

Electronic Spectra of Chevreul's Salts

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A série isomórfica de sulfitos duplos com fórmula empírica $\text{Cu}_2\text{SO}_3 \cdot \text{MSO}_3 \cdot 2\text{H}_2\text{O}$ (onde M é Cu, Fe, Mn ou Cd) é preparada pela substituição do Cu(II) no sal de Chevreul, $\text{Cu}_2\text{SO}_3 \cdot \text{CuSO}_3 \cdot 2\text{H}_2\text{O}$, por íons de metais de transição, tais como Fe(II), Mn(II) e Cd(II). Como consequência, as espécies isomórficas apresentam colorações distintas. Cálculos de modelagem molecular foram empregados neste trabalho para o centro dimérico $[\text{Cu}_2(\text{SO}_3)_2(\text{SO}_3)_2]^{6-}$. O espectro eletrônico do sal de Chevreul consiste de uma banda de transferência de carga em 425 nm associada ao cromóforo $[\text{Cu}_2(\text{SO}_3)_2(\text{SO}_3)_2]^{6-}$ e duas transições de campo ligante a 785 e 1000 nm envolvendo distorção de Jahn-Teller dos níveis do Cu(II). Além disso, uma banda adicional de transferência de intervalência é observada em 500 nm, sendo responsável pela sua coloração vermelha característica. A substituição do íon Cu(II) pelos íons Fe(II), Mn(II) e Cd(II) não elimina a banda de absorção em 425 nm, associada à transição de transferência de carga centrada nos sítios Cu(I), porém a banda original em 500 nm desaparece, em concordância com a atribuição de transição intervalência.

The isomorphous series of double sulfites with empirical formula $\text{Cu}_2\text{SO}_3 \cdot \text{MSO}_3 \cdot 2\text{H}_2\text{O}$ (where M is Cu, Fe, Mn, or Cd) have been prepared from the Cu(II) replacement by transition metal ions such as Mn(II), Fe(II) and Cd(II) ions in Chevreul's salt, $\text{Cu}_2\text{SO}_3 \cdot \text{CuSO}_3 \cdot 2\text{H}_2\text{O}$. As a consequence, the isomorphous species present distinct colors. Molecular modeling calculations were carried out for the dimeric $[\text{Cu}_2(\text{SO}_3)_2(\text{SO}_3)_2]^{6-}$ center. The electronic spectra of the Chevreul's salt consist of a charge-transfer band around 425 nm associated with the $[\text{Cu}_2(\text{SO}_3)_2(\text{SO}_3)_2]^{6-}$ chromophore and two ligand field transitions at 785 and 1000 nm involving the Jahn-Teller splitting of the Cu(II) levels. An additional intervalence-transfer band, responsible for its characteristic red color, can be found at 500 nm. The replacement of the Cu(II) ions for 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; while the original band at 500 nm disappears, in agreement with its intervalence transfer nature.

Keywords: electronic spectra, Chevreul's salt, isomorphous salts

Introduction

The first known mixed valence sulfite complex, $\text{Cu}^{\text{I}}_2\text{SO}_3 \cdot \text{Cu}^{\text{II}}\text{SO}_3 \cdot 2\text{H}_2\text{O}$, was prepared by M. Chevreul,¹ in 1812. Its crystalline structure was described in terms of coordination polyhedra by Kierkegaard and Nyberg,² consisting of $[\text{SO}_3]$ trigonal pyramids, $[\text{Cu}^{\text{I}}\text{O}_3\text{S}]$ tetrahedra and $[\text{Cu}^{\text{II}}\text{O}_4(\text{H}_2\text{O})_2]$ octahedra linked together, giving a three-dimensional network.

Chevreul's salt derivatives have been prepared from the Cu(II) replacement by transition metal ions such as Mn(II), Fe(II) and Cd(II) ions.³⁻⁵ In such cases, the X-ray diffraction data were similar to those of Chevreul's salt, with minor

changes in "d" spacings,³⁻⁵ forming an isomorphous series, *i.e.*, $\text{Cu}_2\text{SO}_3 \cdot \text{CuSO}_3 \cdot 2\text{H}_2\text{O}$, $\text{Cu}_2\text{SO}_3 \cdot \text{MnSO}_3 \cdot 2\text{H}_2\text{O}$, $\text{Cu}_2\text{SO}_3 \cdot \text{FeSO}_3 \cdot 2\text{H}_2\text{O}$ and $\text{Cu}_2\text{SO}_3 \cdot \text{CdSO}_3 \cdot 2\text{H}_2\text{O}$. 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.

