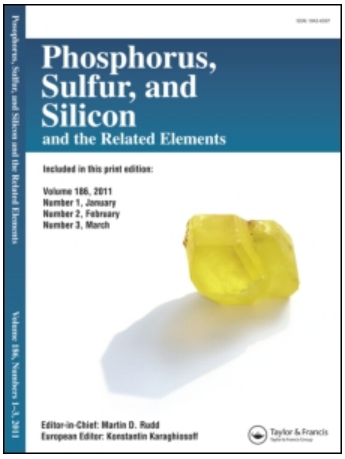

Phosphorus, Sulfur, and Silicon and the Related Elements

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Novel Copper(I) Complexes and Clusters with Phosphorus-Sulfur and Sulfur-Sulfur Containing Ligands

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The synthesis and coordination chemistry of ligands bearing PS donor groups in complexes with copper(I) halides, in particular thiophosphites, thiophosphonites, and thiophosphinites, are described.

Keywords Copper(I) complexes; coordination mode; ligand; structure; thiophosphite; thiophosphinite; thiophosphonite

RESULTS AND DISCUSSION

The following complexes of Cu(I) with ligands bearing PS donor groups have been synthesized: CuX·L [L-(*i*-PrS)$_3$P, (*i*-PrS)$_2$PCl, (*i*-PrS)$_3$P(S), *t*-BuP(SEt)$_2$, PhP(SEt)$_2$, PhP(SEt)Cl, Ph$_2$PSEt, Ph$_2$P(S)SEt], and are characterized by X-ray single crystal diffraction.

Crystals of complexes with bulky P—S ligands, [(CuX · (P(i-PrS)$_3$)], are composed of Cu_4X_4 cubane tetramers with monodentate coordination by P-atom. The same cubane tetramer is formed in crystals of copper(I) halide complexes with thiophosphonites and thiophosphinites, t-BuP(SEt)$_2$ · CuX (X = Br,I) and Ph$_2$ PSEt · CuBr, where one or two P—S bonds are substituted by the P—C bonds.

The break of coordination bonds in complexes with tetrameric cubane-like structure upon the disproportionation or recrystalization results in more stable compounds (various dimers and clusters

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including P–S and S–S ligands of another type of coordination: $[CuX \cdot P(i\text{-}PrS)_3 \cdot (MeCN)]$, $[Cu_2Br_2 \cdot 2MeCN]_n$, $[(Cu_4Cl_4 \cdot (P(i\text{-}PrS)_3)]_n$, $[CuX \cdot (RS)_2]_n$). The structure of the product including P–S ligands, $[(Cu_4Cl_4 \cdot (P(i\text{-}PrS)_3)]_n$, is composed of two-dimensional nets consisting of Cu_8Cl_8 clusters with tridentate coordination mode *via* P and two S atoms. The products that include S–S ligands (disulfides) are of the type $CuX \cdot L$ [L-$(EtS)_2$, $(i\text{-}PrS)_2$; X-Cl, Br] with bidentate coordination *via* two S atoms. Their X-ray crystal structure consists of polymeric clusters $[CuX \cdot (RS)_2]_n$ formed by Cu_2X_2 rings with fused S–S containing cycles.

Thus, copper(I) halides are notable for their ability to form the variety of structures and coordination modes with P–S and S–S ligands: rhomboid Cu_2X_2 dimers and Cu_4X_4 cubane tetramers with monodentate type of coordination; (Cu_2X_2)n stair-step polymers; and (CuX)n chains with bi- or tridentate type of coordination.