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Reactions in CH_3CN:CH_2Cl_2 (2:1) under Ar of the dimethyl-quaterpyridine ligand $C_{22}H_{18}N_4$ (L) with $Mn(ClO_4)_2$, $Fe(BF_4)_2$, $CoCl_2$, $Co(NO_3)_2$, $Zn(NO_3)_2$, $Cd(CH_3COO)_2$ and $HgCl_2$ give complexes of the type $[ML(H_2O)_mX_n]_2[MX_p]$, where X denotes the initial counterions, with $m = 1, n = 1, p = 4$ or $m = 2, n = 0, p = 6$. The complexes have been characterised by spectroscopic techniques and elemental analysis. The solid-state structures of two forms of the $CoCl_2$ complex have been established by X-ray crystallography, enabling an analysis of the interactions occurring in crystals of this type.

Keywords: quaterpyridine; transition metal complexes; polyanionometallates; luminescence

Introduction

The coordination chemistry of polypyridines (*1*) and of bipyridines (*2–4*), terpyridines (*1, 5, 6*) and quaterpyridines (*7, 8*) in particular, is a field of major interest because of the often remarkable physical and chemical properties of the very diverse metal ion complexes of both the parent ligands and numerous sophisticated derivatives (*9*). The range of their applications includes those as molecular machines (*10*), liquid crystals (*11*), catalysts for both organic and inorganic reactions (*9d, 12*), and as both therapeutic and imaging agents in medicine (*13*). While quaterpyridine chemistry has been relatively limited in development because of synthetic inaccessibility, we have recently described (*7*) the rather facile synthesis of the dimethyl-quaterpyridine L (Figure 1) and have shown that it may act as a helical quadridentate ligand forming both mononuclear [with octahedral Co(II) and Zn(II)] and binuclear, 'helicate' [with tetrahedral Cu(I) and Ag(I)] complexes.

In the present work, we extend these studies of the coordination chemistry of L with transition metal ions in the poor anion-solvating solvent acetonitrile (*14*). The consequence of the use of this solvent with the particular metal reactants now chosen is that the solids deposited from the reaction mixtures contain L bound in a cationic species which is associated with a polyanionometallate counterion. The stoichiometry of the isolated solid depends upon the nature of both the metal cation and the simple anion with which it is initially associated.

Experimental section

The metal salts were used without further purification as supplied from Aldrich. The ligand **L** and the complex $[Zn\mathbf{L}(H_2O)_2](CF_3SO_3)_2$ **8** were prepared as described previously (*7*). Solvents were freshly distilled under argon from CaH_2. NMR spectra were run on a Varian Gemini 300 MHz spectrometer and were calibrated against the residual protonated solvent signals (CD_3CN: δ 1.94). Mass spectra for acetonitrile solutions $\sim 10^{-4}$ M were determined using a Waters Micromass ZQ spectrometer. Sample solutions were introduced into the mass spectrometer source with a syringe pump at a flow rate of 40 μL min^{-1} with a capillary voltage of $+3$ kV and a desolvation temperature of 300°C. The source temperature was 120°C. The cone voltage (V_c) was set to 30 V to allow transmission of ions without fragmentation processes. Scanning was performed from $m/z = 200$ to 1000 for 6 s, and 10 scans were summed to obtain the final spectrum. Microanalyses were obtained using a Perkin-Elmer 2400 CHN microanalyser. All absorption spectra were recorded with a Shimadzu UVPC 2001 spectrophotometer, between 200 and 600 nm, in 10×10 mm quartz cells using solutions acetonitrile 10^{-5} M with respect to the metal ion. Excitation and emission spectra were measured at room temperature on a Perkin-Elmer MPF3 spectrofluorimeter with excitation and emission slits at 10 nm.

