

Chloro(2-[[5-(2-hydroxybenzyl-O)-1,5-diaza-1-cyclooctyl-*N,N'*]methyl]-phenolato-O)cadmium(II)

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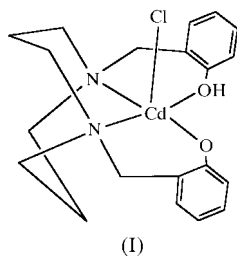
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The crystal structure of the title complex, [Cd(C₂₀H₂₅N₂O₂)Cl], reveals a hydrogen-bonded dimer composed of neutral molecules. The Cd^{II} center is five-coordinated by two O atoms of the pendant arms, two nitrogen donors of the 1,5-diazacyclooctane ring and a chloride anion. The coordination geometry of the complex could be described as a distorted square pyramid. The 1,5-diazacyclooctane backbone adopts a boat/chair configuration and the two phenol/phenolato groups have a dihedral angle of 101.3 (2)° between them. The coordinated phenolate and phenolic groups of inversion-related molecules form strong intermolecular O—H...O hydrogen bonds.

Comment

1,5-Diazacyclooctane (DACO) has several attractive features as a backbone for the development of ligands with exceptionally strong ligand fields (Musker & Hussain, 1966; Musker & Steffen, 1974), unique conformational requirements (Boeyens *et al.*, 1984) and the possibility for further functionalization (Mills *et al.*, 1990; Buonomo *et al.*, 1995). Some derivatives of DACO bearing functional pendant arms have been shown to strongly coordinate to metal centers, and to form a class of compounds having unique conformational



features (five-coordinate square pyramid or four-coordinate square planar) (Musker, 1992). The complexes can act as good functional model complexes for potential applications (Darensbourg *et al.*, 1992; Grapperhaus & Darensbourg,

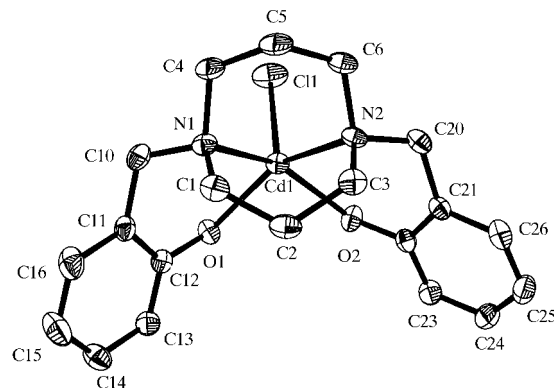


Figure 1
The molecular structure of the title complex with 30% probability displacement ellipsoids and H atoms omitted.

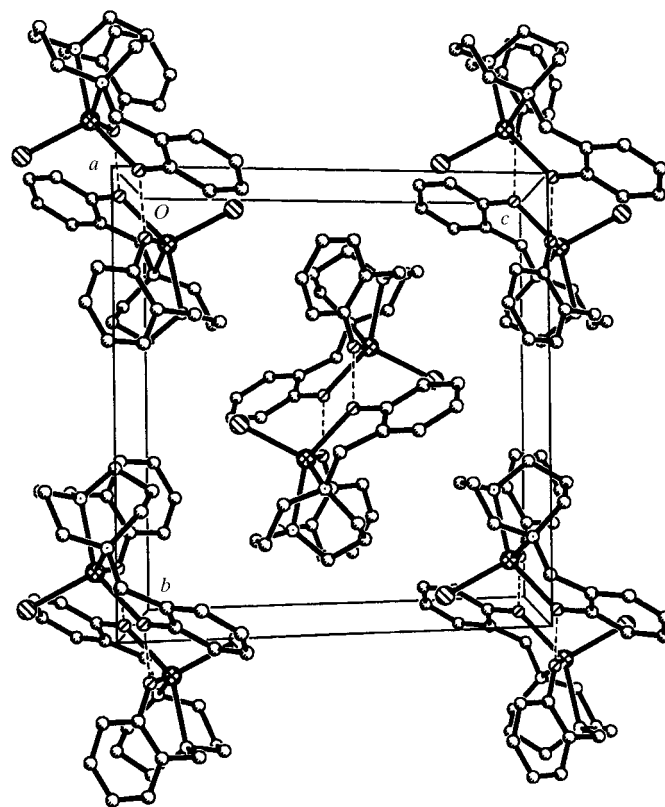


Figure 2
Packing diagram of the unit cell of the title complex.

1998). These interesting chemical properties prompted our investigation of DACO modified with functional donor pendants and novel functional complexes. Recently, we synthesized a new DACO ligand, 1,5-bis(2-hydroxybenzyl)-1,5-diazacyclooctane, and its cadmium(II) complex, (I).

The title complex is a neutral molecule (Fig. 1). The Cd^{II} center is bound to the ligand by two O atoms of the phenol pendants and one pair of nitrogen donors of the DACO ring. A chloride anion completes the coordination polyhedron. Since only one phenol donor is deprotonated, the complex is neutral. The Cd^{II} center is five-coordinate and the coordination geometry is best described as a square pyramid, with the

Table 1

Selected geometric parameters (Å, °).

