$[\{Cu_2[S_2C_2(NCH_2CH_2OH)_2](H_2O)(SO_4)\}(H_2O)]_2$

Crystal Structure and Magnetic Properties of Di-μ-aqua-bis[μ-[N,N'-bis(2-hydroxyethyl)dithiooxamidato(2-)-N,O,S:N',O',S']]-bis[aquacopper(II)sulfatocopper(II)]. A New Example of Very Strong Antiferromagnetic Coupling between Copper(II) Ions Far Away from Each Other

C. CHAUVEL,[1] J. J. GIRERD,*[2a] Y. JEANNIN,*[2b] O. KAHN,*[2a] and G. LAVIGNE[2b]

The title compound, $[\{Cu_2[S_2C_2(NCH_2CH_2OH)_2](H_2O)(SO_4)\}(H_2O)]_2$, was synthesized and its crystal structure solved at room temperature. It crystallizes in the monoclinic system, space group $C2/c$. The lattice constants are $a = 24.211$ (6) Å, $b = 8.173$ (5) Å, $c = 15.179$ (6) Å, and $\beta = 110.68$ (2)°. Least-squares refinement of the structure has led to a conventional R factor of 0.038. The structure is made of binuclear units $\{Cu_2[S_2C_2(NCH_2CH_2OH)_2](H_2O)(SO_4)\}$ doubly bridged by water molecules making tetrameric entities. The coordination of each copper is 4 + 1 in the form of a square pyramid, the apex of which is occupied by a more weakly bonded oxygen atom of the bridging water molecule. This compound (noted B) is isomeric with *catena*-μ-sulfato-μ-[N,N'-bis(2-hydroxyethyl)dithiooxamidato(2-)-N,O,S:N',O',S']-bis[aquacopper(II)] (noted A) the structure of which has been recently reported. The difference between both isomers essentially concerns the positions of H_2O and SO_4^{2-} ligands. The mechanism of the isomerization is discussed. It could involve as an intermediate step a binuclear unit in which one of the Cu(II) ions would be coordinated in the form of a trigonal bipyramid. The temperature dependence of the molar magnetic susceptibility, studied in the range 15–300 K, reveals a large antiferromagnetic coupling characterized by a 523-cm⁻¹ singlet–triplet separation. This coupling is however slightly smaller than that found for the A isomer. The difference is interpreted as resulting from the distortion of the binuclear unit due to the bridging water molecules and from the correlated lengthening of the S–N distances in B with regard to A.

Introduction

In a recent paper,[3] we described the synthesis, the crystal structure, and the magnetic properties of a complex of formula $\{Cu[S_2C_2(NCH_2CH_2OH)_2](H_2O)_2\}SO_4$. In this paper, we shall define this compound as the A isomer. Its structure, shown here, is made of nearly planar binuclear units $\{Cu_2[S_2C_2(NCH_2CH_2OH)_2](H_2O)_2\}^{2+}$ bridged by SO_4 groups building zigzag chains.
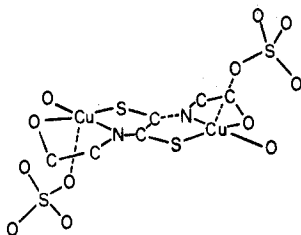
This compound might be considered as the first perfectly defined, well-crystallized copper(II) rubeanate. All previously obtained copper(II) rubeanates were amorphous polymers, of unknown structure.[4-7] The main feature of this new complex arose from its very peculiar magnetic properties. Although the Cu–Cu distance inside the binuclear unit is as large as 5.61 Å, the temperature dependence of the magnetic susceptibility revealed a very strong antiferromagnetic coupling characterized by a 594-cm⁻¹ singlet–triplet separation. To the best of our knowledge, such a strong interaction between transition ions so far away from each other has never been reported before.

Modifying very slightly the conditions of the synthesis, we obtained a new complex, hereafter referred as the B isomer. We herein report the crystal structure and the magnetic properties of this B form. The structure consists of $\{Cu_2[S_2C_2(NCH_2CH_2OH)_2](SO_4)(H_2O)\}$ binuclear units doubly bridged two-to-two by water molecules, making tetrameric entities. In the binuclear units, in spite of the large Cu–Cu distance, 5.65 Å, the Cu(II) ions are again strongly antiferromagnetically coupled, the singlet–triplet separation being 523 cm⁻¹. In this paper, we compare the crystal structure and the magnetic properties of the A and B isomers. This

comparison led us to the two following main results: (i) The isomerization from A to B may be described by displacement of the SO_4^{2-} and H_2O ligands. (ii) The small but significant differences between the magnetic properties of A and B find an elegant interpretation in the frame of an orbital model for the exchange interaction proposed by two of us[8-10] and already used several times.[3,11-13]

Experimental Section

Synthesis. The ligand N,N'-bis(2-hydroxyethyl)dithiooxamide was obtained from dithiooxamide and ethanolamine by the Wallach reaction.[14] The complex was prepared as follows: A solution of 0.53 g (2.5×10^{-3} mol) of N,N'-bis(2-hydroxyethyl)dithiooxamide in 20 cm³ of methanol was slowly poured into a stirred solution of 1.86 g (7.5×10^{-3} mol) of copper(II) sulfate pentahydrate in 40 cm³ of methanol. An amorphous precipitate of a compound with formula $CuS_2C_2(NCH_2CH_2OH)_2$ was formed. To dissolve this precipitate, we added 1 cm³ of concentrated sulfuric acid. The solution was then filtered (solution S) and poured into 100 cm³ of water at room temperature containing 7 g of ammonium sulfate. A clear green crystalline precipitate appeared which was filtered out, washed with water, and dried under vacuum. Anal. Calcd for $Cu_2C_6H_{14}N_2S_3O_8$: C, 15.48; H, 3.03; N, 6.02; S, 20.67. Found: C, 15.54; H, 3.13; N, 5.58; S, 20.05. Compared spacing (Å) of the strongest lines of the powder patterns: A isomer 7.01, 5.00, 3.35; B isomer 7.69, 7.15, 4.27, 3.79, 3.54, 3.38.

