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Coordination properties of the diethyl (pyridin-3-ylmethyl)phosphonate ligand (3-pmpe) with nitrate transition metal salts

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A new series of nitrate transition metal complexes containing diethyl(pyridin-3-ylmethyl)phosphonate (3-pmpe) as a ligand, having a general formula $[M(3\text{-pmpe})_2(H_2O)_2](NO_3)_2$ (M = Cu, Co and Ni) and $[Zn(3\text{-pmpe})_2](NO_3)_2$ were prepared. The complexes were identified and characterized by the elemental analysis, spectroscopic and magnetic studies. Ligands containing two donor atoms, heterocyclic nitrogen and phosphoryl oxygen atoms bind in a bidentate bridging manner *via* the pyridine nitrogen and the phosphoryl oxygen atoms. The magnetic behaviour in the temperature range 1.8–300 K) of the Cu(II), Ni(II), Co(II) complexes as well as their spectroscopic properties suggest polymeric structure of all complexes and the existence of a weak antiferromagnetic exchange coupling between paramagnetic centres inside the dibridged linear chains $[M(3\text{-pmpe})_2M]_n$.

Key words: *N,O ligand; transition metal complexes; spectroscopy; magnetism*

1. Introduction

Ligand species, including some organophosphorus compounds containing phosphonic acids and their esters, derivatives of the pyridine or quinoline and their metal complexes exhibit significant biological and pharmacological activity. These compounds might be considered as analogues of naturally occurring phosphates. During recent years, much attention has been focused on the synthesis of N-heterocyclic phosphonates and their platinum(II) and palladium(II) complexes, because of their potential applications [1] and significant antitumor properties [2–13]. The present paper is a continuation of our earlier investigation of the reactivity of these N,O donor

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ligands with transition metal ions [14–21], i.e. diethyl(pyridin-2-ylmethyl)-, (pyridin-4-ylmethyl)- and (quinolin-2-ylmethyl)phosphonate ligands (2-pmpe, 4-pmpe and 2-qmpe, respectively). The coordination compounds with these ligands were investigated with regard to their spectral and magnetic properties which provide a chemical base for their biological activity. The crystal structure of the representative compounds, i.e. $[Co(2\text{-}pmpe)_2Cl_2]$ [14], $[Co(2\text{-}pmpe)_2(H_2O)_2](ClO_4)_2$ [15], $[Cu(2\text{-}pmpe)_2(ClO_4)_2]$ [16], $[Cd_4(2\text{-}pmpe)_4Cl_8]$ [17] (with N,O-bonded chelate ligand) and $[Co(4\text{-}pmpe)_2(H_2O)_2](ClO_4)_2{\cdot}2H_2O$ (with N,O-bridging ligand) [18] as well as $[M(2\text{-}qmpe)_4(H_2O)_2](ClO_4)_2$ (with O-bonded ligand), where M = Ni, Mn [19] was determined. We found recently that the interaction of 2-pmpe and 2-qmpe with some copper(II) and cobalt(II) salts leads to an unusual oxidative decomposition of the ligands [21, 22]. In this reaction, cleavage of C–P bond occurs and copper–pikolinate, copper– and cobalt–quinaldinate systems are produced.

Recently, we have reported the coordination properties of the 3-pmpe ligand (Fig. 1) with zinc(II) chloride [23]. IR and X-ray analyses show that in the reaction of $ZnCl_2$ with 3-pmpe in methanol, three crystalline polymorphs were found: $[Zn(3\text{-}pmpe)Cl_2]_2$ (**1**) and $[Zn(3\text{-}pmpe)Cl_2]_n$ (**2** and **3**). In **1**, Zn(II) ions are doubly bridged by the 3-pmpe ligand, resulting in the formation of dinuclear species. In polymeric compounds **2** and **3**, Zn(II) ions are singly bridged by the 3-pmpe, resulting in the formation of one-dimensional chains.

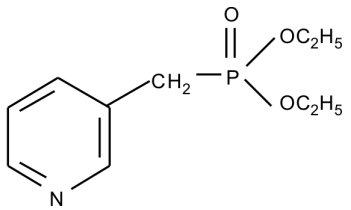

Fig. 1. Schematic drawing of diethyl(pyridin-3-yl)methylphosphonate ligand (3-pmpe)

Here we extend our studies to the synthesis and characterization of nitrate compounds for the purpose of studying the coordination behaviour of the diethyl(pyridin-3-ylmethyl)phosphonate (3-pmpe), stoichiometries and geometrical features of the resulting species. Additionally, our interest is the study of the stability of the metal(II) compounds in solution. Unfortunately, we have not succeeded in preparing the complex crystals suitable for the X-ray studies. The physicochemical properties of the compounds and their possible structures are discussed based on their spectral (infrared, ligand field and EPR spectra) and magnetic features.

