Diaquabis(dimethyl sulfoxide-κO)-disaccharinatocadmium

Fezile S. W. Potwana and Werner E. Van Zyl*

School of Chemistry, University of KwaZulu-Natal, Westville Campus, Private Bag X54001, Durban 4000, South Africa
Correspondence e-mail: vanzylw@ukzn.ac.za

The title compound, $[Cd(C_7H_4NO_3S)_2(C_2H_6OS)_2(H_2O)_2]$, contains a Cd^{2+} cation in an octahedral coordination environment. The metal atom is surrounded by the two different neutral ligands dimethyl sulfoxide (DMSO) and water, each coordinating through the O atom. The anionic saccharinate (sac; 1,1,3-trioxo-2,3-dihydro-$1\lambda^6$,2-benzothiazol-2-ide) ligand coordinates through the N atom. Each of the three similar ligand pairs is in a *trans* configuration with respect to each other. The Cd atom lies on a crystallographic center of symmetry. The DMSO ligand coordinates through the lone pair of electrons on the O atom, as can be seen from the Cd—O—S bond angle of 123.96 (9)°.

Related literature

For a general review article on the coordination chemistry of saccharinate ligands, see: Baran & Yilmaz (2006). For cadmium saccharinate complexes, see: Deng *et al.* (2008) and for cadmium complexes with saccharinate as a non-coordinating ligand, see: Batsanov *et al.* (2011). For a cadmium complex that contains both saccharinate and DMSO, see: Yilmaz *et al.* (2003). For the preparation of cadmium precursor complexes, see: Haider *et al.* (1984).
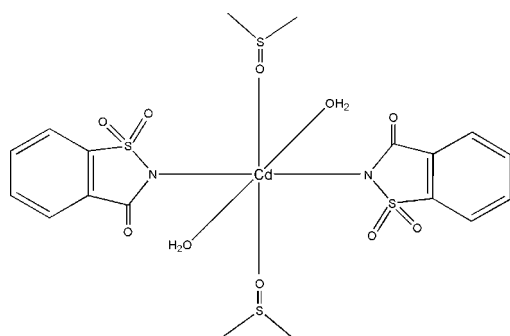
Experimental

Crystal data

$[Cd(C_7H_4NO_3S)_2(C_2H_6OS)_2$ $(H_2O)_2]$	$\beta = 98.889$ (1)°
$M_r = 669.03$	$V = 1250.63$ (11) Å^3
Monoclinic, $P2_1/c$	$Z = 2$
$a = 10.2613$ (5) Å	Mo $K\alpha$ radiation
$b = 15.4294$ (8) Å	$\mu = 1.26$ mm^{-1}
$c = 7.9951$ (4) Å	$T = 173$ K
	$0.14 \times 0.11 \times 0.08$ mm

Data collection

Bruker Kappa DUO APEXII diffractometer	12452 measured reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1997)	3121 independent reflections
	2624 reflections with $I > 2\sigma(I)$
$T_{min} = 0.843$, $T_{max} = 0.906$	$R_{int} = 0.038$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.025$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.061$	
$S = 1.03$	
3121 reflections	$\Delta\rho_{max} = 0.42$ e Å^{-3}
170 parameters	$\Delta\rho_{min} = -0.41$ e Å^{-3}
2 restraints	

Data collection: *APEX2* (Bruker, 2006); cell refinement: *SAINT* (Bruker, 2006); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *SHELXL97*.

References

Baran, E. J. & Yilmaz, V. T. (2006). *Coord. Chem. Rev.* **250**, 1980–1999.
Barbour, L. J. (2001). *J. Supramol. Chem.* **1**, 189–191.
Batsanov, A. S., Bilton, C., Deng, R. M. K., Dillon, K. B., Goeta, A. E., Howard, J. A. K., Shepherd, H. J., Simon, S. & Tembwe, I. (2011). *Inorg. Chim. Acta*, **365**, 225–231.
Bruker (2006). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA
Deng, R. M. K., Dillon, K. B., Goeta, A. E. & Sekwale, M. S. (2008). *Inorg. Chim. Acta*, **361**, 1542–1546.
Haider, S. Z., Malik, K. M. A., Das, S. & Hursthouse, M. B. (1984). *Acta Cryst.* C**40**, 1147–1150.
Sheldrick, G. M. (1997). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Yilmaz, V. T., Hamamci, S. & Thöne, C. (2003). *Z. Anorg. Allg. Chem.* **629**, 711–715.

