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Amino Acid Amides of Dithiooxalic Acid: Spectroscopic, Electrochemical, and Magnetic Properties of Copper(II) Binuclear Complexes and Crystal Structure of [*N*,*N'*-(1,2-Dithioxoethane-1,2-diyl)bis(methyl methioninato)]bis(bromocopper(II))

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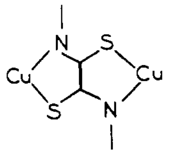
Three novel amino acid amides of dithiooxalic acid were synthesized, namely $C_2S_2(NHCH_2CONHCH_2CONHCH_2CH_2OH)_2$ (**1**), $C_2S_2[NHCH(CH_2CH_2SCH_3)COOH]_2$ (**7**), and $C_2S_2[NHCH(CH_2CH_2SCH_3)COOCH_3]_2$ (**9**). From **1**, two copper(II) binuclear complexes were synthesized: $Cu_2[C_2S_2(NCH_2CONHCH_2CONHCH_2CH_2OH)_2](SO_4)\cdot H_2O$ (**5**) and $\{Cu_2[C_2S_2(NCH_2CONCH_2CONCH_2CH_2OH)_2]\}[N(C_4H_9)_4]_2\cdot 2H_2O$ (**6**). From **7**, $Cu_2\{C_2S_2[NCH(CH_2CH_2SCH_3)COO]_2\}(CH_3OH)\cdot {}^1/_2H_2O$ (**8**) was obtained and from **9**, the three complexes $Cu_2\{C_2S_2[NCH(CH_2CH_2SCH_3)COOCH_3]_2\}X_2$, X = Cl (**10**), Br (**11**), and ClO_4 (**12**) were synthesized. The structures of **5**, **6**, **8**, **10**, and **12** were deduced from the electronic and vibrational spectra. The crystal structure of **11** was solved. **11** crystallizes in the monoclinic system, space group $P2_1/c$: $a = 12.907$ (12), $b = 6.701$ (4), $c = 14.878$ (10) Å; $\beta = 111.06$ (2)°; $Z = 2$. The structure consists of isolated centrosymmetrical binuclear units. The environment of each copper(II) ion is a distorted trigonal bipyramid with the sulfur atoms of the dithiooxamide and the thioether group and the oxygen atom of the ester group in equatorial positions, the nitrogen and bromide atoms occupying the apical sites. The bridging network $CuC_2S_2N_2Cu$ is almost planar with a Cu-Cu separation of 5.666 (3) Å. The electrochemical properties of **6**, **10**, and **11** were investigated. **6** can be oxidized in two successive steps at 0.42 and 0.85 V (vs. SCE). Each step involves one electron. The first step is totally reversible, but the $Cu^{II}Cu^{III}$ species is chemically unstable. **10** and **11** can be reduced by one electron around 0.2 V. This reduction is only slightly reversible. The magnetic properties of **5**, **6**, **10**, and **11** were investigated in the 60-300 K temperature range. All the compounds exhibit a strong antiferromagnetic interaction with a singlet-triplet energy gap in the range 560-730 cm^{-1}.

Introduction

Some years ago, we described the synthesis, the crystal structure, and the magnetic properties of copper(II) binuclear complexes with dithiooxamide derivatives.[2-4] From a structural point of view, these complexes are characterized by the planar bridging network



with copper-copper separations of the order of 5.6 Å. The same kind of bridge is present in the polymeric copper(II) rubeanate.[5] The magnetic behavior of these compounds revealed that, in spite of the large separation between them, the metal centers were strongly coupled in an antiferromagnetic fashion, with singlet-triplet energy gaps around 600 cm^{-1}. Since, to our knowledge, all the mixed-valence copper binuclear complexes were obtained from copper(II) complexes exhibiting a large antiferromagnetic interaction,[6,7] we decided to explore the electrochemical properties of the copper(II) binuclear complexes with dithiooxamide derivatives. To favor the formation of $Cu^{II}Cu^{III}$ or $Cu^{II}Cu^{I}$ species, we used amino acid amides of dithiooxalic acid as polychelating ligands. Indeed, it is now well established that the amino acids can stabilize the unusual oxidation states of copper. For instance, Margerum and co-workers showed that copper(III) can be stabilized when surrounded by peptides.[8,9] Recently the crystal structure of a peptide copper(III) complex was reported.[10] When sulfur-containing amino acids are used, the stabilization of copper(I) may be expected. In fact, copper complexes with sulfur-containing amino acids have been much studied, in relation with the problem of the structure of the blue copper proteins, which exhibit a characteristic intense absorption around 600 nm, attributed to a S(σ) → copper(II) LMCT transition.[11-14] Many models have been synthesized; none of them reproduce the quite peculiar spectroscopic properties of the blue copper proteins. Methionine in principle can be utilized to obtain a copper-S bond. In fact, methionine binds to the metal preferentially by the nitrogen atom of the amine function or the oxygen atom of the carboxylic function. It is however possible to force the coordination of the thioether function by esterification of the carboxylic function.[15] We report here on the first crystal structure of a complex of this kind.

In this paper, we describe the synthesis of three novel amino acid amides of dithiooxalic acid, namely $C_2S_2(NHCH_2CONHCH_2CONHCH_2CH_2OH)_2$ (**1**), $C_2S_2[NHCH(CH_2CH_2SCH_3)COOH]_2$ (**7**), and $C_2S_2[NHCH(CH_2CH_2SCH_3)COOCH_3]_2$ (**9**), abbreviated by DT(glyglyEtOH)$_2$, DT(met)$_2$, and DT(metOMe)$_2$, respectively. From **1**, we prepared two copper(II) complexes $Cu_2[C_2S_2(NCH_2CONHCH_2CONHCH_2CH_2OH)_2](SO_4)\cdot H_2O$ (**5**) and $\{Cu_2[C_2S_2(NCH_2CONCH_2CONCH_2CH_2OH)_2]\}[N(C_4H_9)_4]_2\cdot 2H_2O$ (**6**), abbreviated by

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$Cu_2DT(glyglyEtOH)_2SO_4{\cdot}H_2O$ and $Cu_2DT(glyglyEtOH)_2(NBu_4)_2{\cdot}2H_2O$, respectively. From **7**, we prepared $Cu_2\{C_2S_2[NCH(CH_2CH_2SCH_3)COO]_2\}(CH_3OH){\cdot}{}^1/_2H_2O$ (**8**) abbreviated by $Cu_2DT(met)_2CH_3OH{\cdot}{}^1/_2H_2O$. From **9**, we synthesized the complexes $Cu_2\{C_2S_2[NCH(CH_2CH_2SCH_3)COOCH_3]_2\}X_2$ with X = Cl (**10**), Br (**11**), and ClO_4 (**12**). For these compounds, we used the abbreviation $Cu_2DT(metOMe)_2X_2$. The structures of **5**, **6**, **8**, and **10**–**12** were deduced from the electronic and vibrational spectra. For **10**–**12**, the structure was confirmed by the refinement of the crystal structure of **11**. The electrochemical properties of **6**, **10**, and **11** were investigated, as well as the magnetic properties of **5**, **6**, **10**, and **11**.

