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Bis(saccharinato-κN)zinc(II) complexes with N,N'-bidentate 2-aminomethylpyridine and 2-aminoethylpyridine

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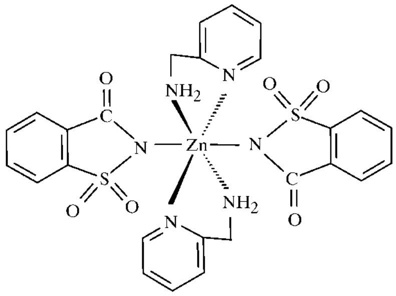
The structures of *trans*-bis[2-(aminomethyl)pyridine-κ^2N,N']bis(saccharinato-κN)zinc(II), $[Zn(C_7H_4NO_3S)_2(C_6H_8N_2)_2]$, (I), and [2-(aminoethyl)pyridine-κ^2N,N']bis(saccharinato-κN)zinc(II), $[Zn(C_7H_4NO_3S)_2(C_7H_{10}N_2)]$, (II), exhibit octa- and tetrahedrally coordinated Zn^{II} atoms, respectively. The diamine ligands behave as N,N'-bidentate ligands, while saccharinate (sac) is coordinated through the N atom. In (I), the complex lies about an inversion centre with the Zn atom disordered and displaced by 0.256 (2) Å from a centre of symmetry towards a sac N atom. The crystal structure of (I) is stabilized by N—H···O hydrogen bonds and the crystal packing of (II) is determined by hydrogen bonding as well as weak π–π stacking interactions between the sac ligands.

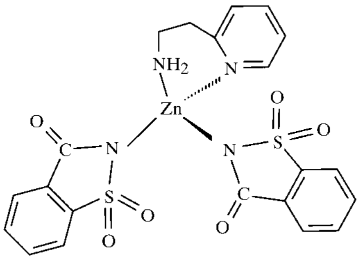
Comment

Saccharin (3*H*-benzisothiazol-3-one 1,1-dioxide or *o*-benzosulfimide) is a well known artificial sweetener and is readily deprotonated to form the corresponding saccharinate anion (sac), which is a versatile polyfunctional ligand (Ager *et al.*, 1998). Sac coordinates to metals both through the negatively charged N atom and through the carbonyl and sulfonyl O atoms as a mono- or bidentate ligand and, in some cases, as a bridging ligand. This study forms part of our continuing research into the synthesis and spectral, thermal and structural characterization of a series of mixed-ligand complexes of sac with other co-ligands. In this work, we used two unsymmetrical diamine ligands, namely 2-(aminomethyl)pyridine (ampy) and 2-(aminoethyl)pyridine (aepy), as co-ligands, since metal complexes of both ligands are rare. This paper reports the structures of *trans*-[Zn(sac)$_2$(ampy)$_2$], (I), and [Zn(sac)$_2$(aepy)], (II), both of which consist of neutral molecules.

In (I) (Fig. 1), the disordered zinc cation is displaced from a centre of symmetry towards a sac N atom [Zn1—N1 = 2.188 (2) Å] and forms a very long Zn1—N1^{i} bond [2.700 (2) Å; see Table 1 for symmetry code] to a symmetry-equivalent N-bonded sac ligand in the *trans* position. This strongly distorted octahedral coordination is completed by two ampy ligands, thus forming the equatorial plane of the coordination polyhedron. The neutral ampy ligand behaves as a bidentate donor to the Zn atom through the two amine N atoms, thus forming a five-membered chelate ring. An alternative model of the structure, which placed the Zn species at the ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$) inversion centre, resulted in slightly higher residuals and identical Zn—N$_{sac}$ bond lengths [2.443 (2) Å]. However, the Zn-atom anisotropic displacement parameters displayed gross anisotropy normal to the Zn(ampy)$_2$ plane and a *PLATON* (Spek, 2003) analysis indicated that the Zn1—N1$_{sac}$ bond failed the Hirshfeld (1976) rigid-bond test by over 100σ. The disorder in the Zn atom also results in non-equivalent Zn—N$_{ampy}$ bond distances, as shown in Table 1.