supplementary materials

Diaquabis(dimethyl sulfoxide-*κO*)disaccharinatocadmium

F. S. W. Potwana and **W. E. Van Zyl**

Comment

Saccharin (*o*-sulfobenzimide; 1,2-benzothiazole-3(2*H*)-one 1,1-dioxide; Hsac) is a widely used artificial sweetening agent. The imino hydrogen is acidic and can be readily deprotonated. The coordination chemistry of this anion is versatile due to the different coordination sites to metallic centers it can accommodate, *i.e.*, one N, one O (carbonylic) and two O (sulfonic) atoms. These donor atoms of the anion can thus readily generate either N– or O-monodentate or bidentate (N, O) coordination. Saccharin is normally used as the sodium or calcium salt which dramatically improves water solubility. Most metal complexes contain the deprotonated form of saccharin, and this saccharinate anion (sac) is commercially available as the sodium salt, used in the present study. The reaction of sodium saccharinate with a variety of divalent transition metal ions results in coordination complexes with general formula [M(sac)$_2$(H$_2$O)$_4$].2H$_2$O, (M = V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd), which all show a clear preference to bind through the deprotonated anionic N-atom (Baran and Yilmaz, 2006). These octahedral complexes contain two N-bonded sac ligands in *trans* positions, and complexes of the type [M(sac)$_2$(H$_2$O)$_4$].2H$_2$O are thus commonly used as precursors in the synthesis of mixed-ligand saccharinate complexes. The aqua ligands in these metal complexes are labile and readily displaced by direct reaction of neutral ligands. The addition of the ligands to the solutions of the complexes usually results in the substitution of all four aqua ligands, thereby forming stable new mixed-ligand complexes. In cases where the incoming neutral ligand is relatively bulky, as in the present study, it causes steric hindrance and only two of the four aqua ligands become displaced in order for the Cd center to remain octahedral. Although there are a number of Cd(II) saccharinate complexes previously reported (Batsanov *et al.*, 2011, and refs. therein), we are aware of only one other report that contains both saccharinate and dmso as ligands in a structurally characterized Cd(II) complex (Yilmaz *et al.*, 2003).

Experimental

[Cd(sac)$_2$(H$_2$O)$_4$].2H$_2$O was prepared as per literature method (Haider *et al.*, 1984). Colorless crystals of [Cd(sac)$_2$(H$_2$O)$_4$].2H$_2$O (1.13 g; 2.10 mmol) was placed in a 100 ml beaker and dissolved in excess amount of dimethyl sulfoxide (dmso) (20 ml). The reaction mixture was gently heated on a heating mantle with stirring to reduce the volume of dmso to ~7 ml. The beaker was removed from the heat source and allowed to stand for 6 days during which time large colorless blocky crystals of the title compound were obtained. Yield (1.30 g, 92%); Mp 114°C; ^{13}C NMR (CD$_3$OD, 101 MHz) d(p.p.m.): 40.39 (CH$_3$-dmso), 121.20 (C$_6$-ring), 124.91 (C$_6$-ring), 133.42 (C$_6$-ring), 134.21 (C$_6$-ring), 134.24 (C$_6$-ring), 144.90 (C$_6$-ring) 171.90 (C=O); IR (ATR) 3481, 3016 n(OH), 1646, 1609 n(C=O), 1583, 1460 n(C=C), 1271, 1256 n(O=S=O); 1054, 1036 n(S=O).

Refinement

All non-H atoms were refined anisotropically. All hydrogen atoms could be found in the difference electron density maps. All, except H5A and H5B on O5, were placed in idealized positions refining in riding models with U_{iso} set at 1.2 or 1.5

times those of their parent atoms. The water hydrogen atoms H5A and H5B were located in the difference electron density maps and refined with independent isotropic temperature factors and simple bond length constraints of d(O—H) = 0.980 (2) Å. The structure was refined to *R* factor of 0.0253.
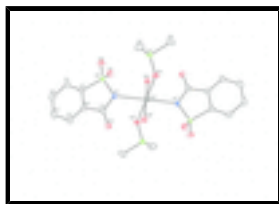
Figures

Fig. 1. The *ORTEP* molecular structure of the title complex, shown with 50% probability ellipsoids. [Symmetry codes: (i) 1-*x*, 2-*y*, -*z*]

Diaquabis(dimethyl sulfoxide)bis(1,1,3-trioxo-2,3-dihydro-1λ^6,2-benzothiazol-2-ido)cadmium

