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Cadmium-containing pyridyl–thiazole complexes: crystal structures and solution behaviour of mononuclear, dinuclear double helicate and dinuclear triple helicate complexes

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Abstract

Reaction of $Cd(ClO_4)_2$ with the potentially tetra- (L^1), penta- (L^2) and hexadentate (L^3) pyridine–thiazole-containing ligands gives $[Cd_2(L^1)_3(H_2O)][ClO_4]_4$ (a dinuclear triple helicate), mononuclear $[Cd(L^2)(ClO_4)_2]$, and $[Cd_2(L^3)_2(ClO_4)(CH_3CN)][ClO_4]_3$ (a dinuclear double helicate), respectively. In $[Cd_2(L^1)_3(H_2O)][ClO_4]_4$ two of the ligands L^1 partition into two bidentate pyridyl–thiazole domains whereas the remaining ligand partitions into a bidentate (pyridyl–thiazole) and monodentate (coordinating pyridyl unit with a pendant thiazole) unit; one Cd(II) centre is coordinated by three bidentate ligand fragments, whereas the other is coordinated by two bidentate and one monodentate ligand fragments as well as a water molecule. This low-symmetry arrangement is retained in solution. In $[Cd(L^2)(ClO_4)_2]$, L^2 acts as a planar pentadentate equatorial ligand with perchlorate anions coordinated at the axial sites; the ligand has a shallow helical twist to minimise steric interactions between the terminal pyridyl H^6 protons, which are directed towards each other. In $[Cd_2(L^3)_2(ClO_4)(CH_3CN)][ClO_4]_3$, the potentially hexadentate ligand L^3 is partitioned into terdentate (pyridyl–thiazole–pyridyl) and bidentate (pyridyl–thiazole) coordination domains with a non-coordinated terminal pyridyl unit; each Cd(II) centre is coordinated by one terdentate and one bidentate ligand fragment, with the sixth site being occupied by MeCN at one Cd(II) site and a perchlorate anion at the other. Again, the low symmetry coordination mode of the ligands is retained in solution although the two metal centres become equivalent.

Keywords: Pyridyl; Crystallography; Hexadentate; Ligand; Helicate

1. Introduction

The study of the assembly of multi-dentate ligands with transition metal ions into double and triple helicate complexes has been a major area of activity. The interplay between parameters such as the stereoelectronic preference of the metal ion, the number and disposition of the binding sites on the ligand, non-covalent interactions between ligands, and even non-covalently bound guest species within the helical framework, all contribute to the assembly process [1–5]. We have recently carried out exploratory coordination chemistry of a new class of multidentate ligands such as L^1–L^4 based on linear arrays of pyridyl and thiazolyl units [6–9]. It has become apparent that the way in which these ligands partition themselves into distinct domains for coordination to metal ions is related to the arrangement of five-membered (thiazolyl) and six-membered (pyridyl) rings in the sequence. For example L^1, although potentially a tetradentate chelate, partitions into two bidentate pyridyl–thiazole units by twisting about the central C–C bond because the two central thiazole units cannot coordinate to the same metal ion. This behaviour leads to formation of dinuclear triple helicates with Cu(II), Zn(II) and Co(II) ions [6,9]. Likewise the ligand L^4 does not act as a tetradentate chelate, but coordinates either as a tridentate chelate

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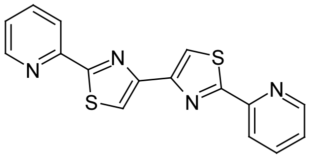
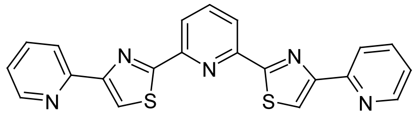
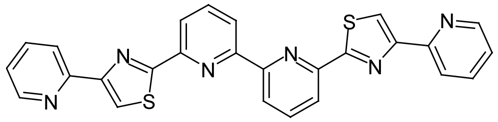
(with a pendant pyridyl group) to Cu(II), or as a bis-bidentate bridging ligand to give a triple helicate with Co(II) [7]. In addition, we have shown that ligand self–self recognition can occur when mixtures of ligands are used to form double helicates with Ni(II), Cu(II) and Zn(II); this recognition process is a consequence of the way each type of ligand partitions into distinct coordination domains according to the position of the thiazolyl and pyridyl units in the sequence [8]. In this paper, we describe the structures of complexes of Cd(II) with ligands L^1–L^3, which show some interesting differences compared to the structures of the complexes with first-row dications.



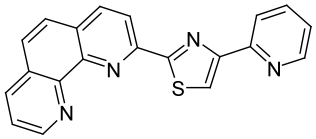
L^1



L^2



L^3



L^4

2. Experimental

2.1. General details

The following instruments were used for routine spectroscopic measurements: ^{1}H NMR spectra, a Bruker Avance DPX400; electrospray mass spectra, a VG Quattro II triple quadrupole mass spectrometer. Ligands L^1–L^3 were prepared according to the previously published methods [9].

