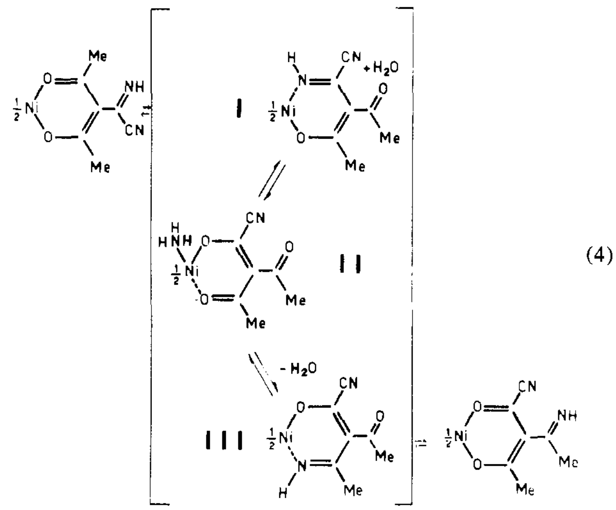

(4)

attack, >C=NH hydrolysis, and ammonia extraction to give a diaminobis(triketoenolate) complex, II. This species can undergo ammonolysis of the metal-coordinated CO groups to give either I or III, which isomerizes to the more stable species $Ni\beta_2$.

Acknowledgment. The cooperation of Mr. L. Turiaco for having carried out the magnetic moment measurements and of Mr. F. Darin for having recorded the IR spectra reported in the text is acknowledged.

Registry No. $Ni\alpha_2$, 71616-26-7; $Bi\beta_2$, 71616-27-8; αH, 71616-10-9; $Ni(acac)_2$, 3264-82-2; C_2N_2, 460-19-5; acac, 123-54-6.

Supplementary Material Available: A listing of structure factor amplitudes (7 pages). Ordering information is given on any current masthead page.

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Unusual Sulfur Insertion in a Copper(I)–Mercaptobenzothiazole Complex: Synthesis and Structural Study of $[Cu^{I}(C_7H_5NS_2)(C_{14}H_8N_2S_5)](ClO_4)\cdot 2CHCl_3$

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The title complex was obtained from a chloroform solution of mercaptobenzothiazole (Hmbt) which was reacted with solid copper(II) perchlorate hexahydrate. The infrared spectrum of this species was consistent with the presence of the ligand under two different forms such as Hmbt and mbt, involving different coordination sites. This was confirmed by an X-ray structure determination which also revealed an unusual sulfur insertion. Crystals are monoclinic, of space group $P2_1/C$, with $a = 14.746$ (6) Å, $b = 10.883$ (5) Å, $c = 12.296$ (6) Å, and $\beta = 94.51$ (1)°. The structure was solved by the heavy-atom method. The final agreement index R_w was 0.06. The perchlorate anion exhibits a statistical distribution between two sites, in the ratio 0.65/0.35. The cuprous complex cation is tetrahedral; it contains mercaptobenzothiazole under two different forms: (i) a Hmbt form S bonded to the metal through the exocyclic sulfur atom (Cu–S = 2.221 (4) Å) and (ii) an unusual oxidized form RSSSR in which an additional sulfur atom has been inserted. This mbt–S–mbt unit is coordinated through both thiazolic nitrogen atoms (Cu–N = 2.04 (1), 2.01 (1) Å) and the central sulfur atom (Cu–S = 2.486 (4) Å). The molecular structure of both forms is discussed.

Introduction

During the last few years, we have been interested in the interaction of organic corrosion inhibitors such as mercaptobenzothiazole (Hmbt) with metallic copper surfaces. For elucidation of the stereochemical aspect of this interaction, models of the surface complex were first derived from carbonyl clusters,[1] with $Ru_3(CO)_{12}$ as a starting material. The most interesting coordination type was found in the triangular cluster $Ru_3H(CO)_9(mbt)$. The infrared spectrum of this complex was closely related to the reflection spectrum of the actual surface complex. Although such a species may be considered as a good model of the ligand's linkage on a bulk metal surface, it concerns ruthenium and not copper.

A second move in our investigation was then to prepare copper complexes in order to check the affinity of the ligand for this metal. Let us first note that recent developments in copper–thiol cluster chemistry[2-4] provide several new compounds which seem interesting for this purpose. The formation

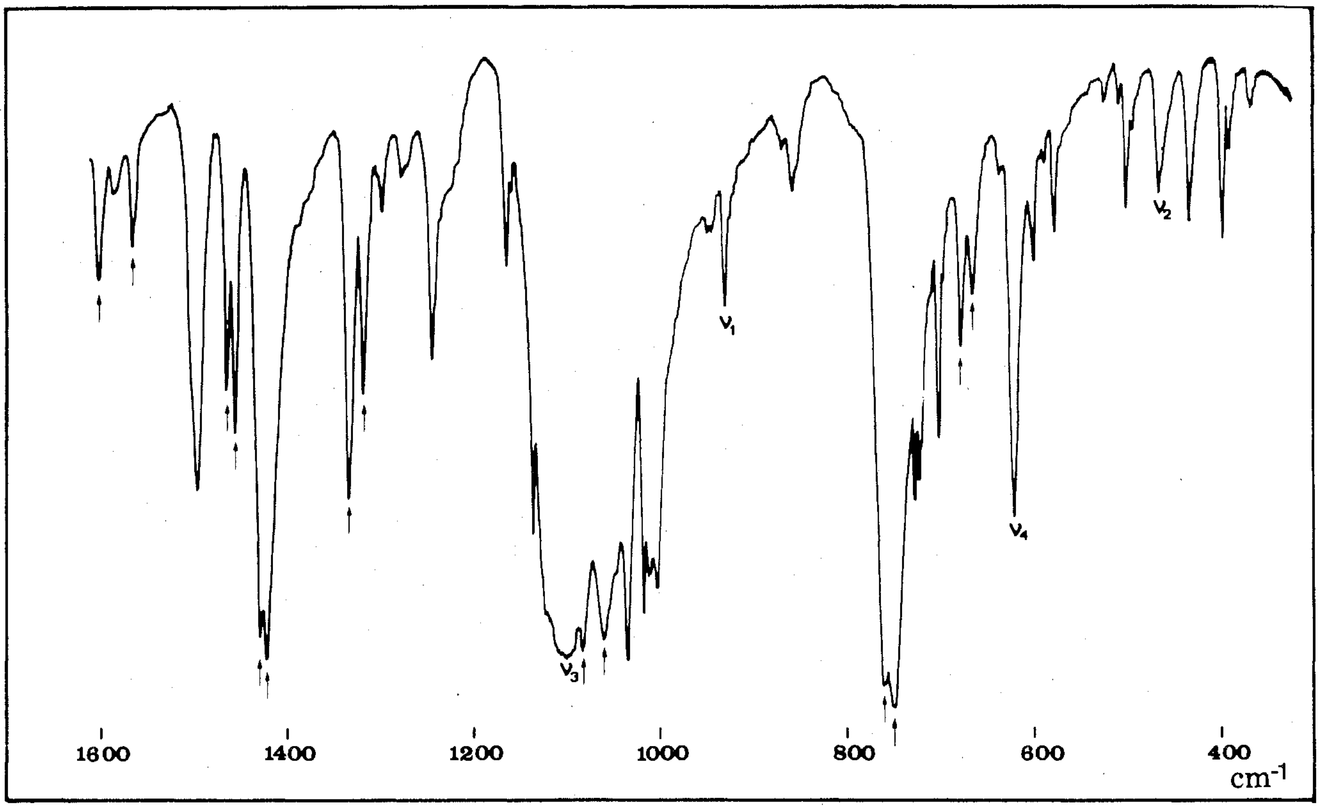

Figure 1. Infrared spectrum showing the splitting of most ligand bands.

of such species sometimes involves the following redox reaction, well-known in biochemistry:[5,6]

$$2Cu^{2+} + 2RS^- \rightleftarrows 2Cu^+ + RSSR$$

This reaction seems also interesting from the corrosion point of view. Indeed, inhibitors may act on a partly oxidized metal surface possibly involving Cu^+ and Cu^{2+}.