2. Experimental

General comments and physical measurements. 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. Elemental analyses were carried out using a Perkin-Elmer elemental analyzer 2400CHN. Infrared spectra (100–4000 cm^{-1}) were recorded on a Bruker IFS 113v spectrophotometer using KBr pellets, and solid state electronic spectra (4000–28 000 cm^{-1}) were performed on a Cary 500 spectrophotometer. ^{1}H and ^{31}P NMR spectra were recorded on a Varian Mercury-300 spectrometer operating at a frequency 300 MHz. Chemical shifts were reported using a standard (δ) notation in ppm with respect to TMS (1%) as an internal standard and H_3PO_4 (85%) as an external standard. The EPR spectra of powder samples were recorded (at 295 and 77 K) on a Bruker ESP 300E spectrometer operating at X-band and equipped with a Bruker NMR. Magnetic measurements of polycrystalline samples were carried out with a Quantum Design SQUID magnetometer (MPMSXL-5 type). The measurements were recorded in a magnetic field of 0.5 T over the temperature range 1.8–300 K. The correction for diamagnetism of the experimental susceptibility was based on subtracting the sample-holder signal and estimating the contribution χ_D from Pascal constants [24]. The effective magnetic moments were calculated from $\mu_{eff} = 2.83(\chi_M T)^{1/2}$, using the temperature-independent paramagnetism of 60×10^{-6} $cm^3\cdot mol^{-1}$ for Cu (**1**), of 220×10^{-6} $cm^3\cdot mol^{-1}$ for Ni (**2**), and of 150×10^{-6} $cm^3\cdot mol^{-1}$ for Co (**3**) [25].

*Synthesis of the ligand***.** Diethyl(pyridin-3-ylmethylphosphonate (3-pmpe) was prepared according to the procedure described in detail elsewhere [23].

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.26 (t, 6H, $^{3}J_{HH}$ = 6.9, 2 CH_3), 3.15 (d, 2H, $^{2}J_{HP}$ = 21.6; py-CH_2P), 4.06 (dq, 4H, $^{3}J_{HH}$ = 6.9; 2 $POCH_2$), 7.24-7.29 (m, 1H, (py) H-C5), 7.67-7.72 (m, 1H, (py) H-C4), 8.43-8.51 (m, 2H, (py) H-C2, H-C6); ^{31}P-NMR (300 MHz, $CDCl_3$): δ = 25.16; IR (film) ν_{max} (cm^{-1}): (py-ring) 1570 (m), 1550(w), (P = O) 1265 (vs), (P–O–C) 1050–1025(vs); (vs – very strong, m – medium, w – weak).

Synthesis of the complexes. The nitrate complexes were prepared by dissolving the appropriate quantity of hydrated metal nitrate (1 mmol) in ethanol (10 cm^3) and adding to a solution of the ligand (3 mmol) in ethanol (20 cm^3). The resulting solutions were filtered off, and left to evaporate slowly at room temperature. Blue (**1**) green (**2**), pink (**3**) and white (**4**) the Cu(II), Ni(II) Co(II) and Zn(II) compounds were obtained.

[Zn(3-pmpe)$_2$](NO$_3$)$_2$. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.26 (t, 6H, $^{3}J_{HH}$ = 6.9, 2 CH_3), 3.38 (d, 2H, $^{2}J_{HP}$ = 21.8; py-CH_2P), 3.94 (dq, 4H, $^{3}J_{HH}$ = 6.9; 2 $POCH_2$), 7.27 (m, 1H, (py) H-C5), 7.74 (m, 1H, (py) H-C4), 8.67 (m, 2H, (py) H-C2, H-C6).

Anal. Found (**1**): C, 29.27; H, 5.92; N, 8.22; Cu, 9.32; Calc. for [$C_{20}H_{40}N_4P_2O_{14}Cu$ (**1**): C, 30.36; H, 6.34; N, 8.41; Cu, 9.15 %

Anal. Found (**2**): C, 35.47; H, 5.96; N, 8.27; Ni, 8.67; Calc. for [$C_{20}H_{40}N_4P_2O_{14}Ni$) (**2**): C, 35.67; H, 5.50; N, 8.51; Ni 8.45 %

Anal. Found (**3**): C, 35.46; H, 5.96; N, 8.27; Co, 8.70; Calc. for [$C_{20}H_{40}N_4P_2O_{14}Co$] (**3**); C, 35.75; H, 6.05; N, 8.54; Co 8.23 %