2.2. Syntheses of metal complexes

Caution: perchlorate salts are potentially explosive and should be treated with due care. Those complexes described below which were isolated as perchlorates were only prepared in small amounts (10–20 mg) and we had no problems with them.

2.2.1. $[Cd_2(L^1)_3(H_2O)][ClO_4]_4$

To a suspension of L^1 (0.010 g, 0.03 mmol) in MeCN (2 cm^3), $Cd(ClO_4)_2 \cdot 6H_2O$ (0.009 g, 0.02 mmol) was added and the suspension stirred until dissolution was complete. Filtration of this solution, followed by slow vapour diffusion of ethyl acetate into the solution, gave $[Cd_2(L^1)_3(H_2O)][ClO_4]_4$ as large colourless crystals, which were isolated by filtration and dried under vacuum. Yield: 0.010 g, 60%. ^{1}H NMR (400 MHz, CD_3NO_2): δ (ppm) 8.60 (1 H, s; tz), 8.22 (10 H, m; py), 8.10 (5 H, m; py), 7.91 (1 H, m; py), 7.85 (1 H, m; py), 7.74 (1 H, m; py), 7.59 (5 H, m; py), 7.58 (5 H, s; tz), 7.30 (1 H, m; py). ESMS: *m*/*z* 1490 $[Cd_2(L^1)_3(ClO_4)_3]^+$. *Anal*. Found: C, 35.9; H, 1.9; N, 11.0%; $C_{48}H_{32}N_{12}S_6Cd_2Cl_4O_{17}$ requires C, 35.8; H, 2.0; N, 10.4%.

2.2.2. $[Cd(L^2)(ClO_4)_2]$

To a suspension of L^2 (0.010 g, 0.025 mmol) in $MeNO_2$ (2 cm^3) $Cd(ClO_4)_2 \cdot 6H_2O$ (0.011 g, 0.025 mmol) was added and the solution stirred until dissolution was complete. Filtration followed by slow vapour diffusion of ethyl acetate into the solution gave $[Cd(L^2)(ClO_4)_2]$ as large colourless crystals, which were isolated by filtration and dried under vacuum. Yield: 0.009 g, 50%. ^{1}H NMR (400 MHz, CD_3CN): δ (ppm) 8.95 (2 H, d, $J=$ 4.9; py), 8.58 (2 H, S; tz), 8.37 (1 H, t, $J=8.2$; py), 8.32 (2 H, d, J 7.9; py), 8.25 (2 H, d, $J=8.2$; py), 8.21 (2 H, dd, $J=7.9$, 1.6 Hz; py), 7.77 (2 H, m; py). ESMS: *m*/*z* 611 $[Cd(L^4)(ClO_4)]^+$. *Anal*. Found: C, 35.0; H, 1.8; N, 10.4%. $C_{21}H_{13}N_5S_2CdCl_2O_8$ requires C, 35.5; H, 1.8; N, 9.8%.

Table 1
Crystallographic data for the two structures

Compound	$[Cd_2(L^1)_3(H_2O)][ClO_4]_4 \cdot 3MeCN$	$[Cd(L^2)(ClO_4)_2] \cdot MeNO_2$	$[Cd_2(L^3)_2(ClO_4)(MeCN] \cdot (ClO_4)_3 \cdot MeCN$
Empirical formula	$C_{54}H_{41}Cd_2Cl_8N_{15}O_{17}S_6$	$C_{22}H_{16}CdCl_2N_6O_{10}S_2$	$C_{56}H_{38}Cd_2Cl_4N_{14}O_{16}S_4$
Forward weight	1872.8	771.8	1657.8
Crystal dimensions (mm)	0.25 × 0.25 × 0.2	0.5 × 0.2 × 0.2	0.3 × 0.2 × 0.1
Crystal system	triclinic	triclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	Cc
a (Å)	12.1864(19)	8.7527(12)	21.559(3)
b (Å)	12.588(2)	11.8637(17)	14.160(2)
c (Å)	23.927(4)	13.8118(19)	21.956(3)
α (°)	76.825(3)	70.037(2)	90
β (°)	87.986(3)	81.553(2)	113.840(3)
γ (°)	66.215(2)	87.664(2)	90
V (Å^3)	3263.6(9)	1333.3(3)	6130.7(16)
Z	2	2	4
ρ_{calc} (g cm^{-3})	1.906	1.922	1.796
Absorption coefficient (mm^{-1})	1.254	1.246	1.087
Reflections collected: total/independent/R_{int}	33 150/4768/0.0492	13 870/6061/0.0289	19 022, 9274, 0.0361
Data/restraints/parameters	14 768/38/883	6061/0/389	9274/2/868
Final R_1, wR_2[a,b]	0.0481, 0.1160	0.0298, 0.0700	0.0333, 0.0681

Data in common: $T = 173$ K; $\lambda = 0.71073$ Å; instrument, a Bruker SMART-CCD diffractometer.

