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trans-Bis(diethanolamine-*N*,*O*)bis(saccharinato-*N*)cadmium(II)

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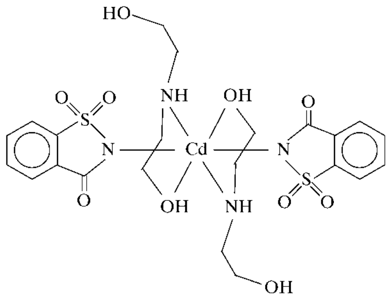
The structure of the title complex consists of isolated $[\mathrm{Cd(C_7H_4NO_3S)_2(C_4H_{11}NO_2)_2}]$ units. The $\mathrm{Cd^{2+}}$ cation lies on an inversion centre and is octahedrally coordinated by two *N*,*O*-bidentate diethanolamine (dea) and two *N*-bonded saccharinate (sac) ligands [saccharin is 1,2-benzisothiazol-3(2*H*)-one 1,1-dioxide]. The dea ligands constitute the equatorial plane of the octahedron, forming two five-membered chelate rings around the $\mathrm{Cd^{II}}$ ion, while the sac ligands are localized at the axial positions. The $\mathrm{Cd-N_{sac}}$, $\mathrm{Cd-N_{dea}}$ and $\mathrm{Cd-O_{dea}}$ bond distances are 2.3879 (12), 2.3544 (14) and 2.3702 (13) Å, respectively. The H atoms of the free and coordinated hydroxyl groups of the dea ligands are involved in hydrogen bonding with the carbonyl and sulfonyl O atoms of the neighbouring sac ions, while the amine H atom forms a hydrogen bond with the free hydroxyl O atom. The individual molecules are held together by strong hydrogen bonds, forming an infinite three-dimensional network.

Comment

This work is part of our extensive research into the synthesis and spectral, thermal and structural characterization of mixed-ligand complexes of the saccharinate ion (sac), also known as *o*-sulfobenzimide, with other bidentate *N*- and *O*-donor ligands, such as ethanolamine (Yilmaz, Andac *et al.*, 2001; Andac *et al.*, 2002), monoethanolethylenediamine (Yilmaz *et al.*, 2002) and diethanolamine (Yilmaz, Topcu *et al.*, 2001). In order to extend this investigation to group IIB metal complexes, we report here the structural characterization of the complex of cadmium(II) saccharinate with diethanolamine (dea), $[\mathrm{Cd(dea)_2(sac)_2}]$, (I).

A view of the molecule of (I) is shown in Fig. 1. The structure is built up of individual molecules, each containing a $\mathrm{Cd^{2+}}$ cation, two sac anions and two neutral dea molecules. The $\mathrm{Cd^{II}}$ ion sits on a centre of symmetry and the coordination around the $\mathrm{Cd^{II}}$ ion is a distorted $\mathrm{CdN_4O_2}$ octahedron, with two *N*-bonded sac and two bidentate dea ligands. Both dea and sac ligands occupy the *trans* positions of the octahedron.

The dea ligands are chelated to the $\mathrm{Cd^{II}}$ ion symmetrically through one hydroxyl O atom and the amine N atoms, forming two five-membered rings, and one ethanol group of the dea ligand remains uncoordinated. The two dea ligands constitute the equatorial plane of the octahedron, while the sac ligands are localized at the axial positions. The $\mathrm{Cd-N_{dea}}$ and $\mathrm{Cd-O_{dea}}$ bond distances are 2.3544 (14) and 2.3702 (13) Å, respectively. The $\mathrm{Cd-N_{sac}}$ bond distance of 2.3879 (12) Å is noticeably longer than those found in $[\mathrm{Cd(sac)_2(H_2O)_4}]\cdot\mathrm{2H_2O}$ (2.323 Å; Haider *et al.*, 1984), $[\mathrm{Cd_2(sac)_2(im)_4}]$ [im is imidazole; 2.323 (5) and 2.367 (5) Å; Jianmin *et al.*, 1997] and $[\mathrm{Cd(sac)_2(bipy)_2}]$ [bipy is 2,2′-bipyridine; 2.320 (4) Å; Johns *et al.*, 2001], and also somewhat shorter than the values reported for $[\mathrm{Cd(sac)_2(NH_3)_4}]$ [2.423 (8) Å; Pascual, 1995] and $[\mathrm{Cd(sac)_2(HydEt\text{-}en)_2}]$ [HydEt-en is (2-hydroxyethyl)-ethylenediamine; 2.412 (4) and 2.525 (5) Å; Yilmaz *et al.*, 2002]. The large differences in the reported $\mathrm{Cd-N_{sac}}$ bond distances seem to be a consequence of the presence of sterically hindered groups in the co-ligands, although $\mathrm{NH_3}$ does not obey the rule. The interatomic distances within both sac and dea ligands are similar to the corresponding values found in the free Hsac molecule (Okaya, 1969) and $[\mathrm{Cu(SCN)_2(dea)_2}]$ (Yilmaz *et al.*, 2000), respectively.