Interestingly, the isomorphous species present distinct colors.⁴ The intense red color of the Chevreul's salt changes to yellowish-brown, after the substitution of Cu(II) by Fe(II). If the substitution is carried out with Mn(II) instead of Fe(II), a gradual transition to yellow color is observed. On the other hand, if Cu(II) is replaced by Cd(II), a faint yellow color is obtained.

Although the interest for this kind of compounds dates from the beginning of the 19th century, only recently the

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spectroscopic properties of the Chevreul's salt have been investigated by Inoue *et al.*⁶ based on EPR measurements and diffuse reflectance absorption spectra. Up to the present time, there is a complete lack of information about the electronic interactions between the constituents of Chevreul's salt derivatives, especially concerning the types of electronic transitions responsible for their different colors. For this reason, this subject is focused in this paper, with emphasis on the theoretical evaluation of the charge-transfer bands in the Chevreul's salt.

Experimental

Materials

All chemicals used in the synthesis of the double sulfites were of analytical reagent grade.

Copper, and mixtures of copper and manganese, copper and iron or copper and cadmium sulfate solutions (see compositions in Table 1) were saturated with sulfur dioxide gas at room temperature to give solutions with pH of approximately 1. These solutions were heated to 78 °C. The pH of the solutions was raised to 3.0-3.5 by dropwise addition of a 20% sodium carbonate solution, under magnetic stirring. The precipitation of the complex sulfites starts at about pH 3.0. The crystalline materials were immediately collected on a filter, washed with deionized water and rinsed with ethanol, followed by air drying. A more detailed account on their syntheses can be found elsewhere.^{4,5}

Table 1. Composition of the starting solutions in the mixed valence sulfite preparations

Double sulfites	MSO ₄ ·nH ₂ O ^a (g)				Solution volume (mL)
	Cu	Fe	Mn	Cd	
Cu ₂ SO ₃ ·CuSO ₃ ·2H ₂ O	2.0	-	-	-	50
Cu ₂ SO ₃ ·FeSO ₃ ·2H ₂ O	1.0	12.2	-	-	50
Cu ₂ SO ₃ ·MnSO ₃ ·2H ₂ O	1.0	-	6.2	-	50
Cu ₂ SO ₃ ·CdSO ₃ ·2H ₂ O	1.0	-	-	10.2	50

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

Measurements

The electronic spectra were recorded on a Guided Wave spectrophotometer, model 260, equipped with a Wand bundle probe for *in situ* reflectance measurements. Total copper, manganese, iron, and cadmium contents were determined using an ICP/AES ARL, model 3410 instrument.

Theoretical Calculations

Molecular modeling calculations were carried out for the dimeric [Cu^I₂(SO₃)₂(SO₃)₂]⁶⁻ center attached to two [Cu^{II}(H₂O)₂(SO₃)₂]²⁻ fragments, starting from the crystallographic bond lengths,² in order to simulate the {Cu^I₂(SO₃)₂[Cu^{II}(H₂O)₂(SO₃)₂]₂}⁶⁻ repetitive group (Figure 1) in the tridimensional structure of the Chevreul's salt² (SO₃²⁻ = S bound sulfite, SO₃²⁻ = O bound sulfite). Geometry optimization was carried out using the MM⁺ method within the HyperChem 6.0 program (Hypercube Inc. Gainesville, USA), and a gradient of 1 x 10⁻⁶ kcal (1 cal = 4.1840 J) as a convergence criterion in a conjugate gradient method. Spectral simulations were carried out in separate for the [Cu^I₂(SO₃)₂(SO₃)₂]⁶⁻ center, but keeping the same previously optimized geometry for the {Cu^I₂(SO₃)₂[Cu^{II}(H₂O)₂(SO₃)₂]₂}⁶⁻ group (Figure 1). SCF molecular orbitals were obtained at the RHF level for the closed-shell Cu(I) ground-state species, using the ZINDO/S method,⁷⁻¹⁰ and the default parameters, for single CI excitations in an active space involving 20 frontier molecular orbitals (10 highest occupied and 10 lowest unoccupied MOs).

