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Synthesis and crystal structure of the cadmium complex of 2-bromobenzaldehyde thiosemicarbazone

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Abstract—The new cadmium iodide complex CdL_2I_2 (where L is a Schiff base ligand, 2-bromobenzaldehyde thiosemicarbazone) has been synthesized and characterized by spectroscopic techniques and single-crystal X-ray analysis. The coordination geometry about the cadmium atom is distorted trigonal bipyramidal with two iodide atoms and one sulfur atom, S(2), from one of the two ligands in the equatorial plane; the iodide atom I(1a) from an adjacent moiety and the other sulfur atom S(1) occupy the axial positions. The iodide I(1a) and I(1) serve as bridges to form a centrosymmetric dimeric structure. © 1997 Elsevier Science Ltd

Keywords: crystal structure; thiosemicarbazone; synthesis.

Recently, there has been considerable interest in the chemistry of Schiff base compounds containing thiosemicarbazones and their metal complexes due to their biological activities [1–3] and nonlinear optical properties [4,5]. IIB group metal complexes of thiosemicarbazone are pale in color and quite thermally stable [1]. It has also been reported that some cadmium complexes of thiosemicarbazides and thiosemicarbazones can show quite large SHG efficiency [4]. It could be expected that the design and synthesis of IIB metal complexes derived from thiosemicarbazones might be a possible way to obtain the potential nonlinear optical materials. Here, a new cadmium iodide complex of the Schiff base ligand 2-bromobenzaldehyde thiosemicarbazone has been designed and structurally characterized.

EXPERIMENTAL

Materials

All chemicals used were of analytical grade without further purification. The ligand 2-bromobenzaldehyde thiosemicarbazone was prepared according to the literature method in our previous work [6].

Preparation of the complex

Ethanol solutions of cadmium iodide (0.73 g, 2 mmol) and the ligand (0.52 g, 2 mmol) were mixed. After refluxing for 4 h the solution was cooled to room temperature and the colorless crystalline solid formed was isolated and dried *in vacuo*. Crystals suitable for X-ray structure determination were obtained by slowly evaporating a dichloromethane solution in air. Found: C, 21.8; H, 1.8; N, 9.3; Calc. for $CdL_2I_2C_{16}H_{16}N_6S_2Br_2CdI_2$: C, 21.8; H, 1.8; N, 9.5%. IR data (KBr discs, cm^{-1}): 3383, 3287, 3160 (N—H, m), 1594, 1547 (C=C, C=N, s), 995 (C=S, s), 227 (M—I, m), 195 (M—S, m). Electronic spectra (nm DMF, log ε): λ_{max} 326(4.45). m.p. 245°C.

Physical measurements

Elemental analyses were performed on a Perkin–Elmer 240 instrument. IR spectra were recorded on a Nicolet FT-IR-170SX instrument (KBr discs) in the

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4000–400 cm^{-1} region. The far-IR spectra (500–100 cm^{-1}) were recorded in Nujol mulls between polyethylene sheets. Electronic absorption spectra were obtained on a Shimadzu VU 3100 spectrophotometer in DMF.

Crystallographic data collection and structure determination

The relevant crystal data and structure parameters are summarized in Table 1. The intensities of the free ligand were collected at 294 K on a Riguka AFC7R diffractometer using Mo-K_α radiation (λ = 0.71073 Å) from a rotating-anode generator operating on 50 kV and 90 mA. Intensity measurements were made at room temperature with the $\theta/2\theta$ scan mode (range $4 < 2\theta < 55°$) and a scan speed varied from 2.0 to 19.5° min^{-1}.

The intensities of the cadmium complex were collected at 294 K on a Rigaku RAXIS-IIC imaging plate diffractometer using Mo-K_α (λ = 0.71073 Å) from a rotating-anode generator operating at 50 kV and 90 mA ($2\theta_{max}$ = 55.2^0) ; 60 oscillation frames in the range 0–180°, exposure at 8 min per frame [7,8].

The structures were solved by direct methods. All non-hydrogen atoms were refined anisotropically by full-matrix least squares. Hydrogen atoms were placed in their calculated position with C—H = 0.96 Å, assigned fixed isotropic thermal parameters and allowed to ride on their respective parent atoms. The contributions of these hydrogen atoms were included in the structure-factor calculations.

All calculations were carried out on a PC-486 computer using the SHELXTL-PC program package [9]. Analytical expressions of neutral-atom scattering factor were employed and anomalous dispersion corrections were incorporated [10]. Selected bond lengths and angles for the title complex are tabulated in Table 2. Additional materials available from the Cambridge Crystallographic Data Center comprise complete lists of atom coordinates and thermal parameters.

