Studies of transition metal sulphites

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STUDIES OF
TRANSITION METAL SULPHITES

by

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MEMORANDUM

The work described in this thesis was carried out on a part-time basis between October 1967 and December 1971. It has not been submitted for any other degree and is the original work of the author except where acknowledged by reference.

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J. Ibbotson.
Hartlepool 1971.

SUMMARY

Sulphito-groups may act as monodentate or polydentate ligands. Bonding may take place through sulphur, sulphur and oxygen or oxygen. The aim of part of this study was to determine the possible mode of bonding in a number of sulphites of the type $M_a(SO_3)_b.nH_2O$ and a number of ammonium complexes of the first row transition metals. These were prepared free of sulphate ions and examined by diffuse reflectance, infrared, and far infrared methods.

The solubility of the compounds was determined qualitatively, in water and aqueous sulphur dioxide solution and an effort made to relate their general insolubility in water and solubility in aqueous sulphur dioxide solution to their structures.

Results of spectroscopic studies suggest that for, (a) $Ni(OH)_2.3NiSO_3{\sim}12H_2O$ the metal is octahedrally co-ordinated probably by the oxygens of water and the sulphito-groups; (b) $ZnSO_3 2.5H_2O$, $MnSO_3 3H_2O$, $CoSO_3 3H_2O$ and $(NH_4)_2Ni_3(SO_3)_4.18H_2O$ the metal is octahedrally co-ordinated, or in the case of zinc possibly tetrahedrally co-ordinated, mainly through oxygen, the sulphito-groups having low symmetry; (c) $(NH_4)_2M(SO_3)_2.nH_2O$ (M = Mn, Co, Ni, Zn) and basic ammonium chromium sulphite the metal is octahedrally co-ordinated by oxygens of sulphito-groups and the C_{3v} symmetry of the free ion is maintained; (d) $(NH_4)_7Cu(SO_3)_4.5H_2O$, the sulphite groups may be present as discrete ions. Results of solubility studies suggest three dimensional or polymeric structures for all the compounds except $(NH_4)_7Cu(SO_3)_4.5H_2O$.

In thermal decomposition studies of transition metal sulphites, in a variety of atmospheres, the final products have been reported variously to include the metals, oxides, sulphides, and sulphates. Thermal gravimetric analyses have been carried out to clarify this situation for all the compounds

mentioned previously in this summary, and for $Cu_2SO_3CuSO_32H_2O$ and NH_4CuSO_3. With the exception of NH_4CuSO_3 the final decomposition products are oxides with possibly minor amounts of sulphide and/or sulphate.

CONTENTS

CHAPTER 1

INTRODUCTION

Many transition metal sulphites have been reported over a period extending from the early 19th century. Unlike most other oxy-anion complexes, little work has been carried out to systematise and correlate their properties, and there is much conflicting data. For example $CoSO_3.6H_2O$[1] is reported to precipitate on the loss of sulphur dioxide from its aqueous sulphur dioxide solution, but other reports refer only to $CoSO_3.H_2O$, $CoSO_3.5H_2O$ and $CoSO_3.3H_2O$.[2]

Some efforts have been made to clarify the situation in individual cases where it was suspected that the sulphite was not a true compound. The formulation of the red complex, $Cu_2SO_3CuSO_3.2H_2O$,[2] for example, has been confirmed, whereas the yellow-green complex, referred to as $Cu_2SO_3CuSO_3.5H_2O$,[2] has a variable composition.[3] Also the formulation of white $Cu_2SO_3.0{\cdot}5H_2O$ has been confirmed but the red material formulated the same, has been shown to be an approximately equimolar mixture of $Cu_2SO_3CuSO_3.2H_2O$ and metallic copper.[4]

An interesting feature of transition metal sulphites is their general insolubility in water.[2] There is little discussion of this aspect in the literature. The insolubility is possibly due to polymeric structures, in which the sulphito-groups are acting as ligands to two or more transition metal ions. Alternatively, it may arise from extensive hydrogen bonding, for example, between oxygens of the sulphito-groups and hydrogens of the water molecules in $NiSO_3.6H_2O$.[5]

At the outset of this work only the crystal structures of $CoSO_3.6H_2O$,[1] $NiSO_3.6H_2O$,[1,6,7] $Cu_2SO_3CuSO_3,2H_2O$[8] and NH_4CuSO_3[9] had been reported. All were reported[2] as being insoluble in water, which is consistent with their three dimensional polymeric structures. The structure of $NiSO_3.6H_2O$ consisted of distorted $[Ni(H_2O)_6]^{2+}$ octahedra and SO_3^{2-} ions, linked three dimensionally by hydrogen bonds.[5] $Cu_2SO_3CuSO_3.2H_2O$ consists of tetrahedral Cu^IO_3S units and Cu^{II} distorted (4 + 2) octahedra formed by two oxygen atoms from water molecules and four oxygens from different sulphito-groups. The units are linked together into a three dimensional network (Fig.1.1).[8]

The crystal structure of NH_4CuSO_3 consists of SO_3 pyramids and CuO_3S tetrahedra, the tetrahedral co-ordination around the copper being three oxygen atoms and one sulphur atom of four SO_3 trigonal pyramids. The CuO_3S tetrahedra and SO_3 pyramids form double layers which are held together by ammonium ions (Fig.1.2).[9,10]

The solubility of transition metal sulphites in aqueous sulphur dioxide solution, is in general greater than that in water.[2] Especially soluble are the sulphites of the types $M_a(SO_3)_b.nH_2O$ and $M_aX_b(SO_3)_c.nH_2O$ ($X = OH, O$). Some sulphites however react with the sulphur dioxide solution. For example, Ag_2SO_3 forms silver metal on standing,[2] and $Cu_2SO_3.0{\cdot}5H_2O$ on prolonged digestion gives a mixture of copper metal and $Cu_2SO_3CuSO_3.2H_2O$.[4] In contrast, $ZnSO_3.2{\cdot}5H_2O$ and $Na_2Hg(SO_3)_2$ are reported to be sparingly soluble.[2]

The equilibria in aqueous sulphur dioxide solutions may be represented as:

$$SO_2 + xH_2O \rightleftharpoons SO_2.xH_2O$$

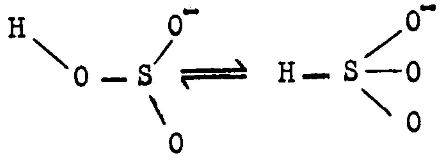
$$[SO_2.xH_2O \rightleftharpoons H_2SO_3 \quad K <<< 1]$$

$$SO_2.xH_2O \overset{K_1}{\rightleftharpoons} HSO_3^-\ (aq) + H_3O^+ + (x - 2)H_2O$$

and the first acid dissociation constant

$$K_1 = \frac{[HSO_3^-][H^+]}{[\text{Total dissolved } SO_2] - [HSO_3^-] - [SO_3^{2-}]} = 1{\cdot}3 \times 10^{-2}$$

According to Golding,[11] HSO_3^- in solution occurs in the following tautomeric forms at low concentrations (ca. $3 \times 10^{-3}M$).



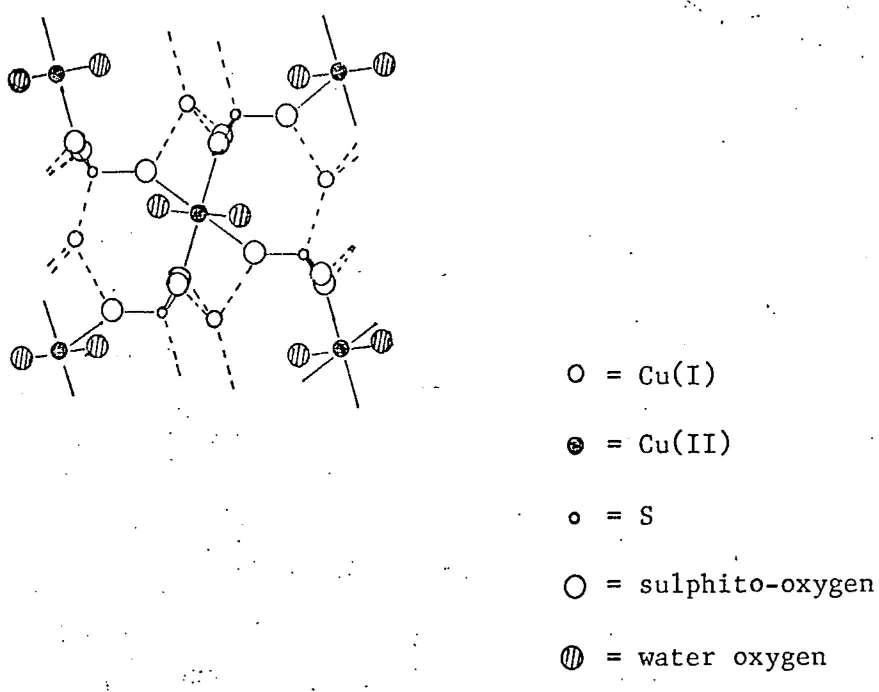


Fig.1.1 The three dimensional network of $Cu_2SO_3CuSO_32H_2O$

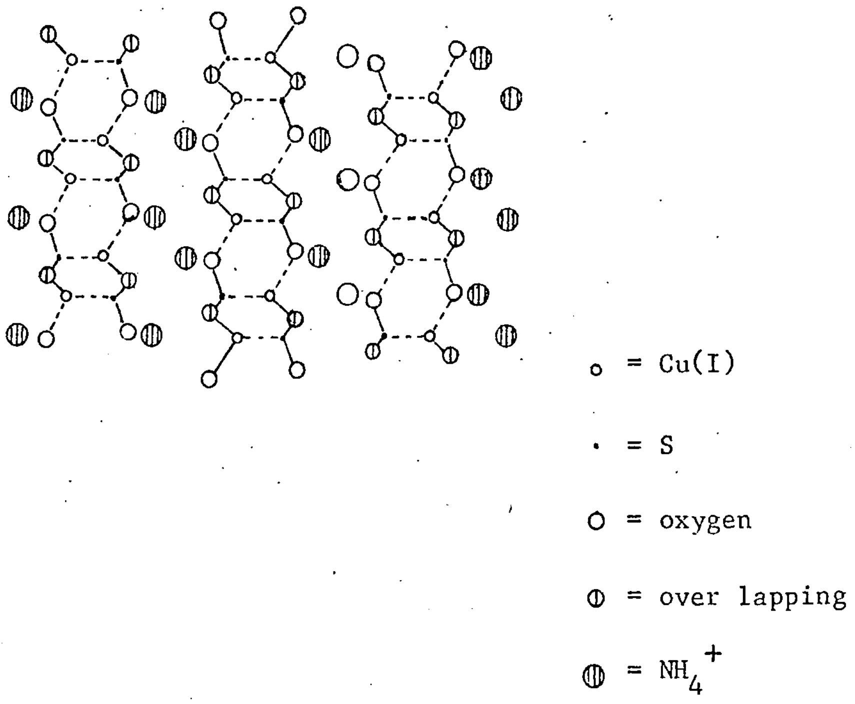
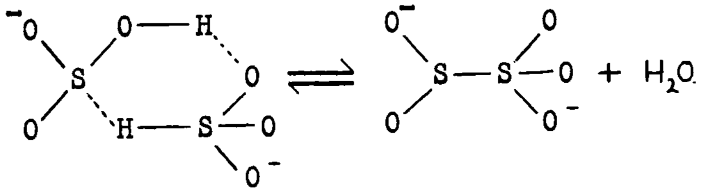


Fig.1.2 The double layers of NH_4CuSO_3

At higher concentrations (<u>ca</u>.10^{-2}M) these interact by hydrogen bonding and are in equilibrium with the pyrosulphite ion.



On this basis, the solubility of $NiSO_3.6H_2O$ can be explained by conversion of SO_3^{2-} on the surface of the crystal to HSO_3^-, thus reducing the hydrogen bonding, followed by possible conversion to the other species at higher concentrations. However it is difficult to account for the reported solubility of $Cu_2SO_3CuSO_3.2H_2O$[2] in aqueous sulphur dioxide solution or the effect of sulphur dioxide on NH_4CuSO_3 to produce metallic copper and $Cu_2SO_3CuSO_3.2H_2O$.[4] Structural determinations have shown that both these sulphites are also polymeric.

The bond order of the S-O bond in SO_3^{2-} has been calculated from Raman spectral data for the ion in solution and in solid Na_2SO_3 to be 1·33[12] and many other workers have suggested a bond order greater than one. X-ray crystal determinations give a S-O bond length of 1·50Å for Na_2SO_3,[13] compared to the normally accepted single bond distance of 1·64Å, and a S=O bond distance of about 1·40Å.[14] Thus apart from σ bonding there must also be π bonding due to overlap of p orbitals of the oxygen atoms with unfilled d orbitals of the sulphur atom.

In transition metal chemistry the sulphito-group forms many complexes in which it apparently acts as a monodentate or polydentate ligand and since there are possible alternative modes of bonding through sulphur or through oxygen this has been the subject of many structural studies particularly using infra-red spectroscopy. The information obtained has been based upon the shift in the S-O stretching frequencies.

In one study,[15] the shifts in stretching frequencies were used to classify the compounds studied as (a) double sulphites; (b) complexes with monodentate sulphito-groups bonded through sulphur or oxygen; (c) complexes with bidentate sulphito-groups. An attempt was made to distinguish between chelating and bridging sulphito-groups. Some structural conclusions made on the basis of i.r. spectroscopy have been confirmed later by X-ray crystallographic studies. For example, for $PdSO_3(NH_3)_3$ a monodentate sulphito-group, bonded to the metal through sulphur was predicted by i.r. studies and later confirmed by a crystal structure determination.[16] NH_4CuSO_3[9,10] a 'so called' double sulphite shows tetrahedral co-ordination around Cu^I of three oxygens and one sulphur atom. Each sulphito-group bonds to four metals through the three oxygens and the sulphur atom.

The thermal decomposition of sulphites of the types $M_a(SO_3)_b.nH_2O$, $M_aX_b(SO_3)_c.nH_2O$ and $Me_aM_b(SO_3)_c.nH_2O$ ($Me = NH_4^+$, Na^+, K^+; M = transition metal; X = OH, O) have been extensively studied[2] in a variety of atmospheres with much conflicting information on the products. Much of this work was complicated by aerial oxidation. More recent work under nitrogen,argon or in vacuum, also show conflicting results. For example, the decomposition of $ZnSO_3.2{\cdot}5H_2O$ is reported to lead to ZnS_2O_3, $ZnSO_4$ and SO_2 when heated in vacuum,[17] whereas when heated in argon, ZnO is the primary product with traces of ZnS and $ZnSO_4$.[18] Oxides, sulphides,sulphates, and in the cases of silver and mercury sulphite complexes, the free metal, are all reported decomposition products of sulphites, but no pattern in the decompositions is apparent and much confusion still exists about the nature of these products.

Much industrial interest has centred on the sulphites of the type $M_a(SO_3)_b.nH_2O$ especially those of zinc and copper. $ZnSO_3.2{\cdot}5H_2O$ has been used in copper fungicidal compositions,[19] its formation, from ZnO, occurring in the recovery of sulphur dioxide from waste gases[20] and in the purification of gases containing sulphur dioxide.[21] The extraction of zinc from zinc muds or sludges containing CdS[22] has involved the use of sulphur dioxide to form $Zn(HSO_3)_2$ solution and the conversion by heat of this solution to substantially pure ZnO.

$Cu_2SO_3.CuSO_3.2H_2O$ is used in molluscididal and fungicidal preparations and is formed at a stage in the extraction of copper metal from its ores.[23] Copper metal can also be obtained from aqueous solution of its salts by treatment with sulphur dioxide.[24] The formation of the complex $(NH_4)_3[Rh(SO_3)_3]$[25] has been used to prepare spectroscopically pure rhodium and the complexing of ruthenium by SO_3^{2-} or HSO_3^- has been used to separate it from thorium and uranium fission products, the complexing rendering it insoluble in organic solvents.[26]

The purpose of this work was to attempt, in a limited number of cases, to rationalise the data reported in the literature over many years, to shed light on the conflicting data, to obtain information on the bonding modes of the sulphito-group and to use modern techniques to achieve these ends.

Most of the research work reported in this thesis was undertaken in a school laboratory where limited apparatus was available. It was found necessary to undertake the filtration,and washing-drying operations in an atmosphere of nitrogen and to de-aerate the materials used in these operations.

CHAPTER 2

REVIEW OF TRANSITION METAL SULPHITES

1. Introduction

In this chapter the transition metal sulphite complexes are reviewed. The various features of their chemistry are treated separately, and comparisons and contrasts are made between complexes of different metals. Conflicting claims have been made for some sulphite complexes, and where directly relevant to the present work, are discussed in detail.

Transition metal sulphites have been known since the late 18th century, and much of the early work was concerned with preparatory aspects and reactions with acids, air, water and ammonia etc. A large number of sulphite containing compounds have been reported, often with elaborate formulations, and many require further study especially using modern techniques. This review is consequently restricted, because of the sheer mass of available data, to the underlying principles established for the transition metal sulphites, with particular reference to preparative methods, structures and thermal decomposition reported in the more recent literature (from ca.1930). These aspects are of direct relevance to the research described in Chapter 3.

2. Preparation of Transition Metal Sulphites

(a) Sulphites of the type $M_a(SO_3)_b.nH_2O$

Sulphites of this type have been prepared by analogous routes to those for the salts of other oxy-acids, namely:

(i) the metal and the acid,

(ii) the metal oxide or hydroxide, and the acid,

(iii) the metal carbonate and the acid,

(iv) metathesis,

and also by the following routes:

(v) from a soluble compound of the metal with the acid or alkali hydrogen sulphite,

(vi) from the metal sulphide and the acid,

(vii) by wet reduction of a chromate with sulphur dioxide,

(viii) by the action of an alkali carbonate followed by acid on a sulphito-complex of the type $Me_a[M_b(SO_3)_2]$,

(ix) by the action of tetramethylammonium pyrosulphite on the anhydrous iodide of the metal.

(i) From metal and acid

This method has been little used, owing to the risk of formation of the thiosulphate from the sulphite,[2] e.g.

$$2Fe + 3SO_2 \longrightarrow FeSO_3 + FeS_2O_3$$

In this instance the sulphite is deposited from the solution before the thiosulphate. Sulphur and iron(II) sulphide are formed also, thus rendering the method unsatisfactory.

Cadmium sulphide is formed as well as the sulphite when cadmium dissolves in sulphurous acid.[2]

(ii) From the metal oxide or hydroxide, and acid

This popular method usually involves the passage of sulphur dioxide into a suspension of the oxide or hydroxide in water, followed, after dissolution, by the removal of sulphur dioxide. The solution on losing sulphur dioxide precipitates the sulphite e.g.

$$2ZnO + 2SO_2 + 5H_2O \longrightarrow 2ZnSO_3.2{\cdot}5H_2O \quad ^{27}$$

Mellor[2] refers frequently to this method. It has been used in manufacturing processes for the extraction of metals[28] and the manufacture of metal sulphites.[29] In the production of copper sulphate from copper oxide ore by the action of sulphur dioxide and air,[30] the precipitation of $CuSO_3.2H_2O$ is prevented by the presence of iron salts together with small amounts of other heavy metal ions. As might be expected MnO_2 does not give the sulphite[31] and this appears true of other higher oxides.

(iii) From the metal carbonate and acid

This popular route[2] was used by Klasens et al.[1] to prepare $MgSO_3.6H_2O$, $CoSO_3.6H_2O$ and $NiSO_3.6H_2O$, and by Cadoret[32] to prepare $NiSO_3.6H_2O$ and Bugli[33] $CoSO_3.2{\cdot}5H_2O$

(iv) By metathesis

Formally:

$$M_xA_y + Me_z(SO_3)_b + nH_2O \longrightarrow M_x(SO_3)_b.nH_2O + Me_zA_y$$

M_xA_y is a soluble salt of the transition metal concerned and $Me_z(SO_3)_b$ is an alkali metal sulphite or ammonium sulphite, more usually the former. To avoid complex formation the ratio of M^{n+} to $SO_3^{\ 2-}$ is usually x:b.

Bugli[34] used this method recently for the preparation of $FeSO_3.3H_2O$ and it has been used also in the manufacture of sulphites.[35]

Pavlyuchencho et al.[36] have reacted Ag_2SO_4 and Na_2SO_3 in the solid phase by grinding or pressing of the reaction mixture at room temperature.

(v) From a soluble compound of the metal with the acid or alkali hydrogen sulphite

$$xM^{y+} + 2zHSO_3^{\ -} + nH_2O \longrightarrow M_x(SO_3)_z.nH_2O + zSO_2 + zH_2O$$

This method is essentially similar to the previous method in that the low solubility of the metal sulphite causes its precipitation leaving other ions in solution.

Its main use has been in the preparation of $Cu_2SO_3CuSO_3.2H_2O$[2,24] and through it the recovery[37] and extraction[23] of copper, and in the preparation of Ag_2SO_3.[2,38]

(vi) From the metal sulphide and the acid

The primary action of sulphurous acid upon the sulphides of iron, zinc and manganese is according to the following equation:[39]

e.g. $$MS + SO_2 + H_2O \longrightarrow MSO_3 + H_2S$$

A corresponding quantity of thiosulphate results from oxidation involving the liberated hydrogen sulphide. There is also the additional problem of the conversion of the sulphite formed into other products such as tetrathionate and pentathionate.[40,41]

(vii) <u>By wet reduction of a chromate with sulphur dioxide</u>

On adding aqueous $(2N)H_2SO_3$ to Ag_2CrO_4, storing in the dark and shaking occasionally over seventy five days the resultant precipitate consisted wholly of Ag_2SO_3.[42]

(viii) <u>By the action of an alkali carbonate followed by acid on a sulphito-complex of the type $Me_a[M_b(SO_3)_2]$</u>

$Hg_2SO_3.HgSO_3.H_2O$ has been prepared in this way from $Na_2[Hg(SO_3)_2]$.[43]

(ix) <u>By the action of tetramethylammoniumpyrosulphite on the anhydrous iodide of the metal</u>

$CoSO_3$ is reported to be prepared in this way from CoI_2, using tetramethylammoniumpyrosulphite in acetone.[44]

(b) <u>Sulphites of the type $[ML_a](SO_3)_b.nH_2O$</u>

These are prepared in the following ways:

(i) <u>By using the components $M_a(SO_3)_b$ and a neutral ligand</u>

The monoamines of zinc[2] and cadmium[2] and the compounds of the formula $M_a(N_2H_4)_b(SO_3)_c.nH_2O$[45] have been prepared by this method.

