Bis(triethanolamine)cadmium(II) and -mercury(II) saccharinates: seven-coordinate complexes containing both tri- and tetradentate triethanolamine ligands

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The structures of the title triethanolamine (tea) complexes of Cd^{II} and Hg^{II} saccharinates, bis(triethanolamine)-$\kappa^3 O,N,O'$;-$\kappa^4 O,N,O',O''$-cadmium(II) 1,2-benzisothiazol-3(2H)-onate 1,1-dioxide, $[Cd(C_6H_{15}NO_3)_2](C_7H_4NO_3S)_2$, (I), and bis(triethanolamine)-$\kappa^3 O,N,O'$;$\kappa^4 O,N,O',O''$-mercury(II) 1,2-benzisothiazol-3(2H)-onate 1,1-dioxide, $[Hg(C_6H_{15}NO_3)_2](C_7H_4NO_3S)_2$, (II), or $[M(\text{tea})_2](\text{sac})_2$, where M is Cd^{II} or Hg^{II} and sac is the saccharinate anion, reveal seven-coordinate metal ions in both complexes. Both complex cations, $[M(\text{tea})_2]^{2+}$, adopt a monocapped trigonal prism geometry in which the two tea ligands exhibit different coordination modes to achieve seven-coordination. One tea ligand acts as a tetradentate ligand using all its donor atoms, while the other behaves as a tridentate O,N,O'-donor ligand, with one of its ethanol groups remaining uncoordinated. The H atoms of the free and coordinated hydroxyl groups of the tea ligands are involved in hydrogen bonding with the amine N atom, and with the carbonyl and sulfonyl O atoms of neighbouring sac ions, forming an infinite three-dimensional network. A weak π–π interaction between the phenyl rings of the sac ions also occurs.

Comment

Triethanolamine (tea) is an amino alcohol used in a number of commercial applications, such as herbicides, surface-active agents, corrosion inhibitors and cement additives (Esker *et al.*, 1999). Because of its double action as both a tertiary amine and a primary alcohol, tea readily coordinates to metal ions to form complexes and also stabilizes the anions by hydrogen bonding (Sen & Dotson, 1970; Brannon *et al.*, 1971; Bajaj & Poonia, 1988). As part of our research effort on the preparation and spectral, thermal and structural characterization of

transition metal complexes of tea (Icbudak *et al.*, 1995; Yilmaz *et al.*, 1997; Topcu *et al.*, 2001a), we report here the structural characterization of the rather unusual seven-coordinate title compounds, (I) and (II).

(I) $M = \text{Cd}$
(II) $M = \text{Hg}$
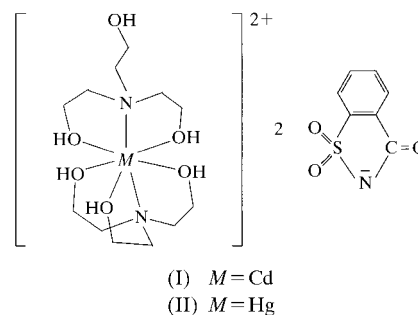
The aim of the present work was to prepare a series of mixed-ligand complexes containing both tea and sac ligands. However, it was observed that the bulky and polydentate tea ligand coordinates to the metal ions completely and does not leave any site available for the coordination of sac (Topcu *et al.*, 2001b). Therefore, the sac ions are present as counter-ions in metal complexes with tea.

The structures of $[Cd(\text{tea})_2](\text{sac})_2$, (I), and $[Hg(\text{tea})_2](\text{sac})_2$, (II), are shown in Figs. 1 and 2, respectively. Tables 1 to 4 list their bond and hydrogen-bonding geometries. The structures resemble each other and consist of a complex cation and two sac ions. In the complex cation, two neutral tea ligands coordinate to the Cd^{II} or Hg^{II} ions. The two tea ligands exhibit
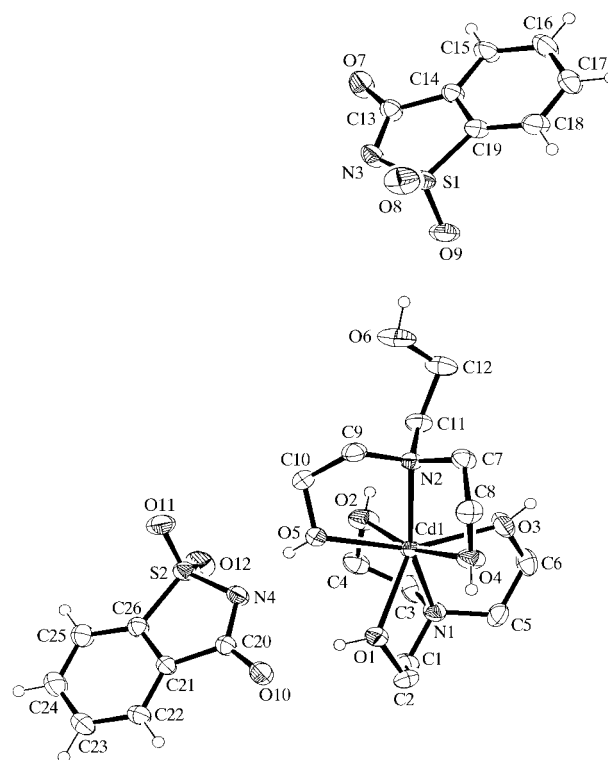

