

Coordination of bis((dimethylphosphinyl)methyl)amine to copper(II). Synthesis and single-crystal structure of its mononuclear octahedral copper(II) complex

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The synthesis and structural characterization of a mononuclear complex of bis((dimethylphosphinyl)methyl)amine, L with a composition $[\text{CuL}_2]\text{Cl}_2 \cdot 3\text{H}_2\text{O}$ has been discussed in a comparison with series of copper(II) complexes in order to study the mode of the ligand coordination as a function of the electronic properties of the metal ion and the particular reaction conditions. All copper(II) coordination compounds of the titled ligand have been obtained as a result of its interaction with $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ at different M:L molar ratios in ethanol and were isolated as neutrals compounds containing different counter ions (Cl^- , AsF_6^-). The compound $[\text{CuL}_2]\text{Cl}_2 \cdot 3\text{H}_2\text{O}$ crystallizes in orthorhombic *Fdd2* space group with unit cell parameters $a = 19.123(16)$, $b = 21.657(16)$, $c = 13.107(11)$ Å and $Z = 8$. Its crystal structure consists of complex $[\text{Cu}^{2+}\text{L}_2]^{2+}$ cations, chloride anions and water molecules. The L ligands are coordinated in a tridentate mode each of them forming two five-membered Cu-O-P-C-N rings. The Cu^{2+} in the CuO_4N_2 -chromophores exhibits tetragonally compressed octahedral coordination.

Keywords: Cu^{2+} complex, tetragonally compressed octahedral coordination, bis((dimethylphosphinyl)methyl)amine.

INTRODUCTION

Among the essential elements, copper has an important role for the biological systems [1]. Many enzymes and proteins have coordinated copper ions and thus their active sites are formed [2]. The biological functions of copper containing proteins and enzymes involve electron transfer, dioxygen transport and control on processes of oxidation, reduction and disproportionation. The importance of copper transporters for the selective cellular uptake of the platinum based antitumor drugs was established [3, 4]. Drug transport, intracellular shuffling and export, carried out by the high-affinity copper transporters contribute cumulatively to the chemo-

sensitivity of platinum drugs and thus for improvement of their mode of action.

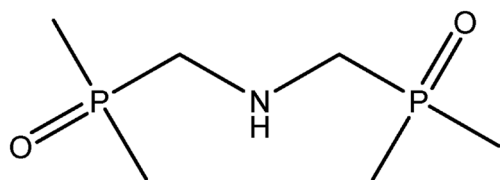
Metallobiomolecules and in particular, copper biomolecules [5] can be considered as complicated coordination complexes whose active sites are constructed from one or more metal ions together with the donor atoms in their inner co-ordination sphere originating from the proteins and enzymes. The complexity of the biological systems makes the detailed study on their mechanism of action very difficult. An approach to circumvent the problem is to elucidate the structures and model mechanisms on simpler coordination compounds. Thus, in order to mimic the physicochemical properties of the metalloproteins numerous new simple coordination compounds have been synthesized.

The investigations on the coordination chemistry of copper(II) is stimulated by the construction of models for copper proteins [6]. An additional

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challenge for the intensive studies in this field is to understand the factors which give rise to the seemingly infinite variety of distortions from regular stereochemistry observed for Cu(II) complexes [7–9]. The copper compounds containing Cu^{2+} with its d^9 electron configuration are strongly affected by the Jahn–Teller effect [10–12]. The metal atom in the copper(II) compounds display square-planar, square pyramidal, trigonal bipyramidal or octahedral coordination which due to the Jahn–Teller effect could be tetragonally compressed or elongated [13–16]. Very few of the Cu^{2+} complexes with regular square pyramidal and trigonal bipyramidal geometry are known as most of the complexes adopt geometries that are intermediate between these extremes [17].

Here we report the synthesis and the single crystal structure of a mononuclear Cu^{2+} complex of bis((dimethylphosphinyl)methyl)amine [18],



Scheme 1. Molecular structure of bis((dimethylphosphinyl)methyl)amine.

Scheme 1, with tetragonally compressed octahedral geometry and composition $[\text{CuL}_2]\text{Cl}_2 \cdot 3\text{H}_2\text{O}$ (Fig. 1).