The copper(I) oxidation state can be stabilized in different ways: (a) Kroneck, Hemmerich, and co-workers[7] reported the formation of a $(Cu\text{–}SR)_n$ complex polymer from monodentate alkylthiols. The recent synthesis of this species from 2-mercaptobenzoxazole[8] shows that the reaction also occurs with thioamides. (b) A different reaction was described by Verani and co-workers[9] in the case of thiazolidine-2-thione (Htzt): $CuX_2 + 4Htzt \rightarrow Cu^I(Htzt)_3X + 0.5(tzt)_2 + 2HX$ (X = Cl, Br). The cuprous complex is here stabilized by neutral ligand molecules.

This paper deals with a particular reaction of mercaptobenzothiazole with cupric perchlorate, leading to a new species which could not be readily characterized from analytical results. The unusual spectral characteristics of this species suggested the presence of the ligand under two different forms. This was confirmed by an X-ray structure determination which also revealed an unusual sulfur insertion. Let us note that the copper(I) site in this structure is closely related to the reduced form of some "blue" copper proteins.[6]

Experimental Section

Reaction of Mercaptobenzothiazole with $Cu(ClO_4)_2 \cdot 6H_2O$. In a first step, the existence of the previously reported[6-8] $(Cu\text{–}SR)_n$ species was checked in the case of mercaptobenzothiazole. Complex formation was obtained in a very simple way by mixing a chloroform solution of the ligand mercaptobenzothiazole (334 mg) to a water solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (370 mg). A pale yellow compound precipitated; it was filtered and washed with alcohol and chloroform solutions and then dried several days with P_4O_{10}. Analytical results are in agreement with the raw formula $[Cu(C_7H_4NS_2)]_n$. Anal. Calcd for $[Cu(C_7H_4NS_2)]_n$: C, 36.6; H, 1.7; N, 6.1; S, 27.9; Cu, 27.6. Found: C, 36.85; H, 1.95; N, 5.72; S, 27.58; Cu, 26.43. The infrared spectrum exhibits the features which were previously related[1] to simultaneous N and S coordination (cm^{-1}): 1562 (w), 1452 (m), 1398 (vs), 1312 (m), 1245 (m), 1080 (m) 1020 (s), 1008 (vs), 748 (vs), 720 (m), 695 (m) (w = weak; m = medium; s = strong; vs = very strong).

A new species was obtained by the following procedure: A chloroform solution (50 mL) of the ligand (1.5 g) was poured onto an excess of solid $Cu(ClO_4)_2 \cdot 6H_2O$ (10 g). After several hours at room temperature, a brown film grew on the solid surface; yellow crystals appeared after 3 days. Analytical results (from 100 mg of crystals) for the raw formula $CuC_{22.3}H_{16.97}N_{2.84}Cl_{6.67}S_{6.80}O_{4.5}$ are as follows (wt %): C, 29.20; H, 1.85; N, 4.34; Cl, 25.83; S, 23.82; Cu, 6.93; $\sum$, 91.97 (the difference from 100 mg was attributed to 8.03 mg of oxygen).

The oxygen/copper ratio suggested the presence of only one perchlorate anion. Thus, the excess of chlorine was attributed to two chloroform molecules. Although the metal/ligand ratio seemed to be 1/3 when calculated from nitrogen, an excess of sulfur was found but not readily explained.

Infrared Spectrum. The infrared spectrum (Figure 1, Table I) of the complex is particularly interesting since most of the ligand bands are split. Although a band splitting may often be related to symmetry considerations, this systematic feature led us to expect the presence of the ligand in two different forms. Indeed, a first series of bands is characteristic of the S–C–NH group. These frequencies are very close to those observed for the free ligand, clearly indicating the absence of strong disturbance in its structure. The presence of the strong absorption at 1496 cm^{-1} (δ(NH), ν(C–N), δ(N–C–S)) is the main proof,[1] showing that the ligand is not deprotonated. Besides, a second series of frequencies reveals a stronger disturbance with respect to the free Hmbt molecule, as previously observed[1] for deprotonated mbt ligand bonded through both nitrogen and sulfur atoms.

X-ray Diffraction Study. Intensity Data. The crystal selected for the X-ray analysis was of parallelepiped habit (0.10 × 0.20 × 0.64 mm), bound by faces 100, 001, and 010. Preliminary Laue and precession photographs indicated monoclinic symmetry with extinction patterns consistent with space group $P2_1/C$. The crystal was mounted on a four-circle diffractometer. Unit cell parameters were obtained from a least-squares fit to the setting angles of the Cu Kα peaks of 12 high-angle reflections: a = 14.746 (6) Å, b = 10.883 (5) Å, c = 12.296 (6) Å, β = 94.51 (1)°. Measurements of intensity data were carried out as described previously:[1] radiation Mo Kα (selected by

Table I. Comparative Table of Infrared Spectra

a) free mercaptobenzothiazole[1] (thione form)
b) copper complex (this work)
c) ruthenium complex[1] (deprotonated mbt under the thiolate form)
The splitting of most infrared bands in the copper complex (b) is in agreement with the presence of Hmbt and mbt forms.

Frequencies (cm^{-1})

(a) Hmbt	(b) $Cu(Hmbt)(mbt\text{-}S\text{-}mbt)(ClO_4)$	(c) $Ru_3H(CO)_9(mbt)$
1604m	1600m	
	1565m	1565w
1505vs	1496s	
1464m	1465m	
	1455m	1458vs
1433vs	1430vs	
	1420vs	1417s
1328vs	1335s	
	1320m	1321m
1251m	1245m	1240s
	1100b (ν_3 ClO_4)	
		1092vs
1080s	1082vs	
	1060vs	
1040vs	1037vs	1035vs
1019	1018vs	1018s
	930m ($\nu_1 ClO_4$)	
	760vs	760vs
753vs	750vs	
	727sh	730s
720sh	722sh	
709sh	700m	708s
672s	678m	
	665w	635s
	620 ($\nu_4 ClO_4$)	

vs = very strong ; s = strong ; sh = shoulder ; b = broad ; m = medium ; w = weak

a graphite monochromator set in front of the counter), takeoff angle 3°, collimator ϕ 1.5 mm, counter window ϕ 3 mm, scan type θ–2θ, scan rate 1°/min (θ), scan length $[1 + (\Delta\lambda/\lambda) \tan \theta]°$, 4962 reflections collected at room temperature up to $(\sin \theta)/\lambda = 0.55$, standards 600 and 023 (intensity variations 3σ).

