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***cis*-bis(Saccharinato)cobalt(II) and -zinc(II) complexes with 2-dimethylaminoethanol: syntheses, crystal structures, spectroscopic and thermal studies**

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***cis*-bis(Saccharinato)cobalt(II) and -zinc(II) complexes with 2-dimethylaminoethanol: syntheses, crystal structures, spectroscopic and thermal studies**

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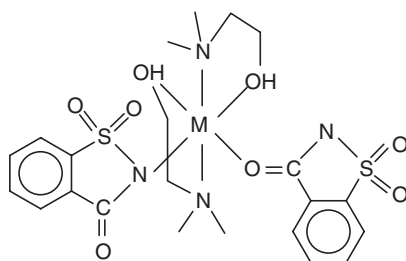
2-Dimethylaminoethanol (dmea) reacted with tetraqua-bis(saccharinato)cobalt(II) and -zinc(II) in *n*-butanol to yield the new complexes *cis*-[Co(sac)₂(dmea)₂] (1), and *cis*-[Zn(sac)₂(dmea)₂] (2) (sac = saccharinate). The complexes were characterized by elemental analyses, IR spectroscopy, DTA-TG and X-ray crystallography. Both complexes are isomorphous and crystallize in the monoclinic space group *P*2₁/*c*. The cobalt(II) and zinc(II) ions are coordinated by two neutral dmea ligands and two sac anions in a distorted octahedral environment. The dmea ligand acts as a bidentate N, O donor through the amine N and hydroxyl O atoms, while the sac ligand exhibits non-equivalent coordination, behaving as an ambidentate ligand; one coordinates to the metal *via* the carbonyl oxygen atom, while the other is *N*-bonded. The packing of the molecules in the crystals of both complexes is achieved by aromatic π (sac)– π (sac) stacking interactions, C–H $\cdots\pi$ interactions and weak intermolecular C–H \cdots O hydrogen bonds involving the methyl groups of dmea and the sulfonyl oxygen atoms of the sac ligands. IR and UV spectra and thermal analysis are in agreement with the crystal structures.

Keywords: 2-Dimethylaminoethanol; Saccharinato; Cobalt(II); Zinc(II); Crystal structure

1. Introduction

Saccharin (C₇H₅NO₃S, also named 1,2-benzisothiazol-3(2*H*)-on-1,1-dioxide or *o*-benzosulfimide) is widely used as a non-caloric artificial sweetener and commercially available as water soluble alkali salts [1]. Interest in the synthesis and characterization of metal complexes of saccharin is due to its possible carcinogenesis and DNA-alerting ability. Studies showed that the presence of three different functional groups such as the imino nitrogen, carbonyl oxygen, or sulfonyl oxygen makes its nitranion, saccharinate (sac), a polyfunctional ligand in coordination chemistry [2, 3]. The most common coordination mode of sac is ligation through the negatively charged nitrogen atom, usually observed in the aqua bis(saccharinato) complexes of first-row transition metals,

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Scheme 1. Structural diagram of *cis*-[M(sac)₂(dmea)₂] (M = Co^{II} and Zn^{II}).

and coordination *via* the carbonyl oxygen occurs in certain cases, especially with alkali, alkaline earth, inner-transition and p-block metals [3].

As part of our studies on the preparation of metal-sac complexes with chelating ligands, especially containing alkyhydroxyl and alkylamine groups, herein we report the synthesis, spectroscopic, thermal and structural characterization of two isomorphous cobalt and zinc complexes of sac with 2-dimethylaminoethanol (dmea), *cis*-[Co(sac)₂(dmea)₂] (**1**) and *cis*-[Zn(sac)₂(dmea)₂] (**2**) (scheme 1).

2. Experimental

2.1. Materials

All reagents were purchased from commercial sources and used as supplied. The starting complex [M(sac)₂(H₂O)₄]·2H₂O (M = Co^{II} and Zn^{II}) was prepared according to the literature method [4].

2.2. Preparation of the complexes

2-Dimethylaminoethanol (dmea) (0.46 g, 0.5 mmol) was added to a solution of [Co(sac)₂(H₂O)₄]·2H₂O (0.13 g, 0.25 mmol) in *n*-butanol (20 cm³) at 50°C, and stirred for 30 min. Dark pink crystals of complex **1** suitable for X-ray diffraction were obtained by slow evaporation of the resulting solution at room temperature within a day. Yield 65%. decomp. p. 127°C (Found: C, 43.7; H, 4.8; N, 9.5; S, 10.5; C₂₂H₃₀N₄O₈S₂Co, Calcd: C, 43.9; H, 5.0; N, 9.3; S, 10.7).

