285 cm^{-1} and 292 cm^{-1}, while for Cs_2ZnBr_4, ν(Zn-Br) is observed at 203 cm^{-1} and 207 cm^{-1}. Complexes containing the $(ZnX_4)^{2-}$ anion would be expected to give rise to only one infrared active vibration in the region studied, namely the triply degenerate antisymmetric stretch $\nu_3(f_2)$, assuming perfect tetrahedral symmetry. The appearance of two bands in the spectrum of Cs_2ZnCl_4 has in fact already been considered in terms of departure from exact tetrahedral symmetry in the crystalline state.[3] The loss of degeneracy results in a splitting of the single absorption band due to metal-halogen stretching. As the complex Cs_2ZnBr_4 has also been shown to have a distorted tetrahedral structure in the crystalline state,[27] the complexity of the band due to ν(Zn-Br) may be similarly explained.

TABLE I.

COMPLEX	ν(Zn-X)
Cs_2ZnCl_4	285sh, 292s
$(NH_3)_2ZnCl_2$	298s, 285s
$(NHEt_2)_2ZnCl_2$	296s
Py_2ZnCl_2	330s, 297s

TABLE 1 (Cont'd).

$(Me_2N \cdot CH_2-)_2ZnCl_2$	334s, 312s
$BipyZnCl_2$	331s, 323sh
1,10-$PhenanZnCl_2$	324s, 314s
$TerpyridylZnCl_2$	288s, 279s
$(PEt_3)_2ZnCl_2$	294s, 277s
$(PMe_2Ph)_2ZnCl_2$	305s, 283s
$(p\text{-}Me_2N \cdot C_6H_4 \cdot PMe_2)_2ZnCl_2$	305s, 289s
$(PPh_3)_2ZnCl_2$	322s, 299s
$(PPh_2 \cdot CH_2-)_2ZnCl_2$	315s, 292s
$(EtS \cdot CH_2-)_2ZnCl_2$	345s, 308s
$(BipyBPh_2)ZnCl_3$	334s, 301s, 238s, 225s
Cs_2ZnBr_4	223m,sh, 215s
$(NH_3)_2ZnBr_2$	210s (broad)
Py_2ZnBr_2	257s, 222 (doubtful)
$(Me_2N \cdot CH_2-)_2ZnBr_2$	263s, 233s
$BipyZnBr_2$	263s, 256sh
1,10-$PhenanZnBr_2$	264s, 232s
$(PEt_3)_2ZnBr_2$	221s (broad)
$(PMe_2Ph)_2ZnBr_2$	239s, 209m
$(p\text{-}Me_2N \cdot C_6H_4 \cdot PMe_2)_2ZnBr_2$	230s, 198m
$(PPh_3)_2ZnBr_2$	235s, 202m
$(PPh_2 \cdot CH_2-)_2ZnBr_2$	243s, 209m

TABLE 1 (Cont'd).

$(EtS{\cdot}CH_2-)_2ZnBr_2$	265s, 229m
$(BipyBPh_2)_2ZnBr_4$	217m, 209s
$(BipyBPh_2)ZnBr_3$	253s, 209s

If in going from the symmetrical species ZnX_4^{2-}, to the neutral complexes L_2ZnX_2, (L is ligand), the ligands being regarded as equivalent to single heavy nuclei, then the symmetry of the species can essentially be regarded as being reduced from T_d to C_{2v}. The triply degenerate vibrational mode $\nu_3(F_2)$ is therefore split into the vibrations $\nu_1(a_1)$, and $\nu_6(b_1)$ of the latter symmetry group.[73] Both modes are infrared active, and correspond to the symmetrical and antisymmetrical stretching frequencies respectively. Two bands due to metal-halogen stretching vibrations were observed in the spectra of all but three of the neutral complexes. The large variation of the difference between the two bands is suprising, ranging from 33 cm^{-1} in the chlorides, and 36 cm^{-1} in the bromides, down to a single strong broad band in three of the complexes. The broad bands presumably contain the unresolved doublet.

It can be seen that there is relatively small change in ν(Zn-X) in passing from the anions ZnX_4^{2-}, to the neutral complexes L_2ZnX_2. For Cs_2ZnCl_4, ν(Zn-Cl) is at 285 cm^{-1} and 292 cm^{-1}, and is at similar frequencies for $(Et_4N)_2ZnCl_4$ and $(Ph_3AsMe)_2ZnCl_4$.[3] These

are near the lower part of, but within the range 277-345 cm^{-1} observed for the neutral complexes. For some tin(IV) complexes,[11,12] ν(Sn-Cl) is in much the same region for $SnCl_6^{2-}$ ions (310 cm^{-1}), as for complexes py_2SnCl_4 (324 cm^{-1}), and $bipySnCl_4$ (327 cm^{-1} and 280 cm^{-1}). The metal-halogen stretching frequencies for some neutral complex of nickel halides are appreciably higher than in the anion, e.g. ν(Ni-Cl) in $(PMe_3)_2NiCl_2$, and $(PPhMe_2)_2NiCl_2$ occurs at 403 cm^{-1}, and 404 cm^{-1} respectively.[7] The ν(Ni-Cl) in $(Et_4N)_2NiCl_4$ occurs at 286 cm^{-1}.[3]

For neutral zinc bromide complexes, ν(Zn-Br) tends to be significantly higher than in the complexes containing $ZnBr_4^{2-}$ ions. Thus ν(Zn-Br) occurs at 215 cm^{-1} and 233 cm^{-1} for Cs_2ZnBr_4, but apart from the complexes $(NH_3)_2ZnBr_2$, and $(Et_3P)_2ZnBr_2$, the higher of the two frequencies observed in the spectra of the neutral complexes was in the range 230-265 cm^{-1}, the lower in the range 198-256 cm^{-1}.

Woodward[15] has shown that for any isoelectronic series AY_4^{2-}, BY_4^-, CY_4, the totally symmetric vibration $\nu_1(a_1)$ decreases from C to A, e.g. $ZnCl_4^{2-}$ (280 cm^{-1}), $GaCl_4^-$ (346 cm^{-1}), and $GeCl_4$ (396 cm^{-1}). As might be expected, the higher the negative charge on an anion, the more ionic become the bonds between the ligands and the central atom, and the lower the stretching force constant. In view of this, larger differences between ν(Zn-X) in the ions ZnX_4^{2-}, and in the neutral complexes L_2ZnX_2 may have been expected.

The variation of the nature of the donor atom does not appear to have a predictable effect on the metal-halogen stretching frequencies, and the only correlation which can be made, is that higher frequencies have a tendency to be associated with chelating ligands. The terpyridyl complex is an exception in that v(Zn-Cl) were very nearly the lowest observed. In view of the fact that the zinc atom is five co-ordinate,[31] and the probability that the $ZnCl_2$ group carries a rather larger negative charge due to co-ordination with three nitrogen atoms, the low values for v(Zn-Cl) are not unexpected.

Indeed, it is surprising that the frequencies fall within the range of tetrahedral complexes.

The boronium complexes are discussed below, together with those of cadmium, and mercury.

Cadmium

Data for the cadmium complexes are given in Table II. As indicated earlier, octahedral complexes of cadmium are very commonly formed, and many compounds whose empirical formula might suggest four co-ordination, in fact contain six co-ordinate cadmium. The infrared spectra of those cadmium complexes which are known to have an octahedral structure, evidently did not contain bands which could be assigned to v(Cd-Cl). The absorption bands may be extremely weak, and therefore not detectable, but it is more likely that they are at frequencies lower than 200 cm^{-1} when the chlorine atom is in either

a bridging or terminal position in an octahedral complex. Thus no bands due to v(Cd-Cl) were observed in the spectra of $(NH_3)_2CdCl_2$,[34] py_2CdCl_2,[35] or NH_4CdCl_3.[33] These complexes all have polymeric structures, the cadmium atom being in a distorted octehedral environment. The octahedra are condensed into chains by sharing edges through bridging chlorine atoms. Cadmium is also surrounded by six chlorine atoms in the salts $(NH_4)_4CdCl_6$, and K_4CdCl_6, the octahedral anions existing as discrete units in the crystalline state.[28] No bands that could be due to v(Cd-Cl) were observed in the spectra of these compounds. The band due to v(Cd-Cl) in $(Et_4N)_2CdCl_4$, presumably containing tetrahedral $CdCl_4^{2-}$ anions, is at 260 cm^{-1}; therefore, it is perhaps not surprising that v(Cd-Cl) should be at less than 200 cm^{-1} for the octahedral anion $CdCl_6^{4-}$. The much bigger negative charge on the latter anion would be expected to render the cadmium chlorine bonds much more ionic, and consequently lower the stretching force constant.

TABLE II.

COMPLEX	v(Cd-X)
$(Me_2N\cdot CH_2-)_2CdCl_2$	228w, 222w
$BipyCdCl_2$	228w
1,10-$PhenanCdCl_2$	227m, 213m
$TerpyridylCdCl_2$	269s, 250s
$(BipyBPh_2)CdCl_3$	271s, 224w
$(PMe_2Ph)CdCl_2$	233s

TABLE II (Cont'd)

$p\text{-}Me_2N\cdot C_6H_4PMe_2CdCl_2$	245s
$(PPh_2\cdot CH_2\text{-})_2CdCl_2$	270s, 258sh
$(EtS\cdot CH_2\text{-})_2CdCl_2$	223w
$(PPh_2\cdot CH_2\text{-})_2CdBr_2$	~195s

In contrast, bands evidently due to cadmium-chlorine stretching vibrations were observed in the spectra of all other complexes of cadmium chloride examined. The bands varied in intensity to a much greater extent than those of similar zinc complexes. No X-ray structural data were available for any of the complexes listed in Table II, except for the terpyridyl complex, which is isomorphous with its trigonal biprismatic five co-ordinate zinc analogue.[31] The bands assigned as being due to v(Cd-Cl) are some 20-30 cm^{-1} lower than those of the corresponding zinc complex, indicating a greater degree of ionic character of the cadmium-chlorine bonds. The same is also true of the chelating phosphine complex $(PPh_2\cdot CH_2\text{-})_2CdCl_2$, v(Cd-Cl) being some 30-45 cm^{-1} lower than v(Zn-Cl) in the zinc analogue. The author feels that of the cadmium chloride complexes examined, with the exception of the 1:1 halogen bridged dimers, the chelating bisphosphine complex $(PPh_2\cdot CH_2\text{-})_2CdCl_2$ is the only one to exist as individual molecules in the crystalline state. The cadmium-chlorine stretching frequency of the chelating bisphosphine complex is in the same range as that found for $(Et_4N)_2CdCl_4$, and for the terpyridyl

complex. The corresponding bromide $(PPh_2.CH_2-)_2CdBr_2$ is probably isostructural, as only in this instance was an absorption observed that could be due to ν(Cd-Br); in all other cases ν(Cd-Br) must be well below 200 cm^{-1}.

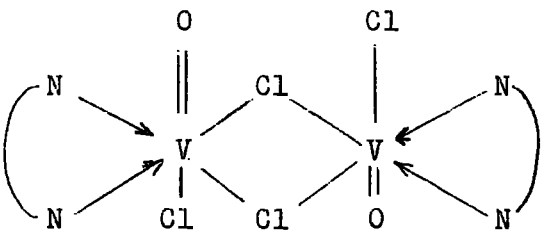
The low frequencies, and low intensities of the cadmium-chlorine absorptions in other complexes which might appear from their empirical formulae to contain tetrahedrally co-ordinated cadmium seem to indicate that there may be interaction between the chlorine atoms of one unit and the cadmium atom of another. This is equivalent to suggesting that the complexes $(Me_2N.CH_2-)_2CdCl_2$, $bipyCdCl_2$, $1,10\text{-}phenanCdCl_2$, and $(EtS.CH_2-)_2CdCl_2$, have distorted octahedral structures; this is reasonable in view of the known tendency of cadmium to be six co-ordinate.

As indicated earlier, various complexes $R_3PCdBr_2(orI_2)$ have been described which are dimeric in solution, and $(Et_3PCdBr_2)_2$ is dimeric in the solid state,[38] having a trans-halogen bridged structure. Analogous cadmium chloride complexes are not so readily prepared, but the spectra of two such complexes examined, $(PMe_2PhCdCl_2)_2$, and $(p\text{-}Me_2N.C_6H_4.PMe_2CdCl_2)_2$, are consistent with their having chlorine bridged dimeric structures. The single strong band due to ν(Cd-Cl) is assumed as being associated with a stretching vibration of the terminal cadmium-chlorine group. It is assumed that the vibrations due to bridging cadmium-chlorine occur at frequencies less than 200 cm^{-1},

and evidence in support of this is discussed below.

Klemperer[74] has made a complete vibrational assignment for Al_2Cl_6 (as gas), and although the comparison between Al_2Cl_6 (symmetry $V_h \equiv D_{2h}$), and $L_2Cd_2Cl_4$ (symmetry C_{2h}) is not strictly correct due to fundamental vibrations having different symmetry, it is of value in that the infrared active stretching vibrations involving terminal chlorines, 484 cm^{-1} and 625 cm^{-1}, are much higher than those involving bridging chlorines, 301 cm^{-1} (calculated) and 420 cm^{-1}. Similarly the Raman active terminal frequencies are higher than the bridging frequencies.

It has been reported[75] that the complex vanadyl chloride $VOCl_2L$ (L is 2,2'-bipyridyl), may be dimeric, having the trans-halogen bridged structure shown below.



It is suggested that the single strong band at 371 cm^{-1} is due to terminal ν(V-Cl), and that the absorption due to bridging chlorines do not occur at frequencies greater than 250 cm^{-1}.

The infrared spectra of the trans-halogen bridged ethylene complex

of palladium chloride $(C_2H_4PdCl_2)_2$, has been reported.[76] The terminal v(Pd-Cl) is assigned at 350 cm^{-1}, and the strong band at 270 cm^{-1} is assigned as being due to the Pd-Cl-Pd stretching vibration.

Similarly, the terminal v(Pt-Cl) in the trans-halogen bridged complex $(Et_3PPtCl_2)_2$ has been assigned[77] at 352 cm^{-1}, and the bridging v(Pt-Cl) at 265 cm^{-1}.

Finally, in complete contrast, Bennett and Clark[78] presume little difference between terminal and bridging vibrations in the transition element carbonyl halides. The assignment of v(Mn-Br) in $Mn(CO)_5Br$ is at 218 cm^{-1}, but in the dimeric halogen bridged compound $(Mn(CO)_4Br)_2$,[79] a band at 215 cm^{-1} is assigned as being due to v(Mn-Br) in the bridging position.

In view of the evidence given above vibrations due to bridging halogens in the complexes studied are assumed to be at some value lower than 200 cm^{-1}; certainly, apart from the single band due to terminal v(Cd-Cl), no other band that could be assigned to v(Cd-Cl) was observed.

Mercury.

Data for some neutral complexes of mercuric halides L_2HgX_2 and $(LHgX_2)_2$ are given in Table III, together with data for a boronium salt.

For complexes which apparently exist in the crystalline state as discrete tetrahedral species, two bands are nearly always observed, the upper one being in the range 279-292 cm^{-1}, and the lower in the range

249-279 cm^{-1}. For the complex $bipyHgCl_2$, a strong broad band at 273 cm^{-1} presumably contains the unresolved doublet, and for the complex $1,10\text{-}phenanHgCl_2$, the lower frequency band could not be assigned as it was obscured by ligand vibrations. The single band observed in the spectra of the halogen bridged complexes occurs within the range 285-307 cm^{-1}. For similar reasons to those discussed in connection with the cadmium complexes, it is assumed that the bridging Hg-Cl-Hg stretching vibrations occur at frequencies of less than 200 cm^{-1}

TABLE III.

COMPLEX	ν(Hg-X)
$(Me_2N\cdot CH_2-)_2HgCl_2$	289s, 277s
$BipyHgCl_2$	273s (broad)
$1,10\text{-}PhenanHgCl_2$	279s
$\left[(PMe_2Ph)HgCl_2\right]_2$	305s
$\left[(p\text{-}Me_2N\cdot C_6H_4PMe_2)HgCl_2\right]_2$	307s
$(PPh_3HgCl_2)_2$	289s
$(PPh_2\cdot CH_2-)_2(HgCl_2)_2$	292s, 279s
$(AsEt_3HgCl_2)_2$	285s (broad)
$(AsEt_3)_2(HgCl_2)_3$	342s, 292s (broad)

TABLE III (Cont'd)

$(AsPh_3HgCl_2)_2$	290s
$(EtS\cdot CH_2-)_2HgCl_2$	288s, 249m
$(TeBu_2^nHgCl_2)_2$	299s
$(BipyBPh_2)HgCl_3$	283s
$(^{Me}{}_2N\cdot CH_2-)_2HgBr_2$	213s, 208sh
$BipyHgBr_2$	Not observed
$1,10\text{-}PhenanHgBr_2$	211s, 205sh
$\left[(p\text{-}Me_2N\cdot C_6H_4\cdot PMe_2)HgBr_2\right]_2$	214s (broad)
$(EtS\cdot CH_2-)_2HgBr_2$	204s (broad)

where a direct comparison can be made, that is, when the metal atoms are in similar environments, it can be seen that v(Hg-Cl) is lower than v(Zn-Cl), but slightly higher than v(Cd-Cl). For example, for the chelating bisphosphine complexes $(PPh_2\cdot CH_2-)_2MCl_2$, v(Zn-Cl) is at 315 cm^{-1} and 292 cm^{-1}, v(Cd-Cl) at 270 cm^{-1} and 258 cm^{-1}, and v(Hg-Cl) at 292 cm^{-1} and 279 cm^{-1}.

The mercury-chlorine stretching frequencies in the neutral complexes are similar to those for the anion $HgCl_4^{2-}$, the symmetrical,[18] and antisymmetrical [6] stretching frequencies of that anion occurring at

269 cm^{-1} and 276 cm^{-1} respectively. In the complex $(Et_4N)_2CdCl_4$, ν(Cd-Cl) occurs at 260 cm^{-1}, [5] this is in agreement with the present authors observations that ν(Hg-Cl) tends to occur at higher frequencies than ν(Cd-Cl).

Where observed, the mercury-bromine stretching frequencies were near the limit of the spectrometer, and were not observed for $bipyHgBr_2$, $(PPh_3)_2HgBr_2$, $(PPh_3HgBr_2)_2$, $(AsPh_3HgBr_2)_2$, $(Et_3P)_2HgBr_2$, and $(PPh_2{\cdot}CH_2-)_2HgBr_2$.

As indicated above, the single band in the spectra of the dimeric halogen bridged complexes $(LHgX_2)_2$ is assigned to terminal ν(Hg-Cl), bridging vibrations not being observed. The complex $(AsEt_3)_2(HgCl_2)_3$ fits this pattern if it has a structure similar to that of the bromide $(AsEt_3)_2(HgBr_2)_3$, which is a molecular lattice compound of $HgBr_2$, and $(AsEt_3HgBr_2)_2$ molecules. [38] The band at 342 cm^{-1} evidently is due to the antisymmetrical stretching vibration of the $HgCl_2$ molecule, and that at 292 cm^{-1}, to the terminal Hg-Cl in the dimer.

The 1,2 -bisdiphenylphosphinoethane complexes were found to be unusual, in that although a complex $(PPh_2{\cdot}CH_2-)_2HgBr_2$ was prepared, attempts to prepare the analogous chloride yielded the complex $(PPh_2{\cdot}CH_2-)_2(HgCl_2)_2$. No band due to ν(Hg-Br) was observed in the spectrum of the bromide, but bands due to ν(Hg-Cl) were observed at 292 cm^{-1} and 279 cm^{-1} in the spectrum of the chloride. Apart from a

band at 350 cm^{-1} the spectrum was entirely consistent with the symmetrical and antisymmetrical stretching frequencies of the more orthodox tetrahedral 1:1 complex $(PPh_2 \cdot CH_2-)_2HgCl_2$. A band in the region of 350 cm^{-1} is found in the spectra of all complexes containing this ligand, although usually it is considerably weaker. In this instance it could possibly coincide with the antisymmetrical stretching absorption of free $HgCl_2$ units (compare v(Hg-Cl) at 342 cm^{-1} for $HgCl_2$ in the triethylarsine complex discussed above), and if so, then the complex must be a molecular aggragate of $HgCl_2$ and $(PPh_2 \cdot CH_2-)_2HgCl_2$ molecules.

The halogen-bridged complexes with dimethylphenylphosphine call for comment. Two compounds with almost identical mercury contents corresponding to the formula $(PMe_2PhHgCl_2)_2$, were found to have quite different infrared spectra in the 450-200 cm^{-1} region. The complex which was prepared by the present author gave a simple spectrum with a single strong band at 305 cm^{-1}, which was assigned as being due to the terminal v(Hg-Cl) of the bridged dimer. The second complex, which had been prepared in the laboratories a long while previous to the present investigation, gave a spectrum consisting of several weak bands, and two strong bands evidently due to v(Hg-Cl) at 317 cm^{-1} and 289 cm^{-1}. The spectrum of the bromo-complex $(PMe_2PhPHgBr_2)$, prepared during the present investigation was found to have several weak bands identical in position to the second chloro-complex, and a band of

medium intensity at 224 cm^{-1}, the strong bands at 317 cm^{-1} and 289 cm^{-1} being absent. The infrared spectra of the complexes in the 2000-400 cm^{-1} region were found to be identical, and the only reason which can be put forward to explain the obvious structural differences, is that both cis, and trans-isomers of the halogen bridged dimeric complex were obtained. The two bands due to terminal v(Hg-Cl) would be consistent with the cis-isomer, while the single band at 305 cm^{-1} is presumably due to the terminal v(Hg-Cl) in the trans-complex.

The only bands in the spectrum of $(PPh_3)_2HgCl_2$ which could be attributed to v(Hg-Cl) were two broad bands of low intensity at 236 cm^{-1} and 221 cm^{-1}, which were absent from the spectrum of the bromo-analogue. The frequencies are much lower than expected for terminal v(Hg-Cl) in a complex containing tetrahedrally co-ordinated mercury. The structure of the complex has not been elucidated but on the basis of the infrared spectrum it is concluded that there is some interaction between the separate molecular species resulting in a shift in v(Hg-Cl) of 50-60 cm^{-1}.

The bistriethylphosphine complex $(PEt_3)_2HgCl_2$, was found to have an infrared spectrum identical to that of the bromide, apart from a very weak broad band at 279 cm^{-1}. This is not characteristic of a covalent tetrahedral complex, and the infrared evidence prompts the author to suggest the possibility of an ionic structure, e.g. $(Hg(PEt_3)_2)^{2+}2Cl^-$. Evidence in support of this is that the complexes

dissolve in water without smell of free phosphine, and addition of silver nitrate to the aqueous solution results in the immediate precipitation of the silver halide. Alternatively, the complex could contain octahedrally co-ordinated mercury in a polymeric structure having halogen bridges between mercury atoms, and phosphorus atoms at the apeces of the octahedra. Such a structure could apply equally as well to the triphenylphosphine complex discussed above. The exsistence of such structures for neutral co-ordination complexes of mercuric chloride has been demonstrated by X-ray diffraction methods,[71] e.g. the 1:1 complex of mercuric chloride with thiophen has been shown to contain distorted octahedrally co-ordinated mercury, and the structure is best described as being composed of $Cl\text{-}Hg\text{-}SC_4H_8^+$ ions and Cl^- ions coupled together to form infinite chains.

The spectrum of the bispyridine complex PY_2HgCl_2 in the 450-200 cm^{-1} region was particularly interesting, since apart from a single band at 418 cm^{-1} where co-ordinated pyridine commonly absorbs,[80] no band was observed. This is in fact contradictory to a recent report [81] that the spectrum of this complex contains a band at 292 cm^{-1}. Grdenić et al [82] have carried out an X-ray structural analysis on this complex and have reported that the mercury atom has two chlorine atoms at 2·34Å, two nitrogen atoms at 2·60Å, and two more chlorine atoms at 3·25Å. The authors regard the structure as containing discrete $HgCl_2$ molecules with pyridine of crystallisation held together by longer Hg.....Cl contacts. In order to confirm this interpretation,

several complexes known to contain virtually two co-ordinate mercury in $HgCl_2$ units were examined, including mercuric chloride itself. Crystalline mercuric chloride was found to absorb at 375 cm^{-1}, in close agreement with a previously reported value,[77] 374 cm^{-1}. The metal is virtually two co-ordinate [83] having two chlorines at 2·25Å, two at 3·34Å, and two more at 3·63Å. It may be mentioned here that the environment of mercury in crystalline mercuric bromide is rather similar [84], and the antisymmetrical stretching frequency was found to occur at 249 cm^{-1}, in good agreement with a previously reported value,[77] 251 cm^{-1}.

In the complex $CsHgCl_3$, the mercury atom is octahedrally surrounded [39] having two chlorines at 2·29Å, and four at 2·70Å; a strong band was observed at 320 cm^{-1}, and one of medium intensity at 284 cm^{-1}. The appearance of two bands in the spectrum is surprising, and would seem to indicate non-linearity of the $HgCl_2$ molecules, thus giving rise to a symmetrical and antisymmetrical stretching frequency. An unresolved broad band centred at 304 cm^{-1} was observed for K_2HgCl_4,H_2O which has a similar structure,[39] with two chlorines at 2·29Å, two at 2·92Å, and two more at 3·13Å. The spectrum of NH_4HgCl_3, in which the metal has two chlorines at 2·34Å, and four at 2·96Å,[40] was similar with an unresolved broad band centred at 309 cm^{-1}.

Thus the description by Grdenić of the structure of py_2HgCl_2 does not seem consistent with the absence of infrared bands in the 300 cm^{-1}

region. On the other hand Dunitz [85] concludes that the complex is isomorphous with its Cu(II) analogue in which the copper atom is in a distorted octahedral environment. The infrared result provides evidence that all of the chlorines in the mercury complex should be regarded as being in bridging rather than in terminal positions, thus supporting the view that the complex is a polymer held together by bridging chlorine rather as in py_2CuCl_2 and α-py_2CoCl_2.

A trigonal oxonium complex $(O(HgCl)_3)^+Cl^-$ gave a spectrum having a complex band due to v(Hg-Cl) namely, 350 cm^{-1}(s), 344 cm^{-1}(s), and 328 cm^{-1}(sh). This may be due to the loss of degeneracy of the v(Hg-Cl), since the cation containing the trigonally co-ordinated oxygen is non-planar.[86]

Organomercuric halides.