Well-shaped single crystals were obtained by the gel technique. The gel was prepared in a tube from an aqueous solution of sodium metasilicate acidified by a few drops of sulfuric acid (pH ~7) and saturated in ammonium sulfate. Crystals appeared at the gel surface after about 2 months.

Intensity Data. The crystal selected for X-ray analysis was shaped as a parallelepiped (0.80 × 0.35 × 0.07 mm) bound by faces {010}, {001}, {100}. Preliminary Laue and precession photographs showed monoclinic symmetry. Systematic absences were consistent with space group $C2/c$. Crystal parameters are $a = 24.211$ (6) Å, $b = 8.173$ (5) Å, $c = 15.179$ (6) Å, $\beta = 110.68$ (2)°, and $V = 2810$ Å³ with $Z = 8$, the asymmetric unit being $\{Cu_2[C_2S_2(NCH_2CH_2OH)_2](H_2O)\}$. Data collection conditions were the same as previously described,[3] with the following characteristics: Mo Kα radiation, dissymmetric θ scan range (−0.6°; +0.7°) + [(Δλ/λ) tan θ]°, 2481 reflections collected at room temperature up to (sin θ)/λ = 0.6, standard reflections 0,0,10 and 408 monitored every 50 reflections. Fluctuations were within 6σ. Intensities were corrected for Lorentz and polarization

Table I. Atomic Coordinates[a]

atom	x	y	z
	Metal Atoms		
Cu(1)	0.61028 (2)	0.10222 (6)	0.15086 (4)
Cu(2)	0.36332 (2)	0.15494 (6)	0.05493 (3)
	Dithiooxamidato Ligand		
S(1)	0.55158 (4)	0.3290 (1)	0.13730 (8)
S(2)	0.42345 (4)	−0.0693 (1)	0.08213 (8)
N(1)	0.5408 (1)	−0.0262 (4)	0.1422 (2)
N(2)	0.4350 (1)	0.2865 (4)	0.1014 (2)
C(1)	0.4868 (2)	0.2231 (5)	0.1176 (3)
C(2)	0.4888 (2)	0.0380 (5)	0.1172 (3)
C(3)	0.5493 (2)	−0.2043 (5)	0.1474 (3)
H(31)	0.536 (4)	−0.24 (1)	0.082 (7)
H(32)	0.531 (4)	−0.24 (1)	0.186 (6)
C(4)	0.6146 (2)	−0.2344 (5)	0.1976 (3)
H(41)	0.623 (4)	−0.33 (1)	0.188 (6)
H(42)	0.618 (4)	−0.22 (1)	0.264 (6)
C(5)	0.4264 (2)	0.4633 (5)	0.1003 (4)
H(51)	0.434 (4)	0.50 (1)	0.043 (6)
H(52)	0.451 (4)	0.51 (1)	0.150 (7)
C(6)	0.3628 (2)	0.4926 (5)	0.0950 (3)
H(61)	0.349 (4)	0.60 (1)	0.087 (6)
H(62)	0.358 (4)	0.47 (1)	0.155 (7)
O(1)	0.6445 (1)	−0.1281 (3)	0.1533 (2)
H(1)	0.676 (5)	−0.14 (1)	0.177 (7)
O(2)	0.3237 (1)	0.3817 (4)	0.0264 (2)
H(2)	0.320 (4)	0.42 (1)	−0.020 (7)
	Water Molecules		
O(3)	0.6699 (1)	0.1230 (4)	0.3216 (2)
H(13)	0.692 (4)	0.19 (1)	0.313 (6)
H(23)	0.689 (4)	0.05 (1)	0.336 (6)
O(4)	0.2913 (1)	0.0449 (4)	−0.0256 (2)
H(14)	0.294 (4)	−0.05 (1)	−0.056 (7)
H(24)	0.269 (4)	0.05 (1)	−0.012 (7)
	SO$_4^{2-}$ Anion		
S(3)	0.71469 (4)	0.3420 (1)	0.16223 (7)
O(31)	0.6785 (1)	0.1897 (3)	0.1270 (2)
O(32)	0.6765 (2)	0.4848 (4)	0.1266 (3)
O(33)	0.7636 (1)	0.3392 (4)	0.1269 (2)
O(34)	0.7362 (1)	0.3407 (4)	0.2663 (2)

[a] Standard deviations are in parentheses.

factors. Absorption corrections were carried out and applied at the end of refinement (μ = 36 cm^{-1}). Minimum and maximum transmission factors were 0.325 and 0.777. Atomic form factors were taken from Cromer and Mann.[15,16] Both the real and imaginary components of anomalous dispersion were taken into account for all nonhydrogen atoms.

The structure was refined by least squares, inverting the full matrix and minimizing the functions $\sum w^2(|F_o| - |F_c|)^2$. The weighting scheme was $w = 1/\sigma_F$; $\sigma_F = \sigma_I/2F_o$. The reliability factors are defined as

$$R = \sum(|F_o| - |F_c|)/\sum|F_o|$$

$$R_w = [\sum w^2(|F_o| - |F_c|)^2/\sum w^2|F_o|^2]^{1/2}$$

Structure Resolution. The structure was solved by the heavy-atom method. A three-dimensional Patterson map showed two copper atoms. Successive Fourier syntheses led to locations of all nonhydrogen atoms. Refinements of coordinates and anisotropic thermal parameters resulted in R = 0.071 and R_w = 0.076. Absorption corrections improved those factors down to R = 0.047 and R_w = 0.052. It was then possible to locate the 14 hydrogen atoms. They were introduced in the refinement with variable coordinates, but fixed isotropic thermal parameters were taken 1 Å higher than the average B's of carbon and oxygen atoms to which hydrogen are bound; i.e., B = 3 Å^2. On consideration of the satisfactory agreement between observed and calculated structure factors at low Bragg angles, it was not found necessary to introduce secondary extinction. Final results concerning 2334 observations with $F_o \geq 3\sigma$ are R = 0.038 and R_w = 0.047.

