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Dedicated to Professor Ionel Haiduc,
President of The Romanian Academy at his 70th anniversary

NEW COPPER(I) AND COPPER(II) TETRAORGANODICHALCOGENOIMIDODIPHOSPHINATES. CRYSTAL AND MOLECULAR STRUCTURE OF THE FIRST MONOTHIOIMIDODIPHOSPHINATO COPPER(I) COMPLEX, $Cu_4[(OPMe_2)(SPPh_2)N]_4{\cdot}6CH_2Cl_2$

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ABSTRACT. New copper complexes containing dichalcogenoimidodiphosphinato ligands, *i.e.* $Cu_4[(OPMe_2)(SPPh_2)N]_4$ (**1**), $(Ph_3P)_2Cu[(SPMe_2)(SPPh_2)N]$ (**2**) and $Cu[(SPMe_2)(SPPh_2)N]_2$ (**3**), were prepared and characterized. The molecular structure of the complex **1**$\cdot 6CH_2Cl_2$ was established by single-crystal X-ray diffraction. The crystal contains discrete tetranuclear units with a distorted Cu_4 tetrahedron [Cu···Cu 2.702(3) and 3.060(2) Å] and bimetallic triconnective monothio ligands [Cu-S 2.258(3), 2.267(4) Å; Cu-O 1.969(9) Å]. All four copper centers are tricoordinated ($CuOS_2$ core), in an almost planar, trigonal arrangement.

Key-words: copper, imidodiphosphinato ligands, solution NMR studies, RES, X-ray diffraction

Introduction

During last decade copper complexes containing dichalcogenoimidodiphosphinato ligands raised considerable interest as structural model compounds for the active-sites in copper-containing enzymes and proteins [1-3], compounds with nonlinear optical properties [4] or precursors for solid state materials [5]. In most cases reported so far phosphorus ligands containing the same chalcogen in the molecular unit were used. When protic solvent conditions were used the reduction of copper(II) salts of dithio ligands resulting in the isolation of copper(I) complexes was observed. Ionic Cu(I) compounds containing tetranuclear cations, *i..e.* $[Cu_4\{(SPPh_2)_2N\}_3][X]$ (X = $[CuCl_2]^-$ [6], $[BF_4]^-$ [7], $[I_3]^-$ [8]), $[Cu_4\{(SePPh_2)_2N\}_3][BF_4]^-$ [7], or a cluster anion in $[Et_4N]_4[Mo_4Cu_8O_4S_{12}\{(SPPh_2)_2N\}_4]$ [4], as well as neutral trinuclear complexes, *i..e.* $[Cu\{(EPPr^i_2)_2N\}]_3$ (E = S [9], Se [5]),

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$[Cu\{(SPPr^i_2)(SPPh_2)N\}]_3$, $[Cu\{(SPPr^i_2)(SP(OPh)_2)N\}]_3$ [9], $[Cu\{(SP(OC_6H_4Bu^t\text{-}2)_2)_2N\}]_3$ [10], were structurally characterized by single-crystal X-ray diffraction. Mononuclear Cu(I) complexes can be obtained in the presence of triphenylphosphine, *e.g.* $(Ph_3P)Cu[(EPPh_2)_2N]$ (E = S [11], Se [12]) and $(Ph_3P)_2Cu[(OPPh_2)_2N]$ [13]. Recently, ionic Cu(I) complexes containing protonated imidodiphosphinato ligands, *i.e.* $[Cu\{(SPPh_2)_2NH\}_2][I_3]$ [8] and $[Cu\{(OPPh_2)_2NH\}_3][PF_6]$ [14], were also reported. Copper(II) complexes were found to be generally stabilized by the use of oxo ligands, *i.e.* monomeric $Cu[\{OP(OPh)_2\}_2N]_2$ [15], $Cu[(OPPh_2)_2N]_2$ [13], and dimeric $[Cu\{(OPPh_2)_2N\}(O_2PPh_2)]_2$ [16]. So far, the molecular structure of only one copper(II) complex containing mixed dichalcogenoimidodiphosphinato ligands, $Cu[(OPPh_2)(SPPh_2)N]_2$ [13], was established by X-ray diffraction.

