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Review

REVIEW OF THERMOANALYTICAL, IR, RAMAN AND X-RAY STUDIES OF SOLID METAL SULPHITES

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1. WHY THIS REVIEW?

Research on SO_2-induced atmospheric corrosion and catalytic oxidation of SO_2 in the polluted air [1,2] indicates that solid metal sulphites and sulphite complexes in solution may play a role as intermediates in such processes. The nitrosyl complexes can react with the absorbed SO_2 to form a variety of products [3–9]. Absorption of NO in mixed solutions of Fe(II)–EDTA and Na_2SO_3 is attributed [10] to NO coordination to Fe(II)(EDTA)(SO_3^{2-}) irreversibly. All this importance and the absence of any recent review on thermal, spectroscopic and X-ray of metal sulphites prompted the present work.

2. INTRODUCTION

The chemistry, especially structure, and IR spectra of metal sulphites have been examined by several authors [11–21]. The structural problems arising in

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TABLE 1

IR and Raman vibrations of Na_2SO_3 (cm^{-1}) [34]

	ν_1 (sym.str.)	ν_3 (asym.str.)	ν_2 (sym.bend)	ν_4 (asym.bend)
Na_2SO_3(solid) (IR)	1010 m	961 s	633 s	496 s
Na_2SO_3 (soln.) (Raman)	967 s	933 m	620 w	469 m

s, strong; m, medium; w, weak.

sulphites have been known for many years and are reviewed by Sidgwick [22]. The sulphite ion is said to form complexes or double salts [23] with Be, Mn, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, Zn, Cd and Hg. The crystal structure of alkali metal sulphites and X-ray data of $PbSO_3$ [24], $FeSO_3$ and $MnSO_3$ have been reported [15,24]. Rare earth element sulphites are a class of compounds that has been comparatively poorly studied. Cuttica [25] first prepared the sulphites of some lanthanides. Vickery [26] showed that complex ionic lanthanide sulphites of $[Ln(SO_3)_3]^{3-}$ exist in solution, and are stable in the narrow pH range 5.5–6.1. Hydrated sulphites of the rare earth elements yttrium and scandium were described for the first time in refs. 27–31. The behaviour of the salts $NaLn(SO_3)_2H_2O$ (where Ln is Ho, Er, Tm, Yb or Lu) on heating has been studied [29] by TG, DTA, X-ray diffraction, IR and chemical analyses.

3. COORDINATION OF SULPHITE ION

From X-ray and Raman spectral investigations [32,33] the simple sulphite ion is known to possess the C_{3v} (pyramidal) symmetry, both in solution and in the solid state. Thus, sulphite compounds having C_{3v} symmetry would be expected to possess four fundamental vibrations as shown in Table 1 for sodium sulphite, all of which are IR and Raman active. The asymmetric fundamentals ν_3 and ν_4 are both doubly degenerate.

Nyberg and Larsson [35] made a detailed study of the IR spectra of a range of solid metal sulphites. Interpretation is not easy, as many of the bands are broad, and the stretching vibrations ν_1 and ν_3 in sulphite are often superimposed. However, it is usually possible to distinguish between ionic sulphite and covalently bonded sulphite. The structures of complexes containing bidentate sulphite groups are rather difficult to deduce from their IR spectra.

In the crystalline state there are several factors which affect the sulphite frequencies. The most dominant factors are the effect on the site symmetry of the ion in the structure and the effect of coordination of the ion. According to the available spectroscopic data sulphites may be classified:

(i) ionic/double sulphites;

(ii) sulphur-bonded/coordinated sulphites;
(iii) oxygen-bonded/coordinated sulphites.

4. INFRARED AND RAMAN SPECTRA AND X-RAY STUDY OF SULPHITES

4.1. Ionic / double sulphites

Newman and Powell [36] classified the following compounds in this category: $M^I_2M^{II}(SO_3)_2$, where $M^I = NH_4^+$, alkali metal, M^{II} = Zn, Cd, Fe, Mn, Co, Ni, Mg. The IR spectra of two of these sulphites are shown in Fig. 1. They are remarkably similar and are closely analogous to the spectrum of sodium sulphite. Four vibrations are found in the region 4000–500 cm^{-1} and results are consistent with the C_{3v} symmetry having been preserved.

The spectra of $MgSO_3 \cdot 3H_2O$ and $MgSO_3$ indicate [37] that sulphite is present as the free ion, which may be loosely attached to the metal ion and hydrogen bonded to water in the case of hydrate. The spectra of $CaSO_3 \cdot 0.5H_2O$ and $CaSO_3$ are more complex than those of the magnesium compounds (Table 2) and suggest some degree of interaction between the metal ion and sulphite, as well as hydrogen bonding between sulphite and water in the hydrate. The water molecules are very strongly attached and the compound exhibits a high thermal stability. The very broad bands obtained [36], particularly noticeable in the salts of Zn(II) and Cd(II), may be due to the state of the crystalline lattice. The two bending vibrations ν_2 and ν_4 occur

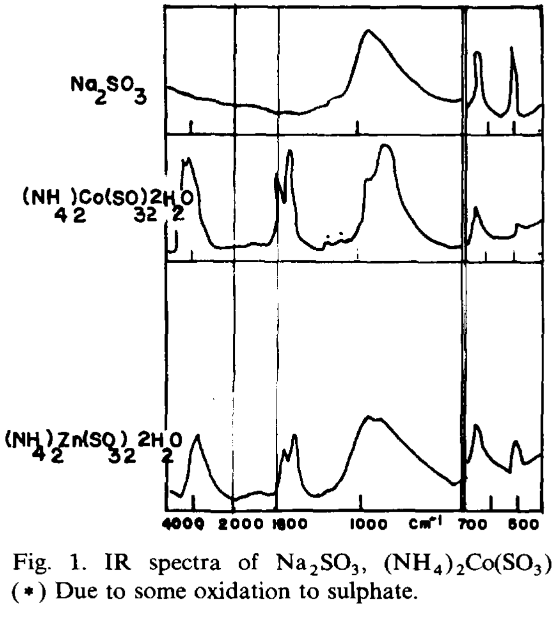


Fig. 1. IR spectra of Na_2SO_3, $(NH_4)_2Co(SO_3)_2 \cdot 2H_2O$ and $(NH_4)_2Zn(SO_3)_2 \cdot 2H_2O$. (*) Due to some oxidation to sulphate.

