

Structure of a Dinuclear Saden(ethanol)cadmium(II) Complex

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Abstract. Bis[μ -{*N*-[2-(2-aminoethylamino)ethyl]salicylideneaminato-*O*}-ethanol]cadmium(II) bisperchlorate, $[\{Cd(C_{11}H_{16}N_3O)(C_2H_5OH)\}_2(ClO_4)_2]$, $M_r = 464.2$, monoclinic, $C2/c$, $a = 13.665$ (5), $b = 12.868$ (3), $c = 20.470$ (6) Å, $\beta = 96.51$ (3)°, $V = 3576$ (2) Å³, $Z = 8$, $D_m = 1.72$ (2), $D_x = 1.724$ (1) Mg m⁻³, Mo $K\alpha$, $\lambda = 0.70926$ Å, $\mu = 1.35$ mm⁻¹, $F(000) = 1872$, $T = 293$ K, $R = 0.058$, 3259 unique observed reflections. The structure consists of dinuclear $[Cd(saden)(EtOH)]_2^{2+}$ (saden = $C_{11}H_{16}N_3O^-$) complexes and perchlorate anions. The environment of Cd is a strongly distorted octahedron, CdN_3O_3 .

Introduction. Complexes with unsymmetrical tetradentate Schiff bases are interesting model systems for investigation of various oxygen-transfer metallo-enzymes (Jones, Summerville & Basolo, 1979). Four structures with the saden ligand, *N*-[2-(2-aminoethylamino)ethyl]salicylideneaminato-*O,N,N',N''* (1-), coordinated to soft metal ions are known: $[Ni(saden)]B(C_6H_5)_4$ (Rotondo, Cusmano Priolo, Romeo, Bruno & Bombieri, 1983), $[Ni(saden)]ClO_4$ (Podlahová, Knižek, Loub & Hašek, 1988), $[Ni(saden)]NCS$ (Loub, Podlahová, Kopf & Weiss, 1989) and $[Pd(saden)]ClO_4$ (Kratohvil, Nováková, Haber, Ondráček & Hájek, 1989). The Cd^{2+} ion can be expected to influence drastically the usual square-planar arrangement of the complexes, mainly because of its larger diameter and d^{10} configuration. The X-ray structural determination of the title compound was therefore undertaken.

Experimental. The complex was prepared from methanol solution containing equal amounts of $Cd(ClO_4)_2 \cdot 6H_2O$ and the ligand Hsaden, to which one equivalent of KOH in water-methanol mixture was added slowly with vigorous stirring. The precipitated $KClO_4$ was filtered off and the yellow filtrate

evaporated to dryness. The crude product was extracted with trichloromethane and dissolved in hot ethanol. The solution was allowed to stand for a few days in air. Pale yellow crystals were obtained. They were unstable in air and stable to X-rays. The density was determined pycnometrically. A spherical crystal of radius $r = 0.12$ mm was used for the X-ray measurements with a Syntex $P2_1$ diffractometer with graphite monochromator. The lattice parameters were obtained by least-squares fit of 15 reflections, $9 \leq 2\theta \leq 25^\circ$. Intensity data were collected using θ - 2θ scan, absorption was ignored ($\mu R = 0.162$); max. $\sin\theta/\lambda = 0.65$ Å⁻¹; h 0→17, k 0→16, l -26→26. Three standard reflections were measured after each 97 reflections. Their intensity variations were less

Table 1. Atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($\text{Å}^2 \times 10^3$) of non-H atoms, with e.s.d.'s in parentheses