We report here on the synthesis and characterization of the first tetranuclear Cu(I) monothioimidodiphosphinate, $Cu_4[(OPMe_2)(SPPh_2)N]_4$, as well as the dithioimidodiphosphinato derivatives $(Ph_3P)_2Cu[(SPMe_2)(SPPh_2)N]$ and $Cu[(SPMe_2)(SPPh_2)N]_2$.

Experimental

The organophosphorus starting materials were prepared according to literature methods: $Na[(OPMe_2)(SPPh_2)N]$ [17], $K[(SPMe_2)(SPPh_2)N]$ [18]. Room-temperature ^1H and ^{31}P NMR spectra were recorded in dried $CDCl_3$ on a BRUKER AVANCE 300 instrument operating at 300.11 and 121.48 MHz, respectively. The chemical shifts are reported in ppm relative to the residual peak of the deuterated solvent (ref. $CHCl_3$: ^1H 7.26 ppm) and H_3PO_4 85%, respectively. ESR measurements were performed on powder compound at room temperature (r.t.) on a Radiopan SE/X-2543 9 GHz ESR spectrometer, using a 100 kHz field modulation.

*Preparation of $Cu_4[(OPMe_2)(SPPh_2)N]_4$ (**1**)*

A mixture of $CuCl_2{\cdot}2H_2O$ (0.170 g, 1 mmol) and $Na[(OPMe_2)(SPPh_2)N]$ (0.663 g, 2 mmol) in CH_2Cl_2 (30 ml) was stirred for 6 h at room temperature. After removing NaCl, the solvent was evaporated to dryness. The remaining colorless solid was recrystallized from a mixture of CH_2Cl_2/n-hexane to afford the title compound. Yield: 0.27 g (74%, with respect to copper), m.p. 127-129°C. ^1H NMR: δ 0.91t (6H, CH_3, $^2J_{PH}$ 13.8 Hz), 7.35m (6H, C_6H_5 – *meta+para*), 7.93ddd (4H, C_6H_5 - *ortho*, $^3J_{PH}$ 13.8, $^3J_{HH}$ 6.0, $^4J_{HH}$ 2.2 Hz). ^{31}P NMR: δ 42.7s (Ph_2PS), 47.7s (Me_2PO).

*Preparation of $(Ph_3P)_2Cu[(SPMe_2)(SPPh_2)N]$ (**2**)*

A mixture of $(Ph_3P)_2CuNO_3$ (0.356 g, 0.55 mmol) and $K[(SPMe_2)(SPPh_2)N]$ (0.199 g, 0.55 mmol) in CH_2Cl_2 (30 ml) was stirred for 6 h at room temperature. The insoluble KNO_3 was filtered off and the solvent was evaporated to dryness under vacuum. The remaining colorless solid was recrystallized from a mixture of CH_2Cl_2/n-hexane to afford the title compound. Yield: 0.4 g (80%), m.p. 132°C. ^1H NMR: δ 1.84d (6H, CH_3, $^2J_{PH}$ 13.1 Hz), 7.34m [30H, $P(C_6H_5)_3$], 7.47m (4H, C_6H_5 – *meta*), 7.71m (2H, C_6H_5 –*para*), 7.89ddd (4H, C_6H_5 - *ortho*, $^3J_{PH}$ 13.3, $^3J_{HH}$ 7.7, $^4J_{HH}$ 1.7 Hz). ^{31}P NMR: δ -3.2s [$P(C_6H_5)_3$], 32.4d (Ph_2PS, $^1J_{PC}$ 109.0, $^2J_{PP}$ 11.8 Hz), 38.3s (Me_2PS, $^1J_{PC}$ 75.7, $^2J_{PP}$ 11.8 Hz).

