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Synthesis, Crystal Structure, and Second-Order Optical Nonlinearity of Bis(2-chlorobenzaldehyde thiosemicarbazone)cadmium Halides (CdL_2X_2; X = Br, I)

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The new Schiff base ligand 2-chlorobenzaldehyde thiosemicarbazone (L, **1**) has been synthesized and characterized by spectral techniques and single-crystal X-ray analysis. Crystals of **1** are monoclinic, space group $P2_1/n$ with $a = 12.964(4)$ Å, $b = 5.131(5)$ Å, $c = 4.970(1)$ Å, $\beta = 94.32(2)°$, and $Z = 4$. The thiosemicarbazone moiety adopts a configuration with N(1) *cis* to N(3) and places the *E* configuration about both the bonds C(1)−N(2) and C(2)−N(3). The monodentate behavior of the neutral ligand (L) has been investigated in two cadmium halides $CdL_2\ Br_2$ (**2**) and CdL_2I_2 (**3**). Compound **2** crystallizes in space group *Cc* with $a = 8.175(1)$ Å, $b = 14.176(1)$ Å, $c = 21.073(1)$ Å, $\beta = 94.02(1)°$, and $Z = 4$. Compound **3** crystallizes in space group $P\bar{1}$ with $a = 10.9577(1)$ Å, $b = 16.174(1)$ Å, $c = 7.878(1)$ Å, $\alpha = 100.50(1)°$, $\beta = 109.39(1)°$, $\gamma = 83.67(1)°$, and $Z = 2$. The coordination geometry about the cadmium(II) atom in compound **2** conforms to a tetrahedral configuration with two sulfur atoms from two unequivalent neutral ligands and two bromide atoms. Whereas the coordination geometry about the cadmium(II) atom in compound **3** is (4 + 1) distorted trigonal bipyramidal with two iodide atoms and one sulfur atom in the equatorial plane, the other thiosemicarbazone sulfur and the iodide atom I(1a) of an adjacent moiety occupy the axial positions. Compound **2** exhibits powder SHG efficiencies *ca.* 20 times that of urea, whereas compound **3** does not exhibit any SHG efficiency. Theory and experiment suggested that intermolecular contact is the main factor controlling the SHG efficiencies of compounds.

Introduction

There is considerable interest in the synthesis of new materials with optical nonlinearities because of their potential use in device applications relative to telecommunications, optical computing, optical storage, and optical information processing.[1−4] Recently, tremendous efforts have been devoted to the synthesis of molecular-based materials, organic polymers, and organometallic compounds with large second order optical nonlinearities.[5−7] And it has been reported that some of those compounds demonstrate SHG efficiencies hundreds times larger than that of urea.[8] However, few of them could be used as applicable materials, owing to the mechanical and thermal instability of organic systems and the intensity of color of transition metal complexes. Group IIB metal complexes of thiosemicarbazides and thiosemicarbazones are among few kinds of metal complexes that are pale in color and quite thermally stable. And it has also reported that some cadmium complexes of those ligands can present quite large SHG efficiencies.[9] It could be expected that the design and synthesis of IIB metal complexes derived from thiosemicarbazones might be a possible way to obtain the applicable nonlinear optical materials. Here, new cadmium halide complexes of the Schiff base ligand 2-chlorobenzaldehyde thiosemicarbazone have been designed and structural characterized. Theoretical and experimental second order optical nonlinearity studies have also been reported, which suggest that intermolecular contact is the main factor controlling the SHG efficiencies of those compounds.

Experimental Section

Materials and Reagents. All chemicals were of reagent grade and were used without further purification.

