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Reactions of Copper(II) Halides (Chloride, Bromide) with the Sulfur-Rich Donor 1,3-Dithiacyclohexane-2-thione (ptc). Synthesis, Crystal Structures, and Characterization of Three Different Copper Compounds: Trinuclear Mixed-Valence $[Cu^{I}_{2}Cu^{II}(ptc)_{4}Cl_{4}]$, Polynuclear $[Cu^{I}_{2}(ptc)Br_{2}]_{n}\cdot(n/2)$THF, and Dinuclear $[Cu^{I}_{2}(ptc)_{4}Br_{2}]$

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Introduction

Cu(II) → Cu(I) reduction is greatly affected by a variety of geometrical and electronic factors: the ligand environment at the metal center, the metal ion stereochemistry, and the nature of the solvent.[1] In particular, it is known that soft bases, such as the sulfur donors, generate a favorable thermodynamic situation for reduction.[2]

We are investigating the coordination of copper(II) halides by a series of polyfunctional sulfur-rich ligands, where the versatility of sulfur donors (which can act as terminal or bridging ligands), coupled with the capability of halide ions to act as terminal or bridging ligands, may produce a variety of stereochemical environments able to stabilize copper(II),[3] copper(I),[4] or mixed-valence derivatives.

In the case of the ligand 1,3-dithiolane-2-thione (dtt), only Cu(I) derivatives have been obtained.[5] The crystal structure of $[Cu_{2}(dtt)Cl_{2}]_{n}$ has shown that two distinct polymeric chains –Cu–Cl–Cu–Cl–, one distorted tetrahedral and the other trigonal in coordination and both held together by the triply bridging μ_3-S ligand through the exocyclic sulfur, are formed.[5]

When one more CH_2 group (ptc) is introduced into the 1,3-dithiolane-2-thione ring and the trithiocarbonate is left group unchanged, significant changes are produced in the final products: the title compounds, including the mixed-valence trimer $[Cu^{I}_{2}Cu^{II}(ptc)_{4}Cl_{4}]$ (I), are obtained.

Experimental Section

Synthesis of the Complexes. Reagents and solvents of reagent grade quality were used as furnished by Aldrich. **1,3-Dithiacyclohexane-2-thione** (ptc) was prepared according to the literature.[6] Anal. Calcd for $C_4H_6S_3$: C, 31.97; H, 4.02; S, 64.00. Found: C, 32.14, H 3.92, S 65.19.

Table 1. Crystallographic Data for $[Cu^{I}_{2}Cu^{II}(ptc)_{4}Cl_{4}]$ (I)

formula: $C_{16}H_{24}Cl_{4}Cu_{3}S_{12}$	$\mu = 132.13$ cm^{-1}
fw = 933.536	temp = 295 K
crystal system: $P2_1/n$ (No. 14)	θ range: 3–70°
$a = 8.756(5)$ Å	scan speed: 2.5–12° min^{-1}
$b = 22.414(7)$ Å	scan width: $(1.20 + 0.142 \tan\theta)°$
$c = 8.580(5)$ Å	no. of measd data: 3147
$\beta = 112.85(2)°$	no. of obsd data: 2340 ($I > 2\sigma(I)$)
$V = 1552(1)$ Å^3	no. of params: 211
$Z = 2$	R; R_w:[a] 0.0405; 0.0585
d(calcd) = 1.99 g/cm^3	weighting scheme: $w = 0.1642/[\sigma^2(F_o) + 0.013075F_o^2]$
λ(Cu Kα): 1.541 838 Å	

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

Table 2. Crystallographic Data for $[Cu^{I}_{2}(ptc)Br_{2}]_{n}\cdot(n/2)$THF (II)

formula: $C_{6}H_{10}Br_{2}Cu_{2}S_{3}O_{0.5}$	temp = 295 K
fw = 473.225	θ range: 3–70°
crystal system: *Fdd*2 (No. 43)	scan speed: 2.5–12° min^{-1}
$a = 25.939(5)$ Å	scan width: $(1.20 + 0.142 \tan\theta)°$
$b = 27.516(5)$ Å	no. of measd data: 1286
$c = 6.947(6)$ Å	no. of obsd data: 771 ($I > 2\sigma(I)$)
$V = 4958(4)$ Å^3	no. of params: 116
$Z = 16$	R; R_w:[a] 0.0341; 0.0460
d(calcd) = 2.54 g/cm^3	weighting scheme: $w = 0.2020/[\sigma^2(F_o) + 0.006861F_o^2]$
λ(Cu Kα): 1.541 838 Å	
$\mu = 162.22$ cm^{-1}	

