Synthesis, Spectroscopy, and Magnetic Properties of Transition-Metal Complexes with the Diethyl 2-Quinolylmethylphosphonate (2-qmpe) Ligand − Crystal Structures of $[Ni(2\text{-qmpe})_4(H_2O)_2](ClO_4)_2$ and $[Mn(2\text{-qmpe})_4(H_2O)_2](ClO_4)_2$ Showing Unexpected O-Binding of the qmpe Ligands

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The synthesis and characterization of transition-metal coordination compounds containing the ligand diethyl 2-quinolylmethylphosphonate (2-qmpe) is described. Complexes of Co^{II}, Mn^{II}, Ni^{II}, Cd^{II}, and Zn^{II} were found to be mutually isomorphous according to their X-ray powder diffraction patterns and IR spectra. The new coordination compounds were identified and characterized by elemental analysis, magnetic measurements, infrared and ligand-field spectra. The crystal structures of the complexes $[M(2\text{-qmpe})_4(H_2O)_2](ClO_4)_2$ (M = Ni, **1**; Mn, **2**) reveal six-coordinate $[M(2\text{-qmpe})_4(H_2O)_2]$ cations with the qmpe ligand coordinating via the oxygen rather than via the nitrogen atom, as well as lattice perchlorate anions. The metal ion is octahedrally surrounded by the four oxygen atoms of the four organic ligands. The non-participation of the pyridine nitrogen atom is unusual. The two water molecules occupy the fifth and the sixth coordination sites in a *trans* configuration. The coordinated water molecules are strongly hydrogen-bonded to the pyridine nitrogen atom of the 2-qmpe, further stabilizing the solid-state structure. The geometry of the metal ion can be described as distorted octahedral. For the Cu^{II} complex, a hydroxo-bridged dinuclear structure of the type $[Cu(2\text{-qmpe})_2(OH)(H_2O)_2]_2(ClO_4)_2$ is proposed, based on its spectroscopic and magnetic properties. Ligand-field spectra of the Co and Ni compounds were found to be in agreement with the tetragonally distorted octahedral geometry.

Introduction

During the last decade there has been a great increase in interest in ligands containing a phosphoryl group and a heterocyclic ring[1]. Organophosphorus derivatives of pyridine and quinoline with the phosphonic chain *ortho* or *para* with respect to the endocyclic nitrogen atom have been shown to possess significant bactericidal and herbicidal activity. Coordination compounds of phosphonic acids and their esters with transition-metal ions have been the subject of several studies due to the fact that complexes of such compounds exhibit biological activity[1][2][3][4][5][6][7][8][9][10][11][12][13][14]. In recent years, platinum(II) complexes of phosphonate ligands have attracted attention as a result of their significant antitumor activity[8]. Phosphonate ligands bearing a heterocyclic ring have some interesting features with regard to their coordination chemistry; they contain two potential donor atoms, the heterocyclic nitrogen and phosphoryl oxygen atoms, in a suitable orientation for chelation. Over the years, we have studied in detail the complex-forming properties of phosphonate ligands towards transition-metal ions. The coordination behaviour of pyridylmethylphosphonate ligands was examined by single-crystal X-ray structure determinations, which showed that various coordination modes are possible[10][28]. In a previous study, the results of spectroscopic and magnetic studies on transition-metal complexes with diethyl 2- and 4-pyridylmethylphosphonate ligands (2-pmpe, 4-pmpe), as well as the structures of high-spin $[Co(4\text{-pmpe})_4(H_2O)_2](ClO_4)_2(H_2O)_2$, where the ligand bridges the cobalt ions with both ends of the molecule coordinating to a different metal ion forming infinite chains, and of $[Co(2\text{-pmpe})_2Cl_2]$, where the 2-pmpe acts as a bidentate N,O-bonded chelate ligand, were reported[10]. As the biological activity of coordination compounds depends on the presence of metal ions[6], we have studied the biological properties of complexes with pyridylmethylphosphonate ligands. Preliminary investigations have shown that 2-pyridylmethylphosphonic acid labelled with technetium (^{99m}Tc) forms a complex, which when administered to rats shows a high re-

