Synthesis and Characterization of Cadmium and Mercury Saccharinate Complexes with 2-Dimethylaminoethanol: cis-[Cd(sac)₂(dmea)₂] and [Hg(sac)₂(dmea)(H₂O)]

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The new cadmium and mercury saccharinate (sac) complexes, cis-[Cd(sac)₂(dmea)₂] (1) and $[Hg(sac)_2(dmea)(H_2O)]$ (2) (dmea = 2-dimethylaminoethanol), have been prepared and characterized by elemental analysis, IR spectroscopy, thermal analysis and single crystal X-ray diffraction. In complex 1, the cadmium(II) ion is coordinated by two neutral dmea ligands and two sac anions in a distorted octahedral CdN₃O₃ coordination geometry. The dmea ligand acts as a bidentate N, O chelate, while the sac ligands behave as an ambidentate ligands. One of them coordinates to the cadmium(II) ion through the carbonyl oxygen atom, while the other is N-bonded. In complex 2, the mercury(II) ion is coordinated by an aqua ligand, a chelating dmea ligand and two N-bonded sac ligands, forming a distorted trigonal bipyramidal coordination HgN₃O₂. The molecules interact with each other through O–H···O hydrogen bonds and aromatic $\pi(sac) \cdots \pi(sac)$ stacking interactions, leading to a three-dimensional supramolecular network.

Key words: Saccharinate, 2-Dimethylaminoethanol, Cadmium, Mercury, Crystal Structure

Introduction

Saccharin (C7H5NO3S; also named 1,2-benzisothiazoline-3-(2H)one 1,1-dioxide or o-benzosulfimide) and its water soluble alkali and earth-alkali salts are widely used as non-caloric artificial sweeteners [1]. The presence of several potential donor atoms such as the imino nitrogen, one carbonyl and two sulfonyl oxygen atoms makes sac an interesting polyfunctional ligand in coordination chemistry. While metal complexes of neutral saccharin are not known, its deprotonated anion, saccharinate (sac), readily coordinates to various metal ions [2, 3]. Sac exhibits different coordination modes using these donor atoms, behaving as a Nor O-monodentate, bidentate (N,O), tridentate (N,O,O)chelating and/or bridging ligand, forming complexes from monomers to coordination polymers [3]. A lesscommon coordination characteristic of the ligand is the ambidentate coordination behavior, or the formation of M-N and M-O bonds with two different sac ligands in the same complex [3].

As a part of our continuing research on the synthesis and characterization of mixed-ligand complexes of



sac with N- and O-donor ligands, we reported a helical polymeric complex of copper(II)-sac with 2-dimethylaminoethanol (dmea), $[Cu_2(sac)_2(\mu-dmea)_2(\mu-dm$ H_2O]_n [4], and in this paper, we describe the synthesis, spectral, thermal and structural characterization of new bis(saccharinato)cadmium and mercury complexes with the same co-ligand, namely cis-[Cd(sac)2- $(dmea)_2$ (1) and $[Hg(sac)_2(dmea)(H_2O)]$ (2).

Results and Discussion

Complexes 1 and 2 are obtained by the direct reaction of the dmea ligand with the starting complexes $[Cd(sac)_2(H_2O)_4] \cdot 2H_2O$ and $[Hg(sac)_2]$, respectively, in reasonable yields. Complex 1 is soluble in water, methanol, ethanol, and n-butanol, but sparingly solu-

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| Table | 1. | Selected | bond | lengths | and | angles, | and | hydrogen |
|--------|----|----------|---------------|---------|-----|---------|-----|----------|
| bondir | ıg | geometry | of 1 . | | | | | |