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

Table 3. Crystallographic Data for $[Cu^{I}_{2}(ptc)_{4}Br_{2}]$ (III)

formula: $C_{16}H_{24}Br_{2}Cu_{2}S_{12}$	$\mu = 127.15$ cm^{-1}
fw = 887.986	temp = 295 K
crystal system: $P2_1/c$ (No. 14)	θ range: 3–70°
$a = 9.123(5)$ Å	scan speed: 2.5–12° min^{-1}
$b = 10.797(6)$ Å	scan width: $(1.20 + 0.142 \tan\theta)°$
$c = 15.857(7)$ Å	no. of measd data: 2941
$\beta = 106.28(2)°$	no. of obsd data: 2369 ($I > 2\sigma(I)$)
$V = 1499(1)$ Å^3	no. of params: 146
$Z = 2$	R; R_w:[a] 0.0523; 0.0748
d(calcd) = 1.95 g/cm^3	weighting scheme: $w = 1.0000/[\sigma^2(F_o) + 0.004715F_o^2]$
λ(Cu Kα): 1.541 838 Å	

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

$[Cu^{I}_{2}Cu^{II}(ptc)_{4}Cl_{4}]$ (I). This compound was prepared by refluxing for 20 min under N_2 a THF solution (25 mL) of anhydrous $CuCl_2$ (44.8 mg) with a THF solution (25 mL) of ptc in a 1:2 molecular ratio. The solution became orange-yellow. On long standing (4 weeks), the solution turned yellow and well-formed brown crystals precipitated. The solid was collected and washed with methanol/diethyl ether. Anal. Calcd for $Cu_3(ptc)_4Cl_4$: C, 20.59; H, 2.59; S 41.21. Found: C, 20.67; H, 2.62; S, 41.31. Diffuse-reflectance spectrum (cm^{-1} × 10^3), KBr pellet: 10.5 w, 12.5 w, 23.8 vs, 30.0 vs, 41.0 m.

$[Cu^{I}_{2}(ptc)Br_{2}]_{n}\cdot(n/2)$THF (II). II was prepared following the same procedure described above for the Cl derivative, by reacting $CuBr_2$ (74mg) with ptc in a 1:2 molecular ratio. Shining brown crystals separated from the orange-red mother liquor (50 mL) after 3 weeks. Anal. Calcd for $Cu_2(ptc)Br_2\cdot{}^1/_2$THF: C, 15.23; H, 2.13; S, 20.33. Found: C, 15.51; H, 2.04; S, 20.12.

$[Cu^{I}_{2}(ptc)_{4}Br_{2}]$ (III). III was obtained when CH_3CN instead of THF was used as solvent. After 20-min reflux, the dark green solution, left to the air, turned orange-red, giving ruby-colored crystals on slow evaporation of the solvent (2 weeks). The crystals were washed by using the usual procedure. The same compound was obtained by starting from CuBr. Anal. Calcd for $Cu(ptc)_2Br$: C, 21.64; H, 2.72; S, 43.33. Found: C, 21.75; H, 2.71; S, 43.13.

X-ray Structure Determination. A summary of the crystallographic data is given in Tables 1–3 for compounds I–III, respectively. Crystals of approximate dimensions 0.33 × 0.17 × 0.15, 0.15 × 0.08 × 0.05, and 0.53 × 0.29 × 0.23 mm were utilized for I–III, respectively. All diffraction measurements were made on a Siemens AED diffractometer with Ni-

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Table 4. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters ($Å^2 \times 10^4$) (One-Third the Trace of the Diagonalized Matrix), with Esd's in Parentheses, for **I**

atom	*x/a*	*y/b*	*z/c*	U_{eq}
Cu(1)	5000	5000	0	254(3)
Cu(2)	5618.8(8)	3741.9(3)	1886.8(9)	360(3)
Cl(1)	3581.8(12)	4546.5(5)	1408.3(14)	303(3)
Cl(2)	7404.5(11)	4506.0(5)	1741.0(14)	309(3)
S(1)	4344.8(13)	3092.6(5)	−361.6(14)	309(4)
S(2)	1926.5(15)	3114.8(6)	−3771.0(16)	414(4)
S(3)	4580.4(12)	4079.2(5)	−2423.4(13)	274(3)
S(4)	5985.0(15)	3119.5(5)	4043.8(14)	371(4)
S(5)	8085.4(13)	4054.4(5)	6168.9(14)	327(4)
S(6)	7518.4(15)	2854.3(5)	7549.4(15)	359(4)
C(1)	3605(4)	3440(2)	−2232(5)	240(13)
C(2)	1374(7)	3574(3)	−5662(7)	473(19)
C(3)	1684(6)	4233(3)	−5328(7)	398(18)
C(4)	3507(6)	4377(2)	−4544(6)	325(15)
C(5)	7209(5)	3362(2)	5967(5)	248(13)
C(6)	9300(7)	4188(3)	8410(7)	407(18)
C(7)	10023(6)	3635(3)	9439(7)	401(17)
C(8)	8703(5)	3217(2)	9540(6)	339(16)

