

Λ -{1,4,7,10-Tetrakis[(*S*)-2-hydroxypropyl- κ O]-1,4,7,10-tetraazacyclododecane- κ^4 N}cadmium(II) bis(2,4,6-trinitrophenolate) acetonitrile solvate

Christopher B. Smith,^a Stephen F. Lincoln,^b Max R. Taylor^a and Kevin P. Wainwright^{a*}

^aSchool of Chemistry, Physics and Earth Sciences, The Flinders University of South Australia, GPO Box 2100, Adelaide, SA 5001, Australia, and ^bDepartment of Chemistry, University of Adelaide, Adelaide, SA 5005, Australia
Correspondence e-mail: kevin.wainwright@flinders.edu.au

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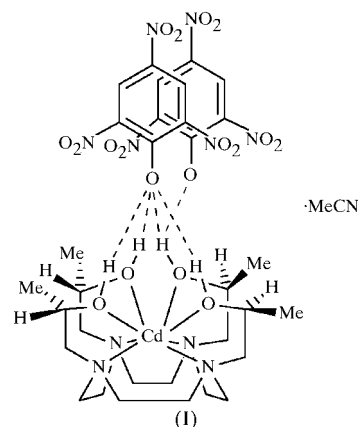
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Crystallization of [Cd(S-thpc12)](ClO₄)₂·H₂O {S-thpc12 is 1,4,7,10-tetrakis[(*S*)-2-hydroxypropyl]-1,4,7,10-tetraazacyclododecane} in the presence of two equivalents of sodium picrate monohydrate (sodium 2,4,6-trinitrophenolate monohydrate) diastereoselectively produces a neutral receptor complex, *viz.* the title compound, Λ -[Cd(C₂₀H₄₄N₄O₄)]-(C₆H₂N₃O₇)₂·CH₃CN. In this complex, two picrate anions hydrogen bond, *via* their phenolate moieties, to the pendant hydroxyl groups of the receptor which, together with the four N atoms, themselves bond to Cd^{II} in an approximately cubic arrangement. One picrate anion hydrogen bonds to all four hydroxyl groups, one of which also acts as the sole hydrogen-bond donor to the second picrate anion.

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 distorted cube or 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 Δ or Λ depending on 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 pseudo-*C*₄ axis (Dhillon *et al.*, 1995). Our 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, in particular aromatic anions (Smith *et al.*, 1999, 2002). In the present work, the attached group is the methyl group and it was of interest to us

to determine if, by using it, association with picrate (2,4,6-trinitrophenolate), which appears to be too large to be included within complexes having more enclosed cavities (Smith *et al.*, 2002), could be induced.



The cation of the title compound, (I), shows the expected approximately cubic coordination geometry about the Cd atom, with Cd–N bond lengths in the range 2.440 (2)–2.525 (3) Å and Cd–O(hydroxyl) bond lengths in the range 2.378 (2)–2.845 (2) Å (Table 1 and Fig. 1). The plane of the four O atoms is rotated clockwise by *ca* 14° with respect to the plane of the four N atoms, giving the complex the Λ helicity (left-handed screw form of the N–O chelating arms around

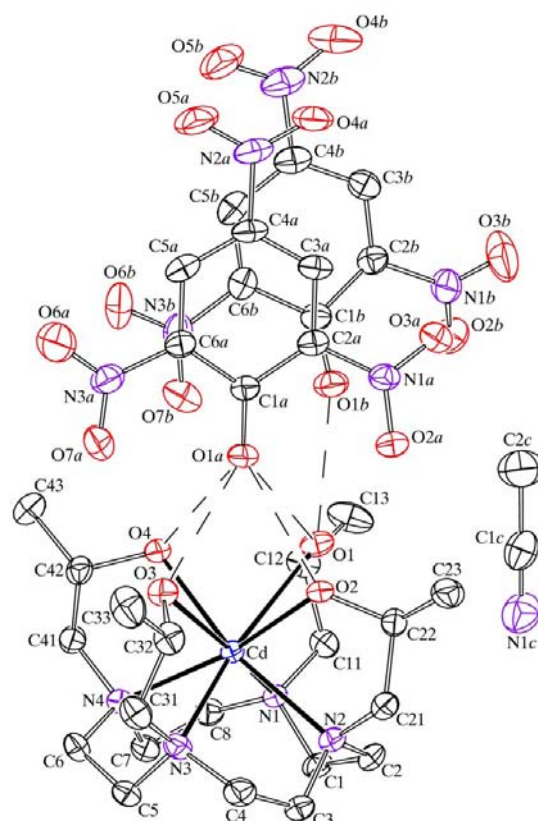


Figure 1
View of the title compound, showing the atom-labelling scheme. Hydrogen bonds are shown as dashed lines. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted.

