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{Δ-1,4,7,10-Tetrakis[(*S*)-2-hydroxypropyl-κ*O*]-1,4,7,10-tetraazacyclododecane-κ^4*N*}cadmium(II) 4-nitrophenolate perchlorate hydrate

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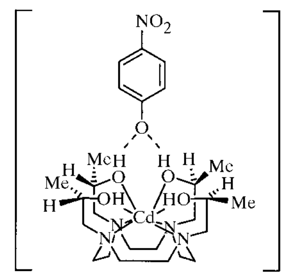
Crystallization of [Cd(*S*-thpc12)]$(ClO_4)_2\cdot H_2O$ {*S*-thpc12 is 1,4,7,10-tetrakis[(*S*)-2-hydroxypropyl]-1,4,7,10-tetraazacyclododecane} in the presence of sodium *p*-nitrophenolate forms the title complex, $[Cd(C_{20}H_{44}N_4O_4)](C_6H_4NO_3)(ClO_4)\cdot H_2O$, in which *p*-nitrophenolate and water separately hydrogen bond to a different pair of *cis*-related pendant hydroxyl groups which, together with the four N atoms, are themselves bound to Cd^{II} in an approximately square antiprismatic arrangement. The diastereoselectivity of the complex-forming process is apparent from the fact that both different disymmetric cations in the asymmetric unit have the same Δ helicity.

Comment

The ability of optically active pendant hydroxyl donor macrocyclic ligands based on cyclen (cyclen is 1,4,7,10-tetraazacyclododecane) to coordinate in a diastereoselective manner has been noted previously (Dhillon *et al.*, 1997, 1998). The structures of such complexes generally approximate to that of a square antiprism (Buøen *et al.*, 1982; Chin *et al.*, 1994; Hancock *et al.*, 1988; Luckay *et al.*, 1995) and as such have an inherent helicity which may be described as Λ or Δ according to whether the four hydroxyl donors are displaced anticlockwise or clockwise with respect to the N atom to which each is attached when the molecule is viewed from the plane of the hydroxyl groups towards the plane of the four N atoms along the C_4 axis (Dhillon *et al.*, 1995). Recent research has been directed towards attaching aromatic groups to each of the pendant arms in such a way that they will juxtapose to form a cavity suitable for the inclusion of smaller guest molecules (Smith *et al.*, 1999). In the present work, the attached group is the smaller methyl group and it was of interest to determine whether association with potential guest molecules for the larger complexes would occur in the absence of aromatic attachments.

There are two formula units of Δ[Cd(*S*-thpc12)] *p*-nitrophenolate perchlorate hydrate, (I), in the asymmetric unit which, apart from their orientation in the crystal, are very nearly identical, so they will be discussed as one (Fig. 1). There is a high degree of pseudosymmetry in the structure with average weak intensity data indicating approximate glide planes and a space group that tends towards *Pcab*. This space group is precluded because of the presence of enantiomerically pure chiral cations. Fig. 2 shows the relationship between the crystallographically independent species and illustrates one of the approximate glide planes.



(I)

The structures of the two cations (*A* and *B*) show the expected approximately square-antiprismatic geometry with Cd—O(hydroxyl) bond lengths in the range 2.349 (5)–2.626 (5) Å and Cd—N bond lengths in the range 2.435 (7)–

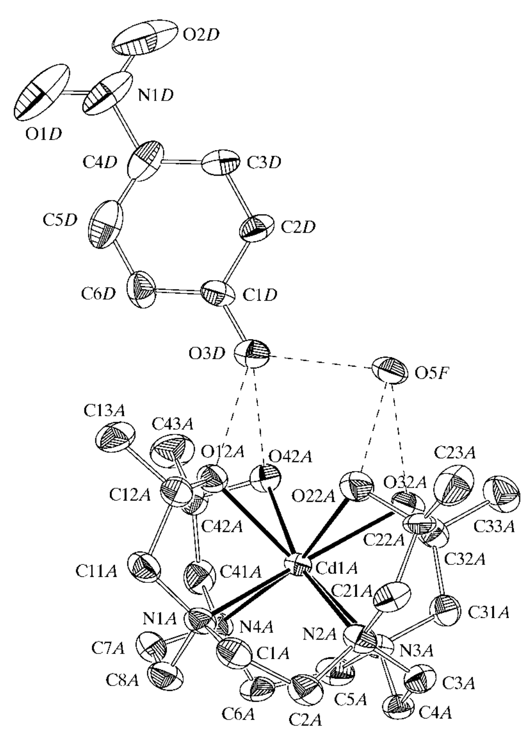


Figure 1
A perspective view of one of the crystallographically independent units in the structure. Hydrogen bonds are shown as dashed lines. Displacement ellipsoids are at the 50% probability level.

