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Use of Cu²⁺ as a Metal Ion Probe for the EPR Study of Metal Complexation Sites in the Double Sulfite $Cu^I_2SO_3 \cdot Cd^{II}SO_3 \cdot 2H_2O$

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A estrutura dos sítios metálicos na rede de $Cu^I_2SO_3 \cdot Cd^{II}SO_3 \cdot 2H_2O$ foi avaliada pela técnica de ressonância paramagnética eletrônica (EPR), empregando o íon paramagnético Cu^{II} como íon sonda. Essa metodologia foi capaz de distinguir os sítios de complexação dos íons M^I e M^{II} na estrutura de $Cu^I_2SO_3 \cdot Cd^{II}SO_3 \cdot 2H_2O$. Os resultados indicam que $Cu^I_2SO_3 \cdot Cd^{II}SO_3 \cdot 2H_2O$ é dopado com íons Cu^{II} nas duas posições dos íons metálicos. Os valores baixos da razão $g_\parallel/A_\parallel$ para o íon sonda no sítio octaédrico resultam da interação do cobre com átomos de oxigênio em ambiente tetragonal distorcido com alongamento da molécula na direção z. A baixa constante de acoplamento hiperfino A_{33} é explicada considerando a mistura dos orbitais $d_{x^2-y^2}$ e d_{z^2} e uma estrutura quase piramidal trigonal para o outro sítio.

An evaluation was made of the presence of paramagnetic ions in the host lattice of $Cu^I_2SO_3 \cdot Cd^{II}SO_3 \cdot 2H_2O$ by the electron paramagnetic resonance (EPR) technique, using copper(II) ions as paramagnetic probes. The existing M^I and M^{II} complexation sites in the double sufite structure were successfully differentiated. The results indicate that the $Cu^I_2SO_3 \cdot Cd^{II}SO_3 \cdot 2H_2O$ structure was doped with Cu^{II} ions in the two metal ion substitutional positions. The low $g_\parallel/A_\parallel$ ratio for the Cu^{II} probe in the distorted octahedral site resulted from the interaction of copper ions with oxygen donor atoms in a distorted tetragonal environment, with elongation of the molecule in the z direction. The very low value of the A_{33} hyperfine coupling constant was explained considering the admixture of the $d_{x^2-y^2}$ and d_{z^2} orbitals and the almost trigonal pyramidal structure of the other site.

Keywords: electron paramagnetic resonance, EPR, Chevreul's salt, double sulfites

Introduction

EPR spectroscopy is a suitable tool for the study of paramagnetic metal ion complexes and may provide useful information about the oxidation states, modes of coordination, geometry and type of ligand sites.

Solid Chevreul's salt is known as a stable mixed-valence sulfite. Environmentally, the precipitation of Chevreul's salt and similar complexes is a key stage in hydrometallurgical processes[1] and is 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.[2,3]

An X-ray study revealed the presence of two types of copper atoms, one with a distorted octahedral coordination, $CuO_4(H_2O)_2$, and the other with a distorted tetrahedral coordination, CuO_3S (Figure 1).[4] The former is in the Cu^{II} state and the latter in the Cu^I state. The occurrence 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.[5] These results support the formula $Cu^I_2SO_3 \cdot Cu^{II}SO_3 \cdot 2H_2O$.

Chevreul's salt derivatives have been prepared from the replacement of Cu^{II} by Cd^{II} ions and transition metal ions such as Mn^{II} and Fe^{II}. In such cases, the X-ray diffraction data were similar to those of Chevreul's salt (Figure 1), with minor changes in "d" spacings, forming an isomorphic series.[6-9] As a consequence, a gradual substitution of the Cu^{II} ions by the transition metal ions is also possible, giving rise to a variety of mixed compositions. The isomorphic series has been found to have the general formula of $Cu^I_2SO_3 \cdot M^{II}SO_3 \cdot 2H_2O$

