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Copper(II) and Nickel(II) Trinuclear Species with Dithiooxamide Derivative Ligands: Structural, Magnetic, Spectroscopic, and Electrochemical Properties

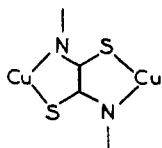
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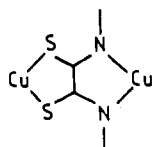
The new binucleating ligands $C_2S_2(NH(CH_2)_nSCH_2CH_2OH)_2$ ($n = 3$ (1) and 2 (3)) derived from dithiooxamide were synthesized as well as the related copper(II) and nickel(II) trinuclear species $[M_3\{C_2S_2(N(CH_2)_nSCH_2CH_2OH)_2\}_2]X_2$ ($M = Cu$, $n = 3$, $X = NO_3$ (5) and ClO_4 (6); $M = Cu$, $n = 2$, $X = NO_3$ (7); $M = Ni$, $X = NO_3$, $n = 3$ (8) and 2 (9)). The crystal structure of 6 was solved. 6 crystallizes in the orthorhombic system, space group $Pbca$, with $a = 15.638$ (6) Å, $b = 18.254$ (9) Å, $c = 29.437$ (7) Å, and $Z = 8$. The structure consists of trinuclear cations and noncoordinated perchlorate anions. The central copper atom is in a square-planar CuS_4 chromophore and the terminal copper atoms in $CuS_2N_2O_2$ chromophores with 4 + 2 coordination. In the $Cu_3C_2S_2N_2Cu$ bridging network, the dithiooxamide group is in a syn conformation. The magnetic and EPR properties of 5 were investigated and revealed a strong antiferromagnetic interaction between nearest-neighbor copper(II) ions with a doublet ground state stabilized by 483 and 725 cm^{-1} with regard to the doublet and quartet excited states, respectively. The magnetic properties of 8 were also investigated and showed that the central nickel(II) ion is diamagnetic and the terminal ones paramagnetic with essentially non-interacting $S = 1$ states. The electrochemical properties of 5 and 7 gave evidence of a one-step two-electron oxidation leading to a $Cu(III)Cu(II)Cu(III)$ mixed-valence species. This process is partially reversible, but the oxidized species react with the solvent.

Introduction

In the last years, we have described several copper(II) binuclear complexes with dithiooxamide derivatives.² All these complexes were characterized from a structural viewpoint by the planar bridging network



with the dithiooxamido group in an anti position and from a physical viewpoint by a very strong intramolecular antiferromagnetic interaction in spite of a copper-copper separation of the order of 5.6 Å. In this paper, we report on the first copper(II) polynuclear complex with the same kind of ligand, in which the bridging network is



with the dithiooxamide group in a syn conformation. This occurs in trinuclear species synthesized from the novel ligands $C_2S_2[NH(CH_2)_nSCH_2CH_2OH]_2$, with $n = 2$ or 3, in which the central copper atom is in a planar environment of four sulfur atoms. We describe the synthesis of these compounds, the crystal structure of one of them, namely $[Cu_3\{C_2S_2(NCH_2CH_2CH_2SCH_2CH_2OH)_2\}_2](ClO_4)_2$ and their magnetic, spectroscopic, and electrochemical properties. With the same ligands, we also prepared the related nickel(II) complexes where the central nickel(II) ion is diamagnetic and the terminal ones paramagnetic.

Whereas a large number of binuclear complexes with $C_2X_2Y_2$ -bis bidentate bridging ligands have been studied so far,⁶ only one paper, to our knowledge, deals with trinuclear species with the

same kind of bridges,⁷ and more generally the physics of the trinuclear systems has been by far less investigated than that of the binuclear systems. This paper has also as a goal to contribute to a better understanding of the coupled trinuclear species.

Experimental Section

Syntheses. $C_2S_2(NHCH_2CH_2CH_2SCH_2CH_2OH)_2$ (1) was prepared in two steps. The first step consisted of preparing $NH_2CH_2CH_2CH_2SCH_2CH_2OH$ (2) by mixing 20 g of chloro-3-propylamine hydrochloride with 12 g of mercaptoethanol in 200 mL of ethanol. Then 17.5 g of KOH was added, and the mixture was heated at reflux for 5 h. KCl precipitated and was eliminated by filtration. The solvent was removed and 2 was distilled under vacuum (bp = 140 °C (0.1 mmHg)). 1 was then prepared by adding 2 g of 2 to a solution of 1 g of dithiooxamide in 20 mL of methanol. The mixture was heated at 40 °C for 6 h, and then the methanol was removed and replaced by ether. The solution was washed with dilute HCl. Ether was removed, and 1 was obtained as an orange oil.

$C_2S_2(NHCH_2CH_2SCH_2CH_2OH)_2$ (3) was prepared in the same manner as 1 by replacing chloro-3-propylamine hydrochloride by chloro-2-ethylamine hydrochloride in the first step, leading to $NH_2CH_2CH_2SCH_2CH_2OH$ (4). Anal. Calcd for $C_4H_{11}NOS$ (4): C, 36.58; H, 6.10; N, 8.56. Found: C, 36.56; H, 6.18; N, 8.45. 3 precipitated as orange crystals from a cooled methanolic solution.

$[Cu_3\{C_2S_2(NCH_2CH_2CH_2SCH_2CH_2OH)_2\}_2]X_2$ ($X = NO_3^-$ (5); $X =$

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- (19) The expression of J in (7) only differs from that obtained for a copper(II) binuclear complex by the term in kS^2 . Indeed, in this latter case, J is found as $4tS + 2j - 2kS^2$. More generally, this term in kS^2 depends on the topology of the system. For instance, for four electrons at the vertices of a regular tetrahedron or eight electrons at the vertices of a cube, J is found as $4tS + 2j - 10kS^2$.
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ClO_4^- (6). A 500-mg sample of copper(II) nitrate or perchlorate was dissolved in 100 mL of methanol. **1** was added dropwise in stoichiometric proportion. **5** or **6** was obtained as small single crystals by slow evaporation of the green solution. Anal. Calcd for $\text{C}_{24}\text{H}_{44}\text{N}_4\text{O}_{12}\text{S}_8\text{Cl}_2\text{Cu}_3$ (**6**): C, 26.23; H, 4.00; N, 5.10; O, 17.49; S, 23.32; Cl, 6.46. Found: C, 26.20; H, 3.96; N, 5.18; O, 17.35; S, 23.04; Cl, 6.67. *Warning!* The use of ClO_4^- was necessary to get good structural data. Nevertheless we prepared **6** only in small amounts due to its potential explosive nature.