The ligand belongs to the group of aminophosphine oxides [19] and especially to functionalized nitrogen-containing tertiary phosphine oxides (AmPOs). The organophosphorus compounds, including AmPOs are extensively studied in the past years because of their various industrial applications and ability of the phosphorus substituents to regulate important cellular processes. It is proved already that the introduction of organophosphorus functionalities in simple synthons may afford useful substrates for the preparation of biologically active compounds [20]. AmPOs have additional N-containing functional groups that together with highly basic P=O groups and the substituents at the pentavalent phosphorus atom determine their special behavior in regard to coordination ability, flexibility, lipophilicity, etc. The diverse properties of the AmPOs are the basis for their application as molecular precursors to produce new polymeric materials, in catalytic organic reactions, in selective separation mostly for lanthanides and actinides, etc.. Due to their biological importance there has been growing interest in coordination chemistry [21, 22] of this class of ligands. Here, we discuss the mode of coordination of bis((dimethylphosphinyl)methyl)amine as a function of the copper(II) nature and the reaction conditions on the basis of a series of complexes (Scheme 2).

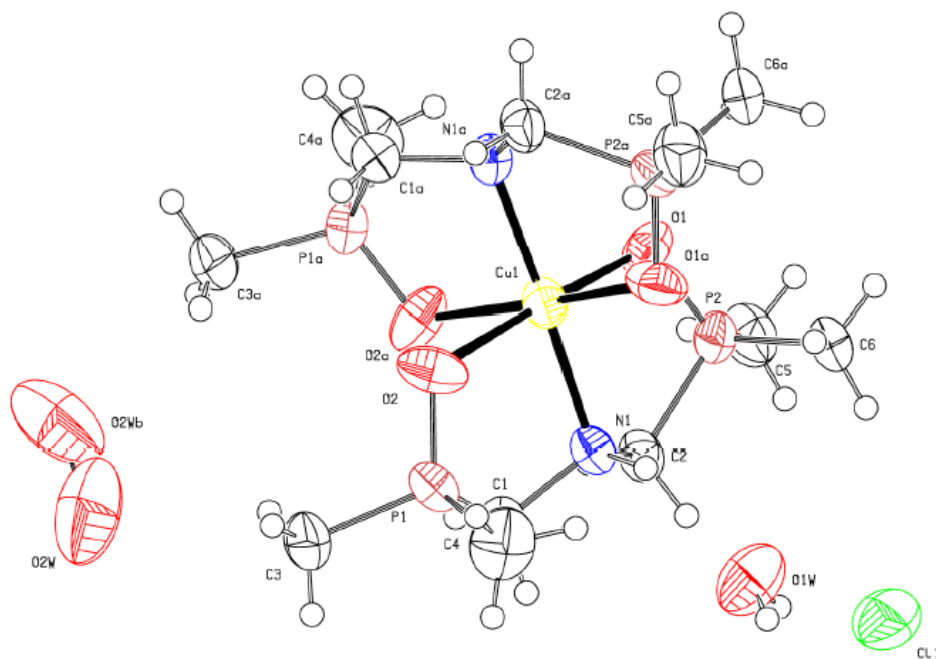
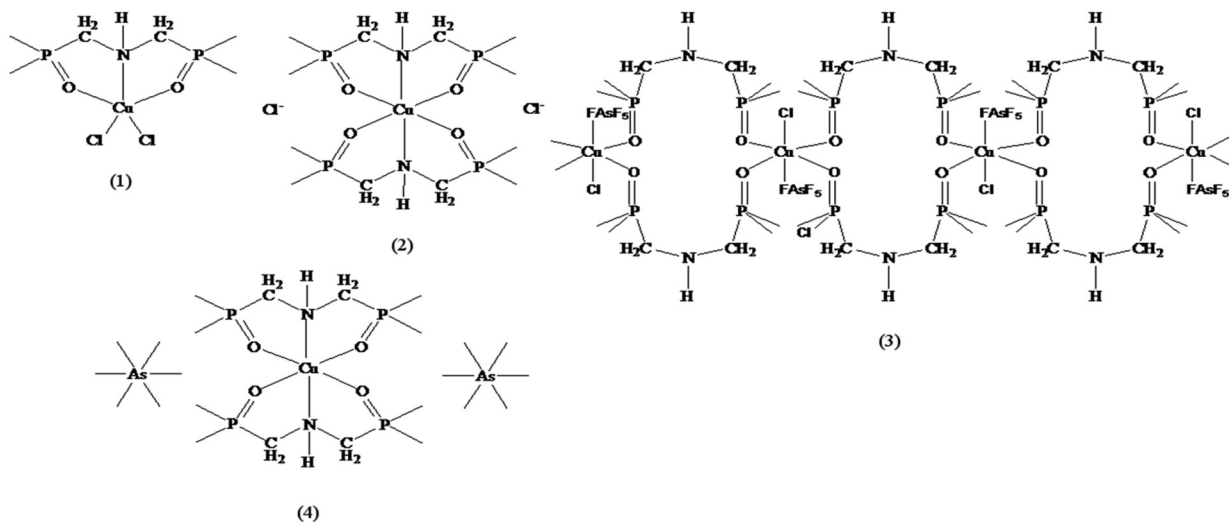