Experimental Section

Syntheses. $\mathbf{C_2S_2(NHCH_2CONHCH_2CONHCH_2CH_2OH)_2}$ **(1).** **1** was prepared in four steps. First the phthalylglycylglycine **2** was obtained by heating up to 150 °C a mixture of 4 g of phthalic anhydride and 2 g of glycylglycine. The mixture became liquid and then solidified. **2** was recrystallized in hot water. The yield (with regard to the glycylglycine) was 98%. The ethyl phthalylglycylglycinate **3** was obtained as follows: 3.80 g of **2** was dissolved in 50 mL of ethanol containing 1 mL of sulfuric acid and was heated at reflux for 1 h. **3** was precipitated by cooling, filtered, and washed with ethanol. The yield was 83%. The ethanolamide of glycylglycine, **4**, was prepared by dissolving **3** in the minimum amount of ethanolamine. The mixture was stirred overnight. **4** was precipitated, filtered, and washed with ethanol. The yield was 79%. Anal. Calcd for $C_6H_{13}N_3O_3$ (**4**): C, 41.14; H, 7.43; N, 24.0; O, 27.43. Found: C, 41.30; H, 7.35; N, 23.85; O, 27.54.

Finally **1** was obtained by dissolving 500 mg of **4** and 150 mg of dithiooxamide in the minimum amount of water. The solution was allowed to stand overnight. **1** precipitated as a pale brown polycrystalline powder and was recrystallized in hot water. Anal. Calcd for $C_{14}H_{24}N_6O_6S_2$ (**1**): C, 38.53; H, 5.50; N, 19.27; O, 22.02; S, 14.68. Found: C, 38.27; H, 5.64; N, 18.97; O, 21.90; S, 14.54.

$\mathbf{Cu_2[C_2S_2(NCH_2CONHCH_2CONHCH_2CH_2OH)_2](SO_4){\cdot}H_2O}$ **(5).** A solution of 114.5 mg of copper(II) sulfate in 5 mL of water was added to a suspension of 100 mg of **1** in 5 mL of water. The solution became limpid, and **5** was obtained by slow evaporation. Anal. Calcd for $C_{14}H_{24}N_6O_{11}S_3Cu_2$ (**5**): C, 24.88; H, 3.55; N, 12.44; O, 26.07; S, 14.22; Cu, 19.34. Found: C, 24.80; H, 3.66; N, 11.89; O, 25.41; S, 14.24; Cu, 19.60.

$\mathbf{Cu_2[C_2S_2(NCH_2CONCH_2CONCH_2CH_2OH)_2][N(C_4H_9)_4]_2{\cdot}2H_2O}$ **(6).** A solution of 114.5 mg of copper(II) sulfate in 5 mL of water was added to a suspension of 100 mg of **1** in 5 mL of water. Then, an aqueous solution of tetrabutylammonium hydroxide was added dropwise until the pH was 11. The solution became limpid red. It was dried off, and the residue was redissolved in acetone and filtered. **6** was obtained by slow evaporation as a red polycrystalline powder. Anal. Calcd for $C_{46}H_{96}N_8O_8S_2Cu_2$ (**6**): C, 51.27; H, 8.54; N, 10.40; O, 11.89; S, 5.94; Cu, 12.20. Found: C, 51.72; H, 8.69; N, 10.17; O, 12.15; S, 5.85; Cu, 12.14.

$\mathbf{C_2S_2[NHCH(CH_2CH_2SCH_3)COOH]_2}$ **(7).** A 1.240-g amount of methionine and 200 mg of NaOH were dissolved in 20 mL of water. A 500-mg amount of dithiooxamide was added. The solution was allowed to stand overnight and then concentrated HCl was added until the pH was 1. **7** precipitated as an orange polycrystalline powder and was filtered and recrystallized in hot water. Anal. Calcd for $C_{12}H_{20}N_2S_4O_4$ (**7**): C, 37.46; H, 5.24;, N, 7.29; O, 16.65; S, 33.26. Found: C, 37.70; H, 5.26; N, 7.11; O, 16.94; S, 33.22.

$\mathbf{Cu_2\{C_2S_2[NCH(CH_2CH_2SCH_3)COO]_2\}(CH_3OH){\cdot}{}^1/_2H_2O}$ **(8).** A 100-mg amount of **7** and 193 mg of copper(II) perchlorate were dissolved in 20 mL of methanol. Small crystals of **8** appeared from this solution. Anal. Calcd for $C_{13}H_{21}N_2O_{5.5}S_4Cu_2$ (**8**): C, 28.46; H, 3.83; N, 5.11; O, 16.05; S, 23.35. Found: C, 28.55; H, 3.75; N, 5.12; O, 16.00; S, 22.97.

$\mathbf{C_2S_2[NHCH(CH_2CH_2SCH_3)COOCH_3]_2}$ **(9).** Two grams of **7** was dissolved in 20 mL of methanol with a few drops of concentrated HCl. The solution was heated at reflux for 3 h and then cooled down to −10 °C. **9** precipitated and was filtered and washed with cold acetone. Anal. Calcd for $C_{14}H_{24}N_2O_4S_4$ (**9**): C, 40.78; H, 5.82; N, 6.80; O, 15.53; S, 31.07. Found: C, 40.91; H, 5.96; N, 7.09; O, 16.08; S, 30.44.

Table I. Atomic Coordinates and Thermal Isotropic Parameters with Esd's in Parentheses

atom	x/a	y/b	z/c	B_{eq}, Å^2
Cu	0.18663 (9)	0.2717 (2)	0.50473 (8)	3.26 (4)
Br	0.31041 (9)	0.2246 (2)	0.42465 (7)	4.22 (4)
S(1)	0.0665 (2)	0.4599 (5)	0.3865 (2)	3.59 (8)
S(2)	0.1697 (2)	−0.0700 (5)	0.5471 (2)	4.09 (9)
O(1)	0.3261 (6)	0.335 (1)	0.6715 (5)	4.7 (3)
O(2)	0.3147 (5)	0.292 (1)	0.8173 (4)	4.0 (2)
N	0.1068 (6)	0.365 (1)	0.5858 (5)	2.7 (2)
C(1)	0.0182 (8)	0.469 (2)	0.5530 (6)	3.0 (3)
C(2)	0.1483 (8)	0.302 (2)	0.6879 (6)	3.1 (3)
C(3)	0.2736 (7)	0.314 (2)	0.7230 (6)	2.8 (3)
C(4)	0.115 (1)	0.082 (2)	0.6994 (8)	4.0 (4)
C(5)	0.4348 (8)	0.293 (3)	0.8633 (8)	5.6 (4)
C(6)	0.182 (1)	−0.076 (2)	0.6737 (9)	5.0 (4)
C(7)	0.295 (1)	−0.200 (2)	0.556 (1)	5.7 (5)

[a] $B_{eq} = {}^1/_3\Sigma_i\Sigma_jB_{ij}a^*_ia^*_j\bar{a}_i\bar{a}_j$.