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nal clearance value[15a]. Recently, we investigated the effect of *cis*-$[PtCl_2(4\text{-pmpe})_2]$ and *cis*-$[PtCl_2(NH_3)_2]$ on murine mast cells[11] and on the aggregation of platelet-rich plasma[12]. Both of the complexes tested were found to activate mast cells so as to secrete histamine by a non-cytotoxic, active secretory process[11]. *cis*-Platinum complexes incorporating diethyl 2-, 3-, or 4-pyridylmethylphosphonate ligands showed in vivo cytostatic activity against mice Sa180 sarcoma solid tumours[13] and were found to exhibit alkylating activity in vitro[14]. In order to broaden the scope of this work and to determine the effects of the additional benzene ring, we have now extended our studies to the diethyl 2-quinolylmethylphosphonate ligand (2-qmpe). The 2-qmpe ligand, which has the desired 2-quinolyl group as well as a phosphonate group, can act either as a monodentate N-bonded, as a monodentate O-bonded, or as a bidentate N,O-bonded chelate ligand in forming coordination compounds with transition-metal ions. In the present work, we report on a modification of a previously[15] reported synthesis of diethyl 2-quinolylmethylphosphonate that simplifies the procedure and results in improved yields. We also report on the synthesis, spectroscopic and magnetic properties of coordination compounds of the 2-qmpe ligand with several transition-metal ions and perchlorate ions. These were investigated with regard to their structural and magnetic properties, which provide a chemical basis for the biological activity. The representative compounds $[Ni(2\text{-qmpe})_4(H_2O)_2](ClO_4)_2$ (**1**) and $Mn(2\text{-qmpe})_4(H_2O)_2](ClO_4)_2$ (**2**) were chosen for X-ray crystallographic studies in an attempt to determine which of the potential binding sites of the 2-qmpe ligand, N or O, is attached to the metal centre, as well as to allow comparison with the previously published crystal stucture of $[Co(4\text{-pmpe})_2(H_2O)_2](ClO_4)_2(H_2O)_2$. The structure of **2** is described in detail.

Results and Discussion

General

The condensation of 2-chloromethylquinoline with triethyl phosphite affords diethyl 2-quinolylmethylphosphonate (2-qmpe). The synthesis of 2-qmpe from 2-chloromethylquinoline by the reaction with diethyl sodium phosphite has been reported previously[15]. In the present investigation, we modified a previously reported[15a] synthesis of 2-qmpe, resulting in a simplified procedure and increased yields. The ligand was synthesized by the phosphorylation of 2-chloromethylquinoline with triethyl phosphite and checked for purity by spectroscopic and analytical methods.

The 2-qmpe system is a powerful ligand able to form coordination compounds of the types $[M(2\text{-qmpe})_4(H_2O)_2]_2(ClO_4)_2$, [M = Co^{II}, Ni^{II}, Mn^{II}, Cd^{II}, or Zn^{II}] and $[Cu(2\text{-qmpe})_2(OH)(H_2O)_2]_2(ClO_4)_2$. The structures of the complexes were unambiguously confirmed by a combination of NMR and IR experiments and by elemental analyses. Analytical data are reported in Table 1. A hydroxo-bridged structure is proposed for the Cu^{II} compound, which is supported by chemical and physical evidence. Dinuclear copper compounds having one or two OH groups as bridging ligands are known[16] and are magnetically interesting.

Table 1. Analytical[a] data for the diethyl 2-quinolylmethylphosphonate complexes

No.	Complex	Analysis (%) M	H	C	N	P	M.p. [°C]
1	$[Co(2\text{-qmpe})_4$-	4.21	5.35	47.33	3.66	8.85	122–125
	$(H_2O)_2](ClO_4)_2$	(4.18)	(5.43)	(47.67)	(3.97)	(8.78)	
2	$[Ni(2\text{-qmpe})_4$-	4.32	5.28	47.65	3.86	8.63	124–126
	$(H_2O)_2](ClO_4)_2$	(4.16)	(5.43)	(47.68)	(3.97)	(8.78)	
3	$[Mn(2\text{-qmpe})_4$-	3.85	5.34	47.22	3.77	8.75	122–124
	$(H_2O)_2](ClO_4)_2$	(3.90)	(5.44)	(47.81)	(3.98)	(8.81)	
4	$[Cu(2\text{-qmpe})_2$-	8.35	5.18	43.56	3.87	8.18	131–134
	$(OH)(H_2O)_2]_2(ClO_4)$	(8.21)	(5.34)	(43.42)	(3.62)	(8.00)	
5	$[Cd(2\text{-qmpe})_4$-	7.77	5.20	45.78	3.93	8.65	171–172
	$(H_2O)_2](ClO_4)_2$	(7.68)	(5.23)	(45.93)	(3.83)	(8.46)	
6	$[Zn(2\text{-qmpe})_4$-	4.87	5.56	47.24	3.91	8.56	103–105
	$(H_2O)_2](ClO_4)_2$	(4.61)	(5.40)	(47.45)	(3.95)	(8.74)	

[a] Calculated values are given in parentheses.

Spectroscopic Studies

Ligand-field spectra (Table 2) of the nickel(II) compound exhibit three spin-allowed bands which, in order of decreasing energy, are assigned to the $^3T_{1g}(P) \leftarrow {}^3A_{2g}$ (υ_3), $^3T_{1g}(F) \leftarrow {}^3A_{2g}$ (υ_2), and $^3T_{2g} \leftarrow {}^3A_{2g}$ (υ_1) transitions[17]. In addition, a shoulder at ca. 21050 cm^{-1} in-forbidden [$^1T_{2g} \leftarrow {}^3A_{2g}$ (υ_5)] and a weak absorption at 15750 cm^{-1} [$^1E_g \leftarrow {}^3A_{2g}$ (υ_4)] are observed. The origin of the υ_4 band has been discussed elsewhere[17][18]. The υ_1 band shows weak signs of a splitting, which can be attributed to the lower, tetragonal symmetry of the nickel(II) compound. A complete assignment of the components in D_{4h} symmetry was not considered as meaningful, in view of the broad bands. The calculated value for D_q is in the lower range for Ni^{II}, reflecting the weak ligand field for phosphoryl ligands. Spectroscopic studies dealing with spectral and magnetic characterization of the nickel compounds have recently been reported[19].

