



Novel bicyclic hexanuclear copper(I) aggregate: Structure and solid state ^{31}P CPMAS NMR spectra of $[(\text{Cu}_3\text{L}_3)_2]$ and $[\text{Cu}(\text{PPh}_3)_2\text{L}]$ complexes of *N*-(diisopropoxythiophosphinyl)-*N'*-phenylthiourea (HL)

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ABSTRACT

A new complex of *N*-thiophosphorylthiourea $\text{PhNHC}(\text{S})\text{NHP}(\text{S})(\text{OiPr})_2$ (**HL**) of formula $[(\text{Cu}_3\text{L}_3)_2]$ has been synthesized and characterized by single crystal X-ray diffraction, FT-IR, ^1H , ^{31}P NMR in solution and by ^{31}P CPMAS NMR spectroscopy in the solid state. A comparison of the structure and the spectral parameters of $[(\text{Cu}_3\text{L}_3)_2]$ with those of the mononuclear analogue $[\text{Cu}(\text{PPh}_3)_2\text{L}]$ was performed. In the solid state the aggregate $[(\text{Cu}_3\text{L}_3)_2]$ represents the first example of a spontaneous “side-by-side” association of two neutral cyclic $[\text{Cu}_3\text{L}_3]$ moieties using two Cu–S–Cu bridges formed by the sulfur atoms of the PS-groups. The values of the $^1J(^{31}\text{P}_{-63,65}\text{Cu})$ and $^2J(^{31}\text{P}_{-31}\text{P})$ coupling constants of the $[\text{Cu}(\text{PPh}_3)_2]^+$ moiety in the solid state spectra are reported.

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1. Introduction

Data available in the literature demonstrate, that complexes of coinage metal cations with 1,3- and 1,5-bidentate ligands derived from sulfur- or selenium-containing phosphines, exhibit a clear propensity to form oligo- and polynuclear assemblies with structural features which depend on the conditions employed for their preparation and the nature of the ligand [1–3]. The investigation of the structure of such compounds, as a rule, is impossible without the use of single crystal X-ray diffraction techniques. The situation is further complicated by the problems encountered when attempting to grow single crystals and the tendency for form oligomeric aggregates.

Therefore the development of spectroscopic methods has been the focus of recent interest as such techniques not only provide information on the structure of a given compound but can also shed light on the mechanism of its formation. The literature contains reports on the successful application of solid state nuclear magnetic resonance for this purpose. For example, the solid-state ^{31}P and ^{65}Cu NMR spectroscopy allowed to determine successfully selected structural parameters of some polynuclear copper(I)

complexes like $[\text{Cu}_4\{\text{S}_2\text{P}(\text{OR})_2\}_4]$, $[\text{Cu}_6\{\text{S}_2\text{P}(\text{OR})_2\}_6]$ and $[\text{Cu}_8\{\text{S}_2\text{P}(\text{OR})_2\}_6(\mu^8\text{-S})]$ ($\text{R} = \text{alkyl}$) [3,4].

This type of researches is important not only for the understanding of the fundamental laws of polynuclear coordination structure formation, but also open the ways for further use of the formed molecules. The complexes of phosphorus-, sulfur- or selenium-containing ligands with coinage metals cations are of great interest due to their photophysical properties [5,6], their application for creation of chalcogenide nanoparticles [1c], and as models for biological objects [7].

Contrary to the dithiophosphate ligands, there is a lack of information about the structures of polynuclear copper(I) complexes containing *N*-thiophosphorylated thioureas and thioamides, $\text{RC}(\text{S})\text{NHP}(\text{S})\text{R}'_2$ ($\text{R} = \text{R}'_2\text{N}$, alkyl, aryl). The molecular structures of three polynuclear Cu^{I} complexes namely the cyclic trimers $[\text{Cu}_3\{\text{Et}_2\text{NC}(\text{S})\text{NP}(\text{S})(\text{OPh})_2\}_3]$ [8], $[\text{Cu}_3\{\text{MfC}(\text{S})\text{NP}(\text{S})(\text{OiPr})_2\}_3]$ ($\text{Mf} = \text{morpholyn-N-yl}$) [9] and of an ionic aggregate $[\text{Cu}_{10}\{\text{PhNHC}(\text{S})\text{NP}(\text{S})(\text{OEt})_2\}_9]\text{ClO}_4$ [10], have been reported.

