

# Structure and characterization of copper(II) perchlorate with diethyl(pyridin-2-ylmethyl) phosphonate (2-pmpe) ligand: $[\text{Cu}(2\text{-pmpe})_2(\text{ClO}_4)_2]$

B. ŻUROWSKA<sup>1\*</sup>, A. BIAŁOŃSKA<sup>1</sup>, J. OCHOCKI<sup>2</sup>

<sup>1</sup>Faculty of Chemistry, University of Wrocław, Joliot-Curie 14, 50-383 Wrocław, Poland

<sup>2</sup>Department of Bioinorganic Chemistry, Faculty of Pharmacy, Muszyńskiego 1, Medical University, 90-151 Łódź, Poland

Copper(II) mononuclear compound  $[\text{Cu}(2\text{-pmpe})_2(\text{ClO}_4)_2]$  (2-pmpe = diethyl(pyridin-2-ylmethyl) phosphonate) was synthesized and studied. Examination of the crystal structure by the X-ray diffraction method revealed two crystallographically unrelated molecules,  $[\text{Cu}(1)(2\text{-pmpe})_2(\text{ClO}_4)_2]$  (**1**) and  $[\text{Cu}(2)(2\text{-pmpe})_2(\text{ClO}_4)_2]$  (**2**) in an asymmetric part of the unit cell. The geometry about the Cu(**1**) and Cu(**2**) chromophores shows elongated octahedra, resulting from the didentate N,O-bonded two chelate 2-pmpe ligands and two coordinated perchlorate ions around the Cu(II) cations (CuN<sub>2</sub>O<sub>4</sub> chromophore). Similarly to **1**, molecules **2** are linked to each other by weak C–H...O hydrogen bonds and  $\pi\cdots\pi$  stacking interactions. Additionally, both **1** and **2** molecules are linked to each other through weak C–H...O hydrogen bonds and C–H... $\pi$  contacts, resulting in a 3D polymeric network arrangement. Magnetic data indicate a very weak intermolecular exchange interaction between copper(II) ions ( $zJ' = -0.20 \text{ cm}^{-1}$ ) transmitted through non-covalent interactions in the crystal lattice. The spectral properties are in accordance with the structural and magnetic data.

Key words: *copper(II); phosphonic acid ester; crystal structure, spectroscopy; magnetism*

## 1. Introduction

Structure and bond properties of copper(II) complexes have been of constant interest in inorganic chemistry and biochemistry [1, 2] similarly as various ligand phosphonate derivatives due to their broad spectrum of biological properties. In recent years, much attention has been focused on the synthesis of phosphonate and phosphate esters of N-heterocyclic systems (pyridine or quinoline) and their platinum(II) and palladium(II) complexes, because of their potential applications [3] and significant

---

\*Corresponding author, e-mail: zurowska@chem.uni.wroc.pl

antitumor activity [4–15]. Recently, we have demonstrated a high reactivity of these phosphonate with transition metal ions [16–23]. Our interest has also been focused on the magnetic properties of these compounds because it may allow the estimation of the strength of the magnetic coupling between magnetic centres through intramolecular covalent and/or intermolecular non-covalent interactions.

Studies of very weak non-covalent intermolecular interactions are of fundamental importance for further development of inorganic supramolecular chemistry and the prediction of crystal structures. These contacts generate or have an influence on interesting supramolecular properties such as electrical, optical and magnetic ones, and play a major role in the functioning of biological macromolecules [24–27].

The present paper is a continuation of our earlier investigation on the coordination properties of the N-heterocyclic phosphonate diesters including structural, spectroscopic and magnetic properties of obtained species.

It is worth mentioning that the interaction of the (pyridin-2-ylmethyl)phosphonate and (quinolin-2-ylmethyl)phosphonate diesters (2-pmpe and 2-qmpe, respectively) with some copper(II) and cobalt(II) salts leads to copper–picolinate or copper– and cobalt–quinaldinate systems through the oxidative decomposition of these ligands with cleavage of the C–P bond [22, 28].

In this work, the crystal structure of the mononuclear copper(II) compound with diethyl(pyridin-2-ylmethyl)phosphonate ligand (2-pmpe) was investigated (Fig. 1), having the formula  $[\text{Cu}(2\text{-pmpe})_2(\text{ClO}_4)_2]$ . Spectroscopic and magnetic properties are presented with reference to the crystal structure.

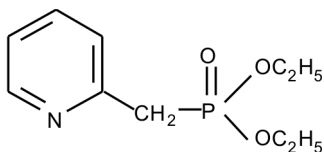


Fig. 1. Molecule of the diethyl(pyridin-2-ylmethyl) phosphonate (2-pmpe) ligand

## 2. Experimental

*Synthesis of the  $\text{Cu}(2\text{-pmpe})_2(\text{ClO}_4)_2$  complex*<sup>\*</sup>. The diethyl(pyridin-2-ylmethyl) phosphonate (2-pmpe) ligand was obtained according to procedure described in detail elsewhere [17]. The perchlorate complex was synthesized by dissolving the hydrated copper(II) perchlorate (1 mmol) in ethanol (10 cm<sup>3</sup>) and adding dropwise under stirring to the solution of the ligand (2 mmol) in ethanol (20 cm<sup>3</sup>). The crystalline blue product was obtained by slow evaporation of the solvent at room temperature.

<sup>\*</sup>Although no problem was encountered in this work, perchlorate salts containing organic ligands are potentially explosive. They should be prepared in small quantities and handled with care.

Anal. calcd. for  $\text{C}_{20}\text{H}_{32}\text{Cl}_2\text{CuN}_2\text{O}_{14}\text{P}_2$ : C, 33.32; H, 4.48; N, 3.89; Cu, 8.82. Found: C, 33.55; H, 4.56; N, 3.69; Cu, 8.63 %.