(I)

A packing diagram with the hydrogen-bonding scheme is shown in Fig. 2. Both sac ions are essentially planar, with an

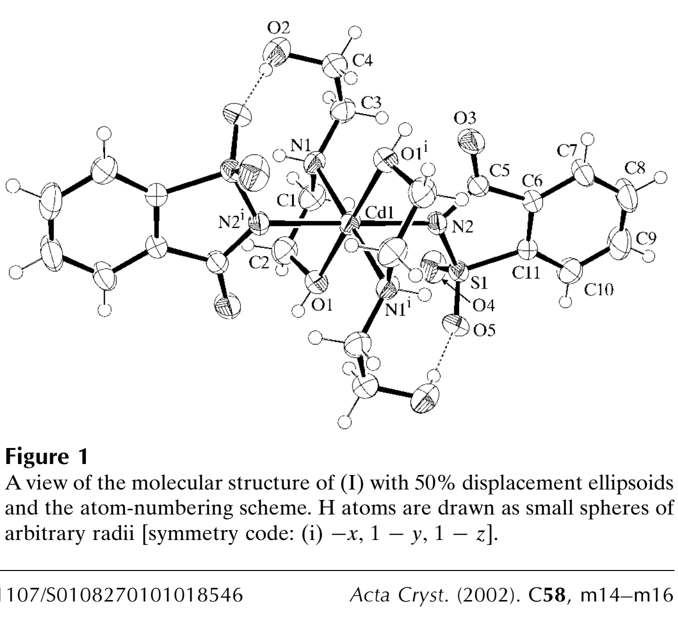


Figure 1
A view of the molecular structure of (I) with 50% displacement ellipsoids and the atom-numbering scheme. H atoms are drawn as small spheres of arbitrary radii [symmetry code: (i) $-x, 1-y, 1-z$].

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r.m.s. deviation of 0.02 Å. The sac ions of adjacent molecules are almost perpendicular to each other and the dihedral angles between the corresponding planes with symmetry code $1 - x$, $y - \frac{1}{2}, \frac{3}{2} - z$ are 86.44 (3)°. The individual molecules are linked by intermolecular hydrogen bonds, forming infinite three-dimensional zigzag chains.

The H atom of the free hydroxyl group (O2) of the dea ligand forms a relatively strong intramolecular hydrogen bond with the sulfonyl O atom (O5) of the sac ligand [O2···O5 2.785 (2) Å; symmetry code: $-x, 1 - y, 1 - z$], while the H atoms of the coordinated hydroxyl (O1) and amine (N1) groups of the dea ligand are involved in intermolecular hydrogen bonding with the carbonyl O atom [O1···O3 2.818 (2) Å; symmetry code: $x - 1, y, z$] and the free hydroxyl O atom [N1···O2 3.205 (2) Å; symmetry code: $-x, -y, 1 - z$] of neighbouring molecules, respectively. Furthermore, some weak interactions between the phenyl H atoms on C7 and C10 and the hydroxyl and sulfonyl O atoms (O1, O4 and O5) also occur (Table 2).

The sum of the van der Waals radii of H and O [1.20 + 1.52 = 2.72 Å; calculated using *PLATON* (Spek, 2000)] is somewhat longer than the distances found for the C7—H7···O5 (2.53 Å) and C10—H10···O4 (2.58 Å) interactions, with C—H···O angles of 133 and 169°, respectively, and somewhat shorter than the distance found for C7—H7···O1 (2.84 Å), with a C—H···O angle of 144°. Therefore, the C10—H10···O4 interaction, with a nearly linear angle, may be considered as a weak hydrogen bond, while the C7—H7···O5 and C7—H7···O1 interactions, with highly deviated angles, are classical van der Waals contacts (Steiner, 1997; Steiner & Desiraju, 1998). Additionally, the phenyl H atom on C9 interacts with the ring centroid, *Cg*, of the phenyl ring of the sac anion, forming a non-conventional hydrogen bond of the C—H···π type (Madhavi *et al.*, 1997). The hydrogen bonds maintain the crystal structure by forming an infinite three-dimensional lattice.

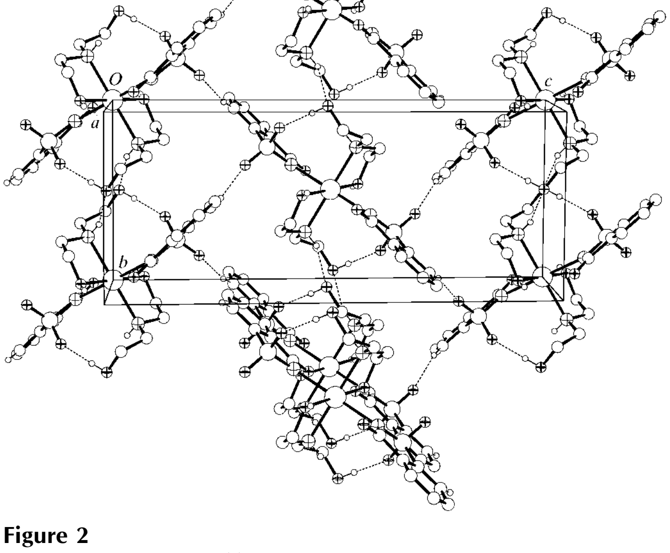

Figure 2
A packing diagram for (I) showing the hydrogen-bonding scheme.

