Structural, Spectroscopic, and Thermal Behaviour of *Bis*-(thiosaccharinate)-aqua-cadmium(II)

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Summary. The crystal structure of the title complex, $[Cd(tsac)_2(H_2O)]$, has been determined by single crystal X-ray diffraction methods. It crystallizes in the monoclinic space group C2/c ($a = 12.236(3)$, $b = 8.919(3)$, $c = 16.655(3)$ Å, $\beta = 96.18(2)°$, $Z = 4$). The molecular structure was solved from 1705 independent reflections with $I > 2\sigma(I)$ and refined to $R_1 = 0.0489$. Infrared and *Raman* spectra of the complex were recorded and are briefly discussed. Its thermal behaviour was investigated by thermogravimetry and differential thermal analysis.

Introduction

The coordination chemistry of metal thioamides has received increasing attention during the last decades taking into account the participation of sulfur-containing molecules and ions in a variety of biological systems and processes [1, 2].

Simple cyclic thioamides like imidazole-2-thione, benzimidazole-2-thione, thiazolidine-2-thione, benzothiazolidine-2-thione, pyridine-2-thione, and their derivatives show interesting and versatile coordination behaviour. They can act as monodentate ligands through their nitrogen or sulfur atoms or as bridging ligands using simultaneously both atoms [3, 4].

As an extension of our investigation on metal complexes of saccharin [5–15], we have now started some studies with its sulfur analogue, thiosaccharin (1,2-benzothiazol-3(2*H*)-thione 1,1-dioxide), a cyclic thioamide potentially able to produce the tautomeric equilibrium shown in Fig. 1.
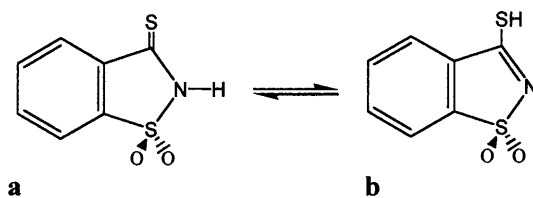
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Fig. 1. Tautomeric equilibrium of thiosaccharin

Only the crystal structures of thiosaccharin itself [16] and of its sodium [17] and potassium [18] salts have been reported so far. Additionally, some of its transition metal complexes have recently been characterized by IR spectroscopy; the results suggested coordination through the nitrogen atom [19].

Considering the interesting coordination possibilities of the tautomeric form **b** (Fig. 1), we simultaneously started theoretical studies of the electronic properties of the thioamide [20] and experimental ones about its interaction with some heavy metal cations which should be favoured by *Pearson*'s rule [1, 21]. We could isolate insoluble compounds with Ag(I), Cd(II), Hg(II), Pb(II), and Tl(I). However, only in the case of Cd(II) we were able to obtain single crystals adequate for structural analysis.

In this paper we report the synthesis of this new complex, the results of the single crystal X-ray investigation, and its vibrational spectroscopic as well as thermal behaviour.

Results and Discussion

Structural analysis

Crystal parameters and details of the applied refinement procedures are given in Table 1, whereas Fig. 2 shows a PLUTON2 [22, 23] plot of the structure of [Cd($tsac$)$_2$(H$_2$O)] including the atom labelling of the non-hydrogen atoms. Selected interatomic distances and angles are compiled in Table 2.

The Cd(II) ion is located on a crystallographic two fold-axis in a five-fold environment. It is coordinated to four symmetry related thiosaccharinate anions through the thiocarbonyl sulfur atoms (d(Cd-S) = 2.467(1) Å) and one of the sulfonyl O-atoms (d(Cd-O(2)) = 2.512(3) Å). These ligands reside at the corners of a distorted tetrahedron, squashed along the two-fold axis (S-Cd-S and O-Cd-O bond angles of 134.52(6) and 139.2(2)°, respectively). The fifth ligand is a water molecule located on the axis (d(Cd-O(3)) = 2.219(6) Å). This distance is lower than the sum of the Cd(II) ionic radius and the *van der Waals* radius of oxygen [24].

The Cd-S bonds are in the order of the shortest known metal-sulfur distances of covalently bonded thiolates or thioamidates [25–27], suggesting the existence of a negative charge at the sulfur atom. The Cd-O bond distances, on the other hand, are of the order of the sum of the Cd(II) ionic radius and the *van der Waals* radius of oxygen, indicating only a weak interaction between these atoms.