*Preparation of $Cu[(SPMe_2)(SPPh_2)N]_2$ (**3**)*

A mixture of $CuCl_2·2H_2O$ (0.143 g, 0.84 mmol) and $K[(SPMe_2)(SPPh_2)N]$ (0.614 g, 1.69 mmol) in CH_2Cl_2 (30 ml) was stirred for 6 h at room temperature. The resulted KCl was filtered off and the solvent was evaporated to dryness under vacuum. The remaining yellow-brown solid was recrystallized from a mixture of CH_2Cl_2/n-hexane to afford the title compound. Yield: 0.26 g (43%), m.p. 285°C. ^{31}P NMR: δ 21.2s, 38.0s (broad signals). ESR (X band): $g_{||}$ 2.78±0.01, $g_{\perp}$ 2.77±0.01.

X-ray Crystallographic Study

Data were collected with a SMART APEX diffractometer (*National Center for X-Ray Diffractometry*, “Babes-Boyai” University, Cluj-Napoca, Romania) at 297 K, using a graphite monochromator to produce a wavelength (Mo-$K\alpha$) of 0.71073 Å. The crystal structure measurement and refinement data for compound **1**·$6CH_2Cl_2$ are given in Table 1. Absorption corrections were applied using the multi-scan (Bruker SAINT) method [19]. The structure was solved by direct methods (full-matrix least-squares on F^2). All non hydrogen atoms were refined with anisotropic thermal parameters. For structure solving and refinement a software package SHELX-97 was used [20]. The drawings were created using the Diamond program by Crystal Impact GbR [21].

Table 1.

Crystallographic data for compound **1**·$6CH_2Cl_2$

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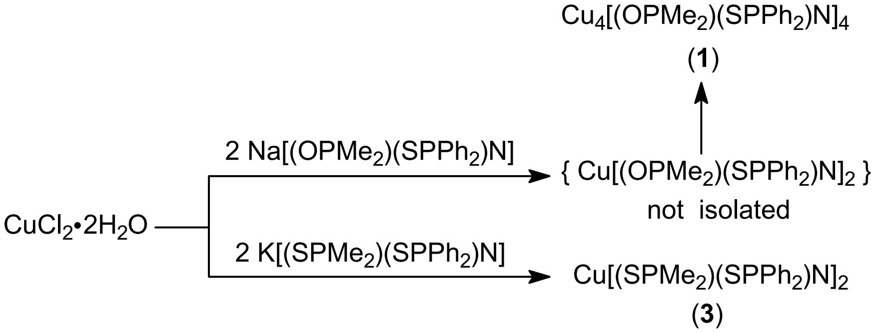
Empirical formula	$C_{62}H_{76}Cl_{12}Cu_4N_4O_4P_8S_4$		
Formula mass	1996.91	*F*(000)	2024
Crystal system	Tetragonal	Crystal size [mm]	0.48x0.34x0.30
Space group	*P4(2)/n*	μ(Mo-Kα) [mm^{-1}]	1.633
a [Å]	14.742(6)	θ range [°]	1.72-26.36
b [Å]	14.742(6)	No. of reflections collected	22761
c [Å]	19.858(16)	No. of independent reflections	4408 (R_{int} = 0.0928)
α [°]	90	No. of parameters	224
β [°]	90	R_1 [$I > 2\sigma(I)$]	0.1644
γ [°]	90	wR_2	0.3123
V [Å^3]	4316(4)	GOF on F^2	1.381
Z	2	Largest difference electron density [e/Å^3]	1.838/-0.810
$D_{calcd.}$ [g/cm^3]	1.537		

CCDC-642236 (**1**·$6CH_2Cl_2$) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Results and discussion

Synthesis and spectroscopic characterization

The reaction of $CuCl_2·2H_2O$ with $Na[(OPMe_2)(SPPh_2)N]$ affords the isolation of the tetranuclear $Cu_4[(OPMe_2)(SPPh_2)N]_4$ (**1**), formed by reduction of the intermediate copper(II) species, $Cu[(OPMe_2)(SPPh_2)N]_2$, which could not be isolated under the conditions used. By contrast, the reaction of $CuCl_2·2H_2O$ with $K[(SPMe_2)(SPPh_2)N]$ resulted in the isolation of the copper(II) species, $Cu[(SPMe_2)(SPPh_2)N]_2$ (**3**):



