J. Braz. Chem. Soc., Vol. 15, No. 2, 170-177, 2004.
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0103 - 5053 $6.00+0.00

Isomorphic Series of Double Sulfites of the $Cu_2SO_3.MSO_3.2H_2O$ (M = Cu, Fe, Mn, and Cd) Type – A Review

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Embora o primeiro sulfito duplo de valência mista, $Cu_2SO_3.CuSO_3.2H_2O$, tenha sido preparado no início do século XIX por M. Chevreul, o interesse por compostos dessa natureza ressurgiu só depois da metade do século XX com a determinação da estrutura cristalina deste composto e a caracterização de seu espectro de absorção na região do infravermelho. Nos últimos anos, os estudos referentes a este tema têm se intensificado, especialmente após a descoberta da possibilidade de substituição isomórfica do Cu(II) no sal de Chevreul por diversos cátions com o mesmo estado de oxidação, gerando uma série de compostos cujas propriedades são fortemente dependentes da natureza do cátion M(II). Devido às suas propriedades interessantes, esses sistemas de valência mista podem ser usados como modelos para identificar intermediários em processos de corrosão atmosférica, bem como para avaliar o papel de metais de transição como catalisadores de autooxidação de S(IV) na conversão do SO_2 na atmosfera.

Although the first mixed valence double sulfite, $Cu_2SO_3.CuSO_3.2H_2O$, was prepared in the early 19th century by M. Chevreul, interest in this type of compound was only rekindled in the mid-1960s, when the crystalline structure of Chevreul's salt was determined and its infrared spectrum characterized. Studies of this type of compound have been intensified in recent years, especially after the discovery that the isomorphic Cu(II) in Chrevreul's salt could be replaced by a divalent metal ion, forming an isomorphic series whose properties are strongly dependent on the nature of the M(II) cation. Because of their interesting properties, these mixed valence systems can be used as models to identify intermediates in atmospheric corrosion processes, and to evaluate the role of transition metals as catalysts of S(IV) autoxidation in the conversion of SO_2 in the atmosphere.

Keywords: Chevreul's salt, double sulfites, mixed valence systems, isomorphic series

1. Introduction

Mixed valence systems are of considerable interest in chemistry because their properties rarely represent only the sum of the ions separately. The first known mixed valence sulfite complex, $Cu_2SO_3.CuSO_3.2H_2O$, was prepared by M. Chevreul in 1812.[1] However, it was only in 1965 that its crystalline structure was determined by Kierkegaard and Nyberg in terms of coordination polyhedra (Figure 1).[2,3] The structure consists of $[SO_3]$ trigonal pyramids, $[Cu^IO_3S]$ tetrahedra and $[Cu^{II}O_4(H_2O)_2]$ octahedra linked together, giving a three-dimensional network pertaining to the $P2_{1/n}$ spatial group. The structure is monoclinic, with the unit cell containing two formula units and dimensions of: a = 5.5671 Å; b = 7.7875 Å; c = 8.3635 Å and $\beta = 91.279^o$.

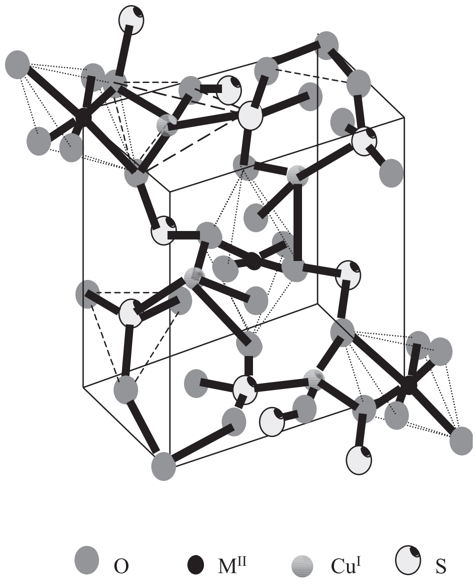

Figure 1. Unit cell of Chevreul's salt.

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The first optical approach to identify Chevreul's salt was published in 1973, when Nyberg and Larson[4] studied sulfite ion coordination types using fundamental active infrared modes. X-ray diffraction results indicate that the free sulfite ion is pyramidal (C_{3v} symmetry), with the sulfur at the apex.[5] This model gives rise to four fundamental active infrared modes: ν_1 (symmetric stretch), ν_2 (symmetric bend), ν_3 (asymmetric stretch), and ν_4 (asymmetric bend). The two asymmetric modes are doubly degenerated. Because the Na-O bonds in Na_2SO_3 are very weak, this compound can be used as a free sulfite ion standard for comparison with other metal sulfites. The infrared spectrum of the Na_2SO_3 in the solid state presents the following bands (in cm^{-1}): $\nu_1 = 1010$ (medium), $\nu_2 = 633$ (strong), $\nu_3 = 961$ (strong), and $\nu_4 = 469$ (strong).[6]

Assuming that the 3d orbitals of sulfur participate in bonding, the S-O bond shows a partially double bond character and two of the resonance structures of the sulfite ion can be written as shown in the Figure 2.

