Organic and hydride chemistry of beryllium

N.A Bell

ORGANIC AND HYDRIDE CHEMISTRY OF BERYLLIUM

by

N.A. BELL.

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Memorandum.

The work described in this thesis was carried out in the University of Durham between September 1961 and May 1964. This work has not been submitted for any other degree and is the original work of the author except where acknowledged by reference.

Summary.

Mixed methyl- and ethyl-beryllium hydrides have been prepared in ether solution by reaction between the sodium hydridodialkylberyllates $Na(R_2HBe)$, and beryllium chloride. Ether can be removed from the product which has the overall composition $R_4Be_3H_2$ ($R= -CH_3$, $-C_2H_5$). After evaporation of ether from solutions of '$Me_4Be_3H_2$' which probably contains many complex species in equilibrium, heating at low pressure causes disproportionation into volatile dimethylberyllium and involatile beryllium hydride still containing some methyl groups. A similar disproportionation occurs more readily when the ethyl analogue is heated and the influence of excess sodium hydridodiethylberyllate and beryllium chloride on this reaction has been studied.

Ethereal solutions containing '$Et_4Be_3H_2$' have been shown to react with sodium hydride to form sodium hydridodiethylberyllate and a sodium hydridoberyllate which has not been characterised.

Although a pure alkylberyllium hydride $(RBeH)_n$ could not be obtained from the above mixed hydride ('$R_4Be_3H_2$'), coordination compounds of methylberyllium hydride have, however, been isolated. Reaction between trimethylamine and '$Me_4Be_3H_2$' gives a mixture of the known compound $Me_2Be.NMe_3$

and $(MeHBe.NMe_3)_2$ which have been separated and the vapour pressure and vapour phase association of this latter complex have been studied. The diamine $(Me_2NCH_2-)_2$ gives the previously described compound $(Me_2NCH_2-)_2BeMe_2$ together with an insoluble, involatile and probably polymeric complex $\left[(Me_2NCH_2-)_2(BeMeH)_2\right]_n$. The analogous ether $(MeOCH_2-)_2$ reacts in a similar way forming the previously described compound $(MeOCH_2-)_2BeMe_2$ and a colourless viscous oil $\left[(MeOCH_2-)_2(BeMeH)_2\right]_n$. A 2,2'-bipyridyl complex of methylberyllium hydride could not be isolated since this red complex decomposes in solution to form a brown tarry material.

Reaction between trimethylamine hydrochloride and sodium hydridodiethylberyllate in ether resulted in the evolution of both hydrogen and ethane and this was therefore not a satisfactory method for the preparation of an ethylberyllium hydride-trimethylamine complex. However, reaction between triethylstannane and diethylberyllium resulted in the formation of ethylberyllium hydride which was characterised by conversion into its trimethylamine complex.

Hydride ion has been shown to displace trimethylamine from the liquid complex diethylberyllium-trimethylamine in boiling ether, with formation of the hydridodiethylberyllate salt.

The infrared spectrum of dimethylberyllium in the gas phase and the spectra of organoberyllium and organoberyllium hydride coordination complexes have been studied and correlations established for these compounds, with particular respect to beryllium-hydrogen frequencies.

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INTRODUCTION

INTRODUCTION.

The work described in this thesis is concerned with the preparation of organo-beryllium hydrides, their reactions with donor molecules, and an infrared spectroscopic study of these and other beryllium compounds.

In this introduction, the chemistry of compounds relevant to these topics is discussed. First, the preparation, properties, and coordination compounds of organo-beryllium compounds are considered, including a review of the bipyridyl complexes of beryllium which are covered separately. Preparative methods for and reactions of beryllium hydride are included, together with the relevant hydride chemistry of other Group II and Group III elements. Finally spectroscopic data, relevant to the compounds studied, are described.

Beryllium, having the electronic configuration $1s^2 2s^2$, almost exclusively forms covalent compounds due to the small size and therefore high polarising power of the dipositive cation Be^{2+} . The atomic radius of beryllium is 0.89Å and the calculated ionic radius of Be^{2+} is 0.34Å . The high ionisation potentials of beryllium, the first being 215 and the second 420 kcal./mole, would suggest that free divalent ions of beryllium in its compounds do

not exist. Beryllium fluoride, which might be expected to be the most ionic compound of beryllium, is a poor conductor of electricity in the fused state and beryllium oxide has only about 40 per cent ionic character.

Compounds of beryllium have covalencies of two, three or four for the metal atom but there are no known compounds with a coordination number greater than four, since the atomic orbitals of principal quantum number three are of too high an energy to participate in bond formation and no hybrid orbitals involving d-orbitals can be expected for beryllium. The coordination number of two arises from the use of sp hybrid orbitals by the beryllium to give a linear molecule as is found in the case of beryllium chloride at high temperature when it exists as a monomer[4] and, beyond reasonable doubt, in monomeric di-tertiarybutylberyllium[48]. The rather unusual coordination number of three is found, for example, in dimethylberyllium-trimethylamine[5], in which the beryllium atom must make use of sp^2 hybrid orbitals. Beryllium, however, has a strong tendency to form four covalent compounds using sp^3 orbitals to give tetrahedral bonding. The viscosities, conductivities and freezing points of solutions of beryllium salts[63] show that the beryllium ion is more strongly hydrated than any other divalent

cation and its salts always have four molecules of water of crystallisation for each beryllium atom. The ionic mobilities at 25°C are :

Be	Mg	Ca	Sr	Ba	Ra
30	55.5	59.8	59.8	64.2	67

The phthalocyanine complex of beryllium is exceptional in that it has a square-planar configuration due to the shape of the phthalocyanine molecule[6].

Organo-Beryllium Compounds.

Beryllium dialkyls and diaryls have been prepared in small quantities by the action of beryllium metal on the dialkyl or diaryl derivatives of mercury at elevated temperatures, often with traces of mercuric chloride as catalyst.[7-13,21,22,23]. On larger scales, the reaction between beryllium chloride and a Grignard[13,14,37]. or lithium reagent[14] in ether is better :

$$BeCl_2 2Et_2O + 2RMgX \longrightarrow BeR_2 + MgCl_2 + MgX_2$$

or $$BeCl_2 2Et_2O + 2RLi \longrightarrow BeR_2 + 2LiCl.$$

When prepared by this method, complete separation of the beryllium compound from traces of ether is usually difficult.

Dialkylberyllium compounds are also formed when alkylberyllium halides are cautiously heated[8] and by the

reaction of free methyl or ethyl radicals with metallic beryllium[16]. Some alkyl- and aryl- beryllium halides have been prepared by heating beryllium metal with the appropriate alkyl halide.[8,17].

All the organo-beryllium compounds must be prepared and handled in the absence of oxygen, moisture and in some instances carbon dioxide, with which they react rapidly.

Dialkylberyllium compounds react with hydrogen peroxide in ether solution producing beryllium peroxide[18]. and with phenyl isocyanate to form the corresponding anilide.[13].

Alkylberyllium compounds have been used for the polymerisation of alkenes, and as intermediates as exemplified by :-

$$Et_2Be + MePr^nC{=}CH_2 \longrightarrow MeEtPr^nCCH_2BeEt. \quad [19.]$$

They react with ethylene stepwise, in a similar manner to aluminium and lithium alkyls, and Ziegler has reviewed this class of reaction thoroughly.[20].

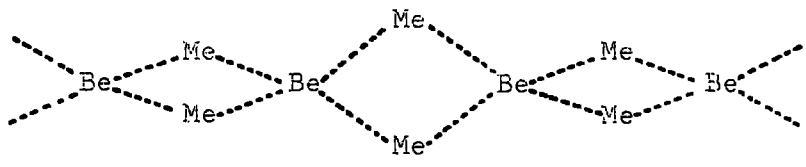
The electronic unsaturation of beryllium alkyls leads to the formation of coordination compounds with donor molecules.

Dimethylberyllium.

Small quantities of dimethylberyllium are most conveniently prepared by the reaction of dimethylmercury and excess powdered beryllium metal at 100°C.[11,12,21,22,23]. The product can be sublimed from the reaction mixture under high vacuum, and traces of mercury can be removed with gold foil.[21].

Preparation from the Grignard or lithium reagent presents some difficulties. The product of this reaction can be isolated free from dissolved salts by a process of 'ether distillation' at atmospheric pressure,[13,15,24]. but complete separation from ether is difficult. The use of dimethyl sulphide as a solvent has been suggested,[25]. since dimethyl sulphide does not coordinate to dimethylberyllium[5], but the method has not been examined experimentally.

Solid dimethylberyllium has a polymeric structure similar to silicon disulphide. X-ray diffraction methods[26]. have shown that there is an approximate tetrahedral distribution of methyl groups round each beryllium atom with all the beryllium - carbon bonds equivalent and of length 1.92Å , the Be-C-Be angle being 66° :



The extrapolated sublimation temperature, 217°C , and the interchain distances in the polymer, exclude an ionic structure. Both beryllium and carbon atoms make use of four tetrahedral (sp^3) atomic orbitals and it is probable that three-centre molecular orbitals $Be(sp^3)$ + $C(sp^3)$ + $Be(sp^3)$ are formed from these.

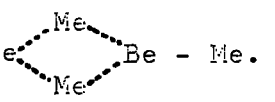
Dimethylberyllium forms colourless needles when condensed from the vapour phase but has not been observed to melt. The vapour pressure of the solid is given by the equations[27] :

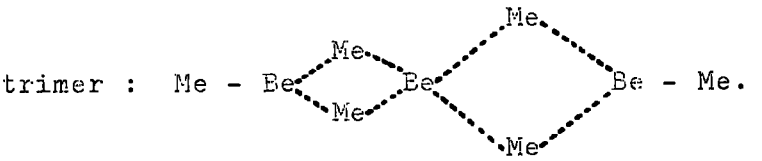
$$100\text{-}150^{\circ}C : \quad \log_{10}P(mm.) = 12.530 - 4771/T.$$

$$155\text{-}180^{\circ}C : \quad \log_{10}P(mm.) = 13.292 - 5100/T.$$

Vapour density measurements have been made between 160 and 200°C and from a study of the pressure - dependence of the vapour density, it was shown that the vapour consists of monomer, dimer and trimer molecules, together with higher polymers which only become important at near-saturation conditions. Heat and entropy terms have been obtained for the monomer-dimer and monomer-trimer equilibria and structures have been proposed for the monomer, dimer and trimer[27]. :

monomer : Me - Be - Me.

dimer : 

trimer : 

In these formulae, dotted lines represent half bonds.

Thermal decomposition starts to occur at 202°C with the formation of $(BeCH_2)_n$ as intermediate product and at 220-230°C beryllium carbide is formed as end product :

$$n(CH_3)_2Be \xrightarrow{202^\circ} nCH_4 + (BeCH_2)_n \xrightarrow{220^\circ} \frac{n}{2} Be_2C + \frac{n}{2} CH_4 \quad [29]$$

Beryllium metal can be deposited by the electrolysis of a mixture of dimethylberyllium and beryllium chloride in ethereal solution.[15].

Dimethylberyllium reacts with diborane above room temperature, the reaction taking place in several stages.[7]. Trimethylborane, methylberyllium borohydride $(MeBeBH_4)_n$ as an intermediate product, beryllium borohydride and an involatile substance which is probably $(BeBH_5)_n$ are formed during the reaction.

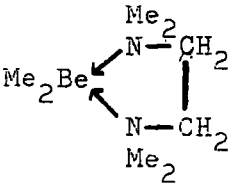
Dimethylberyllium will only coordinate with molecules which are strong enough to break down its polymeric structure. It forms coordination compounds with trimethylamine, trimethylphosphine, dimethyl- and diethyl-ether, but not with trimethylarsine or dimethylsulphide and the properties of these compounds indicate that the order of heat of

coordination is N > P > O > As,S [5]. This same order is found with trimethylaluminium[30]. and trimethylgallium[31]. when the acceptor atom is of the type that forms simple coordination links without complications due to double bonding or any similar influence of d-orbitals.

Dimethylberyllium forms a 1:1 compound ($Me_2Be{\leftarrow}NMe_3$) melting at 36°C ,with trimethylamine. This is stable to 180°C and is monomeric in the gas phase[5] , although slightly associated in benzene solution[32]. Below 9-10°C, a compound $(Me_2Be)_2(NMe_3)_3$ can be obtained but this begins to dissociate on warming

In the reaction of dimethylberyllium with trimethylphosphine, complex equilibria result from the similarities between the affinities of dimethylberyllium molecules for trimethylphosphine and for each other. A considerable range of compounds $(Me_3P)_x(Me_2Be)_y$ where x= 2,3,1,2,2,2 and y= 1,2,1,3,4,5. respectively are formed, each being stable in a certain range of temperature and pressure of trimethylphosphine. All the trimethylphosphine can be removed in vacuo at room temperature. One peculiarity is that two molecules of phosphine can coordinate to one molecule of dimethylberyllium, whereas the analogous trimethylamine complex is unknown even though nitrogen is a stronger donor to beryllium than is phosphorus, as shown

by the dissociation pressures of these compounds. The non-formation of $Me_2Be(NMe_3)_2$ must be due to an entropy rather than a steric effect since the phosphine analogue would be more sterically hindered and the compound

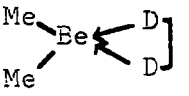


forms.[33].

With dimethylether, the compounds $Me_2Be.OMe_2$, $(Me_2Be)_2(OMe_2)_3$, $(Me_2Be)_3(OMe_2)_2$ and $(Me_2Be)_2OMe_2$ have been observed but all are less stable than the phosphine complexes.

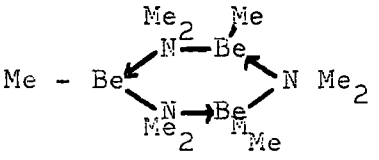
With diethylether, there was no indication of a compound of definite composition being formed.

Colourless crystalline needles, m.p. 91-92°C ,of dimethyldipyridineberyllium were isolated from the reaction of pyridine with dimethylberyllium in ether.[33].

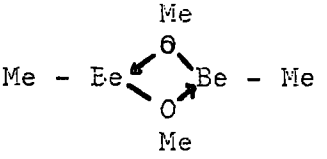
Bidentate ligands form very stable 1:1 chelate complexes with dimethylberyllium.[33]. N,N,N',N',- tetramethylethylenediamine and the chelating diether 'Monoglyme' both form well-defined complexes with dimethylberyllium of the type  where D is the donor atom. Both compounds must have very small dissociation pressures since they can be sublimed unchanged in vacuo. In benzene

solutions, the ether complex is monomeric but the amine is about ten per cent associated.

Donor molecules containing reactive hydrogen atoms also react readily with dimethylberyllium with the elimination of methane and formation of di- ,tri-, or polymeric products. Dimethylamine forms the adduct $Me_2Be \leftarrow NHMe_2$ which melts at 44°C with the evolution of methane, leaving the white crystalline trimeric compound $(MeBeNMe_2)_3$ to which a cyclic structure has been assigned (I) and which does not react with trimethylamine below 50°C.



(I) m.p. 55-56°C



(II)

Methanol and dimethylberyllium react with the immediate evolution of methane forming a dimeric product (II) which disproportionates to dimethylberyllium and beryllium methoxide ($Be(OMe)_2$) above 120°C. [34].

Di<u>iso</u>propylamine[32] and dimethylberyllium form a fairly stable monomeric adduct ($Me_2Be \leftarrow NHPr^i_2$) which starts to lose methane slowly at about 100°C in the presence of excess amine. Loss of methane was not quantitative

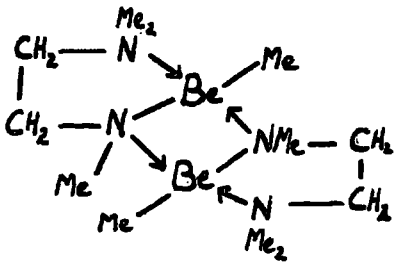
however, even after refluxing with excess amine for several days, and this is probably due to steric hindrance by the isopropyl groups.

Methylamine and methanethiol will also liberate methane from dimethylberyllium but the other product of the reaction were not characterised.[34] Methylamine appears to displace trimethylamine from dimethylberyllium-trimethylamine and therefore the reaction follows a similar course to the reaction of dimethylberyllium and methylamine.[32]

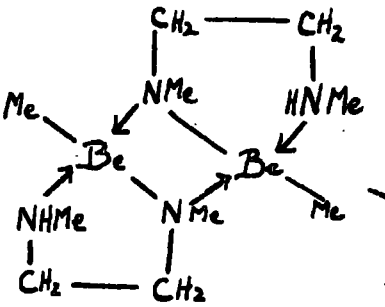
N- methyl substituted primary and secondary diamines also yield products in which the coordinative unsaturation of beryllium is relieved by association or polymerisation.[33]

N,N,N'- Trimethylethylenediamine loses a mol. of methane at room temperature with dimethylberyllium, forming the dimeric product (III) which melts at 116-118°C.

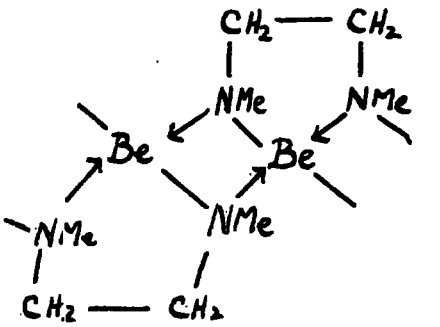
One mol. of methane is also liberated from N,N' - dimethylethylenediamine and dimethylberyllium in ether as soon as the mixture melts. The product, which is believed to have the structure (IV), sublimes slowly at 90°C. and at 145°C about eighty per cent of the remaining methyl bound to beryllium is evolved as methane. When (IV) is heated in tetralin solution, methane is evolved quantitatively at 140-150°C. and an insoluble polymeric product (V) is formed.



(III)



(IV)



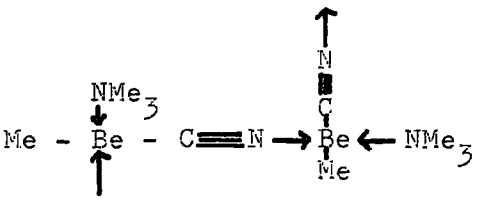
(V)

Unsymmetrical N,N- dimethylethylenediamine liberates one mol. of methane from dimethylberyllium in ether just below room temperature, giving a product analogous to (IV). This product sublimes at 115°C, and at 170°C it melts with a vigorous evolution of methane and, on cooling, a hard glass is produced.

Ethylenediamine liberates about eighty per cent of the methyl from dimethylberyllium at room temperature with the formation of a white, amorphous, evidently polymeric material. Even after heating to 45°C, about six per cent of the methyl groups is retained but this is released on hydrolysis.

The reaction between hydrogen cyanide and dimethylberyllium has also been investigated[35,36]. Beryllium dicyanide is precipitated when ethereal dimethylberyllium is added slowly to excess hydrogen cyanide in benzene and this does not react with trimethylamine nor dissolve in solvents with which it does not react, since it no doubt has a cross-linked polymeric structure. Equimolar amounts of

the above reactants form methane and the soluble methylberyllium cyanide from which the ether can be removed by pumping at 70°C but the residue does not redissolve and is no doubt polymeric. No method for purifying this compound was found but its coordination complex with trimethylamine was isolated as an involatile amorphous product from the reaction of dimethylberyllium-trimethylamine and hydrogen cyanide.



Diethylberyllium.

This compound cannot be prepared from diethylmercury and beryllium metal[13,23]. but is conveniently obtained from the reaction of ethylmagnesium bromide and beryllium chloride in ether.[13,37]. Separation from ether is difficult but prolonged pumping, followed by vacuum distillation gives a colourless product boiling at 63°C/0.3mm.Hg., containing about two per cent ether.[37]. Some of the purest material solidifies as white crystals melting between -13°C and -12°C.[13]. Diethylberyllium has recently been prepared[64]. by treating beryllium chloride with triethylaluminium at

100°C for one hour. The beryllium compound is separated from the latter by distillation after the addition of an electron-donor complexing agent for the aluminium compound.

The vapour pressure is given approximately by the equation :

$$\log_{10} p \text{ (mm.)} = 7.59 - 2200/T.$$

whence the extrapolated boiling point is 194°C. [37].

Diethylberyllium is monomeric in dioxan, but is associated in cyclohexane and benzene, its molecular weight being time dependent (160 and 140 respectively two days after the preparation of the solution and 212 and 224 respectively after 240 days).[28].

The apparent dipole moment of diethylberyllium in various solvents is intermediate between those of diethylmagnesium and - zinc. Its moment is 1.0D in heptane, 1.69D in benzene, in both of which it is associated, and 4.3D in dioxan.[39,40].

Diethylberyllium decomposes slowly at 85°C and rapidly at 190-200°C. resulting in the formation of ethane, ethylene, and butene, together with small amounts of 3-hexene, 1-3-cyclohexadiene and benzene. The residue is a mixture of an oil, which can be distilled at 95-100°C/0.1-0.2mm. having the approximate formula $((H \div Be - CH_2 -)_2)_n$, and a crystalline solid $(Be(CH_2)_3)_n$.[37].

Methanol, isopropanol and hydrogen chloride, all react explosively with diethylberyllium.[37.]

Little study of the coordination compounds of diethylberyllium has been made. It forms an orange crystalline complex (Et_2BePy_2) with pyridine[33.] and diphenylamine forms the polymeric compound $(Be(NPh_2)_2)_n$ and ethane.[41.] The reactions between diethylberyllium and also between its trimethylamine complex and the methyl hydrazines have been investigated. In general, liberation of ethane was not quantitative and polymeric materials were formed, although a 1:1 adduct ($Me_2NNMeH.BeEt_2$) was formed with trimethylhydrazine and a 2:1 adduct $(Et_2Be)_2Me_2NNMe_2$ with tetramethylhydrazine.[3.]

Strohmeier and co-workers[42,43,44.] have prepared in recent years a series of ether-free salts of diethylberyllium of the type $MX(BeEt_2)_n$ where M represents an alkali metal, X represents halide or cyanide and n = 1,2,or 4.

Potassium fluoride dissolves in ethereal diethylberyllium at 65°C over three hours and the crystalline material $KF(BeEt_2)_2$ can be isolated. At 70°C in benzene this compound decomposes to form the insoluble material $KFBeEt_2$ and pure, ether-free diethylberyllium which can be distilled out. Ether-free diethylberyllium can also be obtained by heating $KF(BeEt_2)_2$ at 100-130°C. Rubidium

and caesium fluorides also form similar compounds but ~~either~~ sodium cyanide, sodium fluoride, lithium fluoride, caesium chloride and potassium chloride either do not appear to react or, at least, no pure compound could be isolated from their reaction. Potassium cyanide forms the product $KCN.(BeEt_2)_4$ which loses pure diethylberyllium at 100-150°C in vacuo and tetra-ethylammonium chloride forms a viscous liquid product at room temperature of the type $Et_4NCl.(BeEt_2)_2$. The tendency for complex formation has been investigated, and the order of reactivity appears to be $CsF > RbF > KF > NaF$.

A crystalline pyrophoric material $(NaBeEt_2H)_n$ melting at 198°C, has been isolated from the reaction of diethylberyllium and sodium hydride in ether. Lithium hydride reacts with diethylberyllium at 110°C but a pure product was not isolated and magnesium hydride does not appear to react.[45].

Di-isopropylberyllium.[46].

This material has been prepared by the reaction between isopropylmagnesium bromide and beryllium chloride in ether. An ether-free product can be obtained by refluxing with continuous pumping for a long time. The ether-free product which is a colourless, slightly viscous liquid,

freezes at -9.5°C and is soluble in benzene in which it is dimeric. Its vapour pressure, (0.17mm. at 20°C and 0.53mm. at 40°C) and extrapolated boiling point (280°C) are consistent with a dimeric structure.

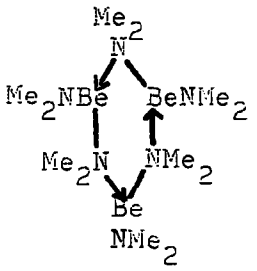
Propene is slowly evolved from di-isopropylberyllium at 50°C and rapidly at 200°C with the formation of a viscous, non-volatile polymer of isopropylberyllium hydride, which reacts with dimethylamine at room temperature liberating propane and hydrogen in the ratio 2.5 : 1, and which decomposes at 220-250°C forming propane, propene, hydrogen, beryllium and an orange residue. The liquid adduct ($Pr^i_2Be \leftarrow NMe_3$) is formed with trimethylamine and this is monomeric in benzene solution. At 200°C di-isopropylberyllium-trimethylamine loses a mol. of propene forming feathery needles of $(Pr^iBeH.NMe_3)_n$ but this product has not yet been further studied.

Di-isopropylberyllium reacts with methanol giving propane and $(Pr^iBe.OMe)_n$ m.p. 133°C.

With one mol. of dimethylamine, di-isopropylberyllium forms a mol. of propane and the liquid dimethylaminoisopropylberyllium $(Pr^iBe.NMe_2)_n$ which at 100°C evolves propene leaving the glassy product dimethylaminoberyllium hydride $(HBe.NMe_2)_n$.

Addition of two mols. of dimethylamine to di-isopropyl-

beryllium at just above room temperature affords two mols. of propane and bisdimethylaminoberyllium which is trimeric in both benzene solution and the vapour phase and probably has the cyclic structure as shown below:



m.p. 94°C.

Di-tertiary-butylberyllium [47].

This was prepared from ethereal solutions of tert.-butylmagnesium chloride and beryllium chloride. It decomposes slowly at room temperature with the evolution of isobutene and is therefore best kept at low temperature. It has been obtained ether-free by treating the product of the above reaction with beryllium chloride which has a higher affinity for ether, followed by distillation of the di-tert.-butylberyllium.[48]. This latter product is more volatile than the ether complex; it freezes at -16°C, has a vapour pressure of 35mm. at 25°C and is therefore probably monomeric.

Di-tert.-butylberyllium reacts with trimethylamine[47]. but the product has not been well characterised and no other coordination compounds have been studied.

Diphenylberyllium.

This has been obtained by heating diphenylmercury and beryllium metal for one to two hours at 210-220°C followed by recrystallisation from benzene,[49,39.] and by heating the same two reagents in dry xylene in a sealed tube for three days at 150°C.[9.] It melts at 244-248°C with decomposition and its dipole moment is 1.64D in benzene, 4.33D in dioxan and zero in heptane.[39,40.]

A crystalline dietherate m.p. 28-32°C has been isolated from an ethereal solution of diphenylberyllium, and this compound loses ether in vacuo at 130°C.[50.]

The complex salt $Li(BePh_3)$ can be isolated from the reaction of phenyl-lithium and diphenylberyllium in ether at room temperature, followed by recrystallisation from xylene. Crystallisation from dioxan yields a product $(Li(BePh_3)(dioxan)_4)$ containing four molecules of solvent. Diphenyl -magnesium, -cadmium, and -zinc also form similar compounds.[9.]

A complex hydride, $Li(BePh_2H)OEt_2$, has been formed by the reaction of diphenylberyllium etherate and lithium hydride at 160-165°C.[50.]

Dessy[51] has shown that there is no exchange between diphenylberyllium and isotopically labelled beryllium bromide in ether solution and suggests that the complex formed may

be formulated as $Ph_2Be.BeBr_2$. Since similar claims were made in respect of phenylmagnesium bromide, now known to exist as monomer $PhMgBr(OEt_2)_2$, by X-ray diffraction,[61] there is now some doubt about the isotopic exchange results for both beryllium and magnesium compounds.

Beryllium Borohydride.

The most convenient preparation of beryllium borohydride is from the reaction of lithium or sodium borohydride with beryllium halides at elevated temperatures.[62]

It is a white, volatile solid, monomeric in the vapour phase, melting at 123°C and its vapour pressure is 760mm.Hg at 91.3°C.[7]

Beryllium borohydride undergoes reaction with trimethylamine in several stages. It absorbs the amine at -80°C forming the 1 : 1 complex, which is monomeric in the gas phase and does not react with diborane at 70°C. At 100°C in the presence of the amine, it reacts further forming $BH_3.NMe_3$ and $BeBH_5NMe_3$. This latter product loses the amine reversibly above room temperature but not all the amine can be removed.[7]

Bipyridyl Complexes.[33]

A remarkable series of coloured bipyridyl complexes of the organo and halide compounds of beryllium has been prepared. These compounds, their colours, their long-wavelength absorption bands (λ max.), and molar extinction coefficients are listed below.

X in X_2bipy Be.	Colour.	λmax(mμ).	Molar extinction coefficient, x10^3.
Cl	White	352 infl.	1.2
Br	Pale cream	364	2.4
I	Yellow	368	7.0
Ph.	Yellow	353 infl.	0.5
Me.	Yellow	395	2.7
Et.	Red	461	3.7

The bipyridyl complexes of di-isopropylberyllium, isopropylberyllium hydride and di-n-butylberyllium decomposed readily to brown tars.

The increase in molar extinction coefficient as the electronegativity of X decreases and their colours are explained by electron-transfer from the Be-X bonds to the lowest unoccupied molecular orbital of the bipyridyl.

Two black crystalline complexes of beryllium have also

been prepared, - bisbipyridylberyllium ($bipy_2Be$) from the dilithium adduct of bipyridyl and dichloro(bipyridyl)beryllium in 'monoglyme' and crystallised from benzene; lithium bisbipyridylberyllate from lithium bipyridyl and dichloro-(bipyridyl)beryllium in ether. This latter product reacts with bromine to form dibromo(bipyridyl)beryllium.

The magnetic properties of ($bipy_2Be$) and its deep colour are consistent with its formulation as a coordination complex of the bipyridyl anion ($(bipy^-)_2Be^{2+}$).

Beryllium Hydride.

Many methods for preparing beryllium hydride have been investigated, and varying degrees of purity have been obtained.

It was first reported by Schlesinger and co-workers [52.] from the reaction between lithium aluminium hydride and dimethylberyllium in ether. The white, insoluble, involatile material which contains ether, decomposed to beryllium and hydrogen at 125°C and reacted vigorously with water, but not with dry air. Later workers however, showed this product to be inseparably contaminated with aluminium and lithium.[48.]

Coates and Glockling[47.] found that 63mole per cent di-tert-butylberyllium, the rest being ether which could not be removed, starts to decompose at 100°C and at 150°C a

white, apparently non-crystalline solid formed. The volatile products, ether and isobutene were removed and the residue was shown by hydrolysis to be 89mole per cent beryllium hydride. Pyrolysis at 210°C, during which time a little hydrogen was formed, yielded 96.3 mole per cent beryllium hydride, the rest being tertiary butyl groups. Beryllium hydride prepared by this method was remarkably resistant to water, even at room temperature and acid was required to complete the hydrolysis. Pyrolysis at 240-290°C caused increasing liberation of hydrogen which became rapid at 300°C.

Pyrolysis of ether-free di-tert-butylberyllium[48]. at 200°C afforded 97 mole per cent beryllium hydride which has a density of 0.57 gms/cc., and an X-ray powder photograph showed no lines attributable to the hydride.