(ii) <u>By replacement of certain ligands in a complex, by other ligands at the same time producing a sulphite</u>

$[Co(NH_3)_5H_2O]_2(SO_3)_3H_2O$ is prepared from $[Co(CO_3)(NH_3)_4Cl]$ or $[Co(NH_3)_5Cl]^{2+}$ using an ammoniacal solution of $(NH_4)_2SO_3$[2] and $[Pt(NH_3)_4]SO_3$ from $(NH_4)_2[PtCl_3(HSO_3)]$ by warming with ammonia.[2]

(iii) By replacing counter ions of a complex by sulphite ions. e.g. $[Co(NH_3)_6]ClSO_3$ from $[Co(NH_3)_6]Cl_3$ by passing sulphur dioxide into a hot solution in dilute ammonia.[2]

(c) Sulphites of the type $Me_aM_b(SO_3)_c.nH_2O$

These have been prepared as follows:

(i) By mixing solutions containing the component ions, or ions which give component ions on reduction with SO_2

Mellor[2] refers frequently to this method. Hahn et al.[46] used the metal chloride or acetate with an alkali sulphite or hydrogen sulphite to prepare compounds of the type $Me_2M(SO_3)_2$ (Me = NH_4^+; M = Zn, Cd, Fe, Mn, Co, Ni; whereas when Me = Na, K; M = Co, Mn). $Na_3[Co(SO_3)_3]$ was obtained using the nitrate.

The effect of temperature, acidity and molar ratios of the components on the formation of this type of complex has been investigated.[47,48,49]

(ii) By replacement of anionic ligands by sulphito-groups

This method has not been as extensively used as the previous method. $Na_6[Pt(SO_3)_4].2H_2O$[50] and $(NH_4)_3[Rh(SO_3)_3].2H_2O$[51] were synthesised by the reactions of Na_2SO_3 with $K_2[PtCl_4]$ and $(NH_4)_2SO_3$ with $H_3[RhCl_6]$ respectively, whilst the production of $[Hg(SO_3)_2]^{2-}$ is involved in estimations of atmospheric sulphur dioxide by colorimetric methods.[52]

$$[HgCl_4]^{2-} + 2SO_2 + 2H_2O \longrightarrow [Hg(SO_3)_2]^{2-} + 4Cl^- + 4H^+$$

(iii) By replacement of both anionic and neutral ligands in a complex

This method has been little used, but Lebedinskii et al.[25] have prepared $(NH_4)_3[Rh(SO_3)_3]$ from $[Rh(NH_3)_3Cl_3]$ using $(NH_4)_2SO_3$ in their route to spectroscopically pure rhodium metal

$$Rh(NH_3)_3Cl_3 + 3(NH_4)_2SO_3 \longrightarrow (NH_4)_3[Rh(SO_3)_3] + 3NH_4Cl + 3NH_3$$

(d) Sulphites of types $Me_a[M(SO_3)_bL_c].nH_2O$, $[M(SO_3)_aL_b].nH_2O$ and $[M(SO_3)_aL_b]X_c.nH_2O$

These three types of sulphites may be prepared by the same routes which are classified as follows:

(i) The replacement of neutral ligands by sulphite ions

Lyubimova[53] used this method for the preparation of $[Pt\{(NH_2)_2CS\}_3SO_3]$ and $Na_2[Pt\{(NH_2)_2CS\}_2(SO_3)_2]$ from $[Pt\{(NH_2)_2CS\}_4]Cl_2$ using Na_2SO_3.

(ii) The replacement of anionic ligands by sulphite ions

Syrtsova et al.[54] prepared $Na_3[Co(SO_3)_2(mg)_2]$ (mgH = methylglyoxime) from $Na[Co(NO_2)_2(mg)_2]$ and Na_2SO_3 using molecular ratios of 1:2. Cobalt,[55] rhodium[56] and platinum[57] complexes have also been prepared by this route.

(iii) The replacement of sulphito-groups by anionic ligands

Sulphito-groups in cobalt complexes were replaced by chloride ions using a dry solution of hydrogen chloride in absolute alcohol at room temperature.[58]

(iv) The replacement of sulphito-groups by neutral ligands

Klement[59] prepared $Na[(SO_3)_2Co(NH_3)_2].2H_2O$ from $Na_3[Co(SO_3)_3]$ dissolved in an aqueous $(NH_4)_2SO_3$ solution.

(v) The replacement of neutral ligands by stronger neutral ligands

Syrtsova and Korletyanu[60] used this method for the preparation of a number of $[Co(SO_3)(dmg)_2amine]^-$ complexes from $[Co(SO_3)(dmg)_2H_2O]^-$ (dmgH = dimethylglyoxime). Cobalt complexes containing 1,10-phenanthroline have been prepared by Palade.[61] Many other workers have used this method in connection with other cobalt[58,59,62] and palladium[63] complexes.

(vi) The replacement of neutral ligands by anionic ligands

Within the last ten years a number of cobalt complexes[64,65] have been prepared by this method, e.g. $[CoX(SO_3)(NH_3)_4]$ (X = NO , NCS or CN) by treating finely ground $[Co(SO_3)(NH_3)_5]Cl$ with an excess of concentrated aqueous solutions of $NaNO_2$, NaNCS and KCN respectively.[65]

(vii) The replacement of anionic ligands by neutral ligands

$NH_4[Pt(SO_3)_2(NH_3)_2].4H_2O$ was prepared from $PtCl_2(SO_3)_2$ in cold ammonia solution.[50]

(viii) By metathesis

$[Pt(NH_3)_2SO_3]$ was prepared from $[Pt(NH_3)_2Cl_2]$ using Na_2SO_3 (1:1),[53] $[IrCl(SO_3)en_2]$ from cis-$[IrCl_2en_2]Cl$ using Na_2SO_3.[66] (1:3), and $PdSO_3(H_2O)_3$ from $PdCl_2$ and Ag_2SO_3 when ground together in water.[63]

(ix) From the component ions, or ions which give the component ions on oxidation with air

This was a most widely used method of early workers[2], and examples are the preparations of $K_6[Co_2SO_3(CN)_{10}]$,[67,68] $(NH_4)_2[Fe(SO_3)_2OH]$ and $(NH_4)[Fe(SO_3)_2(NH_3)(H_2O)]$,[47] and $K_3[Rh(NH_3)_3(SO_3)_3]3 \cdot 5H_2O$.[51] The composition of the rhodium complex formed depends critically on the molar quantities of reactants used.[50,64] Cis and trans isomers differ in the course of their reactions owing to the strong trans effect of the sulphito-group.

The preparation of hydrogen sulphites

In comparison with the sulphites a far smaller number of hydrogen sulphites have been reported but they can be classified in a similar way.

(a) Hydrogen sulphites of the type $M_a(HSO_3)_b.nH_2O$

No transition metal hydrogen sulphites of this type are known in the solid state, though solutions of the corresponding sulphites in sulphur dioxide solution are presumed to contain these compounds.[2] Evaporation to concentrate the solution, causes loss of sulphur dioxide and probably upsets the equilibria in the solution i.e.

$$2HSO_3^- \rightleftharpoons SO_2 + H_2O + SO_3^{2-}$$

Even though the equilibrium lies well to the left in sulphur dioxide solution, precipitation of the sparingly soluble metal sulphite will displace the equilibrium to the right and reduce the possibility of forming hydrogensulphito-complexes. Alternatively the equilibrium

$$HSO_3^- + H_2O \rightleftharpoons H_3O^+ + SO_3^{2-}$$

is displaced to the right through the insolubility of the metal sulphite.

(b) Hydrogen sulphites of the type $ML(HSO_3)_2.nH_2O$

Few are known, but $MN_2H_4(HSO_3)_2.nH_2O$[45] (M = Co, Mn, Cd, Zn) were prepared from the components, the metal sulphite & aqueous SO_2 solution in the presence of hydrazine. Recently Duff[69] prepared $ML(HSO_3)_2$ ($L = 1,2\text{-}C_6H_4(NH_2)_2$, M = Zn, Cu, Ni or Co) by suspending ML_nX_2 (X = halide, NO_3^- or ClO_4^-; n = 1, 2 or 3), in sulphur dioxide solution.

These examples[45,69] may or may not contain hydrosulphito ligands but Mellor[2] has described the preparation of $[Pt(NH_3)_2(HSO_3)Cl]$ by the action of sulphur dioxide on a solution of $[PtCl_2(NH_3)_2]$ or $PtCl_2(NH_3)_4$.

(c) Hydrogen sulphites of the type $Me_aM_b(HSO_3)_c(SO_3)_d.nH_2O$

The early workers[2] prepared these compounds using the components e.g. $K_4[Cu(HSO_3)_3(SO_3)]$ was prepared from $K_3[Cu(HSO_3)_2(SO_3)].2{\cdot}5H_2O$ using excess $KHSO_3$ or from K_2CO_3 and basic copper(II) carbonate by saturation with sulphur dioxide while cooled in ice. Treatment of $K_6[Pt(SO_3)_4]H_2O$ with dilute sulphuric acid gave $K_4[Pt(SO_3)_2(HSO_3)_2]$ and its tetrahydrate.[70]

(d) Hydrogen sulphites of the type $Me_a[M_b(HSO_3)_cL_d]$ and $[M_a(HSO_3)_bL_c]X_d$

Early workers[2] used the action of sulphur dioxide solution on a chloro complex of the metal e.g. $(NH_4)_2[PtCl_3(HSO_3)]$ was prepared from $(NH_4)_2PtCl_4$ and warm concentrated sulphur dioxide solution.

Mineral acids have been used on complexes containing sulphito-groups[56,70-73] e.g. the action of excess concentrated hydrochloric acid on $K_6[Pt(SO_3)_4]H_2O$ produced $K_3[PtCl_2SO_3(HSO_3)]$.[70]

In some cases[71] the anion of the acid also replaces one sulphito-group of a disulphito-complex, the other one being converted to a hydrosulphito-group, or alternatively, neutral ligands such as water are, in a monosulphito complex, replaced by the anion of the acid.[56] Dilute nitric or perchloric acids are reported to convert $[Co(SO_3)_2(Df)_2]^{3-}$ to $[Co(SO_3H)(Df)_2H_2O]$ by hydrolysis[72] and hydrochloric acid to convert the dihydrosulphito complex $(NH_4)[Co(SO_3H)_2(mg)_2]$ to $NH_4[Co(SO_3H)Cl(mg)_2]$,[73] (where HDf = benzildioxime and mgH = methylglyoxime).

To conclude, hydrogen sulphites have been prepared in acid conditions using alkali metal hydrogen sulphites, through the reaction of sulphur dioxide with suitable compounds such as halide complexes,[69] or by the reactions of mineral acids on suitable sulphito or hydrosulphito complexes. The identity of the acid and its concentration influence the complex formed.

The preparation of basic sulphites

As with basic compounds of other salts and complexes, the methods of preparation are as for the normal salts, but with the additional route of the action of heat on a normal sulphite. If the normal sulphite can be prepared, then the conditions used for the basic sulphites are those more likely to lead to hydrolysis, i.e. the conditions are less acidic.

For compounds of the type $M_aX_b(SO_3)_c.nH_2O$ (X = OH,O) the methods most often referred to by Mellor[2] are methods (ii), (iv) and (v) for the normal sulphites.

Where it is possible to form a normal sulphite of the metal, the most usual method has been method (iv), occasionally modified to aid hydrolysis e.g. $2MnSO_3.Mn(OH)_2.2H_2O$ was prepared by slowly mixing a large excess of Na_2SO_3 or K_2SO_3 with a boiling 20 to 25% aqueous solution of $MnSO_4$.[2]

Basic sulphites may be the product of a reaction which for other metal systems would produce a normal sulphite. For example $Fe_2O_2(SO_3)6H_2O$[2] has been obtained by dissolving $Fe(OH)_3$ in ice cold sulphur dioxide solution. The same conditions apply for the preparation of other basic sulphites, e.g. $K_2PtO(SO_3)_2H_2O$[2] is prepared by passing sulphur dioxide into a suspension of PtO_2, until a clear solution results, followed by treatment with K_2SO_3 and K_2CO_3 solutions. Hydrolysis of $KHgClSO_3$ with moist Ag_2O or with KOH gave $K_2O.3HgO.3SO_2$.[2]

Studies of the formation conditions of basic sulphites have included the effect of concentrations on the sulphites formed in the reaction between boiling Na_2SO_3 solution and chromium sulphate,[74] and the eutonic point where $2ZnSO_3.3ZnO.3H_2O$ coexists with $ZnSO_3.2{\cdot}5H_2O$, in the system zinc hydroxide-water-sulphur dioxide at 20^o.[75]

That there may be other novel methods of preparing basic sulphites has been shown by Simon et al.[76] who obtained $1{\cdot}5ZnO.SO_3$ by heating together equimolecular mixtures of ZnO and $ZnSO_4$.

The existence and stability of complex ions in solutions

A number of potentiometric, conductometric and solubility studies have been carried out, to determine the existence and nature of complex ions in solutions containing suitable components, in a wide variety of systems.[77-84]

Simple complexes, and some mixed complexes of mercury,[77,78,79] silver,[80,81,83] copper,[80] iridium,[82] and lanthenum[84] have been established or suggested, some of which have been isolated in the solid form, and in some cases[79,80,81] the dissociation constants have been determined.

3. General Properties

(a) Physical Properties

There is extensive reference to qualitative solubility in water in the literature but little quantitative work has been carried out. In general terms the vast majority of sulphites are slightly, sparingly or insoluble in water. However Mellor[2] refers to some compounds of the type $M_aM_b(SO_3)_c.nH_2O$ (M = Pt, Au, Cu, Os) and some mixed complexes of cobalt as soluble. A few quantitative studies are referred to e.g. 100 cm^3 of water at 20^o dissolve 5.37 g. of $Na_2[Pt(NH_3)(SO_3)_2]$.

More recently the solubility of $Hg^+SO_3^{--}$,[85] Ag_2SO_3[86] and $Cu_2SO_3CuSO_3.2H_2O$[87] have been determined.

In an interesting study[88] $Li_3[Co(SO_3)_3]$ which appeared to be moderately soluble in water was shown to be only slightly soluble by conductivity measurements and use of an ultramicroscope.

Extensive reference to solubility in organic solvents shows that sulphites are as expected generally less soluble than in water, and one instance of its use has been in the separation of a ruthenium sulphite complex from thorium and uranium fission products.[26]

Densities have been determined generally in cases where crystal structures have been under investigation but a few are referred to by Mellor[2] and more recently Weigel[89] showed, by density determination, that polymorphs of $NiSO_3.6H_2O$ exist.

Equivalent and molecular conductivities, and depression of freezing point determinations have been carried out to determine the number of ions present in the solution of complexes both by early workers[2] and more recently.[90,60]

4. Chemical Reactions

With water

The effect of water on sulphites was extensively reported by early workers[2] in a qualitative way and almost all reports refer to decomposition to a variety of products such as the metal, the hydroxide or oxide. The extent of decomposition even in boiling water depends on the nature of the metal sulphite and in some cases is slight. For example, $[Co(SO_3)_3]^{3-}$ is only slowly decomposed by boiling water whereas $CuO.2CuSO_3.nH_2O$ completely decomposes in a few minutes.[2]

With strong alkalis and alkali metal carbonates

Early reports[2] suggest that compounds of the type $M_a(SO_3)_b.nH_2O$ tend to hydrolyse easily whilst complexes of the type $M_aM_b(SO_3)_c.nH_2O$, (M = Pt, Pd, Rh) are resistant to hydrolysis. The simple sulphites of mercury of the type $Hg_a(SO_3)_b.nH_2O$ are interesting in that they produce $K_2[Hg(SO_3)_2]$ and Hg_2O with an aqueous solution of KOH.

In one recent study[72] $K[CoSO_3(Df)_2H_2O]$ (Df = anion of α-benzildioxime) was prepared by treatment of $[Co(SO_3H)(Df)_2H_2O]$ with K_2CO_3 solution.

With acids

The effect of sulphur dioxide solution has been confined to early studies. Mellor[2] refers mainly to sulphites of the types $M_a(SO_3)_b.nH_2O$ and $M_aX_b(SO_3)_c.nH_2O$, where X is OH or O, and these sulphites are almost without exception soluble, presumably forming the hydrogen sulphite. Silver and mercury sulphites have been reported as giving the metal.

The action of mineral acids on sulphites has been extensively investigated.[2] In general with hydrochloric acid, sulphur dioxide is liberated and the chloride(s) of the metal(s) are formed, or in the case of mixed complexes the chloro-mixed complex.

However, as noted in the preparation of hydrosulphito complexes, it has been possible to convert the sulphito-ligand to the hydrosulphito-ligand, using hydrochloric acid. At the same time a second hydrosulphito- or sulphito-group in the same complex is replaced by the chloride ion.[56,70,71,73] Also by using the theoretical quantity of concentrated hydrochloric acid, $[Co(NH_3)_5SO_3]_2SO_3.H_2O$ can be converted to $[Co(NH_3)_5SO_3]Cl$.[2]

With nitric and sulphuric acids their oxidizing properties and the fact that they are oxy-acids influence the products formed. The mercury sulphites are remarkable in that the dilute acids do not react.[2] The action of dilute sulphuric acid on $K_6[Pt(SO_3)_4]$ gives $K_4[Pt(SO_3)_2(SO_3H)_2]$[70] and that of dilute nitric or perchloric acid on $[Co(SO_3)_2(Df)_2]^{3-}$, (Df = anion of benzildioxime) causes hydrolysis to form $[Co(SO_3H)(Df)_2H_2O]$.[72] The rate of decomposition of $ZnSO_3.2{\cdot}5H_2O$ by sulphuric acid has been measured.[91]

The action of the weak acids oxalic and malonic on $[CoL_4(SO_3)_2]^-$ complexes, ($L = NH_3$, $\frac{1}{2}$en, or propylenediamine), causes liberation of the free sulphurous acid which then reduces the trivalent cobalt.[92] Acetic and oxalic acids cause the partial decomposition of $Na_3Au(SO_3)_2.1{\cdot}5H_2O$.[2]

5. Oxidation and Reduction

Many references have been made to oxidation in air[2] mainly in connection with sulphites of the types $M_a(SO_3)_b.nH_2O$, $M_aM_b(SO_3)_c.nH_2O$ and $M_aX_b(SO_3)_c.nH_2O$ (X = OH or O). Their stability to oxygen varies from remarks such as 'stable in air' to 'readily oxidised in air'.

There is a singular lack of reference in the case of complexes of platinum and cobalt(III) in which the sulphito-group is known to be bonded to the metal through sulphur.

Hahn et al.,[46] said that the compounds $Me_a[M(SO_3)_2]nH_2O$ ($Me = NH_4^+$; M = Zn, Cd, Fe, Mn, Co, Ni and when $Me = Na^+$, K^+; M = Co, Mn) which they obtained were so coarsely crystalline that the salts which were normally easily oxidized had good stability in air.

A few rate studies have been carried out.[19,87,93] In the oxidation of $FeSO_3.3H_2O$ in dry air, the sulphite content fell regularly and continuously. The purer and drier the original sample, the more slowly it decomposed.[93] The rate of oxidation of $ZnSO_3$ in fungicidal preparations is decreased by the addition of Al_2O_3 or iron oxide,[19] and the rate of oxidation of $Cu_2SO_3CuSO_3.2H_2O$

in contact with its solution, increases with the oxygen content of the gas passed through and with the $CuSO_4$ content of the solution.[87]

Other stronger oxidizing agents, other than acids are reported[2] to oxidize all types of sulphites. The reagents used include solutions of $KMnO_4$ and the halogens. However Feigl[94] reports that even MnO_4^- fails to oxidize $[Hg(SO_3)_2]^{2-}$ except at a very slow rate. An unusual oxidation of anhydrous $CoSO_3$ and $NiSO_3$, has been reported,[95] involving the use of liquid sulphur dioxide and dimethyl sulphoxide to produce $MS_2O_7.6Me_2SO$.

The auto-reduction of silver complexes has been investigated. Steigmann[96] showed that $NaAgSO_3$ was auto-reduced, the reaction being strongly catalysed by traces of copper, with or without excess of sulphite. More recently a comprehensive study[97] has shown that the rate of decomposition decreases with increasing concentrations of sulphite ion and is 2nd order with respect to it. The products, and dependence of total rate of decomposition on the concentration of the various complexes present are also reported.

The internal oxidation and reduction of <u>trans</u>-$[Co(en)_2SO_3OH_2]^+$ in a range of $HClO_4$ media up to 7M have been investigated[98], the complex disproportionating according to the reaction,

$$[Co(en)_2SO_3OH_2]^+ + 3H^+ \longrightarrow Co(aq)^{2+} + HSO_3 + 2enH^+$$

The HSO_3 radical gives dithionic acid. The reaction is acid catalysed, and protonation is complete above 1M $HClO_4$.

In a reduction of 'so called' $ZnSO_3$ solution by magnesium the products include sulphur dioxide, ZnO, ZnS and $ZnSO_4$[2] whilst reduction of $ZnSO_3$ using zinc amalgam[99] under the action of carbon dioxide proceeds according to the equation,

$$2ZnSO_3 + 2H_2CO_3 + Zn \longrightarrow ZnS_2O_4 + 2ZnCO_3 + 2H_2O.$$

Polarographic reduction of various cobalt complexes has been investigated.[100,101,102]

Maki et al[100] found that most of the Co(III) complex ions of the bisethylene diammine series were reduced irreversibly in two steps at the dropping mercury electrode. The first diffusion current corresponded to the reduction Co(III) → Co(II) and the second Co(II) → Co(0).

The complexing ability of the sulphito-group has been compared using polarographic techniques with a wide range of other anionic groups, particularly carboxylic acid groups in a series of chromium complexes. Two separate studies conflict markedly in their conclusions of the relative donor strength of the sulphito-group.[103,104]

6. The Effects of Radiation

It has long been known that silver salts in general are decomposed by ultra violet and visible radiation. A number of studies of this phenomenon have centred on or included Ag_2SO_3.[105,106,107] These have shown that it fluoresces at liquid air temperature when irradiated with radiation below a wavelength of 3650Å and that this radiation causes blackening at room temperature. The presence of excess of the anion makes the salt susceptible to silver deposition.[107] It is supposed that defects in the lattice of Ag_2SO_3 play an important role. In a study of the effects of impurities on its stability to ultraviolet radiation an increase in stability was noted on the addition of 5% Cd^{++}, and a decrease on the addition of 5% PO_4^{3-}. The results of irradiation agree well with those of thermal decomposition. The mechanism of the effect of additions is identical with that of heterovalent impurities on the thermal decomposition of ionic salts, namely, that there is an increase in the probability of interstitial Ag^+ occupying lattice positions in the sulphite, because of the additional vacancies formed by the introduction of Cd^{++}. The introduction of PO_4^{3-} also results in an increase in the concentration of anion vacancies and also an increase in the rate of photolysis.[108]

Scharz and Tede[109] investigated the photochemical decomposition of compounds of the type $[Co(NH_3)_4X_2]Y$ in solution and found that hydrolysis gives $Co(OH)_3$, NH_4X, NH_4Y and NH_3. The relative stability of the complex is a function of the acid ligand X and not of the light absorption.