*Physical measurements.* Metal content was determined using a Carl Zeiss Jena atomic absorption spectrophotometer and an ARL model 3410 ICP spectrometer. Elemental analyses were carried out using a Perkin-Elmer elemental analyzer 2400CHN. Solid-state electronic spectrum (28000–4000  $\text{cm}^{-1}$ ) was performed on a Cary 500 spectrophotometer. Solid state EPR spectra were recorded at room temperature and at 77 K on a Bruker ESP 300E spectrometer operating at X-band, equipped with a Bruker NMR gaussmeter ER 0.35 M and a Hewlett Packard microwave frequency counter HP 5350B. Magnetic measurements were carried out with a Quantum Design SQUID magnetometer (type MPMSXL-5). The measurements were recorded in a magnetic field of 0.5 T in the temperature range 1.8–300 K. Corrections for diamagnetic contributions are based on subtracting the sample holder signal and estimating the contribution  $\chi_D$  from the Pascal constants [29]. The effective magnetic moments were calculated from  $\mu_{\text{eff}} = 2.83(\chi_M T)^{1/2}$  using temperature-independent paramagnetism of  $60 \times 10^{-6} \text{ cm}^3 \cdot \text{mol}^{-1}$  for Cu(II) ion [30].

*Determination of the crystal structure of  $[\text{Cu}(2\text{-pmpe})_2(\text{ClO}_4)_2]$ .* X-ray data were collected on a Kuma KM4CCD diffractometer (Mo  $\text{K}_\alpha$  radiation,  $\lambda = 0.71073 \text{ \AA}$ ). X-ray data were collected at 100 K using an Oxford Cryosystem device. Data reduction and analysis were carried out with the CrysAlice 'RED' program [31]. The space group was determined using the XPREP program. The structure was determined by direct methods using the XS program and refined using all the  $F^2$  data, as implemented by the XL program [32]. Non-hydrogen atoms were refined with anisotropic displacement parameters. All H atoms were placed at calculated positions. Before the last cycle of refinement, all H atoms were fixed and were allowed to ride on their parent atoms.

### 3. Results and discussion

#### 3.1. Description of the structure of $[\text{Cu}(2\text{-pmpe})_2(\text{ClO}_4)_2]$

Two crystallographically unrelated molecules,  $[\text{Cu}(1)(2\text{-pmpe})_2(\text{ClO}_4)_2]$  (**1**) and  $[\text{Cu}(2)(2\text{-pmpe})_2(\text{ClO}_4)_2]$  (**2**), exist in the asymmetric part of the unit cell (Fig. 2). The Cu(**1**) and Cu(**2**) copper ions are located in a special position. The crystallographic parameters are summarized in Table 1. The selected bond lengths and angles are listed in Table 2.

Diethyl(pyridin-2-ylmethyl)phosphonate (2-pmpe) ligands acting as a didentate bonding, chelate to the Cu(**1**) and Cu(**2**) atoms through the pyridyl nitrogen and the phosphoryl oxygen atoms resulting in six-membered rings. The P=O group is arranged in a *trans* position. The O atoms of the perchlorate anions complete a distorted octahedral surrounding of Cu(**1**) and Cu(**2**) atoms. As presented in Table 2, the Cu–N and Cu–O bond length between the Cu atoms and the 2-pmpe ligands are shorter than

Cu–O bonds between Cu atoms and perchlorate anions. It causes a significant distortion of the coordination polyhedron around the Cu(1) and Cu(2) ions (CuN<sub>2</sub>O<sub>4</sub> chromophore). In the crystal under investigation, the Cu–O (coordinated perchlorate) distances (2.482(3) and 2.433(3) Å) are longer than the Cu–O (coordinated perchlorate) distances found in crystals of related Cu(II) compounds with N-heterocyclic phosphate ligand (2.409 (2) Å) [33].

Table 1. Crystal data and structure refinement for [Cu(2-pmpe)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub>]

Empirical formula	C <sub>20</sub> H <sub>32</sub> Cl <sub>2</sub> CuN <sub>2</sub> O <sub>14</sub> P <sub>2</sub>	$D_c$ , Mg·m <sup>-3</sup>	1.680
Formula weight	720.86	Absorption coefficient, mm <sup>-1</sup>	1.137
Temperature, K	100(2)	$F(000)$	742
Wavelength, Å	0.71073	Crystal size, mm	0.26 x 0.11 x 0.09
Crystal system	triclinic	$\theta$ range for data collection, deg	3.11 - 27.00
Space group	$P\bar{1}$	Ranges of $h, k, l$	-10=>10, -14=>14, -19=>18
$a$ , Å	8.442(3)	Reflections collected	15969
$b$ , Å	11.158(3)	Independent reflections, $R_{int}$	6220 (0.0759)
$c$ , Å	15.248(4)	Completeness to $2\theta = 54.00$	99.7%
$\alpha$ , deg	87.30(3)	Absorption correction	analytical
$\beta$ , deg	84.23(3)	Data/parameters	6220/373
$\gamma$ , deg	86.35(3)	Goodness-of-fit, $F^2$	1.151
Volume, Å <sup>3</sup>	1424.9(7)	Final $R/wR$ indices, $I > 2\sigma I$	0.0723/0.1028
$Z$	2	Largest diff. peak/hole, e·Å <sup>-3</sup>	0.429/-0.484

Table 2. Bond lengths (Å) and angles (°) for [Cu(2-pmpe)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub>]