The direct synthesis from beryllium and both molecular and atomic hydrogen at high temperature and pressure has been tried unsuccessfully.[53,54].

A surface reaction between lithium hydride and beryllium chloride has been noticed but no product was isolated.[55].

Dimethylberyllium reacts with dimethyl aluminium hydride in the absence of solvent.[52]. Although trimethylaluminium was formed as indicated by the equation below, a product free from methyl groups could not be obtained:

$$2Me_2AlH + Me_2Be \longrightarrow 2Me_3Al + BeH_2.$$

This may be due to the intermediate occurrence of a reversible reaction:

$$Me_2AlH + Me_2Be \longrightarrow Me_3Al + MeBeH.$$

No better results than the above could be obtained in isopentane solution.

Beryllium hydride[47.] reacts with two mols. dimethylamine at 160°C liberating hydrogen and forming bisdimethylamino-beryllium; with diborane at 95°C forming beryllium borohydride, but fails to react with trimethylamine even at 210°C.

Hydride Chemistry of other Group II elements.

Alkyl-hydrogen exchange reactions for the preparation of Group II metal hydrides have been investigated but a high degree of purity was never obtained.

Lithium aluminium hydride reacts with some dialkyl derivatives of magnesium, zinc, and cadmium in ether solutions in a somewhat similar, but apparently rather more straightforward way to the reaction with dimethylberyllium, forming the metal hydrides as white, involatile, insoluble powders.[52.] Zinc and cadmium hydrides are obtained ether-free by this method but contain small amounts of other impurities. The

former decomposes at room temperature and the latter at 0°C. into the corresponding metal and hydrogen, whilst dimethylmercury reacts with lithium aluminium hydride at -80°C. forming mercury and liberating hydrogen. Zinc hydride is insoluble in pure ether but dissolves in ether containing a large excess of dimethylzinc presumably with the formation of a methylzinc hydride. Zinc hydride can also be obtained in a similar degree of purity to the above from dimethylaluminium hydride and dimethylzinc.

Magnesium hydride as precipitated from the reaction of diethylmagnesium and ethereal lithium aluminium hydride, contains ether and often aluminium, depending on the proportion of reactants, order of addition, and concentration of solutions.

It is of interest to note that the decomposition temperatures, and therefore the purity of the Group II metal hydrides, varies considerably depending on the method of preparation (compare above method of preparation of beryllium hydride with Coates and Glockling's preparation[47].). It seems probable that these electron-deficient hydrides prepared as above, are contaminated to various extents with other electron-deficient molecules such as aluminium hydride, or with lithium hydride, or their methyl analogues, all of which may be formed during the reaction.

Zinc[65]., cadmium[66]., and mercury (II)[66]. iodides as well

as diphenylmercury[77]. are reduced by lithium aluminium hydride but pure hydrides were not obtained. A third but less satisfactory preparation of zinc hydride involves the use of zinc chloride and aluminium chlorohydride.[65].

Alkyl-hydrogen exchange reactions between the diethyl derivatives of magnesium, zinc, cadmium and mercury and diethylaluminium hydride in the absence of solvent, have been investigated.[67]. Although triethylaluminium was isolated in every case, the only hydride isolated was that of magnesium in a purity of 97%. (No mention of the impurity was made). The zinc and cadmium compounds decomposed liberating hydrogen and depositing the metal under the reaction conditions used (temperatures in the range 25-50°C). Diethylmercury reacts with diethylaluminium hydride with the formation of ethane , hydrogen and mercury. The presence of ethane in the reaction products reflects the intermediate formation of ethylmercury hydride and this mainly breaks down to ethane and mercury or reacts with diethylaluminium hydride to give mercury hydride which subsequently breaks down to mercury and hydrogen.

An apparently polymeric mixed hydride-borohydride $(HZnBH_4)_n$. is formed from dimethylzinc and diborane.[68].

Organo-zinc compounds also form anionic hydride complexes. Diphenylzinc[50]. forms an ether complex $Li(ZnPh_2H)OEt_2$ with lithium hydride in a similar way to the analogous beryllium compound. Recently the compound $(NaH(Et_2Zn)_2)_n$.

has been formed by the reaction of sodium hydride with diethylzinc in 'monoglyme' or 'diglyme' but attempts to isolate it resulted in its decomposition. No reaction was observed in ether, tetrahydrofuran, aromatic or aliphatic hydrocarbons. Sodium hydride also reacts with zinc chloride in glycol ethers forming $(NaH(ZnCl_2)_2)_n$ which could not be isolated, but two competing reactions appear to take place since sodium chloride and zinc metal are deposited together with some gas evolution which is more rapid at elevated temperatures.[69].

The Grignard reagent ($HMgX$) derived from hydrogen has been obtained as bis-tetrahydrofuran and ether crystalline complexes from the reactions of ethylmagnesium halides with diborane in the appropriate solvent at -25°C.[70].

$$B_2H_6 + 6EtMgX \longrightarrow 6HMgX + 2Et_3B.$$

Analogous solvent-free products have been obtained from the pyrolysis of Grignard reagents.[71,72].

$$C_2H_5MgBr \xrightarrow{220^{\circ}C} C_2H_4 + HMgBr.$$

Later workers[73]. have described this compound, possibly incorrectly, as an equimolar mixture of magnesium hydride and bromide since at 300-350°C. it decomposes into magnesium, hydrogen and magnesium bromide.

Some dialkylmagnesium compounds decompose at elevated temperatures evolving olefin and leaving magnesium hydride as

residue, although side reactions also take place resulting in the formation of some paraffin.[73,74]. Magnesium hydride prepared by this method decomposes into its elements at 280-300°C.

The reactions between diborane and diethylmagnesium appear to be relatively complex.[74,111,112,113]. In ether solution and with excess diethylmagnesium, magnesium hydride is formed; with excess diborane, magnesium borohydride is formed, surprisingly as a white microcrystalline precipitate[74]. but the reactions appear to go through several intermediate stages.

Pure diethylmagnesium (containing no aluminium) absorbs diborane with the formation of $MgH_2(BEtH_2)_2$ (I) which reacts with more $MgEt_2$ forming $EtMgH_2BEtH$ (II) and this reverts to I on reaction with diborane. Both I and II are colourless air-sensitive viscous and therefore possibly polymeric liquids at room temperature which decompose above 80°C, into magnesium hydride and $EtBH_2$ and Et_2BH respectively. The mixed boron-magnesium compounds I and II are further de-alkylated by reaction with Et_2BH;[111].

$$MgH_2(BEtH_2)_2 + Et_2BH \longrightarrow Mg(BH_4)_2 + 2Et_3B.$$

$$2EtMgH_2BRH + 6Et_2BH \longrightarrow 2MgH_2(BRH_2)_2 + 4Et_3B.$$

When aluminium is present (as triethylaluminium), more complete disproportionation is catalysed, producing

ether-insoluble $EtMgBH_4$ and $MgH_2.BEt_3$. The former is stable in the presence of tri-ethylaluminium and diethylmagnesium but decomposes above 100°C. producing $Mg(BH_4)_2$ and Et_2Mg which recombine forming $2MgH_2 + 2EtBH_2$ or if sufficient Et_2Mg is present;

$$Mg(BH_4)_2 + 3Et_2Mg \longrightarrow 4MgH_2 + 2Et_3B.$$

The latter (MgH_2BEt_3) decomposes above 80°C. into MgH_2 and Et_3B. In the presence of aluminium, $EtMgH_2BEtH$ and $HMgH_2BEt_2$ recombine to form MgH_2BEt_3 and $EtMgBH_4$. Addition of tri-ethylaluminium to a stable solution of $EtMgH_2BEtH$ initiates the reaction and the same products are obtained as if aluminium were present during the reaction of Et_2Mg and B_2H_6.[112].

In the presence of aluminium alkyls, $Mg(BH_4)_2$ is formed by the reaction of Et_2Mg and B_2H_6 at room temperature, but when aluminium is absent, a series of complex intermediates is formed which require heating to 100°C. to decompose the intermediates in order to give the borohydride.[113].

The high pressure and temperature reaction of magnesium and hydrogen in the presence of magnesium iodide also results in the formation of magnesium hydride.[75].

A slow reaction between diethylmagnesium and silane in ether results in the gradual deposition of crystalline $(HMgOEt)_n$ which is stable to 200°C.[76].

A comparison of decomposition temperatures of these hydrides, whatever their method of preparation, shows that their stability decreases considerably with increasing atomic weight of the metal atom. However, it is apparent that the investigation of the Group II metal hydrides has been somewhat inadequate, and that there is much scope for further study in this area.

Hydride Chemistry of the Group III elements.

Much work has been done on the hydrides and on reactions of alkali metal hydride complexes of the organo compounds of boron and aluminium, very much less having been reported concerning the remaining Group III elements.

Lithium hydride and triphenylborane form a 1:1 complex at 180°C, the product retaining five mols. of dioxan when recrystallised from that solvent but losing three mols. when heated to 100°C. *in vacuo*.[78] Similar compounds are formed from sodium hydride and triphenylborane in ether[79], and from sodium hydride and triethylborane in ether, 'diglyme' or hexane,[80] but these last two products retain no solvent of crystallisation. The latter product, $NaBEt_3H$, which is a colourless viscous oil, decomposes at 135°C. *in vacuo*. into sodium hydride and triethylborane, and disproportionates in 'diglyme' at 170°C. into sodium borohydride and sodium

tetra-ethylborate. Triarylborane-alkali metal compounds react with methanol also forming an anionic boron hydride derivative.[79.]

$$2Ph_3B^{\cdot}\ Na^+ + MeOH \longrightarrow Na^+(Ph_3B.OMe)^- + Na^+(Ph_3BH)^-$$

The rest of the very extensive hydride chemistry of boron is less relevant to this thesis, and is not discussed further.

Alkali metal hydrides react with organo-aluminium compounds in a similar way to those of boron and beryllium. Sodium hydride reacts with both triethylaluminium and diethylaluminium hydride in heptane at 80°C.[81.] and lithium hydride reacts with triphenylaluminium at 250-260°C.[82.], forming 1:1 complexes. Two products, however, can be obtained from the reaction of triethylaluminium and lithium hydride.[83.] The liquid 1:1 complex is formed by heating this mixture at 130°C. and when this product is mixed with triethyl-aluminium, two phases are formed, the lower layer having the composition $LiH(AlEt_3)_2$. Hydride complexes $NaAlEt_3H$, $NaAlEt_2H_2$ but not $NaAlEtH_3$ can be prepared by heating sodium tetra-ethylaluminate and sodium aluminium hydride together in the right proportions at 80-100°C. [84.]

The reactions between alkali metal hydrides and alkylaluminium halides have been used for the preparation of alkylaluminium hydrides and their alkali metal hydride

adducts.[85,86,87,88].

$$MH + R_2AlCl \longrightarrow MCl + R_2AlH \xrightarrow{MH} MR_2AlH_2.$$

(M represents an alkali metal)

$$3EtAlCl_2 + 7NaH \longrightarrow Et_2AlH + EtAlH_2 + NaAlH_4 + 6NaCl$$

Dimethylaluminium hydride is obtained from the reaction between lithium aluminium hydride and the trimethyl derivatives of boron, aluminium and gallium.[89]. It is trimeric in hydrocarbon solvents, but its vapour consists of a mixture of dimer and trimer molecules. Amines and ethers dissociate the trimers with the formation ofcoordination complexes and an infrared spectroscopic investigation of these compounds has led to the suggestion that the trimers are associated by means of hydrogen bridges and the heat of dissociation is estimated as 15-20 kcals. per hydrogen bond as compared with 10 kcals. for a methyl bridge.[89,90].

Recently dialkylaluminium hydrides have been prepared from trialkylaluminium compounds and tri-alkyl tin hydrides at 80°C. Ethers and tertiary amines inhibit the reaction and thus the electron-deficient state of the aluminium is important since a transition state involving the tin and aluminium compounds is probably first formed.[108].

Alkylaluminium hydride trimethylamine complexes can also be prepared by the alkylation of trimethylamine-alane with dialkylmercury compounds or the equilibration of

trimethylamine-alane with organo-aluminium trimethylamine complexes.[91].

The coordination compounds of alane (aluminium hydride) especially the trimethylamine complexes have been the subject of several studies in recent years. Spectroscopic investigation of the mono- and bis- trimethylamine complexes has shown that both compounds are monomeric in the gas phase[92]. and the bis compound also in the solid state,[93]. in which the five co-ordinate trigonal biprismatic structure has been confirmed by X-ray analysis. The mono-amine complex is prepared from lithium aluminium hydride and trimethylamine hydrochloride in ether below room temperature and this reacts reversibly with trimethylamine forming the bis compound.

$$LiAlH_4 + Me_3NHCl \longrightarrow H_2 + LiCl + Me_3NAlH_3 \xrightarrow{Me_3N} (Me_3N)_2AlH_3.$$

Similarly a 1:1 complex is formed with N,N,N¦N¦-tetramethylethylenediamine from the diamine dihydrochloride in the amine as solvent and lithium aluminium hydride; or from the diamine and bis-trimethylamine alane. This compound is dimeric in the gas phase, association probably occuring by means of hydrogen bridges.[94].

Dialkylammonium halides react with lithium aluminium hydride forming N,-dialkylamino-alanes[95]., which like the tertiary amino-alanes,[95]. react with metal hydrides (Li,Na,

Ca, but not Mg.) forming metal aluminium hydrides.[96]

$$Me_3NAlH_3 + NaH \longrightarrow NaAlH_4 + Me_3N$$

$$2AlH_2NMe_2 + NaH \longrightarrow NaAlH_4 + HAl(NMe_2)_2.$$

Soluble aluminium hydride is prepared from three mols. of lithium aluminium hydride and one mol. of aluminium chloride in ether, but quickly polymerises into an insoluble product.[97] When the above reaction is carried out in the presence of donor molecules, such as dioxan, tetrahydrofuran or amines, the corresponding coordination compounds of alane are formed.[98,99,100,101]

Coordination compounds of aluminium alkyls, aryls, and halides can be prepared from the coordination compounds of alane and an organometallic compound.[102]

$$H_3AlNMe_3 + 3/2\ R_2Hg \longrightarrow R_3AlNMe_3 + 3/2\ Hg + 3/2\ H_2$$

R represents aryl, alkyl or halogen.

$$3H_2AlNMe_2 + 6BuLi \longrightarrow (Bu_2AlNMe_2)_3 + 6LiH$$

Lithium aluminium hydride reacts with the hydrides of the fifth group of elements, liberating hydrogen and forming $LiAl(EH_2)_4$ (where E = N, P or As) but more hydrogen atoms can be replaced, depending on the ratio of the reactants. The above compounds react with water releasing the fifth group hydrides.[107]

Mono- and bis- trimethylamine gallanes are prepared from lithium gallium hydride in a similar way to the alanes.[103,104]

Boron trifluoride acts as a stronger acceptor to trimethylamine and removes it from trimethylamine-gallane leaving gallium hydride which decomposes into its elements at room temperature. When this reaction is carried out in the presence of other donors, different coordination compounds of gallane can be prepared.[105,106].

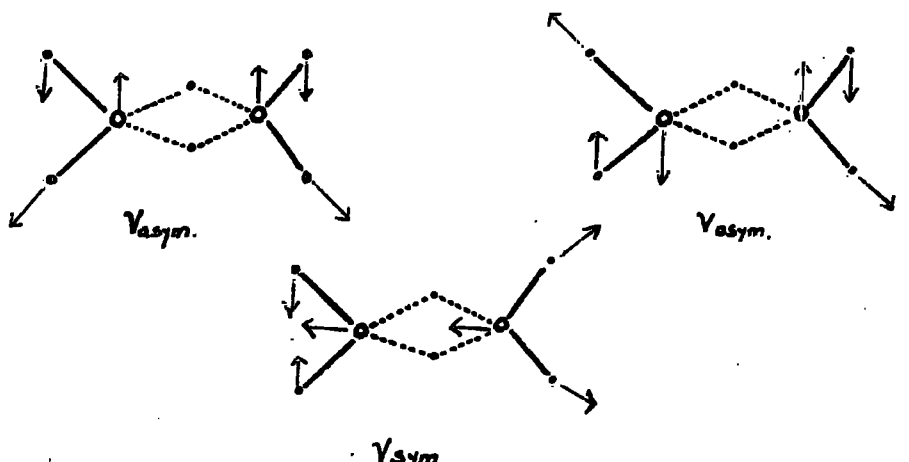
Spectroscopic Background.

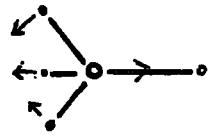
The infrared spectra of beryllium compounds have not been studied to any great extent. The infrared and Raman spectra of solid dimethyl-beryllium have shown that this polymeric material has D_{2h} symmetry with six vibrations active in the infrared and six in the Raman spectrum. The assignment of frequencies for this material and its thermal decomposition product, beryllium carbide, are listed in Table I[29]. Significantly, there was no absorption in the 1400-1500 cm^{-1} region where most compounds containing methyl groups absorb strongly on account of the methyl asymmetric deformation (δ_{asym} CH_3) but there were two very strong bands at 1243 cm^{-1} and 1255 cm^{-1} (Raman 1255 cm^{-1}) which are due to deformations of the bridging methyl groups. In related compounds, Me_2Zn[116], Me_3B[117], Me_6Al_2 and $Me_4Al_2Cl_2$[118,119]., absorptions due to $\delta_{asym.}$ CH_3 are much weaker than those due

to $\delta_{sym.}\ CH_3$.

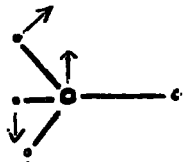
The spectra of organo-aluminium compounds have been extensively studied.[118,119]. In trimethylaluminium the methyl-metal stretching vibration does not differ greatly in frequency from the methyl rocking vibration, and this has made the interpretation of spectra more difficult than might have been expected. The relative weakness of $\delta_{asym.}CH_3$ at 1440 cm^{-1} in $(CH_3)_6Al_2$ and 1140 cm^{-1} in $(CD_3)_6Al_2$ contrasts with the strong absorption due to $\delta_{sym.}\ CH_3$ at 1255 cm^{-1} (bridging) and 1208 cm^{-1} (terminal) which move to 1036 cm^{-1} and 955 cm^{-1} respectively on deuteration. This results in part from the symmetric deformation having some of the character of the aluminium-carbon stretching vibrations which are strong and are listed below:

	$\nu_{asym.}(cm^{-1})$	$\nu_{sym.}(cm^{-1})$
$(CH_3)_6Al_2$	772	616
$(CD_3)_6Al_2$	677	570
$(CH_3)_4Al_2Cl_2$	720	585
$(CD_3)_4Al_2Cl_2$	664	530





$\delta_{sym}\ CH_3$



$\delta_{asym}\ CH_3$

Modes exhibiting shifts on deuteration in the range 1.2-1.3 were considered to be primarily associated with vibrations of the methyl group itself. Stretching vibrations v(Aℓ-Me) in which the methyl group moves as a unit should change much less on deuteration. If the CH_3 and CD_3 groups are regarded as atoms of atomic weight 15 and 18 respectively, then ν_H/ν_D should be $\sqrt{18/15} = 1.096$ if the mass of the aluminium is regarded as infinite or 1.06* if it is taken as 27. Thus a relatively low value of ν_H/ν_D may be taken to indicate a metal-methyl stretching vibration, and higher values 1.2-1.3 may be taken to indicate rocking or deformation modes of the methyl groups.

* $\left(\frac{18 \times 27}{18 + 27} - \frac{15 \times 27}{15 + 27}\right)^{\frac{1}{2}} = 1.059$

Monomeric dimethylberyllium, which presumably is linear, will no doubt have a similar spectrum to dimethylzinc and dimethylmercury which both have D_{3h}, symmetry with essentially free rotation of methyl groups. The assignments for these two compounds are listed in Table II and the C-Hg and C-Zn stretching force constants have been calculated to be 2.45×10^5 and 2.39×10^5 dynes/cm. respectively.[116].

The absorption band at 830 cm^{-1} in beryllium acetyl-

acetonate and substituted derivatives has been assigned to the stretching vibration of the beryllium-oxygen bond, with a force constant of 2.3 x 10^5 dynes/cm.[120]. A study of the ether complexes of beryllium chloride from 1500-650 cm^{-1} includes the range (750-900 cm^{-1}) in which the stretching vibrations of the beryllium-oxygen bond are stated to be found and these frequencies are listed below :[121].

$Cl_2Be(OMe_2)_2$	888	s	s=strong m=medium
$Cl_2Be(OEt_2)_2$	860	m	
Cl_2Be(tetrahydrofuran)$_2$	887	s	
Cl_2Be(tetrahydropyran)$_2$	864	s	
Cl_2Be(dioxan)$_2$	906	s	
$Cl_2Be(OH_2)_4$	890, 905, 927.		

The very strong bands at 800 cm^{-1} and 1090 cm^{-1} in beryllium hydroxide have been assigned as ν(Be-OH) and δ(OH) respectively.[122].

No beryllium-nitrogen frequencies have been assigned but these are stated to occur below 650 cm^{-1} in $Cl_2Be(HNMe_2)_2$ and $Cl_2Be(NMe_3)_2$.[123]. In boron coordination compounds of the type $R_3B.NR_3$, the B-N stretching frequency usually occurs in the 700-800 cm^{-1} region but in compounds of the type $R_2B.NR_2$ the B-N frequency is found at considerably higher wavelengths (1330-1530 cm^{-1}).[124]. The variation in these frequencies has

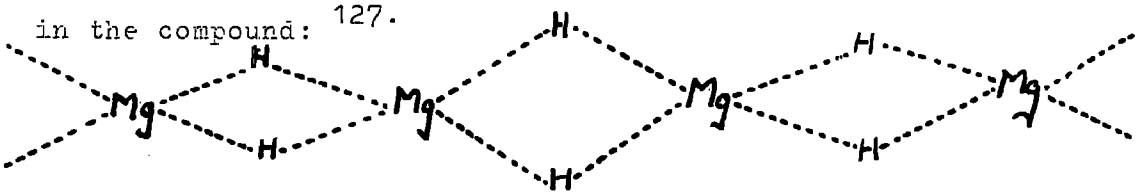
generally been interpreted as being mainly due to a change in the multiplicity of the B-N bond so the high frequency 1552 cm^{-1} observed in the case of the dimeric compound $Ph_2B.NH_2$ in which the B-N bond must surely be single, seems remarkably high. However vibrational modes due to the stretching of boron-nitrogen bonds in a ring can scarcely be expected to be closely comparable to those due to an isolated B-N bond in a monomeric compound.[125]. Beryllium-nitrogen stretching frequencies would probably not be far displaced to lower wavelengths from boron-nitrogen frequencies in similar types of compounds.

Four bands were observed in the absorption spectrum at 500° of beryllium chloride (mostly dimer) of which only two were observed in the emission spectrum at 1000°. These two bands at 1113 cm^{-1} and 482 cm^{-1} were assigned to the asymmetric stretching and bending modes respectively in monomeric beryllium chloride, but it is possible that other polymer bands are masked by the monomer band at 482 cm^{-1} and particularly by the 1113 cm^{-1} band.[126].

Examination of the spectra of beryllium salts containing fluorine has led to the conclusion that ν(Be-F) occurs in the 800-1000 cm^{-1} region.[122].

The infrared spectrum of magnesium hydride contains a broad band (900-1600 cm^{-1}) with a maximum at 1160 cm^{-1}

which has been interpreted as being due to hydrogen bridging in the compound: [127].



The primary feature of the absorption spectra of thin films of lithium hydride and deuteride at room temperature is a broad absorption centred on 588cm^{-1} for the hydride and 446cm^{-1} for the deuteride, and these are probably due to lattice vibrations.[128]. The infrared spectrum of lithium hydride vapour at 1000° consists of rotational fine structure extending from 1600-1100cm^{-1}. The position of the non-existent Q branch in this spectrum has been calculated (from data on the P and R branches) as 1406cm^{-1}.

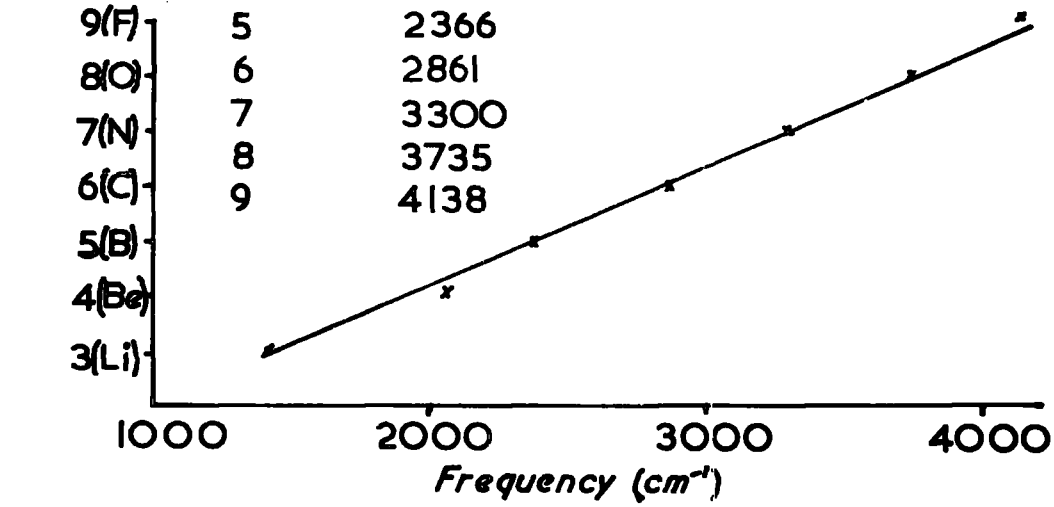
The infrared spectra of trimethylamine complexes have been quite extensively studied; the frequencies observed and the assignments made both for the free base [130,131]. and for trimethylamine-borane [132]. are listed in Tables III and IV respectively.

In this work, assignments of the beryllium-methyl and -hydride infrared frequencies have been made. As a guide to the regions where these frequencies may be expected to be found the two graphs shown in Figure I have been drawn. The graph of the stretching frequencies derived from the electronic spectra for the mono-hydrides of the first period

FIGURE 1.

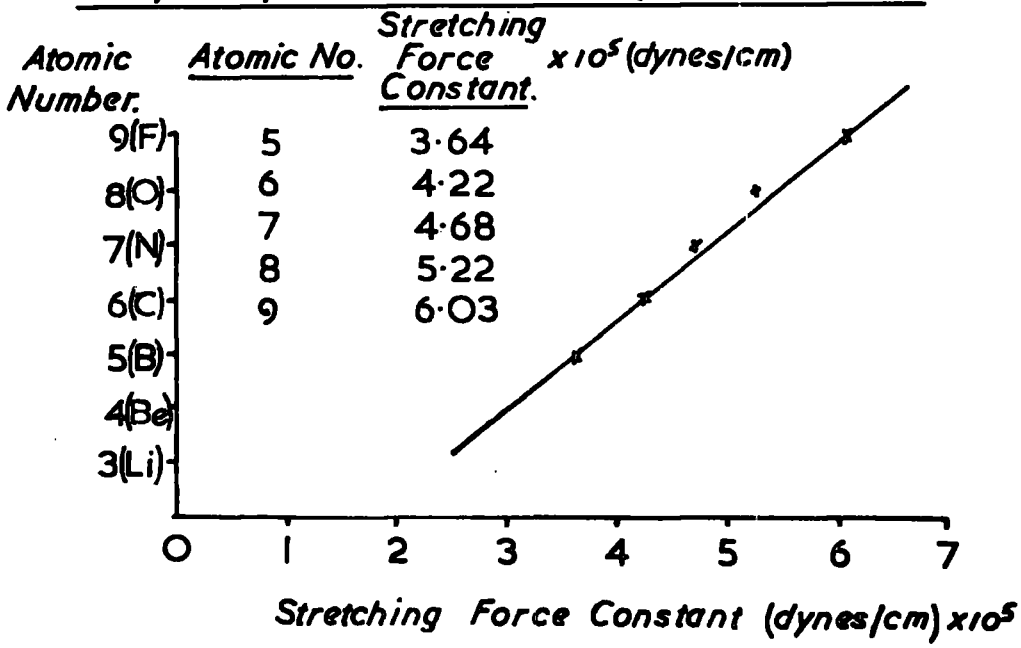
Mono-hydrides of the first period elements.

Atomic No.	Frequency (cm^{-1})
3	1406
4	2059
5	2366
6	2861
7	3300
8	3735
9	4138



Methyl compounds of the first period elements.

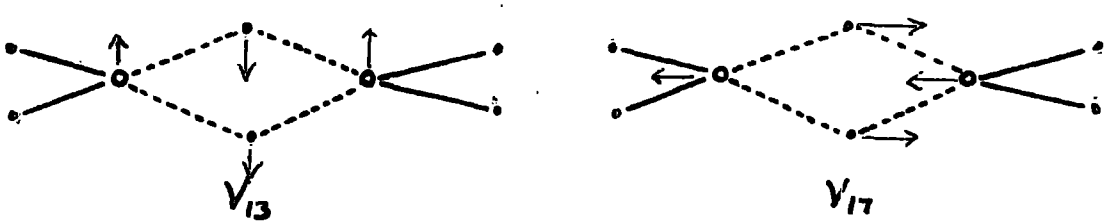
Atomic No.	Stretching Force Constant. $\times 10^5$ (dynes/cm)
5	3·64
6	4·22
7	4·68
8	5·22
9	6·03



elements approximates closely to a straight line from which the extrapolated beryllium-hydrogen stretching frequency is 1880 cm^{-1} although the calculated value is 2059 cm^{-1}.[135]. Thus the terminal beryllium-hydrogen stretching frequency is expected in the range 1850-2100 cm^{-1}. Association involving hydrogen bridges would cause the beryllium-hydrogen frequencies to occur at lower frequency as is found in the boron hydrides: [134].

	$\nu_{13}(cm^{-1})$	$\nu_{17}(cm^{-1})$
B_2H_6	1915	1606
$Me_4B_2H_2$	1972	1605
$Me_3B_2H_3$	1880	1605
$Et_4B_2H_2$	1850	1582

where ν_{13} and ν_{17} are the symmetric out of phase and the asymmetric in phase ring stretches respectively.



The terminal boron-hydrogen stretching frequency usually occurs at about 2500 cm^{-1}.

From the graph of the force constants of the methyl

derivatives of the first period of elements,[135] (in fully methylated compounds) the extrapolated beryllium-methyl force constant is 3.0 dynes/cm. from which the approximate stretching frequency is calculated to be 950 cm^{-1} (the methyl group is considered as an atom of mass 15).

TABLE I.