The spectra of alkyl- and aryl- mercury halides all contain, as expected, a single band due to mercury-halogen stretching. The band is always strong in the spectra of the chlorides, and considerably weaker in those of the bromides. The frequencies (Table IV) are in the region between those found in the spectra of tetrahedral complexes and those of $HgCl_2$ and $HgBr_2$.

TABLE IV

HALIDE	ν(Hg-Cl)	HALIDE	ν(Hg-Br)
$HgCl_2$	375s	$HgBr_2$	249s
MeHgCl	315s	MeHgBr	214w
EtHgCl	314s	EtHgBr	209w
Pr^nHgCl	322s	Pr^nHgBr	214w
Bu^nHgCl	316s	Bu^nHgBr	246m
$CH_2{:}CH{\cdot}HgCl$	323s	$CH_2{:}CH{\cdot}HgBr$	216m
$PhC{:}C{\cdot}HgCl$	345s		
CCl_3HgCl	335s	$CCl_3{\cdot}HgBr$	238s
PhHgCl	331s	PhHgBr	214m
$p\text{-}CH_3{\cdot}C_6H_4{\cdot}HgCl$	325s	$p\text{-}CH_3{\cdot}C_6H_4{\cdot}HgBr$	246m
$p\text{-}CF_3{\cdot}C_6H_4{\cdot}HgCl$	324s	$p\text{-}CF_3{\cdot}C_6H_4{\cdot}HgBr$	230m
$p\text{-}Cl{\cdot}C_6H_4{\cdot}HgCl$	330s		
$p\text{-}Me_2N{\cdot}C_6H_4{\cdot}HgCl$	323s	$p\text{-}Me_2N{\cdot}C_6H_4{\cdot}HgBr$	233m

The mercury-chlorine stretching frequencies fall within the range 314-345 cm^{-1}, and there is no apparent relation to the nature of the organic group, apart from the fact that the aryl derivatives are in the upper half of the range (323-345 cm^{-1}), whereas with the exception of trichloromethyl mercuric chloride (335 cm^{-1}), the alkyls are in the lower half (314-323 cm^{-1}). Mercury-bromine stretching frequencies vary

rather more, 209-246 cm^{-1} , the high values of v(Hg-Br) in n-butyl- and p-tolyl- mercuric bromides are remarkable being nearly the same as in mercuric bromide.

Results relating to some trifluoromethyl[87] and pentafluorophenyl[88] mercury compounds are given in Table V.

TABLE V.

Compound	v(Hg-CF_3)	v(Hg-X)	C_6F_5 vibrations
CF_3HgCl	252m	339vs, 327?	-
CF_3HgBr	270s	233m	-
CF_3HgI	255s	-	
C_6F_5HgMe	-	549w	221m, 278m, 310m, 358s
C_6F_5HgCl	-	344s	230m, 312w, 362s, 379s
C_6F_5HgBr	-	246s	223s, 281w, 310m, 360s
$(C_6F_5)_2Hg$	-	-	226sh, 231s, 279s, 310s, 357s, 368s, 375sh

The mercury-halogen stretching frequencies are within the ranges given above, although in the higher regions.

The trifluoromethyl- mercury stretching frequencies v(Hg-CF_3) are in the same range as previously reported values. Downs[89] has made a complete vibrational assignment of bis-trifluoromethyl mercury, and assigns the symmetrical v(Hg-CF_3) at 226 cm^{-1}, the antisymmetrical v(Hg-CF_3) being

assigned at 274 cm^{-1} .

The spectra of the pentafluorophenyl mercury compounds all contain a characteristic band pattern due to the C_6F_5 group, that of $(C_6F_5)_2Hg$ differing only in that the lowest frequency band is split into two, and the 360 cm^{-1} band is split into three components.

Bipyridylyldiphenylboronium salts.

Since other work on these was in progress in the laboratory, the following salts were prepared containing the large cation, and zinc, cadmium, and mercury halogeno-anions: $B^+ZnCl_3^-$, $B^+ZnBr_3^-$, $B_2^{2+}ZnBr_4^{2-}$, $B^+CdCl_3^-$, $B^+CdBr_3^-$, $B^+HgCl_3^-$, and $B^+HgBr_3^-$ (B is $bipyBPh_2$). Only in one instance could a salt be prepared containing the tetrahedral MX_4^{2-} anion, namely $B_2^{2+}ZnBr_4$. The zinc-bromine stretching frequencies at 217 cm^{-1} and 209 cm^{-1} are quite close to those in the caesium complex Cs_2ZnBr_4 (223 and 215 cm^{-1}). The complexity of the band is indicative of a distorted tetrahedral arrangement within the anion. The salts of empirical formula $B^+MX_3^-$ could contain three co-ordinate anions, or more probably binuclear anions such as $ZnCl_6^{2-}$ containing two bridging halogen atoms. The four strong bands evidently due to v(Zn-Cl) at 334, 301, 238, and 225 cm^{-1} observed in the spectrum of the complex $BZnCl_3$ are difficult to reconcile with the presence of a mononuclear anion. The present author suggests that the bands at 334 and 301 cm^{-1} are associated with terminal v(Zn-Cl), and the lower frequency bands with bridging chlorine. In the spectrum of the bromide $BZnBr_3$, the bands at 253 and 209 cm^{-1}

would be due to terminal ν(Zn-Br), and the bridging modes would be expected to be well below 200 cm^{-1}. For the cadmium complex the bands at 271 cm^{-1} and 224 cm^{-1} may be explained on the same basis, but the single band at 283 cm^{-1} in the spectrum of the mercury complex is surprising. However, in view of the fact that in the complex $(NMe_4)^+HgBr_3^-$, the mercury atom is trigonally co-ordinated in discrete $HgBr_3^-$ anions,[42] than the single band in the spectrum of $B^+HgCl_3^-$ may be due to the antisymmetrical stretching vibration of a planar $HgCl_3^-$ anion.

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P.A R T II

SOME ALKOXY-, THIO-, AND AMINO- DERIVATIVES

OF

METHYL-, AND ETHYL- ZINC.

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INTRODUCTION.

PART II

INTRODUCTION

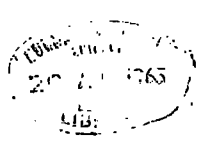
The work described in Part II of this thesis is concerned with the chemistry of organo-zinc compounds. In particular it is concerned with the nature of the zinc-containing products obtained by reactions of organo-zinc compounds of the type R_2Zn, with 'weak acids'. The term 'weak acid' , as well as including commonly recognized weak acids such as carboxylic and phosphinic acids also includes organic compounds in which the protonic character of a hydrogen atom is sufficiently enhanced to cause cleavage of a zinc-carbon bond. The general reaction may be represented thus,

$$R_2Zn + HA \longrightarrow RH + RZnA.$$

In many cases the reaction between the products(much of the interest in which lies in the possibility of their containing co-ordinatively unsaturated zinc), and a strong donor ligand, e.g. a tertiary base, has also been investigated.

An investigation of the reaction of organo-zinc compounds with several unsaturated systems has been included in the present study with a view to isolating the zinc analogues of Grignard intermediates.

The relevant data are included in the introduction together with a concise account of the preparation and properties of organo-zinc compounds, and a discussion of the coordination chemistry of zinc and some other Group II organo-metallic compounds.



Preparative methods for organo-zinc compounds.

Nearly all organo-zinc compounds are rapidly decomposed by oxygen and moisture, the lower alkyls being spontaneously inflammable in air. Complete oxygen and moisture-free conditions must therefore be employed during their preparation, and during any subsequent manipulation of the pure compounds.

Zinc dialkyls were first prepared by Frankland [1] in 1853, by heating methyl iodide and zinc metal in a sealed tube. This original method still forms the basis for the very convenient preparation of zinc alkyls by thermal disproportionation of alkyl zinc iodides [2], the latter being obtained by direct reaction between alkyl iodides, or mixtures of bromides and iodides, and a zinc-copper couple, e.g.

$$Zn + EtI \longrightarrow EtZnI$$

$$2EtZnI \longrightarrow Et_2Zn + ZnI_2$$

The reactions are carried out in an inert atmosphere of nitrogen (carbon dioxide was used in the earliest work), without isolation of the organo-zinc halides which normally appear as white crystalline substances. The formation of alkyl zinc iodides usually requires a period of refluxing before reaction starts, but several authors [3,4] have recently shown that alkyl iodides react spontaneously and vigorously with zinc dust in solvents such as 1,2 - dimethoxyethane, dimethyl sulphoxide, and dimethylformamide, giving good yields of the solvated species.

Improvements on the original method of Frankland have mainly concerned the use of suitable zinc-copper alloys,[2] or special methods for the preparation of the zinc-copper couple (e.g. from zinc dust and cupric citrate[5]).

Zinc alkyls have been obtained in high yield by the reaction of trialkyl aluminium or alkyl aluminium sesquihalides with zinc halides, either alone or in the presence of an inert solvent.[6,7,8,9]

Solutions of di-alkyl and di-arylzinc, and of organo-zinc halides in ether may be obtained by addition of anhydrous zinc chloride in ether, to a Grignard solution:

$$ZnCl_2 + RMgX \longrightarrow RZnCl + MgXCl$$

Excess of Grignard reagent gives the dialkyl (or aryl) derivatives, and the more volatile products may be distilled from the reaction mixture,[10] although difficulty has apparently been experienced in obtaining dimethylzinc entirely ether-free by distillation from ethereal solutions.[11] A successful separation will obviously depend to a large extent on the choice of ether.

Small quantities of organo-zinc compounds, particularly the lower alkyls, can be prepared conveniently by metal exchange reactions involving the use of mercury alkyls. The latter reagents are easily prepared, and have the advantage that they are unaffected by both oxygen and moisture due to the relatively low affinity of oxygen for mercury. The diaryls of zinc may be obtained by this method, the reaction being

carried out in boiling xylene solution.[13] More recently [14,15] good yields of zinc di-aryls have been obtained from anhydrous zinc chloride and the appropriate lithium reagent in ether solution.

A series of unsymmetrical zinc alkyls of the type $RZnR'$ have been prepared by the reaction of a Grignard reagent with an alkyl zinc halide. These compounds can be distilled only under reduced pressure, and they disproportionate into the symmetrical alkyls even on standing at room temperature.[16]

Properties of organo derivatives of other elements of Group II.

The physical and chemical properties of organo-metallic compounds are determined by the polarity of the M - C bond, the theoretical extreme being an ionic lattice of cations, and carbanions. Thus the organo derivatives of sodium and heavier alkali metals are non - volatile solids, and are insoluble in hydrocarbon solvents. Their intense chemical reactivity may be ascribed to the presence of carbanions. Methyl - , and ethyl-lithium are involatile solids, but the latter is soluble in saturated hydrocarbons.[10] The crystal structures of both these compounds have recently been determined by X-ray analysis,[15] methyl-lithium having eight monomer units in the unit cell, associated as tetramers. Ethyl-lithium[16] has sixteen monomer units in the unit cell, and these are also associated as tetramers though in a more complicated way. Systems of electron deficient bonding have been discussed for both structures. The difference in structure between organo-lithium, and

organo-sodium compounds is due to the small size and high polarising power of the lithium ion, and is even more marked when large polarisable organic radicals are considered, e.g. n - butyl lithium is a colourless liquid soluble in paraffin solvents, and is presumably largely covalent.

In Group II the gradation in physical and chemical properties is much more marked, and a transition from saline to completely covalent character is observed. The trend parallels the change in electronegativity of the elements.

The alkyls of calcium, strontium, and barium have been little studied, but where they have been isolated they have been found to be extremely reactive, undergoing metallation reactions, and adding to ethylenic double bonds.[17] They appear to be rather similar to the alkali metal alkyls, and are presumably of similar constitution.

The alkyls of beryllium and magnesium are essentially covalent, and are highly reactive resembling organo-lithium reagents in many respects. The neutral metal atoms having an outer electronic configuration ns^2 have more low energy orbitals than valence electrons, and when combined with atoms or groups containing no unshaired pairs, delocalisation of bonding can occur so as to make use of all of the low energy bonding orbitals of the metal atom. Such is the case for the organo-beryllium and organo-magnesium compounds, both of the methyl compounds being solids of low volatility. X-Ray diffraction methods have shown that both dimethylberyllium,[18] and dimethylmagnesium[19] exist in the solid state

as linear polymers, the metal atoms being connected by pairs of methyl bridges with an almost tetrahedral arrangement of four methyl groups around each metal atom. A comparison of bond distances indicates that in the latter compounds the bonds are stronger, and this probably explains the lower volatility of the magnesium compound. Diethylmagnesium and higher homologues are also white solids, and apparently non-volatile,[20] whereas the higher homologues of beryllium are presumably of more covalent character, e.g. diethylberyllium [21] is a liquid, easily soluble in benzene, although the low vapour pressure does indicate association (b.pt. ca. 0·4 mm. is 90-95°). Di-tert-butylberyllium[22] is considerably more volatile and is assumed to be monomeric. The apparently more covalent nature of the beryllium alkyls is due beyond reasonable doubt to the greater electronegativity of the beryllium atom relative to the magnesium atom.

Both series of organo-metallic compounds are extremely reactive, being hydrolysed with explosive violence, and igniting spontaneously in air. The methyl derivatives have been reported to ignite in carbon dioxide.[10] The reactions of di-alkyl and di-arylmagnesium compounds are typified by those of the Grignard reagents, [23] and it is probably due to the easy preparation of the latter that the chemistry of the magnesium dialkyls and diaryls has been little studied. Dimethylberyllium undergoes several reactions typical of Grignard reagents, e.g. with benzophenone, diphenylmethylcarbinol is formed,[24] and with

phenylisocyanate, acetanilide is obtained [25](after hydrolysis), but it appears to be somewhat less reactive than dimethylmagnesium or methylmagnesium halides.

The large increase in electronegativity in going from the typical elements to those of the B sub-group, is reflected in the properties of their organic derivatives. Thus zinc, cadmium, and mercury all form covalent organo derivatives, the alkyls being volatile liquids, easily soluble in paraffin solvents, and monomeric in liquid and vapour phases. The bonding in these types of molecules is generally described in terms of 'normal' sp - hybridization, the C-M-C axis being linear. The reactivity of the compounds show a marked decrease with increasing atomic weight, e.g. the lower zinc alkyls ignite spontaneously in air, cadmium alkyls smoke, and are not as vigorously hydrolysed. The mercury alkyls are unaffected by both oxygen and moisture, and are stable even towards dilute aqueous acids. This change in reactivity is not necessarily a measure of the metal-carbon bond strength, but is due more to a decrease in affinity of the metal atom for oxygen. However, bond dissociation energies have been measured by a study of the behaviour of the methyl derivatives on pyrolysis. [26] For the reaction:

$$Me_2M \longrightarrow Me + MeM$$

the values obtained were: Me_2Hg (50 Kcals/mole.), Me_2Cd(46 Kcals/mole), and Me_2Zn(47 Kcals/mole). Spectroscopic evidence [27] also indicates the above order, e.g. from an infrared study of the dimethyl derivatives, the

stretching force constants of the M-C bonds were calculated to be: Hg-C, $2{\cdot}45 \times 10^5$ dynes/cm., Cd-C, $2{\cdot}05 \times 10^5$ dynes/cm; Zn-C, $2{\cdot}39 \times 10^5$ dynes/cm.

As expected, the zinc, cadmium and mercury alkyls are not as reactive as organo- magnesium or beryllium compounds, a fact which resulted in the chemistry of zinc alkyls not being as fully developed as might have been expected for compounds which have been known for more than one hundred years. The development of the much more reactive and more readily prepared Grignard reagents resulted in organo-zinc compounds being almost entirely replaced as synthetic reagents. However, zinc alkyls are sometimes preferred when a Grignard reagent is too reactive, e.g. for the synthesis of ketones from acid chlorides. The Grignard reagent in this case reacts further with the ketone, the final product being a tertiary alcohol.

Organo-zinc compounds are generally thought to be unaffected by light. However, higher alkyls of zinc have been observed slowly to deposit black precipitates of zinc after several weeks even when stored in sealed ampoules.[28] With the exception of the methyl derivatives, organo-cadmium and organo-mercury compounds are generally light sensitive.

Properties of some organo-zinc compounds.

Dimethylzinc

This is colourless liquid at room temperature which can be distilled at atmospheric pressure without decomposition at 44°, and which freezes at -29°.[29] The variation of vapour pressure with temperature between $-6{\cdot}2^\circ$ and $16{\cdot}6^\circ$ is given by:[30]

$$\log_{10}p = -\frac{1480}{T} + 7{\cdot}52$$

The latent heat of evaporation is given as 6,840 cals/mole, and the Trouton constant as 21·4. An X-ray diffraction study of solid dimethylzinc [31] has shown that within the tetragonal crystals, the Zn-C distances in the monomers are 1·94Å. This is shorter than the sum of the two covalent radii, 2·02Å, suggesting that apparently vacant valence orbitals allow some multiple bond character in the Zn-C bonds by a hyperconjugation effect.

Diethylzinc

The liquid can be distilled unchanged at atmospheric pressure at 117·6°, [29] and it freezes at -30°. The variation of vapour pressure between 17·2° and 79·8° can be expressed by: [30]

$$\log_{10}p = -\frac{1910}{T} + 7{\cdot}695$$

The latent heat of evaporation is given as 8,780 cals/mole, and the Trouton constant as 22·2. Diethylzinc has a specific conductivity of 2×10^{-11} ohms^{-1}cm^{-1} at 20°. Although itself non-polar it is reported to have a solvent character intermediate between ionizing and non-polar solvents.

Di-n-propylzinc.

The liquid freezes at -81°, and on attempted distillation begins to decompose at 70°. The extrapolated b.pt. is given as 139·4°. [29]

Diphenylzinc.

Like all of the aryl derivatives, this is a crystalline solid,

m.pt. 105°. It can be distilled with only slight decomposition at 280-285°. [32]

The co-ordination chemistry of Group II organo-metallic compounds. Beryllium and magnesium.

The co-ordination chemistry of organo-derivatives of calcium, strontium, and barium has not been studied, whereas that of the Group IIB elements has been investigated in much more detail. The methyl derivatives of beryllium and magnesium, being electron deficient, would be expected to form electron donor-acceptor complexes readily thus relieving the electron deficiency. Only molecules with relatively strong donor properties combine with these molecules, since the heat of co-ordination must exceed the heat of polymerisation.[10] Dimethylmagnesium is apparently a more strongly bound polymer than dimethylberyllium, since the former is only slightly soluble in ether [20] whereas the latter is easily soluble. The chemical evidence has found support in the recent X-ray structural analysis of dimethylmagnesium. [19] An unstable crystalline mono-ether complex of diethylmagnesium has been reported, [32] and vapour pressure measurements of some solutions of diethyl- and dipropylmagnesium in ether - tetrahydrofuran mixtures show that an equilibrium exsists in solution:[33]

$$R_2Mg.Et_2O + THF = R_2Mg\cdot THF + Et_2O.$$

Dimethylmagnesium reversibly absorbs trimethylamine, [10] and some volatile chelate complexes of R_2Mg with NNN'N' tetramethyl-ethylenediamine

(R = Et, Pr, Pr^i and Bu^n) have recently been described.[34] The tetramethylethylenediamine complexes of dimethyl- and diphenylmagnesium are also described as crystalline solids, as are the 1,2-dimethoxyethane complexes, and a bis-tetrahydrofuran complex of diphenylmagnesium.[35] Finally, diphenylmagnesium reacts reversibly in ether solution with phenyl-lithium, and a crystalline anionic complex $Li(MgPh_3)$ can be obtained by addition of xylene.[36]

As indicated above, dimethylberyllium is easily soluble in ether presumably due to co-ordination, and a series of unstable complexes with dimethyl ether have been detected by vapour pressure measurements.[37] The same authors found that when dimethylberyllium was heated in a closed system with the **stronger** donor, trimethylphosphine, increase in temperature brought about a succession of phase changes, and vapour pressure measurements indicated a considerable range of compounds $(Me_2Be)_x (PMe_3)_y$, each one being stable over a range of temperature and pressure. It was concluded that in this particular system the heat of co-ordination was comparable with the heat of polymerisation and that the ligand was acting as a polymer chain-stopper. With trimethylamine, a low melting solid 1:1 adduct is formed, this is monomeric in the vapour phase, and stable to 180°. At low temperatures the formation of 2:3 complex $(Me_2Be)_2(NMe_3)_3$ is reported to occur.[37] Crystalline, presumably chelate complexes of dimethylberyllium with 1,2-dimethoxyethane, and tetramethylethylenediamine have been described, as well as a series of coloured complexes with

2,2′-bipyridyl, bipy BeR_2. The colour was found to depend on the electronegativity of the group R, and was ascribed to an electron transfer from one of the Be - R bonds into the lowest unoccupied orbital of 2,2′-bipyridyl. The dark green complex $bipy_2Be$ is thought, on the evidence of magnetic moment measurements, to be represented by the equilibrium:[38]

$$(bipy_2^- \; Be^{2+}) \rightleftharpoons (bipy^{2-} \; bipy^{o} \; Be^{2+}).$$

The presence of two unpaired electrons has been confirmed by electron spin resonance spectra.[38a] Anionic complexes of organo- beryllium compounds have also been reported, e.g. $LiBePh_3$,[36] and $NaBeEt_2H$.[39] The latter complex crystallises from ether with one mole of solvent, which is associated with the sodium cations.[40]

Mercury.

The organo derivatives of the remaining elements of Group II might be expected to be poor acceptors due to the higher electronegativities, and consequent reduction in the polarity of the M - C bond. This is particularly true in the case of mercury, e.g. mercury alkyls and aryls can be recovered unchanged from solutions containing pyridine, and ethylenediamine,[41] and dimethylmercury can be recovered unchanged from 2,2′-bipyridyl.[38] The dipole moment of diphenylmercury is very low in dioxan, indicating that the linear C-Hg-C bond undergoes little, or no readjustment to a tetrahedral configuration.[42] When the electronegativity of the alkyl group is increased, e.g. by

fluorination, then stable neutral complexes are formed. Bis-pentafluorophenylmercury forms stable 1:1 complexes with 2,2′-bipyridyl and 1,2-bis(diphenylphosphine)-ethane,[43] and several other donors.[44] Bis-trichloromethylmercury also forms a stable 1:1 complex with 2,2′-bipyridyl, the adduct being a well defined crystalline solid.[45]

Cadmium

Cadmium alkyls and aryls form neutral co-ordination complexes, some of which are not particularly stable. A number of colourless, crystalline 1:1 complexes of di-arylcadmium compounds with 1,4-dioxan have been described.[46] The complexes lose dioxan when they are heated to approximately 80-100°. Similar complexes of mixed cadmium aryls ArCdAr′, have been described (Ar = phenyl, Ar′ = 2-thienyl).[47] Crystalline complexes of dimethylcadmium with 1,4-dioxan, N,N,N′,N′-tetramethylethylenediamine, 2,2′-bipyridyl, and 1,10-phenanthroline are reported to be quite stable thermodynamically, whereas 1:1 complexes formed with unidonor molecules like tetrahydrofuran or pyridine, are liquids which readily dissociate at room temperature, and in benzene solution.[48] In contrast to the above, the yellow complex formed from dimethylcadmium and 2,2′-bipyridyl is said to be unstable, having an appreciable dissociation pressure at room temperature.[38] Anionic complexes of organo-cadmium compounds are known, e.g. diphenylcadmium and phenyl-lithium are reported to react reversibly in ether solution, an unsolvated crystalline complex $LiCdPh_3$ being obtained on addition of

xylene.[36] A complex cadmium acetylide, $K_2 Cd(C{\equiv}CH)_4$ has also been described.[49]

Zinc

The co-ordination chemistry of organo-zinc compounds was until quite recently confined to complexes in which the organo-zinc moiety appeared as part of a complex anion. This type of complex was first reported in 1858 when Wanklyn[50] obtained a low melting crystalline solid from sodium metal and diethylzinc. The analyses correspond to sodium triethylzincate, $NaZnEt_3$. Since then various anionic organo-zinc complexes have been reported in the literature, although several of these were not described in detail. The complex mentioned above has also been prepared by dissolving ethyl sodium in diethylzinc, and removing the excess of the latter. The complex is said to be a associated in benzene, and the authors suggest that it is best represented by the dimeric formula $(NaEt.ZnEt_2)_2$.[51] Support for this formulation has been found in a dipole moment study, the conclusion of which is that the complex contains the dimeric anion $Zn_2Et_6^{2-}$, in which each zinc atom is tetrahedrally surrounded by an ethyl group.[52] A rubidium complex $RbZnEt_3$ has been obtained, from diethylzinc and the alkalimetal, as a crystalline solid m.pt. 70-75°.[53] The formation of similar complexes has been observed in the preparation of organo-derivatives of Group IIA elements from the metal and diethylzinc in benzene solution. Addition of ether, and filtration from solid matter yields a solution containing the

complexes having the formula $MZnEt_4$, (M = Ca, Sr, Ba).[54] The strontium complex has been obtained without the use of ether, and is described as a reddish-brown crystalline solid which decomposes at 170° with deposition of a metallic mirror, and evolution of diethylzinc.[55] Lithium tetramethylzincate has been obtained as a mono etherate by the reaction of methyl-lithium with an excess of dimethylzinc in ether solution and subsequent removal of all of the volatile material. The complex does not lose ether even when heated to 60° under vacuum.[56] The formation of complexes with organo-lithium reagent in tetrahydrofuran solution has been detected by the shift in the ultra-violet absorption of the lithium alkyl. A 1:1 complex was formed, and the reaction was found to be completely reversible;[57]

$$(R^- Li^+) + Et_2Zn \rightleftharpoons (RZnEt_2)^- Li^+$$

Phenyl-lithium adds reversibly to diphenylzinc in ether solution to give a 1:1 complex, which can be obtained solvent free by addition of xylene. The complex is a grey powder which decomposes at 164°; when recrystallised from dioxan it crystallises with four molecules of solvent. A less stable complex $Li_3Zn_2Ph_7$ can also be obtained, but this is highly dissociated in boiling ether, whereas the 1:1 complex $LiZnPh_3$ is essentially monomeric.[36]

Anionic complexes in which hydride ions act as ligands have been reported. Lithium hydride adds to diphenylzinc in ether solution to yield a 1:1 complex which crystallises as a mono etherate, $LiPh_2ZnH \cdot OEt_2$.