(I)



(II)

In (II) (Fig. 2), the Zn atom exhibits a distorted tetrahedral coordination geometry, with a neutral bidendate aepy ligand and two anionic sac ligands, thus forming a ZnN$_4$ chromophore. The four Zn—N bond distances in (II) are practically identical (Table 3), but the N—Zn—N bond angle associated with the aepy grouping is significantly less than the nominal tetrahedral angle of 109.5°. The Zn—N$_{sac}$ bond distance in (II) is similar to those observed in [Zn(sac)$_2$(py)$_2$] [1.977 (2) Å; py is pyridine; Quinzani *et al.*, 1997] but considerably shorter than the corresponding values found in previously reported zinc(II) complexes with sac, *viz.* 2.200 (4) Å in [Zn(sac)$_2$(H$_2$O)$_4$]·2H$_2$O (Haider *et al.*, 1984), 2.157 (5) Å in [Zn(sac)$_2$(bpy)$_2$]·H$_2$O (Johns *et al.*, 2001), 2.2423 (9) Å in [Zn(sac)$_2$(mea)$_2$] (Yilmaz *et al.*, 2001), 2.159 Å in [Zn(H$_2$O)(bpy)$_2$(sac)](sac) (Grupce *et al.*, 2001) and 2.1167 (16) Å in [Zn(sac)$_2$(mpy)$_2$] (Yilmaz *et al.*, 2002), where bpy, mea and mpy are 2,2′-bi-

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pyridine, monoethanolamine and 2-pyridylmethanol, respectively.

It seems that the difference in the coordination geometry of complexes (I) and (II) may be the consequence of the steric hindrance created by the chelate rings, so that the aepy ligand prevents the coordination of a second aepy ligand, resulting in a tetrahedral coordination. Large distortions in the coordination polyhedra of both complexes are clearly evident from the N—Zn—N bond angles, which deviate significantly from ideal values. The largest deviations occur at the bite angles of the ampy and aepy ligands.

The sac ligands in both complexes are essentially planar. The r.m.s. deviations from the planes formed by atoms C1–C7, N1, O3 and S1 in (I), by atoms C1–C7, N1 O1 and S1 in (II), and by atoms C8–C14, N2, O4 and S2 in (II) are 0.014, 0.024 and 0.030 Å, respectively. The pyridine rings of the ampy and aepy ligands are also planar, with r.m.s. deviations of 0.013 Å for atoms C8–C13 and N3 in (I), and 0.004 Å for atoms C15–C20 and N3 in (II). For (II), atoms C21 and N4 deviate from the pyridine plane by 1.135 (3) and 0.846 (3) Å, respectively. The ampy and sac ligands in (I) are almost perpendicular to one another, with a dihedral angle of 89.67 (7)° between their planes.

Packing diagrams of (I) and (II) are shown in Figs. 3 and 4, respectively. In (I), the amine H atoms of the ampy ligand form intramolecular hydrogen bonds with the carbonyl and sulfonyl O atoms of the sac ligands (Table 2). The individual molecules of (I) are connected by relatively weak intermolecular C—H···O interactions, involving one of the py H atoms and the sulfonyl O atom of the sac ligand in a neighbouring unit. The molecules of (II) are linked by a strong hydrogen bond between the amine H atom of the aepy ligand and the sulfonyl O atom of the sac ligand of an adjacent molecule (Table 4). Furthermore, weak π–π interactions between the sac rings in (II) [$Cg\cdots Cg^{iii} = 3.690$ Å; symmetry code: (iii) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; Cg is the centroid of the sac ring] contribute to the formation of a three-dimensional network.

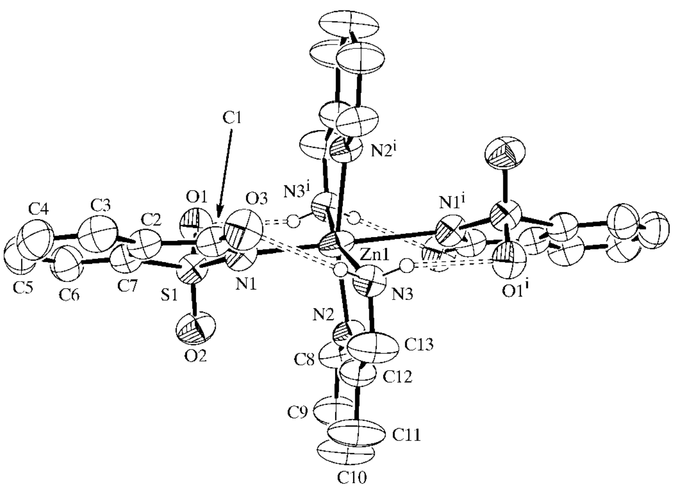

Figure 1
A view of the molecule of (I), showing displacement ellipsoids at the 50% probability level. The symmetry code is as given in Table 1. Atom Zn1 shows positional disorder and the site-occupation factor is 0.5. Atom Zn1^i and H atoms bonded to C atoms have been omitted for clarity. Hydrogen bonds are indicated by double dashed lines.