Structure Solution. Intensities were corrected for Lorentz and polarization factors and for absorption ($\mu = 15.8$ cm^{-1}). Atomic form factors were taken from Cromer and Mann,[10] including the real and imaginary components of anomalous dispersion for all nonhydrogen atoms. The weighting scheme and refinement procedure were the same as previously described.[1]

The structure was solved by the heavy-atom technique. The copper atom was located in a Patterson map. Subsequent Fourier syntheses revealed three ligand molecules, a perchlorate ion, two chloroform units, and an additional sulfur atom, leading to the formula $Cu(Hmbt)(mbt\text{–}S\text{–}mbt)(ClO_4)\cdot 2CHCl_3$, in agreement with analytical results and density measurements. Anal. Calcd for $Cu(Hmbt)(mbt\text{–}mbt)(ClO_4)\cdot 2CHCl_3$: C, 29.62; H, 1.50; N, 4.50; Cl, 26.61; S, 24.07; Cu, 6.86. Observed: C, 29.20; H, 1.85; N, 4.34; Cl, 25.83; S, 23.82; Cu, 6.93. Density: measured, 1.734 g cm^{-3}; calculated, 1.736 g cm^{-3}.

Treatment of Disordered Molecules. Although the copper atom and surrounding ligand molecules could be well refined, the perchlorate anion and chloroform molecules were found to be disordered.

Evidence of a disordered perchlorate anion was obtained from a Fourier difference map which displayed six peaks surrounding the chlorine atom. The geometry of this set (Figure 2) suggested a statistical distribution between two sites, as shown in Figure 3, despite the absence of splitting for O(1), O(2), and Cl peaks. Indeed, these three atoms exhibit a strongly anisotropic electron density, in agreement with the presence of two sites too close to be distinguished. The probability of both orientations of the perchlorate was determined as follows: O(3), O(4), O(5), and O(6) were first introduced with fixed coordinates and fixed isotropic thermal parameters (B terms were chosen equal to the mean value found for O(1) and O(2)) but variable occupancy factors which were refined. For $\bar{m} = 0.67$: O(3), 0.70 (2); O(4), 0.64 (2). For $\bar{m} = 0.36$: O(5), 0.44 (2); O(6), 0.27 (2). In a second step, these occupancies were fixed to 0.65 and 0.35 while atomic coordinates and anisotropic thermal parameters were refined. Although the two sites of the chlorine atom could not be separated, an evaluation of their distance was made from the positions of O(4) and O(5): O(4)–Cl and O(5)–Cl distances are respectively 0.09 and 0.08 Å greater than the usual value 1.43 Å. These deviations can be considered as a good estimate of the distance between the two sites of chlorine: 0.15 Å.

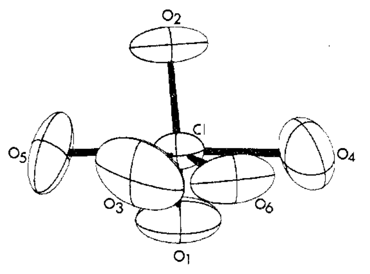

Figure 2. ORTEP view of the disordered perchlorate anion.

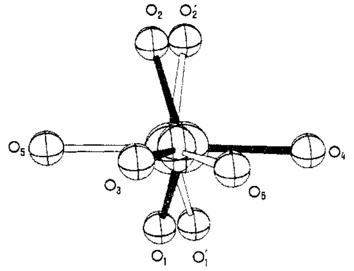

Figure 3. Disordered perchlorate: statistical distribution between two sites.

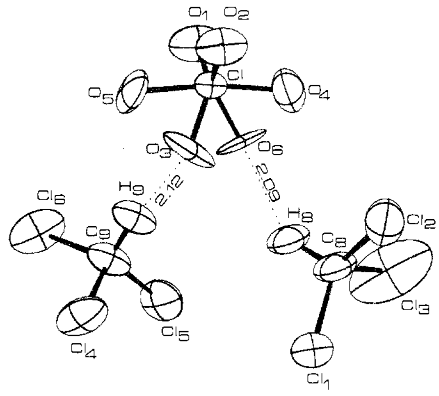

Figure 4. ORTEP view showing molecular packing of the perchlorate anion and chloroform molecules.

Such a disorder requires for the perchlorate anion more space than necessary for its size. A careful examination of its surrounding leads to the following remarks.

(a) The O(2)···N(1) distance (2.91 Å) suggests hydrogen bonding with the Hmbt molecule (Figure 6) (N(1)–H···O(2)). This is confirmed by several features: (i) the ν(NH) stretching vibration which would arise near 3400 cm^{-1} in free thioamides[19] is shifted to 3025 cm^{-1}; (ii) the O(2) atom has the smallest ellipsoid, indicating that its splitting is limited by the O(2)···H–N interaction.

(b) Besides the NH group, the surrounding of the perchlorate anion includes chloroform molecules as shown in Figure 4. The particular position of these chloroform molecules is helpful to understand the problems which were encountered in their refinement: although the Fourier difference map did not display any splitting of the chlorine peaks, these atoms exhibit abnormally large and strongly anisotropic thermal ellipsoids (Table III). These characteristics should be assigned to the fact that each chloroform molecule exists in two sites too close to be distinguished. The explanation of such a disorder should be as follows. It can be observed that two intermolecular distances are shorter than van der Waals bonds: O(3)···C(9), 3.12 Å; O(6)···C(8), 3.02 Å. Moreover, the orientation of both chloroform molecules (Figure 4) is such that hydrogen atoms H(8) and H(9) (computed position) point toward O(6) and O(3), respectively, leading to the

Table II. Final Atomic Coordinates in $[Cu(C_7H_5NS_2)(C_{14}H_8N_2S_5)]ClO_4 \cdot 2CHCl_3$ with Esd's in Parentheses