$\mathbf{Cu_2\{C_2S_2[NCH(CH_2CH_2SCH_3)COOCH_3]_2\}X_2}$ **with X = Cl (10), Br (11), and** $\mathbf{ClO_4}$ **(12).** A 100-mg amount of **9** and 82.75 mg of copper(II) chloride (or 108.50 mg of copper(II) bromide) were dissolved in 50 mL of methanol. **10** (or **11**) precipitated and was recrystallized in dichloromethane. Anal. Calcd for $C_{14}H_{22}N_2O_4Br_2S_4Cu_2$ (**11**): C, 24.10; H, 3.16; N, 4.02; O, 9.18; Br, 22.95; S, 18.36. Found: C, 24.24; H, 3.25; N, 4.13; O, 9.02; Br, 23.05; S, 17.95.

12 was prepared as follows: 100 mg of **9** and 180 mg of copper(II) perchlorate were dissolved in 25 mL of methanol and then 50 mL of ether was added. Small black-violet crystals of **12** appeared at −10 °C. *Caution*! **12** is explosive. Anal. Calcd for $C_{14}H_{22}N_2O_{12}Cl_2S_4Cu_2$ (**12**): C, 22.85; H, 2.99; N, 3.81; O, 26.0; S, 17.41. Found: C, 22.98; H, 3.12; N, 3.93; O, 26.01; S, 17.44.

Crystallographic Data Collection and Refinement of the Structure of 11. The crystal selected for X-ray analysis was shaped as a parallelepiped (0.35 × 0.075 × 0.025 mm^3). Preliminary precession and Laue photographs showed the crystal to be monoclinic. Systematic absences were consistent with the space group $P2_1/c$. Lattice parameters are a = 12.907 (12) Å, b = 6.701 (4) Å, c = 14.878 (10) Å, β = 111.06 (2)°, and V = 1201 Å^3 with Z = 2 (D_{exptl} = 1.92 g cm^{-3}). A total of 1576 independent reflections were collected at room temperature on a homemade diffractometer with Mo Kα radiation in the θ–2θ scan mode up to $2\theta_{\max}$ = 46°. The scan width was $\Delta\theta = 0.8 + 0.345 \tan\theta$, taking into account the Kα_1–Kα_2 dispersion. Three standard reflections (013, 132, 220) were monitored every 100 reflections. No significant variation was observed. Intensities were corrected for Lorentz and polarization factors. A total of 280 reflections with $I < 3\sigma(I)$ were omitted from further calculations. The intensities were corrected for absorption (μ = 55 cm^{-1}). Minimum and maximum transmission coefficients were 0.37 and 0.90.

The structure was solved by the heavy-atom method. Successive Fourier syntheses led to the positions of all non-hydrogen atoms. Full-matrix least-squares refinement of atomic coordinates and thermal (isotropic and then anisotropic) parameters led to the final values $R = \sum(|F_o| - |F_c|)/\sum|F_o| = 0.045$ and $R_w = (\sum w(|F_o| - |F_c|)^2/\sum|F_o{}^2|)^{1/2} = 0.051$ with $w = 1.0$. Hydrogen atoms were introduced to calculated positions.[16a] In the last least-squares cycle Δ/σ was less than 0.2. The real and imaginary parts of the scattering factor of copper were taken from ref 16b. Atomic coordinates are listed in Table I.

Electrochemistry. Materials. Dichloromethane (Prolabo) was purified by fractional distillation over P_2O_5 under a stream of argon. The supporting electrolyte Bu_4NPF_6 (Fluka) was deoxygenated and dehydrated by melting under vacuum.

Apparatus. Electrochemical experiments were carried out in a three-electrode cell. The 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. For the polarographic and cyclic voltammetric measurements, the working electrode was a carbon disk. Coulometry and preparative electrolyses were carried out in a similar three-compartment cell, the working electrode being a 35-cm^2 carbon tissue. The working electrode compartment contained about 30 mL of solution stirred with a magnetic stirrer. The reference electrode was an aqueous standard

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(16) (a) All calculations were performed on the IRIS 80 computer of the Université Pierre et Marie Curie, using the program SHELX 76. (b) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, p 99.

Table II. UV-Visible Spectroscopic Data[a]

compd	λ (ε)	assignt
$Cu_2DT(glyglyEtOH)_2SO_4 \cdot H_2O$ (5)[b]	670	d-d
	405	S → Cu
$Cu_2DT(glyglyEtOH)_2(NBu_4)_2$ (6)[c]	440	S → Cu
$Cu_2DT(met)_2CH_3OH \cdot {}^1/_2H_2O$ (8)[d]	670	d-d
	460	S → Cu
$Cu_2DT(metOMe)_2X_2$		
X = Cl (10)[e]	880 (530)	d-d
	690 (1080)	
	525 (1960)	S → Cu
	470 (1580)	>S → Cu
X = Br (11)[e]	920 (560)	d-d
	650 (1750)	
	560 (2630)	S → Cu
	490 (1980)	>S → Cu
X = ClO_4 (12)[e]	880 (400)	d-d
	690 (950)	
	488 (2000)	S → Cu + >S → Cu
$Cu_2DT(EtOMe)_2Cl_2$ (13)[f]	700	d-d
	525	S → Cu
$Cu_2DT(glyOMe)_2Cl_2$ (14)[f]	650	d-d
	490	S → Cu
$Cu_2DT(glygly)_2{}^{2-}$ (15)[b]	540 (400)	d-d
	420 (1100)	S → Cu
$Cu_2DT(EtOH)_2(SO_4) \cdot 2H_2O$ (16)[g]	678 (300)	d-d
	426 (1000)	S → Cu

[a] The wavelengths are in nm. The absorption coefficients are given in parentheses; they are expressed in M^{-1} cm^{-1} and are unconvoluted. Legend: S → Cu, S(thioamide, σ) → copper(II) LMCT transition; >S → Cu, S(thioether, σ) → copper(II) LMCT transition. [b] In water. [c] In water + NBu_4OH. [d] In KBr pellet. [e] In dichloromethane. [f] In Nujol. [g] In methanol.

calomel electrode (SCE) and the auxiliary electrode a platinum or aluminum wire.

All electrochemical studies were performed under an argon atmosphere. Cyclic voltammetry and polarography were performed with Tacussel PRT 100X1X and TP-PRT instruments using for polarography the EDI Tacussel rotating electrode. Coulometry and preparative electrolyses were performed with a Tacussel PRT 100X1X potentiostat and a IG 5N electronic integrator.