[a] Structure was refined on $F_o{}^2$ using all data; the value of R_1 is given for comparison with older refinements based on F_o with a typical threshold of $F \geqslant 4\sigma(F)$.

[b] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2]^{1/2}$ where $w^{-1} = [\sigma^2(F_o^2) + (aP)^2 + bP]$ and $P = [\max(F_o^2, 0) + 2F_c^2]/3$.

2.2.3. $[Cd_2(L^3)_2(ClO_4)(CH_3CN)][ClO_4]_3$

To a suspension of L^3 (0.010 g, 0.02 mmol) in MeCN (2 cm^3), $Cd(ClO_4)_2 \cdot 6H_2O$ (0.009 g, 0.02 mmol) was added and the suspension stirred until dissolution was complete. Filtration followed by slow vapour diffusion of ethyl acetate into the solution gave $[Cd_2(L^3)_2](ClO_4)_4$ as large pale yellow crystals, which were isolated by filtration and dried under vacuum. Yield: 0.020 g, 59%. ^{1}H NMR (400 MHz, CD_3CN): δ (ppm) (1 H, d, J 7.8; py), 8.51 (1 H, s; tz), 8.47 (1 H, t, J 7.8; py), 8.35 (1 H, d, J 7.8; py), 8.35 (1 H, s; tz), 8.13 (1 H, d, J 8.8; py), 8.09 (1 H, t, J 7.4; py), 8.02 (1 H, d J 7.4; py), 7.91 (3 H, m; py), 7.75 (1 H, d, J 7.2; py), 7.70 (1 H, d, J 3.6 Hz; py), 7.40 (1 H, m; py), 7.21 (1 H, m; py), 7.01 (1 H, m; py). ESMS: m/z 1476 $[Cd_2(L^3)_2(ClO_4)_3]^+$. *Anal*. Found: C, 40.9; H, 1.9; N, 11.8%. $C_{54}H_{35}N_{13}S_4Cd_2Cl_4O_{16}$ requires C, 40.1; H, 2.2; N, 11.3%.

2.3. Crystallography

Suitable crystals of $[Cd_2(L^1)_3(H_2O)][ClO_4]_4 \cdot 3MeCN$, $[Cd(L^2)(ClO_4)_2] \cdot MeNO_2$ and $[Cd_2(L^3)_2(ClO_4)(CH_3CN)][ClO_4]_3 \cdot CH_3CN$ were mounted on a Siemens SMART-CCD diffractometer under a stream of cold N_2 at −100 °C and all subsequent crystallographic studies were carried out at this temperature. The software used was SHELXS-97 for structure solution [10]; SHELXL-97 for structure refinement [10]; and SADABS for the absorption correction [11]. Details of the crystal parameters, data collection and refinement are collected in Table 1, and selected metric parameters are in Tables 2–4. None of the solutions or refinements presented any significant problems. The complexes $[Cd_2(L^1)_3(H_2O)]$-$[ClO_4]_4 \cdot 3MeCN$ and $Cd_2(L^3)_2(ClO_4)(CH_3CN)][ClO_4]_3 \cdot CH_3CN$ crystallise as racemates, with equal numbers of opposite enantiomers in achiral unit cell.

3. Results and discussion

3.1. Synthesis and crystal structure of $[Cd_2(L^1)_3(H_2O)][ClO_4]_4$

Previously we have shown that L^1, upon coordination to Co(II), Cu(II) or Zn(II), partitions into two pyridyl–thiazole domains, resulting in formation of triple helicates in which each metal centre is approximately octahedral coordinated by three bidentate pyridyl–thiazole units [6,9].

Reaction of $Cd(ClO_4)_2 \cdot 6H_2O$ with one equivalent of L^1 in MeCN gives upon slow precipitation with ethyl acetate a colourless crystalline material whose analytical and mass spectroscopic data were in agreement with the formation of the dinuclear complex $[Cd_2(L^1)_3](ClO_4)_4$. The crystal structure confirms the formation of a dinuclear triple helicate (Fig. 1) in which both metal ions are six-coordinate. However, there is one significant difference between this structure and those of the triple helicates with the first-row dications reported earlier. Whilst two of the ligands are partitioned into two pyridyl–thiazole bidentate domains and are accordingly acting in the expected manner, the third ligand is only terdentate, acting as a bidentate chelate to one metal but as a monodentate pyridyl donor to the other, with the

Table 2
Selected bond distances (Å) and angles (°) for $[Cd_2(L^1)_3(H_2O)][ClO_4]_4 \cdot 3MeCN$