Preparation of the complexes: general procedures

All complexes were prepared under similar conditions. A mixture of appropriate metal salt (27 μmol) and ligand **L** (9 mg, 27 μmol) in 2:1 $CH_3CN–CH_2Cl_2$ (10 mL) was stirred at room temperature for 48 h under argon. The volume was reduced under vacuum until crystallisation commenced and the mixture was then allowed to stand to equilibrate. The product was obtained as a powder and

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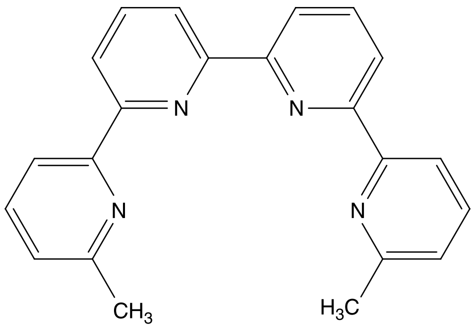

Figure 1. The ligand **L**.

was washed on the filter with CH_2Cl_2. The yields were 88–97%.

Mn(II) complex (1)

ESI-MS(+) := 492 (40) $[Mn\mathbf{L}(ClO_4)]^+$, 195 (100) $[Mn\mathbf{L}]^{2+}$. ESI-MS(−): *m/z* (%) = 352 (100) $[Mn(ClO_4)_3]^-$, 226 (40) $[Mn(ClO_4)_4]^{2-}$. Elemental analysis (%) calcd. for $[Mn(C_{22}H_{18}N_4)(ClO_4)(H_2O)]_2[Mn(ClO_4)_4]$ (1474.36): C, 35.84; H, 2.73; N, 7.60; found: C, 35.81; H, 2.80; N, 7.61.

Fe(II) complex (2)

^1H NMR (300 MHz, CD_3CN): $\delta = 8.66$ (d, 2H, $J = 5.7$ Hz), 8.49 (t, 2H, $J = 6.9$ Hz), 8.07 (t, 2H, $J = 5.7$ Hz), 7.70 (d, 2H, $J = 2.4$ Hz), 7.54 (d, 2H, $J = 6.3$ Hz), 7.21 (d, 2H, $J = 5.7$ Hz), 3.09 (s, 6H, CH_3). ESI-MS(+): *m/z* (%) = 429 (100) $[Fe\mathbf{L}Cl]^+$, 198 (40) $[Fe\mathbf{L}]^{2+}$. ESI-MS(−): *m/z* (%) = 202 (40) $[Fe(BF_4)_4]^{2-}$, 145 (15) $[Fe(BF_4)_6]^{4-}$. Elemental analysis (%) calcd. for $[Fe(C_{22}H_{18}N_4)(H_2O)_2]_2[Fe(BF_4)_6]$ (1438.17): C, 36.77; H, 3.09; N, 7.80; found: C, 36.74; H, 3.07; N, 7.77.

Co(II) complex (3)

ESI-MS(+): *m/z* (%) = 432 (80) $[Co\mathbf{L}Cl]^+$, 237 (55) $[Co\mathbf{L}(CH_3CN)(H_2O)_2]^{2+}$, 207 (5) $[Co\mathbf{L}(H_2O)]^{2+}$, 199 (20) $[Co\mathbf{L}]^{2+}$. ESI-MS(−): *m/z* (%) = 164 (100) $[CoCl_3]^-$; 101 (13) $[CoCl_4]^{2-}$. Elemental analysis (%) calcd. for $[Co(C_{22}H_{18}N_4)Cl(H_2O)]_2[CoCl_4]$ (1102.36): C, 47.94; H, 3.66; N, 10.16; found: C, 47.81; H, 3.65; N, 10.03.

Co(II) complex (4)

ESI-MS(+): *m/z* (%) = 459 (25) $[Co\mathbf{L}(NO_3)]^+$, 199 (30) $[Co\mathbf{L}]^{2+}$. ESI-MS(−): *m/z* (%) = 245 (45) $[Co(NO_3)_3]^-$, 154 (40) $[Co(NO_3)_4]^{2-}$. Elemental analysis (%) calcd. for $[Co(C_{22}H_{18}N_4)(NO_3)(H_2O)]_2[Co(NO_3)_4]$ (1261.67): C, 41.89; H, 3.20; N, 15.54; found: C, 41.84; H, 3.17; N, 15.50.

