



# Novel bicyclic hexanuclear copper(I) aggregate: Structure and solid state $^{31}\text{P}$ 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)

Felix D. Sokolov<sup>a</sup>, Maria G. Babashkina<sup>a</sup>, Franck Fayon<sup>b,c</sup>, Aydar I. Rakhmatullin<sup>b,c</sup>, Damir A. Safin<sup>a,\*</sup>, Tania Pape<sup>d</sup>, F. Ekkehardt Hahn<sup>d</sup>

<sup>a</sup> A. M. Butlerov Chemistry Institute, Kazan State University, Kremlevskaya St. 18, 420008 Kazan, Russian Federation

<sup>b</sup> CEMHTI-CNRS, 1D Avenue de la Recherche Scientifique, 45071 Orléans Cedex2, France

<sup>c</sup> Université d'Orléans, Faculté des Sciences, Avenue du Parc Floral, BP 6749, 45067 Orléans Cedex2, France

<sup>d</sup> Institut für Anorganische und Analytische Chemie, Westfälische Wilhelms-Universität Münster, Corrensstrasse 36, D-48149 Münster, Germany

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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,  $^1\text{H}$ ,  $^{31}\text{P}$  NMR in solution and by  $^{31}\text{P}$  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  $^{31}\text{P}$  and  $^{65}\text{Cu}$  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  $\text{Cu}^{\text{I}}$  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  $\text{Cu}^{\text{I}}$  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.

\* Corresponding author. Fax: +7 843 254 37 34.

E-mail address: damir.safin@ksu.ru (D.A. Safin).

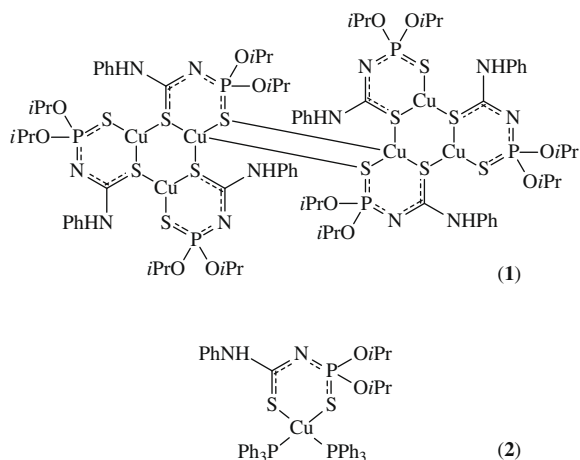


Chart 1. R = PhNH, R' = OiPr.

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  $\text{Cu}^{\text{I}}$  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  $638\text{ cm}^{-1}$  [12]. The band is shifted to lower wavenumbers in the spectra of the complexes **1** and **2** due to  $\text{Cu}^{\text{I}}$  coordination. A single absorption peak has been observed in the spectra of the mononuclear complex **2**, while three new bands at 561, 567, and  $589\text{ cm}^{-1}$  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  $1530\text{ cm}^{-1}$  (**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  $3200\text{ cm}^{-1}$ . 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  $^{31}\text{P}$  NMR spectra of complexes **1** and **2** ( $\text{CDCl}_3$  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  $^{31}\text{P}$  NMR spectrum of **1** is highfield shifted by 4.7 ppm relative to the parent thiourea **HL**.

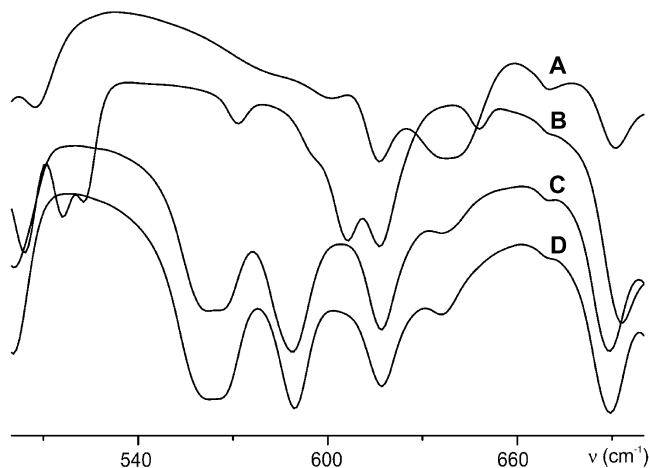


Fig. 1. Comparison of a section of the IR spectra (Nujol) of **HL** (A),  $[\text{Cu}(\text{PPh}_3)_2\text{L}]$  (**2**) (B), and  $[\text{Cu}_3\text{L}_2]_2$  (**1**) obtained by reaction with  $\text{CuI}$  (C) and  $\text{Cu}(\text{NO}_3)_2$  (D).