The complex is easily soluble in tetrahydofuran, but sparingly soluble in benzene, and, rather surprisingly, in ether.[57] In glycol ethers diethylzinc adds sodium hydride to yield a complex of unexpected stoichiometry. With "monoglyme" or "diglyme" as a solvent, a complex containing one mole of hydride for every two moles of diethylzinc is obtained, i.e. $Na(Et_2Zn)_2H$.[58] Attempts at isolating the complex by removal of solvent only results in decomposition, and the fact that the reaction would not take place in hydrocarbons, diethyl ether or tetrahydrofuran suggests that the chelating ethers are somehow involved in the bonding of the species in solution. The solution reacts with ethylene at 100°, and 450p.s.i. presumably to give sodium triethylzincate, since ethane is the only gaseous hydrolysis product.

Finally, the ethynyl complex $K_2\ Zn(C\equiv CH)_4$ and the complex cyanide $K_2Zn(CN)_4$ may be included since they contain zinc-carbon bonds. The former complex, prepared from potassium acetylide and the diammine of zinc thiocyanate[59] in liquid ammonia, functions as a 2:1 electrolyte in that solvent, and though it is neither sensitive to shock nor explosive when heated, it is rapidly hydrolysed by water. The latter complex, and the iso-nitrile complexes $Zn(CN)_2.2RNC$[60] are thought to be stabilised by some sort of mesomeric effect involving $d_\pi \rightarrow p_\pi$ bonding.

Due to the low polarity of the zinc-carbon bond, organo-zinc compounds have generally been thought of as being unable to form neutral

electron donor-acceptor complexes, indeed triethylamine and triethylphosphine have been reported not to react with diethylzinc.[60] Quite recently however, the first examples of well defined co-ordination complexes have been described. An indication of their existence was the observation of Frankland[61] in 1859, who noted that the use of dimethyl- or diethylether as a solvent greatly facilitates the formation of dimethylzinc from zinc and methyl iodide, but that complete separation from the product proved to be impossible. The Me_2O/Me_2Zn system has recently been reinvestigated by Thiele,[62] who has demonstrated the formation of a 1:1 complex. However by distillation of the 1:1 complex through an efficient fractionating column, a complete separation can be achieved. A series of liquid adducts with cyclic ethers was also reported. They could be distilled at atmospheric pressure without decomposition, but dissociated in benzene solution. The strength of the bond between the dimethylzinc and the ether molecules, and the possibility of co-ordination of a second ether molecule was found to increase from ethylene oxide to pentamethyleneoxide. Thus, only 1:1 complexes are formed with ethylene oxide and trimethylene oxide, whereas with tetrahydrofuran, and pentamethylene oxide 2:1 complexes are obtained. On steric grounds the reverse trend might have been expected, and it was concluded that the major influencing factor was the orientation and character of the oxygen orbitals, which vary with the ring size of the ether.

Dimethylzinc yields crystalline, and presumably chelate, 1:1

complexes with 1,4-dioxan and 1,4-thioxan. These cannot be distilled without decomposition. Aliphatic ethers like 1,2-dimethoxyethane yield liquid complexes containing two ether molecules to one zinc atom. The complexes can be distilled without decomposition, but they dissociate in benzene solution into a 1:1 complex and free ether.[63] Similar 1:1 complexes of di-arylzinc compounds with 1,4-dioxan have been reported,[64] and as already mentioned, the preparation of organo-zinc halides in donor solvents always affords the solvated species.[3,4,65]

With tertiary amines, dimethylzinc yields definite co-ordination complexes. One or two molecules of trimethylamine react with one molecule of dimethylzinc to give liquid adducts, the 1:1 complex distilling without decomposition at 84°. The 1:2 complex distills at 84·5°, suggesting that dissociation into the 1:1 complex and free amine takes place; such a process is definitely observed when the complex is dissolved in benzene. Triethylamine and pyridine afford only 1:2 complexes, which are a liquid and a crystalline solid respectively; both dissociate in benzene solution yielding the respective amine and the 1:1 complex. N,N,N′,N′- tetraethylethylenediamine, 2,2′-bipyridyl, and 1,10-phenanthroline react with dimethylzinc forming crystalline chelate compounds which may be sublimed without decomposition in vacuum.[66] The sensitivity of the co-ordination complexes to atmospheric oxygen is small compared to that of dimethylzinc, and it is reported that the chelate complexes can be handled in air for a short time.

The pale yellow chelate complex obtained from dimethylzinc and

2,2′-bipyridyl and the orange compound bipy $ZnEt_2$ have also been reported by Coates and Green[38] in connection with a study of a series of coloured bipyridyl complexes of beryllium alkyls. More recently the 2,2′-bipyridyl, and 1,10-phenthroline complexes of various organo-zinc compounds have been prepared, and have been the subject of an ultra-violet and visible spectroscopic study.[67] The colour of the complexes $L \cdot ZnR_2$ (L = 2,2′-bipyridyl or 1,10-phenanthroline) was found to depend on the electronegativity of the alkyl group, and the results for the bipyridyl complexes are given in Table I.

TABLE I

R	Colour	max(mμ)	logemax	E(Kcals/mole)
Pr^i	dark red	480	2·63	59
Bu^n	red	425	2·56	67
Et	orange red	420	2·77	67
C_6H_5	pale yellow	350	2·91	82
C_6F_5	colourless	309	4·15	92

The authors conclude that the observed spectra are due to a charge-transfer process involving donation of electrons from the ZnR_2 group into the lowest unoccupied molecular orbitals of the ligand. Unlike the beryllium complexes however, the intensity of the charge-transfer band increases with increasing electronegativity of R, and it is suggested that participation of the '3d' orbitals of zinc is important.

A similar sort of charge-transfer process is likely to be responsible for the colour of the bright yellow crystalline 1:1 complex formed from diethylzinc and isoquinoline.[68]

Finally, a series of complexes of di-n-butylzinc, diphenylzinc, and bis-pentafluorophenylzinc with a variety of donor ligands has been described.[69] Chelate complexes with 1,2-dimethoxyethane, N,N,N′,N′- tetramethylethylenediamine, 1,2-diphenylphosphinoethane, and O-phenylene-bis dimethylarsine were characterised, together with 1:2 complexes of ZnR_2 and triphenylphosphine. The effect of increasing electronegativity of R was shown to have a considerable effect on the stability of the complexes. Dibutylzinc forms a thermally very unstable complex with 1,2-dimethoxyethane (complete dissociation at 40° and 0.01mms Hg), and fails to complex with triphenylphosphine. Similarly the liquid complex with the chelating arsine slowly loses dibutylzinc when heated in vacuum. In contrast the phenyl and pentafluorophenyl derivatives form very stable complexes which are crystalline solids as opposed to liquid, and in all cases the melting points of the complexes increased in the order: $Bu_2Zn < Ph_2Zn < (C_6F_5)_2Zn$. The increasing electronegativity of R brings about a corresponding increase in electron affinity of the vacant orbitals of the zinc atom, causing it to become a stronger electron acceptor.

"Internal" co-ordination complexes.

In recent years a large amount of work has been done to try to

determine the factors affecting the formation of molecular addition compounds. The inorganic and organometallic compounds of the Group III elements have attracted most attention in this respect, and the very considerable amount of data have been the subject of two review articles.[70,71] The most important factors contributing to the formation, and to the stability of molecular complexes are now well understood. What is not so clearly understood is the relative importance, and nature of the factors involved in determining the degree of polymerisation of so-called "internal" co-ordination complexes. The term applies to the compound produced when a molecular complex, usually of an organometallic compound with a ligand containing 'acidic hydrogen', undergoes irreversible decomposition with evolution of one or more moles. of hydrocarbon, e.g.

$$Me_3Al\cdot NMe_2H \longrightarrow CH_4 + (Me_2AlNMe_2)_n$$

The product, if monomeric, would contain a co-ordinatively unsaturated metal atom attached to a donor atom of enhanced donor character, due to the dipole, e.g. $Al^{\delta+}—N^{\delta-}$. In fact these compounds generally associate to form oligomers where n = 2,3, or 4, and polymers. It is the unpredictability of the degree of association which is perplexing, and will continue to be so until more data are available.

Clearly, the most important characteristic of these compounds is the molecular weight, and again it is the hydrido- and organo-derivatives of the Group III elements which have received the most attention.

Some of the "internal" complexes which have been reported in the literature are discussed below.

The adduct of trimethylboron with ammonia can be thermally decomposed under pressure to yield aminodimethyl borane $Me_2B.NH_2$, and methane.[72] Co-ordination saturation can be achieved by dimerization to give a crystalline solid, or it can remain as a monomeric gas; a reversible monomer-dimer equilibrium can be observed in the gas phase at room temperature. The ability of this type of compound to remain as a monomeric species is confined to boron, and several such examples are known e.g. $Me_2B.NMe_2$,[73,74] $Me_2B.NHMe$,[75] Me_2BOMe,[74,76] and Me_2BSMe.[77] Similarly trisdimethylaminoboron $(Me_2N)_3B$,[78] and methyl borate $(MeO)_3B$ are monomeric. The existence of some of these boron compounds as monomers has been ascribed to $p_\pi \rightarrow p_\pi$ bonding in the B-N, and B-O bonds.[70] Thus when boron is attached to a donor atom from the second or later rows of the periodic system, conditions for orbital overlap are unfavourable and polymers result, e.g. $Me_2B.PMe_2$ is a cyclic trimer, and the compound $Me_2P.BH_2$ forms exceptionally stable cyclic trimers and tetramers.[76] The latter degree of association may be due to a steric effect similar to that which causes association of $H_2B.NHMe$,[79] and $H_2B.NH_2$[80,81] to cyclic trimers, a polymeric form of the latter also being known.[82] The monomeric compound $Me_2B.SMe$ appears anomalous, but the lack of association has been ascribed to the weak σ-bonding power of sulphur to boron being insufficient to hold a polymer together.[70]

The compounds $Me_2M.NMe_2$ (M = Al,[83] Ga,[84] In,[85] Tl[85]) are all dimeric in either the vapour phase or in benzene solution, the first three existing in both crystalline and glassy forms. It is believed that the latter consist of cyclic oligomers or polymers.[86] A crystalline dimeric compound, diphenylaminodimethylaluminium has been reported together with the dimers $(Me_2M{\cdot}PPh_2)_2$, (where M = Al, and Ga) and the arsenic analogues $(Me_2M{\cdot}AsPh_2)_2$ (where M = Al, Ga, and In).[87] Both the dimers $(Me_2Al{\cdot}PPh_2)_2$ and $(Me_2AlAsPh_2)_2$ absorb trimethylamine reversibly in contrast to the cyclic trimer $(Me_2Al{\cdot}PMe_2)_3$.[83] This is due to the fact that donor atoms bound to phenyl groups are less powerful donors than those attached to alkyl groups.

Trimethylgallium and trimethylindium react with dimethylphosphine and dimethylarsine at elevated temperatures to give compounds exemplified by $(Me_2Ga.PMe_2)_x$, which are polymeric glasses in the condensed state at room temperature but cyclic trimers in benzene solution. Phenylphosphine and phenylarsine gave compounds exemplified by MeAl·AsMe, which are nonvolatile polymers.[88] Analogous aluminium compounds formed from triphenyl-aluminium and aniline are crystalline tetramers, $(PhAlNPh)_4$, but when ortho substituents are present on the amine, the crystalline dimers $(Ph_2AlNHAr)_2$ are obtained.[89] Preliminary X-ray structural examination indicates that the tetramers have a cubic structure having twelve essentially equal Al-N bond lengths.[90]

Dimethylaluminium methoxide is a cyclic trimer[83] like the indium

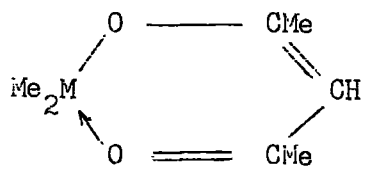
analogue,[85] whereas the gallium[91] and thallium[92] analogues are dimeric. Diethylaluminium methoxide is also trimeric, but diethylaluminium ethoxide,[93] and t-butoxide are dimeric. The aluminium compounds illustrate the steric factor governing association, there being less steric interference between bulky substituents in a dimer than in the corresponding trimer. The same effect is presumably operative when the trimer $(Me_2Al\cdot PMe_2)_3$ is reduced to a dimer when the dimethylphosphino residue is replaced by a diphenylphosphino group.

The compounds $Me_2M.SMe$ (M = Al,[83] Ga,[91] In,[85] Tl[85]) are all dimers stable in the vapour phase, although the first two are depolymerised by trimethylamine. It has been suggested that in the latter two compounds, the internal co-ordination is strengthened by $d_\pi - d_\pi$ interaction.[71] The reason that no higher polymers than dimers have been observed for the thio-derivatives and some seleno-analogues, is probably the fact that atoms of high atomic number undergo valence angle deformation much easier than lighter elements.[95] The same factor also probably accounts for the dimers $(Me_2M^{III}NMe_2)_2$[86] and trimers $(Me_2M^{III}PMe_2)_3$[88] existing as glassy solids. The valence angle deformation is gradually relieved with the formation of larger cyclic oligomers and polymers. The tetrameric dimethylaluminium cyanide and its gallium, and indium analogues[96] provide another illustration of the importance of resistance to valence angle deformation determining the extent of polymerisation.

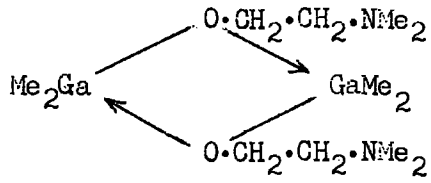
The remaining factors affecting the degree of polymerisation are the

entropy effect, and the nature of the reaction intermediate, as mentioned below. The former effect will always favour dimers as the associated species since the number of molecules per unit mass will be at a maximum. It has been suggested[88] that the latter effect might be most important. Polymeric intermediates formed by an intermolecular condensation would favour the observed polymer, tetramer or trimer as the isolated species. Those reactions which go through a monomeric intermediate formed by an intramolecular condensation, would favour the dimer as the associated species.

Several 'internal' co-ordination complexes, in which the donor atoms are part of a chelate group, have been described. Trimethylgallium,[91] -indium,[85] and -thallium[97] all react with acetylacetone to give methane and chelate monomers.



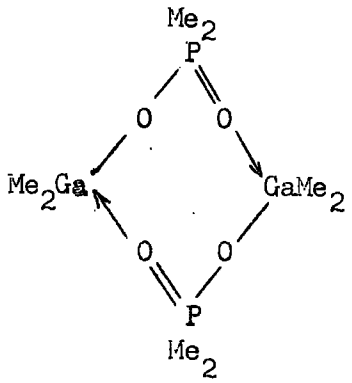
Trimethylgallium also reacts with salicylaldehyde with the elimination of methane and formation of a similar chelate monomer. With dimethylethanolamine however, which might be expected to form a chelate compound, a dimeric product is obtained which forms a dimethiodide with methyl iodide.[91] The complex is formulated as,



A similar dimer is obtained from triethylaluminium and 2-ethoxyethanol, the ethereal oxygen atoms not being involved in co-ordination.[93]

Some acetoxyboranes $R_2BOOCCH_3$ have been assigned monomeric structures on infrared evidence. The lowered carbonyl stretching frequency indicated the presence of a chelating acetate group. The fact that the relative intensity of the band due to ν(C-O) remained constant over a large concentration range in solution suggested the absence of an acetate bridged dimer.[99]

A similar infrared spectroscopic study[100] of some dimethyl-gallium and -aluminium derivatives of oxy- and thio- acids has shown that the dimeric acetates contain bridging acetate groups in an eight-membered cyclic structure. The dimeric dimethylphosphinates, diphenylthiophosphinates, and benzenesulphinates have also been formulated eight-membered ring structures as a result of similar molecular weight and infrared studies, and the cyclic structure of the phosphinate, $Me_2GaO_2PMe_2$, has been confirmed by an X-ray single crystal analysis.[98]

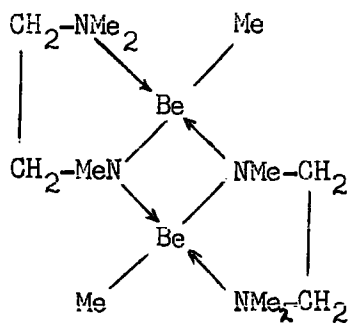


In contrast, the dimethyldithiophosphinates were found to be chelate monomers.

"Internal" co-ordination complexes of organo-derivatives of Group II elements have apparently been of much less interest than their Group III analogues. This is surprising since even the associated products could be co-ordinatively unsaturated, and consequently the formation of compounds containing metal atoms of unusual co-ordination number is to be looked for.

Dimethylberyllium reacts with dimethylamine eliminating methane and forming the volatile cyclic trimer $(MeBe{\cdot}NMe_2)_3$, which is formulated as having a six-membered Be-N ring; the beryllium atom is necessarily three co-ordinate. Methylamine reacts similarly to give an involatile polymer, as does methane-thiol. Methanol reacts rapidly to give the dimeric alkoxide $(MeBe.OMe)_2$, which disproportionates into dimethylberyllium and beryllium methoxide at 120°. [101] N,N,N,′-Trimethylethylenediamine with dimethylberyllium yields methane and a

crystalline solid $MeBeN(Me)CH_2CH_2NMe_2$, which is dimeric in benzene and has been formulated with the following structure.



Ethylendiamines with two or more acidic hydrogens give polymeric products.[38] Diethylberyllium reacts with N-methylhydrazine to yield a solid compound $EtBeN(Me)NH_2$, which is tetrameric in benzene and is said to be associated through nitrogen and ethyl bridges.[102] bis-Diphenylaminoberyllium,[103] formed from diethylberyllium and diphenylamine, is insoluble in hydrocarbons and presumably polymeric.

Ethylmagnesium ethoxide, a volatile solid, has been described by Birnkraut,[104] but the molecular weight of the compound was not determined. However, the same species, formed when an ethereal solution of diethylmagnesium is treated with a deficiency of oxygen, has been shown by vapour pressure measurements of the ether solutions to be a trimer.[105] n-Butylmagnesium isopropoxide has been obtained as a

colourless oil, soluble in benzene, but the molecular weight of the species was not determined.[106]

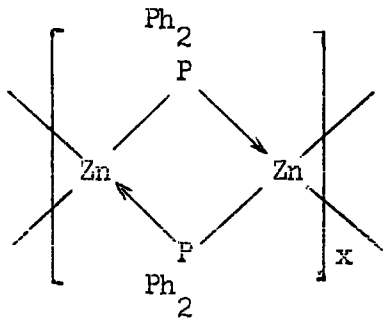
Dimethylzinc reacts with a deficiency of oxygen to yield methylzinc methoxide, MeZnOMe.[107,108] The same compound may also be obtained from dimethylzinc and methanol, an excess of the latter yielding zinc methoxide.[109] The molecular weight of the methylzinc methoxide, a colourless crystalline solid, was not determined. Similar data are lacking for the more recently prepared ethylzinc isopropoxide, a colourless solid which is soluble in heptane.[110] Acetoxime in excess reacts rapidly with diethylzinc in ether solution to give an insoluble presumably polymeric compound $Zn(ON{=}CMe_2)_2$. When a 1:1 ratio of reactants is used ethylzinc acetoximate is obtained. It is extremely soluble in ether, but can be obtained as a crystalline solid from very concentrated solutions. No molecular weight data are available.[111]

The acidolysis of zinc alkyls by p-toluidine has been the subject of a kinetic study, but the intermediates $RZn{\cdot}NHC_6H_4{\cdot}CH_3$ were not isolated.[112] Organo-zinc amides have recently been prepared and isolated as either liquids e.g. $EtZnNEt_2$, or crystalline solids e.g. $PhZnNPh_2$, but no molecular weight data are available.[113]

Diphenylzinc reacts slowly with an excess of phenylacetylene in ether solution to yield the insoluble compound $Zn(C{\equiv}CPh)_2$.[114] The

compound may be polymeric, the multiple bond providing a source of electrons to form a π-complexed polymer. If this is the case, the co-ordination is not very strong since it is easily soluble in the strong donor solvents, tetrahydrofuran, and dimethylformamide.[115]

Diethylzinc and a two-fold excess of diphenylphosphine slowly react in paraffin solvents to yield bis-diphenylphosphino-zinc.[116] The compound is insoluble in hydrocarbon solvents, ether, dioxan, and tetrahydrofuran, and is presumably polymeric, having the following structure.



The zinc amides $Zn(NH_2)_2$,[117] $Zn(NH{\cdot}Et)_2$,[60] and $Zn(NEt_2)_2$[117] obtained from diethylzinc and the corresponding amine all probably have similar polymeric structures.

Some organo-metallation reactions.

The first examples of reactions of this type were those of the Grignard reagents; these have proved particularly useful in syntheses,[23] some of the more well-known examples being reactions with compounds containing $\rangle C{=}O$ and $-C{\equiv}N$ groups, e.g. the carbonation by carbon dioxide,

$$CO_2 + MeMgX \longrightarrow MeC(=O)-OMgX \xrightarrow{H_2O} MeC(=O)-OH$$

the formation of alcohols from aldehydes and ketones,

$$RCHO + MeMgX \longrightarrow R-\underset{Me}{CH}-OMgX \xrightarrow{H_2O} RMeCHOH$$

$$RRCO + MeMgX \longrightarrow R-\underset{R}{CMe}-OMgX \xrightarrow{H_2O} RR\underset{Me}{C}OH$$

and the formation of ketones from nitriles,

$$RCN + MeMgX \longrightarrow R-\overset{Me}{C}=NMgX \xrightarrow{H_2O} RMeCO$$

Recently Lappert[118] and other workers[119] have commented on the generality of this reaction, and the fact that it is becoming evident that organo-metallation is merely an example taken from a wider class, in which derivatives of metals or metalloids act as 1,2-dipolarophiles with respect to unsaturated substrates. Some examples of other types of metallation reaction are briefly discussed below.

a. Hydrometallation

The addition of dialkyl aluminium hydrides to alkynes followed by hydrolysis, is a well-known possibility for a partial or complete reduction of acetylene and its homologues. The reaction allows a smooth synthesis of many pure cis- 1,2-disubstituted ethylenes.[120] Dialkylaluminium hydrides also add to other multiple bonds, and are

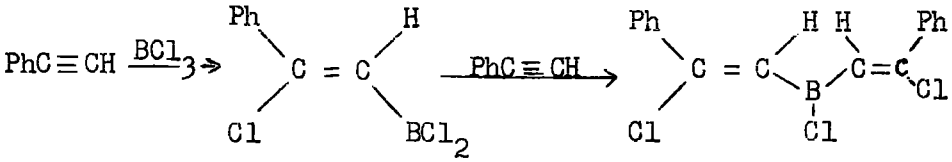
convenient reducing agents for the groups -CHO, >C=O, -COOR, -C≡N and others.[121] A more recently discovered example of this type of reaction is the hydroboration of olefinic and acetylenic compounds.[122] The reaction intermediate from tetramethyldiborane and methyl cyanide has been isolated, and identified as the dimeric dimethylethylideneaminoborane $(MeCH{=}NBMe_2)_2$.[123] It exists in cis and trans isomeric forms. Trialkyltin hydrides have been shown to add to compounds containing -CHO, >C=O, and -C=N- groups,[124] e.g.

$$Et_3SnH + PhCHO \longrightarrow Et_3SnOCH_2Ph$$

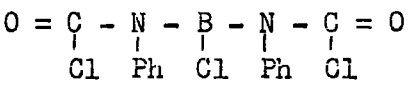
The 1:1 adducts formed from the reaction of similar hydrides with phenylisocyanate and phenylisothiocyanate are formulated as having structures in which addition has taken place across the N=C bond.[124a]

b. Halogenometallation

Boron trichloride reacts with phenylacetylene in two stages,[125] e.g.



The chloride has also been shown to react with phenylisocyanate to yield the substituted aminoborane,[126]



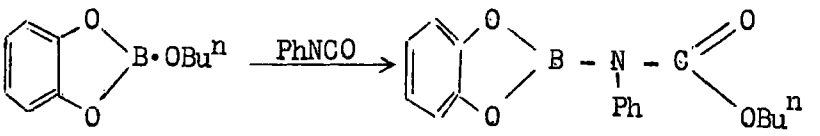
c. Alkoxymetallation

A new series of compounds, the N-stannyl-carbamates has been prepared by the addition reaction of trialkyltin alkoxides with organic isocyanates.[127] For example, tributyltin methoxide and 1-naphthylisocyanate react at room temperature to give methyl N-tributylstannyl- N-1-naphthylcarbamate, the addition therefore having occurred across the N=C bond. Tributyltin methoxide also undergoes addition reactions with aldehydes, the product not being particularly stable as the reaction is reversible.[128] A similar reaction occurs with aldehydes and bis(trialkyltin) oxides, and it was suggested that such reactions would be common to alkoxides of many other metals. The formation of N-mercuricarbamates from mercuric alkoxides and aryl isocyanates has recently been reported,[129] e.g.

$$Hg(OMe)_2 + 2PhNCO \longrightarrow Hg(NPh\cdot COOMe)_2$$

Phenylmercury methoxide likewise adds exothermically to phenyl isocyanate giving methyl N-phenyl-N-phenylmercuricarbamate PhHg.NPh.COOMe.

Finally, the first example of alkoxyboration[130] has been effected by the reaction of phenylisocyanate with n-butoxy-1,3,2-benzodioxaborole,



d. Aminometallation.