Anal. Found (**4**): C, 37.07; H, 5.61; N, 8.65; Zn, 10.09; Calc. for [$C_{20}H_{36}N_4P_2O_{12}Zn$] (**3**); C, 37.25; H, 5.48; N, 8.50; Zn 10.48 %

3. Results and discussion

The stoichiometry of the investigated complexes was established from the elemental analysis and metal determination. The analytical and spectroscopic results (see below) demonstrated that 3-pmpe is a ligand able to form coordination compounds with M(II) nitrate salts having the M(II) to ligand molar ratio 1:2 of the following stoichiometries: $[M(3\text{-pmpe})_2(H_2O)_2](NO_3)_2$, M = Cu (**1**), Ni (**2**), Co (**3**) and $[Zn(3\text{-pmpe})_2](NO_3)_2$ (**4**)]. The compounds are stable in solution when exposed to air.

3.1. Infrared and ligand field spectra

The selected infrared spectral bands are shown in Table 1.

Table 1. Selected infrared spectroscopic frequencies (cm^{-1}) of the metal complexes with 3-pmpe

Compound	ν(C = C) ν(C = N)	ν(P = O)	δ(PO–C)	ν(P–OC)	δ(C = N)[a]	δ(C = N)[b]	ν(M–N)
3-pmpe	1633w[c] 1592w 1576m	1250vs 1240sh	1163w 1133vw	1054vs 1027vs	600w	400w	
Cu (**1**)	1609s 1584m	1226vs 1197vs	1162m	1050vs 1021vs	613w	417w	278w
Ni (**2**)	1607m 1571m-w	1214vs 1191vs	1167m-w 1142w	1041vs 1024vs	610w	419w	278w
Co (**3**)	1607m 1584w	1228vs 1190vs	1162w 1141w	1048vs 1024vs	611w	413w	278vw
Zn (**4**)	1582m 1609w	1200vs 1215vs	1163w 1140w	1040vs 1025vs	611w	418w	270w

[a]In-plane pyridine ring deformation.
[b]Out-of-plane pyridine ring deformation.
[c]Abbreviations: v = very, s = strong, m = medium, w = weak, sh = shoulder.

The IR spectra of all the complexes are different in their line shapes and relative intensities, indicating that there is no isomorphism within these groups of compounds. In the infrared spectra of the complexes studied, the bands due to the stretching modes of the pyridine ν(C = C) and ν(C = N) observed in the region 1600–1500 cm^{-1} are not shifted appreciably, whereas the characteristic out-of-plane and in-plane deformation bands of the 3-substituted pyridine ring are shifted to higher frequencies, suggesting coordination of the pyridyl nitrogen donor atom (Table 1). The band at 967 cm^{-1} is associated with a pyridine ring breathing mode of vibration, and is characteristically shifted to higher energy on coordination. Thus, the band observed at 976, 975, 974 and 970 cm^{-1} for **1**, **2**, **3** and **4** compounds, respectively, indicates the coordination of pyridine residues. The very strong band at 1250 cm^{-1} which corresponds to the P=O

stretching frequencies of the free ligand in the spectra of the all complexes, is shifted towards lower frequencies, indicating the coordination of the phosphoryl oxygen to the metal ion. Other ligand bands characteristic of the phosphonate moiety, δ(PO-C) at 1130–1170 cm^{-1} and ν(P–OC) at 1030–1050 cm^{-1}, do not show any significant shifts upon the formation of the M(II) complex. The far IR region of all the compounds shows one band attributed to the ν(M–N) stretching vibration.

The infrared spectra of all the studied compounds show a very strong band at 1384 cm^{-1}, characteristic of an ionic nitrate [26, 27]. The presence of water molecules in the compounds is deduced from the elemental analysis and the IR spectrum [27]. The strong band at about 3420–3440 cm^{-1}, corresponding to ν(OH) stretching mode, is observed in the IR spectra of the Cu(II), Ni(II) and Co(II) compounds. These bands indicate the presence of coordinated water molecules in the hydrogen bonds [28]. The IR spectrum of the Zn(II) compound shows the absence of all vibrations which might be attributed to the presence of water molecules.

