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Crystal Structure and Magnetic Properties of *catena*-μ-Sulfato-[*N*,*N'*-bis(2-hydroxyethyl)dithiooxamido(2−)-*N*,*O*,*S*:*N'*,*O'*,*S'*]bis[aquacopper(II)]: A Chain of Copper(II) Dinuclear Units with a 594-cm^{-1} Singlet–Triplet Separation and a 5.61-Å Copper–Copper Distance

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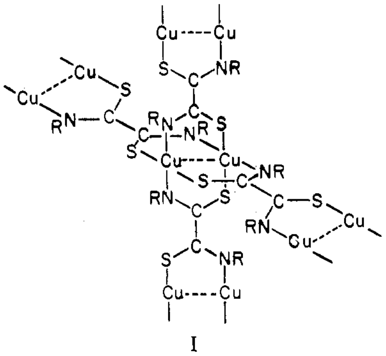
The title compound, $\{Cu_2[S_2C_2(NCH_2CH_2OH)_2](H_2O)_2\}SO_4$, was synthesized and its crystal structure determined at room temperature. It crystallizes in the monoclinic system, space group $C2/c$. The lattice constants are $a = 21.47$ (5) Å, $b = 7.49$ (1) Å, $c = 9.75$ (2) Å, and $\beta = 111.93$ (10)° with $Z = 4$. Least-squares refinement of the structure has led to a conventional R factor of 0.048. The structure is made of the 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. Copper coordination is 4 + 1, in the form of a square pyramid, the apex of which is occupied by a weakly bonded oxygen of a sulfate group (Cu–O = 2.442 Å). Although the Cu–Cu distance in the binuclear unit is 5.61 Å, the temperature dependence of the magnetic susceptibility, studied in the range 20–300 K, shows a strong antiferromagnetic coupling with a singlet–triplet separation of 594 cm^{-1}. This very peculiar magnetic behavior is explained as follows: (i) The copper unpaired electrons are strongly delocalized toward the sulfur and nitrogen atoms bonded to copper. (ii) Owing to the rather short S–N distance (2.68 Å) and to the diffuseness of 3p sulfur orbitals, the in-plane S–N overlaps are important so that the energy gap between the two singly occupied molecular orbitals in the triplet state is very large. A semiquantitative estimate of the antiferromagnetic exchange parameter is given.

Introduction

Extensive work has been carried out on the copper(II) rubeanates of general formula $CuS_2C_2(NR)_2 \cdot xH_2O$ with R = H, alkyl, alkyl ester, cycloalkyl, and benzyl.[2-7] The interest for these compounds arises from the fact that they exhibit at the same time an electric behavior of semiconductors and a magnetic behavior of polymeric systems in which the Cu(II) ions are very strongly coupled in an antiferromagnetic way. Unfortunately so far, it has not been possible to give a satisfactory interpretation of these physical properties because the geometrical structures of these compounds were unknown; all copper(II) rubeanates with a 1:1 copper–ligand ratio were obtained as amorphous powders; all attempts to grow single crystals were unsuccessful. Two types of structures, I and II, were postulated. In structure I,[7] of the copper(II) acetate type, the shortest Cu–Cu distance would be ca. 2.8–3 Å. In structure II,[2-5] of the iron(II) oxalate type,[8] the shortest Cu–Cu distance should be larger than 5 Å. Taking into account the magnitude of the antiferromagnetic coupling, structure I was claimed to be the most likely.[7] However, the mechanism of the exchange interaction in copper(II) rubeanates was far from clear and it appeared to us that it would be of great interest to prepare a new complex from Cu(II) and a dianion $[S_2C_2(NR)_2]^{2-}$ derived from dithiooxamide, which would be perfectly defined and suitable for X-ray study and which would exhibit the same type of magnetic behavior as the amorphous copper(II) rubeanates.



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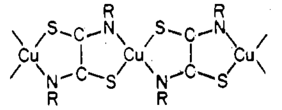


II

We note here that the copper(II) rubeanates are not the only known compounds in the copper(II)–dithiooxamide system. Complexes of formula $\{Cu[S_2C_2(NHR)_2]_2\}(ClO_4)_2$ and $Cu[S_2C_2(NHR)_2]Cl_2$ were also synthesized.[9] They look well crystallized; however, their magnetic behaviors do not reveal any interaction between the Cu(II) ions, except at very low temperature, i.e., below 10 K.

Attempts to synthesize a well-crystallized compound exhibiting the strongly antiferromagnetic properties of the copper(II) rubeanates led us to a new complex of formula $[Cu_2S_2C_2(NCH_2CH_2OH)_2(H_2O)_2]SO_4$. Well-formed single crystals were obtained. Crystal and magnetic studies revealed a quite exceptional situation: the structure contains Cu(II) binuclear units linked to each other by sulfate bridges making zigzag chains. In the binuclear unit, the Cu(II) ions are strongly antiferromagnetically coupled. The singlet–triplet separation is 594 cm^{-1} although the Cu–Cu distance is as large as 5.61 Å. We herein propose a semiquantitative interpretation of this result.

In the last few years, several attempts have been made to correlate the magnetic properties of binuclear complexes with structural data.[10-16] The most striking results were obtained with Cu(II) dimers.[17,18] This work is intended to be an experimental and theoretical contribution to the study of the exchange interaction in polynuclear systems.