In this study, we describe the synthesis and the structural characterization of the new *N*-thiophosphorylthiourea $\text{PhNHC}(\text{S})\text{NHP}(\text{S})(\text{OiPr})_2$ (**HL**) and of its polynuclear Cu^{I} aggregate $[(\text{Cu}_3\text{L}_3)_2]$ (**1**) (Chart 1). To the best of our knowledge, compound **1** represents the first example for the spontaneous “side-by-side” association of the two neutral cyclic $[\text{Cu}_3\text{L}_3]$ moieties to give a hexameric unit.

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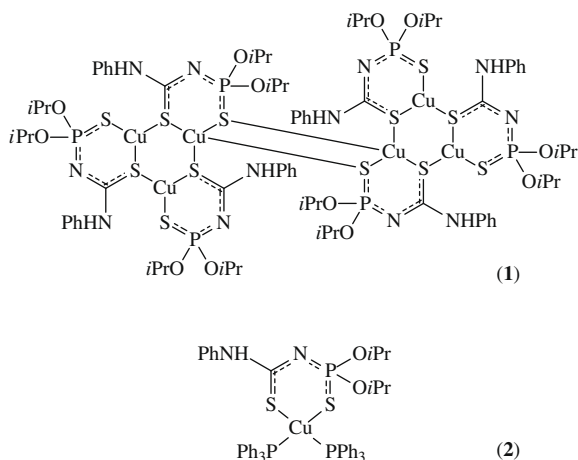


Chart 1. R = PhNH, R' = OiPr.

The structural and spectral parameters of the aggregate are discussed in comparison with the mononuclear analog $[\text{Cu}(\text{PPh}_3)_2\text{L}]$ (**2**), which has been reported earlier [11].

2. Results and discussions

Reaction of the potassium salt **KL** with copper(I) iodide leads, according to microanalytical data, to the formation of a complex **1** having the composition $[\text{CuL}]$. The reaction of **KL** with copper(II) nitrate in ethanol leads to the same product. The identity of the compounds received by these two methods, was confirmed by spectroscopic methods (NMR, IR in the fingerprint area) and single crystal X-ray diffraction.

The mononuclear complex $[\text{Cu}(\text{PPh}_3)_2\text{L}]$ (**2**) has been obtained by the reaction of **KL** with $[\text{Cu}(\text{PPh}_3)_3\text{I}]$. Complexes **1** and **2** were purified by slow crystallization from a $\text{CH}_2\text{Cl}_2/\text{C}_6\text{H}_{14}$ solvent mixture.

Electrospray ionization (ESI-MS) mass spectra of complex **1** did not exhibit the $[\text{M}+\text{H}]^+$ peak. The heaviest ion at m/z 1643 (20%) corresponds to the cation $[\text{Cu}_5\text{L}_4]^+$. The most intensive peaks in the spectra correspond to the cation $[\text{Cu}_4\text{L}_3]^+$ with m/z 1247. This peak has also been observed for all mononuclear or polynuclear Cu^{I} complexes of *N*-thiophosphorylthioureas [9,11]. Medium-intensity (10–12%) peaks for $[\text{Cu}_3\text{L}_2]^+$ cations were also observed in the spectra of **1** and **2**.

The IR spectra of the thiourea **HL** exhibit a medium strong band for the P=S group stretching vibration centered at 638 cm^{-1} [12]. The band is shifted to lower wavenumbers in the spectra of the complexes **1** and **2** due to Cu^{I} coordination. A single absorption peak has been observed in the spectra of the mononuclear complex **2**, while three new bands at 561, 567, and 589 cm^{-1} appear for the polynuclear aggregate **1** (Fig. 1).

The broad and strong absorption peaks for the conjugated SCN group at $1500\text{--}1530\text{ cm}^{-1}$ (**1**) and 1530 cm^{-1} (**2**) are characteristic for the formation of *S,S'*-chelates [13]. The NH stretching vibrations of NHP and NHPH groups in the thiourea **HL** are observed as two peaks at 3100 and 3200 cm^{-1} . Unique bands related to the NHPH groups in the $3320\text{--}3350\text{ cm}^{-1}$ region were observed in the spectrum of the complexes **1** and **2**.

The ^{31}P NMR spectra of complexes **1** and **2** (CDCl_3 solution) exhibit a singlet for the phosphorus atom of the NPS group and one set of signals of the protons of the ligand. No broadening of the signals and no indications for the presence of additional complexes were found in the NMR spectra.

The signal for the phosphorus atom in the ^{31}P NMR spectrum of **1** is highfield shifted by 4.7 ppm relative to the parent thiourea **HL**.

