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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) salicylate perchlorate hemihydrate

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Key indicators

Single-crystal X-ray study
T = 168 K
Mean σ(C–C) = 0.010 Å
H-atom completeness 99%
Disorder in solvent or counterion
R factor = 0.037
wR factor = 0.061
Data-to-parameter ratio = 8.4

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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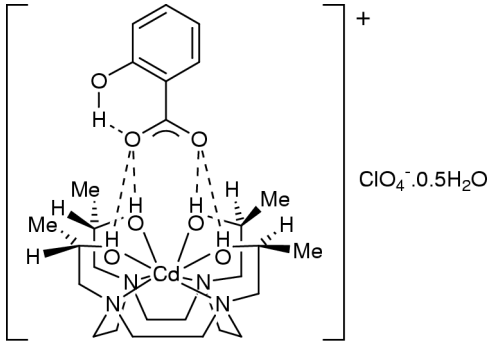
Crystallization of [Cd(*S*-thpc12)](ClO$_4$)$_2$·H$_2$O {*S*-thpc12 is 1,4,7,10-tetrakis[(*S*)-2-hydroxypropyl]-1,4,7,10-tetraazacyclododecane} in the presence of sodium salicylate (sodium *o*-hydroxybenzoate) forms a receptor complex, namely the title compound, [Cd(C$_{20}$H$_{44}$N$_4$O$_4$)(C$_7$H$_5$O$_3$)]ClO$_4$·0.5H$_2$O, in which salicylate is hydrogen bonded, *via* each of its two carboxylate O atoms, to pairs of *cis*-related pendant hydroxyl groups which, together with the four N atoms, are themselves bound to Cd^{II} in an approximately square *anti*-prismatic arrangement. The diastereoselectivity of the complex-forming process is apparent from the fact that only molecules having Δ helicity, associated with the spiralling of the pendant arms, are formed.

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 depending on whether the four hydroxyl donors are displaced anti-clockwise 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 pseudo-C_4 axis (Dhillon *et al.*, 1995). Recent research has been directed towards attaching aromatic groups to each of the pendant arms in such away that they will juxtapose to form a cavity suitable for the inclusion of smaller guest molecules (Smith *et al.*, 1999, 2002).



(I)

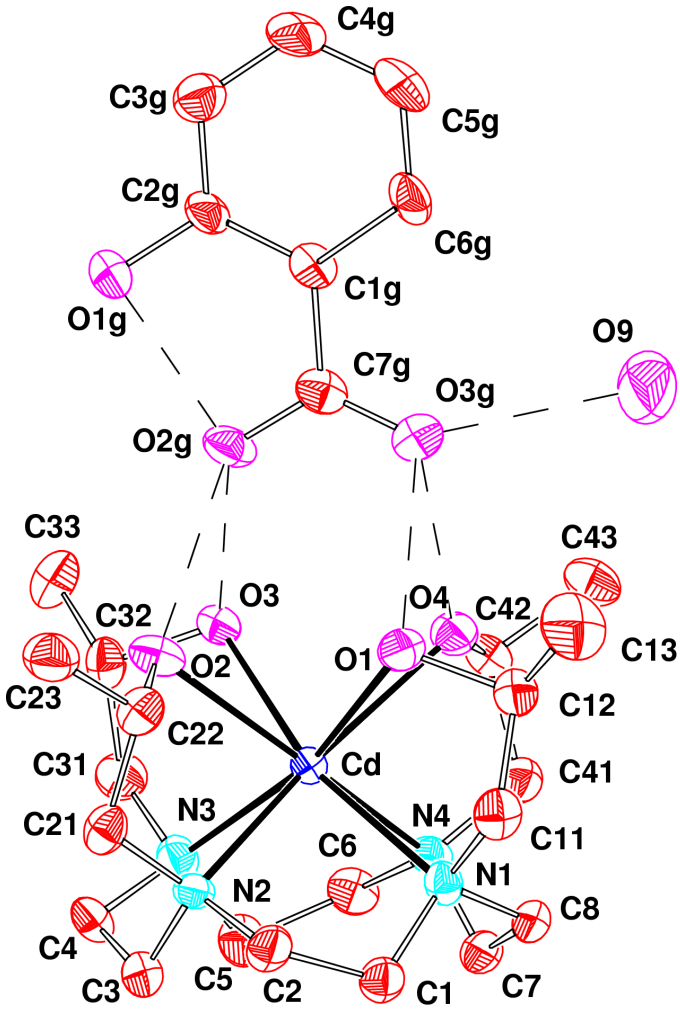


Figure 1
The structure of the title compound showing the atom labels. Hydrogen bonds are shown as dashed lines. Displacement ellipsoids are at the 50% probability level. H atoms and the perchlorate ion are not shown. O9 is the water molecule O atom.

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.