The compound is arranged in the crystal as a layered structure parallel to the *ab* plane. In each layer, the Cd(II) ions form a centered rectangular lattice, with nearest

Table 1. Summary of crystal data, X-ray measurements, and structure refinements

Empirical formula	$C_{14}H_{10}N_2O_5S_4Cd$
Formula weight	526.88
Crystal system	Monoclinic
Space group	C2/c
Unit cell dimensions	$a = 12.236(3)$ Å
	$b = 8.919(3)$ Å
	$c = 16.655(3)$ Å
	$\beta = 96.18(2)°$
	$V = 1807.0(8)$ Å^3
Z	4
$\rho_{calc}/g \cdot cm^{-3}$	1.937
Absorption coefficient/mm^{-1}	14.280
θ-range for data collection	5.34 to 69.89°
$F(000)$	1040
Index ranges	$0 \leq h \leq 14, 0 \leq k \leq 10, -20 \leq I \leq 20$
Reflections collected	1924
Independent reflections	1713 (R(int) $= 0.042$)
Observed reflections ($I > 2\sigma(I)$)	1705
Data/restraints/parameters	1713/0/120
Goodness-of-fit on F^2	1.127
Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.0489; wR_2 = 0.1249$
R indices (all data)	$R_1 = 0.0490; wR_2 = 0.1249$
Largest diffraction peak and hole	0.76 and -2.25 e $\cdot$ Å^{-3}
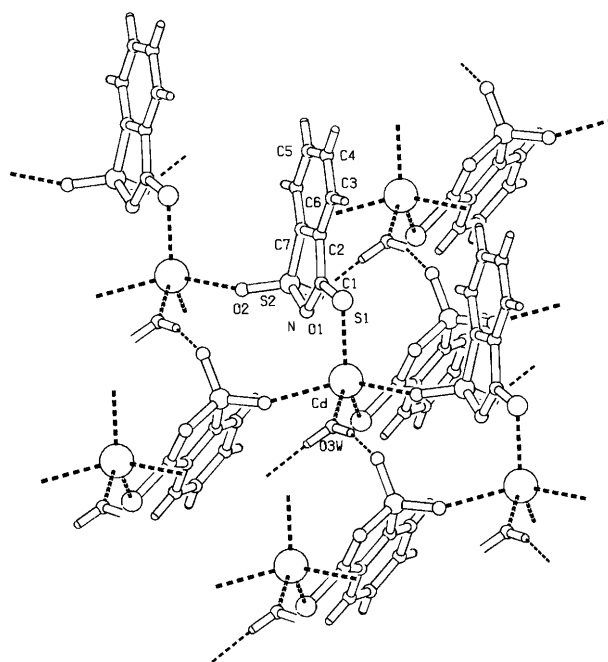
Fig. 2. Plot of [Cd(*tsac*)₂(H₂O)] showing the labelling of the non-H atoms and part of the layered structure; Cd-ligand and O$_{Water}$-H$\cdots$O bonds are emphasized by thick and thin dashed lines, respectively

Table 2. Selected interatomic distances (Å) and bond angles (°) for [Cd(*tsac*)$_2$(H$_2$O)]

Bond distances			
Cd-O(3w)	2.219(6)	S(2)-O(1)	1.432(1)
Cd-S(1)#1	2.467(1)	S(2)-O(2)	1.441(3)
Cd-S(1)#2	2.467(1)	S(2)-N	1.639(4)
Cd-O(2)	2.512(3)	C(7)-S(2)	1.756(5)
Cd-O(2)#3	2.512(3)	C(1)-N	1.303(6)
Cd-S(1)#4	2.467(1)	C(1)-S(1)	1.708(4)
Bond angles			
O(3w)-Cd-S#1	112.74(3)	C(1)-S(1)-Cd#4	94.2(2)
O(3w)-Cd-S#2	112.74(3)	O(1)-S(2)-O(2)	115.8(2)
S(1)#1-Cd-S(1)#2	134.52(6)	O(1)-S(2)-N	110.4(2)
O(3w)-Cd-O(2)	69.60(9)	O(2)-S(2)-N	108.9(2)
S(1)#1-Cd-O(2)	102.5(1)	O(1)-S(2)-C(7)	112.0(2)
S(1)#2-Cd-O(2)	93.0(1)	N-S(2)-C(7)	96.8(2)
O(3w)-Cd-O(2)#3	69.60(9)	S(2)-O(2)-Cd	149.3(2)
S(1)#1-Cd-O(2)#3	93.0(1)	C(1)-N-S(2)	110.2(3)
S(1)#2-Cd-O(2)#3	102.5(1)	N-C(1)-C(2)	116.1(4)
O(2)-Cd-O(2)#3	139.2(2)	N-C(1)-S(1)	123.0(3)