The metathesis reaction between $(Ph_3P)_2CuNO_3$ and $K[(SPMe_2)(SPPh_2)N]$ resulted in the expected mononuclear copper(I) complex, $(Ph_3P)_2Cu[(SPMe_2)(SPPh_2)N]$ (**2**):

$$(Ph_3P)_2CuNO_3 \xrightarrow{K[(SPMe_2)(SPPh_2)N]} (Ph_3P)_2Cu[(SPMe_2)(SPPh_2)N]$$

(**2**)

The copper(I) complexes were isolated in good yield as colorless solids, while the copper(II) complex was obtained as a yellow-brown solid. They are air-stable compounds, soluble in common organic solvents.

All compounds were investigated by NMR spectroscopy (^1H, ^{31}P) in $CDCl_3$ solutions. For copper(I) species the solution NMR spectra of the isolated products are consistent with the formation of the complexes **1** and **2**. The ^1H NMR spectra, recorded in $CDCl_3$, showed the resonances for the organic groups attached to phosphorus atoms, with the expected splitting due to phosphorus-proton. The ^{31}P NMR spectra exhibit two resonances, consistent with non equivalent phosphorus atoms in a dichalcogenoimidodiphosphinato unit. The signals were assigned by comparison with the spectra of the free acids or the alkali salts used as starting materials. For compound **2** the ^{31}P signals are surrounded by satellites and the magnitude of the phosphorus-carbon couplings is consistent with the assignments for the corresponding resonances. In addition, for compound **2** a resonance at δ -3.2 ppm was also observed, which is indicative for the presence of the Ph_3P ligands coordinated to the metal centre.

The ^{31}P NMR spectrum of compound **3** exhibits two very broad resonances, a behavior which is indicative for a copper(II) species. Evidences for its paramagnetic nature were provided by the ESR spectrum which shows two lines located at about 2392 and 2399 Gs, respectively. The half width of the lines is very close to the values of 2.23 and 2.67 Gs. We consider these lines to appear due to the Cu^{2+} ions in an axial symmetry. The *g*-factors are 2.78 and 2.77, respectively, and they represent the middle of the parallel and perpendicular spectra. However, it was not possible to observe the hyperfine structure due probably to (*i*) the very high concentration of the paramagnetic ions, (*ii*) the covalent nature of the compound, and/or (*iii*) the exchange interactions between the paramagnetic ions.

On the basis of the spectroscopic data monomeric structures with tetrahedral CuP_2S_2 and CuS_4 cores are proposed for compounds **2** and **3**, respectively. Similar structures were established for $(Ph_3P)_2Cu[(OPPh_2)_2N]$ and $Cu[(OPPh_2)_2N]_2$ [13].

Single-crystal X-ray diffraction studies

Single-crystals of **1**$\cdot 6CH_2Cl_2$, suitable for X-ray diffraction studies, were obtained by slow diffusion from a mixture of CH_2Cl_2 and hexane (1/4, v/v). The crystal consists of discrete tetranuclear $Cu_4[(OPMe_2)(SPPh_2)N]_4$ units separated by normal van der Waals distances. The ORTEP diagram of the molecular structure of **1** (solvent molecules were omitted for clarity), with the atom numbering scheme, is shown in Figure 1. Selected interatomic distances and angles are listed in Table 2.

The tetranuclear unit contains a central Cu_4 core of distorted tetrahedral geometry. Alternatively, the Cu_4 core can be described as a folded square system [dihedral angle Cu(1)Cu(1a)Cu(1c) / Cu(1)Cu(1b)Cu(1c) 86.8°] and strong transannular copper-copper interactions [Cu(1)-Cu(1c) 3.060(2) Å]. The Cu···Cu distances [Cu(1)-Cu(1a) 2.702(3) Å] in the folded square system are significantly shorter than those observed in the $[Cu_4\{(SPPh_2)_2N\}_3]^-$ cations [range 2.763(3)-2.815(3) Å [6], 2.773(2)-2.844(2) Å [7], 2.758(1)-2.837(1) Å [8]), but in the range [2.658(5)-2.757(5) A] found for the related dithiocarbamate $Cu_4(S_2CNEt_2)_4$ [22]. The transannular Cu···Cu distances in **1** compare well with the longest metal-metal distances [3.092(2) Å] found in the tetranuclear $Cu_4[SC(NH_2)_2]_6(NO_3)_4\cdot 4H_2O$ [23].