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Cd	-503.4 (3)	2073.4 (4)	3251.8 (2)	48.7 (4)
Cl	3504 (2)	43 (2)	1031 (1)	78 (1)
O(1)	934 (3)	1785 (4)	2844 (2)	53 (1)
O(2)	3468 (6)	1115 (4)	1128 (4)	128 (2)*
O(3)	3805 (8)	-454 (7)	1612 (4)	230 (4)*
O(4)	4190 (6)	-156 (6)	582 (4)	156 (2)*
O(5)	2591 (5)	-305 (7)	756 (5)	182 (3)*
O(6)	-1019 (5)	297 (5)	3430 (4)	89 (3)
N(1)	-1147 (5)	3719 (5)	3039 (3)	72 (2)
N(2)	-1560 (5)	2402 (6)	4096 (3)	68 (2)
N(3)	511 (5)	2033 (6)	4207 (3)	72 (3)
C(1)	-2065 (6)	3848 (7)	3360 (4)	71 (3)
C(2)	-1826 (7)	3502 (7)	4061 (5)	80 (3)
C(3)	-1048 (8)	2085 (8)	4698 (5)	91 (4)
C(4)	-12 (8)	2404 (14)	4777 (4)	117 (5)
C(5)	1436 (6)	1821 (7)	4296 (4)	72 (3)
C(6)	2105 (5)	1652 (6)	3811 (4)	55 (2)
C(7)	1850 (5)	1672 (5)	3121 (3)	49 (2)
C(8)	2609 (5)	1559 (6)	2730 (4)	55 (2)
C(9)	3580 (5)	1463 (6)	2995 (4)	64 (3)
C(10)	3837 (6)	1398 (7)	3666 (4)	78 (3)
C(11)	3091 (6)	1486 (6)	4060 (4)	67 (3)
C(12)	309 (12)	-838 (17)	3523 (11)	183 (11)
C(13)	-796 (15)	-751 (21)	3244 (14)	240 (17)

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* U_{iso} .

Table 2. *Interatomic distances (Å) and angles (°)*

Cd—Cd ⁱ	3.511 (1)	O(1)—Cd—O(1 ⁱ)	75.4 (1)
Cd—O(1)	2.250 (4)	O(1)—Cd—O(6)	100.4 (2)
Cd—O(1 ⁱ)	2.284 (4)	O(1)—Cd—N(1)	114.2 (2)
Cd—O(6)	2.432 (6)	O(1)—Cd—N(2)	155.9 (2)
Cd—N(1)	2.315 (6)	O(1)—Cd—N(3)	80.9 (2)
Cd—N(2)	2.413 (6)	O(1 ⁱ)—Cd—O(6)	87.0 (2)
Cd—N(3)	2.266 (6)	O(1 ⁱ)—Cd—N(1)	85.0 (2)
O(1)—O(1 ⁱ)	2.772 (6)	O(1 ⁱ)—Cd—N(2)	128.6 (2)
Cl—O(2)	1.395 (7)	O(1 ⁱ)—Cd—N(3)	155.3 (2)
Cl—O(3)	1.372 (9)	O(6)—Cd—N(1)	141.0 (2)
Cl—O(4)	1.408 (8)	O(6)—Cd—N(2)	81.4 (2)
Cl—O(5)	1.384 (8)	O(6)—Cd—N(3)	90.5 (2)
N(1)—C(1)	1.489 (11)	N(1)—Cd—N(2)	74.3 (2)
C(1)—C(2)	1.502 (13)	N(1)—Cd—N(3)	111.4 (2)
C(2)—N(2)	1.461 (12)	N(2)—Cd—N(3)	75.1 (2)
N(2)—C(3)	1.405 (12)	Cd—O(1)—Cd ⁱ	101.5 (1)
C(3)—C(4)	1.464 (16)	O(2)—Cl—O(3)	110.5 (5)
C(4)—N(3)	1.511 (12)	O(2)—Cl—O(4)	108.0 (5)
N(3)—C(5)	1.286 (9)	O(2)—Cl—O(5)	109.5 (5)
C(5)—C(6)	1.440 (11)	O(3)—Cl—O(4)	109.0 (6)
C(6)—C(7)	1.416 (10)	O(3)—Cl—O(5)	111.7 (6)
C(7)—O(1)	1.322 (8)	O(4)—Cl—O(5)	108.2 (5)
C(7)—C(8)	1.388 (10)	N(1)—C(1)—C(2)	106.7 (6)
C(8)—C(9)	1.381 (10)	C(1)—C(2)—N(2)	111.2 (7)
C(9)—C(10)	1.381 (11)	C(2)—N(2)—C(3)	114.9 (7)
C(10)—C(11)	1.374 (12)	N(2)—C(3)—C(4)	113.3 (7)
C(11)—C(6)	1.402 (11)	C(3)—C(4)—N(3)	111.4 (7)
C(12)—C(13)	1.564 (30)	C(4)—N(3)—C(5)	120.0 (6)
C(13)—O(6)	1.443 (26)	N(3)—C(5)—C(6)	128.7 (6)
		C(5)—C(6)—C(7)	125.5 (6)
		C(6)—C(7)—C(8)	117.2 (6)
		C(7)—C(8)—C(9)	122.0 (6)
		C(8)—C(9)—C(10)	121.4 (7)
		C(9)—C(10)—C(11)	117.2 (7)
		C(10)—C(11)—C(6)	123.1 (7)
		C(5)—C(6)—C(11)	115.6 (6)
		C(7)—C(6)—C(11)	118.9 (6)
		C(6)—C(7)—O(1)	122.9 (5)
		O(1)—C(7)—C(8)	119.8 (5)
		C(12)—C(13)—O(6)	101.1 (1.7)

