trans-Bis(saccharinato)zinc and -cadmium Complexes with N-(2-Aminoethyl)piperazine: Synthesis, Crystal Structures and IR Spectra

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The reactions of N-(2-aminoethyl)piperazine (aeppz) with tetraaqua-bis(saccharinato)zinc(II) and -cadmium(II) in ethanol solution yield the new complexes *trans*-[Zn(sac)$_2$(aeppz)$_2$] (**1**), and *trans*-[Cd(sac)$_2$(aeppz)$_2$] (**2**) (sac = saccharinate), respectively. The complexes were characterized by elemental analyses, IR spectroscopy and X-ray crystallography. Both complexes **1** and **2** are mononuclear of C_i symmetry. The zinc(II) and cadmium(II) ions are coordinated by two neutral aeppz ligands and two sac anions in an elongated distorted octahedral environment. The aeppz ligand acts as a bidentate N, N' donor through the central heterocyclic N atom and the N atom of the aminoethyl group, while the sac ligand is *O*-coordinated *via* the carbonyl O atom. The packing of the molecules in the crystals in both complexes is consolidated by arene $\pi - \pi$ stacking interactions between the sac rings and by intermolecular hydrogen bonds involving the amine groups of aeppz and the sulfonyl oxygen atoms of the sac ligands.

Key words: N-(2-Aminoethyl)piperazine, Saccharinate, Zinc(II), Cadmium(II), Crystal Structure

Introduction

Although its safety has been questioned in the past, saccharin, alternatively named 1,2-benzisothiazoline-3-(*2H*)one 1,1-dioxide or *o*-sulphobenzimide, and its water soluble alkali and earth-alkali salts are currently the most widely used non-caloric artificial sweetener in the world [1]. The presence of several potential donor sites such as the imino nitrogen, one carbonyl and two sulfonyl oxygen atoms makes saccharin an interesting ligand. Saccharin has a dissociable amine proton and is readily deprotonated to form the corresponding saccharinate (sac) anion. Although no metal complexes of neutral saccharin are known, the corresponding, deprotonated, anion sac readily coordinates metal ions, acting as a polyfunctional ligand. The negative charge is mostly located on the nitrogen atom and therefore, sac usually interacts with divalent transition metal ions through its deprotonated N atom as observed in tetraaqua-bis(saccharinato) complexes [2 – 6]. However, *O*-coordination including carbonyl and sulfonyl groups usually occurs in the case of *s*- or *p*-block metals [7 – 13].

sac   aeppz

This work is part of our continuing research on the synthesis and characterization of mixed-ligand complexes of sac with secondary ligands especially containing hydroxyalkyl and aminoalkyl groups. As an extension of these studies, we describe here the synthesis, spectroscopic, thermal and structural characterization of zinc(II) and cadmium(II) complexes of sac with N-(2-aminoethyl)piperazine (aeppz), namely *trans*-[Zn(sac)$_2$(aeppz)$_2$] (**1**) and *trans*-[Cd(sac)$_2$(aeppz)$_2$] (**2**).

Results and Discussion

Synthesis and properties

In the preparation of mixed-ligand transition metal complexes of sac, it became a common practice to

Fig. 1. Molecular structure of **1** with the atom labelling scheme and 40% thermal ellipsoids (arbitrary spheres for the H atoms). All C-H hydrogen atoms are omitted for clarity. Symmetry code (i) = $-x, -y, -z$.
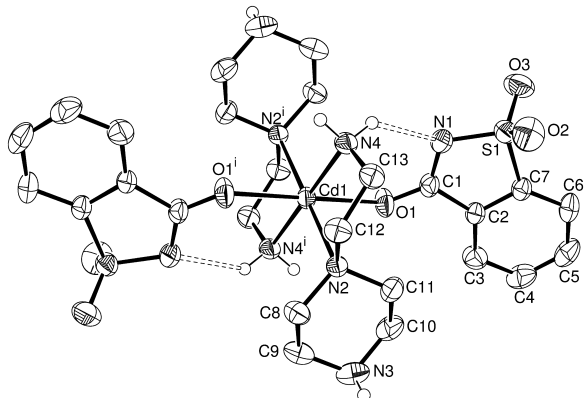