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(M = Cu, Fe, Mn and Cd). These compounds have a monoclinic crystal structure with space group $P2_1/n$ and the unit cell containing two formula units (Z = 2).
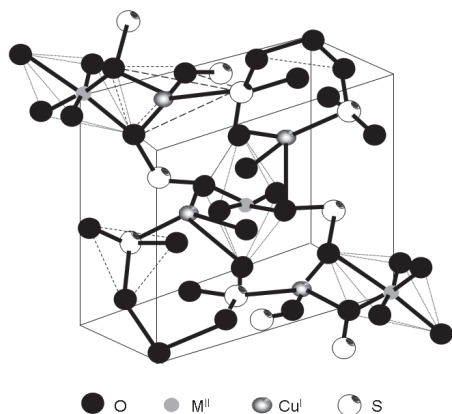

Figure 1. Unit cell of Chevreul's salt and other mixed valence double sulfites of the isomorphic series $Cu_2SO_3 \cdot MSO_3 \cdot 2H_2O$ (M = Cu, Fe, Mn and Cd).

The electronic spectrum of Chevreul's salt consists of a charge-transfer band around 425 nm associated with the $[Cu^I_2(SO_3)_2(\underline{SO_3})_2]^{6-}$ chromophore 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.[8] An additional intervalence-transfer band, which is responsible for the red color, is located 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 at the Cu^I sites. A less intense band at 860 nm for the Fe^{II} derivative is consistent with a Laporte forbidden ligand field transition for high spin octahedral iron(II) complexes, 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 $[Cu^I_2(SO_3)_2(\underline{SO_3})_2]^{6-}$ chromophore, considering the lack of characteristic electronic transitions for Mn^{II} and Cd^{II} ions in that region.[8]

Although the interest for this kind of compound dates from the beginning of the 19th century, it was only in 1999[5,9] that Chevreul's salt began to be investigated by EPR measurements. To date, there is no EPR study of Chevreul's salt derivatives, especially with respect to the use of residual Cu^{2+} as a paramagnetic probe.

In the present work, we evaluated the presence of diamagnetic and paramagnetic ions in the host lattice of the $Cu^I_2SO_3 \cdot Cd^{II}SO_3 \cdot 2H_2O$ by the electron paramagnetic resonance (EPR) technique, which is used to study paramagnetic ions as probes in host lattices. This type of study provides valuable information about the site symmetry of transition metal ions. Copper(II) ion is the simplest paramagnetic probe that enters easily into a number of host lattices.

Experimental

Preparation of double sulfite $Cu_2^ISO_3 \cdot Cd^{II}SO_3 \cdot 2H_2O$

A solution containing 1.0 g of copper sulfate and 10.2 g of cadmium sulfate was saturated with sulfur dioxide gas at room temperature to produce a solution with a pH of approximately 1. This solution was heated to 78 °C. The pH of the solution was raised to 3.0-3.5 by the drop-wise addition of a 20% sodium carbonate solution under magnetic stirring. The precipitation of the complex sulfite started at about pH 3.0. The crystalline material was immediately collected on a filter, washed with deionized water and rinsed with ethanol, followed by air-drying. A more detailed description of this synthesis can be found elsewhere.[5-9]

Compound characterization

Total copper and cadmium contents were determined using an ICP OES ARL model 3410 apparatus. Sulfur analysis was performed by the Shöniger volumetric method. Infrared spectra were recorded on a BOMEM MB-102 FTIR spectrophotometer and X-ray powder diffraction patterns were obtained using a SIEMENS model D5000 diffractometer.

Physical measurements

The EPR spectrum of the powdered sample was recorded at liquid nitrogen temperature (77 K) in quartz tubes. A Bruker ESP 300E spectrophotometer (LABEPR/DQ/UFPR) was used, operating at a frequency of 9.7 GHz (X-band), with a 100 kHz modulation frequency, 2.024 G modulation amplitude and ~20 mW microwave power. Simulations of EPR spectra were carried out using Win-EPR® and SimFonia® computer programs.