$[\text{Cu}_3[\text{C}_2\text{S}_2(\text{NCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{OH})_2]_2](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ (**7**) was prepared in the same manner as **5** by using **3** instead of **1**. Anal. Calcd for $\text{C}_{20}\text{H}_{38}\text{N}_6\text{O}_{11}\text{S}_8\text{Cu}_3$ (**7**): C, 24.83; H, 3.72; N, 8.69; O, 16.55; S, 26.48. Found: C, 24.62; H, 3.77; N, 8.57; O, 16.76; S, 26.55.

$[\text{Ni}_3[\text{C}_2\text{S}_2(\text{NCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{OH})_2]_2](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ (**8**) was prepared in the same manner as **5** by replacing the copper(II) salt by the nickel(II) salt. **8** was obtained as red crystals. Anal. Calcd for $\text{C}_{24}\text{H}_{46}\text{N}_6\text{O}_{11}\text{S}_8\text{Ni}_3$ (**8**): C, 28.06; H, 4.48; N, 8.18; S, 24.95. Found: C, 28.36; H, 4.47; N, 8.35; S, 24.87.

$[\text{Ni}_3[\text{C}_2\text{S}_2(\text{NCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{OH})_2]_2](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ (**9**) was prepared in the same manner as **7** by using nickel(II) nitrate instead of copper(II) nitrate. **9** was obtained as red crystals. Anal. Calcd for $\text{C}_{20}\text{H}_{38}\text{N}_6\text{O}_{11}\text{S}_8\text{Ni}_3$ (**9**): C, 24.74; H, 3.92; N, 8.65; S, 26.38. Found: C, 24.73; H, 3.98; N, 8.58; S, 24.77.

X-ray Analysis for Compound 6. Crystal Data. $\text{C}_{24}\text{H}_{44}\text{O}_4\text{Cu}_3\text{S}_8\text{N}_2$ (ClO_4)₂, $M_r = 1098.69$, orthorhombic, space group $Pbca$ with cell constants $a = 15.638$ (6) Å, $b = 18.254$ (9) Å, $c = 29.437$ (7) Å, $V = 8402.7$ Å³, and $D_{\text{calcd}} = 1.74$ g cm⁻³ for $Z = 8$ and $F_{000} = 4408$, Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å), $\mu(\text{Mo } K\alpha) = 21.4$ cm⁻¹.

Intensity Measurements. A dark green parallelepipedic crystal ($0.5 \times 0.4 \times 0.58$ mm³) was mounted in the air on an Enraf Nonius CAD4 diffractometer. The cell dimensions were obtained from the least-square fit of 25 automatically centered reflections in the range $6 < \theta < 17^\circ$. Data collection was performed at room temperature with graphite-monochromated Mo $K\alpha$ radiation in the θ - 2θ scan mode up to $2\theta_{\text{max}} = 40^\circ$. A variable scan speed (from 1 to 16°/min) and a variable scan range ($0.8 + 0.345(\tan\theta)$) were used with a 25% extension at each end of the scan range for background determination. Among 3923 independent collected reflections, 3033 with $I > 3\sigma(I)$ were considered as observed and kept for further calculations. Two standard reflections were monitored every 100 reflections and remained constant during data collection. Lorentz and polarization corrections were applied while absorption corrections were not considered necessary (transmission factors from 1.0 to 1.02).

Structure Solution and Refinement. The structure was solved by using direct method (MULTAN). Full matrix least squares and successive Fourier syntheses led to the atomic coordinates of all non-hydrogen atoms. The second carbon of two of the four lateral chains appeared disordered; they were refined with a 0.5 occupancy factor. At this stage the R factor was 0.13, and the oxygen atoms of the ClO_4 groups were not located since disorder appeared. With anisotropic thermal parameters on all atoms of the trinuclear cation, R dropped to 0.092. It can be then possible to find seven weak peaks around each chlorine atom. This is attributed to a rotation of the oxygen atoms of the perchlorate group around a O-Cl bond. The oxygen atoms were kept isotropic with three oxygen atoms having a 0.5 occupancy factor. In the last least-square cycles, hydrogen atoms were introduced in theoretical calculated positions. The ratio last shift/standard deviation was less than 0.2. The real and imaginary part of the anomalous dispersion for copper, chlorine, and sulfur atoms were introduced. (scattering factors were taken from ref 25.) The final R values were $R = 0.059$ and $R_w = 0.062$ with $R = \sum F_o - F_c / \sum F_o$ and $R_w = (\sum w(F_o - F_c)^2 / \sum w f_o^2)^{1/2}$ with $w = 1.0$. The atomic coordinates are listed in Table I. All calculations were performed on a DEC-VAX 725 computer using the program CRYSTALS.²⁴

Magnetic Measurements. These were performed with a Faraday type magnetometer equipped with a helium continuous-flow cryostat. Independence of the magnetic susceptibility vs. the magnetic field was checked at room temperature. $\text{HgCo}(\text{SCN})_4$ was used as a susceptibility standard. Diamagnetic corrections were estimated at -460×10^{-6} for **5** and **8**.

EPR. The spectrum of **5** was recorded at X-band frequency with a Bruker ER 200 spectrometer equipped with a helium continuous-flow cryostat, a Hall probe, and a Hewlett-Packard frequency meter.

UV-Visible Spectroscopy. The spectra were recorded with a Cary 2300 spectrometer at room temperature.

Electrochemistry. The electrochemical measurements were carried out with DACFAMOV equipment in a three-electrode cell under argon

Table I. Atomic Coordinates and Thermal Isotropic Parameters with Esd's in Parentheses for Compound **6**