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. $HgCo(SCN)_4$ was used as a susceptibility standard. Diamagnetic corrections were estimated at -390×10^{-6} cm^3 mol^{-1} for **5**, -775×10^{-6} cm^3 mol^{-1} for **6**, -356×10^{-6} cm^3 mol^{-1} for **10**, and -384×10^{-6} cm^3 mol^{-1} for **11**.

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

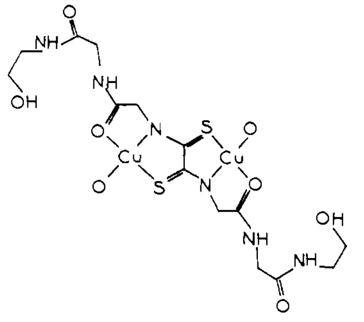
UV-Visible Spectroscopy. The spectra were recorded with a Cary 2300 spectrophotometer at room temperature.

IR Spectroscopy. The spectra were recorded with a Beckman 4250 spectrophotometer on KBr pellets.

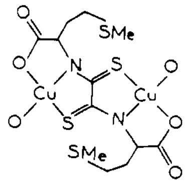
Structures

UV-Visible Spectroscopy. The spectroscopic data for the bimetallic complexes **5**, **6**, **8**, and **10**–**12** are given in Table II, as well as the data concerning other dithiooxamide derivatives (**13**–**16**) previously studied in our group.[2,4,17]

First, we discuss these data from a structural viewpoint. $Cu_2DT(glyglyEtOH)_2SO_4 \cdot H_2O$ (**5**) exhibits a weak band at 670 nm and a strong one at 405 nm. The same holds for $Cu_2DT(met)_2CH_3OH \cdot {}^1/_2H_2O$ (**8**). The spectra of these compounds are similar to that of $Cu_2DT(EtOH)_2(SO_4) \cdot 2H_2O$ (**16**), the structure of which has been solved;[2,3] **16** contains two $CuNSO_2$ chromophores. The low-energy band is a d–d transition for Cu(II) in a square-planar environment, and the high-energy band is a S(σ) → copper(II) LMCT transition. Therefore, we can propose the structures shown for **5** and **8**.

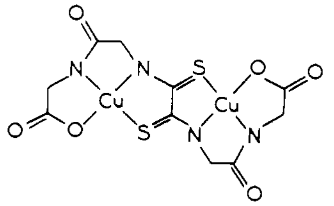


partial structure of 5

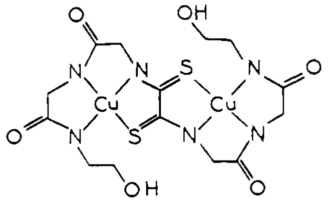


partial structure of 8

We have recently described the complex $[Cu_2DT(glygly)_2]^{2-}$ (**15**), where the ligand diglycylglycyldithiooxamide is deprotonated.[4] The ligand field is stronger in the CuN_2SO chromophore than in the $CuNSO_2$ chromophore, so that the d–d band in **15** appears at 540 nm. $Cu_2DT(glyglyEtOH)_2(NBu_4)_2$ (**6**) exhibits a unique intense band at 440 nm. The ligand field is likely so strong that the d–d band is hidden by the low-energy tail of the LMCT band. This is consistent with its structure.



15



partial structure of 6

Following a paper by Kozlowski et al.,[15] we wanted to check whether by esterification of methionine we could obtain the otherwise rather elusive thioether–Cu(II) bond. In fact the spectra of $Cu_2DT(metOMe)_2X_2$ show two d–d bands, at 880 and 690 nm for X = Cl (**10**) and ClO_4 (**12**) and at 920 and 650 nm for X = Br (**11**). As pointed out by Duggan et al.[18] two d–d bands in this region are found for the trigonal-bipyramidal environment in $[Cu(tren)(NH_3)]^{2+}$ (658 and 877 nm) and for the square-pyramidal environment in $[Cu(NH_3)_5]^{2+}$ (654 and 877 nm). It follows that the spectra of **10**–**12** are strongly indicative of a ligation of thioether to the Cu(II) ion. The refinement of the structure of **11** (vide infra) confirms this result and specifies the actual environment of the metal centers.

We propose to discuss now the assignments of the charge-transfer bands in $Cu_2DT(metOMe)_2X_2$ (**10**–**12**). Among the copper(II) dithiooxamide derivatives, the compounds **10**–**12** arise as unique in having a dark violet color in the solid. In solution, they exhibit a characteristic strong absorption (ε = 2000) around 500 nm. Recently, the electronic spectra of copper(II) ion in a sulfur environment has been much studied in order to understand the optical properties of blue copper proteins.[19] In particular, in plastocyanine, copper(II) is linked

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(17) Girerd, J. J. Thesis, Université de Paris Sud, 1982.

(18) Duggan, M.; Ray, N.; Hathaway, B.; Tomlinson, G.; Brint, P.; Pelin, K. *J. Chem. Soc., Dalton Trans.* **1980**, 1342–1348.

Table III. Infrared Data[a]

	ν_{OH}	ν_{NH} (CONH)	ν_{NH} (CSNH)	ν_{CO} (CON)	ν_{CN} (CON)	ν_{CN} (CSN)
$DT(glyglyEtOH)_2$ (4)	3460	3350 3300	3200	1690 1650	1540	1515
$Cu_2DT(glyglyEtOH)_2SO_4\cdot H_2O$ (5)		3370 3320 3250		1690 1670 1640	1580	1560
$Cu_2DT(glyglyEtOH)_2(NBu_4)_2$ (6)	3520			1600	1570	

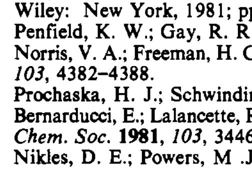
	ν_{NH} (CSNH)	ν_{CO} (CO_2)	ν_{CN} (CSN)		ν_{NH} (CSNH)	ν_{CO} (CO_2)	ν_{CN} (CSN)
$DT(met)_2$ (7)	3230	1715	1490	$DT(metOMe)_2$ (9)	3180	1740	1520
$Cu_2DT(met)_2CH_3OH\cdot{}^1/_2H_2O$ (8)		1570		$Cu_2DT(metOMe)_2X_2$ (10–12)		1700	1540

[a] The frequencies are in wavenumbers.

to the thioether function of methionine and the thiolato function of cysteine.[14] It has been clearly established that the characteristic band of blue copper proteins is due to a $RS^-(\sigma) \rightarrow$ copper(II) LMCT transition,[19] but the thioether → copper(II) transition has not been clearly identified. So, it was of interest to assign this transition in complexes of known structure, particularly in our complexes **10–12**, where the thioether function comes from a methionine ligand.

