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Bis(2-pyridylmethanol)bis(saccharinato)zinc(II) and -cadmium(II) at 120 K: three-dimensional structures containing both *N*-and *O*-coordinated ambidentate saccharinate ligands

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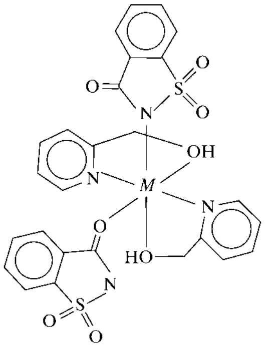
The title complexes [M(sac)$_2$(mpy)$_2$] [sac is saccharinate ($C_7H_4NO_3S$) and mpy is 2-pyridylmethanol (C_6H_7NO)], with M = Zn^{II} and Cd^{II}, are isostructural and consist of neutral molecules. The Zn^{II} or Cd^{II} cations are octahedrally coordinated by the two neutral mpy and two anionic sac ligands. The mpy ligand acts as a bidentate donor through the amine N and hydroxyl O atoms. The sac ligands exhibit an ambidentate coordination behaviour; one is *N*-coordinated and the other is *O*-coordinated within the same coordination octahedron. The crystal packing is determined by C—H···O-type hydrogen bonding, as well as by weak py–py and sac–sac aromatic π–π-stacking interactions.

Comment

Saccharin and its deprotonated form, saccharinate (sac), are versatile polyfunctional ligands in coordination chemistry. Sac may bond to metals through four sites, *viz.* the negatively charged imino N atom, the carbonyl O atom and the two sulfonyl O atoms. The sac ligand can behave as a mono- or bidentate ligand and, in some cases, can act as a bridging ligand between two metals. In this work, we report the crystal structures of new bis(saccharinato)zinc(II) and -cadmium(II) complexes with 2-pyridylmethanol (mpy), namely [Zn(sac)$_2$(mpy)$_2$], (I), and [Cd(sac)$_2$(mpy)$_2$], (II), containing ambidentate *N*- and *O*-coordinated sac ligands within a coordination polyhedron.

The molecular structures of [Zn(sac)$_2$(mpy)$_2$] and [Cd(sac)$_2$(mpy)$_2$] are shown in Figs. 1 and 2, respectively. The crystal structures are isomorphous and consist of individual neutral molecules of [M(sac)$_2$(mpy)$_2$]. The Zn^{II} and Cd^{II} atoms are six-coordinated by two mpy and two sac ligands, forming an MN_3O_3 core. The mpy ligand behaves as a bidentate donor through the amine N and methanol O atoms, forming a five-membered chelate ring. The N atoms of the two mpy ligands are in *trans* positions, while the hydroxyl O atoms occupy the *cis* positions of the octahedron. The sac anion usually interacts with transition metal ions through its deprotonated N atom. The coordination of sac to the transition metal ions through donor groups other than the amine N atom is unusual and only a few examples of the *O*-coordination of sac have been reported previously, *e.g.* in metal–sac complexes with pyridine (Cotton *et al.*, 1986; Quinzani *et al.*, 1999), dipyridylamine (Deng *et al.*, 2001) and triphenylphosphine (Falvello *et al.*, 2001). Recently, *O*-coordinated sac complexes of trivalent lanthanides and yttrium have been reported by Piro *et al.* (2002). Therefore, the most interesting feature of complexes (I) and (II) is the coordination of the sac ligands, which occur in two distinct manners. Both sac ligands are monodentate, but one is *N*-coordinated and the other is *O*-coordinated.