TABLE 2

IR bands of ionic metal sulphites (cm^{-1}) [37]

	ν_1 (sym.str.)	ν_3 (asym.str.)	ν_2 (sym.bend)	ν_4 (asym.bend)
$MgSO_3$	942 m		625 m	480 w
$MgSO_3 \cdot 3H_2O$	940 s		620 m	480 w
$CaSO_3$	950 s	970 s	650 m 665 m	480 w 520 w
$CaSO_3 \cdot \frac{1}{2}H_2O$	950 s	975 s	650 m 668 m	485 w 520 w

s, strong; m, medium; w, weak.

near 500 and 650 cm^{-1}, respectively. Consequently, it appears that, despite the insolubility of these compounds, they are double salts.

4.2. *Sulphur-bonded/coordinated sulphites*

It is anticipated [38] that coordination of the sulphite group through sulphur will shift the stretching bands to higher frequencies compared with the free ion and the C_{3v} symmetry is essentially preserved, whereas coordination through oxygen may shift them to lower or higher [39] frequencies. On the basis of these criteria, Newman and Powell [36] showed that the sulphite groups in $K_6[Pt(SO_3)_4] \cdot 2H_2O$ and $[Co(NH_3)_5(SO_3)]Cl$ are S-bonded. The compounds $Pd(SO_3)(NH_3)_3$ [40] and $Co(en)_2SO_3NCS \cdot 2H_2O$ (en = ethylenediamine) [41] have metal–sulphur bonds and the crystals are composed of discrete molecules held together by hydrogen bonds. The spectra have stretching frequencies above 975 cm^{-1} (Table 3). The spectra are all consistent with the site symmetry of the anion. On the basis of observed [35] frequencies of $Na_2[Hg(SO_3)_2]$ (Table 3) a structure with an Hg–S bond was proposed.

Several metal sulphites [42] furnish evidence of bonding between sulphur and metal atoms with a tetrahedral coordination around sulphur comprising, in addition to the metal atom, the three sulphite oxygen atoms. In Ag_2SO_3 [43] one of the Ag atoms belongs to the tetrahedron surrounding the S atom, while the other is exclusively bonded to oxygen atoms. The effects of the Ag atoms on the S–O bond distance thus counteract each other and the average S–O distance is rather close to that present in Na_2SO_3. Even more complicated schemes of bonding are found in the copper sulphites NH_4CuSO_3 [44] and $Cu^I_2Cu^{II}(SO_3)_2 \cdot 2H_2O$ [45]. The monovalent Cu atoms of the former have a tetrahedral environment comprising one sulphur and three oxygen atoms and are likely to affect both these kinds of atoms. This results in an S–O bond distance not very different from the value found in Na_2SO_3. The structure of the copper sulphite, $Cu^I_2Cu^{II}(SO_3)_2 \cdot 2H_2O$ is characterized by a bonding scheme similar to, but more complicated than that of NH_4CuSO_3. The new complexes $[Os(SO_3)(NH_3)_4]Cl$ and $[Os_2N$-

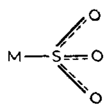
TABLE 3

IR bands (cm^{-1}) of some sulphur-bonded sulphites

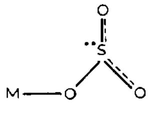
	ν_1 and ν_3	ν_2	ν_4	Ref.
$PdSO_3(NH_3)_3$	1095, 1077, 989	643	510, 481	40
NH_4CuSO_3	965	660	483	40
$Co(en)_2SO_3NCS \cdot 2H_2O$	1095, 1089, 1050	625	500, 475	40, 41
$Co(NH_3)_5SO_3Cl$	1110, 985	633	519	36
Ag_2SO_3	1035, 970, 908	632	500, 494	40
$K_6Pt(SO_3)_4 \cdot 2H_2O$	1082, 1057, 964	660	540	36, 46
$Na_2Hg(SO_3)_2$	1125, 1020, 975	640	520, 510, 495	45
$(NH_4)_2Hg(SO_3)_2$	1117, 1023, 967	643	514	36
$K_3Rh(SO_3) \cdot 2H_2O$	1150, 1112, 970, 945	687, 640	550, 530	46
$K_4Os(SO_3)_3(H_2O)_3$	1120, 1070, 1030, 980	600	508	46
$Na_7Ir(SO_3)_4Cl_2 \cdot 7H_2O$	1110, 1070, 965	635, 625	525	47
$Os_2N(NH_3)_8(SO_3)(H_2O)Cl_3$	1090, 1045, 957	625	508	46

$(NH_3)_8(SO_3)(H_2O)]Cl_3$were also suggested [46] to contain S-bonded sulphite.

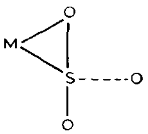
Infrared spectra of sulphite complexes show multiple splitting, and it is difficult to draw conclusions as to the mode of bonding involved. Hall and Griffith [46] reported both Raman and IR data on complexes of types **I**, **II** and **III** and showed that, by using the full symmetry of the complex, reasonable assignments of modes could be made.



(I) C_{3v}



(II) C_s

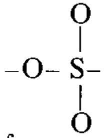


(III) C_1

As in work [35,36,47–50] on the infrared spectra of sulphite complexes, the four vibrational modes ν_1–ν_4 of the free sulphite ion are used as approximate descriptions of the vibrations of the coordinated ligand. The strongest Raman modes are assumed to arise from symmetric rather than asymmetric vibrations. Deuteration has been used in three cases: $Pd(SO_3)(NH_3)_3$ and $(NH_4)_3[M(SO_3)_3(NH_3)_3]$ ($M = Rh$, Ir), the SO_3^{2-} vibrations being relatively unaffected while the NH_3 modes are greatly shifted.

Single-crystal X-ray studies suggest that the complex anion in *trans*-$(NH_4)_5[Ir(SO_3)_2Cl_4]$ has an idealised C_{2h} symmetry [51]. Hall and Griffith [46] found the Raman and infrared spectra of $(NH_4)_5[Ir(SO_3)_2Cl_4] \cdot H_2O$ and $K_5[Ir(SO_3)Cl_4] \cdot 6H_2O$ to be very similar. For $Na_3[Ir(SO_3)_2(NH_3)_2Cl_2] \cdot 6H_2O$ three Raman and four infrared active bands were observed, suggesting a *trans* structure (idealised C_{2h} symmetry).