Molecule (1)	Molecule (2)
Cu(1)–N(1) 1.952(3)	Cu(2)–O(1A) 1.966(3)
Cu(1)–N(1) 2.058(3)	Cu(2)–N(1A) 2.060(4)
Cu(1)–O(11) 2.482(3)	Cu(2)–O(21) 2.433(3)
P(1)–N(1) 1.499(3)	P(1A)–O(1A) 1.493(3)
P(1)–O(3) 1.546(3)	P(1A)–O(3A) 1.554(3)
P(1)–N(1) 1.558(3)	P(1A)–O(2A) 1.564(3)
N(1)–P(1)–O(3) 115.50(17)	O(1A)–P(1A)–O(3A) 114.90(18)
N(1)–P(1)–N(1) 111.94(16)	O(1A)–P(1A)–O(2A) 113.05(18)
O(3)–P(1)–N(1) 105.98(18)	O(3A)–P(1A)–O(2A) 103.93(17)
N(1)–P(1)–C(7) 110.7(2)	O(1A)–P(1A)–C(7A) 109.84(19)
O(3)–P(1)–C(7) 102.59(19)	O(3A)–P(1A)–C(7A) 104.9(2)
N(1)–P(1)–C(7) 109.64(19)	O(2A)–P(1A)–C(7A) 109.74(19)
N(1)–Cu(1)–N(1) <sup>i</sup> 88.06(13)	O(1A)–Cu(2)–N(1A) <sup>ii</sup> 86.90(13)
N(1)–Cu(1)–N(1) 91.94(13)	O(1A)–Cu(2)–N(1A) 93.10(13)
N(1)–Cu(1)–O(11) 95.59(11)	O(1A)–Cu(2)–O(21) 97.79(12)
N(1)–Cu(1)–O(11) 90.55(12)	N(1A)–Cu(2)–O(21) 88.24(13)
N(1)–Cu(1)–O(11) <sup>ii</sup> 84.41(11)	O(1A)–Cu(2)–O(21) <sup>ii</sup> 82.21(12)
N(1)–Cu(1)–O(11) <sup>ii</sup> 89.45(12)	N(1A)–Cu(2)–O(21) <sup>ii</sup> 91.76(13)

Symmetry transformations used to generate equivalent atoms: (i)  $-x+2, -y, -z+1$ , (ii)  $-x+1, -y+1, -z$

The P(1)-N(1) and P(1A)-O(1A) bond lengths of the phosphoryl P=O group of both crystallographically unrelated ligands are equal to 1.499(3) and 1.493(3) Å, respectively, and are smaller than the P–O bond lengths of the phosphonate groups (Table 2). Analysis of the geometric parameters indicates that the environment of the P(1) and P(1A) atoms is distorted tetrahedral i.e. the angles deviate from the ideal value of  $109.5^\circ$ , observed for other phosphonate diesters [34].

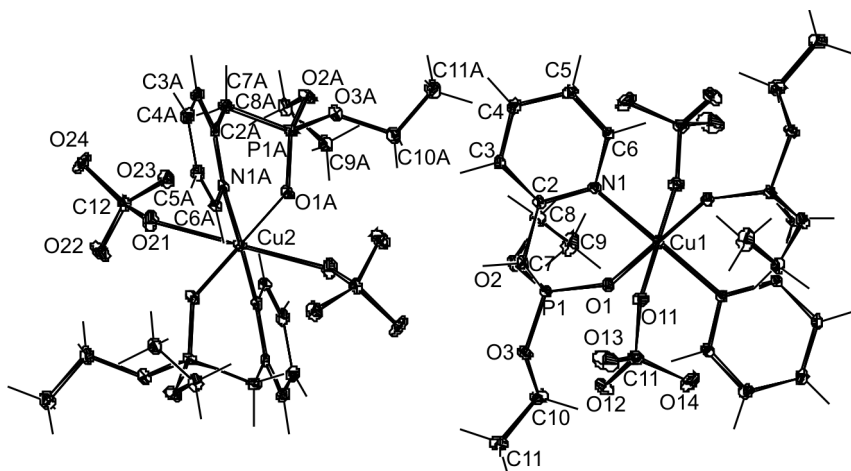


Fig. 2. Relative orientation of the molecules **1** and **2** in the crystal of  $[\text{Cu}(2\text{-pmpe})_2(\text{ClO}_4)_2]$  showing the atomic numbering. Symmetry codes are given in Table 2

Crystallographically unrelated molecules,  $[\text{Cu}(1)(2\text{-pmpe})_2(\text{ClO}_4)_2]$  (**1**) and  $[\text{Cu}(2)(2\text{-pmpe})_2(\text{ClO}_4)_2]$  (**2**) are linked by  $\pi\cdots\pi$  interaction, formed between pyridyl rings, resulting in ribbons extended in the [100] direction. The ribbons are stabilized by C–H $\cdots$ O hydrogen bonds formed between the aromatic C–H group of the pyridine rings and coordinated perchlorate oxygens [C(4)–H(4) $\cdots$ O(11)<sup>iii</sup> and C(4A)–H(4A) $\cdots$ O(21)<sup>vi</sup>] (symmetry codes are given in Table 3). The ribbons are linked to each other by C–H $\cdots$ O hydrogen bonds and C–H $\cdots\pi$  contacts. Additionally, the molecules **1** and **2** are stabilized by intramolecular C–H $\cdots$ O hydrogen bonds (Table 3).