A list of structure factors is given as supplementary material.

Atomic coordinates are in Table I, anisotropic thermal parameters in Table II, interatomic distances in Table III, and bond angles in Table IV.

Table II. Anisotropic Thermal Parameters[a]

atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{23}	B_{33}
			Metal Atoms			
Cu(1)	1.09 (2)	1.29 (2)	2.67 (2)	−0.12 (1)	0.65 (1)	0.04 (1)
Cu(2)	1.11 (2)	1.47 (2)	2.20 (2)	−0.07 (1)	0.49 (1)	−0.04 (1)
			Dithiooxamidato Ligand			
S(1)	1.36 (3)	1.28 (3)	3.26 (5)	−0.19 (3)	0.64 (3)	−0.01 (3)
S(2)	1.17 (3)	1.39 (4)	3.24 (5)	−0.19 (3)	0.58 (3)	−0.08 (3)
N(1)	1.6 (1)	1.4 (1)	2.2 (1)	−0.3 (1)	0.7 (1)	−0.1 (1)
N(2)	1.4 (1)	1.4 (1)	2.4 (1)	−0.1 (1)	0.5 (1)	−0.0 (1)
C(1)	1.6 (1)	1.4 (1)	1.6 (1)	−0.1 (1)	0.6 (1)	0.0 (1)
C(2)	1.4 (1)	1.4 (1)	1.6 (1)	0.0 (1)	0.6 (1)	−0.0 (1)
C(3)	1.8 (1)	1.0 (1)	2.7 (2)	0.0 (1)	0.8 (1)	0.2 (1)
C(4)	2.0 (2)	1.4 (1)	2.7 (2)	−0.0 (1)	1.0 (1)	0.1 (1)
C(5)	2.0 (2)	1.4 (2)	3.4 (2)	−0.1 (1)	0.6 (1)	−0.1 (1)
C(6)	1.9 (2)	1.7 (2)	3.1 (2)	0.2 (1)	1.0 (1)	−0.4 (1)
O(1)	1.3 (1)	1.8 (1)	2.4 (1)	0.14 (8)	0.63 (9)	0.27 (9)
O(2)	1.5 (1)	2.0 (1)	2.7 (1)	−0.01 (9)	0.54 (9)	0.4 (1)
			Water Molecules			
O(3)	1.9 (1)	1.9 (1)	2.4 (1)	0.3 (1)	1.1 (1)	0.3 (1)
O(4)	1.4 (1)	3.3 (1)	2.6 (1)	−0.5 (1)	0.8 (1)	−1.4 (1)
			SO$_4^{2-}$ Anion			
S(3)	1.47 (3)	1.33 (4)	1.85 (4)	−0.30 (3)	0.59 (3)	−0.11 (3)
O(31)	1.8 (1)	1.8 (1)	2.5 (1)	−0.64 (8)	1.07 (9)	−0.66 (9)
O(32)	3.8 (1)	1.9 (1)	3.2 (1)	0.87 (9)	1.5 (1)	0.5 (1)
O(33)	2.0 (1)	2.4 (1)	3.3 (1)	−0.60 (9)	1.3 (1)	−0.4 (1)
O(34)	2.6 (1)	2.8 (1)	1.8 (1)	−1.2 (1)	0.3 (1)	−0.2 (1)

[a] They enter the expression of the structure factor in the form $\exp[-0.25(B_{11}a^{*2}h^2 + B_{22}b^{*2}k^2 + B_{33}c^{*2}l^2 + 2B_{12}a^*b^*hk + 2B_{13}a^*c^*hl + 2B_{23}b^*c^*kl)]$ and have units of A^2.

Table III. Interatomic Distances (A)[a]

Copper–Copper Distances

Tetranuclear Unit
Cu(1)···Cu(2)	5.648 (1)	Cu(1)···Cu(2)*	4.304 (2)

Shorter Packing Distance
Cu(1)···Cu(2)**	3.999 (1)

Metal–Ligand Bonds

Cu(1) Surrounding
Cu(1)-S(1)	2.300 (1)	Cu(1)-O(31)	1.949 (3)
Cu(1)-N(1)	1.947 (3)	Cu(1)-O(3)	2.487 (3)
Cu(1)-O(1)	2.052 (3)		

Cu(2) Surrounding
Cu(2)-S(2)	2.286 (1)	Cu(2)-O(4)	1.958 (3)
Cu(2)-N(2)	1.950 (3)	Cu(2)-O(3)*	2.300 (3)
Cu(2)-O(2)	2.061 (3)		

Dithiooxamidato Ligand
S(1)-C(1)	1.723 (4)	C(3)-C(4)	1.512 (6)
S(2)-C(2)	1.721 (4)	C(4)-O(1)	1.439 (5)
C(1)-C(2)	1.514 (5)	N(2)-C(5)	1.459 (5)
N(1)-C(2)	1.291 (5)	C(5)-C(6)	1.532 (6)
N(2)-C(1)	1.297 (5)	C(6)-O(2)	1.451 (6)
N(1)-C(3)	1.468 (5)		

SO$_4^{2-}$ Anion
O(31)-S(3)	1.506 (3)	O(33)-S(3)	1.464 (3)
O(32)-S(3)	1.468 (3)	O(34)-S(3)	1.478 (3)

C–H Bonds
C(3)-H(31)	1.0 (1)	C(5)-H(51)	1.00 (9)
C(3)-H(32)	0.9 (1)	C(5)-H(52)	0.9 (1)
C(4)-H(41)	0.9 (1)	C(6)-H(61)	0.9 (1)
C(4)-H(42)	0.98 (9)	C(6)-H(62)	1.0 (1)

O–H Bonds
O(1)-H(1)	0.7 (1)	H(23)	O(3)-H(2,3)	0.7 (1)
O(2)-H(2)	0.8 (1)	H(14)	O(4)-H(1,4)	0.9 (1)
H(13) O(3)-H(1,3)	0.8 (1)	H(24)	O(4)-H(2,4)	0.6 (1)

[a] Standard deviations are in parentheses. Starred atoms are in equivalent positions: (*) $-x, y, \frac{1}{2} - z$; (**) $-x, -y, -z$.