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  $\text{PPh}_3$  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  $\text{L}^-$ . 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  $\mu^2$ -sulfur atoms of the CS-groups. The hexamer is formed by the  $\mu^2$ -sulfur atoms of the PS-groups of the ligands.

The  $\text{Cu}(1)$  and  $\text{Cu}(3)$  atoms are found in a trigonal  $\text{S}_3$  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,  $2.80\text{ \AA}$  [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  $\text{Cu--S--C--N--P--S}$  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

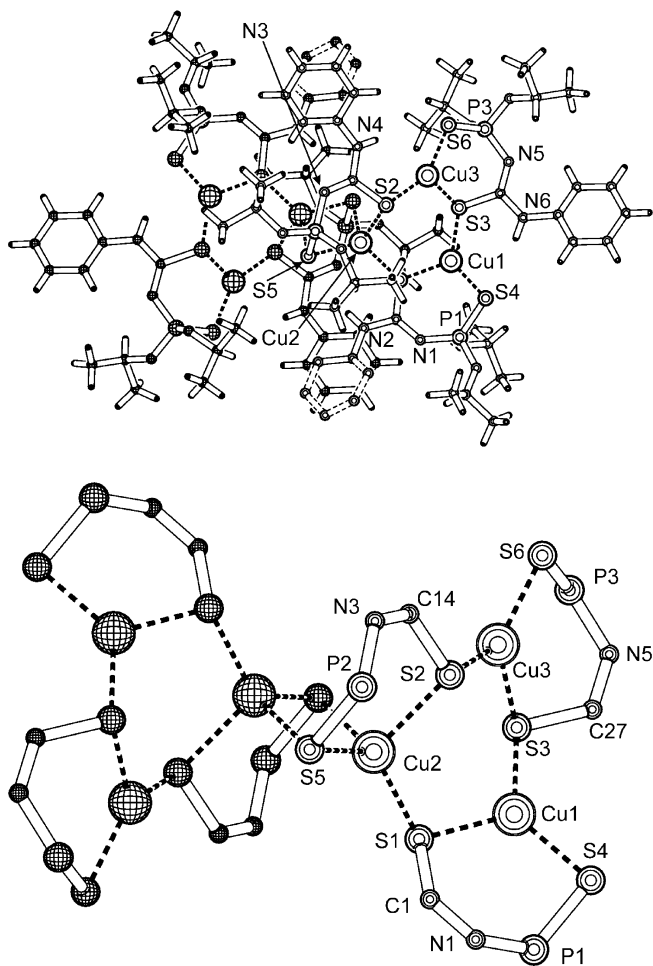


Fig. 2. Crystal structure of complex  $[(\text{Cu}_3\text{L}_3)_2]$  (**1**) (top) and the structure of the polynuclear complex backbone (substituents are omitted for clarity).

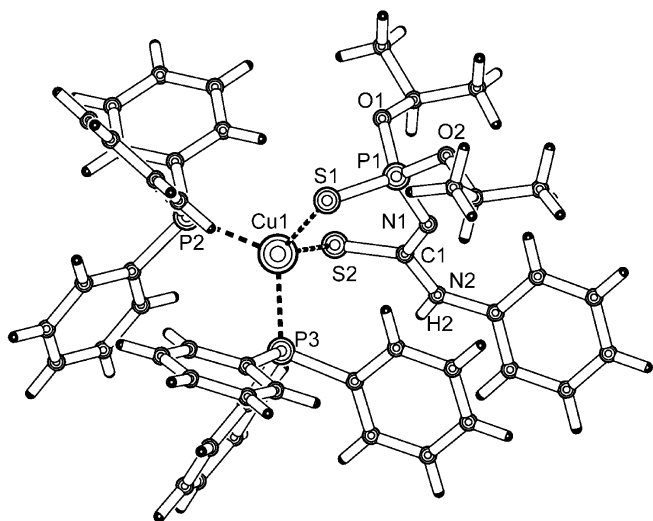


Fig. 3. Crystal structure of complex  $[\text{Cu}(\text{PPh}_3)_2\text{L}]$  (**2**).

a range which is characteristic for the complexes of *N*-thioacylamidophosphates and *N*-thiophosphorylated thioureas [13].

The four-membered metallocycle  $\{\text{Cu}(2)-\text{S}(5)-\text{Cu}(2),-\text{S}(5),\}$  is flat. The six-membered metallocycle  $\{\text{Cu}(1)-\text{S}(1)-\text{Cu}(2)-\text{S}(2)-\text{Cu}(3)-\text{S}(3)\}$  is in a twist-boat conformation with tops at the Cu(1) and S(2) atoms. The dihedral angle between root-mean-

Table 1  
Crystal data, data collection and refinement details for **1** and **2**.

