Materials Science-Poland, Vol. 25, No. 4, 2007

Coordination properties of the diethyl 2-quinolilmethylphosphonate ligand with chloride and nitrate transition-metal salts

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A new series of the chloride and nitrate transition metal complexes containing the ligand diethyl 2-quinolylmethylphosphonate (2-qmpe) of general formula M(2-qmpe)$(NO_3)_2$ (M = Cu, Co), [Zn(2-qmpe)$(H_2O)_2NO_3$]$NO_3\cdot$ H_2O, [Ni(2-qmpe)$(H_2O)_2NO_3$]NO_3, M$(2\text{-qmpe})_2Cl_2$ (M = Cu, Ni, Co, Pd) and M(2-qmpe)Cl_2 (M = Co, Zn) were prepared. The complexes were identified and characterized by elemental analysis, spectroscopic and magnetic studies. Ligand containing two donor atoms, heterocyclic nitrogen and phosphoryl oxygen atoms exhibits different coordination properties. It was shown that the ligand binds in a bidentate chelate manner via the quinoline nitrogen and the phosphoryl oxygen atoms (complexes with 1:1 metal to ligand molar ratio) and it can also acts as a monodentate ligand coordinated through the nitrogen in the Pd(II) or oxygen atom in the Cu(II) and Co(II) complexes (complexes with 1:2 metal to ligand molar ratio). The magnetic behaviour of the Cu(II), Ni(II) and Co(II) and spectroscopic investigation of Zn(II) complexes suggests mononuclear structure of all the complexes and the existence of a weak intermolecular exchange coupling between magnetic centres inside crystal lattice.

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

1. Introduction

Many of chelating ligands containing nitrogen and oxygen donor atoms show biological activity and are of special interest due to a variety of ways in which they are bonded to metal ions [1, 2]. The ligand species include some organophosphorus compounds containing phosphonic acids and their esters, derivatives of pyridine or quinoline. These ligands and their metal complexes exhibit significant biological and pharmacological activity [3–7]. These compounds might be considered as analogues of

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naturally occurring phosphates. Aminophosphate complexes of platinum group metals have attracted attention as a result of their potential antitumor agents [3–8]. Biological activity of coordination compounds depends on the presence of metal ions [10]. Hence the investigation of interaction between the phosphonate ligands containing mononitrogen aromatic bases such as pyridine and quinoline with various metal ions may contribute to a better understanding of their biological activity and facilitate meaningful biochemical and pharmacological studies.

It is worth noting that quinoline derivatives, contrary to pyridine derivatives are barely studied groups of ligands in coordination chemistry. A structural study of these ligands seen also as pyridine derivatives seems interesting and useful in view of numerous applications [11].

The present paper is a continuation of our earlier investigation of the coordination compounds of the diethyl 2-pyridyl-, 4-pyridyl and 2-quinolylmethylphosphonate (Fig. 1) ligands (2-pmpe, 4-pmpe, 2-qmpe, respectively), containing two potential donor atoms, the heterocyclic nitrogen and phosphoryl oxygen atoms, with the several transition-metal ions and various anions [9, 13–17]. These were investigated with regard to their spectral and magnetic properties, which provide a chemical bases for their biological activity.

The crystal structures 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] (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) [9] as well as $[M(2\text{-qmpe})_4(H_2O)_2](ClO_4)_2$ (with O-bonded ligand), where M = Ni, Mn [16] were determined. It is worth noting that the interaction of 2-pmpe and 2-qmpe with some copper(II) salts leads to a novel oxidative P-dealkylation/dephosphorylation reaction of the ligand [17] in which pyridyl-2-carboxylate and quinolil-2-carboxylate, respectively ligands are produced. The results of structural and physicochemical studies of such complexes, as has been shown by us earlier [9, 14–17], are interesting from the point of view of inorganic and bioinorganic chemistry as well as their activity in biological systems.