Zn(II) complex (5)

^1H NMR (300 MHz, CD_3CN): $\delta = 8.58$ (d, 2H, $J = 8.7$ Hz), 8.48 (t, 2H, $J = 6.4$ Hz), 8.18 (t, 2H, $J = 5.4$ Hz), 7.50 (d, 2H, $J = 6.6$ Hz), 7.44 (d, 2H, $J = 7.2$ Hz), 7.18 (d, 2H, $J = 6.0$ Hz), 2.98 (s, 6H, CH_3). ESI-MS(+): *m/z* (%) = 263 (80) $[Zn\mathbf{L}(CH_3CN)_3]^{2+}$, 210 (15) $[Zn\mathbf{L}(H_2O)]^{2+}$, 203 (20) $[Zn\mathbf{L}]^{2+}$. ESI-MS(−): *m/z* (%) = 250 (100) $[Zn(NO_3)_3]^-$, 157 (40) $[Zn(NO_3)_4]^{2-}$. Elemental analysis (%) calcd. for $[Zn(C_{22}H_{18}N_4)(NO_3)(H_2O)]_2[Zn(NO_3)_4]$ (1281.04): C, 41.25; H, 3.15; N, 15.31; found: C, 41.29; H, 3.18; N, 15.30.

Cd(II) complex (6)

^1H NMR (300 MHz, CD_3CN): $\delta = 8.49$ (d, 2H, $J = 8.4$ Hz), 8.41 (t, 2H, $J = 5.7$ Hz), 8.31 (d, 2H, $J = 7.8$ Hz), 8.16 (d, 2H, $J = 7.5$ Hz), 7.99 (t, 2H, $J = 7.8$ Hz), 7.50 (d, 2H, $J = 7.5$ Hz), 2.22 (s, 6H, CH_3). ESI-MS(+): *m/z* (%) = 511 (100) $[Cd\mathbf{L}(CH_3OO)]^+$, 339 (30) $[\mathbf{L}H]^+$, 306 (10) $[Cd\mathbf{L}(CH_3CN)_4]^{2+}$, 244 (20) $[Cd\mathbf{L}(CH_3CN)]^{2+}$, 225 (15) $[Cd\mathbf{L}]^{2+}$. ESI-MS(−): *m/z* (%) = 289 (50) $[Cd(CH_3COO)_3]^-$, 174 (40) $[Cd(CH_3COO)_4]^{2-}$, 136 (30) $[Cd(CH_3COO)_5]^{3-}$. Elemental analysis (%) calcd. for $[Cd(C_{22}H_{18}N_4)(CH_3COO)(H_2O)]_2[Cd(CH_3COO)_4]$ (1404.34): C, 47.89; H, 4.16; N, 7.98; found: C, 47.91; H, 4.19; N, 8.01.

Hg(II) complex (7)

^1H NMR (300 MHz, CD_3CN, 25°C): $\delta = 8.89$ (d, 2H, $J = 8.3$ Hz), 8.78 (t, 2H, $J = 7.4$ Hz), 8.58 (t, 2H, $J = 6.4$ Hz), 8.41 (d, 2H, $J = 6.1$ Hz), 7.94 (d, 2H, $J = 7.5$ Hz), 7.38 (d, 2H, $J = 6.5$ Hz), 2.48 (s, 6H, CH_3). ESI-MS(+): *m/z* (%) = 301 (100) $[Hg\mathbf{L}(CH_3CN)(H_2O)]^{2+}$, 277 (35) $[Hg\mathbf{L}(H_2O)]^{2+}$, 270 (25) $[Hg\mathbf{L}]^{2+}$. ESI-MS(−): *m/z* (%) = 307 (60) $[HgCl_3]^-$, 170 (45) $[HgCl_4]^{2-}$, 127 (40) $[HgCl_5]^{3-}$, 102 (100) $[HgCl_6]^{4-}$. Elemental analysis (%) calcd. for $[Hg(C_{22}H_{18}N_4)(H_2O)_2]_2[HgCl_6]$ (1563.36): C, 33.80; H, 2.84; N, 7.17; found: C, 33.83; H, 2.86; N, 7.20.

