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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: $\text{CuX} \cdot \text{L}$ [$\text{L}-(i\text{-PrS})_3\text{P}$, $(i\text{-PrS})_2\text{PCl}$, $(i\text{-PrS})_3\text{P(S)}$, $t\text{-BuP(SET)}_2$, PhP(SET)_2 , PhP(SET)Cl , Ph_2PSEt , $\text{Ph}_2\text{P(S)SEt}$], and are characterized by X-ray single crystal diffraction.

Crystals of complexes with bulky P–S ligands, $[(\text{CuX} \cdot (\text{P}(i\text{-PrS})_3)]$, 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, $t\text{-BuP(SET)}_2 \cdot \text{CuX}$ ($\text{X} = \text{Br}, \text{I}$) and $\text{Ph}_2\text{PSEt} \cdot \text{CuBr}$, 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 recrystallization 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: $[\text{CuX} \cdot \text{P}(i\text{-PrS})_3 \cdot (\text{MeCN})]$, $[\text{Cu}_2\text{Br}_2 \cdot 2\text{MeCN}]_n$, $[(\text{Cu}_4\text{Cl}_4 \cdot (\text{P}(i\text{-PrS})_3))_n]$, $[\text{CuX} \cdot (\text{RS})_2]_n$. The structure of the product including P–S ligands, $[(\text{Cu}_4\text{Cl}_4 \cdot (\text{P}(i\text{-PrS})_3))_n]$, 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 $\text{CuX} \cdot \text{L}$ [$\text{L} = (\text{EtS})_2$, $(i\text{-PrS})_2$; $\text{X} = \text{Cl}, \text{Br}$] with bidentate coordination *via* two S atoms. Their X-ray crystal structure consists of polymeric clusters $[\text{CuX} \cdot (\text{RS})_2]_n$ 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; $(\text{Cu}_2\text{X}_2)_n$ stair-step polymers; and $(\text{CuX})_n$ chains with bi- or tridentate type of coordination.