Schiff Base Ligand [$(C_6H_5Cl)CHNNHCSNH_2$] (L, 1). Five drops of acetic acid were added to a mixture of thiosemicarbazide (0.91 g, 10 mmol) and 2-chlorobenzaldehyde (1.40 g, 10 mmol) in refluxing ethanol. The solution was further refluxed for 2 h, and a white solid formed. The solid was filtered off by suction and dried *in vacuo* over P_2O_5. Yield: 1.80 g (84%). Crystals suitable for X-ray structure analysis were obtained from slow evaporation of an ethanolic solution in the air. IR data (KBr disks, cm^{-1}): 3415, 3246, 3153 (N−H, m), 1611, 1592 (C=C, C=N, s), 1102 (C=S, s). Electronic spectra [nm, DMF (log ϵ)]: λ_{max} 326 (4.48). Mp: 185 °C. ^1H NMR (δ, ppm): 10.93 (br, 1H), 8.60 (s, 1H), 8.22 (d), 8.03 (br, 2H), 7.48 (d, 1H), 7.43 (t, 1H), 7.38 (t, 1H). Anal. Calcd for L ($C_8H_8N_3SCl$): C, 44.98; H, 3.77; N, 31.58. Found: C, 44.74; H, 3.56; N, 31.45.

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Table 1. Crystallographic Data for the Free Ligand **1** and Two Cadmium Complexes **2** and **3**

	compd		
	1	**2**	**3**
chem formula	$C_8H_8N_3SCl$	$C_{16}H_{16}N_6S_2Cl_2Cd_2Br_2$	$C_{16}H_{16}N_6S_2Cl_2Cd_2I_2$
fw	213.6	699.6	793.6
a, Å	12.964(4)	8.175(1)	7.862(2)
b, Å	5.131(5)	14.176(1)	10.547(2)
c, Å	14.970(1)	21.073(1)	16.099(3)
α, deg	90	90	83.86(2)
β, deg	94.33(2)	94.02(1)	79.86(2)
γ, deg	90	90	70.54(2)
V, $Å^3$	933(1)	2433.0(12)	1236.06
Z	4	4	2
μ(Mo Kα), mm^{-1}	0.541	4.589	3.78
d(calcd), g cm^{-3}	1.429	1.910	2.132
temp, K	293	294	294
λ, Å	0.710 73	0.710 73	0.710 73
R,[a] R_w[b]	0.045, 0.059	0.072, 0.093	0.060, 0.089

[a] $R = \sum(||F_o| - |F_c||)/|F_o|$ for the ligand **1** and $R = \sum(||F_o|^2 - |F_c|^2|)/|F_o|^2$ for the two cadmium complexes; $w^{-1} = \sigma^2(F_o)$ for all three compounds.

Cadmium Bromide Complex [CdL_2Br_2] (2). An ethanol solution of **1** (0.43 g, 2 mmol) and cadmium bromide (0.69 g, 2 mmol) were mixed. The colorless crystalline solid formed after refluxing for 4 h was isolated, washed with ethanol, and dried *in vacuo* over P_2O_5. Crystals suitable for X-ray structure determination were obtained by slowly evaporating a dichloromethane solution in air. Yield: 85%. IR data (KBr disks, cm^{-1}): 3432, 3280, 3170 (N−H, m), 1593, 1534 (C=C, C=N, s), 1027 (C=S, s), 238 (Cd−Br, m), 195 (Cd−S, m). Electronic spectra [nm, DMF (log ϵ)]: λ_{max} 326 (4.45). Mp: 253 °C. Anal. Calcd for CdL_2Br_2 ($C_{16}H_{16}N_6S_2Cl_2CdBr_2$): C, 27.47; H, 2.27; N, 12.01. Found: C, 27.45; H, 2.31; N, 11.98.

Cadmium Bromide Complex [CdL_2Br_2] (3). The complex was obtained as colorless prism crystals in a similar manner. Yield: 85%. IR data (KBr disks, cm^{-1}): 3455, 3253, 3174 (N−H, m), 1592, 1534 (C=C, C=N, s), 1029 (C=S, s), 235 (Cd−Br, m), 195 (Cd−S, m). Electronic spectra [nm, DMF (log ϵ)]: λ_{max} 326 (4.78). Mp: 223 °C. Anal. Calcd for CdL_2I_2 ($C_{16}H_{16}N_6S_2Cl_2CdI_2$): C, 24.21; H, 2.03; N, 10.59. Found: C, 24.12; H, 2.23; N, 10.45.

Physical Measurements. Elemental analyses were performed on a Perkin-Elmer 240C analytical instrument. IR spectra were recorded on a Nicolet FT-IR-170SX instrument (KBr disks) in the 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 UV-3100 spectrophotometer in DMF. The proton NMR spectrum was measured on a Bruker Cryospec WM 250 (250 MHz) spectrometer.