The electronic spectra of the cobalt(II) compound exhibit three spin-allowed bands, corresponding to the $^4T_{2g} \leftarrow {}^4T_{1g}(F)$ (υ_1), $^4A_{2g} \leftarrow {}^4T_{1g}(F)$ (υ_2), and $^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$ transitions. The υ_2 transition usually appears as a weak peak, so that accurate determination of the band maximum is not possible. A shoulder at ca. 21000 cm^{-1} on the high-energy side of the visible band is assigned to spin-orbit components and to a spin-forbidden transition[20]. The asymmetric near-IR band υ_1 gives evidence for octahedral stereochemistry, albeit tetragonally distorted[17]. The crystal-field parameters B and D_q were calculated using well-known methods[20]. The relatively high values of the ligand-field Racah parameter B might reflect the deviation from octahedral geometry[17].

The copper(II) complex exhibits one broad asymmetric d-d band at 13200 cm^{-1}, associated with the $^2T_{1g} \leftarrow {}^2E$ transition in O_h symmetry. The position and shape of this band indicate tetragonally elongated octahedral geometry[21][22].

The extremely low values of the intensities of the bands for the octahedral manganese(II) complex are not unusual[17]. The spectrum shows bands as shoulders on a high-energy ligand or CT band at ca. 25000 cm^{-1} and ca.

19000 cm^{-1}, which can be assigned to $^4A_{1g}$, $^4E_g(G) \leftarrow {}^6A_{1g}$ and $^4T_{1g}(G) \leftarrow {}^6A_{1g}$ transitions, respectively. The other characteristic bands for 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.

In general, the IR spectra of all the complexes appear complicated and a complete assignment of each spectrum is difficult. Only some observations concerning the major bands will therefore be discussed. The IR spectra of the complexes of Co^{II}, Ni^{II}, Mn^{II}, Cd^{II}, and Zn^{II} are very similar with respect to band positions, shapes, and relative intensities, indicating a similar conformation for the five compounds. X-ray powder patterns also showed these five complexes to be mutually isomorphous. The IR spectrum of the Cu^{II} compound, however, indicates quite different structural features.

Evidence for the presence of ClO_4^- was obtained from the infrared spectra. All of the perchlorate compounds show a strong band near 1100 cm^{-1} (asymmetric stretch), a sharp band at 625 cm^{-1} (asymmetric bend) and a very weak absorption at 930−935 cm^{-1} (symmetric stretch), indicative of uncoordinated perchlorate anions[23][24].

The absorption bands attributed to the C=C and C=N of the quinoline ring, observed in the region 1600−1500 cm^{-1} in the free ligand, remain unchanged upon complex formation, confirming non-involvement of the quinolyl nitrogen atom in the metal coordination. In the far-IR region, no metal−nitrogen stretching vibrations are observed.

The absorption band at 1255 cm^{-1}, which corresponds to the P=O stretching of the ligand, is shifted by ca. 15−20 cm^{-1} towards lower frequencies in the spectra of all the complexes, in agreement with coordination of the phosphoryl group to the metal(II) ion[25].

In all the complexes, coordinating water is present. The δ(H−O−H) bending vibrations of coordinated water are observed at 1600−1650 cm^{-1}, whereas the O−H stretching bands are observed around 3400−3600 cm^{-1}. In the spectrum of the Cu^{II} compound, bands at 884 cm^{-1} and 530 cm^{-1} are assigned to H_2O rocking and wagging modes, respectively. On the other hand, the band observed at 440 cm^{-1} is attributable to Cu−O (for coordinated water) stretching vibrations[23]. A very sharp infrared peak at 3540 cm^{-1} can be assigned as the υ(OH) stretching frequency of the hydroxo bridge[26]. Furthermore, the investigated complex exhibits the bridging (Cu−OH) bending mode at 950 cm^{-1}. Support for the assignment of the bridge between two copper centres comes from the absorption at about 520 cm^{-1}, which appears as a doublet (asymmetric and symmetric modes) due to υ(Cu−O) copper−oxygen stretching OH vibrations[27].