| Bond lengths (| Å) and angl | es (°): | | |
|-------------------------|-----------------|-----------------------------|------------------|-------------------------|
| Cd1-N2 | 2.29 | 9(7) | N2-Cd1-O8 | 92.4(2) |
| Cd1-N3 | 2.32 | 3(8) | N3-Cd1-O3 | 93.7(3) |
| Cd1-N4 | 2.35 | 1(7) | N3-Cd1-O7 | 78.4(3) |
| Cd1-O3 | 2.26 | 2(5) | N3-Cd1-O8 | 98.3(3) |
| Cd1–O7 | 2.40 | 0(6) | N4-Cd1-O3 | 92.2(3) |
| Cd1-O8 | Cd1–O8 2.331(7) | | N4-Cd1-O7 | 85.1(3) |
| N2-Cd1-N3 | 97.9(| 3) | N4-Cd1-O8 | 73.4(3) |
| N2-Cd1-N4 | 97.9(| 3) | O3-Cd1-O7 | 89.3(2) |
| N3-Cd1-N4 | 162.4(3 | 3) | O3-Cd1-O8 | 163.9(2 |
| N2-Cd1-O3 | 96.5(2 | 2) | O7-Cd1-O8 | 82.6(3) |
| N2-Cd1-O7 | 173.3(2 | 2) | | |
| Hydrogen bond | ds: | | | |
| $D\!\!-\!\!H\!\cdots A$ | D-H (Å) | $H \cdots A (\mathring{A})$ | $D \cdots A$ (Å) | $D-H\cdots A(^{\circ})$ |
| O8–H8···O6 | 0.93 | 2.62 | 2.848(11) | 95 |



Fig. 1. A view of the molecular structure of complex 1, showing 30% displacement ellipsoids (arbitrary spheres for the H atoms). Intramolecular hydrogen bonds are indicated by dashed lines.

ble in isopropanol, while complex **2** is slightly soluble in water and ethanol, but highly soluble in methanol. Both complexes are non-hygroscopic and stable in air. Complexes **1** and **2** do not melt, but decompose at 86 and 28 $^{\circ}$ C, respectively.

Description of the crystal structures

The molecular structure of complex **1** with the atom labeling scheme is shown in Fig. 1 and selected bond distances and angles are listed in Table 1. Complex **1** consists of individual neutral molecules of $[Cd(sac)_2(dmea)_2]$, in which cadmium(II) is octahedrally coordinated by two neutral dmea ligands and two sac anions, constituting a distorted meridional CdN₃O₃ chromophore. Each dmea ligand acts as a bidentate N, O-ligand, forming a fivemembered metallocyclic chelate ring. The sac ligand is usually involved in the formation of *N*- or *O*-bonded mononuclear complexes. In the starting complex $[Cd(sac)_2(H_2O)_4]\cdot 2H_2O$, both sac ligands are *N*-



Fig. 2. Packing diagram of 1, showing $\pi(sac) \cdots \pi(sac)$ stacking interactions. All C–H hydrogen atoms are omitted for clarity.

coordinated at *trans* positions. During complex formation, the sac coordination geometry was switched from *trans* to *cis*. Furthermore, complex **1** exhibits a lesscommon coordination characteristic of the sac ligand: both sac ligands are monodentate, but one is *N*-bonded, while the other one is coordinated through the carbonyl O atom behaving as an ambidentate ligand as observed only in the following complexes: $[Cu(sac)_2(py)_3]$ (py = pyridine) [5], $[Cu(sac)_2(dipy)(H_2O)]$ (dipy = dipyridylamine) [6], ApyH[Cu(H_2O)_2(sac)_3] (ApyH = 2-aminopyridinium) [7], and $[M(sac)_2(pym)_2]$, where pym = 2-pyridylmethanol, M = Co^{II} [8], Ni^{II} [12], Zn^{II} [9], and Cd^{II} [9].

The Cd–N_{sac} and Cd–O_{sac} bond distances are similar to those reported for $[Cd(sac)_2(pym)_2]$: 2.2612(14) and 2.2755(17) Å [9]. The M–N_{dmea} and M–O_{dmea} bond distances in complex 1 are slightly longer than the Cd–N_{sac} and Cd–O_{sac} bond distances. Significant distortions are evident from the angles in the coordination octahedron as seen from Table 1. The largest deviations from the ideal values were observed in the bite angles of the dmea ligands.