X-ray crystallography

Both forms of the cobalt complex crystallised simultaneously from the acetonitrile solution as the blue prisms. Diffraction data were collected at room temperature (**3A**) and 100(1) K (**3B**) by the ω-scan technique, on a KUMA-KM4CCD diffractometer (*15*) with graphite-monochromated MoK_α radiation ($\lambda = 0.71073$ Å). The temperature was controlled by an Oxford Instruments Cryosystems cooling device. The data were corrected for Lorentz polarisation and absorption effects (*15*). Accurate unit-cell parameters were determined by a least-squares fit of 2236 (**3A**) and 8354 (**3B**) reflections of highest intensity, chosen from the whole experiment. The structures were solved with SHELXS97 (*16*) and refined with the full-matrix least-squares procedure on F^2 by SHELXL97 (*16*). Scattering factors incorporated in SHELXL97 were used. All non-hydrogen atoms were refined anisotropically and hydrogen atoms of water fragment in **3B** were found in difference Fourier map but all other hydrogen atoms were located geometrically and refined as 'riding model' with their U_{iso}'s set at 1.2 (1.4 for CH_3 groups) of the U_{eq}'s of the appropriate carrier atoms. In the structure of **3B** the anionic fragment is disordered over two positions, sharing two common Cl atoms; the site occupation factors refined at 0.826(3) and 0.174(3). Relevant crystal data are listed in Table 1, together with refinement details.

Crystallographic data (excluding structure factors) for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, Nos. CCDC-690352 (**3A**) and CCDC-690353 (**3B**). Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK. Fax: +44(1223)336-033, E-mail: deposit@ccdc.cam.ac.uk or www: www.ccdc.cam.ac.uk.

Results and discussion

In contrast to the results of our earlier work, where reactions of Co(II) and Zn(II) salts with an equimolar quantity of L in acetonitrile produced crystalline materials containing the M(II) in a complex cation only, reactions of different salts of Co and Zn, as well as of salts of other M(II) species, in acetonitrile:dichloromethane (2:1) have provided solids in which the present evidence is that the metal ions are present in both cationic and anionic species. Thus, despite the use of preparative mixtures containing the metals and L in a 1:1 molar ratio, the materials precipitated were found from elemental microanalysis to have these components present in 3:2 ratio (M:L). The blue colour of the Co(II) complexes, in particular, was suggestive of the presence of tetrahedral anionometallates ($[CoCl_4]^{2-}$ and $[Co(NO_3)_4]^{2-}$) and X-ray structure determinations (see below) of two different solvates of the complex derived from $CoCl_2$ showed the presence of $[CoCl_4]^{2-}$, associated with two $[CoL(OH_2)Cl]^+$ cations, in both. Although attempts to obtain crystals suitable for structure determinations failed with all other complexes, in all cases electrospray mass spectra did provide evidence that anionometallate species could be present in the solids. Whilst it is somewhat surprising that complexes of perchlorate and tetrafluoroborate anions might be obtained under the preparative conditions used, the solvent mixture used should be a particularly poor anion solvator and, from the stoichiometry of the isolated solids, it is clear that even allowing for metal ion bridging by water ligands, at least some degree of metal ion/anion binding must occur in all cases. Thus, with cautionary acknowledgements that 'double salts' in general adopt a multitude of forms, that oligomeric rather than mononuclear anionometallates

Table 1. Crystal data, data collection and structure refinement.

Compound	**3A**	**3B**
Formula	$[Co(C_{22}H_{18}N_4)Cl(H_2O)]_2\ [CoCl_4]$	$[Co(C_{22}H_{18}N_4)Cl(H_2O)]_2\ [CoCl_4] \times 2CH_3CN$
Formula weight	1102.34	1184.44
Crystal system	Monoclinic	Monoclinic
Space group	*C2/c*	*C2/c*
a (Å)	25.950(12)	16.4768(5)
b (Å)	13.283(5)	14.1032(5)
c (Å)	14.237(7)	22.9752(8)
β (°)	112.36(4)	92.547(3)
V (Å^3)	4538(3)	5333.6(3)
Z	4	4
D_x (g cm^{-3})	1.61	1.48
F (000)	2236	2412
μ (mm^{-1})	1.49	1.27
Crystal size (mm)	0.05 × 0.05 × 0.3	0.15 × 0.2 × 0.2
Θ range (°)	2.9–20.0	2.6–25.0
Reflections:		
Measured	6905	21,200
Unique (R_{int})	2083 (0.077)	4675 (0.041)
With $I > 2\sigma(I)$	1350	3395
Number of parameters	287	330
$R(F)$ $[F^2 > 2\sigma(F^2)]$	0.079	0.059
$wR(F^2)$ [all refl.]	0.203	0.185
Goodness-of-fit	1.05	1.14
Max/min $\Delta\rho$ (eÅ^{-3})	1.00/−0.43	2.42/−0.50