	x	y	z
	Metal		
Cu	0.1557 (1)	0.2405 (1)	0.23330 (7)
	Hmbt Ligand		
S(1)	0.1955 (3)	0.0671 (3)	0.1898 (2)
C(1)	0.2480 (9)	0.111 (1)	0.1278 (6)
S(2)	0.2561 (3)	0.2613 (4)	0.1053 (2)
N(1)	0.2872 (8)	0.035 (1)	0.0931 (5)
C(2)	0.316 (1)	0.222 (1)	0.0450 (6)
C(3)	0.328 (1)	0.091 (1)	0.0451 (6)
C(4)	0.375 (1)	0.036 (1)	0.0005 (7)
C(5)	0.412 (1)	0.108 (2)	−0.0417 (8)
C(6)	0.402 (1)	0.233 (2)	−0.0423 (7)
C(7)	0.350 (1)	0.290 (1)	0.0016 (7)
	Perchlorate Anion		
Cl	0.7149 (3)	0.1906 (3)	0.4462 (2)
O(1)	0.712 (1)	0.071 (1)	0.4307 (7)
O(2)	0.714 (1)	0.269 (1)	0.3965 (5)
O(3)	0.683 (3)	0.235 (3)	0.494 (2)
O(4)	0.818 (3)	0.188 (3)	0.460 (1)
O(5)	0.612 (3)	0.200 (5)	0.442 (2)
O(6)	0.754 (5)	0.218 (4)	0.496 (2)
	Chloroform 1		
C(8)	0.151 (2)	0.591 (2)	0.4225 (8)
Cl(1)	0.1961 (5)	0.4852 (9)	0.3766 (3)
Cl(2)	0.1117 (5)	0.5064 (8)	0.4801 (3)
Cl(3)	0.059 (1)	0.664 (1)	0.3905 (6)
	mbt–S–mbt Ligand		
S	0.0552 (2)	0.3925 (4)	0.1776 (2)
S(21)	0.1400 (3)	0.5413 (4)	0.1826 (2)
C(21)	0.2376 (9)	0.485 (1)	0.2198 (6)
N(21)	0.2531 (7)	0.3743 (9)	0.2420 (4)
S(22)	0.3317 (3)	0.5842 (3)	0.2293 (2)
C(22)	0.396 (1)	0.464 (1)	0.2624 (6)
C(23)	0.3447 (9)	0.361 (1)	0.2652 (6)
C(24)	0.3812 (9)	0.250 (1)	0.2892 (5)
C(25)	0.4715 (9)	0.252 (1)	0.3098 (5)
C(26)	0.5244 (9)	0.359 (1)	0.3059 (6)
C(27)	0.488 (1)	0.466 (1)	0.2811 (6)
S(31)	−0.0354 (2)	0.4175 (4)	0.2416 (2)
C(31)	0.0052 (8)	0.325 (1)	0.3010 (6)
N(31)	0.0737 (7)	0.250 (1)	0.3011 (4)
S(32)	−0.0501 (3)	0.3300 (3)	0.3668 (2)
C(32)	0.0263 (8)	0.218 (1)	0.3976 (6)
C(33)	0.0870 (9)	0.188 (1)	0.3557 (6)
C(34)	0.1556 (9)	0.102 (1)	0.3688 (6)
C(35)	0.159 (1)	0.046 (1)	0.4266 (7)
C(36)	0.098 (1)	0.081 (2)	0.4676 (7)
C(37)	0.029 (1)	0.166 (1)	0.4520 (7)
	Chloroform 2		
C(9)	0.592 (2)	0.345 (2)	0.1102 (9)
Cl(4)	0.5426 (5)	0.2054 (5)	0.1250 (3)
Cl(5)	0.6709 (5)	0.3835 (7)	0.1689 (4)
Cl(6)	0.5073 (7)	0.4553 (5)	0.1014 (3)

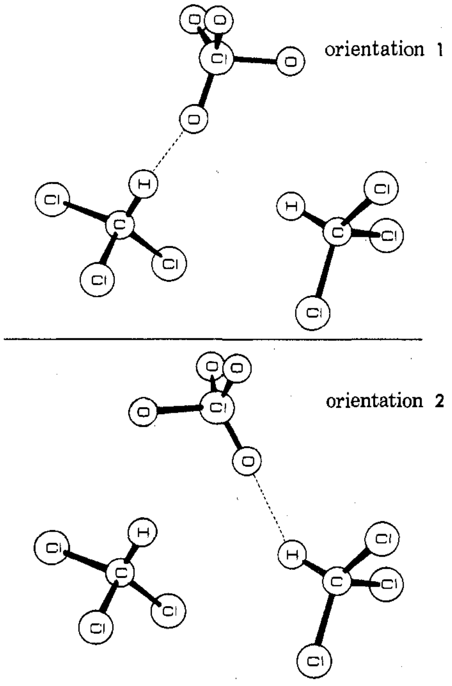

Figure 5. Alternate connection between perchlorate anion and chloroform molecules.

following short contacts: O(6)···H(8), 2.09 Å; O(3)···H(9), 2.12 Å. This suggests hydrogen bonding since the hydrogen atom in chloroform has some positive charge. Let us recall that O(6) and O(3) sites are alternately occupied in the ratio 0.35/0.65. Consequently, the two chloroform molecules would be also alternately retained through hydrogen bonding. So, the site of each chloroform molecule would be slightly different, depending upon the ClO_4 orientation (Figure 5). Thus, it is obvious that ClO_4 and chloroform disorders are related.

Final Refinements. Hydrogen atom positions were computed at 1 Å from the atoms to which they are bound. Their positions were fixed and their thermal parameters were isotropic (empirically taken 1 Å^2 greater than those of the atoms to which H was bonded). The highest residue of the difference Fourier map corresponded to the Cl(3) position and was slightly lower than 1 e/Å^3. The final refinement concerned 2994 observations with $F_o > 2\sigma$. Considering the satisfactory agreement between F_o and F_c at low diffraction angle, it was not found necessary to introduce a secondary extinction parameter. Final refinements led to $R_w = 0.060$ and $R = 0.089$. These relatively high values may be related to the observed disorder which concerns 27% of the whole electron density. The disorder would also be responsible for the weak intensity diffracted (40% of the F_o are smaller than 2σ) despite the size of the crystal.

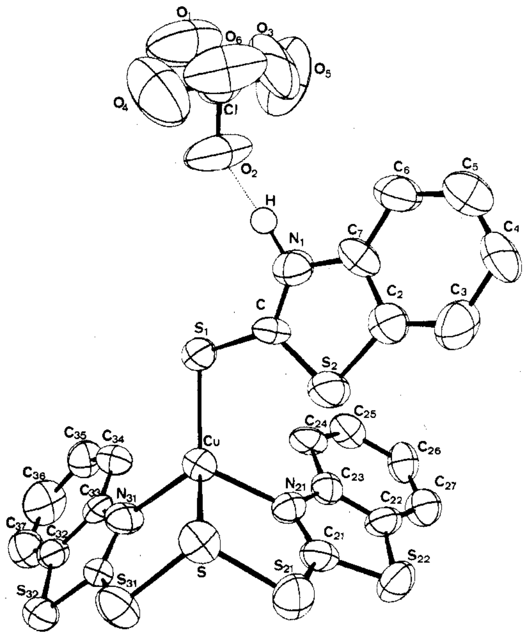

Figure 6. Geometry of the complex cation and disordered perchlorate anion.

Results and Discussion

The X-ray structure determination leads to an unusual formula for this tetrahedral cuprous complex: $[Cu^I(Hmbt)(mbt{-}S{-}mbt)](ClO_4) \cdot 2CHCl_3$. It contains mercap-

Table III. Anisotropic Thermal Parameters[a] in $[Cu(C_7H_5NS_2)(C_{14}H_8N_2S_5)]ClO_4\cdot 2CHCl_3$ with Esd's in Parentheses