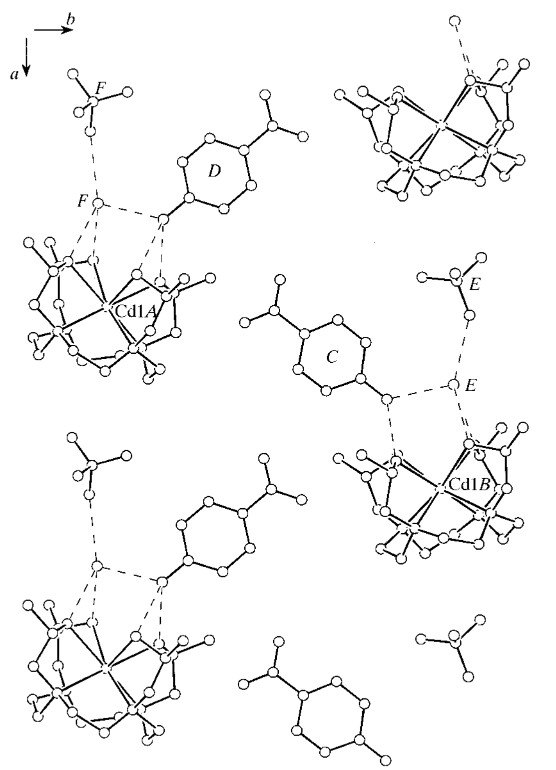


Figure 2
A view of one layer of the structure looking down **c**. *A*, *D* and *F* are related to *B*, *C* and *E* by the pseudo-*a*-glide plane perpendicular to **b**. Cations labelled *A* and *B* have the same chirality. Letters correspond to atom labels in Table 1.

2.492 (7) Å. The twist angles for the cations are *ca* +12.5° giving both complexes the Δ helicity. This is similar to the configuration for [K(*S*-thpc12)]$^+$ predicted by molecular orbital calculations (Dhillon *et al.*, 1997). The *p*-nitrophenolate is associated with two adjacent pendant hydroxyl donors *via* hydrogen bonds (Fig. 1 and Table 1). The Cd^{II}–phenolate O distances are 4.005 (6) and 3.993 (6) Å for *A* and *B*, respectively, eliminating the possibility of significant ionic interaction between these two charged centres. The displacement ellipsoids of the nitro groups indicate that there is considerable positional freedom for the *p*-nitrophenolate anions (Fig. 1). There are no base-stacking interactions between the *p*-nitrophenolates. The other pair of adjacent hydroxyl groups is hydrogen bonded to the water molecule (Fig. 1 and Table 1). The water molecule also acts as the donor in hydrogen bonds to phenolate and perchlorate O atoms.

The results of the crystal structure of (I) described here, show that *p*-nitrophenolate and water can both associate with the complex in the solid state. The electrical conductivity of the complex in *N,N*-dimethylformamide (DMF) solution (92 Ω^{-1} cm^2 mol^{-1}), however, is above the range normally shown by 1:1 electrolytes in this solvent (65–90 and 130–170 Ω^{-1} cm^2 mol^{-1}) for 1:1 and 1:2 electrolytes, respectively (Geary, 1971), showing that the *p*-nitrophenolate, at least, is partially dissociated in DMF, and probably more so in solvents of higher dielectric constant.

Experimental

[Cd(*S*-thpc12)]$(ClO_4)_2\cdot H_2O$: a solution of cadmium perchlorate hexahydrate (356 mg, 0.84 mmol) in dry ethanol (4 ml) was added over several minutes to a refluxing solution of *S*-thpc12 (229 mg, 0.56 mmol) in dry ethanol (10 ml). The solution was heated under reflux for 1 h, then allowed to cool slowly overnight. Very large white needles formed that were filtered off and washed with cold ethanol (2 ml) (yield 328 mg, 81%). ^{13}C NMR (DMSO-d_6) δ 62.01 (4C), 59.42 (4C), 49.99 (4C), 48.03 (4C), 20.96 (4C) p.p.m. Analysis calculated for $C_{20}H_{46}CdCl_2N_4O_{13}$: C 32.73, H 6.32, N 7.63%; found: C 32.88, H 5.98, N 7.64%; conductivity 153 Ω^{-1} cm^2 mol^{-1} (0.001 *M*, DMF) (1:2).

The title compound was prepared by adding sodium *p*-nitrophenolate (46 mg, 0.28 mmol) to a solution of [Cd(*S*-thpc12)]$(ClO_4)_2\cdot H_2O$ (205 mg, 0.28 mmol) in dry acetonitrile (15 ml). The yellow solution was then heated under reflux for 2 h, cooled and the solvent removed *in vacuo*. The yellow solid residue that remained was dissolved in boiling ethanol (10 ml) and allowed to cool slowly. Fine pale yellow needles formed that were collected by filtration and dried under vacuum (yield 131 mg, 60%). ^{13}C NMR (DMSO-d_6) δ 177.16 (1C), 131.77 (1C), 127.19 (2C), 118.94 (2C), 61.79 (4C), 59.77 (4C), 50.06 (4C), 48.09 (4C), 20.98 (4C) p.p.m. Analysis calculated for $C_{26}H_{50}CdClN_5O_{12}$: C 40.42, H 6.52, N 9.07%; found C 40.67, H 6.40, N 9.10%. Crystals suitable for X-ray analysis were grown by diffusion of ether into a solution of the complex in acetonitrile.