(I) M = Zn
(II) M = Cd

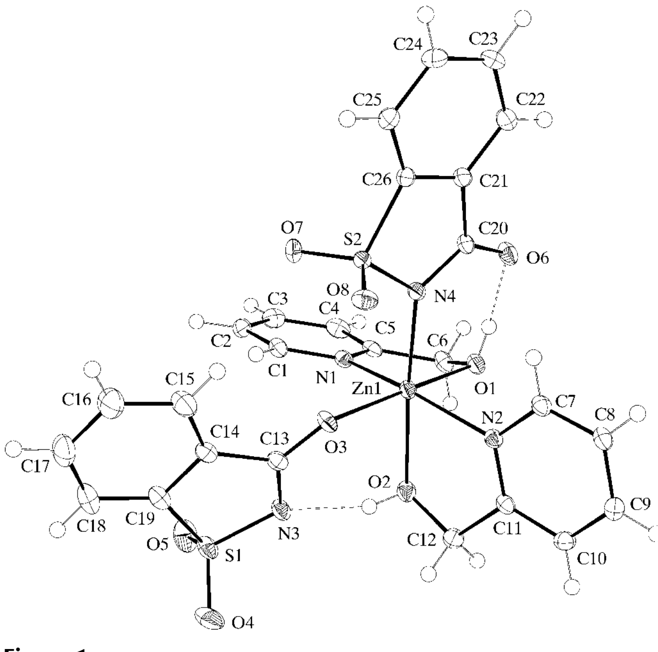


Figure 1
A view of the molecular structure of (I), showing the atom-numbering scheme and 50% displacement ellipsoids. H atoms are shown as small spheres of arbitrary radii.

The $\mathrm{Zn-N_{sac}}$ bond distance in (I) (Table 1) is significantly longer than the distance of 1.977 (2) Å found in [Zn(sac)$_2$(py)$_2$] (py is pyridine; Quinzani *et al.*, 1997), but also markedly shorter than the distances of 2.157 (5) and 2.2423 (9) Å reported for [Zn(sac)$_2$(bipy)$_2$]·H$_2$O (bipy is 2,2′-bipyridine; Johns *et al.*, 2001) and [Zn(sac)$_2$(mea)$_2$] (mea is monoethanolamine; Yilmaz *et al.*, 2001), respectively. The $\mathrm{Cd-N_{sac}}$ bond distance in (II) (Table 3) is much shorter than that observed in [Cd(sac)$_2$(HydEt-en)$_2$] (Yilmaz *et al.*, 2002), where HydEt-en is *N*-(2-hydroxyethyl)ethylenediamine, while it is longer than those found in [Cd(sac)$_2$(bipy)$_2$] (Johns *et al.*, 2001) and [Cd$_2$(sac)$_4$(im)$_2$] (im is imidazole; Jianmin *et al.*, 1997). It seems that the differences in the $M-\mathrm{N_{sac}}$ bond distances in these structures are a consequence of the steric effects of the co-ligands, such as bipy, mea, HydEt-en and im. Large distortions in the coordination polyhedra from ideal octahedral geometry are clearly evident from the N—*M*—N, N—*M*—O and O—*M*—O bond angles. The bite angles of the mpy ligand in the Zn$^{\rm II}$ and Cd$^{\rm II}$ complexes are significantly smaller than the ideal *cis* angles of a regular octahedron (90°) and, as a result, these complexes may be regarded as having a distorted octahedral structure.