The structure of Δ-[Cd(*S*-thpc12)(salicylate)]ClO_4.0.5H_2O, (I) {*S*-thpc12 is 1,4,7,10-tetrakis[(*S*)-2-hydroxypropyl]-1,4,7,10-tetraazacyclododecane} (Fig. 1) shows the expected approximately square antiprismatic geometry with Cd–ligand atom bond lengths given in Table 1. The plane of the four O atoms is rotated clockwise by *ca* 15.0°, with respect to the plane of the four N atoms, giving the complex the Δ helicity. The salicylate anion associates with the complex through hydrogen bonding between pendant-arm hydroxyl groups and the carboxylate group; each carboxylate O atom of the salicylate acts as the receptor, and a pair of *cis*-related hydroxyl groups of the complex act as donors, with detailed geometry given in Table 2 and shown in Fig. 1. The hydroxyl group of the salicylate is internally hydrogen bonded to the adjacent carboxylate O atom and does not interact with the complex. Neither the perchlorate anion nor the water molecule play a direct role in the host–guest interaction. The Cd^{II}–carboxylate O distances are 3.918 (3) and 4.131 (3) Å, precluding the possibility of significant ionic interaction between these charged centres. There is a marked similarity in the configuration of hydrogen bonds from the Cd(*S*-thpc12)$^{2+}$ species to the guest in (I) and that found in the corresponding 4-nitrophenolate adduct (Davies *et al.*, 2000), although in the latter, the second *cis* pair of hydroxyl groups is hydrogen bonded to a water O atom.

The crystal structure of (I) shows that salicylate associates with the complex in the solid state. The electrical conductivity for the receptor complex in DMF solution (86 Ω^{-1} cm^2 mol^{-1}), however, is at the high end of 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), suggesting that the salicylate may be partially dissociated in DMF, and probably more so in solvents of higher dielectric constant.

Experimental

The title compound was prepared by adding sodium salicylate (sodium *o*-hydroxybenzoate) (53 mg, 0.33 mmol) to a solution of [Cd(*S*-thpc12)]$(ClO_4)_2\cdot H_2O$ (233 mg, 0.33 mmol) (Davies *et al.*, 2000) in dry methanol (15 ml). The sodium salt dissolved and after 5 min the solution became turbid. After heating under reflux for 2 h, the then clear solution was cooled overnight. Large colourless rod-like crystals of the pure product formed and were collected by filtration. Yield: 171 mg, 67%. ^{13}C NMR (DMSO-d_6): δ 172.72 (C=O), 161.73, 132.48, 130.53, 119.33, 117.21, 116.10, 61.55, 59.67, 50.32, 47.98, 20.97. Analysis calculated for $C_{27}H_{50}CdClN_4O_{11.5}$: C 42.53, H 6.61, N 7.35%; found: C 42.29, H 6.42, N 7.21%.

Crystal data

$[Cd(C_{20}H_{44}N_4O_4)(C_7H_5O_3)]ClO_4\cdot 0.5H_2O$
M_r = 762.57
Monoclinic, $P2_1$
a = 9.608 (2) Å
b = 12.423 (3) Å
c = 14.549 (4) Å
β = 107.47 (1)°
V = 1656.5 (7) Å^3
Z = 2
D_x = 1.531 Mg m^{-3}
Mo Kα radiation
Cell parameters from 6178 reflections
θ = 2.8–26.4°
μ = 0.80 mm^{-1}
T = 168 (2) K
Plate, colourless
0.35 × 0.28 × 0.07 mm

Data collection

Bruker *P*4 SMART diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Bruker, 1997)
T_{min} = 0.769, T_{max} = 0.945
6081 measured reflections
3539 independent reflections
3421 reflections with $F^2 > 0$
R_{int} = 0.032
θ_{max} = 26.4°
$h = -11 \rightarrow 11$
$k = -15 \rightarrow 13$
$l = -18 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.061
S = 1.42
3421 reflections
406 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + (0.01F_o^2)^2]^{1/2}$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.80 e Å^{-3}
$\Delta\rho_{min}$ = −0.90 e Å^{-3}
Absolute structure: Flack (1983), 2542 Friedel pairs
Flack parameter = 0.04 (3)

Table 1
Selected interatomic distances (Å).

Cd—O1	2.457 (5)	Cd—N1	2.467 (8)
Cd—O2	2.580 (5)	Cd—N2	2.473 (8)
Cd—O3	2.428 (4)	Cd—N3	2.440 (9)
Cd—O4	2.499 (5)	Cd—N4	2.490 (8)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*o*···O3*g*	0.92	1.87	2.776 (8)	170
O2—H2*o*···O2*g*	0.93	2.01	2.766 (7)	138
O3—H3*o*···O2*g*	0.99	1.90	2.814 (7)	153
O4—H4*o*···O3*g*	1.01	1.88	2.791 (7)	150
O1*g*—H1*g*···O2*g*	0.93	1.61	2.507 (4)	161
O9···O3*g*			2.792 (12)	
O9···O8^{i}			2.774 (12)	

Symmetry code: (i) $x, y, 1 + z$.

The occupancy of the water molecule O atom, O9, refined to 0.522 (12). As this was not significantly different from 0.5 and this fitted the analytical data, the occupancy of O9 was fixed at 0.5 in the final cycles. H atoms of the water molecule were not found. All other H atoms were observed in a difference map. Hydroxyl H-atom positions were obtained from the difference map and others were placed in calculated positions. Checking software shows that the structure has an approximate mirror plane. The existence of a true mirror plane is precluded by the presence of enantiomerically pure chiral cations and the successful refinement of a Flack parameter; Friedel-related reflections were treated as independent.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2000) and *Xtal*3.7 *ADDREF SORTRF* (Hall *et al.*, 2000); program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1994); program(s) used to refine structure: *Xtal*3.7 *CRYLSQ*; molecular graphics: *Xtal*3.7; software used to prepare material for publication: *Xtal*3.7 *BONDLA CIFIO*.

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