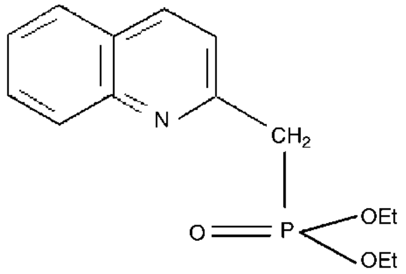

Fig. 1. Formula of the 2-quinolylmethylphosphonate (2-qmpe) ligand

Recently, we have reported the coordination properties of the 2-qmpe ligand towards perchlorate transition-metal salts [16]. In this case, the ligand is able to coordinate only by phosphoryl oxygen atom. The quinolil nitrogen atom is not included in the coordination. Here we extend our studies to the synthesis and characterization of new nitrate and chloride compounds for the purpose of study the coordination behaviour of diethyl 2-quinolilmethylphosphonate (2-qmpe), stoichiometries and geometric preferences of the resulting species. Additionally, our interest is the study of stability in solution metal(II) compounds. Unfortunately, we have not succeeded in preparing crystals suitable for the X-ray studies of the complexes. Physicochemical properties of the compounds and their possible structures are discussed based on the spectral (infrared, electronic and EPR spectra) and magnetic studies. Our findings on these complexes will be compared with results of our previous studies of the perchlorate metal-transition compounds with 2-qmpe.

2. Experimental

Reagents and physical measurements. The starting materials and solvents for synthesis were obtained commercially and used as received. 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 spectra (28 000–4000 cm^{-1}) were determined with a Cary 500 spectrophotometer. Solid-state EPR spectra were recorded at room temperature and at 77K 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 on solid polycrystalline samples by the Faraday method in the temperature range 77–300 K by using a sensitive Sartorius M-25D electrobalance. The susceptometer was equipped with an Oxford Instruments CF-1200 continuous-flow cryostat and an electromagnet operating at 5.25 kG. The calibrant employed was $HgCo(NCS)_4$ for which the susceptibility was assumed to be $16.44\times10^{-6}cm^3\cdot g^{-1}$ [18]. The corrections for diamagnetism of the constituent atoms were made by use of Pascal constants [19] and the effective magnetic moments were calculated from $\mu_{eff} = 2.83(\chi_M T)^{1/2}$ using temperature-independent paramagnetism (TIP) [20–22] of [$cm^3\cdot mol^{-1}$] 60×10^{-6} for Cu (**1**), 235×10^{-6} for Ni (**2**), 150×10^{-6} for Co (**3**), 522×10^{-6} for Co (**7**) and 568 for Co (**8**) compounds.

Synthesis of ligand and complexes. 2-qmpe was prepared by phosphorylation of 2-chloromethylquinoline with diethyl phosphine according to the procedure described in detail elsewhere [16] and checked for purity by spectroscopic and analytical methods. The nitrate complexes were prepared by dissolving the appropriate hydrated metal nitrate (1 mmol) in ethanol (10 cm^3) and adding to a solution of the ligand (1 or 2 mmol) in ethanol (15 cm^3). After filtration of the hot reaction mixture to remove any impurities, the complexes crystallized on cooling. In some cases, however, evaporation of a part of the solvent was necessary before the crystallization would occur.

The chloride complexes 1:1 and 1:2 were prepared as described above using metal chloride hexahydrate and 2-qmpe ligand (1 mmol) and (2 mmol), respectively. Their calculated and determined compositions are as follows:

Anal. calc. for [$C_{14}H_{18}N_3PO_9Cu$] (**1**):	C, 36.01; H, 3.89; N, 9.00; Cu, 13.61 %
Found	C, 36.65; H, 3.40; N, 8.59; Cu, 13.76 %
Anal. calc. for [$C_{14}H_{22}N_3PO_{11}Ni$] (**2**):	C, 33.76; H, 4.46; N, 8.44; Ni, 11.78 %
Found:	C, 33.65; H, 4.30; N, 8.59; Ni, 11.12%
Anal. calc. for [$C_{14}H_{18}N_3PO_9Co$] (**3**):	C, 36.37; H, 3.93; N, 9.09; Co,12.75%
Found:	C, 36.42; H, 3.58; N, 9.29; Co, 12.65%
Anal. calc. for [$C_{14}H_{24}N_3PO_{12}Zn$] (**4**):	C, 32.17; H, 4.64; N, 8.04; Zn, 12.51 %
Found:	C, 32.65; H, 4.30; N, 8.59; Zn, 12.65%
Anal. calc. for [$C_{28}H_{36}N_2P_2O_6Cl_2Cu$] (**5**):	C, 48.52; H, 5.25; N, 4.04; Cu, 9.17 %
Found:	C, 49.14; H, 5.50; N, 4.29; Cu, 9.33%
Anal. calc. for [$C_{28}H_{36}N_2P_2O_6Cl_2Ni$] (**6**):	C, 48.86; H, 5.28; N, 4.07; Ni, 8.53%
Found:	C, 48.65; H, 5.30; N, 4.32; Ni, 8.66%
Anal. calc. for [$C_{14}H_{18}NPO_3Cl_2Co$] (**7**):	C, 41.10; H, 4.44; N, 3.42; Co, 14.40, %
Found:	C, 41.61; H, 4.56; N, 3.66; Co, 14.62%
Anal. calc. for [$C_{28}H_{36}N_2P_2O_6Cl_2Co$] (**8**):	C, 48.85; H, 5.28; N, 4.07; Co, 8.56%
Found:	C, 49.01; H, 5.30; N, 4.59; Co, 8.65%
Anal. calc. for [$C_{14}H_{28}NPO_3Cl_2Zn$] (**9**):	C, 40.46; H, 4.37; N, 3.37; Zn, 15.73 %
Found:	C, 40.65; H, 4.30; N, 3.59; Zn, 15.65%
Anal. calc. for [$C_{28}H_{36}N_2P_2O_6Cl_2Pd$] (**10**):	C, 45.69; H, 4.94; N, 3.81; Pd, 14.46 %
Found:	C, 45.65; H, 4.30; N, 3.59; Pd, 14.65%

3. Results and discussion

The stoichiometry of the investigated complexes was established from the elemental analysis and metal determination. The analytical results demonstrated that the 2-qmpe is a ligand able to form coordination compounds with M(II) nitrate and chloride salts with the M(II) to 2-qmpe ligand molar ratio 1:1 and 1:2 with the following stoichiometries: M(2-qmpe) $(NO_3)_2$, [M = Cu (**1**), Co (**3**)], [Ni(2-qmpe)$(H_2O)_2NO_3$]NO_3 (**2**), [Zn(2-qmpe)$(H_2O)_2NO_3$]NO_3 ·H_2O (**4**), M(2-qmpe)Cl_2 (M = Co (**7**), Zn (**9**)) and M$(2\text{-qmpe})_2Cl_2$ [M = Cu (**5**), Ni(**6**), Co (**8**), Pd (**10**)]. The interaction of 2-qmpe with $CuCl_2$ salt produces an unstable compound of the formula Cu$(2\text{-qmpe})_2Cl_2$ (**5**), [17] undergoing an oxidative decomposition when exposed to air. In this reaction, the compound of the formula Cu$(2\text{-qca})_2\cdot H_2O$ (2-qca – quinoline-2-carboxylate ion) is formed as has been presented elsewhere [17].

3.1. Spectroscopic properties

In general, the IR spectra of the all complexes are very complex and complete assignment of the bands is difficult. Only these bands which are diagnostic for the nature of the metal(II) to ligand bonding have been analysed (Table 1).