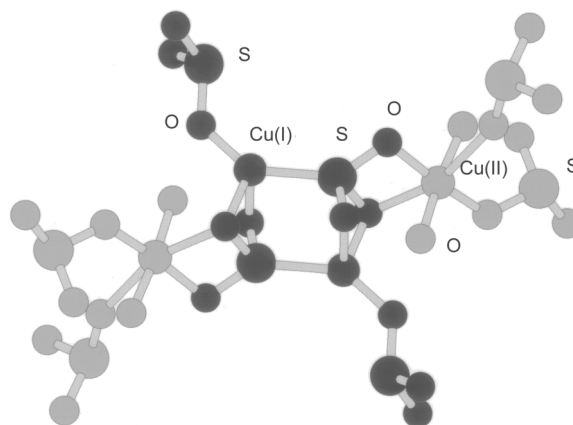


Figure 1. ZINDO/1 optimized molecular structure for the {Cu^I₂(SO₃)₂[Cu^{II}(H₂O)₂(SO₃)₂]₂}⁶⁻ characteristic group in the Chevreul's salt, showing the [Cu^I₂(SO₃)₂(SO₃)₂]⁶⁻ unity in the center (dark) and the [Cu^{II}(H₂O)₂(SO₃)₂]²⁻ fragments (light).

Results and Discussion

The diffuse reflectance electronic spectrum of the Chevreul's salt reported by Inoue *et al.*⁶ in the 400-800 nm range, consists of two broad bands at 785 and 425 nm. The first one has been ascribed to a d-d transition of the octahedral Cu(II) ions.⁶ The second band (at 425 nm) has been tentatively assigned to an intervalence transition between the tetrahedral Cu(I) sites and the octahedral Cu(II) ones. This transition is responsible by the intense dark red color of the Chevreul's salt.

In this work, the electronic spectrum of the Chevrel's salt has been extended to the near-infrared region, as illustrated in Figure 2. The spectra of the corresponding derivatives with Fe(II), Mn(II) and Cd(II) ions are also shown in Figure 2, for comparison purposes.

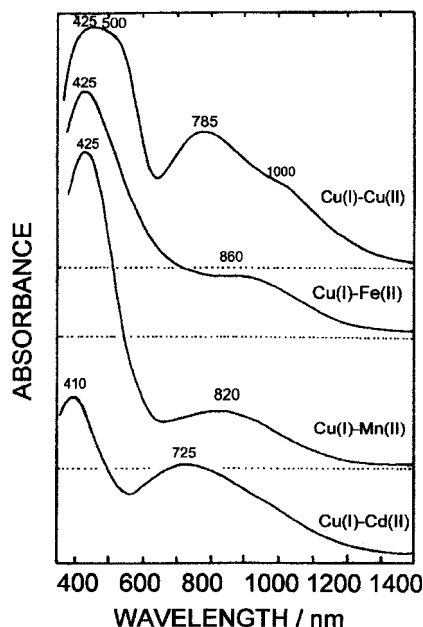


Figure 2. Diffuse reflectance spectra of the mixed valence Cu(I)-Cu(II) and related Cu(I)-M(II) Chevrel's salts, $\text{Cu}_2\text{SO}_3\cdot\text{MSO}_3\cdot 2\text{H}_2\text{O}$ ($M = \text{Cu}, \text{Fe}, \text{Mn}, \text{and Cd}$).

As can be seen in Figure 2, all the Chevrel's salt derivatives exhibit an absorption band around 425 nm and a less intense band in the visible region. This feature has also been recently reproduced from photoacoustic measurements.¹¹ However, the absorption profile is markedly distinct for the Chevrel's salt, in which case the comparison with the series clearly reveals the composite nature of the absorption band in the 400-500 nm range. A new component can be observed at 500 nm, and another one at 1000 nm, in the near-infrared region not accessed by the previous work.⁶

The high energy band at 425 nm seems to be a common feature of the Chevrel's salt derivatives (see Figure 2) and accordingly, it would be better ascribed to a transition in the Cu(I)-sulfite chromophore, rather than to an intervalence transfer transition. In the last case, the electronic transition would be strongly dependent on the nature of the M(II) ion. For this reason, semi-empirical theoretical calculations were carried out for the Cu(I)-sulfite chromophore, in order to elucidate the characteristic electronic transitions associated with this group.