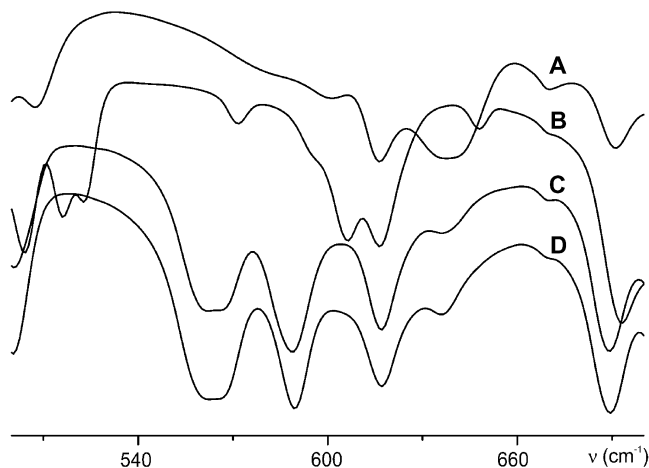


Fig. 1. Comparison of a section of the IR spectra (Nujol) of **HL** (A), $[\text{Cu}(\text{PPh}_3)_2\text{L}]$ (**2**) (B), and $[(\text{Cu}_3\text{L}_3)_2]$ (**1**) obtained by reaction with CuI (C) and $\text{Cu}(\text{NO}_3)_2$ (D).

For complex **2** no such highfield shift has been observed ($\Delta\delta_{\text{p}} = 0.2\text{ ppm}$). This observation can be related to the smaller electron-deficiency of the tetracoordinated copper(I) atom, coordinated by two PPh_3 donor groups in comparison with the coordinatively unsaturated tricoordinated copper atom in complex **1**. An increase in the Cu–S(P) bond order leads to an increase of the electron density at the phosphorus atom and causes its shielding. This effect can be presented schematically, as an increase of the contribution of the mesomeric structure $[\text{S}=\text{C}-\text{N}=\text{P}-\text{S}^-]$ during the negative charge delocalization in L^- . The internuclear distances in the molecular structure (see below) also testify to a greater degree of participation of the sulfur atom of the P=S group in the formation of the Cu–S(P) bonds in complex **1** in comparison with the similar bonds in the mononuclear analogue **2**.

The molecular structures of the hexameric **1** (Fig. 2) and mononuclear complex **2** (Fig. 3) were determined by single crystal X-ray diffraction (Table 1). Crystals of the complexes have been obtained by slow crystallization from a dichloromethane/*n*-hexane solution, 1:2 (v/v).

In the crystalline state complex **1** is a hexamer containing two cyclic trimeric units $[\text{Cu}_3\text{L}_3]$ connected by a pair of $\text{Cu}(2)\text{--S}(5)\text{--Cu}(2)$ bridges. Symmetry transformations used to generate equivalent atoms: (*) $1-x, -y+1, -z+1$. The trimers are formed by the bridging action of the μ^2 -sulfur atoms of the CS-groups. The hexamer is formed by the μ^2 -sulfur atoms of the PS-groups of the ligands.

The $\text{Cu}(1)$ and $\text{Cu}(3)$ atoms are found in a trigonal S_3 environment. Atom $\text{Cu}(2)$, participating in the bridging between trimers, is coordinated in a distorted tetrahedral $\text{S}_3\text{S}'$ environment. The values of the bond angles $\text{S}(1)\text{--Cu}(2)\text{--S}(5)$ and $\text{S}(2)\text{--Cu}(2)\text{--S}(5)$, are significantly distorted from the perfect tetrahedron value (Table 2).

The bridging distances $\text{Cu}(2)\text{--S}(5)$, is longer than the other Cu–S bonds in the molecule (Table 2). The Cu–S bond distances in the cycle $\text{Cu}(2)\text{--S}(2)\text{--C}(14)\text{--N}(3)\text{--P}(2)\text{--S}(5)$ are noticeably increased compared with the cycles at the $\text{Cu}(1)$ and $\text{Cu}(2)$ atoms.

The $\text{Cu}(2)\text{--Cu}(2)$, separation of $2.8016(9)\text{ \AA}$ measures close to twice the van der Waals radius of Cu, 2.80 \AA [14]. The other Cu...Cu distances fall in the range $3.62\text{--}3.80\text{ \AA}$, showing no metal–metal interactions.

The values of the bond distances in the six-membered cycles Cu--S--C--N--P--S differ slightly. In comparison with the parent ligand **HL** [15] lengthening of the C=S and shortening of the C–N bonds are observed upon complex formation. The same changes, but to a lesser degree, has been observed for the P–N and P=S bonds. The measured values for the internuclear distances are in

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