Cd1—O1	2.241 (2)	Cd1—N2	2.357 (3)
Cd1—O2	2.242 (2)	Cd1—Cl1	2.4253 (10)
Cd1—N1	2.347 (3)		
O1—Cd1—O2	90.35 (8)	N1—Cd1—N2	78.80 (9)
O1—Cd1—N1	86.43 (9)	O1—Cd1—Cl1	107.24 (7)
O2—Cd1—N1	148.33 (9)	O2—Cd1—Cl1	104.40 (7)
O1—Cd1—N2	144.70 (9)	N1—Cd1—Cl1	106.64 (7)
O2—Cd1—N2	86.02 (9)	N2—Cd1—Cl1	107.67 (7)

chloride anion occupying the axial position. The τ value used to describe the degree of trigonal distortion is 0.06 (Addison *et al.*, 1984), which is nearly zero and indicates that the distortion is very small. The Cd^{II} center is 0.6493 (3) Å above the mean plane formed by four donors (N1, N2, O1 and O2) towards the apical chloride anion. The dihedral angle between the two phenol pendants is 101.3 (2)°.

The ligand adopts a chair/boat configuration, and gives rise to two six-membered chelate rings with an N2—Cd1—O2 angle of 86.18 (10)° and an N1—Cd1—O1 angle of 86.48 (10)°. The distances are all normal. The DACO ring of the ligand takes a chair/boat configuration and is bent so that the central methylene CH₂ (C2H₂) group of the boat form of the metalladiazacyclohexane ring (C1, C2, C3, N2, N1 and Cd) shields the metal center in the complex with an H···Cd distance of 2.80 Å. Thus, this methylene H atom effectively blocks the sixth coordination position to give the unusual five-coordinate complex. The distance between the N atoms (N1 and N2) of the DACO ring is thereby restricted, so that the N1—Cd—N2 bond angle [78.81 (11)°] is in a limited range and smaller than the O1—Cd—O2 angle [90.32 (10)°] due to the stereochemical requirements. Furthermore, the coordinated phenolate and phenolic groups between two adjacent ligands form strong intermolecular O—H···O hydrogen bonds [O···O 2.443 (4) Å and O—H···O 165.24 (3)°] (Fig. 2).

Experimental

The cyclooctyl ligand was prepared by the reaction of 1,5-diazacyclooctane hydrobromide (Buhle *et al.*, 1943; Billman & Dorman, 1962) and bromomethylphenyl acetate (Range, 1971) in toluene solution in the presence of KOH, and the final product was obtained by recrystallization from methanol as a white solid. Further details will be published elsewhere. A mixture of CdCl₂·2.5H₂O (114 mg, 0.5 mmol) and the 1,5-bis(2-hydroxybenzyl)-1,5-diazacyclooctane ligand (163 mg, 0.5 mmol) was dissolved in a mixture of methanol and acetone (20 ml). The colorless solution was filtered and left to stand at room temperature. Clear colorless single crystals were obtained within 1 d.

Crystal data

[Cd(C₂₀H₂₅N₂O₂)Cl]

$M_r = 473.27$

Monoclinic, $P2_1/c$

$a = 10.7364$ (11) Å

$b = 14.0507$ (13) Å

$c = 13.5546$ (13) Å

$\beta = 105.104$ (2)°

$V = 1974.1$ (3) Å³

$Z = 4$

$D_x = 1.592$ Mg m⁻³

Mo $K\alpha$ radiation

Cell parameters from 3450 reflections

$\theta = 1.96$ – 26.42 °

$\mu = 1.258$ mm⁻¹

$T = 298$ (2) K

Prism, colorless

$0.25 \times 0.20 \times 0.15$ mm

Data collection

Bruker SMART 1000 diffractometer
 ω scans
 Absorption correction: by integration (North *et al.*, 1968)
 $T_{\min} = 0.744$, $T_{\max} = 0.885$
 9248 measured reflections
 4048 independent reflections

2866 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.042$
 $\theta_{\text{max}} = 26.42$ °
 $h = -12 \rightarrow 13$
 $k = -17 \rightarrow 17$
 $l = -16 \rightarrow 8$
 Intensity decay: <1%

Refinement

Refinement on F^2

$R(F) = 0.033$

$wR(F^2) = 0.061$

$S = 0.935$

4048 reflections

239 parameters

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0274P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.013$

$\Delta\rho_{\text{max}} = 0.54$ e Å⁻³

$\Delta\rho_{\text{min}} = -0.68$ e Å⁻³

Extinction correction: *SHELXL97*

(Sheldrick, 1997)

All the H atoms were placed geometrically and in calculated positions, except for H20, which was refined isotropically [O2—H20 1.149 (2) Å].

Data collection and cell refinement: *SMART1000 Software* (Bruker, 1998); data reduction: *SAINT* (Bruker, 1998); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1996).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1538). Services for accessing these data are described at the back of the journal.

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