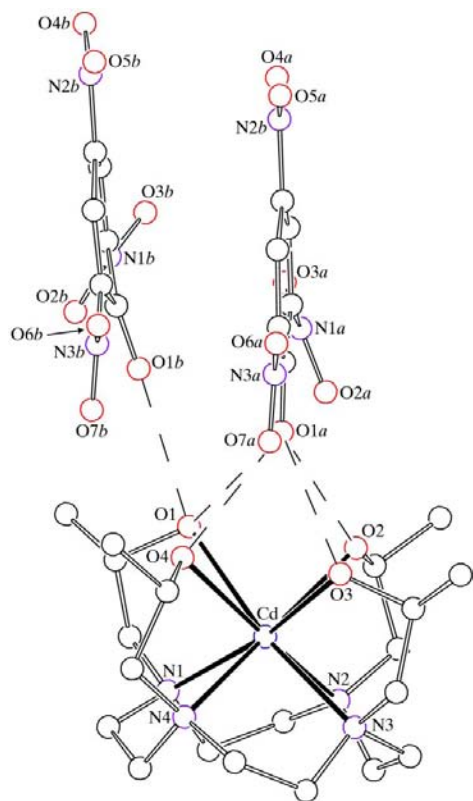


Figure 2

View of the title compound nearly edge-on to the trinitrophenolate planes. Hydrogen bonds are shown as dashed lines. Atoms are shown as spheres of arbitrary size and H atoms have been omitted.

the local fourfold axis). One picrate anion is located centrally above the cation, held in place by hydrogen bonds from all four hydroxyl O atoms to O1a, while the other anion packs in the crystal beside it and is hydrogen bonded only to hydroxyl atom O1 (Table 2 and Fig. 2). The planar regions of the two anions are approximately parallel, with a mean separation of 3.22 Å, and are offset in such a way as to prevent the eclipsing of any of the atoms (Fig. 3). The extra stability conferred on the crystal structure by the stacking of the anions and the steric factors involved in the formation of the bifurcated hydrogen bond from O1 to the electron-rich O1b centre apparently combine to weaken the Cd–O1 bond, which is 0.219 Å longer than any such bond currently recorded in the Cambridge Structural Database (Version 5.24; Allen, 2002). The Cd^{II} to phenolate O1a distance is 3.656 (2) Å, eliminating the possibility of significant ionic interaction between these charged centres. No association of the acetonitrile molecule present in the crystal lattice with the complex is apparent.

As judged from the range of hydrogen-bond donor–acceptor distances in (I) [2.840 (3)–3.197 (4) Å], the picrate anions are held less strongly than are 4-nitrophenolate anions in similar complexes; corresponding distances are 2.627–2.797 Å in {1,4,7,10-tetrakis[(*S*)-2-hydroxypropyl- κ O]-1,4,7,10-tetraazacyclododecane- κ^4 N]cadmium(II) 4-nitrophenolate perchlorate hydrate (Davies *et al.*, 2000), and 2.546 and 2.630 Å (twice) in {1,4,7,10-tetrakis[(*S*)-2-hydroxy-3-phenoxypropyl- κ O]-1,4,7,10-tetraazacyclododecane- κ^4 N]cadmium(II)

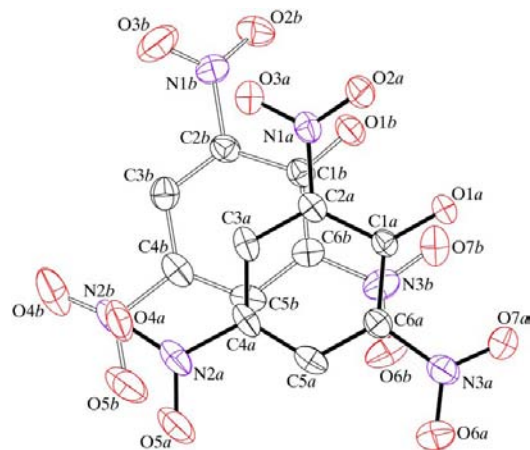


Figure 3

The stacking of the trinitrophenolate rings, viewed strictly normal to the least-squares plane. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted.

di-4-nitrophenolate (Smith *et al.*, 2002). This probably arises for two reasons: (i) the greater delocalization of the negative charge away from the O atom on the picrate corresponding to short C–O1a/O1b bonds (Table 1) compared with corresponding distances in the 4-nitrophenolate anions in the above structures [1.293 (10) and 1.277 (4) Å, respectively], making these picrate O atoms more like neutral hydrogen-bond acceptors, and (ii) a steric constraint is possibly more marked when associated with forming four hydrogen bonds to the same acceptor (O1a) rather than two, *i.e.* if the phenolate O atom moves any closer to the Cd atom, the hydrogen bonds will shorten, but the O–H...O angles will deviate further from linearity than they have already.

The crystal structure of (I) shows that both picrate anions associate with the complex cation in the solid state. The electrical conductivity for the receptor complex in *N,N*-dimethylformamide (DMF) solution ($128 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$), however, is almost in the range normally shown by 1:2 electrolytes in this solvent (130 – $170 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$; Geary, 1971), suggesting that both picrate anions are substantially dissociated in DMF, and probably more so in solvents of higher dielectric constant.