Symmetry transformations used to generate equivalent atoms: (#1): $-x - 1/2,\ y - 1/2,\ -z + 1/2$; (#2): $x + 1/2,\ y - 1/2,\ z$; (#3): $-x,\ y,\ -z + 1/2$; (#4): $x - 1/2,\ y + 1,\ z$

neighbour Cd(II) ions bridged by a thiosaccharinate moiety through its sulfur atom and one of the sulfonyl oxygen atoms. The layers are further stabilized by H-bonds involving the water molecule and the other sulfonyl O-atom (H$_{Water}$···O(1) distance: 1.876 Å; O$_{Water}$-H···O(1) angle: 164.6°).

The thiosaccharinate moieties are almost planar. The principal features of the thioamidic functional group are that the C(1)-S(1) distance is larger and the C(1)-N distance is shorter than in the thiosaccharin molecule (C(1)-S(1) = 1.622 Å, C(1)-N = 1.384 Å [16]). This observation is in agreement with the results of our theoretical calculations about the electronic structure of the thiosaccharin molecule and its anion [20], indicating that after deprotonation the negative charge at the nitrogen atom is essentially transferred to the C(1)-N bond which acquires double bond character. Simultaneously, thiocarbonyl π-bonding electrons are transferred to the sulfur atom, and the C(1)-S(1) bonds adopt single bond character, thus increasing the negative charge at the heteroatom and facilitating the Cd(II)-sulfur interaction expected from *Pearson*'s rule [1, 21].

It should be noted that in most heavy metal saccharinates, like mercury derivatives (cf. Ref. [28] and references cited therein) or [Cd(*sac*)$_2$(H$_2$O)$_2$] [29], the ligand binds through the imidic N-atom. In a few cases, additional interactions between the carbonyl oxygen and the metallic centers are observed, producing chelated structures like in [Pb(*sac*)$_2$(H$_2$O)] [30] and [Pb(*sac*)$_2$(*ophen*)(H$_2$O)$_2$] [13] or bridging structures as in [Cd(*sac*)$_2$(*im*)$_2$] [31]. It is also interesting that the CdS$_2$O$_3$ environment found for the Cd(II) cation of the title compound seems to be rather uncommon. Apparently, it has so far only been observed in a complex with an arenephosphinothiol ligand [32].

Vibrational spectra

Infrared and *Raman* data of the complex, compared with those of the free thio-saccharin molecule [33], are shown in Table 3. The proposed assignments are based on previous investigations on saccharinate complexes [7, 8, 10, 12, 34], free thiosaccharin [16, 33], sodium and potassium thiosaccharinate [35], general literature data on thioamidates [36], and simple compounds containing SO and CS groups [37–39].

In a simplified analysis the 42 internal vibrational modes of the thiosaccharinate anion can be divided into aromatic ring motions, sulfothiocarboximide (C(S)NSO₂) group motions, and isoindole group motions. Most of the aromatic ring vibrations, particularly CH stretchings and bendings, CC stretchings, and CCC deformations, have been identified on the basis of our previous studies of saccharinate compounds [7, 8, 10, 12] complemented by the theoretical study of *Binev et al.* [40] and data from related substances like benzothiophene [41] and phthalimide [42].