	<b>1</b>	<b>2</b>
Empirical formula	$\text{C}_{78}\text{H}_{120}\text{Cu}_6\text{N}_{12}\text{O}_{12}\text{P}_6\text{S}_{12}$	$\text{C}_{49}\text{H}_{50}\text{CuN}_2\text{O}_2\text{P}_3\text{S}_2$
Formula mass	2369.64	919.48
Crystal form	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
<i>a</i> (Å)	13.1158(19)	13.5916(19)
<i>b</i> (Å)	14.102(2)	13.6610(19)
<i>c</i> (Å)	16.142(2)	14.1437(19)
$\alpha$ (°)	105.228(3)	117.705(3)
$\beta$ (°)	100.058(3)	92.922(3)
$\gamma$ (°)	107.719(3)	99.910(3)
<i>V</i> (Å <sup>3</sup> )	2636.7(7)	2264.4(5)
<i>Z</i>	1	2
<i>D</i> <sub>calc</sub> (mg/m <sup>3</sup> )	1.492	1.349
Temperature (K)	233(2)	153(2)
<i>F</i> (000)	1224	960
$\mu$ [cm <sup>-1</sup> ]	15.75	7.22
Number of recorded reflections	15204	10404
Number of independent reflections	9185 ( <i>R</i> <sub>int</sub> = 0.0378)	7842 ( <i>R</i> <sub>int</sub> = 0.0427)

Table 2  
Selected bond lengths (Å), and bond angles (°) for **1**.

Bond lengths			
Cu(1)–S(3)	2.2045(10)	S(5)–P(2)	2.0035(14)
Cu(1)–S(4)	2.2143(13)	S(6)–P(3)	1.9896(13)
Cu(1)–S(1)	2.2182(11)	P(1)–N(1)	1.592(4)
Cu(3)–S(2)	2.1886(10)	P(2)–N(3)	1.602(3)
Cu(3)–S(6)	2.2177(11)	P(3)–N(5)	1.602(3)
Cu(3)–S(3)	2.2499(10)	N(1)–C(1)	1.293(5)
Cu(2)–S(1)	2.2795(10)	N(3)–C(14)	1.314(4)
Cu(2)–S(2)	2.3187(10)	N(5)–C(27)	1.303(4)
Cu(2)–S(5)	2.3302(10)	N(2)–C(1)	1.353(5)
Cu(2)–S(5)	2.4942(10)	N(2)–C(2)	1.415(5)
S(1)–C(1)	1.757(4)	N(4)–C(14)	1.352(4)
S(2)–C(14)	1.750(3)	N(4)–C(15)	1.417(4)
S(3)–C(27)	1.763(4)	N(6)–C(27)	1.341(4)
S(4)–P(1)	1.954(2)	N(6)–C(28)	1.420(4)
Bond angles			
S(1)–Cu(2)–S(2)	109.24(4)	S(2)–Cu(2)–S(5)	95.68(3)
S(1)–Cu(2)–S(5)	126.16(4)	S(5)–Cu(2)–S(5)	109.09(3)
S(2)–Cu(2)–S(5)	106.71(4)	Cu(2)–S(5)–Cu(2)	70.91(3)
S(1)–Cu(2)–S(5)	105.74(4)		

square planes of the  $\{\text{Cu}_2\text{S}_2\}$  and  $\{\text{Cu}_3\text{S}_3\}$  cycles measures 70.93°. Hydrogen bonds are not observed in the crystal structure of complex **1**.

In the molecular structure of complex  $[\text{Cu}(\text{PPh}_3)_2\text{L}]$  (**2**) (Fig. 3), the copper(I) cation is in a  $\text{P}_2\text{S}_2$  tetrahedral environment. The weak distortion relative to a perfect tetrahedron (Table 3) reveal the absence of major steric hindrance.

The structures of the six-membered cycles of **1** and **2** have many common features, typical for similar compounds [9,11], like the flat N–C(S)–N–P–O fragment. The six-membered Cu(1)–S(2)–C(1)–N(1)–P(1)–S(1) metallocycle in the mononuclear analogue **2**, as well as in complex **1**, are in a boat conformation. The P(1) and S(2) atoms occupy apical positions.

The Cu(1)–S(2) bond is 0.04 Å longer than the Cu(1)–S(1) distance, which indicates the greater contribution of the S-enolic form of  $\text{L}^-$ . It is interesting to note, that the interatomic distances Cu(1)–S(1) in the six-membered cycle of the complex **2** is significantly larger than the distances Cu(1)–S(4), Cu(2)–S(5), Cu(3)–S(6) in the complex **1**. The lengthening of the Cu–S(P) bond in complex **2** is caused by the smaller acceptor ability of the coordinative-saturated copper atom in a  $\text{P}_2\text{S}_2$  environment in comparison with the copper in a trigonal  $\text{S}_3$  or distorted-tetrahedral  $\text{S}_3\text{S}'$  environment.