The ligand field spectrum of the Cu(II) compound shows a broad asymmetric band centred at 15 200 cm^{-1}, associated with the $^2E \rightarrow {}^2T_{1g}$ transition in the O_h symmetry. Ligand field spectra of the Ni(II) and Co(II) compounds have the typical representative features of divalent metal ions having high spin in an octahedral environment [29]. The ligand field spectrum of the Ni(II) complex exhibits three spin-allowed bands in O_h symmetry (25 575, 14 925, 8620 cm^{-1}), which, in order of decreasing energy, are assigned to the, $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g} \rightarrow {}^3T_{2g}$ transition. The spin-forbidden absorption at about 13 590 cm^{-1} is observed as a shoulder. For the Co(II) complex, spin-allowed bands in O_h symmetry at 21 280 (sh), 19 340 and 8330 cm^{-1} are observed, corresponding to the $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$, $^4T_{1g}(F) \rightarrow {}^4A_{2g}$ and $^4T_{1g}(F) \rightarrow {}^4T_{2g}$, respectively. Asymmetric band for Cu(II) and in the near IR region for Ni(II) and Co(II) compounds show that the metal ions are in an octahedral, tetragonally distorted environment. The calculated [30, 31] spectrochemical parameters D_q and B for Ni (860, 975 cm^{-1}, respectively) and for Co (910, 830 cm^{-1}, respectively) indicate that the nickel and cobalt compounds according to the literature [30, 31] are not isomorphous. Relative high values of the parameter *B* might reflect the deviation from the octahedral geometry.

3.2. EPR and magnetic properties

The EPR spectrum of the Cu(II) compound is of an axial type, with *g* values at room temperature of $g_{||} = 2.24_7$ and $g_{\perp} = 2.08_5$. The spectrum is independent of temperature. The EPR spectrum of the Co(II) compound shows no lines at room temperature, but does show one broad line at 77 K, with $g \approx 3.90$. The Ni(II) compound does not exhibit an X-band spectrum.

The magnetic behaviour of the **1**–**3** complexes is shown in Fig. 2 in the form of the plot $\chi_M T$ vs. T (χ_M being the magnetic susceptibility per mole of the metal atoms).

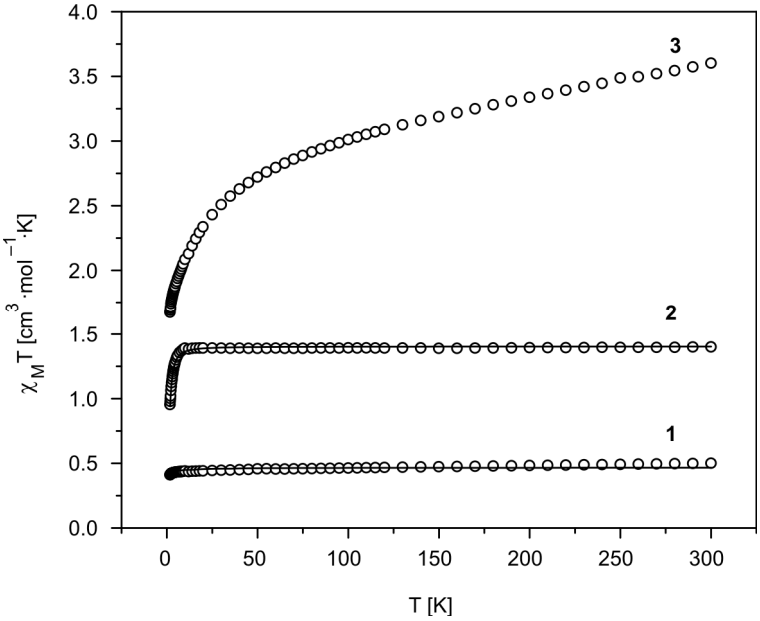

Fig. 2. Plot of $\chi_M T$ versus T for $[Cu(3\text{-pmpe})_2(H_2O)_2](NO_3)_2$ (1), $[Ni(3\text{-pmpe})_2(H_2O)_2](NO_3)_2$ (2) and $[Co(3\text{-pmpe})_2(H_2O)_2](NO_3)_2$ (3). Solid lines correspond to the best theoretical fit (see text)

The effective magnetic moments at room temperature for the Cu(II) ($\mu_{eff} = 2.00\mu_B$), Ni(II) ($\mu_{eff} = 3.35\mu_B$) and the Co(II) ($\mu_{eff} = 5.37\mu_B$) complexes are within the usually observed range of experimental values for the complexes in octahedral configuration [32]. The negative value of the Weiss constant (θ), obtained from the equation $\chi_M = [C/(T - \theta)]$ within the measured temperature region, equal to –0.47 K for the Cu(II) compound, may suggest the possibility of a very weak magnetic interaction between magnetic centres. The value of the Weiss constant (θ) for the Ni(II) compound is –1.40 K. Since the zero-field splitting parameters of isolated Ni(II) ions are usually large and lie in the range 4–8 cm^{-1} [33, 34], the decrease of $\chi_M T$ at lower temperatures observed for the nickel(II) compound (Fig. 2) can be explained by weak antiferromagnetic interactions and/or zero-field splitting effects [34]. The Co(II) compound behaves as a Curie–Weiss paramagnet, at temperatures above 100 K. The negative Weiss constant of –24.8 K obtained in the range 100–300 K is due to the effect of spin coupling, resulting in a gradual transformation of an isotropic $s = 3/2$ at high temperature to an anisotropic $s_{eff} = 1/2$ at low temperature. Because the value of the Weiss constant of –24.8 K differs from that expected for an isolated Co(II) ion with a spin-orbit coupling of –170 cm^{-1}, i.e. –20 K [35], antiferromagnetic exchange interaction between cobalt ions is also expected.