Experimental Section

Synthesis. The ligand *N*,*N'*-bis(2-hydroxyethyl)dithiooxamide was obtained from dithiooxamide and ethanolamine by the Wallach reaction.[19] 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 cm^3 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 cm^3 of methanol. An amorphous precipitate of a compound with formula $CuS_2C_2(NCH_2CH_2OH)_2$ was formed. To dissolve this precipitate, 1 cm^3 of concentrated sulfuric acid was added. The solution was then filtered (solution A) and poured into 100 cm^3 of water at 80 °C

Table I. Atomic Coordinates (× 10^4) and Thermal Parameters[a]

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	3453.1 (2)	6175.2 (7)	2640.4 (5)	1.71 (2)	2.03 (2)	1.50 (1)	−0.29 (1)	0.02 (1)	0.19 (1)
S_1	2641.4 (5)	4740 (1)	777 (1)	2.34 (4)	1.89 (4)	2.07 (4)	−0.17 (3)	−0.36 (3)	0.29 (3)
S_2	5000 (0)	4433 (2)	2500 (0)	1.47 (4)	2.13 (5)	1.21 (4)	0.0000	0.11 (3)	0.0000
N	3177 (2)	8350 (4)	1501 (3)	1.7 (1)	2.0 (1)	1.9 (1)	0.04 (9)	0.18 (9)	0.14 (9)
C_1	2665 (2)	8386 (5)	258 (4)	1.5 (1)	1.8 (1)	1.6 (1)	0.1 (1)	0.3 (1)	0.08 (9)
C_2	3542 (2)	9975 (6)	2186 (5)	2.1 (1)	2.0 (1)	2.2 (1)	−0.1 (1)	−0.2 (1)	0.2 (1)
H_{12}	3553 (34)	727 (97)	1442 (80)						
H_{22}	3301 (35)	698 (99)	2609 (79)						
C_3	4182 (2)	9398 (7)	3441 (5)	2.4 (2)	2.8 (2)	2.7 (2)	−0.6 (1)	−0.5 (1)	0.4 (1)
H_{13}	4312 (36)	274 (100)	4113 (82)						
H_{23}	4585 (37)	8886 (109)	3091 (81)						
O_1	4391 (1)	5541 (5)	1876 (3)	2.5 (1)	3.7 (1)	1.8 (1)	1.1 (1)	0.65 (9)	0.48 (9)
O_2	5072 (1)	3299 (5)	1324 (3)	2.1 (1)	3.4 (1)	2.6 (1)	−0.2 (1)	0.59 (9)	−1.1 (1)
O_3	3754 (1)	4071 (4)	3923 (3)	2.3 (1)	2.6 (1)	1.5 (9)	0.05 (9)	0.35 (8)	0.28 (9)
$H_1(O_3)$	3922 (35)	4260 (98)	4799 (80)						
$H_2(O_3)$	4093 (38)	3784 (109)	3918 (76)						
O_4	4011 (2)	7907 (4)	4170 (3)	2.3 (1)	2.6 (1)	1.8 (1)	0.08 (9)	−0.30 (9)	0.08 (9)
$H(O_4)$	4327 (38)	7595 (108)	4717 (79)						

[a] See Figure 4 for identifying the atoms. The anisotropic thermal parameters have units of $Å^2$. They enter the expression for the structure factor in the form $\exp[-0.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

containing 7 g of ammonium sulfate. A dark green crystalline precipitate appeared, which was filtered out, washed with water, and dried under vacuum. Anal. Calcd for $Cu_2C_6H_{14}N_2S_3O_8$: Cu, 27.30; C, 15.48; H, 3.03; N, 6.02; S, 20.67. Found: Cu, 26.65; C 15.64; H, 3.04; N, 6.06; S, 20.53.

Well-formed single crystals, suitable for X-ray study, were obtained by very slow evaporation of solution A at room temperature.

Structure Solution and Refinement. The crystals are slightly air unstable. The crystal selected for X-ray analysis was roughly cubic (edge: 0.24 mm). Preliminary Laue and precession photographs led to a monoclinic unit cell. Lattice constants were measured from diffractometer settings. For space group $C2/c$ the following values were obtained: $a = 21.47$ (5) Å, $b = 7.49$ (1) Å, $c = 9.75$ (2) Å, $\beta = 111.93$ (10)°, $V = 1455$ Å^3, $Z = 4$, $\rho_{calcd} = 2.13$ g cm^{-3}, and $\rho_{measd} = 2.16$ g cm^{-3} (flotation in a tribromomethane–tetrachloromethane mixture).

The crystal was introduced into a Lindemann tube which was then sealed and set up on a 300-mm Eulerian craddle along its $h00$ axis.

Intensity data were collected at room temperature on a homemade automatic diffractometer: radiation, Mo Kα; takeoff angle, 2°; crystal–focus distance, 230 mm; crystal–counter distance, 230 mm; scan type, θ–2θ scan technique (1.7° min^{-1}); scan length, 1° symmetrical scan at zero Bragg angle, corrected for Kα_1–Kα_2 dispersion; background measurements, 10 s in fixed positions before and after every scan. The scintillation counter was connected to a pulse-height analyzer set on Mo Kα energy so that 90% of the intensity was counted. The graphite monochromator was set in front of the counter window. Two standard reflections, 12,0,0 and 040, were measured every 100 reflections. Observed variations never exceeded 6σ during data collection. A total of 1756 independent reflections were collected up to $\theta_{Bragg} = 28°$.

Treatment of Intensity Data. Intensities were corrected for Lorentz and polarization factors. Attempts to correct intensities from absorption at the end of the refinement gave no improvement of the R value. For every observed structure factor F_o, a standard deviation σ was computed: $\sigma = F_o\Delta c/2c$, where c is the integrated intensity and Δc the error on it. $\Delta c = (I_1 + I_2 + I_3)^{1/2}$, where I_1 is the measured intensity, I_2 is the background intensity, and I_3 is the count loss correction if the counting rate is above 10 000 counts/s.[20] Atomic form factors were taken from Cromer and Waber[21] for all atoms except hydrogen atoms for which values of Stewart, Davidson, and Simpson[22] were applied. The copper atom was corrected for the real and imaginary parts of anomalous dispersion.[21]

Refinements were made by full-matrix least squares, minimizing the R_w factor $R_w = [\sum_i(w_i|F_o - kF_c|)^2/\sum_i|w_iF_o|^2]^{1/2}$, where w is $1/\sigma$ and k is the scale factor. A three-dimensional Patterson map showed copper and all sulfur atoms. Refinement of their coordinates led to $R = 0.375$.

Successive Fourier syntheses and refinements dropped R to 0.113 with isotropic temperature factors and R to 0.065 with anisotropic temperature factors. The introduction of hydrogen atoms led to $R = 0.051$.