Figure 1
A view of the molecule of (I) shown with 40% probability displacement ellipsoids. Selected H atoms are shown as small spheres of arbitrary radii and the remainder have been omitted for clarity.

metal-organic compounds

different coordination modes in the same coordination polyhedron. One of them is coordinated to the central metal ion as a tetradentate ligand using all its donor atoms, *i.e.* the amino N atom and all three hydroxyl O atoms, while the other is bonded to the metal ion tridentately through its N atom and two hydroxyl O atoms, one hydroxyl O atom being non-coordinated. A similar inequivalency of two tea ligands coordinated to the Mn^{II} ion in a distorted pentagonal bipyramidal geometry has been reported for the [Mn(tea)$_2$](CF$_3$COO)$_2$ complex (Andruh *et al.*, 1993). A coordination polyhedron containing the same ligand with two different coordination modes was also reported for the monoethanolamine complex of the Cu^{II} ion (Bombicz *et al.*, 1997).

The tri- and tetradentate coordinations of the two tea ligands result in a coordination number of seven for the metal ion, which is relatively rare for Cd^{II} and unusual for Hg^{II}, since Cd^{II} and Hg^{II} usually possess octahedral as well as tetrahedral geometry (Holloway & Melnik, 1995). Although eight-coordinate Sr^{II} (Naiini *et al.*, 1995; Poonia *et al.*, 1999) and Y^{III} (Naiini *et al.*, 1995) complexes containing two tetradentate tea ligands have recently been reported, only one Cd^{II} complex with eight-coordination, *viz.* [Cd(tea)$_2$](NO$_3$)$_2$, has been reported in the literature to date (Naiini *et al.*, 1995). It should be noted that the tea complexes of Cd^{II} reported in this paper and in the literature have different coordination numbers and geometries. This may be attributed to the presence of different counter-ions, such as nitrate or saccharinate.

The seven-coordinate geometry around the Cd^{II} and Hg^{II} ions in (I) and (II) is described as a monocapped trigonal prism (C_{2v}). The dihedral angles between the least-squares

Figure 3
A packing diagram for (I).

planes are as follows for (I) and (II), respectively: 53.2 (1) and 46.0 (1)° between O2/O3/O4/O5 (plane 1) and O2/N1/O1/O5 (plane 2), 50.8 (1) and 51.2 (1)° between O3/O4/O1/N1 (plane 3) and plane 1, and 76.0 (1) and 82.9 (2)° between planes 2 and 3. The dihedral angle between two triangular planes, O2/O3/N1 and O5/O4/O1, is only 8.5 (1)° for (I) and 12.4 (4)° for (II). The dihedral angles between these triangular and square planes are in the range 83.6 (1)–87.5 (1)° for (I) and 73.6 (2)–85.9 (2)° for (II). The central Cd^{II} and Hg^{II} ions are located 0.362 (1) and 0.378 (1) Å, respectively, from plane 1.

All the ethylene C atoms (C1–C6) of the tetradentately coordinated tea ligand and the free hydroxyl O atom (O6) of the tridentate tea ligand in (I) are noticeably disordered over two positions, with occupancies of 31 (1) and 69 (1)% for the C atoms, and 56 (1) and 44 (1)% for atom O6. In addition, atom O1 in (II) is slightly disordered; this disorder was not resolved.