Bond distances			
Cd(1)–N(151)	2.311(4)	Cd(2)–N(201)	2.305(4)
Cd(1)–N(131)	2.336(4)	Cd(2)–N(251)	2.314(3)
Cd(1)–N(101)	2.376(4)	Cd(2)–N(231)	2.365(3)
Cd(1)–N(141)	2.424(3)	Cd(2)–N(221)	2.380(3)
Cd(1)–O(1)	2.447(3)	Cd(2)–N(211)	2.407(4)
Cd(1)–N(111)	2.468(3)	Cd(2)–N(241)	2.411(4)
Bond angles			
N(151)–Cd(1)–N(131)	106.94(13)	N(201)–Cd(2)–N(251)	86.14(13)
N(151)–Cd(1)–N(101)	128.01(13)	N(201)–Cd(2)–N(231)	169.51(12)
N(131)–Cd(1)–N(101)	109.02(12)	N(251)–Cd(2)–N(231)	103.60(12)
N(151)–Cd(1)–N(141)	150.27(12)	N(201)–Cd(2)–N(221)	100.48(12)
N(131)–Cd(1)–N(141)	70.65(12)	N(251)–Cd(2)–N(221)	159.82(13)
N(101)–Cd(1)–N(141)	78.13(12)	N(231)–Cd(2)–N(221)	71.66(12)
N(151)–Cd(1)–O(1)	77.32(12)	N(201)–Cd(2)–N(211)	72.30(13)
N(131)–Cd(1)–O(1)	80.04(12)	N(251)–Cd(2)–N(211)	122.91(12)
N(101)–Cd(1)–O(1)	73.41(12)	N(231)–Cd(2)–N(211)	98.75(12)
N(141)–Cd(1)–O(1)	129.19(11)	N(221)–Cd(2)–N(211)	77.23(12)
N(151)–Cd(1)–N(111)	80.68(12)	N(201)–Cd(2)–N(241)	106.39(13)
N(131)–Cd(1)–N(111)	169.54(12)	N(251)–Cd(2)–N(241)	70.57(12)
N(101)–Cd(1)–N(111)	69.93(12)	N(231)–Cd(2)–N(241)	80.90(12)
N(141)–Cd(1)–N(111)	99.14(11)	N(221)–Cd(2)–N(241)	89.26(12)
O(1)–Cd(1)–N(111)	109.05(11)	N(211)–Cd(2)–N(241)	165.77(11)

Table 3
Selected bond distances (Å) and angles (°) for $[Cd(L^2)(ClO_4)_2] \cdot CH_3NO_2$

Bond distances			
Cd(1)–N(21)	2.320(2)	Cd(1)–N(51)	2.465(2)
Cd(1)–N(11)	2.330(2)	Cd(1)–N(31)	2.525(2)
Cd(1)–O(11)	2.360(2)	Cd(1)–N(41)	2.565(2)
Cd(1)–O(21)	2.418(2)		
Bond angles			
N(21)–Cd(1)–N(11)	127.93(7)	N(11)–Cd(1)–N(31)	67.26(7)
N(21)–Cd(1)–O(11)	93.77(7)	O(11)–Cd(1)–N(31)	95.13(7)
N(11)–Cd(1)–O(11)	86.06(7)	O(21)–Cd(1)–N(31)	82.68(7)
N(21)–Cd(1)–O(21)	87.93(7)	N(51)–Cd(1)–N(31)	97.42(7)
N(11)–Cd(1)–O(21)	94.62(8)	N(21)–Cd(1)–N(41)	63.93(7)
O(11)–Cd(1)–O(21)	177.24(7)	N(11)–Cd(1)–N(41)	64.04(7)
N(21)–Cd(1)–N(51)	68.16(7)	O(11)–Cd(1)–N(41)	87.60(7)
N(11)–Cd(1)–N(51)	163.53(8)	O(21)–Cd(1)–N(41)	95.11(7)
O(11)–Cd(1)–N(51)	89.51(7)	N(51)–Cd(1)–N(41)	131.67(7)
O(21)–Cd(1)–N(51)	89.10(7)	N(31)–Cd(1)–N(41)	130.89(7)
N(21)–Cd(1)–N(31)	162.98(7)		

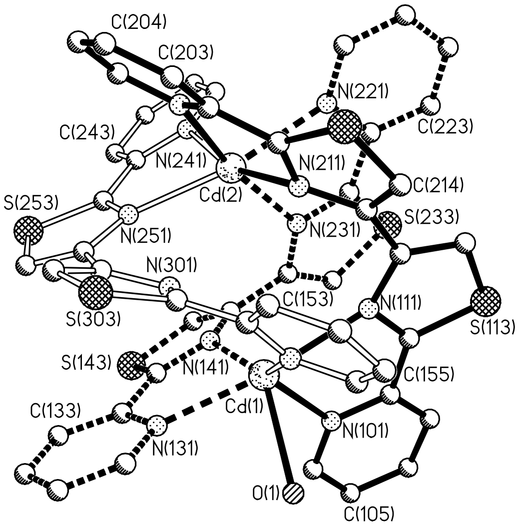


Fig. 1. Structure, showing one enantiomer, of the complex cation of $[Cd_2(L^1)_3(H_2O)][ClO_4]_4 \cdot 3MeCN$.