Fig. 1. ORTEP drawing of the molecular structure of the compound 2. The thermal displacement ellipsoids are drawn at the 50% probability.



Scheme 2. A series of copper(II) complexes of bis((dimethylphosphinyl)-methyl)amine.

EXPERIMENTAL

Synthesis

The ligand bis((dimethylphosphinyl)methyl)amine was synthesized as described in the literature [18]. All other reagents were of analytical grade and were used without further purification and drying; $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and LiAsF_6 (Fluka) and $\text{C}_2\text{H}_5\text{OH}$ (Merck).

Synthesis of $[\text{CuLCl}_2]$, **1**: 0.0170 g (0.10 mmol) of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and 0.0381 g (0.19 mmol) L ($\text{L}:\text{Cu}^{2+}=2$) were dissolved each in 5 mL $\text{C}_2\text{H}_5\text{OH}$. Then the two solutions were mixed, stirred magnetically and heated (40 °C) for 3 hours. The complex was obtained as blue crystals by slow evaporation at room temperature for a week. *Anal. Calc. for 1*, $\text{C}_6\text{H}_{17}\text{NP}_2\text{O}_2\text{Cl}_2\text{Cu}$ ($\text{MM}=331.60$ g/mol); $\text{C}\%=21.73$, $\text{H}\%=5.17$, $\text{N}\%=4.22$; *Found*: $\text{C}\%=21.74$, $\text{H}\%=5.13$, $\text{N}\%=4.23$).

Synthesis of $[\text{CuL}_2]\text{Cl}_2 \cdot 3\text{H}_2\text{O}$, **2**: 0.0085 g (0.05 mmol) of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ was dissolved in 2 mL $\text{C}_2\text{H}_5\text{OH}$ and 0.0394 g (0.2 mmol) of the ligand was dissolved in 5 mL $\text{C}_2\text{H}_5\text{OH}$ ($\text{L}:\text{Cu}^{2+}=4$). Then, both solutions were mixed, stirred and heated at 60 °C for 4 hours. The complex was obtained as light blue crystals suitable for X-ray analysis after repeated recrystallization in ethanol. Compound **2** crystallizes in orthorhombic $Fdd2$ space group with cell parameters $a=19.123(16)$, $b=21.657(16)$, $c=13.107(11)$ Å and $Z=8$.

Synthesis of $\{[\text{Cu}(\text{L})\text{Cl}(\text{AsF}_6)] \cdot \text{H}_2\text{O}\}_n$, **3**: An ethanol solution (3 mL) of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.0171 g, 0.1 mmol) was mixed with an ethanol solution (3 mL) of the ligand (0.0395 g, 0.2 mmol) ($\text{L}:\text{Cu}^{2+}=2$). Then the reaction mixture was stirred and heated