Infrared studies on $Na_5(NH_4)[Ir(SO_3)_3(NH_3)_3]$ have been interpreted in terms of the sulphite ligands being bonded with a *fac* configuration [47] and infrared spectra for $K_3[(Rh(SO_3)_3]\cdot 3\frac{1}{2}H_2O$ have been interpreted on the basis of S-bonded monodentate sulphite ligands being present [36,49].

The main features of the infrared and Raman spectra of $Na_3[Ir(SO_3)_3(NH_3)_3]\cdot 7H_2O$, $(NH_4)_3[Rh(SO_3)_3(NH_3)_3]\cdot 1\frac{1}{2}H_2O$ and the new complex $K_4[Os(SO_3)_3(H_2O)_3]$ are similar, suggesting the same basic stereochemistry [46] for the anions. The complex $K_3[Rh(SO_3)_4]\cdot 2H_2O$ may contain bidentate SO_3^{2-} ligands, but the complexity of the spectra, together with the very low solubility of the compound and its amorphous character with respect to X-ray studies, suggests a polymeric structure probably with  $-O-\overset{\overset{\large O}{|}}{\underset{\underset{\large O}{|}}{S}}-$ bridges. It is interesting that bands are seen in the same region as for monodentate S-bonded sulphite groups.

The infrared spectrum of $Na_7[Ir(SO_3)_4Cl_2]$ [47] suggests monodentate S-bonded sulphite groups. Infrared spectra of $K_6[Pt(SO_3)_4]$, $Na_6[Pd(SO_3)_4]\cdot 2H_2O$ and $K_6[Pt(SO_3)_4]\cdot 6H_2O$ suggest that these also contain S-bonded ligands [48]. $K_4[Os(SO_3)_3(H_2O)_3]$ has monodentate S-bonded sulphite groups [46]. Its vibrational spectra are very similar to those for *fac*-$[M(SO_3)_3(NH)_3]^{3-}$ ($M = Rh$, Ir). The infrared and Raman spectra of $[Os_2N(NH_3)_8(SO_3)(H_2O)]Cl_3$ suggest that the sulphite group is coordinated via the sulphur atom.

4.3. *Oxygen-bonded/coordinated sulphites*

Applying the Nyberg and Larsson [35] criterion, Lutz and Suradi [52] concluded that calcium, strontium, barium, lead and cadmium sulphites are oxygen coordinated. However, sulphites of calcium and magnesium have been found to be ionic [37]. A structural determination [53] confirmed the formula $2CdSO_3\cdot 3H_2O$. The determination revealed coordination of the sulphite ion through oxygen. The observed S–O bond lengths (152–155 pm) and angles (101.3–106.1°) are in good agreement with the reported value of 150–153 pm for sulphites and 105.7° for OSO in Na_2SO_3 [54], respectively. The vibrations at 950 and 500 cm^{-1} show that the site symmetry of none of these sulphites agrees with the SO_3^{2-} ion (C_{3v}). The spectra of sulphites reveal relatively large splitting. Lutz et al. [55] reported high-temperature Raman and IR spectra, X-ray and thermoanalytical analyses of magnesium and zinc sulphites with a view to obtain hitherto unknown lower hydrates of these compounds. In the system $MgSO_3\cdot XH_2O$ hydrates ($X = 6$, 3 and 2) have been definitely characterized [39,56,57]. The existence of a monohydrate was reported by Szendrei and Ho-Tun [56]. In the system $ZnSO_3\cdot XH_2O$, a relatively large number of hydrates is known, namely compounds with $X = 3, 2\frac{1}{2}$ (three forms: α, β and γ), 2 and 1 [39,57,58]. In the literature so far [39,58,59], the monohydrate was reported to be a semihydrate. From structure analysis [57], however, it was found that this hydrate is in fact $ZnSO_3 \cdot 1H_2O$. The thermal decomposition of the hydrates of $MgSO_3$ and $ZnSO_3$ has been investigated several times in the literature [39,56–59]. The results obtained are not in good agreement because different hydrates are formed under the same conditions [58].

$MgSO_3 \cdot 2\frac{1}{2}H_2O$ crystallizes in the tetragonal $CoSO_3 \cdot 2\frac{1}{2}H_2O$ form [39,57,58] (space group $p4_12_12 - D_4$, $Z = 8$) with $a = 944.4(1)$ and $c = 1025.5(1)$ pm; $MgSO_3 \cdot 2H_2O$ in the monoclinic $ZnSeO_3 \cdot 2H_2O$ form [58,60] (space group $P2_1/n - C^5_{2h}$, $Z = 4$) with $a = 635.9(1)$ $b = 854.7(1)$, $c = 754.4(1)$ pm and $\beta = 98.73(1)°$; $MgSO_3 \cdot 1H_2O$ (and β-$ZnSO_3 \cdot 1H_2O$) in the monoclinic $MnSO_3 \cdot 1H_2O$ form [39,57] (space group $P2_1/n$, $Z = 4$) with $a = 469.9(3)$, $b = 1282.3(10)$, $c = 563.2(4)$ pm and $\beta = 90.26(5)°$.

The IR and Raman spectra of the lower hydrates and of the amorphous anhydrous $MgSO_3$ are given in Figs. 2 and 3. From recent studies [61,62] it is shown that in both the SO stretching (850–1100 cm^{-1}) and the SO_3 bending regions, H_2O rotatory modes, i.e., H_2O liberations, can appear. This fact was not considered in earlier work [36,39], in which it was assumed that only the bending modes of the sulphite ion may coincide with H_2O liberations.