Magnetic Measurements. The magnetic measurements were carried out on a polycrystalline sample with a previously described Fara-
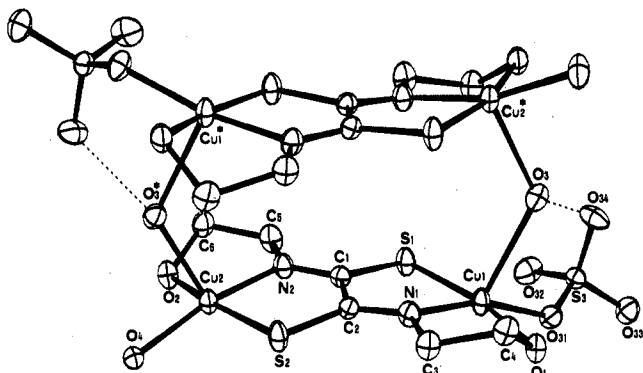
Figure 1. ORTEP drawing of the tetrameric entity $[\{Cu_2[S_2C_2(NC-H_2CH_2OH)_2](H_2O)(SO_4)\}_2(H_2O)_2]_2$ with 50% probability thermal ellipsoids. Starred atoms and nonlabeled atoms are in equivalent position $\bar{x}, y, {}^1/_2 - z$. Dashed lines indicate intramolecular hydrogen bonding.

day-type magnetometer.[3] The correction for diamagnetism was estimated at -235×10^{-6} cm^3 mol^{-1} from the atomic values of Pascal.[17]

Results: Comparison of A and B Isomers

Structure Description. The asymmetric unit consists in a binuclear association of two independent copper atoms through a hexadentate dithiooxamidato ligand (Figure 1). The coordination geometry of this ligand is closely related to that observed in the previously reported A isomer.[3] The difference is concerning the position of H_2O and SO_4^{2-} ligands.

Let us recall the A isomer structure: the binuclear unit is centrosymmetric. The square-pyramidal geometry of both copper atoms is achieved with a water molecule in the basal plane and a SO_4^{2-} anion on the apex. This SO_4^{2-} ligand is bridging two neighbor binuclear units, leading to infinite chains, as referred to the steps of a staircase. The situation is different in the B isomer studied here. The SO_4^{2-} anion is not bridging, but only bound to Cu(1) and located in its basal plane. The corresponding site about Cu(2) is occupied by a water molecule. The apical sites on both square pyramids are thus available for the second water molecule, which bridges two neighbor units, leading to a tetranuclear association (Figure 1). The whole molecule has C_i symmetry.

The main features of this structure are discussed below.

Metal–Metal Distances. The shortest copper–copper distance in the lattice results from molecular packing of two neighboring tetranuclear units: Cu(1)⋯Cu(2) (equivalent position $\bar{x}, \bar{y}, \bar{z}$) = 3.999 (1) Å.

Intramolecular distances Cu(1)–Cu(2)* = 4.304 (2) Å and Cu(1)–Cu(2) = 5.648 (1) Å are found across the H_2O bridge and across the dithiooxamidato ligand, respectively. The latter distance is slightly greater than in the A isomer (5.61 (1) Å). This change comes about from the slight lengthening of Cu–S

Table IV. Bond Angles (deg)[a]

Cu(1) Surrounding		Cu(2) Surrounding	
S(1)–Cu(1)–N(1)	86.4 (1)	S(2)–Cu(2)–N(2)	87.0 (1)
N(1)–Cu(1)–O(1)	80.8 (1)	N(2)–Cu(2)–O(2)	82.5 (1)
O(1)–Cu(1)–O(31)	88.7 (1)	O(2)–Cu(2)–O(4)	92.1 (1)
O(31)–Cu(1)–S(1)	103.0 (1)	O(4)–Cu(2)–S(2)	96.5 (1)
O(3)–Cu(1)–S(1)	98.7 (1)	O(3)*–Cu(2)–S(2)	98.3 (1)
O(3)–Cu(1)–N(1)	106.0 (1)	O(3)*–Cu(2)–N(2)	106.9 (1)
O(3)–Cu(1)–O(1)	87.8 (1)	O(3)*–Cu(2)–O(2)	90.2 (1)
O(3)–Cu(1)–O(31)	87.2 (1)	O(3)*–Cu(2)–O(4)	88.1 (1)

Dithiooxamidato Ligand and Chelated Rings			
Cu(1)–S(1)–C(1)	96.1 (1)	Cu(2)–S(2)–C(2)	96.0 (1)
S(1)–C(1)–C(2)	118.3 (3)	S(2)–C(2)–C(1)	118.9 (3)
N(2)–C(1)–C(2)	115.4 (3)	N(1)–C(2)–C(1)	115.7 (3)
S(1)–C(1)–N(2)	126.3 (3)	S(2)–C(2)–N(1)	125.3 (3)
Cu(1)–N(1)–C(2)	122.0 (3)	Cu(2)–N(2)–C(1)	121.7 (3)
Cu(1)–N(1)–C(3)	115.4 (3)	Cu(2)–N(2)–C(5)	115.9 (3)
C(2)–N(1)–C(3)	121.5 (3)	C(1)–N(2)–C(5)	121.5 (3)
N(1)–C(3)–C(4)	106.9 (3)	N(2)–C(5)–C(6)	107.0 (3)
C(3)–C(4)–O(1)	105.9 (3)	C(5)–C(6)–O(2)	109.2 (3)
C(4)–O(1)–Cu(1)	107.2 (2)	C(6)–O(2)–Cu(2)	105.9 (2)
C(4)–O(1)–H(1)	109 (7)	C(6)–O(2)–H(2)	105 (7)
Cu(1)–O(1)–H(1)	117 (7)	Cu(2)–O(2)–H(2)	117 (7)