It has been shown by Amundsen et al.[12] that this thioether → 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 (see also ref 21). Apparently, in our complexes this transition occurs at lower energy (470 nm for **10**, 490 nm for **11**, and and 488 nm for **12**). The Cu–S< bond length of 2.405 (3) Å in **11** does not explain this displacement since (1,5-diamino-3,6-dithiaoctane)(1-methylimidazole)copper(II) perchlorate with slightly longer Cu–S< bond lengths (2.414 and 2.560 Å)[23] absorbs in solution at 323 nm (ϵ = 3000).[12,24] The low intensity of this band in our $Cu_2DT(metOMe)_2X_2$ compounds (ϵ = 500 per copper(II)) is consequent with a relatively bad overlap between $>S(\sigma)$ and the singly occupied d metal orbital. Finally, we can notice that a >S → copper(II) LMCT transition with methionine methyl ester has already been observed at 450 nm.[15]

In all the copper(II) dithiooxamide derivatives, the S-(thioamide) → copper(II) LMCT band seems rather sensitive to the nature of the other nearest neighbors of the metal center; it occurs at 426 nm for $Cu_2DT(EtOH)_2(SO_4)\cdot 2H_2O$ (**16**), at 525 nm for $Cu_2DT(EtOMe)_2Cl_2$ (**13**), and at 490 nm for $Cu_2DT(glyOMe)_2Cl_2$ (**14**). This S(thioamide) → copper(II) transition appears at lower energy when the ligand field is weak (halogen donor atom) than when the ligand field is strong (oxygen donor atom). So, for **10** (X = Cl), it appears at 525 nm and for **11** (X = Br) at 560 nm. For **12** ($X = ClO_4$), this transition is likely hidden under the broad band at 488 nm. The intensity of this transition in the $Cu_2DT(metOMe)_2X_2$ compounds is as strong as in the compounds with planar chromophores. This indicates a good $S(\sigma)$–copper overlap, which is consistent with the magnetic properties of **10** and **11** (vide infra).



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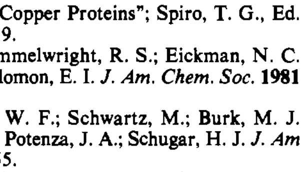

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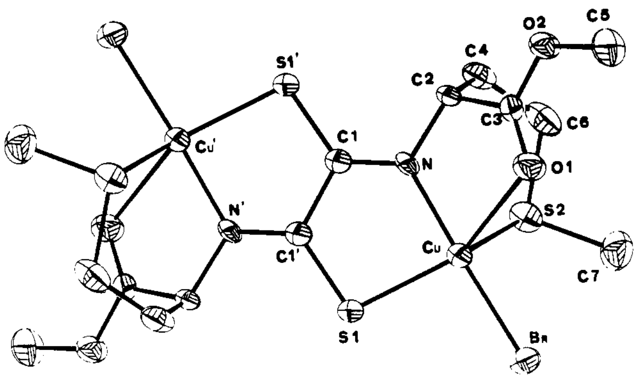


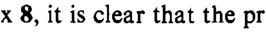
Figure 1. ORTEP view of $Cu_2DT(metOMe)_2Br_2$ (**11**).

Table IV. Interatomic Distances (Å) with Esd's in Parentheses

Cu–N	1.950 (7)	S(2)–C(7)	1.79 (1)
Cu–S(1)	2.265 (3)	C(1)–C(1)'	1.53 (2)
Cu–S(2)	2.405 (3)	C(2)–C(3)	1.51 (1)
Cu–Br	2.332 (1)	C(2)–C(4)	1.56 (2)
Cu–O(1)	2.524 (7)	C(3)–O(1)	1.20 (1)
N–C(1)	1.28 (1)	C(3)–O(2)	1.32 (1)
N–C(2)	1.48 (1)	C(4)–C(6)	1.51 (2)
S(1)–C(1)	1.72 (1)	O(2)–C(5)	1.45 (1)
S(2)–C(6)	1.83 (1)		

Infrared Spectroscopy. Infrared spectroscoy was used to confirm the structures of $Cu_2DT(glyglyetOH)_2SO_4\cdot H_2O$ (**5**), $Cu_2DT(glyglyEtOH)_2(NBu_4)_2$ (**6**), and $Cu_2DT(met)_2CH_3OH\cdot{}^1/_2H_2O$ (**8**) proposed from the chemical analyses and the electronic spectra of the compounds. The data are given in Table III.

The comparison of the IR spectra of **5** and of the ligand **4** clearly shows that a partial deprotonation has occurred. Also the ν_{CO} region has broadened, reflecting the nonequivalence of the CO groups in **5**. In **6**, the ν_{NH} vibrations have completely disappeared and the ν_{CO} and ν_{CN} bands have fused in a unique broad band as CN groups have gained and CO groups have lost some double-bond character according to



As for the complex **8**, it is clear that the protons of the thio-

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(19) Gray, H. B.; Solomon, E. I. In "Copper Proteins"; Spiro, T. G., Ed.; Wiley: New York, 1981; pp 1–39.

(20) Penfield, K. W.; Gay, R. R.; Himmelwright, R. S.; Eickman, N. C.; Norris, V. A.; Freeman, H. C.; Solomon, E. I. *J. Am. Chem. Soc.* **1981**, *103*, 4382–4388.

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(22) Nikles, D. E.; Powers, M .J.; Urbach, F. L. *Inorg. Chem.* **1983**, *22*, 3210–3217.

(23) Richardson, J. F.; Payne, N. C. *Inorg. Chem.* **1978**, *17*, 2111–2114.

(24) In contrast, a short >S–Cu distance (2.311 Å) is observed in [1,8-bis-(2-pyridyl)-3,6-dithiaoctane]copper(II) perchlorate, for which the $S(\sigma) \rightarrow$ copper(II) LMCT transition occurs at 360 nm with ϵ = 5560.[22] For the structure, see: Brubaker, G. R.; Brown, J. N.; Yoo, M. K.; Kinsey, R. A.; Kutchan, T. N.; Mottel, E. A. *Inorg. Chem.* **1979**, *18*, 299–302.