A series of monoaminoboranes $R_2B.NR^1R^2$, and bis-aminoboranes $R.B(NR^1R^2)_2$ undergo aminoboration[130] reactions with phenylisocyanate to yield mono-, or bis-ureidoboranes $>B.NPh.\underset{\underset{O}{\|}}{C}.NR^1R^2$. Similarly, aminostannylation reactions occur when trialkyltin amides react with carbon dioxide, carbon disulphide, ketene, organic isocyanates, and several other unsaturated compounds.[131,132]

Finally, organozinc amides have been shown to undergo aminozincation[113] reactions with phenylisocyanate, and phenyl isothiocyanate, carbon dioxide and carbon disulphide. With the former two reagents, addition is regarded as taking place across the -C=N bond.

e. Organometallation

The Grignard reactions mentioned previously have also been shown to occur with other less reactive organo-metallic derivatives. This has found application in the preparation of ketones from acid chlorides, where Grignard reagents have a tendency to react further providing, on hydrolysis, the tertiary alcohol. The less reactive organo-zinc and -cadmium compounds afford only the ketones,[23] although the formation of

tertiary alcohols from α-nitro ketones and organo-cadmium compounds has recently been reported.[133]

The relative Grignard activity for some organo-metallic derivatives has been established by Gilman[134] as; $RMgX > R_3Al > R_2Zn > R_2Cd$. Thus although Grignard reagents and organo-aluminium compounds are readily carbonated, diethylzinc only reacts under pressure at 160°.[135] Di-p-tolylzinc is rather more reactive yielding, on hydrolysis in one experiment, 21% of p-toluic acid when carbon dioxide was bubbled through a refluxing xylene solution.[134] Addition to the $>C=O$ group occurs at much the same relative rates, e.g. with benzophenone at room temperature, and in ether solution, triphenylaluminium yields, on hydrolysis, 16% triphenylcarbinol. The reaction with diphenylzinc only proceeds to the same extent in refluxing xylene solution.[134] Diethylzinc and acetaldehyde after refluxing, yield a white crystalline solid which has not been isolated. Hydrolysis of the product affords methylethylcarbinol.[136]

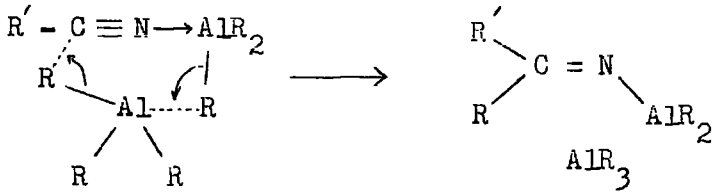
Triphenylaluminium, diphenylzinc, and diethylzinc are all reported to react with phenylisocyanate at room temperature, the yields of the anilides being greater with the aluminium compounds.[134] Aliphatic isocyanates react exothermically with triethylaluminium, giving on hydrolysis, good yields of the corresponding priopionamide. The addition is assumed to take place across the C=O bond although no intermediates were isolated,[137] and there is no evidence about their structures.

Small yields of ketones have been obtained from benzonitrile and tri-p-tolylaluminium, and di-p-tolylzinc.[134] The reactions only proceed at high temperatures e.g. refluxing xylene solutions, as does that between trimethylaluminium and benzonitrile. When present in a 1:1 molar ratio, the latter begin to react at 85°, reaching a maximum reaction rate at 140°. The authors regard the reaction as a two stage process,

a. complex formation, $R'.C{\equiv}N{\rightarrow}AlR_3$, which is exothermic and,

b. the formation of $\begin{matrix} R' \\ \diagdown \\ \quad C = NAlR_2 \\ \diagup \\ R \end{matrix}$, which is slow and rate determining.[138]

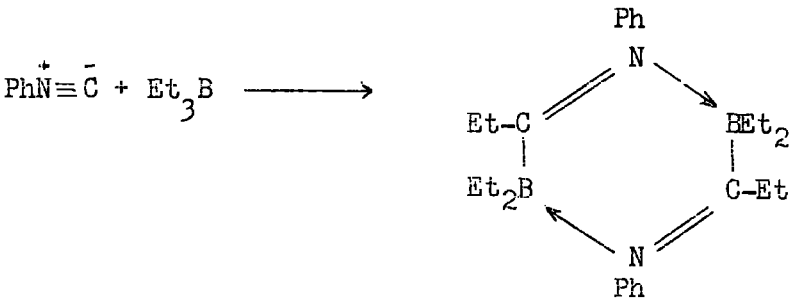
This would seem to be the case since other workers have shown that by using a 2:1 molar ratio of triethylaluminium to benzonitrile, very high yields of propiophenone can be obtained by refluxing the reactants in benzene solution. A mechanism involving nucleophilic attack by the migrating group, on the carbon of the nitrile has been suggested,[137]



however, no intermediates were isolated.

The primary interest in the reactions discussed above has usually been applicability for syntheses, and reaction intermediates have not been isolated. Details of molecular complexity of intermediates may provide useful information for kinetic studies on analogous systems, this is particularly true of Grignard reactions. In only very few instances are such data available.

The dimeric compound $(Ph_2MeC\cdot O\cdot AlMe_2)_2$ has been isolated from the reaction between benzophenone and trimethylaluminium.[139] The latter and other aluminium alkyls also react with benzonitrile with the formation of benzylideneamino derivatives exemplified by $(PhMeC{=}N\cdot AlMe_2)_2$. The intermediates are dimeric, and the proton magnetic resonance spectra support a nitrogen-bridged structure for the dimers, with <u>cis</u> and <u>trans</u>-isomers present in the case of the compound formulated above.[140] Triethylboron adds readily to phenylisocyanide to yield a six-membered cyclic dimer.[141]



A similar compound has been obtained by reaction of triethylboron with ethylisocyanide,[142] although trimethylboron and t-butylisocyanide yield, rather surprisingly, the monomer $Me_3CN{=}CMe\cdot BMe_2$.[143]

EXPERIMENTAL.

Experimental methods and apparatus.

Nitrogen supply.

The nitrogen used was purified by passing the gas through a furnace containing reduced wire-form copper at ca.400°, then through a furnace containing 'BTS' catalyst at ca.100°, and finally through two traps at -196°. The 'oxygen-scrubbers' were periodically regenerated with hydrogen.

Glove box.

Samples for analysis and infrared spectra were transferred and manipulated under a nitrogen atmosphere in a glove box of the conventional type (Lintott, IIB). The nitrogen was purified as described above, and a small pump fitted inside the box provided a continuous recycling of nitrogen through the purification system when the box was not in use. A tri-isobutylaluminium bubbler included in the purification system was found to give very dry, oxygen-free nitrogen, but great difficulty was encountered in trying to remove aluminium oxide 'smoke' from the gas stream.

Vacuum system.[144]

A vacuum system (Photograph 1.) was constructed for the manipulation of many of the compounds used in the present investigation. It consisted of three sections: a, storage section; b, gas measuring section; and c, fractionation section.

a. The storage section had large (3 litre) bulbs for the storage of gases, e.g. dimethylamine, and smaller (100 c.c.) bulbs for the storage of low boiling liquids, e.g. dimethylzinc. Each storage bulb was isolated from the main manifold by a mercury float valve.

b. The gas measuring section consisted of a large bulb and cold finger (approx. 4 litres), connected by a mercury float valve to a smaller bulb and cold finger (approx. 400 c.c.). A single limb manometer was connected to the smaller section so that either a small volume of gas could be measured with the large bulb isolated, or a larger amount in the combined sections. The bulbs were calibrated to a reference mark on the manometer by condensing in known amounts of carbon dioxide.

Calibration for measuring system

Combined volume of large and small bulbs	=	4512 c.c.
Volume of small bulb	=	389·6 c.c.
Internal radius of manometer	=	0·520 cm.
For 1cm. drop on manometer the increase in volume	=	0·849 c.c.
For 1cm. drop on manometer the rise in the reservoir	=	0·0304 cm.

The bulbs were used to measure condensible gases and the bulk of partly condensible ones, e.g. methane. The remainder of the partly condensible gas could be measured using a Töpler pump and gas burette, which was fitted in the line.

c. The fractionation section consisted of three U-traps connected

by mercury float valves, each one being independantly connected to the main manifold through a float valve. A single inlet point through an S·19 socket was fitted, and evacuation was accomplished using a rotary oil pump and a mercury diffusion pump. A rotary oil pump was also used for the secondary vacuum line controlling the mercury reservoirs.

Reactions were usually done in a double Schlenck tube, the compounds being purified either by recrystallization or sublimation in one of the limbs. Sealed tubes, when reactions were complete, were opened when the tube was attached through a suitable adaptor to the vacuum line, so that the volume of gas produced during a reaction could be measured conveniently. The tubes were then sealed again under vacuum, transferred into a glove box where they were opened, and the contents scraped into a small two-necked flask. This was removed from the glove box, and the solid compound transferred under a flow of dry nitrogen into a double Schlenck tube where it was subsequently purified, for example by crystallization.

Analyses

Carbon and hydrogen analysis.

Analyses for these elements were carried out in this department by various members of the analytical staff. Relatively few of the compounds prepared in the course of this work were sufficiently air-stable to permit analysis by conventional combustion methods.

Hydrolyses.

The great majority of the compounds prepared were readily hydrolysed by moisture causing cleavage of a zinc-carbon bond and corresponding evolution of hydrocarbon. This was used as a basis for analysis, a weighed sample being hydrolysed under controlled conditions in a small two-necked flask attached to the vacuum line. The compounds were hydrolysed initially with a few c.c. of 2-methoxyethanol followed by dilute sulphuric acid, run into the flask through a dropping funnel. The liberated gases, after fractionation, were measured in the gas burette using the Töpler pump. In the case of phenyl-zinc compounds, hydrolysis was accomplished by allowing the compound to stand in contact with dry hydrogen chloride at approximately 45° for about an hour. The benzene produced was measured in the small gas measuring bulb.

Zinc analysis.

The organic matter in the hydrolysate, obtained as described above, was destroyed by boiling with a mixture of nitric and sulphuric acids, and finally the zinc was determined by the 'EDTA' method described in Part 1 of this thesis.

Amines.

Aliphatic amines were determined by the Kjeldahl method. After cautiously hydrolysing a weighed sample of compound with concentrated hydrochloric acid, the hydrolysate was transferred to a small Kjeldahl

flask, made alkaline with strong caustic soda, and boiled. The amine was steam distilled into a flask containing a known amount of standard acid, and the excess titrated with standard alkali solution.

Diphenylamine was determined by ether extraction of an alkaline hydrolysate, and after removing the ether under vacuum, the diphenylamine was sublimed onto a previously weighed 'cold finger'.

Phosphorus

This was determined as phosphate by precipitation with quinoline molybdate.[144a] A suitable weight of sample was combusted in an 'oxygen-flask' as described in Part I of this thesis. After absorbing the combustion products in dilute aqueous acid and diluting to a known volume a suitable aliquot was taken and a little citric acid added. This prevented interference from silicate ions. The solution was boiled and the phosphate precipitated by the slow addition of quinoline molybdate solution. The mixture was allowed to cool and the precipitate filtered on a paper pulp pad. It was washed until completely free of acid and then quantitatively transferred to the original flask. An excess of standard sodium hydroxide was added and the precipitate dissolved by shaking the stoppered flask. The excess alkali was determined by back-titration with standard (0·1N) hydrochloric acid using phenolphthalein as an indicator.

Molecular weight measurements.

Molecular weights were determined where possible cryoscopically in

benzene. The benzene, of analytical reagent purity, was dried over sodium wire and calibrated (in respect of its freezing point constant) using freshly sublimed biphenyl. The usual Beckmann apparatus was used, and since most of the compounds were air-sensitive, a slow current of dry nitrogen was passed through the apparatus during each determination. This did not cause a significant loss of solvent by evaporation.

Infrared spectra

Infrared spectra were recorded on a Grubb-Parsons Spectromaster prism-grating spectrometer. The spectra of solid compounds were recorded as Nujol mulls between potassium bromide discs; those of liquids and gases were recorded using a potassium bromide liquid cell, and 7cm. gas cell respectively.

Nuclear magnetic resonance spectra

These were recorded on an A.E.I. R.S.2 spectrometer operating at 60 Mc./s. Samples were dissolved in benzene or deutero-toluene, with tetramethylsilane as a reference compound. The sample tubes were filled by syringing the sample solution through a constriction, against a counter current of nitrogen. They were then cooled to approximately -100°, evacuated, and a suitable quantity of tetramethylsilane condensed in. Finally, the tubes were sealed-off at the constriction, under vacuum.

Preparation of starting materials.

Methylmercuric chloride

145

This was prepared by a method already described in the literature. Methylaluminium sesquichloride and mercuric chloride reacted in methylene chloride solution to yield methylmercury chloride in almost quantitative yield.

$$Me_3Al_2Cl_3 + 3HgCl_2 \longrightarrow 3MeHgCl + Al_2Cl_6$$

A 5-litre, three-necked flask was fitted with a heavy stirrer, a condenser, a dropping funnel, and a nitrogen inlet and outlet. Mercuric chloride (698gms.) and methylene chloride (1500 c.c.) were placed in the bottom of the flask, and the apparatus purged with nitrogen. Methylaluminium sesquichloride (185gms.) in methylene chloride (250 c.c.) was slowly added through the dropping funnel over a period of about forty minutes, the solution being stirred continuously. The solvent refluxed under the heat of reaction, and was kept refluxing overnight. The slight excess of methylaluminium sesquichloride, and aluminium chloride were hydrolysed by the slow addition of 2% aqueous hydrochloric acid (1250 c.c.). The aqueous layer was separated, and washed with methylene chloride (200 c.c.). This was separated and the organic layer added to the main bulk of methylene chloride which was removed by distillation, and the crude methylmercury chloride pumped dry under vacuum. The product was

purified by vacuum sublimation, and was obtained as white shining plates, m.p. 172-173°. (Lit.,[146] 173°). The yield was 625gms. (97%).

Dimethylmercury.

This was prepared by a modification of the method of Gilman and Brown[147] whose method involved the reaction of mercuric chloride with a two molar excess of Grignard reagent. A considerably improved yield has been obtained in the present method by using methylmercuric chloride and an equimolar amount of methylmagnesium bromide.

Magnesium turnings (44gms.) and dry ether (2 litres) were placed in a 5-litre three-necked flask. The flask, which had previously been purged with dry oxygen-free nitrogen, was fitted with a heavy stirrer, a dropping funnel, and a 'cold finger' maintained at -78°. The dropping funnel was cooled by surrounding it with powdered solid carbon dioxide, and filled with a solution of methyl bromide (173 gms.) in ether (400 c.c.). The reaction was initiated with a few drops of ethylene dibromide, and the methyl bromide solution added at such a rate that the solution refluxed gently. The mixture was stirred continuously, and was allowed to reflux for a further thirty minutes after addition had been completed. The concentration of the Grignard reagent was not determined, and a 95% conversion of methyl bromide was assumed when calculating the amount of methylmercuric chloride required for the subsequent reaction.

The 'cold finger' was replaced by a Soxhlet extracter fitted with

a sintered disc, and having a water condenser fitted to the top. Methylmercuric chloride (435gms.) was placed on the sintered disc and caused to be extracted by refluxing the mixture for a total of thirty hours. In order to ensure complete reaction, the solution was concentrated by distilling off about 1500 c.c. of ether; this was returned to the main reaction flask later. The mixture was hydrolysed with aqueous acid (500 c.c.), the ether layer separated, and the aqueous layer washed with ether (3 x 50 c.c.). The washings were added to the main bulk of ether, which was dried by standing over anhydrous magnesium sulphate. The ether was distilled off through an efficient fractionating column until pieces of porous pot in the distillation flask began to float on the surface of the liquid. The distillation apparatus was allowed to cool, a smaller fractionating column fitted, and after distilling of the remaining ether, the dimethylmercury was distilled as a clear colourless liquid, b.pt. 93°. (Lit.,[10] 92·0°). A total of 342 gms. of dimethylmercury were obtained (87% yield).

Dimethylzinc.

Dimethylzinc was prepared by an alkyl exchange reaction between zinc metal and dimethylmercury. The reaction was carried out in an all-glass apparatus, which consisted of a 250 c.c. reaction flask to which was attached an efficient fractionating column, and a constricted side-arm. A side-arm at the top of the column led to a 'cold-finger' and a mercury cut-off, which could be raised or lowered when taking off

a fraction from the top of the fractionating column. The apparatus was thoroughly purged with dry oxygen-free nitrogen, and the reaction carried out under such an atmosphere.

Zinc filings (70gms. approximately 100% excess), and a few crystals of methylmercuric chloride (as catalyst) were placed in the round bottomed reaction flask and dimethylmercury (121gms.) was syringed through the constricted side-arm against a counter-current of nitrogen. The flask and contents were cooled to -78°, and the side-arm sealed off. The reaction mixture was heated so that the dimethylmercury began to reflux, and after approximately thirty minutes the temperature of the liquid refluxing at the top of the column was 44°. Fractions boiling between $43{\cdot}5^{\circ}$ and $44{\cdot}0^{\circ}$ were removed from the apparatus at regular intervals, the reaction being completed after seven hours. The yield of dimethylzinc was 44gms, corresponding to a yield of 90%, based on the amount of dimethylmercury used. The dimethylzinc was distilled onto the vacuum line for storage, and no further fractionation was found to be necessary. The vapour pressure at 0° was found to be 123·9mm. (Lit.,[148] 125mm.).

Diethylzinc

This was prepared by the method described by Noller,[2] and consisted of the preparation and thermal disproportionation of ethylzinc iodide.

A zinc/copper couple was prepared in a 500 c.c., three necked flask

by heating a mixture of zinc dust (120gms.), and cupric oxide powder (10gms) in an atmosphere of hydrogen. The temperature was increased until the metal just began to fuse, and this temperature was maintained until all of the water vapour had been driven out of the exit gas lead. The flask was allowed to cool, and the hydrogen atmosphere replaced by one of nitrogen. While the flask was continuously purged with nitrogen, it was fitted with a dropping funnel, a condenser, and a heavy stirrer.

A mixture of ethyl iodide (78gms.) and ethyl bromide (54gms.), was added to the zinc-copper couple, and the mixture refluxed under an atmosphere of nitrogen. After approximately twenty minutes the reaction started, and proceeded quite vigorously. The mixture was refluxed for a further sixty minutes, and the flask allowed to cool to room temperature. The contents of the flask solidified, probably due to the reformation of ethylzinc iodide and bromide. The stirrer was removed from the flask, a distilling head fitted, and the diethylzinc obtained by heating the ethylzinc halides under reduced pressure, a trap cooled to -78° being used to freeze the product out. The yield of diethylzinc was 51gms.(85%).

The frozen product melted to give a clear colourless liquid, but after approximately twenty minutes the liquid became dark-grey, probably due to finely divided metallic zinc. The diethylzinc was distilled at atmospheric pressure, b.pt. 118° (Lit.,[29] $117{\cdot}6^{\circ}$) to give again a clear

colourless liquid. This again became cloudy due to the precipitation of metallic zinc and it was concluded that the material was light sensitive. Although similar behaviour has been observed with the higher alkyls,[28] the light sensitivity of diethylzinc has not been reported previously. The product was distilled onto the vacuum line where it was stored in a vessel wrapped in black paper.

Diphenylzinc.

This compound was prepared by a previously described method,[13] and involved a metal-aryl exchange reaction between zinc and diphenylmercury.

Diphenylmercury (30gms.) and zinc dust (24gms.) were placed in a two-necked flask with dry xylene (150 c.c.), and the flask purged with nitrogen. The flask was fitted with a nitrogen inlet, and an outlet at the top of the condenser. The mixture was heated until the xylene began to reflux, and the temperature maintained for several hours. The hot xylene solution was then filtered under an atmosphere of nitrogen, and the clear solution cooled in an ice-salt mixture. The colourless crystals of diphenylzinc were filtered and washed several times with hexane before pumping dry under vacuum. The yield of diphenylzinc was 10gms.(80%), and the m.p. 105-106° (Lit.,[13] 105-106°).

Dimethylamine.

The N-nitrosamine was already available, and the free amine was obtained by hydrolysis of the former.

Dimethyl-N-nitrosamine (10gms) were refluxed for twelve hours with

concentrated hydrochloric acid (35 c.c.), and after distilling off most of the acid, the solution of the amine hydrochloride was allowed to fall onto potassium hydroxide pellets. The latter were contained in an evacuated flask, and the free amine was condensed onto caustic pellets in a receiving flask cooled to -78° . Finally, the amine was distilled onto the vacuum line through two traps cooled to -80°, and the volume measured. The volume of dimethylamine was found to be 2,490 Nc.c. corresponding to an 85% yield. The vapour pressure at -23° (melting carbon tetrachloride) was found to be 176·1 mm. (Lit.,[149] 174·9 mm.)

Dimethylphosphine.

A sample of impure phosphine was available, and this was purified by fractionation through two traps cooled to -78°, into two traps cooled to -96°. A small amount of the dimethylphosphine which passed through the latter trap was discarded, and the remainder transferred to the storage section of the vacuum line. The vapour pressure at 0° was measured, and found to be 338·2 mm. (Lit.,[150] 338 mm.).

The remainder of the compounds used during the present investigation were commercial products which were purified either by distillation, vacuum sublimation, or recrystallization.

The solvents which were used were dried and stored over sodium wire, or in the case of ethers and some amines, distilled from lithium aluminium hydride and then stored over sodium. Pyridine cannot be

purified by this method and was refluxed with solid caustic soda, and, after fractionating through an efficient column, stored over sodium hydroxide pellets.

Reactions with amines.

Reaction of NNN′N′-tetramethylethylenediamine with dimethylzinc- formation of the adduct $Me_2NCH_2CH_2NMe_2 \cdot ZnMe_2$

Dimethylzinc (0·48g., 5·05 m.mole) was condensed onto the amine (0·54g., 5·0 m.mole) contained in a sublimation tube attached to the vacuum line. The mixture was allowed to warm to room temperature, and the white solid which was formed was purified by vacuum sublimation (0·01 mm. 40°) as large glistening crystals, m.p. 57-58°.

(Found: Zn, 30·7; hydrolysable Me, 14·10%; M, cryoscopically in 0·75, 0·86 wt. % benzene solution, 225,219. $C_8H_{22}N_2Zn$ requires Zn, 30·9; hydrolysable Me, 14·19%; M, 211).

The complex slowly decomposed in air, but was rapidly hydrolysed by moisture.

The infrared spectrum (below 2000 cm^{-1}) of the complex, recorded as a Nujol mull contained bands at the following frequencies:
1441vs, 1379s, 1356s, 1287vs, 1250s, 1178s, 1159vs, 1145vs, 1130vs, 1098s, 1065s, 1034vs, 1016s, 950s, 791vs, 770s, 649vs(br), 610s(sh), 553m, 510vs, 453s, 431m.
vw = very weak, w = weak, m = medium, s = strong, vs = very strong, sh = shoulder, br = broad.

Reaction of NNN′- trimethylethylenediamine with dimethylzinc- formation of the dimer $(MeZnNMeCH_2CH_2NMe_2)_2$.

Dimethylzinc (0·87g., 9·15 m.mole) was condensed onto the amine

(0·93g., 9·21 m. mole) contained in a sublimation tube. On warming the mixture to room temperature a white crystalline complex was formed, which melted at approximately 40° with the slow evolution of methane. At 50° a vigorous gas evolution occurred leaving a white crystalline mass which was purified by vacuum sublimation (0·01mm. 75°) as glistening plates, m.p. 110-111° (shrinking at 99°).

(Found: Zn, 36·3; hydrolysable Me, 8·32%; M, cryoscopically in 1·22, 2·43 wt. % benzene solution, 358, 365. $C_{12}H_{32}N_4Zn_2$ requires Zn, 36·1; hydrolysable Me, 8·27%; M, 363).

The compound was apparently slowly decomposed in air but was rapidly hydrolysed by moisture. The infrared spectrum recorded as a Nujol mull contained bands at: 1460vs, 1449vs(sh), 1410w, 1404w, 1370m, 1344m, 1276m, 1253m, 1242w(sh), 1186w, 1175w, 1148s, 1143s(sh), 1112s, 1099s(sh), 1058m, 1030s, 1003m, 938m, 848s, 836s(sh), 780s, 627vs(br), 592m, 506vs(br).

Reaction of dimethylamine with dimethylzinc- formation of bisdimethylaminozinc $Zn(NMe_2)_2$.

Dimethylzinc (229 N c.c., 10·2 m.mole) and dimethylamine (226 N c.c., 10·1 m. mole) were measured on the vacuum line and condensed into a reaction tube which was then sealed off at a constriction. When the liquid mixture was warmed to room temperature, evolution of methane was observed to take place very slowly; at 70° the reaction was quite rapid and was considered to be complete after

approximately two hours. The tube contained a white solid, as well as gaseous products which, on opening the tube were found to be methane (224 N c.c., 10·0 m.mole), and dimethylzinc (115 N c.c., 5·13m.mole). The gaseous products were identified by their infrared spectra. The white solid was involatile and insoluble in either benzene, ether or dimethylformamide. Solutions of 2,2′-bipyridyl in these solvents also failed to dissolve the compound, as did refluxing pyridine. The compound decomposed without melting at 270-290°, and was rapidly hydrolysed by moisture.

(Found: Zn, 42·9; hydrolysable Me_2N, 57·3%. $C_4H_{12}N_2Zn$ requires Zn, 42·6; hydroysable Me_2N, 57·4%).

The infrared spectrum of the compound recorded as a Nujol mull contained bands at the following frequencies: 1439vs, 1215m, 1142m(sh), 1130s, 1043m, 930m(sh), 916vs.

Reaction of diphenylamine with dimethylzinc- formation of methyl (diphenylamino)zinc dimer, $(MeZnNPh_2)_2$.

Dimethylzinc (151 N c.c., 6·74 m.mole) was condensed onto freshly sublimed diphenylamine (1·14g., 6·75 m.mole) contained in a reaction tube which was then sealed off at a constriction. The mixture was heated at 70° overnight, a white crystalline solid being formed. On opening the tube methane (150 N c.c., 6·67 m.mole) was obtained as the only gaseous product. The solid was recrystallised from benzene as small colourless plates, m.p. 185-195° (shrinking at

160°).

(Found: Zn, 26·2; hydrolysable Me, 6·0%; M, cryoscopically in 0·74, 1·48 wt. % benzene solution, 465, 475. $C_{26}H_{26}N_2Zn_2$ requires Zn, 26·3; hydrolysable Me, 6·0%; M, 497).

The compound easily decomposed in air and moisture, and when heated under vacuum began to disproportionate into dimethylzinc and bisdiphenylaminozinc at 130°, disproportionation occurring rapidly at 150°. The latter compound was not investigated, but dimethylzinc was identified by its infrared spectrum.

The infrared spectrum of the compound, recorded as a Nujol mull contained bands at: 1587s, 1562s(sh), 1538m(sh), 1460s, 1333w, 1307w, 1227s, 1176s(sh), 1163s, 1156s(sh), 1075m, 1027m, 985w, 917m, 877w, 862m, 830s, 813m(sh), 755vs, 746vs(sh), 699vs(sh), 689vs, 667s(sh)(br), 575m, 548s, 499s(sh), 489s.

Reaction of methyl(diphenylamino)zinc with 2,2′-bipyridyl.

When a benzene solution of 2,2′-bipyridyl was added to a benzene solution of methyl(diphenylamino)zinc, a very dark red colour was produced immediately. The colour was assumed to be due to the presence of a 1:1 chelate adduct, but repeated attempts to obtain an analytically pure sample by crystallizing from solution, failed. The conditions of crystallisation were found to affect the colour of the product, e.g. when hexane was added to the dark red benzene solution, and the mixture allowed to stand overnight, dark red crystals were

obtained which according to analytical data contained approximately 90% of the chelate adduct $MeZnNPh_2 \cdot bipy$. However, in another experiment, most of the benzene was removed under vacuum, and hexane added to precipitate the complex quickly. Buff-coloured crystals which contained hardly any $Zn-CH_3$ group, were obtained. The crystals dissolved when heated in the pale-brown supernatant solution resulting in the reformation of the dark red colour.