Fig. 2. Molecular structure of **2** with the atom labelling scheme and 40% thermal ellipsoids (arbitrary spheres for the H atoms). All C-H hydrogen atoms are omitted for clarity. Symmetry code (i) = $-x, -y, -z$.

utilize $[M(sac)_2(H_2O)_4] \cdot 2H_2O$ [M = zinc(II) or cadmium(II)] as a starting compound. The two sac ligands occupy the *trans* positions and addition of the secondary ligands results in the replacement of weakly coordinated aqua ligands, thereby forming the new complex. The title complexes **1** and **2** are obtained in this way by the direct reaction of the aeppz ligand in ethanol, with the sac coordination mode switching from the imino N to the carbonyl O atoms. The new complexes were obtained in high yields (over 90%) and the analytical data (C, H, N and S contents) are consistent with the proposed formulation of the complexes, which is also confirmed by X-ray studies. The molar ratio M:sac:aeppz in both complexes is 1:2:2. Both complexes are insoluble in common sol-

Table 1. Selected bond lengths and angles, and the hydrogen bonding geometry for **1**[a].

Bond lengths [Å] and angles [°]			
Zn1-N2	2.3997(10)	N2-Zn1-O1	92.44(3)
Zn1-N4	2.0679(10)	N2^i-Zn1-O1	87.56(3)
Zn1-O1	2.1654(8)	N4-Zn1-O1	91.95(4)
N2-Zn1-N4	81.34(4)	N4^i-Zn1-O1	88.05(4)
N2^i-Zn1-N4	98.66(4)		

Hydrogen bonds				
D-H···A	d(D–H)	d(H···A)	d(D···A)	⟨(D-H···A)
N4-H18···N1	0.90	2.28	2.9932(14)	136
N4-H19···N3^{ii}	0.90	2.34	3.1631(15)	152
N3-H17···O2^{iii}	0.96	2.12	3.0647(17)	169
C4-H2···O3^{iv}	0.93	2.52	3.3537(17)	150
C13-H15···O2^v	0.97	2.56	3.4061(16)	146

[a] Symmetry operations: ^{i} $-x, -y, -z$; ^{ii} $x-1, y, z$; ^{iii} $1-x, 1-y, -z$; ^{iv} $1+x, y, z$; ^{v} $-x, 1-y, -z$.

Table 2. Selected bond lengths and angles, and the hydrogen bonding geometry for **2**[a].

Bond lengths [Å] and angles [°]			
Cd1-N2	2.4705(10)	N2-Cd1-O1	93.11(4)
Cd1-N4	2.2892(10)	N2^i-Cd1-O1	86.89(4)
Cd1-O1	2.3341(10)	N4-Cd1-O1	91.55(4)
N2-Cd1-N4	77.31(4)	N4^i-Cd1-O1	88.45(4)
N2^i-Cd1-N4	102.69(4)		

Hydrogen bonds				
D-H···A	d(D–H)	d(H···A)	d(D···A)	∠(D-H···A)
N4-H18···N1	0.90	2.36	3.0616(16)	135
N4-H19···N3^{ii}	0.90	2.27	3.1196(16)	158
N3-H17···O2^{iii}	0.92	2.14	3.058(2)	171
C4-H2···O3^{iv}	0.93	2.54	3.3680(19)	148
C13-H15···O2^v	0.97	2.55	3.4128(18)	148

[a] Symmetry operations: ^{i} $-x, -y, -z$; ^{ii} $x-1, y, z$; ^{iii} $1-x, 1-y, -z$; ^{iv} $1+x, y, z$; ^{v} $-x, 1-y, -z$.

vents such as water, MeOH and EtOH, but sparingly soluble in warm MeOH. **1** and **2** are non-hygroscopic and stable in air.