RESULTS AND DISCUSSION

The cadmium complex was prepared by the reaction of 2-bromobenzyldehyde thiosemicarbazone with cadmium iodide in a 1 : 2 molar ratio. The ligand can, in principle, coordinate to the metal atom either as a chelating ligand with N and S as donors or as a monodentate S donor [11–13]. The ν(M—N) band at *ca* 350–450 nm is absent from the IR spectra of the metal complex, but ν(M—I) at 230 cm^{-1} and ν(M—S) at 195 nm are present, indicating that in the solid state the ligand is coordinated to the cadmium atom as a monodentate S donor. The ν(C═S) band is less than 1000 cm^{-1}, also suggesting that the ligand coordinated to cadmium is the C═S → Cd form.

Description of the crystal structure of the ligand

Figure 1 shows an ORTEP drawing of the molecule with the atom numbering scheme. The thiosemicarbazone moiety shows an *E* configuration about both the C(2)—N(3) and C(1)—N(2) bonds, as found in most thiosemicabazides [14–16] and thiosemi-

Table 1. Summary of crystallographic data and parameters for the free ligand and cadmium complex

Compound	Ligand	Cadmium complex
Formula	$C_8H_8N_3SBr$	$C_{16}H_{16}N_6S_2Br_2CdI_2$
Formula weight	258.1	882.5
Color/habit	Colorless prism	Colorless needle
Size (mm)	0.25 × 0.30 × 0.40	0.12 × 0.15 × 0.51
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P1$
a (Å)	14.9850(10)	10.547(2)
b (Å)	5.0470(10)	16.099(3)
c (Å)	15.0650(10)	7.862(2)
α (°)		100.50(3)
β (°)	117.310(10)	109.46(3)
γ (°)		83.86(3)
V (Å^3)	1012.4(5)	1236.5(6)
Z	4	2
μ (mm^{-1})	4.233	6.796
d(calcd) (g cm^{-3})	1.694	2.370
Reflections unique	1164	4356
Reflections observed	377 [$F > 6.0\sigma(F)$]	3241[$F > 6.0\sigma(F)$]
R, Rw	0.067, 0.086	0.072, 0.094
GOF	1.92	1.65
$\Delta(\rho)_{max,min}$ (e Å^{-3})	0.46, −0.54	2.19, −2.10

Table 2. Selected bond lengths (Å) and angles (°) for the free ligand (L) and complex CdL_2I_2

Free ligand			
S(1)—C(1)	1.651(4)	N(1)—C(1)	1.365(5)
N(2)—N(3)	1.379(4)	N(2)—C(1)	1.365(5)
N(3)—C(2)	1.284(6)	C(2)—C(8)	1.452(4)
Br(1)—C(3)	1.860(4)	C(3)—C(4)	1.393(4)
C(3)—C(8)	1.393(6)	C(4)—C(5)	1.389(6)
C(5)—C(6)	1.397(3)	C(6)—C(7)	1.397(4)
C(7)—C(8)	1.396(5)		
N(3)—N(2)—C(1)	122.4(4)	N(2)—N(3)—C(2)	116.6(4)
S(1)—C(1)—N(1)	123.2(3)	S(1)—C(1)—N(2)	122.7(3)
N(1)—C(1)—N(2)	113.7(3)	N(3)—C(2)—C(8)	122.5(2)
Br(1)—C(3)—C(8)	121.6(3)	Br(1)—C(3)—C(8)	120.5(2)
C(4)—C(3)—C(8)	121.6(3)	C(3)—C(4)—C(7)	119.0(3)
C(4)—C(7)—C(6)	121.0(3)	C(5)—C(6)—C(7)	119.0(3)
C(6)—C(7)—C(8)	120.7(4)	C(2)—C(8)—C(3)	123.0(3)
C(2)—C(8)—C(7)	118.1(4)	C(3)—C(8)—C(7)	118.6(3)
Cadmium complex			
Cd(1)—I(1)	2.738(1)	Cd(1)—I(2)	2.770(1)
Cd(1)—S(1)	2.621(2)	Cd(1)—S(2)	2.541(3)
Cd(1)—I(1a)	4.105(6)	S(2)—C(9)	1.698(5)
S(1)—C(1)	1.726(5)	N(4)—C(9)	1.328(5)
N(2)—N(3)	1.359(6)	N(2)—C(1)	1.330(6)
N(1)—C(1)	1.297(4)	Br(1)—C(3)	1.804(3)
I(1)—Cd(1)—I(2)	115.8(1)	S(1)—Cd(1)—S(2)	101.1(1)
I(1)—Cd(1)—S(2)	115.3(1)	I(2)—Cd(1)—S(2)	117.8(1)
Cd(1)—S(1)—C(1)	99.5(1)	Cd(1)—S(2)—C(9)	105.8(2)
N(3)—N(2)—C(1)	119.2(3)	N(2)—N(3)—C(2)	116.0(3)
S(1)—C(1)—N(1)	121.9(4)	N(1)—C(1)—N(2)	119.5(4)

Symmetry code: (a) $-x, 1-y, -z$.