Crystal data

$[Cd(C_7H_4NO_3S)_2(C_2H_6OS)_2(H_2O)_2]$	$F(000) = 676$
$M_r = 669.03$	$D_x = 1.777$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 12452 reflections
$a = 10.2613$ (5) Å	$\theta = 2.0$–$28.4°$
$b = 15.4294$ (8) Å	$\mu = 1.26$ mm^{-1}
$c = 7.9951$ (4) Å	$T = 173$ K
$\beta = 98.889$ (1)°	Plate, colourless
$V = 1250.63$ (11) Å^3	$0.14 \times 0.11 \times 0.08$ mm
$Z = 2$	

Data collection

Bruker Kappa DUO APEXII diffractometer	3121 independent reflections
Radiation source: fine-focus sealed tube	2624 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.038$
0.5° φ scans and ω scans	$\theta_{max} = 28.4°$, $\theta_{min} = 2.0°$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1997)	$h = -13 \rightarrow 13$
$T_{min} = 0.843$, $T_{max} = 0.906$	$k = -20 \rightarrow 19$
12452 measured reflections	$l = -10 \rightarrow 10$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.025$	Hydrogen site location: inferred from neighbouring sites

$wR(F^2) = 0.061$

$S = 1.03$

3121 reflections

170 parameters

2 restraints

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.026P)^2 + 0.4033P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{max} = 0.42$ e Å^{-3}

$\Delta\rho_{min} = -0.41$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	$U_{iso}*/U_{eq}$
Cd1	0.5000	1.0000	0.0000	0.01487 (7)
S1	0.52294 (5)	0.80523 (4)	0.19576 (7)	0.02107 (12)
S2	0.26624 (5)	0.99004 (4)	0.27847 (6)	0.01863 (12)
O1	0.37534 (15)	1.02578 (12)	0.39322 (19)	0.0269 (4)
O2	0.23352 (16)	0.90145 (11)	0.3102 (2)	0.0286 (4)
O3	0.17818 (14)	1.06754 (10)	−0.15887 (18)	0.0236 (3)
O4	0.52173 (15)	0.85326 (10)	0.02902 (18)	0.0226 (3)
O5	0.62293 (15)	1.02147 (11)	0.25981 (19)	0.0219 (3)
H5A	0.7063 (14)	0.9905 (16)	0.261 (4)	0.053 (10)*
H5B	0.599 (3)	1.0050 (18)	0.3695 (18)	0.056 (11)*
N1	0.28899 (17)	1.00406 (12)	0.0832 (2)	0.0187 (4)
C1	0.12665 (19)	1.05728 (14)	0.2691 (3)	0.0173 (4)
C2	0.0586 (2)	1.08352 (15)	0.3962 (3)	0.0226 (5)
H2	0.0842	1.0655	0.5101	0.027*
C3	−0.0494 (2)	1.13759 (16)	0.3494 (3)	0.0285 (5)
H3	−0.0998	1.1564	0.4329	0.034*
C4	−0.0848 (2)	1.16459 (17)	0.1830 (3)	0.0315 (6)
H4	−0.1590	1.2016	0.1548	0.038*
C5	−0.0139 (2)	1.13854 (15)	0.0564 (3)	0.0240 (5)
H5	−0.0382	1.1572	−0.0574	0.029*
C6	0.09327 (19)	1.08447 (14)	0.1024 (3)	0.0173 (4)
C7	0.1890 (2)	1.05113 (14)	−0.0059 (3)	0.0181 (4)
C8	0.3957 (2)	0.72722 (17)	0.1524 (3)	0.0338 (6)
H8A	0.3100	0.7565	0.1340	0.051*
H8B	0.3996	0.6874	0.2485	0.051*

