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Transformation of Copper(I) Thiophosphite Complexes into Copper(I) Clusters Bridged by Diisopropyldisulfides and Diethyldisulfides

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ABSTRACT: *The cleavage of coordination bonds in copper(I) halide thiophosphite complexes with the following transformation of the P—S containing ligands in metal coordination sphere results in new cluster compounds bridged by disulfides. Thus, polymeric and tetrameric complexes of Cu(I) halides with thiophosphite ligands (triethyltrithiophosphites and triisopropyltrithiophosphites) were found to be transformed at the storage or upon recrystallization in polar solvents ($CHCl_3$, CH_3CN) into polymeric copper(I) clusters with Cu···Cu short contacts: $[Cu_2X_2{\cdot}L]_n$ (where $L = (EtS)_2$, $(i\text{-}PrS)_2$; $X = Cl$, Br). A completely different new polymeric complex was obtained by direct interaction of copper bromide with diethyl disulfide.* © 2006 Wiley Periodicals, Inc. Heteroatom Chem 17:542–546, 2006; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20274

INTRODUCTION

Coordination properties of thiophosphites were found to be essentially different from their oxygen and nitrogen analogues [1–6]. It has been shown earlier that the diversity of coordination modes of copper(I) complexes with P(III) thioesters was determined by the electronic structure and lability of thiophosphite ligands. Thiophosphite ligands are conformationally flexible in these complexes, which result in their rotational disorder and conformational inhomogeneity [6]. This flexibility and the presence of several donor atoms in these ligands determine the copper coordination chemistry, which appeared to be diverse and unexpected. The dimeric, tetrameric step-like and cuban-like, as well as the polymeric chain and two-dimensional polymeric structures have been realized in studied complexes [3–8].

Coordination bonds Cu—P and Cu—S in copper(I) thiophosphite complexes were found to be rather weak and were able to break in special conditions (affected by steric strain, solvent, etc.) causing the disproportionation of ligands and their full or partial substitution in metal coordination sphere as well as other transformations. These result in structural changes: from polymeric or cuban-like complexes to dimeric structures as well as in the chemical transformations of ligands [3,4,7,8].

RESULTS AND DISCUSSION

We have revealed that some complexes of Cu(I) halides with thioesters of the P(III) acids may be transformed into copper(I) clusters with Cu···Cu short contacts, e.g., $[(i\text{-}PrS)_3P{\cdot}Cu_4Cl_4]_n$. Copper

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clusters are bound via bridge trithiophosphite molecules, the unusual tridentate Cu coordination by P and two S atoms being realized in crystals [8].

However, the ability of coordination bonds to break easily may cause more crucial changes of the ligands in metal coordination sphere. In the present work, we describe chemical transformations observed in polymeric and tetrameric Cu(I) complexes with thiophosphite ligands upon recrystallization and storage. It was shown that tetrameric cuban-like derivatives with monodentate coordination of copper atoms, $[(RS)_3P{\cdot}CuX]_4$, **1** and **2**, as well as the polymeric bidentate complexes $[(RS)_3P{\cdot}CuX]_n$, **3**, whose structures were determined earlier [6,8], are transformed into polymeric clusters $[(RS)_2{\cdot}2CuX]_n$ **4–6** at the storage or upon recrystallization in polar solvents ($CHCl_3$ and CH_3CN):

$$\underset{\mathbf{1\text{–}3}}{(RS)_3P{\cdot}CuX} \rightarrow \underset{\mathbf{4\text{–}6}}{[(RS)_2{\cdot}2CuX]_n}$$

$$R = i-\mathrm{Pr},\ X = \mathrm{Br}(\mathbf{1},\ \mathbf{4});\ R = i-\mathrm{Pr},\ X = \mathrm{Cl}(\mathbf{2},\ \mathbf{5});$$

$$R = \mathrm{Et},\ X = \mathrm{Br}(\mathbf{3},\ \mathbf{6})$$

Such transformations most easily occur for complexes containing bulky ligands because of the large strain present in tetrameric cuban-like structures. For this reason, our attempts to determine the structure of complex **2** failed, the latter compound being immediately transformed into another **5** [8]. These clusters **4–6** are shown by X-ray single crystal diffraction to include bridge S—S ligands instead of P–S containing ligands. A series of 2:1 products, 2 $CuX{\cdot}L$ (where $L = (EtS)_2$, $(i\text{-}PrS)_2$; X = Cl, Br), were obtained. These are polymeric clusters $[Cu_2X_2{\cdot}(RS)_2]_n$ formed by four-membered cycles Cu_2X_2 with copper atoms bridged by the S—S fragments (Figs. 1 and 2). It should be noted that in a few works, especially concerning copper(I) halide dialkyl disulfide complexes, the tendency of copper(I) to form clusters has been discussed [10–12].