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

N-Cu-Br	166.1 (2)	Cu-S(2)-C(6)	107.8 (5)
N-Cu-S(1)	86.3 (2)	Cu-S(2)-C(7)	108.5 (5)
N-Cu-S(2)	91.5 (3)	C(6)-S(2)-C(7)	99.5 (7)
N-Cu-O(1)	71.7 (3)	Cu-O(1)-C(3)	103.9 (6)
Br-Cu-S(1)	94.7 (1)		
Br-Cu-S(2)	98.6 (1)	C(3)-O(2)-C(5)	117.0 (7)
Br-Cu-O(1)	98.5 (2)	C(1)-C(1)-N	116.3 (9)
S(1)-Cu-S(2)	129.2 (1)	C(1)-C(1)-S(1)	116.5 (8)
S(1)-Cu-O(1)	135.8 (2)	N-C(1)-S(1)	127.1 (9)
S(2)-Cu-O(1)	90.2 (2)		
Cu-N-C(1)	122.6 (6)	N-C(2)-C(3)	106.7 (7)
Cu-N-C(2)	117.8 (6)	N-C(2)-C(4)	111.6 (9)
C(1)-N-C(2)	119.5 (8)	C(3)-C(2)-C(4)	108.4 (8)
Cu-S(1)-C(1)	97.7 (4)	C(2)-C(3)-O(1)	124.4 (8)
		C(2)-C(3)-O(2)	109.5 (7)
		O(1)-C(3)-O(2)	126.1 (8)
		C(2)-C(4)-C(6)	115.4 (9)
		C(4)-C(6)-S(2)	113.5 (9)

Table VI. Mean Least-Squares Planes[a]

atom	dist, Å	atom	dist, Å
Plane 1 Equation: $-0.88296x + 0.15966y + 0.44146z - 3.92721 = 0$			
S(1)*	0.000 (5)	Cu	−0.287 (2)
S(2)*	0.000 (5)	N	1.602 (13)
O(1)*	0.000 (14)	Br	−2.617 (2)
Plane 2 Equation: $0.45925x + 0.84242y + 0.28181z - 3.5512 = 0$			
N*	−0.003 (7)	C(1)′*	−0.010 (9)
N′*	0.003 (7)	Cu	−0.176 (1)
S(1)*	0.002 (3)	S(2)	−2.144 (3)
S(1)′*	−0.002 (3)	Br	0.176 (1)
C(1)*	0.010 (9)		

[a] Asterisks denote atoms included in the calculation of the plane.

amide groups have been lost and that the CO groups are strongly coordinated as represented in the proposed structure for **8**. For the *N*,*N*′-(1,2-dithioxoethane-1,2-diyl)bis(methyl methionine) complexes **10–12**, the infrared spectra show the deprotonation of the thioamide groups and the weak coordination of the carbonyl groups of the ester functions.

Crystal Structure of $Cu_2DT(metOMe)_2Br_2$ (11). The structure of **11** is made up of isolated centrosymmetrical binuclear units. A view of this structure is shown in Figure 1. Bond lengths and bond angles are given in Tables IV and V.

The better description of the environment of each copper(II) ion is that of a distorted trigonal bipyramid. The two sulfur atoms S(1) and S(2) and the atom O(1) of the ester group of the ligand **9** form the equatorial plane; the nitrogen and bromide atoms occupy the apical positions. The metal atom lies 0.287 (5) Å out of the trigonal plane on the same side as the bromide atom (see Table VI). The trigonal axis does not show too much distortion from linearity, ∠NCuBr being 166.1 (2)°. However, the angles in the equatorial plane depart significantly from the theoretical 120° value, with values 90.2 (2), 129.2 (1), and 135.8 (2)°. Moreover, the Cu–O(1) bond length in the equatorial plane, which involves the lightest atom, is larger than the two Cu–S bond lengths. This means that the atom O(1) of the ester group is much more weakly bound to the metal than the atom S(2) of the thioether group.

An alternative description of the environment of the metal ion would be that of a strongly distorted square-based pyramid with O(1) in an apical position. However, N, S(1), S(2), and Br are far from being coplanar, S(2) lying more than 2 Å below the NS(1)Br plane.

The two copper(II) ions are bridged by the C(1), C(1)′, S(1), S(1)′, N, and N′ atoms of the dithiooxamide ligand. These atoms are coplanar, their deviation with regard to the mean plane being less than 0.01 Å. The two metal ions lie ±0.176 (1) Å out of this plane (see Table VI). The Cu···Cu separation is 5.666 (3) Å.

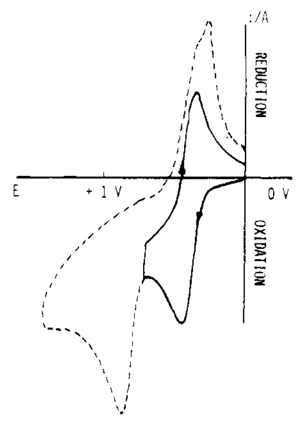
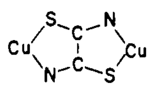


Figure 2. Cyclic voltammogram at 20 °C of a 3 × 10^{-3} M solution of $Cu_2DT(glyglyEtOH)_2(NBu_4)_2 \cdot 2H_2O$ (**6**) at a carbon electrode (scan rate 50 mV s^{-1}) in CH_2Cl_2.

The structure of **11** significantly differs from that of a previously described copper(II) binuclear complex with a derivative of dithiooxamide, namely $\{Cu_2[C_2S_2(NCH_2CH_2OH)_2](H_2O)_2\}(SO_4)$.[2] In this latter compound, the environment of the metal ions is a genuine square-based pyramid, and the two basal planes are coplanar. On the other hand, in both compounds, the bridging networks



are quite similar with bond lengths equal within 0.03 Å. The Cu···Cu separation is 5.61 (1) Å in $\{Cu_2[C_2S_2(NCH_2CH_2OH)_2](H_2O)_2\}(SO_4)$ (5.666 (3) Å in **11**). As for the separation between the S and N atoms bound to the same C atom of the bridge, which was postulated to play a key role in the magnetic properties, it is equal to 2.686 (13) Å in **11** and 2.674 (6) Å in $\{Cu_2[C_2S_2(NCH_2CH_2OH)_2](H_2O)_2\}(SO_4)$.

Electrochemical Properties

The electrochemical properties of three compounds were investigated, namely **6**, **10**, and **11**.

Figure 2 shows the cyclic voltammogram for the oxidation of $Cu_2DT(glyglyEtOH)_2(NBu_4)_2$ (**6**) in CH_2Cl_2 containing 0.2 M of NBu_4PF_6 at a glassy-carbon electrode. The oxidation of **6** occurs in two successive steps at 0.42 and 0.85 V vs. SCE. The first step appears to be totally reversible (ΔE^p = 80 mV, $I_{ox}{}^p/I_{red}{}^p = 1$) even for scan rates of 0.02 V s^{-1}. The second step is irreversible even for scan rates of 10 V s^{-1}. A coulometric experiment indicates that one electron is involved in each step. The cyclic voltammetry performed after the electrolysis, on the plateau of the first oxidation wave, does not show any cathodic peak around 0.4 V, indicating that the first electron transfer is chemically irreversible. On the time scale of the electrolysis, a chemical reaction takes place after the one-electron oxidation leading to the decomposition of the $Cu^{II}Cu^{III}$ mixed-valence complex that has been generated (an EC process). The chemical instability of this mixed-valence complex is confirmed by the bulk electrolysis. The electrogenerated products are metallic copper and polymeric copper(II) rubeanate. These results are consistent with the following scheme, where D denotes here the ligand DT(glyglyEtOH)$^{6-}$ involved in **6**:

$$Cu^{II}Cu^{II}D^{2-} \underset{}{\overset{E_1 = 0.42\ V}{\rightleftharpoons}} e^- + Cu^{II}Cu^{III}D^-$$

$$Cu^{II}Cu^{III}D^- \xrightarrow{E_2 = 0.85\ V} e^- + Cu^{III}Cu^{III}D$$

On the electrolysis time scale

$$\mathrm{Cu^{II}Cu^{III}D^-} \rightarrow \mathrm{Cu} + [\mathrm{CuC_2S_2(NR)_2}]_n$$

Therefore, $\mathrm{Cu^{II}Cu^{III}D^-}$ is chemically instable. It decomposes, probably through an internal oxidation–reduction process occurring between Cu(III) and the ligand; indeed, when the electrolysis is performed in an EPR cavity, a signal corresponding to a short-lived organic radical (g = 2.006) is detected.