thiazolyl N atom [N(301)] not coordinated to Cd(1); there is a weak interaction however with the Cd(1)···N(301) separation being 2.767 Å. Cd(1) has a water molecule to complete its highly irregular six-coordinate environment; Cd(2) however has a more conventional and regular tris-chelate six-coordinate environment. As always in structures of this type there is substantial aromatic p-stacking between overlapping and approximately parallel domains of adjacent ligands.

Somewhat surprisingly, this low-symmetry structure is retained in solution (Fig. 2a). If a symmetric structure were adopted in which N(301) reattached and the coordinated water ligand at Cd(1) were displaced, we would expect to see just five resonances in the aromatic region (four pyridyl H, one thiazolyl H) since all bidentate half-ligand fragments would be equivalent in the D_3 symmetry. Instead, the spectrum shows two closely-spaced sets of aromatic signals in a 5:1 ratio. The larger component is assigned as corresponding to the five bidentate pyridyl–thiazole units, which—although

Table 4
Selected bond distances (Å) and angles (°) for $[Cd_2(L^3)_2(CH_3CN)(ClO_4)][ClO_4]_3 \cdot CH_3CN$

Bond distances			
Cd(1)–N(131)	2.296(4)	Cd(2)–N(211)	2.340(4)
Cd(1)–N(121)	2.330(4)	Cd(2)–N(21)	2.345(5)
Cd(1)–N(111)	2.347(4)	Cd(2)–N(231)	2.359(4)
Cd(1)–N(101)	2.354(5)	Cd(2)–N(201)	2.374(5)
Cd(1)–O(11)	2.357(6)	Cd(2)–N(221)	2.377(5)
Cd(1)–N(141)	2.576(5)	Cd(2)–N(241)	2.573(5)
Bond angles			
N(131)–Cd(1)–N(121)	163.05(18)	N(211)–Cd(2)–N(21)	155.52(16)
N(131)–Cd(1)–N(111)	72.13(15)	N(211)–Cd(2)–N(231)	71.91(15)
N(121)–Cd(1)–N(111)	116.58(16)	N(21)–Cd(2)–N(231)	84.90(18)
N(131)–Cd(1)–N(101)	125.71(17)	N(211)–Cd(2)–N(201)	85.29(16)
N(121)–Cd(1)–N(101)	70.91(17)	N(21)–Cd(2)–N(201)	103.58(18)
N(111)–Cd(1)–N(101)	84.11(15)	N(231)–Cd(2)–N(201)	127.63(17)
N(131)–Cd(1)–O(11)	83.61(19)	N(211)–Cd(2)–N(221)	120.27(15)
N(121)–Cd(1)–O(11)	90.06(17)	N(21)–Cd(2)–N(221)	84.14(17)
N(111)–Cd(1)–O(11)	152.85(19)	N(231)–Cd(2)–N(221)	161.86(18)
N(101)–Cd(1)–O(11)	101.0(3)	N(201)–Cd(2)–N(221)	69.24(18)
N(131)–Cd(1)–N(141)	97.88(16)	N(211)–Cd(2)–N(241)	109.92(15)
N(121)–Cd(1)–N(141)	66.06(16)	N(21)–Cd(2)–N(241)	80.35(18)
N(111)–Cd(1)–N(141)	107.27(15)	N(231)–Cd(2)–N(241)	97.94(17)
N(101)–Cd(1)–N(141)	136.08(14)	N(201)–Cd(2)–N(241)	134.35(17)
O(11)–Cd(1)–N(141)	87.6(3)	N(221)–Cd(2)–N(241)	65.96(18)

not symmetrically identical—are sufficiently similar in the ^{1}H NMR to be coincident. The smaller component is assigned to the unique monodentate pyridyl–thiazole fragment [the rings containing N(301) and N(151)].