Table 3. Geometry of the hydrogen bonds [Å] and contacts for  $[\text{Cu}(2\text{-pmpe})_2(\text{ClO}_4)_2]$  [deg]

D–H $\cdots$ A	d(D–H)	d(H $\cdots$ A)	d(D $\cdots$ A)	$\angle(\text{DHA})$
1	2	3	4	5
Interactions for molecule (1)				
Intra				
C(7)–H(7B) $\cdots$ O(11)	0.99	2.54	3.286(6)	132
C(6)–H(6) $\cdots$ O(12) <sup>i</sup>	0.95	2.57	3.338(5)	138
Inter				
C(4)–H(4) $\cdots$ O(11) <sup>iii</sup>	0.95	2.45	3.274(6)	144

Table 3 continued

1	2	3	4	5
Interactions for molecule (2)				
Intra C(8A)–H(8D)···O(23)	0.99	2.33	3.318(6)	174
Inter C(4A)–H(4A)···O(21) <sup>vi</sup>	0.95	2.61	3.354(6)	136
Interactions between (1) and (2) molecules				
C(3)–H(3)···O(22) <sup>ii</sup>	0.95	2.64	3.463(6)	146
C(7)–H(7A)···O(22) <sup>ii</sup>	0.99	2.54	3.472(6)	157
C(11)–H(11A)···O(23) <sup>vii</sup>	0.98	2.55	3.314(6)	134
C(5)–H(5)···O(2A) <sup>viii</sup>	0.95	2.54	3.434(6)	156
C(9)–H(9B)···CP2 <sup>ix</sup>	0.98	3.02	3.919(6)	153
Interactions between (2) and (1) molecules				
C(10A)–H(10C)···O(13) <sup>v</sup>	0.99	2.57	3.342(6)	134
C(7A)–H(7C)···O(12) <sup>iv</sup>	0.99	2.28	3.251(6)	167

Symmetry transformations used to generate equivalent atoms: (i)  $-x+2, -y, -z+1$ ; (ii)  $-x+1, -y+1, -z$ ; (iii)  $-x+1, -y, -z+1$ ; (iv)  $x-1, y+1, z$  (v)  $x, y+1, z$  (vi)  $-x, -y+1, -z$  (vii)  $-x+2, -y+1, -z$ ; (viii)  $-x+1, -y+1, -z+1$ ; (ix)  $x+1, y, z$ .

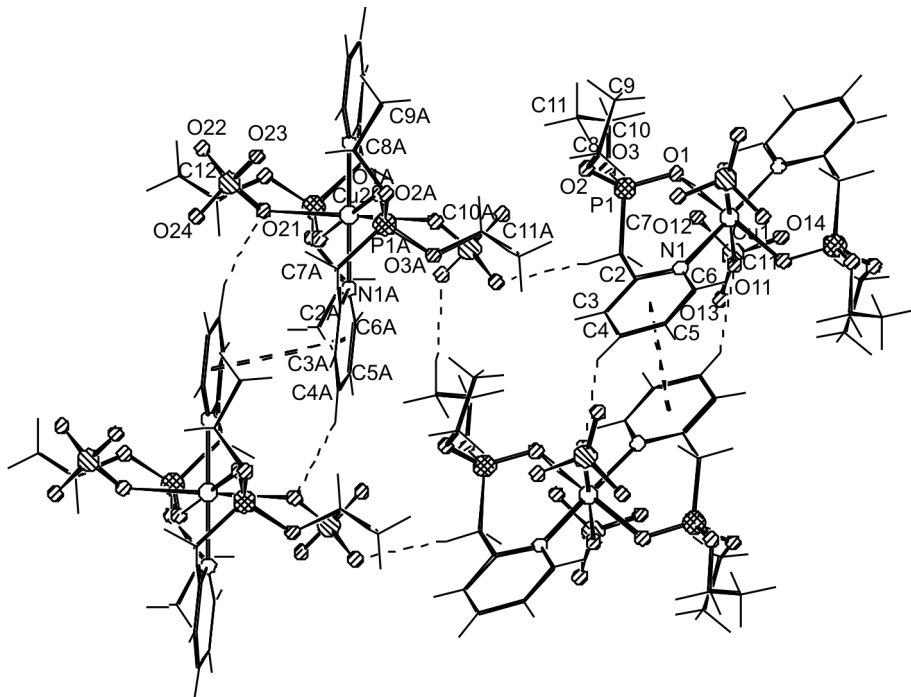


Fig. 3. Arrangement of the molecules **1** and **2** in the crystal of  $[\text{Cu}(\text{2-pmpe})_2(\text{ClO}_4)_2]$  and their linkage through weak C–H···O hydrogen bonds and  $\pi$ – $\pi$  interactions (dashed lines). Other hydrogen contacts linked to the molecules **1** and **2** are listed in Table 3

The dihedral angle between planes defined by  $\text{N}(1)$ ,  $\text{N}(1)$ ,  $\text{N}(1)^i$ ,  $\text{N}(1)^j$  and  $\text{N}(1\text{A})$ ,  $\text{O}(1\text{A})$ ,  $\text{N}(1\text{A})^i$ ,  $\text{O}(1\text{A})^i$  atoms is equal to  $67.68^\circ$ . Arrangement of the molecules **1** and **2** in the crystal of  $[\text{Cu}(2\text{-pmpe})_2(\text{ClO}_4)_2]$  is shown in Fig. 3. The  $\text{C}-\text{H}\cdots\text{O}$  hydrogen bonds,  $\text{C}-\text{H}\cdots\pi$  contacts and  $\pi\cdots\pi$  interactions, given in detail in Tables 3 and 4 stabilize the structure and give rise to a three-dimensional (3D) network. Crystal packing of the molecules **1** and **2** is shown in Fig. 4.

Table 4.  $\pi\cdots\pi$  interactions [ $\text{\AA}$ ] and [deg]

$\text{Cp1}\cdots\text{Cp1}^i$	Cp-Cp	Interplanar angle	Cp (perp)	Slippage
$\text{Cp2}\cdots\text{Cp2}^v$	3.628	0.00(20)	3.486(3)	1.01
	3.798	0.00(22)	3.637(3)	1.09

Symmetry transformations used to generate equivalent atoms: (i)  $-x+2, -y, -z+1$ , (v)  $x, y+1, z$ ; Cp1 – centroid of  $\text{N}(1)$  C(2) C(3) C(4) C(5) C(6) ring; Cp2 – centroid of  $\text{N}(1\text{A})$  C(2A) C(3A) C(4A) C(5A) C(6A) ring.