The internal motions of the water molecules could also be clearly identified. The O-H stretching vibrations are of medium intensity, relatively broad, and centered

Table 3. Assignment of IR and *Raman* bands (cm^{-1}) for thiosaccharin and [Cd(*tsac*)₂(H₂O)]

Thiosaccharin		[Cd(*tsac*)₂(H₂O)]		
IR	*Raman*	IR	*Raman*	Assignment
		3610 m, br	3642 w	ν(OH) (H₂O)
3341 vs				ν(NH)
	3093 w	3070 vw		ν(CH)
	3060 w	3050 vw	3057 m	ν(CH)
	3010 w	3000/2990 vw		ν(CH)
		1636 m		δ(HOH) (H₂O)
1590 w	1590 vs	1612 m	1578 w	ν(CC), δ(CH)
1455 s	1460 m	1460 s	1462 w	ν(CC)
1376 vs	1375 m, br	1301 vs	1300 w	ν_{as}(SO₂)
1318 s				δ(NH)
1283 m	1282 s	1285 s	1284 vw	ν(CC), δ(CH)
1247 m	1248 s	1418 s	1419 s	ν(CN), ν(φS)
1218 s	1222 s	1234 s	1235 s	δ(CH)
1156 vs	1155 m	1156 vs	1150 m	ν_{s}(SO₂), ν(CC)
1120 m	1120 vw	1118 s	1127 w	ν_{s}(SO₂), δ(SN)
1039 m		1005 s		ν(CS) (cf. text)
817 vs	820 vw	823 s	823 vw	ν(NS), δ(CCC)
769 s		774 m		γ(CH)
700 vw	700 m	698 vw	701 vw	δ(CCC)
610 w	610 vw	624 w		γ(CCC)
591 s	582 w	591 m		γ(SO₂)
545 w		541 w		γ(CCC)
527 s	530 vw	523 vw		ν(isoindol)
403 vw	405 vw	411 vw		γ(isoindol)
		378 vw	374 m	ν(Cd-S) ?

vs: very strong; s: strong; m: medium; w; weak; vw: very weak; br: broad

around $3610\,\mathrm{cm^{-1}}$ in the IR spectrum. The HOH bending mode produces a IR band at $1636\,\mathrm{cm^{-1}}$, near to a stretching vibration of the thiosaccharinate ligand.

The spectroscopic behaviour of the five-membered ring, including the chalcogen atom and the SO_2 moiety, seems to be of special interest because this part of the molecule must reflect the properties of the metal-ligand interactions. In the same way as for the saccharinate anion, the stretching vibrations of the SO_2 group are related to some of the most intense IR bands. These vibrations are expected to appear at lower wavenumbers in the Cd(II) complex compared to thiosaccharin due to the increased S-O bond lengths $(d(\mathrm{S\text{-}O}) = 1.431/1.425\,\text{Å}$ in thiosaccharin [16], $1.441/1.432\,\text{Å}$ in the complex (cf. Table 2)) as a consequence of the interaction of this group with the metallic center and the electronic charge reorganization after deprotonation [20]. As can be seen from Table 3, this expectation is clearly fulfilled for $\nu_{as}(SO_2)$.

The assignment of the respective symmetric stretching mode is not so straightforward, because this mode is coupled with other vibrations of the isoindole moiety. In free thiosaccharin, this band has been found at $1155\,\mathrm{cm^{-1}}$ [16, 19]. However, due to the interaction of the Cd(II) cation with the O-atoms of the sulfonyl groups, for this vibrational mode a frequency lowering may be expected, too. On this basis we assume that the strong IR band at $1118\,\mathrm{cm^{-1}}$ is mostly related to this mode. Therefore, the very strong IR band at $1156\,\mathrm{cm^{-1}}$ and the medium intensity *Raman* line at $1150\,\mathrm{cm^{-1}}$, found at almost the same position as in thiosaccharin, must be essentially related to breathing modes of the five-membered ring.

A comparison of the C(1)-S(1) and C(1)-N bond lengths in the thiosaccharinate complex and in the free ligand (1.622 and $1.384\,\text{Å}$, respectively [16]), shows a lengthening of the first one with a concomitant important reduction of the latter one, in good agreement with the results of our theoretical study of the electronic structures of both species [20]. Thus, one can assume that the band related essentially to the C(1)-N bond stretching ($1247\,\mathrm{cm^{-1}}$ in the IR spectrum of thiosaccharin) may be strongly displaced to higher wavenumbers in the cadmium complex, and we have assigned the $1418\,\mathrm{cm^{-1}}$ entity to this vibration. On the other hand, and although the C=S stretching mode is not a good group vibration because it is coupled with other motions of the sulfothioamide skeleton [16], the band mainly related to the C(1)-S(1) stretching motion ($1039\,\mathrm{cm^{-1}}$ in thiosaccharin) should be displaced to lower energies in the complex, in which it is actually found at $1005\,\mathrm{cm^{-1}}$ (cf. Table 3).