Results and Discussion

The results of the elemental analysis were in good agreement with the $Cu_2SO_3 \cdot CdSO_3 \cdot 2H_2O$ empirical formula (calculated: Cu, 30.2%; Cd, 25.9%; S, 14.7%, found: Cu, 29.5%; Cd, 24.9%; S, 13.7%). The infrared spectrum of $Cu_2SO_3 \cdot CdSO_3 \cdot 2H_2O$ is similar to that of Chevreul's salt and may be assigned similarly. The vibrational bands of the sulfite group were assigned by comparison with data reported in the literature.[5-10] The

four fundamental vibrational modes of the sulfite ion were identified at $\nu_1 = 1114(m)$; $\nu_3 = 965(s)$ and $993(s)$; $\nu_2 = 653(m)$ and $618(m)$; $\nu_4 = 479(m)$ cm^{-1}. The appearance of strong S-O stretching band above and below 975 cm^{-1} (ν_3) is an indication of S-bonded and O-bonded sulfite, respectively. The splitting of the ν_3 mode is typical of double sulfites infrared spectra.

The X-ray diffraction data (Table 1) provided evidence for Cu^{II} replacement by Cd^{II} in Chevreul's salt. As can be seen, the patterns of the substituted sulfite resemble those of Chevreul's salt with minor changes in "d" spacings.[5-9]

Table 1. Powder X-ray diffraction data

Cu$_2$SO$_3$·CuSO$_3$·2H$_2$O	Cu$_2$SO$_3$·CdSO$_3$·2H$_2$O
d / Å	d / Å
5.6828	
4.9704	4.7862
4.6596	
4.1834	4.0959
3.9832	
3.5337	3.6192
3.0681	3.0222
2.9780	
2.7928	2.8742
	2.5956
2.5390	2.5513
2.5101	2.5153
2.4780	
2.2618	2.2480

The diamagnetic host ions possess a closed outer electronic shell, heightening the local symmetry of the host lattice. When Cu^{II} replace diamagnetic Cu^{I} and Cd^{II} centers in such host lattices, local distortions take place because of the mismatch of the size of Cu^{II} ions to that of host ions and in response to dynamic effects such as Jahn-Teller effects.[11]

Figure 2 shows the experimental (a) and simulated (b) EPR spectra using the spin Hamiltonian parameters listed in Table 2 for the Cu$_2^I$SO$_3$·Cd^{II}SO$_3$·2H$_2$O sample in a 1200 G field sweep range. The simulated spectrum is, in fact, the sum result of two other simulated spectra: (c) one considering a fraction of the paramagnetic Cu^{II} ion probe in a site with axial symmetry (M^{II}) and the other (d) considering another fraction of the paramagnetic Cu^{II} ion probe in a nonaxial (M^I) site.

Through an interactive process, the intensity of the two added simulated spectra was varied to resemble the experimental spectrum. The agreement between the simulated and experimental spectra is good (Figure 2). One of the simulated EPR spectra (Figure 2c) indicates Cu^{II} ion probe in a distorted octahedral environment, which is in good agreement with the X-ray determined structure.
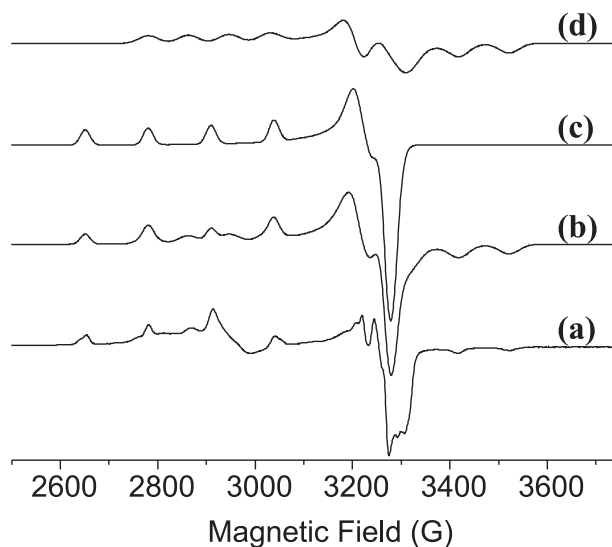

Figure 2. Experimental (a) and simulated (b) spectra. The simulated spectrum (b) represents the sum result of two other simulated spectra (c) and (d).