Description of the crystal structures

The molecular structures of **1** and **2** are shown in Figs 1 and 2, and their selected bond lengths and angles are listed in Tables 1 and 2, respectively. $[Zn(sac)_2(aeppz)_2]$ and $[Cd(sac)_2(aeppz)_2]$ are isostructural and contain individual neutral molecules of $[M(sac)_2(aeppz)_2]$. The zinc(II) or cadmium(II) ions occupy an inversion center and are six-coordinated by two neutral aeppz and two anionic sac ligands forming a MN_4O_2 core. Each aeppz ligand behaves as a bidentate ligand using the central heterocyclic N atom and the N atom of the aminoethyl group, and forms a five-membered metallocyclic chelate ring, while each sac ligand is *O*-bonded through the carbonyl O atom and placed at *trans* positions.

The most common coordination mode of sac is ligation through the charged nitrogen atom. In the case of zinc(II) and cadmium(II), the coordination of sac using a donor group other than the amine N atom is unusual, and [Zn(sac)$_2$(mpy)$_2$] and [Cd(sac)$_2$(mpy)$_2$] [14] are the only other examples of *O*-coordinated sac with these metal ions (mpy = 2-pyridylmethanol). Therefore, the most interesting feature of the title complexes is the *O*-coordination of the sac ligands *via* the carbonyl oxygen atom. The Zn-O$_{sac}$ bond distance of 2.1654(8) Å and the Cd-O$_{sac}$ bond distance of 2.3341(10) Å are somewhat longer than the equivalent distances found in [Zn(sac)$_2$(mpy)$_2$] [2.0717(14) Å] and [Cd(sac)$_2$(mpy)$_2$] [2.2612 (14) Å] [14]. The M-O$_{sac}$ and M-N$_{ethylamino}$ bond distances are similar, but the M-N$_{ppz-ring}$ bond distances of 2.3099(11) [Zn] and 2.4705(10) Å [Cd] are significantly longer than the other four bonds, resulting in an elongated distorted octahedral geometry along the N2-M-N2^i (i = −x, −y, −z) bond axis. This may be due to the molecular conformation of the ppz ring. The puckering parameters [15] of the ppz ring system in **1** are $q = 0.5377(16)$ Å and $\theta = 5.44(17)°$, and in **2**, $q = 0.5422(15)$ Å and $\theta = 4.12(19)°$, suggesting that the ppz rings exhibit an essentially "undistorted" (cyclohexane like) chair conformation. The sp^3 lone pair on the N2 atom thus may not completely overlap with the valence orbitals of the adjacent metal ion. The Zn and Cd atoms are axial to the ring atoms, and the poor overlap results in a lengthening of the M-N$_{ppz-ring}$ bonds. The bond angles involving the metal(II) and N2 atoms [Zn-N2-C8 = 117.52(7)°, Zn-N2-C11 = 115.99(8)°, Zn-N2-C12 = 97.43(6)°, and Cd-N2-C8 = 114.63(8)°, Cd-N2-C11 = 115.56(8)°, Cd-N2-C12 = 99.06(7)°] also show the deviation from that of a regular tetrahedron. The deviation of the metal coordination sphere from octahedral geometry is revealed in significant deviations of the *cis* angles from ideal values as shown in Tables 1 and 2.

The sac ligand is essentially planar in both compounds with root-mean-square (rms) deviations from the best least-squares planes of 0.021 and 0.028 Å in **1** and **2**, respectively. The Zn and Cd atoms deviate from the best planes of sac by 0.7844(13) and 0.9589(14) Å. Since the structures are identical in terms of molecular interactions, only the packing of the molecules of **1** is presented in Fig. 3. The amine hydrogen atoms of the aeppz ligands form intra- and intermolecular hydrogen bonds with the imino N, carbonyl or sulfonyl O atoms of the adjacent sac ligands. Some of the phenyl hydro-

Table 3. Selected IR data^a for **1** and **2**.