atom	x/a	y/b	z/c	U_{eq} , Å ²
Cu(1)	0.15745 (9)	0.30861 (8)	0.12709 (5)	0.0449
Cu(2)	-0.1275 (1)	0.40261 (8)	0.23367 (6)	0.0485
N(3)	-0.0367 (7)	0.4450 (5)	0.1952 (4)	0.0502
C(31)	-0.025 (1)	0.5230 (7)	0.1855 (5)	0.0605
C(32)	-0.020 (1)	0.5671 (9)	0.2266 (8)	0.0911
C(33)	-0.103 (1)	0.5855 (9)	0.2502 (8)	0.1072
S(8)	-0.1697 (4)	0.5142 (3)	0.2703 (2)	0.1054
C(34)	-0.137 (2)	0.500 (1)	0.325 (1)	0.1385
C(35)	-0.063 (2)	0.471 (2)	0.3341 (9)	0.1318
O(3)	-0.045 (1)	0.417 (1)	0.3024 (6)	0.1595
C(3)	0.0117 (7)	0.3988 (6)	0.1757 (4)	0.0366
C(4)	-0.0089 (7)	0.3188 (6)	0.1866 (4)	0.0343
N(4)	-0.0753 (6)	0.3098 (5)	0.2107 (3)	0.0410
C(41)	-0.1013 (8)	0.2336 (7)	0.2214 (5)	0.0560
C(421)	-0.201 (2)	0.227 (2)	0.220 (1)	0.0677
C(422)	-0.161 (2)	0.225 (1)	0.2646 (9)	0.0424
C(43)	-0.244 (1)	0.2539 (8)	0.2574 (6)	0.0700
S(7)	-0.2440 (2)	0.3506 (2)	0.2707 (1)	0.0605
C(44)	-0.3282 (9)	0.3868 (9)	0.2356 (6)	0.0763
C(45)	-0.311 (1)	0.391 (1)	0.1865 (8)	0.1135
O(4)	-0.2328 (7)	0.4287 (7)	0.1781 (4)	0.0982
S(4)	0.0537 (2)	0.2505 (2)	0.1663 (1)	0.0465
S(3)	0.0941 (2)	0.4181 (2)	0.1397 (1)	0.0501
Cu(3)	0.4242 (1)	0.20768 (8)	0.01191 (5)	0.0503
N(1)	0.3436 (6)	0.1687 (5)	0.0564 (3)	0.0483
C(1)	0.3002 (7)	0.2157 (6)	0.0774 (4)	0.0365
S(1)	0.2209 (2)	0.1984 (2)	0.1160 (1)	0.0501
C(2)	0.3212 (7)	0.2937 (6)	0.0656 (4)	0.0419
N(2)	0.3868 (7)	0.3014 (5)	0.0399 (4)	0.0481
C(21)	0.413 (1)	0.3758 (7)	0.0260 (6)	0.0678
C(22)	0.506 (1)	0.3845 (8)	0.0143 (7)	0.0750
C(23)	0.533 (1)	0.349 (1)	-0.0292 (7)	0.0871
S(5)	0.5392 (2)	0.2507 (2)	-0.0300 (1)	0.0630
C(24)	0.6229 (9)	0.234 (1)	0.0101 (6)	0.0815
C(25)	0.623 (1)	0.161 (1)	0.0283 (7)	0.0987
O(2)	0.5437 (7)	0.1419 (6)	0.0497 (4)	0.0823
S(2)	0.2597 (2)	0.3645 (2)	0.0853 (1)	0.0542
C(11)	0.331 (1)	0.0902 (8)	0.0673 (6)	0.0647
C(121)	0.372 (3)	0.032 (1)	0.038 (1)	0.0623
C(122)	0.302 (2)	0.050 (2)	0.029 (2)	0.0794
C(13)	0.364 (1)	0.037 (1)	-0.0104 (7)	0.1095
S(6)	0.4260 (3)	0.1041 (2)	-0.0356 (1)	0.0760
C(14)	0.372 (1)	0.133 (1)	-0.0840 (7)	0.1193
C(15)	0.304 (1)	0.183 (2)	-0.0793 (7)	0.1132
O(1)	0.3197 (7)	0.2431 (7)	-0.0514 (4)	0.0926
Cl(101)	0.0329 (4)	0.2533 (3)	0.8494 (2)	0.1122
Cl(202)	0.3217 (6)	0.0745 (5)	0.3829 (4)	0.1558
O(101)	0.035 (2)	0.236 (1)	0.8035 (8)	0.099 (9)
O(102)	-0.010 (1)	0.3148 (9)	0.8631 (5)	0.168 (6)
O(103)	-0.049 (2)	0.219 (2)	0.842 (1)	0.22 (2)
O(104)	0.118 (2)	0.263 (2)	0.874 (1)	0.18 (1)
O(105)	0.007 (2)	0.190 (1)	0.870 (1)	0.121 (9)
O(106)	0.068 (1)	0.260 (1)	0.8074 (7)	0.072 (7)
O(107)	0.065 (3)	0.212 (2)	0.883 (1)	0.17 (1)
O(201)	0.350 (3)	0.139 (2)	0.400 (2)	0.20 (2)
O(202)	0.406 (3)	0.052 (4)	0.379 (2)	0.34 (3)
O(203)	0.242 (2)	0.048 (2)	0.3833 (9)	0.29 (1)
O(204)	0.349 (2)	0.066 (1)	0.3373 (8)	0.118 (8)
O(205)	0.305 (3)	0.076 (3)	0.430 (1)	0.24 (2)
O(206)	0.306 (4)	0.152 (2)	0.378 (2)	0.29 (3)
O(207)	0.346 (3)	0.009 (2)	0.411 (2)	0.23 (2)

atmosphere. Reference and auxiliary electrodes were separated from the solution by a tube with a glass frit in its extremity containing the electrolytic solvent and the supporting electrolyte. The working electrode was a platinum electrode, the reference electrode was an aqueous standard calomel electrode, and the auxiliary electrode again was a platinum electrode.

Crystal Structure of $[\text{Cu}_3[\text{C}_2\text{S}_2(\text{NCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{OH})_2]_2](\text{ClO}_4)_2$ (**6**)

The structure of **6** consists of trinuclear cations and uncoordinated perchlorate anions. The perspective view of the cation with the labeling of the atoms is shown in Figure 1. Bond lengths and bond angles are given in Tables II and III.

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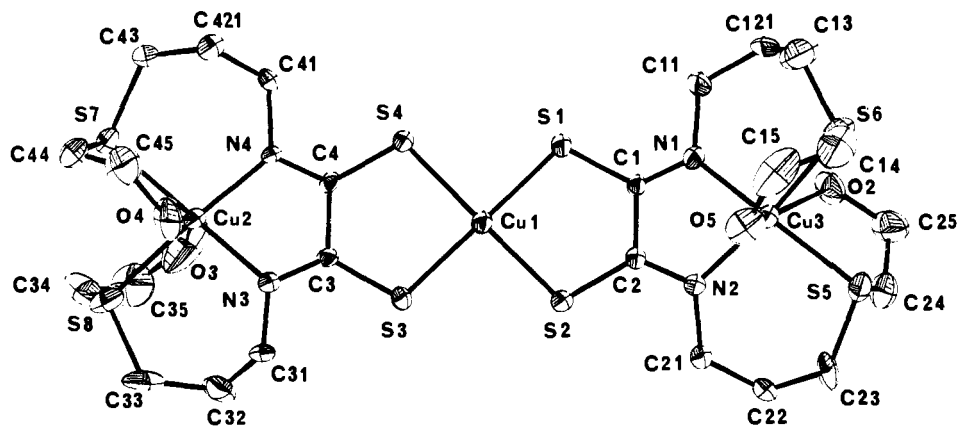


Figure 1. Perspective view of the trinuclear cation $[Cu_3[C_2S_2(NCH_2CH_2SCH_2CH_2OH)_2]_2]^+$ in 6. For the sake of clarity, disordered lateral chains are drawn as non disordered.