filtered Cu Kα radiation. Accurate unit-cell parameters were obtained by least-squares treatment of the setting angles of 30 reflections in the θ ranges 18–40, 12–40, and 18–38° for **I–III**, respectively. The data were collected using the θ-2θ scan method. The check of the standard reflections showed no significant decrease. The space groups were unambiguously deduced from systematic absences. Intensity data were corrected for Lorentz and polarization factors and for absorption (maximum and minimum values: 1.2299 and 0.8395 for **I**, 1.1856 and 0.8050 for **II**, 1.2552 and 0.7870 for **III**) by following the empirical method of Walker and Stuart.[7] The structures were solved by Patterson and Fourier methods. Blocked-matrix least-squares refinement for compound **I** and full-matrix least-squares refinement for compounds **II** and **III** were carried out initially with isotropic thermal parameters for all atoms, followed by anisotropic thermal parameters for all non-hydrogen atoms, excluding those of the solvent molecule in **II**. The latter molecule was found to be disordered and to have the two carbon atoms bonded to the oxygen atom lying on a 2-fold axis. The corresponding atoms out of the 2-fold axis were inserted into two positions with site occupancy factors of 0.50. In compound **I** the hydrogen atoms were located from a ΔF map, and their coordinates were introduced in the last cycle. The coordinates of the hydrogen atoms in compounds **II** and **III**, placed at their geometrically calculated positions, were not refined and were introduced in the final structure factor calculation with the constrain C-H = 0.96 Å and with a unique refined isotropic thermal parameters [U = 0.0827(232) and 0.1313(119) $Å^2$ for **II** and **III**, respectively]. The hydrogen atoms of tetrahydrofuran in **II** were not considered. Scattering factors and corrections for anomalous dispersion effects were from ref 8. Calculations were carried out on a Gould Powernode 6040 computer at the Centro di Studio per la Strutturistica Diffrattometrica del CNR (Parma, Italy). The system of computer programs SHELX 76[9] and the programs ABSORB,[10] PARST,[11] PLUTO,[12] and ORTEP[13] were used. Final atomic coordinates are reported in Tables 4–6; selected bond distances and angles, in Tables 7–9.

Physical Measurements. X-Band EPR spectra were obtained at room and liquid N_2 temperatures with a Varian E9 spectrometer equipped with a cryostat for low-temperature measurements. Magnetic susceptibility was measured by a Quantum Design SQUID magnetometer, Model MPMS, down to 4.2 K. The polycrystalline sample was fixed inside a cellulose capsule which was inserted into a long polyethylene tube. This tube was then placed in the sample holder. An external magnetic field of up to 5 T was supplied by a superconducting solenoid. Temperature measurements were based on a calibrated carbon glass resistor up to 40 K and on a Pt sensor above this temperature. The magnetic susceptibility data were corrected for diamagnetism as calculated from the known diamagnetic susceptibility of the constituents of the title compounds, i.e. -4.5972×10^{-4} emu/mol.

Table 5. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters ($Å^2 \times 10^4$) (One-Third the Trace of the Diagonalized Matrix), with Esd's in Parentheses, for **II**

atom	*x/a*	*y/b*	*z/c*	U_{eq}
Cu(1)	−712(1)	2874(1)	−895(6)	521(8)
Cu(2)	−762(1)	2776(1)	4205(6)	487(8)
Br(1)	−1328(1)	2639(1)	1536	455(5)
Br(2)	−1011(1)	3383(1)	6547(4)	520(5)
S(1)	110(1)	2726(1)	3693(7)	398(12)
S(2)	−163(2)	3486(1)	1007(7)	436(13)
S(3)	909(1)	3010(1)	1025(7)	415(13)
C(1)	288(5)	3086(5)	1929(25)	360(47)
C(2)	158(7)	3877(7)	−773(38)	646(68)
C(3)	556(7)	3611(7)	−2017(31)	628(73)
C(4)	1030(6)	3469(6)	−757(33)	512(55)
O	328(15)	5186(15)	4017(75)	2208(123)
C(5)	0	5000	2360(63)	1463(144)
C(6)	−344(13)	4601(12)	2913(51)	453(76)
C(7)	−103(16)	4539(15)	4651(62)	697(116)
C(8)	0	5000	5614(60)	1125(115)