3.2. Synthesis and crystal structure of $[Cd(L^2)(ClO_4)_2]$

Reaction of L^2 with $Cd(ClO_4)_2 \cdot 6H_2O$, as described above, gave a colourless crystalline material for which

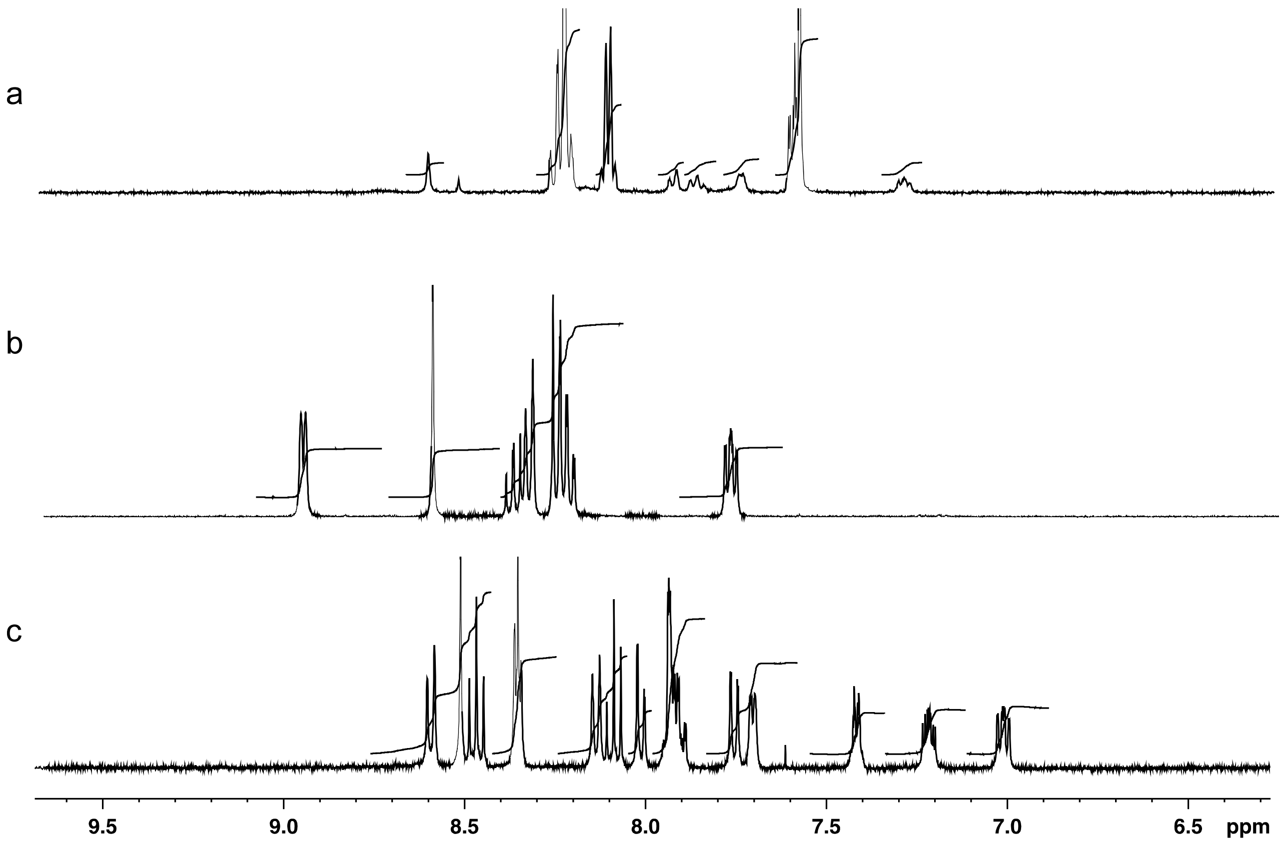


Fig. 2. Aromatic regions of the ^{1}H NMR spectra of $[Cd_2(L^1)_3](ClO_4)_4$ (**a**), $[Cd(L^2)(ClO_4)_2]$ (**b**) and $[Cd_2(L^3)_2][(ClO_4)_4]$ (**c**).

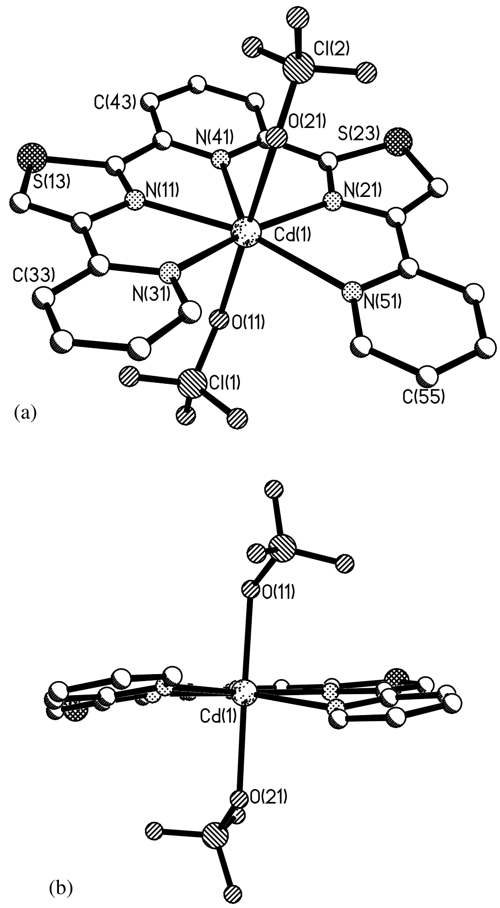


Fig. 3. (a) Structure of the complex unit of $[Cd(L^2)(ClO_4)_2]\cdot MeNO_2$; (b) an alternative view emphasising the slight helical twist of the ligand.