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
			Metal			
Cu	4.48 (8)	3.88 (7)	4.89 (8)	0.14 (8)	1.36 (6)	−0.22 (7)
			Hmbt Ligand			
S(1)	6.4 (2)	3.6 (2)	5.2 (2)	−0.6 (2)	2.4 (2)	−0.5 (1)
C(1)	4.5 (7)	3.4 (7)	5.2 (7)	0.4 (6)	1.4 (6)	−1.6 (6)
S(2)	7.6 (2)	4.2 (2)	5.1 (2)	0.7 (2)	2.6 (2)	0.4 (2)
N(1)	5.4 (6)	4.4 (5)	4.5 (6)	−0.3 (5)	0.4 (5)	−0.7 (5)
C(2)	6.3 (8)	5.0 (8)	4.8 (8)	−0.1 (7)	1.7 (7)	0.0 (6)
C(3)	5.1 (8)	6.1 (8)	3.3 (6)	0.8 (7)	1.3 (6)	−0.3 (6)
C(4)	9 (1)	5.1 (8)	5.2 (8)	0.7 (8)	2.6 (8)	−0.9 (7)
C(5)	9 (1)	8 (1)	5 (1)	−1 (1)	3.1 (9)	−1.9 (9)
C(6)	9 (1)	8 (1)	5 (8)	−0 (1)	4.4 (8)	0.6 (8)
C(7)	10 (1)	5 (8)	5 (8)	−1.4 (8)	1.9 (8)	0.8 (7)
			mbt-S-mbt Ligand			
S	4.6 (2)	5.7 (2)	4.1 (2)	0.6 (2)	0.3 (1)	0.6 (2)
S(31)	5.0 (2)	5.0 (2)	7.6 (3)	0.5 (2)	0.5 (2)	2.0 (2)
C(21)	4.7 (7)	3.8 (7)	4.5 (7)	1.1 (6)	0.8 (6)	−0.0 (6)
S(22)	5.2 (2)	3.8 (2)	7.7 (2)	−0.3 (2)	0.0 (2)	1.4 (2)
N(21)	4.1 (5)	3.2 (5)	3.7 (5)	0.2 (4)	0.2 (4)	0.1 (4)
C(22)	5.9 (8)	2.9 (6)	4.7 (7)	0.6 (6)	0.9 (6)	0.2 (5)
C(23)	4.0 (6)	4.5 (6)	3.2 (6)	−0.6 (6)	0.7 (5)	−0.8 (6)
C(24)	6.3 (8)	3.2 (6)	4.6 (6)	2.5 (7)	1.7 (6)	1.5 (6)
C(25)	4.6 (7)	5.1 (9)	4.2 (8)	1.7 (7)	0.6 (6)	1.6 (7)
C(26)	3.4 (7)	6.5 (9)	5.2 (8)	−1.0 (7)	0.1 (6)	0.2 (7)
C(27)	3.7 (7)	5.2 (8)	6.0 (8)	−0.3 (6)	−0.3 (6)	−0.2 (6)
S(31)	4.6 (2)	6.3 (2)	5.2 (2)	1.8 (2)	1.0 (2)	1.0 (2)
C(31)	3.3 (6)	2.8 (5)	5.3 (7)	−0.0 (5)	1.4 (5)	−0.4 (5)
S(32)	5.0 (2)	4.1 (2)	5.2 (2)	0.3 (2)	1.7 (1)	−0.1 (1)
N(31)	5.5 (6)	4.3 (5)	3.3 (5)	0.3 (6)	0.7 (4)	−0.8 (5)
C(32)	4.5 (6)	3.1 (6)	3.7 (6)	−0.1 (5)	0.7 (5)	−0.1 (5)
C(33)	4.8 (7)	2.2 (5)	4.9 (7)	−0.5 (5)	1.2 (6)	0.1 (5)
C(34)	4.5 (7)	4.3 (7)	4.8 (7)	0.9 (6)	0.4 (6)	−0.4 (6)
C(35)	5.2 (8)	4.8 (8)	5.6 (8)	0.2 (7)	0.3 (7)	1.6 (7)
C(36)	10 (1)	7 (1)	4.2 (8)	−1 (1)	1.6 (8)	2.2 (8)
C(37)	5.7 (9)	6.2 (9)	5.6 (9)	0.2 (8)	1.2 (7)	−0.0 (8)
			Disordered Perchlorate Anion			
Cl	7.6 (3)	4.1 (2)	5.0 (2)	0.2 (2)	0.8 (2)	0.4 (2)
O(1)	23 (2)	6.1 (8)	10 (1)	−1 (1)	2 (1)	0.4 (7)
O(2)	18 (1)	5.3 (6)	7.9 (8)	−0.2 (8)	0.8 (8)	2.4 (6)
O(3)	19 (3)	13 (2)	13 (2)	1 (3)	13 (3)	−2 (2)
O(4)	8 (1)	19 (3)	12 (2)	−2 (1)	3 (1)	1 (2)
O(5)	6 (2)	14 (4)	15 (4)	2 (2)	−5 (2)	−4 (3)
O(6)	19 (6)	6 (2)	3 (2)	−3 (3)	−5 (3)	−1 (1)
			Chloroform Molecules			
C(8)	14 (2)	13 (2)	5 (1)	−3 (1)	−0 (1)	−2 (1)
Cl(1)	12.0 (5)	20.7 (7)	13.3 (5)	−2.5 (5)	2.2 (4)	−8.6 (5)
Cl(2)	10.6 (4)	18.9 (7)	12.5 (5)	−3.1 (5)	0.4 (4)	−0.0 (5)
Cl(3)	42 (2)	15.0 (7)	28 (1)	11 (1)	−19 (1)	0.3 (8)
C(9)	14 (2)	6 (1)	9 (1)	−0 (1)	6 (1)	−1 (1)
Cl(4)	16.8 (6)	7.3 (3)	14.4 (5)	−3.8 (3)	−4.4 (4)	3.3 (3)
Cl(5)	12.3 (5)	12.8 (5)	15.7 (6)	−6.7 (4)	0.1 (4)	1.7 (4)
Cl(6)	24.5 (9)	6.3 (3)	14.4 (6)	2.3 (4)	−2.7 (5)	−2.0 (3)

[a] These anisotropic thermal parameters have units of Å². They enter the expression for the structure factor in the form $\exp[-0.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

tobenzothiazole under two forms (Figure 6): (i) A Hmbt molecule, which is not deprotonated, is S bonded to the metal through the exocyclic sulfur atom (Cu–S(1) = 2.221 (4) Å) and associated through hydrogen bonding with the ClO_4 anion (N(1)–H···O(2)). (ii) An oxidized form of mercaptobenzothiazole, in which an additional sulfur atom has been inserted, is symmetrically coordinated to the metal through both nitrogen atoms (Cu–N(21) = 2.04 (1) Å; Cu–N(31) = 2.01 (1) Å) and the central sulfur atom (Cu–S = 2.486 (4) Å). Thus, the existence of two forms which was expected from the infrared spectra is confirmed.