Symmetry code: (i) = $-x, y, \frac{1}{2} - z$.

than 2%. 4850 reflections were measured of which 4133 were unique and 3259, with $I \geq 1.96\sigma(I)$, were subsequently used. The structure was solved by the heavy-atom method. F magnitudes were used in full-matrix least-squares refinement. All H atoms, except H(O6), were placed in calculated positions (Sheldrick, 1976) assuming sp^3 or sp^2 hybridization at the C and N atoms, and C—H and N—H distances of 1.08 Å. All positional parameters except those of H atoms were then refined. The ClO_4^- anion was first refined using the bond-length constraints Cl—O 1.39 (1) Å and O—O 2.27 (1) Å. Anisotropic thermal parameters of Cd, Cl, O(1), O(6), N and C atoms, and isotropic thermal parameters of O(2)—O(5) and the H atoms were refined [one for H bonded to N and C(1)—C(4), one for H bonded to C(5) and C(8)—C(11), and one for H bonded to C(12) and C(13)]. The final error indicators are $R = 0.058$ and $wR = 0.089$ with weights $w = 3.1/[\sigma^2(F_o) + 0.0009F_o^2]$; in the last refinement cycle $(\Delta/\sigma)_{\max} = 0.276$ [for $U_{12}C(12)$]; $\Delta\rho_{\max}/\Delta\rho_{\min} = 1.15/-1.00 \text{ e } \text{Å}^{-3}$; 201 parameters were refined. Atomic scattering factors and corrections for anomalous dispersion were from *Inter-*

national Tables for X-ray Crystallography (1974); ICL 4-72 computer, programs *SHELXS86* (Sheldrick, 1986) and *SHELX76* (Sheldrick, 1976).*

Discussion. The final atomic parameters are given in Table 1. Selected intramolecular distances and angles are given in Table 2. The structure consists of $[\text{Cd}(\text{saden})(\text{EtOH})]_2^{2+}$ dimeric cations and perchlorate anions. A projection of the cation onto the ac plane is depicted in Fig. 1. The cation possesses twofold rotation symmetry with the axis normal to the ac plane. The Cd atoms are slightly asymmetrically bridged by the O(1) and O(1ⁱ) atoms ($i = -x, y,$

* Lists of H-atom parameters, anisotropic thermal parameters and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52452 (23 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

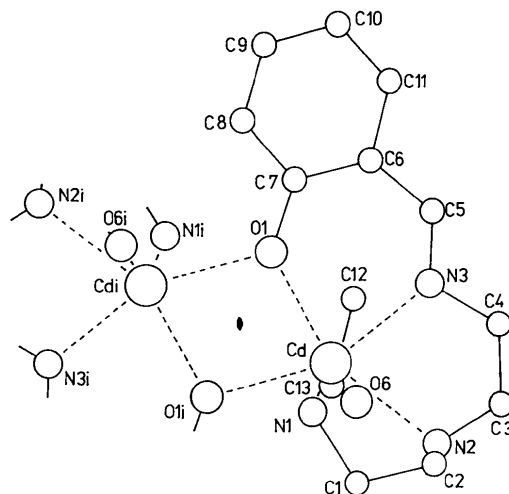
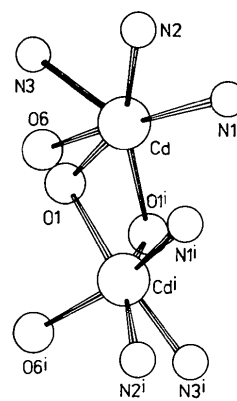
Fig. 1. Projection of the complex cation onto the ac plane with atom numbering (H atoms omitted).