Table 6. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters ($Å^2 \times 10^4$) (One-Third the Trace of the Diagonalized Matrix), with Esd's in Parentheses, for **III**

atom	*x/a*	*y/b*	*z/c*	U_{eq}
Cu	103(1)	1326(1)	5467(1)	425(3)
Br	525(1)	720(1)	3997(0)	421(2)
S(1)	2102(1)	2355(1)	6372(1)	340(4)
S(2)	5352(2)	2469(2)	6957(1)	628(6)
S(3)	3709(2)	126(1)	6144(1)	540(5)
S(4)	−1996(2)	2585(1)	4866(1)	551(5)
S(5)	−3094(3)	5067(1)	4768(1)	733(7)
S(6)	−986(2)	4051(2)	6464(1)	538(5)
C(1)	3744(5)	1610(4)	6488(3)	298(13)
C(2)	7025(6)	1460(7)	7155(5)	587(23)
C(3)	6700(7)	127(6)	7233(4)	536(21)
C(4)	5668(7)	−392(7)	6390(5)	593(23)
C(5)	−1998(5)	3923(5)	5384(3)	350(15)
C(6)	−3184(10)	6404(6)	5449(4)	651(26)
C(7)	−2739(9)	6160(6)	6415(4)	587(23)
C(8)	−1187(8)	5655(7)	6767(4)	647(25)

Table 7. Selected Bond Distances (Å) and Angles (deg), with Esd's in Parentheses, for **I**

Cu(1)–Cl(1)	2.281(1)	S(3)–C(4)	1.820(5)
Cu(1)–Cl(2)	2.334(1)	S(4)–C(5)	1.671(4)
Cu(1)–S(3)	2.850(2)	S(5)–C(5)	1.710(4)
Cu(2)–Cl(1)	2.456(2)	S(5)–C(6)	1.825(5)
Cu(2)–Cl(2)	2.355(2)	S(6)–C(5)	1.710(5)
Cu(2)–S(1)	2.326(2)	S(6)–C(8)	1.811(5)
Cu(2)–S(4)	2.239(2)	C(2)–C(3)	1.510(8)
S(1)–C(1)	1.672(4)	C(3)–C(4)	1.506(7)
S(2)–C(1)	1.712(4)	C(6)–C(7)	1.511(8)
S(2)–C(2)	1.821(6)	C(7)–C(8)	1.517(8)
S(3)–C(1)	1.707(4)		
Cl(1)–Cu(1)–Cl(2)	89.5(1)	Cu(2)–S(4)–C(5)	116.4(2)
Cl(1)–Cu(1)–S(3)	97.0(1)	C(5)–S(5)–C(6)	108.1(3)
Cl(2)–Cu(1)–S(3)	87.3(1)	C(5)–S(6)–C(8)	107.8(2)
S(1)–Cu(2)–S(4)	99.5(1)	S(2)–C(1)–S(3)	126.5(3)
Cl(2)–Cu(2)–S(4)	127.7(1)	S(1)–C(1)–S(3)	117.5(3)
Cl(2)–Cu(2)–S(1)	121.7(1)	S(1)–C(1)–S(2)	116.0(3)
Cl(1)–Cu(2)–S(4)	117.2(1)	S(2)–C(2)–C(3)	114.7(4)
Cl(1)–Cu(2)–S(1)	103.7(1)	C(2)–C(3)–C(4)	112.0(5)
Cl(1)–Cu(2)–Cl(2)	84.9(1)	S(3)–C(4)–C(3)	114.5(4)
Cu(1)–Cl(1)–Cu(2)	84.6(1)	S(5)–C(5)–S(6)	126.6(3)
Cu(1)–Cl(2)–Cu(2)	85.8(1)	S(4)–C(5)–S(6)	114.2(3)
Cu(2)–S(1)–C(1)	112.7(2)	S(4)–C(5)–S(5)	119.1(3)
C(1)–S(2)–C(2)	107.3(3)	S(5)–C(6)–C(7)	114.9(4)
Cu(1)–S(3)–C(4)	109.5(2)	C(6)–C(7)–C(8)	112.6(5)
Cu(1)–S(3)–C(1)	117.7(2)	S(6)–C(8)–C(7)	113.2(4)
C(1)–S(3)–C(4)	108.7(3)		

Diffuse-reflectance spectra for KBr-diluted samples were measured on a Cary 5 spectrophotometer equipped with a diffuse-reflectance accessory.