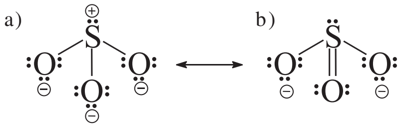


Figure 2. Resonance structures of the sulfite ion.

In an oxygen-coordinated compound (Figure 2a), the symmetry of the group changes to C_s and the number of fundamental active infrared modes increases to six, due to the removal of degeneracy from ν_3 and ν_4. This is a consequence of the decrease in the bond order (S-O) following the decrease in the stretching frequency. If the sulfite group is coordinated with the metal through sulfur (Figure 2b), the C_{3v} symmetry is preserved, but the stretching modes should shift to higher frequencies than those of the free ion because of the higher bond order. The sulfite group can coordinate to the metal as a monodentate sulfur (I) or oxygen (II) donor or, in bidentate form, via oxygen (III) or oxygen and sulfur (IV) (Figure 3).[7]

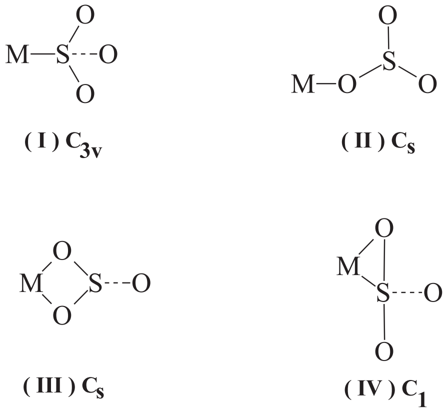


Figure 3. Different possibilities of coordination between the sulfite ion and a metal ion.

According to Nyberg and Larson,[4] the structure of sulfite compounds can be divided into three groups after coordination of the sulfite ion: (*i*) compounds without sulfur coordination (under 975 cm^{-1}); (*ii*) compounds with both sulfur and oxygen coordination (over and under 975 cm^{-1}); and (*iii*) compounds with dominant sulfur coordination (over 975 cm^{-1}). Chevreul's salt spectrum shows stretching frequencies of high intensity over and under 975 cm^{-1}, suggesting that the compound belongs to group (*ii*), with both metal-sulfur bonds and metal-oxygen bonds.

The presence of both Cu(I) and Cu(II) in the structure of Chevreul's salt was confirmed by the presence of two distinct $2p_{1/2}$ and $2p_{3/2}$ copper bands with their associated satellites in the photoelectron spectrum.[8] The binding energy of the $2p_{1/2,3/2}$ sulfur band confirmed the expectation that sulfur is present in only one oxidation state.[8] The magnetic susceptibility of the $Cu^{2+}(Cu^{+})_2(SO_3^{2-})_2(H_2O)_2$ formula gives the magnetic moment 1.90 M.B. for the paramagnetic Cu^{2+} ion. The latter value agrees with the magnetic moment calculated from EPR g factors determined by Inoue *et al.*[9] These magnetic properties support the formula proposed by Chevreul.[1]

2. Isomorphic Series

After Chevreul first prepared his salt, several simple sulfites of transition metals – Zn, Ni, Ag, Pd, Co, and Cd – and double sulfites consisting of transition metals and an alkali metal or ammonium ion were prepared and characterized.[4,10-13] Although Cu(II) sulfite ($CuSO_3$) seems never to have been isolated, the literature contains references[14] to two simple sulfites of Cu(I), commonly distinguished as Étard's salt, $Cu_2SO_3.1/2H_2O$, and Rogojski's salt, $Cu_2SO_3.H_2O$. The color, diamagnetism, infrared spectrum and elemental analysis of Étard's salt confirm its formulation.[15] However, Dasent and Morrison[15] proved that Rogojski's salt is an approximately equimolar mixture of $Cu_2SO_3.CuSO_3.2H_2O$ and metallic copper. They suggested that its preparation method involved a partial disproportionation of the Cu(I) compound:

$$Cu_2SO_3 \rightarrow Cu + CuSO_3 \quad (1)$$

followed by the immediate combination of the resulting Cu(II) sulfite with unchanged Cu_2SO_3 to form Chevreul's salt:

$$CuSO_3 + Cu_2SO_3 + 2H_2O \rightarrow Cu_2SO_3.CuSO_3.2H_2O \quad (2)$$

The resulting red mixture of Cu and $Cu_2SO_3.CuSO_3.2H_2O$ has the same composition as $2Cu_2SO_3.H_2O$.[15]