The *M*—N bond distances are 2.375 (2) and 2.392 (2) Å for (I), and 2.234 (5) and 2.239 (5) Å for (II). The *M*—O bonds are in the range 2.327 (2)–2.415 (2) Å for (I) and 2.468 (5)–2.730 (5) Å for (II). The bond lengths in (I) are somewhat shorter than those of the eight-coordinate Cd^{II} complex with tea (Naiini *et al.*, 1995).

Both sac ions are essentially planar, with r.m.s. deviations of 0.0057 and 0.0292 Å in (I), and 0.023 and 0.024 Å in (II). In both complexes, the sac ions adopt a parallel alignment, and the dihedral angles between the corresponding planes are 3.5 (1) and 1.1 (1)° for (I) and (II), respectively. Thus, the phenyl rings are approximately superimposed on each other and are connected by weak π–π interactions of 4.166 (1) Å in (I) and 4.038 (1) Å in (II).

The crystals of the two complexes feature numerous hydrogen bonds (Figs. 3 and 4). The H atoms of the free and
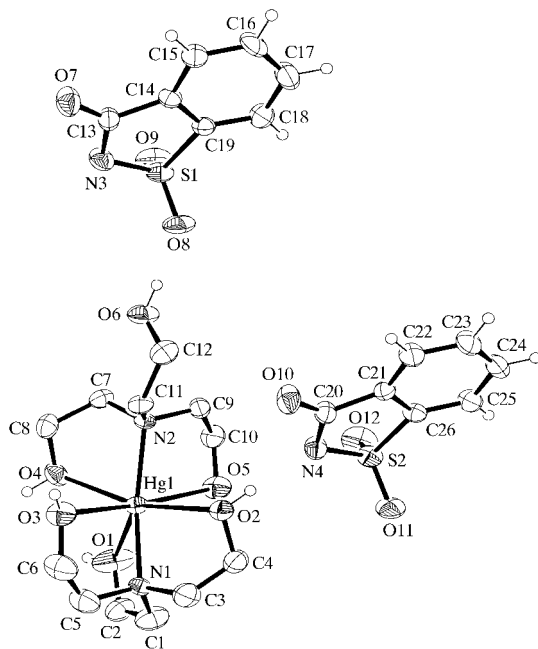

Figure 2
A view of the molecule of (II) shown with 40% probability displacement ellipsoids. Selected H atoms are shown as small spheres of arbitrary radii and the remainder have been omitted for clarity.
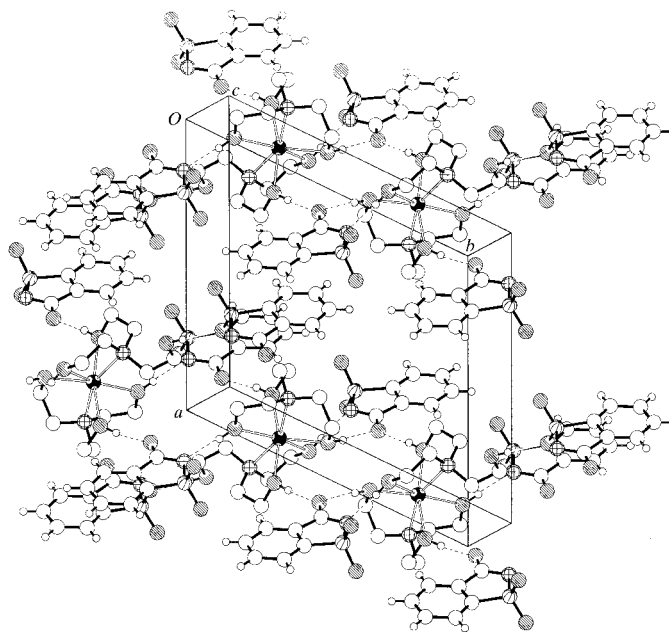
coordinated hydroxyl H atoms of the tea ligands are involved in intermolecular hydrogen bonding with the negatively charged amine N atoms and the carbonyl and sulfonyl O atoms of neighbouring sac ions. An extensive network of
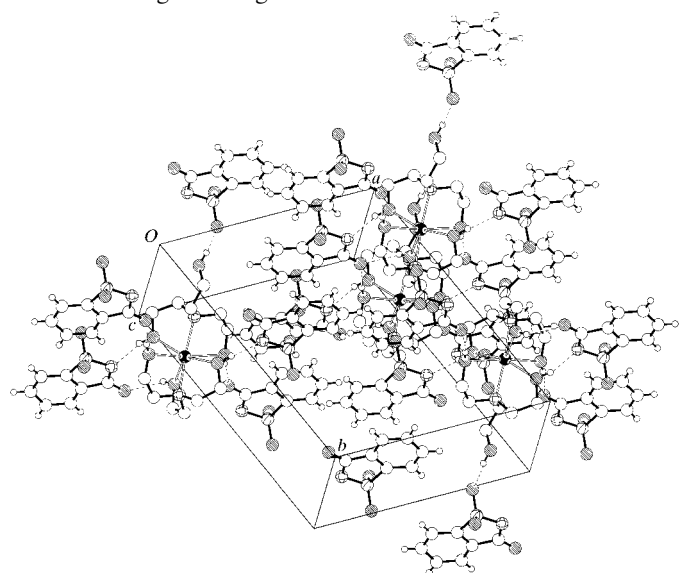