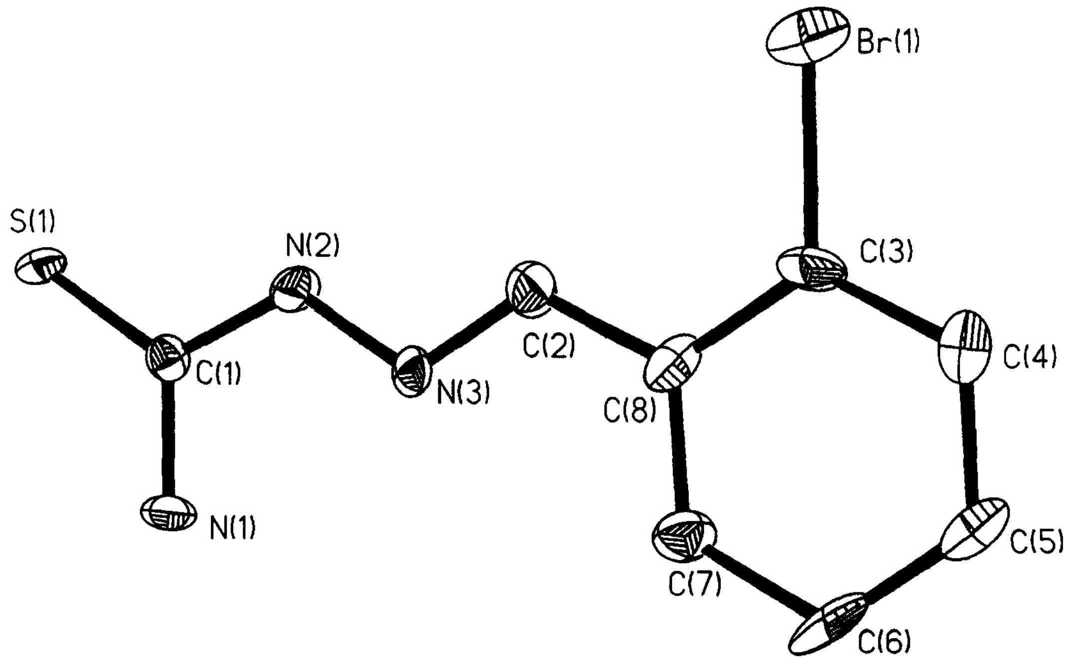
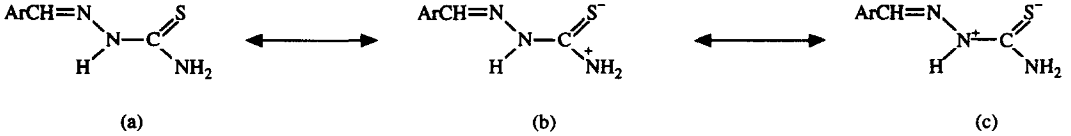


Fig. 1. Molecular structure and atom numbering of the free ligand $C_6H_4BrCH{=}NNHC(S)NH_2$ (L). The thermal ellipsoids are drawn at the 30% probability level.



Scheme. I.

carbazones [17–19]. The C—S bond distance of 1.651(4) Å agrees well with those in related compounds, being intermediate between 1.82 Å for a C—S single bond and 1.56 Å for a C=S double bond [20]. The corresponding C(1)—N(1) and C(1)—N(2) [1.365(3) Å] bond distances are indicative of some double-bond character, in agreement with the resonance forms (b) and (c) in Scheme I.

Description of the structure of the complex

The complex has dimeric structure with crystallographic $\bar{1}$ symmetry. The coordination geometry about the Cd^{II} ion is trigonal bipyramidal, as illustrated in Fig. 2. The two iodide atoms I(1) and I(2), as well as the thiosemicarbazone sulfur S(2), comprise the equatorial plane, whereas the axial positions are occupied by the other thiosemicarbazone sulfur S(1) and the I(1a) [Cd(1)—I(1a), 4.100 Å] of the symmetry-related half of the dimer. The Cd(1) atom is placed 0.52 Å above the equatorial plane toward the axis site of S(1). The other axis coordination site of the complex is very soft, Cd(1)—I(1a) more than 4.0 Å, and may well be omitted in a simplified bonding description. However, this contact is very important in the crystallization of centrosymmetric space group crystals. It has also been reported [21] that in the related cadmium complexes derived from the ligand 2-chlorobenzaldehyde thiosemicarbazone, the corresponding cadmium bromide complex can crystallize in a noncentrosymmetric space group and give quite large SHG efficiency, while the related cadmium iodide complex crystallizes in a centrosymmetric space group and in the dimeric structure as the title complexes and shows no SHG efficiency.