Complex **2** forms centrosymmetric dimers due to formation of intermolecular hydrogen bonds N(2)–H(2)⋯S(2). Hydrogen bond

**Table 3**  
Selected bond lengths (Å), and bond angles (°) for **2**.

Bond lengths			
Cu(1)–P(2)	2.2623(7)	S(2)–C(1)	1.744(2)
Cu(1)–P(3)	2.3181(7)	P(1)–N(1)	1.6149(19)
Cu(1)–S(2)	2.3303(7)	N(1)–C(1)	1.312(3)
Cu(1)–S(1)	2.3730(7)	N(2)–C(1)	1.355(3)
S(1)–P(1)	1.9716(9)	N(2)–C(2)	1.412(3)
Bond angles			
P(2)–Cu(1)–P(3)	115.00(3)	S(2)–Cu(1)–S(1)	105.80(2)
P(2)–Cu(1)–S(2)	113.83(2)	P(1)–S(1)–Cu(1)	98.93(3)
P(3)–Cu(1)–S(2)	107.22(3)	C(1)–S(2)–Cu(1)	101.24(8)
P(2)–Cu(1)–S(1)	107.95(3)	N(1)–P(1)–S(1)	118.45(8)
P(3)–Cu(1)–S(1)	106.41(2)	C(1)–N(1)–P(1)	126.92(16)

parameters are as follows:  $d(\text{NH})$  0.8400 Å,  $d(\text{HS})$  2.6700 Å,  $d(\text{NS})$  3.4704 Å,  $\angle(\text{NHS})$  161.0°. Symmetry transformations used to generate equivalent atoms: (\* ) 1 – x, 1 – y, 1 – z.

To obtain information about the solid state structures of the  $\text{Cu}^{\text{I}}$  complexes we have investigated polycrystalline samples of these complexes using  $^{31}\text{P}$  MAS NMR spectroscopy (Table 4).

The crystal structure of **1** shows a centrosymmetric molecule, containing three types of the phosphorus atoms (P1, P2, P3). This observation is in good agreement with the CPMAS NMR data, containing three singlets (Fig. 4). Simulation of the spectrum using the DMFIT program [16] has enabled us to determine the exact values of the chemical shifts of the phosphorus atoms and a ratio of the integrated intensities 1/1/1 (Table 4).

A similar picture emerged previously in the spectrum of the trimeric associate  $[\text{Cu}_3\{\text{MfC}(\text{S})\text{NP}(\text{S})(\text{OiPr})_2\}_3]$  [9]. The  $^{31}\text{P}$  CPMAS NMR data indicate the expected presence of three nonequivalent P-sites in the solid state. This could be used for the identification of the asymmetric trimeric fragment  $\{\text{Cu}_3[\text{RC}(\text{S})\text{NP}(\text{S})(\text{OiPr})_2]\}$  in the structure of the polynuclear complexes.

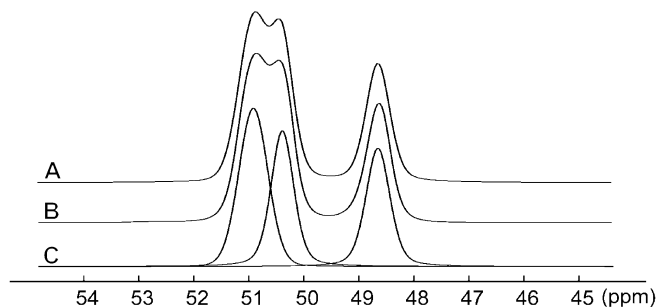
Obviously, the  $^{31}\text{P}$  chemical shifts in the  $[\text{Cu}_3\text{L}_3]$  and  $[(\text{Cu}_3\text{L}_3)_2]$  aggregates cannot be identical due to nonequivalent electronic situation on the phosphorus nuclei and different environment in a crystal. The  $^{31}\text{P}$  CPMAS NMR spectra containing the only one sets of signals, that proves the formation of the only type of the complexes in the obtained crystal samples, not the mix of the  $[\text{Cu}_3\text{L}_3]$  and  $[(\text{Cu}_3\text{L}_3)_2]$  aggregates.