^{1}H-NMR spectroscopy is a useful tool for the investigation of complexes of methylphosphonate ligands with N-heterocyclic rings, since coordination of the metal ion via N gives rise to a characteristic downfield shift of the proton signals of the CH_2−P methylene group[28] and this seems to be a general trend in such complexes[2]. We observed[28] a remarkable downfield shift for *trans*-dichlorobis(diethyl 2-pyridylmethylphosphonato-*N*)palladium(II), [Pd(2-pmpe)$_2$Cl$_2$]. Most notable is the downfield shift of 1.17 ppm for the CH_2 signal, which may be explained by the decrease in electron density in the pyridine ring caused by the coordination to the metal ion. In fact, a crystal-structure determination[28] of *trans*-[Pd(3-pmpe)$_2$Cl$_2$] confirmed that the metal ion is bound in a monodentate fashion to the pyridine-N. Comparison of the chemical shifts of the cadmium(II) (**5**) and zinc(II) (**6**) coordination compounds with those of the free 2-qmpe ligand enables us to make an assignment of the ^{1}H-NMR signals. The ^{1}H-NMR spectra of complexes **5** and **6** show the signals hardly shifted in comparison with those of the free ligand. The signal that appears as a doublet due to ^{31}P-^{1}H coupling is assigned to the CH_2−P protons and is not shifted upon coordination to the transition-metal centre. This clearly implies a lack of electron transfer from the quinoline to the metal centre and indicates that the pyridine nitrogen atom does not participate in coordination.

The effective magnetic moments (Table 2) of the cobalt(II), nickel(II), and manganese(II) complexes are within the usually observed ranges of experimental values for high-spin complexes in octahedral configurations[29]. Cadmium(II) and zinc(II) complexes are diamagnetic. Variable-temperature (4.2−294 K) magnetic susceptibility measurements (Table 2, Figure 1) of the Cu^{II} complex clearly indicate a magnetic interaction between the paramagnetic centres, suggesting a hydroxo-bridged $[Cu(2\text{-qmpe})_2(OH)(H_2O)_2]_2(ClO_4)_2$ dinuclear structure. The susceptibility curve for this compound increases with decreasing temperature until a maximum is reached at 73 K. Below 73 K, the susceptibility χ_M (and μ_{eff}) decreases markedly with decreasing temperature. The μ_{eff}(Cu) at 294 K is 1.91 B.M., which is in the range expected for an octahedral Cu^{II} ion. In the molecular antiferromagnetics under study, the magnetic interactions are limited to two magnetic centres, the singlet-triplet separation defined as $2J$ being a measure of this effect. This parameter was determined by fitting the results to the modified Bleaney-Bowers expression[30]

$$\chi_{Cu}^{corr} = \frac{Ng_{av}^2\beta^2}{3kT}[1 + 1/3(e^{-2J/kT})]^{-1}(1-x) + (\frac{Ng_{imp}^2\beta^2}{4kT})$$

where $\chi_{Cu}{}^{corr}$ is the molar magnetic susceptibility calculated per copper(II) ion, J is the exchange parameter in the Heisenberg-Dirac-van Vleck Hamiltonian ($\mathrm{H} = -2JS_1S_2$), p is the percentage of monomeric form of the complex, and other symbols have their usual meaning. In the least-squares fitting procedure, two parameters were calculated, the singlet-triplet $2J$ energy gap and g; these values amounted to −80 cm^{-1} and 2.34, respectively. The agreement factor R was found to be 3.97×10^{-3}, where $R = \Sigma_i[(\chi_i{}^{exptl} - \chi_i{}^{calcd})^2/(\chi_i{}^{exptl})^2]$

The EPR X-band powder spectrum of the Cu^{II} compound does not exhibit absorption, suggesting a strong

Table 2a. Electronic spectral data for $[M(2\text{-qmpe})_4(H_2O)_2](ClO_4)_2$ and $[Cu(2\text{-qmpe})_2(OH)(H_2O)_2]_2(ClO_4)_2$

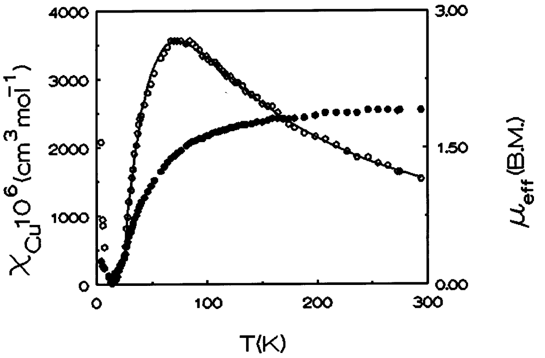
Compound	Band position [cm^{-1}]	[cm^{-1}]	[cm^{-1}]	Dq[a] [cm]	B[a] [cm]
$[Co(2\text{-qmpe})_4(H_2O)_2]$-$(ClO_4)_2$	20760 (sh)	19050 υ_3	7270 υ_1	790	855
$[Ni(2\text{-qmpe})_4(H_2O)_2]$-$(ClO_4)_2$	24690 υ_3	12990 υ_2	7810 υ_1	780	950
$[Mn(2\text{-qmpe})_4(H_2O)_2]$-$(ClO_4)_2$	25000 (sh)	19000 (sh)			
$[Cu(2\text{-qmpe})_2(OH)$-$(H_2O)_2]_2(ClO_4)_2$	13200				