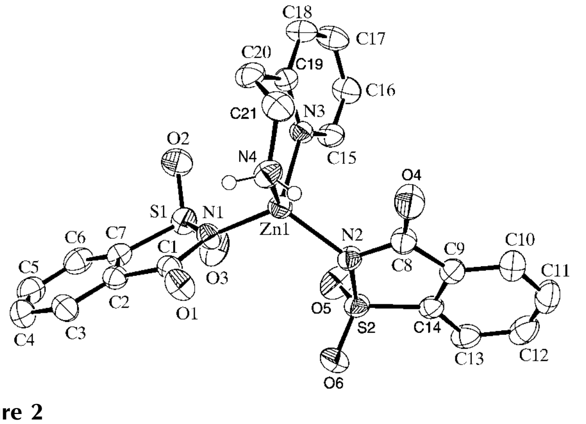

Figure 2
A view of the molecule of (II), showing displacement ellipsoids at the 50% probability level. H atoms bonded to C atoms have been omitted for clarity.

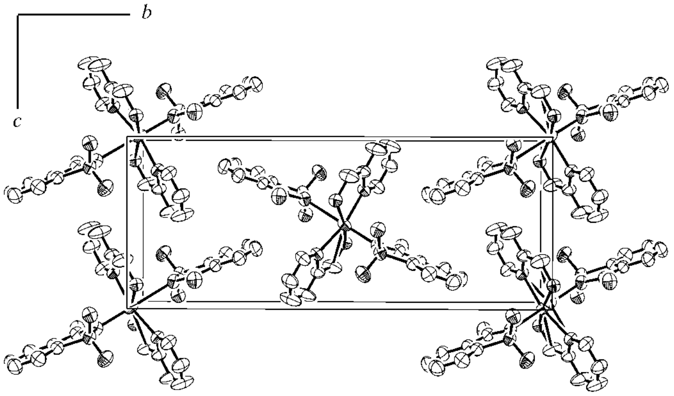

Figure 3
A packing diagram for (I). All H atoms have been omitted for clarity.

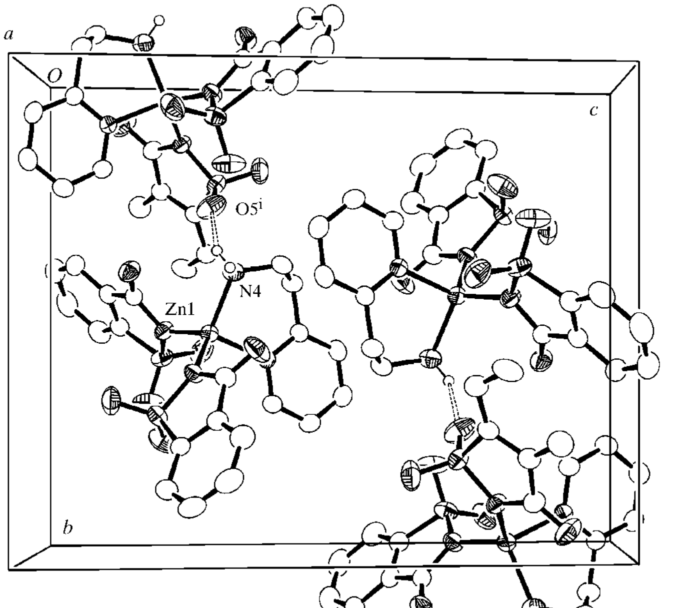

Figure 4
A packing diagram for (II). H atoms bonded to C atoms have been omitted for clarity. Hydrogen bonds are indicated by double dashed lines.

Experimental

Tetraaquabis(saccharinato)zinc(II) dihydrate, $[\mathrm{Zn(sac)_2(H_2O)_4}]\cdot2\mathrm{H_2O}$, was prepared according to the method of Haider *et al.* (1984). For the preparation of (I) and (II), an aqueous solution (25 ml) of $[\mathrm{Zn(sac)_2(H_2O)_4}]\cdot2\mathrm{H_2O}$ (0.27 g, 0.5 mmol) was mixed at 333 K with ampy (1 mmol) and aepy (1 mmol), respectively. In each case, the precipitated white polycrystalline solid was dissolved in a methanol–water mixture (1:2 *v*/*v*) and the resulting solution was left to stand at room temperature and allowed to evaporate slowly over a few days. Colourless crystals of (I) and (II) suitable for X-ray diffraction analyses were collected separately by suction filtration and dried in air.