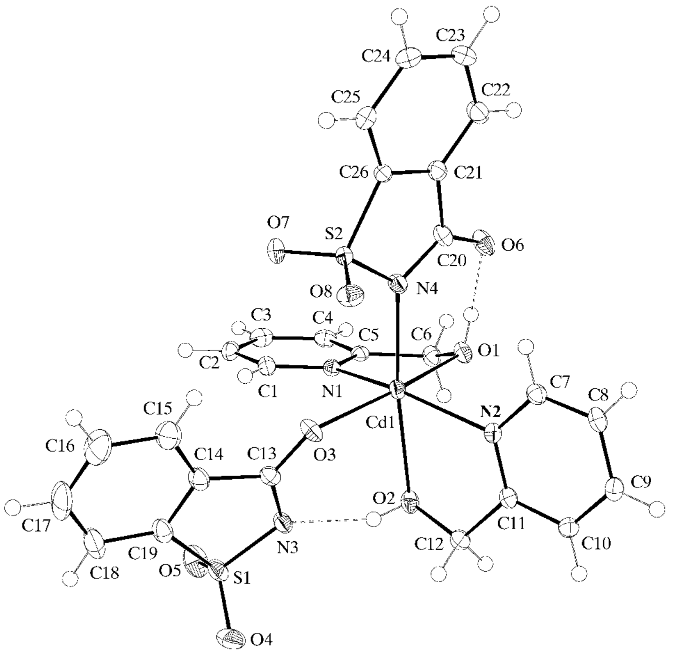


Figure 2
A view of the molecular structure of (II), showing the atom-numbering scheme and 50% displacement ellipsoids. H atoms are shown as small spheres of arbitrary radii.

The sac ligands in the two title complexes are essentially planar, with r.m.s. deviations of *ca* 0.03 Å. The py rings of the mpy ligands are also planar, with r.m.s. deviations of *ca* 0.01 Å, but the hydroxyl O and methylene C atoms deviate slightly from the py planes by *ca* 0.38 (2) and 0.02 (1) Å, respectively. The mpy ligands in (I) and (II) are roughly perpendicular to each other, with dihedral angles of 80.07 (5) and 87.46 (5)°, respectively, while the dihedral angle between the best planes of the sac ligands is 22.60 (5)° in (I) and 19.19 (5)° in (II). As the two structures are isomorphous, the packing of only one of the structures, (I), is given (Fig. 3). The hydroxyl H atoms of

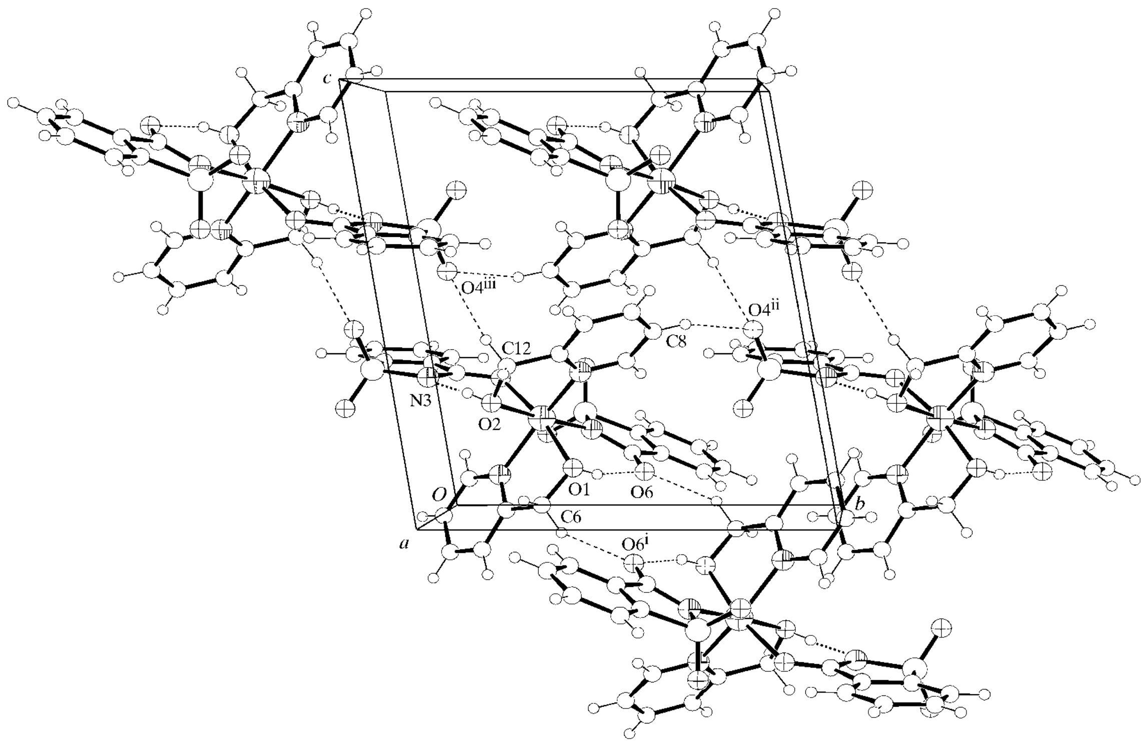


Figure 3
A packing diagram for (I). The symmetry codes are as given in Table 2.