Water Molecules			
Cu(1)–O(3)–Cu(2)*	128.0 (1)	H(14)–O(4)–H(24)	117 (11)
H(13)–O(3)–H(23)	103 (9)		

$SO_4{}^{2-}$ Anion			
Cu(1)–O(31)–S(3)	131.4 (2)	O(32)–S(3)–O(33)	111.3 (2)
O(31)–S(3)–O(32)	108.4 (2)	O(32)–S(3)–O(34)	109.8 (2)
O(31)–S(3)–O(33)	107.5 (2)	O(33)–S(3)–O(34)	111.4 (2)
O(31)–S(3)–O(34)	108.4 (2)		

[a] Standard deviations are in parentheses.

Table V. Deviations (Å) from the Mean Planes 1, 2, and 3

Plane 1: S(1), N(1), O(1), O(31)

S(1)	+0.049	O(31)	-0.037
N(1)	-0.117	Cu(1)	+0.16
O(1)	+0.095		

Plane 2: S(1), C(1), N(2), S(2), C(2), N(1)

S(1)	-0.149	S(2)	-0.040
C(1)	+0.024	C(2)	+0.018
N(2)	+0.142	N(1)	+0.029

Plane 3: S(2), N(2), O(2), O(4)

S(2)	+0.054	O(4)	-0.047
N(2)	-0.075	Cu(2)	+0.19
O(2)	+0.071		

and Cu–N bonds, related to a more distorted metal surrounding.

Coordination Geometry. The binuclear unit is not planar as in the A isomer. Atoms are found in three planes involving (1) Cu(1) basal surrounding, (2) dithiooxamidato ligand but the hydroxyethyl chain, and (3) Cu(2) basal surrounding, as shown in Figure 3. These deformations can be evaluated from
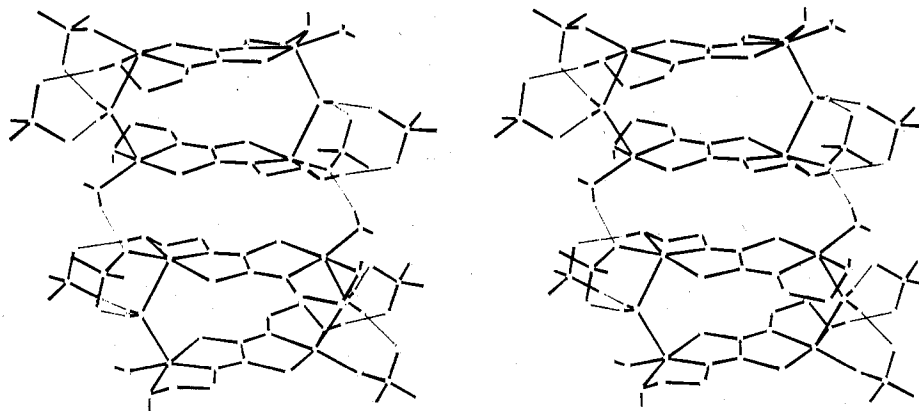

Figure 2. Stereopair partial view of molecular packing within the unit cell. Tetranuclear units are related through an inversion center.
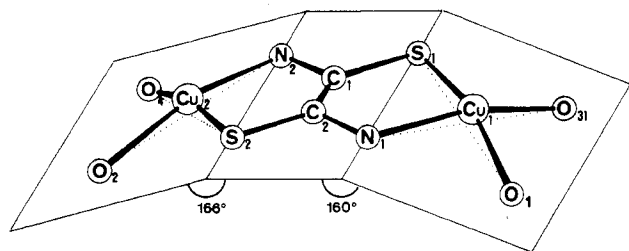
Figure 3. Distortions in the binuclear unit (see text).

dihedral angles between these planes.

Atom deviations from the mean planes are reported in Table V. Cu(1) and Cu(2) are displaced 0.16 and 0.19 Å, respectively, out of the mean planes toward the apical water molecules. These different deviations seem to be well correlated with the magnitude of copper–water interactions (Cu(1)–O(3) = 2.487 Å; Cu(2)–O(3)* = 2.300 Å). This behavior is normal for five-coordinate tetragonal-pyramidal Cu(II) complexes.[18] It can also be observed that the signs of deviations in plane 2 (dithiooxamidato ligand) indicate a slight twist of ca. 8° around the C(1)–C(2) axis.

Another feature concerns the similar distortion of both square pyramids. It is obvious from Table IV that the three copper–oxygen bonds form a quasi-orthogonal set while both angles involving the apical oxygen atom and either sulfur or nitrogen are significantly larger.

Bridging Water Molecule. We assumed a possible influence of the bridging water molecules on the distortion described above. Indeed, it seems likely that the oxygen atom exhibits a tendency to reduce this bridge angle in order to preserve a nearly tetrahedral basis set of orbitals. This cannot be completely achieved since the bridge angle Cu(1)–O(3)–Cu(2) is 128°. However, such a constraint on oxygen–copper directions should induce a strong distortion of square pyramids. The bending of binuclear units can therefore be regarded as an attempt by copper to keep the Cu–O direction as normal as possible to the basal plane of the metal coordination sphere. Indeed, the angles between both Cu–O directions and corresponding basal planes of the copper coordination sphere are 80.6 and 80.2°, respectively.