Structure factors were then corrected for secondary extinction, with an extinction factor equal to 2.89×10^{-7}. R dropped to 0.048, which is significant at the 0.005 level of Hamilton's test.[23] Three reflections were excluded because $|F_c - F_o|$ differences were higher than 15. The final reliability factors were as follows: nonweighted R excluding 79 zeros, 0.047; weighted R excluding 79 zeros, 0.042. $F(000) = 844$. The average of parameter changes during the last refinement cycle was one-tenth of the standard deviations for all nonhydrogen atoms. The atomic parameters are shown in Table I. Main interatomic distances and bond angles are shown in Table II.

Two ORTEP[24] diagrams were computed with 50% probability thermal ellipsoids (Figures 2 and 4).

Magnetic Measurements. The magnetic measurements were carried out on a powder sample with a Faraday-type magnetometer, equipped with a continuous-flow cryostat designed by Oxford Instruments. The temperature is given by a gold-iron/chromel thermocouple. A magnetic induction of about 9 kG was used. The independence of the susceptibility from the magnetic induction was checked at room temperature; this gives evidence of the absence of ferromagnetic impurities in the sample. Mercuritetrathiocyanatocobaltate(II) was used as a susceptibility standard. The absolute accuracy on temperature is estimated at ±0.1 K and the relative accuracy on the apparent increase of the weight of the sample when the magnetic field is applied is about 1%. The correction for diamagnetism is estimated at -235×10^{-6} cm^3 mol^{-1} from the atomic values of Pascal.[25]

Results

Magnetic Properties. In Figure 1 is shown the temperature dependence of the molar magnetic susceptibility χ_M of $\{Cu_2[S_2C_2(NCH_2CH_2OH)_2](H_2O)_2\}SO_4$ in the range 20–300 K. At room temperature χ_M is only 760×10^{-6} cm^3 mol^{-1} and decreases upon cooling from 300 to 118 K. Such behavior is characteristic of a strong antiferromagnetic coupling between the Cu(II) ions. Upon cooling below 118 K, χ_M increases. This is most likely due to the presence of traces of noncoupled Cu(II) ions as an impurity in our sample. By assuming that the magnetic behavior of this impurity obeys Curie law above 20 K, it is very easy to correct our experimental data in order to eliminate the effect of this impurity. This is made in Figure 1. The magnetic curve is then perfectly described by the expression giving the temperature dependence of χ_M for a Cu(II) binuclear complex, where $-J$ is the energy separation between the spin singlet and the spin triplet (eq 1). The values

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

of g, J, and $N\alpha$ leading to the best agreement between experiment and theory are $g = 2.24$, $J = -594$ cm^{-1}, and $2N\alpha = 35 \times 10^{-6}$ cm^3 mol^{-1}. The theoretical curve is compared

Table II. Selected Interatomic Distances and Angles[a,b]

Distances (Å)			
Copper Surrounding (Cf. Figure 4)			
Cu-N	1.935 (5)	Cu-O_3	1.967 (5)
Cu-S_1	2.265 (5)	Cu-O_1	2.442 (2)
Cu-O_4	2.002 (4)		
Dinuclear Unit (Cf. Figure 4)			
N-C_1	1.297 (5)	S_1-N^c	2.919 (5)
C_1-C_1*	1.499 (8)	Cu-Cu*^{c}	5.61 (1)
C_1*-S_1	1.710 (4)	C_2-H_{12}	0.92 (8)
N-C_2	1.466 (6)	C_2-H_{22}	0.95 (8)
C_2-C_3	1.523 (6)	C_3-H_{13}	0.89 (8)
C_3-O_4	1.441 (6)	C_3-H_{23}	1.099 (9)
S_1-N*^{c}	2.674 (6)	O_4-H(O_4)	0.72 (7)
SO_4 Group			
S_2-O_1	1.470 (3)	S_2-O_2	1.486 (4)
Hydrogen Bonds (Cf. Figure 4)			
Interchain			
O_3-O_1	2.702 (7)	O_4-O_2	2.616 (7)
O_3-H_1(O_3)	0.80 (7)	O_4-H(O_4)	0.73 (7)
H_1(O_3)-O_1	1.90 (7)	H(O_4)-O_2	1.89 (8)
Intrachain			
O_3-O_2	2.683 (7)	H_2(O_3)-O_2	1.90 (8)
O_3-H_2(O_3)	0.79 (8)		
Copper-Copper Distances (Cf. Figure 3)			
Cu(1)-Cu(6)	5.61 (1)	Cu(1)-Cu(7)	5.478 (8)
Cu(1)-Cu(4)	5.18 (1)	Cu(1)-Cu(3)	6.75 (1)
Angles (deg)			
Copper Surrounding			
N-Cu-O_4	81.5 (2)	O_1-Cu-S_1	97.9 (1)
S_1-Cu-N	87.7 (2)	O_1-Cu-N	97.7 (2)
S_1-Cu-O_3	96.0 (2)	O_1-Cu-O_4	91.3 (2)
O_3-Cu-O_4	94.6 (2)	O_1-Cu-O_3	85.8 (2)
Dinuclear Unit			
N-Cu-O_4	81.5 (2)	N-Cu-S_1	87.7 (2)
Cu-O_4-C_3	109.1 (3)	Cu-S_1-C_1*	95.5 (2)
O_4-C_3-C_2	107.3 (4)	S_1-C_1*-C_1	119.9 (3)
C_3-C_2-N	107.5 (4)	C_1*-C_1-N	115.2 (4)
C_2-N-Cu	116.0 (3)	C_1-N-Cu	121.6 (3)
Nitrogen Surrounding			
Cu-N-C_1	121.6 (3)	C_1-N-C_2	122.1 (4)
Cu-N-C_2	116.0 (3)		
SO_4 Group			
O_1(1)-S_2-O_1(3)	112.0 (3)	O_1(3)-S_2-O_2(1)	108.0 (2)
O_1(1)-S_2-O_2(1)	109.6 (2)	O_1(3)-S_2-O_2(3)	109.6 (2)
O_1(1)-S_2-O_2(3)	108.0 (2)	O_2(1)-S_2-O_2(3)	109.5 (3)
Water Molecule			
H_1(O_3)-O_3-H_2(O_3)	90 (7)	O_3(1)-H_2(O_3)-O_2(3)	173 (8)
O_1(4)-O_3-O_2(3)	90.0 (2)	H_2(O_3)-O_3-Cu	107 (6)
O_3(1)-H_1(O_3)-O_1(4)	173 (7)	H_1(O_3)-O_3-Cu	116 (5)

[a] Estimated standard deviations of the least significant figures are given in parentheses. [b] In this table and through the text, equivalent positions referring to a given atom (numbered in Figure 3 caption) are shown by a number in parentheses appearing after the symbol of this atom. [c] Not bound.

with the corrected experimental points in Figure 1.