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the mpy ligands form strong intramolecular hydrogen bonds with the carbonyl O and the negatively charged N atoms of neighbouring sac ligands. The methylene and phenyl H atoms are involved in weak intermolecular C—H···O interactions with the sulfonyl and carbonyl O atoms. Furthermore, there are weak π–π interactions between the centroids (Cg) of the mpy rings [$Cg\cdots Cg^{\rm i}$: 3.443 (1) Å in (I) and 3.460 (1) Å in (II); symmetry code: (i) $1 - x$, $1 - y$, $1 - z$] and the sac rings [$Cg\cdots Cg^{\rm ii}$: 3.801 (1) Å in (I) and 3.979 (1) Å in (II); symmetry code: (ii) $-x$, $-y$, $1 - z$]. The molecules are held together by weak hydrogen bonds (Tables 2 and 4) and π–π interactions, thereby forming a three-dimensional network.

Experimental

The mpy ligand (0.218 g, 2.0 mmol) dissolved in methanol (15 ml) was added dropwise with continuous stirring to solutions of tetraaquabis(saccharinato)zinc(II) dihydrate (1 mmol) and tetraaquabis(saccharinato)cadmium(II) dihydrate (1 mmol) in methanol–2-propanol (*v*:*v* 1:1, 30 ml) at room temperature. The resulting solutions were left to stand and allowed to evaporate slowly over a period of a few days, whereupon crystallization occurred. Crystals of both compounds suitable for X-ray diffraction analysis were collected by suction filtration, and were then washed with acetone and dried in air.

Compound (I)

Crystal data

$[Zn(C_7H_4NO_3S)_2(C_6H_7NO)_2]$
$M_r = 647.97$
Triclinic, $P\overline{1}$
$a = 8.9874$ (2) Å
$b = 11.1630$ (2) Å
$c = 13.1879$ (3) Å
$\alpha = 99.1532$ (8)°
$\beta = 95.0138$ (9)°
$\gamma = 95.729$ (2)°
$V = 1292.52$ (5) Å^3
$Z = 2$
$D_x = 1.665$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 11 819 reflections
$\theta = 2.9$–27.5°
$\mu = 1.17$ mm^{-1}
$T = 120$ (2) K
Needle, colourless
0.25 × 0.10 × 0.05 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans to fill Ewald sphere
Absorption correction: multi-scan (Blessing, 1995)
$T_{\rm min} = 0.869$, $T_{\rm max} = 0.943$
16 550 measured reflections
5684 independent reflections
4863 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.042$
$\theta_{\rm max} = 27.5°$
$h = -10 \rightarrow 11$
$k = -14 \rightarrow 14$
$l = -17 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.081$
$S = 1.04$
5684 reflections
376 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0312P)^2 + 0.9518P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.38$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.53$ e Å^{-3}

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

Zn1—O3	2.0717 (14)	Zn1—N1	2.1244 (17)
Zn1—N2	2.0887 (17)	Zn1—O1	2.1788 (14)
Zn1—N4	2.1167 (16)	Zn1—O2	2.2323 (14)
O3—Zn1—N2	101.67 (6)	N4—Zn1—O1	93.84 (6)
O3—Zn1—N4	93.40 (6)	N1—Zn1—O1	76.74 (6)
N2—Zn1—N4	99.10 (6)	O3—Zn1—O2	88.05 (5)
O3—Zn1—N1	94.17 (6)	N2—Zn1—O2	76.74 (6)
N2—Zn1—N1	156.92 (6)	N4—Zn1—O2	175.80 (6)
N4—Zn1—N1	96.58 (6)	N1—Zn1—O2	87.24 (6)
O3—Zn1—O1	168.97 (5)	O1—Zn1—O2	85.32 (5)
N2—Zn1—O1	85.38 (6)		

