

Synthesis, spectroscopy and magnetic properties of transition-metal complexes with aminophosphonate derivatives of pyridine

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The compounds of general formula $[ML_2](ClO_4)_2$ [$M = Cu(II), Ni(II), Co(II)$]; $L =$ diethyl 3-pyridylmethyl[N-(butyl)amino]phosphonate (3-pmape) or diethyl 4-pyridylmethyl[N-(butyl)amino]phosphonate (4-pmape) were prepared. The new complexes were identified and characterized by elemental analysis, infrared, electronic spectral studies and magnetic measurements. The complexes are sixcoordinate. Metal ions are octahedrally surrounded by two pyridine and two amine nitrogens, and two oxygens of the phosphoryl groups. The results of the magnetic studies suggest polymeric chain structure of the above complexes and indicate weak antiferromagnetic interaction between the magnetic centers. The magnetic behavior of Co(II) complexes is characteristic for cobalt(II) system with an important orbital contribution via spin-orbit coupling.

Keywords: *aminophosphonate ligand, transition-metal complexes; spectroscopy; magnetism*

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1. Introduction

Phosphorus compounds of the type aminophosphonic acids and their esters might be considered as analogues of naturally occurring amino acids. This class of compounds are of considerable interest because of their occurrence in numerous organisms and their useful biological and chemical activity [1, 2]. Hence, the investigation of their interaction with various metal ions may contribute to a better understanding of these activities [3], which are greatly influenced by the structure of the ligand coordinated to metal ions. In recent years, transition metal complexes with phosphonate [4–9] and phosphate [10, 11] diesters bearing N-heterocyclic donor atom have been the object of intensive investi-

gations, because of their potential [12] or significant antitumor activity [13–25].

These compounds were examined by structural and spectroscopic studies. Additionally, the magnetic studies were presented for the complexes with paramagnetic centers. These studies provided important information on the magnetic exchange interaction between the magnetic centers through covalent and/or non-covalent interactions. The biological relevance of the phosphonate and phosphate derivatives with N-heterocyclic system and their high reactivity toward transition metal ions prompted us to synthesize and design the new class of organophosphorus compounds, i.e. aminophosphonate diesters, derivatives of pyridine. Coordination chemistry of these *N,N,O*-donor ligands (Fig. 1) has not been recognized until now.

In this work, we present the synthesis, spectroscopic (infrared, ligand field, EPR) and magnetic

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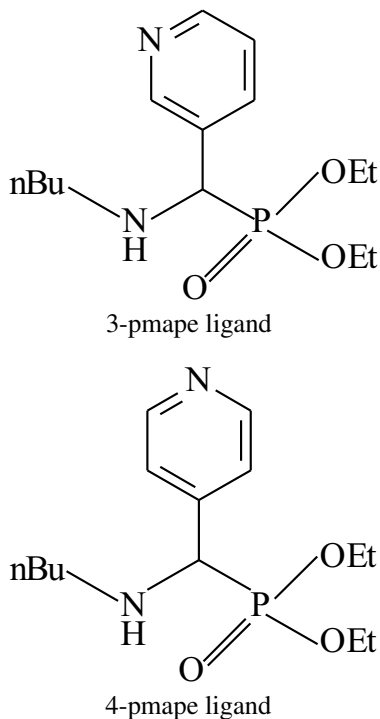


Fig. 1. Scheme of the 3-pmpe (3-pyridylmethyl[N-(butyl)amino]phosphonate) and 4-pmpe (4-pyridylmethyl[N-(butyl)amino]phosphonate) ligands.

measurements in order to determine coordination properties of the aminophosphonate ligands and stereochemistry of their coordination compounds with perchlorate $M(II) = Cu, Ni, Co$ salts. These studies provide a chemical basis for the biological activity of the ligands.

Although we have not succeeded in obtaining crystals of the complexes suitable for X-ray studies, the arrangement of metal ions in the solid (as monomer, dimer, chain etc.) can be determined from magnetic experiments. On the other hand, complementary information concerning local environments of the metal ions can be deduced from spectroscopic measurements.