might be present in some of the solids and that well-studied Hg(II) systems have shown that the relationship between stoichiometry and structure can be very varied, we present the materials isolated as forming two series $[ML(H_2O)_mX_n]_2[MX_p]$, where X denotes the initial counterions, with $m = 1$, $n = 1$, $p = 4$ (**1**, M = Mn, X = ClO_4^-; **3**, **4**, M = Co, X = Cl^-, NO_3^-; **5**, M = Zn, X = NO_3^-; **6**, M = Cd, X = $CH_3CO_2^-$) or $m = 2$, $n = 0$, $p = 6$ (**2**, M = Fe, X = BF_4^-; **7**, M = Hg, X = Cl^-).

Crystallographic characterisation of complex 3

In both structures, there are different Co complexes: one di-anionic $CoCl_4^{2-}$ and two cations, in which Co central ion is coordinated by four nitrogen atoms of **L** and chlorine atom and water molecule. In the complex **3B**, there is an additional solvent–acetonitrile molecule that occupies the empty spaces in the crystal structure. It might be noted that the crystal structure of **3B** is less efficiently packed as can be deduced from the differences in the calculated densities (cf. Table 2).

Figures 2 and 3 show the perspective views of the cations with the numbering scheme, while Table 3 lists relevant geometrical parameters of the structural elements for both crystals.

The anions are close to ideal tetrahedrons; in **3B** the anions are disordered over two alternative positions, and the shape of the less-occupied molecule is distorted, but that might be the artefact of the disorder itself.

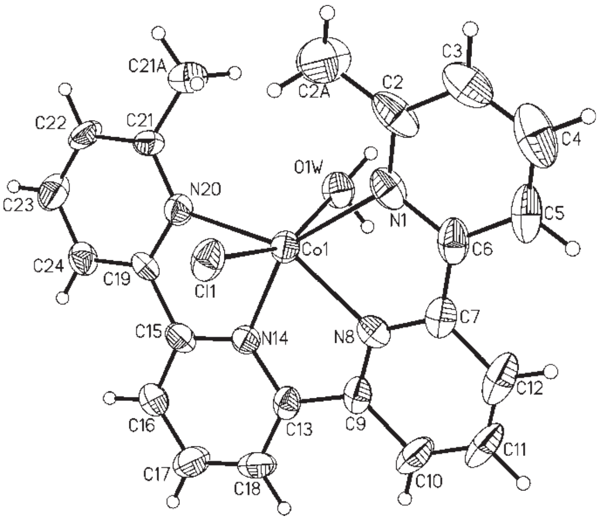

Figure 2. Perspective view of the cation $Co(\mathbf{L}ClH_2O)^+$ in **3A** together with the numbering scheme. The displacement ellipsoids are drawn at 25% probability level.

The coordination polyhedron of Co in cationic complexes is a distorted octahedron (or tetragonal bipyramid). Four nitrogen atoms of **L** make the basal plane (maximum deviation from the least-squares plane through four atoms is 0.074(5) Å in **3A** and 0.005(2) Å in **3B**), and Cl and O atoms are on the opposite sites. The central Co atom is slightly but significantly out of the basal plane (by 0.161(5) Å in **3A** and 0.119(2) Å in **3B**), always the deviation is towards the Cl atom.

Table 2. Selected bond distances (Å) and angles (°) and torsion angles with e.s.d. in parentheses.