at 50 °C for 1 hour. LiAsF_6 (0.0782 g, 0.4 mmol) was dissolved in 4 mL $\text{C}_2\text{H}_5\text{OH}$ and then the solution was added to the initial mixture. A light blue powder was precipitated for a few minutes. The interaction was continued with stirring and heating (50 °C) for 2 more hours. The obtained precipitate was filtered while the solution was left for evaporation on air at room temperature. Dark blue crystals of a polymeric compound were obtained after repeated evaporation of the solvent. *Anal. Calc. for 3*, $\{\text{C}_6\text{H}_{19}\text{NP}_2\text{O}_3\text{ClF}_6\text{AsCu}\}_n$ ($\text{MM}(\text{monomer})=502.08$ g/mol); $\text{C}\%=14.32$, $\text{H}\%=3.81$, $\text{N}\%=2.78$; *Found*: $\text{C}\%=14.07$; $\text{H}\%=3.73$, $\text{N}\%=2.79$.

Synthesis of $[\text{CuL}_2](\text{AsF}_6)_2 \cdot 2\text{H}_2\text{O}$, **4**: $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.0171 g, 0.1 mmol) was dissolved in 3 mL $\text{C}_2\text{H}_5\text{OH}$ and 0.0395 g (0.2 mmol) of the ligand was dissolved in 5 mL $\text{C}_2\text{H}_5\text{OH}$. Then, both solutions were mixed ($\text{L}:\text{Cu}^{2+}=2$), stirred and heated at 50 °C for 1 hour. An amount of 0.0782 g (0.4 mmol) of LiAsF_6 was dissolved in 4 mL $\text{C}_2\text{H}_5\text{OH}$ and was added to the reaction mixture. A light blue powder precipitated after a few minutes (~4–5 min). The interaction was continued with stirring and heating (50 °C) for 2 more hours. The obtained complex was filtrated and recrystallized repeatedly from ethanol solution. *Anal. Calc. for 4*, $\text{C}_{12}\text{H}_{38}\text{N}_2\text{O}_6\text{P}_4\text{F}_{12}\text{As}_2\text{Cu}$ ($\text{M}=871.70$ g/mol); $\text{C}\%=16.53$, $\text{H}\%=4.39$, $\text{N}\%=3.21$; *Found*: $\text{C}\%=16.36$; $\text{H}\%=4.15$, $\text{N}\%=3.18$.

Single-crystal XRD structural analysis

A light blue crystal of complex **2** suitable for X-ray analysis with size $0.50 \times 0.48 \times 0.20$ mm³ was selected for data collection at room temperature. The crystal was mounted on a Bruker SMART

X2S diffractometer using a monochromatic Mo-K α ($\lambda = 0.71073 \text{ \AA}$) radiation from a micro-focus source and APEX-II CCD detector. Data collection, cell refinement and data reduction were performed using APEXII software [23]. SADABS-2014/5 (Bruker, 2014/5) was used for absorption correction [23]. The ratio of minimum to maximum transmission is 0.6538. The structure was solved by *ab-initio* methods using ShelXD and refined with the ShelXL [24]. All hydrogen atoms were placed on calculated positions. To refine the structure, the program SHELXL97 [24], version 2014/7 implemented in program OLEX2 [25] was used. Full-matrix least-squares refinement was carried out till the final refinement cycles converged to an $R = 0.0650$ and $wR(F^2) = 0.1457$ for all observed data. The OLEX software was applied to prepare the materials for publication. The crystallographic, X-ray data collection and refinement statistics for the compound are given in Table 1. Selected bond lengths and bond angles are summarized in Table 2 and hydrogen bonding interactions are given in Table 3. ORTEP diagram for the studied compound is shown on Fig. 1. The crystallographic data for **2** were deposited at the Cambridge Crystallographic Data

Centre and allocated the deposition number CCDC 1831416. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; tel: +441223762910; fax: +441223336033; e-mail: deposit@ccdc.cam.ac.uk; <http://www.ccdc.cam.ac.uk/deposit>. The drawings were prepared using Mercury version 3.3 [26].