H8C	0.4071	0.6945	0.0505	0.051*
C9	0.6623 (2)	0.73625 (17)	0.2127 (4)	0.0379 (6)
H9A	0.6571	0.7007	0.1103	0.057*
H9B	0.6642	0.6985	0.3116	0.057*
H9C	0.7428	0.7714	0.2254	0.057*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cd1	0.01608 (10)	0.01350 (11)	0.01516 (10)	0.00098 (8)	0.00279 (7)	0.00131 (8)
S1	0.0264 (3)	0.0166 (3)	0.0201 (2)	0.0016 (2)	0.0034 (2)	0.0023 (2)
S2	0.0167 (2)	0.0241 (3)	0.0156 (2)	0.0032 (2)	0.00400 (19)	0.0044 (2)
O1	0.0193 (8)	0.0431 (10)	0.0180 (8)	0.0014 (7)	0.0016 (6)	0.0029 (7)
O2	0.0331 (9)	0.0243 (9)	0.0296 (9)	0.0055 (7)	0.0089 (7)	0.0086 (7)
O3	0.0227 (8)	0.0323 (9)	0.0156 (7)	0.0056 (7)	0.0027 (6)	0.0038 (7)
O4	0.0322 (9)	0.0142 (8)	0.0219 (8)	0.0017 (6)	0.0060 (7)	0.0041 (6)
O5	0.0233 (8)	0.0270 (9)	0.0156 (7)	0.0019 (6)	0.0039 (6)	−0.0007 (6)
N1	0.0180 (8)	0.0238 (10)	0.0149 (8)	0.0040 (7)	0.0045 (7)	0.0028 (8)
C1	0.0144 (9)	0.0180 (10)	0.0191 (10)	−0.0006 (8)	0.0013 (8)	0.0018 (8)
C2	0.0245 (11)	0.0245 (12)	0.0194 (10)	−0.0031 (9)	0.0055 (9)	0.0010 (9)
C3	0.0290 (12)	0.0309 (13)	0.0286 (12)	0.0065 (10)	0.0136 (10)	−0.0020 (11)
C4	0.0244 (12)	0.0355 (14)	0.0356 (13)	0.0106 (11)	0.0076 (10)	0.0008 (12)
C5	0.0220 (11)	0.0272 (13)	0.0225 (10)	0.0047 (9)	0.0026 (9)	0.0031 (10)
C6	0.0155 (9)	0.0181 (10)	0.0179 (10)	−0.0020 (8)	0.0017 (8)	−0.0013 (8)
C7	0.0165 (9)	0.0202 (11)	0.0176 (10)	−0.0009 (8)	0.0029 (8)	0.0007 (9)
C8	0.0393 (14)	0.0272 (13)	0.0339 (13)	−0.0102 (11)	0.0024 (11)	0.0086 (11)
C9	0.0325 (13)	0.0331 (15)	0.0490 (16)	0.0124 (11)	0.0089 (12)	0.0184 (13)

Geometric parameters (Å, °)

Cd1—O5^i	2.2817 (15)	C1—C2	1.379 (3)
Cd1—O5	2.2817 (15)	C1—C6	1.388 (3)
Cd1—O4	2.2833 (15)	C2—C3	1.391 (3)
Cd1—O4^i	2.2833 (15)	C2—H2	0.9500
Cd1—N1^i	2.3620 (17)	C3—C4	1.388 (3)
Cd1—N1	2.3620 (17)	C3—H3	0.9500
S1—O4	1.5236 (15)	C4—C5	1.394 (3)
S1—C8	1.770 (2)	C4—H4	0.9500
S1—C9	1.771 (2)	C5—C6	1.384 (3)
S2—O2	1.4393 (17)	C5—H5	0.9500
S2—O1	1.4429 (17)	C6—C7	1.498 (3)
S2—N1	1.6286 (17)	C8—H8A	0.9800
S2—C1	1.761 (2)	C8—H8B	0.9800
O3—C7	1.237 (2)	C8—H8C	0.9800
O5—H5A	0.979 (2)	C9—H9A	0.9800
O5—H5B	0.979 (2)	C9—H9B	0.9800
N1—C7	1.364 (3)	C9—H9C	0.9800
O5^i—Cd1—O5	180.0	C2—C1—S2	129.98 (17)