Infrared Spectra. The observed splitting of most infrared bands (Figure 1, Table I) is consistent with the presence of Hmbt and mbt–S–mbt forms. The first series of bands is assigned to the Hmbt unit. The second series is related to the mbt–S–mbt unit, in agreement with a stronger disturbance of the structure with respect to free Hmbt. Some comments are necessary to complete our previous discussions[1] about the spectrum of mercaptobenzothiazole: (a) The most characteristic band in the spectra of thioamides arises in the 1500-cm^{-1} region and results from a rather complicated coupling (ν(C$\cdots$N), δ(N$\cdots$C$\cdots$S), δ(NH)).[11-20] No splitting occurs for this band (1496 cm^{-1}) which can be assigned to the Hmbt unit. Indeed, we previously noted its total disappearance[1] in the spectrum of the deprotonated ligand, in agreement with several authors.[15,20] (b) The band at 1565 cm^{-1} does not exist in free mercaptobenzothiazole, but it was found in the spectra of mbt[1,15,20] and related ligands[21] when deprotonated and coordinated through the nitrogen atom. It should be assigned to the ν(C═N) vibrations in mbt–S–mbt. (c) The 1433-cm^{-1}

Table IV. Interatomic Distances (Å) in $[Cu(C_7H_5NS_2)(C_{14}H_8N_2S_5)]ClO_4 \cdot 2CHCl_3$ with Esd's in Parentheses

	Metal Environment		
Cu–N(21)	2.04 (1)	Cu–S	2.486 (4)
Cu–N(31)	2.012 (9)	Cu–S(1)	2.221 (4)
	S–S Bonds		
S–S(21)	2.044 (5)	S–S(31)	2.050 (5)
	Hmbt Ligand		
S(1)–C(1)	1.71 (1)	C(3)–C(4)	1.40 (2)
C(1)–N(1)	1.29 (1)	C(4)–C(5)	1.37 (2)
N(1)–C(3)	1.41 (2)	C(5)–C(6)	1.36 (2)
C(1)–S(2)	1.72 (1)	C(6)–C(7)	1.43 (2)
S(2)–C(2)	1.72 (1)	C(7)–C(2)	1.35 (2)
C(2)–C(3)	1.43 (2)		
	mbt–S–mbt Ligand		
S(21)–C(21)	1.71 (1)	S(31)–C(31)	1.73 (1)
C(21)–N(21)	1.32 (2)	C(31)–N(31)	1.30 (2)
N(21)–C(23)	1.42 (2)	N(31)–C(33)	1.39 (2)
C(21)–S(22)	1.76 (1)	C(31)–S(32)	1.74 (1)
S(22)–C(22)	1.74 (1)	S(32)–C(32)	1.76 (1)
C(22)–C(23)	1.36 (2)	C(32)–C(33)	1.39 (2)
C(23)–C(24)	1.41 (2)	C(33)–C(34)	1.39 (2)
C(24)–C(25)	1.37 (2)	C(34)–C(35)	1.42 (2)
C(25)–C(26)	1.41 (2)	C(35)–C(36)	1.39 (2)
C(26)–C(27)	1.38 (2)	C(36)–C(37)	1.39 (2)
C(27)–C(28)	1.39 (2)	C(37)–C(38)	1.34 (2)
	Chloroform 1		
C(8)–Cl(1)	1.71 (2)	C(8)–Cl(3)	1.68 (3)
C(8)–Cl(2)	1.72 (2)		
	Chloroform 2		
C(9)–Cl(4)	1.73 (2)	C(9)–Cl(6)	1.73 (2)
C(9)–Cl(5)	1.73 (2)		
	Disordered Perchlorate Anion		
Cl–O(1)	1.35 (1)	Cl–O(4)	1.53 (2)
Cl–O(2)	1.40 (1)	Cl–O(5)	1.52 (4)
Cl–O(3)	1.29 (3)	Cl–O(6)	1.26 (4)
	Hydrogen Bonds		
N(1)···O(2)	2.91 (2)	O(6)···C(8)	3.02 (4)
O(3)···C(9)	3.12 (4)		

band in mercaptobenzothiazole is often assigned to the benzene ring.[13] Its sensitivity to N coordination would support the hypothesis that it also receives a contribution from ν(C–N) (C belonging to the benzene ring). As a matter of fact, we previously noted[1] a shift to lower frequencies upon N coordination while the band remains unchanged upon S coordination (for $Ru(mbt)_2(CO)_2(py)_2$ 1430 cm^{-1}).[22] The splitting of this band (1430–1420 cm^{-1}) is in agreement with the presence of Hmbt (S bonded) and mbt–S–mbt (N bonded). (d) The last noticeable feature is the splitting (678–665 cm^{-1}) of the 672-cm^{-1} band (ν(CS) contribution[14,20,23]) which would be related to slightly different multiplicities of the CS bonds in Hmbt and mbt–S–mbt.

Molecular Structure. A comparison of C–S and C–N bond lengths in both ligand units in the complex is helpful for an understanding of the molecular structure: for the free ligand mercaptobenzothiazole,[24] C–S = 1.66 Å and C–N = 1.35 Å; for mbt–S–mbt, C(21)–S(21) = 1.715 (13) Å, C(21)–N(21) = 1.318 (16) Å, C(31)–S(31) = 1.733 (12) Å and C(31)–N(31) = 1.299 (16) Å; for the Hmbt unit, C(1)–S(1) = 1.706 (14) Å and C(1)–N(1) = 1.295 (18) Å. Considering these data, we can make the following remarks.

(1) Bond lengths in the mbt–S–mbt unit are in agreement with a thiolate form. This tendency is however limited with respect to previous examples[25] ($[Re(CO)_3(mbt)]_2$: SC, 1.76 Å; CN, 1.25 Å). A residue of π-electron density on the C–S bond is therefore likely. It would explain the absence of free rotation around C(21)–S(21) and C(31)–S(31) bonds, resulting in the perfect planarity of both chelated rings. (See Table VI.)

Table V. Bond Angles (Deg) in $[Cu(C_7H_5NS_2)(C_{14}H_8N_2S_5)]ClO_4 \cdot 2CHCl_3$ with Esd's in Parentheses

	Metal Environment		
S–Cu–S(1)	121.0 (2)	S(1)–Cu–N(21)	116.0 (3)
S–Cu–N(21)	87.7 (3)	S(1)–Cu–N(31)	124.4 (3)
S–Cu–N(31)	88.5 (3)	N(21)–Cu–N(31)	110.7 (4)
	Chloroform 1		
Cl(1)–C(8)–Cl(2)	105 (1)	Cl(2)–C(8)–Cl(3)	105 (2)
Cl(1)–C(8)–Cl(3)	114 (1)		
	Chloroform 2		
Cl(4)–C(9)–Cl(5)	110 (1)	Cl(5)–C(9)–Cl(6)	111 (1)
Cl(4)–C(9)–Cl(6)	108 (1)		
	Hmbt Ligand		
Cu–S(1)–C(1)	105.6 (4)	C(7)–C(2)–C(3)	120 (1)
S(1)–C(1)–N(1)	124 (1)	N(1)–C(3)–C(2)	112 (1)
S(1)–C(1)–S(2)	123.2 (7)	N(1)–C(3)–C(4)	129 (1)
N(1)–C(1)–S(2)	113 (1)	C(2)–C(3)–C(4)	120 (1)
C(1)–N(1)–C(3)	115 (1)	C(3)–C(4)–C(5)	119 (1)
C(1)–S(2)–C(2)	92.3 (7)	C(4)–C(5)–C(6)	122 (2)
S(2)–C(2)–C(3)	109 (1)	C(5)–C(6)–C(7)	119 (1)
S(2)–C(2)–C(7)	132 (1)	C(6)–C(7)–C(2)	120 (1)
	Disordered Perchlorate Anion		
O(1)–Cl–O(2)	112.8 (8)	O(2)–Cl–O(4)	97 (1)
O(1)–Cl–O(3)	124 (1)	O(2)–Cl–O(5)	88 (2)
O(1)–Cl–O(4)	92 (1)	O(2)–Cl–O(6)	122 (2)
O(1)–Cl–O(5)	92 (2)	O(3)–Cl–O(4)	105 (2)
O(1)–Cl–O(6)	118 (2)	O(5)–Cl–O(6)	115 (4)
O(2)–Cl–O(3)	116 (2)		
	mbt–S–mbt Ligand		
Cu–S–S(21)	99.3 (2)	S(21)–S–S(31)	106.6 (2)
Cu–S–S(31)	97.8 (2)		
S–S(21)–C(21)	103.3 (5)	S–S(31)–C(31)	104.4 (4)
S(21)–C(21)–N(21)	128 (1)	S(31)–C(31)–N(31)	126.2 (9)
S(21)–C(21)–S(22)	117.7 (8)	S(31)–C(31)–S(32)	118.0 (7)
N(21)–C(21)–S(22)	114 (1)	N(31)–C(31)–S(32)	116 (1)
Cu–N(21)–C(21)	121.1 (9)	Cu–N(31)–C(31)	122.8 (9)
Cu–N(21)–C(23)	127.2 (8)	Cu–N(31)–C(33)	125.6 (9)
C(21)–N(21)–C(23)	111 (1)	C(31)–N(31)–C(33)	111 (1)
C(21)–S(22)–C(22)	89.4 (6)	C(31)–S(32)–C(32)	88.8 (6)
S(22)–C(22)–C(23)	111 (1)	S(32)–C(32)–C(33)	109 (1)
S(22)–C(22)–C(27)	127 (1)	S(32)–C(32)–C(27)	129 (1)
C(27)–C(22)–C(23)	122 (1)	C(37)–C(32)–C(33)	122 (1)
N(21)–C(23)–C(22)	115 (1)	N(31)–C(33)–C(32)	115 (1)
N(21)–C(23)–C(24)	123 (1)	N(31)–C(33)–C(34)	124 (1)
C(22)–C(23)–C(24)	122 (1)	C(32)–C(33)–C(34)	121 (1)
C(23)–C(24)–C(25)	116 (1)	C(33)–C(34)–C(35)	117 (1)
C(24)–C(25)–C(26)	121 (1)	C(34)–C(35)–C(36)	120 (1)
C(25)–C(26)–C(27)	122 (1)	C(35)–C(36)–C(37)	121 (1)
C(26)–C(27)–C(22)	117 (1)	C(36)–C(37)–C(32)	119 (1)