RESULTS AND DISCUSSION

Syntheses and crystallography

The ligand bis((dimethylphosphinyl)methyl)amine is well soluble in ethanol. All copper coordination compounds the synthesis we report here were obtained as a result of the interaction ligand (L) with $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (M) at a different molar L:M ratio in ethanol (with traces of water). The complexes were isolated as neutral compounds with the counter ions (Cl^- or AsF_6^-). Complexes **1** and **2** were obtained solely from the interaction of the starting copper salt and ligand L with successively substitution of solvate (complex **1**) and Cl^- (complex **2**) ligands from Cu^{2+} -inner coordination sphere with one and

Table 1. Crystal data and structure refinement for **2**

Empirical formula	$\text{C}_{12}\text{H}_{38}\text{Cl}_2\text{CuN}_2\text{O}_7\text{P}_4$
Formula weight	580.10
Temperature/K	300.15
Crystal system	<i>orthorhombic</i>
Space group	<i>Fdd2</i>
$a/\text{\AA}$	19.123(16)
$b/\text{\AA}$	21.657(16)
$c/\text{\AA}$	13.107(11)
$\alpha/^\circ \equiv \beta/^\circ \equiv \gamma/^\circ$	90
Volume/ \AA^3	5428(8)
Z	8
$\rho_{\text{calc}} \text{ g/cm}^3$	1.420
μ/mm^{-1}	1.268
F(000)	2421.0
Crystal size/ mm^3	$0.5 \times 0.48 \times 0.2$
Radiation	MoK α ($\lambda = 0.71073$)
2θ range for data collection/ $^\circ$	5.684 to 50.048
Index ranges	$-22 \leq h \leq 22, -24 \leq k \leq 25, -15 \leq l \leq 15$
Reflections collected	12187
Independent reflections	2369 [$R_{\text{int}} = 0.1762, R_{\text{sigma}} = 0.1572$]
Data/restraints/parameters	2369/1/141
Goodness-of-fit on F^2	0.953
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0650, wR_2 = 0.1278$
Final R indexes [all data]	$R_1 = 0.1092, wR_2 = 0.1457$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.42/-0.56
Flack parameter	0.00(4)
CCDC number	1845615

Table 2. Geometrical parameters for the complex cation of the compound **2** (Å, °)

Bond Lengths			
Cu(1)–O(1) ¹	2.159(9)	P(1)–C(3)	1.786(12)
Cu(1)–O(1)	2.159(9)	P(1)–C(4)	1.781(12)
Cu(1)–O(2)	2.211(9)	P(2)–O(1)	1.505(7)
Cu(1)–O(2) ¹	2.211(9)	P(2)–C(5)	1.789(11)
Cu(1)–N(1)	2.026(8)	P(2)–C(6)	1.776(11)
Cu(1)–N(1) ¹	2.026(8)	P(2)–C(2)	1.829(11)
P(1)–O(2)	1.517(8)	N(1)–C(1)	1.502(14)
P(1)–C(1)	1.830(10)	N(1)–C(2)	1.481(12)
Bond Angles			
O(1) ¹ –Cu(1)–O(1)	95.1(4)	O(2)–P(1)–C(4)	111.7(6)
O(1) ¹ –Cu(1)–O(2) ¹	174.1(3)	C(3)–P(1)–C(1)	109.1(6)
O(1) ¹ –Cu(1)–O(2)	174.1(3)	C(4)–P(1)–C(1)	107.3(6)
O(1)–Cu(1)–O(2)	90.0(3)	C(4)–P(1)–C(3)	108.0(7)
O(1)–Cu(1)–O(2) ¹	90.0(3)	O(1)–P(2)–C(5)	114.8(6)
O(2) ¹ –Cu(1)–O(2)	85.1(4)	O(1)–P(2)–C(6)	111.9(5)
N(1) ¹ –Cu(1)–O(1) ¹	89.1(3)	O(1)–P(2)–C(2)	106.6(5)
N(1)–Cu(1)–O(1) ¹	92.4(3)	C(5)–P(2)–C(2)	106.9(5)
N(1) ¹ –Cu(1)–O(1)	92.4(3)	C(6)–(2)–C(5)	107.8(6)
N(1)–Cu(1)–O(1)	89.1(3)	C(6)–P(2)–C(2)	108.6(5)
N(1) ¹ –Cu(1)–O(2)	90.7(3)	P(2)–O(1)–Cu(1)	108.7(5)
N(1)–Cu(1)–O(2) ¹	90.7(3)	P(1)–O(2)–Cu(1)	109.7(5)
N(1) ¹ –Cu(1)–O(2) ¹	87.6(3)	C(1)–N(1)–Cu(1)	109.0(7)
N(1)–Cu(1)–O(2)	87.6(3)	C(2)–N(1)–Cu(1)	110.2(6)
N(1) ¹ –Cu(1)–N(1)	177.7(5)	C(2)–N(1)–C(1)	113.7(8)
O(2)–P(1)–C(1)	108.1(5)	N(1)–C(1)–P(1)	108.5(7)
O(2)–P(1)–C(3)	112.5(6)	N(1)–C(2)–P(2)	108.4(7)