Table II. Interatomic Distances (Å) with Esd's in Parentheses for Compound 6

Cu(1)-S(4)	2.256 (3)	Cu(1)-S(3)	2.261 (3)
Cu(1)-S(1)	2.267 (3)	Cu(1)-S(2)	2.260 (4)
Cu(2)-N(3)	1.98 (1)	Cu(2)-S(8)	2.396 (5)
Cu(2)-O(3)	2.42 (2)	Cu(2)-N(4)	1.999 (9)
Cu(2)-S(7)	2.326 (4)	Cu(2)-O(4)	2.37 (1)
N(3)-C(31)	1.46 (2)	N(3)-C(3)	1.27 (1)
C(31)-C(32)	1.46 (2)	C(32)-C(33)	1.52 (3)
C(33)-S(8)	1.77 (2)	S(8)-C(34)	1.71 (3)
C(34)-C(35)	1.31 (3)	C(35)-O(3)	1.38 (3)
C(3)-C(4)	1.53 (2)	C(3)-S(3)	1.70 (1)
C(4)-N(4)	1.27 (1)	C(4)-S(4)	1.69 (1)
N(4)-C(41)	1.48 (1)	C(41)-C(421)	1.56 (3)
C(41)-C(422)	1.59 (3)	C(421)-C(43)	1.40 (3)
C(422)-C(43)	1.42 (3)	C(43)-S(7)	1.81 (1)
S(7)-C(44)	1.80 (2)	C(44)-C(45)	1.47 (2)
C(45)-O(4)	1.43 (2)	Cu(3)-N(1)	1.953 (9)
Cu(3)-N(2)	1.987 (9)	Cu(3)-S(5)	2.318 (4)
Cu(3)-O(2)	2.48 (1)	Cu(3)-S(6)	2.351 (4)
Cu(3)-O(1)	2.56 (1)	N(1)-C(1)	1.26 (1)
N(1)-C(11)	1.48 (2)	C(1)-S(1)	1.71 (1)
C(1)-C(2)	1.50 (2)	C(2)-N(2)	1.28 (1)
C(2)-S(2)	1.71 (1)	N(2)-C(21)	1.47 (2)
C(21)-C(22)	1.50 (2)	C(22)-C(23)	1.50 (2)
C(23)-S(5)	1.79 (2)	S(5)-C(24)	1.79 (2)
C(24)-C(25)	1.43 (2)	C(25)-O(2)	1.43 (2)
C(11)-C(121)	1.51 (3)	C(11)-C(122)	1.42 (4)
C(121)-C(13)	1.43 (4)	C(122)-C(13)	1.53 (4)
C(13)-S(6)	1.72 (2)	S(6)-C(14)	1.74 (2)
C(14)-C(15)	1.41 (3)	C(15)-O(1)	1.40 (2)

Inside the trinuclear cation, the metal centers are aligned. The central copper atom Cu(1) is located in an almost perfect square-planar CuS_4 environment (plane I) with Cu-S bond lengths of 2.26 Å. Each terminal copper atom Cu(2) or Cu(3) is in a 4 + 2 environment with a strongly distorted basal plane made up of two sulfur and two nitrogen atoms and two oxygen atoms of the alcoholic groups in apical position. The average value of the Cu-N bond lengths is 1.98 Å and that of the Cu-S bond lengths is 2.35 Å, i.e. significantly larger than the Cu-S bond lengths around the central copper atom. The Cu-O apical bond lengths are in the range 2.37–2.56 Å. Each Cu-O bond is bent toward the Cu-S bond involving a sulfur atom belonging to the same chain $S-CH_2-CH_2OH$. For instance, S(7)-Cu(2)-O(4) and S(8)-Cu(2)-O(3) are equal to 82.1 (3) and 71.1 (5)°, respectively. It follows that the angles O(3)-Cu(2)-O(4) and O(1)-Cu(3)-O(2) deviate significantly from linearity with an average value of 158°.

Two nearest-neighbor copper atoms Cu(1) and Cu(2) or Cu(1) and Cu(3) inside the trinuclear entity are bridged by a planar $S_2C_2N_2$ group with a syn conformation. Cu(1) and Cu(2) lie at -0.15 and -0.07 Å, respectively, with regard to the S(3)S(4)C(3)C(4)N(3)N(4) mean plane (plane II), and Cu(1) and Cu(3) lie at 0.20 and 0.27 Å, respectively, with regard to the S(1)S(2)C(1)C(2)N(1)N(2) mean plane (plane III). Plane I makes angles of 5.7 and 7.6°, respectively, with planes II and III. Planes