Other bands in the spectral range below $1000\,\mathrm{cm^{-1}}$ are more difficult to assign. They are usually of complex origin and involve strong couplings of different motions. Therefore, the assignment proposed in Table 3 for some of these bands is only tentative. It was also difficult to identify with certainty a band related to the Cd-S stretching mode. The band assigned to this vibration in Table 3 lies in the spectral range usually found for this mode in other complexes containing *M*-S bonds [43].

Thermal behaviour

The analysis of the TG and DTA curves shows a weight loss of 3.6% between 75 and 128°C as the first TG step, accompanied by a weak and relatively broad

endothermic DTA-signal centered at about 115°C. This corresponds to the loss of the bonded water molecule (theoretical loss: 3.42%). Subsequently, three further TG-steps are observed between 128–310, 310–450, and 450–750°C. The first one is related to a well-defined and medium intensity exothermic DTA peak at 295°C, whereas the last two are associated to a unique, broad, and flat exothermic signal extending between 450 and 650°C. These three successive processes are related to the gradual decomposition of the thiosaccharinate ligands, involving a total weight loss of 69.1% (theoretical value: 69.2%). The final pyrolysis residue was identified as CdS by IR spectroscopy.

Experimental

Synthesis

Thiosaccharin was prepared by reaction of saccharin (Mallinckrodt) with *Lawesson*'s reagent (Fluka) in toluene according to the procedure of *Schibye et al.* [44]. The cadmium complex was obtained by slow addition of 0.4 mmol of cadmium nitrate dissolved in 10 cm^3 of water to 0.8 mmol of thiosaccharin dissolved in 40 cm^3 of water under continuous stirring. The precipitated solid complex was filtered off, washed several times with small portions of cold water, and finally dried over CaCl$_2$. Amber-like single crystals adequate for X-ray studies were grown by slow evaporation from saturated aqueous solutions.

Crystal structure determination

Single crystal data collection was performed at 293(2) K on an Enraf-Nonius CAD-4 diffractometer using graphite monochromated CuK_α radiation ($\lambda = 1.54184$ Å) in the ω-2θ scan mode employing a single crystal of the approximate dimensions 0.4×0.4×0.2 mm. Unit cell parameters were refined by least-squares of $(\sin\theta/\lambda)^2$ using 22 reflections in the range $18.78 < \theta < 45.24°$. Intensities were corrected for *Lorentz*, polarization, and numerical absorption effects [22]. The structure was solved by *Patterson* and *Fourier* methods, and the final result was obtained by anisotropic full-matrix least-squares refinement of the non-hydrogen atoms. The programs used were XCAD-4 [45], PLUTON [22, 23], SHELXS-97 [46], and SHELXL-97 [47].

All hydrogen atoms were found among the first nine peaks of a difference *Fourier* map. However, the thiosaccharinate H-atoms were positioned stereochemically and refined with the riding model. During the refinement, the independent water hydrogen atom was kept fixed at its located position.

Tables containing complete information on atomic coordinates and equivalent isotropic parameters, bond distances, angles, anisotropic thermal parameters, and hydrogen atomic positions are available from the authors upon request and have been deposited at the Cambridge Crystallographic Data Centre (reference number CCDC 157696).

Spectroscopic measurements

Infrared spectra were recorded up to 400 cm^{-1} on a Perkin Elmer GXFT-IR instrument using the KBr pellet technique. Spectra obtained from suspensions of the powdered samples in Nujol gave identical results. *Raman* spectra of the powdered sample in a capillary tube were scanned on a Spex Ramalog double-monochromator spectrometer using the 514.5 nm line of a Spectra Physics Ar$^+$ laser for excitation.

Thermal analysis

Thermogravimetric (TG) and differential thermal analysis (DTA) were carried out on a Rigaku Denki Thermoflex instrument under a nitrogen flow of 30 cm$^3 \cdot$ min^{-1} up to a final temperature of 750°C.

The heating rate was $5°C \cdot min^{-1}$, and employed sample masses were about $10\,mg$. Al_2O_3 was used as a DTA reference standard.

Acknowledgements

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