Table 1. Selected infrared frequencies [cm^{-1}] of metal complexes with 2-qmpe

Compound	ν(P=O)	δ(C=N)[a]	δ(C=N)[b]	ν(M–N(L)	ν(M–O) ν(M–Cl)	Other bands of NO_3
2-qmpe	1254 vs	620w	396 w			
Cu(2-qmpe)$(NO_3)_2$ (**1**)	1172 s	640w	408 w	279 m	309 m, 327 m	1013 vs[c], 1274 vs, 1516 vs
[Ni(2-qmpe)$(H_2O)_2NO_3$]NO_3 (**2**)	1190 m	640w	415 w	276 v,br	300 v, br	1020 vs[c], 1292 s, 1384 vs, 1496 s
Co(2-qmpe)$(NO_3)_2$ (**3**)	1160 s	640w	410 w	268 m	300 m	1005 vs[c], 1245 vs, 1470 vs
[Zn(2-qmpe)$(H_2O)_2NO_3$]$NO_3 \cdot H_2O$ (**4**)	1190 s	636w	408 w	283 w	310 m	1005 vs[c], 1270 s, 1384 vs, 1510 s
Cu(2-qmpe)$_2Cl_2$ (**5**)	1225 s	635w	415 w		310 m	
Ni(2-qmpe)$_2Cl_2$ (**6**)	1187 m	635w	412 w	275 m	212 m	
Co(2-qmpe)Cl_2 (**7**)	1189 vs	636w	404 w	262 w	308 m, 338 m	
Co(2-qmpe)$_2Cl_2$ (**8**)	1224 s	627w	399 w		303 m, 334 m	
Zn(2-qmpe)Cl_2 (**9**)	1180	638	416	270 m	306 vs, 337 vs	
Pd(2-qmpe)$_2Cl_2$ (**10**)	1260 vs	640w	418 w	272 w	352 m	

[a] In-plane-ring quinoline deformation.
[b] Out-of-plane ring deformation.
[c] Overlapped with ν(P–OC).

In the IR spectra of the complexes studied (except Cu(2-qmpe)$_2Cl_2$ (**5**) and Co(2-qmpe)$_2Cl_2$ (**8**)), the bands due to stretching modes of the quinoline C=C and C=N bands in the region 1600–1500 cm^{-1} are not shifted appreciably, whereas the characteristic out-of-plane and in-plane ring deformation bands of the 2-substituted quinoline ring (observed at 396 and 620 cm^{-1}, respectively, in free ligand) are shifted to higher frequencies by ca. 8–22 cm^{-1} and 16–20 cm^{-1}, respectively, suggesting coordination of the quinolyl nitrogen donor atom [23, 24]. In the spectrum of Cu(2-qmpe)$_2Cl_2$ (**5**) and Co(2-qmpe)$_2Cl_2$ (**8**) compounds, characteristic deformation bands of the quinoline ring remain at the same position as for free ligand, indicating that the quinolyl nitrogen atom is not involved in the coordination sphere.

The strong absorption band at 1254 cm^{-1} corresponding to the P=O stretching frequencies of a free ligand, in the spectra of all complexes (except Pd(2-qmpe)$_2Cl_2$ (**10**)) is shifted by ca. 30–70 cm^{-1} towards lower frequencies, indicating coordination of the phosphoryl oxygen to the metal ions. A larger shift of this band is observed when 2-qmpe acts as N,O-bonded chelate ligand. Thus the spectrum of **5** indicates that 2-qmpe acts as O-bonded monodentate ligand. In the spectrum of **10** containing the N-bonded quinoline group, the characteristic ligand band assigned to the P=O group remains almost at the same position as in the free ligand, indicating monodentate coordination of 2-qmpe. In fact, X-ray structural determination [25] of *trans*-[Pd(2-qmpe)$_2$Cl$_2$] confirmed that the metal ion is bound in a N-monodentate way to the pyridine. Other ligand bands characteristic of the phosphonate moiety, δ(PO-C) at 1130–1170 cm^{-1} and ν(P–OC) at 1050–1030 cm^{-1} do not show any significant shifts upon M(II) complex formation. These assignments are consistent with our earlier observation of the IR spectral features of this ligand [16].

For Cu(2-qmpe)(NO$_3$)$_2$ (**1**) and Co(2-qmpe)(NO$_3$)$_2$ (**3**) it appears that the nitrate group is chelating bidentate in nature. For these compounds, nitrate ions form strong splitting bands at 1499–1470 cm^{-1} and 1274–1245 cm^{-1} with large separation (204–225 cm^{-1}). The $\nu_1 + \nu_4$ region of the spectrum contains two weak broad bands at about 1720–1770 cm^{-1} supportive for this assignment. The band of the ionic nitrate is not observed.