ES mass spectrometry and elemental analysis suggested the formula of $[Cd(L^2)(ClO_4)_2]$. The ^1H NMR spectrum in CD_3CN shows that the 13 aromatic protons occur in seven environments (six of intensity 2H, and one of intensity 1H) with the signals occurring between 7.7 and 9.0 ppm (Fig. 2b). This indicates that the two ligand halves are equivalent in solution, with the unique proton being H^4 of the central pyridyl ring. This is explained by the crystal structure (Fig. 3), which shows a mononuclear seven-coordinate Cd(II) complex. The ligand L^2 acts as a near-planar pentadentate 'equatorial' ligand, with the two perchlorate anions acting as monodentate axial ligands. The Cd–N bonds range from 2.32 to 2.57 Å, with the longest bond being to the central pyridyl ring [N(41)]. The ligand is not exactly planar but has a shallow helical twist (Fig. 3b) which allows the H^6 protons of the two terminal pyridyl ligands to avoid one another; this ligand conformation is very similar to that observed in the near-planar five-coordinate complex $[Ag(qpy)]^+$ (qpy = $2,2':6',2'':2'',6''':2''',6''''$-quinquepyridine) [12]. The structure of $[Cd(L^2)(ClO_4)_2]$ may be contrasted with that of the dinuclear double helicate $[Cu_2(L^2)_2]^{4+}$ which contains two four-coordinate Cu(II) centres, with the central pyridyl ring of each ligand L^2 not coordinated [9]. The difference between the two types of structure may be ascribed partly to the larger ionic radius of Cd(II) compared to Cu(II) which clearly makes it a good fit for the ligand cavity, and partly to the absence of stereoelectronic preferences for the d^{10} Cd(II) ion.

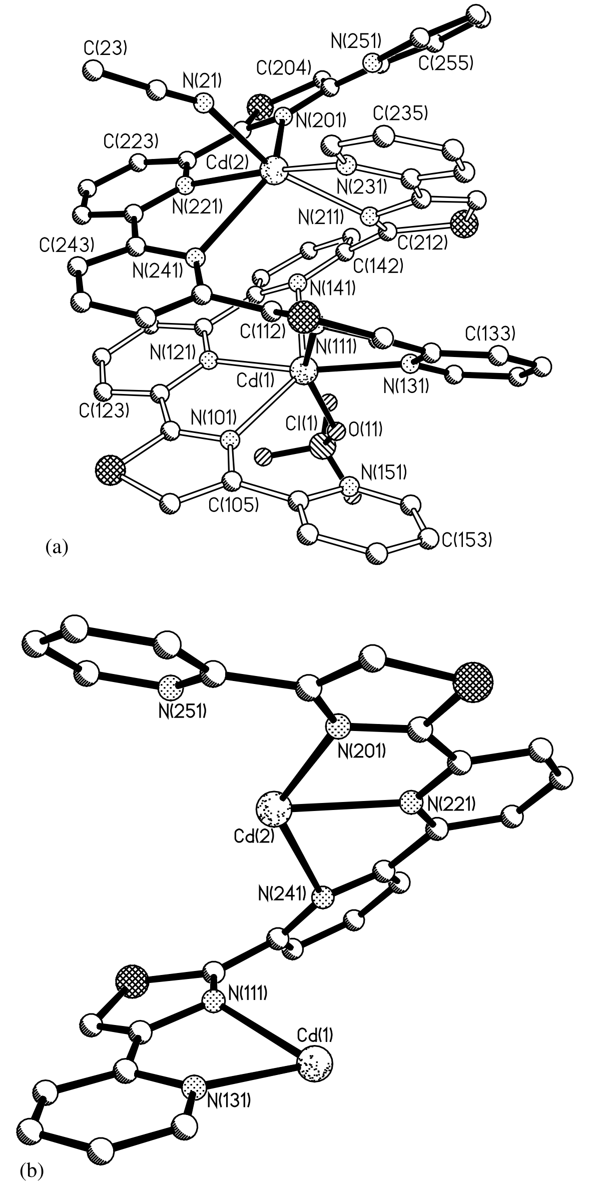


Fig. 4. (a) Structure, showing one enantiomer, of the complex cation of $[Cd_2(L^3)_2(ClO_4)(CH_3CN)][ClO_4]_3\cdot CH_3CN$; (b) an alternative view emphasising the asymmetric coordination mode of each ligand.