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Table 8. Bond Distances (Å) and Angles (deg), with Esd's in Parentheses, for **II**[a]

Cu(1)–Br(1)	2.414(4)	S(3)–C(1)	1.74(1)
Cu(1)–Br(2^{i})	2.391(4)	S(2)–C(2)	1.84(2)
Cu(1)–S(1^{iii})	2.291(4)	S(3)–C(4)	1.80(2)
Cu(1)–S(2)	2.571(5)	C(2)–C(3)	1.53(3)
Cu(2)–Br(1)	2.394(4)	C(3)–C(4)	1.56(3)
Cu(2)–Br(2)	2.420(4)	O–C(5)	1.52(6)
Cu(2)–S(1)	2.294(4)	O–C(8)	1.49(6)
Cu(2)–S(3^{iv})	2.533(5)	C(5)–C(6)	1.47(4)
S(1)–C(1)	1.64(2)	C(6)–C(7)	1.37(6)
S(2)–C(1)	1.73(1)	C(7)–C(8)	1.46(5)
Br(1)–Cu(1)–Br(2^{i})	117.5(2)	Cu(1)–S(2)–C(1)	98.5(5)
Br(1)–Cu(1)–S(1^{iii})	110.2(1)	Cu(1)–S(2)–C(2)	106.8(6)
Br(1)–Cu(1)–S(2)	100.5(1)	C(1)–S(2)–C(2)	108.4(8)
Br(2^{i})–Cu(1)–S(1^{iii})	123.4(2)	C(1)–S(3)–Cu(2^{iii})	98.2(5)
S(2)–Cu(1)–Br(2^{i})	100.3(2)	C(4)–S(3)–Cu(2^{iii})	106.4(6)
S(2)–Cu(1)–S(1^{iii})	99.2(2)	C(1)–S(3)–C(4)	109.0(8)
Br(1)–Cu(2)–Br(2)	117.8(2)	S(1)–C(1)–S(2)	118.0(9)
Br(1)–Cu(2)–S(1)	118.4(1)	S(1)–C(1)–S(3)	117.3(8)
Br(1)–Cu(2)–S(3^{iv})	99.2(2)	S(2)–C(1)–S(3)	124.6(8)
Br(2)–Cu(2)–S(3^{iv})	102.3(1)	S(2)–C(2)–C(3)	113.9(14)
Br(2)–Cu(2)–S(1)	114.1(2)	C(2)–C(3)–C(4)	109.5(15)
S(1)–Cu(2)–S(3^{iv})	100.1(2)	S(3)–C(4)–C(3)	115.2(13)
Cu(1)–Br(1)–Cu(2)	95.4(1)	C(5)–O–C(8)	97.4(30)
Cu(2)–Br(2)–Cu(1^{ii})	90.5(1)	O–C(5)–C(6)	113.2(20)
Cu(2)–S(1)–Cu(1^{iv})	134.1(2)	C(5)–C(6)–C(7)	92.6(27)
C(1)–S(1)–Cu(1^{iv})	109.6(5)	C(6)–C(7)–C(8)	112.4(32)
Cu(2)–S(1)–C(1)	110.9(5)	O–C(8)–C(7)	93.5(23)

[a] Key to symmetry operations: (i) $x, y, z - 1$; (ii) $x, y, 1 + z$; (iii) $-x, {}^1/_2 - y, z - {}^1/_2$; (iv) $-x, {}^1/_2 - y, {}^1/_2 + z$.

Table 9. Bond Distances (Å) and Angles (deg), with Esd's in Parentheses, for **III**[a]

Cu–Br	2.552(1)	C(2)–C(3)	1.481(10)
Cu–Br^{i}	2.490(2)	C(3)–C(4)	1.510(9)
Cu–S(1)	2.270(2)	S(4)–C(5)	1.663(5)
Cu–S(4)	2.323(2)	S(5)–C(5)	1.712(5)
S(1)–C(1)	1.665(5)	S(6)–C(5)	1.709(5)
S(2)–C(1)	1.719(5)	S(5)–C(6)	1.818(7)
S(3)–C(1)	1.690(5)	S(6)–C(8)	1.820(7)
S(2)–C(2)	1.829(6)	C(6)–C(7)	1.494(8)
S(3)–C(4)	1.808(7)	C(7)–C(8)	1.473(10)
Br–Cu–Br^{i}	101.1(1)	S(2)–C(2)–C(3)	114.6(5)
Br–Cu–S(1)	113.7(1)	C(2)–C(3)–C(4)	112.1(6)
Br–Cu–S(4)	95.3(1)	S(3)–C(4)–C(3)	114.1(5)
S(1)–Cu–Br^{i}	116.1(1)	C(1)–S(3)–C(4)	107.2(3)
S(4)–Cu–Br^{i}	114.7(1)	Cu–S(4)–C(5)	114.9(2)
S(1)–Cu–S(4)	113.4(1)	S(4)–C(5)–S(5)	115.2(3)
Cu–S(1)–C(1)	111.8(2)	S(4)–C(5)–S(6)	119.4(3)
Cu–Br–Cu^{1}	78.9(0)	S(5)–C(5)–S(6)	125.4(3)
S(1)–C(1)–S(2)	114.8(3)	C(5)–S(5)–C(6)	110.5(3)
S(1)–C(1)–S(3)	119.2(3)	S(5)–C(6)–C(7)	115.1(4)
S(2)–C(1)–S(3)	126.0(3)	C(6)–C(7)–C(8)	114.2(6)
C(1)–S(2)–C(2)	108.8(3)	S(6)–C(8)–C(7)	114.2(5)
		C(5)–S(6)–C(8)	106.0(3)

[a] Key to symmetry operation: (i) $-x, 1 - y, -z$.