The simplest polymeric structure is observed for complex $2CuBr{\cdot}(SPr\text{-}i)_2$ **4** (Fig. 1a). It is a step-like chain polymer formed by four-membered Cu_2Br_2 cycles fused via opposite CuBr bonds. Each copper atom is bound to a sulfur atom of the ligand so that S—S bonds bridge two copper atoms belonging to neighboring four-membered cycles. All copper atoms have similar tetrahedral coordination with three bromine atoms and one sulfur atom in the nearest coordination sphere.

Complex $2CuCl{\cdot}(SPr\text{-}i)_2$ **5** has more complicated structure (Fig. 1b) with twisted step-like chain due to alternating position of four-membered ring condensation. Thus, one of the chlorine atoms, namely

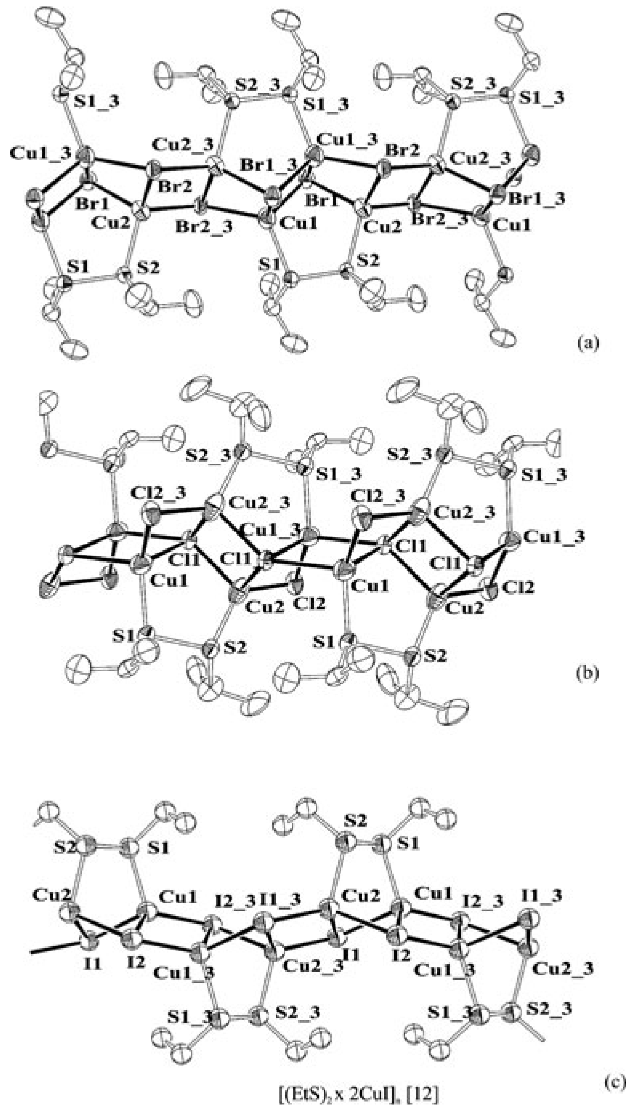

FIGURE 1 Crystal structures of cluster complexes **4** and **5** and $[(EtS)_2{\cdot}2CuI]_n$ [12] (hydrogen atoms are not shown).

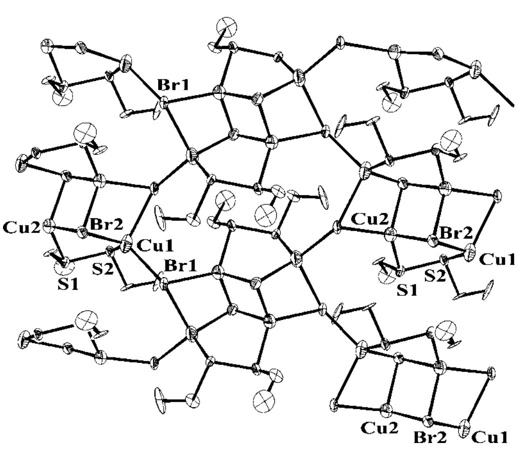

FIGURE 2 Crystal structure of cluster complex **6** (hydrogen atoms are not shown).

Cl1, has a distorted tetrahedral coordination in contrast to Cl2 which is two coordinated. Both copper atoms have distorted tetrahedral coordination with one copper–chlorine bond being extremely long, Cu2–Cl1 2.679(2) Å, while the shortest is Cu2–Cl2 2.233(2) Å.