Reaction of methyl(diphenylamino)zinc with pyridine.

a. With an excess, (formation of diphenylamino(methyl)bispyridinezinc), $Mepy_2ZnNPh_2$.

To a solution of methyl(diphenylamino)zinc (1g., 4m.mole) in benzene (15 c.c.), pyridine (1·6g., 20·0m.mole) was added, and the solution immediately became bright yellow. Hexane (25 c.c.) was added and a bright yellow solid was precipitated. It was recrystallized from the benzene-hexane mixture as yellow feathery needles, m.p. 185-195°. This melting point was that of a partially decomposed material, since by placing a specimen in a melting point apparatus which had previously been heated to various temperatures, a sharp melting point of 110° was observed.

(Found: Zn, 16·2; hydrolysable Me, 3·74%; M, cryoscopically in 1·26, 1·58, 1·66 wt. % benzene solution 370, 385, 390. $C_{23}H_{23}N_3Zn$ requires Zn, 16·1; hydrolysable Me, 3·69%; M, 406).

The complex was rapidly decomposed by air, and the infrared spectrum

recorded as a Nujol mull contained bands at the following frequencies: 1600s, 1575s, 1431s, 1425s, 1418m(sh), 1379m, 1342s, 1307s(br), 1290m, 1235w, 1212s, 1183m, 1163m, 1149m, 1064s, 1037s, 1031m, 1015m, 999w, 985s, 943w, 917m, 877m, 851s, 833w, 746s(br), 694s(br), 651w, 633w, 621s(br), 516m(sh), 505s(br).

b. With an equimolar amount, - formation of bisdiphenylaminobispyridine-zinc. $py_2Zn(NPh_2)_2$.

To a solution of methyl(diphenylamino)zinc (2g., 8·0m.mole) in hot benzene (20 c.c.), was added pyridine (0·64g., 8·0m.mole); the colourless solution changed to a very pale yellow colour, and after the addition of hexane (10 c.c.) and benzene (10 c.c.), the mixture was heated to 80° and allowed to cool slowly. Large, very pale yellow crystals m.p. 210-211°, separated overnight; the crystals were only slowly decomposed by air.

(Found: Zn, 11·5; hydrolysable Ph_2N, 60·6%; M, cryoscopically in 1·02, 1·14 wt. % benzene solution, 553, 571. $C_{34}H_{30}N_4Zn$ requires Zn, 11·7; hydrolysable Ph_2N, 60·1%; M, 559).

The infrared spectrum recorded as a Nujol mull contained bands at the following frequencies: 1600vs, 1577vs, 1562s(sh), 1493vs, 1443vs, 1412w, 1333s, 1316s(sh), 1299vs, 1242w, 1209s, 1176m, 1163w(sh), 1148m, 1078m, 1066s, 1040s, 1025m, 1010m, 995w, 988s, 957m, 900m, 873s, 851s, 758s(sh), 741vs, 737vs(sh), 690vs(br), 633m, 516s(sh), 500s.

Reaction of diethylzinc with diphenylamine - formation of ethyl(diphenylamino)zinc dimer $(EtZnNPh_2)_2$.

Diethylzinc (1·18g., 9·60m.mole) and diphenylamine (1·62g., 9·60m.mole)

were placed in a glass reaction tube, and after evacuating all of the nitrogen, the tube was sealed off at a constriction, and heated at 50-60° overnight. A white solid product and ethane (213 N c.c. 9·51m.mole) were obtained. The solid, which was very soluble in benzene, was recrystallised from hexane at -70° as small colourless plates, m.p. 99-100° (shrinking at 89°).

(Found: Zn, 24·8; hydrolysable Et, 11·02%; M, cryoscopically in 1·5, 1·79 wt. % benzene solution 514, 540. $C_{28}H_{30}N_2Zn_2$ requires Zn, 24·9; hydrolysable Et, 11·05%; M, 525).

The infrared spectrum contained bands at the following frequencies: 1592s, 1587s(sh), 1504m(sh), 1493vs, 1449s(sh), 1408w, 1333m, 1307m, 1282m, 1235vs, 1176s(sh), 1163s, 1156m, 1081w, 1075m, 1031m, 990m, 956m, 930w, 917m, 877w, 862s, 833s, 755vs, 746s(sh), 697vs(br), 641w, 620s(br), 578m, 518s(br), 488s(sh), 481s(br).

Reaction of dimethylphosphine with dimethylzinc - formation of bisdimethylphosphinozinc $Zn(PMe_2)_2$.

Dimethylzinc (58·5 N c.c., 2·61m.mole) and dimethylphosphine (58·6 N c.c., 2·61m.mole) were measured on the vacuum line and condensed into a reaction tube, which was then sealed off at the constriction. The reaction tube was heated at 70° for seventy hours, after which time a white solid had formed. On opening the tube, methane (25 N c.c. 1·11m.mole) and unreacted starting materials were recovered. The reaction was repeated at 110° using 10m.mole of each reactant, but no

solid was observed to form at this temperature. The temperature was gradually lowered until solid began to deposit on the inside of the tube; this occurred at 95°. After maintaining the tube at 95° for two weeks it was opened, and methane (222 N c.c., 9·91m.mole) and dimethylzinc (113 N c.c., 5·05m.mole) were obtained together with a white solid which is involatile, and insoluble in ether, benzene, dimethylformamide, and pyridine. It decomposed without melting at 270° and was readily hydrolysed by moisture.

(Found: Zn, 34·7; P, 33·4%. $C_4H_{12}P_2Zn$ requires Zn, 34·9; P, 33·1%).

The infrared spectrum recorded as a Nujol mull contained bands at: 1418s, 1289w, 1272w, 1145w, 932vs, 887vs, 709s, 649s(br), 503s(br).

Reactions with alcohols.

Reaction of methyl alcohol with dimethylzinc, - formation of methylzinc methoxide tetramer, $(MeZnOMe)_4$.

Methyl alcohol (0·65g., 20·3m.mole) in hexane (10 c.c.) was slowly added to a solution of dimethylzinc (460 N c.c., 20·5m.mole) in hexane (40 c.c.), which was cooled to -70°. The mixture was allowed to warm, and at about -30° rapid methane evolution occurred and a white crystalline solid was deposited. The mixture was heated to about 60°, and the clear, colourless solution allowed to stand at room temperature.

Methylzinc methoxide slowly crystallised as broad needles, m.p. 190-191°. The sample became white and opaque at 150-170°, and the melt evolved dimethylzinc (identified by infrared spectrum).

(Found: Zn, 58·8; hydrolysable Me,13·6%; M, cryoscopically in 1·12, 1·69 wt. % benzene solution 461,458. $C_8H_{24}O_4Zn_4$ requires Zn, 58·7; hydrolysable Me, 13·5%; M, 446).

Methylzinc methoxide was found to sublime unchanged at 60° (10^{-4} mm.), but when heated under an atmosphere of dry nitrogen, it disproportionated at its melting point leaving a residue which was insoluble in benzene; the residue was probably polymeric zinc methoxide. Methylzinc methoxide dissolved readily in pyridine, but addition of hexane caused no precipitation of a co-ordination complex, and removal of all volatile material under vacuum yielded the unchanged starting material, (identified by infrared).

The colourless crystals of the compound rapidly became white and opaque on exposure to air, and were rapidly hydrolysed by moisture. The infrared spectrum recorded as a Nujol mull contained bands at: 1449s, 1370m, 1170w(sh), 1160m, 1058m(sh), 1022vs, 678vs(br), 546vs, 397s, 287s.

The proton magnetic resonance spectrum of the above compound in benzene solution and in toluene solution using tetramethylsilane as an internal standard, was recorded.

Results in benzene solution at room temperature.

Peak 1 (doublet); Zn-Me; τ 10·366 and 10·407

Peak 2 (doublet); O-Me; τ 6·842 and 6·802

When the solution in toluene was heated, the Zn-Me doublet collapsed over a range of about ten degrees and became a sharp singlet at 45°. The methoxy-doublet, in contrast, remained as such even at 100°, and the splitting of the components increased slightly from 0·0686p.p.m. at 23° to 0·0873p.p.m. at 100°.

The density of the compound was determined by floatation on a series of organic liquids and found to be 1·75g./c.c. These operations were carried out in the glove box.

Reaction of t-butanol with dimethylzinc, - formation of methylzinc t-butoxide tetramer, $(MeZnOBu^t)_4$.

t-Butanol (0·89g., 12·0m.mole) in hexane (10 c.c.) was slowly added to a solution of dimethylzinc (271 N c.c., 12·1m.mole) in hexane (20 c.c.) cooled to -80°. As the mixture warmed to room temperature vigorous gas evolution occurred at about -40°, and a clear solution was obtained. The product was crystallised by cooling the solution to -70°. The white solid began to decompose without melting at approximately 250°.

(Found: C, 38·9; H, 7·6; Zn, 42·8%; M, cryoscopically in 1·71, 2·43 wt. % benzene solution 595, 603. $C_{20}H_{48}O_4Zn_4$ requires C, 39·1; H, 7·8; Zn, 42·6%; M, 612).

The product could be sublimed unchanged at 95° (10^{-4}mm.) but when

it was heated under an atmosphere of nitrogen, isobutene (identified by infrared) was evolved at 270°. It was sufficiently stable to air to permit combustion analyses by conventional methods, and was decomposed only slowly by a boiling mixture of acetone and dilute sulphuric acid.

Like the methoxide it was recovered unchanged from pyridine, and the infrared spectrum recorded as a Nujol mull contained bands at: 1453s, 1370s, 1241s, 1179s(sh), 1174s, 1029m, 900vs, 754s, 675s(br), 544s(br), 463s.

The proton magnetic resonance spectrum of the compound in benzene solution using tetramethylsilane as an internal standard, was recorded.

Results in benzene solution at room temperature.

Peak 1 (singlet); Zn-Me; τ 10·179.

Peak 2 (singlet); O-Bu^t; τ 8·698.

Reaction of t-butanol with diethylzinc - formation of ethylzinc t-butoxide tetramer, $(EtZnOBu^t)_4$.

A solution of t-butanol (1·39g., 18·8m.mole) was slowly added to a solution of diethylzinc (2·35g., 19·1m.mole) in hexane (30 c.c.) which was cooled to -80°. The mixture was allowed to warm to room temperature during which time gas evolution was observed. The resulting clear solution was cooled to about -60° to crystallise the product. The compound decomposed without melting at approximately 250°, but could be sublimed unchanged at 105° (10^{-4}mm.). Like the methyl analogue, it was hydrolysed by a boiling mixture of acetone and

dilute sulphuric acid only very slowly, and was analysed for carbon and hydrogen by normal combustion methods.

(Found: C, 42·7; H, 8·2; Zn, 38·8%; M, cryoscopically in 1·43, 2·86 wt. % benzene solution 691,680. $C_{24}H_{56}O_4Zn_4$ requires C, 43·0; H, 8·4; Zn, 39·1%; M, 668).

The infrared spectrum recorded as a potassium bromide disc contained bands at: 1460m, 1418w, 1389s, 1370vs, 1242s, 1179vs, 1026w, 1010w, 967w, 926m, 903vs, 755s, 611s, 540vs, 495w, 462m.

Reaction of isopropanol with diethylzinc. - formation of ethylzinc isopropoxide tetramer, $(EtZnOPr^i)_4$.

A solution of isopropanol (0·6g., 10·0m.mole) in hexane (10 c.c.) was slowly added to diethylzinc (1·23g., 10·0m.mole) in hexane (20 c.c.) cooled to -60°. Ethane was evolved as the mixture warmed to room temperature, and the resulting clear solution had to be cooled to -80° to cause crystallization of the white solid product. It melted with decomposition at 258-260°, and became opaque at 190-200°.

(Found: Zn, 43·0; hydrolysable Et, 19·1%; M, cryoscopically in 1·51, 2·26 wt % benzene solution 599,632. Calc. for $C_{20}H_{48}O_4Zn_4$ Zn, 42·6; hydrolysable Et, 18·9%; M, 614).

The compound quickly decomposed in air, and was rapidly hydrolysed by moisture. The infrared spectrum recorded as a Nujol mull contained bands at: 1439m, 1418w, 1370vs, 1342s, 1274w, 1235w, 1163m, 1136s, 1117vs, 990m, 947vs, 926m(sh), 824vs, 613vs, 541vs(br), 518vs(br).

Reaction of 2-methoxyethanol with dimethylzinc - formation of methylzinc 2-methoxyethoxide tetramer, $(MeZn\cdot OCH_2CH_2\cdot OMe)_4$.

A solution of 2-methoxyethanol (0·75g., 9·9m.mole) in hexane (20 c.c.) was added to a solution of dimethylzinc (235 N c.c., 10·5m.mole) in hexane (20 c.c.), cooled to -80°. Vigorous methane evolution occurred at about -30°, and removal of the solvent from the clear solution yielded a liquid product. This was purified by vacuum distillation (70°/0·01mm.), but only with difficulty since the compound slowly decomposed under these conditions.

(Found: Zn, 41·8; hydrolysable Me, 9·5%; M, cryoscopically in 1·83, 2·29 wt. % benzene solution 624,631. $C_{16}H_{40}O_8Zn_4$ requires Zn, 42·1; hydrolysable Me, 9·65%; M, 622).

The infrared spectrum recorded as a liquid film between potassium bromide discs contained bands at: 1449vs, 1389m, 1361vs, 1333w, 1282m, 1235s, 1198s, 1160s, 1124s(br), 1111s(sh), 1064s(br), 1025s(sh), 990m, 965m, 930w, 893s, 881s(sh), 671vs(br), 578s(br), 540vs(br).

Reaction of phenol with dimethylzinc, - formation of methylzinc phenoxide tetramer, $(MeZnOPh)_4$.

A solution of phenol (0·95g., 10·1m.mole) in benzene (5 c.c.) was added to a solution of dimethylzinc (232 N c.c. 10·4m.mole) in hexane (30 c.c.) cooled to -80°. A vigorous gas evolution occurred as the mixture warmed to about -30°, with the corresponding formation of a white solid. The mixture was warmed to about 60°, and the resultant clear

solution allowed to cool slowly. Methylzinc phenoxide was obtained as colourless prisms, m.p. 219-221° (decomp.). When heated under vacuum, the product evolved dimethylzinc (identified by infrared) at 120°, and was decomposed rapidly by moisture.

(Found: Zn, 37·6; hydrolysable Me, 8·7%; M, cryoscopically in 1·77, 3·05 wt. % benzene solution 684,720. $C_{28}H_{32}O_4Zn_4$ requires Zn, 37·7; hydrolysable Me, 8·65%; M, 694).

The infrared spectrum of the solid recorded as a Nujol mull contained bands at: 1587vs, 1493vs, 1484vs, 1469s, 1283w, 1250m, 1220vs(sh), 1205vs, 1163s, 1153m, 1099w, 1075m, 1026m, 1000w, 975w, 885m, 826vs, 813vs, 760vs, 685vs, 621m, 578m, 565s, 559vs, 552vs(sh), 546s, 516s(br).

The proton magnetic resonance spectrum of a solution of the compound in D_8-toluene using tetramethylsilane as an internal standard, was recorded.

Results in D_8-toluene solution at room temperature

Peak 1 (singlet); Zn-Me; τ 10·289.

Peak 2 (triplet); O-C_6H_5; τ 2·981, 2·945, 2·905.

Reactions of methylzinc phenoxide with pyridine - formation of methyl(pyridine)zinc phenoxide dimer, $(MepyZnOPh)_2$.

To a solution of methylzinc phenoxide (1·0g., 5·8m.mole) in benzene (15 c.c.) was added pyridine (3·0g., 38·0m.mole), and the mixture allowed to stand at room temperature. After several minutes

colourless crystals were deposited, and more was obtained by the addition of hexane (20 c.c.). The product was recrystallised from benzene-hexane mixture, as small colourless prisms, m.p. 193-200°.

(Found: Zn, 25·8; hydrolysable Me, 6·10%; M, cryoscopically in 1·10, 1·11, 1·34 wt. % benzene solution 513,515,520. $C_{24}H_{26}N_2O_2Zn_2$ requires Zn, 25·9; hydrolysable Me, 5·94%, M, 505).

The complex was only soluble in benzene to an extent of about 2·5 wt. % at room temperature. The infrared spectrum recorded as a Nujol mull contained bands at: 1613m, 1600s, 1493s, 1282vs, 1250w(sh), 1220m, 1163m, 1156m(sh), 1075m, 1042m, 1020m, 995m, 943w, 885w, 844s, 820m, 769vs, 754s, 695vs, 653m(br), 633s, 625w, 563s, 521m, 508m.

Reaction of dimethylzinc with acetoxime - formation of methylzinc acetoximate tetramer, $(MeZnON{=}CMe_2)_4$.

To a solution of dimethylzinc (224 N c.c., 10·0m.mole) in diethylether (30 c.c.) at -100° was added acetoxime (0·8g., 10·6m.mole) dissolved in ether (10 c.c.). Reaction occurred at about -80°, and the white solid, which was present when the solution was warmed to room temperature, was filtered off. Ether was removed from the colourless filrate by pumping under vacuum, and when the volume had been reduced to about 10 c.c., the filtrate was cooled to about -70°, and the product was obtained as a white solid. It decomposed without melting at 170°.

(Found: Zn, 42·5; hydrolysable Me, 9·65%; M, cryoscopically in 1·64, 2·28 wt. % benzene solution 650,624. $C_{16}H_{36}N_4O_4Zn_4$ requires Zn, 42·9; hydrolysable Me, 9·85%; M, 610).

The infrared spectrum recorded as a Nujol mull contained bands at: 1629m, 1449vs, 1370vs, 1274m, 1160m, 1081vs, 1000vs, 966s(sh), 943m, 719w, 694vs, 547m, 524m, 435s(br).

Reaction of diethylzinc with 2,-dimethylaminoethanol - formation of ethylzinc 2,-dimethylaminoethoxide trimer, $(EtZnOCH_2CH_2NMe_2)_3$.

2,-Dimethylaminoethanol (0·90g., 10·1m.mole) was added to a solution of diethylzinc (1·3g., 10·6m.mole) in hexane (25c.c.) at room temperature. When the mixture was warmed to about 40°, rapid evolution of ethane occurred, leaving a clear colourless solution. White crystals of the product, m.p. 148-150° (shrinking at 130°) were obtained by cooling the solution to -70°.

(Found: Zn, 35·7; hydrolysable Et, 15·7%; M, cryoscopically in 1·98, 2·24 wt. % benzene solution 547,560. $C_{18}H_{45}N_3O_3Zn_3$ requires Zn, 35·9; hydrolysable Et, 15·9%; M, 547).

The product was recovered unchanged from a hexane solution containing methyl iodide. It was identified by m.p. and infrared, the spectrum containing bands at: 1449vs, 1379s, 1370m, 1274m, 1258w, 1250w, 1183w, 1163w, 1099m, 1081vs, 1070s, 1036s, 952s, 885s, 784m, 617m, 592m, 517m, 490m.

Reactions with thiols

Reaction of methane thiol with dimethylzinc - formation of methyl methylzinc sulphide, $(MeZnSMe)_x$.

Methane thiol (225 N c.c., 10·1m.mole) was condensed into a solution of dimethylzinc (240 N c.c., 10·7m.mole) in hexane (50 c.c.) at -80°. Some gas evolution occurred at low temperature (-80°) but became more rapid as the solution warmed. The white solid which was precipitated was insoluble in hexane, and in benzene; it was therefore filtered and washed with much hexane before pumping dry under vacuum. The product a white powder, did not melt below 360°, but when heated in vacuum it evolved dimethylzinc at 90°.

(Found: Zn, 51·0; hydrolysable Me, 11·5%. C_2H_6SZn requires Zn, 51·3; hydrolysable Me, 11·8%).

Reaction of methyl methylzinc sulphide with pyridine.

The product, although insoluble in benzene, dissolved readily in pyridine, but addition of hexane failed to cause crystallization of an adduct; only an emulsion was obtained. All of the solvent was removed under vacuum leaving a colourless syrup which slowly lost pyridine on pumping, leaving a white solid. The white solid was shown to be methyl methylzinc sulphide by its infrared spectrum, which contained bands at: 1435s, 1321w, 1161m, 963m, 695m, 655vs, 525vs, 299s, 225s.

Reaction of n-propyl thiol with dimethylzinc - formation of methylzinc n-propyl sulphide, $(MeZnSPr^n)_x$.

A solution of n-propyl thiol (0·75g., 9·9m.mole) in hexane (10 c.c.) was added to a solution of dimethylzinc (230 N c.c., 10·3m.mole) in hexane (30 c.c.) at -80°. As the mixture warmed to room temperature methane evolution occurred with the formation of a white solid which was insoluble in hexane, and benzene. The product did not melt, but disproportionated at 70° when heated under vacuum.

(Found: Zn, 41·7; hydrolysable Me, 9·40%. $C_4H_{10}SZn$ requires Zn, 42·0; hydrolysable Me, 9·65%).

The infrared spectrum recorded as a Nujol mull contained bands at: 1460vs, 1342w, 1299w, 1266w, 1250s, 1163m, 1099m, 1064m, 1031w, 909m, 787w, 723s, 719s, 654vs(br), 521vs.

Reaction of isopropyl thiol with dimethylzinc - formation of isopropyl methylzinc sulphide hexamer, $(MeZnSPr^i)_6$.

To a solution of dimethylzinc (224 N c.c., 10·0m.mole) in hexane (50 c.c.) cooled to -80°, a solution of isopropyl thiol (0·75g., 9·9m.mole) in hexane (10 c.c.) was added. Methane was evolved as the mixture warmed up to room temperature and a clear solution was obtained. The solvent was removed under vacuum, and the white solid product recrystallised from hexane as colourless prisms, m.p. 90-105° (shrinking at 75°). When heated under vacuum the product evolved dimethylzinc at 95°.

(Found: Zn, 41·5; hydrolysable Me, 9·4%; M, cryoscopically in

1·66, 1·97, 2·03, 2·49 wt. % benzene solution 942,942, 966,919. $C_{24}H_{60}S_6Zn_6$ requires Zn, 42·0; hydrolysable Me, 9·65%; M, 934).

The infrared spectrum recorded as a Nujol mull contained bands at: 1449vs, 1370vs, 1250vs, 1156s, 1058s, 1053s, 922w, 885m, 669vs, 617m, 606m, 531s, 519s.

Reaction of t-butylthiol with dimethylzinc - formation of methylzinc t-butylsulphide pentamer, $(MeZnSBu^t)_5$.

To a solution of dimethylzinc (257 N c.c., 11·0m.mole) in hexane (20 c.c.) at -70°, was added t-butyl thiol (1·0g., 11·1m.mole) dissolved in hexane (10 c.c.). Methane evolution occurred with the corresponding formation of a white solid product. The mixture was warmed to about 50° and the clear solution which was obtained allowed to stand at room temperature. The product slowly crystallised as long colourless needles, m.p. > 360°, the crystals became white and opaque at 155-160°. When heated under vacuum, the product evolved dimethylzinc at 100°.

(Found: Zn, 38·4; hydrolysable Me, 8·9%; M, cryoscopically in 2·49, 3·05, 3·47 wt. % benzene solution 875, 846, 861. $C_{25}H_{60}S_5Zn_5$ requires Zn, 36·6; hydrolysable Me, 8·9%; M, 847).

The infrared spectrum of the product, recorded as a Nujol mull contained bands at: 1458vs, 1370vs, 1217w, 1152vs, 1027w, 931w, 813m, 665vs(br), 586m, 566s, 531vs.

The density was measured by floatation on a variety of organic

solvents and found to be 1·39g./c.c.

Reaction of methylzinc t-butyl sulphide with pyridine. - formation of methyl(pyridine)zinc t-butyl sulphide dimer, $(MepyZnSBu^t)_2$.

An excess of pyridine (2g., 25·0m.mole) was added to a solution of methylzinc t-butyl sulphide (1g., 5·9m.mole) in benzene (10 c.c.) Removal of all of the solvent under vacuum yielded a white solid which was recrystallised from a benzene-hexane mixture as small white feathery needles, m.p. 147-155° (decomp.).

(Found: Zn, 26·4; hydrolysable Me, 6·10%; M, cryoscopically in 0·87, 1·75 wt. % benzene solution 470,481. $C_{20}H_{34}N_2S_2Zn_2$ requires Zn, 26·3; hydrolysable Me, 6·05%; M, 497).

The infrared spectrum recorded as a Nujol mull contained bands at: 1613s, 1577m, 1481s, 1449vs, 1361s, 1220s, 1156s, 1064s, 1037s, 1010s, 943w, 820m, 752s, 697vs, 676w, 654m, 639s(br), 625vs, 592m, 515s, 506s, 418m(br).

Reaction of t-butylthiol with diethylzinc - formation of ethylzinc t-butyl sulphide pentamer, $(EtZnSBu^t)_5$.

A solution of the thiol (0·80g., 6·7m.mole) in hexane (10 c.c.) was added to a solution of diethylzinc (1·15g., 9·3m.mole) in hexane (20 c.c.) at -70°. The solvent was removed from the clear solution which was obtained after reaction had occurred, and the white solid recrystallised from hexane at -70°. The crystals did not melt below 360°, but became white and opaque at 120°.

(Found: Zn, 35·9; hydrolysable Et, 15·9%; M, cryoscopically in 2·67, 3·64 wt. % benzene solution 940, 954. $C_{30}H_{70}S_5Zn_5$ requires Zn, 35·7; hydrolysable Et, 15·8%; M, 917).

The infrared spectrum of the solid recorded as a Nujol mull contained bands at: 1458vs, 1370vs, 1235w, 1220w, 1156vs, 1027w, 1010m, 980m, 962m, 920m, 816m, 610s, 569s, 500s(br).

Reaction of thiophenol with dimethylzinc- formation of methylzinc phenyl sulphide, $(MeZnSPh)_x$.

A solution of thiophenol (0·85g., 7·7m.mole) in hexane (10 c.c.) was added slowly to a solution of dimethylzinc (200 N c.c., 8·9m.mole) in hexane (40 c.c.), the solution being vigorously stirred throughout the addition. Reaction occurred at -80°, a white solid being precipitated; the product was insoluble in benzene, and by removing all solvent under vacuum it was obtained as a white powder, m.p. 186-203 (decomp.). When heated under vacuum the product evolved dimethylzinc at 60°.