The Ni(2-qmpe)(H$_2$O)$_2$NO$_3$]NO$_3$ (**2**) and Zn(2-qmpe)(H$_2$O)$_2$NO$_3$]NO$_3$·H$_2$O (**4**) complexes contain both ionic and bidentate coordinated NO$_3$ groups [26,27]. Very strong band at 1384 cm^{-1} assigned as ν_3 of ionic nitrate and the splitting of the band ν_3 at 1510–1496 cm^{-1} as the ν_1 and ν_4 modes of coordinated NO$_3$ is observed. The position of ν_1 and ν_4 and their separation of 204–240 cm^{-1} clearly indicate bidentate coordination of the nitrate groups. The presence of both ionic and coordinated nitrate is also demonstrated by the occurrence of three distinct absorption bands at 1700–1800 cm^{-1} (ν_1 + ν_4) due to combination of vibrational modes of ionic and coordinated nitrate. The ν_2 modes about 810 and 830 cm^{-1} were also observed. The band observed at far IR region at 300–327 cm^{-1} in the spectrum of the nitrate compounds has been assigned to a ν(M-O) mode for coordinated nitrate ligand [28].

The analysis of nitrate compounds by IR spectroscopy was carried out both as dispersion in KBr and, where appropriate, as mulls in fluorinated mineral oil (Kel-F). It was because of the compounds Ni and Zn (recorded in KBr) complexes displaying a strong band at 1390 cm^{-1} characteristic of the asymmetric stretch of free nitrate anion in addition to coordinated nitrate bands. Grinding of the complexes with KBr can give rise to displacement of a part of the nitrate ions by bromide under moderate pressure and uncertain assignment to be made of a free nitrate ion. This phenomenon has been observed in nitrate complexes [29, 30]. In this study, substantial differences between samples prepared in KBr and Kel-F have not been observed.

The presence of water molecules in the compounds is deduced from the elemental analysis and IR spectrum [26]. The IR spectrum of Zn(2-qmpe)(H$_2$O)$_2$NO$_3$]NO$_3$·H$_2$O (**4**) have a sharp δ(OH$_2$) bending mode at 1656 cm^{-1} and broad, jagged ν(OH) absorption bands with maxima at 3240 and 3430 cm^{-1}, confirming the presence of lattice water molecules linked by the hydrogen bond and coordinated water, respectively. The Ni(2-qmpe)(H$_2$O)$_2$NO$_3$]NO$_3$ (**2**) compound shows in the O–H stretching and bending region only the presence of coordinated water molecules (3410 and 1655 cm^{-1}, respectively). IR spectra of the Cu(II) (**1**, **5**), Co(II) (**7**, **8**), Zn (**9**),) and Pd(II) (**10**) compounds show the absence of all vibrations which might be assigned to water molecules.

The far IR region of Pd(2-qmpe)$_2$Cl$_2$ (**10**) shows one band at 352 cm^{-1} attributed to the Pd–Cl stretching vibration, suggesting that the compound is the *trans* square-planar in the D_{2h} symmetry according to X-ray crystal structure determination [25]. For chloride copper (**1**) and nickel (**2**) compounds the bands at 310 and 210 cm^{-1} are observed, respectively. The ν(M-Cl) symmetric and asymmetric frequencies in other chloride compounds are consistent with a pseudotetrahedral environment [26, 31–34]. Namely, for Zn(2-qmpe)Cl$_2$ (**9**) strong bands at 306 and 337 cm^{-1} are observed. It is interesting that the interaction of the CoCl$_2$ with 2-qmpe leads to the formation of compounds displaying different stoichiometries, i. e. Co(2-qmpe)Cl$_2$ (dark blue) (**7**) and Co(2-qmpe)$_2$Cl$_2$ (dark green-blue) (**8**). In the far IR region, very strong bands at 303 and 334 cm^{-1} as well as at 308 and 339 cm^{-1}, respectively, are observed, characteristic of tetrahedral environment of the cobalt(II) ion.