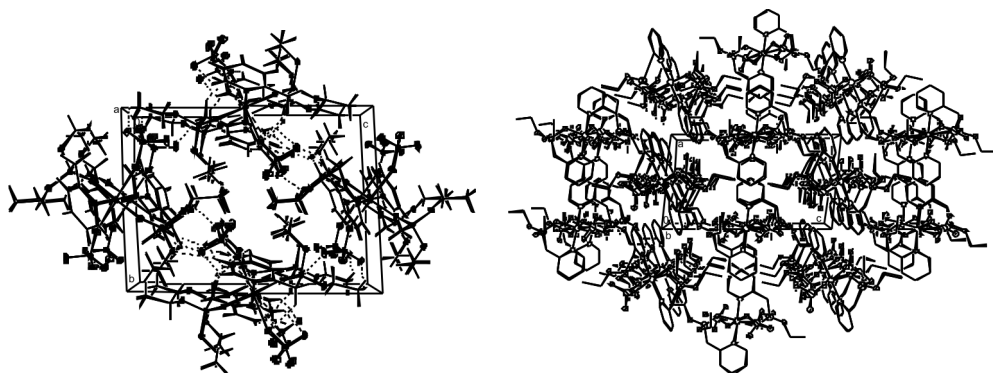


Fig. 4. Crystal packing of the molecules **1** (left) and **2** (right) in the crystal of  $[\text{Cu}(2\text{-pmpe})_2(\text{ClO}_4)_2]$  viewed down the  $a$ -axis and  $b$ -axis, respectively. The  $\text{C}-\text{H}\cdots\text{O}$  hydrogen bonds are shown with dashed lines

The shortest intermolecular metal–metal separations for  $\text{Cu}(1)\cdots\text{Cu}(1)^{ix}$  and  $\text{Cu}(2)\cdots\text{Cu}(2)^{ix}$  ( $ix = 1+x, y, z$ ) are of  $8.442(3)$   $\text{\AA}$ . For  $\text{Cu}(1)\cdots\text{Cu}(2)$ ,  $\text{Cu}(1)\cdots\text{Cu}(2)^{ix}$  and  $\text{Cu}(1)\cdots\text{Cu}(2)^x$  ( $x = x, y, 1-z$ ), these separations are:  $10.322(4)$ ,  $9.979(4)$  and  $10.080(4)$   $\text{\AA}$ , respectively.

### 3.2. Spectroscopic properties

In the infrared spectrum of the compound studied, the bands corresponding to the stretching modes of the pyridine  $\nu(\text{C}=\text{C})$  and  $\nu(\text{C}=\text{N})$  observed at  $1589$ ,  $1570$   $\text{cm}^{-1}$  for the free ligand are shifted to the higher frequencies in the complex ( $1610$ ,  $1571$   $\text{cm}^{-1}$ ). The characteristic out-of-plane and in-plane deformation bands of the 2-substituted

pyridine ring (405 and 602  $\text{cm}^{-1}$ , respectively) are also shifted to higher frequencies (416 and 616  $\text{cm}^{-1}$ , respectively), suggesting coordination of the pyridyl nitrogen atom. The band at 967  $\text{cm}^{-1}$  associated with a pyridine ring breathing mode is characteristically shifted to higher energy (972  $\text{cm}^{-1}$ ) on coordination.

A very strong band at 1250  $\text{cm}^{-1}$ , which corresponds to the P=O stretching frequencies of the free ligand in the spectrum of the title compound, is shifted towards lower frequencies by 75  $\text{cm}^{-1}$ , indicating the coordination of the phosphoryl oxygen atom to the metal ion and suggests, that 2-pmpe acts as a N,O-bonded chelate ligand. For monodentate coordination of 2-pmpe through the oxygen atom a shift about 20–30  $\text{cm}^{-1}$  is observed [21]. The strong non-splitting absorption band of uncoordinated perchlorate anion at about 1110  $\text{cm}^{-1}$  in the IR spectrum of  $[\text{Cu}(2\text{-pmpe})_2(\text{ClO}_4)_2]$  is distinctly split to two components, observed at around 1090 and 1120  $\text{cm}^{-1}$ . Also a strong absorption band characteristic of uncoordinated perchlorate ion, centred at 620  $\text{cm}^{-1}$  is significantly split (610 and 628  $\text{cm}^{-1}$ ) in the spectrum of the compound. These features indicate unidentate coordination of the perchlorate group [34–36]. The far-IR region of the compounds reveals one band at ca. 270  $\text{cm}^{-1}$  attributed to the  $\nu(\text{M-N})$  stretching vibration.

A broad asymmetric band centred at 14 800  $\text{cm}^{-1}$  with a shoulder of ca. 12 700  $\text{cm}^{-1}$  observed in the ligand field spectrum is characteristic of tetragonally distorted octahedral complexes [37], consistent with the structural analysis.

### 3.3. Magnetic properties

The EPR X-band powder spectrum of the copper compound is of the axial type with  $g$  values of  $g_{\parallel} = 2.28_6$  and  $g_{\perp} = 2.06_6$  at room temperature. The spectrum is independent of temperature. The  $g_{\parallel}$  value is in agreement with that observed for  $\text{CuN}_2\text{O}_4$  chromophore [38]. The spectrum of copper(II) compound in a frozen solution of ethanol was also recorded. This spectrum shows  $g$  values similar to the  $g$  values of the powder spectra, which indicates that the complex is stable in solution.