Table 2b. Magnetic data for $[M(2\text{-qmpe})_4(H_2O)_2](ClO_4)_2$ and $[Cu(2\text{-qmpe})_2(OH)(H_2O)_2]_2(ClO_4)_2$

	T [K]	Magnetic susceptibility $10^6 \times c_M$ [cm^3/mol]	μ_{eff} [B.M.]	Curie constant C [cm^3/mol]	Weiss constant [K]	R[b]
$[Co(2\text{-qmpe})_4$-$(H_2O)_2](ClO_4)_2$	77 294	28300 8870	4.29 4.60	2.80	−19.9	$7.37 \cdot 10^{-7}$
$[Ni(2\text{-qmpe})_4$-$(H_2O)_2](ClO_4)_2$	77 294	12900 3610	2.95 2.93	1.05	3.0	$2.03 \cdot 10^{-7}$
$[Mn(2\text{-qmpe})_4$-$(H_2O)_2](ClO_4)_2$	77 294	54000 14500	5.94 5.92	4.28	3.3	$2.43 \cdot 10^{-7}$
$[Cu(2\text{-qmpe})_2$-$(OH)(H_2O)_2]_2$-$(ClO_4)_2$	4.2[d] 77 294	2080 3520 1540	0.26 1.52 1.91		−65.4[c]	$4.89 \cdot 10^{-8}$

[a] Calculated from refs.[18][20]. – [b] $R = \Sigma_i[(\chi_i^{exptl} - \chi_i^{calcd})^2 / (\chi_i^{exptl})^2]$. – [c] In the range 100 K to room temperature. – [d] All experimental points are presented in Figure 1.

Figure 1. Relation of the magnetic susceptibility (χ_{Cu}): circles, experimental susceptibility; dashed line, calculated and experimental magnetic moment (μ_{eff}) vs. *T* for $[Cu(2\text{-qmpe})_2(OH)(H_2O)_2]_2(ClO_4)_2$



magnetic interaction, e.g. as in a dinuclear unit. Such interactions can be transmitted by hydroxy ligands, resulting in an EPR-silent spectrum[31].

The nickel compound does not exhibit an X-band EPR spectrum. The cobalt compound shows no lines at room temperature, but one line is seen at 77 K at $g = 5.80$. The EPR spectrum of the Mn^{II} complex consists of a single, broad, asymmetric line. A hyperfine structure (6 lines) typical for a $^{55}Mn^{II}$ ion is not resolved, and only some fine-structure due to zero-field splitting is visible, which is not uncommon for Mn^{II}[32].

Crystal Structure Determination

Relevant bond-length and bond-angle information for $[Ni(2\text{-qmpe})_4(H_2O)_2](ClO_4)_2$ (**1**) is given in Table 3. The Ni atom has crystallographically imposed inversion symmetry and is in a distorted octahedral environment, of which the equatorial coordination sphere is formed by the four O-donor atoms of the phosphoryl groups of the 2-qmpe ligands. The axial ligands are two water molecules. The molecular structure is stabilized by hydrogen bonds donated by these water molecules to the quinoline nitrogen atoms (see Table 4). The isomorphous Mn compound **2** displays the same molecular structure and crystal packing. The molecular structure of $[Mn(2\text{-qmpe})_4(H_2O)_2](ClO_4)_2$ is shown in Figure 2. The water molecules bound to the manganese ion are also hydrogen-bonded to the nitrogen atom at a very short distance O−H···N = 2.799 Å. The structure as a whole is stabilized by intramolecular hydrogen-bond interactions.

Conclusions

A number of new coordination compounds with the diethyl 2-quinolylmethylphosphonate ligand have been synthesized. To the best to our knowledge, the results described herein show for the first time that, unexpectedly, the ligand 2-qmpe coordinates to M^{II} through the oxygen atom of the phosphonate group, and not through the pyridine nitrogen atom. This may be attributable to steric factors. Intramolecular O−H···N hydrogen bonds from H_2O toward N seem to stabilize the complexes. The complexes of Co^{II}, Ni^{II}, Mn^{II}, Cd^{II}, and Zn^{II} are six-coordinate, having four 2-qmpe ligands and two *trans* water molecules in a tetragonally elongated octahedral stereochemistry (MO_6 chromophore), as revealed by the crystal-structure determinations. The non-participation of the pyridine group is unusual. A contribution of the pyridine nitrogen atoms was observed in related ligands in an earlier study[10][28], when the reactivity of pyridylmethylphosphonate ligands towards transition-metal ions was studied. For the Cu^{II} compound, a hydroxo-bridged dinuclear structure is proposed, i.e. $[Cu(2\text{-qmpe})_2(OH)(H_2O)_2]_2(ClO_4)_2$; this is supported by chemical analysis and the antiferromagnetic coupling evident from the magnetic susceptibility data.