Table 2. Electronic and EPR spectral data of the metal complexes with 2-qmpe

Compound	Wavenumber [cm^{-1}]	D_q [cm^{-1}]	B [cm^{-1}]	Splitting factor g	
				298 K	77 K
Cu(2-qmpe)(NO$_3$)$_2$ (**1**)	14 280			$g_\parallel \cong 2.3$ $g_\perp = 2.10_2$	$g_\parallel = 2.31_1$ $g_\perp = 2.07_7$
[Ni(2-qmpe)(H$_2$O)$_2$NO$_3$]NO$_3$ (**2**)	24 690, 21 050 sh, 14 710, 13 070 sh, 8560	860	910	no line	
Co(2-qmpe)(NO$_3$)$_2$ (**3**)	21050, 19050, 8170	890	865		
Cu(2-qmpe)Cl$_2$ (**5**)	12 100	780	800	$g_\parallel = 2.37_7$ $g_\perp = 2.10_4$	$g_\parallel = 2.32_3$ $g_\perp = 2.09_4$
Ni(2-qmpe)$_2$Cl$_2$ (**6**)	23 250, 28 840, 13 160, 7810	400	750	no line	
Co(2-qmpe)Cl$_2$ (**7**)	16 345, 6930	368	778	no line	$g = 2.11$
Co(2-qmpe)$_2$Cl$_2$ (**8**)	16 310, 6400			no line	$g = 2.16$

Basic features of the absorption spectra of the studied compounds are presented in Table 2. The electronic spectrum of Cu(2-qmpe)(NO$_3$)$_2$ (**1**) shows one broad asymmetric band with the maximum at 14280 cm^{-1} characteristic of the transition in O_h symmetry. The position as well as the shape of this band suggests CuNO$_5$ chromophore in a tetragonally elongated octahedral geometry [35]. The electronic spectrum of the nitrate (**2**) and chloride nickel(II) (**6**) complexes exhibit spin-allowed bands and also spin-forbidden absorption observed as a shoulder typical of high-spin octahedral structure [36]. The d-d spectrum of Co(2-qmpe)(NO$_3$)$_2$ (**3**) also show bands typical of high-spin an octahedral environment [37, 38].

The spectrochemical parameters (D_q and B) for octahedral compounds calculated with well-known methods [36, 37] are D_q = 860, 890 and 780 cm^{-1} for (**2**), (**3**) and (**6**) compounds, respectively. The values of D_q for (**2**) and (**3**) are in good agreement with those expected for isomorphous nickel and cobalt compounds [36, 37]. The D_q value of (**6**) ($N_2O_2Cl_2$) is lower than this obtained for (**2**) (N_2O_4), reflecting weak ligand field produced by the chloride ligand. A rather high value of *B* calculated for **2** and **3** (910, 865 cm^{-1}, respectively) may suggests a distorted octahedral geometry [36, 37].

The electronic spectrum of Cu(2-qmpe)$_2$Cl$_2$ (**5**) shows one broad asymmetric band with the maximum centred at 12 100 cm^{-1} and shoulder at about 9100 cm^{-1}. Bands lower in energy than ca. 25 000 cm^{-1} in the spectra of the chloride complexes may be assigned to chlorine-to-copper(II) charge transfer bands and confirm their coordination to the Cu(II) centre [38]. Therefore, yellow colour of **5** for which the tetrahedral coordination is proposed is due to the charge-transfer band observed at 24 700 cm^{-1} [39].

The electronic spectra of **7** and **8** are typical of pseudotetrahedral ligand arrangements around Co(II) [35, 38, 39]. In the spectra, two sets of the bands can be distinguished; one in the visible region and the other in the near infrared one. The presence of three bands in the near-infrared region is typical of ligands which differ significantly in strength. The centres of the multiple visible bands appears at 16 340 and 16 310 cm^{-1} for **7** and **8**, respectively. Splitting of the band is probably due to the interaction with a doublet through spin-orbit coupling [40]. The near-IR multiple bands are perceptibly broadened and show a long tail towards lower wavenumbers. The complexity is caused by the components of $^4T_1(F)$ level which becomes allowed transition in the C_{2v} symmetry [41]. A large splitting of ν_2 bands (4000 cm^{-1}) can be attributed to a large distortion from the ideal tetrahedral symmetry [40–42]. The calculated parameters D_q and *B* using the secular equation for tetrahedral cobalt(II) transition energies [43, 44] are based on the centres of gravity of the respective multiplets. These values (400, 750 cm^{-1} and 370, 780 cm^{-1}, respectively for **7** and **8** are consistent with those reported for tetrahedral Co(II) complexes [39, 41] and are in agreement with mixed nitrogen-oxygen donation [45]. The higher value of D_q and lower value of *B* calculated for Co(2-qmpe)Cl$_2$ (**7**) are consistent with contribution of the nitrogen atom of the quinoline ring to the ligand field in this complex.