	3A	3B
Co—Cl (anion)	2.244(4)	2.276(1)
	2.279(4)	2.293(1)
Co—Cl (cation)	2.305(4)	2.3503(15)
Co—O1W	2.111(8)	2.046(4)
Co—N	2.126(10)	2.113(4)
	2.129(11)	2.117(4)
	2.345(11)	2.392(4)
	2.393(10)	2.401(4)
Cl—Co—Cl (anion)	114.7(2)	108.34(8)
	109.20(14)	108.43(5)
	107.28(15)	114.38(5)
Cl—Co—O1W	155.7(3)	155.8(1)
Cl—Co—N	89.5(3)	102.8(1)
	100.3(3)	88.4(1)
	94.4(3)	88.9(1)
	91.0(3)	102.0(1)
O1W—Co—N	99.0(3)	96.3(2)
	94.4(3)	96.9(2)
	81.7(4)	83.0(1)
	81.2(3)	82.6(1)

The structural units are made of two cations and a dianion. In **3A** the $O-H\cdots Cl$ hydrogen bonds connect both water hydrogen atoms (H1 and H2) with different Cl atoms of the anions (Figure 4); the geometry of these hydrogen bonds is quite typical (Table 3).

These symmetrical units – the dianion occupies the special position, on the two-fold axis – are packed into the sheets of approximately parallel cations (the dihedral angle between the planes of the rings in the unit is about 6°),

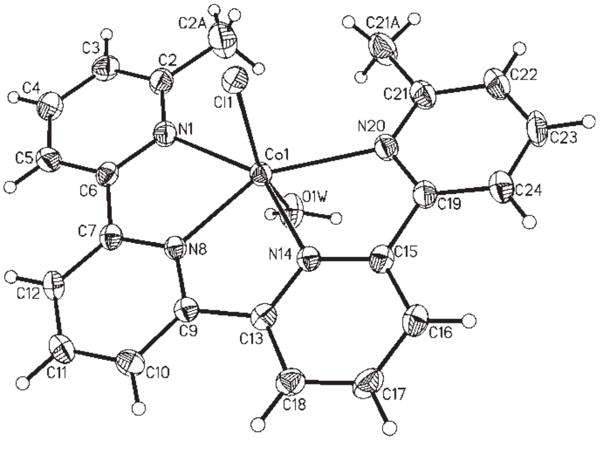

Figure 3. Perspective view of the cation $Co(\mathbf{L}ClH_2O)^+$ in **3B** together with the numbering scheme. The displacement ellipsoids are drawn at 50% probability level.

Table 3. Hydrogen bond data.

D	H	A	D—H	H···A	D···A	D—H···A
			3A			
O1W	H1	Cl2	0.90	2.32	3.158(3)	154
O1W	H2	Cl3($-x$, y, $-z-1/2$)	0.90	2.34	3.192(3)	158
			3B			
O1W	H1	Cl2	0.96	2.26	3.192(1)	164
O1W	H2	Cl3($-x$, y, $3/2-z$)	0.92	1.98	2.862(6)	162

separated by dianion–water systems and chlorine atoms from the cations (Figure 5). This structure is densely packed, and this tendency probably causes relatively large folding of the ligand **L**. The dihedral angle between least-squares plane of the terminal rings is 12.7(4)°.

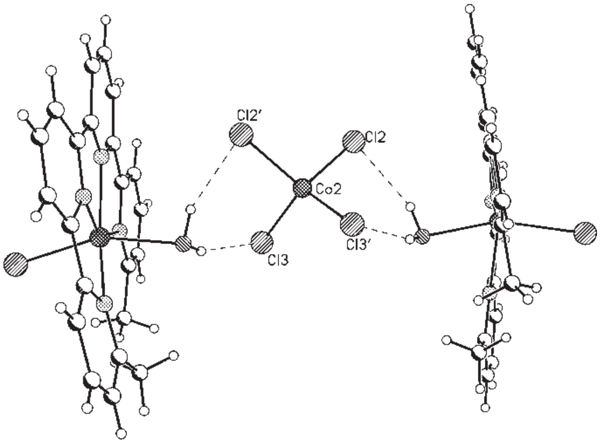

Figure 4. The structural unit in **3A**. Hydrogen bonds are depicted as dashed lines, two cations are related by the two-fold axis of symmetry that also halves the anion.