2. Experimental

2.1. Reagents and physical measurements

The starting materials and solvents for the synthesis were obtained commercially and used as received. Metal content was determined using a Carl

Zeiss Jena atomic absorption spectrophotometer and a ARL Model 3410 ICP spectrometer. Elemental analyses were carried out using a Vario El III CHNS elemental analyzer. Solid-state electronic spectra ($28000\text{--}4000\text{ cm}^{-1}$) were 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. Magnetic measurements were carried out with a Quantum Design SQUID magnetometer (type MPMSXL-5). The measurements were recorded at a magnetic field of 0.5 T in the temperature range 1.8–300 K. Corrections for diamagnetic contribution are based on subtracting the signal of sample holder and estimating the contribution χ_D from the Pascal constants [26]. The effective magnetic moments were calculated from $\mu_{eff} = 2.83(\chi_M T)^{1/2}$ using temperature-independent paramagnetism of $60 \times 10^{-6}\text{ cm}^3\text{ mol}^{-1}$ for Cu, $150 \times 10^{-6}\text{ cm}^3\text{ mol}^{-1}$ for cobalt(II) ion and $220 \times 10^{-6}\text{ cm}^3\text{ mol}^{-1}$ for Ni [27].

2.2. Synthesis of the ligands and compounds

The ligands were prepared from the corresponding pyridine imines and diethyl phosphonate, according to the procedures described earlier [25, 26]. Spectroscopic data (1H , ^{31}P NMR) of the ligands are given in [29].

The perchlorate complexes were prepared by dissolving an appropriate hydrated metal perchlorate (1 mmol) in ethanol (10 cm^3) and adding this compound to the solution of the ligand (2 mmol) in ethanol (20 cm^3). The resulting solutions were filtered and left to evaporate slowly at room temperature.

Anal. Calc. for $C_{28}H_{50}N_4O_{14}P_2Cl_2Cu$ (**1**) (%): C, 38.94; H, 5.85; N, 6.49; Cu, 7.36. Found: C, 38.75; H, 5.98; N, 6.44; Cu, 7.03.

Anal. Calc. for $C_{28}H_{50}N_4O_{14}P_2Cl_2Ni$ (**2**) (%): C, 39.16; H, 5.88; N, 6.49; Ni, 6.62. Found: C, 39.65; H, 5.92; N, 6.34; Ni, 6.53.

Anal. Calc. for $C_{28}H_{50}N_4O_{14}P_2Cl_2Co$ (**3**) (%): C, 39.16; H, 5.88; N, 6.53; Co, 6.86. Found: C, 39.58; H, 5.63; N, 6.42; Co, 6.43.

Anal. Calc. for $C_{28}H_{50}N_4O_{14}P_2Cl_2Cu$ (**4**) (%): C, 38.94; H, 5.85; N, 6.49; Cu, 7.36. Found: C, 38.78; H, 5.37; N, 6.14; Cu, 7.71.

Anal. Calc. for $C_{28}H_{50}N_4O_{14}P_2Cl_2Ni$ (**5**) (%): C, 39.16; H, 5.88; N, 6.49; Ni, 6.62. Found: C, 39.85; H, 5.23; N, 6.07; Ni, 6.33 %.

Anal. Calc. for $C_{28}H_{50}N_4O_{14}P_2Cl_2Co$ (**6**) (%): C, 39.16; H, 5.88; N, 6.53; Co, 6.86. Found: C, 39.38; H, 5.48; N, 6.26; Co, 6.87.

In spite of all the efforts no crystals suitable for X-ray determination were obtained.

Caution! Although no problems encountered in this work, perchlorate salts containing organic ligands are potentially explosive. They should be prepared in small quantities and handled with care.

3. Results and discussion

We synthesized a series of M(II) (M = Cu, Ni and Co) perchlorate complexes with diethyl 3-pyridylmethyl[N-(butyl)amino]phosphonate (3-pmape) and diethyl 4-pyridylmethyl[N-(butyl)amino]phosphonate (4-pmape) ligands. The stoichiometry of the complexes was established from the elemental analysis and metal determination data. The analytical results demonstrated that the ligands were able to form coordination compounds with M(II) perchlorate salts in 1:2 metal to ligand molar ratio, with the following stoichiometries: $[M(L)_2](ClO_4)_2$.

3.1. Spectroscopic properties

In the IR spectra of the complexes, the strong band due to the stretching mode of the C=N aromatic ring in ca. 1595 cm^{-1} region in free ligands is slightly shifted about 20 cm^{-1} to somewhat higher frequencies as expected upon metal coordination. Additionally, the characteristic out-of-plane and in-plane ring deformation bands of the substituted pyridine ring (observed at ca. 400 and 620 cm^{-1} , respectively, in free ligand) are shifted to higher frequencies by ca. 20 cm^{-1} and 35 cm^{-1} , respectively. These also suggest the coordination of the pyridyl nitrogen donor atom [30, 31].