Initially, molecular modeling calculations were carried out for the dimeric $[\text{Cu}^1_2(\text{SO}_3)_2(\text{SO}_3)_2]^{6-}$ center attached to

two $[\text{Cu}^{\text{II}}(\text{H}_2\text{O})_2(\text{SO}_3)_2]^{2-}$ fragments, reproducing very closely the $\{\text{Cu}^1_2(\text{SO}_3)_2[\text{Cu}^{\text{II}}(\text{H}_2\text{O})_2(\text{SO}_3)_2]_2\}^{6-}$ characteristic group in the tridimensional structure of the Chevrel's salt.² After the geometry optimization using the ZINDO/1 program, the two $[\text{Cu}^{\text{II}}(\text{H}_2\text{O})_2(\text{SO}_3)_2]^{2-}$ fragments were removed, leaving the $[\text{Cu}^1_2(\text{SO}_3)_2(\text{SO}_3)_2]^{6-}$ center. In this way one can simulate the electronic properties of the $[\text{Cu}^1_2(\text{SO}_3)_2(\text{SO}_3)_2]^{6-}$ moiety, in separate, but keeping the same original structural arrangement found in Chevrel's salt. This particular chromophore is rather unusual, since it contains a dimeric, tetrahedral Cu(I) complex attached to sulfur bound, bidentate oxygen bound and monodentate oxygen bound sulfite ions, as illustrated in Figure 1.

ZINDO/S calculations for the $[\text{Cu}^1_2(\text{SO}_3)_2(\text{SO}_3)_2]^{6-}$ center led to the HOMOs and LUMOs involved in the electronic transitions. As shown in Table 2, the three highest occupied molecular orbitals (HOMO levels number 60, 61 and 62) exhibit predominantly Cu(I) character, but incorporate a substantial contribution from the S-bound sulfite ion. The lowest unoccupied molecular orbital (LUMO 63) has a strong S-bound sulfite ion character (83%), containing only a small contribution from the Cu(I) ion. The next level (LUMO 64) has also predominantly S-bound sulfite ion character (63%), while the succeeding level (LUMO 65) involves a nearly equivalent mixture of the Cu(I) and S-bound sulfite ions.

Table 2. HOMO and LUMO composition for the $\text{Cu}^1_2(\text{SO}_3)_2(\text{SO}_3)_2$ moiety in the Chevrel's salts

Type	MO Number	Composition ^a
HOMO	60	0.625 (Cu ^I) + 0.256 (SO ₃ ²⁻) + 0.119 (SO ₃ ²⁻)
HOMO	61	0.586 (Cu ^I) + 0.387 (SO ₃ ²⁻) + 0.027 (SO ₃ ²⁻)
HOMO	62	0.544 (Cu ^I) + 0.429 (SO ₃ ²⁻) + 0.027 (SO ₃ ²⁻)
LUMO	63	0.135 (Cu ^I) + 0.833 (SO ₃ ²⁻) + 0.012 (SO ₃ ²⁻)
LUMO	64	0.320 (Cu ^I) + 0.635 (SO ₃ ²⁻) + 0.045 (SO ₃ ²⁻)
LUMO	65	0.547 (Cu ^I) + 0.363 (SO ₃ ²⁻) + 0.090 (SO ₃ ²⁻)

a) (SO₃²⁻) = S bound; (SO₃²⁻) = O bound

According to the ZINDO/S calculations, the lowest, moderately intense, spin-allowed electronic transitions occurs at 620 (oscillator strength $f = 0.033$) and 577 nm ($f = 0.078$), involving the excitation from HOMO 62 to LUMO 64, and from a combination of the HOMO 61 and 62 levels, to a combined level from LUMO 63 and 65, respectively. The next theoretically allowed transition occurs at 401 nm ($f = 0.098$), corresponding to the excitation from HOMO 60 to LUMO 63. Therefore the $[\text{Cu}^1_2(\text{SO}_3)_2(\text{SO}_3)_2]^{6-}$ chromophore is expected to exhibit three absorption bands in the visible region, ascribed to

molecular orbital transitions displaying substantial Cu^I-sulfite charge-transfer character, as deduced from the HOMO and LUMO compositions.

The octahedral Cu(II) sites exhibit the metal ion bound to six oxygen donor ligands, and the visible band around 785 nm has been associated with the characteristic ligand field transition in the copper(II) ions.¹² Actually, the metal ion is bound to two water molecules ($d = 1.92 \text{ \AA}$)² and to two pairs of non-equivalent, oxygen bound sulfite ions, at $d = 2.03$ and 2.46 \AA . These bonding distances characterize a substantial distortion, as expected from the Jahn-Teller effect associated with the d^9 ions.¹³ One of the consequences of the Jahn-Teller effect is the splitting of the ligand field bands in the copper(II) ions. Although this aspect has not been previously reported⁶ for the Chevrel's salt, the observed bands at 785 and 1000 nm are in good agreement with the ligand field theory, reflecting the Jahn-Teller distortion in the copper(II) sites. The expected, weak charge-transfer bands in the $[\text{Cu}^{\text{I}}_2(\text{SO}_3)_2(\text{SO}_3)_2]^{6-}$ moiety at 620 and 577 nm are probably superimposed to the ligand field bands in the visible.

