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Diiodobis(4-methoxybenzaldehyde thiosemicarbazone-S)cadmium(II)

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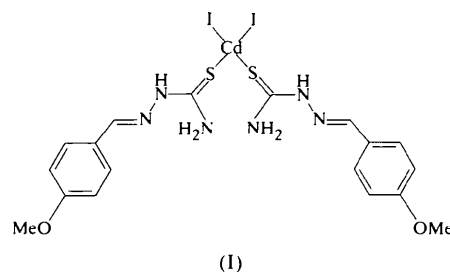
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Abstract

The title complex, $[\text{CdI}_2(\text{C}_9\text{H}_{11}\text{N}_3\text{OS})_2]$, contains distorted tetrahedral $[\text{CdI}_2L_2]$ units (where L is 4-methoxybenzaldehyde thiosemicarbazone), in which L molecules are S -bonded in a monodentate mode to the cadmium ion. Principal dimensions include Cd—S 2.5875 (10) and 2.5795 (10) Å, and Cd—I 2.7020 (4) and 2.7470 (4) Å.

Comment

Transition metal complexes of thiosemicarbazones have been studied extensively and have been the subject of several recent reviews (Campbell, 1975; Padhye & Kauffman, 1985; Lukevics *et al.*, 1995). Thiosemicarbazones have been shown to exhibit a range of biological activities, which is considered to be related to their ability to chelate metals. Recently, there has been considerable interest in the chemistry of Schiff base compounds containing thiosemicarbazones and their IIB group metal complexes, due to their non-linear optical properties (Xu *et al.*, 1987; Hu *et al.*, 1995; Tian *et al.*, 1997). It might be expected that the design and synthesis of IIB metal complexes derived from thiosemicarbazone may be a possible way of obtaining potential non-linear optical materials. In this paper, the synthesis and crystal structure of the title complex, (I), are reported.



The molecular structure of (I), together with the atom-labelling scheme, is shown in Fig. 1. The crystals contain individual neutral $[\text{CdI}_2L_2]$ molecules. In (I), the Cd—S [2.5875 (10) and 2.5795 (10) Å] and Cd—I [2.7470 (4) and 2.7020 (4) Å] distances are almost equal, and are comparable with compounds with terminal $M—S$ and $M—I$ bonds. Thus, the strong distortion in the tetrahedral environment of the four donor atoms in (I) is explained on the basis of strong stereo interactions between the two molecules of the ligand in the complex. Comparing (I) with the free ligand (Tian *et al.*, 1997), some bond distances are different. The obvious lengthening of the C—S bond distances in (I) is as expected for a C=S double bond, and reflects the coordination of the ligand to the S atom. The angles around the Cd atom in (I) vary from 100.02 (3) to 115.73 (1)°. The bond lengths in the two thiosemicarbazone groups show slight differences and the C=N , N—N , N—C_{sp^2} and C=S bond distances are similar to the values reported in the literature (Fun *et al.*, 1995; Tian *et al.*, 1996), which shows that the molecule is in the keto tautomeric form. The C=N bond is in the E configuration.

In similar thiosemicarbazone derivatives, there is crystallographic evidence of both N,S -chelates and monodentate S - or N -ligands. $[\text{CdI}_2L_2]$ complexes present crystallographic evidence for S -bonding. The preference for S atoms (a softer donor than N) is not