Crystal Structure. The crystal structure (Figure 2) consists of chains built from roughly planar dinuclear units $\{Cu_2[S_2C_2(NCH_2CH_2OH)_2](H_2O)_2\}^{2+}$ linked by SO_4 groups as with steps of a staircase; the angle between two successive steps is equal to 20.4°. Each SO_4 group is bound through two oxygen atoms to two copper atoms belonging to two successive units, its sulfur atom being located on the twofold axis. These chains run parallel one to each other and the translation from Cu(7) to Cu(3) is $^1/_2$, $^1/_2$, 0 (Figure 3).

Dinuclear Unit and Copper Coordination. Figure 4 shows the atomic positions in the dinuclear unit. The nearly planar

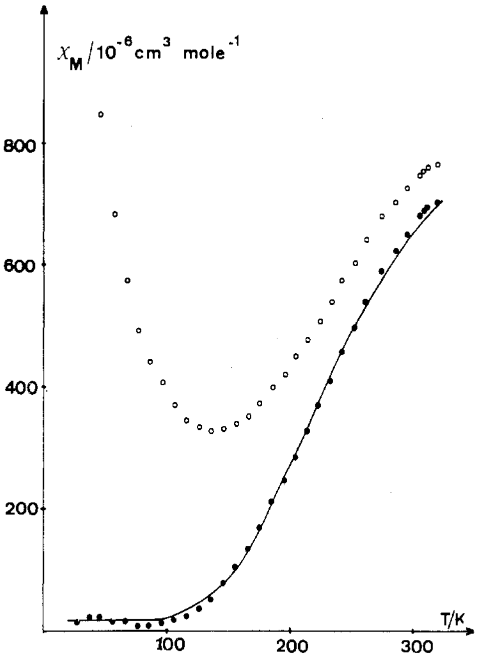


Figure 1. Experimental and theoretical temperature dependence of the molar magnetic susceptibility: (○) experimental points, (●) points corrected of the noncoupled Cu(II) impurity, (—) theoretical curve.

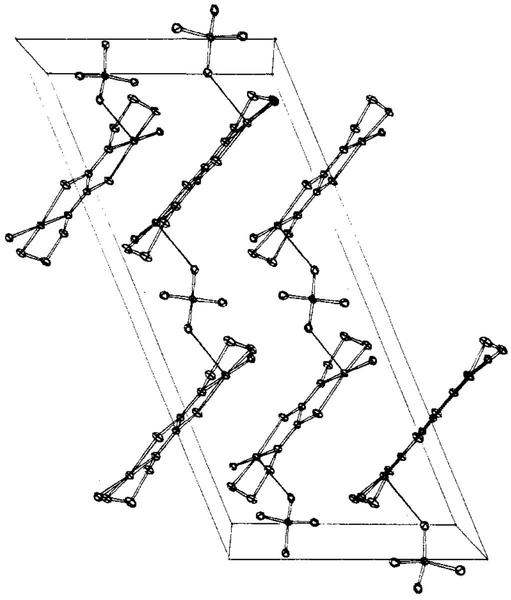


Figure 2. ORTEP drawing of packing in the unit cell, with 50% probability thermal ellipsoids.

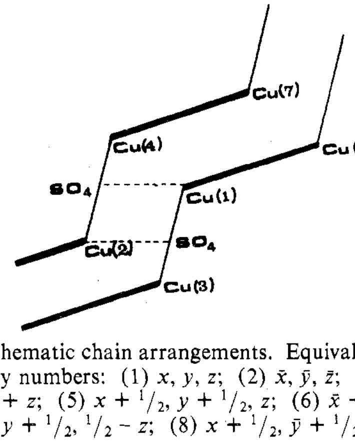


Figure 3. Schematic chain arrangements. Equivalent positions are designated by numbers: (1) x, y, z; (2) $\bar{x}, \bar{y}, \bar{z}$; (3) $\bar{x}, y, {}^1/_2 - z$; (4) $x, \bar{y}, {}^1/_2 + z$; (5) $x + {}^1/_2, y + {}^1/_2, z$; (6) $\bar{x} + {}^1/_2, \bar{y} + {}^1/_2, \bar{z}$; (7) $\bar{x} + {}^1/_2, y + {}^1/_2, {}^1/_2 - z$; (8) $x + {}^1/_2, \bar{y} + {}^1/_2, {}^1/_2 + z$.

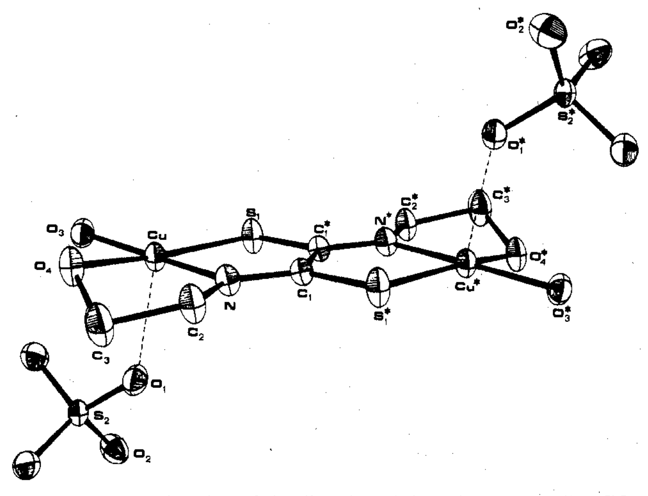


Figure 4. ORTEP drawing of the dinuclear unit and corresponding SO_4 groups, with 50% probability thermal ellipsoids. Starred atoms are in equivalent position 6: $\bar{x} + {}^1/_2, \bar{y} + {}^1/_2, z$.