The accidental discovery of a Cu, Fe, Mn triple sulfite in the mid 60s, when a hydrometallurgical study was designed to obtain precious metals from deep-sea manganese nodules, gave rise to preliminary studies involving complex sulfites, which resulted in preparation of non-stoichiometric compound mixtures, including the Chevreul's salt.[16-18] Almost two centuries after Chevreul's salt preparation, Cipriano,[18] Miguel and de Andrade[19] studied the chemistry and preparation of double sulfites involving Cu(I) and a divalent metal ion, M(II), establishing the best conditions to obtain the complete replacement of Cu(II) by transition metal ions such as Fe(II), Mn(II) and Cd(II) ions. In this case, their X-ray diffraction data were similar to those of Chevreul's salt, with minor changes in "d" spacings, forming an isomorphic series: $Cu_2SO_3.CuSO_3.2H_2O$, $Cu_2SO_3.FeSO_3.2H_2O$, $Cu_2SO_3.MnSO_3.2H_2O$, and $Cu_2SO_3.CdSO_3.2H_2O$.[20-22]

Sghyar *et al.*[22] determined the structure and crystallographic parameters of isomorphic series of doubles sulfite such as $Cu_2SO_3.MSO_3.2H_2O$ (M = Cu, Fe, Mn, and Cd):

Table 1. Crystallographic parameters of the isomorphic series of double sulfites such as $Cu_2SO_3.MSO_3.2H_2O$ (M = Cu, Fe, Mn, and Cd) (selected from ref. 22)

M(II)	Cu	Fe	Mn	Cd
r_i / Å	0.73	0.77	0.82	0.95
a / Å	5.5671	5.694	5.712	5.696
b / Å	7.7875	7.874	7.936	8.065
c / Å	8.3635	8.093	8.156	8.260
β / °	91.279	93.1	92.8	92.4
V / Å^3	362.5	362.3	369.3	379.1
ρ_x / (g cm^{-3})	3.57	3.46	3.40	3.82

Note: r_i = ionic radii; a, b, c and β = network parameters; V = unit cell volume; ρ_x = density.

The infrared spectra of $Cu_2SO_3.FeSO_3.2H_2O$, $Cu_2SO_3.MnSO_3.2H_2O$ and $Cu_2SO_3.CdSO_3.2H_2O$ are similar to that of Chevreul's salt and may be assigned in a similar way.[20,21] The vibrational bands of the sulfite group were assigned by comparing them with data reported in the literature. The four fundamental bands of the sulfite ion vibrations were identified.

Copper(II) and copper(I) have different bonding characteristics. Copper(I) is a class b metal or soft base and follows the trend of having increased polarizability over Cu(II) and of having a decreased number of coordination sites (four, instead of five or six). Copper(I) preferentially complexes with soft sulfur-containing ligands. Copper(II) is sometimes classified as class b, but it can show characteristics of both classes (a or b).[23-25] In $Cu^I_2SO_3.Cu^{II}SO_3.2H_2O$, Cu(I) is bonded to SO_3^{2-} through both oxygen and sulfur bonds, while Cu(II) is bonded through oxygen bonds and its hard character prevails. Thus, considering M(II) cations of the isomorphic series, the hardness order is: Cu(II) > Fe(II) > Mn(II) > Cd(II). Pearson[26] proposed that a hard acid prefers to combine with a hard base, and a soft acid prefers to combine with a soft base; hence, since M(II) is bonded only through oxygen, which is a hard acid, a preference is expected for the formation of $Cu_2SO_3.CuSO_3.2H_2O$.

Selectivity evaluation studies[20] of the incorporation of M(II) during the formation of salt have shown that, contrary to expectation, the replacement of Cu(II) by M(II) takes place preferentially in decreasing order of hardness. Sghyar *et al.*[22] calculated the unit cell volumes of several double sulfites, considering isomorphic substitution (Figure 4). It is worth noting that, in the incorporation of M(II), the unit cell expands proportionally to the increase in ionic radius, confering a supplementary stability on the sulfite network. This fact may justify the preference for Cu(II) replacement by the soft cation. Nevertheless, this replacement only occurs if there is an excess of M(II) cations.