Crystallography. The relevant crystal data and structural parameters are summarized in Table 1. The intensities of compound **1** were collected at 293 K on a Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo Kα ($\lambda = 0.710\ 73$Å) radiation using the $\omega/2\theta$ scan mode and CONTROL.[10] Intensity data were corrected for Lorentz−polarization effects and absorption. The structure was solved by direct methods using MITHRIL[11] and refined by full-matrix least-squares methods with anisotropic temperature factors for all the non-hydrogen atoms. H atoms were placed in their idealized locations and included in the structure factor calculations. All calculations were performed on a Micro VAX3100 using the TEXSAN[12] system of computer programs.

The intensities of the cadmium complexes **2** and **3** were collected at 293 K on a MSC/Rigaku RAXIS-IIC imaging plate system using Mo Kα radiation ($\lambda = 0.710\ 73$ Å) from a rotating anode operating at 50 kV, 90 mA ($2\theta_{max} = 55.2°$); there were 60 oscillation frames in the range 0−180°, exposed 8 min per frame for **2** and **3**[13] and corrected for absorption using the DIFABS program.[14] The structures were solved by direct methods. All non-hydrogen atoms were refined anistropically. Hydrogen atoms of the ligand were generated geometrically (C−H = 0.96 Å), assigned fixed isotropic thermal parameters, and included in the structure factor calculations. All the computations were carried out on a PC 486 using the SHELXTL-PC program package.[15] Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated.[16]

Nonlinear Optical Property Measurement. The second-order nonlinear optical intensities are estimated by measuring powder of 76−154 μm diameter in the form of a pellet. The thickness of a pellet is about 0.8 mm. The pressure in compacting the pellet is 300 MPa. The experimental arrangement for the nonlinear optical properties utilizes a M200 high-power mode-locked Nd:YAG laser with 200 ps pulse at a repetition rate of 5 Hz. The selected wavelength is 1064 nm. After the selection of the wavelength, the laser beam is split into two parts, one to generate the second harmonic signal in the sample and the other to generate the second harmonic signal in the reference (urea pellet). According to the principle proposed by Kurtz and Perry,[17] we estimate that the strong SHG efficiency of compound **2** is larger than that of urea by about 22 times. The reflectance spectra show that the cadmium complexes have a new absorption band range from 400 to 510 nm which is absent in the free ligand. The new absorption band in the complexes is assigned to metal to ligand or ligand to metal charge transfer, which may be associated with large second-order optical nonlinearities.[18]

Results and Disscusion

The new Schiff base ligand **1** was prepared by the reaction of thiosemicarbazide with 2-chlorobenzaldehyde in a 1:1 molar ratio. This ligand can, in principle, exhibit thione−thiol tautomerism, since it contains a thioamide −HN−C=S functional group.[19−21] The ν(S−H) band at 2570 cm^{-1} is absent from the IR spectra of the Schiff base, but ν(N−H) at *ca.* 3150 cm^{-1} is present, indicating that in the solid state the ligand remains as the thione tautomer. The ^1H NMR spectrum in CH_3Cl-*d* does not show any peak at *ca.* 4.0 ppm attributable to the S−H proton, suggesting that the thiol tautomeric form is absent even in solution.

Crystal Structure of Ligand 1. The coordinates and thermal parameters of the non-hydrogen atoms of the ligand **1** are listed in Table 2. For comparison, the main bond distances and bond angles of the free ligand **1** and the two cadmium complexes **2** and **3** are shown in Table 3. Figure 1 shows a PLUTO drawing of the molecule with numbering scheme. The thiosemicarbazone moiety shows an *E* configureation about both C(2)−N(3) and C(1)−N(2) as found in most thiosemicarbazides[22−24] and thiosemicarbazones.[25−27] The molecule, though nonplanar as