Nonlinear optical properties calculation

Based on MNDO Hamiltonian [22] and PM3 parametrization [23] with the MOPAC program package [24], the molecular hyperpolarizability, β_μ, the vector component along the dipole moment direction, of the free ligand and the cadmium complex are calculated to be -9.2×10^{-30} and -13.6×10^{-30} esu, respectively,

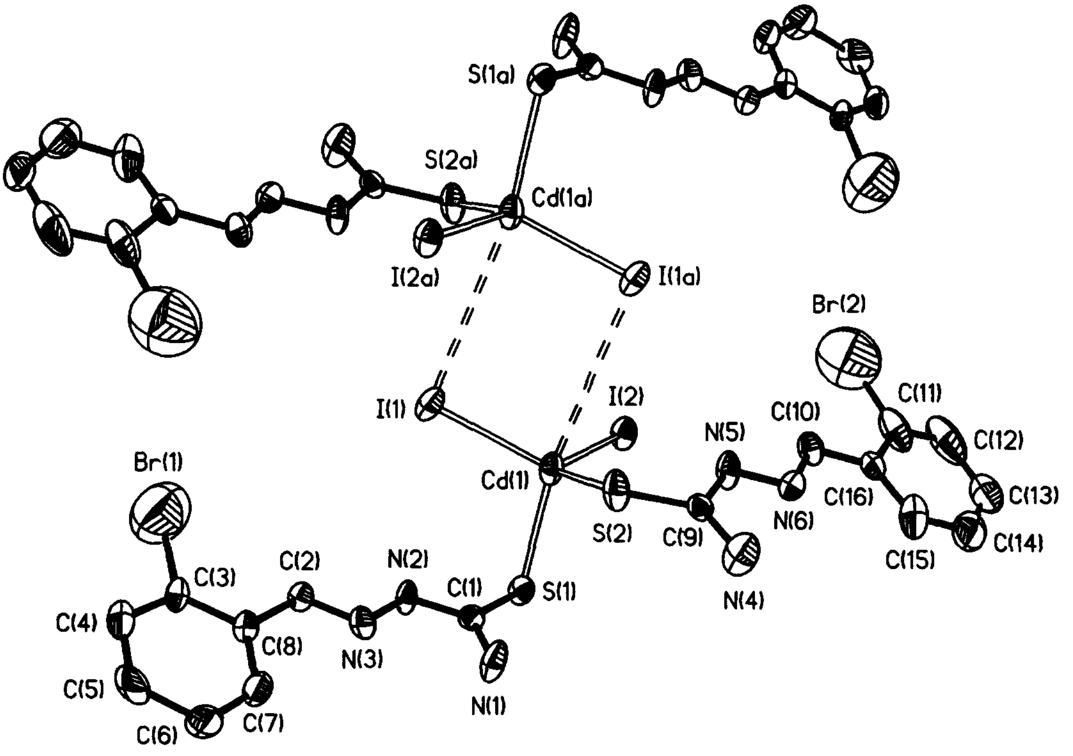


Fig. 2. Molecular structure and atom numbering of the cadmium complex CdL_2I_2. The thermal ellipsoids are drawn at the 30% probability level; symmetry code: (a) $-x$ $1-y$, $-z$.

which are comparable with that of *p*-nitroaniline (PNA, 6.3×10^{-30}) and are much greater than that of urea (0.14×10^{-30}). The negative sign of β_μ can be explained by the smaller dipole moment of the lowest excited state than that of the ground one. The difference of β_μ in magnitude between the ligand and its cadmium complex is small. The similarity of β_μ can be readily understood by their similar contribution from a low-energy transition. The linear absorption spectra of the ligand and the cadmium complex in a solution of DMF exhibit one intense band ($\log \varepsilon = 4.54, 4.75$) near 326 nm. The PM3 electronic spectrum calculation for the ligand and its cadmium complex give a strong electron transition near *ca* 317 nm with oscillator strength 0.797, consistent with the above linear absorption spectra. The optical transition associated with this band is mainly the contribution of $\pi^* \leftarrow \pi$ or $\pi^* \leftarrow n$ transition of nonbonding electron pairs of N and S atoms, according to the analysis of molecular orbital components for ligand and cadmium complexes. Unfortunately, the free ligand and complex crystals show a vanishing SHG response due to their centrosymmetric space groups in crystallization, although they have large microscopic second-order nonlinear susceptibility β.

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