7. Trans effect

The sulphite group exhibits a strong trans-effect. For example, the action of Na_2SO_3 on cis-$[PtPy_2Cl_2]$, where Py is pyridine, gives $Na_6[Pt(SO_3)_4]$, whilst its action on the trans-isomer produces trans-$Na_2[PtPy_2(SO_3)_2]$[57] trans-$Na_4[PtCl_2(SO_3)_2]$ with cold NH_4OH gives colourless trans-$Na_2[Pt(SO_3)_2(NH_3)_2].4H_2O$. The labilisation of the two Cl groups indicates a strong trans-effect.[50] Analogous conclusions have been made for sulphito-cobalt(III) complexes. When aqueous solutions of $[CoSO_3(dmg)_2amine]^+$ are heated the amine is displaced indicating a strong trans-influence of the sulphito-group.[60] Syrtsova[90] has placed the sulphito-group according to the following series, in order of increasing trans-effect: $NO_2^- < SCN < SO_3^{2-} = CN^-$, by studying the reactions of $[CoX(SO_3)(dmg)_2]$ ($X = SCN^-$, NO_2^- or CN^-; dmgH = dimethylglyoxime. In complexes of the type trans-$[Co(X)_2mg)_2].nH_2O$, ($X = SCN^-, CN^-, SO_3^{2-}$ ~~$M = 3Na^+, 3NH_4^+, [Co(NH_3)_6]^{3+}, [Co(en)_3]^{3+}$~~; mgH = methylglyoxime) the trans-effect has the same order of decreasing strength as in analogous dimethylglyoxime complexes.[54]

8. Kinetic studies of the reactions of sulphito-and hydrosulphite-complexes or their formation reactions

Many reactions of cobalt, and to a lesser extent iron and chromium complexes have been investigated recently in an effort to obtain information on the trans-effect of the sulphito-and hydrosulphito-groups. Many suggestions concerning mechanisms have been concerned with the aquation of complexes. Holly Ho Chen et al.,[110] investigated the complexes $[Co(CN)_4(SO_3)_2]^{5-}$ and $[Co(CN)_5(SO_3)]^{4-}$, and found that the rate of aquation of the first sulphito-ligand in $[Co(CN)_4(SO_3)_2]^{5-}$ is very much greater than that in $[Co(CN)_4(SO_3)OH_2]^{3-}$ or $[Co(CN)_5(SO_3)]^{4-}$, strongly suggesting a large trans-activation of the sulphito-ligand. Infra-red and

Raman spectra support a trans-configuration for $[Co(CN)_4(SO_3)_2]^{5-}$. Halpern et al.,[111] found that the kinetics of the reaction:

$$CoA_4SO_3(X) + Y \longrightarrow CoA_4SO_3(Y) + X$$

where X = NH_3; Y = $^{15}NH_3$, OH^-, CN^-, NO_2^- or SCN^-; X = OH^-; Y = NH_3 or CN^- and X = SCN^-; Y = NH_3, agree with a limiting S_N1 mechanism through a common intermediate $[CoA_4SO_3]^+$, the reactions reflecting the marked trans-labilising influence of a sulphur bonded sulphito-ligand. Tewari et al.,[112] carried out the displacement of water in $[Co(CN)_4(SO_3)OH_2]^{3-}$ by CN^- at 25° in the presence of a large excess of CN^-. Each experiment gave pseudo first order kinetics and a limiting S_N1 mechanism. It is also suggested that this labilisation of trans-ligand to the sulphito-group is not connected with strong metal to ligand π bonding. Syrtsova and Sui Luong have investigated the kinetics of the aquation of Na $[CoCl(SO_3H)(DH)_2]$[113] and $NH_4[CoCl(SO_3H)(MH)_2]$[73] in water and aqueous organic media, and found that the exchange of H_2O for Cl shows first order kinetics and that the rate of aquation of $[CoClX(DH)_2]^-$ is inversely proportional to the trans-effects of X, where X = HSO_3, NO_2 or Cl. The aquation of $NH_4[CoCl(HSO_3)(mg)_2]$ is practically irreversible and proceeds by an associative mechanism. In a study of hydrolysis of several ferrocyanide complexes[114] it was found that the reaction:

$$H_2O + [FeSO_3(CN)_5]^{5-} \longrightarrow [FeH_2O(CN)_5]^{3-} + SO_3^{2-}$$

did not go to completion. The reaction was first order with respect to the complex and most rapid at low pH. Murray et al.,[115] have shown that the rates of substitution reactions of a number of cobalt(III) sulphito-complexes is fast, and suggest that weakening of the ligand bond trans- to a sulphur bonded sulphito ligand is the prime cause of the strong labilising effect of this ligand. Above pH 12 the substitution reaction of trans-$[Co(en)_2(SO_3)OH]$ with SO_3^{2-} to form $[Co(en)_2(SO_3)_2]^-$ is reversible and the mechanism is a reversible two step limiting S_N1 mechanism, OH^- ion being at least fifty times more reactive than

SO_3^{2-} ion towards the intermediate $[Co(en)_2SO_3]^+$.[116] At pH 8.1, substitution of trans-$[Co(en)_2SO_3OH_2]^+$ by SO_3^{2-} is virtually complete and has a limiting S_N1 mechanism.

Carlyle and King[117] have found that Cr(III) in aqueous acidic sodium sulphite solution forms a sulphite complex ion $[CrOSO_2]^+$ rapidly and reversibly, suggesting that it forms without breaking the Cr-O bond in the $Cr(H_2O)_6^{3+}$ ion. The rates of several ligand substitution reactions of Cr(III) ions in the presence of sulphite-ions are first order with respect to sulphite ions. They also suggest that the oxygen donating sulphito-ligand exerts less trans-influence than a sulphur donating sulphito-ligand. Carlyle[118] from a study of the reaction represented by:

$$Fe^{3+} + HSO_3^- \longrightarrow FeSO_3^+ + H^+$$

finds that the kinetic evidence agrees with a sulphur bonded $FeSO_3^+$ species. The reaction of sulphite ions with $[Pd(Et_4dien)Br_2]Br$,[119] (Et_4dien = $Et_2NCH_2CH_2NHCH_2CH_2NEt_2$), follows a first order path as found previously for other ligands with this substrate. Hague and Halpern[120] have reported meaaurements for a number of anation reactions of trans-$[Co(dmg)_2(NO_2)OH_2]$ and trans-$[Co(dmg)_2(I)OH_2]$. The reactions exhibited second order kinetics, consistent with S_N1 or S_N2 mechanisms.

9. Thermal and Thermodynamic properties

Heats of formation of sulphites of the type $M_a(SO_3)_b$ have been determined. Those of silver [121] and cadmium[122,123] have been determined experimentally, and Erdos[124] calculated a large number using an equation which reproduces heats of formation of sulphates with an average deviation of ± 1.5 kcal/mole. Entropies and heat capacities have been calculated in a similar manner,[125] and thermodynamic values for a number of simple sulphites discussed.[126]

The thermal decomposition of sulphites, mainly simple sulphites, have been studied extensively[2] in a variety of atmospheres. The solid products are oxides, sulphides and sulphates but there appears to be no simple pattern.

At 100° Ag_2SO_3 gives sulphur dioxide, silver and silver sulphate, but at or above red heat, silver, oxygen and sulphur dioxide are detected.[2] Ag_2SO_3 did not decompose in hydrogen to silver and sulphur trioxide up to 100°, but the sulphur dioxide produced caused auto-acceleration.[127] At 100° and under nitrogen,[128] the reaction is firstly:

$$Ag_2SO_3 \longrightarrow 2Ag + (O) + SO_2$$

The oxygen then oxidizes more Ag_2SO_3 to Ag_2SO_4 giving the overall equation:

$$2Ag_2SO_3 \longrightarrow 2Ag + SO_2 + Ag_2SO_4$$

The mechanism is thought to involve the formation of SO_3 radicals followed by the reaction:

$$Ag_2SO_3 + SO_3 \longrightarrow Ag_2SO_4 + SO_2$$

and the rate of decomposition to depend upon lattice defects.[129,130,131] Addition of Pb^{2+} and VO_3^-, lowers the activation energy of the decomposition process but the rate is reduced also.[131] Savel'ev et al., have suggested that $Ag_2S_2O_6$ is formed between 100-150°[132] and that the formation of a new modification is complete at 151-5°.[133] The effects of applied electric fields and the addition of various semi conductors on the decomposition process have been studied.[134]

Early work[2] suggested that $ZnSO_3.2{\cdot}5H_2O$ at 100° lost all its water, and at 200° sulphur dioxide was evolved and the residue was ZnO together with some $ZnSO_4$. Industrially the production of $ZnSO_3$ is important, so its thermal decomposition in air has been the subject of a number of studies with an industrial bias.[20,21,22,135] It is generally suggested that the final product is ZnO. A number of workers[18,136,137] have carried out more detailed studies in air. The decomposition is considered by Okabe et al.[135] to occur according to:

$$ZnSO_3.2{\cdot}5H_2O \xrightarrow{120^\circ} ZnSO_3.H_2O \xrightarrow{200^\circ} ZnSO_3 \xrightarrow{270^\circ} ZnO$$

but the following alternative scheme has been suggested:[137]

$$ZnSO_3.2{\cdot}5H_2O \xrightarrow{90\text{-}110^\circ} ZnSO_3.0{\cdot}5H_2O \longrightarrow \text{mixture } (ZnSO_3 + ZnO) \xrightarrow{320^\circ}$$

$$ZnSO_3.yZnO \xrightarrow{854^\circ} 2ZnSO_4.ZnO \text{ and } ZnO$$

Increase in the oxygen content of the atmosphere[18] (21% to 100%) increased the amount of $ZnSO_4$ (4.03 to 6.91% at 500°, 2.04 to 4.52 at 300°). Similar increases were obtained by addition of 10% by weight of Cr_2O_3 or Fe_2O_3.

Under argon[18,138] the decomposition route:

$$4ZnSO_3.2{\cdot}5H_2O \xrightarrow{96\text{-}100^\circ} 4ZnSO_3.2H_2O \xrightarrow{131\text{-}45^\circ} 4ZnSO_3.H_2O \xrightarrow{189\text{-}210^\circ}$$

$$3ZnSO_3.ZnO \xrightarrow{283\text{-}300^\circ} 2(ZnSO_3.ZnO) \xrightarrow{371\text{-}82^\circ} 4ZnO$$

results in the generation of steam and sulphur dioxide. Above 350° traces of ZnS and $ZnSO_4$ decreased as the temperature increased. Decomposition under nitrogen[139] (up to 600°) gave the oxide, sulphur dioxide, and traces of sulphide and sulphate. Under vacuum (200-340°) ZnS_2O_3, $ZnSO_4$ and sulphur dioxide, were products.[17] Between 200 and 260° the following reaction occurred:

$$2ZnSO_3 + SO_2 \longrightarrow 2ZnSO_4 + \tfrac{1}{2}S_2$$

but became progressively slower due to the production of $ZnSO_4$. A mixture of $ZnSO_3$ and $MgSO_3$ (10:1) decomposed in an analogous manner to $ZnSO_3$. This work[139,17,18] has been reviewed by Margulis and Grishankina[27] who suggested the following decomposition stages under argon or dry air:

(i) at temperatures $\geqslant$ 100°,

$$3(ZnSO_3.2{\cdot}5H_2O) \xrightarrow{-6H_2O} 3ZnSO_3.1{\cdot}5H_2O \xrightarrow{-SO_2} ZnO.2ZnSO_3.1{\cdot}5H_2O$$

(ii) at temperatures $\geqslant$ 220°,

$$3ZnSO_3.1{\cdot}5H_2O \xrightarrow{-1.5H_2O} 3ZnSO_3 \xrightarrow{-SO_2} ZnO.2ZnSO_3$$

$$ZnO.2ZnSO_3.1{\cdot}5H_2O \longrightarrow ZnO.2ZnSO_3 + 1{\cdot}5H_2O$$

$$3ZnSO_3 \longrightarrow ZnO.2ZnSO_3 + SO_2$$

(iii) at temperatures $\geqslant$ 320°,

$$ZnO.2ZnSO_3 \longrightarrow 3ZnO + 2SO_2$$

The concentration of sulphate sulphur did not exceed 5% of the total sulphur content in the decomposition products in dry air. The decomposition of $ZnSO_3$ was examined kinetically[140] at constant temperature between 270-300° and found to be first order with an activation energy of 26.7 kcal/mole.

Pechkoyskii and Ketov[136] have reported that $CdSO_3$ decomposes in argon at 467-581° according to:

$$CdSO_3 \longrightarrow CdO + SO_2$$

$$SO_2 + 2CdSO_3 \longrightarrow 2CdSO_4 + S$$

$$2CdO + 3S \longrightarrow 2CdS + SO_2$$

and at 765-837° and 871-904°

$$3CdSO_4 + CdS \longrightarrow 4CdO + 4SO_2$$

whilst Cola and Tarantino[139] found that up to 600° dissociation takes place to give the oxide and sulphur dioxide with the formation of only minor quantities of sulphide and sulphate. More recently,[141] in results of decomposition under argon, the thermograms indicate dehydration at 175°,

$$4CdSO_3 \longrightarrow CdS + 3CdSO_4 \text{ at } 217°,$$

$$3CdSO_3 \longrightarrow 2CdO.CdSO_3 + 2SO_2 \text{ at } 415^{\circ},$$

and total decomposition of $CdSO_3$ at 517° presumably to the oxide. These reactions also occur in air but are paralleled by oxidation of the $CdSO_3$. Aerial oxidation also complicated earlier work.[2]

Thermal decompositios of $MnSO_3$[2,136] and $Cu_2SO_3CuSO_3.2H_2O$,[2,48] in a variety of atmospheres, have been studied. The thermal decomposition products of $MnSO_3$ are reported to be sulphur dioxide, MnS and $MnSO_4$ up to 300°.[139] At higher temperatures (ca. 420°) large amounts of Mn_3O_4 are formed.

The thermal decompositions of a number of cobalt(III) complexes have been studied[54,65] and it has been shown that $[Co(SO_3)(NH_3)_5]Cl$ decomposes at 150°, with initial loss of $4NH_3$ followed by NH_4Cl. At 360° the residue is $CoSO_3$ with a very small quantity of NH_4Cl. Thermogravimetric curves are reported[54] for the decomposition of $Na_3[Co(SO_3)_2(mg)_2]H_2O$, $Na_3[Co(SO_3)_2(dmg)_2]12H_2O$, $(NH_4)_3[Co(SO_3)_2(mg)_2]5{\cdot}5H_2O$ and $(NH_4)_3[Co(SO_3)_2(dmg)_2]2H_2O$.

10. Structural Properties

The structural properties of sulphites have been investigated in a variety of ways depending upon the structural problem to be solved.

(a) Spectroscopic properties

Several infrared spectral studies have been undertaken mainly in an effort to determine the symmetry of the sulphite group in individual sulphito-complexes and through this the mode of bonding to the metal. The sulphite-group may be monodentate, bidentate or polydentate and may bond through sulphur or oxygen or both.

The sulphite ion has C_{3v} symmetry giving rise to four infrared and Raman active modes[142,143] ν_1(symmetric stretch), 970 cm^{-1}, ν_3(asymmetric stretch), 930 cm^{-1}, ν_2(symmetric bend), 630 cm^{-1}, ν_4(asymmetric bend), 480 cm^{-1} (Fig.2.1). For dimethylsulphoxide complexes bonded through sulphur the S-O stretching frequency is expected to increase due to an increase in $p\pi \rightarrow d\pi$ bonding from oxygen to sulphur and conversely if bonded through oxygen.[144]

If bonded through sulphur the sulphite group will maintain its C_{3v} symmetry and there will be no splitting of ν_3 (asymmetric stretch). On the other hand if bonded through oxygen the symmetry would be lowered to C_s and three stretching vibrations would then be expected, two due to removal of the degeneracy of ν_3.[15]

On this basis and the possible structures proposed by Sidgwick[145] for bidentate groups, Newman and Powell[15] classified the sulphito-complexes in the following groups: (a) double sulphites, (b) complexes with monodentate sulphito-groups, (c) complexes with bidentate sulphito-groups. They found that in the monodentate sulphito-complexes of Hg^{II}, Pd^{II}, Pt^{II}, Co^{III} and Rh^{III} such as $[PdSO_3(NH_3)_3]$ and $[Co(NH_3)_5SO_3]Cl$, two strong peaks are observed, one near 960 cm^{-1} which they assigned to ν_1 and a broad peak (1050-1150 cm^{-1}) assigned to ν_3. They concluded that the move of ν_3 to higher frequencies indicated M-S bonding. A number of other studies[146-149] of unidentate sulphito-complexes of Ir^{III}, Pt^{II}, Co^{III} and Rh^{III} have shown similar changes in stretching frequencies and the same conclusions have been drawn. Only for $Tl_2[Cu(SO_3)_2]$,[132] in which three peaks have been noted for the S-O stretching vibrations, two of which are at lower frequencies than for SO_3^{2-} is it suggested that co-ordination takes place through oxygen.

Because there was no shift in the fundamental frequencies for compounds of the type $(NH_4)_2M(SO_3)_2.nH_2O$ (M = Mg, Zn, Cd, Fe, Mn, Co, Ni) and NH_4CuSO_3 compared with Na_2SO_3, and only four fundamental vibrations were found, Newman et al., concluded that these sulphites were double salts. The crystal structure of NH_4CuSO_3[9,10] has recently been determined and shows that Cu^I is tetrahedrally co-ordinated by one sulphur and three oxygen atoms of four different sulphite groups. Thus the sulphur and three oxygen atoms of each sulphite group are co-ordinated to metals and their symmetry is little changed from that of the sulphite ion. All complexes classed as double sulphites may consequently be considered as containing similarly co-ordinated sulphite groups.

Complexes containing apparently bidentate sulphito-groups such as $Na_3[Co(SO_3)_3]4H_2O$ and $K_3[Rh(SO_3)_3]2H_2O$ show four absorptions (ν_1 and ν_3)[15,150] one of which is probably an overtone,[15] indicating a reduction in symmetry of the sulphite group from C_{3v} to C_s as stated previously. From a consideration of the structures proposed for bidentate groups[145] and bridging groups (Fig.2.2), Newman et al. doubted whether infrared spectroscopy could differentiate between structures (I), (III) and (IV), structure (II) being sterically improbable. The compounds $K_3[Rh(SO_3)_3]$ and $(NH_4)_3[Rh(SO_3)_3]$ show three complex absorption bands of about the same intensity in the region expected for ν_1 and ν_3, which suggest a reduction in symmetry from C_{3v} to C_s and bidentate or bridging sulphito-groups.[149] The infrared spectra cannot distinguish between these two possibilities. However the same workers[151] report that the infrared spectra of the compounds $Na_3[Co(SO_3)_3]4H_2O$, $K_3[Rh(SO_3)_3]$ and $(NH_4)_3Rh(SO_3)_3$ support a bridging structure, since there is no reduction of stretching frequencies compared with the sulphite ion and thus structures (I) and (II) are not possible. Examples of each of the three types of spectra, taken from the work of Newman and Powell[15] are given in Tables 2.1, 2.2 and 2.3.

The infrared spectra of a number of sulphites of the type $M_a(SO_3)_b.nH_2O$ have been determined[142,152] and it is suggested that the sulphite groups have C_{3v} symmetry. The infrared spectra of individual sulphites of this kind have also been reported[136,137,153,4] in various detail associated with the identification of products in thermal decomposition[136,137] and the formulation of particular species, e.g. to show that the red compound previously reported as $CuSO_3.0.5H_2O$[2] was in fact a mixture of $Cu_2SO_3CuSO_3.2H_2O$ and metallic copper.[4]

More recently the spectrum of cis-$NH_4[Co(SO_3)_2en_2]$ has been reported,[154] and the spectra of $Pd(dien)SO_3$, $Pd(Et_4dien)SO_3$ ($Et_4dien = Et_2NCH_2CH_2NHCH_2CH_2NEt_2$) and $Pd(H_2O)_2SO_3$[119] interpreted as showing that the compounds contain monodentate sulphur bonded sulphito-groups. Baranovskii et al[66] have determined

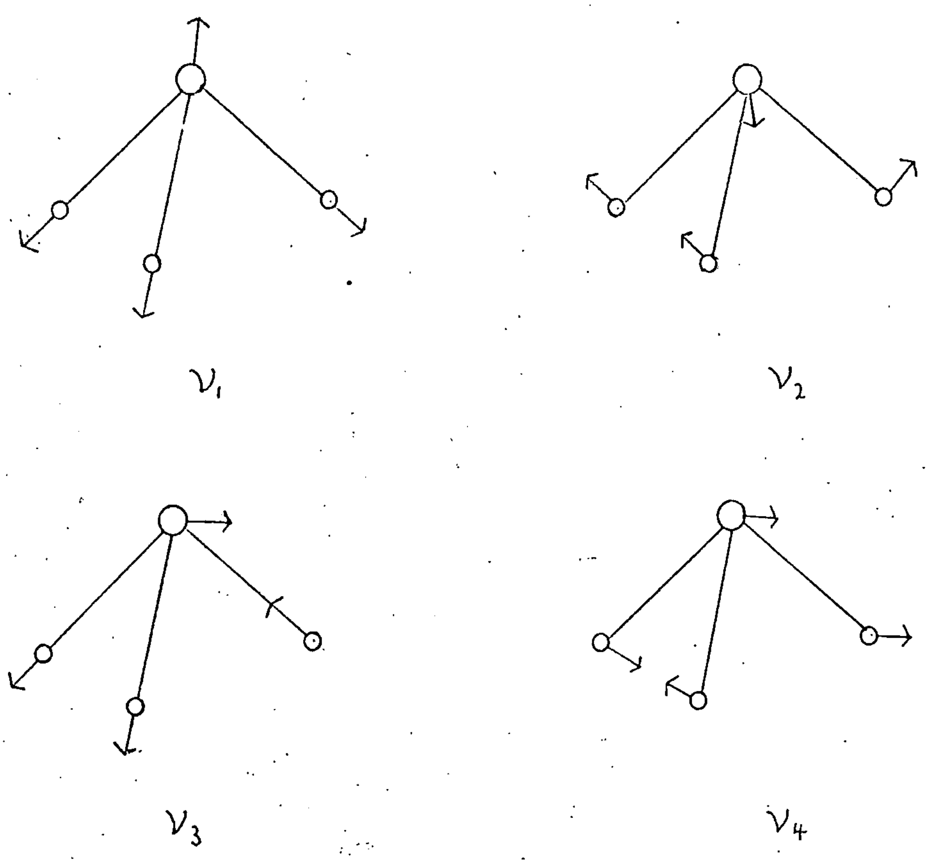


Fig.2.1 Normal modes of vibration of the sulphite ion

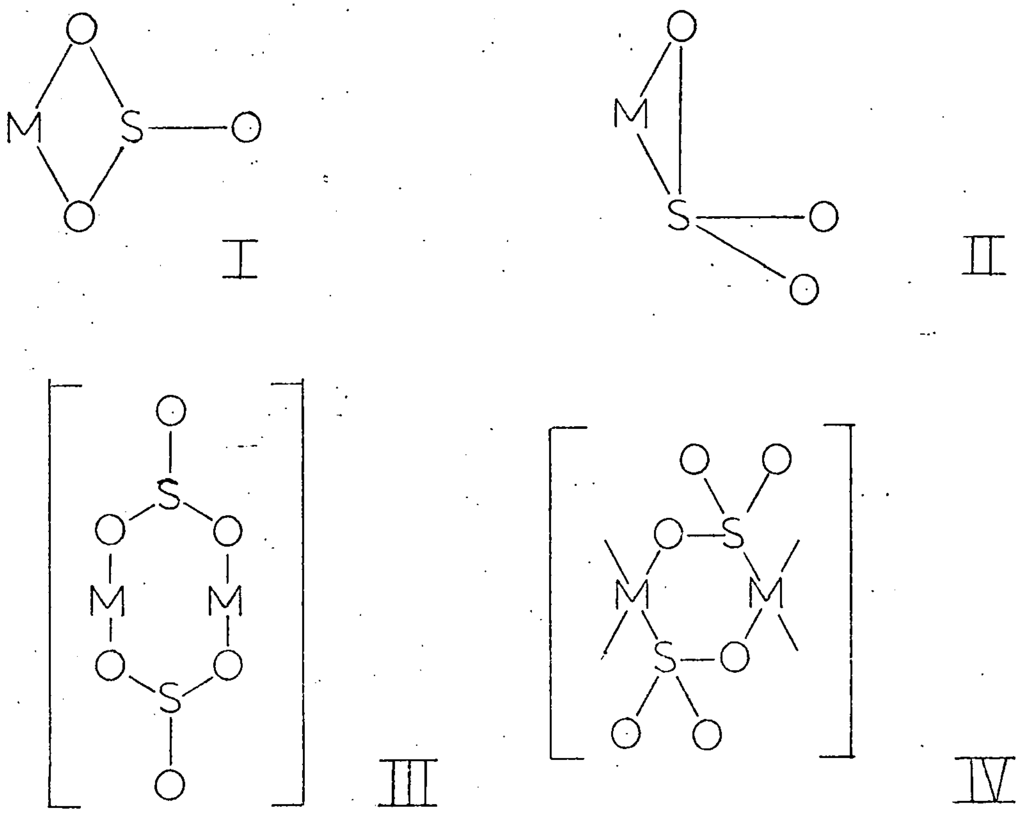


Fig.2.2 Possible structures for bidentate sulphito-groups

Table 2.1

Compounds of the type $M_2^{I}M^{II}(SO_3)_2$ and $M^{I}CuSO_3$ recorded in the region 2000-400 cm^{-1}

NH_4CuSO_3	963s		669m		497ms
$(NH_4)_2Fe(SO_3)_2 2H_2O$	959sh	895vs	663m		487w
$(NH_4)_2Zn(SO_3)_2 2H_2O$	952-857s		650m		486m
$(NH_4)_2Mn(SO_3)_2$	964sh	907vs	655w		482w
$(NH_4)_2Co(SO_3)_2 2H_2O$	957sh	890vs	672mw	616w	490m
$(NH_4)_2Ni(SO_3)_2 2H_2O$	958sh	880vs	674w	632m	495w

Absorption peaks due to NH_4^+ and H_2O are omitted.