In summary, we have demonstrated that the P=O donor atom in the 2-qmpe ligand has a very high affinity towards divalent transition-metal ions. These observations may have important consequences, as subsequent studies will deal with platinum pyridyl- and quinolylmethylphosphonate complexes, which can be regarded as antitumour agents.

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Table 3. Selected bond lengths [Å] and angles [°] for **1** and **2** with e.s.d.'s in parentheses[a]

Compound	**1**	**2**
Bond Lengths		
M (1)−O(10)	2.019(5)	2.132(3)
M (1)−O(30)	2.046(5)	2.169(4)
M (1)−O(50)	2.079(6)	2.204(4)
P(10)−O(10)	1.500(5)	1.467(4)
P(10)−O(11)	1.550(6)	1.557(4)
P(10)−O(12)	1.555(7)	1.567(4)
P(10)−C(20)	1.781(8)	1.771(5)
P(30)−O(30)	1.470(6)	1.479(4)
P(30)−O(31)	1.580(6)	1.558(5)
P(30)−O(32)	1.519(8)	1.564(5)
P(30)−C(40)	1.803(9)	1.775(6)
Bond Angles		
O(10)−M(1)−O(30)	90.3 (2)	89.37(14)
O(10)−M(1)−O(50)	91.2(2)	92.32(13)
O(10)−M(1)−O(10)a	180.00	180.00
O(10)−M(1)−O(30)a	89.7(2)	90.63(14)
O(10)−M(1)−O(50)a	88.8(2)	87.68(13)
O(30)−M(1)−O(50)	89.0(2)	88.04(14)
O(10)a−M(1)−O(30)	89.7(2)	90.63(14)
O(30)−M(1)−O(30)a	180.00	180.00
O(30)−M(1)−O(50)a	91.0(2)	91.92(14)
O(10)a−M(1)−O(50)	88.8	87.68(13)
O(30)a−M(1)−O(50)	91.0(2)	91.92(14)
O(50)−M(1)−O(50)a	180.00	180.00
O(10)a−M(1)−O(30)a	90.3(2)	89.37(14)
O(10)a−M(1)−O(50)a	91.2(2)	92.32(13)
O(30)a−M(1)−O(50)a	89.0(2)	88.08(14)

[a] Suffix denotes symmetry operation −*x*, −*y*, 1 − *z*.

Figure 2. Perspective drawing of **2**; non-hydrogen-bonding hydrogen atoms and the counter ions are omitted for clarity; only the major disorder component is shown

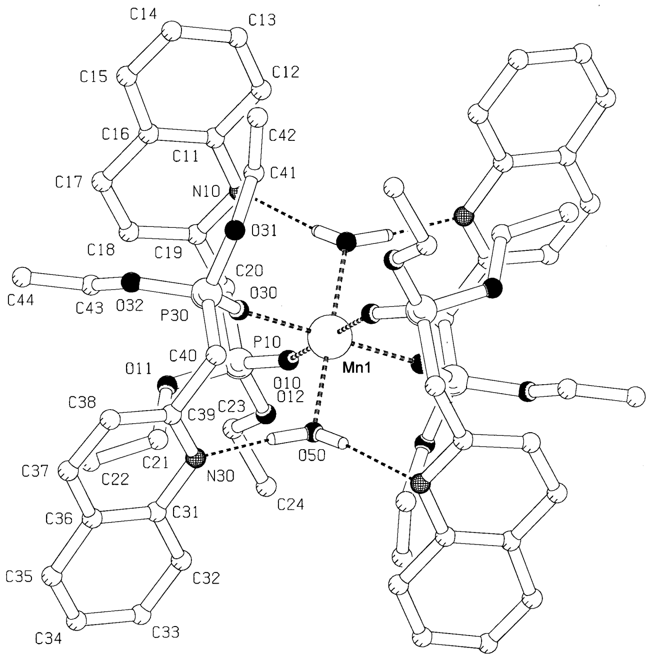

Table 4. Relevant interatomic distances [Å] and angles [°] for the hydrogen-bonding interactions in [Ni(2-qmpe)$_4$(H$_2$O)$_2$](ClO$_4$)$_2$ (**1**) and in [Mn(2-qmpe)$_4$(H$_2$O)$_2$](ClO$_4$)$_2$ (**2**) with e.s.d.'s. in parentheses

D−H···A	D−H	H···A	D···A	D−H···A
Compound **1**				
$O_{50}-H_{501}\cdots N_{10}$[a]	0.79(8)	2.14(9)	2.921(9)	174(9)
$O_{50}-H_{502}\cdots N_{30}$	0.87(9)	1.97(9)	2.811(10)	161(8)
Compound **2**				
$O_{50}-H_{502}\cdots N_{10}$[b]	0.72(7)	2.13(6)	2.919(6)	167(7)
$O_{50}-H_{501}\cdots N_{30}$	0.80(6)	2.09(7)	2.799(6)	168(7)

[a] Denotes symmetry operation −*x*, −*y*, 1 − *z*. − [b] Denotes symmetry operation −*x*, −*y*, 1 − *z*.