INFRARED (cm^{-1})	RAMAN (cm^{-1})	ASSIGNMENTS
DIMETHYLBERYLLIUM.[29]		
403 s	412	δBe_2C
	455, 510	ν Be_2C
535 s		
567 m		
835 vs	923	ρ CH_3
1243 vs		δ CH_3
1255 vs		
2885 s		$\nu_{asym.}$ CH_3
2912 vs	2912	$\nu_{sym.}$ CH_3
BERYLLIUM CARBIDE.		
430 vs		
555 s		
1125 vs		combination band(2x555).

TABLE II.

DIMETHYLMERCURY		DIMETHYLZINC		ASSIGNMENTS.[116]
I.R.(cm^{-1})	Raman(cm^{-1})	I.R.(cm^{-1})	Raman(cm^{-1})	
	2910		2898	v C-H
	1182		1158	CH_3 bending
	515		504	v C-M-C
2880		2870		v C-H
1205		1185		δ_{sym} CH_3
550		615		v C-M-C
2966		2940		v C-H
1475		1444		δ_{asym} CH_3
787		707		ρ CH_3
	156		144	C-M-C bending
	2869		2833	v C-H
	1443		1388	δ CH_3
	700		620	ρ CH_3

TABLE III.

TRIMETHYLAMINE [130,131].

INFRARED (cm^{-1})	ASSIGNMENT.
2967,2777,2822	v C-H
1466,1402	CH_3 bending
1272,1183,1104	ρ CH_3
1043	$v_{asym.}$ C-N
826	$v_{sym.}$ C-N

cf. In dimethylamine $v_{asym.}$ C-N occurs at 1024 cm^{-1} and $v_{sym.}$ C-N at 930 cm^{-1}.

TABLE IV.

$Me_3N.BH_3$.	$Me_3N.BD_3$.	ASSIGNMENT[132].
2270 s	1656 m	v B-H(D)
1340 vs	1355 m	δ CH_3
1255 m	1248 m	v B-N
1117 m	840 s	δ $BH_3(D_3)$
850 s	850 s	ρ CH_3
2372 s	1780 vs	v B-H(D)
1480 ms	1480 ms	δ CH_3
1450 ms	1460 ms	δ CH_3
1402 m	1402 w	δ CH_3
1169 vs	860 s	δ $BH_3(D_3)$
1115 m	1115 w	ρ CH_3
1005 s	995 s	w CH_3
1005 s	995 s	v CN
913 m	720 (Raman)	ρ $BH_3(D_3)$

In the above Tables, the following abbreviations have been used.

δ = deformation

ρ = rocking

v = stretching

w = wagging

vs = very strong

s = strong

ms = medium strong

m = medium

w = weak.

Object of the Investigation.

This was principally to explore the potentiality of the recently prepared compound, sodium hydridodiethylberyllate[45]. and its analogues, as intermediates for the preparation of some alkylberyllium hydrides, beryllium hydride and their coordination compounds.

As there was a paucity of infrared data appertaining to organo-beryllium compounds, it was hoped that the establishment of such correlations would be derived from the present work.

EXPERIMENTAL

Apparatus and Techniques.

Nitrogen supply.

As most of the compounds studied react rapidly with oxygen and moisture, almost all the work was carried out in an atmosphere of dry, oxygen-free nitrogen.

The nitrogen used for this work was first freed from oxygen by passage through a column containing copper at 350°, prepared by reducing copper oxide with a stream of hydrogen gas, and then through a column packed with molecular sieve to dry the gas. The molecular sieve was regenerated periodically by pumping at 200°.

Techniques for handling beryllium compounds.

As beryllium oxide is very toxic, beryllium compounds must be handled with great care, particularly when fumes of beryllium oxide are formed on exposure to the air. Many reactions were therefore carried out in a fume cupboard, and volatile compounds were handled in the vacuum system. Compounds were usually transferred from one vessel to another in a glove box filled with dry nitrogen.

Starting materials such as dimethyl- and diethyl-beryllium were stored as ether solutions in two-necked flasks fitted with a nitrogen lead and serum cap. These solutions could then be conveniently transferred using a hypodermic syringe and needle, thus preventing any exposure to the air.

Many reactions were carried out in which ethereal organoberyllium compounds required refluxing for many hours. As greases will dissolve under such conditions, ' Teflon ' sleeves were used at the ground glass joints but these were never used whenever vacuum work was involved.

Glove Box.

The glove box (Lintott III B) was set up in such a way that after purging the transfer tube and introducing the materials required into the box, the nitrogen could be recycled for several hours (or days if necessary) through the nitrogen purification system. This involved the use of a small pump fitted inside the box, thus removing small traces of oxygen and moisture which may have been introduced from the transfer tube.

The box was found to be contaminated with an appreciable amount of water, so a liquid air trap was fitted in the

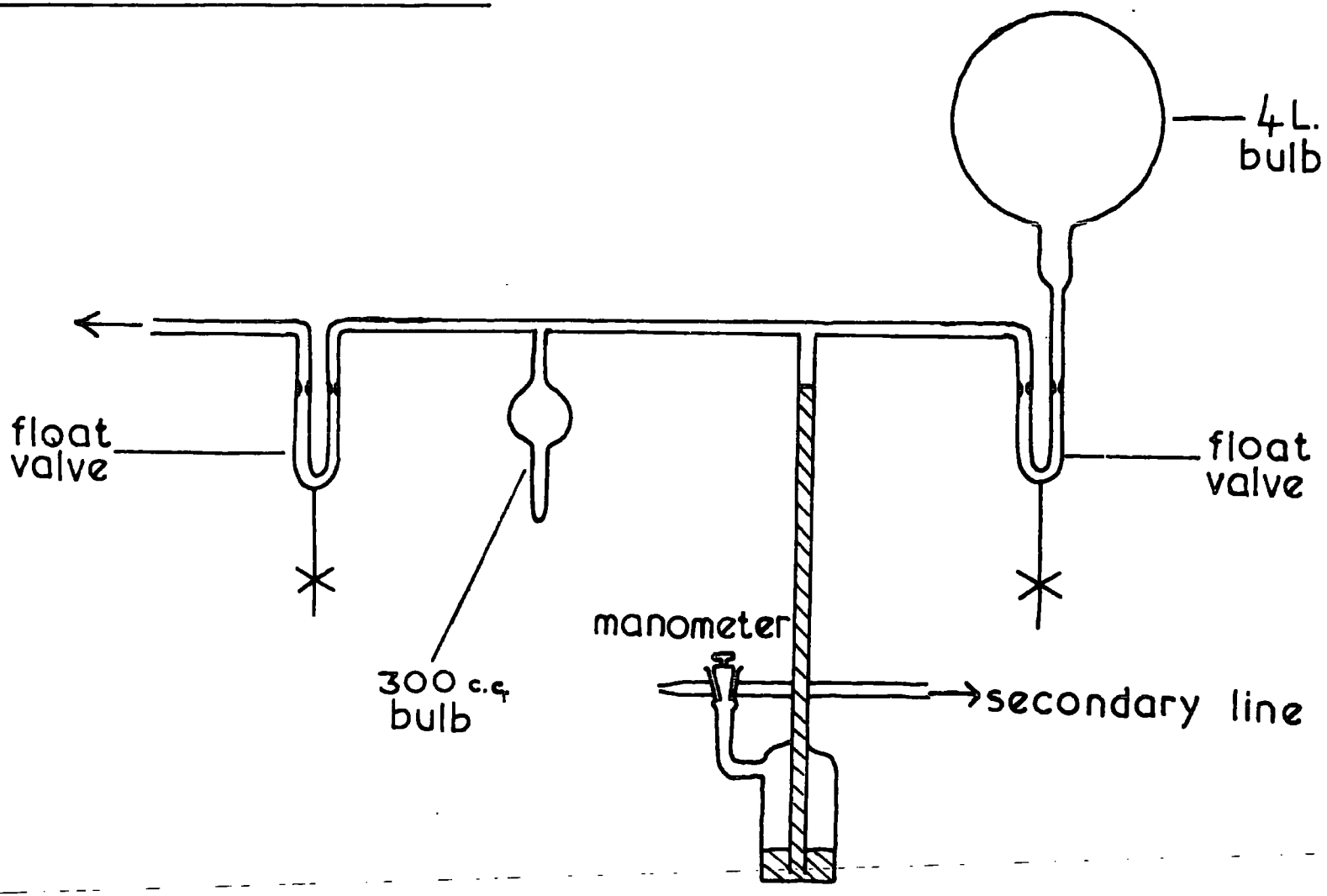
recycling system before the nitrogen purifier to remove this water (and on some occasions organic vapours) which may have desorbed from flasks inside the box. A second liquid air trap was inserted after the purifier as the molecular sieve did not appear to be efficient at the high flow rates required for purging the transfer tube.

Vacuum Apparatus.

Many reactions were carried out in a vacuum apparatus which was also designed to be used for gas analyses.

The apparatus had a section to which a reaction flask could be attached and this was connected to the rest of the line through three traps. A Töpler pump and gas burette were also included so that gases (normally methane and hydrogen) not completely condensed by liquid nitrogen could be measured. Two calibrated bulbs attached to a manometer were included for the measurement of condensable gases, - the smaller one for volumes up to about 100N-cc. and the larger one for volumes greater than this. (a normal c.c., written as N-cc., is one c.c. at N.T.P.). An infrared spectrometer cell or a combustion bulb for analyses of gas mixtures (normally methane and hydrogen) could be attached to the apparatus as required. The whole apparatus could be

Gas measurement bulbs.



filled with nitrogen let in through a needle valve.

Infrared Spectroscopy.

Infrared spectra were recorded using a Grubb-Parson's GS 2A prism-grating spectrophotometer having a range of 2-25μ.

Specimens of air-sensitive compounds were prepared for spectroscopic examination in the glove box. The spectra of involatile compounds at room temperature but sufficiently volatile below 200° were recorded using a Perkin-Elmer G...B.H. heated gas cell, having sodium chloride windows with a range 2-14μ or potassium bromide windows, 2-25μ.

Analyses.

Beryllium analyses.

Beryllium was estimated by treating an aqueous acid solution of each compound with excess ammonium hydroxide. The white gelatinous precipitate of beryllium hydroxide was separated by filtration using a 'Whatman 541' filter paper, and ignited to beryllium oxide in a weighed crucible with pumice until a constant weight was achieved. The purpose of

the pumice was to retain the very finely divided oxide produced in the crucible during the ignition.

Gas analyses.

Compounds evolving gases on hydrolysis were analysed by running degassed 2-methoxyethanol on to a weighed sample which was cooled in liquid air. The mixture was allowed to warm slowly to room temperature during which time gas evolution occured. Sometimes cooling was required to prevent vigorous gas evolution, as side reactions can take place under these conditions. The hydrolysis was completed with dilute sulphuric acid and the liberated gases were fractionated, measured in the vacuum line, and identified by their infrared spectra.

Mixtures of methane and hydrogen cannot be separated in the vacuum line as neither is completely condensable in liquid nitrogen. (Both these gases are hereafter described as uncondensable although this is not strictly correct) The following procedure was therefore adopted. A measured volume of gas was mixed with excess oxygen inside the combustion bulb and ignited by passing an electric current through the platinum filament inside the bulb. The combustion products, carbon dioxide and water, were separated and the

carbon dioxide measured. The water produced in the combustion was estimated by condensing it on to lithium aluminium hydride and measuring the hydrogen produced.

Amine analyses.

These were estimated by steam distillation of an alkaline solution containing the amine into excess standard acid. The excess acid was determined by back-titration with standard alkali.

Sodium.

Estimation of sodium was carried out using an 'EEL' flame photometer which had been calibrated with standard sodium sulphate solutions, and the unknown solution was compared with a standard solution of approximately equal strength.

Cryoscopic molecular weight measurements.

'Analar' benzene, dried with sodium wire for several days, was used as solvent. Cryoscopic constants for the benzene were determined using biphenyl which had been recrystallised from ethanol and dried.

Preparation And Purification Of Starting Materials And Solvents

All solvents were purified and stored under an atmosphere of nitrogen.

Diethyl Ether.

'Anhydrous Methylated Ether' was dried over sodium wire for several days, and was distilled from lithium aluminium hydride just before use.

'Monoglyme' (1,2-Dimethoxyethane or Ethylene Glycol Dimethyl Ether.)

This was purified by refluxing it with potassium for several hours, followed by distillation. The process was repeated a second time and the distillate stored. Final purification was carried out just before use by refluxing with, and distillation from, lithium aluminium hydride.

'Diglyme' (Diethylene Glycol Dimethyl Ether or 2,5,8,-Trioxanonane.)

This was purified in a similar way to 'Monoglyme' using sodium instead of potassium.

Benzene.

'Analar' benzene was dried by allowing it to stand over sodium wire for several days.

Pentane.

Drying was carried out in exactly the same way as diethyl ether.

Trimethylamine.

Trimethylamine was dried with phosphorus pentoxide and subsequently stored over this drying agent and distilled off as required. The vessel used for storage was fitted with a 'Teflon' tap and would withstand pressures slightly greater than atmospheric.

N,N,N',N',-Tetramethylethylenediamine.

This amine was purified by refluxing with sodium, followed by fractional distillation.

Dimethylamine.

$$Me_2NH_2Cl + NaNO_2 \longrightarrow NaCl + Me_2NNO + H_2O.$$

Dimethylamine hydrochloride usually contains traces of ammonium chloride, methylamine hydrochloride, and trimethylamine hydrochloride, so pure dimethylamine was obtained by the following method.[60]

An aqueous acid solution of the salt was heated at 75-80° with excess sodium nitrite for two hours. The solution was then saturated with sodium carbonate: the pale yellow oil which separated was isolated and the aqueous solution extracted with ether. The ethereal extracts and the oil were combined and dried with potassium carbonate. Subsequent fractional distillation gave a 96% yield of the pale yellow N,-dimethylnitrosamine. b.p. 148-150°.

$$Me_2NNO + 2HCl \longrightarrow NOCl + Me_2NH_2Cl.$$

This nitrosamine was refluxed with two moles of 4N hydrochloric acid until the solution became very pale coloured. The amine was liberated by treatment with aqueous potassium hydroxide solution, dried by passage through a column packed with potassium hydroxide pellets and stored in a vacuum apparatus.

2,2'-Bipyridyl.

As bipyridyl goes brown in air and light over a period of time, purification was effected by vacuum sublimation just before use to obtain a white crystalline solid melting at 70-71°.

N,N,N',N',-Tetramethyl-o-phenylenediamine.

o-Phenylenediamine was boiled with a mixture of concentrated hydrochloric acid, an aqueous solution of stannous chloride and animal charcoal and then filtered whilst hot. Concentration of the filtrate was brought about by distillation and this was followed by cooling in ice to form colourless crystals of o-phenylenediamine dihydrochloride in about 90% yield, which were filtered off and pumped dry *in vacuo*[2].

The amine dihydrochloride was heated with excess methanol in a bomb at 175-185° for eight hours. The mixture was removed from the bomb, pumped dry *in vacuo* and subsequently treated with excess aqueous sodium hydroxide solution. After extracting the product with ether and drying with potassium hydroxide, a colourless oil was isolated which boiled over a range of 215-256° and which slowly went black[57].

This mixture of N-methylated o-phenylenediamines was further treated with equal volumes of methanol and methyl iodide at 180-185° for ten hours and the product (B.p.218-220°) isolated as above.[58].

Infrared examination of this product showed the presence of a small amount of free N-H, which was removed by heating the amine to 50-60° with p-toluene sulphonyl chloride, followed by vacuum distillation. The distillate was treated with caustic soda solution and after extraction with ether, the pure colourless oil which boiled at $36°/10^{-3}$ mm Hg. was isolated in 50% yield. As N,N,N',N',-tetramethyl o-phenylenediamine tends to go dark-coloured in air and light, it was stored under vacuum at -20° in the absence of light.

Trimethylamine Hydrochloride.

Equal volumes of trimethylamine and hydrogen chloride were condensed into an evacuated flask, containing a little ether, which was cooled in liquid air. The mixture was allowed to warm slowly to room temperature, care being taken to ensure that the pressure inside the flask was kept below atmospheric pressure. The ether was removed under vacuum and the white, crystalline, hygroscopic amine hydrochloride

which remained was stored under nitrogen.

Sodium Hydride.

This was obtained from L.Light & Co. Ltd., as a 50% slurry in oil and the oil was removed by repeatedly washing the hydride with dry pentane under nitrogen in a double Schlenk tube. The grey hydride was pumped dry, stored under nitrogen and transferred, when required, in a glove box.

Sodium Deuteride.

Sodium deuteride was obtained as one gram samples 97 atom % deuterated, in oil from 'Metal Hydrides Incorporated' and purified in the same way as sodium hydride. Mass spectrometry investigation of the gaseous hydrolysis products from a sample of sodium deuteride, showed that it was actually 96 atom % deuterated.

Oil for Lithium Shot Preparation.

A 200-240^{o} petroleum fraction was washed several times with concentrated sulphuric acid to remove unsaturated hydrocarbons then twice with water, followed by drying with

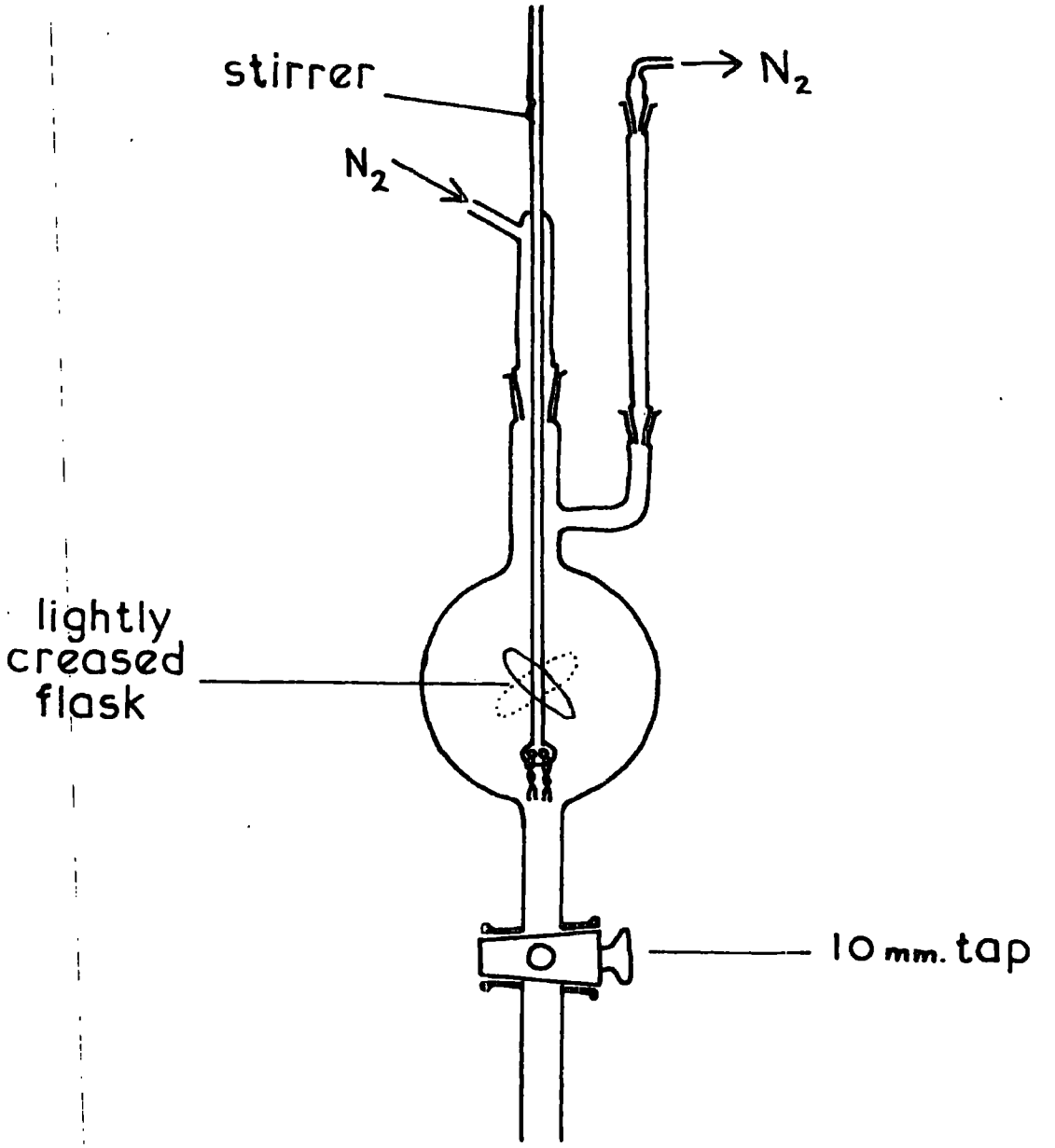
potassium hydroxide. On distillation, the fraction boiling between 200° and 240° was collected.

Preparation of Lithium Shot.[1]

Weighed pieces of lithium metal were placed in the apparatus shown in Figure II which was almost half-filled with the oil described above, under an atmosphere of nitrogen. The oil was heated with a ring burner until it was refluxing well when the lithium will have melted (m.p. 180°). The heating was stopped and the oil stirred vigorously to cause the lithium metal to break down into tiny globules. Stirring was continued until the shot solidified. The oil together with dirt and corrosion products which sink to the bottom of the oil, were run off. The lithium shot which floats on all solvents, was washed with the solvent to be used in the reaction and then rinsed into the reaction flask against a counter current of nitrogen.

During the preparation the nitrogen flow must be kept as slow as possible since molten lithium is attacked appreciably by nitrogen; consequently an argon atmosphere is preferable.

Lithium shot apparatus. ***Figure II***



Lithium Reagents.

Methyl-, ethyl-, and phenyl-lithium were prepared in 80-90% yields from the corresponding alkyl or aryl halide and lithium shot in ether.

Grignard Reagents.

These were prepared from the reaction of alkyl bromides with magnesium in about 90% yield in ether.

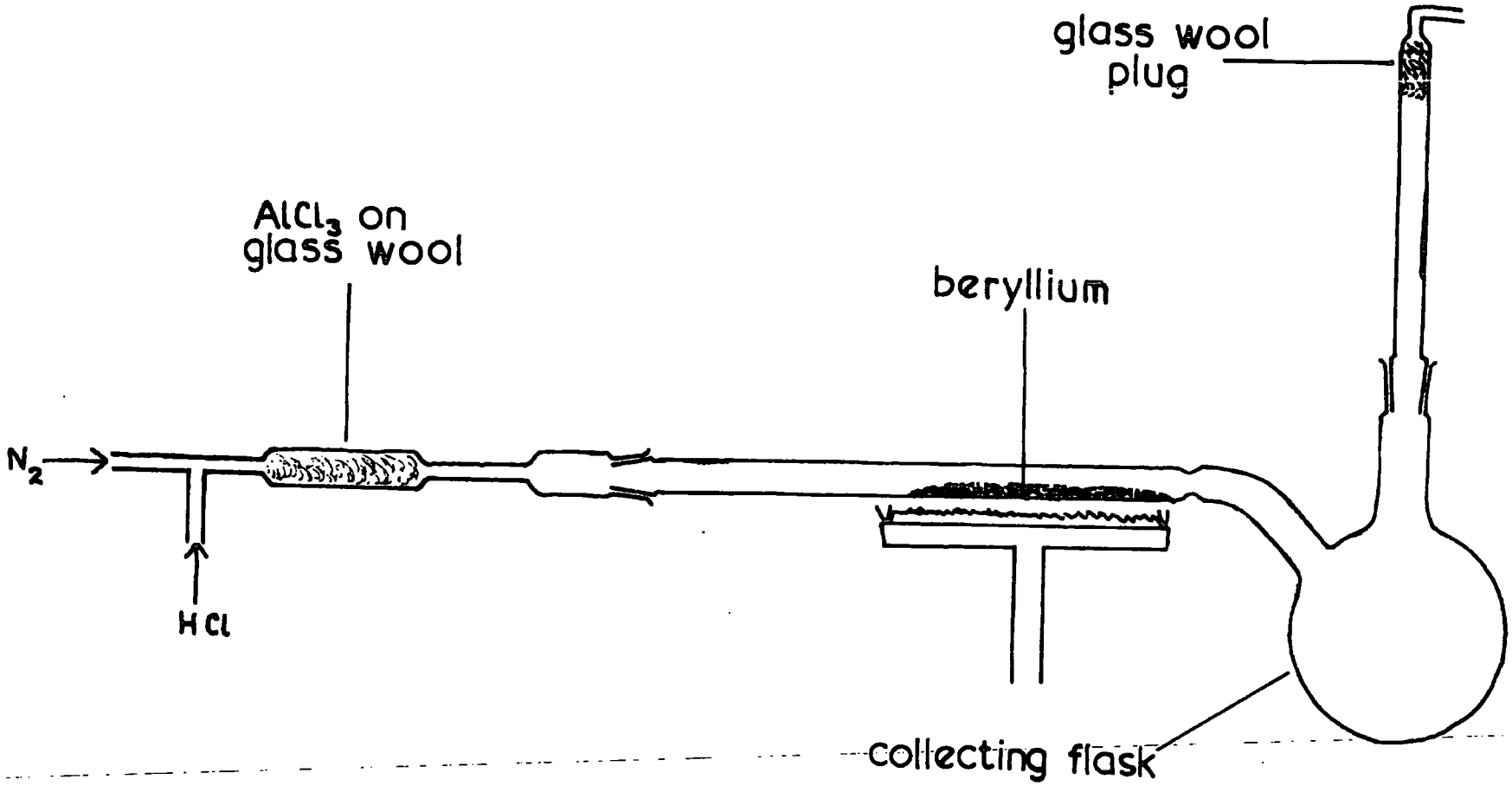
Beryllium Chloride.[4,37,52]

This was prepared in 90-95% yield by heating beryllium flakes in a stream of dry hydrogen chloride gas in the apparatus shown in Figure III. The product was sublimed off and collected as white needles in the flask which was then sealed off from the reaction tube.

The hydrogen chloride was supplied from a Kipp's apparatus containing ammonium chloride and concentrated sulphuric acid and was dried by passage of the gas through glass wool on which some anhydrous aluminium chloride had been sublimed.

Beryllium chloride apparatus.

Figure III



Dimethylberyllium.

Ethereal solutions of dimethylberyllium were prepared in 70-80% yield both by the addition of two mols. of methyl-lithium to one mol. of beryllium chloride and by the addition of two mols. of methylmagnesium bromide to one mol. of beryllium chloride in ether. The solution was decanted from precipitated salts, which were washed with ether and most of the ether removed by distillation. Purification of the dimethylberyllium was achieved by a process of continuous 'ether distillation' at 200° for many hours, (about 25 hours for half a mole of dimethylberyllium), to separate it from dissolved salts.[13]. The solution was analysed by hydrolysis for methane and beryllium.

Diethylberyllium.[13].

This was prepared in 70-80% yield both by the addition of two mols. of ethyl-lithium to one mol. of beryllium chloride and by the addition of two mols. of ethylmagnesium bromide to one mol. of beryllium chloride in ether. The solution was decanted from precipitated salts which were washed with ether and distilled down to small volume. The remaining ether was removed under vacuum followed by distillation

of the diethylberyllium at 60-65°/0.3mm. Hg. The solution was analysed by hydrolysis for ethane and beryllium.

There was little difference in yield when a Grignard or lithium reagent was used. However the lithium reagent is preferable as the precipitated salts settle better than in the preparations involving Grignard reagents.

Diphenylmercury.

A good yield of diphenylmercury was obtained by the reduction of phenylmercuric chloride with hydrazine hydrate in boiling ethanol for one hour, followed by filtration from mercury and subsequent crystallisation and sublimation.[59].

Diphenylberyllium.

It was found impossible to isolate a crystalline product of diphenylberyllium etherate from the reaction in ether of two mols of phenyl-lithium with one mol. of beryllium chloride. However a crystalline product was obtained by a modification of Wittig's method.[49].

Beryllium powder was activated in a double Schlenk tube by allowing it to stand in an ethereal solution of

diethylberyllium for a while. The diethylberyllium solution was removed and the powder washed with ether and pumped dry. Diphenylmercury was added to the beryllium powder under nitrogen and heated at 200° for one hour, during which time droplets of mercury formed on the beryllium. Unreacted diphenylmercury was removed by sublimation in vacuo and the diphenylberyllium purified by crystallisation from benzene. Diphenylberyllium dietherate was isolated as a white crystalline solid (m.p. 32°) by crystallisation of diphenylberyllium from ether solution.

Tri-ethylstannane.

$$4EtMgBr + SnCl_4 \longrightarrow Et_4Sn + MgBrCl.$$

Anhydrous stannic chloride (125g., 0.078 mole.) was added dropwise to an ice-cold ether solution of ethylmagnesium bromide, which had been prepared from 375g.(3.44 mole.) of ethylbromide and 75g.(3.09 mole.) of magnesium. When the addition was complete, the ether was distilled off to concentrate the reactants, and after returning the ether to the flask (which was then cooled in ice) the excess Grignard reagent was decomposed with 125c.c. of ice-cold water followed by 600cc. of ice-cold 10% hydrochloric acid. When the solutions became clear, the ether layer was separated, the

aqueous layer extracted twice with 150cc. of ether and the combined extracts dried over calcium chloride, before removal of the ether by distillation. The tetra-ethyltin thus prepared was distilled under reduced pressure (b.p. 55-57°/11mm.Hg.) and then shaken in turn with 5% sodium hydroxide solution and 5% hydrochloric acid to convert any traces of bromide into the corresponding chloride, before being extracted, dried, and distilled as before in 81% yield.[114].

$$3Et_4Sn + SnCl_4 \longrightarrow 4Et_3SnCl.$$

A mixture of 35.6g.(0.13 mole.) freshly distilled stannic chloride and 91g.(0.39 mole.) of tetra-ethyltin were heated in a flask fitted with an air-condenser for one hour at 100°, followed by two hours at 200°. The product, tri-ethyltin chloride, was distilled through a short column packed with glass helices at 82.0-82.5°/10mm. and collected as a colourless liquid in 80% yield.[114].

$$4Et_3SnCl + LiAlH_4 \longrightarrow 4Et_3SnH + LiCl + AlCl_3.$$

Tri-ethyltin chloride (102g.,0.423 mole.) in 200cc. of ether was added dropwise to an ice-cooled suspension of lithium aluminium hydride (10g., 0.264 mole.) in 300cc. of ether. This mixture was stirred for three hours at room temperature and then most of the ether removed by distillation through a short column, the rest being removed under reduced

pressure before distillation of the product at 23°/2.5mm. The tri-ethylstannane was redistilled at 44°/16mm. and collected in an ice-bath as a colourless liquid in 66% yield. It was thought that this compcund might deposit metallic tin over a long period of time, consequently it was stored under nitrogen at -20°. [115].

Compounds prepared mainly with a view to Spectroscopic Studies.

The first few compounds described, and the deuterides which are described immediately after the analogous hydrides, were prepared with a view to establishing infrared correlations for organic and hydride compounds of beryllium.