Figure 4
A packing diagram for (II).

hydrogen bonds and other intermolecular interactions maintains the crystal structure by forming an infinite three-dimensional lattice.

Experimental

The preparation and spectral characterization of tea complexes of first-row divalent transition metal saccharinates, including the present Cd^{II} and Hg^{II} saccharinates, have been reported elsewhere by Topcu *et al.* (2001*b*). The polycrystalline solid complexes (I) and (II) were crystallized from solutions in methanol–propan-2-ol (1:1, *v/v*) at room temperature in order to obtain suitable single crystals for X-ray analysis.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.115$
$S = 1.02$
11 203 reflections
478 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.047P)^2 + 0.051P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.80$ e Å^{-3}
$\Delta\rho_{min} = -0.87$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (I).

Cd1—O4	2.3274 (19)	Cd1—O2	2.3862 (19)
Cd1—O5	2.3464 (19)	Cd1—N1	2.392 (2)
Cd1—O1	2.3676 (19)	Cd1—O3	2.415 (2)
Cd1—N2	2.375 (2)		
O4—Cd1—O5	102.28 (8)	O5—Cd1—N1	125.92 (7)
O4—Cd1—O1	81.81 (7)	O1—Cd1—N1	72.11 (7)
O5—Cd1—O1	72.95 (7)	N2—Cd1—N1	154.11 (7)
O4—Cd1—N2	74.86 (7)	O2—Cd1—N1	73.97 (8)
O5—Cd1—N2	73.64 (7)	O4—Cd1—O3	80.07 (8)
O1—Cd1—N2	133.59 (7)	O5—Cd1—O3	158.08 (7)
O4—Cd1—O2	166.01 (7)	O1—Cd1—O3	128.66 (7)
O5—Cd1—O2	82.73 (8)	N2—Cd1—O3	86.21 (7)
O1—Cd1—O2	112.18 (7)	O2—Cd1—O3	90.46 (8)
N2—Cd1—O2	94.39 (7)	N1—Cd1—O3	71.15 (7)
O4—Cd1—N1	111.99 (8)		

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

D—H$\cdots$A	D—H	H$\cdots$A	$D\cdots$A	D—H$\cdots$A
O1—H1$\cdots$O10	0.86	1.90	2.749 (3)	171
O2—H2$\cdots$O7^{i}	0.86	1.83	2.679 (3)	173
O3—H3$\cdots$N3^{ii}	0.86	1.95	2.804 (3)	178
O4—H4$\cdots$O10^{iii}	0.86	1.86	2.715 (3)	175
O5—H5$\cdots$N4	0.86	1.86	2.714 (3)	172
O6A—H6$A\cdots$O9	0.88	1.97	2.778 (15)	152
O6B—H6$B\cdots$O9	0.88	1.93	2.78 (2)	162

Symmetry codes: (i) $-x, -y, -1 - z$; (ii) $x, y, 1 + z$; (iii) $-x, 1 - y, 1 - z$.

Compound (I)

Crystal data

[Cd(C$_6$H$_{15}$NO$_3$)$_2$](C$_7$H$_4$NO$_3$S)$_2$
$M_r = 775.12$
Triclinic, $P\bar{1}$
$a = 13.2825$ (9) Å
$b = 14.9093$ (11) Å
$c = 8.9376$ (10) Å
$\alpha = 98.002$ (8)°
$\beta = 102.662$ (8)°
$\gamma = 63.762$ (5)°
$V = 1547.2$ (2) Å^3

$Z = 2$
$D_x = 1.664$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 24 reflections
$\theta = 10.5–13.2°$
$\mu = 0.91$ mm^{-1}
$T = 293$ (2) K
Prism, colourless
$0.4 \times 0.2 \times 0.2$ mm