Table 5. Crystallographic data for compounds **1** and **2**

Compound	**1**	**2**
Crystal data		
Formula	$C_{55}H_{76}N_4NiO_{14}P_4 \cdot$ 2 ClO_4	$C_{55}H_{76}N_4MnO_{14}P_4 \cdot$ 2 ClO_4
Molecular weight	1410.73	1406.97
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a [Å]	11.7164(14)	11.7027(9)
b [Å]	12.623(3)	12.7259(11)
c [Å]	12.784(4)	12.8297(10)
α [°]	66.79(2)	66.956(7)
β [°]	72.91(2)	73.273(7)
γ [°]	85.74(2)	85.969(7)
V [Å^3]	1659.1(8)	1681.9(3)
$D_{calcd.}$ [g cm^{-3}]	1.412	1.389
Z	1	1
F (000)	738	735
μ [$^{-1}$] (Mo-$K_α$)	5.4	4.3
Crystal size [mm]	0.4 × 0.4 × 0.2	0.4 × 0.4 × 0.2
Data collection		
T [K]	298	293
$θ_{min}$, $θ_{max}$ [°]	1.76, 27.50	1.74, 27.50
Wavelength (Mo-$K_α$) [Å]	0.71073 (graphite monochr.)	0.71073 (Zr-filtered)
Scan type	ω/2θ	ω/2θ
Δω [°]	1.61 + 0.35 tan θ	0.90 + 0.35 tan θ
Horiz., vert. aperture [mm]	4.15, 4.00	2.44, 5.00
X-ray exposure time [h]	43	113
Linear decay (%)	3	2
Reference reflections	$2\ 0\ 3,\ 2\ 2\ 2,\ \bar{5}\ 1\ \bar{2}$	$2\ \bar{2}\ 1,\ 0\ \bar{2}\ \bar{3},\ 4\ 0\ 2$
Data set	−15/15, −10/16, −15/16	−15/15, −16/16, −16/16
Total data	10240	8770
Total unique data	7594 [R_{int} = 0.067]	7720 [R_{int} = 0.050]
DIFABS corr. range	0.656, 1.468	0.609, 1.157
Refinement		
No. of refined parameters	409	440
Final R[a]	0.120 [2312 $F_o > 4σ(F_o)$]	0.073 [2984 $F_o > 4σ(F_o)$]
Final $wR2$[b]	0.209	0.185
Goodness of Fit	1.15	0.88
Weighting scheme[c]	$[σ^2(F^2) + (0.0400P)^2]^{-1}$	$[σ^2(F^2) + (0.0773P)^2]^{-1}$
$(Δ/σ)_{av}$, $(Δ/σ)_{max}$	0.026, −0.363	0.000, 0.004
Min. and max. residual density [e Å^{-3}]	−0.94, 0.58	−0.51, 0.42

[a] $R = Σ||F_o| - |F_c||/Σ|F_o|$. − [b] $wR2 = \{Σ[w(F_o^2 - F_c^2)^2]/Σ[w(F_o^2)^2]\}^{1/2}$. − [c] $P = [\max(F_o^2,0) + 2F_c^2]/3$.

Experimental Section

General: All commercial reagents were ACS reagent grade. − IR spectra (50−4000 cm^{-1}) were recorded with a Perkin-Elmer 180 spectrophotometer using KBr pellets. − Solid-state electronic spectra (28000−50000 cm^{-1}) were measured with a Beckman UV 5240 spectrophotometer fitted with a reflectance attachment, using MgO as a reference. − EPR spectra were recorded with a Radiopan SE/X 2543 spectrometer at X-band frequencies at room temperature and at 77 K (liquid nitrogen). Solid diphenylpicrylhydrazyl (dpph) was used as the reference and magnetic fields were calibrated with proton and lithium NMR probes. − NMR: ^{1}H-NMR spectra were recorded with a Bruker MSL-300 spectrometer employing a frequency of 300 MHz, TMS as internal standard. − ^{31}P-NMR spectra were recorded with a Bruker MSL-300 instrument at 121.496 MHz with 85% phosphoric acid as external standard. − Magnetic susceptibility measurements: See below.

2-Chloromethylquinoline: 1.0 g (5.0 mmol) of 2-chloromethylquinoline hydrochloride was dissolved in 75 ml of water and the solution was brought to pH ≈ 8 by the addition of Na_2CO_3. The yellow product was filtered and dried in vacuo. Yield: 0.7 g (84%), m.p. 43−45°C (petroleum ether). − IR (KBr): $\tilde{\nu}$ = 700−900 cm^{-1} (CH), 1400−1700 (C=N), 3000−3800 (CH). − ^{1}H NMR ($CDCl_3$): δ = 4.82 (s, 2 H, CH_2Cl), 7.52−8.20 (m, 6 H, aromatic H).