3.3. Synthesis and crystal structure of $[Cd_2(L^3)_2][ClO_4]_4$

Previously we have shown that L^3 forms dinuclear double helicates with Zn(II), Cu(II) and Ni(II). Although this ligand is potentially hexadentate, the double helicates $[Zn_2(L^3)_2]^{4+}$ and $[Cu_2(L^3)_2]^{4+}$ contain four-coordinate metal ions because the ligand coordinates via the terminal bidentate thiazole–pyridyl units with the central bipyridyl unit of each ligand is not coordinated. In contrast, the dinuclear double helicate $[Ni_2(L^3)_2]^{4+}$ [in which the metal ion has a greater stereoelectronic preference for octahedral coordination than is the case with Zn(II) and Cu(II)] contains six-coordinate metal ions with L^3 coordinating as a hexadentate ligand, using two terdentate pyridyl–thiazolyl–pyridyl units. This variability in coordination modes shown by L^3 (compared, for example to the all-pyridine analogue 2,2′:6′,2″:6″,2‴:6‴,2⁗:6⁗,2‴″-sexipyridine) [13] can be ascribed to the inclusion of thiazole units into the backbone. Terdentate coordination of a pyridyl–thiazolyl–pyridyl fragment is sterically hampered by the presence of a 5-membered ring at the central position; the donor set is less optically organised for coordination, and the pyridine donors have to 'stretch' further to coordinate, than is the case with e.g. a terpyridyl unit. This problem can be avoided by bidentate pyridyl–thiazole coordination with a pyridyl unit pendant, as occurs with L^3 in its Cu(II) and Zn(II) complexes.

Reaction of $Cd(ClO_4)_2 \cdot 6H_2O$ with one equivalent of L^3 in MeCN gives upon slow precipitation with ethyl acetate a pale yellow crystalline material, whose analytical data and ES mass spectra were in agreement with the formation of dinuclear $[Cd_2(L^3)_2](ClO_4)_4$. The crystal structure (Fig. 4) confirms formation of a dinuclear helicate, but also reveals some differences compared to the structures observed earlier with Ni(II), Cn(II) and Zn(II). The crystalline material is $[Cd_2(L^3)_2(MeCN)(ClO_4)][ClO_4]_3 \cdot MeCN$, in which a new coordination mode of L^3 is observed: the ligand is pentadentate, with one bidentate pyridyl–thiazole domain, one terdentate pyridyl–pyridyl–thiazole domain, and the terminal pyridyl ring of each ligand is not coordinated (Fig. 4b). In this way the ligand avoids having to use the sterically unfavourable pyridyl–thiazolyl–pyridyl terdentate units as binding sites. The irregular six-coordinate environment about each Cd(II) ion thus comprises a terdentate unit from one ligand, a bidentate unit from the other, and an additional monodentate ligand [MeCN at Cd(1), and a perchlorate anion at Cd(2)]. The ligands are arranged in a 'head-to-tail' arrangement such that the pendant pyridyl units are at opposite ends of the helicate. The N atoms of these are directed towards the Cd(II) centres, but these separations [Cd(1) ···N(151), 3.15 Å; and Cd(2)···N(251), 3.09 Å] are too large to represent significant bonding interactions. The remaining bond distances around the Cd(II) centres are largely unremarkable, in the range 2.3–2.4 Å, with the exception of Cd(1)–N(141) and Cd(2)–N(241) [2.576(5) and 2.573(5) Å, respectively] whose length may be ascribed to steric crowding at the centre of the helicate.

^1H NMR and $^1H/^1H$ correlation (COSY) spectra of $[Cd_2(L^3)_2(MeCN)(ClO_4)][ClO_4]_3$ in CD_3CN show the presence of 16 proton environments with chemical shifts lying between 6.9 and 8.6 ppm, consistent with the asymmetric coordination mode seen in the crystal structure with all proton environments in L^3 being inequivalent (Fig. 2c). The fact that the two ligands are equivalent in solution (16 resonances seen, not 32) means however that the sites occupied by terminal monodentate ligands—perchlorate and MeCN in the crystal—are equivalent in solution, which is to be expected in a coordinating solvent.

4. Concluding remarks

The structures of the Cd(II) complex with L^1, L^2 and L^3 show several significant differences to the structures of the complexes prepared with first-row transition metal dications Ni(II), Cu(II), Co(II) and Zn(II). Notably, the helical complexes of Cd(II) with L^1 and L^3 both have lower symmetry than the complexes with the first-row ion, and the seven-coordinate complex with L^2 is completely different, being monomeric due to the good fit of the Cd(II) ion in the pentadentate ligand cavity.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre CCDC Nos. 183 834–183 836 for the compounds $[Cd_2(L^1)_3(H_2O)][ClO_4]_4 \cdot 3MeCN$, $[Cd(L^2)(ClO_4)_2] \cdot MeNO_2$ and $[Cd_2(L^3)_2(MeCN)(ClO_4)][ClO_4]_3$, respectively. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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