The values of the EPR parameters obtained for Cu^{II} complexes are significantly influenced by the donor atoms and the geometry. Hard donors and planarity distortion increase $g_\parallel$ while soft donors and planar geometry decrease $g_\parallel$. The EPR spectrum of the Cu^{II} ion probe in the octahedral site presents an axial symmetry, with $g_z = g_\parallel$ and $g_x = g_y = g_\perp$, $A_z = A_\parallel$ and $A_x = A_y = A_\perp$, and, $g_\parallel > g_\perp > 2$ (Table 2), indicating a tetragonal distortion with elongation at the molecule z axis. The values of the $g_\parallel/A_\parallel$ ratio may be used to estimate the extent of this distortion. In CuN$_4$ units this value ranges from about 105 to 135 cm for a square-planar structure, or octahedral with tetragonal distortion, and this quotient increases upon the introduction of tetrahedral deformation in the chromophore, or upon substitution of N donor atoms by O donors.[11]

In the present case, as the axial structure was indicated by the $g_\parallel > g_\perp > 2$ relationship, the $g_\parallel/A_\parallel$ ratio of 150 cm

Table 2. Spin Hamiltonian parameters calculated from the Cu^{II} spectra in different host lattices

Hamiltonian parameters	Cu^{II} in a substitutional position of Cu^{I}	Cu^{II} in a substitutional position of Cd^{II}
g_{11}	2.001	-
g_{22}	2.065	-
g_{33}	2.320	-
A_{11} /10^{-4} cm^{-1}	88.7	-
A_{22} /10^{-4} cm^{-1}	9.6	-
A_{33} /10^{-4} cm^{-1}	97.5	-
$g_\parallel$	-	2.370
$g_\perp$	-	2.080
$A_\parallel$ / 10^{-4} cm^{-1}	-	158
$A_\perp$ /10^{-4} cm^{-1}	-	15
$A_\parallel/g_\parallel$ / cm	-	150

(Table 2) results from the presence of the CuO_4 unit in the square-planar portion of the octahedral site.[12]

Observing the values of the EPR parameters for the other Cu^{II} complexation site (Table 2), we note that they differ significantly from the more familiar copper complexes. For example, the value of the A_{33} hyperfine coupling constant is appreciably lower than the value of $A_\parallel$ generally found for a copper(II) ion.[11] The very low values of the hyperfine coupling constants for the $Cu^{II}O_4$ structure in the distorted tetrahedral site was explained by considering the admixture of d_{z^2} with the $d_{x^2-y^2}$ ground state orbital. It was found that a 10% admixture of $d_{x^2-y^2}$ and d_{z^2} orbitals results in a 20% reduction in dipolar anisotropy, lowering hyperfine coupling constants.[10] This indicates that, based on the EPR measurement, this site will have an approximately trigonal pyramidal structure.

Conclusions

EPR spectroscopy was used successfully to differentiate the existing M^I and M^{II} complexation sites in the $Cu^I_2SO_3 \cdot Cd^{II}SO_3 \cdot 2H_2O$ structure when used in combination with Cu^{II} ions as probes. The results indicate that the $Cu^I_2SO_3 \cdot Cd^{II}SO_3 \cdot 2H_2O$ structure was doped with Cu^{II} ions in the two metal ion substitutional positions. The low values of the $g_\parallel/A_\parallel$ ratio for the Cu^{II} probe in the octahedral site resulted from the interaction of copper ions with oxygen donor atoms in a distorted tetragonal manner with elongation for the molecule in the z direction. The very low value of the A_{33} hyperfine coupling constant was explained by considering the admixture of the $d_{x^2-y^2}$ and d_{z^2} orbitals and an almost trigonal pyramidal structure for the other site.

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