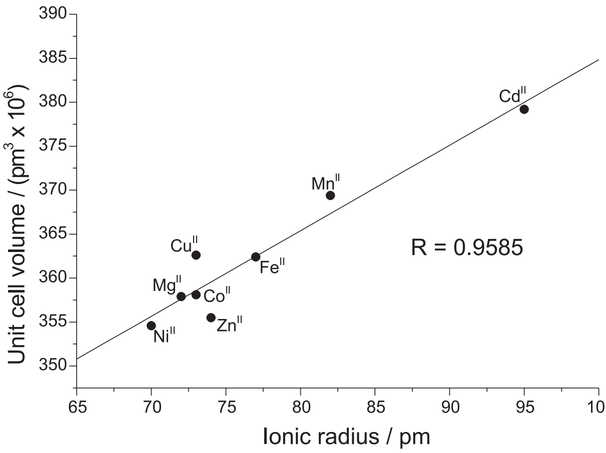


Figure 4. Changes in unit cell volume as a function of the ionic radius.

3. Considerations About Synthesis

Chevreul's salt has been synthesized by various procedures. Up to the 1960s, the most common preparation method described for this substance in the literature consisted of passing sulfur dioxide through an aqueous solution of Cu(II) sulfate at about 70 °C for two hours,[2,27] after which the gas stream was interrupted and a brick red solid precipited. In 1967, Scarbo *et al.*[18] described a new synthesization procedure to obtain Chevreul's salt from diluted Cu(II) solution, replacing the prolonged heating time by adding an alkali solution. In that protocol, Chevreul's salt is prepared by precipitation from a copper sulfate solution (1 g/100 mL) by the passage of SO_2 at ambient temperature. After saturation with sulfur dioxide, the solution temperature is raised to 78 ± 2 °C and the pH value is adjusted to 3.0 – 3.5 with the addition of a hydroxide or carbonate solution, at which point Chevreul's salt precipites.

The isomorphic series was prepared according to Skarbo's procedure, adding, besides Cu(II) sulfate, an excess of M(II) sulfate to each of the initial solutions. The compositions of the starting solutions are given in Table 1. Further details of the steps involved in isomorphic series synthesis are discussed elsewhere.[18-22]

Table 2. Composition of the starting solutions in mixed valence sulfite preparations

Double sulfites	$MSO_4.nH_2O^a$/g				Vol. Solution
	Cu	Fe	Mn	Cd	(mL)
$Cu_2SO_3.CuSO_3.2H_2O$	2.0	-	-	-	50
$Cu_2SO_3.FeSO_3.2H_2O$	1.0	12.2	-	-	50
$Cu_2SO_3.MnSO_3.2H_2O$	1.0	-	6.2	-	50
$Cu_2SO_3.CdSO_3.2H_2O$	1.0	-	-	10.2	50

[a] Cu (n = 5); Fe (n = 7); Mn (n = 1); Cd (n = 8/3).

When carbonate or hydroxide solution is used as a neutralizing agent, a substantial increase of the pH occurs at the point where the drop reaches the solution, causing the cation, usually Na^+, K^+ or NH_4^+, to become incorporated as an impurity in the sulfite structure. In the specific case when alkali is a sodium carbonate solution, Na^+ can replace Cu^+ in the crystalline structure because these two cations have the same charge, +1, and their ionic radii are very similar (Na^+, 97 pm and Cu^+, 96 pm).

To avoid incorporation of the base cation, Silva *et al.*[20] suggested two alternative methods to raise the pH, replacing the addition of alkali with the removal of excess SO_2: *i*) by reducing the internal pressure of the system associated with the ultrasonic bath at 60 °C; *ii*) by burbling N_2 in the sulfur dioxide saturated solution.

In both cases, the salts obtained displayed high degrees of purity. While the traditional method (the addition of Na_2CO_3) leads to a contamination by Na^+ of about 0,8% (m/m), the use of the new procedure results in sodium concentrations at blank levels.[20]

4. Redox Chemistry of Cu(II)-S(IV) Complexes

Transition metal complexes are important in aqueous atmospheric systems (e.g., cloud droplets and haze aerosols), where trace metal catalysis of the autoxidation of S(IV) has been postulated as an important pathway for SO_2 conversion.[28-41] The Cu(II)-S(IV) system was proposed by Conklin and Hoffmann[29] for use as a model for transition metals that are active catalysts for SO_2 autooxidation. This system is similar to the preparation of Chevreul's salt.

According to Conklin and Hoffmann,[30] copper(II) forms transient complexes with S(IV) in solution. These complexes react to form a mixture of Cu(I), Cu(II), SO_4^{2-} and SO_3^{2-} in apparent equilibrium with Chevreul's salt ($Cu^I_2SO_3.Cu^{II}SO_3.2H_2O$). However, the reduction of Cu(II) by S(IV), in terms of the predominant Cu(II) and S(IV) species, is thermodynamically unfavorable:

$$Cu^{2+} + e^- \rightleftharpoons Cu^+ \qquad E^o = 0.153\ V \qquad (3)$$

$$HSO_3^- \rightleftharpoons H^+ + e^- + SO_3^- \qquad E^o = -0.84\ V \qquad (4)$$

The unfavorable ΔG^o for this reaction indicates that other processes must be taken into account. These processes include the stabilization of the products and the energy released by precipitation.