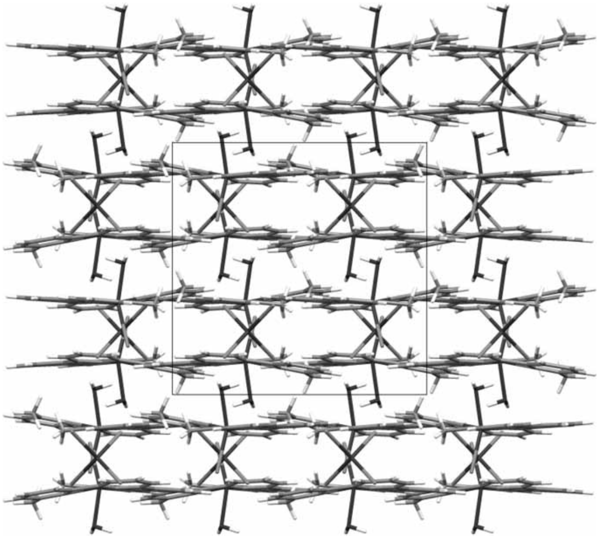

Figure 5. The crystal packing – supramolecular architecture in **3A** as seen along *a*-direction.

In **3B** also the hydrogen bonds between water molecules and anions organise the structural unit. In this case, however, due to the disorder in the structure the water molecule uses only one hydrogen bond for each alternative positions of the anion (Figure 6).

This disorder (over pseudo-mirror plane of symmetry) leads to the less dense packing, which causes more planar conformation of the ligand: dihedral angle between the terminal rings is as small as 1.2(3)°. What is more, this packing leads to the huge empty spaces in the crystal structures which are occupied by the solvent–acetonitrile molecules (Figure 7).

Electronic absorption spectra and luminescence properties

Absorption spectra of solutions of the ligand **L** and complexes **1**–**7** in acetonitrile are characterised by high-energy absorptions at about 210 nm and low-energy bands at ca. 300 and 340 nm, respectively. The electronic absorption spectra in the UV-region show the typical $\pi-\pi^*$ ligand-based transitions.

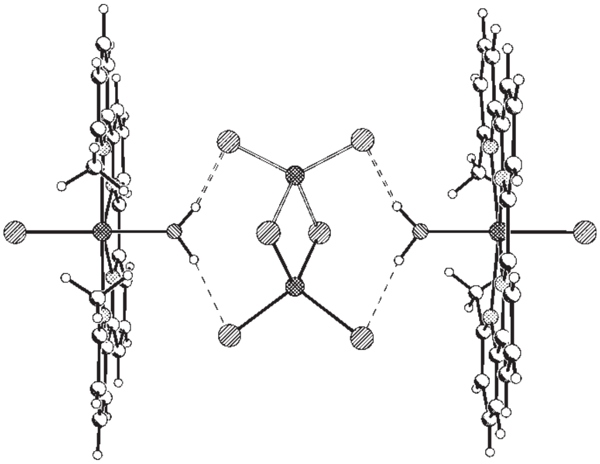

Figure 6. The structural unit in **3B**. Hydrogen bonds are depicted as dashed lines, two cations are related by the two-fold axis of symmetry that also halves the anion. The open lines show the anion of lesser occupancy.

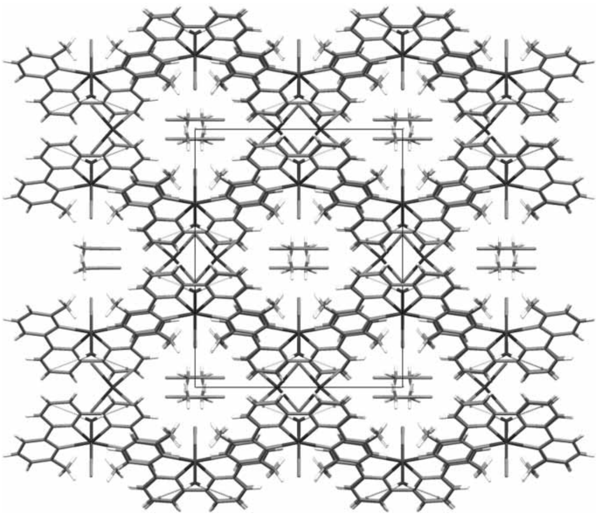

Figure 7. The crystal packing – supramolecular architecture in **3B** as seen along *a*-direction. The free spaces, occupied by the solvent molecules, are clearly seen.