$MnSO_3 \cdot H_2O$ (pale pink) and $FeSO_3 \cdot 3H_2O$ (pale green) have colours in accord with octahedrally coordinated metal ions [37]. The central metal ion is probably surrounded by oxygen-bonded sulphite groups and by water oxygen atoms. This is borne out by the complexity of the IR peaks in the

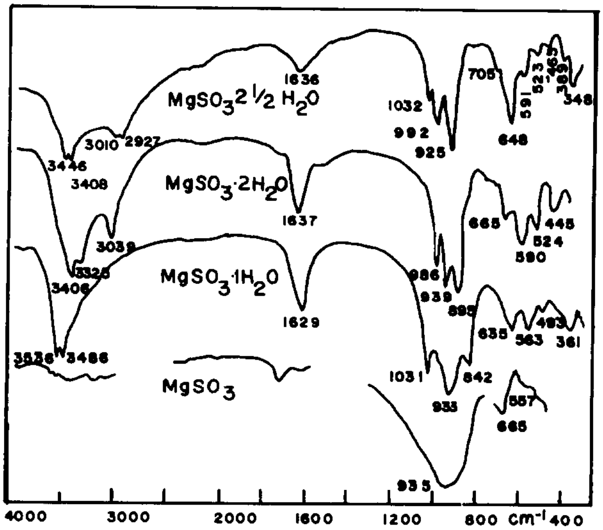


Fig. 2. IR spectra of $MgSO_3 \cdot 2\frac{1}{2}H_2O$, $MgSO_3 \cdot 2H_2O$, $MgSO_3 \cdot 1H_2O$ (KBr discs) and amorphous $MgSO_3$ (Nujol) (Perkin-Elmer 283).

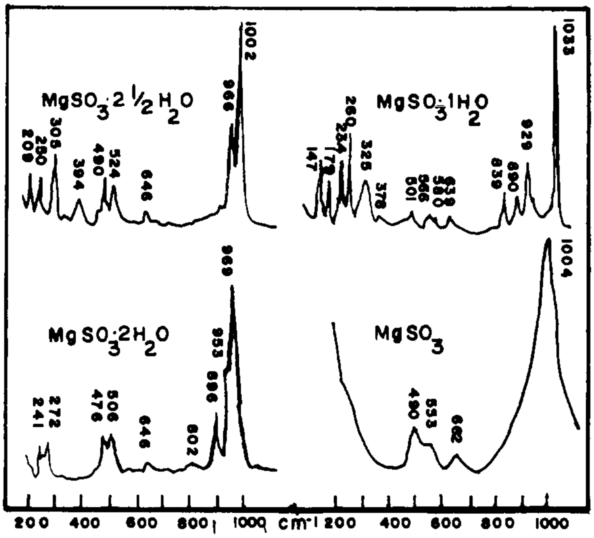


Fig. 3. Raman spectra of $MgSO_3 \cdot 2\frac{1}{2}H_2O$, $MgSO_3 \cdot 2H_2O$, $MgSO_3 \cdot 1H_2O$ and amorphous $MgSO_3$ (Coderg T 800, 488.0 nm).

region 1020–880 cm^{-1} and the crystal structure [63] of monoclinic α-iron(II) sulphite trihydrate. The S–O distances were in the range 152.1(1)–155.1(1) pm. The Fe ion is approximately octahedrally surrounded by sulphite and water oxygen atoms with Fe–O distances ranging from 205.1 to 222.7 pm.

Besides α-$FeSO_3 \cdot 3H_2O$ and $FeSO_3 \cdot 2.5H_2O$, Lutz et al. [15] obtained and definitely characterized γ-$FeSO_3 \cdot 3H_2O$ and $FeSO_3 \cdot 2H_2O$. Anhydrous crystalline $FeSO_3$ was obtained in ref. 64. IR and Raman spectra for various iron and nickel sulphites are reported in ref. 15 (Figs. 4–7). Goodall and co-workers [37,65] studied some anhydrous, hydrated transition and non-transition metal sulphites in order to ascertain the influence of metal ion and water of hydration on the characteristics of the oxyanion.

The iron complex $(NH_4)_9[Fe(OSO_2)_6]$ has been shown by an X-ray study [66] to contain monodentate oxygen donor sulphite ligands, the ion being at the centre of an FeO_6 octahedron.

Rare earth element (REE), oxygen-bonded sulphites

Crystalline hydrated sulphites of lanthanum and certain rare earth elements (Nd, Sm, Gd and Dy) have been studied [67,68]. Moskalenko et al. [69] isolated and studied sulphites of composition $Ln_2(SO_3)_3 \cdot 3H_2O$ (where Ln is Ho, Er, Tm, Yb or Lu). X-ray diffraction patterns reveal that these compounds are isostructural. Their IR spectra are also similar. The group of intense bands in the range 800–1200 cm^{-1} belongs to the stretching vibrations of the greatly distorted SO_3^{2-} ion. In the range of the SO_3^{2-} deformation vibrations (500–700 cm^{-1}), five bands are observed. Coordination of

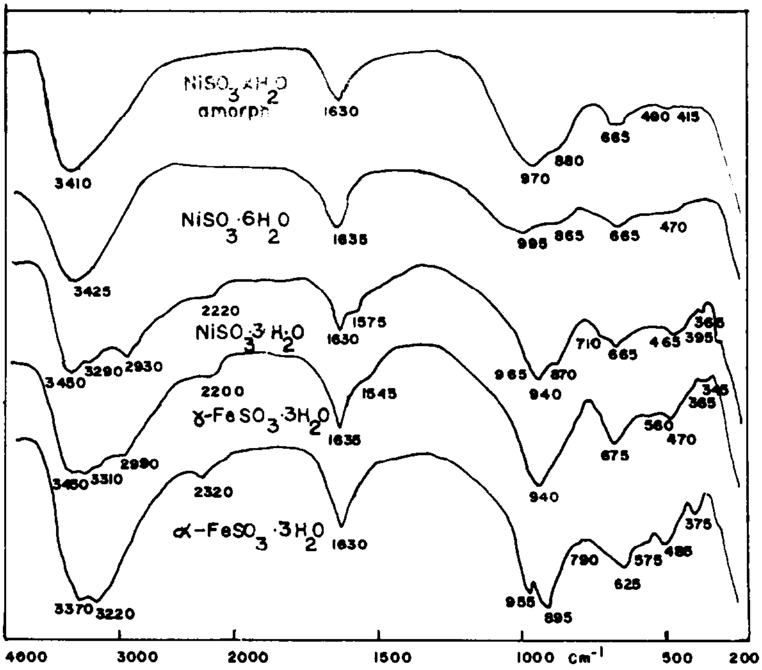


Fig. 4. IR spectra of $NiSO_3 \cdot 6H_2O$, α-$FeSO_3 \cdot 3H_2O$, γ-$FeSO_3 \cdot 3H_2O$, $NiSO_3 \cdot 3H_2O$ and $NiSO_3 \cdot xH_2O$.

