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Coordination properties of diethyl (pyridyn-2-ylmethyl)phoshate ligand with chloride transition metal salts

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A new series of chloride transition metal complexes containing a diethyl (pyridyn-2-ylmethyl) phosphate (2-pmOpe) ligand, of the general formula $[M(2\text{-pmOpe})_2Cl_2]$ (M = Cu, Ni, Mn) and $[M(2\text{-pmOpe})Cl_2]$ (M = Co, Zn), were synthesized and studied. The stoichiometry and stereochemistry of the compounds were confirmed by elemental analysis, spectroscopic and magnetic studies. The ligand containing two donor atoms, heterocyclic pyridyl nitrogen and phosphoryl oxygen atoms, binds in a didentate chelate manner in all complexes. The octahedral (Cu, Ni, Mn) and tetrahedral (Co, Zn) coordination sphere complete chloride ions included in coordination. The magnetic behaviour (for paramagnetic centres) and spectroscopic analyses of the complexes indicate a mononuclear structure and suggest existence of a very weak exchange coupling between the metal centres in the crystal lattice.

Keywords: *transition metal complexes; N,O-donor ligand; spectroscopy; magnetism*

1. Introduction

The title compounds have been synthesized and investigated as a part of the program of research regarding metal complexes of the N-heterocyclic phosphonate and phosphate ligands. Recently, much attention has been focused on the synthesis of phosphonate and phosphate diesters, derivatives of pyridine or quinoline and their platinum(II) and palladium(II) complexes, because of their potential [1] and significant [2–14] anti-tumour activity. In previous studies, the authors have demonstrated high reactivity of pyridyl- and quinolyl-substituted phosphate diesters to transition metal ions [15–26]. However, the interaction of the new class of organophosphorous compounds, i.e. phosphate esters, derivatives of pyridine, with transition metal ions is

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still little known. Studies on the structure and biological activity of platinum(II) and palladium(II) complexes with diethyl (pyridin-2,-3- and -4-ylmethyl)phosphate (2-pmOpe, 3-pmOpe and 4-pmOpe, respectively) have been published [1, 14]. Recently, we reported the coordination properties of 2- and 4-pmOpe ligand with perchlorate metal(II) salts [25, 26] and chloride zinc(II) [27]. Further investigation of the reactivity of the N-heterocyclic phosphate ligands to transition metal salts concern the interaction of 2-pmOpe ligand (Fig. 1) with chloride transition metal salts.

In this paper, interactions of chloride metal(II) salts with 2-pmOpe ligand have been analysed, and stoichiometries as well as geometrical arrangements of the resulting species have been proposed. Physicochemical properties of the compounds and their possible structures were discussed based on their spectral properties (infrared, ligand field spectra) and magnetism analyses.

2. Experimental

Reagents and physical measurements. The starting materials and solvents for the syntheses obtained commercially were used as received. The compositions of the metals were 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 spectra (28 000 –4000 cm^{-1}) were obtained on a Cary 500 spectrophotometer. Magnetic measurements were carried out with a Quantum Design SQUID magnetometer (MPMSXL-5 type). The measurements were recorded at the magnetic field strength of 0.5 T in the temperature range 1.8–300 K. Corrections for diamagnetic contributions were based on subtracting the sample holder signal 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 60×10^{-6} $cm^3\cdot mol^{-1}$ for Cu(II) ions, of 500 type 10^{-6} $cm^3\cdot mol^{-1}$ for Co(II) ions and of 220×10^{-6} $cm^3\cdot mol^{-1}$ for Ni(II) ions [29].

Synthesis of 2-pmOpe ligand. The diethyl (pyridyn-2-ylmethyl)phosphate (2-pmOpe) (Fig. 1) ligand was prepared according to the procedure described elsewhere [1].