Table VI. Atom Deviations from the Mean Plane of Both Chelated Rings (Å)

Cu	−0.012	Cu	−0.010
S	+0.016	S	+0.000
S(21)	−0.019	S(31)	+0.012
C(21)	+0.011	C(31)	−0.032
N(21)	+0.004	N(31)	+0.030

(2) Although a thione form could be expected from the presence of the imino hydrogen in the Hmbt ligand, bond lengths in this unit reveal a change in molecular structure with respect to free mercaptobenzothiazole. This evolution could be related to a strong metal–ligand interaction: an electron donation from the sulfur atom to the metal might induce a decrease in the π-electron density along the C–S bond. This would result in a charge displacement from the nitrogen lone pair to the CN bond, in agreement with the observed CN shortening. The Cu–S(1) bond length, 2.221 (4) Å, could be determined by steric requirements about the copper atom. Indeed, comparison with closely related tetrahedral species[26-28] reveals that this bond length is intermediate between the mean

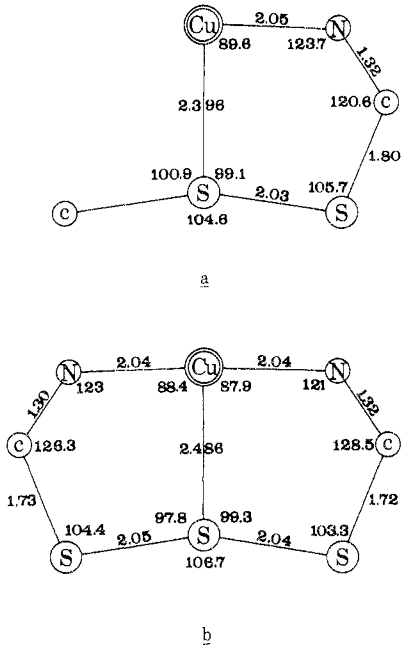

Figure 7. Geometry of chelated rings in (a) bis(2-pyridyl disulfide)copper(I) perchlorate[30] and (b) [Cu(Hmbt)(mbt–S–mbt)]-(ClO_4)·2$CHCl_3$.

value 2.34 Å related to a CuS_4 set[26] and the short value 2.19 Å found in a $CuSN_3$ type complex.[28]

Coordination of the Oxidized Ligand mbt–S–mbt. Literature provides several examples[29-31] of oxidized thiol derivatives in copper(I) complexes. Seff et al.[29] found that disulfide species, resulting from the reduction of Cu(II) to Cu(I) by aminethiols, act as ligands in a binuclear tetrahedral species $Cu_2(C_8H_{20}N_2S_2)_2^{2+}$. The study by the same authors of bis(2-pyridyl disulfide)copper(I) perchlorate[30] shows the ability of such ligands to give various coordination types involving nitrogen and sulfur atoms. The mbt–S–mbt ligand is well adapted to simultaneous N and S coordinations involving two chelated rings. A closely related five-membered ring (Cu–N–C–S–S) exists in the previously reported species.[30] A comparison of both geometries (Figure 7) leads to the following remarks concerning the mbt–S–mbt coordination: (a) The Cu–N bonds in our complex (2.011, 2.042 Å) are close to the values found in some copper complexes involving pyridyl or amide nitrogen atoms[28,30,32] but shorter than in the case of a saturated nitrogen atom (2.13 Å).[29] Such a difference is sometimes assigned to the possibility of some π back-bonding into low-lying 2pπ^* orbitals.[29] (b) The Cu–S bond is weak with respect to other examples.[29-32] Let us note that this weak interaction seems correlated with the absence of S–S lengthening[31] (2.05, 2.04 Å). Although the internal angles about the sulfur atom are imposed by the ring size, the external angle value S(21)–S–S(31) (106.6°) would suggest tetrahedral sulfur hybridization. (c) The trithio ligand coordination results in a very distorted copper environment. Bond angles vary from 88 to 124° (Table V); dihedral angles are far from these, corresponding to a regular tetrahedron (Table VII).

Assumptions about Complex Formation. We described the formation of this complex from a light brown film which grew on solid cupric perchlorate hexahydrate. Analysis of this compound revealed a 1/1 metal/ligand ratio, in agreement with the formula $(Cu\text{-}mbt)_n$. The redox reaction leading to such a $(Cu\text{-}SR)_n$ type complex[7] yields the oxidized form RSSR. Multiple reactions can therefore occur between $(Cu\text{-}SR)_n$, Cu^{2+}, the X^- anion, RSH, and RSSR. This could explain the wide range of compounds such as (i) mononuclear $Cu(RSH)_nX^-$ complexes,[9] (ii) mononuclear or polymeric species involving RSSR,[29,30] and (iii) clusters[4] or mixed-valence complexes,[2] which can be obtained from a minor change in reaction conditions.