Nearly all the beryllium compounds involved in this work are sensitive to air and moisture, so preparations were carried out in a nitrogen atmosphere, and care was taken to exclude air and moisture at all stages.

Diethylberyllium-trimethylamine, $Et_2Be.NMe_3$.

Diethylberyllium (0.0278 mole, 10cc. of a 2.78M. ethereal solution.) was placed in a flask attached to the vacuum apparatus. The solution was pumped for about fifteen minutes to remove as much ether as possible, and then trimethylamine (0.030 mole., 672 N-cc.) was condensed on to the compound cooled in liquid air. The mixture was allowed to warm slowly to room temperature and although no visible reaction could be seen, the pressure in the apparatus did not increase appreciably. The flask was again cooled and then allowed to warm up to ensure complete reaction. Ether and excess amine were removed under reduced pressure after passage through a

receiving flask at -40°. The colourless liquid remaining distilled slowly at room temperature into this receiver.

The complex fumes strongly when exposed to traces of air, melts below -40° and reacts vigorously with water with effervescence.

Found: Be, 7.25, 7.23; Me_3N, 45.8; hydrolysable ethyl, 45.5, 45.1. $C_7H_{19}BeN$ ($Et_2Be.NMe_3$) requires Be, 7.15; Me_3N, 46.5; hydrolyzable ethyl, 45.6%.

cyclo-μμ'μ"-Trisdimethylaminotrimethyltriberyllium.[34]

Dimethylberyllium (96.3 N-cc., 0.0043 mole., 4.6cc. of a 0.929M. solution in ether.) was transferred by syringe to one limb of a double Schlenk tube and the ether was then removed under vacuum. Dimethylamine (166.5 N-cc., 0.00742 mole.) was condensed on to the beryllium compound, cooled in liquid air. The mixture was allowed to warm to room temperature and then the excess amine (71.2 N-cc.) was removed. Some methane was evolved at room temperature and at 44° the compound melted and more gas was evolved (total volume of methane collected, 90.5 N-cc.). The temperature was maintained at 60° until gas evolution ceased and then the compound was sublimed in vacuum at 45-50° as white crystals melting at 55°. (literature value, 55-56°).

Lithium hydridodiphenylberyllium etherate, $LiBePh_2HOEt_2$. [50.]

Diphenylberyllium dietherate (3.1g.,0.01 mole.) was intimately mixed in a double Schlenk tube with lithium hydride (0.8g., 0.1 mole.) which had been ground to a powder with a percussion mortar inside a glove box. The mixture was heated at 160-165° until the liquid mass became a hard cake. The mixture was allowed to cool and several extractions with ether yielded colourless rhombic crystals, which were filtered on the sintered disc connecting the two limbs of the Schlenk tube and pumped dry.

Attempted reaction of sodium hydride with diphenylberyllium dietherate.

Excess sodium hydride did not react with diphenylberyllium dietherate either when boiled with reflux in ether for two days or when the two were heated in the absence of solvent at 165° for two hours. (the supernatant solution of the products in ether did not evolve hydrogen on hydrolysis).

Reaction of sodium hydride with diethylberyllium. [45.]

$$NaH + Et_2Be \longrightarrow NaBeEt_2H.$$

Diethylberyllium (0.0417 mole.,15cc. of a 2.78M. ethereal solution)

was transferred by syringe to a flask containing a suspension of 2.1g. (0.0875 mole.) of sodium hydride in 70cc. of ether. The mixture was stirred vigorously under reflux for eight hours during which time a colourless crystalline deposit formed. The mixture was transferred under nitrogen to one limb of a double Schlenk tube and the crystalline material extracted from excess sodium hydride into the other limb with hot ether (the same ether was used for each extraction and was recovered by distillation from one limb to the other under reduced pressure). The solution was pumped down to small volume (about 10cc.), cooled to about -50°(acetone-CO_2) and the crystalline material separated by filtration on the sintered disc connecting the two limbs of the Schlenk tube to remove any unreacted diethylberyllium, and finally pumped dry. The complex, sodium hydridodiethylberyllate, was obtained in 90% yield as colourless, pyrophoric, crystalline needles melting at 197.5° without decomposition in a sealed tube under vacuum. The complex is only slightly soluble in benzene and reacts explosively with water.

Found: Be, 9.86; hydrolyzable-ethyl, 62.5; - hydride, 1.08, no ether was detected in the compound. Solubility, 0.23mole/litre. at 20°. $C_4H_{11}BeNa$ ($NaBeEt_2H$) requires Be, 9.90; Hydrolyzable ethyl, 63.7; - hydride, 1.10%.

Sodium deuterodiethylberyllate.

$$NaD + Et_2Be \longrightarrow NaBeEt_2D.$$

Sodium deuterodiethylberyllate was obtained as colourless needles, melting at 200-201° in a sealed tube under vacuum, in a similar way to the analogous hydride compound, using 0.2655g.(0.0106 mole.) of sodium deuteride and 7.0cc. of a 1.5M. solution of ethereal diethylberyllium (0.0105 mole.) in 60cc. of ether.

Found: Hydrolyzable-ethyl, 63.1; -deuteride, 2.19. The hydrogen deuteride evolved on hydrolysis was shown by mass spectrometry to be 48.4 atom % deuterated (required, 48.0 on the basis of the sodium deuteride used in the reaction being 96.0 atom % deuterated). $C_4H_{10}BeDNa$ ($NaBeEt_2D$) requires hydrolyzable-ethyl, 63.0; - deuteride, 2.17%.

Reaction of sodium hydride with diethylberyllium-trimethylamine.

$$Et_2Be.NMe_3 + NaH \longrightarrow NaBeEt_2H + NMe_3.$$

Diethylberyllium-trimethylamine (1.6g., 0.013 mole.) and sodium hydride (2.0g., 0.083 mole.) were boiled in 100cc. of ether for twelve hours. The supernatant liquid was shown by hydrolysis of a small sample to contain hydride and ethyl in the ratio 1:2.9. The ethereal solution was transferred

to a double Schlenk tube, and sodium hydridodiethylberyllate (identified by infrared spectrum and melting point) was isolated by ether extraction from excess sodium hydride and crystallisation from ether solution. Gases evolved during the preparation were passed through dilute hydrochloric acid which on evaporation yielded 0.45g.,(0.0047 mole.) of trimethylamine hydrochloride (identified by infrared spectrum).

Reaction of sodium hydride with dimethylberyllium.

$$NaH + Me_2Be \longrightarrow NaBeMe_2H.$$

Dimethylberyllium (0.0352 mole., 20cc. of a 1.76M. solution in ether) was transferred by syringe to a flask containing 1.2g.,(o.o5 mole.) of sodium hydride and 80cc. of ether. Heating this mixture under reflux with vigorous stirring for about eight hours resulted in the deposition of a white insoluble material. The complex was less soluble than the analogous ethyl compound, and extraction in a double Schlenk tube proved to be laborious.

The compound was therefore extracted from excess sodium hydride with boiling ether for several days using a sintered disc Soxhlet extractor. The compound, sodium hydridodimethyl-beryllate, crystallised as tiny needles in the ether solution during the extraction. When sufficient material was obtained,

the mixture was transferred to a double Schlenk tube and the compound filtered off and pumped dry on the sintered disc connecting the two limbs.

The compound is pyrophoric, reacts explosively with water and melts at 195-196° in a sealed tube under vacuum.

Other experiments showed that two to three days refluxing were required for complete reaction, and the use of tetrahydrofuran as solvent resulted in no apparent increase in the rate of reaction.

Found: Be, 14.98, 14.80; hydrolyzable-methyl, 47.8, 46.8; -hydride, 1.59, 1.62. No ether was detected in the products of hydrolysis. C_2H_7BeNa ($NaBeMe_2H$) requires Be, 14.3; hydrolyzable-methyl 47.5; -hydride 1.60%.

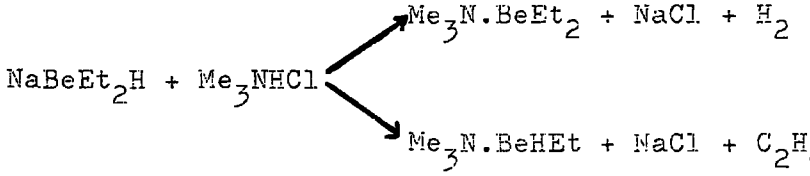
Sodium deuterodimethylberyllate.

$$NaD + Me_2Be \longrightarrow NaBeMe_2D.$$

This colourless crystalline compound, melting at 196° in a sealed tube under vacuum, was prepared in a similar way to the analogous hydride compound from 0.1389g.(0.0056mole.) of sodium deuteride and 7.0cc. of a 0.929M. solution of ethereal dimethylberyllium (0.0065 mole.).

Found: Hydrolyzable-methyl, 46.9; -deuteride, 3.1. C_2H_6BeDNa ($NaBeMe_2D$) requires hydrolyzable-methyl 46.9; -deuteride, 3.1%.

Reaction of sodium hydridodiethylberyllate with trimethylamine hydrochloride.



2.2g.(0.023 mole.) of trimethylamine hydrochloride, transferred in a glove box, was added in small quantities to 1.9858g. (0.022 mole.) of sodium hydrido-diethylberyllate in 50cc. of ether at -78°(acetone-CO_2.). After each addition the mixture was allowed to warm slowly to room temperature until gas evolution ceased, then a further quantity of the amine hydrochloride was added. At room temperature, slow evolution of gas occurred and the solution became cloudy due to the formation of sodium chloride. The gas evolved consisted of 168.7 N-cc. of hydrogen and 196.0 N-cc. of ethane. Thus the reaction must have produced at least two products, diethyl-beryllium- and ethylberyllium hydride-trimethylamine complexes, which were considered difficult to separate. Hydrolysis of the residual solution yielded 318.1 N-cc. of hydrogen and 774.0 N-cc. of ethane.

This type of reaction is therefore not a satisfactory method for the preparation of ethylberyllium hydride complexes. A successful preparation of the ethylberyllium hydride-trimethylamine complex by another method is described later.

Reaction of Sodium Hydridodimethylberyllate with Beryllium Chloride and the Thermal Decomposition of '$Me_4Be_3H_2$'

For most reactions between the hydridodimethylberyllates and beryllium chloride it was found unnecessary to undertake the time-consuming operation of isolating the hydridodimethylberyllate free from excess sodium hydride as this latter compound did not interfere with the reaction.

Dimethylberyllium (0.0352 mole., 20cc. of a 1.76M. solution in ether) was refluxed with 1.0g.(0.0417 mole.) of sodium hydride in 100cc. of ether for two days. The solution was allowed to cool to room temperature, and hydrolysis of a sample of the supernatant liquid showed that most of the dimethylberyllium had reacted to form an evidently very sparingly soluble compound (solubility 2.64×10^{-2} mole/litre at 20°). Beryllium chloride (1.5g., 0.0817 mole.) dissolved in 50cc. of ether was slowly added to the refluxing reaction mixture with rapid stirring. An exothermic reaction appeared to take place and a white precipitate of sodium chloride immediately formed. The mixture was refluxed overnight, then cooled to room temperature and the precipitate allowed to settle. A sample of the supernatant liquid was then removed by syringe and analysed. Found; 0.7cc. gave 3.0 N-cc. of hydrogen, 5.8 N-cc. of methane on hydrolysis; Be, 0.0018g.

The ratio methyl:hydrogen:beryllium = 3.894:2.003:3.000, and therefore the reaction appeared to have gone according to the equation:

$$2nNaBeMe_2H + nBeCl_2 \longrightarrow 2nNaCl + (Me_4Be_3H_2)_n.$$

As no chloride was found in the solution after hydrolysis, all the beryllium chloride must have reacted and the sodium chloride formed has a negligible solubility in ether.

The product which hereafter will be denoted by '$Me_4Be_3H_2$', although probably consisting of many complex species combined with ether in equilibrium, is completely soluble in ether; thus insoluble material (sodium hydride and sodium chloride) can be removed by filtration.

Most of the ether was distilled off under atmospheric pressure until only about 30cc. remained. The rest of the ether was condensed, under reduced pressure, into a receiver cooled in liquid air, leaving a colourless viscous oil, which slowly forms solid material on its surface on pumping for many hours. No beryllium could be detected in the distillate but the condensate consisted of ether together with a negligible amount (about 0.00024 mole.) of dimethylberyllium measured by hydrolysis and also identified by the formation of a small amount of the characteristic yellow bipyridyl complex.[33] Hydrolysis of a sample of the oil

yielded 12.7 N-cc. of methane, 5.8 N-cc. of hydrogen; Be, 0.00396g. and thus the ratio methyl:hydrogen:beryllium = 4.00:1.84:3.10.

Action of heat on '$Me_4Be_3H_2$'.

About 1.1g. of the viscous oil was heated under vacuum, and at 51° the oil started to bubble and 153.3 N-cc.(0.505g.) of ether were evolved, leaving a white solid (about 0.6g.) which evolved no more ether at higher temperatures although a white solid started to sublime at 60°. Assuming the solid residue was entirely '$Me_4Be_3H_2$' , the oil consisted of approximately 0.007 mole. of '$Me_4Be_3H_2$' and 0.007 mole. of ether, corresponding to the composition $Me_4Be_3H_2.OEt_2$.

The solid residue was transferred to a sublimation apparatus and then heated under vacuum. At 60° a white pyrophoric solid started to sublime and the sublimation was continued at 120° for ten days, after which both sublimate and the white residue of amorphous appearance which neither caught fire nor fumed in the air, were analysed.
Sublimate: Be, 22.5; hydrolyzable methyl, 77.2. C_2H_6Be (Me_2Be) requires Be, 23.1; hydrolyzable methyl, 77.0%. Hydrolysis was rapid with 2-methoxyethanol at low temperature.
Residue; Samples evolved 5.2 N-cc., 5.7 N-cc. of methane and

11.3 N-cc., 12.3 N-cc. of hydrogen respectively on hydrolysis which was slow with 2-methoxyethanol even at room temperature although rapid with acid. Methyl:hydrogen = 0.461,0.463:1.

N,N,N',N'-tetramethylethylenediamine (78.0 N-cc.) was condensed on to 0.0584g. of this residue, cooled in liquid air, and the mixture was allowed to warm to room temperature. Excess amine (38.0 N-cc.) was removed, and the residue heated under vacuum. At 50-60°, a colourless crystalline compound sublimed but insufficient was obtained for identification. The white amorphous-looking residue was shown by hydrolysis to have a methyl:hydrogen ratio of 0.43:1.

Although this reaction has removed some methyl groups from the residue, probably as the known compound, $Me_2Be(Me_2NCH_2-)_2$ [33]. insufficient reaction had occurred to warrant further investigation.

As '$Me_4Be_3H_2$' was apparently disproportionating into volatile dimethylberyllium and involatile beryllium hydride, still containing some methyl groups, further experiments were undertaken to determine how high the hydride content of the residue could be raised by pyrolysis.

A solution containing '$Me_4Be_3H_2$', prepared from 60cc. of a 1.76M. solution of ethereal dimethylberyllium (0.106mole.), 3.5g.(0.145 mole.) of sodium hydride and 4.2g.(0.0526 mole.) of beryllium chloride in 400cc. of ether, was pumped at room

temperature to remove ether. The colourless oil which remained liberated more ether at 51°, under vacuum, leaving a white solid. This latter was heated at 170-180° under vacuum for three days during which time a white solid sublimed leaving a white residue as before.

Residue; Samples on hydrolysis, which was very slow with 2-methoxyethanol, liberated 1.8 N-cc., 1.0 N-cc. of methane and 18.6 N-cc., 10.5 N-cc. of hydrogen respectively, Therefore the hydrogen:methyl ratio is 10.30,10.25:1.

A further sample of the same solution, after removal of the solvent was heated at 200-210° for eight hours under vacuum.

Residue: A sample on hydrolysis gave 1.2 N-cc. of methane and 13.0 N-cc. of hydrogen, therefore the hydrogen:methyl ratio was 10.4:1.

In one experiment, 2.3 N-cc. of uncondensable gas were evolved during the pyrolysis. This volume is quite small and was probably due to the presence of small amounts of moisture in or on the glass.

The limit of the hydrogen:methyl ratio in the residue appears to be about 10:1. This corresponds to the residue being 91 mole per cent beryllium hydride if the remainder is assumed to be dimethylberyllium.

Preparation of Methylberyllium Hydride Coordination Compounds.

The reactions of solutions of '$Me_4Be_3H_2$' in ether with donor molecules proved to be a route for the preparation of methylberyllium hydride coordination compounds.

N,N,N',N'-Tetramethylethylenediamine.

An ethereal solution (10cc.) containing '$Me_4Be_3H_2$' prepared from 3.5g.(0.145 mole.) of sodium hydride, 60cc. of a 1.76M. solution of ethereal dimethylberyllium (0.106 mole.) and 4.2g.(0.0526 mole.) of beryllium chloride in 400cc. of ether and concentrated by distillation to about 100cc. was transferred by syringe into one limb of a double Schlenk tube. Excess of the diamine was condensed on to the solution, cooled in liquid air, and on allowing the mixture to warm to room temperature an insoluble white material was deposited. The mixture was shaken for a few minutes to ensure complete mixing, then the solid material was separated by filtration, being collected on the sintered disc connecting the two limbs of the Schlenk tube. Ether was distilled back under vacuum through the sintered disc, and this allowed the solid to be washed with ether by repetition of the above process. This washing operation was repeated once more, and then the ether

and excess amine were removed under vacuum. Colourless crystals remained when the filtrate was evaporated and these were sublimed at 30-40° under vacuum. This material was shown by its melting point 81°(literature value 81-82°) and its infrared spectrum to be the known compound dimethyl-(N,N,N',N'-tetramethylethylenediamine)-beryllium, $Me_2Be(Me_2NCH_2-)_2$ [33].

The insoluble material was an apparently amorphous white powder which hydrolysed moderately rapidly with 2-methoxyethanol and neither fumed nor caught fire in air.

The compound was involatile, insoluble in carbon disulphide, carbon tetrachloride and benzene. At 248° a small sample under vacuum in a sealed tube became semi-liquid and at 280-290°, a colourless crystalline solid sublimed, leaving a brown-yellow residue.

Found: Be, 11.0; diamine, 69.4; hydrolyzable-methyl, 17.9; -hydride, 1.20. $C_8H_{24}Be_2N_2$ $[(MeBeH)_2(Me_2NCH_2-)_2]$ requires Be, 10.85; diamine, 69.9; hydrolyzable-methyl, 18.05; -hydride, 1.21%.

1,2-Dimethoxyethane. ('monoglyme')

An ethereal solution (60cc.) containing '$Me_4Be_3H_2$' prepared from 1.6g.(0.0677 mole.) of sodium hydride, 60cc. of

a 0.929M. solution of ethereal dimethylberyllium (0.0558 mole.) and 2.2g.,(0.0275 mole.) of beryllium chloride in 150cc. of ether, was transferred by syringe on to excess 'monoglyme' (about 10g.). The clear solution was swirled for a few minutes and then the ether removed under vacuum, leaving an oil and a white solid. The white solid slowly went oily on pumping and at 48-50° a colourless crystalline solid sublimed. This temperature was maintained until no further material appeared to sublime. The crystalline solid was identified as (1,2-dimethoxyethane) dimethylberyllium, m.p.101°, (literature value 100-101°)[33].

The viscous oily residue was involatile and insoluble in benzene, and no method for its purification could be found. Found: Be, 13.1, 13.2; hydrolyzable-methyl, 21.6, 21.5; -hydride, 1.38, 1.37. $C_6H_{18}Be_2O_2$ $[(MeBeH)_2(CH_3OCH_2-)_2]$ requires Be, 12.9; hydrolyzable-methyl, 21.4; -hydride, 1.44%.

The course of the reaction did not differ when 'monoglyme' was added to the beryllium compound.

2,2'-Bipyridyl.

The addition of excess 2,2'-bipyridyl in ether to an ethereal solution of '$Me_4Be_3H_2$' resulted in the immediate deposition of a yellow solid (bipyridyldimethylberyllium) and

the formation of a deep red solution. Complete separation of these two materials could not be effected as bipyridyldimethylberyllium is slightly soluble in ether and after a short while the deep-red colour of the supernatant liquid disappeared leaving a dark-brown tarry material.

Trimethylamine.

Trimethylamine (314 N-cc., an excess) was condensed on to 15cc. of an ethereal solution of '$Me_4Be_3H_2$', cooled in liquid air in one limb of a double Schlenk tube, which had been prepared from 3.5g.(0.145 mole.) of sodium hydride, 60cc. of a 1.76M. solution of ethereal dimethylberyllium (0.106 mole.) and 4.2g.(0.0526 mole.) of beryllium chloride in 400cc. of ether and concentrated by distillation to 100cc. The mixture was allowed to warm to room temperature, then cooled and allowed to warm up again to ensure complete reaction. The ether and excess amine were removed from the clear solution under vacuum, leaving colourless crystals. On pumping continuously through a liquid air trap, colourless crystals sublimed into the trap. This compound melted at 36° and was the known compound dimethylberyllium-trimethylamine (literature value 36°).[5] The residue was heated at 40-45° with continuous pumping through the liquid air trap

when colourless crystals (prisms) sublimed up the walls of the Schlenk tube, condensing on the cooler parts.
Found: Be, 10.8; Me_3N, 70.5; hydrolyzable-methyl, 17.5,17.7; -hydride, 1.20, 1.20; M, cryoscopically in benzene, 166,154 in 0.4,0.2 weight % solutions. $C_8H_{26}Be_2N_2$ $(MeHBe.NMe_3)_2$ requires Be, 10.7; Me_3N, 70.3; hydrolyzable-methyl, 17.8; -hydride, 1.20; M, 168.

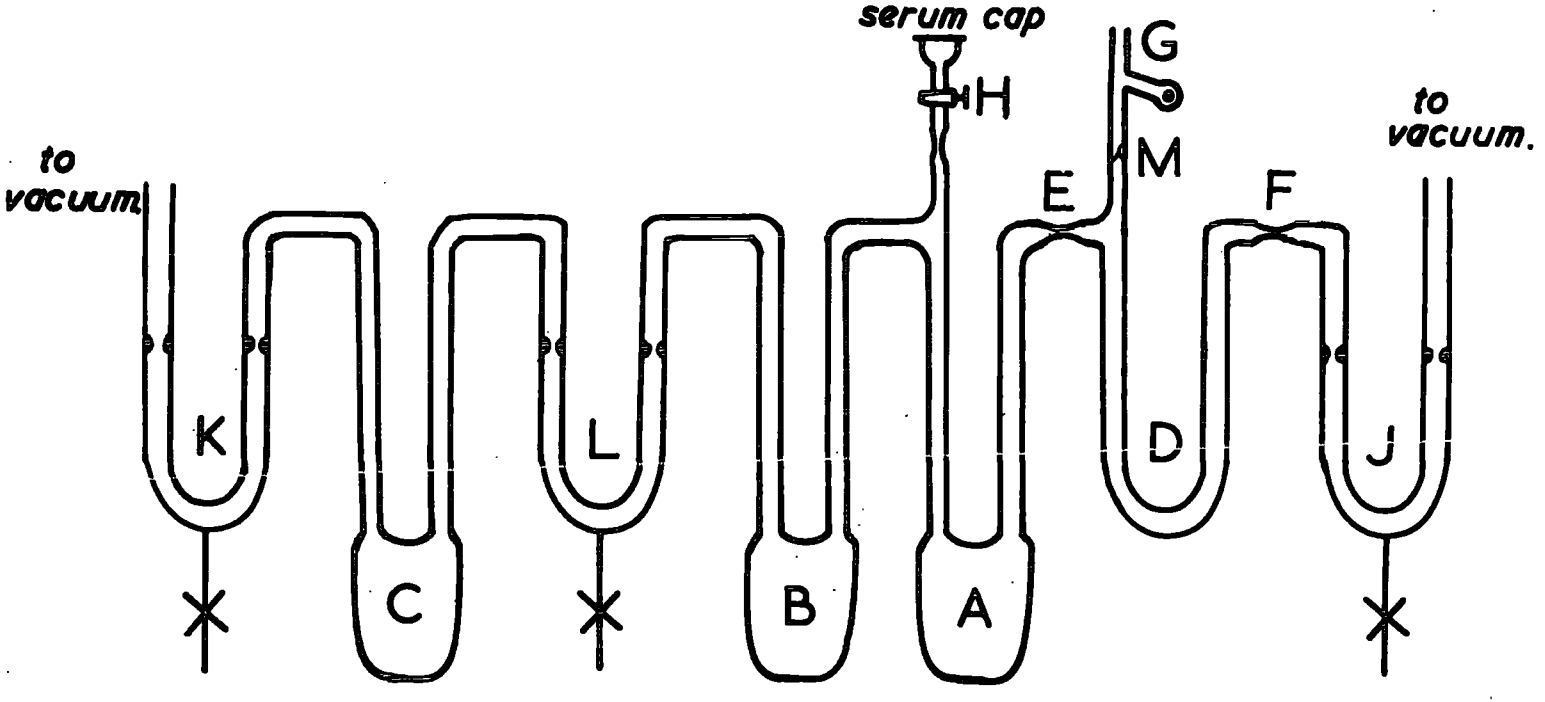
The molecular weight measurements correspond to degrees of association of 1.97 and 1.83 respectively in the two solutions measured.

When larger samples of this amine complex were prepared for further experiments, this method of fractional sublimation for purification was not satisfactory as the sublimate had a methyl:hydrogen ratio greater than one, and a second sublimation did not produce a pure compound, ie. the sublimate was contaminated with small amounts of dimethyl-beryllium-trimethylamine and it melted over the range 60-80°. Consequently fractional condensation methods were used for the isolation of a pure compound.

The apparatus shown in Figure IV. was used and it was designed so that trap-to-trap fractionations under vacuum, could be carried out without vapours coming into contact with greased joints or taps. The apparatus was attached to the vacuum system in which trimethylamine had been stored; it was

FIGURE IV

MeHBe.NMe$_3$ apparatus.



then evacuated and finally filled with nitrogen.

A 0.929M. solution of ethereal dimethylberyllium (60cc. 0.0557 mole.) was heated under reflux with 1.6g. (0.0667 mole.) of sodium hydride suspended in 100cc. of ether for two days with continuous stirring. Reaction was presumed to be complete since hydrolysis of 2cc. of the supernatant liquid evolved only 2.3 N-cc. of uncondensable gas, whereas the original dimethylberyllium present would have given 31.2 N-cc. per 2cc. on hydrolysis. Beryllium chloride (2.2g., 0.0275 mole.) in 50cc. of ether was added to the refluxing reaction mixture with the immediate formation of a white precipitate. The mixture was boiled with reflux overnight and then the solution allowed to cool before being filtered. No chloride could be detected after the hydrolysis of a 2cc. sample of the clear filtrate which evolved 26.0 N-cc. of uncondensable gas. The volume of the solution was reduced to about 80cc. by distillation, and the solution was then transferred by syringe through the serum cap and tap 'H' into trap 'A' (Figure IV). The constriction below 'H' was sealed off and with 'A' frozen in liquid air, the apparatus was evacuated. Excess trimethylamine (1000 N-cc.) was condensed into 'A' and the mixture warmed to room temperature and frozen again two or three times to ensure complete reaction. Ether and excess amine were removed under vacuum,

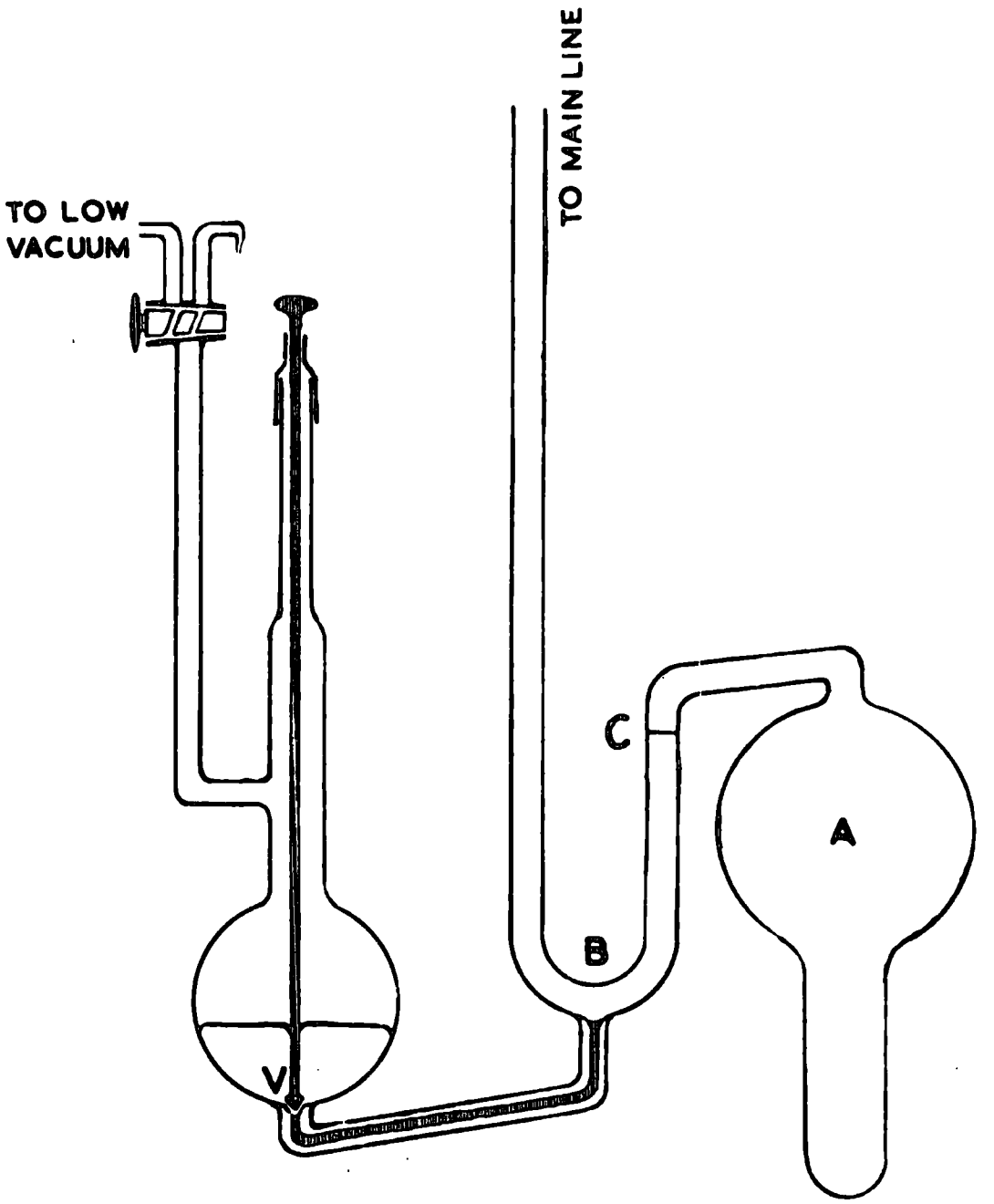
leaving a colourless crystalline solid. With float valves 'J' shut, 'K' and 'L' open, traps 'B' cooled to 0° in ice-water and 'C' cooled in liquid air, the compound was sublimed with continuous pumping at 20-30°. When all the material had sublimed from trap 'A', the melting point of the colourless crystalline solid in 'C' was 36° (i.e. dimethylberyllium-trimethylamine[5]), and that of the colourless crystalline solid in 'B' was 73-74°. As the material in 'B' had a sharp melting point, it was presumed to be pure and was therefore sublimed from 'B' into 'D' with 'J' open and 'K' and 'L' shut and finally the apparatus was sealed under nitrogen at 'E' and 'F'.