SO₄²⁻ Anion. The position of this ligand in the basal site of Cu(1) favors a strong interaction with the metal as shown by (i) the short Cu(1)–O(31) distance 1.949 (3) Å, (ii) the significant lengthening of O(31)–S(3), 1.506 (3) Å, with respect to the other oxygen–sulfur distances (O(32)–S(3) = 1468 (3) Å, O(33)–S(3) = 1.464 (3) Å, O(34)–S(3) = 1.478 (3) Å), and (iii) a weak but significant distortion of the sulfur tetrahedral surrounding, consisting of a slight decrease of the three angles adjacent to the bonding oxygen O(31) (107.5 (2)°, 108.4 (2)°, 108.4 (2)°) with respect to others (111.3 (2)°, 111.4 (2)°, 109.8 (2)°).

Molecular Packing. Tetranuclear units are packed through a network of hydrogen bonds involving alcoholic OH groups, H₂O molecules, and SO₄²⁻ anions. Evidence of such interactions has been obtained from oxygen–oxygen distances and from the positions of hydrogen atoms.

A partial view of the molecular packing is given in Figure 2. Considering the parallel arrangement of tetranuclear units and taking the mean plane of dithiooxamidato ligand as a reference, one could distinguish the in-plane packing (Figure 4a) from the out-of-plane packing (Figure 4b).

(a) The in-plane association of neighbor units is only made through the Cu(1) surrounding as shown in Figure 4a: two oxygen atoms of the SO₄²⁻ anion, O(33) and O(34), are connected to a neighbor unit through hydrogen bonds involving the bridging water molecule (O(33)···O(3) = 2.773 (5) Å; O(33)···H(23) = 2.0 (1) Å) and the alcohol function (O-(34)···O(1) = 2.721 (5) Å; O(34)···H(1) = 2.0 (1) Å). The
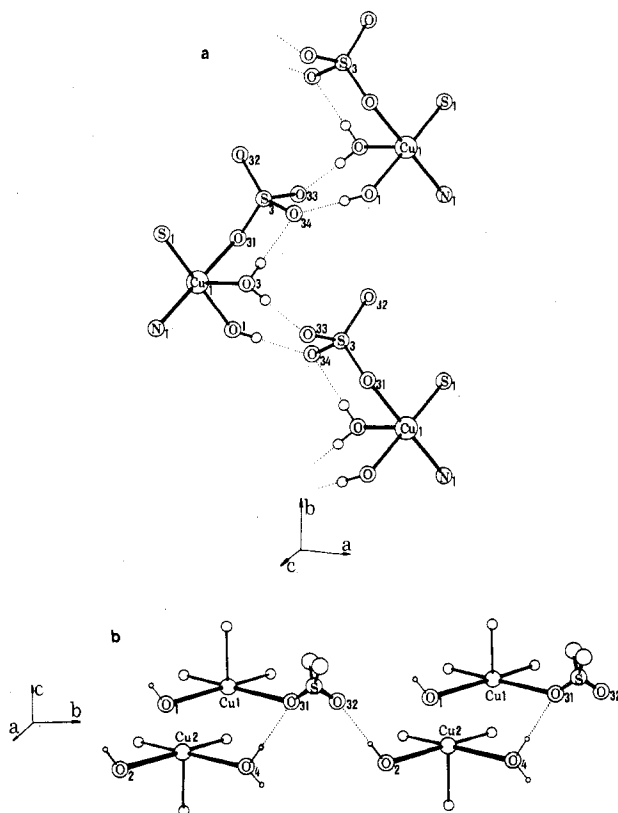

Figure 4. Hydrogen bonds: (a) in-plane connection between Cu(1) basal planes (dashed lines indicate hydrogen bonds); (b) out-of-plane connection between Cu(1) and Cu(2) basal planes.

bridging water molecule is therefore involved in intramolecular and intermolecular hydrogen bonds running around the helicoidal axis.

(b) The out-of-plane packing results from the connection of the SO₄²⁻ anion (Cu(1) surrounding) with the Cu(2) basal plane of two neighbor units. This association is made through two hydrogen bonds sketched in Figure 4b: the first one connects O(31) to the terminal water molecule (O(31)···O(4) = 2.715 (5) Å; O(31)–H(14) = 1.9 (1) Å); the second one connects O(32) to the alcohol function O(2) (O(32)···O(2) = 2.563 (5) Å; O(32)···H(2) = 1.8 (1) Å).

It seems likely that all these hydrogen bonds participate in the bending of binuclear units.

A–B Isomerization. We have pointed out the structural differences between A and B isomers. Formally, one can pass from the one to the other one by a concerted rotation of both a water molecule and a sulfato anion around one of the SCuO(H) axes in the binuclear unit. This rotation might correspond to the actual mechanism of the isomerization. In the solution S (see Synthesis), the two binuclear species α and β shown in 1 and 3 would be in equilibrium. The isomerization might occur owing to the intermediate step 2 in which the coordination around one of the Cu(II) ions is trigonal bipyramidal, with N, O(H₂), and O(SO₃) atoms in the basal plane, and S and O(H) atoms on the equatorial axis. Such a mechanism has already been proposed for 4 + 2 coordinated Cu(II) complexes.[19,20]