The very strong band at ca. 1245 cm^{-1} , which corresponds to the P=O stretching frequencies of

the free ligands, in the spectra of the all complexes is shifted towards lower frequencies by ca. $20\text{--}30\text{ cm}^{-1}$, as consequence of the coordination of the phosphoryl oxygen atom to the metal ion. The ligands exhibit one absorption band at $3300\text{--}3315\text{ cm}^{-1}$ associated with the NH group [32, 33]. This band in all complexes is shifted about 70 cm^{-1} upon M(II) complex formation, suggesting that the amino group participates in the coordination. Strong absorption bands of the perchlorate ion observed around 1100 cm^{-1} , and a sharp band at 625 cm^{-1} observed for all complexes, are characteristic for uncoordinated perchlorate anions [34, 35].

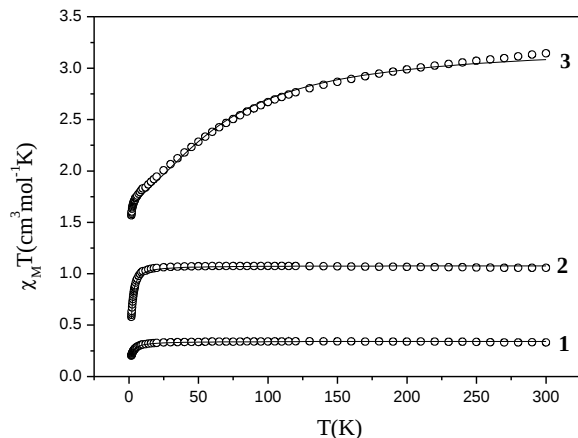
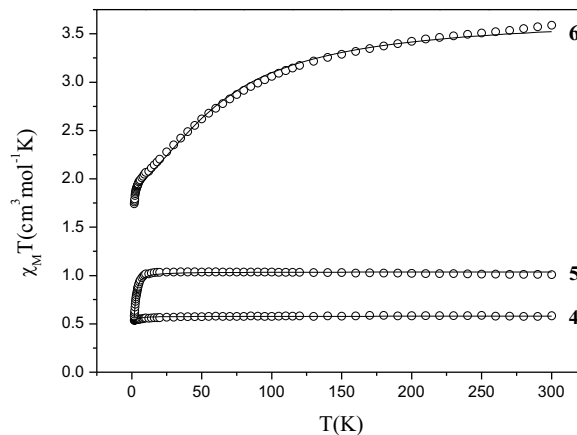
The far-IR region of the compounds reveals one band at ca. 270 cm^{-1} attributed to the metal-nitrogen stretching vibrations, which are in good agreement with those reported for the pyridine complexes [36]. We conclude that the IR spectra imply a N_4O_2 chromophore around the metal ions for all complexes. The 3- and 4-pmape ligands combine the pyridine ring and phosphoryl group, but in a sterically unfavourable position to form a chelate. These ligands form polymeric compounds with both ligands ends coordinating to different metal ions.

The ligand field spectral data of all complexes are presented in Table 1.

The ligand field spectra of the Cu(II) compounds reveal one broad asymmetric band associated with the ${}^2E \rightarrow {}^2T_{1g}$ transition in O_h symmetry [37]. The position, as well as the shape of this band suggests the presence of CuN_2O_4 chromophore in a tetragonally elongated octahedral geometry. The d-d spectra of the Ni(II) complexes exhibit three spin-allowed bands in O_h symmetry, which in order of decreasing energy, are assigned to the ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ and ${}^3A_{2g} \rightarrow {}^3T_{2g}$ transition. The Co(II) complexes display two bands typical for a high-spin octahedral environment of metal ion corresponding to the ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$, ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}$ and ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}$, respectively [38, 39]. The calculated [35, 36] spectrochemical parameters D_q and B are in a good arrangement with those expected for isomorphous cobalt and nickel compounds (**2** and **3**, respectively and **5** and **6**, respectively) as suggested in the [38] and [39]. Relative high values of the parameter B might reflect the deviation from the octahedral geometry.

Table 1. Electronic spectra data for $[\text{ML}_2](\text{ClO}_4)_2$.