Vapour pressure and vapour density measurements.

The apparatus was sealed at 'G' as close as possible to the 'high temperature bulb' (Figure V) on the vacuum system. The break-seal 'M' was broken by means of a small ball-bearing and a magnet and some of the compound sublimed under vacuum into bulb 'A' which was cooled in liquid air. The mercury cut-off 'B' was raised and the bulb immersed in an oil thermostat. Pressure readings were taken about every 10° between 20° and 170° and are listed in Table V.

Before each reading the mercury cut-off 'B' was raised to the standard mark 'C'. Temperatures were measured by a

FIG. V THE 'HIGH TEMPERATURE BULB'



standardised mercury thermometer reading to tenths of a degree. At the end of the experiment, the quantity of compound present was determined by hydrolysis of the material and measurement of the uncondensable gas liberated.

Vapour Pressure - over the temperature range in which the material was not all present in the gas phase (56-115°) a plot of log $p_{mm.}$ against temperature^{-1}(°K) was linear and the observed vapour pressures for the liquid from 73-115° are closely represented by the linear equation:

$$73\text{-}115^{\circ} : \log_{10} p_{mm.} = 7.483 - \frac{2439}{T}$$

Observed vapour pressures are compared in TableV with those calculated from the above equation.

The extrapolated boiling point is 257°, the latent heat of vapourisation 11.2 kcal.per mole., and the Trouton constant 21.1.

Vapour-phase association.

The vapour density measurements when all the material was present in the gaseous phase over the range 144-172° indicate that the compound is monomeric but shows signs of association.

Temp(°C)	144.2	156.2	165.3	172.3
Molecular Weight	101.6	95.1	90.8	82.5
Degree of Association	1.21	1.13	1.08	0.98.

Table V.

Vapour pressure of trimethylamine-methylberyllium hydride.

Obs.press.(mm.)	Vap.press.(mm.)	Temp.(°C)	Calc.press.(mm.)
0.26	0.26	23.0	
0.42	0.42	30.6	
0.44	0.43	39.4	
0.80	0.79	47.0	
1.15	1.13	55.8	1.170
1.98	1.94	65.9	1.941
3.09	3.02	75.2	3.025
4.96	4.84	85.6	4.849
7.97	7.75	96.0	7.513
11.31	10.96	104.8	10.64
15.96	15.38	114.7	15.58
21.92	20.94	125.8	
25.90	24.43	134.8	
30.00	27.81	144.2	
34.16	30.57	156.2	
37.82	32.70	165.3	
43.20	36.56	172.6	

Reaction of $(MeBeHNMe_3)_2$ with 2,2'-bipyridyl.

Excess bipyridyl in ether was added to a small sample of trimethylamine-methylberyllium hydride dissolved in ether. Immediately a deep red solution formed which decomposed either when precipitated by the addition of hexane, or on allowing the solution to stand for a few hours, or on pumping down the solution to small volume, to form a dark-brown tarry material.

Reaction of $(MeBeH.NMe_3)_2$ with dimethylamine.

20.9 N-cc. of dimethylamine were condensed on to 0.0783g.(20.8 N-cc. of monomer) of trimethylamine-methylberyllium hydride cooled in liquid air. At room temperature slow evolution of gas occurred and the mixture was left until gas evolution ceased. 20.8 N-cc. of a mixture of methane and hydrogen were evolved and thus a mixture of compounds was formed which was not further investigated.

Trimethylamine-methylberyllium deuteride.

Sodium deuteride (0.53g., 0.021 mole.) and 8cc. of a 2.42M. solution of ethereal dimethylberyllium (C.0194 mole.)

were boiled in 200cc. of ether for two days. Hydrolysis of a 2cc. sample of the supernatant liquid yielded only 2.1 N-cc. of uncondensable gas. Beryllium chloride (0.65g.,0.008 mole.) in 50cc. of ether was added to the refluxing reaction mixture and boiling continued for a further hour and then the solution was filtered. The filtrate, which did not contain chloride was transferred to the apparatus described for the isolation of the analogous hydride (Figure IV.) and 1100 N-cc. of trimethylamine condensed on to it. Methylberyllium deuteride-trimethylamine was then isolated as colourless crystals melting at 75-76° in the same way as its hydride analogue. Found: Hydrolyzable-methyl, 17.6; -deuteride, 2.29. $C_4H_{12}BeDN$ ($MeDBe.NMe_3$) requires hydrolyzable-methyl, 17.6; -deuteride, 2.35%.

Neither N,N,N',N'-tetramethylethylenediamine nor 1,2-dimethoxyethane appears to form a chelate complex with methylberyllium hydride, in which a terminal beryllium-hydrogen bond might be expected to be present. It was thought that N,N,N',N'-tetramethyl o-phenylenediamine, because of its steric configuration, might induce methylberyllium hydride to form a chelate complex which would thus have a terminal beryllium-hydrogen bond. Since the preparative method would also have resulted in the formation of the dimethylberyllium complex, the latter was first prepared and characterized.

Reaction of dimethylberyllium with N,N,N',N'-tetramethyl-o-phenylenediamine.

N,N,N',N'-tetramethyl o-phenylenediamine (2.0g., 0.0122 mole.) was added by syringe to 10cc. of a 0.929M. solution of ethereal dimethylberyllium (0.00929 mole.), contained in one limb of a double Schlenk tube. A slightly exothermic reaction took place and the mixture was swirled for a few minutes to ensure complete mixing. The clear solution was pumped down and at low volume colourless crystals appeared. These were pumped dry under good vacuum for one hour to remove excess amine and then vacuum sublimed (at 80-90°/10^{-2}mm.) up the tube as colourless prisms, melting at 103-104° in a sealed tube under vacuum. The compound fumes slowly in the air but does not catch fire and reacts vigorously with water.

Found: Be, 4.52, 4.29; hydrolyzable-methyl, 14.6; M, cryoscopically in benzene, 215, 211, 206 in 0.92, 0.65, 0.42 weight % solutions respectively. $C_{12}H_{22}BeN_2$ requires Be, 4.42; hydrolyzable-methyl, 14.8%, M, 203.

The molecular weight measurements correspond to degrees of association of 1.05, 1.03, 1.01 respectively.

Reaction of Sodium Hydridodiethylberyllate with Beryllium Chloride and the Thermal Decomposition of '$Et_4Be_3H_2$'

Diethylberyllium (0.03 mole, 20cc. of 1.5M. solution in ether) was heated under reflux for one day with 1.0g., (0.04 mole.) of sodium hydride in 100cc. of ether. 1.2g., (0.015 mole.) of beryllium chloride in 50cc. of ether was added slowly to the refluxing reaction mixture, which was then boiled with reflux for a further hour before being allowed to cool to room temperature. A 2cc. sample of the supernatant liquid was removed by syringe and hydrolysed, and gave 9.1 N-cc. of hydrogen and 18.2 N-cc of ethane, as would be expected according to the overall equation:

$$2NaH + 2Et_2Be + BeCl_2 \longrightarrow 2NaCl + 'Et_4Be_3H_2'$$

Action of heat on '$Et_4Be_3H_2$'

The solution was filtered and 20cc. of the clear filtrate was transferred by syringe to a flask joined by a distillation arm to a receiving flask attached to the vacuum system. The ether was removed under vacuum into the receiver which was cooled in liquid air, leaving a colourless oil and this latter evolved ether at about 50° under vacuum leaving a viscous glassy residue. This residue was heated to

50-60°, the minimum temperature at which diethylberyllium distils, when a colourless liquid distilled into the receiver leaving a colourless glassy-like residue. The ethereal distillate evolved only ethane on hydrolysis and evidently consisted of diethylberyllium.

A sample of the solid residue on hydrolysis evolved 13.4 N-cc. of hydrogen and 17.7 N-cc. of ethane.

In another experiment using a further 10cc. of the above solution of '$Et_4Be_3H_2$' and heating at 70-80° for eight hours, a sample of the residue evolved 10.1 N-cc. of hydrogen and 11.6 N-cc. of ethane.

A small sample of this solid residue was heated to 110° under vacuum in one limb of a double Schlenk tube. A colourless liquid distilled up the walls of the tube, leaving a white residue and after half an hour, heating was stopped. The residue was washed twice with ether removing the liquid product, and pumped dry. Hydrolysis of this white, apparently non-crystalline residue, was remarkably slow with 2-methoxyethanol although quite rapid with acid, 16.7 N-cc. of hydrogen and 0.35 N-cc. of ethane were evolved and thus the hydrogen:ethyl ratio is 47.7:1. If the product were a mixture of beryllium hydride and diethylberyllium only, then this corresponds to 98.0 mole % beryllium hydride.

A further experiment using 20cc. of the solution of

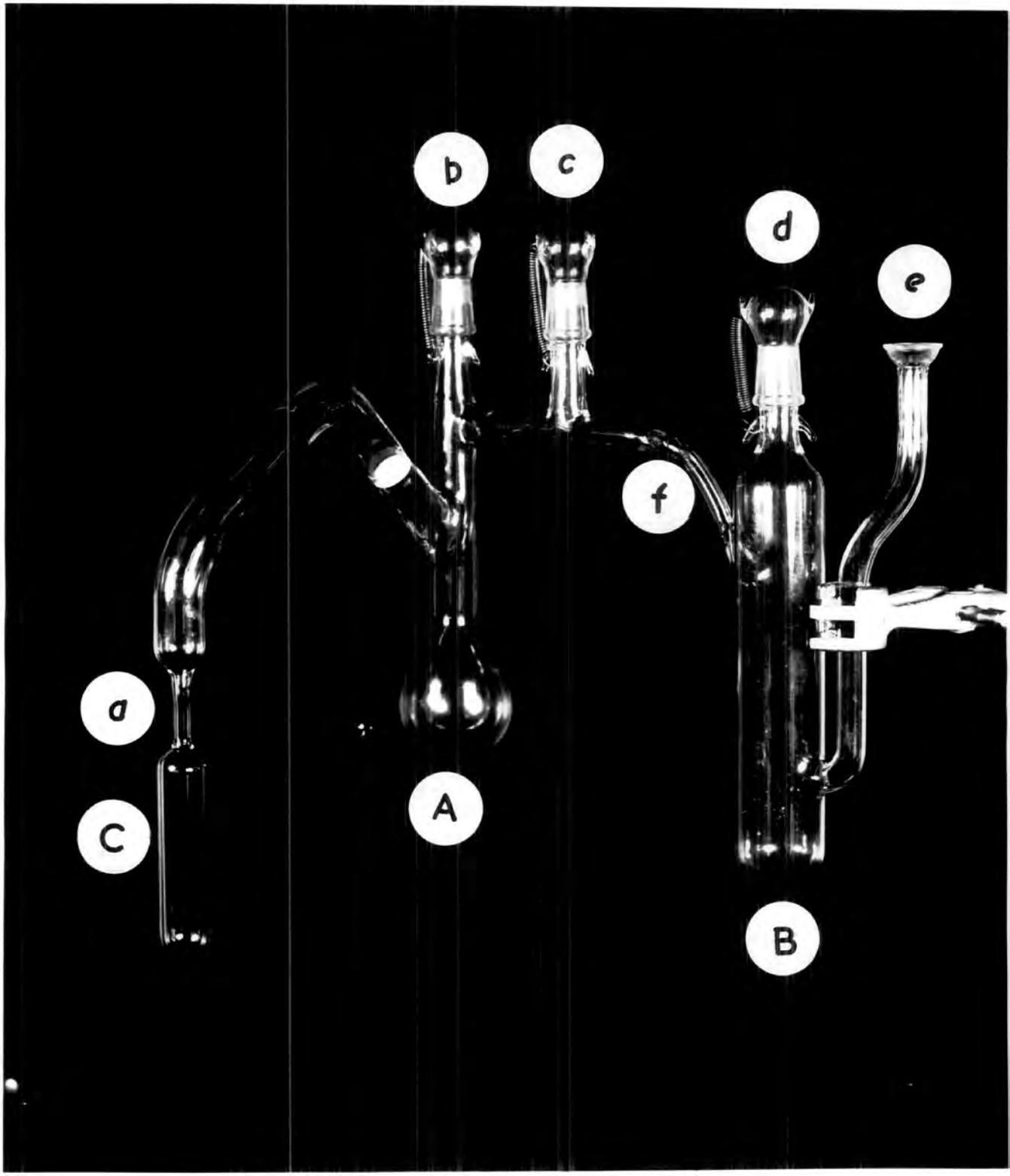
'$Et_4Be_3H_2$' was carried out using similar apparatus. The ether was removed under vacuum, followed by heating to 60° for four hours and subsequently heating to 110-120° for two hours. During this period no permanent gas was evolved. Residue Found: Be, 79.3%; 0.0090g. gave 35.7 N-cc. of hydrogen and 0.9 N-cc. of ethane on hydrolysis. BeH_2 requires Be, 81.8%; 36.6 N-cc. of hydrogen.

(a). Addition of beryllium chloride to sodium hydridodiethylberyllate without prior filtration from sodium hydride.

The apparatus, shown in Photograph I. was designed such that quantitative isolation and analysis of both products could be obtained. It also enabled the residue to be washed with ether without removal from the apparatus.

$$'Et_4Be_3H_2' \xrightarrow{180^\circ} 2Et_2Be + BeH_2.$$

Diethylberyllium (0.06 mole, 40cc. of a 1.5M. solution in ether) was transferred by syringe into a suspension of 2.0g. (0.083 mole.) of sodium hydride in 100cc. of ether. After the reaction mixture had been boiled with reflux for 24 hours, 2.4g. (0.03 mole.) of beryllium chloride, dissolved in 50cc. of ether were added and boiling continued for a further hour. The reaction mixture was allowed to cool and then filtered. Two 3.0cc. samples of the filtrate were



Photograph I

hydrolysed and yielded 23.2, 23.1 N-cc. of hydrogen and 46.6, 46.5 N-cc. of ethane.

Another sample (31.3cc.) of the same filtrate was transferred through 'b' to bulb 'A' of the apparatus illustrated in Photograph I. This apparatus was connected to the vacuum line by ball-joint 'e'. Bulb 'A' was cooled (acetone-CO_2), the apparatus evacuated, and as 'A' was allowed to warm to room temperature the ether which evaporated was condensed in the vacuum apparatus and stored.

Bulb 'B' was then cooled in liquid nitrogen, the glass between the top of 'A', the joint 'b', and extending down to bulb 'C' was wound with heating tape kept at 60-70°, and bulb 'A' was slowly warmed to 70° and maintained at or near that temperature for 24 hours. During this time diethylberyllium, probably accompanied by some ether, condensed in 'B'.

The temperature of the oil bath surrounding 'A' was then raised to 120° for a further 24 hours, during which time the contents of 'A' partially liquefied and then solidified as a white material. At the end of this period, a small amount of colourless crystalline material had condensed just above the level of the oil bath, but this was removed by raising the level of the latter about an inch. Finally the oil bath was heated to 180° for 8 hours.

Bulb 'B' was allowed to warm to -96°(CH_2Cl_2 bath) and 14.0 N-cc. of ethylene (identified by infrared spectrum) was collected in a trap at -196°. No gas that could not be condensed at -196° was produced during the reaction.

The apparatus was then filled with nitrogen, and, against a countercurrent of nitrogen cap 'c' was replaced by a nitrogen lead. The left hand side of the apparatus was then separated from 'B' by sealing off at 'f'.

Analysis of the diethylberyllium.

Cap 'd' was removed against a countercurrent of nitrogen and replaced by a dropping funnel containing de-gassed 2-methoxyethanol. After the nitrogen had been pumped out, addition of 2-methoxyethanol to 'B' (initially at -196°, then allowed slowly to warm to room temperature) followed by water and finally dilute sulphuric acid yielded 476.5 N-cc. (0.02126 mole.) of ethane (identified by infrared spectrum), a little ether (also identified by its infrared spectrum) and no gas that was not condensed by liquid nitrogen (e.g. no hydrogen). Bulb 'B' was detached from the vacuum line and its contents washed into a standard volumetric flask and made up to 250cc. Two 50cc. aliquots yielded 0.0536 and 0.0539g. of BeO, so bulb 'B' had contained 0.01074 mole. beryllium and 0.02126 mole. hydrolyzable ethyl, Et:Be = 1.977:1.

Analysis of the involatile residue.

Against a countercurrent of nitrogen entering through the gas lead attached at 'c', cap 'b' was replaced by an adaptor which connected the apparatus to the vacuum line via a stopcock. When the nitrogen had been pumped out, dry ether (about 10cc., stored from an earlier stage of the preparation) was condensed on the white residue in 'A'. The apparatus was separated from the vacuum line, bulb 'A' swirled a few times and the ether filtered into the side-arm 'C'. Ether was then condensed back in 'A' and the operation repeated twice more. The apparatus was then re-connected to the vacuum line and the ether removed; no residue could be observed in 'C', which was sealed off at 'a' after nitrogen had been let in.

Cap 'c' was replaced by a dropping funnel containing de-gassed 2-methoxyethanol, the nitrogen pumped away, bulb 'A' was cooled to -196° and 2-methoxyethanol slowly run in. As bulb 'A' was allowed to warm to room temperature a very slow gas evolution was seen, and the hydrolysis was mainly accomplished by the subsequent addition of water and finally dilute sulphuric acid at room temperature. The gases evolved during hydrolysis were pumped through traps at -128°(pentane) and -196° (two in series) by means of a Töpler pump. 242 N-cc. (0.01080 mole.) of hydrogen and 1.80 N-cc.(0.0000803 mole,

identified by infrared spectrum) of ethane were collected; no ether was detected. The solution remaining in 'A' was washed into a standard volumetric flask and made up to 250cc. Two 50cc. aliquots yielded 0.0272 and 0.0279g. BeO, so 'A' had contained 0.00550 mole. beryllium, so the ratio H:Be in the hydride was 1.965:1.

From the volumes of hydrogen and ethane the mole.% hydride would be $\frac{242.0}{243.8} \times 100 = 99.3\%$ or 95.9 weight % BeH_2, on the assumption (soon shown to be incorrect) that the only other component was diethylberyllium.

The remainder of the ether solution containing '$Et_4Be_3H_2$' was treated in exactly the same way and the following reactions carried out on the involatile residue left after pyrolysis.

(1). After removal of most of the hydride from bulb 'A' the apparatus was re-attached to the vacuum system and pumped out. With the apparatus shut off from the pump but open to a manometer, the bulb and its contents were heated slowly in a silicone oil bath. At 280° slow evolution of hydrogen occurred and the white solid started to turn black. At 300° 15.5 N-cc. of hydrogen were evolved over a period of 7-8 minutes. The black powder remaining did not catch fire in air.

(2). The hydride did not catch fire nor fume in air. After two hours in air, small samples of the hydride liberated hydrogen when water was added to them but after three hours no evolution of gas was noticeable even when acid was added.

(3). The infrared spectrum recorded as a mull in perfluoromethyldecalin showed the absence of C-H vibrations in the 3μ region. (The spectrum recorded as a nujol mull is discussed elsewhere).

(4). Diethylberyllium (0.006 mole, 4cc. of a 1.5M. solution in ether) was added to 0.0647g.(0.0059 mole.) of the hydride. The hydride did not dissolve after two hours at room temperature nor at 90° over 4 hours after removal of the solvent by distillation. The hydride did not dissolve on the further addition of 10cc. of the solution of diethylberyllium followed by refluxing for several hours.

(5). A list of the interplanar spacings (d) and their relative intensities (I) from the X-ray powder photograph of a sample of this hydride using copper radiation is shown overleaf in Table VI.

Table VI.

X-ray Powder Data for the Pyrolysis Product.

Interplanar spacings (A^{o}) are represented by d.

Relative intensities of the lines is represented by I.

(maximum 200.)

d	I	d	I	d	I
6.178	18	1.852	8		
4.538	20	1.799	18	1.085	5
3.765	15	1.767	13	1.068	5
3.228	200	1.717	3	1.024	10
3.108	8	1.652	3	0.992	5
3.038	8	1.602	18	0.941	1½
2.990	3	1.568	5	0.901	1½
2.913	150	1.553	10	0.888	3
2.731	3	1.488	13	0.879	3
2.661	120	1.457	1½	0.855	1½
2.499	5	1.439	1½	0.804	1½
2.441	120	1.384	18		
2.341	20	1.353	1½		
2.263	5	1.327	1½		
2.168	5	1.296	5		
2.078	3	1.252	5		
2.049	18	1.230	10		
1.991	3	1.217	5		
1.934	5	1.189	3		
1.881	35	1.164	3		

(6). A small sample of the hydride was transferred in a glove box to a small weighing capsule fitted with B14. ground glass joints. The capsule was opened inside a flask filled with nitrogen and the contents hydrolysed with distilled water followed by dilute sulphuric acid. The hydrolysis of 0.02494g. gave 44.5 N-cc. of hydrogen, and 0.5 N-cc. of ethane.

Found: Na, 43; Be, 30.9; hydrolyzable-hydride, 8.72; -ethyl, 2.6%. neither chloride nor ether could be detected. This analysis accounts for only 85% of the total weight so some oxygen may have been present, possibly as beryllium oxide. BeH_2 Requires Be, 81.7; H, 18.3%. A mixture of $3Na_2Be_2H_6 + 5BeH_2$ requires Na, 52; Be,37.3; H, 10.6%.

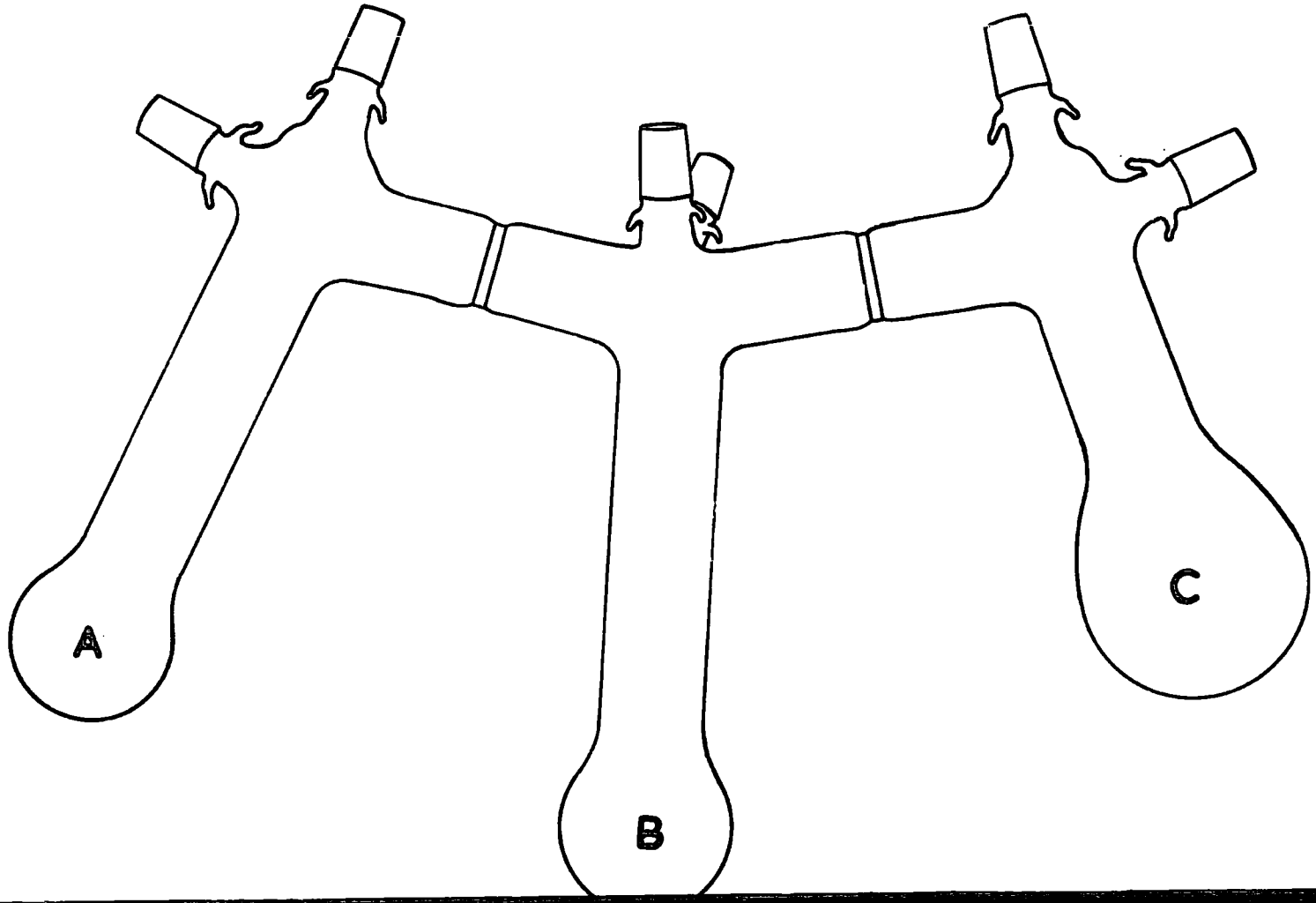
(b) Modified procedure for '$Et_4Be_3H_2$' pyrolysis, with control of the sodium content.

A solution of approximately 3.3g. of beryllium chloride in 250cc. of ether was made up shortly before use (the solution turns yellow after 3-4 days) such that only one phase was present. The solution was standardised by removing an aliquot with a pipette, hydrolysis with water and titration of the free acid with standard sodium hydroxide solution.

Sodium hydride (2.0g., 0.0833 mole.) and 30cc. of a 1.57M. solution of ethereal diethylberyllium (0.0471 mole.) were refluxed in 250cc. of ether with stirring for three days. The mixture was poured into limb 'A' of the triple Schlenk tube (Figure VI) and the sodium hydridodiethyl-beryllate extracted with ether from excess sodium hydride into limb 'B'. Most of the ether was then distilled under vacuum into 'A' (cooled to -196°) and the residual solution cooled to -60°(acetone-CO_2). The mother liquor was decanted into 'A', leaving the crystalline hydridodiethylberyllate in 'B'. Ether was distilled back from 'A' into 'B' (cooled to -196°) under vacuum up to a standard mark (180cc. at room temperature) and the salt dissolved by gently swirling and warming the solution. Two 0.7cc. samples were removed by syringe, hydrolysed with distilled water and acid and made up to standard volume with distilled water. Analysis of these solutions for sodium showed that the ether solution in 'B' contained 0.842g.(0.0366 mole.) of sodium. 108.5cc. of the 0.1675M. solution of ethereal beryllium chloride (0.01818 mole.) were added by pipette to the solution in 'B' and an immediate white precipitate formed. The mixture was gently swirled to ensure complete mixing and then the precipitate allowed to settle. Analysis of a sample of the supernatant liquid showed that only a small amount of sodium was present

Figure VI

The Triple Schlenk Tube.



in solution and chloride could not be detected. The solution was filtered into limb 'C' and the clear solution was distilled down to about 70-80cc. The solution was transferred by syringe into the pyrolysis apparatus, previously described , and the pyrolysis was carried out as described in the previous experiment. 76.2 N-cc. of ethylene (identified by its infrared spectrum.) were evolved during the pyrolysis and the residue was washed four times with ether and pumped dry.

The hydrolysis was carried out as previously described, using a small capsule fitted with ground joints in which to weigh the hydride.

Hydrolysis of 0.0185g. produced 70.4 N-cc. of hydrogen and 0.3 N-cc. of ethane. Chloride could not be detected in the product. Found: Na, 5.7; Be, 81; hydrolyzable-H, 17.1%. BeH_2 requires Be, 81.7; H, 18.3%. A composition $Na_2Be_2H_6$ + $65BeH_2$ or Na_2BeH_4 + $66BeH_2$ requires Na, 5.8; Be, 77; H, 17.4%.

The X-ray powder photograph showed that this product was amorphous.

(c). Effect of chloride on the preparation of beryllium hydride.

In order to determine the effect of chloride on the pyrolysis, a further experiment was tried using 1.0g. (0.0417 mole.) sodium hydride and 20cc. of a 1.57M. solution of ethereal diethylberyllium (0.0314 mole.) in 100cc. of

ether. After the hydridodiethylberyllate had been extracted and dissolved in ether in the triple Schlenk tube as before, analysis of a sample of the solution showed that the total solution (80cc.) contained 0.2673g.(0.0116 mole.) of sodium. 29.0cc. of a 0.2003M. solution of beryllium chloride (0.00581 mole.) in ether was added, and after mixing, the supernatant liquid shown to contain no sodium but a small amount of chloride. The solution was treated as in the previous experiments, but at 120°, the contents of the pyrolysis vessel became liquid and did not solidify below 140° even after several hours at this temperature. At 180°, the solid began to darken after about an hour so the vessel was allowed to cool and the residue washed four times with ether. During the pyrolysis, 25.0 N-cc. of a mixture (shown by infrared spectrum) of ethane and ethylene were formed.
Found: 0.02416g. on hydrolysis produced 17.6 N-cc. of hydrogen and 6.9 N-cc. of ethane on hydrolysis. The residual solution after hydrolysis contained chloride but no sodium.

In one experiment only (out of about six or seven) aimed at the preparation of beryllium hydride by the pyrolysis process, hydrolysis of the residue produced a relatively small amount (30.2 N-cc.) of isobutane (identified by its infrared spectrum).

Reactions between '$Et_4Be_3H_2$' and Sodium Hydride.

Methods for increasing the hydrogen:ethyl ratio by reaction of '$Et_4Be_3H_2$' with sodium hydride, with a view to obtaining ethylberyllium hydride or its sodium hydride complex are now described.

Sodium hydride (2.3g.,0.0958 mole.) and 20cc. of a 2.78M. solution of ethereal diethylberyllium (0.0556 mole.) were refluxed in 100cc. of ether for 24 hours. 2.2g.(0.0275 mole.) of beryllium chloride in 60cc. of ether were added and after refluxing for 1 hour, the mixture was filtered. Hydrolysis of a 1.0cc. sample of filtrated solution liberated 6.5 N-cc. of hydrogen and 13.7 N-cc. of ethane. The ethyl: hydrogen ratio is 2.1:1, thus '$Et_4Be_3H_2$' has been formed.

2.5g.(0.0104 mole.) of sodium hydride was added to the above filtrate and the mixture refluxed with stirring for several hours. 2.0cc. samples of the supernatant liquid were removed at various intervals and analysed by hydrolysis.