¹ 1-X, 1-Y,+Z**Table 3.** Hydrogen bonds and weak C–H...O interactions (Å, °) in the crystal structure of **2**

D—H...A	d(D-H)	d(H-A)	d(D-A)	D-H-A
O(1W)—H(1WA)...O(2) ¹	0.85	1.97	2.807(12)	170.2
O(1W)—H(1WB) Cl(1)	0.85	2.33	3.135(11)	157.9
C(2)—H(2A) O(1W) ²	0.97	2.54	3.477(16)	162.2

¹ 5/4-X,-1/4+Y,-1/4+Z; ² -1/4+X, 3/4-Y,1/4+Z

two bis((dimethylphosphinyl)methyl)amine molecules (Scheme 2) for **1** and **2** respectively. Complex **1** was obtained from a comparatively concentrated reaction mixture (2×10^{-2} mol/L in respect of Cu^{2+}) at molar ratio M:L=1:1.9 (some insufficiency of L in respect to L:M = 2) for approximately 3 hours. Whereas complex **2** was prepared from a more diluted system (5×10^{-3} mol/L in respect of Cu^{2+}) at molar ratio M:L=1:4 for a slightly longer period (~4 hours). The complexes **3** and **4** were obtained from the M:L=1:2 reaction system (concentration of $\text{Cu}^{2+} \sim 1 \times 10^{-2}$ mol/L) with a four-fold excess of AsF_6^- . Although AsF_6^- counter-anions exhibit very

weak coordinating tendencies towards transition metals, it was found that the competition between $[\text{F-AsF}_5]^-$ and Cl^- for the inner coordination sphere of copper(II) in the reaction system directs the mode of coordination of bis((dimethylphosphinyl)methyl)amine. Thus, the complexes **3** and **4** were isolated from the filtrate and from the powder of one and the same reaction system (Scheme 2).

Light blue crystals of $[\text{CuL}_2]\text{Cl}_2 \cdot 3\text{H}_2\text{O}$, **2** suitable for X-ray analysis were obtained after repeated recrystallization from ethanol. Crystallographic data of complex **2** are summarized in Table 1. The data for the bond lengths and angles are listed in

Table 2. Molecular structure and hydrogen bonds together with weak C–H...O interactions (Table 3) are shown in Figs. 1 and 2. The Cu²⁺ ion is situated in a special crystallographic position and is surrounded by two symmetrically equivalent bis((dimethylphosphinyl)methyl)amine molecules (L) to form complex [CuL₂]²⁺ cation. The organic molecules are bonded as a tridentate ligands through secondary amino group and two tertiary phosphine oxide donors thus forming two five-membered rings. The Cu–O bond lengths are not equal and differ with 0.051(1) Å (Cu–O1 = 2.159(9) and Cu–O2 = 2.211(9) Å. As it is expected the Cu–N bonds are shorter than the Cu–O ones being 2.026(8) Å. The O–Cu–O angles vary between 85.1(4)° to 95.1(4)° and only O(1)–Cu–O(2) in the coordination plane is 90.0(3)°. The N–Cu–O angles differ in the range 87.6(3)° to 92.4(4)° while N–Cu–N is 177.7(5)°. Thus the octahedral coordination geometry of the complex cation can be described as axially compressed octahedra. The distance Cu–Cl (Cl[−]) of 6.270 Å shows that the chloride ions are in the outer coordination sphere of the complex **2**. The Cl[−] ions together with the water molecules and O(2) from the coordinated P=O group build up the hydrogen-bonding network (Table 3).