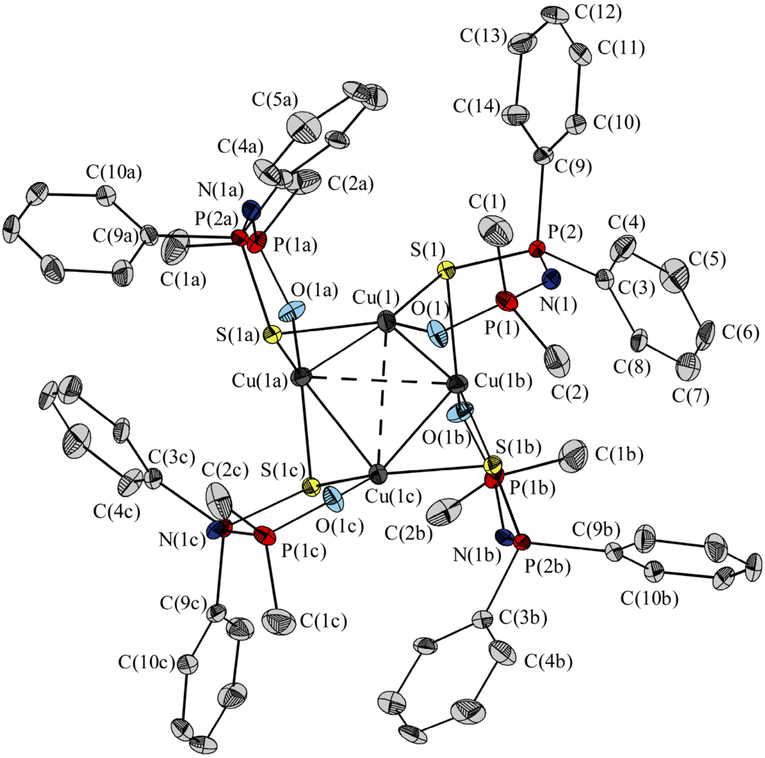


Figure 1. ORTEP representation at 20% probability and atom numbering scheme for $Cu_4[(OPMe_2)(SPPh_2)N]_4 \cdot 6CH_2Cl_2$ (**1**) (for clarity, solvent molecules and hydrogen atoms are not shown).

The central Cu_4 core is surrounded by four monothioimidodiphosphinato ligands, each exhibiting a *bimetallic triconnective* coordination pattern. The oxygen atom of a ligand unit is bound to one copper atom [Cu(1)-O(1) 1.969(9) Å], while the sulfur atom is bridging two metal centers in a symmetrical fashion [Cu(1)-S(1) 2.267(4) Å, Cu(1b)-S(1) 2.258(3) Å]. The lengths of the Cu-O and Cu-S bonds in **1** compare well with those observed in the tetrahedral isomer of $Cu[(OPPh_2)(SPPh_2)N]_2$ [Cu-O 1.940(2) / 1.934(2) Å; Cu-S 2.284(1) / 2.293(1) Å], but are considerably shorter than those observed in the copper(I) species $(Ph_3P)_2Cu[(OPPh_2)_2N]$ [Cu-O 2.122(2)/ 2.165(2) Å] and $(Ph_3P)_2Cu(S_2PMe_2)$ [Cu-S 2.434(1) / 2.480(1) Å] [13].

As result of the coordination pattern of the monothioimidodiphosphinato ligands, the copper atoms achieve a distorted trigonal environment, with the S-Cu-S angle more opened on the expense of the O-Cu-S angles (Table 1). The metal atom is 0.186 Å out of the plane defined by the oxygen and the two sulfur atoms, being displaced towards the centre of the Cu_4 core.

Table 2.