Both sac ligands in complex 1 are essentially planar. The planes of the two sac ligands are nearly coplanar with a dihedral angle of $8.84(34)^\circ$. The packing diagram of complex 1 is presented in Fig. 2. Complex 1 exhibits an intra-molecular O–H…O hydrogen bond, and packing of the molecules of 1 is achieved

Table 2. Selected bond lengths and angles, and hydrogen bonding geometry of **2**.

| Bond lengths (\mathring{A}) and angles (\circ) : | | | | | |
|--|------------|------------------------|-------------------------|--|--|
| Hg1–N1 | 2.154(9) | N1-Hg1-O1W | 94.9(4) | | |
| Hg1–N2 | 2.108(9) | N1-Hg1-O7 | 95.8(3) | | |
| Hg1–N3 | 2.349(12) | N2-Hg1-O1W | 90.9(4) | | |
| Hg1–O1W | 2.820(9) | N2-Hg1-O7 | 96.6(4) | | |
| Hg1–O7 | 2.541(9) | N3-Hg1-O1W | 82.5(4) | | |
| N1-Hg1-N2 | 138.4(4) | N3-Hg1-O7 | 72.2(4) | | |
| N1-Hg1-N3 | 101.8(4) | O1W-Hg1-O7 | 154.1(4) | | |
| N2-Hg1-N3 | 119.8(4) | | | | |
| Hydrogen bond | s: | | | | |
| $D - H \cdots A$ | D–H (Å) H… | $A(Å) D \cdots A(Å) D$ | $-H \cdots A(^{\circ})$ | | |

| D-II···A | $D = \Pi(\Lambda)$ | $\Pi \cdots A(A)$ | DA (A) | $D=11\cdots A()$ |
|--------------------|--------------------|-------------------|-----------|------------------|
| O1W−H1W···O1 | 0.84(9) | 2.39(11) | 2.898(13) | 119(10) |
| $O7-H7\cdots O1^i$ | 0.93 | 2.02 | 2.761(13) | 135 |

¹ Symmetry operation x, y - 1, z.



Fig. 3. A view of the molecular structure of complex 2, showing 30% displacement ellipsoids (arbitrary spheres for the H atoms). Intramolecular hydrogen bonds are indicated by dashed lines.

by an aromatic $\pi(\operatorname{sac})-\pi(\operatorname{sac})$ stacking interaction between the phenyl rings of the neighboring sac units with a $C_g \cdots C_g^i$ (C_g = centroid of atoms) distance of 3.693(4) Å [ⁱ: x, 1/2 - y, -1/2 + z].

Fig. 3 shows the molecular structure of complex 2 with the atom labeling. Selected interatomic distances and angles are listed in Table 2, together with the hydrogen bonding geometry. In complex 2, the mercury(II) cation exhibits a distorted trigonal bipyramidal coordination geometry with a neutral bidendate (N,O)dmea ligand and two N-bonded sac ligands, thus forming a HgN₃O₂ chromophore. The N atoms form the trigonal plane, while the O atoms occupy the apical positions. The Hg-Nsac bond distances are similar to the corresponding values found in previously reported mercury(II) complexes with sac: 2.037, 2.049, 2.029 and 2.058 Å in [Hg(sac)₂] [10], 2.019 Å in [Hg(Cl)-(sac)] [11], 2.120 and 2.140 Å in [Hg(sac)₂(bipy)] [12], 2.106(7) and 2.209(7) Å in [Hg₂(Cl)₂(sac)₂(py)] [13], 2.087(2), 2.117(2), 2.182(2) and 2.193(2) Å in [Hg-(sac)₂(pyet)] [14], 2.094(2) and 2.106(2) Å in [Hg₂-

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

| Assignments | 1 | 2 |
|--------------------------|-----------------------|----------------|
| v(OH) | 3336s,br | 3440s,br |
| v(CH) | 3106vw, 2978vw, 2802w | 3060vw, 2953vw |
| v(CO) | 1651vs, 1600vs | 1624vs |
| v(CC) | 1472s | 1458m |
| $v_{\rm s}({\rm CNS})$ | 1344m | 1384vs |
| $v_{\rm as}({\rm SO}_2)$ | 1268vs | 1285vs, 1250vs |
| $v_{\rm s}({\rm SO}_2)$ | 1165vs | 1153vs |
| $v_{\rm as}({\rm CNS})$ | 961vs | 965s |
| | | |

^a Frequencies in cm⁻¹; b = broad; w = weak; vs = very strong; s = strong; m = medium; sh = shoulder.



Fig. 4. Packing diagram of **2**, showing hydrogen bonds and $\pi(\operatorname{sac}) \cdots \pi(\operatorname{sac})$ stacking interactions. All C–H hydrogen atoms are omitted for clarity. Hydrogen bonds are indicated by dashed lines.