Mode of coordination of bis((dimethylphosphinyl)methyl)amine

The ligand bis((dimethylphosphinyl)methyl)amine has polydentate nature due to its three func-

tional donor groups, namely a secondary amino group and two tertiary phosphine oxide groups. The mode of coordination has been studied by IR spectra analysis. The solid state IR spectral data about the ligand and its copper(II) complexes are represented in Table 4. The assignments of the bands are made in accordance with IR data and NCA published [27, 28] for transition metal complexes of aminomethylphosphine oxides.

In order to assess the mode of coordination the analysis of the IR data has been done on the basis of the IR spectrum of compound **2** since X-ray single-crystal structure data for **2** is available. In this spectrum as well as in the spectra of the compounds **1** and **4** (Table 4) all bands concerning the secondary amino group and phosphoryl groups are affected from the coordination. The bands for NH-stretching and CNH deformation together with P=O stretching vibrations are shifted to lower frequencies. Only in the spectrum of compound **3**, the bands for NH-stretching and CNH deformation are poorly affected and this indicates only for participation of the amino group in hydrogen bonding formation. In addition, the new bands assigned to Cu–O, Cu–N as well Cu–Cl vibration modes prove the composition of inner coordination sphere of the complexes. These results together with the elemental analysis data show that the interaction between the CuCl₂·2H₂O and L in ethanol solution proceeds with consistent coordination of two bis((dimethylphosphinyl)methyl)amine molecules. In the complex **1**, the ligand is coordinated as a tridentate O,N,O ligand

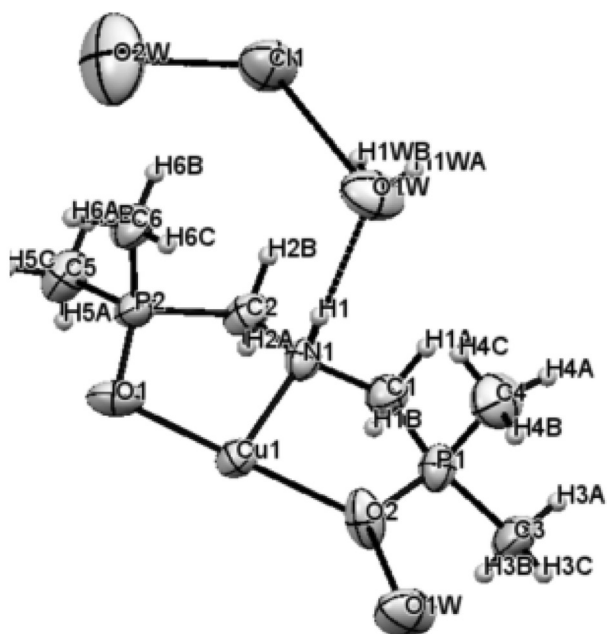


Fig. 2. An asymmetric unit with hydrogen-bonding in the crystal structure of **2**.

Table 4. Selected frequencies from the infrared spectra of the free ligand and its Cu²⁺ complexes

Bands, cm ⁻¹	Compounds				Assignment
	[CuLCl ₂]	[CuL ₂]Cl ₂ ·3H ₂ O	{[Cu(L)ClAsF ₆] _n ·H ₂ O}	[CuL ₂](AsF ₆) ₂ ·2H ₂ O	
L	1	2	3	4	
		3405br	3423br	3430br	v ^{as,a} (H ₂ O)
3317s	3139s	~3227w Overlapped from v ^{as,a} (H ₂ O)	3265	3113s	v(NH)
2956	3002	2987	2989	3016	v ^{as,a} (CH ₃ , CH ₂)
2925	2979	2916	2919	2979	
2870	2967			2926	
2850	2931			2902	
2811	2911				
2791	2898				
		1662	1655 1638	1630	δ(H ₂ O)
1560vw 1545vw	1460s	1543w 1489w	1560w 1548w	1487w 1458w	δ(CNH)
1458	1419	1422	1430	1425	δ(CH ₃ , CH ₂)
1446	1411	1392	1420	1422	
1436	1402			1403	
1428	1392				
1405					
1378 1364					
1332	1321	1301	1326	1238	δ(P-CH ₃)
1317	1314	1272	1311	1216	
1303	1304		1304		
1294	1291				
1286	1261				
1258 1236					
1161s	1104	1138	1105	1143	v(P=O)
1119m	1090	1100	1089	1097	
1077	1067	1039	1040	1087	
1042					
954	974	947	955	957	ρ(P-CH ₃)
924	953	905	924	939	
906	915	866	905	902	
892	905		865	862	
755	762	758	764	697	δ(P-CH ₂)
750	743	745	747	681	
734		733	699		
724					
	509	484	520 498	518	v(Cu-O)
	473	457 447		465	v(Cu-N)
	410		447		v(Cu-Cl)
			697	699	v ₃ (AsF ₆)
			574		v(Cu-F-AsF ₃)