Table III. Bond Angles (deg) with Esd's in Parentheses

S(3)-Cu(1)-S(4)	91.0 (1)	S(1)-Cu(1)-S(4)	88.3 (1)
S(1)-Cu(1)-S(3)	178.8 (1)	S(2)-Cu(1)-S(4)	177.7 (2)
S(2)-Cu(1)-S(3)	90.0 (1)	S(2)-Cu(1)-S(1)	90.7 (1)
S(8)-Cu(2)-N(3)	97.0 (3)	O(3)-Cu(2)-N(3)	93.0 (5)
O(3)-Cu(2)-S(8)	71.1 (5)	N(4)-Cu(2)-N(3)	81.1 (4)
N(4)-Cu(2)-S(8)	170.0 (3)	N(4)-Cu(2)-O(3)	99.1 (6)
S(7)-Cu(2)-N(3)	172.9 (3)	S(7)-Cu(2)-S(8)	85.4 (2)
S(7)-Cu(2)-O(3)	94.1 (4)	S(7)-Cu(2)-N(4)	97.6 (3)
O(4)-Cu(2)-N(3)	91.4 (4)	O(4)-Cu(2)-S(8)	87.1 (4)
O(4)-Cu(2)-O(3)	158.1 (6)	O(4)-Cu(2)-N(4)	102.7 (4)
O(4)-Cu(2)-S(7)	82.1 (3)	C(31)-N(3)-Cu(2)	125.5 (8)
O(3)-N(3)-Cu(2)	115.3 (8)	C(3)-N(3)-C(31)	119.0 (10)
C(32)-C(31)-N(3)	112.5 (13)	C(33)-C(32)-C(31)	116.8 (16)
S(8)-C(33)-C(32)	119.7 (12)	C(33)-S(8)-Cu(2)	108.3 (7)
C(34)-S(8)-Cu(2)	102.3 (9)	C(34)-S(8)-C(33)	104.9 (11)
C(35)-C(34)-S(8)	120.9 (25)	O(3)-C(35)-C(34)	109.2 (24)
C(35)-O(3)-Cu(2)	122.4 (15)	C(4)-C(3)-N(3)	114.4 (10)
S(3)-C(3)-N(3)	126.5 (9)	S(3)-C(3)-C(4)	119.1 (8)
N(4)-C(4)-C(3)	114.4 (10)	S(4)-C(4)-C(3)	120.5 (8)
S(4)-C(4)-N(4)	125.1 (9)	C(4)-N(4)-Cu(2)	114.5 (8)
C(41)-N(4)-Cu(2)	127.7 (8)	C(41)-N(4)-C(4)	117.6 (10)
C(421)-C(41)-N(4)	109.7 (14)	C(422)-C(41)-N(4)	114.9 (13)
C(43)-C(421)-C(41)	115.6 (23)	C(43)-C(422)-C(41)	112.7 (20)
S(7)-C(43)-C(421)	120.9 (15)	S(7)-C(43)-C(422)	108.7 (13)
C(43)-S(7)-Cu(2)	107.5 (5)	C(44)-S(7)-Cu(2)	98.8 (5)
C(44)-S(7)-C(43)	103.4 (8)	C(45)-C(44)-S(7)	117.0 (12)
O(4)-C(45)-C(44)	110.6 (17)	C(45)-C(44)-S(7)	112.5 (10)
C(4)-S(4)-Cu(1)	10.4 (4)	C(3)-S(3)-Cu(1)	104.5 (4)
N(2)-Cu(3)-N(1)	81.2 (4)	S(5)-Cu(3)-N(1)	168.9 (3)
S(5)-Cu(3)-N(2)	99.0 (3)	O(2)-Cu(3)-N(1)	90.5 (4)
O(2)-Cu(3)-N(2)	116.9 (4)	O(2)-Cu(3)-S(5)	79.5 (3)
S(6)-Cu(3)-N(1)	96.5 (3)	S(6)-Cu(3)-N(2)	160.4 (3)
S(6)-Cu(3)-S(5)	87.0 (2)	S(6)-Cu(3)-O(2)	82.4 (3)
O(1)-Cu(3)-N(1)	99.7 (4)	O(1)-Cu(3)-N(2)	84.0 (4)
O(1)-Cu(3)-S(5)	91.3 (3)	O(1)-Cu(3)-O(2)	158.0 (4)
O(1)-Cu(3)-S(6)	77.2 (3)	C(1)-N(1)-Cu(3)	115.4 (8)
C(11)-N(1)-Cu(3)	125.9 (8)	C(11)-N(1)-C(1)	118.6 (10)
S(1)-C(1)-N(1)	126.3 (9)	C(2)-C(1)-N(1)	114.6 (10)
C(2)-C(1)-S(1)	119.1 (9)	C(1)-S(1)-Cu(1)	104.4 (4)
N(2)-C(2)-C(1)	114.6 (10)	S(2)-C(2)-C(1)	121.0 (9)
S(2)-C(2)-N(2)	124.5 (9)	C(2)-N(2)-Cu(3)	112.6 (8)
C(21)-N(2)-Cu(3)	126.7 (8)	C(21)-N(2)-C(2)	119.1 (10)
C(22)-C(21)-N(2)	115.4 (12)	C(23)-C(22)-C(21)	115.5 (16)
S(5)-C(23)-C(22)	117.3 (12)	C(23)-S(5)-Cu(3)	107.0 (6)
C(24)-S(5)-Cu(3)	99.1 (5)	C(24)-S(5)-C(23)	101.7 (9)
C(25)-C(24)-S(5)	114.1 (13)	O(2)-C(25)-C(24)	113.1 (14)
C(25)-O(2)-Cu(3)	109.6 (9)	C(2)-S(2)-Cu(1)	104.0 (4)
C(121)-C(11)-N(1)	119.5 (15)	C(122)-C(11)-N(1)	111.6 (19)
C(13)-C(121)-C(11)	119.5 (26)	C(13)-C(122)-C(11)	118.7 (26)
S(6)-C(13)-C(121)	115.3 (19)	S(6)-C(13)-C(122)	125.0 (17)
C(13)-S(6)-Cu(3)	107.9 (6)	C(14)-S(6)-Cu(3)	103.7 (8)
C(14)-S(6)-C(13)	107.5 (10)	C(15)-C(14)-S(6)	118.9 (15)
O(1)-C(15)-C(14)	115.5 (16)	C(15)-O(1)-Cu(3)	109.9 (11)

II and III make an angle of 2.6°, which means that the three planes are in a very flat chair conformation. The C-C, C-N, and C-S distances inside the bridging networks are quite similar to

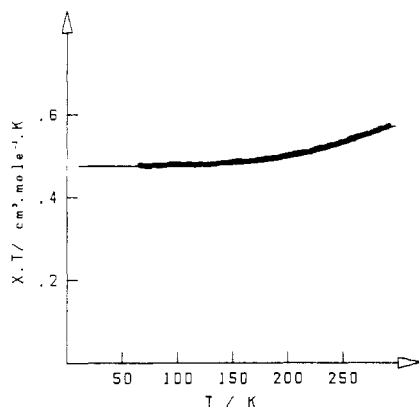


Figure 2. Experimental (□) and calculated (—) temperature dependence of $\chi_M T$ for $[\text{Cu}_3\{\text{C}_2\text{S}_2(\text{NCH}_2\text{CH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{OH})_2\}_2](\text{NO}_3)_2$ (**5**).

what was found in the other dithioamide derivatives where the dithioamide group is in an anti conformation. The Cu...Cu distances inside the trinuclear entity are Cu(1)–Cu(2) = 5.714 (2) Å, Cu(1)–Cu(3) = 5.683 (2) Å, and Cu(2)–Cu(3) = 11.389 (2) Å. The shortest Cu...Cu separations are between Cu(1) atoms of a trinuclear cation and Cu(2) and Cu(3) atoms belonging to another trinuclear cation. These distances are 5.572 (2) and 5.490 (2) Å respectively.

We have not been able to grow single crystals of **8** (or **9**) suitable for X-ray work. However, the IR spectrum of this compound is almost identical with that of **5**. This very strongly suggests that the structure of the $[\text{Ni}_3\{\text{C}_2\text{S}_2(\text{CH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{OH})_2\}_2]^{2+}$ cation is very similar to that shown in Figure 1, with a NiS_4 square-planar central chromophore and two $\text{NiS}_2\text{N}_2\text{O}_2$ octahedral terminal chromophores.

Magnetic Properties

Cu(II) Trinuclear Species. The magnetic investigation was carried out on complex **5**. The results are represented in Figure 2 in the form of the temperature dependence of the product $\chi_M T$ of the molar magnetic susceptibility by the temperature. When the complex is cooling down from room temperature, $\chi_M T$ slightly decreases, then reaches a plateau below 220 K with $\chi_M T = 0.48 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$. This plateau corresponds to the Curie law expected for a doublet ground state very separated in energy from the excited states.