3.2. Magnetic properties

The X-band EPR spectrum (Table 2) of a polycrystalline sample of **1** shows at room temperature a resonance line with broad perpendicular and parallel components ($g_{||} \cong 2.30$, $g_\perp = 2.08_2$). At liquid nitrogen temperature, the spectrum indicates the same line with $g_{||} = 2.31_1$, $g_\perp = 2.07_7$). The spectrum is characteristic of elongated tetragonal stereochemistry [46]. The high value of $g_{||}$ suggests planar geometry of CuNO$_3$with relatively strong axial bonding. The spectrum of **5** at room temperature is of axial type with $g_{||} = 2.37_7$, $g_\perp = 2.10_4$ normal for copper in a tetrahedral environment [46, 47]. The spectrum is independent of temperature. It is interesting to note that we observed lack of a transition in the $\Delta M = 2$ region of the spectra (i.e. 1600 G). This seems to indicate that these complexes are monomeric in their nature, as is confirmed by magnetic measurements. Nickel **2** and **6** compounds do not exhibit X-band spectra, and **3,**

7 and **8** show no lines at room temperature but a single broad line was observed at 77 K for the cobalt(II) compounds ($g = 2.14$, 2.11 and 2.16, respectively).

Table 3. Magnetic data of metal complexes with 2-qmpe ligand

Compound	C [$\mathrm{cm^3 \cdot mol^{-1} \cdot K}$]	Θ [K]	$10^6\chi_M$ [$\mathrm{cm^3 \cdot mol^{-1}}$]	μ_{eff} [B.M.]	
				298 K	77K
(**1**) $\mathrm{Cu(2\text{–}qmpe)(NO_3)_2}$	0.47	–2.2	1560	1.92	1.93
(**2**) $\mathrm{[Ni(2\text{–}qmpe)(H_2O)_2NO_3]NO_3}$	1.35	–1.9	4760	3.31	3.28
(**3**) $\mathrm{Co(2\text{–}qmpe)(NO_3)_2}$	19.9	–6.4	9260	4.60	4.29
(**5**) $\mathrm{Cu(2\text{–}qmpe)_2Cl_2}$	0.42	–1.6	1410	1.83	1.84
(**6**) $\mathrm{Ni(2\text{–}qmpe)_2Cl_2}$	1.10	–3.0	4160	3.12	3.10
(7) $\mathrm{Co(2\text{–}qmpe)Cl_2}$	2.38	–1.4	8010	4.37	4.36
(**8**) $\mathrm{Co(2\text{–}qmpe)_2Cl_2}$	2.84	–0.8	9630	4.76	4.77

Variable-temperature (77–300 K) magnetic susceptibility data were collected for all studied paramagnetic complexes (Table 3). The effective magnetic moments for **1**, **2**, **3** and **6** compounds are within usually observed range of experimental values for high-spin complexes in octahedral environment [48]. The magnetic moments of $\mathrm{Co(2\text{-}qmpe)Cl_2}$ (7) and $\mathrm{Co(2\text{-}qmpe)_2Cl_2}$ (**8**) are in accordance with tetrahedral stereochemistries [48]. The negative values of the Weiss constants (θ) obtained from the equation $\chi_M = C/(T - \theta)$ within the measured temperature range may suggest the possibility of weak magnetic interaction between magnetic centres inside the crystal lattice at lower temperatures. Based on the spectral and magnetic data, a mononuclear structure is proposed for all studied compounds.