without displacement of the two Cl^- ions. In the complex **2**, the second L molecule is coordinated by displacing of the Cl^- and as a result the formation of a CuO_4N_2 -chromophore with compressed octahedral coordination is observed. In the presence of AsF_6^- , the complicated equilibrium is directed toward a substitution of Cl^- with AsF_6^- . As a result, the displacement of Cl^- with AsF_6^- produces two different complexes in which the ligand in addition of the tridentate coordination is also coordinated with two the phosphoryl O-donors. Despite the preferred N-containing donor functional groups from Cu^{2+} , in all complexes presented here, the ligand is bonded only through (compound **3**) or with the participation of phosphoryl O-donor atoms (compounds **1**, **2**, **4**). The determined protolytic constant (pK_a) of 2.54 for the ligand [18] proves the low basicity of the nitrogen donor. The decreased electron density around the nitrogen atom in the molecular structure of the ligand is a consequence of the electronegative effects of the phosphoryl groups. This results in a comparatively equal affinity of these two donor functional groups to copper(II). The structure of the complexes is additionally stabilized from the formation of chelate rings.

CONCLUSION

A series of copper(II) coordination compounds has been synthesized with a ligand belonging to the family of tertiary phosphine oxides functionalized with secondary amino groups. The complexes were obtained from the interaction of the ligand with copper(II) in ethanol solution in the presence of Cl^- and AsF_6^- as counterion. The investigation on the structures of the complexes was done on the basis of X-ray data for the complex with composition $[\text{CuL}_2]\text{Cl}_2 \cdot 3\text{H}_2\text{O}$, IR spectra and elemental analysis. The studied ligand as a chelating ligand, coordinates by formation of two five-membered N,O-chelate rings in mononuclear complexes or as a bridging O,O-linker between metal ions in polynuclear structures.

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КООРДИНАЦИЯ НА БИС((ДИМЕТИЛФОСФИНИЛ)МЕТИЛ)АМИН КЪМ МЕД(II). ПОЛУЧАВАНЕ И КРИСТАЛНА СТРУКТУРА НА МОНОЯДРЕН ОКТАЕДРИЧЕН КОМПЛЕКС НА МЕД(II)

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(Резюме)

Получаването и структурата на моноядрен комплекс на бис((диметилфосфинил)метил)амин, L, със състав $[\text{CuL}_2]\text{Cl}_2 \cdot 3\text{H}_2\text{O}$, са обсъдени в сравнение със серия мед(II) комплекси на този лиганд, с цел да бъде изучен начина на координация на лиганда в зависимост от природата на металния йон и конкретните реакционни условия. Всички комплекси са получени от взаимодействието на лиганда с $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ в етанол при различни M:L молни съотношения и са изолирани като неутрални съединения с противойоните Cl^- , AsF_6^- . Комплексът $[\text{CuL}_2]\text{Cl}_2 \cdot 3\text{H}_2\text{O}$ кристализира в орторомбична *Fdd2* пространствена група с параметри на елементарната клетка $a = 19.123(16)$, $b = 21.657(16)$, $c = 13.107(11)$ Å и $Z = 8$. Кристалната структура се състои от комплексни катиони със състав $[\text{Cu}^{2+}\text{L}_2]^{2+}$, два хлоридни аниона и три водни молекули. Лигандите L се координират като тридентатни, като всеки от тях образува по два петчленни Cu-O-P-C-N хелатни пръстена. Cu^{2+} в комплекса е с тетрагонално деформирана октаедрична координация.