Experimental

To synthesize (I), previously prepared $[Cd(sac)_2(H_2O)_4]\cdot 2H_2O$ (1.17 g, 2.0 mmol) was dissolved in 40 ml of a methanol–2-propanol mixture (1:1) at 333 K with stirring. Next, dea (0.21 g, 4.0 mmol) was added dropwise at 333 K and the solution was cooled to room temperature. The resulting solution was maintained at room temperature until evaporation resulted in the formation of colourless crystals of (I) suitable for X-ray diffraction analysis.

Crystal data

$[Cd(C_7H_4NO_3S)_2(C_4H_{11}NO_2)_2]$
$M_r = 687.02$
Monoclinic, $P2_1/c$
$a = 7.8444$ (3) Å
$b = 8.4654$ (3) Å
$c = 20.4378$ (8) Å
$\beta = 94.188$ (1)°
$V = 1353.57$ (9) Å^3
$Z = 2$
$D_x = 1.686$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 6160 reflections
$\theta = 2.6$–30.0°
$\mu = 1.02$ mm^{-1}
$T = 298$ (2) K
Chunk, colourless
0.36 × 0.25 × 0.18 mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)
$T_{min} = 0.687$, $T_{max} = 0.832$
11 324 measured reflections
3933 independent reflections
3314 reflections with $I > 2\sigma(I)$
$R_{int} = 0.025$
$\theta_{max} = 30°$
$h = -10 \rightarrow 11$
$k = -9 \rightarrow 11$
$l = -28 \rightarrow 28$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.025$
$wR(F^2) = 0.064$
$S = 1.03$
3933 reflections
187 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0361P)^2 + 0.0284P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.30$ e Å^{-3}
$\Delta\rho_{min} = -0.30$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cd1—N1	2.3544 (14)	O2—C4	1.417 (2)
Cd1—N2	2.3879 (12)	O3—C5	1.2303 (19)
Cd1—O1	2.3702 (13)	C1—C2	1.500 (3)
S1—O4	1.4291 (13)	C3—C4	1.502 (3)
S1—O5	1.4368 (13)	C5—C6	1.492 (2)
S1—N2	1.6252 (13)	C6—C11	1.382 (2)
S1—C11	1.7610 (16)	C6—C7	1.384 (2)
N1—C3	1.477 (2)	C7—C8	1.379 (3)
N1—C1	1.483 (2)	C8—C9	1.372 (3)
N2—C5	1.3606 (19)	C9—C10	1.397 (3)
O1—C2	1.430 (2)	C10—C11	1.374 (2)
N1—Cd1—O1	75.04 (5)	O1—Cd1—N2	86.44 (4)
N1—Cd1—N2	88.22 (5)		

H atoms on O and N atoms were found in difference maps and were refined positionally with geometric restraints (O—H = 0.82 Å and N—H = 0.89 Å) and with $U_{iso}(H) = 1.2U_{eq}(N,O)$. The remaining H atoms were placed in calculated positions and refined with a riding model, with C—H = 0.93–0.97 Å and $U_{iso}(H) = 1.2U_{eq}(C)$.

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

*Cg*1 is the centroid of the phenyl ring of the sac anion.

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1N$\cdots$O2$^{\rm i}$	0.88 (2)	2.40 (2)	3.205 (2)	152 (2)
O1—H1O$\cdots$O3$^{\rm ii}$	0.80 (2)	2.05 (2)	2.819 (2)	159 (2)
O2—H2O$\cdots$O5$^{\rm iii}$	0.81 (2)	1.98 (2)	2.785 (2)	177 (2)
C7—H7$\cdots$O5$^{\rm iv}$	0.93	2.53	3.231 (2)	133
C7—H7$\cdots$O1$^{\rm iv}$	0.93	2.84	3.637 (2)	144
C10—H10$\cdots$O4$^{\rm v}$	0.93	2.58	3.502 (2)	169
C9—H9$\cdots$*Cg*1$^{\rm vi}$	0.93	2.85	3.707 (2)	153

Symmetry codes: (i) $-x, -y, 1-z$; (ii) $x-1, y, z$; (iii) $-x, 1-y, 1-z$; (iv) $1+x, y, z$; (v) $-x, \frac{1}{2}+y, \frac{3}{2}-z$; (vi) $1-x, \frac{1}{2}+y, \frac{3}{2}-z$.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1092). Services for accessing these data are described at the back of the journal.

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