The spin Hamiltonian appropriate to describe the magnetic properties of **5** is^{7,8-11}

$$\mathcal{H} = -J(\hat{S}_1 \cdot \hat{S}_2 + \hat{S}_3 \cdot \hat{S}_2) - j\hat{S}_1 \cdot \hat{S}_3 + \sum_{i=1}^3 \beta g_i \hat{S}_i \cdot \vec{H} \quad (1)$$

where J and j denote the exchange parameters between nearest-neighbor and terminal copper(II) ions, respectively, and g_i denotes the local g factors.²⁶ The low-lying states are a spin doublet taken as energy origin, another spin doublet is located at $-J + j$ and a spin quartet at $-3J/2$, and the expression of the magnetic susceptibility is

$$\chi_M = \left(\frac{N\beta^2}{4kT} \right) \frac{g_a^2 + g_b^2 \exp\left(\frac{J-j}{kT}\right) + 10g_c^2 \exp\left(\frac{3J}{2kT}\right)}{1 + \exp\left(\frac{J-j}{kT}\right) + 2 \exp\left(\frac{3J}{2kT}\right)} \quad (2)$$

with^{10,12}

$$g_a = \frac{1}{3}(4g_1 - g_2) \quad g_b = g_2 \quad g_c = \frac{1}{3}(2g_1 + g_2) \quad (3)$$

The only effect of j is to modify the position of the excited doublet

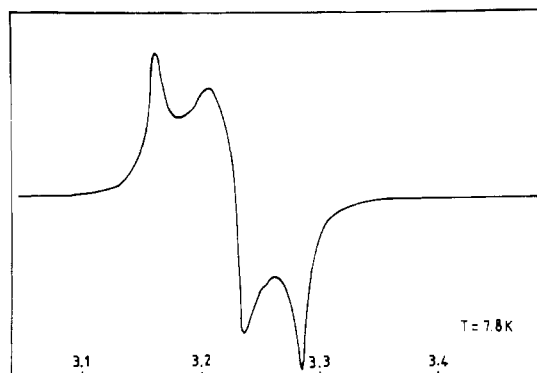


Figure 3. X-Band powder EPR spectrum of **5** at 7.8 K.

state, the other two states remaining unchanged. Therefore, its influence on the magnetic properties is negligible. An excellent agreement between calculated and experimental data was obtained by imposing $j = 0$, the other parameters being found as

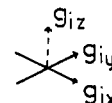
$$j = -483 \text{ cm}^{-1} \quad g_1 = 2.25 \quad g_2 = 2.21$$

The agreement factor defined as $\sum(\chi_M T^{\text{valcd}} - \chi_M T^{\text{obsd}})^2 / \sum(\chi_M T^{\text{obsd}})^2$ is then equal to 6×10^{-6} .

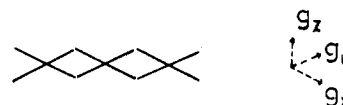
The X-band powder EPR spectrum at room temperature exhibits a broad and almost symmetrical feature centered at $g = 2.09$. When the sample is cooled down below 150 K, the spectrum is resolved and exhibits the features characteristic of a doublet state in a rhombic symmetry with $g_x = 2.062$, $g_y = 2.102$, and $g_z = 2.149$. Since this spectrum, shown in Figure 3, is visible at 4.2 K, it is associated with the doublet ground state $^2B_{2u}$. For this state, the relation between its g tensor and the local g tensors is^{10,12}

$$\mathbf{g} = \frac{1}{3}(2g_1 - g_2 + 2g_3) \quad (4)$$

Each copper(II) ion is roughly in an elongated tetragonal environment, so that its local g tensor is oriented as shown



with $g_{iz} > g_{ix}$ and g_{iy} . It follows from (4) that \mathbf{g} would be expected to be oriented as shown



with the largest principal value g_z along the direction perpendicular to the average molecular plane and an almost axial symmetry. In fact, \mathbf{g} is found to be far from axial, and a full understanding of the \mathbf{g} tensor requires a single-crystal investigation that we intend to perform in the near future.

Ni(II) Trinuclear Species. The magnetic properties of **8** are shown in Figure 4, again in the form of $\chi_M T$ vs. T . From room temperature down to about 40 K, $\chi_M T$ is constant and equal to $2.56 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$, which exactly corresponds to what is expected for two uncoupled nickel(II) ions in a spin-triplet state. These paramagnetic nickel(II) ions clearly are the terminal ions too far away from each other to interact significantly. The central ion in the S_4 planar environment is diamagnetic. Below 40 K, $\chi_M T$ decreases upon cooling down and reaches the value of $1.4 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 4.2 K. This behavior is likely due to the local anisotropy of the terminal nickel(II) ions. A simple model taking into account only the axial zero-field splitting characterized by the D parameter leads to a very good fitting of the experimental data with $|D| = 8.3 \text{ cm}^{-1}$ ($R = 9 \times 10^{-5}$).

A model based on an isotropic interaction between the terminal ions leads to an isotropic exchange parameter of -1.8 cm^{-1} , which

(26) In this section as well as in the Discussion, the indices 1 and 3 refer to the terminal ions and the index 2 refers to the central one.

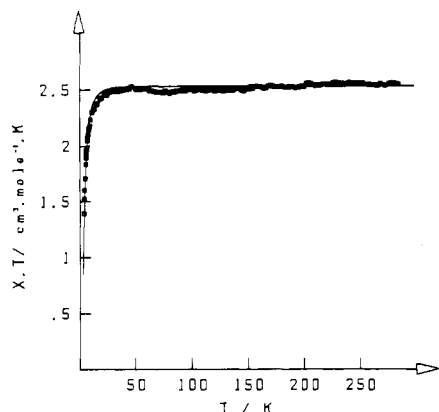


Figure 4. Experimental (\square) and calculated (—) temperature dependence of $\chi_M T$ for $[\text{Ni}_3\text{C}_2\text{S}_2(\text{NCH}_2\text{CH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{OH})_2]_2(\text{NO}_3)_2$ (**8**).

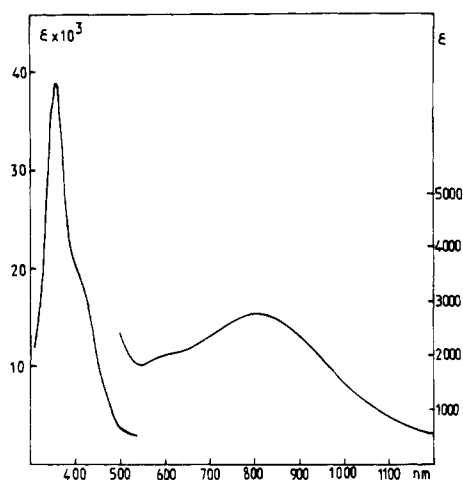


Figure 5. UV-visible spectrum of **5** in methanolic solution.

Table IV. UV-Visible Spectroscopic Data for the Copper(II) Trinuclear Species **5** and **7**^a

compd	in methanol	in KBr
5	820 (2800)	800
	600 (2200)	
	400 (1700)	400
	350 (39000)	350
7	700 (5000)	740
	520 (5500)	
	450 (6000)	450
	350 (59200)	350

^a The wavelengths are in nm. The absorption coefficients are given in parentheses; they are expressed in $\text{M}^{-1} \text{cm}^{-1}$ and are unconvoluted.

is by far too large a value. Moreover, the fitting is then less satisfactory ($R = 2 \times 10^{-4}$). As expected, **8** is EPR silent.