Table III. Mean Planes in the Dinuclear Unit

atom	dev, Å	atom	dev, Å
Mean Plane of Cu, S_1, N, O_4, O_3, C_1, Cu*, S_1*, N*, O_4*, O_3*, C_1*			
Cu	−0.09	Cu*	+0.09
S_1	−0.00	S_1*	+0.00
N	−0.15	N*	+0.15
O_4	+0.09	O_4*	−0.09
O_3	+0.03	O_3*	−0.02
C_1	−0.04	C_1*	+0.04
C_2	−0.20	C_2*	+0.20
C_3	−0.60	C_3*	+0.60
Mean Plane of S_1, N, O_4, O_3			
S_1	+0.06	O_4	+0.06
N	−0.06	O_3	−0.05
Cu	−0.09	O_1	−2.52

(Table II) hexadentate ligand is bonded to each copper atom through one of its sulfur atoms, one of its nitrogen atoms, and one of its oxygen atoms, building around both copper atoms a set of four five-membered chelate rings. The crystallographic inversion center is located at the middle point of the C_1–C_1* bond.

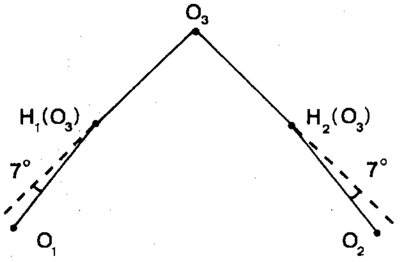
The square pyramid surrounding each copper atom is completed by a water molecule (O_3) in the basal plane and by a SO_4 oxygen atom (O_1) at the top of the pyramid. Table II gives distances between copper and its five neighbors. It can be seen that the sulfate ion is weakly bound to copper; indeed, the corresponding copper–oxygen (Cu-O_1) distance is equal to 2.442 Å, instead of 1.967 or 2.002 Å for the bonds between copper and a water molecule or an alcohol group. Such a lengthening of the copper–ligand bond in axial positions is generally observed in copper complexes.[26–32]

In our complex, the mean plane of the four atoms bound to copper in the basal plane has been calculated (Table III). The copper atom is 0.09 Å above this plane toward the axial SO_4 ligand, which supports a weak interaction between copper and oxygen O_1.

Concerning bond angles, Table II shows that the four angles in the basal plane vary from 81.5 to 96.1°: the copper coordination arrangement is a slightly distorted square. The angles between the Cu–OSO_3 bond and the four coordination bonds of the basal plane are larger than 90°, except for the water molecule (86°); this is in relation with the observed copper shift from the computed mean plane. Let us note that the surrounding of the nitrogen atom is a triangular one (Table II); this proves, if necessary, the departure of hydrogen from NH in spite of the acid solution required for crystal synthesis.

Copper–Copper Distances. Because of the very particular magnetic properties, it was interesting to look at Cu–Cu interatomic distances. The shortest distance is an interchain distance, equal to 5.18 Å. Inside the chain, there are two Cu–Cu distances: through the sulfate ligand, equal to 6.75 Å, and inside the dinuclear unit, equal to 5.61 Å (Table II); this last one is not very different from what is observed in copper complexes involving oxalate bridges[30] (5.410 Å in $[Cu_2(Et_5dien)_2C_2O_4]^{2+}$ and 5.468 Å in $[Cu_2(dien)_2C_2O_4]^{2+}$). Conversely it is twice as long as those found in others dinuclear units as in copper(II) succinate dihydrate[33] where two copper atoms are connected by four ligand molecules; herein, there is a 2.610-Å copper–copper distance, which is not very different from Cu–Cu = 2.465 Å in $Cu(CH_3COO)_2 \cdot C_6H_5N$.[34]

Hydrogen Bonds. The oxygen van der Waals radius is about 1.5 Å.[35] Thus, from oxygen–oxygen observed distances, it can be concluded that two neighboring chains are connected by two kinds of interchain hydrogen bonds. The first one is between the alcohol oxygen atom O_4 coordinated to Cu(2) and a SO_4 nonbonded oxygen atom O_2 belonging to the neighbor chain (Figure 3): O_2–O_4 = 2.62 Å. The second one links oxygen O_3 of the water molecule coordinated to Cu(1) with the SO_4 oxygen O_1 bound to Cu(4) (Figure 3): O_1–O_3 = 2.70 Å. In other respects, a hydrogen atom of the water molecule is involved in an intrachain bond with the nonbonded oxygen O_2 of the SO_4 group belonging to the same chain: O_2–O_3 = 2.68 Å. Each water molecule thus builds two hydrogen bonds, each one involving one hydrogen atom. They bind the water molecule to the O_1 atom of one SO_4 group and to one of the O_2 atoms of another SO_4 group. The bending of the two hydrogen bonds is 7°. It is much smaller than those observed in $(COOH)_2 \cdot H_2O$ (24 and 13°), or in $CuSO_4 \cdot 5H_2O$ (26°);[36] authors explain this by the fact that the tetrahedral geometry around the oxygen has to be kept. However, in the title compound, the H–O_3–H angle is equal to 90.7°, quite smaller that the usual angle in H_2O vapor, although hydrogen is very close to the straight line joining the oxygen atoms.