Table 2.2

Bidentate or bridging sulphito-complexes recorded in the region 2000-400 cm^{-1}

$Na_3[Co(SO_3)_3]4H_2O$	1641m	1129vs	1070vs	1000s	968vs		661m		520mw		
$K_2[Pt(SO_3)_3]2H_2O$	1646m	1166vs	1092s	1036s	977s						
$K_3[Rh(SO_3)_3]2H_2O$	1638s	1157s	1113s	1058vs	939s		690m		647ms	527w	
$K_2Pd(SO_3)_2$		1157s	1099s	1056s	933s	904s	664m	637m	563m	516m	497w

Table 2.3

Monodentate sulphito-complexes recorded in the region 2000-400 cm^{-1}

$(NH_4)_2[Hg(SO_3)_2]$			1413 vs					1117 vs	1023 w	967 s						643 vs				514 s		
$Co[Co(NH_3)_3(SO_3)_3]$	1627 m			1421 m	1350 m	1326 m		1107 s	1053 s	1008 s	958 s		849 w			643 m				515 w		
$PdSO_3(NH_3)_3$	1618 w		1559 w		1297 m	1275 m		1157 w	1091 s	1074 s	983 s	913 w	838 w	813 w		642 s			524 m	510 m	493 w	471 w
Cis-$K_2[Pd(SO_3)_2(NH_3)_2]$	1724 m	1698 m				1266 m		1093-1056 s		995 m	977 w	958 s	831 w	792 w	771 m	655 m	622 m	568 w	522 w	506 w		
Trans-$K_2[Pd(SO_3)_2(NH_3)_2]$	1610 m				1299 m	1273 m	1250 m	1074 s	1056 s	986 s		958 w	837 w	812 w		646 s			525 w	511 w		
$K_3[Rh(SO_3)_3(NH_3)_3]3.5H_2O$	1629 m				1288 w	1250 m		1107 s		1017 w	954 s		800 w			638 m			524 m			
$Tl_2Cu(SO_3)_2$										989 m	902 m		862 m			673 m	602 w			506 w	460 w	

the spectra of a number of new cis-diethylene diamine complexes of iridium. The splitting of the ν(SO) stretching vibrations in bis-sulphito-compounds is reported to be due to the cis-positions of the sulphito-groups.

Visible and ultra violet spectra have also been studied in an effort to determine structure. An early study of cobalt(III) complexes was that of Kiss and Czegledy.[155] Visible and ultra violet spectra of the brown dihydrate of $Na[Co(NH_3)_4(SO_3)_2]$ and the yellow tetrahydrate of its isomer.indicate that the sulphite group is co-ordinated to the cobalt by the sulphur lone pair of electrons and that the brown and yellow forms are the trans- and cis- forms respectively.[156] For complexes of the type $[CoA_4X_2]$ the trans-isomer has a large ϵ_{max} if X has more hyperchromic and trans-pairing effects than A. This is the case with $Na[Co(NH_3)_4(SO_3)_2]$ where for the first band of the trans- and cis-isomers respectively, $\nu = 66.6 \times 10^{13}$ cycles/sec^{-1} and 65.9×10^{13} sec^{-1} and log ϵ = 2.32 and 2.26.[157]

The spectrochemical series for cobalt(III) complexes has been redetermined by Shimura and Tsuchida[158] who determined the visible and ultra violet absorption of eighty six complexes including sulphito-complexes. Visible and ultra violet spectra have been determined in a number of other studies to assess the ligand properties of the sulphito-group.[65,119,150]

Absorption spectra in other regions of the electromagnetic spectrum have been studied e.g. the microwave spectrum of $Cr_2(SO_3)_3$[159] and the X-ray absorption spectra of $(NH_4)_2[Pt(SO_3)_2]H_2O$, $(NH_4)_2[PtCl_3(HSO_3)]$ and $(NH_4)_2[Pt(NH_4SO_3)_4]$.[160]

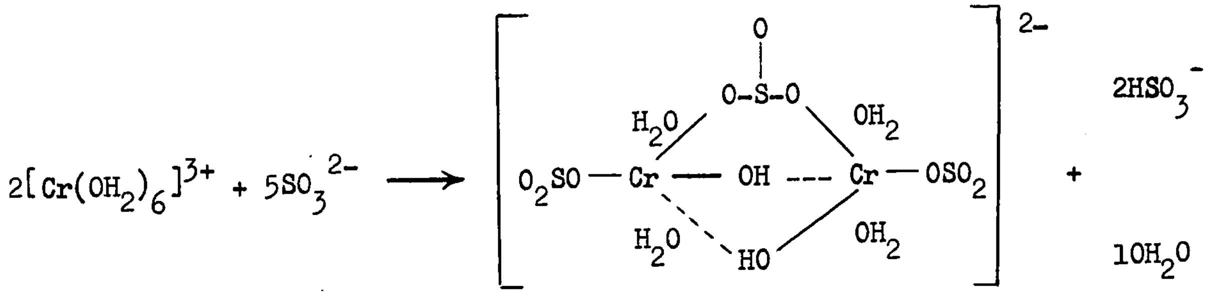
(b) Miscellaneous Structural Studies

A variety of structural problems have been investigated by studying chemical and/or physical properties. Earwicker[63] on examining sulphito- and sulphite-ammine complexes of palladium found that they showed strong similarities in their chemical properties to known thiosulphato, but little to sulphato-complexes, and concluded that they probably all contain sulphur to metal bonds. He also tentatively suggested that the anions of the disulphitopalladates are polymeric. When $[Pt(SO_3)_2(NH_3)_2]^{2-}$ was treated with ethylenediamine, $[Pt(SO_3)_2en]^{2-}$ was formed indicating a <u>cis</u>-configuration for $[Pt(SO_3)_2(NH_3)_2]^{2-}$.[53] As a result of oxidation-reduction between the compound reported by Ray[67] as $K_6Co_2(SO_3)(CN)_{10}$ and ammoniacal silver salts, Cambi and Paglia concluded that the complex corresponds to $K_6\ (CN)_5Co^{III}S^{II}O_2Co^{III}(CN)_5$.[68] The reaction of Na_2SO_3 with <u>trans</u>-$[Copn_2Cl_2]Cl$ (pn = propylenediamine) gives $[\ Copn_2SO_3]^+$, in which the sulphito-group acts as a bidentate group,[55] as shown by the fact that its rotatory dispersion curve is similar to that of <u>cis</u>-$[Coen_2SO_3]^+$ and that $[Coen_2SO_3]^+$ could be dehydrated without change in colour or loss of optical activity. In a consideration of the reactions:

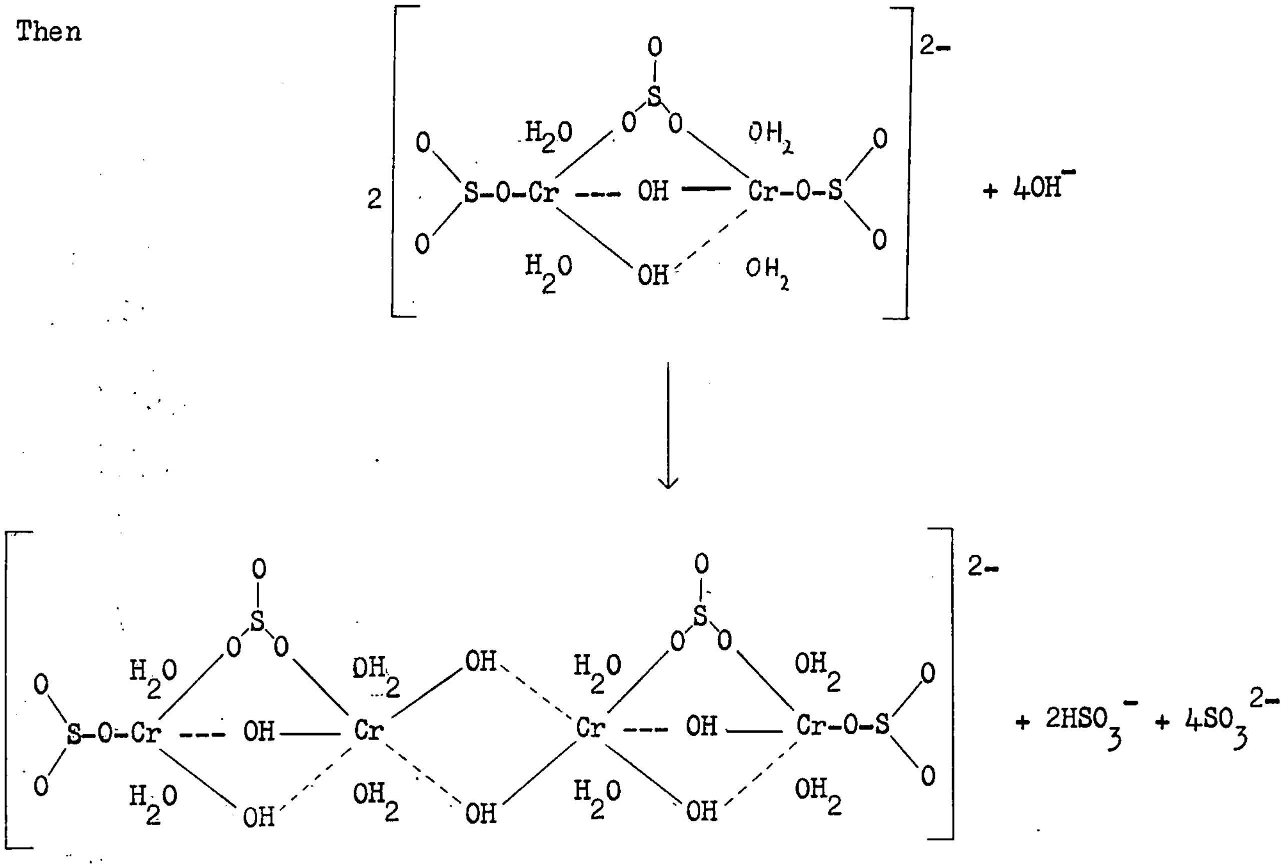
$$\underline{cis}\text{-}NH_4[Co(NH_3)_4(SO_3)_2] \xrightarrow{en} \underline{cis}\text{-}NH_4[Coen(NH_3)_2(SO_3)_2] \xrightarrow{HCl} [Coen(NH_3)_2Cl_2]\,Cl$$

it is believed that aqueous hydrochloric acid gives green <u>trans</u>- $Coen(NH_3)_2Cl_2\ Cl$ since $[Coen(NH_3)_2(SO_3)_2]$ when treated with hydrogen chloride in absolute alcohol gives nearly pure violet <u>cis</u>-$[Coen(NH_3)_2Cl_2]Cl$.[161]

Studies of the reaction between Na_2SO_3 and a chromium(III) salt in aqueous solution[162,163] using conductometric titrations, light absorption measurements and determination of particle size by dialysis have led to the elucidation of the structures of sulphito-chromium(III) complexes and their mechanism of condensation to polynuclear complexes. The following is suggested:



Then



The absolute configuration of $NH_4[Co(l\text{-}pn)(NH_3)_2(SO_3)_2]$ has been investigated[164] by determination of circular dichroism and the absorption spectrum. Magnetic properties have also been used in efforts to determine structures e.g. the magnetic moments of the compounds $[Ni(N_2H_4)_a]SO_3.nH_2O$ have all been determined[165] as have the magnetic properties of decacyano dicobaltate(III) complexes[166] containing the complex ion $[\{(CN)_5Co\}_2SO_2]^{6-}$ previously thought to be $[\{(CN)_5Co\}_2SO_3]^{6-}$.

(c) Crystallographic Studies

The external features of crystals of a few sulphites were investigated by early workers.[2] For example, the axial ratios of $NH_4[Co(NH_3)_4(SO_3)_2]$ have been determined as a:b:c = 0.859:1:0.534 and $\beta = 111^\circ\ 23'$. The microscopic observation of the crystalline product of the reaction of sulphite ions with $[Co(NH_3)_6]Cl_3$, $[Co(NH_3)_5Cl]Cl_2$, $[Co(NH_3)_5H_2O]Cl_3$, $[Co(NH_3)_6](NO_3)_3$ and $[Co(NH_3)_4CO_3]_2SO_4$ has been investigated[167] for use in the detection of sulphite ion. Polymorphs have been found,[33,89] e.g. $NiSO_36H_2O$ crystallises in the hexagonal and tetragonal systems with densities 2.027 and 1.825/cm^3 respectively. Cadoret[10] has studied the growth of crystals of $NiSO_3.6H_2O$ in supersaturated solutions. The trigonal prisms formed at high supersaturation are considered to result from an interaction with the solvent. Photomicrographs have been obtained of crystals of some copper sulphites.[48] More commonly X-ray diffraction patterns have been obtained[33,34,48,49] in the identification of sulphites or in the determination of crystal structures.

The crystal structures of a number of sulphites have been fully determined by X-ray diffraction methods. An early determination was that of Klasens et al.[1] who found that the hexahydrates of nickel and cobalt consisted of units of octahedral $[M.6H_2O]^{n+}$ groups at the corners of rhombohedrons with SO_3 groups at the centres.

Interest in the shape of the sulphito-group and its mode of bonding to the metal in complexes and in simple sulphites was stimulated by the determination and discussion of infrared spectra in the early 1960's. A number of calculations of force constants, bond order and bond lengths of the sulphite ion[12,168,169] and co-ordinated sulphite group,[170] and a study of the dependence of the force constants on the interatomic distance of the S-O bond have also been reported.[171]

Grand-Jean et al[6,7] found that the asymmetric structure of $[Ni(H_2O)_6]\ SO_3$ is due to hydrogen bonding between $SO_3^{\ 2-}$ and the water molecules of $[\ Ni(H_2O)_6]^{2+}$. The principal interatomic distances are S-O, 1.45 ± 0.03; $Ni-(H_2O)_I$ 2.05 ± 0.02; $Ni-(H_2O)_{II}$ 2.11 ± 0.02. The O-S-O valence angles were determined as 95°26'. Two types of water molecule are found. One is 2.54 or 2.89Å from sulphite oxygen and the other distance is always 2.54Å. A re-investigation of this structure[5] has shown the S-O bond length to be 1.536 ± 0.007Å and the O-S-O angle to be 103.6 ± 0.6°, markedly different from the previous determination.[6,7] The crystal structure can be considered to be composed of two separate crystallographic entities, namely the sulphite ion which has C_{3v} symmetry and the $[Ni(H_2O)_6]^{2+}$ complex ion in which the co-ordination round the Ni^{2+} is that of a deformed octahedron which has three equivalent Ni-O bonds of length 2.043 ± 0.008Å and three of length 2.076 ± 0.008Å in general agreement with the previous determination. There is three dimensional linking of these ions by hydrogen bonds.[5]

The crystal structure of the sulphites of copper, $Cu_2SO_3CuSO_3.2H_2O$[8] and NH_4CuSO_3[9,10] have been investigated. In $Cu_2SO_3CuSO_3.2H_2O$ the co-ordination around the copper(I) atoms is distorted tetrahedral, formed by three oxygen atoms and one sulphur atom with Cu(I)-O(S) distances of 2.11-2.14Å. The arrangement round the copper(II) atoms is the distorted (4 + 2) octahedral one formed by two "water" oxygen atoms, with $Cu-O(H_2O)$ lengths 1.92Å and four sulphito-oxygens at distances 2.03Å and 2.47Å. The dimensions of the sulphito-group, the distorted copper(II) octahedron, the copper(I) tetrahedron and $Cu-SO_3$ arrangement are shown in Fig.2.3, 2.4, 2.5 and 2.6 respectively.

The structure of NH_4CuSO_3[9,10] can be described in terms of SO_3 trigonal pyramids and CuO_3S tetrahedra. The tetrahedral co-ordination around copper is provided by three oxygen atoms and one sulphur atom of four sulphito-groups. The CuO_3S tetrahedra and SO_3 pyramids form double layers which are held together by the ammonium ions. The distances and angles are nearly the same as those found in $Cu_2SO_3CuSO_3.2H_2O$ for $Cu(I)O_3S$ tetrahedra and SO_3 pyramids.

The structure of Ag_2SO_3[38] also consists of pyramidal SO_3^{2-} groups each of which is bonded to one silver atom. The co-ordination around one of the two nonequivalent silver atoms is tetrahedral, consisting of three oxygen atoms from different SO_3^{2-} groups and one sulphur atom. The other silver atom is surrounded by a very distorted tetrahedron comprising four oxygen atoms each from a different sulphite group. The sulphite groups are all crystallographically equivalent. The Ag-S distance (2.465 ± 0.008A) shows that π-

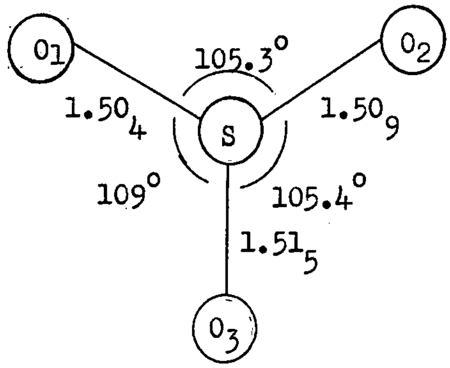


Fig. 2.3

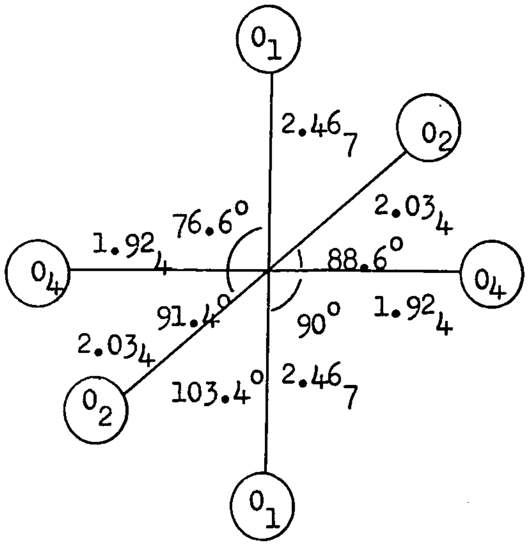


Fig.2.4

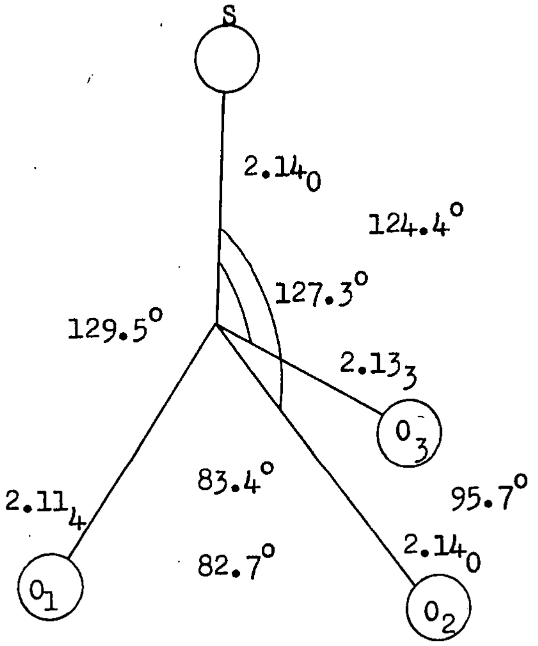


Fig.2.5

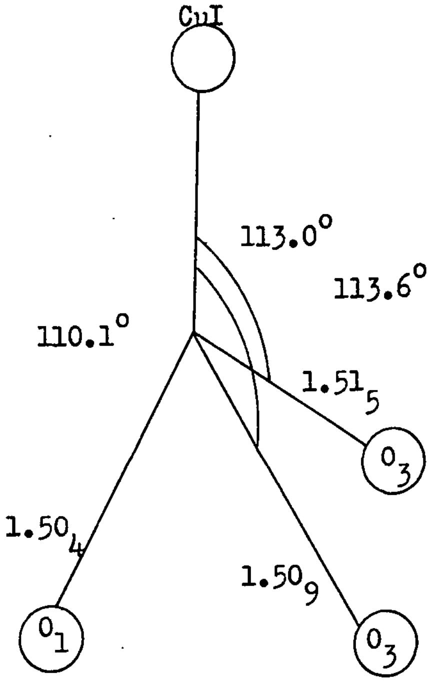


Fig.2.6

The dimensions of the sulphito-group, the distorted copper(II) octahedron, the copper(I) tetrahedron and Cu-SO_3 arrangement in $Cu_2SO_3CuSO_3.2H_2O$

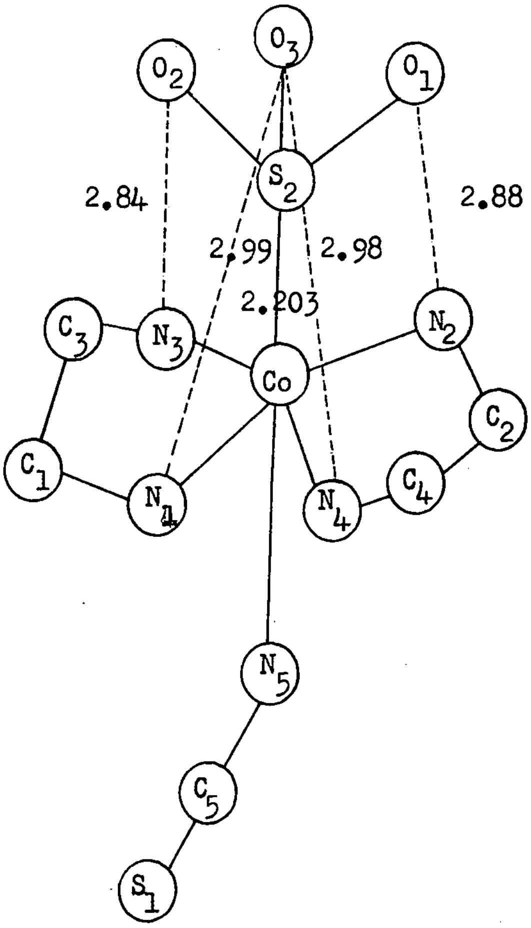
bonding between Ag and S may exist as the bond length is 0.10Å shorter than the sum of Pauling's covalent radii.