Results and Discussion

Crystal Structures. [$Cu^{I}_2Cu^{II}(ptc)_4Cl_4$] (I). The structure of the trinuclear mixed-valence Cu(I)–Cu(II) (2:1) complex and the corresponding atom-labeling scheme are shown in Figure 1. The two independent organic ligands present different behaviors: one coordinates a Cu(I) atom through the thione sulfur and a Cu(II) atom through an endo sulfur and the other is terminal. As the two independent chlorine atoms bridge the two above mentioned Cu atoms and Cu(II) lies on a symmetry center, two six-membered rings with the Cu(1)S(3)C(1)S(1)Cu(2) moiety in common are formed. Cu(II) presents an elongated octahedral coordination (4 + 2 stereochemistry) with two endocyclic S(3) atoms of two bridging ligand molecules at the apices [Cu(1)–S(3) = 2.850(2) Å] and with four bridging chlorine atoms in the equatorial plane. To the best of our knowledge, this is the first example of a $CuCl_4S_2$ polyhedron. The long axial Cu–S_{endo} distance (2.850(2) Å) is not an intrinsic property of the endo sulfur, since the Cu–S_{endo} distances in **II** are 2.533(5) and 2.571(5) Å, but is a consequence of the requirement of the typical Jahn–Teller-distorted coordination sphere for the copper(II) ion.[14] Very similar axial Cu–S distances have been found in bis(1,3-bis(5-phenyl-2-imidazolyl-2-thiapropane))copper(II) diperchlorate (Cu–S = 2.824(5) Å);[15] shorter axial Cu–S distances have been found in [Cu(bidhx)Cl(BF_4)] and [Cu(bidhx)NCS(NO_3)] (bidhx = 1,6-bis(4-imidazolyl)-2,5-dithiahexane) (Cu–S = 2.747(1) and 2.746(4) Å, respectively).[16] A longer Cu–S distance (2.940(1) Å) has been reported for bis(pentafluorothiophenolato)(1,4,8,-11-tetrazacyclotetradecane)copper(II).[17] More weakly axially interacting sulfur donors at the borderline of the nonbonding interactions give rise to Cu–S distances in the 3.1–3.2-Å range.[18,19]

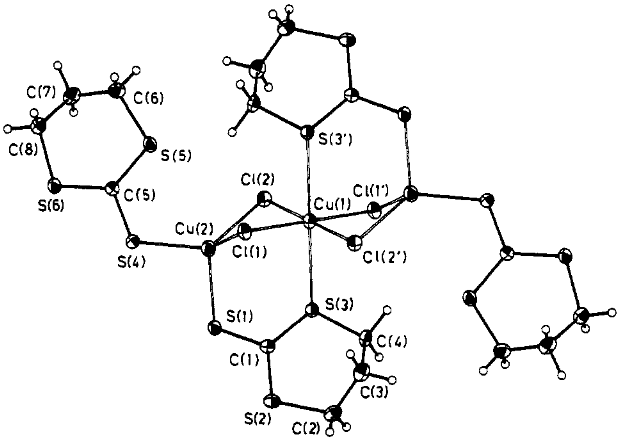

Figure 1. Perspective view of complex **I** (30% probability ellipsoids).

Cu(I) presents a tetrahedral coordination involving the two chlorine atoms and the two independent organic molecules via their thione sulfurs. The Cu–Cl bond distances are asymmetric, and those implied in the coordination of the Cu(I) atom are longer than the others. A similar trend is observed also for the planar-square coordinated bridging chlorine atoms.[20] The Cu(2)–S bond distances are asymmetric, and the longest is that involving the bridging organic molecules. The Cu(1)–Cl–Cu(2) bond angles are smaller than 90° [(84.6(1) and 85.8(1)°]; the Cl(1)–Cu–Cl(2) bond angles are 89.5(1) and 84.9(1)° for Cu(II) and Cu(I), respectively. The interaction between the Cu(I) and Cu(II) atoms is 3.191(1) Å. The S–CSS moieties of the two independent organic molecules are planar and are nearly coplanar, the corresponding dihedral angle being 14.6(1)°. The Cu–S_{thione}–C bond angles are in good agreement with those observed in [$Cu_2(dtt)Cl_2]_n$.[5] With the exception of the contacts Cl(1)···C(4)(x,y,1+z) = 3.520(6) Å and Cl(1)···C(7)(x−1,y,z−1) = 3.556(5) Å, there are no intermolecular contacts smaller than the sum of the van der Waals radii.