(Found: Zn, 34·3; hydrolysable Me, 7·75%. C_7H_8SZn requires Zn, 34·5; hydrolysable Me, 7·9%).

Methylzinc phenyl sulphide dissolved readily in pyridine although a co-ordination complex could not be obtained by addition of hexane. Removal of solvent left a colourless syrup which very slowly lost pyridine under vacuum.

The infrared spectrum of methylzinc phenyl sulphide contained bands at: 1587m, 1488s, 1449m, 1158w, 1081m, 1026s, 1000m, 901w, 735vs, 690vs, 675s,

666s(sh), 526m, 472m.

Reaction of selenophenol with dimethylzinc - formation of methylzinc phenyl selenide, $(MeZnSePh)_x$.

To a solution of dimethylzinc (200 N c.c., 8·9m.mole) in hexane (30 c.c.) at -80°, was added selenophenol (1·4g., 8·9m.mole) in the same solvent (10 c.c.). The mixture was stirred throughout the addition, reaction occurring rapidly at -80°. The white solid product was insoluble in hexane, and benzene; it melted with decomposition at 150-195°, and when heated in vacuum it evolved dimethylzinc at 50°.

(Found: Zn, 27·4; hydrolysable Me, 6·1%. C_7H_8SeZn requires Zn, 27·7; hydrolysable Me, 6·4%).

The product dissolved readily in pyridine, but like the sulphur analogue, no complex could be isolated.

The infrared spectrum of the compound contained bands at: 1582m, 1443m, 1152w, 1071m, 1024m, 1000m, 730vs, 688s, 667s, 526m, 460m.

Reaction of acetic acid with dimethylzinc - formation of methylzinc acetate, $(MeZnOOCMe)_x$.

Acetic acid (0·85g., 14·2m.mole) dissolved in hexane (10 c.c.) was added very slowly to a solution of dimethylzinc (377 N c.c., 16·8m.mole) in the same solvent (30 c.c.) at -80°. Vigorous reaction occurred at that temperature, and a white solid was precipitated.. The product was insoluble in hexane and benzene, and melted at 204-210° with decomposition. When heated under vacuum, the compound evolved

dimethylzinc at 75°.

(Found: Zn, 46·7; hydrolysable Me, 10·6%. $C_3H_6O_2Zn$ requires Zn, 46·9; hydrolysable Me, 10·8%).

The infrared spectrum of methylzinc acetate contained bands at: 1600vs, 1449s, 1408vs, 1348s, 1169w, 1053m, 1031m, 952w, 680s, 613m, 540s(br).

Reaction of methylzinc acetate with pyridine - formation of methyl (pyridine)zinc acetate dimer, $(MepyZnOOMe)_2$.

Pyridine (2·0g., 25·3m.mole) was added to a suspension of methylzinc acetate (2·0g., 14·4m.mole) in benzene (20 c.c.), and the solid dissolved to give a clear solution. Addition of hexane precipitated a white solid which was recrystallised from benzene-hexane mixture as very small white feathery needles, m.p. 106-108°.

(Found: Zn, 29·9; hydrolysable Me, 6·9%; M, cryoscopically in 0·81, 1·62 wt. % benzene solution, 420,427. $C_{16}H_{22}N_2O_4Zn_2$ requires Zn, 29·9; hydrolysable Me, 6·9%; M, 436).

The infrared spectrum of the solid recorded as a Nujol mull contained bands at: 1608m, 1562s(sh), 1550s, 1515m(sh), 1481m(sh), 1449vs, 1220m, 1156w, 1147m, 1071m, 1042m, 1010m, 943w, 760m, 698s, 683m, 654s, 650s(sh), 629m, 614w, 506s, 418m. The infrared spectrum of the complex recorded in pyridine solution showed no band in the 1650-1750 cm^{-1} region, where C=O would be expected to absorb.

Reaction of dimethylphosphinic acid with dimethylzinc - formation of methylzinc dimethylphosphinate, $(MeZnOOPMe_2)_x$

A mixture of dimethylzinc (262 N c.c., 11·7m.mole) and dimethylphosphinic acid (1·1g., 11·7m.mole) in hexane (50 c.c.) was stirred overnight at 40°. Reaction occurred very slowly and the product was obtained as a white powder insoluble in both hexane and benzene. The compound melted at 250-260° with decomposition, and when heated under vacuum it evolved dimethylzinc at 140°.

(Found: Zn, 37·6; hydrolysable Me, 8·6%. $C_3H_9O_2PZn$ requires Zn, 37·7; hydrolysable Me, 8·7%).

The infrared of the solid, recorded as a Nujol mull contained bands at: 1470s, 1429s, 1316s, 1310s, 1156vs, 1152vs, 1026vs(br), 926m, 870vs, 752s, 709m, 662vs(br), 535vs, 483m(br), 437m(br).

Reaction of methylzinc dimethylphosphinate with pyridine - formation of methyl(pyridine)zinc dimethylphosphinate dimer, $(MepyZnOPOMe_2)_2$.

Pyridine (4·0g., 50·5m.mole) was added to a suspension of methylzinc dimethylphosphinate (1·5g., 8·7m.mole) in a benzene-hexane mixture; the solid dissolved when the solution was warmed to about 40°. By the addition of hexane, and cooling the solution, the product was obtained as colourless crystals, m.p. 85-92° with decomposition (shrinking at 70°).

(Found: Zn, 25·8; hydrolysable Me, 5·9%; M, cryoscopically in 0·98, 1·96, 2·75 wt. % benzene solution, 350, 406, 440. $C_{16}H_{28}N_2O_4P_2Zn_2$ requires Zn, 25·9; hydrolysable Me, 5·9%; M, 504).

The infrared spectrum contained bands at: 1613s, 1493m, 1460s, 1429w, 1303s, 1299s, 1250w, 1220w, 1176vs, 1163vs, 1156s, 1143s, 1075s, 1053vs, 1042s, 1015m, 1010w, 862vs, 763s, 738s, 714s, 702s, 654w, 638s, 623s, 514s, 472s(br), 455s(br), 444s(br), 418m(br).

The principal bands in the 2000-1000 cm^{-1} region of a solution of the compound in pyridine were: 1307s, 1299s, 1176vs, 1058vs.

The infrared spectrum of a benzene solution of the product contained bands at: 1605w, 1588w, 1449m, 1439m, 1307s, 1299s, 1183vs, 1163vs, 1062vs, 1042s(sh).

Reaction of diethylzinc with iodine - formation of ethylzinc iodide, $(EtZnI)_x$.

To a solution of iodine (2·50g., 9·9m.mole) in benzene (30 c.c.) was added diethylzinc (1·25g., 10·2m.mole) in the same solvent. The deep mauve colour of the iodine was immediately discharged leaving a clear colourless solution. Removal of the solvent under vacuum yielded a white solid which slowly came out of solution as very small satin plates m.p., 79° (decomp). The product was insoluble in hexane, and also could not be redissolved in benzene after it had been pumped to dry it. It rapidly turned yellow on exposure to air.

(Found: Zn, 27·4; hydrolysable Et, 11·2%. C_2H_5IZn requires Zn, 29·5; hydrolysable Et, 13·1%).

The infrared spectrum recorded as a Nujol mull contained bands at: 1225w, 1160m, 991m, 952w, 920m, 625s, 517m.

Organometallation reactions

Reaction of acetone with dimethylzinc - attempted preparation of methylzinc t-butoxide, ($MeZnOBu^t$).

Dimethylzinc (230 N c.c., 10·3m.mole) and acetone (0·60g., 10·3 m.mole) contained in a sealed glass tube, were heated at 90° for approximately one hour. A yellow solid was formed, and on opening the tube, methane (228 N c.c. 10·2m.mole) was recovered. Methylzinc t-butoxide could not be sublimed from the solid, and the latter was not investigated further.

Reaction of benzophenone with dimethylzinc - attempted preparation of methylzinc methyldiphenylmethoxide, ($MeZnOCPh_2Me$).

Dimethylzinc (258 N c.c., 11·5m.mole), benzophenone (0·90g., 5·0m.mole) and toluene (15 c.c.) were placed in a glass reaction tube which was then evacuated and sealed off. The very pale yellow coloured solution was heated at 120° for approximately twenty hours. On opening the tube dimethylzinc (256 N c.c.) was recovered, and after removing the toluene, the remaining crystalline solid was identified by m.p. and infrared, as benzophenone.

Reaction of benzophenone with diethylzinc - formation of ethylzinc diphenylmethoxide trimer, $(EtZnOCHPh_2)_3$.

Diethylzinc (2·40g., 19·5m.mole) was added to a solution of benzophenone (1·80g., 9·9m.mole) in toluene (30 c.c.) and the resulting pale yellow solution refluxed overnight. The solvent was removed under vacuum leaving a very viscous liquid which dissolved readily in hexane

(40 c.c.). When the solution was cooled to about -50°, the product was obtained as small white crystals; these were filtered and washed several times with hexane at -80° before pumping dry. The product melted with decomposition at 156-158° after shrinking at 130°, and was rapidly hydrolysed by moisture. Benzhydrol was identified as the hydrolysis product by carbon and hydrogen analyses, m.p., and its infrared spectrum.

(Found: Zn, 23·4; hydrolysable Et, 10·4%; M, cryoscopically in 2·15, 3·08 wt. % benzene solution, 841, 865. $C_{45}H_{48}O_3Zn_3$ requires Zn, 23·6; hydrolysable Et, 10·5; M, 833).

The infrared spectrum of the product recorded as a Nujol mull contained bands at: 1587w, 1493m, 1449vs, 1351w, 1190m, 1087w, 1031w, 1000m(sh), 990s, 962w(sh), 926w, 917m, 860m, 768s, 741s, 704vs, 696s, 666m, 621s, 612s, 575w, 505m, 467w(br).

Reaction of benzophenone with diphenylzinc - formation of phenylzinc triphenylmethoxide dimer, $(PhZnOCPh_3)_2$.

A solution of diphenylzinc (1·7g., 7·7m.mole) and benzophenone (0·7g., 3·9m.mole) in toluene (25 c.c.) was refluxed for about thirty hours. After removing the solvent under vacuum, the white solid which remained was washed with cold benzene (2x10c.c.) to remove the excess diphenylzinc, and finally recrystallised from the same solvent. The product melted with decomposition at 236-242°.

(Found: Zn, 16·1; hydrolysable Ph, 19·0%; M, cryoscopically in

2·98, 4·18 wt. % benzene solution, 785,760. $C_{50}H_{40}O_2Zn_2$ requires Zn, 16·3; hydrolysable Ph, 19·2%; M, 803).

Hydrolysis of the product yielded triphenyl carbinol which was identified by carbon and hydrogen analyses, m.p., and its infrared spectrum.

The infrared spectrum of the product recorded as a Nujol mull contained bands at: 1600w, 1575w, 1481m, 1449vs, 1198w, 1156m, 1149m, 1075w, 1042w, 1032m, 1010s, 917w, 901m, 780m(sh), 769s, 763s, 752s, 725m, 699vs, 676w, 662w, 645m, 637m, 546w, 483w, 465w.

Reaction of diethylzinc with phenylisocyanate - formation of N-ethylzinc-N-phenyl-propionamide tetramer, $(EtZnNPh(C{:}O)Et)_4$.

A mixture of diethylzinc (1·2g., 9·8m.mole), phenylisocyanate (1·1g., 9·7m.mole), and benzene (25 c.c.) was refluxed for two hours after which the solvent was removed under vacuum. The white solid which remained was recrystallised from hexane as small colourless prisms, m.p. 148-160 (decomp. shrinking at 130°).

(Found: Zn, 26·7, hydrolysable Et, 11·8%; M, cryoscopically in 2·06, 2·47 wt. % benzene solution, 984,968. $C_{44}H_{60}N_4O_4Zn_4$ requires Zn, 27·0; hydrolysable Et, 12·0%; M, 970).

The infrared spectrum recorded as a Nujol mull contained bands at: 1562vs, 1538s(sh), 1493w, 1389s, 1361s, 1250m, 1222m, 1170w, 1149w, 1081m, 1070m, 1026w, 1000m, 990w(sh), 952w, 926s, 813m(br), 797m, 758s, 719w, 696s, 658m, 606m, 565m, 508m(br), 417w(br).

Hydrolysis of the product yielded propionanilide which was identified by carbon and hydrogen analyses, m.p. and its infrared spectrum. An identical compound to that described above was obtained from the reaction of diethylzinc and propionanilide, the product was identified by its m.p. and infrared spectrum; it was also tetrameric in benzene solution.

Reaction of diphenylzinc with phenylisocyanate - formation of N-phenylzinc-N-phenyl-benzamide tetramer, $(PhZnNPh(C{:}O)Ph)_4$.

Diphenylzinc (1·7g., 7·8m.mole), and phenylisocyanate (0·93g., 7·8m.mole) were refluxed in benzene (40 c.c.) overnight. The solvent was removed under vacuum, and the white solid recrystallised from benzene as small colourless broad needles, m.p. 220-254° (decomp., shrinking at 190°).

(Found: Zn, 19·1; hydrolysable Ph, 22·5%; M, cryoscopically in 2·96, 3·71 wt. % benzene solution, 1398,1379. $C_{72}H_{60}N_4O_4Zn_4$ requires Zn, 19·3; hydrolysable Ph, 22·8%; M, 1354).

Hydrolysis of the product gave benzanilide which was identified by carbon and hydrogen analyses, m.p., and its infrared spectrum.

The infrared spectrum of the product contained bands at : 1585m, 1538s(sh), 1529vs, 1493s, 1449vs, 1418m, 1361vs, 1316w, 1299w, 1242m, 1130m, 1075m, 1031m, 926m, 917m, 807w, 778m, 746s, 699vs, 680m, 671s, 629w, 614w, 513m(br), 444m(br).

Reaction of methylisocyanate with dimethylzinc - formation of N-trimethylisocyanurate, $(MeNCO)_3$.

Dimethylzinc (224 N c.c., 10·0m.mole) and methylisocyanate (220 N c.c., 9·8m.mole) were condensed into a reaction tube containing benzene (25 c.c.). After evacuating the nitrogen, the tube was sealed, and the contents allowed to warm to room temperature. After about forty eight hours the tube was opened and dimethylzinc (223 N c.c.) was recovered, together with a crystalline solid which was purified by vacuum sublimation. The compound melted over the range 110-163°.

(Found: C, 41·9; H, 5·2%; M, cryoscopically in 0·88 wt. % benzene solution, 164. Calc. for $C_6H_{18}N_3O_3$: C, 42·1; H, 5·25%; M, 171).

The infrared spectrum of the solid recorded as a Nujol mull contained bands at: 1689vs, 1316m, 1053m, 943m, 758s, 752s, 483m, 420s.

Reaction of ethylisocyanate with diethylzinc - formation of N-triethylisocyanurate, $(EtNCO)_3$.

A mixture of diethylzinc (1·2g., 9·8m.mole), ethylisocyanate (0·70g., 9·9m.mole) and hexane (40 c.c.) was maintained at room temperature overnight. Removal of all volatile material yielded a white solid product which was purified by vacuum sublimation. It melted at 86-90°.

(Found: C, 51·0; H, 7·1%; M, cryoscopically in 0·80 wt. % benzene solution, 204. Calc. for $C_9H_{15}N_3O_3$: C, 50·7; H, 7·05%; M, 213).

The infrared spectrum of the solid recorded as a Nujol mull contained bands at: 1692vs, 1328s, 1093m, 1070m, 1005m, 877s, 810m, 762vs, 754s(sh), 719w, 506s, 495s, 454m.

Reaction of phenyl cyanide and dimethylzinc - formation of triphenyl triazine, $(PhCN)_3$.

Dimethylzinc (485 N c.c., 21·2m.mole) and phenyl cyanide (1·0g., 9·5m.mole) were heated together in a sealed tube at 100-110° overnight. A green liquid containing large needle-like crystals was obtained. On opening the tube, dimethylzinc (479 N c.c.) was recovered, and the solid, after washing with cold benzene, was recrystallised from the same solvent as very pale yellow needles, m.p. 235-263° (Lit.,[151] 232°)

(Found: C, 81·2; H, 4·95%. Calc. for $C_{18}H_5N$: C, 81·6; H, 4·85%).

The infrared spectrum (below 2000 cm^{-1}) recorded as a potassium bromide disc, contained bands at: 1589m, 1527vs, 1447m, 1366vs, 1299m, 1175m, 1145w, 1070m, 1029m, 1000w, 971vw, 938w, 926vw, 840m, 742vs, 692m(sh), 683vs, 644s, 481m.

DISCUSSION.

DISCUSSION

As indicated in the introduction, the "internal" co-ordination complexes of Group II organo-metallic compounds have not been studied in detail, and very little is known about their constitution. Zinc alkyls have been used to determine "acidic" hydrogen in a variety of organic compounds by measuring the volume of hydrocarbon produced during the reaction.[152] Similarly, relative rates of reaction of several dialkylzinc compounds with p-toluidine have recently been reported.[112] In both of the above studies, the zinc-containing products were not isolated. Various workers have isolated such products from the reactions between zinc alkyls and various alcohols[107] and amines;[117] however, only the empirical formulae were established.

The interest in compounds of the type, RZnA lies in the fact that if monomeric they would contain co-ordinatively unsaturated zinc atoms bound to donor atoms of enhanced donor character, the increase in donor character depending on the polarity of the Zn-A bond. The species would therefore be expected to associate in order to satisfy the co-ordination expansion requirements of the zinc atom. All of the compounds of this type which have been investigated in the present study have been found to be associated. Several compounds have been found to be associated to a degree which, in view of the previous knowledge of Group III "internal" co-ordination complexes, seems surprising.

The difference must be due to the fact that the zinc compounds, even after association, sometimes contain co-ordinatively unsaturated metal atoms. The present investigation was undertaken to determine what effects this factor has on the behaviour and structure of compounds of this type.

With regard to the nature of the compounds which have been prepared, all except the alkylzinc t-butoxides are sensitive to moisture. The apparent stability of the latter compounds is discussed later in connection with their structures. Attempted sublimation of many of the products resulted in their disproportionation, in which volatile zinc alkyls were evolved leaving an involatile and presumably polymeric bis-compound.

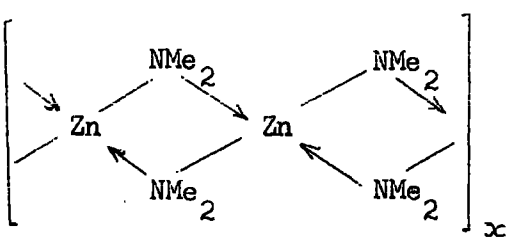
$$2(RZnA)_n \longrightarrow nZnR_2 + n(ZnA_2)_x$$

The disproportionation process probably involves an intermolecular condensation of molecules containing three co-ordinate zinc. Compounds which contain four co-ordinate zinc, e.g. $ZnMe_2 \cdot L$ (where L = 2,2′-bipyridyl, 1,10-phenanthroline,[66] and NNN′N′-tetramethyl-ethylenediamine) all sublime without decomposition.

Since disproportionation of the compounds which apparently contain co-ordinatively unsaturated zinc occurs quite readily (50-150°), the melting points which are quoted are probably better described as decomposition temperatures, or melting points of partially decomposed materials.

Reactions with amines.

The reactions between zinc alkyls and secondary amines occur only slowly at room temperature, and were therefore usually done at temperature of 50-70°. The nature of the product evidently depends on the particular amine involved in the reaction, e.g. in its reaction with dimethylzinc, dimethylamine afforded bisdimethylaminozinc, $(Me_2N)_2Zn$, together with unreacted dimethylzinc. The product is involatile and insoluble in strong donor solvents, e.g. dimethylformamide and pyridine. It did not dissolve in benzene solutions of 2,2′-bipyridyl, and had a very high decomposition temperature (270°). In view of its properties bisdimethylaminozinc can reasonably be assumed to be a co-ordination polymer having the structure shown below.



Evidently the donor character of the dimethylamino-group when bound to zinc is so enhanced that even bipyridyl causes no displacement. An attempted preparation of $(Me_2N)_2Zn$ bipy from the dimethylzinc complex, Me_2Zn bipy and dimethylamine at 80°, yielded only black, involatile and insoluble material in addition to methane. It is not known whether the bisamino-compound is formed by disproportionation of

$(MeZnNMe_2)_n$, or by further reaction of this with dimethylamine. The latter is unlikely since the recently described ethyl(diethylamino)zinc is said to be stable in the presence of excess diethylamine.[113]

The structure of the involatile, insoluble bisdimethylphosphinozinc is probably analogous to that described for bisdimethylaminozinc. The fact that dimethylphosphine did not react with dimethylzinc at 110°, yet reacted slowly at 95°, can be explained on the basis that the co-ordination complex is too highly dissociated at that temperature, and on the assumption that the methyl groups of free dimethylzinc have insufficient anionoid character to react with the P-H bond of dimethylphosphine. The anionoid character of the CH_3-Zn groups would be increased by co-ordination of the metal with an electron donor.

An alkylaminomethylzinc complex was obtained from dimethylzinc and NNN′- trimethylethylenediamine; it sublimes under vacuum without difficulty and without decomposition. The product has a sharp melting point and is dimeric in benzene solution. The stability of the product to disproportionation may be attributed to the zinc being four co-ordinate, the ligand functioning as a bidentate donor. The structure (fig.1) is thought to be analogous to that proposed for a previously described methylberyllium complex.[38]

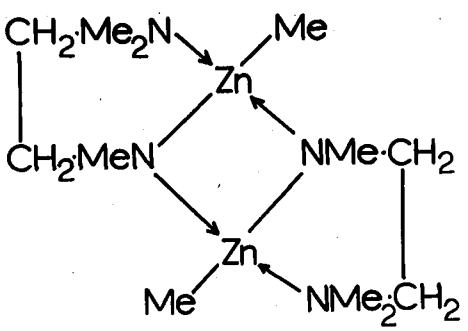
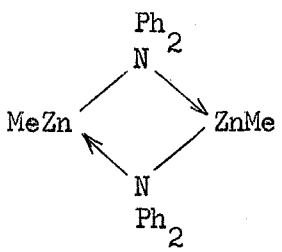


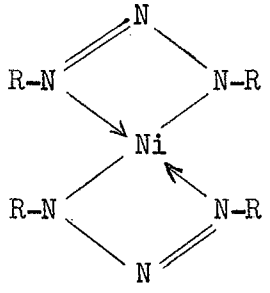
Fig.1

With diphenylamine, dimethyl- and diethyl-zinc yield products which cannot be formulated with anything other than a structure (shown below) in which the zinc atoms are three co-ordinate, forming part of a four-membered Zn-N ring.



Although four-membered rings are quite common in inorganic chemistry due to the differences in atomic sizes and the easier distortion of valence angles of heavier elements,[95] such a ring would be expected to be subject to valence angle strain. Evidence for such strain is found in the unusual complexes of nickel with triazines. The complexes are monomeric in boiling benzene and are

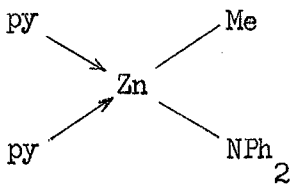
formulated as having the following structure:



The complexes dimerise in concentrated solution and at low temperature; it is suggested that the process is one of relieving ring strain by ring opening and cross-linking.[153] A similar explanation has been put forward for the observation that the amino derivatives of Group III organo-metallic compounds, e.g. $(Me_2AlNMe_2)_n$, are dimeric in benzene solution but form glassy solids when solvent free. It is thought that by ring opening and cross-linking, cyclic oligomers are formed in the solid state.[86,88] The zinc compounds show no molecular weight trend with concentration, and in the solid state they are stable crystalline solids. The zinc atoms can therefore apparently withstand considerable valence angle strain.

The presence of co-ordinatively unsaturated zinc in the alkyl(diphenylamino)zinc compounds is reflected in the fact that they disproportionate when heated, and methyl(diphenylamino)zinc reacted with an excess of pyridine to give diphenylamino(methyl)bispyridinezinc, $Mepy_2ZnNPh_2$, which is monomeric in benzene, and which must surely

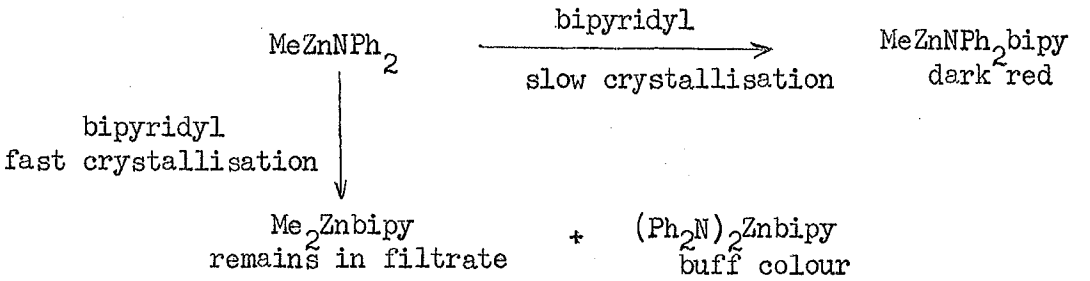
have the following structure:



The bright yellow colour of the compound may be attributed to a charge transfer process in which an electron from the Zn-C bond or possibly from the Ph_2N group is promoted to the lowest anti-bonding orbital of the pyridine rings. The very dark red colour which was obtained by adding 2,2′-bipyridyl to a solution of methyl(diphenylamino) zinc may be similarly explained; the diphenylamino-group is almost certainly involved in the charge transfer process since the bipyridyl complex of dimethylzinc is yellow.

The reaction of methyl(diphenylamino)zinc with 2,2′-bipyridyl was found to be peculiar in that different coloured products giving different analyses could be obtained by crystallising at different rates. For example, by very slow crystallisation, dark red crystals were obtained which contained about 90% $MeZnNPh_2bipy$. The estimate is based on the analysis for hydrolysable methyl. Rapid crystallisation afforded buff-coloured crystals and a pale brown filtrate. The crystals redissolved in the filrate when heated, to give the dark red solution characteristic of the bipyridyl complex described above. It was concluded that a disproportionation reaction was competing with

the normal addition reaction thus:



The above was confirmed by reaction of methyl(diphenylamino)zinc with one molar equivalent of pyridine in benzene solution. Very pale yellow crystals of bisdiphenylaminobispyridinezinc, $py_2Zn(NPh_2)_2$ slowly crystallised from solution. The presence of dimethylzinc in the filtrate was evident from the effect of admitting a trace of air. Complete disproportionation had taken place according to the equation:

$$2MeZnNPh_2 + 2py \longrightarrow Me_2Zn + py_2Zn(NPh_2)_2$$

In view of the disproportionation of $(MeZnNPh_2)_2$ under the influence of bases, the unsatisfactory analytical data for the bipyridyl complex is hardly surprising.