23 hours. 9.4 N-cc. of hydrogen and 23.0 N-cc. of ethane, ethyl:hydrogen = 2.44.

52 hours. 8.8 N-cc. of hydrogen and 22.6 N-cc. of ethane, ethyl:hydrogen = 2.58.

100 hours. 8.9 N-cc. of hydrogen and 24.4 N-cc. of ethane, ethyl:hydrogen = 2.73.

The ether was distilled off, the mixture heated at 75-80° for 24 hours and then the ether replaced and the mixture refluxed for 1 hour.

124 hours. 6.5 N-cc. of hydrogen and 13.0 N-cc. of ethane, ethyl:hydrogen = 1.99.

The solution was poured into a double Schlenk tube and a crystalline solid was extracted with ether from excess sodium hydride. The solution was distilled down to small volume, cooled to -40° and the colourless needles filtered off on the sintered disc connecting the two limbs of the Schlenk tube and pumped dry.

Found: Be, 9.84; hydrolyzable-ethyl, 63.7; -hydride, 1.1; $C_4H_{11}BeNa$ ($NaBeEt_2H$) requires Be, 9.9; hydrolyzable-ethyl, 63.7; -hydride, 1.1%.

Sodium hydridodiethylberyllate was obtained in 91% yield on the basis of the equation shown below:

$'Et_4Be_3H_2'$ + NaH ⟶ $NaBeEt_2H$ + an insoluble product inseparable from sodium hydride (as discussed on p.119)

In a similar experiment, the ethereal solution of $'Et_4Be_3H_2'$ was added to sodium hydride in 'diglyme', diethyl-ether distilled off and the mixture heated to 80-85° for 36 hours. At the end of this period, the gaseous hydrolysis products from a sample of the solution which was dark-brown, were very small, consequently decomposition has taken place.

As '$Et_4Be_3H_2$' reacts with sodium hydride as though it contains diethylberyllium, it was thought that reaction of this product with beryllium chloride would produce more '$Et_4Be_3H_2$' and so on. The overall reaction can be represented by the equation below:

$$2NaH + Et_2Be + BeCl_2 \longrightarrow 2NaCl + 2EtBeH.$$

Diethylberyllium (0.03 mole, 20cc. of a 1.5M. solution in ether) was refluxed with 1.5g.(0.0625 mole.) of sodium hydride in 400cc. of ether for 1 day. 2.5g.(0.031 mole.) of beryllium chloride in 50cc. of ether was added over two hours to the refluxing reaction mixture which was rapidly stirred and refluxed for several days. 5cc. samples of the supernatant liquid were removed by syringe at various intervals and hydrolysed.

1 day. 8.3 N-cc. of hydrogen and 15.2 N-cc. of ethane

3 days. 9.1 N-cc. of hydrogen and 19.9 N-cc. of ethane.

The solution was then filtered on to 0.9g.(0.0375 mole.) of sodium hydride and again refluxed.

1 day. 8.5 N-cc. of hydrogen and 18.2 N-cc. of ethane

7 days. 15.0 N-cc. of hydrogen and 27.5 N-cc. of ethane.

This type of reaction is therefore unsatisfactory for the preparation of ethylberyllium hydride, probably due to coating of sodium hydride by chloride.

Reaction between Tri-ethylstannane and Diethylberyllium.

$$Et_3SnH + Et_2Be \longrightarrow Et_4Sn + EtBeH.$$

Tri-ethylstannane (5.2g., 0.0252 mole.) and 16.0cc. of a 1.57M. solution of ethereal diethylberyllium (0.0251 mole.) were transferred by syringe into the reaction flask 'A' (Figure VII) and heated at 40° for 2 hours,(the apparatus being attached to the vacuum system via ball-joint C and joints D and E being closed with caps). The temperature was then raised to 75° during which time ether distilled into the receiver 'B' and this temperature was maintained for 2 hours. The flask was allowed to cool to room temperature, 'B' cooled in liquid air and the system evacuated so that all volatile matter was collected in 'B' over 14 hours. After continuous pumping at 35° for 2 hours, the flask 'A' contained a viscous glassy residue, which became a white solid after prolonged pumping.

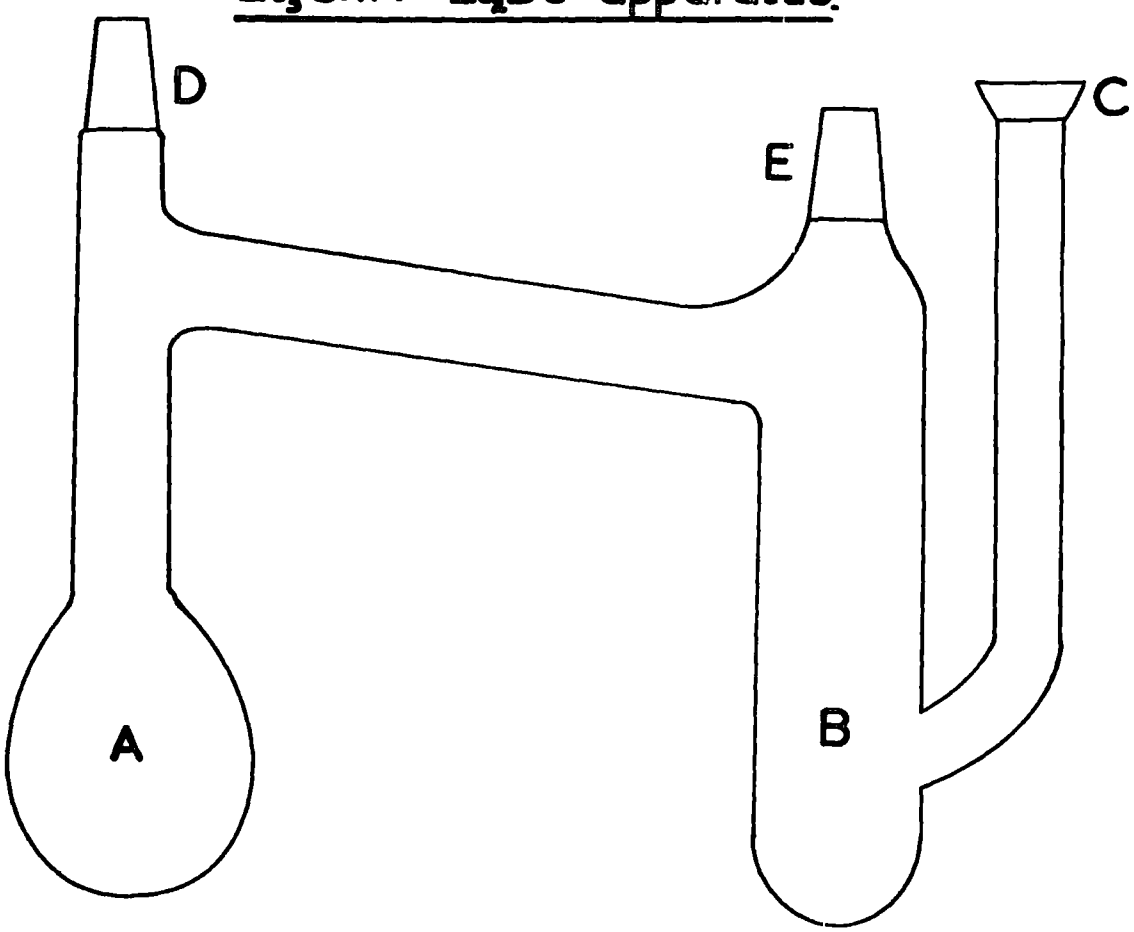
The distillate was removed by syringe, the receiver 'B' washed with more ether, and these were combined and made up to standard volume (25cc.) with ether.

Approximately 20cc. of ether was condensed on to the contents of 'A' and the clear solution removed by syringe and stored in a flask under nitrogen.

Distillate. Two 5cc. aliquots were removed by pipette and

FIGURE VII

$Et_3SnH - Et_2Be$ apparatus.



fractionated through a trap at -50° which collected 0.82g., 0.80g. of tetra-ethyltin containing a trace of tri-ethylstannane (shown by infrared spectrum). The total quantity of tetra-ethyltin isolated was 4.05g.(71% of the theoretical, the remainder may have been trapped in the residue).

Residue. Hydrolysis of 2cc. of the ethereal solution gave 31.0 N-cc. of hydrogen, 31.5 N-cc. of ethane and 0.0155g. of beryllium (38.5 N-cc.)

The remaining solution of the beryllium compound was transferred by syringe to one limb of a double Schlenk tube, and 500 N-cc.(excess) of trimethylamine were condensed on to the solution which was cooled in liquid air. The mixture was allowed to react at room temperature and then ether and excess amine removed under vacuum. The colourless crystalline material which remained, was sublimed up the walls of the Schlenk tube as prisms at 40-45°. The compound melts at 90-91° in a sealed tube under vacuum, fumes in air, and reacts vigorously with water with effervescence.

Found: Be, 9.3; hydrolyzable-ethyl, 29.0; -hydride, 1.0%; M, cryoscopically in benzene, 193, 200, 202, in 0.36, 0.55, 0.78 weight % solutions. $C_{10}H_{30}Be_2N_2$ $(EtHBe.NMe_3)_2$ requires Be, 9.2; hydrolyzable-ethyl, 29.6; -hydride, 1.03%; M,196. The molecular weight measurements correspond to degrees of association of 1.97, 2.04, 2.06 respectively.

DISCUSSION

Discussion.

In contrast to sodium hydridodiethylberyllate[45], which may readily crystallised from diethylether in unsolvated form (solubility about 30g/litre at 20°), the analogous methyl compound is only sparingly soluble (about 1.6g/litre at 20°) and may be crystallised only very slowly by the use of a Soxhlet extractor. The lower solubility of the methyl compound is expected in view of its probably greater molecular symmetry. No evidence has been obtained for the degree of association of these salts but X-ray data for sodium hydridodiethylberyllate, at present being studied, have shown that this material is monoclinic with space group $P2_1/c$ (No.14). The unit cell dimensions are, a=5.04, b=11.2, c=20.9Å and the monoclinic angle (β) is 101° 15'.

For the preparation of many derivatives, isolation of the salt, $NaBeMe_2H$, is fortunately not necessary. When a suspension of sodium hydride (in excess) in ethereal dimethylberyllium is boiled, the concentration of the latter gradually falls, as indicated by the amount of methane evolved when samples of supernatant liquid are hydrolysed. No further change appears to take place after about 48 hours, but addition of half a mol. ethereal beryllium chloride then causes

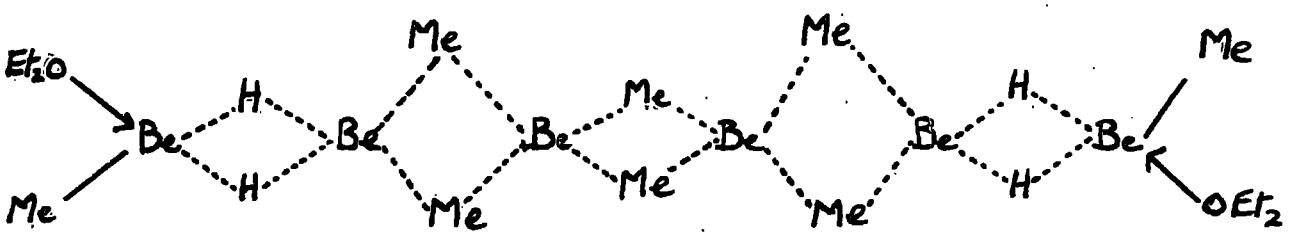
precipitation of sodium chloride and all the beryllium together with hydrolyzable methyl and hydrogen to reappear in solution in molar ratio 3:4:2. Filtration from sodium chloride and excess sodium hydride yields a solution containing '$Me_4Be_3H_2$'. Sodium hydridodiethylberyllate[45], prepared from sodium hydride and diethylberyllium in ether reacts in a similar way with beryllium chloride,

$$NaH + Et_2Be \longrightarrow NaBeEt_2H$$

$$2NaBeEt_2H + BeCl_2 \longrightarrow 2NaCl + 'Et_4Be_3H_2'$$

There is little evidence about the constitution of these solutions and the product '$Me_4Be_3H_2$' could be a 2:1 mixture of methylberyllium hydride $(MeBeH)_n$ and dimethylberyllium, or a 1:2 mixture of beryllium hydride $(BeH_2)_n$ and dimethylberyllium. However, since beryllium hydride is insoluble in ether[52] the latter possibility seems unlikely. On the basis of their reaction with tertiary amines, it is reasonable to believe the main solute species are solvated dimethylberyllium and solvated methylberyllium hydride though significant concentrations of trinuclear (e.g. '$Me_4Be_3H_2$') or more complex species could be present. The colourless viscous oily residue obtained when solvent is removed from ethereal '$Me_4Be_3H_2$' at room temperature, has the approximate composition $Me_4Be_3H_2OEt_2$. Most of the ether is lost when this oily material is heated to about 50°

under vacuum. Since dimethylberyllium is an electron-deficient polymer[26], insoluble or at least very sparingly soluble in solvents with which it does not react[27], the viscous oil could be regarded as some kind of electron-deficient complex between dimethylberyllium and methylberyllium hydride such as,

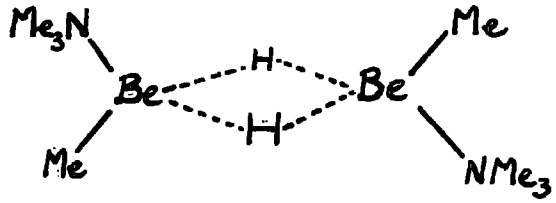


containing an element of the dimethylberyllium polymer chain.

Reactions with donor molecules.

Addition of trimethylamine to ethereal '$Me_4Be_3H_2$' yields a mixture of the dimethylberyllium complex $Me_2Be.NMe_3$ [5] and the trimethylamine complex (I) of methylberyllium hydride. The complex (I), m.p. 73.0-73.2°, is dimeric in benzene and is considerably less volatile than $Me_2Be.NMe_3$. Whereas the vapour pressure of $Me_2Be.NMe_3$ is 1.8mm. at 30°, that of (I) is 1.8mm. at 64° ($\log_{10}p_{mm.} = 7.438 - \frac{2439}{T}$, for the liquid from 73-115°), and the two complexes may be separated by fractional condensation. The hydride (I) is formulated with a hydrogen rather than a methyl bridge because the complex is not decomposed by excess of trimethylamine whereas the methyl bridges between beryllium atoms in the dimethylberyllium polymer

are cleaved by trimethylamine.[5]



(I)

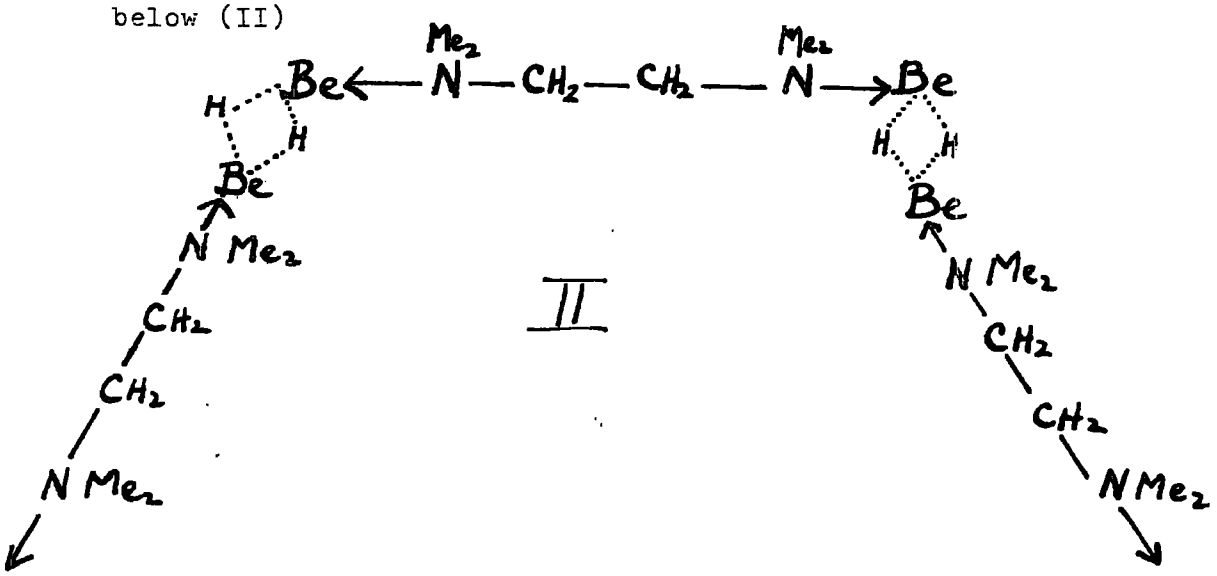
Studies on reactions between dialkylaluminium hydrides and donor molecules have shown that the hydrogen bridges in these compounds are less readily cleaved than are the methyl bridges in trimethylaluminium.[90,99]

From the vapour pressure equation, the latent heat of vaporization is 11.2 kcal. $mole^{-1}$, the extrapolated boiling point 257° and the Trouton constant 21.1. The normal Trouton constant suggests there is no change in the degree of association during the process of vaporization, thus it is likely that the vapour, at least up to about 110°, consists mainly of dimer. An attempt to measure the molecular weight of (I) as vapour at higher temperatures (145-175°) was not entirely successful on account of some decomposition; however, the vapour appeared to be monomeric at 175° and to become more associated at lower temperatures.

Attempts to prepare monomeric complexes, L_2BeMeH, of methylberyllium hydride by the use of donor substances which readily form chelate complexes have not been successful. Addition of bipyridyl to ethereal '$Me_4Be_3H_2$' results in an immediate yellow precipitate of bipy.$BeMe_2$[33], the solution becoming deep red.

Though it is possible that the red colour was due to bipy.BeMeH, the red soon turned to a dark brown and only tarry matter could be obtained on removal of the solvent. When bipyridyl was added to (I), a red colour was produced which underwent a similar decomposition to that described above, These observations may be explained by attack of the hydride across the azo-methine bond of the bipyridyl as occurs with other metal hydride complexes such as bipyridyl aluminium hydride.[109].

Reaction with N,N,N',N'-tetramethylethylenediamine results in the formation of the known chelate complex of dimethylberyllium[33]. and the precipitation of a white apparently amorphous substance, which is insoluble in ether, benzene, carbon disulphide and carbon tetrachloride. Since the analysis of the insoluble product corresponds to the formula, $[(MeBeH)_2.Me_2NC_2H_4NMe_2]_n$ it appears that the hydrogen bridge is present resulting in a polymeric constitution as shown below (II)



II

This involatile complex (II) is neither pyrophoric nor does it fume in air.

Reactions with 1,2-dimethoxyethane and subsequent evaporation of ether gives a mixture of solid and liquid products. When this is heated to about 50° in vacuum, the 1,2-dimethoxyethane complex of dimethylberyllium[33] sublimes from the reaction vessel, leaving a very viscous oil which is insoluble in benzene. Since the analysis of the oil corresponds to the formula $\left[(MeBeH)_2MeOC_2H_4OMe\right]_n$ its constitution is probably similar to that of the tetramethylethylenediamine complex (II).

Reactions between a secondary amine or a tertiary amine hydrochloride and a beryllium compound containing both alkyl and hydride groups, produces a mixture of hydrogen and hydrocarbon as gaseous products. Dimethylamine and trimethylamine-methylberyllium hydride react at about room temperature liberating a mixture of methane and hydrogen. This resembles the reaction between the secondary amine and isopropylberyllium hydride which evolved propane and hydrogen in the ratio 2.5:1[46]. A mixture of ethane and hydrogen in the ratio 1.16:1 was liberated from trimethylamine hydrochloride and sodium hydridodiethylberyllate in ether solution at room temperature. This latter reaction was not considered to be a good method for the preparation of trimethylamine-ethylberyllium hydride

since, no doubt, an approximately equimolar amount of the diethylberyllium complex is also formed. A satisfactory method for the preparation of trimethylamine-ethylberyllium hydride by another route is discussed below.

Reaction between diethylberyllium and triethylstannane in ether solution results in the formation of tetra-ethyltin and ethylberyllium hydride; hydrolysis of the involatile residue left after evaporation of the tetra-ethyltin yielded ethane and hydrogen in the ratio 1.016:1. The hydrogen-alkyl exchange which takes place when tri-ethylstannane is heated with tri-ethylaluminium (giving Et_2AlH) is inhibited by ethers or tertiary amines.[108] On the assumption that the exchange with tri-ethylaluminium involves an electron-deficient intermediate, it is reasonable to expect that exchange should be inhibited by reagents which remove the electron-deficient character of the aluminium alkyl by forming coordination complexes. Since there is evidence that electron-deficient bridges persist in dimethylberyllium in the presence of ethers and trimethylphosphine,[5] it is not surprising that the tin hydride-alkylberyllium exchange reaction takes place in the presence of diethylether. Ethylberyllium hydride prepared by this method has been characterised by conversion into its trimethylamine complex $(EtHBe.NMe_3)_2$ which is dimeric in benzene solution like its methyl analogue (I). It is possible

that this method could be used for the preparation of a wide range of organoberyllium hydride coordination complexes.

Diethylberyllium forms a 1:1 liquid complex with trimethylamine; if more than one mol. of amine coordinates, it can be removed by pumping at -40° whereas dimethylberyllium[5] forms a stable 1:1 complex with trimethylamine and an unstable 2:3 complex $(Me_2Be)_2(NMe_2)_3$ which readily loses a mol. of amine.

N,N,N',N'-tetramethyl o-phenylenediamine forms a crystalline complex with dimethylberyllium in a similar way to the N,N,N',N'-tetramethylethylenediamine complex.[33] Both these crystalline compounds are monomeric in benzene solution and can be sublimed unchanged in vacuo.

In the preparation of the sodium hydridodialkylberyllates, it is probable that hydride ion displaces coordinated ether (used as solvent):

$$H^- + R_2Be.OEt_2 \longrightarrow \frac{1}{n}(R_2BeH)_n^{n-} + OEt_2$$

Hydride ion also displaces trimethylamine,

$$NaH + Et_2Be.NMe_3 \longrightarrow NaBeEt_2H + Me_3N.$$

in a reaction very similar to the formation of sodium aluminium hydride from sodium hydride and trimethylamine-alane.[96]

$$NaH + H_3Al.NMe_3 \longrightarrow NaAlH_4 + Me_3N.$$

Thermal decomposition of alkylberyllium hydride-dialkylberyllium mixtures.

Attempts to prepare methylberyllium hydride by sublimation under reduced pressure of dimethylberyllium from the solid residue of approximate composition '$Me_4Be_3H_2$' (from $2NaBeMe_2H + BeCl_2$) were not successful. At about 10^{-3}mm. pressure slow sublimation of dimethylberyllium is apparent from 60°, but no indication of any pause in the evolution of dimethylberyllium at a stage corresponding to a residue of methylberyllium hydride was obtained. In several experiments (detailed below), sublimation in the range 170-210° resulted in extensive disproportionation,

$$Me_nBe_{\frac{n}{2}} + {}_{\frac{m}{2}}H_m \longrightarrow Me_{n-2}Be_{\frac{n}{2}} + {}_{\frac{m}{2}-1}H_m + Me_2Be \ ,$$

which continued until the hydride:methyl ratio in the residue (m:n-2) was a little more than 10:1. Attempts to obtain products with a greater hydride:methyl ratio by means of reactions at higher temperatures were not successful on account of thermal decomposition of dimethylberyllium, shown by the formation of some methane.

Diethylberyllium separates rather more easily when the viscous residue, left after the evaporation of ether from solutions of approximate composition '$Et_4Be_3H_2$', is heated.

For example, a glassy residue evidently consisting mainly of ethylberyllium hydride was obtained after 8hours heating at 70-80°. The course of further reaction at higher temperature is greatly affected by the composition of the diethylberyllium-ethylberyllium hydride solution.

In some early experiments, solutions of sodium hydridodiethylberyllate were prepared by stirring sodium hydride in excess with boiling solutions of diethylberyllium in ether. The $NaBeEt_2H$ content of the supernatant liquid was then determined by hydrolysis of a small sample and exactly one half mol. of beryllium chloride in ether was added, without previous filtration from unreacted sodium hydride. Filtration from the mixture of sodium hydride and precipitated sodium chloride gave solutions originally believed to be of the composition '$Et_4Be_3H_2$', whose pyrolysis was studied. In one experiment, in which the residue after evaporation of ether from a solution prepared in this way, was heated <u>in vacuo</u> at 60° for 4 hours and then at 110-120° for 2 hours; an involatile residue was obtained which contained 17.8% hydride hydrogen. This result indicated that the reaction

$$Et_4Be_3H_2 \longrightarrow 2Et_2Be + BeH_2$$

had taken place giving a product consisting mainly of beryllium hydride, since the hydrogen content of pure beryllium hydride is 18.3%. Later work suggested this was a misleading result

which is now attributed to the presence of a very small amount of $NaBeEt_2H$ in the '$Et_4Be_3H_2$'. Further experiments showed that solutions of '$Et_4Be_3H_2$' dissolve more sodium hydride and that the presence of some alkali metal is necessary for extensive disproportionation to take place. In one experiment described in the Experimental section (p.**93**), the residue after pyrolysis (finally 8 hours at 180°) contained 43% sodium as well as 31% beryllium, 8.7% hydride hydrogen, and 2.6% ethyl. This residue was shown to be crystalline or mainly crystalline (X-ray powder photograph); it decomposed at about 280° <u>in vacuo</u> but failed to react with diethylberyllium. Though some oxygen was probably present, as the analysis accounted for only 85% of the total weight, the composition of the residue roughly corresponded to a mixture of 5mols. BeH_2 + 3 mols. $Na_2Be_2H_6$ or 8 mols. BeH_2 + 3 mols. Na_2BeH_4. As reaction with cold water was relatively slow, the sodium is probably present as a complex sodium beryllium hydride rather than as free sodium hydride.

Further evidence for the existence of a sodium beryllium hydride, evidently insoluble in ether, was obtained from experiments in which solutions of '$Et_4Be_3H_2$' in ether were boiled with an excess of sodium hydride for periods up to several days. The hydrolysis of samples of solution showed that the ethyl:hydride ratio (in solution) was always at least 2:1,

but since concentration of the filtered solution yielded $NaBeEt_2H$, showing that sodium had entered solution, it is evident that hydride must have left solution as some insoluble complex hydride. The formation of ether-insoluble lithium salts BeH_2nLiH has been reported in a preliminary communication.[55]

Having found that solutions of '$Et_4Be_3H_2$' react with sodium hydride, the experimental procedure for the preparation of beryllium hydride was modified to allow the preparation of ethereal $NaBeEt_2H$ of known concentration and free from both diethylberyllium and sodium hydride. The presence of beryllium oxide, and alkoxide or failure to balance exactly the sodium salt with the beryllium chloride is shown by the presence of these involatile, insoluble materials in the residue. Consequently the following precautions were necessary for the preparation of pure beryllium hydride since no method of purification could be found; (1) the rigorous drying of apparatus before use by washing with ethereal diethylberyllium ; (2) isolation of the hydridodiethylberyllate, thus removing ether-soluble oxidation or hydrolysis products formed in the first step of the preparation; (3) the avoidance of unnecessary transferences of the hydrido-diethyl beryllate once it has been prepared; and finally, (4) the re-use of the same ether throughout the preparation without removal from the apparatus. The triple Schlenk tube shown in Figure VI (in the Experimental

Section) fitted the requirements listed above.

In one such experiment an amount of beryllium chloride was added which resulted in the presence of 1 mol. chloride in excess for every 870 mols. beryllium. Pyrolysis (180°) of the filtrate after separation of sodium chloride yielded a product in which the H:Et ratio was only 2.55:1. A trace of chloride but no sodium was detected in this product.

Finally, addition of about 1% less than the theoretical amount of beryllium chloride to a solution of $NaBeEt_2H$, followed by filtration from sodium chloride, evaporation of ether and pyrolysis (180°) gave an amorphous (X-ray powder photograph) product of approximate composition $Na_2Be_2H_6$ + 65 BeH_2 (or Na_2BeH_4 + 66 BeH_2) evidently consisting mainly of beryllium hydride (approximately 91 wt.%). The infrared spectrum of this product differed from that of beryllium hydride containing more sodium in having a relatively broad and strong absorption centred on 1754 cm^{-1} instead of absorptions at 1760 and 1629 cm^{-1}. The infrared spectrum of this latter product showed no apparent absorption in the 3μ region when examined as a mull in perfluoromethyldecalin.

A purer hydride has been obtained by this method (approximately 91 wt.%) than by other known preparations and there appears to be no reason to doubt that still smaller proportions of sodium (or better still lithium) in excess of

the exact stoichiometric proportion would result in the formation of pyrolysis products more closely approaching pure beryllium hydride. Previously other workers had studied the reaction between lithium aluminium hydride and dimethyl-beryllium[52]. forming a hydride which was contaminated to a large extent with aluminium hydride, lithium hydride and ether[45]. and this was no doubt responsible for its relatively low decomposition temperature (125°) and its reactivity. The pyrolysis of di-tertiary-butyl beryllium etherate yielded 96.3 mole % beryllium hydride (71 wt.%)[47]. and pyrolysis of the ether-free compound yielded 97 mole % beryllium hydride (80 wt.%).[48]. Recently a new synthesis of beryllium hydride has been extensively examined; triphenylphosphine and beryllium borohydride react in xylene at 140° forming triphenylphosphine-borane (soluble) and precipitating 99.1 mole % beryllium hydride (80.7 wt.%).[110]. A negligible amount of the impurity, triphenylphosphine-borane, was removed by prolonged sublimation and by the use of boiling benzene and this impurity must therefore be occluded or bound in some way in the beryllium hydride polymer chain.

The Interpretation and Discussion of Spectroscopic Data.

Section I.

Dimethylberyllium.

The unsaturated and saturated vapour phase infrared spectra of this compound were recorded between 100° and 200° using the heated gas cell. The frequencies observed below 2000cm^{-1} in typical spectra are listed below in Tables VII and VIII. It is perhaps of interest to note that whenever a band at 1307cm^{-1}, due to methane (presumably formed by accidental hydrolysis in the cell) was observed, a band at 842-847cm^{-1} was also observed. The 842-847cm^{-1} band is therefore due to hydrolysis or oxidation products and is in the expected region for νBe-O.