[$Cu^{I}_2(ptc)Br_2]_n$·(n/2)THF (II). The structure of this compound (Figure 2) consists of -Cu-Br-Cu-Br- polymeric chains running parallel to c, held together in pairs by the bridging ligand molecule, which acts as a μ-S-tridentate ligand through all sulfur atoms. In fact the thione sulfur is bridging and each of the two Cu atoms

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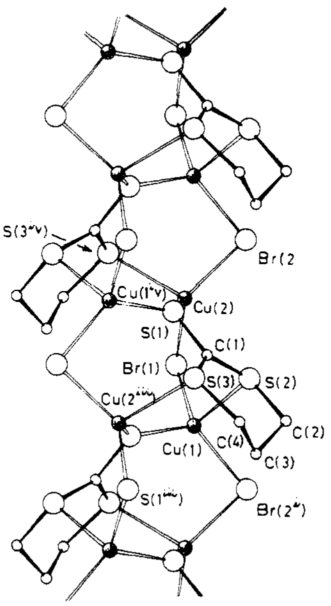

Figure 2. Perspective view of the chain of **II** running parallel to *c*.

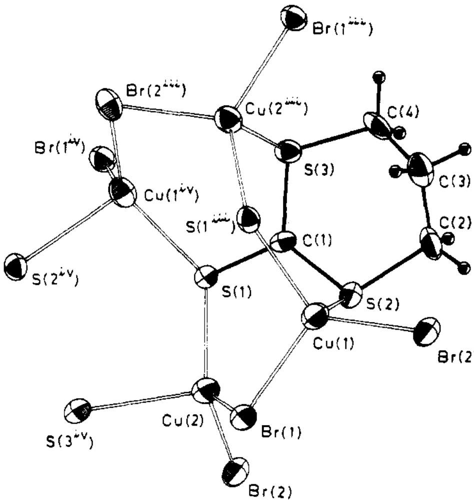

Figure 3. Perspective view of the μ-S tridentate ligand molecule in **II** (30% probability ellipsoids).

bonded to it are in turn bonded to an endo sulfur atom of two different organic molecules. As a consequence, the ptc molecule is bonded to four Cu atoms (Figure 3), which are out of the SCSS plane by 0.402(3), 0.449(3), 2.434(3), and 2.477(3) Å for Cu(2), Cu(1^{iv}), Cu(2^{iii}), and Cu(1), respectively, the larger values being referred to the metal atoms bonded to the endo sulfur. Three six-membered rings are present in the chain Cu(1)S(2)C(1)S(1)Cu(2)Br(1), Cu(1)S(2)C(1)S(3)Cu(2)S(1), and Cu(1)Br(2)Cu(2)S(3)C(1)S(1). In the slightly distorted tetrahedral coordination around each metal atom, two bridging bromide atoms, an exo- and an endocyclic sulfur of two different bridging ligand molecules, are involved. A remarkable asymmetry is observed between the Cu–S_{thione} and Cu–S_{endo} bond distances, and the interaction between the two independent Cu atoms is 3.556(6) Å.

[$Cu^I_2(ptc)_4Br_2$] (III). The structure of this dinuclear complex and the corresponding atom-labeling scheme are shown in Figure 4. The Cu atom presents a tetrahedral coordination involving the bromide atom and the thione sulfur of two ptc molecules, which act as terminal ligands. The dinuclear complex is formed through a symmetry center. The Cu–Br and Cu–S bond distances are slightly asymmetric; the value of the dihedral angle between the two planar CS_3 moieties is 52.5(1)°, and the interaction between the two metal atoms is 3.205(2) Å. The dimensions of the ptc molecules in all compounds are very similar, notwithstanding that these molecules can coordinate with various combinations. The ring in the organic ligand shows a half-boat conformation with the carbon opposite the C–S_{thione} bond, out of the plane determined by the other atoms. This conformation, the values of the endocyclic SCS angles [in the 124.6(8)–126.6(3)° range], and the CSC angles [in the 106.0(3)–110.5(3)° range], which are greater than those observed in the corresponding saturated rings,[21,22] are consequences of the electron delocalization within the planar CS_3 group. The Cu–S_{thione}–C bond angles are in good agreement with those observed in $[Cu_2(dtt)Cl_2]_n$.[5]