It is well known that weak non-covalent interactions not only stabilize crystal structure, but may also provide pathways for magnetic superexchange. Since the above analysis of the structure of the Cu(II) compound indicates that small but not negligible intermolecular magnetic exchange interaction cannot be excluded, we performed a magnetic study of this compound.

The magnetic properties of the compound, represented in the form of  $\chi_{\text{Cu}}T$  and  $1/\chi_{\text{Cu}}$  vs. temperature plots in the 1.8–300 K temperature range, are shown in Fig. 5 ( $\chi_{\text{Cu}}$  is the molar magnetic susceptibility per Cu(II) ions). The effective magnetic moment  $\mu_{\text{eff}}$  at room temperature ( $\mu_{\text{eff}} = 1.93 \mu_{\text{B}}$ ,  $\chi_{\text{M}}T = 0.466 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$ ) is within the usually observed range of experimental values for complexes in the octahedral configuration [39, 40]. At 1.8 K, the effective magnetic moment  $\mu_{\text{eff}}$  is equal to  $1.83\mu_{\text{B}}$  ( $\chi_{\text{M}}T = 0.418 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$ ). The best fit values of the Curie ( $C$ ) and Weiss ( $\theta$ ) constants, obtained from the equation  $\chi_{\text{M}} = (C/(T-\theta))$  within the measured temperature



region, are equal to  $0.460 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$  and  $-1.44 \text{ K}$ , respectively. The negative Weiss constant ( $\theta$ ) suggests the possibility of a very weak magnetic interaction between magnetic centres via the non-covalent bond system in the crystal lattice at lower temperatures.

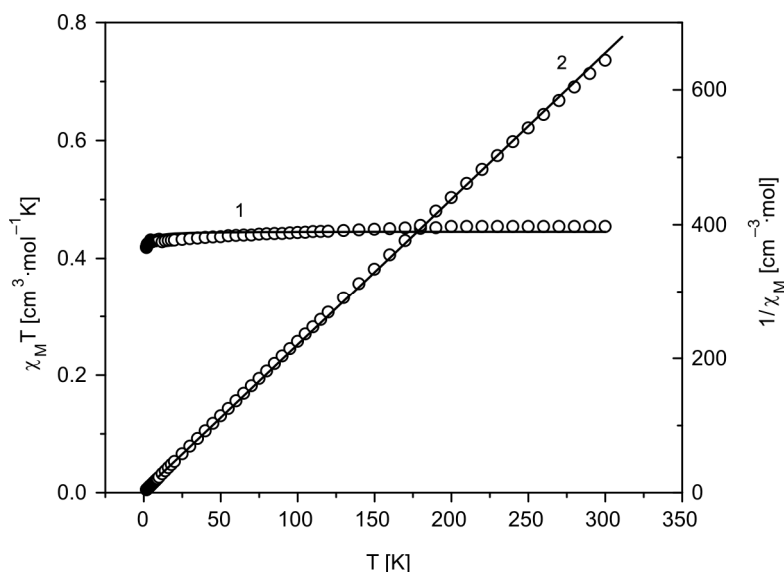


Fig. 5. Temperature dependences of  $\chi_{\text{Cu}} T$  (1) and  $1/\chi_{\text{Cu}}$  (2) for  $[\text{Cu}(\text{2-pmpe})_2(\text{ClO}_4)_2]$ . Solid lines correspond to the best theoretical fit (see text)

Therefore, in order to evaluate the intermolecular interactions of the magnetic centre of the  $[\text{Cu}(\text{2-pmpe})_2(\text{ClO}_4)_2]$  compound, a molecular exchange field model was used [41]:

$$\chi_M = \frac{N\beta^2 g^2}{3kT} S(S+1) \quad (1)$$

$$\chi_M^{\text{corr}} = \frac{\chi_M}{1 - \frac{2zJ'}{N\beta^2 g^2} \chi_M} \quad (2)$$

where  $\chi_M$  is the equation for the magnetic susceptibility of paramagnetic centre,  $\chi_M^{\text{corr}}$  is the measured experimental susceptibility,  $zJ'$  is the intermolecular exchange parameter,  $z$  is the number of nearest neighbours. In the frame of this model, the best fit parameters obtained by the least squares fit are the following:  $zJ' = -0.21 \text{ cm}^{-1}$ ,  $g = 2.18$  with the value of  $R = 6.87 \cdot 10^{-6}$ , where  $R$  is the agreement factor, defined as

$$R = \sqrt{\frac{\sum_i \frac{(\chi_i^{\text{exp}} - \chi_i^{\text{calc}})^2}{(\chi_i^{\text{exp}})^2}}{\sum_i \frac{1}{(\chi_i^{\text{exp}})^2}}}$$

The temperature dependence of the experimental and calculated values of  $\chi_M T$  of the Cu(II) compound is shown Fig. 5.

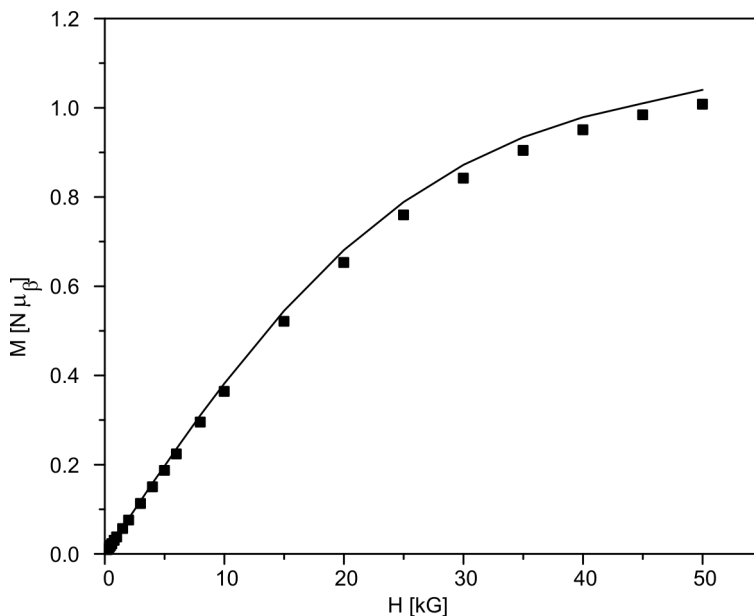


Fig. 6. Molar magnetization in function of the magnetic field, experimental (■). The solid line represents the Brillouin function, assuming  $g = 2.18$  (the value of the fit)