Reactions with alcohols.

The reaction between zinc alkyls and alcohols is extremely rapid at room temperature, but by the slow addition of alcohol to a dilute

solution of zinc alkyl cooled to -80°, and with vigorous stirring as reaction proceeded, compounds of the type RZnOR' were obtained. For similar reasons to those discussed in connection with the organozinc amides, the products would be expected to be associated by relatively strong co-ordination. In the absence of complicating factors, the alkylzinc alkoxides would be expected to be dimers analogous to the amides. The formation of dimers would be favoured relative to that of trimers, tetramers, or more associated species on entropy grounds, i.e. the number of independant molecules per unit mass would tend to a maximum. The objections to the dimeric structure are first that it involves three co-ordinate (and still co-ordinatively unsaturated) zinc, and secondly that both the oxygen and, more particularly, the metal atoms would be subject to some degree of angular strain. Neither objection can be of overwhelming importance as the nitrogen analogues have been prepared, and are discussed above. Also dimeric alkylmetal alkoxides of Group III are known, and methylberyllium methoxide has been shown to be dimeric;[101] the latter compound would not be expected to tolerate valence angular strain as easily as the zinc analogue.

Almost all of the alkylzinc alkoxides prepared during the present investigation are tetrameric in benzene solution and can reasonably be assumed to have eight-membered cyclic structures; there are several possible conformations of the latter (fig.2) assuming the C-Zn-O

angles are about 120° and the Zn-O-Zn angles about 105-110°. However since the zinc atoms can obviously tolerate angular strain, the cubic structure (fig.2) should also be considered.

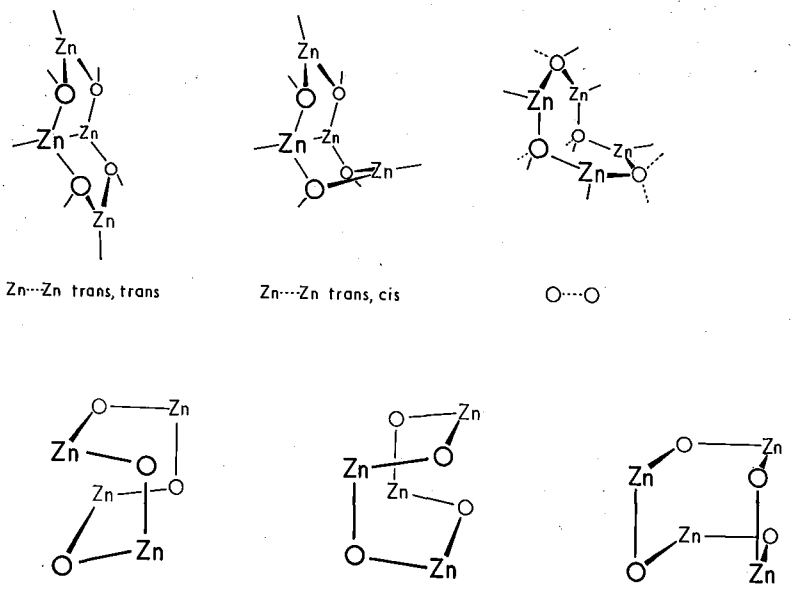


Fig.2

The cubic structure has the advantage of bringing positive and negative centres relatively close together, and if there is some degree of interaction between adjacent zinc and oxygen atoms, shown as non-bonded in Fig.2, this would have the effect of increasing the effective co-ordination number both of zinc and oxygen. Indeed, methylzinc methoxide and the alkylzinc t-butoxides behave as if the zinc atoms are four co-ordinate, e.g. they can be sublimed unchanged and also they are recovered unchanged from solutions containing pyridine. It is likely that the six possible forms of the cubic structure would interconvert rapidly, in which case the time-average

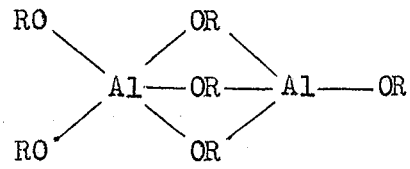
structure would be cubic. This is analogous to the structure of the phenylaluminium anilide tetramer $(PhAlNPh)_4$, the cubic structure of which has been confirmed by X-ray diffraction methods.[90] The cubic structure of thallium methoxide has also been confirmed by X-ray structure analysis, although it is thought that it is better described as a distorted cube consisting of two interpenetrating tetrahedra of different sizes.[154] Dr. H.M.M. Shearer and Mr. C. Spencer of this department are at present carrying out an X-ray crystallographic study of crystals of methylzinc methoxide. Observations have shown the crystals to be orthorhombic of space group $P2_12_12_1$ with unit cell dimensions a = 7·48, b = 7·67, c = 29·41Å. From these data and from the measured density (1·75gm. c.c.$^{-1}$) there are four tetramers in the unit cell.

The proton magnetic resonance spectrum (60Mc./s.) of methylzinc methoxide in benzene solution consists of two double peaks, one due to Zn-Me at τ10·366 and 10·407, and the other at τ6·842 and 6·802. The components of the Zn-Me doublet are of about equal intensity and the splitting is very slightly less in toluene (0·036p.p.m.) than in benzene (0·041 p.p.m.). The components of the methoxy-doublet are unequal and the splitting is a little greater in toluene than in benzene. When the solution in toluene is heated, the Zn-Me doublet collapses over a range of about ten degrees and becomes a sharp singlet at 45°. The methoxy-doublet, in contrast, remains as such even at 100°. The proton magnetic resonance spectrum of the tertiary

butoxide $(MeZnOBu^t)_4$ consists only of two sharp single peaks, one due to Zn-Me at τ 10·179 and the other due to $\cdot OBu^t$ at τ 8·698. These results may indicate that isomeric forms are accessible to the methoxy compound but denied to the t-butoxy-derivative on account of steric hindrance. However it is difficult to accommodate the fact that the methoxy doublet does not collapse at high temperature. If isomeric forms were being interconverted at high temperature then all of the methyl groups, whether bound to zinc or oxygen, would be expected to be affected to the same degree.

Alternatively it may be argued that a disproportionation process occurs in solution to give dimethylzinc and oligomeric zinc methoxide. This is doubtful since the solid does not disproportionate until about 200°, and it can also be recovered unchanged from a benzene solution to which pyridine has been added. If an equilibrium mixture of the type suggested above were present in solution, the pyridine would be expected to complex with either or both of the products and so drive the disproportionation to completion.

A remaining possible explanation of the unexpected proton magnetic resonance spectrum of the methoxy compound is that of intramolecular alkoxide exchange, similar to that proposed for the trimeric form of aluminium iso-propoxide. It is thought that alkoxide exchange in the latter compound occurs by the formation of another Al-O bridge giving an intermediate structure which is more easily represented by a dimeric aluminium alkoxide.



This is followed by fission of one of the bridging Al-O bonds, and reformation of the normal dimeric structure having only two bridging alkoxide groups.[155] It is conceivable that a similar exchange could take place diagonally across the cube of methylzinc methoxide, (Fig.3).

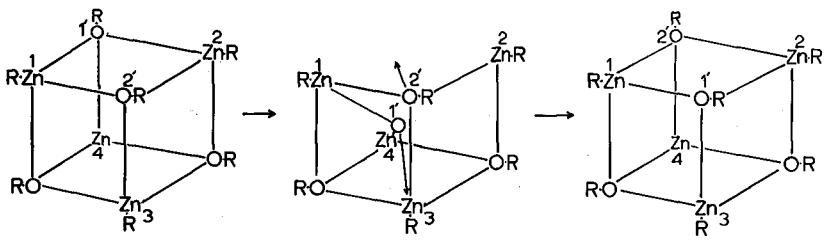


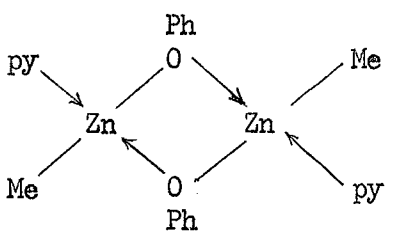
Fig. 3

The process may involve rupture of the bond between oxygen(1′) and zinc (2), the oxygen atom co-ordinating to zinc (3). This is followed by the rupture of the bond between oxygen (2′) and zinc (3), and a similar fission of the bond between oxygen (1′) and zinc (4). Finally the cubic structure is reformed by formation of bonds between oxygen (2′) and zinc (4), and also between oxygen (1′) and zinc (2). If the

process occurs sufficiently slowly then the magnetic non-equivalence of methyl groups bound to atoms which are directly involved in the exchange would be expected to produce splittings in the proton resonances. However, the fact that the Zn-Me doublet collapses at high temperature while the O-Me doublet remains as such is perplexing, and attempts to explain the experimental observations must be regarded as speculative until the structure of the compound is known. The fact that methylzinc t-butoxide gives a proton magnetic resonance spectrum consisting of two singlets is consistent with the above postulate since exchange of such bulky groups would be sterically hindered. The lack of evidence for alkoxide exchange within dimeric aluminium t-butoxide has been similarly explained.[155]

In connection with the stability of alkylzinc t-butoxides towards moisture, the steric effects of the bulky t-butoxy groups must be important. It is likely that the zinc atoms are so well shielded, that the water molecules cannot co-ordinate easily. As a consequence, the hydrolysis of the zinc-carbon bond is an extremely slow process.

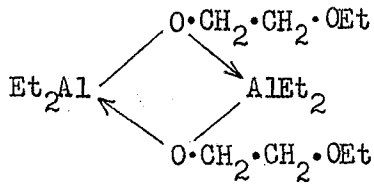
Methylzinc phenoxide tetramer behaves quite differently from the alkoxides. It disproportionates when heated (120°), and with pyridine forms the dimeric adduct, methyl(pyridine)zinc phenoxide.



The behaviour of the phenoxide may be attributed to the weaker donor character of the oxygen when bound to a phenyl group than when bound to an alkyl group. Another factor which must be considered is that the oxygen valence bond angles tend to be larger when bound to aromatic ring systems. It is though that the C - O bonds aquire some double bond character by partial delocalisation of the lone pair electrons into the aromatic system, and the bond angle increases to greater values than the tetrahedral angle (compare 108^{o} and 124^{o} in Et_2O and Ph_2O respectively).[95] The phenoxy group is therefore a less powerful donor and the oxygen atom would be expected to be subject to more valence angle strain than in the corresponding alkoxy compound. It is likely that if the methylzinc phenoxide has a cubic structure, it is only weakly held together, and the zinc atoms approach three co-ordinate rather than four co-ordinate behaviour. The proton magnetic resonance spectrum of the compound in fully deuterated toluene consists of a sharp singlet due to Zn-Me at τ 10·289 and a triplet due to phenyl groups at τ 2·981, 2·945 and 2·905.

The liquid product $(MeZn\cdot O\cdot CH_2\cdot CH_2\cdot OMe)_4$, from dimethylzinc and 2-methoxyethanol, evidently resembles the other tetrameric alkoxides, the alkoxy-oxygen atoms being co-ordinated to the metal in preference to the ether oxygens. Zinc alkyls form co-ordination complexes with ethers (relatively unstable with simple,[62] but much more stable with chelating,[63,69] ethers), and the product may therefore have been expected

to be dimeric. However, the acceptor character of the metal is likely to be enhanced by replacement of one of the carbon atoms by the more electronegative oxygen, and also the donor character of oxygen is enhanced when one of the carbon atoms of an ether is replaced by a more electropositive atom, e.g. a metal. It is not surprising therefore that the ether oxygen atoms are not involved in co-ordination and the structure may be regarded as a cubic arrangement of the eight-membered Zn-O ring with the ether chain protruding from the corners of the cube. This is not unreasonable since the compound $Et_2Al{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}OEt$ is formulated with the structure shown below, rather than as a chelate monomer.[93]



The reaction between diethylzinc and acetoxime has been described previously and although ether soluble ethylzinc acetoximate was obtained as a crystalline solid, no molecular weight data were recorded.[111] Methylzinc acetoximate was prepared in the present investigation in order to determine its molecular weight. The crystalline product was found to be tetrameric in benzene solution, and can therefore be formulated with either of two structures. The tetramer may have the cubic arrangement of the eight-membered Zn-O ring similar to that proposed for the alkylzinc alkoxides. This would mean that the $-N{=}CMe_2$ groups

would protrude from the corners of the cube in the same way as that suggested for the ether side chains in the 2-methoxy-ethoxide. The low symmetry of such a molecule is probably responsible for the fact that methylzinc 2-methoxy-ethoxide is a liquid. Methylzinc acetoximate is a crystalline solid and therefore much more easily packed into the crystal lattice. The infrared spectrum of the compound contains a band of medium intensity at 1629 cm^{-1} which is in a region where one would expect a stretching vibration of the $\rangle C{=}N-$ group to occur. This compares with 1669 cm^{-1} in acetoxime. The shift in $\rangle C{=}N-$ stretching frequency could conceivably be due to the nitrogen being co-ordinated to the zinc. In this case, a tetrameric structure may be explained by the interaction of two six-membered rings as shown in Fig. 4. This is reasonable in view of the apparent stability of the cubic arrangement of eight-membered Zn-O systems.

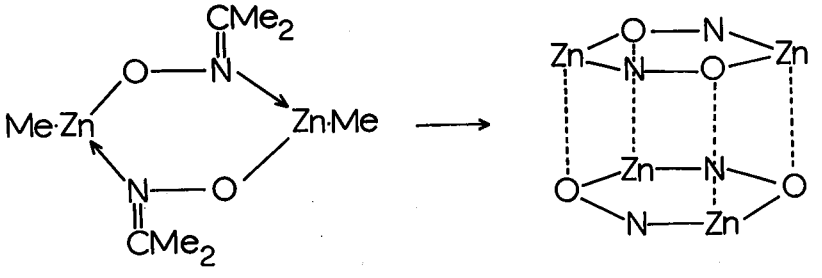
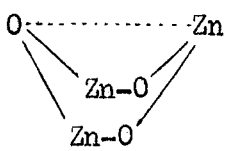


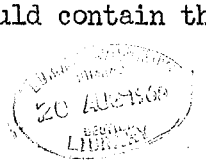
Fig. 4

The crystalline product obtained from diethylzinc and

2-dimethylaminoethanol was found to be trimeric in benzene solution. The product does not form a quaternary salt with methyl iodide, showing that the dimethylamino- groups are chelated to the zinc atoms. A dimeric structure analogous to the product from dimethylzinc and NNN′- trimethylethylenediamine (fig. 1) would reasonably have been expected. However the molecular weight data obtained in benzene solution exclude this possibility. It is likely that the structure consists of a six-membered Zn-O ring, with the dimethylamino- groups chelated to adjacent zinc atoms. The preferred orientation of the six-membered ring can only be determined by a X-ray structural analysis, but it seems likely that the 'boat' form will be preferred since initially this would have the effect of bringing an oxygen and zinc atom close together.



Once formed, the 'boat' form could not interchange with the 'chair' form due to the chelation of the dimethylamino- groups. An unusual feature of the infrared spectrum of this compound is that it contains two bands due to $Zn-CH_2$ rock, and two bands due to $Zn-CH_2$ stretch. The bands occur at 617, 592 cm^{-1}, and 517, 490 cm^{-1} respectively. If such 'stem-stern' interaction occurred in a 'boat' form of the Zn-O ring, the result would be that the ring would contain three zinc atoms, one



of which would be in a different co-ordination environment. Although this would explain the infrared evidence, a complete X-ray analysis would be required to confirm the structure.

Reactions with thiols.

In marked contrast to the dimethylmetal methylsulphides of Group III, all of which are dimeric[83,91,85] except the boron compound which is monomeric,[77] zinc alkyls reacted with a variety of thiols to yield polymeric products as well as a hexamer, and a pentamer. Dimethylzinc reacts with the thiols $R'SH(R' = Me, Pr^n, Ph)$ to give products of empirical formula, MeZnSR, which are insoluble in benzene and are assumed to have polymeric structures. The products all behave as if they contain three co-ordinate zinc since they disproportionate with evolution of dimethylzinc when heated at $90^o(R' = Me)$, $70^o(R' = Pr^n)$, $60^o(R' = Ph)$. The product, $(MeZnSePh)_x$, from dimethylzinc and selenophenol is also insoluble in benzene and disproportionates at 50^o. All of the compounds dissolve readily in benzene to which pyridine has been added, giving mobile solutions. A depolymerisation process must take place, but attempts to isolate the pyridine adducts failed since only syrups were obtained except in the case of the methylthio-derivative. This dissolves in pyridine but the ligand is lost slowly under reduced pressure:

$$(MeZnSMe)_x \underset{\text{vacuum}}{\overset{py}{\rightleftharpoons}} (MepyZnSMe)_n$$

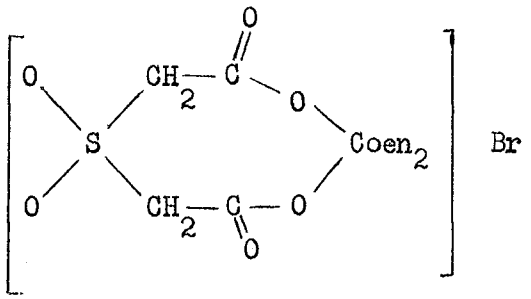
With branched chain thiols quite different products are obtained, dimethyl- and diethylzinc with t-butylthiol afford pentamers, $(RZnSBu^t)_5$, and dimethylzinc with iso-propylthiol affords a hexamer, $(MeZnPr^i)_6$. All of these compounds disproportionate when heated, and methylzinc t-butyl sulphide, $(MeZnSBu^t)_5$, with pyridine affords the dimeric crystalline complex, $(MepyZnSBu^t)_2$. The structure is probably analogous to that described for methyl(pyridine)zinc phenoxide. For reasons discussed in connection with the alkoxides, the products exemplified by RZnSR' would be expected to be dimeric. The zinc atoms can apparently withstand angular strain (see organozinc-amides,), and the existence of the dimeric Group III analogues, e.g. $(Me_2M^{III}SMe)_2$ confirms that the sulphur atoms can also tolerate such strain. The organo-zinc sulphides behave as if they contain co-ordinatively unsaturated zinc, and this may be the reason for apparently extensive polymerisation. The fact that the organozinc diphenylamides also contain co-ordinatively unsaturated zinc yet remain as dimers is probably due to the nitrogen atoms already being four co-ordinate, and any further co-ordination by cross-linking would have the effect of raising their co-ordination to five.

The unexpected degrees of association of thio- compounds may be explained on the basis of a polymeric reaction intermediate. Beachley and Coates[88] have suggested that this may be important and should be taken into consideration. Thus by intermolecular

elimination of hydrocarbon a polymeric product is isolated, unless such influencing factors are present which can reduce the polymer to oligomers. With the straight chain thiols, e.g. MeSH and Pr^nSH, and thiophenol, the product remains polymeric. However, steric factors are presumably important, and with the branched chain thiols, e.g. Pr^iSH, and Bu^tSH, the polymeric products are broken down until a unit is attained which can accommodate the bulky groups without too much steric interaction. Bradley[156] has emphasised the importance of the steric effects of alkyl groups on the degree of polymerisation of metal alkoxides, and for an extensive series of metal amylalkoxides has shown that the degree of polymerisation decreases with increase in branching of the amyl- group.

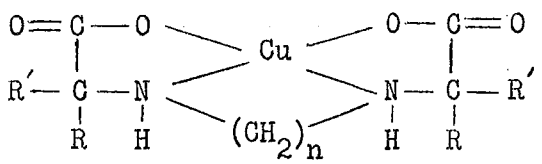
Though no trend of molecular weight with concentration was apparent in the cryoscopic data (benzene solution) on the hexamer and pentamers, additional evidence in support of these unusual degrees of association was required. Dr. H.M.M. Shearer and Mr. G. Adamson of this department are at present carrying out an X-ray structural analysis of $MeZnSBu^t$ and report that the monoclinic crystals have the unit cell dimensions: a = 9·59, b = 39·04, c = 12·13Å, $\beta = 117^\circ 08'$. From these data and the measured density (1·39gm. $c.c.^{-1}$) the unit cell contains twenty monomer units. The space group is $P2_1/c$, the unit cell therefore contains four pentamers. It is possible that the pentamers and hexamer have ten and twelve-membered cyclic structures respectively. The formation of rings of seven or more members is

comparatively uncommon in inorganic chemistry though the existence of structures has been suggested. The product from carbonatobis(ethylenediamine)cobalt(III)bromide and sulphonyldiacetic acid has been assigned the following structure.[157]



However when the sulphone group is replaced by sulphide, no analogous compounds are obtained. This suggests that chelation may involve the oxygen atoms of the sulphone group rather than the carboxyl groups.

A series of complexes of copper with polymethylene bis-α-amino acids have been formulated with the following structure,[158]



where n has the values 2,3,5,7, and 10. Thus if these structures are correct, the rings contain 5,6,8,10 and 13 members. Generally the structures of such large ring compounds are not firmly established. The lack of X-ray structural analyses and the several possible linkages as well as the possibility of polymerisation in

the solid state, tend to make the proposed structures highly speculative.

Methylzinc acetate and dimethylphosphinate.

Methylzinc acetate is insoluble in hexane and benzene, and is probably polymeric. The infrared spectrum contained no band which could have been attributed to ν(C=O), i.e. in the 1700-1750 cm^{-1} region. Intense bands due to symmetric and antisymmetric stretching vibrations of the O-C-O group are observed at 1408 and 1600 cm^{-1} respectively. This suggests that the carboxyl group functions as a chelate ligand as in dimethylgallium-acetate.[100] This compound and several more known to contain bridging acetate groups (from X-ray analysis) have two C-O infrared stretching frequencies[159] in the range 1400-1480 and 1570-1620 cm^{-1}. It is therefore concluded that the zinc compound also contains a bridging acetate group, and that the insolubility is due to cross-linking between the zinc atoms of one dimer unit and oxygen atoms of another. The compound is depolymerised by pyridine and the dimeric adduct, $(MepyZnOAc)_2$ can be isolated. The adduct is thought to have the structure shown in figure 5.

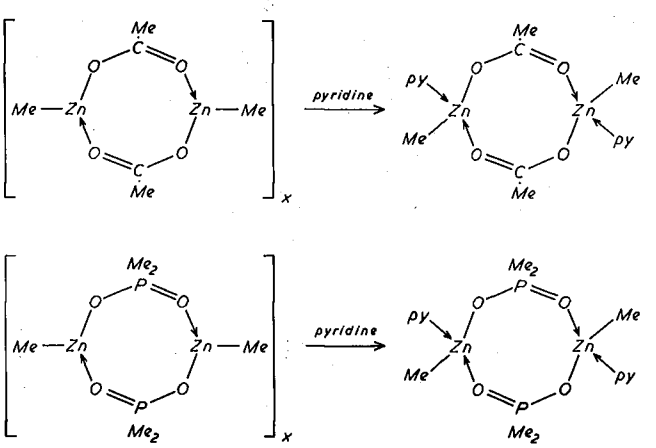


Fig. 5

The infrared spectrum contains bands due to $\nu(CO_2)$ at 1449 and 1550 cm^{-1} which are characteristic of a bridging acetate group. The acetate bridge is not disrupted by excess pyridine since the infrared spectrum of a pyridine solution of the adduct contained no band due to $\nu(C=O)$ in the 1700-1750 cm^{-1} region.

Methylzinc dimethylphosphinate, which is insoluble in benzene, is believed to have a polymeric structure similar to the acetate, but containing bridging phosphinate groups. The infrared spectrum of the compound contained intense absorptions due to $\nu(PO_2)$ at 1026 and 1156 cm^{-1} which are similar to the PO_2 absorptions in the salt, NaO_2PMe_2 (1068 and 1168 cm^{-1}).[160] This is in contrast to the more widely spaced $\nu(PO)$ absorptions, at 1042 and 1230 cm^{-1} of the methyl ester $Me_2P(:O)OMe$.[100] The two P-O bonds in methylzinc dimethylphosphinate are therefore thought to be equivalent as in NaO_2PMe_2, and are present as bridging groups.

Dimethylgallium dimethylphosphinate dimer has an infrared spectrum[100] which contains bands due to $\nu(PO_2)$ at 1164 and 1062 cm^{-1}, and it has been assigned an eight-membered cyclic structure containing bridging phosphinate groups. This structure has been confirmed by an X-ray structural analysis.[198] The recent X-ray structure analysis of di-μ-diphenylphosphinatoacetylacetonatochromium(III) has shown that the ligands around the chromium atoms conform to octahedral symmetry and the bridge structure, $(CrOPO)_2$, is a puckered

eight-membered ring.[160a]

Methylzinc dimethylphosphinate dissolves in benzene to which pyridine has been added, and the dimeric pyridine adduct, $(MepyZnO_2PMe_2)_2$ can be isolated. The adduct has been assigned a structure similar to the acetate adduct (Fig.5) since the infrared spectrum indicates that phosphinate group is bridging. The absorptions due to $\nu(PO_2)$ occur at 1053 and 1163 cm^{-1}. Like the bridging acetate group, the bridging phosphinate group of the pyridine adduct could not be disrupted by excess pyridine. The infrared spectrum of a pyridine solution of the adduct showed no band due to $\nu(P=O)$, and the absorptions due to $\nu(PO_2)$ were almost unchanged at 1058 and 1176 cm^{-1}.

The pyridine adduct is appreciably dissociated in dilute solution in benzene, since the apparent molecular weight decreases as the solution is diluted. The infrared spectrum of such a solution showed no band due to $\nu(P=O)$, the absorptions due to $\nu(PO_2)$ occurred at 1062 and 1163 cm^{-1}. Thus dissociation to a monomeric species does not occur since this would be reflected in the appearance of a band due to P=O. This is substantiated by the obvious resistance to rupture of the O-P-O bridge with excess pyridine. It is therefore concluded that the complex loses pyridine in benzene solution.

Ethylzinc iodide.

Crystalline complexes of organozinc halides with various ligands

have been described. The 2:1 complexes, e.g. $MeZnBr.2Me_2NCHO$[3] are probably monomeric containing four co-ordinate zinc, and analogous to the crystalline dietherates of the Grignard reagent, e.g. $PhMgBr.2Et_2O$, which contains discrete tetrahedral units in the solid state.[161] The 1:1 complexes, e.g. $PhZnI.Et_2O$ may be dimeric by virtue of bridging halogen atoms though no molecular weight data are available for these and the 2:1 complexes. The unsolvated species 'RZnX' may be structurally interesting, and are relevant to the present investigation.