UV-Visible Spectroscopy

The spectroscopic data for the copper(II) trinuclear complexes **5** and **7** are given in Table IV. The spectrum of **5** is shown in Figure 5. These compounds have similar spectra, with four bands in methanolic solution and only three bands in the solid phase. Let us discuss first the assignment of the two bands occurring at higher energy. Amundsen et al.¹³ have shown that the thioether \rightarrow copper(II) transition generally occurs around 350 nm with an intensity depending on the overlap between the σ sulfur orbital and the singly occupied d metal orbital. Therefore, we propose to assign the band at 350 nm to such a transition with, in our case, a very good S(σ)-copper(II) overlap. As for the band around 400 nm, it likely corresponds to a S(thioamide) \rightarrow copper(II) LMCT transition. This transition occurs at lower energy than 400 nm in all the copper(II) dithiooxamide derivatives we have studied so far.²⁻⁵ Coucouvanis¹⁴ found the same energy for the S(thioacid)

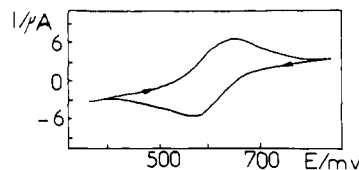


Figure 6. Cyclic voltammogram of **5**.

\rightarrow copper(II) LMCT transition in the copper(II) dithiooxalate anion $[\text{Cu}(\text{C}_2\text{S}_2\text{O}_2)_2]^{2-}$. Let us focus now on the two bands at lower energy. The absorption around 600 nm is most likely due to a d-d transition around the central copper(II) ion. Its relatively strong intensity could arise from the proximity of the even more intense band at lower energy. This assignment is in contradiction with that proposed by Jones et al.,¹⁵ who studied a series of CuS_4 chromophores and suggested that the relatively intense band near 600 nm was due to a S(II) \rightarrow copper(II) transition. It should be noticed, however, that Lever already stated that this band was misassigned and actually was a d-d transition.¹⁶ Finally, the band of lowest energy has quite a surprisingly strong intensity and therefore cannot be assigned to a d-d transition. The d-d band for the terminal copper(II) ions is certainly hidden by this band around 800 nm, of which the origin is not clear to us.

As for the nickel(II) trinuclear complexes **8** and **9**, they essentially exhibit a very intense band at 500 nm, most likely due to a S \rightarrow nickel(II) LMCT transition involving the central metal ion.

Electrochemical Properties

The electrochemical properties of the two copper(II) trinuclear species **5** and **7** were investigated in a 80:20 methanol-dimethylformamide mixture containing 0.1 M of lithium perchlorate. The cyclic voltammograms for **5** and **7** are similar; that of **5** is shown in Figure 6. These voltammograms display a one-step oxidation wave occurring at 0.595 V for **5** and 0.760 V for **7** (vs. SCE). This step is only partially reversible ($I_{p(\text{red})}/I_{p(\text{ox})} \approx 0.95$) even for scan rates of 5 V s^{-1} . A coulometric experiment indicates that two electrons are involved in this step, which supports the point that the oxidation $\text{Cu(II)} \rightarrow \text{Cu(III)}$ concerns the two terminal metal centers. These are surrounded by deprotonated amino groups that are well-known as stabilizers for copper(III).^{21,22} Since the interaction between the terminal metal centers is extremely weak, the two oxidations occur at the same potential.

The difference ΔE_p between the oxidation peak and the reduction peak is 60 mV for **5** and 80 mV for **7** and is essentially independent of the scan rate. Shain and co-workers^{17,18} have established a relation between the peak width $E_p - E_{p/2}$ and the difference between the two redox potentials in the case of a two-electron charge transfer. In **5**, $E_p - E_{p/2}$ is equal to 60 mV, which from this relation corresponds to $E_2^\circ - E_1^\circ$ equal to -40 mV. This value is very close to the value expected for two non-interacting copper(II) ions ($-RT/F \ln 4 = -36 \text{ mV}$).²³

The $\text{Cu(III)Cu(II)Cu(III)}$ compound obtained by electrolysis displays the same cyclic voltammogram as the starting Cu(II)Cu(II) compound, which indicates that the electron transfer is chemically reversible. However, the electrogenerated $\text{Cu(III)Cu(II)Cu(III)}$ species slowly reacts with the solvent to give again the starting compound.

The mixed-valence compound does not show any intervalence band. It certainly belongs to class I of Robin and Day. During the electrolysis, the band at 350 nm decreases and then vanishes, which is consistent with the assignment S(σ) \rightarrow copper(II) LMCT transition proposed in the previous section. As for the band at 800 nm, its intensity decreases and it is shifted toward the higher energies by ca. 50 nm.

Discussion

In this last section, we purpose to discuss in a more thorough manner the mechanism of the interaction in copper(II) trinuclear systems of the type **5-7**.

It is now well understood that the spin Hamiltonian (eq 1) is an effective Hamiltonian that does not correspond to the real mechanisms of the interaction phenomenon. We want to show

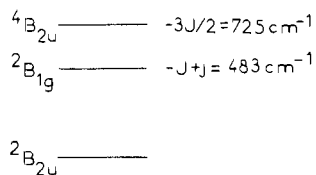


Figure 7. Diagram of the low-lying states in 6.

Table V. Eigenvalues and Eigenfunctions for the Low-Lying States of a Copper(II) Trinuclear System of D_{2h} Symmetry, in the Limit $S \ll 1$ (See Text)

${}^4B_{2u}$	$-4tS - 2j + 4kS^2$	$ a_1a_2a_3 $
${}^2B_{1g}$	$-2tS - j + 2kS^2$	$(2^{1/2}/2)(\bar{a}_1a_2a_3 - a_1a_2\bar{a}_3)$
${}^2B_{2u}$	$2tS + j - 2kS^2$	$(6^{1/2}/6)(\bar{a}_1a_2a_3 - 2 a_1\bar{a}_2a_3 + a_1a_2\bar{a}_3)$

how such an effective Hamiltonian can be built. For that, we assume that the three unpaired electrons of the trinuclear system are described by a_1 , a_2 , and a_3 magnetic orbitals.⁶ Each of them is centered on a metal ion and partially delocalized in an anti-bonding fashion toward the ligands surrounding this ion, with xy symmetry. Let us perform now the two following approximations: (i) the exchange interaction phenomenon is weak with regard to the chemical bond, so that its description from a perturbation theory is legitimate; (ii) only the three unpaired electrons are considered as active, the other electrons of the system only intervening in the potential to which the active electrons are submitted. Then the Hamiltonian of the problem may be written as

$$\mathcal{H} = \sum_{i=1}^3 h(i) + \sum_{i,j>i}^3 \frac{1}{r_{ij}} \quad (5)$$

The detail of the calculation of the eigenvalues of the low lying states is given in the Appendix. This calculation leads to the results of Table V with the notations

$$S = \langle a_1|a_2 \rangle \quad \alpha_i = \langle a_i|h|a_i \rangle \quad \beta = \langle a_1|h|a_2 \rangle$$

$$t = \beta - \left(\frac{\alpha_1 + \alpha_2}{2} \right) S \quad k = \langle a_1a_1|a_2a_2 \rangle \quad (6)$$