The molar magnetization  $M$  of the studied compound was measured in function of the applied magnetic field  $H$  at 2 K (Fig. 6). The magnetization ( $M/N\mu_B$ ) per Cu(II) ion at 5 kGs (5 T) tending to one electron is close to that expected for an isolated Cu(II) ion ( $1 N\mu_B$ ). At intermediate fields, the experimentally determined data points lie below the theoretical curve, indicating a weak antiferromagnetic coupling between the copper(II) ions.

## 4. Conclusions

The reaction of copper(II) perchlorate with diethyl(pyridin-2-ylmethylphosphonate) ligand 2-pmpe leads to crystallization of the  $[\text{Cu}(2\text{-pmpe})_2(\text{ClO}_4)_2]$  complex.

There are two crystallographically unrelated  $[\text{Cu}(2\text{-pmpe})_2(\text{ClO}_4)_2]$  molecules in an asymmetric part of the unit cell. The crystal structure is stabilized by weak C–H...O, C–H... $\pi$  and  $\pi$ ... $\pi$  interactions, resulting in an extensive, three-dimensional network.

Differences between copper(II) and cobalt(II) perchlorate complexes with N-heterocyclic phosphonate or N-heterocyclic phosphate ligands are worth mentioning. While perchlorate anions are coordinated in the Cu(II) complexes, they are uncoordinated in the Co(II) complexes, and water molecules are coordinated to Co(II) ions [19, 42].

In conjugation with structural studies, the magnetic properties of the title compound were investigated. A small value of  $zJ'$  is compatible with the expected limit  $|J'| < 0.5 \text{ cm}^{-1}$  for exchange interactions between the copper(II) ions transmitted through weak intermolecular noncovalent interactions.

Finally, it is worth mentioning that the studied compound is stable in solution when exposed to air. According to our earlier observation [22, 28], the didentate coordination of the 2-pmpe ligand stabilizes the complex preventing oxidative cleavage of C–P bond of the ligand and carboxylate compound formation\*.

#### Acknowledgement

The work was supported by the by the Polish Ministry of Science and Higher Education (Grant No. N405 303236) (J. O.) and by Grants Nos. 503-3016-2 and 502-13-777 (J. O.).

#### References

- [1] MURPHY B.P., HATHAWAY B.J., *Coord. Chem. Rev.*, 63 (1993), 124.
- [2] HATHAWAY B.J., [In:] G. Wilkinson, R.D. Gillard, J.A. McCleverty (Eds.), *Comprehensive Coordination Chemistry*, Vol. 5, Pergamon Press, Oxford, 1987, p. 553.
- [3] KALINOWSKA U., CHĘCIŃSKA L., WALECKA M., ERXLEBEN A., LIPPERT B., OCHOCKI J., *Inorg. Chim. Acta*, 358 (2005), 2464.
- [4] ARANOWSKA K., GRACZYK J., CHĘCIŃSKA L., PAKULSKA W., OCHOCKI J., *Pharmazie*, 61 (2006), 457.
- [5] ZIĘBA R., MALINOWSKA K., WIEWIÓROWSKI M., GRACZYK J., *Acta Pol. Pharm.*, 57 (2000), 136.
- [6] CHĘCIŃSKA L., WALECKA M., OCHOCKI J., ARANOWSKA K., *Acta Cryst.*, E59 (2003) m350.
- [7] BRZEZIŃSKA-BŁASZCZYK E., MIŃCIKIEWICZ M., OCHOCKI J., *Eur. J. Pharmacol.*, 155 (1996), 298.
- [8] KOSTKA B., OCHOCKI J., *Pharmazie*, 51 (1996), 990.
- [9] KAJMAN-BRONŻEWSKA L., OCHOCKI J., *Pharmazie*, 198 (1997), 52.
- [10] ZHAO G., LIN H., YU P., SU H., ZHU S., SU X., CHEN Y., *J. Inorg. Biochem.*, 145 (1999), 73.
- [11] IAKOVIDOU Z., PAPAGEORGIOU A., DEMERTZIS M.A., MIOGLOU E., MOURELATOS D., KOTSLS A., NATH YADAV P., KOVALA-DEMERTZI D., *Anti-Cancer Drugs*, 12 (2001), 65.
- [12] ČURIĆ M., TUŠEK-BOŽIĆ L., VIKIĆ-TOPIĆ D., STARCIA V., FURLANI A., BALZARINI J., DE CLERCQ E., *J. Inorg. Biochem.*, 63 (1996), 125.
- [13] TUŠEK-BOŽIĆ L., ČURIĆ M., BALZARINI J., DE CLERCQ E., *Nucleos. Nucleot.*, 14 (1995), 777.
- [14] TUŠEK-BOŽIĆ L., MATIJAŠIĆ J., BOCELLI G., SGARBOTTO P., FURLANI A., SCARIA V., PAPAIOANNOU A., *Inorg. Chim. Acta*, 185 (1991), 229.