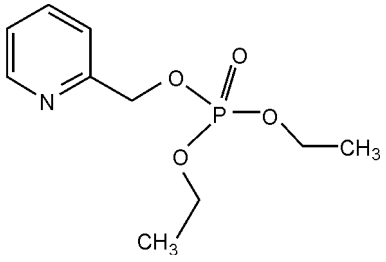

Fig. 1. Formula of the 2-pmOpe ligand

Syntheses of 2-pmOpe complexes. The chloride complexes were synthesized by dissolving an appropriate hydrated metal chloride (1 mmol) in ethanol (10 cm^3) and adding to a solution of the ligand (1 or 2 mmol) in ethanol (20 cm^3). The resulting solutions were filtered and left to evaporate slowly at room temperature. Attempts to obtain monocrystals so suitable for X-ray identification were unsuccessful.

Anal. Calc. for $C_{20}H_{32}Cl_2CuN_2O_8P_2$ (**1**): C, 38.44; H, 5.17; N, 4.48; Cu, 10.17. Found: C, 37.85; H, 5.62; N, 4.44; Cu, 10.31 %.

Anal. Calc. for $C_{20}H_{32}Cl_2NiN_2O_8P_2$ (**2**): C, 38.74; H, 5.21; N, 4.52; Ni, 9.46. Found: C, 38.55; H, 5.82; N, 4.34; Ni, 9.13 %.

Anal. Calc. for $C_{10}H_{16}Cl_2CoNO_4P$ (**3**): C, 32.05; H, 4.31; N, 3.73; Co, 15.71. Found: C, 32.48; H, 4.33; N, 3.42; Co, 15.23 %.

Anal. Calc. for $C_{10}H_{16}Cl_2ZnNO_4P$ (**4**): C, 31.48; H, 4.23; N, 3.67; Zn, 17.41. Found: C, 31.78; H, 4.33; N, 3.42; Co, 17.23 %.

Anal. Calc. for $C_{20}H_{32}Cl_2MnN_2O_8P_2$ (**5**): C, 38.97; H, 5.24; N, 4.55; Mn, 8.91. Found: C, 38.55; H, 5.32; N, 4.34; Mn, 9.13 %.

3. Results and discussion

A series of M(II) (M = Cu, Ni, Co, Mn and Zn) chloride complexes with diethyl (pyridin-2-ylmethyl)phosphate ester (2-pmOpe) have been synthesized. The stoichiometry of the complexes was identified from the elemental analysis and metal determination data. Results of analyses showed that the 2-pmOpe ligand is able to form coordination compounds with M(II) chloride salts in a 2:1 or 1:1 molar ratio, resulting in the following stoichiometries: $[M(2\text{-pmOpe})_2Cl_2]$ (M = Cu, Ni, Mn) and $[M(2\text{-pmOpe})Cl_2]$ (M = Co and Zn). All the studied compounds are stable in solution when exposed to air.

3.1. Spectroscopic properties

In the IR spectra of the complexes under study, the absorption bands were assigned to C=C and C=N stretching modes of a pyridine molecule, and were observed in the 1600–1500 cm^{-1} range for a free ligand. These absorption bands are not shifted appreciably, whereas characteristic bands corresponding to out-of-plane and in-plane ring deformation of the 2-substituted pyridine ring (observed at ca. 400 and 600 cm^{-1}, in a free ligand, respectively) are shifted to higher frequencies by ca. 20 cm^{-1} and 13 cm^{-1}, respectively. This suggests coordination of the pyridyl nitrogen donor atom [30, 31].

A strong absorption band at 1270 cm^{-1} which corresponds to P=O stretching vibrations of a free ligand, in the spectra of all complexes is shifted by ca. 40 cm^{-1} towards lower frequencies, indicating coordination of the phosphoryl oxygen to the metal ions.

The far-IR frequencies of the ν(M–Cl) stretching vibrations corresponding to copper, nickel and manganese compounds are observed at 316, 236 and 317 cm^{-1}, respec-

tively. The ν(M–Cl) symmetric and asymmetric vibrations in [Zn(2-pmOpe)Cl_2] (302, 329 cm^{-1}) and [Co(2-pmOpe)Cl_2] (310, 324 cm^{-1}) are consistent with a pseudotetrahedral environment [32]. It is worth emphasizing that the IR spectrum of Zn(II) complex presented here exhibits significant differences in line shapes, relative intensities and position of the bands, compared with the spectrum of the complex obtained earlier, namely [Zn(2-pmOpe)Cl_2]$_2$ [27], in which the ligand acts as an N,O-bridge, indicating some differences in ligand conformation.