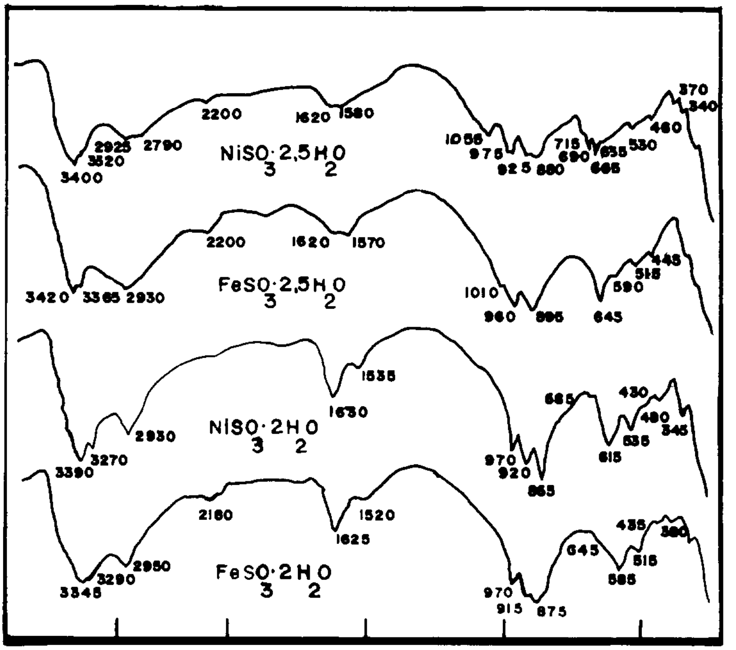


Fig. 5. IR spectra of $FeSO_3 \cdot 2\frac{1}{2}H_2O$, $NiSO_3 \cdot 2\frac{1}{2}H_2O$, $FeSO_3 \cdot 2H_2O$ and $NiSO_3 \cdot 2.5H_2O$ (Perkin-Elmer 325, KBr).

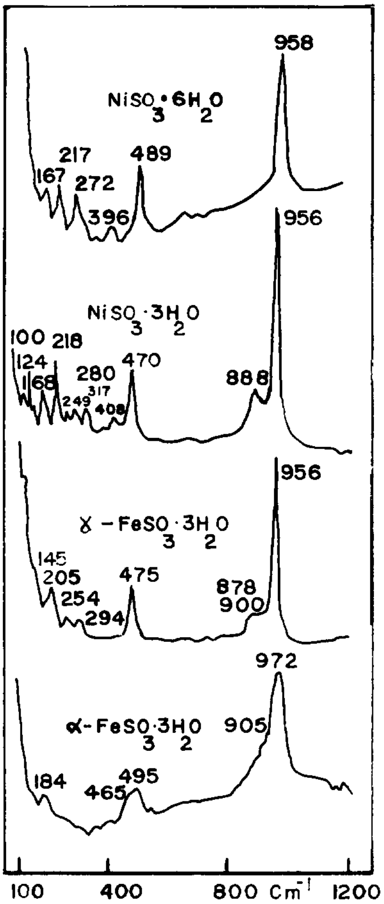


Fig. 6. Raman spectra of $NiSO_3 \cdot 6H_2O$, α-$FeSO_3 \cdot 3H_2O$, γ-$FeSO_3 \cdot 3H_2O$ (Coderg T 800, 4880 and 514.5 nm).

SO_3 groups to Ln is suggested by considerable splitting of the doubly degenerate asymmetric SO_3^{2-} vibrations: stretching (two complex bands, at ~ 850 and 950 cm^{-1}) and deformation (two bands at ~ 530 and 560 cm^{-1}). The presence of two bands (~ 940 and ~ 1120 cm^{-1}) in the range characteristic for the SO_3^{2-} stretching vibration could at least show two types of sulphite groups, differently bonded, in the structure of $Ln_2(SO_3)_3 \cdot 3H_2O$.

When heated in air the rare earth element (REE) sulphites are dehydrated and converted via the oxide sulphate [69] (~ 1000°C) into Ln_2O_3. Hydrated sulphites of the REE yttrium and scandium were described for the first time in refs. 28–30, 69 and 70. Finnish workers [30,70], on the other hand, described the synthesis of the hydrated sulphites of middle REE (Sm, Eu, Tb, Gd and Dy). According to their data, trihydrates exist in the Ln series from Sm to Dy and for the sulphites of the first three of these elements, hexahydrates also exist. The preparation and some properties of Gd_2-

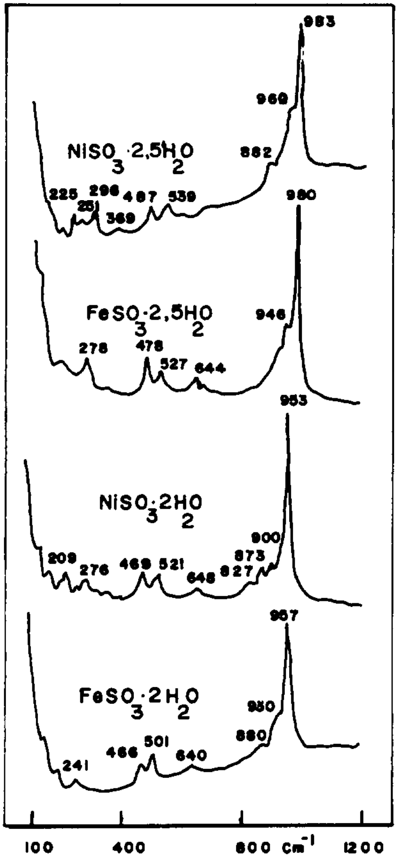


Fig. 7. Raman spectra of $FeSO_3 \cdot 2\frac{1}{2}H_2O$, $NiSO_3 \cdot 2\frac{1}{2}H_2O$, $FeSO_3 \cdot 2H_2O$ and $NiSO_3 \cdot 2H_2O$ (cf. Fig. 6).