The last polymer shown in Fig. 1c for comparison is the structure of $2CuI \cdot (SEt)_2$ studied by Boorman et al. [12]. It is a chain twisted polymer with a different bridging of copper atoms by S—S fragments. In contrast to our structures **4** and **5**, in the latter, S—S bond bridges two copper atoms from the same four-membered cycle. As a result, each second cycle is strongly folded, while the other cycles are planar.

In all studied crystals, short Cu· · ·Cu contacts are observed covering a whole range of distances from the shortest 2.61 Å in $2CuI \cdot (SEt)_2$ [12] to 2.82 in $2CuBr \cdot (SPr\text{-}i)_2$ **4** and 2.87 Å in $2CuCl \cdot (SPr\text{-}i)_2$ **5**.

Similar transformation of polymeric bidentate copper(I) bromide complex with triethyltrithiophosphite ligand, $[(EtS)_3P{\cdot}CuBr]_n$ **3**, into cluster **6**, $2CuBr \cdot (SEt)_2$, is observed upon heating the former compound in CH_3CN.

As shown by X-ray single crystal diffraction, the crystal of this cluster is composed of two-dimensional polymeric nets, consisting of centrosymmetric tetramers Cu_4X_4 bound together by the coordination bonds of two Cu-atoms and two Br-atoms (Fig. 2). Tetramer has a step-like structure with planar central Cu_2Br_2 cycle and two terminal cycles folded by 26.2°. The configuration of Cu-atoms is distorted tetrahedral. Both S atoms of the disulfide ligand participate in metal coordination, forming the five-membered SCuBrCuS cycle. There are also Cu· · ·Cu short contacts (3.081 and 2.975 Å).

Note that in contrast to the known copper(I) halide dialkyl disulfide clusters obtained directly by dissolving Cu(I) salt in the excess of diethyl disulfide [10,12], cluster complexes discussed here resulted from the disproportionation of trithiophosphite ligands in a copper coordination sphere.

It is significant to note that we have obtained a completely different polymeric complex **7** in the model reaction of CuBr with the excess of diethyl disulfide ligand. Its structure (Fig. 3) is different from all other structures described here for complexes of CuHal with the disulfide ligands. Bicyclic clusters are bound by bromine atoms to form chain polymer along the *c*-axis. The clusters are composed of two copper atoms bridged by two disulfide moieties and one bromine atom. The interatomic Cu· · ·Cu distance within the bicycle is much shorter (3.2 Å) than the Cu· · ·Cu distance between the bicycles (3.8 Å), the former being contracted by the disulfide bridge.

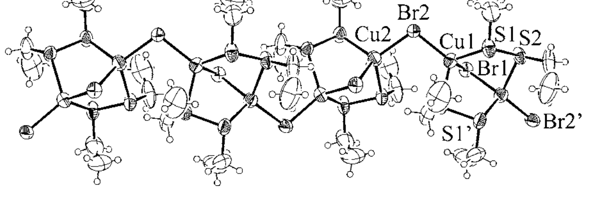

FIGURE 3 Crystal structure of complex **7**.

The difference in structure of these cluster complexes of copper(I) with disulfide ligands may be due to the volume of halogen and also the character of the substituents in the ligand (*i*-Pr, Et) as well. However, one should not exclude the possibility of isomeric transformations being dependent on the conditions of crystal growth.

Thus, the cleavage of coordination bonds in copper(I) halide thiophosphite complexes with the following transformation of the P—S containing ligands in the metal coordination sphere results in the formation of new cluster compounds bridged by disulfides.

EXPERIMENTAL

The IR spectra were recorded on a Specord UR-20 spectrometer. Complexes **1–3** were prepared according to [3,8].

Disopropyl disulfide copper (I) bromide (**4**). 2.3 g complex **1** after long storage was recrystallized from $CHCl_3$. 0.7 g (30%) cluster **4** was isolated. IR (ν/cm^{-1}): 626 (C—S). Found (%): C, 17.0; H, 3.60; S, 14.11; Cu, 29.65. Calcd for $C_6H_{14}S_2Cu_2Br_2$ (%): C, 16.49; H, 3.22; S, 14.67; Cu, 28.97.

Diisopropyl disulfide copper(I) chloride (**5**). 0.6 g (30%) **5** was isolated from 1.7 g complex **2**. IR (ν/cm^{-1}): 630 (C—S). Found (%): C, 21.25; H, 4.70; S, 17.80; Cu, 35.75. Calcd for $C_6H_{14}S_2Cu_2Cl_2$ (%): C, 20.71; H, 4.05; S, 18.43; Cu, 36.39.