In the ligand field spectrum of the Cu(II) compound, only one band is seen at 13 870 cm^{-1}. It is associated with the $^2E_g \rightarrow {}^2T_{2g}$ transition in O_h symmetry, which indicates that the coordination sphere $N_2O_2Cl_2$ produces a weak ligand field [32, 33]. The position, as well as the shape, of this band suggests that CuN_2O_4 chromophore has a tetragonally elongated octahedral geometry.

The ligand field spectrum of the Ni(II) compound displays bands (at 24 450, 14 840, 8290 cm^{-1}) corresponding to the $^3A_{2g} \rightarrow {}^3T_{1g}(P)$, $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g} \rightarrow {}^3T_{2g}$ transitions. Asymmetric bands in the near-IR region show that the Ni(II) ion is in an N_2O_4 octahedral tetragonally distorted [34, 35]. The calculated [34] spectrochemical parameters D_q and B for Ni(II) are 830 and 960 cm^{-1}, respectively. A rather high value of B may suggest a distorted octahedral geometry arising from the different nature of organic and chlorido ligands. The 10Dq value shows that the nearest coordination sphere $N_2O_2Cl_2$ produces a weak ligand field [33].

The ligand field spectrum of a blue cobalt(II) compound is typical of compounds having pseudotetrahedral geometry [36]. The compound shows triply split bands, one in the visible region and the other in the near infrared, with the centre at 16 300 cm^{-1} and about 4000 cm^{-1}. The parameters D_q (370 cm^{-1}) and B (745 cm^{-1}), calculated using the secular equation for tetrahedral cobalt(II) the transition energies [36, 37], are based on the centres of gravity of the respective multiplets. These values are consistent with those reported for tetrahedral Co(II) complexes and are typical of ligands which differ significantly in strength [38].

Extremely low values of the intensities of the bands for the octahedral manganese(II) complex are not unusual [34]. The spectrum shows bands as shoulders on a high-energy ligand or CT band at ca. 25 000 cm^{-1} and ca. 19 000 cm^{-1}, which can be assigned to $^6A_{1g} \rightarrow {}^4A_{1g}$, ^4E_g and $^6A_{1g} \rightarrow {}^4T_{1g}(G)$ transitions, respectively. Other characteristic bands of d-d transitions are masked by UV absorption and are difficult to recognize in the complex, and thus the ligand field parameters cannot be calculated.

3.2. Magnetic properties

The EPR spectrum of Cu(II) compound is of axial type, with g values of $g_{\|} = 2.28_7$, $g_{\perp} = 2.06_4$ normal for copper in a octahedral environment. A high value for $g_{\|}$ suggests a planar geometry with relatively strong axial bonding. The spectrum is independent of the temperature. The EPR spectrum of the octahedral Co(II) compound shows no lines at room temperature, but one broad line at 77 K with g = 5.62. The

nickel(II) compound does not exhibit an X-band spectrum. The EPR spectrum of the manganese(II) displays a hyperfine structure that is typical of ^{55}Mn(II).

Effective magnetic moments of copper(II), nickel(II) and manganese(II) complexes at room temperature (1.92, 3.12, 6.02 μ_B, respectively) are within the usually observed ranges of experimental values for Cu(II), and high-spin Ni(II) and Mn(II) complexes in octahedral configuration [39], and are characteristic of uncoupled metal centres. The magnetic moment of [Co(2-pmOpe)Cl_2] (μ_{eff} = 4.37μ_B) is consistent with tetrahedral stereochemistries [39]. Variable temperature (77–300 K) magnetic susceptibility data were collected for all the studied paramagnetic complexes.