Interatomic bond distances (Å) and angles (°) for compound **1**·$6CH_2Cl_2$.[a]

Cu(1)-Cu(1a)	2.702(3)	Cu(1)-Cu(1b)	2.702(3)
Cu(1a)-Cu(1c)	2.702(3)	Cu(1b)-Cu(1c)	2.702(3)
Cu(1)-Cu(1c)	3.060(2)	Cu(1a)-Cu(1b)	3.060(2)
Cu(1)-O(1)	1.969(9)		
Cu(1)-S(1)	2.267(4)	Cu(1b)-S(1)	2.258(3)
Cu(1)-S(1a)	2.258(3)		
P(1)-O(1)	1.518(9)	P(2)-S(1)	2.052(4)
P(1)-N(1)	1.611(11)	P(2)-N(1)	1.537(12)
P(1)-C(1)	1.756(17)	P(2)-C(3)	1.806(12)
P(1)-C(2)	1.779(16)	P(2)-C(9)	1.828(12)
O(1)···S(1)[b]	3.569(9)		
Cu(1a)-Cu(1)-Cu(1b)	68.97(7)		
Cu(1a)-Cu(1)-Cu(1c)	55.51(5)	Cu(1b)-Cu(1)-Cu(1c)	55.51(5)
O(1)-Cu(1)-S(1)	114.6(3)	S(1)-Cu(1)-S(1a)	128.90(9)
O(1)-Cu(1)-S(1a)	114.3(3)		
O(1)-Cu(1)-Cu(1a)	147.3(3)	S(1)-Cu(1)-Cu(1a)	90.06(12)
O(1)-Cu(1)-Cu(1b)	107.9(3)	S(1)-Cu(1)-Cu(1b)	53.18(10)
O(1)-Cu(1)-Cu(1c)	95.0(3)	S(1)-Cu(1)-Cu(1c)	107.92(9)
S(1a)-Cu(1)-Cu(1a)	53.47(9)	S(1a)-Cu(1)-Cu(1b)	121.45(10)
S(1a)-Cu(1)-Cu(1c)	81.63(9)		
Cu(1)-S(1)-Cu(1b)	73.35(11)		
Cu(1)-O(1)-P(1)	124.1(5)	Cu(1)-S(1)-P(2)	101.28(16)
		Cu(1b)-S(1)-P(2)	100.42(14)
O(1)-P(1)-N(1)	116.6(5)	S(1)-P(2)-N(1)	120.1(4)
P(1)-N(1)-P(2)	136.4(7)		

[a] Symmetry equivalent positions (*y, 1.5-x, 0.5-z*), (*1.5-y, x, 0.5-z*) and (*1.5-x, 1.5-y, z*) are denoted by “a”, “b” and “c”; [b] Non-bonding distances.

Although the phosphorus-nitrogen bonds within the OPNPS skeleton are apparently not equivalent, suggesting a single P_O-N [1.611(11) Å] and a double P_S=N [1.537(12) Å], the difference is not significant in view of the ±3σ parameter (esd). The lengths of the phosphorus-oxygen [1.518(9) Å] and phosphorus-sulfur [2.052(4) Å] bonds are typical for single bonds [c.f. $Ph_2P(=O)OH$ [24]: P–O 1.526(6), P=O 1.486(6) Å; $Me_3Sb(O\text{-}PPh_2\text{=N-}PPh_2\text{=S})_2$ [25]: P-O 1.544(6) / 1.556(5) Å, P=S 1.962(3) / 1.972(3) Å, P_O=N 1.571(7) / 1.564(6) Å, P_S-N 1.601(7) / 1.618(6) Å; Me–S–PPh2=N–PPh2=S [25]: P–S 2.071(1), P=S 1.954(1), P–N 1.610(2), P=N 1.562(2) Å].

The six-membered $CuOSP_2N$ ring is not planar, but folded along the axis joining the phosphorus atoms, with a dihedral angle of 26.7° between the best plane through Cu(1), O(1), S(1), P(1) and P(2) atoms [deviations: Cu(1) -0.001, O(1) -0.126, S(1) 0.013, P(1) 0.016, and P(2) -0.012 Å] and the P(1)N(1)P(2) plane.

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