$(SO_3)_3 \cdot nH_2O$ ($n = 3$ or 6) were described in ref. 71. The IR absorption spectra of hydrated gadolinium sulphites have much in common. The positions of the sulphite group stretches (860–1160 cm^{-1}) are practically the same for the sulphite trihydrates and hexahydrates, and are represented in such IR spectra by six absorption bands. The removal of the degeneracy of asymmetric vibrations (860–1160, 450–660 cm^{-1}) indicates distortion of the sulphite group in the hydrated crystals.

An interesting feature is that in the infrared spectra of the REE sulphite trihydrates of the yttrium subgroup [69], the range corresponding to the SO_3^{2-} stretches is wider (820–1200 cm^{-1}) and the bands are sharper and more clearly defined. This indicates, firstly, that the structure of gadolinium sulphite trihydrate differs from that of the corresponding compounds of the yttrium subgroup and, secondly, that the distortion of the SO_3^{2-} group is greater, possibly due to stronger Ln–SO_3 bonds. This last fact is also confirmed by the thermal data [28].

5. THERMAL ANALYSIS OF SULPHITES

5.1. Rare earth element sulphites and sulphite hydrates

The thermal behaviour of $M_2(SO_3)_3 \cdot 3H_2O$ (M = Sc or Y) and $La_2(SO_3)_3 \cdot 4H_2O$ is strictly individual [29], as studied by TG and DTA.

$$Sc_2(SO_3)_3 \cdot 3H_2O \xrightarrow[\text{endotherm at }150°\text{C}]{50\text{–}150°\text{C}} Sc_2(SO_3)_3 \xrightarrow[\text{endotherm at }385°\text{C}]{150\text{–}400°\text{C}}$$

$$Sc_2O_2SO_4 \xrightarrow{600\text{–}900°\text{C}} Sc_2O_3$$

The course of the thermal decomposition of $Y_2(SO_3)_3 \cdot 3H_2O$ is analogous to those for $Ln_2(SO_3) \cdot 3H_2O$ in the Ho–Lu series [28]

$$Y_2(SO_3)_3 \cdot 3H_2O \xrightarrow[\text{endo effect}]{60°\text{C}} \text{(after a series of intermediate stages)}$$

$$\xrightarrow{60\text{–}300°\text{C}} Y_2SO_3 \xrightarrow[\text{exo effect}]{300\text{–}600°\text{C}} Y_2O_2SO_4 \xrightarrow{850°\text{C}} Y_2O_3 \; La_2(SO_3)_3 \cdot 4H_2O \xrightarrow[\text{endo effect}]{110°\text{C}}$$

$$La_2(SO_3)_3 \cdot 2H_2O \xrightarrow[\text{exo effect }300\text{–}450°\text{C}]{\text{via a series of intermediate hydrates, and apparently anhydrous sulphites}}$$

$$\text{to } La_2O_2SO_4 \xrightarrow[\text{exo effect at }540°\text{C}]{} La_2O_2SO_4 \text{ (stable up to }1100°\text{C)}$$

All the REE double sulphites, $NaLn(SO_3)_2 \cdot H_2O$ (Ln = Ho, Er, Tm, Yb, or Lu), lose their water molecule in the temperature range 150–180°C [72]. When heated further, the anhydrous REE double sulphites are decomposed.

5.2. Sulphites of alkaline earth metals, zinc, cadmium and lead

In the literature [73–79], three hydrates of magnesium sulphite are described: $MgSO_3 \cdot XH_2O$ ($X = 6, 3, 2$). The dehydration of hydrates with $X = 6$ [39,55,56], 3 [37,39,55,56], $2\frac{1}{2}$ [55] and 2 [55,56] have been studied. $MgSO_3 \cdot 6H_2O$ starts dehydration at 70°C. $MgSO_3 \cdot 3H_2O$ is formed in one step by the loss of 3 moles of water. The dehydration of the trihydrate begins at 130°C. Thereby, the remaining water of crystallisation lost along with a partial decomposition (weight loss, 36.8%; calcd. for 3 moles of H_2O, 34.1%) [39]. However, Szendrei and Ho-Tun [56] and Harrison et al. [37] report 100°C as the commencing dehydration temperature. This difference in temperatures may be attributed to different rates of heating and crystallinity of samples. According to IR spectra and the X-ray powder patterns [39], the dehydration products possibly consist of basic magnesium sulphite. The temperature of dehydration was found to increase [37,39,56] with decreasing water content. The endothermicity of dehydration, on the other hand,

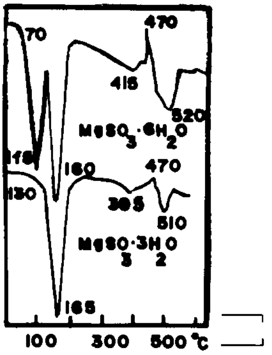


Fig. 8. DTA curves of magnesium sulphites (heating rate, 10° min^{-1}). Peaks: 115°C ($MgSO_3 \cdot 6H_2O$, $MgSO_3 \cdot 3H_2O + 3H_2O$); 160–165°C ($MgSO_3 \cdot 3H_2O$, $MgSO_3 + 3H_2O$), 395–415, 470°C (exotherm), 510–520°C (decomposition of anhydrous magnesium sulphite).

decreased steadily for the lower hydrates. By heating above 400°C, fast decomposition takes place with the formation of a residue consisting mainly of MgO, a little $MgSO_4$ (weight loss, 46.7%; calcd. for 1 mole of SO_2, 61.4%) and MgS [37,39]. Decomposition of $MgSO_3$ is relatively complicated (2 endo and 1 exo effect in DTA as well as 3 peaks in the DTG curve (Figs. 8 and 9)). It is slow, irregular and is not complete up to 1000°C [37].