Diethyl disulfide copper(I) bromide (**6**). 2.7 g (50%) of cluster **6** was isolated upon recrystallization from CH_3CN of the 5 g complex **3**. IR (ν/cm^{-1}): 626 (C—S). Found (%): C, 11.41; H, 2.68; S, 14.11; Cu, 29.88. Calcd for $C_4H_{10}S_2Cu_2Br_2$ (%): C, 11.75; H, 2.46; S, 15.61; Cu, 30.96.

Diethyl disulfide copper(I) bromide (**7**). Complex **7** was prepared by dissolving 0.1 g freshly purified CuBr in an excess of diethyldisulfide (1 g). The reaction mixture was left at the ambient temperature for a long time (~1 month) to slowly crystallize. 0.5 g (55%) of the complex **7** was isolated from the reaction, mp: 76–78°C (decompos.). Single crystals of the complex were obtained by drying on a porous tube. IR (ν/cm^{-1}): 630 (C—S). Found (%): C, 11.50; H, 2.55;

S, 15.0; Cu, 30.78. Calcd for $C_4H_{10}S_2Cu_2Br_2$ (%): C, 11.75; H, 2.46; S, 15.61; Cu, 30.96.

X-Ray Crystallographic Study

The X-Ray diffraction data for the crystals of **4–6** were collected on a CAD4 Enraf-Nonius automatic diffractometer using graphite monochromated Mo K_α (0.71073 Å) radiation. The details of crystal data, data collection, and the refinement are given in Table 1. The stability of crystals and experimental conditions was checked every 2 h using three control reflections, while the orientation was monitored every 200 reflections by centering two standards. No significant decay was observed. An empirical absorption correction based on ψ-scans was applied. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were calculated and refined as riding atoms. Programs used: data collection MoLEN [13], structure solution and refinement SIR [14], SHELXL97 [15], and WinGX [16].

Data set for **7** was collected with a Nonius KappaCCD diffractometer equipped with a molybdenum fine-focus sealed tube at the Institute of Organic Chemistry, Technical University of Dresden, Germany. Programs used: data collection COLLECT (Nonius B.V., 1998), cell refinement Dirax/lsq (Duisenberg & Schreurs, 1989–2000), data reduction EvalCCD (Duisenberg & Schreurs 1990–2000), structure solution SHELXS-97 [17], and structure refinement SHELXL-97 [16].

All figures were made using the program ORTEP3 (University of Glasgow, 2005).

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre CCDC nos. 288129, 288130, 288131, and 288132. Copies of the data can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-(1223)-336033; email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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TABLE 1 Crystallographic Data for Complexes **4–7**

	4	5	6	7
Empirical formula	$C_6H_{14}Br_2Cu_2S_2$	$C_6H_{14}Cl_2Cu_2S_2$	$C_4H_{10}Br_2Cu_2S_2$	$C_4H_{10}BrCuS_2$
Formula weight	437.19	348.31	163.66	265.69
Space group	$P2_1/c$	$P2_1/c$	$P2_1/n$	$C222_1$
a (Å)	7.776 (2)	6.409 (2)	10.649 (3)	11.201 (1)
b (Å)	15.753 (2)	12.499 (7)	7.810 (1)	12.765 (1)
c (Å)	10.856 (2)	15.503 (7)	12.245 (5)	12.785 (1)
α (°)	90	90	90	90
β (°)	109.62 (2)	99.41 (3)	99.47 (3)	90
γ (°)	90	90	90	90
V (Å^3)	1252.6 (4)	1225 (1)	1004.5 (5)	1828.0 (3)
Z	4	4	4	8
D_{calc} (mg m^{-3})	2.32	1.89	2.71	1.931
F(000)	840	696	776	1040
Crystal color	Colorless			
Crystal form	Prismatic			
Crystal size (mm)	0.3 × 0.25 × 0.25	0.4 × 0.4 × 0.35	0.3 × 0.2 × 0.15	0.70 × 0.15 × 0.15
Radiation (Å)		0.71073		
Temperature (K)	293	293	293	293 (2) K
Scan mode	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$	
θ_{max} (°)	26.3	22.75	20.6	25.4
Absorption correction	ψ-scans	ψ-scans	ψ-scans	Multi-scan
μ (cm^{-1})	100.6	41.98	125.34	71.32
Scan speed (deg · min^{-1})		Variable, 1-16.4		
Number of recorded reflections	2728	1796	1097	10721
Number of independent reflections with $I \geq 2\sigma(I)$	1581	1123	501	1696
R (%)	0.033	0.038	0.049	0.031
R_w (%)	0.072	0.076	0.083	0.060
S	1.00	1.016	0.89	1.065

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