Table VII

Dimethylberyllium (unsaturated vapour)

Temperature	150°	175°	185°	Assignment.
Frequency(cm^{-1})				
	1266mw	1266m	1266ms	CH_3 δsym.
	1085mw	1086m	1087ms	
	1062m			CH_3 ρ
	1033ms	1033s	1033s	
	815mw	816m	816s	νBeC_2

The unsaturated vapour consists mainly of monomer and has a relatively simple spectrum in the 5-15μ region. Beyond

reasonable doubt monomeric dimethylberyllium has a linear structure and will therefore have symmetry D_{3h}, and by analogy with dimethylzinc and dimethylmercury, the methyl groups may be assumed to rotate freely.[116.] The odd feature of this spectrum is the absence of $\delta_{asym}\ CH_3$ in the 1480cm^{-1} region, and this is consistent with the spectrum of solid dimethylberyllium in which this absorption is also absent.[29.] Other methyl-metal compounds in which $\delta_{asym}\ CH_3$ is absent or relatively weak are described in the section of the introduction dealing with spectroscopy.

The spectrum of the saturated vapour of dimethylberyllium is far more complex than that of the unsaturated vapour. This is to be expected, since the saturated vapour consists of monomer, dimer and trimer molecules, but the proportion of monomer increases as the temperature increases according to the equilibrium constants K_D and K_T.[27.] In the 11-13μ region, the spectrum became increasingly complex as the temperature was raised. The assignments of $CH_3\ \delta_{sym}$(terminal) to the very strong band observed at 1259-1264cm^{-1} and $CH_3\ \delta_{sym}$(bridge) to the medium strong band at 1211-1214cm^{-1} is due to the observation that as the temperature increases, the relative intensity of the 1259-1264cm^{-1} band increases and the 1211-1214cm^{-1} band decreases and the proportion of monomer (ie. the number of terminal methyl groups) in the

Table VIII.

Dimethylberyllium (saturated vapour).

Temperature	120°	150°	180°	Assignment.
Calculated v.p.(mm) of saturated vapour.[27]	2.45	17.8	109.9	
Frequency(cm^{-1})				
	1484m	1484m	1479m	CH_3 $\delta_{asym.}$
	1456m	1460m	1453m	
	1304mw	1307mw	1305m	
	1259m	1264ms	1259vs	$CH_3\delta_{sym}$(terminal)
	1211ms	1214ms	1212ms	CH_3 δ_{sym}(bridge)
			1182w	
		1152w		
	1096w			
	1072w			
			1050s	
	980m	985s		
	957s	957vs	940vs	
	861ms	864vs	870vs(broad)	
	790ms	790m	801ms	v Be-CH_3?
			758m	
	719w	719w		
		692w	690w	
	668w		668w	

vapour increases as the temperature increases [27]. (and similarly the proportion of bridging methyl groups decreases). In this respect, beryllium appears to differ from aluminium since Hoffmann [118]. has assigned $CH_3\delta_{sym}$(terminal) at 1201cm^{-1} and $CH_3\delta_{sym}$(bridge) at 1255cm^{-1} in Me_6Al_2. Goubeau [29]. has assigned the two strong absorptions at 1243 and 1255cm^{-1} as $\delta_{sym}CH_3$ in the spectrum of solid dimethylberyllium (Table I) and these must undoubtably be bridge vibrations as solid dimethylberyllium has a polymeric structure, all the methyl groups occupying bridging positions. The strong absorptions observed in the 700-900cm^{-1} region are probably methyl rocking vibrations.

Although the assignments listed for dimethylberyllium are purely speculative, a study of the deutero analogue under similar conditions should provide conclusive evidence to enable unambiguous assignments to be made.

Section II.

In this section the infrared spectra of organoberyllium and organoberyllium hydride coordination compounds, the sodium hydridodialkylberyllates and their deutero analogues, and beryllium hydride are discussed. In Tables IX-XVII are given suggested assignments of the characteristic absorption bands below 2500cm^{-1} to the various structural features of

the compounds examined and photographs of the infrared spectra of these compounds are shown after the Tables.

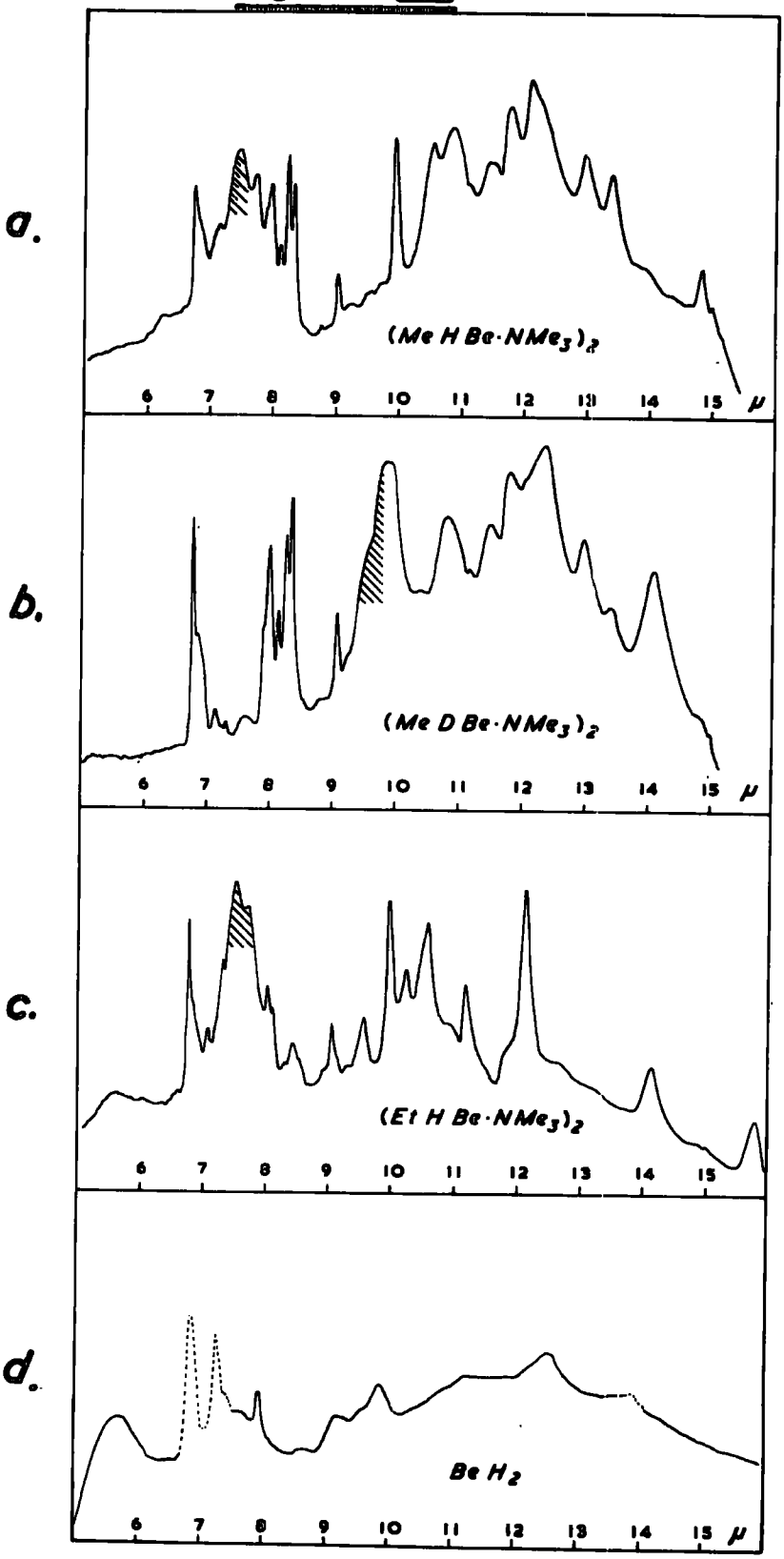
Beryllium-hydrogen vibrations.

The 0→1 vibrational transition of the ground state of the Be-H molecule derived from band heads of emission electronic spectra and band origins [133] is at 2058.6cm^{-1} and at 2087.7cm^{-1} for the first excited state. A terminal Be-H group could therefore be expected to cause absorption near 2100cm^{-1} and a similar conclusion is reached by considering the changes with atomic number of the stretching frequencies of the hydrides of the first short period elements. The vibrational modes, of mainly stretching character of the bridging hydrogen atoms in a BeH_2Be group should cause absorption at frequencies well below 2100cm^{-1}, by analogy with the vibrational modes of the BH_2B group in diborane and the various methyl and ethyl diboranes. Whereas terminal B–H bonds usually cause absorption in the 2200-2500cm^{-1} region, the two modes due to the BH_2B bridge in diborane are at 1915cm^{-1} (ν_{13}, symmetrical out-of-phase) and 1606cm^{-1} (ν_{17}, asymmetric in phase)[130]. (These vibrational modes are illustrated on p.41.) The alkyl diboranes provide a closer analogy to the beryllium compounds formulated as (I) and (II) with BeH_2Be bridges. In the former, the weak absorptions

corresponding to ν_{13} is observed at 1972 ($Me_4B_2H_2$), 1880 ($Me_3B_2H_3$) and 1852cm^{-1} ($Et_4B_2H_2$), whereas the very strong absorption corresponding to ν_{17} is observed at 1605, 1605, and 1582cm^{-1} in the three compounds, changing to 1186, 1183, and 1166cm^{-1} on deuteration.[134]. The spectra of $(MeHBe.NMe_3)_2$, $(MeDBe.NMe_3)_2$, and $(EtHBe.NMe_3)_2$ examined in cyclohexane solution are compared in Figure VIII. The spectrum of (I), Figure VIIIa. contains a strong absorption at 1344cm^{-1} shaded in the Figure, which is clearly due to one of the BeH_2Be stretching modes, since in the spectrum of the deutero analogue $(MeDBe.NMe_3)_2$, Figure VIIIb. it moves to about 1020cm^{-1} (also shaded) and evidently overlaps the absorption at 1007cm^{-1} of (I) which is almost certainly due to $\nu_{asym}(NC_3)$ of the trimethylamine, (see also Figure VIIIc.). Absorption due to $\nu(BeH_2Be)$ is clearly evident at 1333cm^{-1} in the spectrum of the ethyl derivative, $(EtHBe.NMe_3)_2$, Figure VIIIc. It is quite possible that the band at 948cm^{-1} in $(MeHBe.NMe_3)_2$ (moving to 710cm^{-1} on deuteration) may also be a BeH_2Be bridge vibration although it is not known whether these absorptions correspond to ν_{13} or ν_{17} of diborane.

The spectra of the N,N,N',N'-tetramethylethylenediamine complexes of dimethylberyllium and methylberyllium hydride (Table XIII) examined as Nujol mulls are very similar but that of the hydride complex contains a very strong absorption

Figure VIII


a.
(Me H Be·NMe3)2
6 7 8 9 10 11 12 13 14 15 μ
b.
(Me D Be·NMe3)2
6 7 8 9 10 11 12 13 14 15 μ
c.
(Et H Be·NMe3)2
6 7 8 9 10 11 12 13 14 15
d.
Be H2
6 7 8 9 10 11 12 13 14 15 μ

at 1331cm^{-1}, which is almost certainly a vibration of the BeH_2Be bridge, and a weak one at 1754cm^{-1}, both absent from the spectrum of the dimethylberyllium complex.

A comparison of the spectra of $NaBeMe_2H$ and $NaBeMe_2D$, both as Nujol mulls (Table XIV) indicates that absorptions due to Be-H bridging modes are at 1328 and 1165cm^{-1}, those due to Be-D bridges being at 917 and 869cm^{-1}. The absorption at 1328cm^{-1} in the spectrum of $NaBeMe_2H$ is somewhat obscured by the paraffin oil, but it is significant that the spectrum of this compound contains no pronounced features between 800 and 1000cm^{-1} so the very strong absorptions at 869 and 917cm^{-1} in the spectrum of the deutero compound must be due to a Be-D mode. The ratios ν_H/ν_D are 1.45 and 1.34, and though the former is unexpectedly large, the significance of this is doubtful on account of the difficulty in measuring the absorption at 1328cm^{-1}. The spectra of $NaBeEt_2H$ and $NaBeEt_2D$ are more complicated, as expected, but a comparison of the two shows ν(Be-H) at 1294s and 1065vs. cm^{-1} and ν(Be-D) at 951s and 835vs. cm^{-1}, ν_H/ν_D being 1.36 and 1.28. The remaining absorptions are very similar for the two compounds except for a band at 912cm^{-1} in the spectrum of the hydrogen compound.

The spectrum of (I) as saturated vapour using a 10cm. heated gas cell has also been recorded and is very similar to a solution in cyclohexane (Table XI). In the vapour,

$\nu(BeH_2Be)$ is at 1342cm^{-1}, very close to the frequency recorded for a solution in cyclohexane. At 50° (vapour pressure ca.0.9mm.) there was no appreciable absorption between 1500 and 2500cm^{-1}, but at 65° and particularly at 80°, a sharp absorption band at 2141cm^{-1} appeared. This absorption at 2141cm^{-1} is believed to be due to terminal ν(Be-H) in monomeric $MeHBe.NMe_3$ since vapour density measurements indicated extensive dissociation with increasing temperature (145-175°). Between 65° and 80°, the amount of monomer in saturated vapour could begin to be significant. Unfortunately the unsaturated vapour at higher temperatures could not be studied on account of defects in the heated gas cell.

The infrared spectrum of beryllium hydride, examined as Nujol mull is shown in Figure VIIId. This product was of approximate composition $(BeH_2)_{34}NaH$. The most characteristic feature of the spectrum (Table XVIII) is a rather broad absorption centred on 1750cm^{-1}. The material is amorphous by X-ray diffraction like that obtained by the pyrolysis of di tertiary-butylberyllium and has commonly been regarded as a cross-linked disordered polymer. The relatively sharp absorption at 1263cm^{-1} possibly analogous to the 1333-1344cm^{-1} bands in (I) and similar compounds is noteworthy. The other pronounced absorptions are at 1090, 1016, and 799cm^{-1} and are probably associated with beryllium-hydrogen deformations.

The spectrum of a product containing much sodium, ca. $(BeH_2)_{11}(NaH)_6$ (Table XVII) is very similar but differs in that the broad absorption at 1750cm^{-1} is replaced by two sharper absorptions at 1637 and 1771cm^{-1}.

Methyl vibrations.

In the spectra of $Me_2Be.NMe_3$, $(MeHBe.NMe_3)_2$, $(MeDBe.NMe_3)_2$, the symmetric and asymmetric methyl deformations vibrations can almost certainly be assigned to the absorptions occuring above 1200cm^{-1}. However, which absorptions are due to methyl groups attached to beryllium and which are due to methyl groups attached to nitrogen will only be determined by studying the spectrum of an isotopically substituted analogue of one of the above compounds. The complex $(CD_3)_2Be.NMe_3$ will be prepared in due course and examination of the spectrum of this compound should clarify or make it necessary to revise the assignments discussed here. The CH_3 rocking vibrations of the trimethylamine part of the molecule are found at 1115 and 850cm^{-1} in $Me_3N.BH_3$ [132]. and the absorption bands at 1101m(35°) (1105m in cyclohexane) and 840sh.(35°) (824sh.cm^{-1} in cyclohexane) in $Me_2Be.NMe_3$ are assigned to these modes of vibration. The Be-CH_3 rocking vibration is more difficult to assign but it is felt that the band at 941s(35°) (951vs. cyclohexane) may be due to this vibration and if this is a

correct assignment, this absorption will be found at about 660cm^{-1} in the spectrum of the deutero compound. The spectrum of $(MeHBe.NMe_3)_2$ is rather complicated in the 6-14μ region but quite a lot of it is common to the spectrum of $Me_2Be.NMe_3$. Thus it would appear that the N-CH_3 rocking vibration occurs at 1107m and the Be-CH_3 vibration at 922vs in the hydride complex and 1104m and 928s cm^{-1} respectively in the deuteride complex.

Carbon-nitrogen vibrations.

In other trimethylamine coordination complexes, ν_{asym}C-N is always found in the 1000cm^{-1} region, occuring at 1005s in $Me_3N.BH_3$,[132.] 1003 in $Me_3N.GaH_3$ [136.] and 955cm^{-1} in the tetramethylammonium ion.[137.] Thus ν_{asym}C-N can be assigned fairly certainly to the bands occurring at 1000s (35°) (1006vs, cyclohexane) in $Me_2Be.NMe_3$, 1007vs in $(MeHBe.NMe_3)_2$ (cyclohexane), 1016vs in $(MeDBe.NMe_3)_2$, 1001vs in $Et_2Be.NMe_3$ and 1007vs in $(EtHBe.NMe_3)_2$. Other assignments for the spectra of the ethyl compounds have not been made since the spectra of these compounds are complicated by -CH_2- vibrational modes.

No definite assignments have been made for beryllium-carbon and beryllium-nitrogen absorptions although the beryllium-carbon stretching vibrations probably occur about 800cm^{-1} since the strong band at 816cm^{-1} in dimethylberyllium (unsaturated vapour) has been assigned to this mode of vibration.

Table IX.

Infrared spectrum of $Me_2Be.NMe_3$ as saturated vapour.

35°	45°	Assignment.
1475vs	1477vs	
1464vs	1466vs	
1406w	1408w	
1302w	1304w	$\delta(CH_3)$ (d)
1242ms	1245vs	
1232ms	1233vs	
1186vs	1186vs	
1101m	1103m	$\rho(N.CH_3)$ (f)
1037sh	1041sh	
1000s	1000vs	$\nu_{asym}(CN)$ (d)
941s	940vs	$\rho(Be\text{-}CH_3)$ (t)
	874vw	
840sh	841sh	$\rho(NCH_3)$ (f)
800vs	803vs	$\nu(Be\text{-}C)$ (t)
709m	714vs	
671vw		
	608w	
585w		
506m	507w	

In these tables, the degree of certainty of these assignments is shown by the following assignments:

d = definite, f = fairly certain, t = tentative.

Table X.

Infrared spectrum of $Me_2Be.NMe_3$.

Contact film (36°)	Cyclohexane solution	Assignment.
	1484s	
1464vs	1472sh	
1443s	1447sh	
1405w	1408w	$\delta(CH_3)$ (d)
	1245s	
1235s	1235s	
1219s		
1186s	1192vs	
1100m	1105m	$\rho(NCH_3)$ (f)
1037vw	1049vw	
995vs	1006vs	$\nu_{asym}(CN)$ (d)
	951vs	$\rho(Be\text{-}CH_3)$ (t)
937w	893w(sh)	
	874w	
840m	844s	
	824sh	$\rho(NCH_3)$ (f)
800vs	794vs	$\nu(Be\text{-}C)$ (t)
	757sh	
730m(broad)		
	713vs	

Table XI

Infrared spectra of $(MeHBe.NMe_3)_2$ in the gas phase, and in cyclohexane solution and $MeDBe.NMe_3$ in cyclohexane solution.

$(MeHBe.NMe_3)_2$		$(MeDBe.NMe_3)$	
65°	Solution	Solution	Assignment.
2141m			ν(Be-H) (f)
1480s	1484s	1481s	
1458s	1470sh	1466m	$\delta(CH_3)$ (d)
	1400m	1407vw	
		1370vw	
1342s	1344vs		ν(BeH_2Be) (d)
		1317vw	
1304s	1299m		
1286s	1267m	1267sh	$\delta(CH_3)$ (d)
1254s	1253s	1256s	
	1233m	1233m	
1200s	1214vs	1215s	
1187sh	1200s	1203vs	
	1143vw		
1104m	1107m	1104m	$\rho(NCH_3)$ (f)
	1086vw		
	1046vw	1047sh	
1035vs	1032vw		
1002s	1007vs	1016	ν(BeD_2Be) & $\nu_{asym}(NC_3)$ (d)
		965m	
953s	948s		ν(BeH_2Be) (f)
931sh	922vs	928s	$\rho(Be-CH_3)$ (t)
	896s	896m	
870s	875s	870s	

Table XI contd.

65°	Solution	Solution	Assignment.
848vs	847vs	848vs	
		831sh	
826vs	820vs(broad)	810vs	v(Be-C) (t)
	772vs	772s	
745m	747s	746m	
		710ms	v(BeD_2Be) (f)
	722sh		
	699sh		
667m	676m		

Table XII.

Infrared spectra of diethylberyllium-trimethylamine and ethylberyllium hydride-trimethylamine examined as contact film and as a solution in cyclohexane respectively.

$Et_2Be.NMe_3$	$(EtHBe.NMe_3)_2$	Assignment.
1479vs	1484s	
1466s	1468sh	
1451m		
1409m		
	1372m	
	1333vs	$\nu(BeH_2Be)$ (d)
	1299s	
1245m	1250m	
1236m	1235m	
	1206vw	
1193ms	1190w	
	1176sh	
1105mw	1109m	
1076w	1080m	
	1050m	
1001vs	1007vs	$\nu_{asym}(CN)$ (d)
	981s	
954w	948vs	
919w	917sh	
880m	897s	
	851sh	
822vs	826vs	$\nu(Be-C)$ (t)
778m	794sh	
730s(broad)	709m	
667m		
	635m	
621vw		
571vw		

Table XIII.

Infrared spectra of dimethylberyllium and methylberyllium hydride N,N,N',N'-tetramethylethylenediamine complexes examined as Nujol mulls.

Me_2Be complex	MeBeH complex	Assignment.
	1754w	
	1742sh	
1351s	1361vs	δ (CH_3) (d)
	1331vs	ν(BeH_2Be) (d)
1289vs	1302s	δ (CH_3) (d)
1263w	1264m	
1247m	1236m	
1190sh	1200w	
1168vs	1183s	
1122ms	1131m	
1098m	1099m	
1053m	1086s	
1042vs	1038m	
1027vs	1020vs	
1006vs	995vs	
951vs	961vs	
856vs	902s	
	814vs	
	799sh	
767vs	785m	
701vs	694s	
667w	659m	
585s		

Table XIV.

Infrared spectra of sodium hydridodimethylberyllate and its deutero analogue examined as Nujol mulls.

$NaBeMe_2H$	$NaBeMe_2D$	Assignment.
1328s		$\nu(BeH_2Be)$ (d)
1255ms	1261m	
1189s	1199ms	
1165s		$\nu(BeH_2Be)$ (d)
1138vs	1144s	
1086s	1075sh	
1018vs	1015vs	
	917vs	$\nu(BeD_2Be)$ (d)
	869vs	$\nu(BeD_2Be)$ (d)
789vs	797vs	
754m	777s	
612vw	595vw	
557vw		

Table XV.

Infrared spectra of sodium hydridodiethylberyllate and its deutero analogue examined as Nujol mulls.

$NaBeEt_2H$	$NaBeEt_2D$	Assignment.
1605vw		
1294s		$\nu(BeH_2Be)$ (d)
1253s	1256ms	
1235sh	1233vw	
1178s	1178sh	
1147sh	1167ms	
1117sh		
1091vs	1080ms	
1065vs		$\nu(BeH_2Be)$ (d)
1021vs	1014s	
978vs	982vs	
	951s	$\nu(BeD_2Be)$ (d)
936vs	928s	
912m		
894m	858sh	
831vw		
	835vs	$\nu(BeD_2Be)$ (d)
792w	800sh	
672m	667w	
657ms	656mw	

Table XVI.

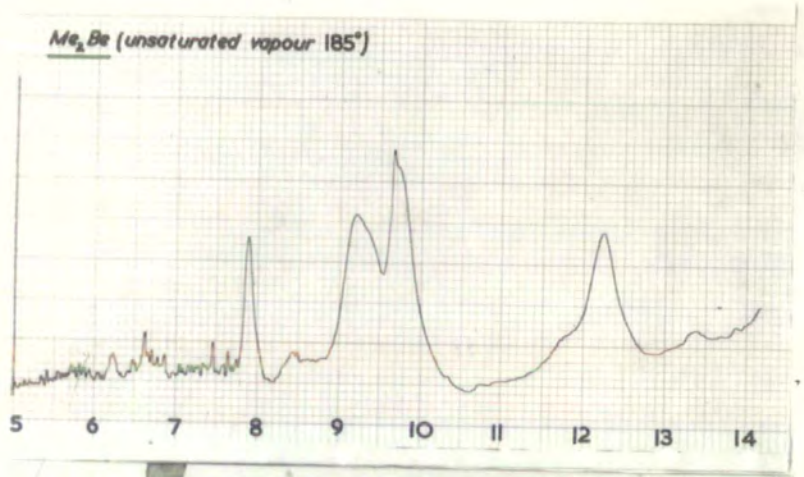
Infrared spectrum of the oil of approximate composition $Me_4Be_3H_2.OEt_2$ examined as a contact film.

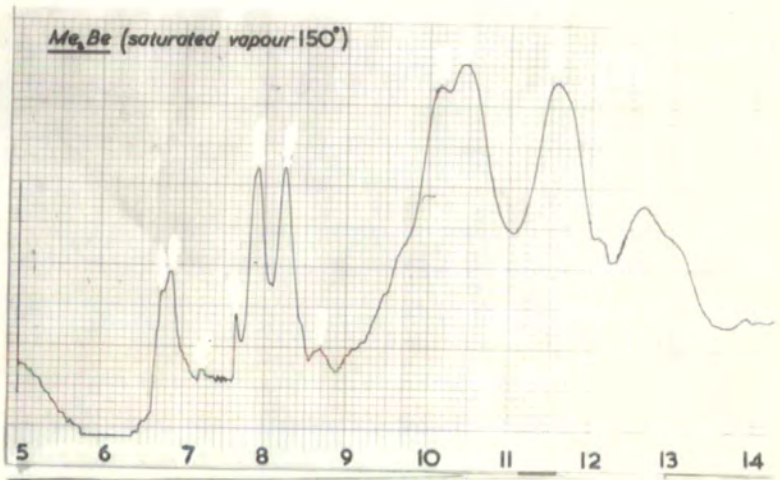
1555w
1479sh
1468m
1449m
1387s
1372sh
1295w
1261s
1240mw
1212s
1199m
1156m
1089m
1033vs
1002sh
962s
917s
848s
800s
784m
676w
668w

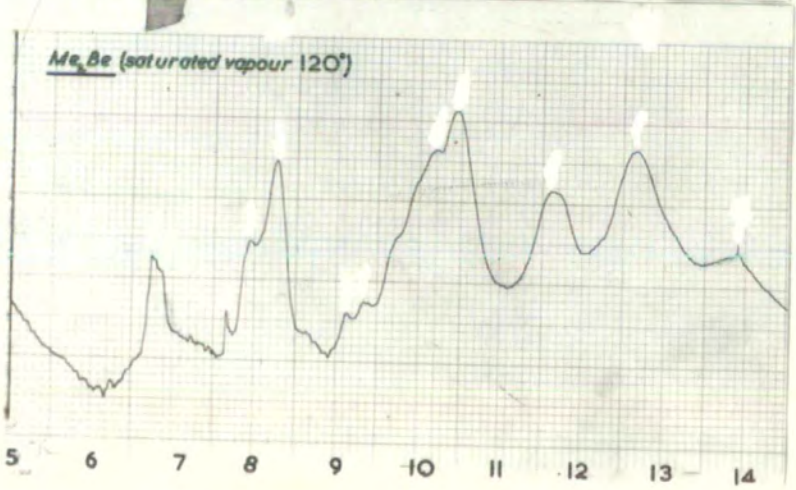
Table XVII.

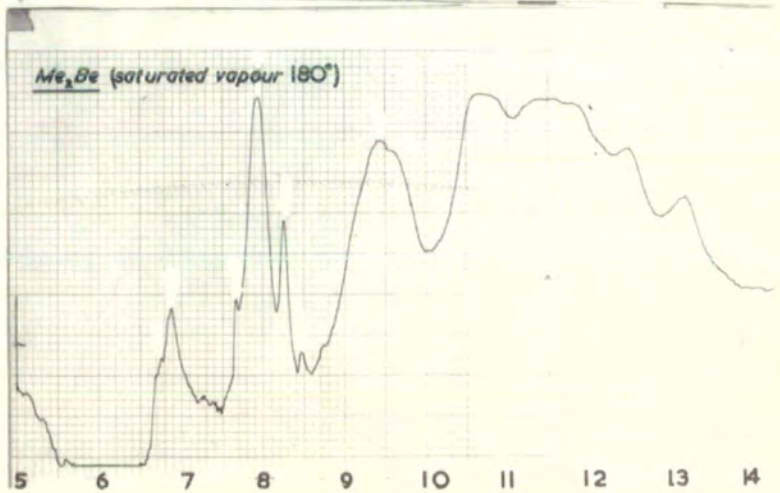
Infrared spectra of beryllium hydride of approximate compositions shown below examined as Nujol mulls.