$\mathrm{Cu_2DT(metOMe)_2X_2}$ (**11** and **12**) exhibits very similar electrochemical behaviors. Figure 3 shows the cyclic voltammogram for the reduction of **11** in $\mathrm{CH_2Cl_2}$/0.2 M $\mathrm{NBu_4PF_6}$ at a glassy-carbon electrode. There is one CV wave in the +1 to −1.7 V range corresponding to a one-electron-transfer process. The half-wave potential measured at the carbon rotating-disk electrode is around 0.14 V for both **11** and **12**. Cyclic voltammetry reveals the corresponding anodic peaks around 0.2 V. The high peak rate $I_{\mathrm{ox}}/I_{\mathrm{red}}$ is less than unity, even for scan rates of 10 V $\mathrm{s^{-1}}$, indicating that the electron transfer is only slightly reversible. In the return scan, two new peaks are detected, around 0.4 and 0.9 V, respectively. Further experiments show that the anodic peak at 0.9 V corresponds to the oxidation of the free halide $\mathrm{X^-}$. Repetitive cyclic voltammetry indicates that the process corresponding to the 0.4 V anodic peak is reversible. This, together with the coulometric experiments, is consistent with the following sequence taking place under CV conditions, where D now denotes the ligand $\mathrm{DT(metOMe)_2}^{2-}$ involved in **10** (X = Cl) and **11** (X = Br):

$$\mathrm{Cu^{II}Cu^{II}DX_2} + e^- \xrightleftharpoons{E\,=\,0.14\ \mathrm{V}} \mathrm{Cu^{II}Cu^{I}DX_2^-}$$

$$\mathrm{Cu^{II}Cu^{I}DX_2^-} \rightarrow \mathrm{Cu^{II}Cu^{I}DX} + \mathrm{X^-}$$

$$\mathrm{Cu^{II}Cu^{I}DX} \xrightleftharpoons{E\,=\,0.4\ \mathrm{V}} e^- + \mathrm{Cu^{II}Cu^{II}DX^+}$$

On the electrolysis time scale, the mixed-valence complex $\mathrm{Cu^{II}Cu^{I}DX}$ is unstable; we were unable to record its EPR spectrum.

Magnetic Properties

The temperature dependences of the molar magnetic susceptibility χ_M for the compounds **5**, **6**, **10**, and **11** were investigated in the 300–50 K temperature range. The four magnetic curves are qualitatively similar. At room temperature, χ_M is in the range 600 × 10^{-6}–800 × 10^{-6} $\mathrm{cm^3\ mol^{-1}}$. When the samples are cooled, χ_M decreases, reaches a minimum around 160 K, and then increases again with a Curie law behavior at low temperature. As a typical example, the magnetic behavior of **11** is displayed in Figure 4. This behavior is characteristic of copper(II) binuclear complexes with a very large antiferromagnetic interaction and a small proportion ρ of noncoupled copper(II) impurity giving the Curie tail at low temperature. χ_M may then be expressed according to

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

where J is the singlet–triplet energy gap and the other symbols have their usual meaning. We assumed that the molecular weight of the impurity is the same as that of the actual compound, so that C is equal to $N\beta^2g^2/2k$. The J, g, ρ, and $N\alpha$ parameters were introduced in the fitting procedure and determined by minimixing the R factor defined as $\sum(\chi_M^{\mathrm{obsd}} - \chi_M^{\mathrm{calcd}})^2/\sum(\chi_M^{\mathrm{obsd}})^2$. The results for J and g are gathered in Table VII. The somewhat too large values for g could be due to the fact that the hypothesis on the expression of C is incorrect. However, it must be noticed that this is without influence on the J values.

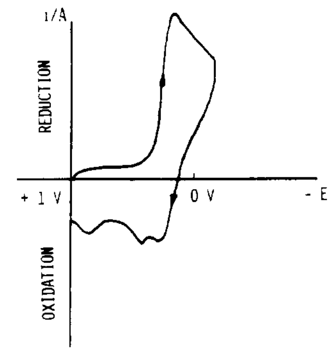


Figure 3. Cyclic voltammogram at 20 °C of a 3 × 10^{-3} M solution of $\mathrm{Cu_2DT(metOMe)_2Cl_2}$ (**10**) at a carbon electrode (scan rate 100 mV $\mathrm{s^{-1}}$) in $\mathrm{CH_2Cl_2}$.

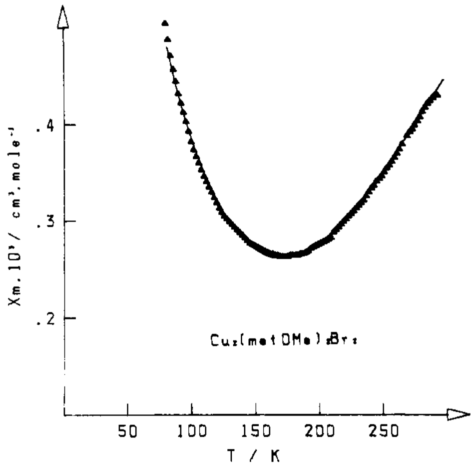


Figure 4. Experimental (▲) and theoretical (—) temperature dependence of the molar magnetic susceptibility of $\mathrm{Cu_2DT(metOMe)_2Br_2}$ (**11**).

Table VII

	J/cm^{-1}	g	R
5	−687	2.29	7.9 × 10^{-4}
6	−566	2.29	3.8 × 10^{-4}
10	−650	2.29	5 × 10^{-5}
11	−730	2.25	8 × 10^{-5}

The singlet–triplet energy gaps in **5**, **6**, **10**, and **11** are similar to the values already obtained for other copper(II) binuclear complexes with derivatives of dithiooxamide.[2–4,25] The strong interaction in spite of the large intramolecular Cu···Cu separation was interpreted in the frameworks of both a semiempirical approach[2,25] and an ab initio calculation.[26,27] The cornerstone of the phenomenon is the overlap of the two magnetic orbitals centered on the two metallic centers. This overlap is favored by both the planarity of the $\mathrm{CuC_2S_2N_2Cu}$ network and the large diffuseness of the sulfur valence orbitals. The structures of **5** and **6** are not known with accuracy. On the other hand, the crystal structure of **11** was refined. It shows that the surroundings of the copper(II) ions are strongly distorted with regard to the square-based pyramid. Nevertheless, the magnitude of the interaction remains unchanged;

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(25) Kahn, O.; Girerd, J. J. In "Sulfur: The Significance for Chemistry, for the Geo-, Bio-, and Cosmophere and Technology"; Müller, A., Krebs, B., Eds.; Elsevier: Amsterdam, 1984, pp 195–220.