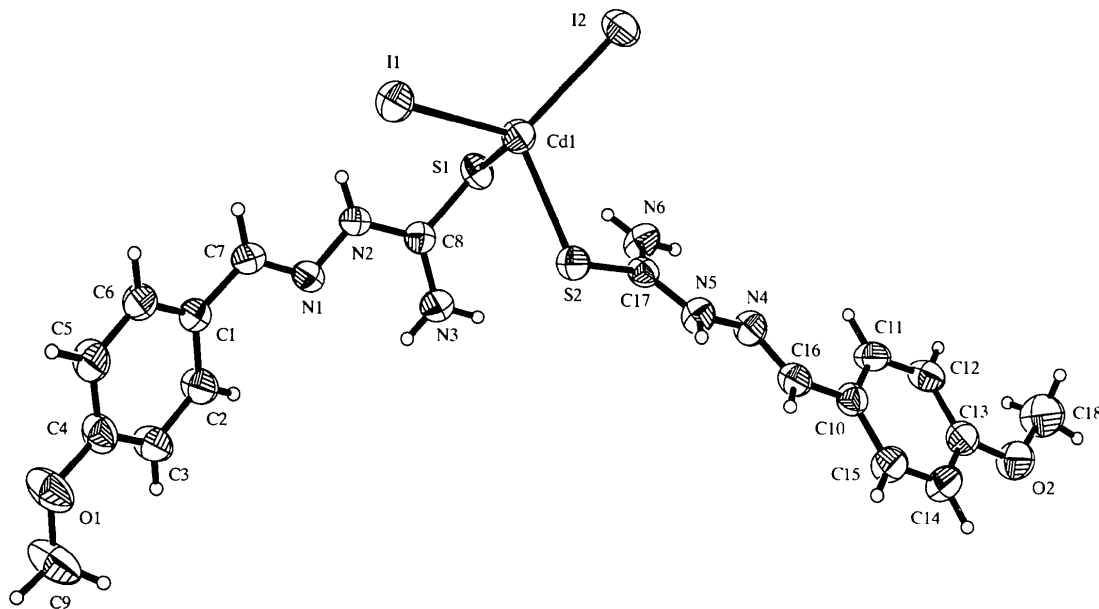


Fig. 1. The structure of complex (I) showing 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms are drawn as spheres of arbitrary radii.

surprising in the case of the soft Cd^{II} ion and acids. Another condition is that $M^{II}X_2$ solutions are acidic during the reaction, which makes it more difficult to coordinate with metal ions as the monodentate ligand. In complex (I), the metal atom is tetracoordinate and surrounded by the two molecules of the ligand (acting as monodentate ligands through the S atoms) and two terminal I atoms. This arrangement yields a strongly distorted tetrahedral environment around the metal ion.

The methoxy group at O1—C9 is coplanar [torsion angle $-2.2(7)^\circ$] and the other methoxy group (O2—C18) is twisted through $10.5(7)^\circ$ out of the plane, with respect to the phenyl rings to which they are attached. The ligands in the complex make an interplanar angle of $48.9(1)^\circ$ with each other. The molecules are packed as helices through N—H...I, N—H...S and N—H...O interactions (Table 2).

Based on *MNDO Hamitan* (Dewar & Thiel, 1977) and *PM3* parameterization with the *MOPAC* program package (Stewart, 1989), the vector component of the molecular hyperpolarizability of (I) along the dipole-moment direction, β_μ , is calculated to be -6.7×10^{-30} e.s.u. The absolute value is much greater than that of urea (0.14×10^{-30} e.s.u.). However, powder SHG (second harmonic generation) studies showed that the complex did not exhibit any SHG efficiency, which is due to its centrosymmetric space group upon crystallization.

Experimental

The thiosemicarbazone ligand was prepared by refluxing equimolar amounts of thiosemicarbazide and 4-methoxybenz-

aldehyde in ethanol solution for 2 h. Upon cooling, a white solid was formed. The title complex was then prepared by mixing an ethanol solution of the thiosemicarbazone and cadmium iodide. The colourless crystalline solid which formed after refluxing for 4 h was isolated and dried under vacuum. Crystals of (I) suitable for X-ray structure analysis were obtained by slow evaporation of an ethanol solution at room temperature.

Crystal data

[CdI₂(C₉H₁₁N₃OS)₂]
 $M_r = 784.74$
 Monoclinic
 $P2_1/c$
 $a = 14.0268(1) \text{ \AA}$
 $b = 15.0988(2) \text{ \AA}$
 $c = 13.3565(2) \text{ \AA}$
 $\beta = 111.16(1)^\circ$
 $V = 2638.02(6) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.976 \text{ Mg m}^{-3}$
 D_m not measured

Mo $K\alpha$ radiation
 $\lambda = 0.71073 \text{ \AA}$
 Cell parameters from 8192 reflections
 $\theta = 2.96\text{--}33.21^\circ$
 $\mu = 3.352 \text{ mm}^{-1}$
 $T = 293(2) \text{ K}$
 Parallelepiped
 $0.48 \times 0.44 \times 0.30 \text{ mm}$
 Yellow