Experimental

The title compound, (I), was prepared by adding sodium picrate monohydrate (159 mg, 0.6 mmol; Siberrad & Phillips, 1908) to a solution of [Cd(S-thpc12)](ClO₄)₂·H₂O (212 mg, 0.3 mmol; Davies *et al.*, 2000) in dry acetonitrile (15 ml). The solid dissolved quickly and a mass of yellow precipitate filled the flask within 20 min. This precipitate was dissolved *in situ* by heating the suspension to the boiling point of the solvent. The resulting solution was then allowed to reflux for 2 h. Upon cooling, large yellow prisms of (I), suitable for X-ray diffraction studies, formed. These were filtered off and dried (yield 228 mg, 76%). ¹³C NMR (DMSO-*d*₆): δ 160.90, 141.96, 125.30, 124.27, 118.16 (CH₃CN), 61.93, 59.36, 49.95, 48.00, 20.94, 1.24 (CH₃CN). Analysis calculated for C₃₄H₅₁CdN₁₁O₁₈: C 40.26, H 5.07, N 15.19%; found: C 40.2, H 5.0, N 15.0%. Conductivity: $128 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ($1 \times 10^{-3} \text{ M}$, DMF).

Crystal data

$[\text{Cd}(\text{C}_{20}\text{H}_{44}\text{N}_4\text{O}_4)](\text{C}_6\text{H}_2\text{N}_3\text{O}_7)_2 \cdot \text{C}_2\text{H}_5\text{N}$	$D_x = 1.597 \text{ Mg m}^{-3}$
$M_r = 1014.25$	Mo $K\alpha$ radiation
Monoclinic, $P2_1$	Cell parameters from 6088 reflections
$a = 10.980 (2) \text{ \AA}$	$\theta = 1.2\text{--}26.4^\circ$
$b = 16.575 (3) \text{ \AA}$	$\mu = 0.61 \text{ mm}^{-1}$
$c = 11.640 (2) \text{ \AA}$	$T = 168 (2) \text{ K}$
$\beta = 95.51 (1)^\circ$	Irregular hexagonal plate, yellow
$V = 2108.6 (7) \text{ \AA}^3$	$0.60 \times 0.42 \times 0.15 \text{ mm}$
$Z = 2$	

Data collection

Bruker P4 diffractometer	4248 reflections with $F^2 > 0$
ω scans	$R_{\text{int}} = 0.016$
Absorption correction: empirical (SADABS; Bruker, 1997)	$\theta_{\text{max}} = 26.4^\circ$
$T_{\text{min}} = 0.779$, $T_{\text{max}} = 0.913$	$h = -13 \rightarrow 13$
15 919 measured reflections	$k = -20 \rightarrow 20$
8289 independent reflections	$l = -14 \rightarrow 14$

Refinement

Refinement on F^2	$\Delta\rho_{\text{max}} = 0.37 \text{ e \AA}^{-3}$
$R(F) = 0.023$	$\Delta\rho_{\text{min}} = -0.31 \text{ e \AA}^{-3}$
$wR(F^2) = 0.057$	Extinction correction: Larson (1970)
$S = 1.24$	Extinction coefficient: $13 (3) \times 10^2$
8289 reflections	Absolute structure: Flack (1983), 3983 Friedel pairs
578 parameters	Flack parameter = 0.018 (14)
H-atom parameters not refined	
$w = 1/[\sigma^2(F_o^2) + (0.05F_o^2)^2]^{1/2}$	
$(\Delta\sigma)_{\text{max}} = 0.001$	

Table 1

Selected interatomic distances (\AA).

Cd—O1	2.845 (2)	Cd—N2	2.440 (2)
Cd—O2	2.404 (2)	Cd—N3	2.525 (3)
Cd—O3	2.566 (2)	Cd—N4	2.469 (2)
Cd—O4	2.378 (2)	O1a—C1a	1.245 (3)
Cd—N1	2.459 (3)	O1b—C1b	1.236 (4)

Table 2

Hydrogen-bonding geometry (\AA , $^\circ$).

$D\text{---}H\cdots A$	$D\text{---}H$	$H\cdots A$	$D\cdots A$	$D\text{---}H\cdots A$
O1—H1 \cdots O1a	0.88	2.62	3.197 (4)	124
O1—H1 \cdots O1b	0.88	2.20	2.913 (3)	137
O2—H2 \cdots O1a	0.81	2.21	2.840 (3)	135
O3—H3 \cdots O1a	0.91	2.34	3.000 (4)	129
O4—H4 \cdots O1a	1.00	2.10	2.894 (3)	135

Hydroxyl H-atom positions were obtained from the four highest peaks in the penultimate difference map and others were placed in calculated positions.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1997) and *Xtal3.7 ADDREF SORTRF* (Hall *et al.*, 2000); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1994); program(s) used to refine structure: *Xtal3.7 CRYLSQ*; molecular graphics: *Xtal3.7*; software used to prepare material for publication: *Xtal3.7 BONDLA CIFIO*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1131). Services for accessing these data are described at the back of the journal.

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