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(27) Charlot, M. F.; Verdaguer, M.; Journaux, Y.; de Loth, P.; Daudey, J. P. *Inorg. Chem.* **1984**, *23*, 3802.

(28) Julve, M.; Verdaguer, M.; Gleizes, A.; Philloche-Levisalles, M.; Kahn, O. *Inorg. Chem.* **1984**, *23*, 3808.

in spite of the distortion, the bridging network $CuC_2S_2N_2Cu$ remains planar with short Cu–N and Cu–S bond lengths. An extended Hückel calculation on the fivefold-coordinated chromophore confirmed that the spin density around each metal center is strongly delocalized toward the nitrogen and sulfur bridging atoms.

The powder EPR spectrum of **11** was recorded. At room temperature, it exhibits an almost symmetrical feature centered at $g = 2.10$ (8), the intensity of which decreases when the sample is cooled as expected for a triplet excited state situated at 730 cm^{-1} above the diamagnetic ground state. Around 120 K, the signal vanishes and the spectrum only shows the signal corresponding to the monomeric impurity detected in magnetism.

Conclusion

We synthesized three novel binucleating dithiooxamide derivatives and from them several copper(II) binuclear complexes.

The magnetic properties of these complexes are quite similar. All exhibit a strong antiferromagnetic interaction with singlet–triplet energy gaps around 600 cm^{-1}. This result confirms the specific ability of the dithiooxamide bridge to propagate the electronic effects between copper(II) ions far away from each other. It is noteworthy that the magnitude of the interaction remains unchanged in $Cu_2DT(metOMe)_2X_2$ (**10** and **11**), where the environments of the metal centers are trigonal bipyramidal instead of coplanar. In other words, the modification of the geometry of the chromophores does not lead to a reversal of the magnetic orbitals, in contrast with what happens in the μ-oxalato copper(II) binuclear complexes.[28]

As opposed to the magnetic properties, the redox properties present great differences. They are strongly influenced by the nature of the amino acid amides of dithiooxalic acid. While $[Cu_2DT(glyglyEtOH)_2]^{2-}(NBu_4)_2\cdot 2H_2O$ (**6**) does not show any reduction step between 0 and −1.7 V (vs. SCE), $Cu_2DT(metOMe)_2X_2$ (**10** and **11**) is very easily reduced. On the other hand, **6** can be reversibly oxidized to the $Cu^{II}Cu^{III}$ species, which unfortunately is chemically unstable. These differences are essentially due to the presence of donating nitrogen atoms in the peptide derivative and to that of a withdrawing sulfur atom in the methionine methyl ester derivatives.

Finally, we wish to emphasize that the compound $Cu_2DT(metOMe)_2Br_2$ (**11**) is the first one in which the coordination of the sulfur atom of the methionine has been structurally characterized.

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

Registry No. **1**, 92957-64-7; **2**, 3916-40-3; **3**, 2641-02-3; **4**, 92957-65-8; **5**, 92957-68-1; **6**, 92984-11-7; **7**, 92957-66-9; **8**, 92957-69-2; **9**, 92957-67-0; **10**, 92957-70-5; **11**, 92984-12-8; **12**, 92984-13-9; phthalic anhydride, 85-44-9; glycylglycine, 556-50-3; dithiooxamide, 79-40-3; methionine, 63-68-3; ethanolamine, 141-43-5.

Supplementary Material Available: Listings of structure factor amplitudes and anisotropic thermal parameters for **11** (7 pages). Ordering information is given on any current masthead page.

Contribution from the Laboratoire de Spectrochimie des Eléments de Transition, ERA No. 672,
Université de Paris-Sud, 91405 Orsay, France, and Laboratoire de Chimie Structurale des Matériaux,
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Crystal Structure and Magnetic Properties of $[Cu_2(tmen)_2(N_3)_3](PF_6)$ (tmen = *N,N,N′,N′*-Tetramethylethylenediamine): A Copper(II) Chain Compound with both Single Symmetrical and Double Dissymmetrical End-to-End Azido Bridges

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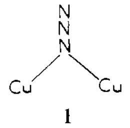
The title compound has been synthesized, and its crystal structure has been solved at room temperature. It crystallizes in the monoclinic system, space group $P2_1/c$. Its lattice constants are $a = 12.713$ (1) Å, $b = 31.240$ (4) Å, $c = 13.259$ (6) Å, and $\beta = 102.17$ (2)° with $Z = 8$ binuclear units. The structure consists of zigzag chains of binuclear cations $[Cu_2(tmen)_2(N_3)_3]^+$ parallel to the c direction and noncoordinated PF_6^- anions. Within the binuclear unit, the copper atoms are bridged by a single azido group in a symmetrical end-to-end fashion with a Cu···Cu mean separation of 4.439 Å. The binuclear units are linked to each other by a double dissymmetrical end-to-end azido bridge with a Cu···Cu mean separation of 5.131 Å. Each copper atom is surrounded by five nitrogen atoms, two from tmen (=*N,N,N′,N′*-tetramethylethylenediamine) and three from the azido groups, occupying the vertices of a slightly distorted square-based pyramid. The two basal planes within a binuclear unit make a mean dihedral angle of 46°. The magnetic properties of the title compound have been investigated in the 30–300 K temperature range. The molar magnetic susceptibility very closely follows the behavior expected for an antiferromagnetically coupled copper(II) binuclear complex with a singlet–triplet energy gap $J = -308.6$ cm^{-1}. The X-band powder EPR spectrum is poorly resolved. It exhibits a resonance in the triplet excited state that vanishes at low temperature. It is shown that the interaction occurs through the symmetrical azido bridge. Its mechanism is discussed, and the concept of spin polarization effect is recalled.

Introduction

The variety of molecular architecture of (μ-azido)copper(II) binuclear complexes leads to a large range of magnetic properties.[2]

When N_3^- bridges in the end-on fashion, as in **1**, the ferromagnetic interaction is favored. Two complexes with two



1

end-on azido bridges have already been described. Both exhibit a spin triplet ground state with a relatively large triplet–singlet

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[2] Magnetostructural correlations in exchange-coupled systems: Gatteschi, D., Kahn, O., Willett, R. D., Eds. *NATO Adv. Study Inst. Ser. C*, in press.

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