Complex (I)

Crystal data

$[\mathrm{Zn(C_7H_4NO_3S)_2(C_6H_8N_2)_2}]$
$M_r = 646.00$
Monoclinic, $P2_1/c$
$a = 7.4169$ (4) Å
$b = 21.5662$ (10) Å
$c = 8.7502$ (4) Å
$\beta = 90.257$ (1)°
$V = 1399.62$ (12) Å^3
$Z = 2$
$D_x = 1.533$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 4514 reflections
$\theta = 2.5$–29.2°
$\mu = 1.08$ mm^{-1}
$T = 293$ (2) K
Block, colourless
0.46 × 0.41 × 0.20 mm

Data collection

Bruker SMART 1000 CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)
$T_{\min} = 0.637$, $T_{\max} = 0.813$
14 105 measured reflections
4077 independent reflections

2798 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.032$
$\theta_{\max} = 30.0°$
$h = -10 \rightarrow 10$
$k = -30 \rightarrow 30$
$l = -12 \rightarrow 12$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.111$
$S = 0.99$
4077 reflections
190 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0612P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.32$ e Å^{-3}
$\Delta\rho_{\min} = -0.23$ e Å^{-3}

Table 1
Selected interatomic distances (Å) for (I).

Zn1—N3	2.046 (3)	Zn1—N2$^{\rm i}$	2.161 (3)
Zn1—N3$^{\rm i}$	2.095 (3)	Zn1—N1	2.188 (2)
Zn1—N2	2.146 (3)	Zn1—N1$^{\rm i}$	2.700 (2)

Symmetry code: (i) $1 - x, 1 - y, 1 - z$.

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

D—H···A	D—H	H···A	D···A	D—H···A
N3—H1···O1$^{\rm i}$	0.90	2.31	3.071 (2)	142
N3—H2···O3	0.90	2.24	3.051 (2)	150
C8—H8···O1$^{\rm ii}$	0.93	2.41	3.334 (3)	171

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

Complex (II)

Crystal data

$[\mathrm{Zn(C_7H_4NO_3S)_2(C_7H_{10}N_2)}]$
$M_r = 551.88$
Monoclinic, $P2_1/n$
$a = 9.1654$ (4) Å
$b = 13.9784$ (6) Å
$c = 17.4679$ (7) Å
$\beta = 100.522$ (1)°
$V = 2200.31$ (16) Å^3
$Z = 4$
$D_x = 1.666$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 5706 reflections
$\theta = 2.4$–29.9°
$\mu = 1.35$ mm^{-1}
$T = 293$ (2) K
Chunk, colourless
0.44 × 0.33 × 0.11 mm

Data collection

Bruker SMART 1000 CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)
$T_{\min} = 0.586$, $T_{\max} = 0.866$
16 660 measured reflections
6434 independent reflections

4512 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.026$
$\theta_{\max} = 30.0°$
$h = -11 \rightarrow 12$
$k = -19 \rightarrow 12$
$l = -23 \rightarrow 24$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.081$
$S = 0.94$
6434 reflections
307 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0424P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.40$ e Å^{-3}
$\Delta\rho_{\min} = -0.33$ e Å^{-3}

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

Zn1—N1	1.9744 (16)	Zn1—N4	2.0207 (16)
Zn1—N2	1.9942 (15)	Zn1—N3	2.0472 (15)
N1—Zn1—N2	115.77 (6)	N1—Zn1—N3	108.50 (6)
N1—Zn1—N4	113.35 (7)	N2—Zn1—N3	105.82 (6)
N2—Zn1—N4	112.98 (6)	N4—Zn1—N3	98.54 (6)

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

D—H···A	D—H	H···A	D···A	D—H···A
N4—H4*A*···O5$^{\rm iii}$	0.90	2.15	2.952 (2)	147

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

All H atoms were placed in idealized positions and treated as riding. The $U_{\rm iso}$(H) values were constrained to $1.2U_{\rm eq}$(parent atom) in all cases.

For both complexes, data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

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Acta Cryst. (2004). C**60**, m35–m38 Veysel T. Yilmaz *et al.* • $[\mathrm{Zn(C_7H_4NO_3S)_2(C_6H_8N_2)_2}]$ and $[\mathrm{Zn(C_7H_4NO_3S)_2(C_7H_{10}N_2)}]$ **m37**

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1151). Services for accessing these data are described at the back of the journal.

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