A mechanism for the anoxic reaction between Cu(II) and S(IV) in the formation of Chevreul's salt was suggested by Conklin and Hoffmann[30] observed that positively charged dimeric Cu(II)-S(IV) complexes are formed upon mixing solutions of Cu(II) and S(IV); the formation of Cu(II)-S(IV) complexes is pH-dependent; the rate of disappearance of the complexes follows biphasic first-order kinetics; two-electron transfer appears to occur with the formation of S(VI); an equilibrium mixture of Cu(II), Cu(I), S(IV), and S(VI) with precipitated $Cu^I_2SO_3.Cu^{II}SO_3.2H_2O$ is established.

A mechanism that is consistent with the above observations is:[30]

$$HSO_3^- \rightleftharpoons H^+ + SO_3^{2-} \qquad (4)$$

$$Cu^{2+} + SO_3^{2-} \rightleftharpoons CuSO_3 \qquad (5)$$

$$Cu^{+2} + CuSO_3 \rightleftharpoons [Cu^{II}SO_3Cu^{II}]^{2+} \qquad (6)$$

$$[Cu^{II}SO_3Cu^{II}]^{2+} + H_2O \rightleftharpoons Cu^{II}SO_3Cu^{II}OH^+ + H^+ \qquad (7)$$

$$[Cu^{II}SO_3Cu^{II}]^{2+} \rightarrow [Cu^IS^VO_3Cu^{II}]^{2+} \qquad (8)$$

$$Cu^{II}SO_3Cu^{II}OH^+ \rightarrow Cu^IS^VO_3Cu^{II}OH^+ \qquad (9)$$

$$[Cu^IS^VO_3Cu^{II}]^{2+} \rightarrow [Cu^IS^{VI}O_3Cu^I]^{2+} \qquad (10)$$

$$Cu^IS^VO_3Cu^{II}OH^+ \rightarrow Cu^IS^{VI}O_3Cu^IOH^+ \qquad (11)$$

$$[Cu^IS^{VI}O_3Cu^I]^{2+} \rightleftharpoons 2Cu^+ + S^{VI}O_3 \qquad (12)$$

$$Cu^IS^{VI}O_3Cu^IOH^+ \rightleftharpoons 2Cu^+ + S^{VI}O_3 + OH^- \qquad (13)$$

$$S^{VI}O_3 + H_2O \rightleftharpoons SO_4^{2-} + 2H^+ \qquad (14)$$

$$2Cu^+ + SO_3^{2-} \rightleftharpoons CuSO_3^- \qquad (15)$$

$$2Cu^+ + Cu^{2+} + 2SO_3^{2-} + 2H_2O \rightleftharpoons Cu^I_2SO_3.Cu^{II}SO_3.2H_2O \qquad (16)$$

5. Oxidation by Air

There is evidence that a significant portion of the airborne sulfur species emitted into the atmosphere may be particulate SO_3^{2-}. Some studies indicate that solid metal sulfite and sulfite complex in solution may play a role as intermediaries in atmospheric corrosion processes.[38] The kinetics of surface oxidation in particles of $Cu_2SO_3.CuSO_3.2H_2O$, Chevreul's salt, was monitored by X-ray photoelectron spectroscopy (XPS) and used as a model compound for characterizing sulfite stability on particle surfaces exposed to air.[31] Several surface reactions of Chevreul's salt exposed to air, including possible oxidation of S(IV) into S(VI) and Cu(I) to Cu(II), were considered. Since no SO_4^{2-} was detected by XPS in the final products, the reaction below is most likely to occur:

$$\tfrac{1}{2}O_2 + Cu_2SO_3.CuSO_3.2H_2O \rightarrow 2CuSO_3 + CuO + 2H_2O \quad (17)$$

This is consistent with the conclusions of Eatough *et al.*[38] that atmospheric S(IV) species, such sulfites, may have long residence times in the environment.

6. Optical Properties

The isomorphic species present distinct colors. The intense red of Chevreul's salt changes to yellow-brown after Cu(II) is replaced by Fe(II). If the substitution involves Mn(II) instead of Fe(II), a gradual transition to yellow is observed. On the other hand, if Cu(II) is replaced by Cd(II), a faint yellow color is obtained.

The spectroscopic properties of Chevreul's salt were investigated recently by Inoue *et al.*[9] based on EPR measurements and diffuse reflectance absorption spectra. A more complete study was made by Silva *et al.*,[42] involving the electronic interactions between the constituents of Chevreul's salt derivatives, particularly insofar as the types of electronic transition responsible for their different colors are concerned, with emphasis on the theoretical evaluation employing molecular modeling calculations.[43-46]

The spectrum of Chevreul's salt and those of the corresponding derivatives with Fe(II), Mn(II) and Cd(II) ions are shown in Figure 5.