At the same time, the given method does not allow to distinguish the trimeric compounds from the centrosymmetric dimer of trimers. This example shows that spectral identification of the structure of polynuclear aggregates in the solid state on the basis of  $^{31}\text{P}$  MAS data should be necessarily supplemented by crystallographic data and additional information using methods sensitive to change of a coordination environment of copper(I).

The X-ray data have shown that complex **2** contains three different types of the phosphorus atoms (the P=S group and two nonequivalent  $\text{PPh}_3$  groups). The solid state  $^{31}\text{P}\{^1\text{H}\}$  CPMAS NMR spectrum of this compound contains a singlet for the phosphorus atom of **L** (Table 4). The signals for the phosphorus atoms of the  $\text{PPh}_3$  ligands were observed as multiplets owing to the indirect spin–spin interaction  $^1J(^{63,65}\text{Cu}-^{31}\text{P})$ , and  $^2J(^{31}\text{P}-^{31}\text{P})$  (Fig. 5). The presence of both two NMR-active copper isotopes ( $^{65}\text{Cu}$  and

**Table 4**  
 $^{31}\text{P}$  isotropic chemical shifts and  $^1J_{\text{P}-\text{Cu}}$  and  $^2J_{\text{P}-\text{P}}$  coupling constants of  $\text{Cu}^{\text{I}}$  complexes **1** and **2**.

	$\delta_{\text{iso}}$ (ppm)	$^1J(^{63}\text{Cu}-^{31}\text{P})$	$^1J(^{65}\text{Cu}-^{31}\text{P})$	$^2J(^{31}\text{P}-^{31}\text{P})$	$I$ (%)
1	48.7 [CuL]				33.0
	50.4 [CuL]				34.1
	50.9 [CuL]				32.9
2	61.5 [CuL]				33.4
	–3.0 [ $\text{PPh}_3$ ]	1124 Hz	1204 Hz	121 Hz	32.0
	–11.8 [ $\text{PPh}_3$ ]	922 Hz	977 Hz	121 Hz	34.6

**Fig. 4.** The experimental (A) and simulated (B, C) of the solid state  $^{31}\text{P}\{^1\text{H}\}$  CPMAS NMR spectrum of the polynuclear complex  $[(\text{Cu}_3\text{L}_3)_2]$  (**1**).

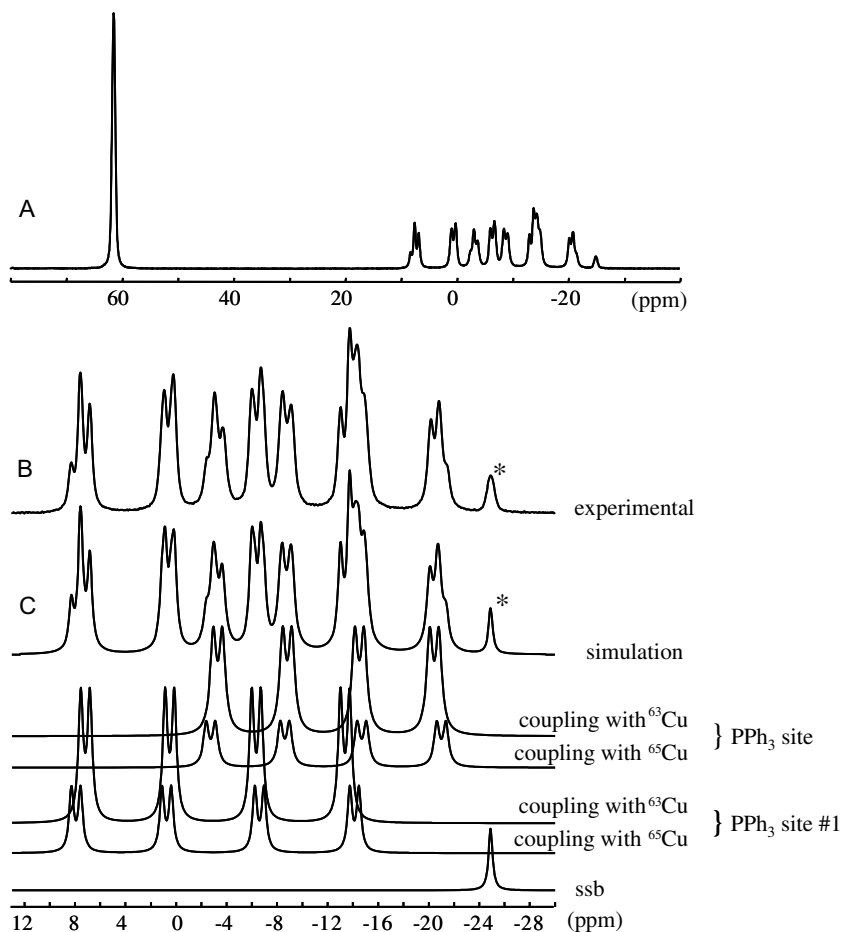
$^{63}\text{Cu}$ ) and a homonuclear  $^2J_{\text{PCuP}}$  coupling of about 121 Hz, which was also measured using a two-dimensional spin echo MAS experiment [17–19] (not shown), leads to a 16-lines multiplet for each of the two inequivalent P sites. Each 16-lines multiplet consists of two distinct quartets of doublets with relative intensities in the ratio of about 2.3, in good agreement with the natural abundance of the two copper isotopes (69.1% for  $^{63}\text{Cu}$  and 30.9% for  $^{65}\text{Cu}$ ). An isotopic effect on the  $^1J_{\text{Cu}-\text{P}}$  scalar coupling is clearly observed and the  $^1J(^{63}\text{Cu}-^{31}\text{P})/^1J(^{65}\text{Cu}-^{31}\text{P})$  ratio determined experimentally is of about 0.938, as expected from the gyromagnetic ratios of the  $^{63,65}\text{Cu}$  isotopes. No isotopic effect on the  $^{31}\text{P}$  isotropic chemical shift was observed experimentally. It should be noted that the  $^1J_{\text{PCu}}$  and  $^2J_{\text{PCuP}}$  couplings were not observed in the solution NMR spectra due to the fast exchange between free and bound triphenylphosphine groups. Table 4 gives the  $^{31}\text{P}$  NMR isotropic chemical shifts and isotropic  $J$ -coupling constants determined from the simulations of the CPMAS spectrum. The coupling constants obtained are comparable to values found previously for complexes with the same  $\text{Cu}_2\text{P}_2$  complex core [9,20]. The P-site quantification obtained from a single pulse spectrum is in agreement with the expected site multiplicities and the  $^{63,65}\text{Cu}$  isotopic abundances. The simulation of the  $J$ -multiplet patterns (shown in Fig. 5) takes in account “residual dipolar” effects due to the dipolar and anisotropic scalar couplings between  $^{31}\text{P}$  and the quadrupolar copper nuclei [21–23]. However, only the magnitude of this term was fitted since both the  $^{63,65}\text{Cu}$  quadrupolar coupling constants and  $J$ -coupling anisotropy are unknown. In order to get more detailed interpretation of this spectrum, additional  $^{63,65}\text{Cu}$  NMR experiments at very high magnetic field allowing to measure the  $^{63,65}\text{Cu}$  quadrupolar coupling parameters are in progress.