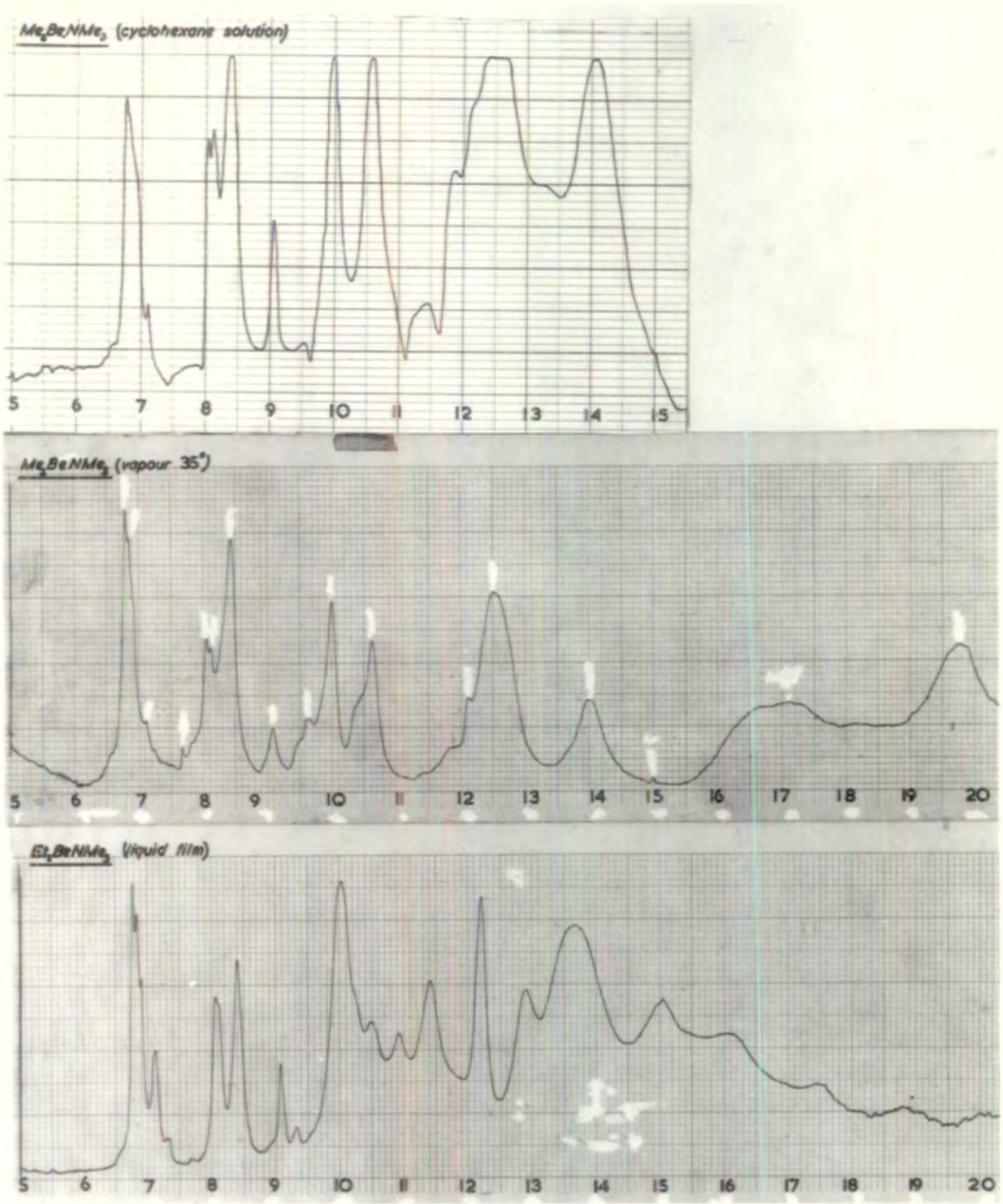
$(BeH_2)_{34}NaH$	$(BeH_2)_{11}(NaH)_6$	Assignment.
1750s(broad)	1771m	
	1637s	
1263vs	1259vs	$\nu(BeH_2Be)$ (t)
	1211vw	
1090m	1088m	
1047m		
1016vs	1013vs	δ (Be-H) (t)
	886 (broad)	
799s	795vs	

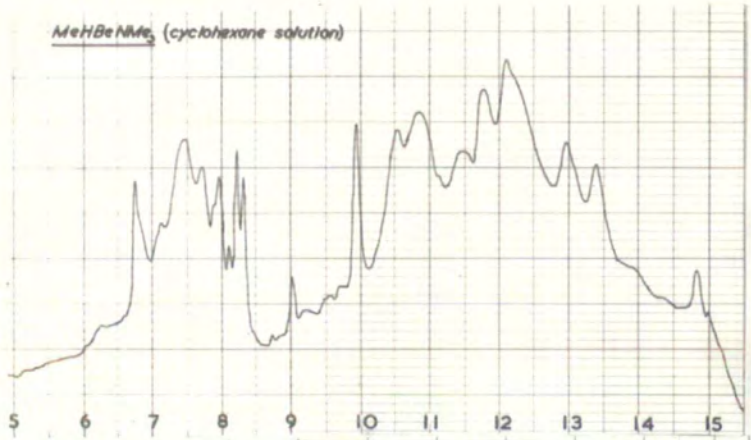

Me_2Be (unsaturated vapour 185°)
5 6 7 8 9 10 11 12 13 14

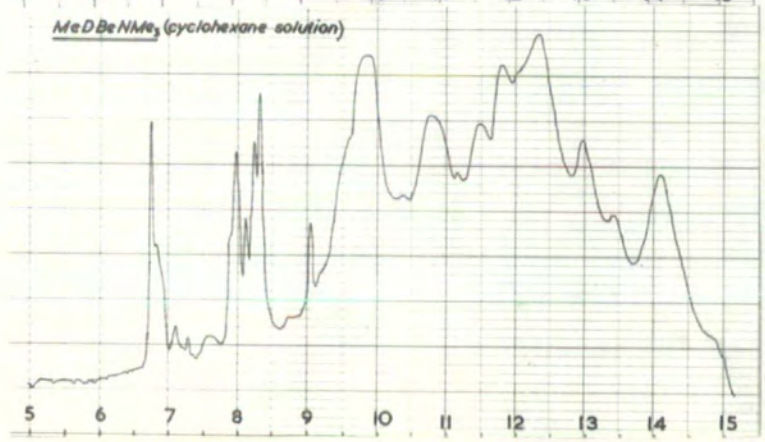

Me_2Be (saturated vapour 150°)
5 6 7 8 9 10 11 12 13 14

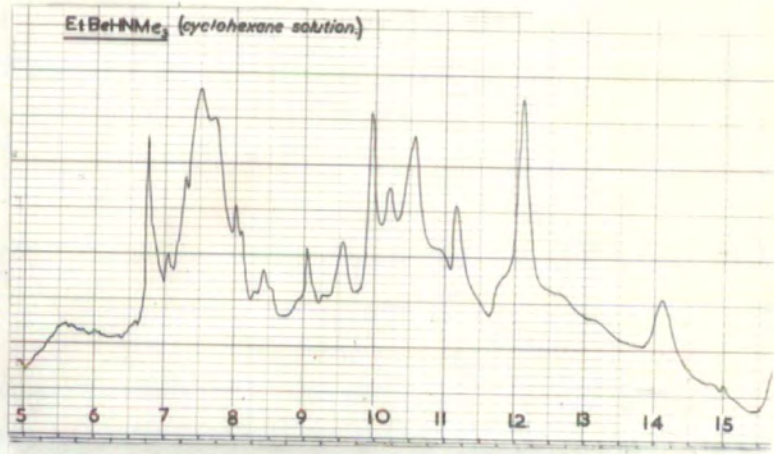

Me_2Be (saturated vapour 120°)
5 6 7 8 9 10 11 12 13 14

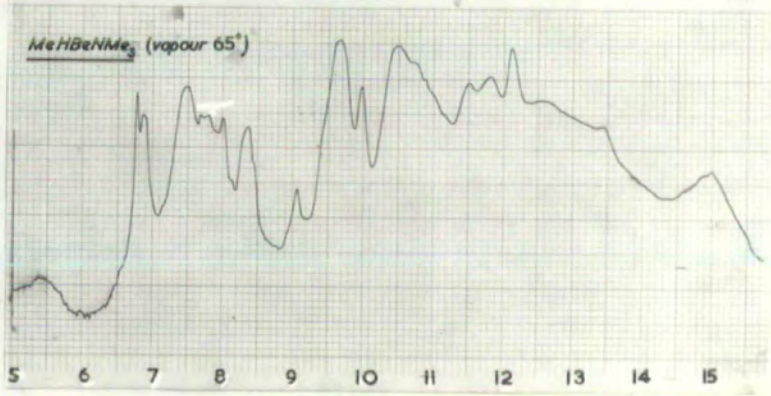

Me_2Be (saturated vapour 180°)
5 6 7 8 9 10 11 12 13 14

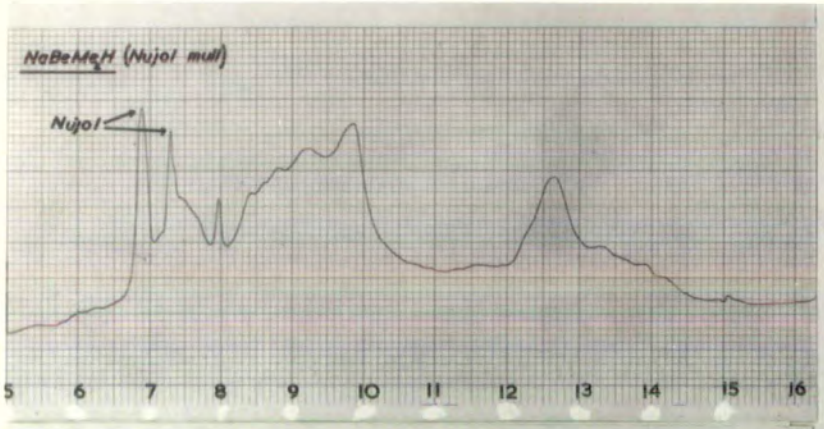

Me2BeNMe2 (cyclohexane solution)
5 6 7 8 9 10 11 12 13 14 15
Me2BeNMe2 (vapour 35°)
5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20
Et2BeNMe2 (liquid film)
5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20

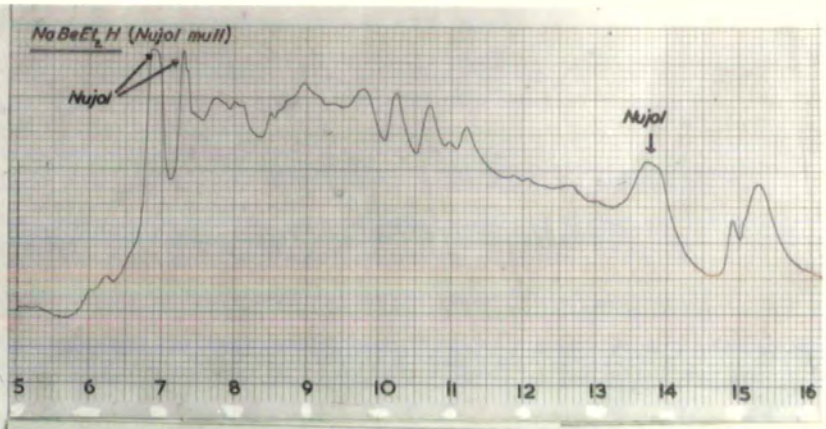

MeHBeNMe2 (cyclohexane solution)
5 6 7 8 9 10 11 12 13 14 15

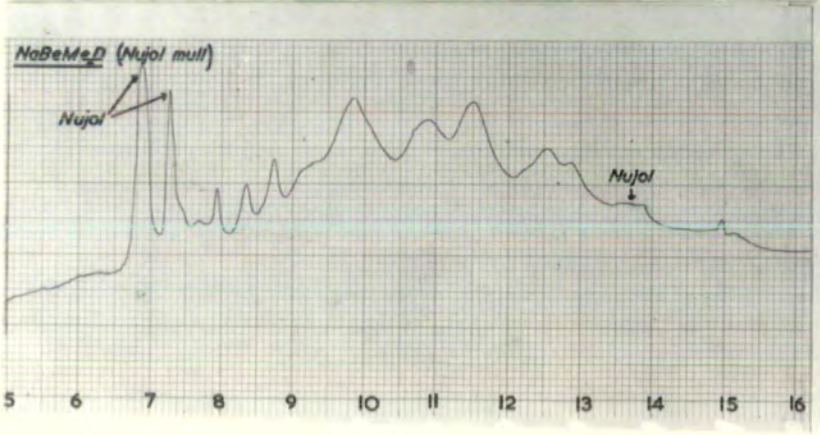

MeDBeNMe2 (cyclohexane solution)
5 6 7 8 9 10 11 12 13 14 15


EtBeHNMe2 (cyclohexane solution)
5 6 7 8 9 10 11 12 13 14 15

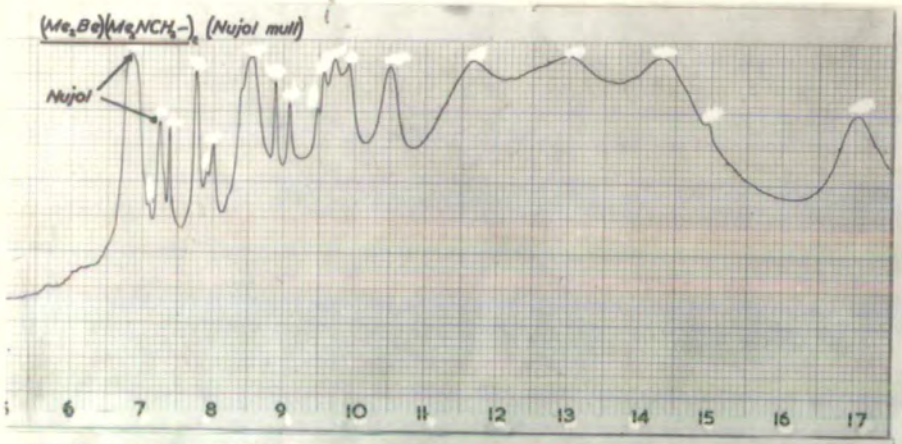

MeHBeNMe2 (vapour 65°)
5 6 7 8 9 10 11 12 13 14 15

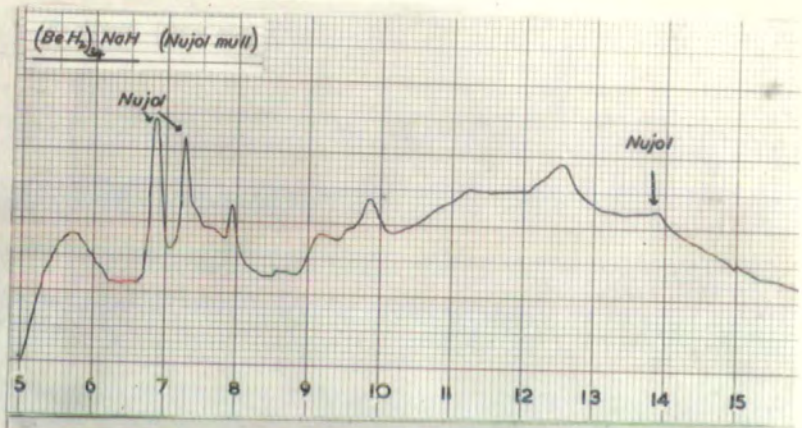

NaBeMe2H (Nujol mull)
Nujol
5 6 7 8 9 10 11 12 13 14 15 16

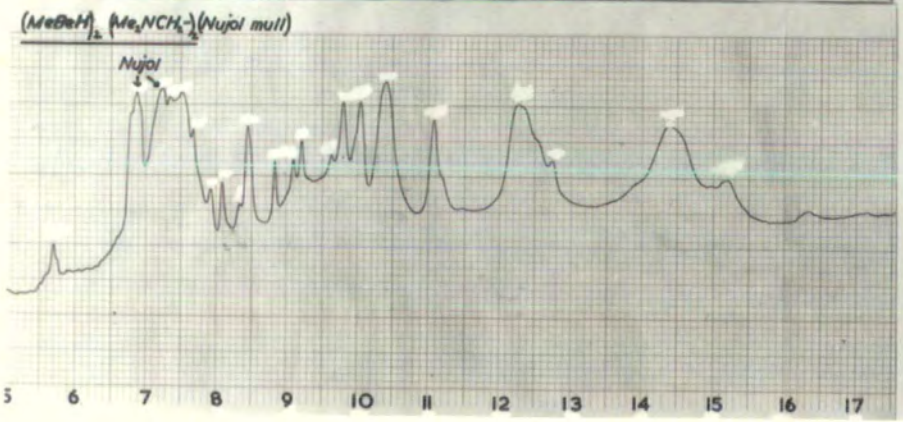

NaBeEt2H (Nujol mull)
Nujol
Nujol
5 6 7 8 9 10 11 12 13 14 15 16

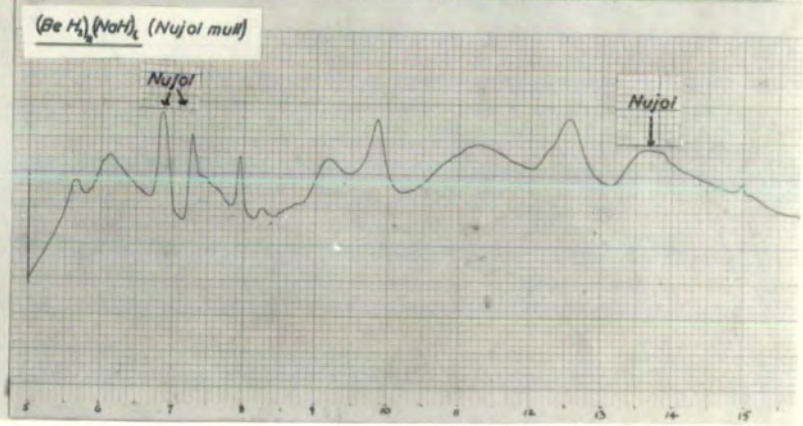

NaBeMe2D (Nujol mull)
Nujol
Nujol
5 6 7 8 9 10 11 12 13 14 15 16


NaBeEt2D (Nujol mull)
Nujol
5 6 7 8 9 10 11 12 13 14 15 16


$(Me_2Be)(Me_2NCH_2-)_2$ (Nujol mull)
Nujol
6 7 8 9 10 11 12 13 14 15 16 17


$(BeH_2)_{3n}NaH$ (Nujol mull)
Nujol
Nujol
5 6 7 8 9 10 11 12 13 14 15


$(MeBeH)_2(Me_2NCH_2-)_2$ (Nujol mull)
Nujol
5 6 7 8 9 10 11 12 13 14 15 16 17


$(BeH_2)_8(NaH)_4$ (Nujol mull)
Nujol
Nujol

REFERENCES

REFERENCES.

(1) COATES G.E. 'Organo-Metallic Compounds' p.4.(Methuen,1960)

(2) Organic Syntheses Vol.II p.502.

(3) FETTER N.R., Canad. J. Chem. , 1964, 42, 861.

(4) NILSON L.F. and PETTERSSON O., Ber., 1884, 17, 987.

(5) COATES G.E. and HUCK N.D., J., 1952, 4501.

(6) LINSTEAD R.P. and ROBERTSON J.M., J., 1936, 1736.

(7) BURG A.B. and SCHLESINGER H.I., J. Amer. Chem. Soc., 1940, 62, 3425.

(8) GILMAN H. and SCHULZE F., J.Amer. Chem.Soc., 1927, 49, 2904.

(9) WITTIG G., MEYER F.J. and LANGE G., Annalen, 1951, 571, 167.

(10) CAHOURS A., Compt. rend.,1873, 76, 1383.

(11) LAVROFF V., Zhur. fiz. Khim., 1884, 16, 93.

(12) LAVROFF V., Bull.Soc.chim.France, 1884, 41, 548.

(13) GILMAN H. and SCHULZE F., J., 1927, 2663.

(14) KRAUSE E. and WENDT B., Ber., 1923, 56, 466.

(15) WOOD G.B. and BRENNER A., J.Electrochem.Soc., 1957, 104, 29.

(16) PANETH F. and LOLEIT H., J., 1935, 366.

(17) ZAKHARKIN L.I., OKHLOBYSTIN O. Yu. and STRUNIN B.N., Izvest. Akad. Nauk S.S.S.R., Otdel.khim.Nauk, 1961, 2254.

(18) PERKINS T., J., 1929, 1687.

(19) ZIEGLER K., B.Patent 763,824 (1956): Chem.Abs., 1958, 52, 1203.

(20) ZIEGLER K., Angew.Chem., 1956, 68, 721 ; Uspekhi-Khim., 1957, 26, 1189.

(21) RABIDEAU S.W., ALEI M. and HOLLEY C.E., Chem.Abs., 1956, 50, 3992.

(22) MUXART R., MELLET R. and JAWORSKY R., Bull.Soc. chim. France, 1956, 445.

(23) SCHULZE F., Iowa State Coll. J. Science, 1933, 8, 225.

(24) GILMAN H. and BROWN R.E., J.Amer.Chem.Soc.,1930,52,4480.

(25) BÄHR G. and THIELE K.H., Chem.Ber., 1957, 90, 1578.

(26) SNOW A.I. and RUNDLE R.E., Acta.Cryst., 1951, 4, 348.

(27) COATES G.E., GLOCKLING F. and HUCK N.D., J.,1952,4496.

(28) STROHMEIER W., HÜMPFNER K., MILTENBERGER K. and SEIFERT F., Z.Elektrochem. , 1959, 63, 537.

(29) GOUBEAU J. and WALTER K., Z.anorg.Chem.,1963, 322, 58.

(30) BROWN H.C. and DAVIDSON N.R., J.Amer.Chem.Soc., 1942, 64, 316.

(31) COATES G.E., J., 1951, 2003.

(32) GREEN S.I.E., Ph.D. Thesis. (DURHAM) 1962.

(33) COATES G.E. and GREEN S.I.E., J., 1962, 3340.

(34) COATES G.E., GLOCKLING F. and HUCK N.D., J., 1952,4512.

(35) COATES G.E. and MUKHERJEE R.N., J., 1963, 229.

(36) MASTHOFF R., Z.Chem. , 1963, 3, 269.

(37) GOUBEAU J. and RODEWALD B., Z.anorg.Chem., 1949,258,162.

(38) SCHREIBE G., BAUMGÄRTNER F. and GENZER M., Angew.Chem., 1955, 67, 512.

(39) STROHMEIER W. and HÜMPFNER K., Z.Elektrochem.,1956,60,1111.

(40) STROHMEIER W. and HÜMPFNER K., Z.Elekrochem.,1957,61,1010.

(41) LONGI P., MAZZANTI G. and BERNARDINI F., Gazzetta, 1960, 90, 180.

(42) STROHMEIER W. and GERNERT F., Z.Naturforsch,1961,16b,760.

(43) STROHMEIER W. and GERNERT F., Z.Naturforsch,1962,17b,128.

(44) STROHMEIER W. and GERNERT F., Chem.Ber., 1962, 6, 1420.

(45) COATES G.E. and COX G.F., Chem.and Ind., 1962, 269.

(46) COATES G.E. and GLOCKLING F., J., 1954, 22.

(47) COATES G.E. and GLOCKLING F., J., 1954, 2526.

(48) HEAD E.L., HOLLEY C.E. and RABIDEAU S.W., J.Amer.Chem.Soc., 1957, 79, 3687.

(49) WITTIG G. and WITTENBERG D., Annalen, 1957, 606, 15.

(50) WITTIG G. and HORNBERGER P., Annalen, 1952, 577, 11.

(51) DESSY R.E., J.Amer.Chem.Soc., 1960, 82, 1580.

(52) BARBARAS G.D., DILLARD C., FINHOLT A.E., WARTIK T., WILZBACH K.E. and SCHLESINGER H.I., J.Amer.Chem.Soc.1951,73,4585.

(53) POWERS J.C., VOSE D.W. and SULLIVAN E.A., Chem.Abs., 1963,58,219.

(54) PIETSCH E., Z.Elektrochem., 1933, 577, 39.

(55) WIBERG E. and BAUER R., Z.Naturforsch,1951,6b,171.

(56) HUMPIDGE T.S., Proc.Roy.Soc. 1885, 39, 10.

(57) PINNOW J., Ber., 1899, 1401.

(58) FISCHER O., Ber., 25, 2826.

(59) GILMAN H. and BARNETT M.M. Rec.Trav.chim.,1936,55,563.

(60) 'Organic Syntheses' Vol.II p.211 and p.290.

(61) STUCKY G.D. and RUNDLE R.E., J.Amer.Chem.Soc.1963,85,1002.

(62) SCHLESINGER H.I., BROWN H.C. and HYDE E.K., J.Amer.Chem.Soc. 1953, 75, 209.

(63) FRICKE R. and SCHÜTZDELLER H., Z.anorg.Chem.,1923,131,132.

(64) 'MONTECATINI' Societa Generale per l'Industria Mineraria e Chimica, Chem.Abs. 1963, 59, 4058 and 14022.

(65) WIBERG E., HENLE H. and BAUER R., Z.Naturforsch, 1951, 6b, 393.

(66) WIBERG E. and HENLE W., Z.Naturforsch, 1951, 6b, 461.

(67) ZAKHARKIN L.I. and KHORLINA I.M. Zhur.obshchei Khim., 1962, 32, 2783.

(68) SCHLESINGER H.I. and BURG A.B., Chem.Rev.,1942,31,36.

(69) KOBETZ P. and BECKER W.E., Inorg.Chem.,1963, 859.

(70) WIBERG E. and STREBEL P., Annalen,1957, 607, 9.

(71) CLAPP D.P. and WOODWARD R.B., J.Amer.Chem.Soc., 1938, 60, 1019.

(72) JOLIBOIS P., Compt.rend., 1912, 155, 353.

(73) WIBERG E. and BAUER R., Chem.Ber. 1952, 85, 593.

(74) WIBERG E. and BAUER R., Z.Naturforsch, 1950,5b,396,397.

(75) WIBERG E., GOELTZER H. and BAUER R., Z.Naturforsch, 1951, 6b, 394.

(76) BAUER R., Z.Naturforsch, 1962, 17b, 201.

(77) BARTON D.H.R. and ROSENFELDER W.J., J., 1951, 2381.

(78) WITTIG G. and RÜCKERT A., Annalen, 1950, 566, 101.

(79) WITTIG G., KEICHER G., RÜCKERT A. and RAFF P., Annalen, 1949, 563, 110.

(80) HONEYCUTT J.B. and RIDDLE J.M., J.Amer.Chem.Soc., 1961, 83, 369.

(81) ZIEGLER K., LEHMKUHL H. and LINDNER E., Chem.Ber., 1959, 92, 2320.

(82) WITTIG G. and BUB O., Annalen, 1950, 566, 113.

(83) ZIEGLER K., KÖSTER R., LEHMKUHL H. and REINERT K., Annalen, 1960, 629, 33.

(84) KOBETZ P., BECKER W.E., PINKERTON R.C. and HONEYCUTT J.B., Inorg.Chem., 1963, 859.

(85) ZAKHARKIN L.I. and KHORLINA I.M., Izvest.Akad.Nauk S.S.S.R, Otdel.khim.Nauk, 1961, 1894.

(86) ZAKHARKIN L.I. and GAVRILENKO V.V., Zhur.obshchei Khim., 1962, 32, 689.

(87) ZAKHARKIN L.I., GAVRILENKO V.V. and KHORLINA I.M., Izvest.Akad.Nauk S.S.S.R., Otdel.khim.Nauk, 1962, 438.

(88) ZIEGLER K., GELLERT H.G., MARTIN H., NAGEL K. and SCHNEIDER J., Annalen, 1954, 589, 91.

(89) WARTIK T. and SCHLESINGER H.I., J.Amer.Chem.Soc., 1953, 75, 835.

(90) HOFFMANN E.G. and SCHOMBURG G., Z.Elektrochem., 1957, 61, 1101.

(91) PETERS F.M., BARTOCHA B. and BILBO A.J., Canad.J.Chem., 1963, 41, 1051.

(92) FRASER G.W., GREENWOOD N.N. and STRAUGHAN B.P., J., 1963, 3742.

(93) HEITSCH C.W., NORDMAN C.E. and PARRY R.W., Inorg.Chem., 1963, 508.

(94) DAVIDSON J.M. and WARTIK T., J.Amer.Chem.Soc., 1960, 82, 5506.

(95) RUFF J.K. and HAWTHORNE M.F., J.Amer.Chem.Soc., 1960, 82, 2141.

(96) RUFF J.K. and HAWTHORNE M.F., J.Amer.Chem.Soc., 1961, 83, 535.

(97) WIBERG E. and SCHMIDT H., Z.Naturforsch, 1951, 6b, 333.

(98) EHRLICH R., YOUNG A.R., LICHSTEIN B.N. and PERRY D.D., Inorg.Chem., 1963, 650.

(99) SCHOMBURG G. and HOFFMANN E.G., Z.Elektrochem. 1957, 61, 1110.

(100) ZEIL W., DAUTEL R. and HONSBERG W., Z.Elektrochem., 1956, 60, 1131.

(101) DAUTEL R. and ZEIL W., Z.Elektrochem., 1960, 64, 1234.

(102) RUFF J.K., J.Amer.Chem.Soc., 1961, 83, 1798.

(103) GREENWOOD N.N., STORR A. and WALLBRIDGE M.G.H., Proc.Chem.Soc., 1962, 249.

(104) SHRIVER D.F. and PARRY R.W., Inorg.Chem., 1963, 1039.

(105) GREENWOOD N.N., STORR A. and WALLBRIDGE M.G.H., Inorg.Chem., 1963, 1036.

(106) GREENWOOD N.N. and WALLBRIDGE M.G.H., J.,1963, 3912.

(107) FINHOLT A.E., HELLING C., IMHOF V., NIELSEN L. and JACOBSON E., Inorg.Chem.,1963, 504.

(108) NEUMANN W.P., NIERMANN H. and SCHNEIDER B., Angew.Chem., 1963, 2, 547.

(109) MUKHERJEE R.N., Ph.D. Thesis, Durham, 1963.

(110) BANFORD L. and COATES G.E., unpublished observation.

(111) BAUER R., Z.Naturforsch, 1961, 16b,557.

(112) BAUER R., Z.Naturforsch, 1961, 16b, 839.

(113) BAUER R., Z.Naturforsch, 1962, 17b, 277.

(114) LUIJTEN J.G.A. and VAN DER KERK G.J.M.. 'Investigations in the field of Organotin Chemistry' p.95,96. (Tin Research Institute. 1959).

(115) DILLARD C.R., McNEILL E.H., SIMMONS D.E. and YELDELL J.B., J.Amer.Chem.Soc., 1958,80,3607.

(116) GUTOWSKY H.S., J.Chem.Phys., 1949, 17, 128.

(117) LEHMANN W.J., WILSON C.C. and SHAPIRO I., J.Chem.Phys., 1958, 28, 777.

(118) HOFFMANN E.G., Z.Elektrochem., 1960, 64, 616.

(119) GRAY A.P., Canad.J.Chem., 1963, 41, 1511.

(120) KORSHAK V.V., KOMAROVA L.I. and SIDOROV T.A., Izvest. Akad.Nauk S.S.S.R., Otdel khim.Nauk., 1963, 813.

(121) TROVA N.YA., SEMENENKO K.N. and NOVOSELOVA A.V., Russ.J.Inorg.Chem., 1963, 452.(Eng.)

(122) KOLDITZ L. and BAUER K., Z.Chem., 1963, 3, 312.

(123) RAKINTZIS N.Th., Diss.Techn.Hochschule Stuttgart.

(124) BECHER H.J. and TAYLOR R.C. International Symposium, Duke University, Durham, North Carolina. (April 1963.)

(125) COATES G.E. and LIVINGSTONE J.G., J., 1961, 1000.

(126) BÜCHLER A and KLEMPERER W., J.Chem.Phys.1958, 29, 121.

(127) MAL'TSEVA N.N. and KHARITONOV Y.Y., Zhur.neorg.Khim., 1962, 7, 947.

(128) ZIMMERMAN W.B. and MONTGOMERY D.J., Phys.Rev., 1960, 120, 405.

(129) JAMES T.C., NORRIS W.G. and KLEMPERER W., J.Chem.Phys., 1960, 32, 728.

(130) BARCELÓ J.R. and BELLANATO J., Spectrochim.Acta., 1956, 8, 27.

(131) SIEBERT H., Z.anorg.Chem., 1953, 273, 161.

(132) RICE B., GALLIANO R.J. and LEHMANN W.J., J.Chem.Phys., 1957, 61, 1222.

(133) HERZBERG G., 'Spectra of Diatomic Molecules ' p.500. (D.Van Nostrand Company Inc. 1950).

(134) LEHMANN W.J., WILSON C.O. and SHAPIRO I. J.Chem.Phys., 1961, 34, 783.

(135) SIEBERT H., Z.anorg.Chem., 1953, 273, 170.

(136) SHRIVER D.F., AMSTER R.L. and TAYLOR R.C., J.Amer.Chem.Soc., 1962, 84, 1321.

(137) EDSALL J.T. J.Chem.Phys., 1937, 5, 225.

(138) NAKAMOTO K., 'Infrared Spectra of Inorganic Coordination Compounds' p.120. (Wiley, New York, 1963) and BELL R.F. and LONGUET-HIGGINS, Proc.Roy.Soc., 1945, A183, 357.