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1O···O6	0.834 (10)	1.811 (12)	2.617 (2)	162 (2)
O2—H2O···N3	0.828 (10)	1.876 (13)	2.667 (2)	159 (2)
C6—H6B···O6$^{\rm i}$	0.99	2.36	3.213 (2)	144
C8—H8···O4$^{\rm ii}$	0.95	2.37	3.247 (3)	153
C12—H12B···O4$^{\rm iii}$	0.99	2.47	3.441 (3)	168

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

Compound (II)

Crystal data

$[Cd(C_7H_4NO_3S)_2(C_6H_7NO)_2]$
$M_r = 695.00$
Triclinic, $P\overline{1}$
$a = 8.7516$ (1) Å
$b = 11.4547$ (1) Å
$c = 13.5442$ (2) Å
$\alpha = 99.8079$ (6)°
$\beta = 96.5191$ (5)°
$\gamma = 95.1327$ (5)°
$V = 1321.03$ (3) Å^3
$Z = 2$
$D_x = 1.747$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 24 147 reflections
$\theta = 2.9$–27.5°
$\mu = 1.04$ mm^{-1}
$T = 120$ (2) K
Block, colourless
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Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans to fill Ewald sphere
Absorption correction: multi-scan (Blessing, 1995)
$T_{\rm min} = 0.738$, $T_{\rm max} = 0.812$
18 640 measured reflections
5886 independent reflections
5437 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.049$
$\theta_{\rm max} = 27.5°$
$h = -11 \rightarrow 11$
$k = -14 \rightarrow 14$
$l = -16 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.066$
$S = 1.06$
5886 reflections
376 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0261P)^2 + 1.0424P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.40$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.85$ e Å^{-3}

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

Cd1—O3	2.2612 (14)	Cd1—N1	2.2952 (16)
Cd1—N2	2.2688 (16)	Cd1—O1	2.3648 (14)
Cd1—N4	2.2755 (17)	Cd1—O2	2.4136 (15)
O3—Cd1—N2	104.10 (6)	N4—Cd1—O1	90.56 (6)
O3—Cd1—N4	95.69 (6)	N1—Cd1—O1	71.76 (5)
N2—Cd1—N4	100.16 (6)	O3—Cd1—O2	84.99 (5)
O3—Cd1—N1	94.13 (6)	N2—Cd1—O2	71.37 (5)
N2—Cd1—N1	152.70 (6)	N4—Cd1—O2	171.35 (5)
N4—Cd1—N1	98.02 (6)	N1—Cd1—O2	90.52 (5)
O3—Cd1—O1	165.28 (5)	O1—Cd1—O2	90.83 (5)
N2—Cd1—O1	87.82 (5)		

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1O···O6	0.833 (10)	1.889 (14)	2.666 (2)	155 (3)
O2—H2O···N3	0.843 (10)	1.904 (13)	2.700 (2)	157 (2)
C6—H6B···O6^{i}	0.99	2.50	3.302 (2)	138
C8—H8···O4^{ii}	0.95	2.36	3.256 (3)	158
C12—H12B···O4^{iii}	0.99	2.59	3.560 (3)	167

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

Hydroxyl H atoms were refined with restraints starting from their locations in a difference map [$U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(O)]. The remaining H-atom positions were calculated [C—H = 0.95 (CH) and 0.99 Å (CH$_2$), and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C)].

For both compounds, data collection: *COLLECT* (Hooft, 1998); cell refinement: *DENZO* (Otwinowski & Minor, 1997); data reduction: *DENZO*; 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).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TR1032). Services for accessing these data are described at the back of the journal.

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