The analytical results and spectroscopic data suggest that two 3-pmpe ligands act as N,O-bridges between metal centres, thus the complexes may be expressed as coordination polymers having the general formula $\{[M(3\text{-pmpe})_2(H_2O)_2](NO_3)_2\}_n$ (M = Cu, Ni, Co) and $\{[Zn(3\text{-pmpe})_2](NO_3)_2\}_n$ (Fig. 3).

The occurrence of intrachain exchange interactions cannot be excluded if the proposed structure is valid. Consequently, we examined the magnetic behaviour of both the Cu(II) and the Ni(II) compounds. Lack of a model for a 3/2 chain system precludes theoretical analysis of the magnetic data of the Co(II) compound.

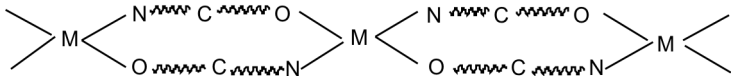

Fig. 3. Scheme of the proposed structure, showing the coordination of 3-pmpe ligand

In order to analyse the magnetic behaviour of the Cu(II) compound, a uniform $S = 1/2$ infinite chain model with Eq. (1) derived by Bonner and Fisher [36, 37] has been used:

$$\chi_{Cu} = \frac{Ng^2\beta^2}{kT} \times \frac{0.25 + 0.14995x + 0.30094x^2}{1 + 1.9862x + 0.68854x^2 + 6.0626x^3} \tag{1}$$

where $x = |J|/kT$ and the other parameters have their usual meanings. Assuming this model, the best-fit parameters obtained for the Cu(II) compound by the least-squares fit are the following: $J = -0.43$ cm^{-1}, $g = 2.13$ with the value of $R = 1.17 \cdot 10^{-4}$, where R is the correlation factor, defined as

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

Experimental magnetic data for the Ni(II) compound were fitted to the Ising chain model [38]. The best fit parameters obtained by the least squares fit are as follows: $J = -0.23$ cm^{-1}, $D = 2.46$ cm^{-1}, $R = 8.85 \times 10^{-5}$. The satisfactory results for the Cu(II) and Ni(II) compounds shown in Fig. 3 confirm their polymeric chain structure and indicate very weak antiferromagnetic exchange interaction between magnetic centres inside the dibridged linear chain. Lack of a single crystal study precludes interpretation of the obtained values of exchange parameters J but suggests that metal–metal distance must be large, leading to observed only very weak antiferromagnetic coupling.

4. Summary

The results described in the present paper have shown that nitrate complexes of Cu(II), Ni(II), Co(II) with 3-pmpe ligand are six-coordinate, formed by two N,O-

bridging 3-pmpe ligand and two water molecules (MN_2O_4 chromophore). The Zn(II) compound is four coordinated (ZnN_2O_2 chromophore). The nitrate ions in the all compounds are ionic. In light of the analytical, spectroscopic and magnetic data (for paramagnetic centres), the investigated compounds may be represented as polymeric chains having the general formula $\{[M(3\text{-pmpe})_2(H_2O)_2](NO_3)_2\}_n$ (M = Cu, Ni, Co) and $\{[Zn(3\text{-pmpe})_2](NO_3)_2\}_n$. The magnetic behaviour of the complexes is explained by very weak magnetic exchange between paramagnetic centres (Cu, Ni and Co) inside the chains.

In summary, in the 3-pmpe ligand, a sterically unfavourable position of the pyridine nitrogen and phosphonate oxygen atoms leads to dimeric [23] and polymeric compounds as presented in Ref. [23], and in this paper, in which ligand acts as an N,O bridge to the metal ions. It is worth mentioning that 3-pmpe ligand reacts with chloride metal(II) ions and $ZnCl_2$ in molar ratios of 1:1 and 1:2 [23], but with metal(II) nitrate it reacts in a 1:2 molar ratio.

Acknowledgements

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