Ethylzinc iodide was prepared in order that an X-ray structural analysis could be carried out. It has been reported that it can be recrystallised from ethyliodide,[163] but all attempts so far to obtain crystals suitable for a structural analysis have failed. It is surprising that the compound, when prepared in benzene, remains in solution. It was therefore isolated by removing the solvent under vacuum, with the object of measuring its molecular weight in benzene solution. However, once the solid had been dried by pumping it would not redissolve in benzene. The unsatisfactory analyses suggested that some disproportionation had occurred at room temperature. This is not surprising since methylzinc iodide is said to dissociate sufficiently at room temperature to cause ignition.[164]

The infrared spectrum of the solid showed bands due to $Zn-CH_2$ rock and $\nu(Zn-CH_2)$ at 625 and 517 cm^{-1} respectively (compare 619 and

562 cm^{-1} in Et_2Zn , and 620 and 518 cm^{-1} in $(EtZnNPh_2)_2$). This may indicate that the co-ordination number of the zinc atom has increased by polymerisation but until structural data are available no real conclusions can be drawn from this.

Organometallation reactions.

As indicated in the introduction, reactions which are typified by those of Grignard reagents are not confined to organo-magnesium compounds, but that several examples of such reactions have been shown to occur with organo- derivatives of other elements. The nature of the intermediates has received very little attention and apparently has not been regarded of any importance. It is evident that if any understanding of a reaction mechanism is to be obtained, then the nature and molecular complexity of the reaction intermediate must surely be taken into account. This particular section of the present work was undertaken to try to provide such information for the zinc analogues of Grignard intermediates.

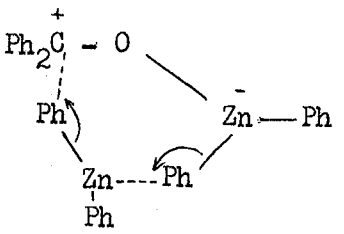
It is well known that organo-zinc compounds react with some unsaturated systems in much the same way as Grignard reagents, but as Gilman[134] has shown they are considerably less reactive. Diethylzinc reacts with acetaldehyde only when the mixture is refluxed,[136] and carbonation of diethylzinc does not normally occur; high pressure and a temperature of 160° are the conditions required.[135]

Reactions with ketones.

In order to see whether intermediates could be isolated, an attempt to prepare methylzinc t-butoxide from dimethylzinc and acetone was undertaken. The product had already been fully characterised by reaction of dimethylzinc and t-butanol. Complications due to enolization occurred and methane was evolved slowly at room temperature. The evolution of methane was quantitative at higher temperatures. The solid product was involatile, insoluble, and was presumably a polymeric isopropenyl derivative, $(CH_2{=}CMeOZnMe)_x$. To avoid such complications, benzophenone was used in subsequent reactions. The organo-zinc compounds were present in a two-molar excess since various workers have shown that under such conditions, addition to the unsaturated system occurs much more readily.[137,165]

Dimethylzinc and benzophenone in toluene at 110° do not react, whereas diphenylzinc and benzophenone under the same conditions react smoothly to form phenylzinc triphenylmethoxide. The difference in reactivity probably lies in the fact that diphenylzinc forms stronger co-ordination complexes than zinc alkyls owing to the greater electronegativity of the phenyl group. This has been demonstrated for a variety of ligands[69] (see introduction). Thus the greater the co-ordinating power of the carbonyl group to the zinc atom, the greater will become the susceptibility of the carbon atom to nucleophilic attack. A six-centre transition state similar to that proposed by

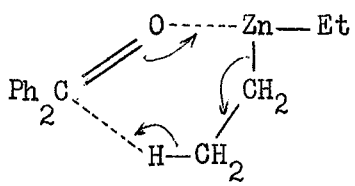
Pasynkiewicz and Sliwa[165] may be envisaged.



Phenylzinc triphenylmethoxide is dimeric in benzene in contrast to the previously described tetrameric alkoxides. This may be ascribed to the steric interactions of phenyl and triphenylmethyl groups.

Diethylzinc reacted with benzophenone in refluxing toluene to yield an ethylzinc alkoxide in quantitative yield. The product was found to be ethylzinc diphenylmethoxide, ($EtZnOCHPh_2$), showing that reduction had occurred in preference to the 'normal' addition. In a similar experiment carried out in a sealed tube one mole of ethylene per mole of benzophenone was obtained when the reaction was completed, and the tube opened. The ethylene was identified by its infrared spectrum. Reduction reactions quite commonly occur with organo-aluminium compounds, particularly tri-isobutylaluminium.[121] However since this slowly evolves iso-butene at room temperature, presumably leaving di-isobutylaluminium hydride, the reaction may reasonably be regarded

as one of hydrometallation. Diethylzinc is reported to react with chloral to yield ethylene and the corresponding primary alcohol.[166] This, and the reaction with benzophenone is extremely unlikely to involve the formation, transient or otherwise, of an alkylzinc hydride (see appendix). The probable mechanism is through the formation of a six-centre transition state similar to that proposed for the Grignard reduction reaction,[167] and for the reduction of ketones by triethylaluminium,[165] i.e. hydride transfer from the β-carbon atom.



Evidence for the existence of such a transition state in the case of the Grignard reagents, is that when benzophenone reacts with isobutylmagnesium bromide which is deuterated at one of the three positions in the carbon chain, only deuterium from the β-position and not from the α- or γ- positions is transferred to the benzophenone.[168]

The product, ethylzinc diphenylmethoxide is trimeric in benzene solution. This contrasts with the previously discussed tetrameric alkoxides. However, steric interactions between the ethyl-groups and the diphenylmethyl- groups would probably be significant in a tetramer,

and result in a lowering of the degree of association. This together with the dimeric phenylzinc triphenylmethoxide provide a further illustration of the importance of steric interaction of substituents on the degree of polymerisation.

Reactions with isocyanates.

Much of the work recently published on organometallation and related reactions has included the addition of various reagents to the very reactive isocyanates. Addition occurs under extremely mild conditions, e.g. diphenyl- and diethylzinc have been reported to react with phenylisocyanate at room temperature.[134] The hydrolysis products are benzanilide, and propionanilide respectively. It is not known whether the addition occurs across the C=N or the C=O bonds, but Arnold et. al have indicated that the electron density is greatest on the oxygen and least on the carbon, the nitrogen atom being intermediate.

$$\underset{\text{(major)}}{R\text{-}N\text{=}C\text{=}O} \longleftrightarrow R\text{-}N\text{=}C\text{=}O \longleftrightarrow \underset{\text{(minor)}}{R\text{-}N\text{-}C\text{=}O}$$

These authors suggest that nucleophilic attack occurs at the carbon atom followed by addition across the N=C bond. Thus with amines, substituted ureas are produced,

$$R\text{-}N\text{=}C\text{=}O + HNR'R'' \longrightarrow RNHC(:O)\text{-}NR'R''$$

and with alcohols, the products are carbamates.

$$R\text{-}N\text{=}C\text{=}O + HOR' \longrightarrow RNHC(:O)\text{-}OR'$$

With electrophiles, isocyanates might reasonably be expected to co-ordinate through the oxygen atom, and the ensuing addition to occur across the C=O bond. This form of addition is favoured for Grignard reagents[170] and organoaluminium compounds[137] though evidence to support this is not available. Various workers favour the addition as occurring across the C=N bond and quote evidence to support this.

Mercuric methoxide adds rapidly to phenylisocyanate[129] to yield the crystalline adduct methyl N-mercuri -N-phenylcarbamate, $Hg(NPh{\cdot}CO_2Me)_2$. The infrared spectrum of the adduct contains a band at 1708 cm^{-1} which is assigned as being due to $\nu(C{=}O)$.

The adducts obtained from trialkyltin alkoxides and organic isocyanates have been formulated as N-stannylcarbamates[127] since alcoholysis of the products regenerates the tin alkoxide and a carbamate, e.g. $R_3SnOR' + PhNCO \rightarrow R_3SnNPhCO_2R' \xrightarrow{R'OH} R_3SnOR' + PhNHCO_2R'$. Had addition occurred across the C=O bond, the adduct containing an Sn-O bond, rather than an Sn-N bond, would not have been expected to be cleaved by alcohol.

A series of adducts from the chloroboration of isocyanates can be exemplified by the reaction of boron chloride and phenylisocyanate.[126]

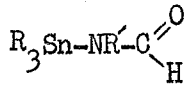
$$BCl_3 + 2PhNCO \longrightarrow Cl - \underset{\underset{O}{\|}}{C} - \underset{\underset{Ar}{|}}{N} - \underset{\underset{Cl}{|}}{B} - \underset{\underset{Ar}{|}}{N} - \underset{\underset{O}{\|}}{C} - Cl$$

The structures of the amidoboranes have been established by several methods, among which are alcoholic degradation and infrared spectra.

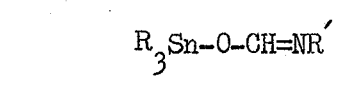
For example, the above adduct with the alcohol ROH, yielded the boric ester, $B(OR)_3$, and the aryl urethane, ArNHCOOR. The infrared spectrum of the adduct contained a band at 1750 cm^{-1} assigned as being due to $\nu(C=O)$, since the infrared spectrum of the thio- analogue was transparent in this region.

Similar infrared evidence supports addition across the C=N bond having occurred in the aminostannylation of phenylisocyanate.[131]

Trialkyltin hydrides react with organic isocyanates to yield 1:1 adducts. Assuming addition occurs across C=O, or C=N, the structures of the two possible adducts can be shown as follows.



(a)



(b)

The ultra-violet spectra of the adducts show a strong band at 239mμ and a weak absorption at 280mμ. This is remarkably like N-phenylformamide, PhNHC(=O)H, but appreciably different to that of ethyl-N-phenylformimidate, Ph-N=CHOEt. The proton magnetic resonance spectrum of the adduct contained a proton signal due to CH group at τ8·34. The spectrum of N-phenylformamide contains a signal due to the C-H group at τ8·40, while for ethyl-N-phenylformimidate the signal occurs at τ 7·60. Both observations favour structure (a).[124a]

Diphenyl- and diethylzinc both reacted smoothly with phenylisocyanate

in refluxing benzene solution to yield 1:1 adducts. The adducts are tetrameric in benzene solution suggesting initially that addition occurs across the C=O bond to yield an alkoxy derivative having the cubic eight-membered cyclic structures, with the -RC=NPh groups bound to the oxygen atoms and protruding from the corners of the cube.

$$PhNCO + R'_2Zn \longrightarrow (R'Zn\text{-}O\text{-}CR'\text{=}NPh)_4$$

However, the nitrogen atom was shown to be bound to the zinc atom since the reaction between diethylzinc and propionanilide yielded the same product (identical I.R. and m.p.) as that obtained from diethylzinc and phenylisocyanate. The infrared spectrum of the product does not contain any bands in the 1700-1750 cm^{-1} region, and it is concluded that the carbonyl group is co-ordinated. The spectrum is complicated by the presence of phenyl bands, but a very intense absorption at 1550 cm^{-1} may be due to the co-ordinated carbonyl group (see methylzinc acetate).

Since both the nitrogen and oxygen atoms are bound to zinc, there is no way of deciding whether addition occurs across the C=O, or the N=C, as the same product would be obtained from each process, assuming an eight-membered cyclic dimeric unit is initially formed (see Fig.6) Presumably association to a tetramer occurs by two of the eight-membered rings linking up as shown (Fig.6). This has the effect of raising the co-ordination of the zinc and the oxygen to four. This is consistent with the observations on the alkylzinc alkoxides.

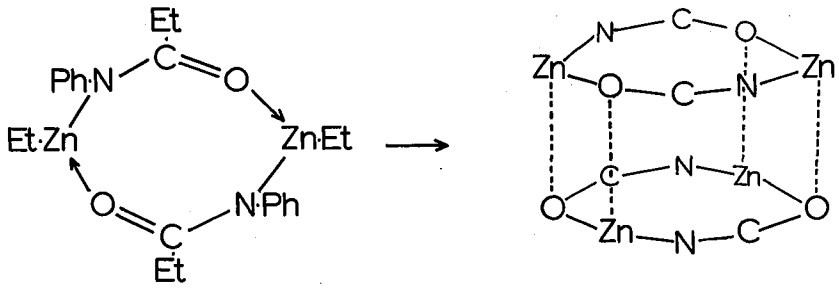


Fig. 6

The structure proposed for the adducts described above is analogous to those proposed for the insoluble methylzinc acetate and dimethylphosphinate. The solubility of the phenylisocyanate adducts may conceivably be due to the steric effects of the phenyl- and ethyl- groups.

Surprisingly, no zinc- containing products were obtained from the reactions between zinc alkyls and methylisocyanate, ethylisocyanate, and phenylcyanide; trimers of the unsaturated reactant were obtained in each case. The isocyanates polymerise readily in the presence of nucleophiles, e.g. tertiaryphosphines and amines,[169] the alkyl compounds even polymerise in the absence of catalysts. Methylisocyanate was found to trimerise slowly even at room temperature. The polymerisation reactions presumably occurs much faster than that of the addition reaction of zinc alkyls.

Phenyl cyanide trimerises in the presence of a variety of catalysts,

e.g. chlorosulphonic acids,[151] sodium,[171] and iron pentacarbonyl.[172] The mechanism of the trimerization, which in view of the variety of catalysts may differ under varying reaction conditions, is unknown. The non-occurrence of an organometallation reaction with dimethylzinc is probably due to the fact that the nitrogen only co-ordinates very weakly to zinc, if at all. The mixture can be separated easily, showing that if any complex is formed, it is highly dissociated. The carbon atom of the cyanide is therefore not as susceptible to nucleophilic attack as, for example, with aluminium alkyls[137] (see introduction).

Infrared characteristics of the Zn-Me group.

The infrared and Raman spectra of dimethylzinc have been analysed in detail,[173] the assignments are tabulated below.

Symmetry class	Frequency	Description
A_1'	2898	ν_1 C-H stretch
	1158	ν_2 CH_3 deformation
	504	ν_3 Zn-C stretch
A_1''	Forbidden	ν_4 torsion
A_2''	2870	ν_5 C-H stretch
	1185	ν_6 CH_3 deformation
	615	ν_7 Zn-C stretch
E'	2940	ν_8 C-H stretch

Symmetry Class.	Frequency	Description
	1444	ν_9 CH_3 deformation
	707	ν_{10} CH_3 rock
	144	ν_{11} C-Zn-C bend
E''	2833	ν_{12} C-H stretch
	1388	ν_{13} CH_3 deformation
	620	ν_{14} CH_3 rock

The molecule has been assigned a linear structure in which the methyl groups rotate freely (symmetry $D_{3h'}$). The infrared active absorptions due to Zn-CH_3 rock (707 cm^{-1}) and Zn-Me stretch (615 cm^{-1}) are very intense, and since they occur in a region where very few other fundamental vibrations occur, they are diagnostically very useful.

Some data are also available[174] on the spectrum of diethylzinc although they are confined to frequencies greater than 650 cm^{-1}. The infrared spectrum of diethylzinc (as a liquid film) was recorded, and absorptions due to Zn-CH_2 rock and Zn-CH_2 stretch found to occur at 619 and 562 cm^{-1} respectively. Since no spectroscopic data are recorded for zinc alkyl co-ordination complexes, absorptions due to Zn-Me and in a few instances Zn-Et groups are collected in the Table. No assignments are included in cases where there may be confusion with absorptions due to the remainder of the compound in question.

Compound	δ(Zn-Me)sym	Zn-Me rock	ν(Zn-Me)
Me_2Zn	1185m	707vs	615vs
Et_2Zn		619vs	562vs
$Me_2Zn(Me_2N{\cdot}CH_2{\cdot})_2$	1178m	645,610vs	510s,453m
$(MeZnNMeC_2H_4NMe_2)_2$	1175m	627s	506s
$(MepyZnOPh)_2$		653s	508s
$(MepyZnSBu^t)_2$		639s	506s
$(MepyZnOAc)_2$	1150m	654s	506s
$(MepyZnO_2PMe_2)_2$	1145m	638s	514s
$(MeZnOMe)_4$	1160m	678vs	546vs
$(MeZnOBu^t)_4$	1174s	675vs	544vs
$(MeZnOPh)_4$	1161m	685vs	552vs
$(MeZnON{=}CMe_2)_4$	1160m	649vs	524s
$(MeZnOCH_2CH_2OMe)_4$		671vs	541vs
$(EtZnOPr^i)_4$		613vs	541vs
$(EtZnOBu^t)_4$		611vs	540vs
$(EtZnOCHPh_2)_3$		612s	505m
$(EtZnOC_2H_4NMe_2)_3$		617,592s	517,490s
$(MeZnSMe)_x$	1161m	655s	525s
$(MeZnSPr^i)_x$	1163m	654vs	521s
$(MeZnSPh)_x$	1158mw	675vs	526s
$(MeZnSePh)_x$	1152mw	667vs	526s
$(MeZnSBu^t)_5$		669vs	531s

Compound	δ(Zn-Me)sym	Zn-Me rock	ν(Zn-Me)
$(MeZnSPr^i)_6$	1156s	669vs	531s
$(EtZnSBu^t)_5$		610vs	505s
$(MeZnOAc)_x$	1169w	680vs	540s
$(MeZnO_2PMe_2)_x$		662vs	535vs
$(MeZnNPh_2)_2$		667s	548s
$Mepy_2ZnNPh_2$	1163m	621vs	505s
$(EtZnNPh_2)_2$		620s	518s
$(EtZnNPhC{:}OEt)_4$		610s	508s
$(EtZnI)_x$		625s	517m

There is a tendency for ν(Zn-Me) to fall as the co-ordination number of the metal increases, from 615 cm^{-1} in dimethylzinc to 506-514 cm^{-1} in those compounds in which the metal is undoubtedly four co-ordinate. The absorptions at 510 and 453 cm^{-1} of the tetramethylethylenediamine complex of dimethylzinc would be due to the antisymmetric and symmetric C-Zn-C stretching modes, respectively. The relatively high frequencies of the alkoxides and thio-derivatives suggest that the metal is three- rather than four co-ordinate in these compounds. The frequencies of these vibrations should not, however, be used as a guide to co-ordination number until reliable structural information becomes available for some of the compounds concerned.

A P P E N D I X.

A P P E N D I X

Zinc hydride and methylzinc borohydride.

Zinc hydride can be conveniently prepared by reaction of dimethylzinc with lithium aluminium hydride in ether,

$$ZnMe_2 + 2LiAlH_4 \longrightarrow ZnH_2 + 2LiAlH_3Me.$$

It is described as a white involatile solid which is insoluble in ether and which slowly decomposes at room temperature (turns grey in one or two days) in an inert atmosphere. Decomposition is rapid at 85°.

The above reaction is reported to yield zinc hydride of 96·5 wt. % purity, and samples of comparable purity have also been obtained by reaction of dimethylzinc with dimethylaluminium hydride in the absence of solvent.

The reaction between dimethylzinc and lithium aluminium hydride in the absence of ether does not go to completion and when the volatile material left after reaction has apparently ceased is evaporated and then condensed, non-volatile zinc hydride is found admixed with the liquid condensate. The authors concluded that the initial reaction produced volatile intermediates, e.g. Me_2AlH or MeZnH or both, and subsequent reaction of such volatile products with each other yielded zinc hydride. Evidence for the exsistence of methylzinc hydride is the reported observation that zinc hydride dissolves in ether containing a considerable excess of dimethylzinc.[175] The following exploratory

reactions were undertaken to try to establish the exsistence of alkylzinc hydrides.

Reaction of lithium aluminium hydride with dimethylzinc- trimethylamine.

Dimethylzinc- trimethylamine (1·8g., 11·6m.mole) in ether (20 c.c.) was added to lithium aluminium hydride (0·42g., 11·0m.mole) also in ether (20 c.c.) at -92°. The resulting clear solution was allowed to warm very slowly. At approximately -40° a white solid suddenly precipitated; this was filtered off, washed with much ether, and finally pumped dry. The product was found to be zinc hydride; it was vigorously hydrolysed by moisture, and decomposed at 90° when heated.

(Found: Zn, 90·1; hydrolysable H, 3·11%. Calc. for H_2Zn: Zn, 97·0; hydrolysable H, 2·97%).

The product was thus 92·9 wt. % zinc hydride, the impurities probably being aluminium hydride, lithium hydride and methylated lithium aluminium hydride. The high H:Zn ratio (2·25:1) is consistent with this.

The hydride was found to be insoluble in N,N,N′,N′-tetramethylethylenediamine, and is probably an electron-deficient polymer.

A suspension of zinc hydride in ether containing a three-molar excess of dimethylzinc was refluxed for about thirty minutes. The zinc hydride did not dissolve, and fractionation of the filtrate showed no evidence of any compound other than ether and dimethylzinc.

The infrared spectrum of zinc hydride recorded as a mull in perfluorokerosene contained a strong broad (half-height width 458 cm^{-1})

band at 1466 cm^{-1} probably due to vibrations involving bridging Zn-H.

Reaction of triethylstannane with diethylzinc.

Alkyl-hydrogen exchange has recently been shown to occur between diethylberyllium and triethylstannane to yield tetraethyltin and ethylberyllium hydride.[40]

Diethylzinc (0·60g., 4·88m.mole) and triethylstannane (1·0g., 4·85m.mole) were placed in a glass tube cooled to -196°, and after evacuating the nitrogen atmosphere the tube was sealed off at a constriction. The mixture was allowed to warm slowly, and at about -10° the clear colourless liquid suddenly turned black. In order to obtain complete reaction it was found necessary to maintain the tube at room temperature for about three weeks. On opening the tube ethane (107 N c.c., 4·78m.mole) and zinc (0·3g., 4·6 m.g. atom) were obtained. A volatile liquid product was identified by its infrared spectrum as tetraethyltin. Zinc was also deposited when the reaction was carried out in the presence of trimethylamine, but the reaction proceeded much more slowly.

The reaction can be expressed by either of the two following equations.

a. $Et_3SnH + Et_2Zn \longrightarrow EtZnH + Et_4Sn$

$EtZnH \longrightarrow EtH + Zn.$

b. $Et_3SnH + Et_2Zn \longrightarrow EtH + Et_3Sn\text{-}ZnEt$

$Et_3Sn\text{-}ZnEt \longrightarrow Et_4Sn + Zn$

It has recently been reported[176] that when diethylzinc reacts with two moles of triethylstannane, two moles of ethane, one equivalent of zinc metal, and hexaethyldi-tin are formed. This seems to favour reaction b, since zinc hydride could reasonably be expected to form if the reaction proceeded by alkyl-hydrogen exchange.

Reaction of dimethylzinc with diborane.

Dimethylzinc and diborane are reported to react to yield involatile $HZnBH_4$, though no experimental conditions are given in the literature.[177]

Diborane (16·1 N c.c., 0·719m.mole) and dimethylzinc (102 N c.c., 4·55m.mole) were maintained at room temperature in a sealed glass tube. After several minutes a white solid formed, and to ensure complete reaction the tube was left at room temperature for a further thirty-six hours. On opening the tube, trimethylborane (16·0 N c.c., 0·715m.mole) and dimethylzinc (70·0 N c.c., 3·125m.mole) were obtained. They were identified by their infrared spectra. Part of the white solid which remained in the tube could be vacuum sublimed at room temperature (10^{-4} mm.), and when left to sublime under its own vapour pressure in a sealed tube it was obtained as very long colourless needles, m.p. 55-60° (decomp.), the melt evolved dimethylzinc (identified by infrared spectrum).

(Found: Zn, 68·2; hydrolysable Me, 15·9; hydrolysable H, 4·06%. CH_7BZn requires Zn, 68·7; hydrolysable Me, 15·8; hydrolysable H, 4·20%). The volatile solid was thus identified as methylzinc borohydride, and

since 0·719m.mole of diborane had reacted with 1·425m.mole of dimethylzinc the reaction can be written thus,

$$B_2H_6 + 2Me_2Zn \longrightarrow Me_3B + MeZnBH_4 + ZnH_2$$

The involatile residue gradually became grey, due to the formation of metallic zinc, as the methylzinc borohydride was removed by sublimation, it was not investigated further.

The vapour pressure of methylzinc borohydride at room temperature (approx. 23°) is 1·1mm., but the fact that it decomposes at its melting point excludes any possibility of determining the molecular weight in the vapour phase. It is also insoluble in benzene. It is rapidly hydrolysed by water and when kept at room temperature in an inert atmosphere or under vacuum it slowly becomes grey (2 days) due to metallic zinc; the dark grey residue reacts with water with explosive violence. Samples of methylzinc borohydride can be kept at least for several months at -30° without any sign of decomposition.

The infrared spectrum of the compound recorded as a Nujol mull contained bands at the following frequencies: 2445m(asym. B-H stretch); 2387m(sym. B-H stretch); 2198vs(br), 2083vs(sh)(bridging B-H-Zn); 1227vs(br)(in-plane BH_2 deformation); 1116w(2x556?); 971m, 947m(out-of-plane BH_2 deformation); 690vs(Zn-Me rock); 556vs(Zn-Me stretch).

Reaction of methylzinc borohydride with trimethylamine.

A tensiometric titration showed that methylzinc borohydride absorbs

one molar equivalent of trimethylamine; the solid liquefies during the addition of the latter. The mixture was separated, with difficulty by fractionation through a trap cooled to -10^{o}, into a volatile liquid and a rather less volatile solid. The liquid was identified as dimethylzinc-trimethylamine (identical IR to a previously prepared sample), and the infrared spectrum of the solid recorded as a Nujol mull contained bands at 2392 (terminal B-H stretch) and a very broad band centred at 2105 cm^{-1} (bridging B-H groups). The spectrum at frequencies of less than 2000 cm^{-1} indicate the presence of co-ordinated trimethylamine.

Trimethylamine thus appears to react with methylzinc borohydride, causing disproportionation. The reaction may be represented by the following equations:

$$MeZnBH_4 + NMe_3 \longrightarrow MeZnBH_4 \cdot NMe_3$$

$$2(MeZnBH_4 \cdot NMe_3) \longrightarrow Me_2Zn \cdot NMe_3 + Zn(BH_4)_2 \cdot NMe_3 .$$

The zinc borohydride adduct has not, at this stage, been investigated in detail.

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