The electronic spectrum of Chevreul's salt consists of a charge-transfer band around 425 nm associated with the $[Cu^I_2(\underline{S}O_3)_2(S\underline{O}_3)_2]^{6-}$ chromophore,[42] and two ligand field transitions at 785 and 1000 nm involving the Jahn-Teller splitting of the Cu(II) levels, an effect that is associated with d^9 ions. An additional intervalence-transfer band, responsible for its red color, can be found at 500 nm. The replacement of the Cu(II) ions by Fe(II), Mn(II) and Cd(II) does not eliminate the absorption band at 425 nm, supporting its assignment as a charge-transfer transition centered on the Cu(I) sites. The less intense band at 860 nm for the Fe(II) derivative is consistent with a Laporte forbidden ligand field transition, while the bands at 820 nm in the case of Mn(II) and at 725 nm in that of Cd(II) have been tentatively attributed to charge-transfer transitions in the $[Cu^I_2(\underline{S}O_3)_2(S\underline{O}_3)_2]^{6-}$ chromophore, considering the lack of characteristic electronic transitions for these ions in this region.

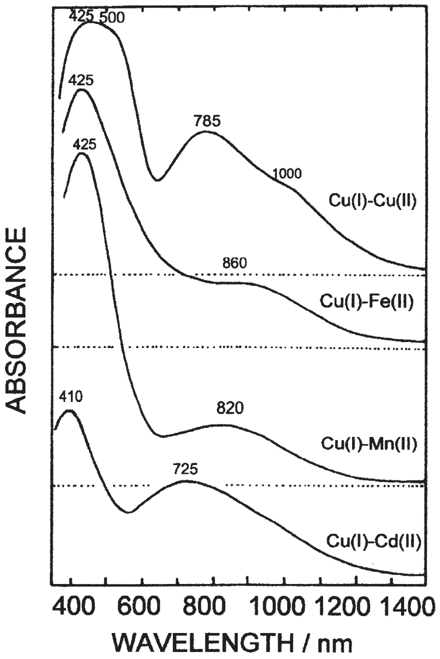


Figure 5. Diffuse reflectance spectra of the mixed valence Cu(I)-Cu(II) and related Cu(I)-M(II) Chevreul's salts, $Cu_2SO_3.MSO_3.2H_2O$ (M = Cu, Fe, Mn, and Cd).

7. Thermal Properties

To gain a better understanding of the chemical nature of mixed valence compounds, Silva *et al.*[47] investigated several thermal properties, such as thermal diffusivity (α), heat capacity (ρc_p), and thermal conductivity (k), as well as the non-radiative relaxation time (τ_R) and the characteristic diffusion time (τ_b) of the excited state of ions in the double sulfites of the isomorphic series, using photoacoustic spectroscopy (PAS) and the rising temperature method.[48-52]

The results in Table 3 show the thermal properties determined by photothermic techniques.[47] The thermal diffusivities have values one order of magnitude higher than some semiconductors and porous silicon.[53-55]

The overall behavior of the thermal parameters seems to reflect the change in the sample structure. It is well known that an amorphous phase is characterized by a slight thermal diffusivity. On the other hand, the high crystallinity of these compounds results in their high diffusivity. In this case, as expected, the heat flows faster

Table 3. Thermal diffusivity, heat capacity, and thermal conductivity of each compound (adapted from ref. 47)

Double Sulfite	α/cm^2 s^{-1}	ρc_p/J cm^{-3} K^{-1}	k/W cm^{-1} K^{-1}
$Cu_2SO_3.CuSO_3.2H_2O$	0.154	0.62	0.10
$Cu_2SO_3.FeSO_3.2H_2O$	0.203	0.57	0.12
$Cu_2SO_3.MnSO_3.2H_2O$	0.148	0.74	0.11
$Cu_2SO_3.CdSO_3.2H_2O$	0.156	0.55	0.09

through crystalline materials. It is noteworthy that the thermal conductivity changes according to the ionic radius of M(II) cations. Their behavior is related to increases in the unit cell volume (Figure 4). Figure 6 shows the results of thermal conductivity as a function of the ionic radius.