 $(sac)_4(mpy)_2$ [15] and [Hg(sac)_2(aepy)] 2.151(4) and 2.233(3) Å [16], but much shorter than 2.739(3) Å in [Hg(ea)_2(sac)_2] [17] and *trans*-[Hg(sac)_2(ampy)_2] 2.7955(16) Å [16], where bipy, py, pyet, mpy, ea, aepy and ampy are 2,2'-bipyridyl, pyridine, 2-pyridylethanol, 2-pyridylethanol, ethanolamine, 2-aminoethylpyridine and 2-aminomethylpyridine respectively. The Hg–N_{dmea} bond distance of 2.349(12) Å is significantly longer than The Hg–N_{sac} bond distances. Among the five coordination bonds in complex **2**, the Hg–OW bond distance of 2.820(9) Å is much longer, indicating a weak interaction of the water molecule with mercury(II).

The sac ligands are planar and the dihedral angle between them is $70.56(20)^{\circ}$. The individual molecules of **2** are linked by O–H···O hydrogen bonds and $\pi(\operatorname{sac})-\pi(\operatorname{sac})$ stacking interactions $[C_g \cdots C_g^i = 3.589(8) \text{ Å}; i 1 - x, 2 - y, -z]$, leading to a three-dimensional network as shown in Fig. 4.

IR spectra

Selected FTIR data of both complexes 1 and 2 are presented in Table 3. The strong and relatively broad bands centered at around 3340 cm⁻¹ are attributed to the v(O-H) vibration of the hydrogen-

bonded hydroxyl groups of the dmea ligand and the aqua ligand in complex 2. The relatively weak absorption bands between 2960-3100 cm⁻¹ are assigned to the v(CH) vibrations. The stretching vibration of the carbonyl group of sac appears as two separate sharp bands at 1651 and 1600 cm^{-1} for complex 1, and as a single band at 1624 cm^{-1} for complex 2. The higher frequency absorption band in the spectrum of complex 1 is characteristics for the N-bonded sac ligand, whereas the lower frequency band is assigned to the sac O-bonded via the carbonyl group, due to the expected weakening of the C=O bond upon coordination. The single carbonyl band in the spectrum of complex 2 clearly indicates that both sac ligands are N-coordinated. The strong absorption bands at around 1460 cm⁻¹ correspond to the v(CC) vibrations of the aromatic ring of sac. The $v_{as}(SO_2)$ vibrations appear as a sharp band centered at 1268 cm^{-1} in complex 1, but as two split bands at 1285 and 1250 cm^{-1} in complex 2, while the $v_s(SO_2)$ mode of sac appears as a very strong band at *ca*. 1160 cm⁻¹.

Thermal analysis

The thermal decomposition processes for complexes **1** and **2** were followed up to 800 °C in a static atmosphere of air. Complex **1** decomposes at two stages. The first stage between 86 and 342 °C corresponds to the endothermic removal of two dmea ligands (mass loss: found 27.0%, calcd. 27.2%). Decomposition of the sac moiety occurs at higher temperatures characterized by two highly exothermic peaks at 471 and 521 °C. The decomposition of **1** ends at 566 °C, giving a solid residue of CdO.

Complex 2 shows a three-step decomposition process. In the first step between 28 and 58 °C, it dehydrates with a mass loss of 3.0% (calcd. 2.7%). In the second step, the elimination of the dmea ligand takes place in the temperature range 65-212 with an endothermic peak at 187 °C. The experimental mass loss of 13.4% is in accord with the calculated value of 13.2%. At higher temperatures, the degradation of the sac ligands occurs with two extremely exothermic peaks at 323 and 479 °C to give an end product of HgO.

Experimental Section

Materials and measurements

All reagents were commercially available and used without further purification. The starting complexes $[Cd(sac)_2(H_2O)_4]\cdot 2H_2O$ and $[Hg(sac)_2]$ were prepared

| Table 4. | Crystal | lographic | data f | or 1 | and 2 . |
|----------|---------|-----------|--------|------|----------------|
|----------|---------|-----------|--------|------|----------------|