Assignment	1	2
ν(NH)	3340m, 3286m	3305m, 3273m
ν(CH)	2978m, 2828w	2972w, 2857w
ν(CO)	1678, 1625vs	1651vs, 1626vs
ν(CN)	1583s	1583s
ν(CC)	1458s	1458vs
ν_s(CNS)	1338m	1335m
ν_{as}(SO$_2$)	1298vs, 1250vs	1271vs, 1251vs
ν_s(SO$_2$)	1171vs	1155vs
ν_{as}(CNS)	966vs	968s

^{a} Frequencies in cm^{-1}. w = weak; vs = very strong; s = strong; m = medium; sh = shoulder.
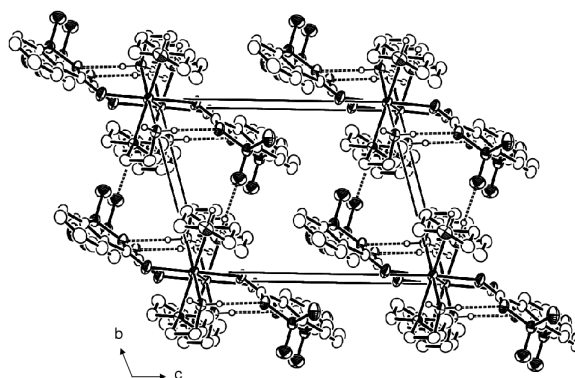

Fig. 3. Packing of molecules of **1** viewed down *a*. All C-H hydrogen atoms are omitted for clarity, and hydrogen bonds are indicated by dashed lines.

gen atoms of sac and the ethylene hydrogen atoms of aeppz are also involved in relatively weak C-H···O interactions with the sulfonyl O atoms of the adjacent sac ligands. Furthermore, the sac ligands form weak $\pi - \pi$ interactions with their inversion-symmetry generated partners [C$_g$···C$_g^i$ 3.8722(9) Å in **1** and 3.9375(9) Å in **2**; C$_g$ = centroid of atoms C2-C7; (i): −x, −y, 1 − z]. Thus, the molecular packing is reinforced by the hydrogen bonds and aromatic $\pi - \pi$ stacking interactions forming a three-dimensional network as shown in Fig. 3.

Infrared spectra

The most important IR bands of complexes **1** and **2**, together with their assignments are listed in Table 3. The absorption bands of the NH groups of aeppz are observed as two separated bands centered at *ca.* 3340 and 3390 cm^{-1} and are significantly shifted to the lower frequency region, compared to the free ligand (3475 and 3415 cm^{-1}). The relatively low frequency of these bands is indicative of strong hydrogen bond-

ing of the NH groups. The relatively weak bands in the range $2980-2828$ cm^{-1} are assigned to the $\nu(CH_2)$ mode of ethylene groups.

Two strong absorption bands of the carbonyl group of sac in **1** are observed at 1678 and 1625 cm^{-1}. The carbonyl stretching vibration frequency of sac in **1** shifts to the lower frequency region by *ca.* 13 cm^{-1} compared to the starting complex [Zn(sac)$_2$(H$_2$O)$_4$]·2H$_2$O with two *N*-bonded sac ligands, in agreement with its participation in bonding. Interestingly, the vibrations related to bending of this group are less affected. However, the carbonyl bands of sac in **2** occur at 1651 and 1626 cm^{-1}, comparable to those (1647 and 1624 cm^{-1}) observed for [Cd(sac)$_2$(H$_2$O)$_4$]·2H$_2$O, in which two sac ligands are *N*-bonded. Based on the IR spectrum of **2**, it may be concluded that the sac ligands are *N*-coordinated. However, Jovanovski and Soptrajanov [16] pointed out that it was not easy to establish clear correlations in the IR spectra of metal-sac complexes, because the position of the carbonyl band is influenced by the whole bonding situation within the sac moiety. The strong bands at 1583 and 1458 cm^{-1} correspond to the ring $\nu(CN)$ and $\nu(CC)$ vibrations, respectively. The $\nu_s(CNS)$ and $\nu_{as}(CNS)$ absorption bands of sac in **1** and **2** are observed at *ca.* 1335 and 967 cm^{-1}, while the $\nu_{as}(SO_2)$ and $\nu_s(SO_2)$ vibration bands appear as very strong bands centered at around 1270 and 1160 cm^{-1}.

Experimental Section

Materials and measurements

All reagents were purchased from commercial sources and used as supplied. The starting complexes [Zn(sac)$_2$(H$_2$O)$_4$]·2H$_2$O and [Cd(sac)$_2$(H$_2$O)$_4$]·2H$_2$O were prepared according to the literature method [17].