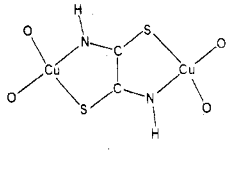


Sulfate Ion. Angles around sulfur atom S_2 vary from 108.1 to 112° (Table II) with a mean value equal to 109.5°. The smallest value corresponds to the O_1–S_2–O_2 angle: these three atoms are involved in the ring $CuO_1S_2O_2(3)O_3$ which includes a hydrogen bond. S–O distances in the sulfate group are 1.470 and 1.486 Å (Table II). The smallest one curiously corresponds to an oxygen atom which is involved in two bonds: the first one is the copper–sulfate interaction; the second one is an interchain hydrogen bond (O_1–O_3 = 2.70 Å). The largest one corresponds to the oxygen atom which is not bound to copper but which is involved in two hydrogen bonds. Sletten and Thorstensen[37] discussed the influence of hydrogen bonds on S–O distances of the SO_4 group in complexes. They found a direct connection between the variation of S–O distance and the number of hydrogen bonds. In the tetraaqua(9-methyladenine)copper(II) sulfate monohydrate, the largest S–O distance (1.500 Å) corresponds to an oxygen atom involved in three hydrogen bonds and the smallest S–O distance (1.462 Å) corresponds to an oxygen atom involved in one hydrogen bond; an intermediate value is found in the case of two hydrogen bonds. Therefore, in our complex, the longest S–O distance, i.e, the most disturbed one with respect to S–O in free sulfate, corresponds to a twice-hydrogen-bonded oxygen; this would suggest that the Cu–OSO_3 bond (2.442 Å) might be weaker than a hydrogen bond.

Discussion

As described earlier, the crystal structure is characterized by the occurrence of three types of Cu–Cu distances between 5 and 6 Å. The two shortest distances are interchain distances of 5.18 and 5.47 Å. The shortest intrachain intermetallic distance is 5.61 Å. This is the Cu–Cu separation inside the binuclear unit $\{Cu_2[S_2C_2(NCH_2CH_2OH)_2](H_2O)_2\}^{2+}$. For completeness, let us remind that the distance between the two copper atoms located on both sides of a sulfate bridge is 6.75 Å. Similarly, in copper(II) sulfate pentahydrate, sulfate bridges link together planar $[Cu(H_2O)_4]^{2+}$ units to form chains.[36,39] The Cu–Cu distance across a sulfate group is 5.65 Å, that is to say significantly shorter than in the studied compound; however, the exchange interaction is extremely weak since J is -2 cm^{-1}.[40] Therefore, the problem is to know how the very strong antiferromagnetic interaction takes place. We have seen that the sulfate groups are very weakly bonded to copper so that it is well founded to consider only the pseudo-square-planar copper surrounding as far as the symmetry of the magnetic orbitals is concerned. Thus the unpaired electron of each Cu(II) ion is described by a magnetic orbital built from the $d_{x^2-y^2}$ metallic orbital pointing toward the oyxgen, sulfur, and nitrogen atoms surrounding the metal. Between the coppers separated by 5.18 or 5.47 Å and belonging to different chains, there is no bridging ligand. Therefore, an interaction would require a direct overlap of δ nature between the magnetic orbitals of symmetry $d_{x^2-y^2}$ centered on both coppers. Such an interaction would indeed be extremely weak; it cannot explain in any way the observed magnetic behavior. On the other hand, in the binuclear unit, although the distance Cu–Cu is slightly greater, the interaction occurs through the bridging ligand dithiooxamide. The two $d_{x^2-y^2}$ metallic orbitals lie in the same molecular plane and can interact via overlap with the in-plane (σ) molecular orbitals of the ligand. Thus, it is easily understood from very simple considerations of geometric structure and of orbital symmetry that the observed exchange interaction occurs within the binuclear units. However, such arguments do not explain at all why this interaction is so important whereas the metallic centers are relatively far away from each other.

Since the pioneer work[38] on copper(II) acetate, the magnetic properties of a large number of Cu(II) binuclear complexes have been studied. In most cases the exchange interaction is of antiferromagnetic nature. More and more frequently, the crystal structures of the complexes have also been determined. To our knowledge, a situation like the one we are herein describing has never been encountered. Very strong antiferromagnetic couplings characterized by J values of -500 or -600 cm^{-1} were found, but only in complexes in which the Cu–Cu distance is of the order of 3 Å. Such is the case, for instance, in $[Cu(tmen)OH]_2Br_2$ with tmen = *N,N,N′,N′*-tetramethylethylenediamine ($J = -510$ cm^{-1} and $d_{Cu-Cu} = 3.00$ Å).[41-42] In other respects, binuclear complexes in which the Cu(II) ions, separated by more than 5 Å, are linked by extended bridges were synthesized, particularly by Hendrickson and coauthors. Relatively important exchange interactions were obtained in $[Cu_2(Et_5dien)_2(C_2O_4)][BPh_4]_2$ ($J = -74$ cm^{-1} and $d_{Cu-Cu} = 5.41$ Å)[30] and in $[Cu_2(tren)_2CN](PF_6)_3$, where tren is 2,2′,2″-triaminotriethylamine and CN is an end-to-end bridging ligand ($J = -176$ cm^{-1}; d_{Cu-Cu} was not determined).[43] We shall notice that in these two complexes, Hendrickson attributed the relatively high values of $|J|$ to the fact the Cu(II) surroundings are such that the magnetic orbitals are built from the d_{z^2} metallic orbitals pointing along the Cu–Cu axis. Such an interpretation cannot be held as far as our complex is concerned. Another complex deserving mention is the hydrogen-bonded copper(II) dimer of the diimine of 2,4-pentanedione and 2-aminoethanol ($J \simeq -100$ cm^{-1} and $d_{Cu-Cu} = 4.98$ Å).[44] Strong antiferromagnetic coupling was also observed in two oxime-bridged copper dimers with Cu–Cu distances of 3.5–3.7 Å.[45-46]



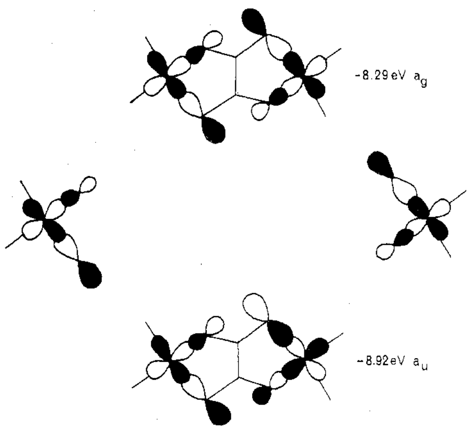


Figure 5. Schematic representation of the magnetic orbitals and of the molecular orbitals built from these magnetic orbitals.