DTA, TG and DTG studies of $CaSO_3 \cdot \frac{1}{2}H_2O$, $PbSO_3$, $2CdSO_3 \cdot 3H_2O$, $CdSO_3$, $SrSO_3$, $BaSO_3$ and $ZnSO_3 \cdot XH_2O$ were reported by Lutz and Suradi [52]. The dehydration of $CaSO_3 \cdot \frac{1}{2}H_2O$ occurs between 300 and 380°C and that of $2CdSO_3 \cdot 3H_2O$ at 115°C, as shown in Figs. 10 and 11. With higher

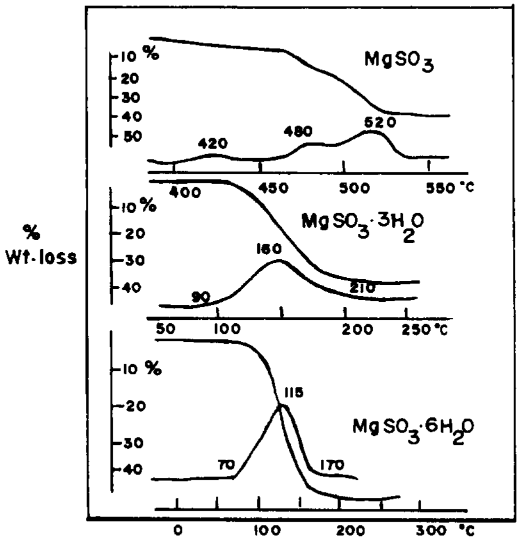


Fig. 9. TG and DTG curves of magnesium sulphites (heating rate, 2° min^{-1}, cf. Fig. 8).

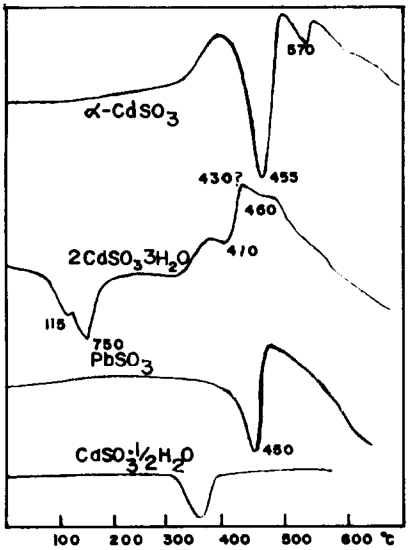


Fig. 10. DTA curves of $CaSO_3 \cdot \frac{1}{2}H_2O$, $PbSO_3$, $2CdSO_3 \cdot 3H_2O$ and α-$CdSO_3$ (heating rate, 10° min^{-1}).

temperatures, decomposition and/or generation of SO_2 takes place with the formation of oxides, sulphides, sulphates, as well as basic sulphates, e.g., $PbO \cdot PbSO_4$, $CdO \cdot CdSO_4$ and $2CdO \cdot CdSO_4$.

DTA of $SrSO_3$, $BaSO_3$ show [52] broad endotherms at 560 and 545°C. These peaks correspond, as supported [52] by IR spectra of the heated samples, to decomposition according to

$$4SrSO_3 \rightarrow 3SrSO_4 + SrS$$

$$4BaSO_3 \rightarrow 3BaSO_4 + BaS$$

The thermal decomposition of Ba, Sr and Pb sulphites was also studied with

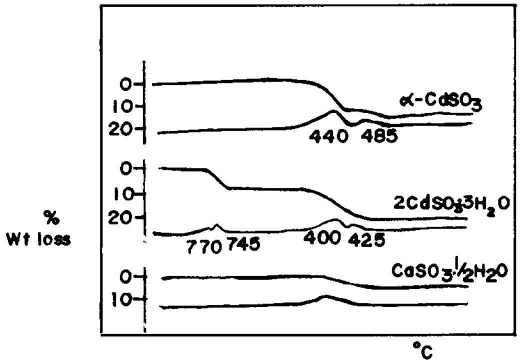


Fig. 11. TG and DTG curves of $CaSO_3 \cdot \frac{1}{2}H_2O$, $2CdSO_3 \cdot 3H_2O$ and α-$CdSO_3$.

the help of high-temperature X-ray diffraction [61], confirming the decomposition to S and SO_4.

The formation of $ZnSO_3 \cdot \frac{1}{2}H_2O$ and $ZnSO_3$ from the thermal decomposition of $ZnSO_3 \cdot 2\frac{1}{2}H_2O$ has been reported [39,59]. Recently [55], however, $ZnSO_3 \cdot \frac{1}{2}H_2O$ was proved to be $ZnSO_3 \cdot 1H_2O$. The high-temperature Raman spectra [39,55] of $ZnSO_3 \cdot 2H_2O$ show that the dehydration occurs firstly to give the hitherto unknown β-$ZnSO_3 \cdot 1H_2O$, then α-$ZnSO_3 \cdot 1H_2O$ (or to mixtures of α- and β-$ZnSO_3 \cdot 1H_2O$) and, finally, anhydrous $ZnSO_3$.

5.3. Sulphites of transition elements

Manganese sulphite hydrates and iron sulphite hydrates

Because of numerous dehydration steps, the thermal decomposition of manganese sulphites is rather complex [58]. The thermograms of $MnSO_3 \cdot XH_2O$ ($X = 2, 2\frac{1}{2}, 3$) are shown in Figs. 12 and 13.

β $MnSO_3 \cdot 3H_2O$ (ortho) lost its water of crystallization from 95°C in 2–3 steps. High-temperature X-ray diffraction showed that the dehydration to $MnSO_3$ results either through crystalline $MnSO_3 \cdot H_2O$ [39] or an intermediate amorphous product. Thus, the thermal decomposition of β-$MnSO_3 \cdot 3H_2O$ is very similar to that of α-$MnSO_3 \cdot 3H_2O$ (mono) [39,80]. The water

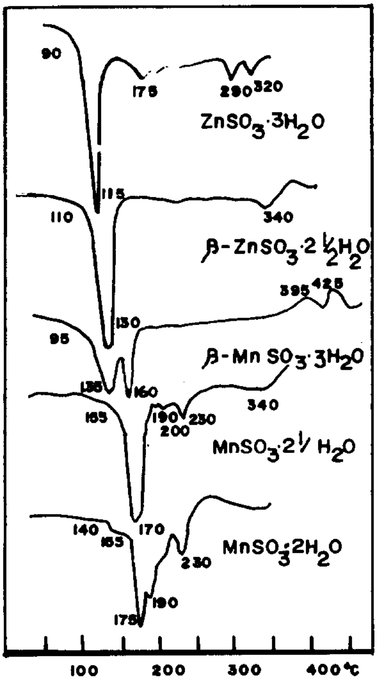


Fig. 12. DTA of manganese and zinc sulphite hydrates (heating rate, 2° min^{-1}). Peaks: 250°C, decomposition of anhydrous sulphites.