The crystal structure of $Pd(NH_3)_3SO_3$[16] shows square planar co-ordination around the Pd atom, the sulphite group being bonded through sulphur and keeping the shape of a trigonal pyramid. The Pd-S distance is 2.254 ± 0.006Å, suggesting a strong Pd-S bond with π character, and, in agreement with the infrared spectrum, the S-O bonds in the complexed sulphite group are stronger than in the sulphite ion. It is possible that O-H-N hydrogen bonds are present.

Investigation of the crystal structure of $[Co(en)_2SO_3NCS]2H_2O$[172] has indicated the general molecular shape shown in Fig.2.7. The difference of the O-S-O bond angle from that in the sulphite ion is due largely to the effect of non-bonded repulsions. There is no evidence of a structural trans-effect. The molecules are held together by hydrogen bonds involving the water molecules and by hydrogen bonds between sulphur atoms of the SCN group and an ammine group of another molecule, i.e. there is a three dimensional bonding network which accounts for the low solubility in non-polar solvents.

The latest determination is that of the dark brown form of $NH_4[Co(SO_3)_2(NH_3)_4]$ (Fig.2.8).[173] The differences in Co-N distances are said to be due to the trans-effect of the sulphite group.

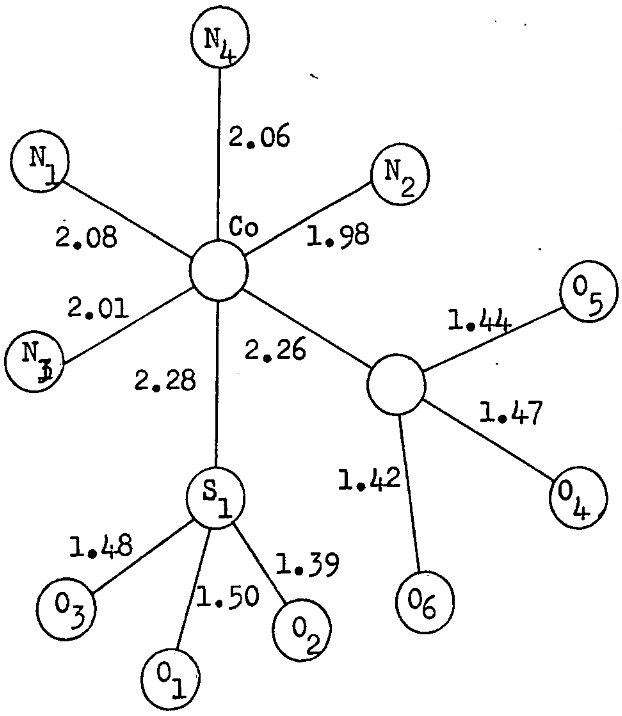
Baggio and Becka[5] have listed the S-O distances and O-S-O angles for sulphites in compounds investigated up to 1969, and these with those of Na_2SO_3,[13] Ag_2SO_3[38] and $NH_4[Co(SO_3)_2(NH_3)_4]3H_2O$[173] are listed in Table 2.4. The non-transition metal sulphites are included for comparison. Average bond lengths and angles are quoted. In sulphite groups bonded to the metal only through sulphur the S-O bond would be expected to shorten and the O-S-O angle widen due to lessening of non-bonded repulsions. This appears to be the case. When bonding to the metal is through both sulphur and oxygen there appears to be little change in dimensions from that of the free ion.



The angles at the cobalt atom are close to 90°

Fig.2.7

The general molecular arrangement of $[Co(en)_2SO_3NCS]2H_2O$ omitting the water molecules.



O_1-S_1-O_2 106°

Fig.2.8

General arrangement of atoms around Co and dimensions of co-ordinated sulphito-groups in $[Co(SO_3)_2(NH_4)_4]^-$

Table 2.4

Crystallographic Data for Sulphites

Compound	(S–O) Å	$O-\hat{S}-O$
$NiSO_3.6H_2O$	1.536(7)	103.6(6)
$(NH_4)_2SO_3H_2O$[174]	1.524(6)	104.8(4)
Ag_2SO_3	1.516(24)	104.6(1.3)
$Cu_2SO_3CuSO_3.2H_2O$	1.509(16)	106.9(8)
NH_4CuSO_3	1.506(12)	105.3(7)
Na_2SO_3	1.504(3)	105.69(17)
$PdSO_3(NH_3)_3$	1.50 (2)	108.6(1.1)
$Pd(SO_3)_2(NH_3)_2Na_2.6H_2O$ [5]	1.478(16)	108.6(9)
$Co(en)_2SO_3NCS.2H_2O$	11.485(12)	110.3(7)
$NH_4[Co(SO_3)_2(NH_3)_4]3H_2O$	1.45	109.5

CHAPTER 3

EXPERIMENTAL WORK

Introduction

The preparations and measurements recorded in this chapter are those for the following transition metal sulphites: $Ni(OH)_2NiSO_3.\sim 12H_2O$, $NiSO_3,6H_2O$, $MnSO_3.3H_2O$, $CoSO_3.3H_2O$, $Cu_2SO_3CuSO_3.2H_2O$, $ZnSO_3.2.5H_2O$, $(NH_4)_2Ni_3(SO_3)_4.18H_2O$, $(NH_4)_2Ni(SO_3)_2$, $(NH_4)_2Mn(SO_3)_2$, $(NH_4)_2Zn(SO_3)_2$, NH_4CuSO_3, $(NH_4)_7Cu(SO_3)_4.5H_2O$ and materials containing ammonium, chromium and sulphite ions of variable composition.

All the sulphites of the type $M_a(SO_3)_b.nH_2O$, apart from $MnSO_3.3H_2O$, were prepared by the acid and carbonate method after preliminary investigations showed mixed materials were obtained by metathetical routes to $CoSO_3.3H_2O$ and $Cu_2SO_3CuSO_32H_2O$. $MnSO_3.3H_2O$ was prepared by metathesis, as the product on analysis was found to agree with the above formulation, and because the method was rapid. The carbonate and acid method was used also but found to have no advantage over metathesis. In general the compounds $(NH_4)_2M(SO_3)_2.nH_2O$ were prepared by the addition of an aqueous solution of NH_4HSO_3 to an aqueous SO_2 solution of the metal salt.

In preliminary investigations, in which the compounds were prepared in air, some oxidation to sulphate was found. This was prevented by washing and drying the compounds under nitrogen, using de-aerated distilled water, de-aerated alcohol and de-aerated ether.

A number of measurements recorded here have been published previously, but as there is some doubt in the literature as to composition, bonding, and thermal decomposition of these sulphites, these measurements were repeated along with new studies in an attempt to clarify the situation.

A. Experimental

(a) Starting materials

The metal salts used were A.R. grade or prepared from A.R. grade materials e.g. cobalt carbonate was precipitated by adding A.R. sodium hydrogen carbonate solution to A.R. cobalt(II) nitrate solution and the precipitate was well washed with distilled water. The ammonium hydrogen sulphite and ammonium sulphite solutions used were prepared using A.R. grade concentrated ammonia solution and B.D.H. liquified sulphur dioxide. 'White spot' nitrogen was used in both the drying operations and as the inert atmosphere in the thermal gravimetric analyses.

(b) Spectra

Infra-red spectra in the range 4000-400 cm^{-1} were recorded using a Grubb-Parson spectromaster. Far infra-red spectra in the range 400-200 cm^{-1} were recorded using a Grubb-Parson DM2 or Perkin-Elmer 457. Diffuse reflectance spectra in the region 1000 mμ - 370 mμ were recorded on a Unicam SP500. Mass spectra and infra-red spectra of the decomposition products of $(NH_4)_2Mn(SO_3)_2$ and $(NH_4)_2Co(SO_3)_2H_2O$ were recorded using an A.E.I. MS9 instrument and Perkin-Elmer 157.

(c) Thermal gravimetric analyses

These were carried out using either a Stanton thermobalance or a Stanton recording balance, both with the modifications for passage of nitrogen around the heated crucible(s).

(d) X-ray diffraction photographs

These were recorded using a Debye-Scherrer powder camera with a Phillips X-ray generator. Cu radiation was used with a nickel filter.

(e) Analyses

All analyses were carried out using standard methods. Procedures adopted for the following elements and groups were those described by Vogel[175] with modifications where necessary: SO_3^{2-}, III, 118 p.354; NH_4^+, III, 18 p.247, - the direct method was employed, using a suitable weight of the ammonium compound, which was added directly to a flask before addition of sodium hydroxide solution; Ni, IV, 12 p.417; Mn, IV, 35 p.468; Co, IV, 33D p.461 and 463 - the cobalt sulphite was oxidised to sulphate using hydrogen peroxide, the excess of which was decomposed by boiling; Cr, III, 70 p.297; Cu, III, 105 p.343 with the included modification of dissolution of the copper compounds in dilute nitric acid by boiling; Zn, III, 145 p.379, the zinc compounds being dissolved in dilute sulphuric acid (approximately 1M) and the solutions boiled for 10-15 minutes to remove any sulphur dioxide present.

B. Preparations

(1) Preparation of sulphites of the type $M_a(SO_3)_b.nH_2O$

(a) Preparation of $NiSO_3.6H_2O$

Nickel carbonate (4 g.) was suspended in distilled water (40-50 ml.) and sulphur dioxide passed through until solution was effected. Any remaining solid material was removed by filtration from the green solution. Removal of excess sulphur dioxide, at ambient temperature, using a stream of nitrogen, produced green crystals of $NiSO_3.6H_2O$ which varied in shade according to their size. The mixture was then filtered, washed with de-aerated distilled water (50 ml.), de-aerated ethanol (25 ml.) and de-aerated ether (200 ml.) under nitrogen and dried by rapid passage of nitrogen under suction for 15-20 minutes. The crystals were immediately checked for sulphate content by the $BaCl_2$ test. In all cases this proved negative. The crystals were stored before use under nitrogen.

All the other simple sulphites with the exception of $MnSO_3.3H_2O$ were prepared in a similar manner, using the same weights and volumes, with the following modifications for the individual sulphites.

(b) Preparation of $Cu_2SO_3.CuSO_3.2H_2O$

The green solution, formed by passage of sulphur dioxide into an aqueous suspension of basic copper carbonate, was warmed gently to 40° when rapid precipitation took place. This was essential, as passage of nitrogen through the solution precipitated a mixture of yellow and red species, and the precipitate formed on allowing the solution to stand at room temperature exposed to air, always contained sulphate which could not be removed by washing.

(c) Preparation of $CoSO_3.3H_2O$

Precipitation of this cobalt complex was effected from the resultant red solution by heating almost to boiling whilst nitrogen was passed through. Precipitation of $CoSO_3.3H_2O$ was not obtained over a long period of time (1 day) at ambient temperatures.

(d) Preparation of $ZnSO_3.2{\cdot}5H_2O$

The method of preparation was identical to that for $NiSO_3.6H_2O$.

(e) Preparation of $MnSO_3.3H_2O$

$Na_2SO_3.7H_2O$ (2·60 g., 0·01 mole) in de-aerated distilled water (20 ml.), was added slowly with stirring to $MnCl_2.4H_2O$ (1·98 g., 0·01 mole) in de-aerated distilled water (20 ml.), at room temperature. The white crystalline precipitate formed was immediately washed and dried in the same way as $NiSO_3.6H_2O$. It was not possible to obtain this compound free of sulphate. However the samples used only contain traces of sulphate as detected by the $BaCl_2$ test.

(2) Preparation of sulphites of the type $(NH_4)_2M(SO_3)_2.nH_2O$ (M = Mn, Co, Ni, Zn)

(a) Preparation of $(NH_4)_2Ni(SO_3)_2.xH_2O$

The green solution, formed by dissolving $NiCl_2.6H_2O$ (2·38 g., 0·01 mole) in distilled water (15-20 ml.), was saturated with sulphur dioxide and added to yellow NH_4HSO_3 solution, prepared by saturating a solution of concentrated ammonia (20 ml.), in distilled water (10 ml.), with sulphur dioxide. The yellow solution formed was evaporated, under reduced pressure at 56°C, until crystals started to separate. The mixture was then allowed to stand for 24 hours to allow more crystals to form. The crystals were washed and dried in the same way as the simple sulphites $M_a(SO_3)_b.nH_2O$, and tested for the presence of chloride and sulphate ions by the usual simple tests. Samples were stored before use under nitrogen.

(b) Preparation of $(NH_4)_2Mn(SO_3)_2$

This preparation was carried out in the same way as the corresponding nickel compound, except that evaporation was continued until an appreciable quantity of crystals (1-2 g.) had formed.

(c) Preparation of $(NH_4)_2Co(SO_3)_2.H_2O$

The method used was similar to that for the corresponding nickel compound, except that, as with the manganese compound, evaporation was continued until an appreciable quantity of crystals had formed. $Co(NO_3)_2.6H_2O$ was used in place of the chloride, as the Analar reagent grade of the chloride was not available. Thus the simple test for the presence of nitrate ions was carried out on the final product. It was noted that, on mixing the reactants, the red colour of the combined solution was similar to that of the original $Co(NO_3)_2.6H_2O$ solution.

(d) Preparation of $(NH_4)_2Zn(SO_3)_2$

Zinc carbonate (1·5 g.) was suspended in distilled water (25 ml.) and the suspension saturated with sulphur dioxide. The solution was then filtered to remove any undissolved solid, and sulphur dioxide again passed through the solution to saturate it, before addition to NH_4HSO_3 solution. The method was then as for the corresponding cobalt and manganese compounds. Only the simple test for sulphate ions was used to test the purity of the product.

(3) Preparation of $(NH_4)_2Ni_3(SO_3)_4.18H_2O$

$(NH_4)_2SO_3$ was prepared by passing sulphur dioxide into aqueous ammonia solution (5 ml. of ammonia solution of S.G. ·880 and 5 ml. of distilled water) until saturated. Then small amounts of ammonia solution (S.G. ·880) were added until the solution was approximately neutral. This solution was then added to $NiSO_3.6H_2O$ in aqueous SO_2 solution, prepared from basic nickel carbonate (8 g.). The mixture was swirled for a few minutes before the green solution deposited light green crystals. A colourless supernatant liquid remained.

(4) Preparation of $(NH_4)_7Cu(SO_3)_4.5H_2O$ and NH_4CuSO_3

(a) Preparation of $(NH_4)_7Cu(SO_3)_4.5H_2O$

Concentrated ammonium sulphite solution was prepared by taking a known volume of ammonia solution (S.G. ·880) and adding one half its volume of distilled water, and then passing into this sulphur dioxide until saturated. A volume, equal to the original volume, of ammonia solution (S.G.·880), was then added.

$Cu(NO_3)_2.3H_2O$ (2·0 g.) in distilled water (25 ml.) was added to ammonium sulphite solution (60 ml.) prepared as above, diluted with distilled water (40 ml.) and the whole was left to stand for 24 hours. Large, colourless, transparent, needle shaped crystals were obtained from the colourless solution. These were washed and dried in the same way as the other sulphites except that only 10 ml. of de-aerated water was used for washing because of the solubility of this compound in water.

(b) Preparation of NH_4CuSO_3

$Cu(NO_3)_2.3H_2O$ solution, of the same strength as in the preparation of $(NH_4)_7Cu(SO_3)_4.5H_2O$, was added slowly with stirring to hot $(NH_4)_2SO_3$ solution (20 ml.), prepared as described previously. The colourless needle shaped crystals which were first formed were dissolved by addition of more $Cu(NO_3)_2 3H_2O$, and the solution became deep reddish-brown in colour before shining colourless platelets were formed. The resultant solution became almost colourless. The crystals were washed and dried in the same way as $NiSO_3.6H_2O$.

(5) Preparation of $Ni(OH)_2 3NiSO_3.{\simeq}12H_2O$

$NiCl_2.4H_2O$ (2·38 g., 0·01 mole) in boiled distilled water (10-15 ml.) was added to Na_2SO_3 (2·60 g., 0·01 mole) in boiled distilled water (20-25 ml.). The light green precipitate formed was washed and dried in a similar way to $NiSO_3.6H_2O$.

(6) Preparation of basic ammonium chromium sulphite

NH_4HSO_3 solution, in twice the quantity used for the preparation of $(NH_4)_2Ni(SO_3)_2$ (see section 2a), was added to $CrCl_3.6H_2O$ (2.7 g.). The procedure was then the same as for the preparation of $(NH_4)_2Co(SO_3)_2.H_2O$.

(7) Preparation of $NiSO_3.2H_2O$

$NiSO_3.6H_2O$ was heated under vacuum at 56° for about 6 hours.

C. General Properties

(a) Colour and Solubility

Table 3.01

Compound	Colour and State	Solubility in water	Solubility in sulphur dioxide solution
$Ni(OH)_2.3NiSO_3.12H_2O$	Light green powder	slightly soluble	soluble
$NiSO_3.6H_2O$	Apple green crystals	sparingly soluble	soluble
$MnSO_3.2H_2O$	White crystals	slightly soluble	soluble
$CoSO_3.3H_2O$	Rose pink crystals	sparingly soluble	soluble
$Cu_2SO_3.CuSO_3.2H_2O$	Red-brown crystals	sparingly soluble	insoluble
$ZnSO_3.2{\cdot}5H_2O$	White crystals	sparingly soluble	soluble
$(NH_4)_2Ni_3(SO_3)_4.18H_2O$	Light green crystals	sparingly soluble	soluble
$(NH_4)_2Ni(SO_3)_2$	Yellow crystals	sparingly soluble	soluble
$(NH_4)_2Mn(SO_3)_2$	White crystals	sparingly soluble	soluble
$(NH_4)_2Co(SO_3)_2.H_2O$	Pink crystals	sparingly soluble	soluble
$(NH_4)_2Zn(SO_3)_2$	White crystals	sparingly soluble	soluble
NH_4CuSO_3	White crystals	sparingly soluble	reacts to form red-brown solid
$(NH_4)_7Cu(SO_3)_4.5H_2O$	White crystals	very soluble giving yellow solution	very soluble
ammonium chromium sulphite	Green powder	slightly soluble	Not investigated

(b) Oxidation

All the sulphite complexes are slowly oxidised in air. The rate of oxidation appears to depend on the size of the particles (crystals), and dryness of the sample. The larger the crystals, and the dryer the sample, the more slowly does oxidation to sulphate take place.

(c) Reactions with dilute acids

All the compounds investigated evolved sulphur dioxide on shaking with dilute hydrochloric acid (2M), and complete solution was obtained, if necessary by heating. The copper compounds first gave a white precipitate with hydrochloric acid, possibly copper(I) chloride, before complete solution was obtained. With dilute nitric and sulphuric acids an accompanying red precipitate, possibly copper metal, was obtained. In the case of nitric acid, this dissolved on boiling.

D. Analyses

Table 3.02

Compound	Found		Theoretical	
	% SO_3^{2-}	% M	% SO_3^{2-}	%M
$Ni(OH)_2.3NiSO_3.12H_2O$	33.2	32.5	33.1	32.4
	33.6	32.8		
	33.8	32.4		
	33.6	32.6		
$NiSO_3.6H_2O$	33.2	23.6	32.4	23.8
	32.5	23.5		
$MnSO_3.2H_2O$*	46.0	32.8	46.8	32.2
	46.3	33.1		
$MnSO_3.3H_2O$*	41.2	28.8	42.3	29.1
	41.0	28.6		
$CoSO_3.3H_2O$	42.0	30.0	41.5	30.3
	42.1	29.9		
$Cu_2SO_3.CuSO_3.2H_2O$		49.0		49.3
		48.9		

Table 3.02 contd.

Compound	Found		Theoretical	
	$\%SO_3^{2-}$	%M	$\%SO_3^{2-}$	%M
$ZnSO_3{\cdot}2{\cdot}5H_2O$	42.2 42.0 42.3 42.1	34.2 34.0 34.4 34.2	42.2	34.3

Compound	$\%SO_3^{2-}$	$\%NH_4^+$	%M	$\%SO_3^{2-}$	$\%NH_4^+$	%M
$(NH_4)_2Ni_3(SO_3)_4{\cdot}5H_2O$	37.9 35.9 36.0 35.4	4.3 4.1 4.1	20.2 20.4 20.6 20.6	37.4	4.2	20.6
$(NH_4)_2Ni(SO_3)_2$	60.2	13.5	22.1	62.8	14.1	23.1
$[(NH_4)_2Ni(SO_3)_2H_2O]$	61.4 61.4 62.5		22.3 22.4	58.7	13.2	21.5
$(NH_4)_2Mn(SO_3)_2$	63.3	14.2	22.0	63.7	14.3	21.9
$[(NH_4)_2Mn(SO_3)_2H_2O]$	63.3 61.8 61.2 59.7 60.2	13.7	21.7	59.5	13.4	20.4
$(NH_4)_2Co(SO_3)_2$	59.1	13.4	21.8	62.9	14.1	23.0
$(NH_4)_2Co(SO_3)_2H_2O$	59.9	14.2 13.7	21.8	58.9	13.2	21.6
$(NH_4)_2Zn(SO_3)_2$	60.2 60.4		25.2 25.4	61.2		25.0
$(NH_4)_7Cu(SO_3)_4{\cdot}5H_2O$			10.6 10.4 10.7			10.6
NH_4CuSO_3			39.2 39.3			39.3
basic ammonium chromium sulphite	47.7 45.8 48.1	5.0 4.8	23.1 21.0			

* The two very different sets of data, obtained for the manganese(II) sulphite, were obtained on the same sample. The set which correspond to $MnSO_3.3H_2O$ being obtained after further washing to remove possible traces of chloride.