Compound **2** was synthesized in a similar manner to **1** except that [Zn(sac)₂(H₂O)₄]·2H₂O was used instead of [Co(sac)₂(H₂O)₄]·2H₂O. Colorless crystals of **2** were formed by slow evaporation at room temperature after 2 d. Yield 35%. decomp. p. 144°C (Found: C, 43.8; H, 4.9; N, 9.4; S, 10.4; C₂₂H₃₀N₄O₈S₂Zn, Calcd: C, 43.5; H, 5.0; N, 9.2; S, 10.6).

2.3. Physical measurements

IR spectra were recorded on a Shimadzu FTIR-8900 spectrophotometer as KBr pellets in the frequency range 4000–400 cm⁻¹. Electronic spectra of aqueous solutions were

measured on a Unicam UV2 in the 200–900 nm range. The elemental analyses (C, H, N and S contents) were performed on a Vario EL Elemental Analyser. Room temperature magnetic susceptibility measurements were carried out using a Sherwood Scientific MXI model Evans magnetic balance. Thermal analysis curves (TG and DTA) were obtained using a Rigaku TG8110 thermal analyzer with a heating rate of 10C min^{-1} in static air, using platinum crucibles. A sample size of 5–10 mg was used and sintered α -alumina was used as the reference material.

2.4. X-ray structure determination

Intensity data for complexes **1** and **2** were collected using a STOE IPDS 2 diffractometer at 293 K. The structures were solved with SHELXS-97 [5] and refined using SHELXL-97 [6]. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms on carbon were included using a riding model in idealised positions, while hydroxyl hydrogen atoms were refined freely. The large residual electron peaks and holes in both structures are due to high U_{ij} values of the methyl carbon atoms. The details of data collection, refinement and crystallographic data are summarized in table 1.

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

Compound	1	2
Empirical formula	$\text{C}_{22}\text{H}_{30}\text{N}_4\text{O}_8\text{S}_2\text{Co}$	$\text{C}_{22}\text{H}_{30}\text{N}_4\text{O}_8\text{S}_2\text{Zn}$
M_r	601.55	607.99
T (K)	293(2)	293(2)
Radiation, λ (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
Unit cell dimensions (Å, °)		
a	14.6980(19)	14.7025(7)
b	12.4950(11)	12.5250(4)
c	15.432(2)	15.4258(8)
β	110.045(10)	110.114(4)
V (Å ³)	2662.4(6)	2667.4(2)
Z	4	4
D_c (g cm ⁻³)	1.501	1.514
μ (mm ⁻¹)	0.854	1.130
$F(000)$	1252	1264
Crystal size (mm ³)	$0.42 \times 0.23 \times 0.18$	$0.49 \times 0.43 \times 0.38$
θ range (°)	2.15–26.00	2.15–27.97
Index range (h, k, l)	–18/18, –15/15, –18/18	–19/19, –16/16, –20/20
Reflections collected	37,281	40,130
Independent reflections (R_{int})	5234 (0.1096)	6391 (0.1197)
Absorption correction	Numerical	Numerical
Min. and max. transmissions	0.634 and 0.766	0.748 and 0.946
Data/restraints/parameters	5234/2/39	6391/2/337
Goodness-of-fit on F^2	0.902	1.071
Final R indices [$I > 2\sigma(I)$]	0.0528	0.0536
R indices (all data)	0.0983	0.0738
wR indices (all data)	0.1447	0.1544
Largest diff. peak and hole (e Å ⁻³)	0.94 and –1.34	1.50 and –1.69

3. Results and discussion

3.1. Synthesis

In the preparation of mixed-ligand transition metal complexes of sac, it is common practice to use $[M(\text{sac})_2(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}$ [$M = \text{Co}^{\text{II}}$ or Zn^{II}] as a starting compound. The two sac ligands are *N*-coordinated and occupy the *trans* positions of the coordination octahedron. Addition of the secondary ligands usually results in the replacement of weakly coordinated aqua ligands. The title complexes **1** and **2** are obtained in this way by the direct reaction of the dmea ligand with the starting complexes of cobalt(II) and zinc(II) in *n*-butanol, forming the solid complexes in reasonable yields. Complex **1** is soluble in water and *n*-butanol, but sparingly soluble in methanol and ethanol, while complex **2** is not soluble in water, ethanol and *n*-butanol, but highly soluble in methanol. Complex **1** is non-hygroscopic and stable in air, whereas complex **2** is somewhat hygroscopic when exposed to air for a long time.