### 3. Experimental

#### 3.1. Physical measurements

$^1\text{H}$  and  $^{31}\text{P}$  NMR experiments in solutions were performed on a Bruker AMX-300 NMR spectrometer.  $^{31}\text{P}$  NMR spectra with continuous wave  $^1\text{H}$  decoupling were acquired using a single pulse of 7  $\mu\text{s}$  duration ( $\pi/4$ ) and a recycle delay varying between 1 and 5 s to ensure no saturation.  $^{31}\text{P}$  solid-state magic angle spinning (MAS) NMR were carried out on a Bruker Avance 400 (9.4 T) spectrometer using a 4 mm probe-head. The  $^{31}\text{P}\{^1\text{H}\}$  cross-polarization (CP) MAS NMR spectra were recorded at a spinning frequency of 14 kHz using a ramped cross-polarization [24] with a contact time of 1 ms and a recycle delay of 2 s.  $^1\text{H}$  decoupling was achieved using the SPINAL-64 sequence [25] with a  $^1\text{H}$  nutation frequency of about 60 kHz. Quantitative MAS spectra were acquired (with and without  $^1\text{H}$  decoupling) using single pulse of 0.5  $\mu\text{s}$  duration ( $\pi/12$ ) and a recycle delay of 1 s. Chemical shifts are referred to  $\text{SiMe}_4$  ( $^1\text{H}$ ) and 85%  $\text{H}_3\text{PO}_4$  ( $^{31}\text{P}$ ) solutions. All MAS NMR spectra were modeled using the DMFIT program [16]. Infrared spectra





**Fig. 5.** The solid state  $^{31}\text{P}\{^1\text{H}\}$  CPMAS NMR spectrum of the mononuclear complex  $[\text{Cu}(\text{PPh}_3)_2\text{L}]$  (**2**) (A). Expansion of the experimental (B) and simulated  $J$ -multiplet patterns (C) of the  $\text{PPh}_3$  ligands. Spinning side-band is marked with an asterisk (\*).