The data, for the ammonium chromium sulphite complex, are all from the same sample, and correspond approximately to $(NH_4)_3Cr_5(SO_3)_6(OH)_6.10H_2O$, but other analytical data showed widely different compositions for this material.

E. Spectra

(a) Diffuse reflectance spectra recorded in the region 28,500-10,000 cm^{-1}

Table 3.03

Compound	Absorption peaks(cm^{-1})
$Ni(OH)_2 3NiSO_3 . 12H_2O$	24,450; 14140sh; 13160
$NiSO_3.6H_2O$	24,810; 13790; 24,270; 13,330
$NiSO_3 . 2H_2O$	23,920; 13,020
$MnSO_3.3H_2O$	colourless
$Cu_2SO_3CuSO_3.2H_2O$	
$CoSO_3.3H_2O$	18,590; 18,900
$ZnSO_3.2.5H_2O$	colourless
$(NH_4)_2Ni_3(SO_3)_4.18H_2O$	25,000; 13,890
$(NH_4)_2Ni(SO_3)_2$	23,360; 12,900 23,360; 12,720
$(NH_4)_2Mn(SO_3)_2$	colourless
$(NH_4)_2Co(SO_3)_2H_2O$	18,730
$(NH_4)_2Zn(SO_3)_2$	colourless
$(NH_4)_7Cu(SO_3)_4.5H_2O$	colourless
NH_4CuSO_3	colourless
NH_4CrSO_3 ?	22,470; 16,370 22,570; 16,450

(b) (i) Infra-red spectra of the sulphites of the type $M_a(SO_3)_b.nH_2O$ and $Ni(OH)_2.3NiSO_3.12H_2O$ recorded in the region 4000-400 cm^{-1} in Nujol mull and KBr disc

Table 3.04

$Ni(OH)_2.3NiSO_3.12H_2O$	(N)	3378sbr			1650m				968svbr		870sh		676m					
	(KBr)	3392svbr			1637w				965s		898sh		658m					480vw
$NiSO_3.6H_2O$	(N)	3344sbr	3257sh		1637m		1112sh		972svbr		891sh		662mvbr					487vw
	(KBr)	3393sbr			1636m		1106sh		973svbr		872sh		663mvbr					490wvbr
$NiSO_3.\ 2H_2O$	(N)	3378m	3205sh		1637w				928svbr				662mvbr					
	(KBr)	3367s	3279sh		1639m				930svbr				661svbr					
$MnSO_3.3H_2O$	(N)		3247s	2257w	1618m			989sh	967s	923sh	899s		645mbr	606mbr				478mvbr
	(KBr)		3268s	2141w	1618m			988sh	965s	922sh	904s		645mvbr	609mvbr				
$Cu_2SO_3CuSO_3.2H_2O$	(N)	3378m			1647m			1013s	975s	926sh	902sh	857s	682s	633s				477m
	(KBr)	3378m	3173mbr		1647w	1255m 1221w	1120m	1008sh	978sh	909s	850sh		675m	636m	620m	565m	520m	476m
$CoSO_3.3H_2O$	(N)																	
	(KBr)																	
$ZnSO_3.2{\cdot}5H_2O$	(N)	3413mbr			1629w	1250w	1147sh 1100sh 1093w	1016m	987s	945s	917s		649m	619w		513m	505m	
	(KBr)	3497s			1621m		1166sh 1139sh 1122s	1017sh	986sh	942s	918sh		648wbr	621m		586w	512wbr 501wbr	

(ii) Infra-red spectra of the sulphites of the type $(NH_4)_aM_b(SO_3)_c.nH_2O$ and basic ammonium chromium sulphite recorded in the region 4000-400 cm^{-1} in Nujol mull and KBr disc

Table 3.05

$(NH_4)_2Ni_3(SO_3)_4.18H_2O$	(N)			3185sh			1672w						955s 935s	895s	779wvbr	604wvbr		487wvbr
	(KBr)	3401s		3155s			1637w	1437sh	1401m	1244w		1006sh	952s 928s	893s	781wvbr	661mvbr		
$(NH_4)_2Ni(SO_3)_2$	(N)		3268sh		3048s		1637vw						960sh	887s		675m		484m
	(KBr)	3390sh	3300m		3067m		1639vw	1473m	1376s				958sh	894s		672m		484m
$(NH_4)_2Mn(SO_3)_2$	(N)		3300m	3135sh	3058sh								961sh	914s		655m		485m
	(KBr)	3401sh	3300s	3115s			1639w	1468m	1389s				959sh	918s		655m		484w
$(NH_4)_2Co(SO_3)_2H_2O$	(N)	3390sh	3279m	3135sh	3058sh		1675vw			1147w	1091w		950sh	903svbr		667m		487w
	(KBr)	3401m	3279m		3096sh		1642vw	1466m	1395sh 1376m	1139w	1111w		956sh	905sbr		667w		488w
	(KBr)	3356m	3289m	3145m			1647vw	1468m	1393sh 1377m	1147m	1104m		954sh	905sbr		667w		488w
$(NH_4)_2Zn(SO_3)_2$	(N)		3279m		3040s								954sh	909sbr		662m		487w
	(KBr)			3145s		2959sbr	1631vw	1468m	1403sh 1381s	1136w			961sh	913sbr		661m	624w	486w
	(N)		3279m	3145sh		1832w	1695vw 1667vw			1155w			967sh	905sbr		661m		487mbr
$(NH_4)_2Zn(SO_3)_2$	(KBr)		3268m		3058m	1818vw	1675vw 1626w	1464m	1393sh 1377s	1121w			955sh	914sbr		660m	619w	486m
	(N)		3289m		3049m	1828vw	1672w						956sh	905sbr		661m		488wbr
	(KBr)		3257sh		3096sbr	1832vw	1675w 1639w	1471m	1403sh 1383s	1131w 1124w			952sh	919sbr		659m	620sh	486mbr

Table 3.05 contd.

$(NH_4)_7Cu(SO_3)_4 \cdot 5H_2O$	(N)	3521sh		3145sh	3021sh	1890w	1718w 1695w 1642w						987sbr	933s	631m		490vwvbr
	(KBr)	3413sh		3135s	3021sh		1637w	1408s		1266w 1241w	1161sh 1112s	1052sh	999m 993sbr 982m	952sh	643sh	617s	579w
NH_4CuSO_3	(N)		3290w										966sbr		663w		490w
	(N)		3268m										961sbr		663m		488wbr
	(KBr)	3390sh	3279sh	3115ms	3012sh	2801sh	1623w	1468sh	1401s	1266w 1241w	1166sh 1142sh 1114s		964sbr		663w	618m	490w
basic ammonium chromium sulphite	(N)	3333sbr					1623m				1109sh		983sh	910sbr		624vwvbr	559vwvbr
	(KBr)		3205sbr				1621m	1562w			1103sh		970sh	915sbr		621vwvbr	540vwvbr
	(N)		3205sbr				1637m						994sh	912 svbr	656mvbr		

w = weak; m = medium; s = strong; v = very; br = broad; sh = shoulder

(c) Far infra-red spectra recorded in the region 400-250 or 200 cm^{-1}

Table 3.06

Compound	Absorption peaks	Limit of measurements (cm^{-1})
$Ni(OH)_2.3NiSO_3.12H_2O$	No peaks from 400-250 cm^{-1}	250
$NiSO_3.6H_2O$	224	200
	332, 236	200
	387m, 291sh, 281s, 265sh, 258sh	250
$NiSO_3.\ 2H_2O$	No peaks from 400-200 cm^{-1}	200
$MnSO_3.2H_2O$	382, 322, 222	200
$Cu_2SO_3.CuSO_3.2H_2O$	359, 247	200 £
	350	250
$CoSO_3.3H_2O$	376, 236	200
	389, 240	200
	358sh, 300s, 286s	250
$ZnSO_3.2{\cdot}5H_2O$	265	200
	344, 300, 285sh	250
$(NH_4)_2Ni_3(SO_3)_4.18H_2O$	360, 214	200
	362m, 306s, 288sh	250
$(NH_4)_2Ni(SO_3)_2$	376, 255	200
$(NH_4)_2Mn(SO_3)_2$	211	200
$(NH_4)_2Co(SO_3)_2H_2O$	209	200
$(NH_4)_2Zn(SO_3)_2$	234	200
	236	200 £
$(NH_4)_7Cu(SO_3)_4.5H_2O$	382, 212	200
	354vw, 338vw	250
	298sh, 221sbr	200 £
NH_4CuSO_3	316sh, 270sh, 261sh	250
basic ammonium chromium sulphite	no peaks from 400-200 cm^{-1}	200

There is some doubt about those results in the region 400-200 cm^{-1} (except those marked $\neq$) as these were carried out on the Grubb-Parson DM2. Other workers have since observed erroneous spectra with this instrument.

Table 3.07

Compound		% losses in weight in recognisable decomposition stages (corrected for buoyancy)						Highest Temperature	Approximate heating rate	Completeness of decomposition	Contents of final product other than oxide	Colour of final product
		1st stage	2nd stage	3rd stage	4th stage	5th stage	Total weight loss	°C	°C/min			
$Ni(OH)_2 3NiSO_3.12H_2O$	I	23.3	33.0				56.3	630	3.3	Not complete	slight trace of S^{2-}	Very dark green
	II	23.8	33.6				57.4	710	1.7	Appeared complete	very slight trace of S^{2-}	Very dark green
$NiSO_3.6H_2O$	I	41.7	27.0				68.7	640	5.2	"	trace of SO_4^{2-}	Black
	II	42.0	20.0	7.6			69.6	800	2.4	"	-	Dark olive green
	III	42.4						260	1.8	Not complete	Not tested	Black
$MnSO_3.3H_2O$	I	30.9	31.8	(2.9)			62.7	870	5.2	Appeared complete	trace of S^{2-}	Dark brown
	II	30.6	32.6	(2.7)			63.2	870	5.2	"	-	Dark brown
$CoSO_3 3H_2O$	I	26.2	32.7				58.9	850	2.3	"	-	Dark grey
	II	26.1	32.7				58.8	870	5.2	"	-	Dark grey
$Cu_2SO_3CuSO_3.2H_2O$	I	35.2	6.3				41.5	700	1.7	"	-	Dark red
	II	35.3	6.4				41.7	750	1.7	"	-	Dark red
$ZnSO_3.2.5H_2O$	I	22.9	9.3	24.0			56.2	650	1.7	Appeared complete	trace of S^{2-} trace of SO_4^{2-}	White
	II	20.6	8.3	26.0			54.9	580	3.4	Appeared complete	more than trace S^{2-} more than trace SO_4^{2-}	Yellow
$(NH_4)_2Ni_3(SO_3)_4.18H_2O$	I	48.6	24.4				73.0	580	1.5	"	S^{2-}	Dark grey
	II	47.2	24.7				71.9	650	4.0	"	S^{2-}	Dark grey
$(NH_4)_2Ni(SO_3)_2$	I	46.8	11.7	10.4	1.6		70.5	650	1.5	Decreasing slightly	S^{2-}	Dark grey
	II	46.2	10.4	12.4	2.1		71.1	700	1.4	"	S^{2-}	Dark grey
$(NH_4)_2Mn(SO_3)_2$	I	47.2	17.7	4.8			69.7	720	1.5	Appeared complete	No S^{2-} Trace of SO_4^{2-}	Brown
	II	45.7	14.8	8.7			69.2	740	1.6	Appeared complete	No S^{2-} Trace of SO_4^{2-}	Brown
$(NH_4)_2Co(SO_3)_2H_2O$	I	48.2	12.2	1.8			62.5	640	1.5	Not complete	Oxidising agent present (liberated chlorine)	Very dark brown
	II	50.9	11.7	1.8	1.8		66.9	720	1.7	Not complete	"	Very dark brown
	III	50.0	12.7	5.0	2.5		70.2	800	1.4	Appeared complete	-	Green
$(NH_4)_2Zn(SO_3)_2$	I	25.7	18.1	14.2	3.8		61.8	650	1.4	Not complete	Not tested	Yellow

Table 3.07 contd.

Compound		% losses in weight in recognisable decomposition stages (corrected for buoyancy)						Highest Temperature	Approximate heating rate	Completeness of decomposition	Contents of final product other than oxide	Colour of final product
		1st stage	2nd stage	3rd stage	4th stage	5th stage	Total weight loss	°C	°C/min			
$(NH_4)_7Cu(SO_3)_4.5H_2O$	I	83.8	4.7+				88.5	650	1.5	Appeared complete	-	Red brown
	II	85.3	2.8+				88.1	820	6.0	"	-	"
NH_4CuSO_3	I	56.4	1.6	2.2			60.2*	780	5.2	"	-	Red
	II	54.2	2.1	2.0			58.3	820	5.5	"	-	Red

* Total % weight loss calculated from weight of residue when cold = 58.7

\+ Three minor decompositions in each case

The contents of the final products were detected by simple tests. In the case of the nickel compounds, these were heated rapidly under nitrogen, and the X-ray powder diffraction patterns of the final decomposition products of $NiSO_3.6H_2O$ and $Ni(OH)_2 3NiSO_3.12H_2O$ were found to be identified with that of B.D.H. NiO, whilst those of $(NH_4)_2Ni_3(SO_3)_4.18H_2O$ and $(NH_4)_2Ni(SO_3)_2$ were identified with those of mixtures of B.D.H. NiO/NiS, in proportions in the range 4:1 to 9:1, which had been heated in a similar manner.

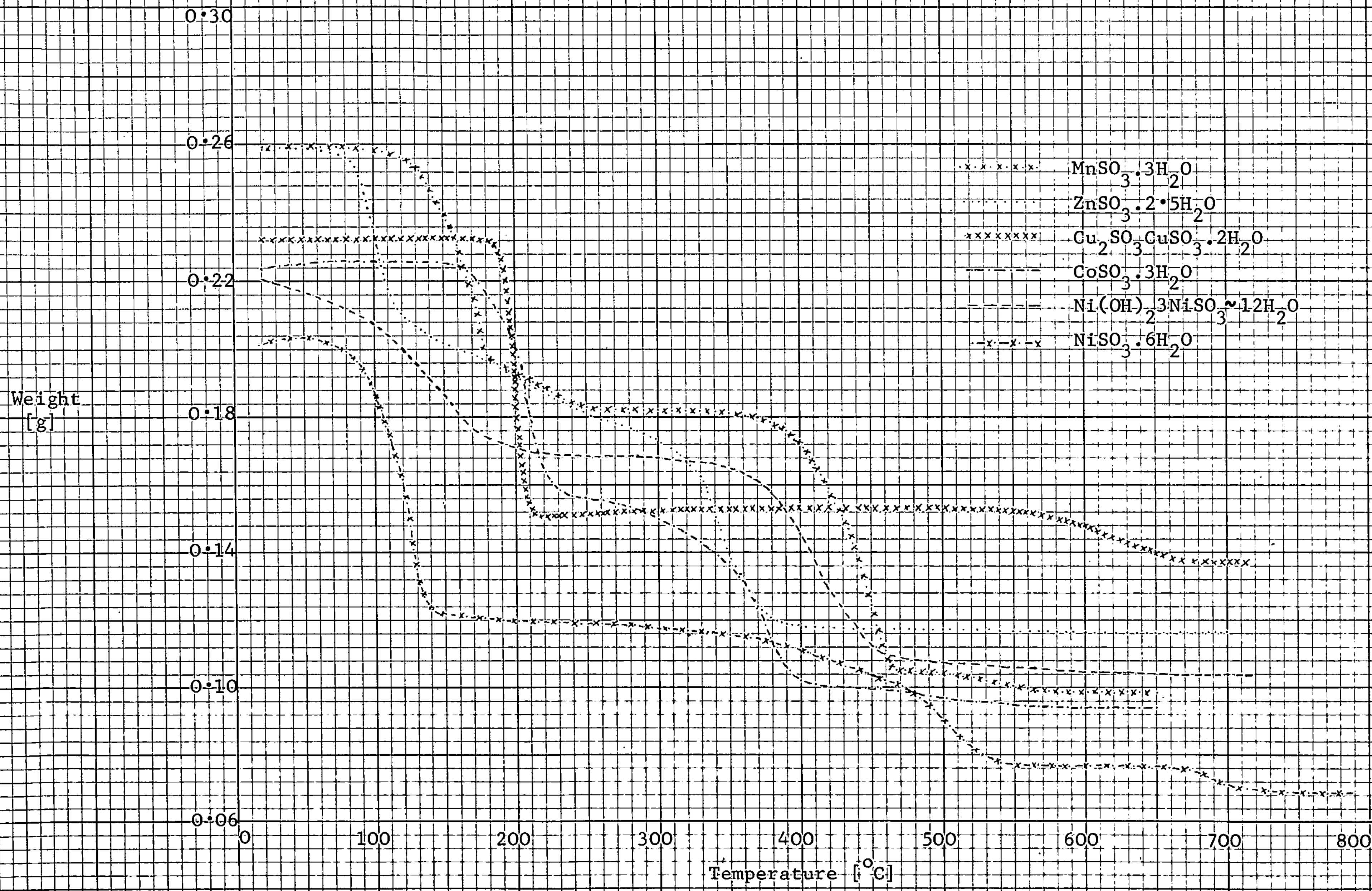


Fig.3.1 Thermal gravimetric analysis curves of $M_a(SO_3)_b.nH_2O$ and $Ni(OH)_2.3NiSO_3\sim12H_2O$ (not corrected for buoyancy)

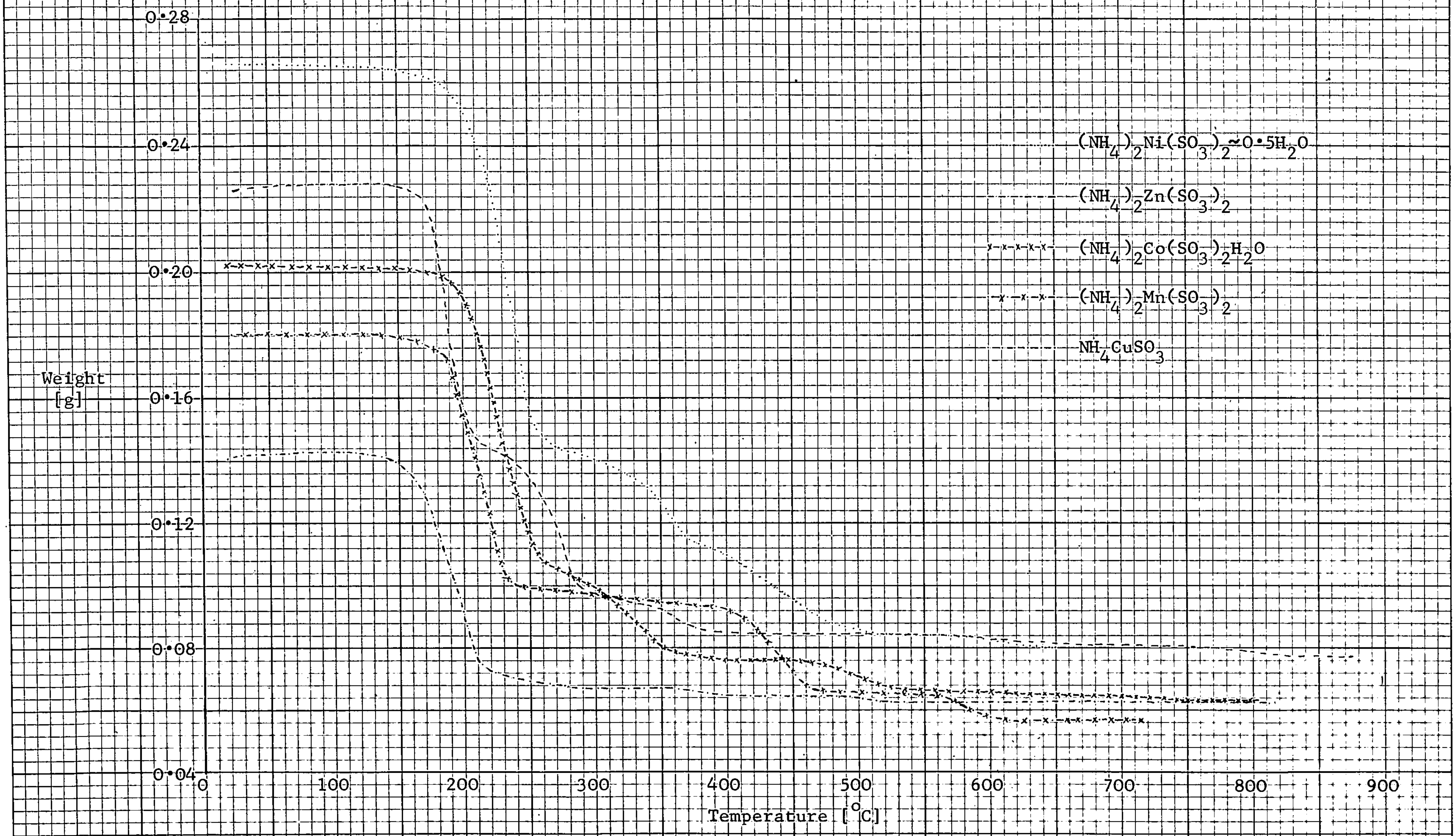


Fig.3.2 Thermal gravimetric analysis curves of $(NH_4)_2M(SO_3)_2.nH_2O$ and NH_4CuSO_3 (not corrected for buoyancy)