Magnetic Properties. The molar magnetic susceptibility χ_M of {Cu₂[S₂C₂(NCH₂CH₂OH)₂](H₂O)(SO₄)}(H₂O) was studied in the temperature range 15–300 K. χ_M decreases upon cooling down from room temperature to about 120 K and then increases again. This behavior is characteristic of both a strong antiferromagnetic coupling in the dimeric entity and a presence of a small amount ρ of monomeric impurity. Assuming that the magnetic behavior of this impurity obeyed a Curie law and
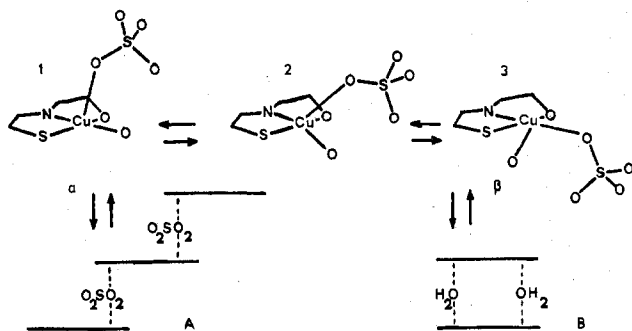
that its molecular weight was half of that of the studied compound, we fitted the experimental data with the expression

$$\chi_M = \frac{2N\beta^2 g^2}{kT}\left[3 + \exp\left(-\frac{J}{kT}\right)\right]^{-1}(1 - \rho) + \frac{N\beta^2 g^2}{2kT}\rho + 2N\alpha$$

where J, g, ρ, and $N\alpha$ were taken as adjustable parameters. Least-squares fitting procedure led to $J = -523$ cm^{-1}, $g = 2.089$, $\rho = 0.066$, and $N\alpha = 36 \times 10^{-6}$ cm^3 mol^{-1}. The agreement factor R defined as $\sum[\chi_{M_{calcd}} - \chi_{M_{obsd}}]^2/\sum\chi_{M_{obsd}}^2$ is then equal to 2.01×10^{-4}. The theoretical curve and experimental data corrected for the monomeric impurity are compared in Figure 5.

We have pointed out earlier that the Cu–Cu distance in the binuclear unit {Cu$_2$[S$_2$C$_2$(NCH$_2$CH$_2$CH$_2$OH)$_2$](H$_2$O)(SO$_4$)} is only the third shortest Cu–Cu distance in the lattice. Nevertheless, it is clear that the strong antiferromagnetic coupling occurs inside this binuclear unit through the dithiooxamido bridging ligand. As a matter of fact, the bridging water molecules are weakly enough coordinated to the Cu(II) ions so that the unpaired electrons around each Cu(II) are described by magnetic orbitals built from the d$_{x^2-y^2}$ metallic orbitals pointing toward the oxygen, sulfur, and nitrogen atoms surrounding the metals. These magnetic orbitals lie in the pseudoplane of the binuclear unit and are strongly delocalized toward sulfur and nitrogen atoms.[3] The interaction takes place owing to the in-plane S–N overlaps and is favored by the diffuseness of the 3p sulfur orbitals. Since the exchange pathways are qualitatively identical in the A and B isomers, we can focus on the quantitative difference between the J values -594 and -523 cm^{-1}, respectively, and attempt to explain it. It has been established[8] that, for a symmetrical Cu(II) binuclear complex, the antiferromagnetic contribution J_{AF} to the exchange interaction parameter J may be expressed according to $J_{AF} = -2S\Delta$, an expression in which S is the overlap integral between the magnetic orbitals centered on the one and the other transition ions and Δ is the energy separation between the two singly occupied molecular orbitals in the triplet state built from the magnetic orbitals. When the binuclear complex is not symmetrical, i.e., when the surroundings of both Cu(II) ions are not strictly identical, J_{AF} must be expressed according to[10] $J_{AF} = -2S(\Delta^2 - \delta^2)^{1/2}$, δ being the energy separation between the two magnetic orbitals. The meaning of Δ and δ for such nonsymmetrical Cu(II) binuclear complexes is defined in Figure 6. We carried out a molecular orbital energy level calculation for the model complex {Cu$_2$[S$_2$C$_2$(NH)$_2$](H$_2$O)$_2$}$^{2+}$ derived from the actual B isomer changing the CH$_2$CH$_2$OH group by a hydrogen atom bonded to the nitrogen and a water molecule coordinated to the metal and replacing the SO$_4^{2-}$ terminal ligand by another water molecule. This model is therefore essentially identical with the one considered to represent the A isomer,[3] the only differences being the exact coordinates of the atoms. In both cases, the coordinates for Cu(II) ions and atoms of the dithiooxamido bridging ligand are those of the actual structures obtained by X-ray study. For the calculation, we used the
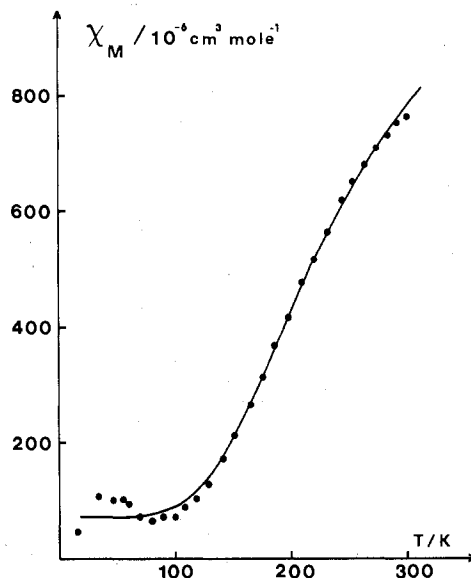

Figure 5. Experimental and theoretical dependence of the molar magnetic susceptibility: (●) points corrected of the noncoupled Cu(II) impurity, (—) theoretical curve.
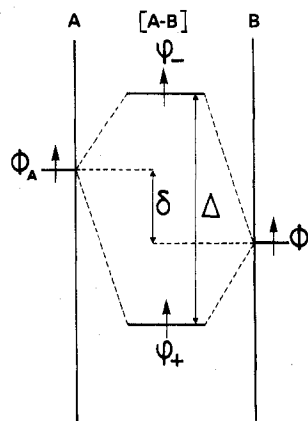

Figure 6. Energy diagram for the magnetic orbitals ϕ_A and ϕ_B and for the molecular orbitals φ_+ and φ_- in the case of interaction between two nonequivalent Cu(II) ions.