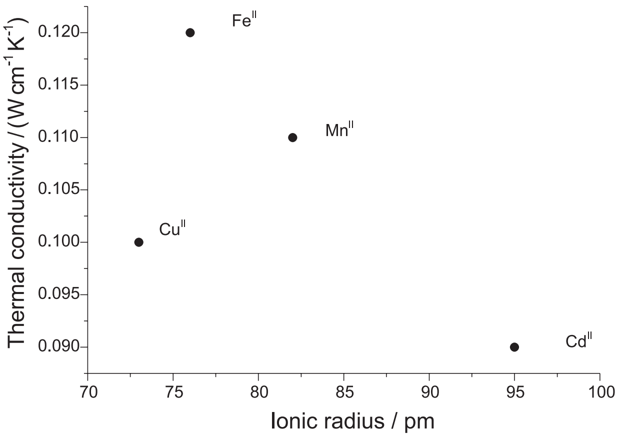


Figure 6. Thermal conductivity of the mixed valence sulfite $Cu_2SO_3.MSO_3.2H_2O$ (M = Fe, Mn, Cu, Cd) as a function of the ionic radius.

The trend indicated in the graph seems to indicate a linear dependence, with the thermal conductivity decreasing as the ionic radii of M(II) cations [Cu(II) < Fe(II) < Mn(II) < Cd(II)], except $Cu_2SO_3.CuSO_3.2H_2O$, increase. The electronic spectrum of Chevreul's salt discussed previously[42] shows an intervalence transfer transition band at 500 nm (see Figure 6) from the tetrahedral Cu(I) ions to the empty $3d_{x^2-y^2}$ level of e_g symmetry of the Cu(II) ions. This band, in addition to being responsible for the salt's red color, is evidence of the strong Cu(I)-Cu(II) interaction and explains the linear correlation (R = 0.9992) observed when one considers the weighted average (88 pm) of the ionic radius of Cu(I) and Cu(II) (Figure 7).[56]

The information concerning the non-radiative relaxation time (t_R) and characteristic diffusion time (t_b) was obtained from measurements of the PA phase angle as a function of the modulation frequency of the maximum absorbance bands (see electronic spectra – Figure 6) using the thermal diffusivity model[51] for a thermally thick sample.[47]

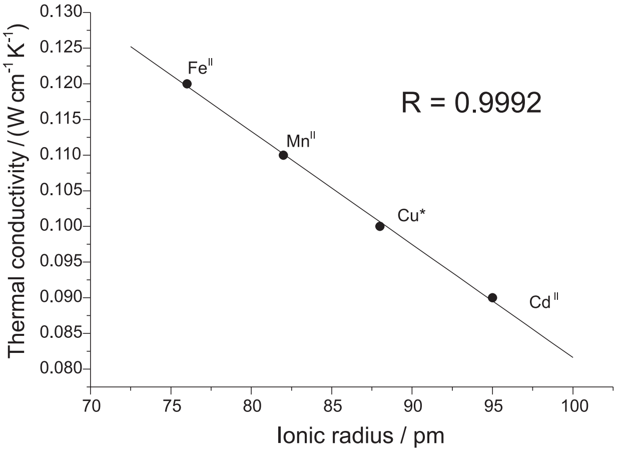


Figure 7. Thermal conductivity of the mixed valence sulfite $Cu_2SO_3.MSO_3.2H_2O$ (M = Fe, Mn, Cu, Cd) as a function of the ionic radius. Note: Cu* is the weighted average of the ionic radius of Cu(I) and Cu(II) (data from ref. 47).

Table 4. Non-radiative relaxation time, τ_R, and characteristic diffusion time, τ_b, of each compound (selected from ref 47)