| | 1 | 2 |
|--|--------------------------------|---|
| Empirical formula | $C_{22}H_{30}N_4O_8S_2Cd$ | C ₁₈ H ₂₁ N ₃ O ₈ S ₂ Hg |
| M _r | 655.05 | 672.11 |
| Crystal system | monoclinic | triclinic |
| Space group | $P2_1/c$ | $P\bar{1}$ |
| a [Å] | 14.3890(7) | 7.6376(9) |
| b [Å] | 12.7790(5) | 7.8699(9) |
| c [Å] | 15.5260(8) | 20.563(2) |
| α [°] | 90 | 94.741(9) |
| β [°] | 109.786(4) | 92.967(9) |
| γ[°] | 90 | 116.765(18) |
| V [Å ³] | 2686.3(2) | 1094.3(3) |
| Ζ | 4 | 2 |
| $D_{\rm c} [\rm g/cm^3]$ | 1.620 | 2.040 |
| $\mu [{ m mm}^{-1}]$ | 1.021 | 7.275 |
| F(000) | 1336 | 652 |
| Crystal size [mm ³] | $0.52 \times 0.35 \times 0.22$ | $0.37 \times 0.33 \times 0.28$ |
| θ Range [°] | 2.12 - 27.87 | 2.00 - 26.00 |
| Index range (h, k, l) | -18/17, | -9/9 , |
| | -16/16, | -9/9 , |
| | -20/20 | -25/25 |
| Reflections collected | 28192 | 14012 |
| Independent refls (R_{int}) | 6368 (0.0828) | 4305 (0.0768) |
| Absorption correction | Numerical | Numerical |
| Min. and max. transmission | 0.773 and 0.825 | 0.082 and 0.127 |
| Data / parameters | 6368 / 322 | 4305 / 278 |
| Goodness-of-fit on F^2 | 1.086 | 1.056 |
| <i>R</i> Indices $[I > 2\sigma(I)]$ | 0.0771 | 0.0603 |
| wR2 (all data) | 0.2365 | 0.1592 |
| Largest diff. peak and hole [e $Å^{-3}$] | 4.2 and -2.0 | 1.5 and -3.2 |

according to the literature methods reported by Haider *et al.* [18] and Kamenar *et al.* [19], respectively.

Elemental analyses (C, H, N and S) were carried out on an Elementar Vario EL elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range $4000 - 400 \text{ cm}^{-1}$ by using a JASCO FT/IR-430 spectrophotometer. Thermal analysis curves (TG and DTA) were obtained using a Rigaku TG8110 thermal analyzer in a static air atmosphere at a heating rate of 10 °C min⁻¹.

Synthesis of the complexes

The dmea ligand (0.09 g, 1.0 mmol) was added drop-wise to a solution of $[Cd(sac)_2(H_2O)_4]\cdot 2H_2O$ (0.29 g, 0.5 mmol) dissolved in a methanol and isopropanol mixture (1 : 1, v : v; 20 cm³) with continuous stirring at 60 °C. Colorless crystals of complex **1** suitable for X-ray diffraction were obtained by slow diffusion of the resulting solution into ether after two days. Yield: *ca.* 40%. d. p. 86 °C. $C_{22}H_{30}N_4O_8S_2Cd$ (655.02); calcd. C 40.3, H 4.6, N 8.6, S 9.8; found C 40.5, H 4.5, N 8.9, S 10.0.

Complex 2 was prepared by a similar synthesis procedure, using $[Hg(sac)_2]$ (0.29 g, 0.5 mmol) instead of $[Cd(sac)_2(H_2O)_4]\cdot 2H_2O$. Colorless crystals of complex 2 were obtained by slow diffusion of the resulting solution

X-ray crystallography

The data collections were performed at 293 K for both complexes on a Stoe-IPDS-2 diffractometer with graphite-monochromated Mo-K_{α} radiation ($\lambda = 0.71073$ Å). The structures were solved by Direct Methods using SHELXS-97 [20] and refined by full-matrix least-squares methods using SHELXL-97 [20]. All non-hydrogen atoms were easily found in a difference Fourier map and refined anisotropically. All hydrogen atoms were refined in the riding mode on their carrier atoms. Atoms C15, C16 and C18 in complex **1** were found to be highly disordered and an isotropic refinement of the disordered atoms split over two positions. The hydrogen atoms of the disordered atoms were positioned by applying the HFIX. Attempts to solve the problem failed. Therefore, the disorder phenomena results in short intra- and intermolecular hydrogen bonds, a short C15–C16 distance and a high residual electron density. The details of data collection, refinement and crystallographic data are summarized in Table 4.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no, CCDC-295608 (1) and CCDC-295609 (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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