(Nujol) were recorded with a Specord M-80 spectrometer in the frequency range  $400\text{--}3600\text{ cm}^{-1}$ . Electrospray ionization mass spectra were measured with a Finnigan-Mat TCQ 700 mass spectrometer on a  $10^{-6}\text{ M}$  solution in  $\text{CH}_3\text{OH}$ . The speed of sample submission was  $2\text{ }\mu\text{L}/\text{min}$ . The ionization energy was  $4.5\text{ kV}$  and the capillary temperature was  $200\text{ }^\circ\text{C}$ . Elemental analyses were performed on a Perkin-Elmer 2400 CHN microanalyser.

### 3.2. Synthesis of **HL**

*N*-(Diisopropoxythiophosphinyl)-*N'*-phenylthiourea (**HL**) was prepared according to the previously described method [12].

### 3.3. Synthesis of $[(\text{Cu}_3\text{L}_3)_2]$ (**1**)

**Path a:** A suspension of **HL** (0.996 g, 3 mmol) in aqueous ethanol (25 mL) was mixed with an ethanol solution of KOH (0.185 g, 3.3 mmol). The resulting mixture was added dropwise to the suspension of CuI (0.570 g, 3 mmol) in aqueous ethanol (20 mL). The mixture was stirred at room temperature for 1.5 h. The obtained precipitate of KI was filtered and the solvent was then removed in vacuum. The residue was recrystallized from a dichloromethane/*n*-hexane mixture 1:5 (v/v). Complex **1** was obtained as light colorless crystals. Yield: 0.782 g, (66%). M.p.  $165\text{ }^\circ\text{C}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) 1.36 (d,  $^3J_{\text{H,H}} = 6.1\text{ Hz}$ , 6H,  $\text{CH}_3$ ), 1.37 (d,  $^3J_{\text{H,H}} = 6.1\text{ Hz}$ , 6H,  $\text{CH}_3$ ), 4.80 (d. sept,  $^3J_{\text{POCH}} = 10.6\text{ Hz}$ ,  $^3J_{\text{H,H}} = 6.1\text{ Hz}$ , 2H, OCH), 7.06–7.11 (m, 1H, *p*- $\text{C}_6\text{H}_5$ ), 7.26–7.31 (m, 2H, *m*- $\text{C}_6\text{H}_5$ ), 7.59–7.61 (m, 2H, *o*- $\text{C}_6\text{H}_5$ ), 8.46 (d,  $^4J_{\text{PNCNH}} = 8.2\text{ Hz}$ , 1H, NH) ppm.  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ) 50.4 ppm. IR: 3354 (NH), 1500–1530 (SCN), 985, 1020

(POC), 561, 567, 589, 637 (P=S)  $\text{cm}^{-1}$ . ES-MS (positive ion):  $m/z$  (%) = 1643 (20)  $[\text{Cu}_5\text{L}_4]^+$ , 1248 (100)  $[\text{Cu}_4\text{L}_3]^+$ , 853 (12)  $[\text{Cu}_3\text{L}_2]^+$ . Anal. Calc. for  $\text{C}_{78}\text{H}_{120}\text{Cu}_6\text{N}_{12}\text{O}_{12}\text{P}_6\text{S}_{12}$  (2369.76): C, 39.53; H, 5.10; N, 7.09. Found: C, 39.68; H, 5.03; N, 7.21%.

**Path b:** A suspension of **HL** (0.996 g, 3 mmol) in aqueous ethanol (25 mL) was mixed with an ethanol solution of KOH (0.185 g, 3.3 mmol). The resulting mixture was added dropwise to the suspension of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (0.363 g, 1.5 mmol) in aqueous ethanol (20 mL). The mixture was stirred at room temperature for 1.5 h. The obtained precipitate of  $\text{KNO}_3$  was filtered and the solvent was then removed in vacuum. The residue was recrystallized from a dichloromethane/*n*-hexane mixture 1:5 (v/v). Complex **1** was obtained as light colorless crystals.