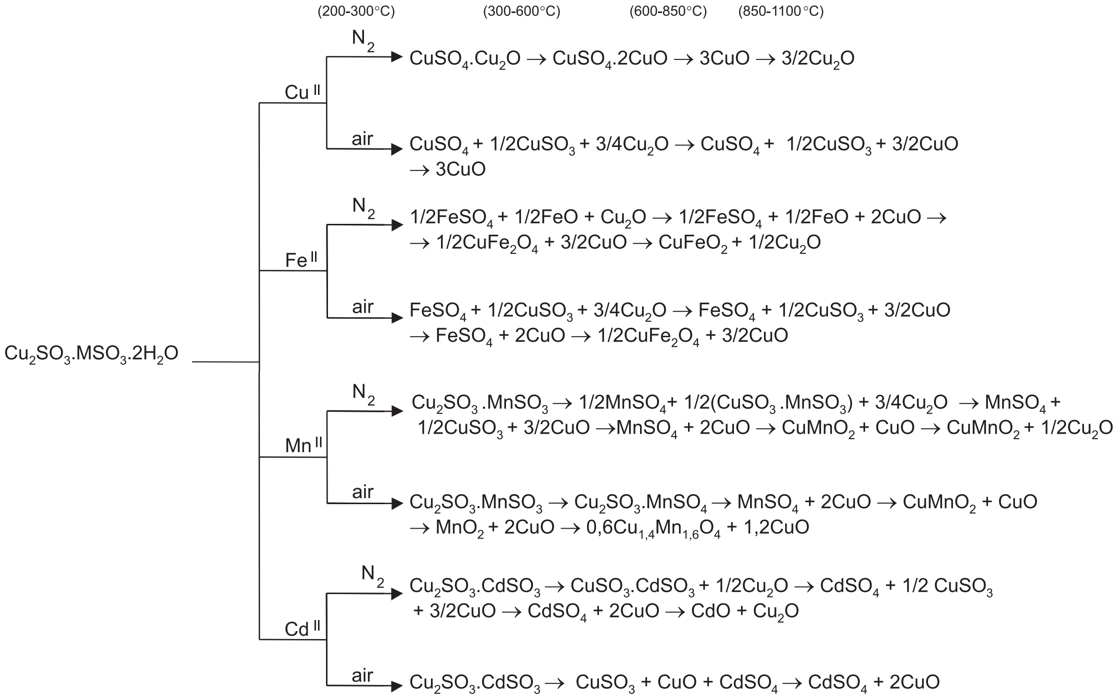
Double Sulfite	Band – 1		Band – 2	
	τ_R/ms	τ_b/μs	τ_R/ms	τ_b/μs
$Cu_2SO_3.CuSO_3.2H_2O$	8.01	1.4	7.66	2.3
$Cu_2SO_3.FeSO_3.2H_2O$	7.21	3.5	9.68	2.0
$Cu_2SO_3.MnSO_3.2H_2O$	10.0	5.0	6.45	1.0
$Cu_2SO_3.CdSO_3.2H_2O$	7.28	1.0	6.29	1.0

Note: Band –1: 360 – 470 nm; Band – 2: 690 – 750 nm.

The photoacoustically measured relaxation time does not necessarily constitute an appropriate representation of the level initially excited in the absorption process, but rather of the average lifetime of a variety of states before energy is lost in the form of heat. Thus, in general, there is a non-unique relaxation pathway consisting of several successive steps, and the measured lifetime is an average lifetime of heat production. For a powder sample, t_R also contains a contribution from the heat exchange time between the powder particle and the transducing gas of the PA cell.

8. Thermal Decomposition

The isomorphic series has been subjected to thermal treatment in helium, nitrogen, air and reductive gaseous mixtures (H_2/Ar) in dynamic atmospheres. The studies revealed that double sulfites are thermally stable up to 200°C under all conditions.[21] Based on the characterization of solid intermediary products and to TG and DSC curve analyses, Silva *et al.*[21] suggested the thermal decomposition reactions of the double sulfites in air and nitrogen atmospheres presented in Scheme 1:



Scheme 1.

The authors[21] found that the sulfite ion coordination structures strongly influence the course of these salts' thermal decomposition (Figure 8). Sulfite species coordinated to the metal through the oxygen atom (a) are more easily oxidized into sulfate than sulfur coordinated species (b),[7,21] leading to the preferential formation of $M^{II}SO_4$ and Cu_2O at the onset of thermal decomposition.[21]

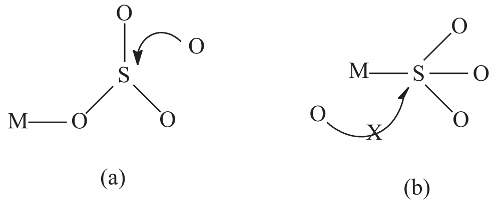


Figure 8. Possibilities of oxygen coordination after sulfite ion oxidation.

The presence of Cu_2O in the solid residue indicates that the evolution of SO_2 during the first step of thermal decomposition takes place through the break of Cu(I)-S and Cu(I)O-S bonds.[21]

Silva *et al.*[21] have reported that the TG curves of all the double sulfites investigated show a weight gain in the second step of thermal decomposition in inert (N_2 and He) and oxidative atmospheres (air) and that they disappear when the salts are heated in a reductive atmosphere (H_2/Ar). This weight gain has been ascribed to the oxidation of Cu_2O to CuO and/or oxidation of $M^{II}SO_3$ to $M^{II}SO_4$, probably by a self-generated atmosphere composed of dense volatile products released in the former step. The oxidation reaction is inhibited in a reductive atmosphere.

9. Final Considerations

Although interest in these types of compounds dates back to the early 19th century, most of the information about double sulfites found in the literature was published after the 1960s. However, these studies have been intensified in recent years, especially in our group, which has drawn a profile of the isomorphic series $Cu_2SO_3.MSO_3.2H_2O$ [M = Cu, Fe, Mn and Cd] in order to gain a better understanding of the chemistry of these compounds.

Acknowledgements

CNPq and FAPESB for financial support.

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Received: June 17, 2003
Published on the web: April 6, 2004