4. Summary

The results described in the present paper have shown that the complexes of 2-qmpe ligand with nitrate salts of Cu(II) and Co(II) are six-coordinate formed by one N,O-bonded chelate 2-qmpe ligand and two bidentate nitrate ions ($\mathrm{MNO_5}$ chromophore), while six-coordination of Ni(II) and Zn(II) nitrate complexes are formed via one N,O-bonded 2-qmpe ligand, one bidentate nitrate ion and two water molecules ($\mathrm{MNO_5}$ chromophore). Unexpectedly, 2-qmpe in its compounds with cobalt chloride adopts monodentate and bidentate mode giving rise to tetrahedral arrangement of cobalt ions in both compounds. In $\mathrm{Co(2\text{-}qmpe)_2Cl_2}$, cobalt ions are coordinated by two chloride ions and two phosphoryl oxygen atoms ($\mathrm{CoO_2Cl_2}$ chromophore). However, in $\mathrm{Co(2\text{-}qmpe)Cl_2}$, 2-qmpe acts in bidentate manner through pyridyl nitrogen and phosphoryl oxygen atoms ($\mathrm{CoNOCl_2}$ chromophore). In the Pd(II) compound, 2-qmpe acts as an N-bonded ligand ($\mathrm{PdN_2Cl_2}$ chromophore). This compound has a *trans* square-planar structure as was demonstrated by the crystal structure [8].

The previous report [16] described the unusual O-monodentate properties of the 2-qmpe ligand towards divalent transition metal perchlorate salts. In this case, the metal(II) ions react with the ligand in 1:4 metal to ligand molar ratio. As has been presented in this paper, 2-qmpe reacts with other metal salts in 1:1 or 1:2 metal to ligand molar ratios and indicates different coordination properties. Namely, 2-qmpe is able to coordinate in a didentate chelate manner via the quinoline nitrogen and the phosphoryl oxygen donor atoms (complexes with 1:1 metal to ligand ratio) and it can also act as a monodentate ligand coordinated through the nitrogen or oxygen atom. Thereby, the 2-qmpe ligand engagement into monodentate coordination prefers coordination by O donor atoms (perchlorate metal compounds, chloride cobalt and copper compounds) in contrast to compound with $PdCl_2$. In this case Pd, as a soft metal, coordinates by N-donor atoms. The non-coordinating behaviour of the pyridine nitrogen atom is probably due to poor donor properties in combination with possible steric constraints and/or crystal packing effects.

It is interesting that the interactions of 2-pmpe and 2-qmpe ligands with some Cu(II) salts studied earlier [17] lead to formation of solid complexes, unstable in solution in air. The results of this studies clearly demonstrate that copper(II) ions promote/enhance decomposition of the ligands and catalyze oxidation by atmospheric oxygen according to the scheme: $R–CH_2P(O)–(OEt)_2 \rightarrow R–COOH + OH–P(O)(OEt)_2$. Other divalent transition metal ions do not exhibit this activity under similar experimental conditions [9, 16, 17].

The results obtained earlier indicate that copper(II) coordination compounds with N,O-bonded (chelate or bridging) ligands 2-pmpe and 4-pmpe with nitrate and perchlorate metal salts [8, 16] are stable in solution. However, those with monodentate coordinating 2-pmpe and 2-qmpe ligands after exposition to air undergo decomposition [17]. The study presented in this paper supports our earlier supposition. Namely, $Cu(2\text{-qmpe})(NO_3)_2$ compound in which 2-qmpe acts as N,O-bonded chelate ligand is stable in solution, is probably stabilized by didentate coordination. However, as mentioned earlier [6], the interaction of 2-qmpe with $CuCl_2$ salt produces an unstable compound in which 2-qmpe acts as O-bonded monodentate ligands. In this case, Cu(II) ion promotes and catalyzes oxidative conversion of 2-qmpe to $R–COO^-$ ligand. However, nitrate and chloride complexes with other divalent metal salts with N,O bonded chelate ligand (Cu, Ni, Zn) and O-bonded ligand (Co) and also N-bonded ligand (Pd) are stable in solution

Finally, it is worth to stress that the chemical degradation of phosphonates, due to their role played in the environment as pesticides and herbicides, is of fundamental importance and will be the subject of further studies.

Acknowledgments

The work was supported by the Polish Ministry of Science and Higher Education (Grant No. 1T09A 12430 (J.M.), and Grant No. 502-13-339 and 503-3016-2 of the Medical University of Łódź (J.O.).

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Received 27 December 2006
Revised 23 April 2007