version Forticon 8 of the extended Hückel method[21] with the parametrization given in ref 3. For the model complex of the B isomer, Δ is found equal to 0.594 eV. This value is compared to the one found for the model complex of the A isomer, 0.623 eV. In contrast to the A isomer, the B isomer is not strictly symmetrical. The surroundings of both Cu(II) ions are, however, close to each other; δ is therefore very small and may be neglected in a first approximation. On the assumption that the overlap integral S is proportional to Δ, $|J_{AF}|$ is expected to vary as Δ^2. In other words, if a small structural modification between A and B isomers leads to a relative variation $d\Delta/\Delta$ of the energy gap between the two singly occupied molecular orbitals in the triplet state, one can expect a relative variation dJ_{AF}/J_{AF} of the antiferromagnetic coupling equal to $-2(d\Delta/\Delta)$. The agreement with this theoretical prediction is fairly good. We observed a decrease of 13% for $|J_{AF}|$ and we calculated a decrease of 5% for Δ. The agreement is even better if we take into account a small δ value for the B isomer. Δ must therefore be replaced by $(\Delta^2 - \delta^2)^{1/2}$ and the variation of $(\Delta^2 - \delta^2)^{1/2}$ is larger than 5%. We have shown[3] that the large Δ value could be explained by (i) the delocalization of the unpaired electrons from the Cu(II) ions toward the sulfur and nitrogen atoms and (ii) the relatively important in-plane S–N overlaps. Consequently the a$_u$ MO in which the S–N overlaps are positive is significantly lower in energy than the a$_g$ MO

in which the S–N overlaps are negative (see below).
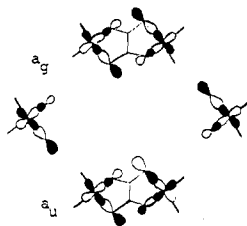
In the B isomer, the delocalization of the unpaired electrons toward sulfur and nitrogen atoms is much the same as in the A isomer. But, owing to both the deviation from planarity of the binuclear unit (see Figure 3) and the slight lengthening of S–N distances (2.702 and 2.682 Å instead of 2.674 Å), the σ S–N overlaps are not so well favored and the Δ energy separation becomes smaller than in the A isomer.

In conclusion, we wish to emphasize that the design of new bridging ligands more efficient than the dithiooxamidato to propagate the interactions in polynuclear systems, in which the transition ions are far away from each other, may be considered as a challenge for inorganic chemists. We would accept with pleasure to compete in this goal.

Registry No. [{Cu$_2$[S$_2$C$_2$(NCH$_2$CH$_2$OH)$_2$](H$_2$O)(SO$_4$)}(H$_2$O)]$_2$, 71276-85-2.

Supplementary Material Available: A listing of structure factor amplitudes (16 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Our colleague C. Chauvel died in an accident on April 9, 1978, just after he obtained the single crystals of the title compound used for the structure study. We would like to dedicate to him this paper, his last paper.
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Structural Determination of [(C₅H₅)₂Mo(H)CO][(C₅H₅)Mo(CO)₃]

M. A. ADAMS, K. FOLTING, J. C. HUFFMAN, and K. G. CAULTON*

On the basis of an X-ray diffraction study at –125 °C, [Cp$_2$Mo(H)CO][CpMo(CO)$_3$] has been established to crystallize in space group $P2_1/c$ with a = 6.370 (2) Å, b = 10.226 (3) Å, c = 27.233 (11) Å, and β = 84.58 (1)°. Refinement of 3931 nonzero reflections leads to $R(F)$ = 0.040 and $R_w(F)$ = 0.064; all hydrogen atoms were refined. The anion CpMo(CO)$_3^-$ suffers only minor distortion from a symmetric "piano stool" configuration with average distances from Mo to cyclopentadienyl and carbonyl carbons of 2.381 and 1.930 Å; the MoCO groups are within 3σ of being linear. In the cation Cp$_2$Mo(H)CO$^+$, the corresponding distances are 2.291 and 1.991 Å. Comparison of these parameters, as well as the C–O distances, supports the idea that back-bonding is enhanced in low oxidation states. Comparison of the structural data for Cp$_2$Mo(H)CO$^+$ with the corresponding values in Cp$_2$MoH$_2$ indicates minimal π donation from CO to Mo(IV) in the cation.

Introduction

Compounds containing one metallic element in disparate oxidation states are unusual, if for no other reason than their potential to react by comproportionation to equalize their oxidation states. Our recent study[1] of the mechanism of carbonylation of Cp$_2$MoH$_2$ revealed the participation of a variety of bimetallic hydrogen-transfer reactions between molybdenum complexes in formal oxidation states IV, II, and I. For example, both reactions 1 and 2 yield compound I, of

$$Cp_2MoCO + CpMoH(CO)_3 \rightarrow I \qquad (1)$$

$$Cp_2MoH_2 + {}^1/_2[CpMo(CO)_3]_2 + CO \rightarrow I \qquad (2)$$
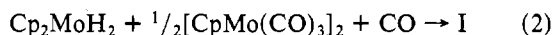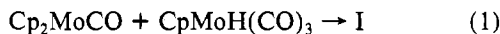
empirical formula Cp$_3$Mo$_2$H(CO)$_4$. Comproportionation or electronegativity equalization reactions necessitate consideration of a structure such as A for compound I. The

Table I. Crystal Data for [(C$_5$H$_5$)$_2$Mo(H)CO][(C$_5$H$_5$)Mo(CO)$_3$]

formula	C$_{19}$H$_{16}$O$_4$Mo$_2$
color	orange
crystal dimensions, mm	0.19 × 0.12 × 0.25
space group	$P2_1/c$
a,^{a} Å	6.370 (2)
b,^{a} Å	10.226 (3)
c,^{a} Å	27.233 (11)
β,^{a} deg	84.58 (1)
Z	4
V, Å^3	1765.8
ρ(calcd), g cm^{-3}	1.878
mol wt	499.21
λ, Å	0.71069
μ(Mo Kα), cm^{-1}	14.07

^{a} Cell dimensions at –125 °C using 12 reflections.

structural study reported here was undertaken to resolve the actual nature of compound I.