Compound	Band position $[\text{cm}^{-1}]$	D_q $[\text{cm}^{-1}]$	B $[\text{cm}^{-1}]$
(1) $[\text{Cu}(3\text{-pmape})_2](\text{ClO}_4)_2$	15550		
(4) $[\text{Cu}(4\text{-pmape})_2](\text{ClO}_4)_2$	15410		
(2) $[\text{Ni}(3\text{-pmape})_2](\text{ClO}_4)_2$	2720, 15770, 9600	960	940
(5) $[\text{Ni}(4\text{-pmape})_2](\text{ClO}_4)_2$	26520, 15620, 9710	910	870
(3) $[\text{Co}(3\text{-pmape})_2](\text{ClO}_4)_2$	20100, 9100	990	810
(6) $[\text{Co}(4\text{-pmape})_2](\text{ClO}_4)_2$	20340, 8310	910	880

Fig. 2. Plot of $\chi_M T$ versus T for $[\text{Cu}(3\text{-pmape})_2](\text{ClO}_4)_2$ (1), $[\text{Ni}(3\text{-pmape})_2](\text{ClO}_4)_2$ (2) and $[\text{Co}(3\text{-pmape})_2](\text{ClO}_4)_2$ (3). Solid lines correspond to the best theoretical fit (see text).Fig. 3. Plot of $\chi_M T$ versus T for $[\text{Cu}(4\text{-pmape})_2](\text{ClO}_4)_2$ (4), $[\text{Ni}(4\text{-pmape})_2](\text{ClO}_4)_2$ (5), $[\text{Co}(4\text{-pmape})_2](\text{ClO}_4)_2$ (6). Solid lines correspond to the best theoretical fit (see text).

3.2. Magnetic properties

The EPR X-band powder spectra of the copper compounds are of the axial type with g values of $g_{\parallel} = 2.248$, and $g_{\perp} = 2.076$ for **1** at room temperature. For **4** one line is observed with $g_{iso} = 2.12$. The spectra are independent of temperature. The nickel compounds do not exhibit the X-band EPR spectrum. The cobalt compounds display no lines at room temperature but one broad line at 77 K with $g = 4.20$ and 4.06 for **3** and **6**, respectively.

Variable-temperature (1.8–300 K) magnetic susceptibility data were collected for all complexes. The variation of the magnetic susceptibility in the form of $\chi_M T$ versus T (χ_M being the magnetic susceptibility per mole of the metal atoms) is depicted in Figs. 2 and 3.

The effective magnetic moments (Table 2) at room temperature for all complexes are within usu-

ally observed range of experimental values for the complexes in octahedral configuration [40].

The negative Weiss constant (Θ) value, obtained from equation $\chi_M = [C/(T - \Theta)]$ within the measured temperature region for the Cu(II) compounds may suggest the possibility of a very weak magnetic interaction between the magnetic centres. Also the small negative Weiss constant (Θ) values for the Ni(II) compounds were observed (Table 1). In this case, two effects can be responsible for the value of Θ and the decrease of $\chi_M T$ in the lowest temperatures (Figs. 2 and 3): weak antiferromagnetic interactions and/or zero-field splitting effects [41, 42].

The analytical results and spectroscopic data suggest that 3- and 4-pmape ligands act as N,N,O -dibridges between the metal centers, thus all complexes may be considered as coordination polymers with the general formula $\{[\text{M}(3\text{-pmape})_2(\text{ClO}_4)_2]_n$ and $\{[\text{M}(4\text{-pmape})_2(\text{ClO}_4)_2]_n$. We can conclude

Table 2. Magnetic data and computed best-fit parameters for $[\text{ML}_2](\text{ClO}_4)_2$.