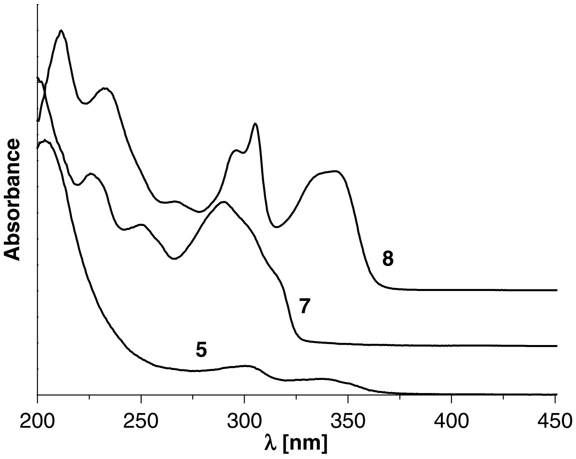

Figure 8. The absorption spectra of **5**, **7** and **8** in acetonitrile (5×10^{-5} M) solution at 298 K.

The complexes **1**, **3–6** and **2**, **7** exhibit a quite similar absorption profiles, respectively, and different for the previously investigated of mononuclear Zn(II) complex $[Zn\mathbf{L}(H_2O)_2](CF_3SO_3)_2$ **8** (*7*). In the UV-region, where the ligand-centred transitions are dominant, the differences in the recorded spectra for the three types of complexes (mononuclear, two types of complexes containing three metal ions) are observed (Figure 8, Table 4). The absorption spectra of **5**, **7** and **8** are depicted in Figure 8.

The luminescence properties of free ligand **L** and its metal complexes **1–7** were also investigated in CH_3CN at room temperature and quantum yield of luminescence was determined. Ligand **L** and complexes exhibit one broad emission band. The emission band maxima of all complexes are red shifted compared to free ligand **L**. The quantum yields of the luminescence of **1**, **4–6** complexes are much lower than that of free ligand under the same conditions. The Mn(II) and Co(II) ions strongly quench the luminescence of **L** ($\phi = 0.0043$ and 0.0067), while Zn(II) and Cd(II) weakly ($\phi = 0.0168$ and 0.0177). Complex **3** does not display luminescence in this solution. The quantum yields of complexes **2** and **7** are higher than the others, but they are lower than the quantum yield of free ligand. The emission of the zinc triflate mononuclear complex (**8**) is much more intense than ligand **L** (*7*). The determined quantum yield of this complex is equal to 0.2151 and it is higher than ligand **L**.

The differences in the luminescence properties of studied complexes, especially zinc complexes, suggest that the emission in those systems is sensitive in respect of coordination changes.

Conclusions

In conclusion, the investigated complexes may be of use in several fields of coordination chemistry. Geometrical parameters for the $[CoCl_4]^{2-}$ anion in complex **3**, whose formation apparently aids the stabilisation of the $[Co\mathbf{L}Cl(H_2O)]^+$ cations in crystal lattice, are similar to those reported previously for these units (*19–29*). The factors of these complexes in solution make these compounds good candidates as luminescence supramolecular nanodevices and laser materials (*30–32*). Transition metal complexes of multidentate ligands have been widely used in modern chemical applications

Table 4. Absorption and luminescence data.

Compound	Absorption, λ/nm ($\varepsilon \times 10^3$/M^{-1} cm^{-1})	Emission (λ/nm)	ϕ^*_{em}
L	209(31), 252(17), 292.5(25)	359	0.0752
1	210(16.9), 234.5(9.7), 267.5(4.0), 307.5(10.6), 338.5(5.4), 350(5.5)	362	0.0043
2	207(29.7), 288.5(9.4)	363	0.0361
3	211(23.7), 253(10.0), 302(5.9), 338.5(3.1)	–	–
4	210(14.3), 301(2.2), 339.5(1.2)	366	0.0067
5	206(13.9), 301.5(1.3) 340(1.0)	365	0.0168
6	206(19.0), 291.5(4.5), 301(4.3), 338(1.1)	365	0.0177
7	207(35.7), 231(29.7), 290(16.1)	366	0.0453

*Quinine sulphate ($\phi = 0.577$ in 0.1 M H_2SO_4) was used as a standard for all systems; experimental error *ca.* 20% (*17, 18*).

including bioinorganic chemistry (*28, 29*) and catalyst development (*33–37*).

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