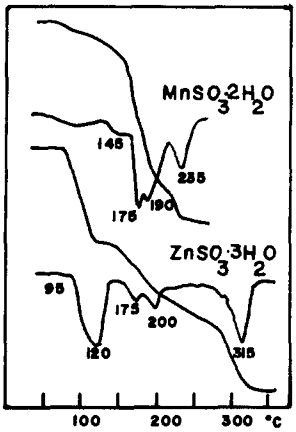


Fig. 13. TG and DTG of $MnSO_3 \cdot 2H_2O$ and $ZnSO_3 \cdot 3H_2O$ (heating rate, 2° min^{-1}). Peaks: 250°C, cf. Fig. 12.

loss of $MnSO_3 \cdot 2H_2O$ (3 peaks in DTA and DTG diagrams) starts at 160°C. Dehydration of either crystalline $MnSO_3 \cdot 1H_2O$ or an intermediate amorphous product by high-temperature X-ray diffraction resulted in $MnSO_3$ [55].

Under the chosen experimental conditions (N_2 current, heating rate, 2° min^{-1}), iron hydrates give [15] the first endothermic (water loss) peak as: $FeSO_3 \cdot 3H_2O$ (monoclinic), 100°C; $FeSO_3 \cdot 3H_2O$ (tetragonal), 120°C; $FeSO_3 \cdot 2.5H_2O$, 120°C; $FeSO_3 \cdot 2H_2O$, 120°C.

Of the two trihydrates of $FeSO_3$ the α-modification is less stable than the γ-form with respect to dehydration [15]. Contrary to this, α-$FeSO_3 \cdot 3H_2O$ at room temperature is less stable in water than γ-$FeSO_3 \cdot 3H_2O$. Unlike the corresponding compounds of other divalent metals [39,52,58], iron and nickel sulphites generally form no lower hydrates during their thermal decomposition. It follows from high-temperature X-ray patterns that the hydrates of $FeSO_3$ first give anhydrous $FeSO_3$ (rhombohedral) [64] which further disproportionates to $FeSO_4 \cdot H_2O$ and FeS_2. The thermal decomposition of nickel sulphite hydrates follows, similarly, without the formation of intermediate lower hydrates (except $NiSO_3 \cdot 6H_2O$ which gives $NiSO_3 \cdot 2H_2O$).

Thermogravimetric investigations [15] showed that the weight loss for the thermal decomposition of iron and nickel sulphites in the first step of disintegration is much higher than the total weight of water of crystallisation present. Under the chosen experimental conditions the dehydration of iron and nickel sulphites takes place with their decomposition [58] and evolution of SO_2. This observation is in agreement with other thermal studies [37,81,82] according to which the divalent metal iron and nickel sulphites are thermally most unstable.

In the thermal decomposition of cobalt sulphite hydrates, the whole of the water of crystallization is lost in one step [39]. Dehydration of $CoSO_3 \cdot 3H_2O$ begins at 120°C, $CoSO_3 \cdot 2\frac{1}{2}H_2O$ at 140°C and that of $CoSO_3 \cdot 2H_2O$ at 150°C.

The sulphites of manganese and iron should be compared with those of cobalt and nickel, which yield the pure oxides CoO and NiO on heating [65,83]. The relative ease with which transition metal sulphites decompose, and the fact that they give an oxide only, favours a fairly strong metal–oxygen bond in these sulphites. The metal sulphite is easily decomposed on heating, with the loss of SO_2, through fission of the oxygen–sulphur bond, which is weaker than in the free sulphite ion. Thermogravimetric studies on transition metal sulphites also indicate [37] that, whilst most of the SO_2 is evolved between 250 and 600°C, in the cases of the hydrated sulphites $FeSO_3 \cdot 3H_2O$, $CoSO_3 \cdot 2.5H_2O$ and $NiSO_3 \cdot 6H_2O$, further loss of SO_2 occurs at rather higher temperatures. This is probably due to the presence in these compounds of some sulphite ion as well as to covalently bonded sulphite.

Compounds containing free sulphite do not decompose substantially until higher temperatures are reached [37] (710°C in the case of $CaSO_3$ and 600°C in the case of $MgSO_3$, neither being completely decomposed up to 1000°C). The decomposition of anhydrous $CoSO_3$ to CoO and of $NiSO_3$ to NiO is complete at 570°C and no secondary loss of SO_2 is observed at higher temperatures. This, together with IR data [65], suggests that these sulphites exclusively contain covalently bonded sulphite groups and no free sulphite ions.

6. CONCLUSIONS

Interpretation of IR and Raman spectra of solid metal sulphites is not easy, as many of the bands are broad, and the stretching vibrations ν_1 and ν_3 are often superimposed. However, it is usually possible to distinguish between ionic sulphite and covalently bonded sulphite. Coordination of the sulphite group through sulphur will shift the stretching bands to higher frequencies compared with the free ion and the C_{3v} symmetry is essentially preserved, whereas coordination through oxygen may, generally, shift them to lower frequencies. Hitherto unknown lower hydrates of magnesium and zinc sulphites have been characterized by the use of high-temperature Raman spectra, IR and thermoanalytical analyses.

IR and thermal studies indicate, firstly, that the structure of gadolinium sulphite trihydrate differs from that of the corresponding compounds of the yttrium sub-group and, secondly, that the distortion of the SO_3^{2-} group is greater, possibly due to stronger $Ln–SO_3$ bonds.

Divalent metal iron and nickel sulphites are thermally most unstable and, unlike other divalent metal sulphites, generally form no lower hydrates during their thermal decomposition. The temperature of dehydration increases with decreasing water content and endothermicity steadily decreases for the lower hydrates. In transition metal sulphites a strong metal–oxygen bond is present as they decompose to their oxides at relatively lower temperatures in comparison to magnesium and calcium sulphites.

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