The negative values for the Weiss constants (θ), obtained from the equation $\chi_M = C/(T - \theta)$] were within the measured temperature range and were found to be –0.24, –0.63, –6.73, –0.12 K for Cu(II), Ni(II), Co(II) and Mn(II) complexes, respectively. They may suggest the possibility of a very weak magnetic interaction between magnetic centres at lower temperatures. Temperature dependences of magnetic susceptibilities $\chi_M T$ for all investigated complexes are shown in Fig. 2.

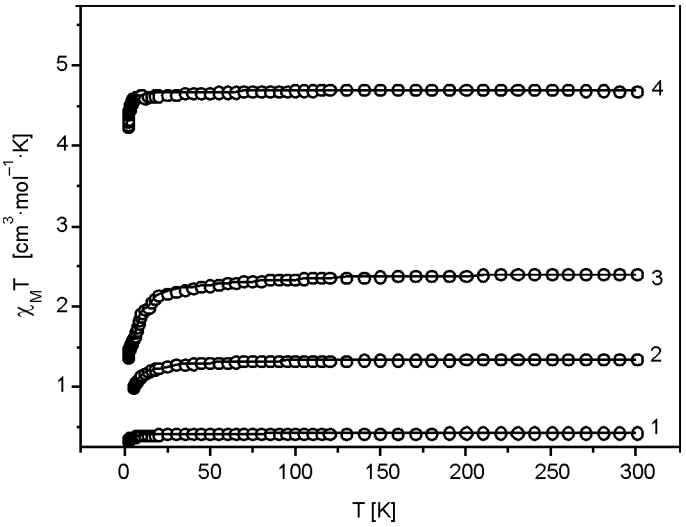

Fig. 2. Temperature dependences of $\chi_M T$ for [Cu(2-pmOpe)$_2$$Cl_2$] (**1**), [Ni(2-pmOpe)$_2$$Cl_2$] (**2**), [Co(2-pmOpe)$Cl_2$] (**3**) and [Mn(2-pmOpe)$_2$$Cl_2$] (**4**)

For all considered complexes, constant values of $\chi_M T$ are observed, decreasing only at the lowest temperatures (Fig. 2). This suggests the possibility of very weak magnetic interactions between magnetic centres inside crystal lattice at lower temperatures. The plot of $\chi_M T$ vs. T for cobalt(II) compound indicates a small contribution of the orbital moment, which is typical of the $^4A_{2g}$ ground state of Co(II) in a slightly distorted tetrahedral site [39].

Assuming all the complexes have monomeric structures**,** the data were analyzed using a molecular exchange field model based on the following equations[40]:

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

$$\chi_M^{\text{corr}} = \frac{\chi_M}{1 - \dfrac{2zJ'}{N\beta^2 g^2}\chi_M} \tag{2}$$

where χ_M is the magnetic susceptibility of a paramagnetic centre, χ_M^{corr} is the measured experimental susceptibility, zJ' is exchange between magnetic ions belonging to different molecules, z is the number of nearest neighbours, and the other symbols have their usual meanings. In the context of this model, the parameter values obtained by least squares fitting are as follows: $zJ' = -0.35$, -0.28, -0.48 and -0.36 cm^{-1} for Cu(II), Ni(II), Co(II) and Mn(II), respectively. The results obtained for the compounds under investigations confirm their monomeric structures and indicate that a very weak antiferromagnetic exchange interaction occurs between magnetic centres in the crystal lattice.

4. Summary

The results described in the present paper have shown that the 2-pmOpe ligand with the Co(II), Ni(II) and Zn(II) chloride salts acts as an N,O-bonded chelate ligand through pyridyl nitrogen and phosphoryl oxygen atoms. Chloride complexes of Cu(II), Ni(II) and Mn(II) are six coordinated ($MN_2O_2Cl_2$ chromophore). The Zn(II) and Co(II) compounds are four coordinated ($MNOCl_2$ chromophore). The results presented here and earlier [27] suggest that in the reaction of $ZnCl_2$ with 2-pmOpe two polymorphic forms are formed. All the studied compounds are stable in solution exposed to air. The magnetism results (for paramagnetic centres) indicate the complexes have monomeric structures, and suggest the possibility of a very weak antiferromagnetic interaction between paramagnetic centres in the crystal lattice.

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