3.2. Spectral and magnetic properties

The most important IR bands of complex **1** and **2** are listed in table 2, together with their assignments. The IR spectra of both complexes are almost identical, indicating structural similarity. The broad and strong absorption bands centered at ca 3450 cm^{-1} characterize $\nu(\text{OH})$ vibrations of the dmea ligand. The relatively weak absorption bands between $2960\text{--}3100\text{ cm}^{-1}$ are assigned to the $\nu(\text{CH})$ vibrations. The stretching vibration of the carbonyl group of sac appears as two separate sharp bands at 1653 and 1624 cm^{-1} for **1**, and 1689 and 1645 cm^{-1} for **2**. The higher absorption band is characteristic for the *N*-bonded sac ligand, whereas the lower band is assigned to the *O*-bonded sac *via* the carbonyl group. The strong absorption bands at 1585 and 1460 cm^{-1} correspond to the $\nu(\text{CC})$ vibrations of the aromatic ring. The absorption bands of the CNS moiety of sac occur at ca 1334 and 960 cm^{-1} . The $\nu_{\text{as}}(\text{SO}_2)$ vibration bands appear as two split bands centered at 1286 and 1268 cm^{-1} in **1**, and 1290 and 1252 cm^{-1} in **2**. The $\nu_{\text{s}}(\text{SO}_2)$ modes of sac appear as a very strong band at approximately 1153 cm^{-1} . The weak bands located at 450 and 485 cm^{-1} are indicative of the M–N and M–O bonds, respectively [7].

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

Assignment	1	2
$\nu(\text{OH})$	3450, 3417s,b	3450s,b
$\nu(\text{CH})$	3093w, 2977w	3085w, 2964vw
$\nu(\text{CO})$	1653vs, 1624vs	1689vs, 1645sh
$\nu(\text{CC})$	1585s, 1461s	1589s, 1462s
$\nu_{\text{s}}(\text{CNS})$	1334s	1333m
$\nu_{\text{as}}(\text{SO}_2)$	1286vs, 1268vs	1290vs, 1252s
$\nu_{\text{s}}(\text{SO}_2)$	1151vs	1155vs
$\nu_{\text{as}}(\text{CNS})$	956vs	964vs
$\nu(\text{MO})$	486w	483vw
$\nu(\text{MN})$	449vw	452vw

^aFrequencies in cm^{-1} . b = broad; w = weak; vw = very weak; s = strong; vs = very strong; sh = shoulder; m = medium.

The electronic spectrum of complex **1** shows several intense bands between 250 and 280 nm assigned to the intra-ligand transitions in dmea and sac, while the broad band at 517 nm is assigned to d–d transitions for the octahedral cobalt(II) species. The room-temperature magnetic moment measurements show that complex **1** is paramagnetic with a μ_{eff} of 4.7 BM, which is significantly higher than the calculated spin-only value of 3.87 BM, suggesting an effective orbital contribution for the high-spin d^7 octahedral configuration.

3.3. Thermal analysis

The thermal decomposition behavior of complexes **1** and **2** were followed up to 800°C under atmospheric conditions. Compound **1** is thermally stable up to 127°C and then begins to decompose. The elimination of two dmea molecules takes place in the temperature range 127–325°C with an endothermic DTA peak at 164°C, leaving a solid residue of $[\text{Co}(\text{sac})_2]$. The experimental mass loss of 28.8% agrees well with the calculated mass loss of 29.6%. The decomposition of the sac residue occurs between 325 and 543°C with two extremely exothermic DTA peaks at 456 and 517°C to give a gray product.

Complex **2** starts to decompose at 144°C and its TG curve indicates a continuous mass loss process, so that it is impossible to distinguish the steps of decomposition. However, the endothermic DTA peaks at 240 and 342°C correspond to removal of the dmea ligands, while highly exothermic DTA peaks at 438 and 512°C characterize the decomposition of the sac moiety [8]. The decomposition of **2** ends at 580°C.