Data collection

Rigaku AFC-7S diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.797, T_{max} = 0.834$
12 760 measured reflections
11 203 independent reflections
7948 reflections with $I > 2\sigma(I)$

$R_{int} = 0.025$
$\theta_{max} = 32.5°$
$h = 0 \rightarrow 20$
$k = -20 \rightarrow 22$
$l = -13 \rightarrow 13$
3 standard reflections every 150 reflections
intensity decay: 7.7%

Compound (II)

Crystal data

[Hg(C$_6$H$_{15}$NO$_3$)$_2$](C$_7$H$_4$NO$_3$S)$_2$
$M_r = 863.31$
Triclinic, $P\bar{1}$
$a = 12.588$ (2) Å
$b = 15.934$ (3) Å
$c = 7.9944$ (14) Å
$\alpha = 91.791$ (14)°
$\beta = 91.343$ (14)°
$\gamma = 72.965$ (13)°
$V = 1532.2$ (4) Å^3

$Z = 2$
$D_x = 1.871$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 20.4–26.8°$
$\mu = 5.23$ mm^{-1}
$T = 293$ (2) K
Thin plate, colourless
$0.50 \times 0.35 \times 0.10$ mm

Data collection

Rigaku AFC-7S diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.113, T_{max} = 0.593$
11 526 measured reflections
11 091 independent reflections
5241 reflections with $I > 2\sigma(I)$

$R_{int} = 0.042$
$\theta_{max} = 32.5°$
$h = 0 \rightarrow 19$
$k = -23 \rightarrow 24$
$l = -12 \rightarrow 12$
3 standard reflections every 150 reflections
intensity decay: 4.1%

metal-organic compounds

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.159$
$S = 0.99$
11 091 reflections
412 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0765P)^2]$
    where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.94$ e Å^{-3}
$\Delta\rho_{min} = -3.76$ e Å^{-3}

Table 3
Selected geometric parameters (Å, °) for (II).

Hg1—N1	2.234 (5)	Hg1—O3	2.618 (5)
Hg1—N2	2.239 (5)	Hg1—O4	2.468 (5)
Hg1—O1	2.581 (7)	Hg1—O5	2.497 (6)
Hg1—O2	2.730 (5)		
N1—Hg1—N2	158.2 (2)	N2—Hg1—O3	96.75 (19)
N1—Hg1—O4	120.61 (19)	O4—Hg1—O3	80.8 (2)
N2—Hg1—O4	75.49 (19)	O5—Hg1—O3	166.47 (19)
N1—Hg1—O5	108.9 (2)	O1—Hg1—O3	112.2 (2)
N2—Hg1—O5	76.2 (2)	N1—Hg1—O2	73.05 (18)
O4—Hg1—O5	108.0 (2)	N2—Hg1—O2	87.82 (18)
N1—Hg1—O1	72.9 (2)	O4—Hg1—O2	159.80 (18)
N2—Hg1—O1	128.7 (2)	O5—Hg1—O2	78.23 (19)
O4—Hg1—O1	69.0 (2)	O1—Hg1—O2	131.2 (2)
O5—Hg1—O1	80.9 (2)	O3—Hg1—O2	90.11 (18)
N1—Hg1—O3	73.5 (2)		

Table 4
Hydrogen-bonding geometry (Å, °) for (II).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1—H1$\cdots$O7^i	0.84	2.24	2.951 (10)	143
O2—H2$\cdots$N4	0.86	1.92	2.775 (8)	177
O3—H3$\cdots$O7^{ii}	0.85	1.91	2.754 (8)	172
O4—H4$\cdots$N3^i	0.85	1.97	2.806 (8)	164
O5—H5$\cdots$O10^{iii}	0.86	1.80	2.650 (8)	167
O6—H6$\cdots$O8	0.86	2.00	2.813 (8)	159

Symmetry codes: (i) $-x, -y, 1 - z$; (ii) $-x, -y, -z$; (iii) $x, y, 1 + z$.

The hydroxyl H atoms were located from a difference map for (II) and were geometrically positioned for (I). All hydroxyl H atoms were refined with a rotating model, with U_{iso} values 1.5 times those of the attached O atoms, while the other H atoms were placed in calculated positions and refined with a riding model, with U_{iso} values 1.2 times those of the attached atoms.

For both compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1994); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1997); 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 (Farrugia, 1997) and *PLATON* (Spek, 2000); software used to prepare material for publication: *SHELXL*97.

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