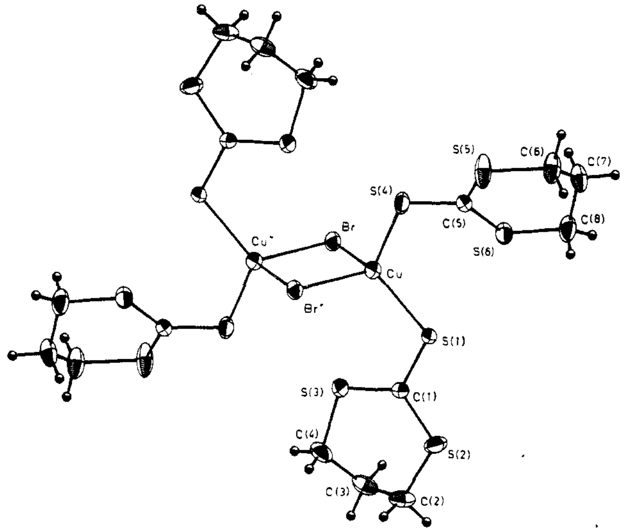

Figure 4. Perspective view of complex **III** (30% probability ellipsoids).

Magnetic Properties. The electron spin resonance spectra of **I**, recorded at room and liquid N_2 temperatures, are quite similar. No hyperfine splitting is observed on lowering the temperature. The EPR spectrum is typical of a Cu(II) ion coordinated in a tetragonally distorted octahedron,[1] in agreement with its molecular structure. The $g_{\parallel}$ and $g_{\perp}$ values measured at room temperature are 2.2718 and 2.0592, respectively, thus indicating the presence of a $d_{x^2-y^2}$ ground state.

It is possible to estimate the d–d electronic transitions expected in this coordination by using the following equations valid for Cu(II) in tetragonally elongated coordination.

$$g_{\perp} = 2.0023 - [2r^2\lambda/(E(d_{xz,yz}) \rightarrow E(d_{x^2-y^2}))] = 2.0592$$

$$g_{\parallel} = 2.0023 - [8r^2\lambda/(E(d_{xy}) \rightarrow E(d_{x^2-y^2}))] = 2.2718$$

where $E(d_{xz,yz})$ and $E(d_{xy})$ are the excited states and $E(d_{x^2-y^2})$ is the ground state. If a free-ion spin–orbit coupling constant of $-829\ cm^{-1}$ is assumed, the two transitions are expected to be at 12 500 and 14 500 cm^{-1}, respectively. These values are at too high an energy as compared to those observed in the optical spectrum, where two maxima at 10 500 and 12 500 cm^{-1} are observed (see Experimental Section) and assigned to d–d electronic transitions arising from the Cu(II) ion in D_{4h} stereochemistry.[23] However, it is known that covalent bonds will reduce the spin–orbit coupling. Using a λ value of about $-700\ cm^{-1}$, a good agreement could be obtained. The behavior of the temperature dependence of the magnetic susceptibility of **I**, corrected for the diamagnetic contribution of the atoms, is Curie-like with a temperature-independent magnetic contribution. The plot could be fitted by using the simple relation $\chi = \alpha + C/T$, where α is

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the temperature-independent paramagnetism and C the Curie constant. The best fit gave the following results: $\alpha = 1.27 \times 10^{-3}$ emu/mol and $C = 0.412$ emu K/mol. The Curie constant is slightly higher than that expected for a one-unpaired spin (0.375 emu K/mol), thus confirming the presence of one Cu(II) ion in the cluster. The experimental C value is also compatible with the value calculated from the g values of the EPR measurements. At low temperatures the $1/\chi$ vs T plot is linear and no intercept on the temperature axis is observed, thus indicating no exchange coupling between adjacent trimers. The isothermal magnetizations as a function of field at three different temperatures, i.e. at $T = 6$, 100, and 200 K, have also been performed. Plots of magnetization vs field are linear in all cases. The best fit gives a C value of 0.413 emu K/mol, in agreement with that found from susceptibility data as a function of temperature. At higher temperatures, the fit comprises also the contribution of the temperature-independent paramagnetism, α. The fit gave a lower value, i.e. $\alpha = 2.7 \times 10^{-4}$ emu/mol, than that estimated from the magnetic susceptibility vs temperature plot. Structural and magnetic properties support a Robin–Day class I classification[24] for **I**, where copper(I) and copper(II) have very different ligand fields and the properties of the compound are—as expected—to be the sum of those of the constituent ions.[24,25]

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Supplementary Material Available: Tables listing detailed experimental data for X-ray diffraction, fractional atomic coordinates of hydrogen atoms, bond distances and angles, and anisotropic thermal parameters for non-hydrogen atoms (5 pages). Ordering information is given on any current masthead page.

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