3.4. Description of the crystal structures

The molecular structure of **1** with the atom-labeling scheme is shown in figure 1 and the structure of **2** is not presented, since both structures are isomorphous with a monoclinic

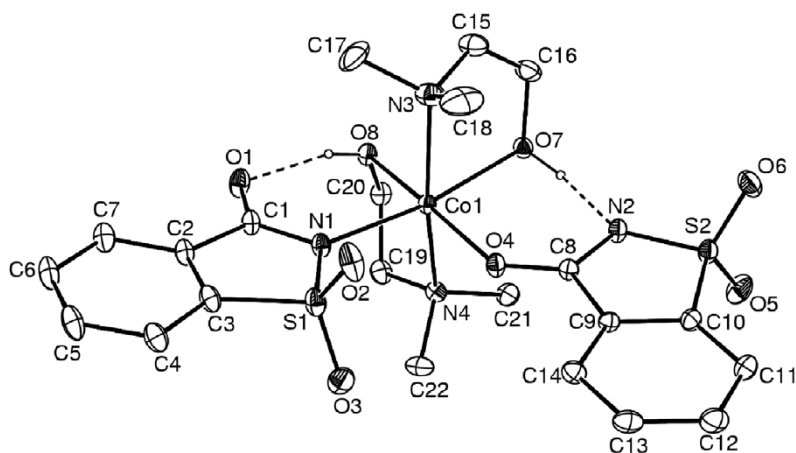


Figure 1. Molecular structure of **1** with the atom labelling scheme and 30% displacement ellipsoids (arbitrary spheres for the H atoms). All the C–H hydrogen atoms are omitted for clarity.

Table 3. Selected bond lengths (Å), angles (°) and hydrogen bonding geometry for **1** and **2**.

	1	2		1	2
M1–N1	2.162(3)	2.147(3)	N1–M1–O8	91.11(13)	92.37(10)
M1–N3	2.214(4)	2.207(3)	N3–M1–O4	94.44(17)	95.31(15)
M1–N4	2.220(4)	2.223(3)	N3–M1–O7	78.66(16)	77.58(12)
M1–O4	2.048(3)	2.054(2)	N3–M1–O8	92.69(17)	91.98(14)
M1–O7	2.193(3)	2.267(2)	N4–M1–O4	91.54(13)	90.91(11)
M1–O8	2.133(3)	2.160(2)	N4–M1–O7	90.00(13)	88.58(10)
N1–M1–N3	94.43(17)	95.69(13)	N4–M1–O8	80.61(13)	80.36(11)
N1–M1–N4	96.38(14)	97.51(11)	O4–M1–O7	92.30(12)	91.83(10)
N4–M1–N3	167.37(16)	164.98(13)	O4–M1–O8	171.58(13)	169.82(10)
N1–M1–O4	92.79(12)	93.96(10)	O8–M1–O7	84.72(13)	82.80(10)
N1–M1–O7	171.72(13)	171.52(11)			
D–H...A	d(D–H)	D(H...A)	d(D...A)	∠(D–H...A)	
1					
O7–H7A...N2	0.87(6)	1.90(6)	2.689(5)	150(6)	
O8–H8A...O1	0.81(7)	1.80(7)	2.583(5)	162(7)	
C18–H18A...O2	0.96	2.38	3.302(11)	160	
2					
O7–H7A...N2	0.81(5)	1.93(5)	2.710(4)	161(5)	
O8–H8A...O1	0.89(5)	1.77(5)	2.606(4)	157(4)	
C17–H17B...O3	0.96	2.47	3.362(9)	154	

space group $P2_1/c$. The selected bond distances and angles are summarized in table 3. Complexes **1** and **2** contain individual neutral molecules of $[M(\text{sac})_2(\text{dmea})_2]$, in which cobalt(II) and zinc(II) sit on inversion centers and are octahedrally coordinated by two neutral dmea ligands and two sac anions, constituting a distorted MN_3O_3 chromophore with a meridional arrangement. Each dmea is bidentate through the amino N and hydroxyl O atoms, forming a five-membered metallocyclic chelate ring. The sac ligand is usually involved in the formation of *N*- or *O*-bonded mononuclear complexes. In the starting complexes, both sac ligands are *N*-coordinated at *trans* positions and during complex formation, the sac coordination geometry switched from *trans* to *cis*. Furthermore, the title complexes present a less-common coordination of sac: both sac ligands are monodentate, but one is *N*-bonded, while the other is coordinated through the carbonyl O atom behaving as an ambidentate ligand as observed only in the following complexes: $[\text{Cu}(\text{sac})_2(\text{py})_3]$ (py = pyridine) [9], $[\text{Cu}(\text{sac})_2(\text{dipy})(\text{H}_2\text{O})]$ (dipy = dipyridylamine) [10], $\text{ApyH}[\text{Cu}(\text{H}_2\text{O})_2(\text{sac})_3]$ (ApyH = 2-aminopyridinium) [11], and $[M(\text{sac})_2(\text{pym})_2]$, where pym = 2-pyridylmethanol, $M = \text{Co}^{\text{II}}$ [12], Ni^{II} [12], Zn^{II} [13], and Cd^{II} [13].