IR spectra were recorded on a Shimadzu FTIR-8900 spectrophotometer as KBr pellets in the frequency range $4000-300$ cm^{-1}. The elemental analyses (C, H, N and S contents) were performed on a Vario EL Elemental Analyser. Thermal analysis curves (TG and DTA) were obtained using a Rigaku TG8110 thermal analyzer in a static air atmosphere. A sample size of $5-10$ mg was used.

Synthesis of the metal complexes

The aeppz ligand (0.26 g, 2.0 mmol) was added dropwise to a solution of [Zn(sac)$_2$(H$_2$O)$_4$]·2H$_2$O (0.54 g, 1 mmol) in EtOH (30 cm^3) and the reaction mixture was stirred for 1 h at room temperature. X-ray quality colorless crystals were obtained by slow diffusion of the resulting solution into ether after two days. Yield 92%. decomp.

Table 4. Crystallographic data for complexes **1** and **2**.

	1	2
Empirical formula	C$_{26}$H$_{38}$N$_8$O$_6$S$_2$Zn	C$_{26}$H$_{38}$N$_8$O$_6$S$_2$Cd
M_r	688.14	735.16
T [K]	298(2)	293(2)
Radiation, λ [Å]	0.71073	0.71073
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions		
a [Å]	8.4501(4)	8.4413(3)
b [Å]	9.3947(4)	9.5724(3)
c [Å]	11.5711(5)	11.6483(4)
α [°]	94.451(1)	94.591(1)
β [°]	110.205(1)	111.079(1)
γ [°]	116.058(1)	115.379(1)
V [Å^3]	745.23(6)	762.25(4)
Z	1	1
D_c [g/cm^3]	1.533	1.602
μ [mm^{-1}]	1.020	0.908
$F(000)$	360	378
Crystal size [mm^3]	$0.49 \times 0.23 \times 0.22$	$0.48 \times 0.38 \times 0.33$
θ Range [°]	2.51/32.52	2.26/32.51
Index range (h, k, l)	$-12/12, -11/14,$ $-17/17$	$-12/12, -14/14,$ $-13/17$
Reflections collected	7764	10013
Independent refls (R_{int})	5165 (0.0120)	5349 (0.0143)
Refls observed ($> 2\sigma$)	4285	5073
Absorption correction	multi-scan	multi-scan
Min. and max. transmission	0.635 and 0.807	0.670 and 0.754
Data / parameters	5165 / 196	5349 / 197
Goodness-of-fit on F^2	1.009	1.045
Final R indices [$I > 2\sigma(I)$]	0.0291	0.0229
$wR2$	0.0819	0.0596
Largest diff. peak and hole [e·Å^{-3}]	0.33 and -0.43	0.36 and -0.38

p. 230 °C. C$_{26}$H$_{38}$N$_8$O$_6$S$_2$Zn (688.14): calcd. C 45.38, H 5.57, N 16.28, S 9.32; found C 45.32, H 5.60, N 16.35, S 9.25.

Complex **2** was prepared by a similar synthesis procedure, using [Cd(sac)$_2$(H$_2$O)$_4$]·2H$_2$O (0.58 g, 1 mmol) and obtained as colorless crystals. Yield: 90%. decomp. p. 240 °C. C$_{26}$H$_{38}$N$_8$O$_6$S$_2$Cd (735.16): calcd. C 42.48, H 5.21, N 15.24, S 8.72; found C 42.40, H 5.32, N 15.30, S 8.65.

X-ray crystal structure determinations

Intensity data for the title compounds were collected using a BRUKER SMART 1000 CCD area detector diffractometer (Mo-K$_\alpha$ radiation, $\lambda = 0.71073$ Å) at 293 K. The structures were solved with SHELXS-97 and refined using SHELXL-97 [18]. All the non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms attached to N were located in difference maps and refined by riding on their parent atom in their as-found positions. H atoms attached to C were included using a riding model in idealised positions. The details of data collec-

tion, refinement and crystallographic data are summarized in Table 4.

indent Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-255255 (**1**) and CCDC-255256 (**2**). Copies of the data can be obtained on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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