Diethyl 2-Quinolylmethylphosphonate: A mixture of 2-chloromethylquinoline (1.77 g, $1\cdot10^{-2}$ mol) and triethyl phosphite (25 ml, $1.4\cdot10^{-1}$ mol) was stirred under reflux for 24 h. After this period, TLC analysis indicated complete phosphorylation. The excess triethyl phosphite was then evaporated yielding a yellow oil. Colorless diethyl 2-quinolylmethylphosphonate was obtained by distillation in vacuo. Yield: 2.2 g (78%). − ^{1}H NMR ($CDCl_3$): δ = 1.23 (t, $^3J_{HH}$ = 7 Hz, 6 H, 2 $POCH_2CH_3$), 3.63 (d, $^2J_{HP}$ = 22 Hz, 2 H, CH_2P), 4.13 (dq, $^2J_{POCH}$ = 7 Hz, $^3J_{HH}$ = 7 Hz, 4 H, 2 $POCH_2CH_3$), 7.36−8.23 (m, 6 H, aromatic H). − $^{31}P\{^1H\}$ NMR ($CHCl_3$): δ = 24.53.

Preparation of the Complexes: The coordination compounds were synthesized by addition of the appropriate hydrated metal perchlorate (1 mmol), dissolved in 10 ml of water, to a solution of 2-qmpe (4 mmol) in 20 ml of ethanol. The resulting solutions were filtered to remove any insoluble material. Following evaporation of the solvent at room temperature, the compounds crystallized after a few days. Crystals of **1** and **2** suitable for single-crystal X-ray diffraction studies were grown from saturated ethanolic solutions of the complexes at room temperature. The Mn, Ni, Co, Cd, and Zn compounds are isomorphous, as shown by X-ray powder diffraction experiments.

Magnetic Measurements: Magnetic susceptibility measurements (80−300 K) were carried out using the Gouy method on a sensitive Cahn RM-2 electronic balance at a magnetic field strength of 9.9 kOe. Over the temperature range 4.2−300 K, measurements were made by the Faraday method, using a Cahn RG-HV electrobalance and a magnetic field of 5.25 kOe. The standard employed for calibration was $HgCo(NCS)_4$, for which the magnetic susceptibility was taken as $16.44\cdot10^{-6}$ cm^3 g^{-1}. Corrections for diamagnetism of the constituent atoms were made by using Pascal constants. The effective magnetic moments were calculated from $\mu_{eff} = 2.83 (\chi^M T)^{1/2}$, after corrections for temperature-independent paramagnetism of $60\cdot10^{-6}$ (Cu^{II}) and $220\cdot10^{-6}$ cm^3 mol^{-1} (Ni^{II}).

X-ray Crystallography: Crystals of **1** and **2** (both colorless) suitable for X-ray diffraction were glued to the tip of a Lindemann glass capillary and transferred to an Enraf-Nonius CAD4 diffractometer on a rotating anode (for **1**) or in a sealed tube (for **2**). Crystals of **1** were of limited quality, as indicated by highly structured broad reflection profiles. Accurate unit-cell parameters and an orientation matrix were determined by least-squares refinement of the setting angles of a set of well-centered reflections (SET4)[33] in the range 9.84° < θ < 13.75° and 4.12° < θ < 12.83° for **1** and **2**, respectively. Reduced-cell calculations did not indicate higher lattice symmetry[34]. Crystal data and details of the data collection and refinement are given in Table 5. Data were corrected for Lp effects and for observed linear decay of the reference reflections. An empirical absorption/extinction correction (DIFABS)[35] was applied for both compounds. The structures were solved by automated Patterson methods and subsequent difference Fourier techniques (DIRDIF-92[37] and SHELX-86[36] for **1** and **2**, respectively). Both compounds were refined on F^2 by full-matrix least-squares techniques (SHELXL-93)[38]; no observance criterion was applied during refinement. 14 deviating reflections displaying an unequal background were omitted during the final refinement cycles of compound **1**. Hydrogen atoms were included in the refinement in calculated positions riding on their carrier atoms, except for water hydrogen atoms of both compounds, which were located on a difference Fourier map and subsequently included in the refinement. Two ethyl groups of compound **2** proved to be disordered; a disorder model consisting of two alternative sites and occupation factors was included in the refinement. Weak bond constraints had to be introduced on this moiety in order to obtain a reasonable geometry. Non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were refined with a fixed isotropic thermal parameter related to the value of the equivalent isotropic thermal parameter of their carrier atoms by a factor amounting to 1.5 for the water and methyl hydrogen atoms, and 1.2 for the other hydrogen atoms, respectively. The relatively high *R* value for **1** is attributed to the rather poor quality of the available crystals. Neutral atom scattering factors and anomalous dispersion corrections were taken from the International Tables for Crystallography[39]. Geometrical calculations and illustrations were performed with the PLATON package[40]; all calculations were performed on a DEC station 5000 cluster. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100672. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44 (0)1223/336033; E-mail: deposit@ccdc.cam.ac.uk].

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