In the last few years, several orbital models were proposed to describe the mechanism of the exchange interaction in binuclear complexes, of which the metallic centers are paramagnetic.[10-18,47] In most of these models, the exchange-interaction parameter J characterizing the singlet–triplet separation ($J < 0$ when the singlet is the ground state), whatever its sign may be, is interpreted as resulting from an antiferromagnetic component J_{AF} and a ferromagnetic component J_F. We shall focus on J_{AF} which is largely dominant in the studied complex. Two of us proposed to express J_{AF} in case of interaction between two spin doublets according to[16,47] $J_{AF} = -2S\Delta$, in which S is the overlap integral between the magnetic orbitals centered on one and the other transition ions and Δ is the energy difference between the two singly occupied molecular orbitals in the triplet state built from the magnetic orbitals. Δ must be calculated from the triplet state in which the two molecular orbitals are singly occupied. We carried out a molecular orbital energy level calculation for the hypothetical complex $\{Cu_2[S_2C_2(NH)_2](H_2O)_2\}^{2+}$ derived from the actual complex changing the CH_2CH_2OH group by an hydrogen atom bonded to the nitrogen and a water molecule coordinated to the metal. For this calculation, we used the version Forticon 8 of the extended Hückel method.[48] The parametrization is given in the Appendix. The two singly occupied molecular orbitals are schematized in Figure 5. In this figure are also schematized the magnetic orbitals defined as the singly occupied molecular orbitals for each monomeric part of the binuclear system consisting in the transition ion surrounded by its nearest neighbors.

The last occupied in-plane (σ) molecular orbitals for the ligand $[S_2C_2(NH)_2]^{2-}$ are very close in energy to the d metallic orbitals, so that the metal–ligand interaction is important and the magnetic orbitals built from the $d_{x^2-y^2}$ metallic orbitals are strongly delocalized toward the nitrogen and sulfur atoms. In other respects, the distance between the nitrogen and the sulfur atoms located on both sides of carbon is only 2.68 Å. Moreover, the 3p sulfur orbitals are very diffuse. Thus, the in-plane S–N overlaps are important. 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 Figure 5). In our calculation, the Δ energy gap between the a_g and a_u MO's turns out to be 0.63 eV. This value may be compared with the Δ value of 0.4 eV for the complex $[Cu(tmen)OH]_2Br_2$ mentioned above, derived by a similar calculation.

By calculating S as described in the Appendix, a J_{AF} value of -490 cm^{-1} is found, which compares in a satisfying manner to the experimentally observed J value.

Conclusion

In this work, we synthesized a new compound in the copper(II)–dithiooxamide system. This compound may be considered as the first perfectly defined, well-crystallized copper(II) rubeanate. So far, all obtained copper(II) rubeanates were amorphous polymers, of unknown structure.

The crystal structure of the title compound leads us to postulate for the amorphous copper(II) rubeanates the ribbon structure (type II in the introduction). We were able to avoid the formation of polymer owing to the two CH_2CH_2OH groups bonded to the nitrogen atoms of the dithiooxamide ligand; as a matter of fact, the formation of two five-membered rings by coordination of the alcoholic oxygen to copper stabilizes the binuclear cation $\{Cu_2[S_2C_2(NCH_2CH_2OH)_2](H_2O)_2\}^{2+}$.

The main feature of this new complex arises from its magnetic properties. Although the Cu–Cu distance inside the binuclear unit is 5.61 Å, the magnetic behavior reveals a very strong antiferromagnetic coupling. Qualitatively, the interpretation of this quite peculiar result can be summarized as follows: (i) the $d_{x^2-y^2}$ metallic orbitals and the last occupied in-plane MO's of the (dithiooxamide)$^{2-}$ dianion are very close in energy. Consequently, the unpaired electrons arising from the Cu(II) ions have a strong probability of presence on the nitrogen and sulfur atoms coordinated to copper. (ii) Owing to the relatively short S–N distance and to the diffuse character of 3p sulfur orbitals, the in-plane S–N overlaps are important, so that both singly occupied MO's, referring to the triplet state, symmetric and antisymmetric, respectively, with respect to the inversion are very different in energy.

The ligands $[S_2C_2(NR_2)]^{2-}$ derived from the dithiooxamide appear particularly able to propagate the interactions in polynuclear systems, in which the transition ions are relatively away from each other. The search for new compounds of this kind is in progress in our group.

Appendix

The calculation performed in this work is of the extended-Hückel type, with charge iteration on all atoms, Madelung corrections, and weighted H_{ij} formulas. The atomic orbitals are simple Slater-type orbitals for hydrogen, carbon, nitrogen, sulfur, and copper except for metallic 3d orbitals for which we choose two-component orbitals. Orbital exponents for the nonmetallic atoms are chosen using Slater's rules; 4s and 4p exponents for copper come from Burns,[49] assuming a 1+ charge on the transition ions in the complex. Exponents and relative weights for metallic 3d orbitals are taken from Richardson and et al.[50] The A_μ, B_μ, C_μ, and $g_{\mu\mu}$ parameters of the method are given in Table IV. The K parameter of the Wolfsberg–Helmholz approximation is taken equal to 1.75.

The overlap integral S between the magnetic orbitals may be approximated as previously shown[51] by

$$S = -\Delta/2(K-1)\epsilon$$

where ϵ is the one-electron energy for each magnetic orbital. In the framework of the EH method, ϵ can be approximate by the half-sum of the energies of the singly occupied a_g and a_u MO's in the triplet state, corrected of the energy shift due to the 2+ charge of the binuclear complex. This leads to $S = 0.048$.

Table IV. Parameters Used in the Iterative Extended-Hückel Calculation

		A_μ	B_μ	C_μ	$g_{\mu\mu}$
Cu	4s	0.942	8.84	7.72	6.5
	4p	1.05	6.639	3.98	4.4
	3d	3.449	6.198	10.646	10.9
S	3s		9.7	22.5	9.7
	3p		9.7	11.94	9.7
C	2s		11.9	20.4	11.9
	2p		11.9	10.6	11.9
N	2s		13.7	26.4	13.7
	2p		13.7	13.4	13.7
O	2s		15.2	33.0	15.2
	2p		15.2	16.4	15.2
H	1s		27.18	13.6	12.8

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Registry No. $[Cu_2S_2C_2(NCH_2CH_2OH)_2(H_2O)_2]SO_4$, 67408-44-0.