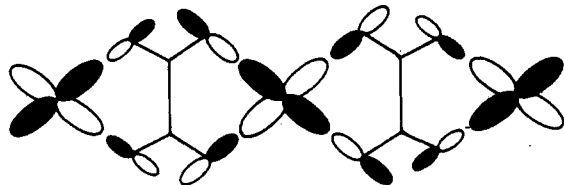
$$j = \langle a_1a_2|a_1a_2 \rangle$$

where we neglected the interaction between a_1 and a_3 and took into account an idealized D_{2h} symmetry for the trinuclear entity. The results of Table V are valid only for $S \ll 1$.

If the energies deduced from (1) are compared with those of Table V, eq 7¹⁹ is obtained, where j and k are positive integrals

$$J = 4ts + 2j - 4kS^2 \quad (7)$$

and tS is negative. The strongly negative value for J found in 5 is attributed to the favorable relative orientations of the magnetic orbitals, which allows a good overlap between them



The overlap is also favored by the presence of sulfur atoms in the bridging networks.²⁰ The spectrum of the low-lying states in 6, as deduced from the magnetic data, is shown in Figure 7.

The EPR properties of the copper(II) complexes described in this paper are also particularly interesting. In fact, compound 5 is, to our knowledge, the copper(II) trinuclear system that exhibits the best resolved EPR spectrum reported so far. We very much hope that a single-crystal investigation will provide new insights on the nature of the ground doublet state in such a system. Particularly, the range of validity and the limits of the relation (eq 4) between this doublet state delocalized on three centers and

the local doublet could be specified.

Acknowledgment. This work was supported by the SNEA, to which we express our gratitude.

Appendix

The low-lying states for the trinuclear unit are two spin doublets and a spin quartet. To find the eigenvalues associated with these states, we have to diagonalize the Hamiltonian (eq 5) by using the eight determinants $|a_i\sigma_i a_j\sigma_j a_k\sigma_k|$ as the basis set. a_i ($i = 1-3$) are the magnetic orbitals and σ_i notes a spin function. For that, we neglect the interaction between a_1 and a_3 , which are centered on metal ions very far away from each other ($\text{Cu}_1 \cdots \text{Cu}_3 = 11.389$ (2) Å) and we assume that $S = \langle a_1|a_2 \rangle$ is small with regard to the unity. This latter approximation corresponds to the description of exchange-coupled nearest-neighbor metal centers.

The function $M_S = 3/2$ associated with the quartet state is $|a_1a_2a_3|$ and its energy is

$$\frac{\langle a_1a_2a_3|\mathcal{H}|a_1a_2a_3 \rangle}{\langle a_1a_2a_3|a_1a_2a_3 \rangle} = 2\alpha_1 + \alpha_2 + \frac{-4tS + 2k - 2j}{1 - 2S^2} \quad (8)$$

In the $M_S = 1/2$ subspace, we have the three basis functions $|\bar{a}_1a_2a_3|$, $|a_1\bar{a}_2a_3|$, and $|a_1a_2\bar{a}_3|$ and the energies are the roots of the secular equation

$$\det([\mathcal{H}] - \epsilon[S]) = 0 \quad (9)$$

with

$$[\mathcal{H}] = \begin{bmatrix} (2\alpha_1 + \alpha_2) \cdot (1 - S^2) - 2tS + 2k - j & -(2\alpha_1 + \alpha_2)S^2 - 0 & 0 \\ -(2\alpha_1 + \alpha_2)S^2 - 2tS - j & (2\alpha_1 + \alpha_2) + 2k & -(2\alpha_1 + \alpha_2)S^2 - 2tS - j \\ 0 & -(2\alpha_1 + \alpha_2)S^2 - 2tS - j & (2\alpha_1 + \alpha_2)(1 - S^2) - 2tS + 2k - j \end{bmatrix}$$

$$[S] = \begin{bmatrix} 1 - S^2 & -S^2 & 0 \\ -S^2 & 1 & -S^2 \\ 0 & -S^2 & 1 - S^2 \end{bmatrix}$$

If we do the transformation

$$\epsilon' = \epsilon - (2\alpha_1 + \alpha_2) - 2k \quad (10)$$

then, in the approximation $S \ll 1$, ϵ' is small with regard to $2\alpha_1 + \alpha_2 + 2k$ so that $\epsilon'S^2$ may be neglected in the off-diagonal terms of the secular equation. (9) may then be written as

$$\begin{vmatrix} -2tS - j + 2kS^2 - \epsilon' & -2tS - j + 0 & 0 \\ -2tS - j + 2kS^2 & -\epsilon' & -2tS - j + 2kS^2 \\ 0 & -2tS - j + 2kS^2 & -2tS - j + 2kS^2 - \epsilon' \end{vmatrix} = 0 \quad (11)$$

of which the roots are identical with the eigenvalues of the spin Hamiltonian

$$\mathcal{H} = -J(\hat{S}_1 \cdot \hat{S}_2 + \hat{S}_1 \cdot \hat{S}_2)$$

in the $M_S = 1/2$ subspace, if we put

$$J = 2tS + 2j - 4kS^2$$

For the quartet state, the energy is

$$\epsilon(S = 3/2) = 2\alpha_1 + \alpha_2 + 2k - 2tS - 2j + 4kS^2 \quad (12)$$

which is identical with (8) in the approximation $S \ll 1$.

The $M_S = 1/2$ eigenfunctions associated with the doublet states given in Table V are easily determined by using (11).

Registry No. 1, 104463-59-4; 2, 37078-78-7; 3, 104463-60-7; 4, 24304-84-5; 5, 104439-63-6; 6, 104528-62-3; 7, 104439-65-8; 8, 104439-67-0; 9, 104439-69-2; 3-chloropropylamine hydrochloride, 6276-54-6; 2-mercaptoethanol, 60-24-2; dithiooxamide, 79-40-3; 2-chloroethylamine hydrochloride, 870-24-6.

Supplementary Material Available: Listing of atomic parameters for hydrogen atoms and anisotropic thermal parameters for non-hydrogen atoms of 6 (3 pages); tables of calculated and observed structure factors (29 pages). Ordering information is given on any current masthead page.