O5^i—Cd1—O4	88.86 (6)	C6—C1—S2	107.30 (15)
O5—Cd1—O4	91.14 (6)	C1—C2—C3	116.8 (2)
O5^i—Cd1—O4^i	91.14 (6)	C1—C2—H2	121.6
O5—Cd1—O4^i	88.86 (6)	C3—C2—H2	121.6
O4—Cd1—O4^i	180.0	C4—C3—C2	121.1 (2)
O5^i—Cd1—N1^i	98.15 (6)	C4—C3—H3	119.4
O5—Cd1—N1^i	81.85 (6)	C2—C3—H3	119.4
O4—Cd1—N1^i	85.58 (6)	C3—C4—C5	121.4 (2)
O4^i—Cd1—N1^i	94.42 (6)	C3—C4—H4	119.3
O5^i—Cd1—N1	81.85 (6)	C5—C4—H4	119.3
O5—Cd1—N1	98.15 (6)	C6—C5—C4	117.6 (2)
O4—Cd1—N1	94.42 (6)	C6—C5—H5	121.2
O4^i—Cd1—N1	85.58 (6)	C4—C5—H5	121.2
N1^i—Cd1—N1	180.00 (9)	C5—C6—C1	120.35 (19)
O4—S1—C8	104.67 (10)	C5—C6—C7	128.20 (19)
O4—S1—C9	104.85 (11)	C1—C6—C7	111.39 (18)
C8—S1—C9	99.72 (13)	O3—C7—N1	124.79 (19)
O2—S2—O1	115.48 (10)	O3—C7—C6	122.33 (19)
O2—S2—N1	111.53 (10)	N1—C7—C6	112.85 (17)
O1—S2—N1	110.29 (9)	S1—C8—H8A	109.5
O2—S2—C1	110.89 (9)	S1—C8—H8B	109.5
O1—S2—C1	110.36 (10)	H8A—C8—H8B	109.5
N1—S2—C1	96.72 (9)	S1—C8—H8C	109.5
S1—O4—Cd1	123.96 (9)	H8A—C8—H8C	109.5
Cd1—O5—H5A	107.3 (19)	H8B—C8—H8C	109.5
Cd1—O5—H5B	126.8 (19)	S1—C9—H9A	109.5
H5A—O5—H5B	102 (3)	S1—C9—H9B	109.5
C7—N1—S2	111.33 (14)	H9A—C9—H9B	109.5
C7—N1—Cd1	121.01 (13)	S1—C9—H9C	109.5
S2—N1—Cd1	122.67 (9)	H9A—C9—H9C	109.5
C2—C1—C6	122.70 (19)	H9B—C9—H9C	109.5
C8—S1—O4—Cd1	124.57 (12)	O1—S2—C1—C2	−58.7 (2)
C9—S1—O4—Cd1	−130.95 (13)	N1—S2—C1—C2	−173.3 (2)
O5^i—Cd1—O4—S1	−143.39 (10)	O2—S2—C1—C6	−111.05 (16)
O5—Cd1—O4—S1	36.61 (10)	O1—S2—C1—C6	119.69 (15)
O4^i—Cd1—O4—S1	140 (100)	N1—S2—C1—C6	5.10 (16)
N1^i—Cd1—O4—S1	118.34 (11)	C6—C1—C2—C3	1.7 (3)
N1—Cd1—O4—S1	−61.66 (11)	S2—C1—C2—C3	179.95 (18)
O2—S2—N1—C7	109.33 (16)	C1—C2—C3—C4	−1.0 (4)
O1—S2—N1—C7	−120.95 (16)	C2—C3—C4—C5	0.1 (4)
C1—S2—N1—C7	−6.30 (17)	C3—C4—C5—C6	0.1 (4)
O2—S2—N1—Cd1	−95.51 (12)	C4—C5—C6—C1	0.5 (3)
O1—S2—N1—Cd1	34.20 (14)	C4—C5—C6—C7	−176.6 (2)
C1—S2—N1—Cd1	148.86 (11)	C2—C1—C6—C5	−1.5 (3)
O5^i—Cd1—N1—C7	−45.91 (16)	S2—C1—C6—C5	179.89 (17)
O5—Cd1—N1—C7	134.09 (16)	C2—C1—C6—C7	176.04 (19)

O4—Cd1—N1—C7	−134.12 (16)	S2—C1—C6—C7	−2.5 (2)
O4^i—Cd1—N1—C7	45.88 (16)	S2—N1—C7—O3	−176.23 (18)
N1^i—Cd1—N1—C7	142 (3)	Cd1—N1—C7—O3	28.1 (3)
O5^i—Cd1—N1—S2	161.27 (12)	S2—N1—C7—C6	5.7 (2)
O5—Cd1—N1—S2	−18.73 (12)	Cd1—N1—C7—C6	−149.94 (14)
O4—Cd1—N1—S2	73.06 (11)	C5—C6—C7—O3	−2.6 (4)
O4^i—Cd1—N1—S2	−106.94 (11)	C1—C6—C7—O3	−180.0 (2)
N1^i—Cd1—N1—S2	−11 (2)	C5—C6—C7—N1	175.5 (2)
O2—S2—C1—C2	70.5 (2)	C1—C6—C7—N1	−1.8 (3)

Symmetry codes: (i) −x+1, −y+2, −z.

Fig. 1