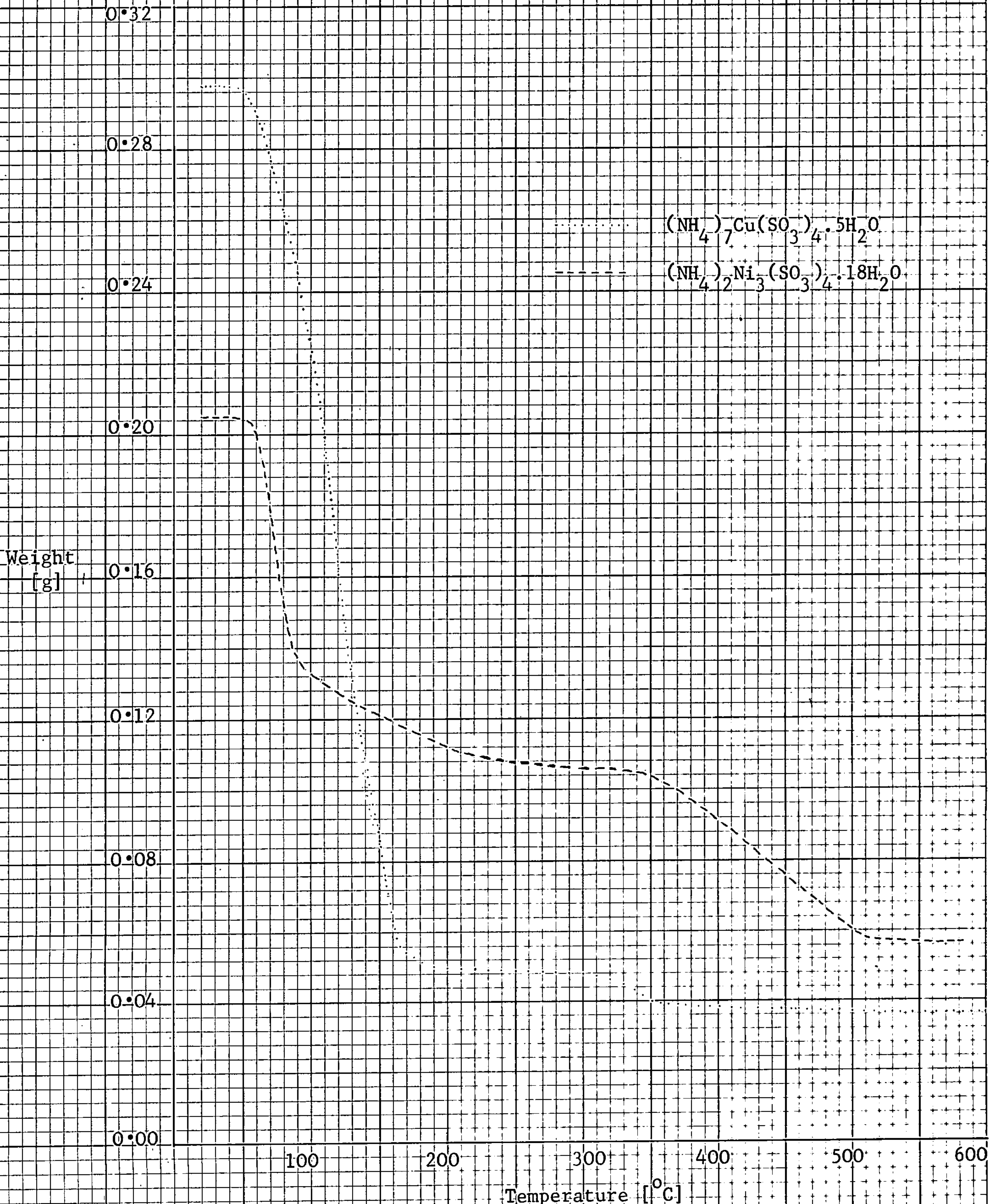


Fig.3.3 Thermal gravimetric analysis curves of $(NH_4)_7Cu(SO_3)_4.5H_2O$ and $(NH_4)_2Ni_3(SO_3)_4.18H_2O$
(not corrected for buoyancy)

CHAPTER 4

DISCUSSION

A. General Features

Attempts were first made to prepare the compounds of the type $(NH_4)_2M(SO_3)_2.nH_2O$ by the methods used by Newman and Powell;[15] however it was found that the methods gave considerable quantities of the sulphates in the final products. It is to be noted that these methods are not those of Hahn et al.,[46] who prepared the compounds from the metal chloride or acetate. The method finally employed in this work was generally that of Hahn et al. The hydrated binary sulphites, except $Ni(OH)_2.3NiSO_3.{\sim}12H_2O$, have all been prepared before by the methods used in this work or by similar methods. The preparation of $Ni(OH)_2.3NiSO_3.{\sim}12H_2O$ resulted from an attempt to prepare $NiSO_3.6H_2O$. Unsuccessful attempts to obtain an X-ray powder diffraction photograph showed the material to be amorphous. A basic sulphite of the composition $Ni(OH)_2.2NiSO_3.6H_2O$, was reported to be prepared by a similar method.[2] Thus the method used was not suitable for the preparation of the normal sulphite.

As reported in Chapter 3, the dry materials oxidise only slowly in air and oxidation appears to depend upon the surface moisture content of the sample. It was noted in the preliminary investigations that material could not be washed free of sulphate if the compound was washed with de-aerated distilled water in air, but that in general this was possible under nitrogen. It is concluded that oxidation takes place on the surface of the crystals or particles when moist and that the process is rapid.

The poor solubility in water of the compounds (Table 3.01), suggests three dimensional structures which arise from hydrogen bonding and/or to polymeric structures. It is known that $NiSO_3.6H_2O$ consists of the distorted octahedra $[Ni(H_2O)_6]^{++}$ and SO_3^{2-} ions held together three dimensionally by hydrogen bonding[5,6,7] and that $Cu_2SO_3CuSO_3.2H_2O$[8] and NH_4CuSO_3[9,10] are polymeric structures due to co-ordination to the metal atoms of the sulphur and the three oxygen atoms of the sulphito-group.

The solubility of all the compounds, except $Cu_2SO_3CuSO_3.2H_2O$ and NH_4CuSO_3, in aqueous sulphur dioxide solution may be due to reaction of H_3O^+ at the surface of the crystals with the sulphite groups to form HSO_3^-, thus reducing hydrogen bonding and enhancing its solubility. This may occur in the case of $NiSO_3.6H_2O$, but $(NH_4)_7Cu(SO_3)_4.5H_2O$ which is very soluble in both water and aqueous sulphur dioxide solution may contain discrete ions with little or no three dimensional bonding.

The analyses obtained were satisfactory and suggest the formulations given in Table 3.02. The variability in sulphite analyses in the ammonium compounds was checked against the gravimetric method involving oxidation of the sulphite to sulphate and its precipitation as $BaSO_4$. The two methods showed satisfactory agreement. Thus it is suggested that for the ammonium complexes of nickel, manganese and cobalt, of the type $(NH_4)_2M(SO_3)_2.nH_2O$, different preparations gave compounds with differing amounts of water. The compound $(NH_4)_2Ni(SO_3)_2$ is reported by Hahn et al.,[46] and Newman and Powell[15] to be the dihydrate; however it has also been reported without water[176] although their analyses suggest a formula $(NH_4)_2Ni(SO_3)_2.\sim0.5H_2O$. The corresponding zinc, magnesium, cadmium, iron and manganese compounds are reported by Hahn et al., to be anhydrous but of these, three, the zinc, magnesium and iron compounds are reported by Newman and Powell as mono- or dihydrates.

The two analyses presented for manganese(II) sulphite indicate that on washing the same precipitate with additional quantities of water it becomes more hydrated and corresponds to the formulation $MnSO_3.3H_2O$. This increase in hydration has been noted previously.[2]

Hydrated cobalt(II) sulphite has been formulated as $CoSO_3H_2O$, $CoSO_3.5H_2O$, $CoSO_3.3H_2O$[2] and $CoSO_3.6H_2O$[1] and recently[33] three species, orange red $CoSO_3.3H_2O$, violet red $CoSO_3.3H_2O$ and red $CoSO_3.2{\cdot}5H_2O$, have been reported in the same preparation. Since the analysis of the material prepared in this study corresponds to $CoSO_3.3H_2O$, from the colour it is possible that the material is the violet red form.

In an attempt to prepare ammonium chromium(III) sulphite, material which was formulated approximately as $(NH_4)_3Cr_5(SO_3)_6(OH)_6.10H_2O$ could be obtained only on one occasion although material containing NH_4^+, Cr^{III} and sulphite ion was always obtained. No normal chromium sulphite has been reported by early workers[2] and so it is probable that no ammonium chromium sulphite can be prepared in aqueous media.

The material whose sulphite content (45.0) corresponded to $NiSO_3.{\sim}2H_2O$ was obtained in an attempt to prepare $NiSO_3.4H_2O$ reported previously.[2] The thermal gravimetric analysis curve (Fig.3.1) shows that all the water is lost from $NiSO_3.6H_2O$ in one stage and the crystal structure[5,6,7] shows that there are two types of water co-ordinated to the nickel in equal numbers. Thus $NiSO_3.{\sim}2H_2O$ is probably not a definite species.

B. Spectroscopic Properties

The nickel compounds $Ni(OH)_2 3NiSO_3{\sim}12H_2O$, $NiSO_3 6H_2O$ and $(NH_4)_2Ni_3(SO_3)_4 18H_2O$ have diffuse reflectance spectra (Table 3.03) which correspond closely to that of $[Ni(H_2O)_6]^{2+}$,[177] with absorptions at 25,000-24,350 cm^{-1} and 14,140-13,160 cm^{-1}, indicating octahedral co-ordination of oxygen around the nickel. $NiSO_3 6H_2O$ is known to contain $[Ni(H_2O)_6]^{2+}$ ions.[1,5,6,7] The positions of the absorption peaks for $(NH_4)_2Ni(SO_3)_2.{\sim}0.5H_2O$ (23,360 and ~12,800 cm^{-1}) are little changed from those of $NiSO_3.6H_2O$ (25,000 and ~14,000 cm^{-1}) and again indicate octahedral co-ordination of nickel(II). The ligand field effects in the former complex are observed to be less than generated by six water molecules and may be consistent with Ni-S bonding in addition to bonding oxygen atoms of other sulphito-groups. This may also be true for the material $NiSO_3{\sim}2H_2O$ since it shows peaks at 23,920 and 13,020 cm^{-1}.

The cobalt(II) compounds $CoSO_3 3H_2O$ and $(NH_4)_2Co(SO_3)_2H_2O$ have absorption peaks in almost the same position as $[Co(H_2O)_6]^{2+}$ ~18,500 cm^{-1} 177 so that here again co-ordination of oxygen around the metal is likely although co-ordination also through sulphur cannot be ruled out. The absorption bands for the basic ammonium chromium sulphite at ~22,500 and 16,400 cm^{-1} are slightly lower than for $[Cr(H_2O)_6]^{3+}$ 177 (24,700 and 17,400 cm^{-1}). As for $(NH_4)Ni(SO_3)_2\ 0.5H_2O$ this may be consistent with Cr-S bonding in addition to bonding to oxygen atoms of other sulphito-groups, hydroxo-groups and water molecules.

Owing to the insolubility, in water and other non-destructive solvents, of the sulphites, all the infrared spectra (Tables 3.04, 3.05) were measured in the solid state. Most of the peaks recorded were broad, so that it may be that individual absorptions are not being observed. Prolonged grinding had no effect on the spectra except that sulphate ions were introduced by aerial oxidation.

For the compounds of the type $M_a(SO_3)_b.nH_2O$ and $Ni(OH)_2.3NiSO_3{\sim}12H_2O$ the peaks in the region 3200-3400 cm^{-1} are assigned to ν(OH). They are generally lower than that of water and so there is the possibility of stronger hydrogen bonding. This is particularly true of $MnSO_3.3H_2O$. The shoulders at 3257 cm^{-1} in the spectrum of $NiSO_3 6H_2O$ and at similar wave numbers in other hydrates are probably due to $2\delta_{(H_2O)}$ (2 x 1630 cm^{-1}). In the Nujol spectra of the ammonium compounds, absorptions assigned to ν(OH) occur at 3401 cm^{-1} for $(NH_4)_2Ni_3(SO_3)_4.18H_2O$, 3390 cm^{-1} for $(NH_4)_2Co(SO_3)_2H_2O$ and 3521 cm^{-1} for $(NH_4)_7Cu(SO_3)_4.5H_2O$. Absorptions in the region of 1640 cm^{-1} are assigned to $\delta(H_2O)$ in all the compounds except $(NH_4)_2Zn(SO_3)_2$ and $(NH_4)_2Mn(SO_3)_2$ where they are absent, in agreement with the analytical data which indicate anhydrous materials. In the ν(NH) stretching region two absorptions are noted for all complexes except $(NH_4)_2Ni_3(SO_3)_4.18H_2O$ and basic ammonium chromium sulphite. In NH_4CuSO_3 a complex band is noted in this region in the KBr disc spectra. In the region of $\delta(NH_4^+)$ two absorptions are observed except for $(NH_4)_7Cu(SO_3)_4.5H_2O$ and basic ammonium chromium sulphite. This splitting may be due to, hydrogen bonding of some N-H bonds and not others, the asymmetry of the NH_4^+ ion in the crystal or possibly to solid state effects.

The potassium bromide disc spectra show absorptions, which are absent in Nujol mull spectra, in the region of 1,100-1,200 cm^{-1}, though in copper compounds this extends to 1270 cm^{-1}. These absorptions are assigned to sulphate asymmetric stretching frequencies, though it is possible that other sulphur oxy-anions are involved especially in the copper compounds. It is also noted that when absorptions appear in this region, absorptions also appear at 620 cm^{-1}. These are assigned to ν_4 (the degenerate bend) of the sulphate ion. Thus it is concluded that the grinding and pressing involved in the making of the disc causes aerial oxidation of the sulphite which in turn causes erroneous absorptions in the spectra of these compounds. Occasionally weak absorptions appear, in the spectra in Nujol mull, in the same regions, presumably due to slight oxidation of sulphite on grinding. Duplicate spectra have been included in Table 3.05 to show that the spectra obtained in Nujol mull and potassium bromide disc were consistent, allowing for oxidation of sulphite on grinding and pressing.

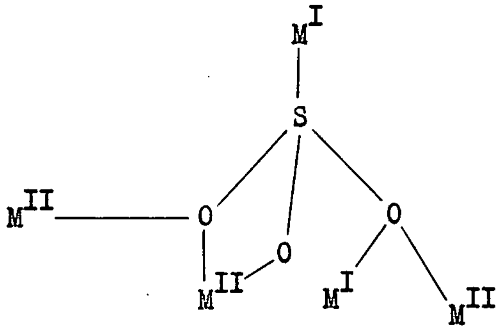
The compounds investigated can be classified into groups according to the number of absorption peaks and positions of those peaks in the S-O stretching frequency region.

Group A: show one peak at about the symmetric stretching frequency of the free ion (ν_1) with a shoulder at a much lower frequency e.g. $NiSO_3.6H_2O$ (972 and 891 cm^{-1}). Group B: show a more complicated series of peaks generally three or more spread over 850-1000 cm^{-1}. Group C: generally show a shoulder between 950-1000 cm^{-1} and a strong broad absorption at <u>ca</u>. 900 cm^{-1}. Group D: show one strong absorption peak in the region of ν_1 for the free ion i.e. <u>ca</u>. 970 cm^{-1} and another at about ν_3 for the free ion i.e. <u>ca</u>.930 cm^{-1}.

	Absorptions [cm^{-1}]
Group A	
$Ni(OH)_2.3NiSO_3{\sim}H_2O$	968svbr, (871sh)
$NiSO_3.6H_2O$	972svbr, (891sh)
Group B	
$Cu_2SO_3CuSO_3.2H_2O$	1013s, 975s, (926sh), 902s, (857sh)
$MnSO_3.3H_2O$	(989sh), 967s (923sh), 899s
$CoSO_3.3H_2O$	1017s, 964s 889sbr
$ZnSO_3.2{\cdot}5H_2O$	1016m, 987s, 945s, 917s
$(NH_4)_2Ni_3(SO_3)_4.18H_2O$	955s, 935s, 895s
Group C	
NH_4CuSO_3	966sbr
$(NH_4)_2Ni(SO_3)_2$	(960sh) 887s
$(NH_4)_2Mn(SO_3)_2$	(961sh) 914s
$(NH_4)_2Co(SO_3)_2H_2O$	(950sh) 903sbr
$(NH_4)_2Zn(SO_3)_2$	(954sh) 909sbr
Ammonium chromium sulphite	(994sh) 912svbr
Group D	
$(NH_4)_7Cu(SO_3)_4.5H_2O$	987sbr 933s

In group A, the symmetry of the sulphite ion in $NiSO_3.6H_2O$ is known to be C_{3v}[5] with all the sulphite-oxygen atoms hydrogen bonded to $[Ni(H_2O)_6]^{2+}$ ions, thus the absorptions at 972svbr, 891sh, 662mvbr and 487vw can be assigned to ν_1, ν_3, ν_2 and ν_4 respectively, of the sulphite ion. There is no splitting of ν_3 and ν_4 which agrees with C_{3v} symmetry. Also $Ni(OH)_2 3NiSO_3{\sim}12H_2O$ which has a very similar spectrum, possibly contains sulphite groups with the same symmetry, and on this evidence alone it may be suggested that it too contains the free ion hydrogen bonded to co-ordinated water molecules. Hydrogen bonding should have the effect of weakening the S-O bond as compared with the sulphite ion, and it is known that in $NiSO_3 6H_2O$[5] the S-O bond is 1.536Å as compared with 1.504Å in Na_2SO_3[13] consistent with a lowering of the frequency for the nickel compound. There appears to be little or no lowering of ν_1, but ν_3 is lowered by ca.40 cm^{-1} for $NiSO_3.6H_2O$, and by ca30-60 cm^{-1} for $Ni(OH)_2.3NiSO_3{\sim}12H_2O$. However the diffuse reflectance spectrum suggests octahedral co-ordination around the nickel in the latter complex and the co-ordination could not be satisfied by water and OH groups alone. Bridging water groups are unlikely, thus some bonding of the sulphite ion to the metal is expected, although this cannot be detected by the i.r. spectral data.

In group B the crystal structure of $Cu_2SO_3CuSO_3.2H_2O$ has been determined[8] (Fig.1.1) and shows that the symmetry of the sulphito-group is very low as shown in I.



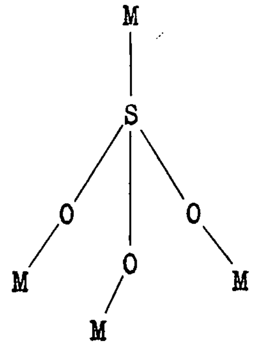
I

Thus splitting of ν_3 for the sulphite ion would be expected on co-ordination. The absorption peaks, in the region of ν_1 and ν_3 for the copper sulphite, are 1013s, 975s, 926sh, 902s and 857sh. Not all of these can be ascribed to removal of the degeneracy of ν_3 arising from a lowering of the symmetry of the sulphito-group, and may be ascribed to solid state effects i.e. the coupling of the vibrations of sulphito-groups in the crystal.

Based on the known structure of $Cu_2SO_3CuSO_3 2H_2O$, and the similarity of infrared spectra, it is reasonable to ascribe $Cu_2SO_3CuSO_3 2H_2O$ type sulphito-groups to $ZnSO_3.2.5H_2O$, $MnSO_3 3H_2O$ and $CoSO_3.3H_2O$, i.e. the symmetry of the sulphito-group in these compounds is very low. However $MnSO_3.3H_2O$ could alternatively be placed with $NiSO_3.6H_2O$ since the absorptions at 989 cm^{-1} and 923 cm^{-1} are only weak shoulders, but the general shape of the absorption band suggests it is better placed with group B.

Group C complexes are characterised by one strong absorption in the 880-970 cm^{-1} region, but may be subdivided into a group consisting of M^{I} derivatives for which the strong absorption occurs <u>ca</u>970 cm^{-1} (NH_4CuSO_3 is the only member of this subgroup), and a group consisting of M^{II} derivatives for which the absorption occurs at <u>ca</u>.900 cm^{-1}. The shoulder on the high side of the latter peaks may be due to an overtone (2 x <u>ca</u>.480 cm^{-1}). No splitting of ν_3 or ν_4 for the sulphite ion is observed, indicating that on co-ordination the symmetry of the sulphite ion is not changed.

Tetrahedral co-ordination of the copper in NH_4CuSO_3 can be achieved only if all the atoms of the sulphito-group bond to copper atoms. The local symmetry determined by X-ray crystallographic studies (shown in Fig.1.2 and II) is the same as that of the sulphite ion. There is little difference in the bond length of the

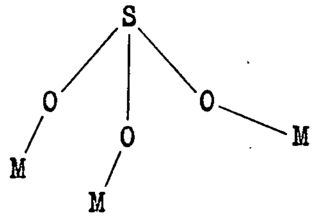


II

sulphito-group in NH_4CuSO_3 (1.506Å)[9,10] compared with that in Na_2SO_3 (1.504Å).[13]

Thus little shift in stretching frequencies is expected, and this is found to be the case in practice.

Since the sulphito-group is the only group in the complexes $[(NH_4)_2M(SO_3)_2]$ capable of co-ordinating to the metals, each sulphito-group must bond to metal atoms through three lone pairs of electrons, since the diffuse reflectance spectra in the visible region indicate octahedral co-ordination for nickel, cobalt, chromium and possibly manganese. If the symmetry of the sulphito-group is to be the same as that of the sulphite ion, as indicated by the single absorption at ca. 900 cm^{-1}, then co-ordination must be through the three oxygen atoms as shown in III. Other possibilities would either alter the symmetry or provide a surplus of co-ordinating groups. 4-Co-ordination is unlikely to occur for the Zn ion in $(NH_4)_2Zn(SO_3)_2$ according to the i.r. spectrum. The C_{3v} symmetry of the sulphite ion is retained in the complex and eliminates the possibility of bidentate attachment. Thus the Zn ions in common with the Cr, Ni, Co, and Mn ions appear to be octahedrally co-ordinated. This uncommon co-ordination to Zn has also been detected for $[Zn(H_2O)_6]^{2+}$ and $[Zn(NH_3)_6]^{2+}$.[177]



III

Co-ordination of the sulphito-groups through three oxygen atoms would lead to a "draining back of electrons" to the oxygens and reduce the π-bonding between the sulphur and the oxygens, lowering the bond order, increasing the bond length and lowering the stretching frequency. For NH_4CuSO_3, bonding through sulphur occurs in addition to bonding through the three oxygen atoms, and will tend to oppose the "draining back" effect. In addition, the presence of a mono-cation rather than a di-cation will reduce the overall tendency for the lowering of the S-O bond order on co-ordination through oxygen, and hence the stretching frequencies are expected to occur at higher frequencies than those observed for $(NH_4)_2M(SO_3)_2$ complexes. This is in good agreement with the frequencies observed.

For group D the only compound with absorption peaks in the positions expected for ν_1 and ν_3 for the sulphite ion is $(NH_4)_7Cu(SO_3)_4.5H_2O$. Coupled with its high solubility in water, this suggests that most sulphite groups are essentially in the state of the free ion with, as previously suggested, little or no three dimensional bonding. The $\nu(OH)$ above $\sim$3400 cm^{-1} also suggests less hydrogen bonding than in all the hydrates except perhaps $ZnSO_3.2{\cdot}5H_2O$.

The absorptions of all the compounds between 676-633 cm^{-1} are assigned to ν_2 (the symmetric bending frequency) of the sulphite group, and those at about 530 - 480 cm^{-1} to ν_4 (the asymmetric bending frequency) of the sulphite group.

Splitting of ν_4 is observed for $CoSO_3.3H_2O$ (528 and 524 cm^{-1}) and $ZnSO_3.2{\cdot}5H_2O$ (513 and 505 cm^{-1}). For $MnSO_3.3H_2O$ and $Cu_2SO_3CuSO_3.2H_2O$ no splitting is observed, but the absorptions are very broad and may consist of two absorptions, in agreement with the low symmetry of the sulphito-groups (previously proposed for group B) which may cause splitting of the doubly degenerate ν_4 mode.