Fig. 2. Perspective view of the coordination environment of the Cd atoms.

$\frac{1}{2}-z$). The resulting four-membered ring is significantly puckered as can be seen from the dihedral angles between the CdO(1)O(1^b) and Cd^bO(1)O(1^b) planes, 156.1 (4)°, and between the CdCd^bO(1) and CdCd^bO(1^b) planes, 150.0 (3)°.

The coordination polyhedron around Cd can be approximated as a strongly distorted octahedron formed by the saden ligand atoms N(1), N(2), N(3), O(1) and O(1^b), and by the O(6) atom of ethanol. The Cd, N(2), N(3), O(1), O(1^b) atoms are coplanar within ± 0.077 (8) Å. Fig. 2 shows a perspective view of the coordination environment of the Cd atom. Since the saden ligand is designed perfectly to accommodate small metal ions into a square planar cage formed by its four donor atoms, it is not surprising that the large Cd²⁺ ion (which moreover displays a profound tendency to higher coordination numbers than four) has a considerably distorted environment in its saden complex. In contrast, distortions within the ligand backbone are relatively small. When compared to, e.g., the Ni (Podlahová, Knížek, Loub & Hašek, 1988) and Pd (Kratochvíl, Nováková, Haber, Ondráček & Hájek, 1989) complexes, the most important difference concerns the N(2)—M ring junction which is *trans* for M = Ni, Pd but *cis* for M = Cd, in agreement with folding of the ligand in order to enable a facial coordination of its N atoms. Further, both five-membered chelate rings of the Cd complex assume a half-chair conformation in contrast to the Ni and Pd complexes where the rings involving N(2) and N(3) are envelopes. Finally, all three chelate rings in the Cd complex are significantly more puckered than their Ni and Pd analogues. This can be demonstrated by the N(1)—

C(1)—C(2)—N(2), N(2)—C(3)—C(4)—N(3) and M—N(3)—C(5)—C(6) torsion angles whose absolute values are 63.0 (5), 54.4 (5) and 6.8 (6)° for Cd, 50.6 (7), 42.1 (6) and 2.3 (5)° for Ni, and 53.2 (7), 46.1 (6) and 3.2 (6)° for Pd. The conformation of the six-membered chelate ring is close to a very flat distorted boat.

The bonding between the complex cations and the perchlorate anions is predominantly ionic, the shortest distance being 3.08 (1) Å between O(2) and N(2^b) with the geometry at H(N2^b) satisfying the criterion for a weak hydrogen bond (Taylor & Kennard, 1982): O(2)⋯H(N2^b) 2.37 Å, O(2)⋯H(N2^b)—N(2^b) 121°.

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Structure of Bis(2-methyl-1,2-propanediamine)nickel(II) Dibromide

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Abstract. [Ni(C₄H₁₂N₂)₂]Br₂, *M_r* = 394.81, triclinic, *P* $\bar{1}$, *a* = 13.4387 (1), *b* = 9.6298 (1), *c* = 5.9928 (1) Å, α = 85.391 (1), β = 84.714 (1), γ = 72.558 (1)°, *V* = 735.60 (2) Å³, *Z* = 2, *D_x* = 1.78 Mg m⁻³, λ (Mo *K* α) = 0.71073 Å, μ = 6.687 mm⁻¹, *F*(000) = 396, *T* = 293 K. Final *R* = 0.034 for 2054 observed reflections and 232 variables. Ni—N(1) and Ni—N(2) average distances are 1.907 (5) and 1.919 (5) Å, respectively, and the average N(1)—Ni—N(2) bite angle is

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86.2 (2)°. The nickel coordination is pseudo square-planar, with two diamine ligands close to a plane. The ligands show an unusual non-centrosymmetric disposition around the central nickel, being related by a pseudo-mirror plane.

Introduction. The present paper reports the crystal and molecular structure of a new complex of nickel(II). The structure of the title compound was

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