---

\*Crystallographic data for the structure have been deposited with the Cambridge Crystallographic Data Centre, CCDC-685325. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int.code +(1223)336-033, e-mail for inquiry: fileserv@ccdc.cam.ac.uk).

- [15] TUŠEK-BOŽIĆ L., MATIJAŠIĆ J., BOCELLI G., CALESTANI G., FURLANI A., STARCIA V., PAPAIOANNOU A., *J. Chem. Soc., Dalton Trans.*, (1991), 195.
- [16] OCHOCKI J., ŽUROWSKA B., MROZIŃSKI J., REEDIJK J., Proc. III Symp. on Inorganic Biochemistry and Molecular Biophysics, and VI Int. Scientific School on Biological Macromolecules, Wrocław –Karpacz, Wrocław 1991, 212.
- [17] OCHOCKI J., KOSTKA K., ŽUROWSKA B., MROZIŃSKI J., GALDECKA E., GALDECKI Z., REEDIJK J., *J. Chem. Soc. Dalton Trans.*, (1992), 2955.
- [18] OCHOCKI J., ŽUROWSKA B., MROZIŃSKI J., KOOIJMAN H., SPEK A.L., REEDIJK J., *Eur. J. Inorg. Chem.*, (1998), 169.
- [19] ŽUROWSKA B., MROZIŃSKI J., CIUNIK Z., OCHOCKI J., *J. Mol. Struct.*, 79 (2006), 98.
- [20] ŽUROWSKA B., MROZIŃSKI J., CIUNIK Z., OCHOCKI J., *J. Mol. Struct.*, 843 (2007), 26.
- [21] ŽUROWSKA B., MROZIŃSKI J., OCHOCKI J., *Mater. Sci.-Poland*, 25 (2007), 1063.
- [22] ŽUROWSKA B., OCHOCKI J., MROZIŃSKI J., CIUNIK Z., REEDIJK J., *Inorg. Chim. Acta*, 357 (2004), 755.
- [23] ŽUROWSKA B., ŚLEPOKURA K., LIS T., OCHOCKI J., *Inorg. Chim. Acta*, 362 (2008), 733
- [24] JEFFREY G.A., SAENGE W., *Hydrogen Bonding in Biological Structures*, Springer, Berlin, 1991; JEFFREY G.A., *An Introduction to Hydrogen Bonding*; Oxford, New York, 1997; ROESKY H.W., ANDRUH M., *Coord. Chem. Rev.*, 91 (2003), 236.
- [25] FISHER B.E., SIGEL H., *J. Am. Chem. Soc.*, 102 (1980), 2998; SUGIMORI T., SHIBAKAWA K., MASUDA H., ODANI A., YAMAUCHI O., *Inorg. Chem.*, 32 (1993), 4951; COSTA-FILHO A.J., MUNTE C.E., BARBERATO C., CASTELLANO E.E., MATTIOLI M.P.D., CALVO R., NASCIMENTO O.R., *Inorg. Chem.*, 38 (1999), 4413; JANIÁK CH., *J. Chem. Soc. Dalton Trans.*, (2000), 3885.
- [26] ZARIĆ S.D., POPOIĆ D.M., KNAPP E-W., *Chem. Eur. J.*, 6 (2000), 3935; ZARIĆ S.D., *Chem. Phys. Lett.*, 77 (1999), 311; PERUTZ M.F., PHILOS M.F., *Trans. R. Soc. A*, 105 (1997), 345; MILČIĆ M., ZARIĆ S.D., *Eur. J. Inorg. Chem.*, (2001), 2143.
- [27] BRILL A.S., *Transition Metals in Biochemistry*; Springer, Berlin, 1977; LIPPARD S.J., BERG J.M., *Principles of Bioinorganic Chemistry*, University Science Books; Mill Valley, CA, 1994.
- [28] ŽUROWSKA B., BRZUSZKIEWICZ A., *Polyhedron*, 27 (2008), 1623.
- [29] KÖNIG E., *Magnetic Properties of Coordination and Organometallic Transition Metal Compounds*, Springer, Berlin, 1966.
- [30] CARLIN R.L., *Magnetochemistry*, Springer, Heidelberg, 1986.
- [31] CrysAlis 'RED', Oxford Diffraction (Poland), Wrocław, 2001, 2003.
- [32] SHELXTL-NT [version 5.1], Bruker AXS Inc., Madison, WI, 1999.
- [33] ŽUROWSKA B., KALINOWSKA-LIS U., BRZUSZKIEWICZ A., OCHOCKI J., *Inorg. Chim. Acta*, 362 (2008), 1435.
- [34] NAKAMOTO K., *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley, New York, 1978.
- [35] HATHAWAY B. J., UNDERHILL A. E., *J. Chem. Soc.*, (1961) 3091.
- [36] LEWIS D.L., ESTES E.D., HODGSON D.J., *J. Cryst. Mol. Struct.*, 67 (1975), 5.
- [37] LEVER A.B.P., *Inorganic Electronic Spectroscopy*, Elsevier, Amsterdam, 1986.
- [38] HATHAWAY B.J., BILLING D.E., *Coord. Chem. Rev.*, 143 (1970), 5.
- [39] MABBS F.E., MACHIN D.J., *Magnetism of Transition Metal Complexes*, Chapman and Hall, London, 1973.
- [40] FIGGIS B.N., LEWIS J., *Prog. Inorg. Chem.*, 37 (1964), 6.
- [41] SMART J.S., *Effective Field Theories of Magnetism*, W.P. Saunders Comp., Philadelphia, 1966, p. 24.
- [42] ŽUROWSKA B., KALINOWSKA-LIS U., BIAŁOŃSKA A., OCHOCKI J., *J. Mol. Struct.*, 889 (2008), 98.

Received 20 June 2008

Revised 16 September 2008