Theoretically, neither the tetrahedral $[\text{Cu}^{\text{I}}_2(\text{SO}_3)_2(\text{SO}_3)_2]^{6-}$ nor the octahedral $[\text{Cu}^{\text{II}}(\text{H}_2\text{O})_2(\text{SO}_3)_4]^{6-}$ sites are expected to exhibit electronic bands around 500 nm. Therefore, the observed absorption at 500 nm in the Chevrel's salt spectrum can only be ascribed to an intervalence transfer transition from the tetrahedral Cu(I) ions to the empty $3d_{x-y}^2$ level of e_g symmetry of the Cu(II) ions. In this case, the intervalence transfer energy can be expressed in terms of the following equation:¹²

$$E_{\text{IT}} = 30,000 [X(\text{Cu}^{\text{I}}) - X(\text{Cu}^{\text{II}})] + 10 Dq$$

where $X(\text{Cu}^{\text{I}})$ and $X(\text{Cu}^{\text{II}})$ are the optical electronegativities of the Cu(I) and Cu(II) sites and $10 Dq$ represents the ligand field splitting in an octahedral Cu(II) ion. From the ligand field transition, $10 Dq$ is approximately $12,700 \text{ cm}^{-1}$. Considering that $E_{\text{IT}} = 20,000 \text{ cm}^{-1}$, and that the optical electronegativity of the octahedral Cu(II) ions is 2.2,¹⁴ the optical electronegativity of the tetrahedral Cu(I) sites in the Chevrel's salt can be calculated as 2.44.

Iron(II), and manganese(II) ions exhibit $3d^6$ and $3d^5$ electronic configurations, respectively. In principle, these electronic configurations can also allow intervalence transitions, since the cations have empty 3d orbitals. However, both ions are not particularly good electron acceptors, and as far we know, intervalence-transfer transitions generating iron(I) or manganese(I) excited species are quite unusual in the literature.

The Mn(II) derivative exhibits an absorption band at 820 nm, while the metal ion, in separate, do not display absorption bands in this particular region. The same

argument can be applied for the Cd^{II} case, which display an absorption band at 725 nm. In the last case, it should be noticed that, from the optical electronegativity,¹⁴ $X(\text{Cd}^{\text{II}}) = 1.35$, the intervalence band in the Chevrel's salt derivative is expected around 300 nm, *i.e.*, in the UV region. Therefore, by ruling out the ligand field and intervalence transfer transitions, the observed bands for the Mn(II) and Cd(II) derivatives at 820 and 725 nm can only be ascribed to the expected low energy transitions in the $[\text{Cu}^{\text{I}}_2(\text{SO}_3)_2(\text{SO}_3)_2]^{6-}$ chromophore, under the influence of the specific interactions with the M(II) ions.

In the case of the Fe(II) derivative, the absorption band at 860 nm coincides with the expected ligand field transition for high spin octahedral iron(II) complexes.¹² The overall absorption profile in this case, as compared with the Mn(II) derivative, is rather broad (see Figure 1) and suggests the existence of additional bands around 600 nm, associated low energy transitions in the $[\text{Cu}^{\text{I}}_2(\text{SO}_3)_2(\text{SO}_3)_2]^{6-}$ chromophore.

Conclusions

The electronic spectrum of the Chevrel's salt consists of a charge-transfer band around 425 nm associated with the $[\text{Cu}^{\text{I}}_2(\text{SO}_3)_2(\text{SO}_3)_2]^{6-}$ chromophore, and two ligand field transitions at 785 and 1000 nm involving the Jahn-Teller splitting of the Cu(II) levels. An additional intervalence-transfer band, responsible for its red color, can be found at 500 nm. The replacement of the Cu(II) ions for 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 and 725 nm in the Mn(II) and Cd(II) cases were tentatively assigned to charge-transfer transitions in the $[\text{Cu}^{\text{I}}_2(\text{SO}_3)_2(\text{SO}_3)_2]^{6-}$ chromophore, respectively, considering the lack of characteristic electronic transitions for these ions, in this region.

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