Table VII. Dihedral Angles in Copper Environment

plane 1	plane 2	angle, deg
S(1)–Cu–N(21)	S(1)–Cu–N(31)	154.5
S–Cu–N(21)	S(1)–Cu–N(21)	147.1
S(1)–Cu–N(21)	N(21)–Cu–N(31)	153.6
S(1)–Cu–N(21)	S(1)–Cu–S	120.8
S(1)–Cu–N(31)	S–Cu–N(31)	136.5
S(1)–Cu–N(31)	N(31)–Cu–N(21)	153.5
S(1)–Cu–N(31)	N(21)–Cu–N(31)	84.7
S–Cu–N(31)	N(21)–Cu–S	125.9
S–Cu–N(31)	N(21)–Cu–N(31)	69.9
S–Cu–N(31)	S–Cu–S(1)	104.2
S–Cu–N(21)	N(21)–Cu–N(31)	59.3
S–Cu–N(21)	S–Cu–S(1)	129.9

A very particular phenomenon in our complex is the insertion of an additional sulfur atom in the oxidized form. It would imply a cleavage of the SS bond, as sometimes discussed.[33] A sulfur release from mercaptobenzothiazole is likely. Indeed, it was yet observed that this ligand could act as a sulfur donor in the following reaction:[34] Hmbt + $Fe_3(CO)_{12} \rightarrow Fe_3(CO)_9S_2$. Moreover, a synthetic route to mercaptobenzothiazole is the reaction of sulfur with benzothiazole under pressure.[35] The reverse reaction could therefore be considered as possible.

Considering the copper environment, a possible precursor of this complex could involve S-bonded and N-bonded mercaptobenzothiazole ligands. Closely related species are known in the chemistry of zinc.[36] Let us remark that such a structure was expected to trap sulfur, leading to $mbtS_x$ species.

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Registry No. Cu(Hmbt)(mbt–S–mbt)(ClO_4)·2$CHCl_3$, 71661-66-0; $[Cu(C_7H_4NS_2)]_n$, 37036-40-1.

Supplementary Material Available: A listing of structure factor amplitudes (20 pages). Ordering information is given on any current masthead page.

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Synthetic and Structural Studies on Monomeric Olefin and Isocyanide Complexes of Copper(I): (Diethylenetriamine)(1-hexene)copper(I) Tetraphenylborate and (*N*,*N*,*N'*,*N'*-Tetramethylethylenediamine)bis(cyclohexyl isocyanide)copper(I) Tetraphenylborate

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The reaction of a suspension of CuI in methanol containing diethylenetriamine (dien) with 1-hexene gives the olefin complex [Cu(dien)(1-hexene)]$^+$, which was isolated as a tetraphenylborate derivative. In the complex cation, dien is coordinated through the three nitrogen atoms to the metal, while the C═C bond of the 1-hexene molecule completes the pseudotetrahedral coordination around copper(I). The reaction of a suspension of CuI in methanol containing ethylenediamine (en) or *N*,*N*,*N'*,*N'*-tetramethylethylenediamine (tmen) with carbon monoxide followed by the addition of CNC_6H_{11} produces [Cu(en)(CNC_6H_{11})$_2$]$^+$ [ν_{CN} (Nujol) 2143 and 2177 cm^{-1}] or [Cu(tmen)(CNC_6H_{11})$_2$]$^+$ [ν_{CN} (Nujol) 2160 and 2180 cm^{-1}], respectively. The tetrahedral structure of the cationic complex in which copper(I) coordinates a chelating tmen and two C-bonded isocyano groups, was confirmed by an X-ray analysis. Both the Cu–C–N and C–N–R moieties are practically linear with Cu–C and C–N bond lengths of 1.899 (8) and 1.895 (7) Å and C–N bond lengths of 1.15 (1) and 1.13 (1) Å. Crystallographic details for [Cu(dien)(C_6H_{12})](BPh_4): space group $P2_1/c$ (monoclinic), $a = 15.835$ (2) Å, $b = 20.346$ (3) Å, $c = 20.219$ (3) Å, $\beta = 96.21$ (2)°, $Z = 8$. The final *R* factor was 11.5% for 4297 observed reflections. Crystallographic details for [Cu(tmen)(CNC_6H_{11})$_2$](BPh_4): space group $P2_1/n$ (monoclinic), $a = 15.626$ (2) Å, $b = 14.753$ (3) Å, $c = 18.024$ (4) Å, $\beta = 97.47$ (2)°, $Z = 4$. The final *R* factor was 6.9% for 3860 observed reflections.

Introduction

Few copper(I) complexes have been used as "model compounds" in homogeneous catalysis because monomeric copper(I) compounds tend not to complex with molecules which could be activated. Copper(I) coordination and organometallic chemistry is dominated by the formation of stable cluster compounds[1,2] or by the disproportionation of copper(I) to copper(II) and copper metal.[1] As a part of our continuing investigation into the synthesis and the chemical and structural properties of copper(I) complexes,[3-6] we report here the synthesis and the structure of [Cu(dien)(C_6H_{12})](BPh_4) (dien = diethylenetriamine, C_6H_{12} = 1-hexene) and [Cu(tmen)(CNC_6H_{11})$_2$](BPh_4) (tmen = *N*,*N*,*N'*,*N'*-tetramethylethylenediamine). Both kinds of complexes could be considered as structural models for electrophilic metal-promoted activation of olefins and isocyanides toward nucleophilic reagents.[7] Moreover, much attention was devoted to the catalytic activity of copper(I)–isocyanide systems, which have been found to promote several versatile organic reactions, such as dimerizations and cycloadditions. In all of these reactions, an organocopper(I)–isocyanide complex is assumed as an active intermediate.[7,8] In spite of a rather rich copper(I)–isocyanide chemistry,[7-10] the polymeric [CuI·$CNCH_3$]$_n$ complex is the only copper(I)–isocyanide compound so far structurally studied.[11]

Experimental Section

Syntheses were carried out under an atmosphere of purified nitrogen. Methanol, ethylenediamine, and *N*,*N*,*N'*,*N'*-tetramethylethylenediamine were dried and distilled before use, and cyclohexyl isocyanide was distilled before use. Infrared spectra were recorded with a Perkin-Elmer 282 spectrophotometer. Considerable difficulty was encountered in obtaining satisfactory elemental analyses, especially for carbon.

Preparation of [Cu(en)(CNC_6H_{11})$_2$](BPh_4). CuI (1.5 g, 7.88 mmol) is suspended in methanol (50 mL) containing ethylenediamine (4 mL, 60 mmol). The blue color disappears when the suspension is reacted with carbon monoxide, producing a nearly colorless solution. Some undissolved CuI is eventually filtered out. On addition of $C_6H_{11}NC$ (2.2 mL, 21.9 mmol), the solution loses carbon monoxide. The further addition of $NaBPh_4$ (2.8 g, 8.19 mmol) dissolved in methanol (10 mL) produces a white crystalline solid (2.7 g, 51.8%) sensitive to oxygen and moisture. Anal. Calcd for [Cu(en)(CNC_6H_{11})$_2$](BPh_4), $C_{40}H_{50}N_4BCu$: C, 72.69; H, 7.57; N, 8.48. Found: C, 71.62; H, 7.70; N, 8.51. The IR spectrum (Nujol) displays two strong bands at 2143 (vs) and 2177 (ms) cm^{-1}.

Synthesis of [Cu(tmen)(CNC_6H_{11})$_2$](BPh_4). CuI (1.0 g, 5.25 mmol) is suspended in CH_3OH (50 mL) containing *N*,*N*,*N'*,*N'*-tetramethylethylenediamine, tmen (2.5 g, 21.5 mmol). Upon exposure

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