Data collection

Siemens SMART CCD area-detector diffractometer
 ω scans
 Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
 $T_{\min} = 0.250$, $T_{\max} = 0.366$
 16 220 measured reflections
 5978 independent reflections

5370 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.026$
 $\theta_{\text{max}} = 27.5^\circ$
 $h = -17 \rightarrow 17$
 $k = 0 \rightarrow 19$
 $l = 0 \rightarrow 17$
 Intensity decay: negligible

Refinement

Refinement on F^2 $R[F^2 > 2\sigma(F^2)] = 0.037$ $wR(F^2) = 0.090$ $S = 1.149$

5978 reflections

280 parameters

H-atom parameters

constrained

 $w = 1/[\sigma^2(F_o^2) + (0.0302P)^2 + 4.3508P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} = 0.001$ $\Delta\rho_{\max} = 1.037 \text{ e } \text{\AA}^{-3}$ $\Delta\rho_{\min} = -1.568 \text{ e } \text{\AA}^{-3}$

Extinction correction: none

Scattering factors from

International Tables for Crystallography (Vol. C)Table 1. Selected geometric parameters (\AA , $^\circ$)

Cd1—S1	2.5875 (10)	O2—C18	1.403 (6)
Cd1—S2	2.5795 (10)	N1—N2	1.384 (4)
Cd1—I1	2.7470 (4)	N1—C7	1.271 (5)
Cd1—I2	2.7020 (4)	N2—C8	1.319 (5)
S1—C8	1.725 (4)	N3—C8	1.327 (5)
S2—C17	1.724 (4)	N4—N5	1.389 (4)
O1—C4	1.372 (5)	N4—C16	1.280 (5)
O1—C9	1.429 (6)	N5—C17	1.326 (5)
O2—C13	1.368 (5)	N6—C17	1.318 (5)
S1—Cd1—I2	110.14 (2)	S2—Cd1—I2	111.93 (2)
S1—Cd1—I1	109.09 (3)	I2—Cd1—I1	115.73 (1)
S2—Cd1—S1	100.02 (3)	C8—S1—Cd1	96.6 (1)
S2—Cd1—I1	108.76 (2)	C17—S2—Cd1	102.6 (1)

Table 2. Hydrogen-bonding geometry (\AA , $^\circ$)

D—H...A	D—H	H...A	D...A	D—H...A
N6—H6C...S1	0.86	2.70	3.522 (4)	160
N2—H2B...S2 ⁱ	0.86	2.60	3.431 (3)	162
N3—H3C...I1 ⁱⁱ	0.86	3.00	3.735 (4)	144
N5—H5B...I1 ⁱⁱⁱ	0.86	3.06	3.901 (4)	167
N6—H6B...O1 ^{iv}	0.86	2.15	2.895 (5)	144

Symmetry codes: (i) $x, \frac{3}{2}-y, z-\frac{1}{2}$; (ii) $1-x, \frac{1}{2}+y, \frac{3}{2}-z$; (iii) $x, \frac{3}{2}-y, \frac{1}{2}+z$; (iv) $x-1, y, z$.

Data collection: SMART (Siemens, 1996). Cell refinement: SAINT (Siemens, 1996). Data reduction: SAINT. Program(s) used to solve structure: SHELXTL (Sheldrick, 1997). Program(s) used to refine structure: SHELXTL. Molecular graphics: SHELXTL. Software used to prepare material for publication: SHELXTL and PLATON (Spek, 1990).

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Dichlorobis(dimethylformamide-*O*)bis-(4-nitrobenzaldehyde thiosemicarbazone-*S*)-cadmium(II)

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Abstract

The title complex, $[\text{CdCl}_2(\text{C}_3\text{H}_7\text{NO})_2(\text{C}_8\text{H}_8\text{N}_4\text{O}_2\text{S})_2]$, crystallizes in space group $P\bar{1}$ with half a molecule in the asymmetric unit. The Cd atom lies on an inversion centre and is octahedrally coordinated to two O atoms from the dimethylformamide ligands, two S atoms from the thiosemicarbazone ligands and two Cl atoms.

Comment

Metal-thiosemicarbazone complexes are emerging as a new class of experimental anticancer compounds which can provide non-platinum therapeutic agents with