Crystal data

$[Cd(C_{20}H_{44}N_4O_4)](C_6H_4NO_3)$-$(ClO_4)\cdot H_2O$	D_x = 1.498 Mg m^{-3}
M_r = 772.57	Mo Kα radiation
Orthorhombic, $P2_12_12_1$	Cell parameters from 25 reflections
a = 13.9929 (11) Å	θ = 15.18–19.39°
b = 19.6661 (11) Å	μ = 0.78 mm^{-1}
c = 24.890 (3) Å	*T* = 200 (1) K
V = 6849.3 (11) Å^3	Tabular, pale yellow
Z = 8	0.40 × 0.24 × 0.20 mm

Data collection

CAD-4/PC diffractometer	R_{int} = 0.025
$\omega/2\theta$ scans	θ_{max} = 25.97°
Absorption correction: Gaussian (*ABSORB*; Hall *et al.*, 1995)	$h = -16 \rightarrow 17$
T_{min} = 0.831, T_{max} = 0.864	$k = 0 \rightarrow 24$
13 751 measured reflections	$l = 0 \rightarrow 30$
7229 independent reflections	3 standard reflections frequency: 120 min
5325 reflections with $I > 2\sigma(I)$	intensity decay: 2%

Refinement

Refinement on F^2	H-atom parameters not refined
$R(F)$ = 0.041	$w = 1/[\sigma^2(F^2)]$
$wR(F^2)$ = 0.070	$(\Delta/\sigma)_{max}$ = 0.003
S = 1.471	$\Delta\rho_{max}$ = 0.576 e Å^{-3}
6622 reflections	$\Delta\rho_{min}$ = −0.819 e Å^{-3}
811 parameters	

Attempts to collect the data at 150 K failed because the crystal appeared to undergo a phase change. At 200 K there was a high degree of streaking in parts of reciprocal space leading to large background imbalances for some reflections. 363 measured reflections where the background ratios were greater than 2:1 were removed from the data set. All reflections (6622) with $F^2 > 0$ were used in the refinement. Bond-length restraints for the bonds of the macrocycle and the phenyl C—C bonds were used in the refinement. The chirality followed from the synthesis. The absolute configuration was checked by refining a Flack (1983) parameter in early refinement cycles [−0.08 (5), 6533 Friedel-related reflections]. No additional rotational symmetry was found by *BUNYIP* (Hester & Hall, 1995).

Table 1
Selected geometric parameters (Å, °).

Distances not involving Cd are hydrogen bonds with the donor atom first.

Cd1*A*—N1*A*	2.492 (7)	Cd1*B*—N1*B*	2.488 (7)
Cd1*A*—N2*A*	2.458 (7)	Cd1*B*—N2*B*	2.435 (7)
Cd1*A*—N3*A*	2.480 (7)	Cd1*B*—N3*B*	2.498 (7)
Cd1*A*—N4*A*	2.454 (7)	Cd1*B*—N4*B*	2.463 (7)
Cd1*A*—O12*A*	2.349 (5)	Cd1*B*—O12*B*	2.359 (5)
Cd1*A*—O22*A*	2.626 (5)	Cd1*B*—O22*B*	2.544 (5)
Cd1*A*—O32*A*	2.438 (5)	Cd1*B*—O32*B*	2.448 (5)
Cd1*A*—O42*A*	2.534 (5)	Cd1*B*—O42*B*	2.543 (5)
O12*A*···O3*D*	2.630 (8)	O12*B*···O3*C*	2.627 (8)
O22*A*···O5*F*	2.746 (8)	O22*B*···O5*E*	2.970 (8)
O32*A*···O5*F*	2.720 (8)	O32*B*···O5*E*	2.645 (8)
O42*A*···O3*D*	2.797 (8)	O42*B*···O3*C*	2.749 (8)
O5*F*···O3*D*	2.627 (9)	O5*E*···O3*C*	2.615 (8)
O5*F*···O1*F*	2.803 (9)	O5*E*···O1*E*	2.798 (9)

Data reduction: *DIFDAT, SORTRF* and *ADDREF* in *Xtal* (Hall *et al.*, 1995); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *CRYLSQ* in *Xtal*; molecular graphics: *Xtal*; software used to prepare material for publication: *BONDLA* and *CIFIO* in *Xtal*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JA1006). Services for accessing these data are described at the back of the journal.

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