Supplementary Material Available: A listing of structure factor amplitudes (12 pages). Ordering information is given on any current masthead page.

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Crystal Structure of Bis(ethanol)(octaethylporphinato)iron(III) Perchlorate–Ethanol

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The crystal structure of the title compound was determined using 2095 reflections (1822 with $I > 2.3\sigma_I$ used in refinement) measured on a four-circle automated diffractometer using monochromatic Mo Kα_1 radiation. The complex crystallized in the monoclinic space group $P2_1$: $a = 11.739$ (4) Å, $b = 18.158$ (7) Å, $c = 10.062$ (3) Å, $\beta = 90.45$ (2)°. The final value for the discrepancy index was $R_1 = 0.055$. The iron atom lies in the plane of the porphine coordinated to the four nitrogen atoms (Fe–N = 2.026 (9)–2.042 (8) Å) and, axially, to the oxygen atoms of two ethanol molecules (Fe–O = 2.113 (8), 2.160 (8) Å). Both the equatorial and axial bonds are considerably longer than those of low-spin porphinatoiron(III) complexes, consistent with a mixed- or high-spin electronic ground state.

In recent years several porphinato iron complexes have been prepared which have intermediate-spin ground states.[1,2] In particular (octaethylporphinato)iron(III) perchlorate (Fe(OEP)ClO$_4$) and Fe(OEP)ClO$_4$·2EtOH have ground states with $S = {}^3/_2$ which have been shown to be single-spin states and not thermally induced spin crossovers. These two compounds were thought to be structurally quite different as there was evidence of iron–perchlorate interactions in Fe(OEP)ClO$_4$ and of iron–ethanol interactions in Fe(OEP)ClO$_4$·2EtOH. It was predicted that the former would have a coordination number of 5 and the latter 6.[1]

This study was initiated to determine the stereochemistry of the solvated species. The geometry about the iron atom was expected to resemble that of low-spin porphinatoiron(III) complexes, but with some small differences in bond lengths owing to changes in the occupancy of some of the d orbitals.

Experimental Section

Fe(OEP)ClO$_4$·2EtOH was prepared by the standard method.[1] Crystals were obtained by the slow evaporation of an ethanol solution of the complex, but if left to stand in the air for any length of time the crystals lost solvent and became unsuitable for X-ray crystallographic studies. To prevent efflorescence, a large crystal was freshly prepared and a prismatic fragment of axial dimensions 0.80 × 0.50 × 0.50 mm cleaved off, immediately covered in grease and sealed in a Lindemann tube. Photographs taken of the crystal fragment with Cu Kα radiation revealed Lauê $2/m$ symmetry and gave approximate unit cell parameters. They also confirmed that the crystal was not decomposing. Accurate cell dimensions were obtained by a least-squares analysis from the setting angles of nine reflections with $2\theta > 25°$ which were accurately centered on a Picker FACS-I four-circle automated diffractometer employing monochromatic Mo Kα_1 radiation. Crystal data are given in Table I. The intensities of 2095 unique reflections with $2\theta < 40°$ were measured and of these 1822 with $I > 2.3\sigma_I$ (σ_I is the standard deviation in the intensity derived from counter statistics) were regarded as observed and used in structure solution and refinement. The average intensity of reflections decreased rapidly with increasing 2θ so data were collected in two shells (see Table II). Two standard reflections were measured after every 75 data points and the data scaled accordingly. No absorption correction was applied.

Table I. Crystal Data

$C_{42}H_{62}ClFeN_4O_7$
space group $P2_1$
$a = 11.739(4)$ Å
$b = 18.158(7)$ Å
$c = 10.062(3)$ Å
$\beta = 90.45(2)°$
$U = 2144.7$ Å^3
$Z = 2$

fw 826.29
$\mu = 4.79$ cm^{-1}
$\rho_o{}^a = 1.27$ g cm^{-1}
$\rho_c = 1.279$ g cm^{-1}
final $R_1{}^b = 0.055$
final $R_2{}^c = 0.061$
final extinction correction 2.2 (4) × 10^{-5}

[a] Flotation in C_6H_6/CCl_4. [b] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma F_o{}^2)^{1/2}$.

Table II. Data Collection

radiation	monochromatic Mo Kα_1 (λ 0.709 26 Å)
takeoff angle	5°
θ-2θ scan	2° min^{-1}
scan width with dispersion cor	$2\theta \leqslant 30°$, $(1.2 + 0.692 \tan\theta)°$; $30° < 2\theta \leqslant 40°$, $(1.1 + 0.692 \tan\theta)°$
stationary-crystal, stationary-counter bgd counts	$2\theta \leqslant 30°$, 4 s at each scan limit; $30° < 2\theta \leqslant 40°$, 10 s at each scan limit

Solution and Refinement of the Structure

The structure was solved by conventional heavy-atom procedures. Least-squares refinement of the nonhydrogen atoms with individual isotropic temperature factors yielded $R_1 = 0.101$. The coordinates of the hydrogen atoms attached to nonmethyl carbons were determined geometrically (sp^2 or sp^3 coordination at the carbon, $r_{C-H} = 0.95$ Å). The H(n1) atoms were assigned the average temperature factor of the C(n1) atoms and the H(n3A) and H(n4A) the average of the eight C(n3A) and C(n4A). These hydrogen atom parameters were not refined, but the scattering contribution was included in all further calculations. In addition, the iron atom and the atoms of the perchlorate were assigned anisotropic temperature factors, the resultant R_1 being 0.072. A difference map using data $2\theta < 32°$ revealed H(5), H(7), and many of the methyl hydrogen atoms. The remaining hydrogens were positioned geometrically from these. Examination

0020-1669/78/1317-3040$01.00/0