The $M\text{--}N_{\text{sac}}$ and $M\text{--}O_{\text{sac}}$ bond distances are similar to those reported for $[\text{Co}(\text{sac})_2(\text{pym})_2]$ [12] and $[\text{Zn}(\text{sac})_2(\text{pym})_2]$ [13]. The $M\text{--}N_{\text{dmea}}$ and $M\text{--}O_{\text{dmea}}$ bond distances in complexes **1** and **2** compare well with those of $[\text{Co}(\text{acac})_2(\text{dmea})_2]$ (acac = 2,4-pentanedionate) [14], but somewhat longer than the corresponding bonds with the sac ligands in the title complexes. Significant distortions are evident from the angles in the coordination polyhedra (table 3). The *trans* and *cis* angles are in the range of $167.4(2)\text{--}171.6(1)^\circ$ and $78.6(2)\text{--}94.4(2)^\circ$, respectively for **1**, and $165.0(1)\text{--}171.5(1)^\circ$ and $77.6(1)\text{--}95.3(1)^\circ$, respectively for **2**. The largest deviations from ideal were observed in the bite angles of the dmea ligands.

Both sac ligands (excluding sulfonyl O atoms) in complexes **1** and **2** are essentially planar and nearly co-planar and the dihedral angles between the corresponding mean

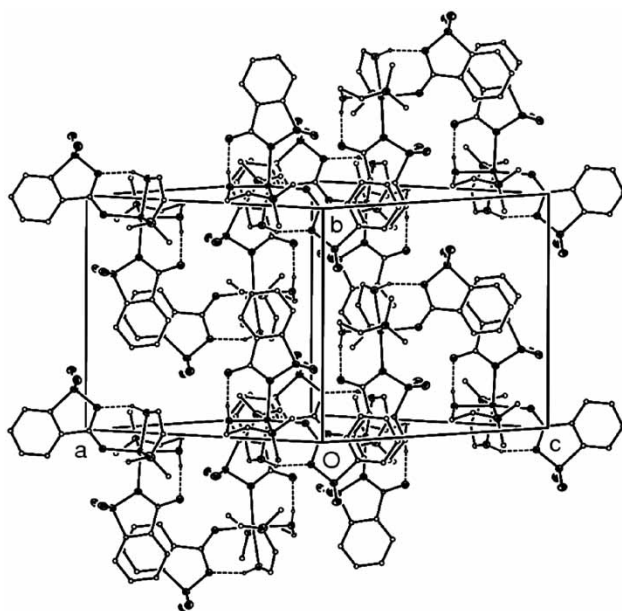


Figure 2. Packing diagram of **1** involving $\pi(\text{sac})-\pi(\text{sac})$ stacking interactions.

planes are $7.6(2)^\circ$ in **1**, and $8.3(2)^\circ$ in **2**. Due to isomorphism, both crystals possess similar packing motifs. Therefore, only the packing diagram of complex **1** is presented in figure 2. Both complexes exhibit intra-molecular $\text{O}-\text{H}\cdots\text{N}$ and $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds and packing of the molecules of **1** and **2** is achieved by an aromatic $\pi(\text{sac})-\pi(\text{sac})$ stacking interaction between the phenyl rings of the neighboring sac ligands and two $\text{C}-\text{H}\cdots\pi(\text{sac})$ interactions. The $\text{C}_g\cdots\text{C}_g^1$ (C_g =centroid of atoms) distances are $3.716(3)$ Å [(i): $x, 1/2 - y, -1/2 + z$] in **1**, and $3.717(2)$ Å [(i): $x, 1/2 - y, 1/2 + z$] in **2**, while the $\text{C}-\text{H}\cdots\pi$ distances are 3.337 and 3.248 Å in **1**, and 3.214 and 3.305 Å in **2**. In addition to these interactions, molecular packing of the title complexes is also reinforced by weak intermolecular $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds involving the methyl groups of dmea and the sulfonyl oxygen atoms of the sac ligands, leading to a three-dimensional network as shown in figure 2.

Supplementary material

Crystallographic data for the structures reported in the article have been deposited at the CCDC as supplementary data, CCDC Nos. 291794 (**1**) and 291795 (**2**). Copies of the data can be obtained on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. Email: deposit@ccdc.cam.ac.uk.

Acknowledgements

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