The infra-red spectra of the compounds of the type $(NH_4)_2M(SO_3)_2.nH_2O$ and NH_4CuSO_3 were investigated by Newman and Powell[15], and the results obtained here are in good agreement (Table 2.1). Of the compounds of the type $M_a(SO_3)_b.nH_2O$, the infrared spectra of $Cu_2SO_3CuSO_3.2H_2O$,[4] $ZnSO_32.5H_2O$[137] and $CoSO_32.5H_2O$[44] have been reported as:

$Cu_2SO_3CuSO_3.2H_2O$		1025m	980m	915m	860w	632s 487s
$ZnSO_32.5H_2O$		1021.5vs	957s	913.5s	862w	
$CoSO_32.5H_2O$	1150w	1020w	965s		899m	848sh 720s 645s 600sh 515m 450w

s = strong; m = medium; w = weak; v = very; sh = shoulder

in agreement with the number of peaks observed in the S-O stretching region in this work. It is noted that in the case of $ZnSO_32.5H_2O$ the reported band was much broader than that observed in these results.

The far infrared data (Table 3.06) may be divided into two groups, (i) the data obtained using a Perkin Elmer 457, (ii) the data obtained using a Grubb Parson DM2. Toward the end of this study it became clear that the Grubb Parson DM2 was giving erroneous spectra and consequently some data in Table 3.06 may be unreliable. Thus discussion of the far infrared data will be restricted to those spectra obtained with the PE457 instrument.

The hydrates all show an absorption peak in the region 387-344 cm^{-1} and other absorptions from about 300-200 cm^{-1}. Hydrated first row transition metal(II) ions are reported to have $\nu(M-OH_2)$ from 310-405 cm^{-1}, commonly about 380 cm^{-1},[178] and MO_2 bending modes from about 300-100 cm^{-1}.[179] Thus all the observed bands may be interpreted as due to co-ordinated water, and to oxygen co-ordinated sulphito-groups. Limited $\nu(M-S)$ data for first row transition metal derivatives are available for dithiocarbamate and xanthate derivatives (350-383 cm^{-1}),[180] and $\nu(M-SO_3)$ may well occur in a similar region. Thus the region associated with $\nu(M-O)$ frequencies includes that associated with (M-S) frequencies, hence based on the limited data available it is not possible to assign the high energy absorption to $\nu(M-O)$ or $\nu(M-S)$. Indeed for those complexes known to have both metal-sulphur and metal-oxygen bonds, only one absorption occurs in the 300-400 cm^{-1} region.

C. Thermal decomposition studies

From thermal gravimetric analyses curves of simple sulphites and $Ni(OH)_2.3NiSO_3$ $12H_2O$ (Fig.3.1), it can be seen that thermal stability increases in the following order $Ni(OH)_2.3NiSO_3{\sim}12H_2O < NiSO_3.6H_2O \sim ZnSO_3 2.5H_2O < MnSO_3.3H_2O < CoSO_3.3H_2O \sim Cu_2SO_3CuSO_3.2H_2O$. The first decomposition stages of $NiSO_3 6H_2O$, $CoSO_3 3H_2O$, $MnSO_3 3H_2O$ and $ZnSO_3 2.5H_2O$ correspond reasonably well to the loss of all the water.

For $NiSO_3 6H_2O$ decomposition II (Table 3.07) may have taken place along a route similar to the following:

at ~70-240°,

$$NiSO_3 6H_2O \longrightarrow NiSO_3$$

at ~240-550°,

$$3NiSO_3 \longrightarrow NiSO_3 2NiO$$

at ~640-750°,

$$NiSO_3 2NiO \longrightarrow 3NiO$$

The theoretical percentage loss in weight due to loss of water is 43.8, and the theoretical percentage loss in weight of $3NiSO_3$ to $NiSO_3 2NiO$ is 17.3. The final product would appear to be NiO, as simple tests for sulphate and sulphide ions were negative, the final percentage weight loss (69.6) corresponds almost exactly to the theoretical for this change (69.7) and the X-ray powder photograph of the products of rapid decomposition under nitrogen were identical with that of NiO. The repeat thermal gravimetric study of $NiSO_3 6H_2O$ differed in the absence of the final decomposition stage although the total percentage loss in weights are very similar. The difference may reasonably be ascribed to the slower heating in the duplicate study (Table 3.07).

$Ni(OH)_2.3NiSO_3{\sim}12H_2O$ appears to lose approximately the equivalent of 9.5 water molecules in the first stage, but the shape of the thermal gravimetric curve indicates that water is lost in the stream of nitrogen from the time the sample is placed in the balance. This loss of water also accounts for the low total weight losses (56.3 and 57.4)compared with a theoretical loss of 58.8% assuming the final product is NiO). The X-ray powder photographs of NiO and the decomposition products of rapid heating were identical indicating the material to be essentially NiO. Traces of NiS were detected by chemical tests, but sulphate ions were absent.

In the case of $MnSO_3.3H_2O$ the actual percentage loss (62.9 average) as compared with the theoretical percentage loss to MnO (62.4) suggests that the final product is MnO. No sulphate ions were detected and only in the decomposition product of one experiment (Table 3.07, I) was there a slight trace of sulphide suggesting that the decomposition is essentially to the oxide. The differences in the final products cannot be explained in terms of heating rates, as these were the same for both experiments. The decomposition corresponds approximately to the following scheme:

at ~90-140°,

$MnSO_33H_2O \longrightarrow MnSO_3$ Theoretical percentage loss = 28.6
Actual percentage loss = 30.7

at ~350-460°,

$MnSO_3 \longrightarrow Mn_3O_4$ Theoretical percentage loss = 31.0
Actual percentage loss = 29.4

at ~460-580°,

$Mn_3O_4 \longrightarrow MnO$ Theoretical percentage loss = 2.8
Actual percentage loss = 2.8

For $CoSO_33H_2O$ it is difficult to decide as to the nature of the final decomposition products. No sulphide nor sulphate ions were detected by the usual simple tests. The material however did not dissolve in dilute hydrochloric acid to any appreciable extent, even on boiling. The material dissolved in concentrated hydrochloric acid on boiling and no sulphide or sulphate ions were detected. However it is doubtful if small amounts of hydrogen sulphide would effect the lead acetate paper, when large quantities of hydrogen chloride are present, as these would give white insoluble $PbCl_2$, probably using up all the Pb^{++} present. Attempts were made to reduce the final decomposition product using zinc metal and dilute hydrochloric acid but still no hydrogen sulphide was detected. The thermal gravimetric analysis curve (Fig.3.1) suggests that loss of sulphur dioxide starts before all the water is lost. A suggested decomposition scheme is:

Temperature ~ 150-250°,

$CoSO_3 3H_2O \longrightarrow CoSO_3$ Theoretical percentage loss = 28.0
Actual percentage loss = 26.2

~ 250-600°,

$CoSO_3 \longrightarrow Co_3O_4$ Theoretical percentage loss = 30.4
Actual percentage loss = 32.7

The total percentage loss in weight of $CoSO_3.3H_2O$ (58.9, 58.8) agrees closely with the theoretical percentage loss calculated for Co_3O_4 as the final product, (58.4) and the dark grey-black colour is also consistent with Co_3O_4.

The decomposition of $Cu_2SO_3CuSO_3.2H_2O$ cannot be interpreted in terms of any simple decomposition scheme. The final products do not contain sulphide or sulphate ions and may consist of copper metal and CuO or a mixture of Cu_2O and CuO. No red material was noted as being insoluble in dilute hydrochloric acid and it is tentatively suggested that the final product is a mixture of Cu_2O and CuO. The decomposition to equal quantities of Cu_2O and CuO would involve a percentage loss of 42.4 compared with that actually found of 41.6 (average). An unusual feature is the gain weight observed between decomposition stages one and two of the thermal gravimetric analysis curve (Fig.3.1). This occurred in both decompositions I and II (Table 3.07) and cannot be explained completely in terms of buoyancy.

$ZnSO_3 2.5H_2O$ shows a complicated thermal gravimetric analysis curve in which one stage overlaps another until the final products are reached. A very tentative scheme of decomposition for I is:

at ~50-160°,

$ZnSO_3 2.5H_2O \longrightarrow ZnSO_3$ Theoretical percentage loss = 23.6
Actual percentage loss = 22.9

at ~160-275°,

$3ZnSO_3 \longrightarrow 2ZnSO_3.ZnO$ Theoretical percentage loss = 11.2
Actual percentage loss = 9.3

at ~275-400°,

$2ZnSO_3.ZnO \longrightarrow 3ZnO$

However traces of sulphide and sulphate ions were found in the final products and decomposition II showed an increase in the amounts of sulphide and sulphate ions formed. This may be due to the increase in the heating rate in decomposition II (Table 3.07). Disproportionation may be taking place in a minor way possibly in the second stage according to:

$$4ZnSO_3 \longrightarrow ZnS + 3ZnSO_4$$

This kind of reaction has been reported as the main reaction in the thermal decomposition of Tl_2SO_3, $SrSO_3$ and $BaSO_4$,[111] and also in the thermal decomposition of potassium and lithium sulphites.[181]

The thermal decomposition of $MnSO_3$ under nitrogen has been reported recently to produce substantial amounts of Mn_3O_4 at temperatures above 420°,[139] and that of $CoSO_3 2.5H_2O$ to produce cobalt oxide progressively when heated to 850°.[44] The solid products of thermal decomposition of $ZnSO_3 2.5H_2O$ have been reported variously as ZnO with minor amounts of ZnS and $ZnSO_4$,[18,139] ZnO and a trace of $ZnSO_4$,[27] and ZnS_2O_3 with $ZnSO_4$.[17] In general these results agree with the work presented here except in the latter two cases where traces of ZnS and

$ZnSO_4$ were found along with ZnO. Early workers[2] reported the decomposition of $Cu_2SO_3CuSO_3.2H_2O$ to give water, sulphur dioxide, Cu_2O and $CuSO_4$ on heating to red heat and out of contact with air, in conflict with these results. They also report the decomposition of $MnSO_3 3H_2O$ out of contact with air to produce sulphur dioxide and a mixture of manganese oxide, sulphate, and sulphide which are also in conflict with the results presented here.

From thermal gravimetric analyses curves of the ammonium complexes (Figs. 3.2, 3.3) it can be seen that for those complexes containing appreciable quantities of water, the thermal stability is much lower than for the other ammonium complexes. These complexes are all of about equal thermal stability, decomposition commencing at about 130-150°C. For all the ammonium complexes the loss in the first decomposition stage corresponds to loss of $(NH_4)_2SO_3$ together with all the water that may be present. The decomposition products in the first stage were investigated by carrying out the decomposition in vacuum at 200°C for $(NH_4)_2Co(SO_3)_2H_2O$ and $(NH_4)_2Mn(SO_3)_2$ and collecting the gaseous and solid decomposition products formed. The infrared and mass spectra of these products showed that $(NH_4)_2SO_3$, SO_2, NH_3, and water were present, suggesting that $(NH_4)_2SO_3$ and H_2O are the main decomposition products in the first stage.

In the decomposition of $(NH_4)_2Ni(SO_3)_2$, the first stage (150-290°) corresponds approximately to the loss of $(NH_4)_2SO_3$ and water (% loss based on $(NH_4)_2Ni(SO_3)_2$ = 45.6 based on $(NH_4)_2Ni(SO_3)_2H_2O$ = 49.1%, Actual loss = 46.5% average). Further decomposition may take place according to:

(i) at 290-390°,

$$2NiSO_3 \longrightarrow NiSO_3.NiO + SO_2$$

(ii) at 390-540°,

$$NiSO_3NiO \longrightarrow 2NiO + SO_2$$

with the disproportionation,

$$4NiSO_3 \longrightarrow 3NiSO_4 + NiS$$

taking place at the same time as either of these two stages but to a small extent. From 550-650° it is possible that the $NiSO_4$ decomposes as follows:

$$2NiSO_4 \longrightarrow 2NiO + 2SO_3 + O_2$$

However it is to be noted that the latter stages do not agree with those of the proposed decomposition scheme for $NiSO_3.6H_2O$, and that each decomposition stage overlaps the next. The above scheme is consistent with the final decomposition products being mixtures of NiO and NiS. The sulphide was detected both by simple tests, and by comparison of the X-ray powder photographs of the final products of rapid decomposition, with those of mixtures of NiO and NiS in various proportions. It is probable that the ratios of NiO/NiS, in the product of rapid decomposition, are between about 4:1 and 9:1, since for these mixtures the X-ray powder photographs most closely corresponded in line intensity and spacing to the product mixture. Thus both analyses and total thermal decomposition (70.9% average), suggest that in this compound water is present, but in such quantities as to suggest a formula $(NH_4)_2Ni(SO_3)_2 0\text{-}1H_2O$. The decomposition of $(NH_4)_2Ni(SO_3)_2$ to NiO, would involve a theoretical percentage loss in weight of 70.7%, and $(NH_4)_2Ni(SO_3)_2H_2O$ to NiO, a loss of 72.6%.

For $(NH_4)_2Mn(SO_3)_2$ the following decomposition scheme is suggested for decomposition I (Table 3.07, Fig.3.2):

at ~140-320°,

$$(NH_4)_2Mn(SO_3)_2 \longrightarrow MnSO_3$$

Theoretical % loss = 46.2
Actual % loss = 47.2

at ~320-510°,

$$MnSO_3 \longrightarrow MnO_2$$

Theoretical % loss = 19.1
Actual % loss = 17.7

at ~510-630°,

$$MnO_2 \longrightarrow Mn_3O_4$$

Theoretical % loss = 4.2
Actual % loss = 4.8

However this may be oversimplified, as decomposition II (Table 3.07), although showing the same general curve and very nearly the same percentage loss in weight, shows significant differences in weight losses in the second and third stages. It is also to be noted that, whereas $MnSO_3 3H_2O$ appears to give MnO as its final decomposition product at about 620°, the ammonium salt appears to give Mn_3O_4 at almost the same temperature. The nature of the final product has been based upon the total weight loss on decomposition, and the product referred to as Mn_3O_4 may alternatively be substantially MnO with small amounts of $MnSO_4$ present. Traces of sulphate ions were detected though no sulphide ions were found.

For $(NH_4)_2Co(SO_3)_2H_2O$ it is interesting to note that in decompositions I and II (Table 3.07) in which the decomposition was not taken to completion, the residue was almost black, and was an oxidizing agent liberating chlorine from dilute hydrochloric acid, suggesting a higher oxide of cobalt. No sulphide ions or sulphate ions were detected in any of the decompositions. The final product of decomposition III (Table 3.07, Fig.3.2) was green suggesting CoO. However decomposition of $(NH_4)_2Co(SO_3)_2H_2O$ to CoO would involve a total percentage loss in weight of 72.5%. In fact the loss is 70.2% which corresponds closely with the decomposition of $(NH_4)_2Co(SO_3)_2$ to CoO (70.6). Not all the final product is soluble in dilute hydrochloric acid even on boiling. The material left is darker in colour and thus may be cobalt sulphide or Co_3O_4. The decomposition of $(NH_4)_2Co(SO_3)_2H_2O$ to Co_3O_4 would involve a percentage weight loss of 70.6. Owing to this uncertainty and the fact that stage one overlaps stage two to quite an appreciable extent it is not possible to suggest a decomposition scheme. From the evidence given, all that can be concluded, is that the final product is principally if not completely oxide(s) of cobalt, since the decomposition of $(NH_4)_2Co(SO_3)_2H_2O$ to CoS would involve a total weight loss of only 66.7%.

For $(NH_4)_2Zn(SO_3)_2$ the first two stages of decomposition I (Table 3.07) correspond fairly closely to loss of $(NH_4)_2SO_3$. In decomposition II (Table 3.07,

Fig.3.2) the percentage weight loss in the first stage differs from the theoretical percentage loss to $(NH_4)_2SO_3$ by about 7%. However stage one overlaps stage two considerably and it is worth noting that the first three stages of decomposition I correspond approximately in % weight loss to the first two stages of decomposition II (58.0, 59.1 respectively). These differences may be attributed to the difference in heating rate in the two decompositions. As only a trace of sulphate ion was found in the final product of decomposition II, the following decomposition scheme is tentatively suggested:

at ~140-330°,

$$(NH_4)_2Zn(SO_3)_2 \longrightarrow ZnSO_3$$

followed by and overlapping,

$$ZnSO_3 \longrightarrow ZnSO_3 2ZnO$$

Theoretical % loss = 60.9
Actual % loss = 59.1

at ~470-850°,

$$ZnSO_3.2ZnO \longrightarrow 3ZnO$$

Theoretical % loss = 8.2
Actual % loss = 8.4

However there are three decomposition stages, on the thermal gravimetric analysis curve (Fig.3.2), (with % losses in weight 4.7, 2.0, 1.7 respectively) which correspond to the suggested simple change in decomposition II of $ZnSO_3.2ZnO \longrightarrow 3ZnO$. Thus the decomposition is probably much more complicated than the above scheme suggests.

For NH_4CuSO_3, decompositions I and II (Table 3.07, Fig.3.2) show similar curves. For decomposition I the actual total percentage weight loss recorded (60.2) by the T.G.A. balance is incorrect due to abnormal buoyancy effects, since using an analytical balance the weight of the final decomposition product corresponded to a total percentage weight loss of 58.7. The percentage weight loss in the first stage (54.2) is slightly less than the theoretical loss of $(NH_4)_2SO_3$ and SO_2 according to:

$$2NH_4CuSO_3 \longrightarrow (NH_4)_2SO_3 + SO_2 + Cu_2O$$

The formation of Cu_2O at the end of this stage however would not explain the two minor decompositions which follow, nor can the final decomposition products be explained by supposing this to take place. Simple chemical tests on the final decomposition product showed that no sulphate or sulphide ion was present. Not all the red material would dissolve in dilute or concentrated hydrochloric acid on boiling, a red residue being left. This residue was soluble in concentrated nitric acid suggesting that it is metallic copper. Since the final product is red, the part soluble in dilute or concentrated hydrochloric acid is almost certainly Cu_2O. These suggestions are also supported by the theoretical percentage losses in weight to Cu_2O of 55.7, and to metallic copper of 60.7 and the actual loss of 58.3%.

For $(NH_4)_2Ni_3(SO_3)_4.18H_2O$ (Table 3.07, Fig.3.3), the % weight loss in the first decomposition stage (48.6, 47.2) is less than the theoretical % weight loss of water and $(NH_4)_2SO_3$ to form $3NiSO_3$ (51.4). It is however fairly certain that these are products in this stage, as the rapid decomposition under nitrogen in a hard glass combustion tube produces a white sublimate and drops of a colourless liquid. Simple tests on the final decomposition product showed that sulphide ion was present but not sulphate. The sulphide may be formed in the first stage. The percentage weight loss in the second stage (24.4, 24.7) is greater than the theoretical % weight loss (22.4), but as the first stage overlaps the second stage it is possible that the major decomposition takes place according to:

(i) at ~50-290°,

$$(NH_4)_2Ni_3(SO_3)_418H_2O \longrightarrow 3NiSO_3 + (NH_4)_2SO_3 + 18H_2O$$

(ii) at ~290-540°,

$$NiSO_3 \longrightarrow NiO$$

With $(NH_4)_7Cu(SO_3)_4.5H_2O$, as for other ammonium compounds, the first stage percentage weight loss (83.8, decomposition I, Table 3.07, Fig.3.3) corresponds approximately with the theoretical percentage loss in weight for the total loss of $(NH_4)_2SO_3$ and water (82.7). The percentage loss in weight in stage two (4.7) corresponds with the loss of sulphur dioxide to form Cu_2O (5.3). Thus a possible decomposition scheme is:

(i) at ~50-250°,

$$(NH_4)_7Cu(SO_3)_4.5H_2O \longrightarrow Cu_2SO_3$$

(ii) at ~250-450°,

$$Cu_2SO_3 \longrightarrow Cu_2O$$

However decomposition II (Table 3.07) shows percentage weight losses of 85.3 and 2.8; thus the decomposition may be more complicated than the above scheme suggests. The final decomposition product contained no sulphide or sulphate ion, and no residue was noted on heating with concentrated hydrochloric, thus it is suggested that the final decomposition product is Cu_2O.

Of those compounds, NH_4CuSO_3 has been reported[182] as giving partly the metal and partly products such as sulphate, oxide and sulphide, depending on the atmosphere used which was never an inert one. The partial production of copper is in agreement with the decompositions discussed previously. $(NH_4)_2Mn(SO_3)_2$ has been reported[2] as decomposing to give final products of a mixture of manganese oxide and sulphide, conflicting with the results presented.

Occurrence of sulphide in the final decomposition does not point to bonding between the metal and sulphur in the original compound as it has been noted previously that for sulphites of potassium and lithium[181] and for those of thallium, strontium and barium[111] the main reaction is that of disproportionation to sulphate and sulphide.

In general the thermal decompositions of the ammonium compounds appear more complicated than for the simple ones. There are more stages of decomposition which frequently overlap, and sometimes minor stages occur within the stages noted (Table 3.07). The products of decomposition for all the compounds also appear to depend to a varying extent on the heating rate. The material used always consisted of small crystals of about the same size. Thus it can be reasonably assumed that partical size played little or no part in producing the differences noted in decompositions carried out on the same compound. Finally it can be concluded, that in general the thermal decompositionsof the sulphites investigated take place with the loss of sulphur dioxide, and water where the compound is hydrated, and with the loss of ammonium sulphite from the ammonium compounds. The final products consist substantially of the metal oxide with, in some cases, small amoumts of sulphide and/or sulphate.

The work presented here suggests that, in general, in the compounds investigated, the sulphite group is co-ordinated to the metal probably mainly through oxygen, and is polydentate. However in $NiSO_3.6H_2O$ the sulphite group is present as the ion[5] and this is possibly the case with $(NH_4)_7Cu(SO_3)_4.5H_2O$. It was hoped at the outset of this work to resolve the exact nature of bonding using methods, the results of which are presented in this thesis. This has not proved possible, due at least in part to the hydration of the compounds which probably causes some of the observed broadening of the absorptions of the S-O stretching frequencies in the infrared spectra, making interpretation difficult. Also in the far infrared spectra, metal-water vibrations cover the same region as those of other metal-oxygen vibrations and also the region in which ν(M-S) for sulphites is likely to occur. Very recently anhydrous sulphites of the type $M_a(SO_3)_b$ have been prepared, and investigations of infrared and far infrared spectra of these compounds may lead to a better understanding of the bonding mode of the sulphito-group. The interpretation of the data presented has been aided considerably by the crystal structures which have been determined recently, some since this work was started, and which have been reviewed in Chapter 2.

The thermal decomposition studies have established that in general the main products of decomposition are oxides, together with small amounts of sulphides and/or sulphates. The decompositions are not simple and need further examination under a variety of different conditions to gain a greater understanding of the factors responsible for the formation of the minor products.

It is also to be noted that only a small number of first row transition metal sulphites have been studied from a very large field of inorganic chemistry. The methods used in the present study, although they have provided additional information on the systems studied, have not been definitive in nature because of the complex chemistry involved. X-ray crystallography has provided the greatest insight into the nature of the interaction of sulphite groups with transition metals, and the greatest contribution to this area of chemistry in the immediate future is again most likely to be provided by X-ray crystallography.

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