Compound	Curie constant ^a C [$\text{cm}^3\text{mol}^{-1}\text{K}$]	Weiss constant ^a Θ [K]	μ_{eff} [B.M] 300 K	Model of magnetic interaction	Parameter	R^b
(1) $[\text{Cu}(3\text{-pmape})_2](\text{ClO}_4)_2$	0.37	−0.29	1.73	Bonner and Fisher chain [44, 45]	$J = -0.93 \text{ cm}^{-1}$ $g = 2.00$	$3.08 \cdot 10^{-5}$
(4) $[\text{Cu}(4\text{-pmape})_2](\text{ClO}_4)_2$	0.53	−0.38	2.06	Bonner and Fisher chain [44, 45]	$J = -0.39 \text{ cm}^{-1}$ $g = 2.18$	$5.07 \cdot 10^{-5}$
(2) $[\text{Ni}(3\text{-pmape})_2](\text{ClO}_4)_2$	1.06	−1.35	2.91	Ising chain [46]	$J = -1.12 \text{ cm}^{-1}$ $D = 2.46 \text{ cm}^{-1}$ $g = 2.13$	$4.98 \cdot 10^{-4}$
(5) $[\text{Ni}(4\text{-pmape})_2](\text{ClO}_4)_2$	1.02	−1.17	2.84	Ising chain [46]	$J = -0.68 \text{ cm}^{-1}$ $D = 2.51 \text{ cm}^{-1}$ $g = 2.21$	$4.80 \cdot 10^{-4}$
(3) $[\text{Co}(3\text{-pmape})_2](\text{ClO}_4)_2$	3.47	−29.9	5.08	Lack of model		
(6) $[\text{Co}(4\text{-pmape})_2](\text{ClO}_4)_2$	3.94	−24.8	5.36	Lack of model		

^aIn the temperature range 100 K to r.t. for **3** and **6**

^b $R = \sum_{i=1}^n (\chi_i^{\text{exp}} - \chi_i^{\text{calc}})^2 / (\chi_i^{\text{exp}})^2$

from the negative Weiss constant (Θ) and the plot of the $\chi_M T$ value for Cu(II) and Ni(II) complexes, that small intramolecular (intrachain) exchange interactions may exist. Therefore, we performed the interpretation of the magnetic behavior on the basis of the proposed structures. Within the assumed models (Table 2), the intermolecular exchange parameters J and zJ' listed in Table 2 were obtained. The satisfactory results (agreement factor, R) for Cu(II) and Ni(II) compounds shown in Figs. 2 and 3 and in Table 2 confirm the polymeric chain structure for all complexes.

The magnetic behaviour of the Co(II) complexes is characteristic of cobalt(II) systems with an important orbital contribution via spin-orbit coupling. Namely, the Co(II) compounds behave as a Curie-Weiss paramagnet above 100 K. The negative Weiss constants (Table 2) obtained in the range 100–300 K is due to the effect of spin-coupling, resulting in a gradual transformation from an isotropic $s = 3/2$ at high temperature to an anisotropic $s_{\text{eff}} = 1/2$ at low temperature. Because the value of the Weiss constant (Table 2) is different from the value expected for an isolated Co(II) ion with a spin-orbit coupling of -170 cm^{-1} i.e. -20 K [47], the antiferromag-

netic exchange interaction between cobalt ions in cobalt complexes is also expected.

From the temperature dependence of the magnetic susceptibility the axial zero-field splitting (ZFS) parameter D has been calculated in fitting procedure [48, 49]. The fitting results provide the following parameters: $|D| = 53.7 \text{ cm}^{-1}$, $g_{\parallel} = 3.21$, $g_{\perp} = 2.30$ for **3**, and $|D| = 49.2 \text{ cm}^{-1}$, $g_{\parallel} = 3.47$, $g_{\perp} = 2.42$ for **6**. The plot of the best fit shown in Figs. 2 and 3 as a solid line, indicates that the cobalt(II) centers are only very weak exchange coupling. The D value is within the typical range for high-spin cobalt(II) ion in an octahedral environment [50–52]. The low-temperature discrepancies below 5 K may have resulted in the occurrence of weak magnetic exchange effects (intramolecular interaction) in the lowest temperatures.

The lack of a model for $S = 3/2$ chain system precludes theoretical analysis of the magnetic data of the complexes **3** and **6**, i.e. the calculation of the exchange of J parameters.

The obtained values of the J parameters for copper and nickel complexes suggest that the metal-metal distance must be large, leading to weak antiferromagnetic coupling. On the basis of the mag-

netic data, the polymeric chain structure for all complexes is proposed.

4. Conclusions

A number of new coordination compounds with the aminophosphonate ligands derivatives of pyridine have been synthesized. The results described above manifested, that the ligands in coordination compounds with perchlorate metal salts act in *N,N,O*-dibridge manner, thus the complexes may be considered as coordination polymers with the general formula $\{[ML_2](ClO_4)_2\}_n$. Weak intrachain magnetic interaction between the magnetic centers was observed.

Although the crystal structures of the studied complexes are unknown, their stoichiometry, results of spectroscopic studies and magnetic data strongly suggest that the polymeric chains are formed with dibridging organic ligands.

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