### 3.4. Synthesis of $[\text{Cu}(\text{PPh}_3)_2\text{L}]$ (**2**)

A suspension of **HL** (0.996 g, 3 mmol) in aqueous ethanol (25 mL) was mixed with an ethanol solution of KOH (0.185 g, 3.3 mmol). A dichloromethane (25 mL) solution of  $[\text{Cu}(\text{PPh}_3)_3]$  (2.931 g, 3 mmol) was added dropwise under vigorous stirring to the resulting potassium salt. The mixture was stirred at room temperature for a further 1 h and a precipitate was filtered off. The filtrate was concentrated until the crystallization began. The residue was recrystallized from a dichloromethane/*n*-hexane mixture 1:5 (v/v). Complex **2** was obtained as colorless crystals. Yield: 1.917 g (87%). M.p.  $145\text{ }^\circ\text{C}$  ( $146\text{ }^\circ\text{C}$ , Ref. [11]).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) 1.28 (d,  $^3J_{\text{H,H}} = 6.2\text{ Hz}$ , 6H,  $\text{CH}_3$ ), 1.31 (d,  $^3J_{\text{H,H}} = 6.1\text{ Hz}$ , 6H,  $\text{CH}_3$ ), 4.74 (d. sept,  $^3J_{\text{POCH}} = 10.8\text{ Hz}$ ,  $^3J_{\text{H,H}} = 6.2\text{ Hz}$ , 2H, OCH), 7.01–7.06 (m, 1H, *p*- $\text{C}_6\text{H}_5$ , L), 7.28–7.41 (m, 30H,  $\text{C}_6\text{H}_5$ ), 7.51–7.54 (m, 2H, *o*- $\text{C}_6\text{H}_5$ ,

L), 7.64–7.71 (m, 2H, *m*-C<sub>6</sub>H<sub>5</sub>, L) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>) –1.2 (s, 2P, PPh<sub>3</sub>), 54.9 (s, 1P, NPS) ppm. IR: 3320 (NH), 1530 (SCN), 976, 995, 1012, 1025 (POC), 606 (P=S) cm<sup>-1</sup>. ES-MS (positive ion): *m/z* (%) = 1248 (12) [Cu<sub>4</sub>L<sub>3</sub>]<sup>+</sup>, 854 (4) [Cu<sub>3</sub>L<sub>2</sub>]<sup>+</sup>, 588 (100) [Cu(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup>. Anal. Calc. for C<sub>49</sub>H<sub>50</sub>CuN<sub>2</sub>O<sub>2</sub>P<sub>3</sub>S<sub>2</sub> (919.53): C, 64.00; H, 5.48; N, 3.05. Found: C, 63.87; H, 5.56; N, 3.10%.

### 3.5. Crystal structure determination and refinement

The X-ray crystal structure determination was performed using a Bruker AXS APEX CCD diffractometer equipped with a rotating anode and graphite-monochromated Mo K<sub>α</sub> radiation. Data were collected over the full sphere and were corrected for absorption using the program SADABS [26]. The structures were solved by direct methods and refined with full-matrix least-squares on *F*<sup>2</sup> using SHELXL-97 [27]. Hydrogen atoms were placed on idealized positions, and refined with fixed isotropic displacement parameters using a riding model.

## 4. Conclusions

The cyclic [Cu<sub>3</sub>L<sub>3</sub>] unit is rather common for copper(I) complexes of *N*-phosphorylthioureas [8,9] and imidodiphosphinate ligands [1,2], but there are no examples of a further assembly between such structure moieties. The structure found in the crystal of the copper(I) complex **1** is the first example of such an association.

Available data testify that the influence of substituents in the ligand on a structure of formed complexes should not be underestimated. Even minor alteration of the ligand structure can have great value. e.g. the example of the versalite coordination towards Ni(II) and Pd(II) cations [28].

In this particular case we also have the new data to bear out this thesis. As it was established recently, the formation of the completely different type of [Cu<sub>*n*</sub>L<sub>*n*</sub>] complexes in a crystal phase take place depending on a structure of the assistant at R in fragment RC(S)NHP(S)(OiPr)<sub>2</sub> groups in the identical experimental conditions. The formation of the trimeric (R = *t*BuNH [29]), tetranuclear (R = Me<sub>2</sub>N [29], Ph [30]) cyclic associates as well, as hexanuclear (R = NH<sub>2</sub> [31]) and octanuclear (R = *i*PrNH [29]) polycyclic associates has been found.

The spontaneous “side-by-side” assembly of the two neutral cyclic [Cu<sub>3</sub>L<sub>3</sub>] moieties could be caused by the comparatively lower steric demand of the PhNH-group in comparison with complexes of *N*-phosphorylthioureas with branched substituents [8–10] and tetraorganoimidodiphosphinate ligands [1,2]. The literature data are too scarce for a reliable comparison, but at the moment we could presume that decreasing of the steric value of the substituents R and R' at the RC(S)NHP(S)R'<sub>2</sub> backbone leads to an increase of the size of the polynuclear aggregate formed. A contribution of weak H-bond intermolecular interactions between [Cu<sub>3</sub>L<sub>3</sub>] with participation of the PhNH-groups could be named as an other possible reason of the further association.

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## Appendix A. Supplementary material

CCDC 652056 and 652057 contains the supplementary crystallographic data for this paper. These data can be obtained free of

charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). Crystallographic data for the structural analyses with thermal parameters and complete tables of interatomic distances and angles. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorgchem.2008.10.010](https://doi.org/10.1016/j.jorgchem.2008.10.010).

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