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Table 2. Atomic Coordinates and Thermal Parameters for the Free Ligand **1**

atom	*x*	*y*	*z*	U_{eq} (Å^2)
Cl(1)	0.2248(1)	−0.2485(2)	0.0658(1)	5.5(1)
S(1)	0.5417(1)	0.8431(1)	0.3701(1)	3.2(1)
N(1)	0.3982(2)	0.6907(4)	0.4764(1)	3.1(1)
N(2)	0.4048(1)	0.4664(4)	0.3458(1)	2.9(1)
N(3)	0.3243(1)	0.3145(4)	0.3692(1)	2.8(1)
C(1)	0.4420(2)	0.6583(4)	0.4003(1)	2.5(1)
C(2)	0.2947(2)	0.1392(5)	0.3131(2)	3.0(1)
C(3)	0.1730(2)	−0.2218(5)	0.2689(2)	3.5(1)
C(4)	0.0946(2)	−0.3940(6)	0.2862(2)	4.5(1)
C(5)	0.0523(2)	−0.3850(6)	0.3670(2)	5.1(1)
C(6)	0.0873(2)	−0.2068(7)	0.4308(2)	4.9(1)
C(7)	0.1659(2)	−0.0335(6)	0.4136(2)	4.0(1)
C(8)	0.2106(2)	−0.0375(4)	0.3311(1)	2.9(1)

[a] Equivalent isotropic U_{eq} defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

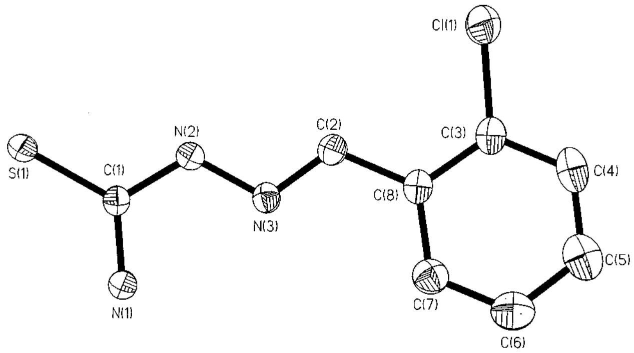

Figure 1. Molecular structure and atom numbering of the free ligand $(C_6H_5Cl)CH{=}NNHCSNH_2$ (L, **1**). The thermal ellipsoids are drawn at the 30% probability level.

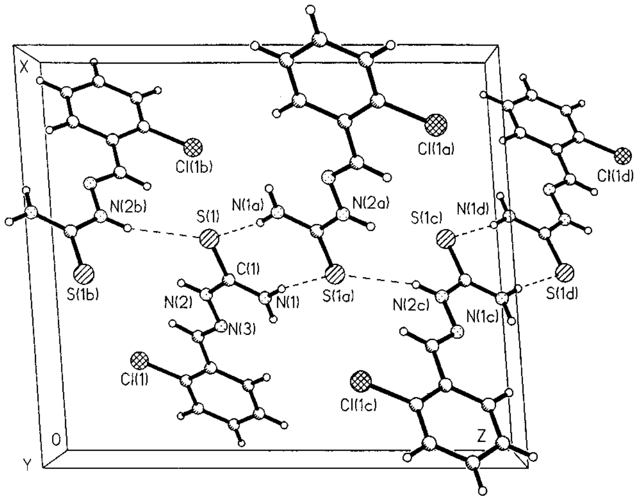

Figure 2. Hydrogen bonding scheme showing an infinite chain in the crystal structure of **1**. Symmetry code: *a*, 1 − *x*, 2 − *y*, 1 − *z*; *b*, 2 − *x*, *y* − 0.5, 0.5 − *z*.

a whole, divides into two planar fragments, a benzyl ring (I) and thiosemicarbazone moiety (II) with the twist angle of 4.9°. The mean deviations from the best plane are 0.0013 and 0.0074 Å for I and II, respectively.

The C−S bond distance of 1.690(3) Å agrees well with that in related compounds. In all cases, the C−S distance is intermediate between a C−S single-bond distance of 1.82 Å and a double-bond distance value of 1.56 Å quoted by Sutton;[28] therefore, the C−S bond in thiosemicarbazones possesses only partial double-bond character. This hypothesis is supported by the bond distances around C(1) (1.322(3) Å and 1.344(3) Å for N(1) and N(2), respectively), which are indicative of some double-bond character. A comparison of the N(2)−N(3) distance of 1.368(3) Å with the corresponding N−N distance of 1.411(2) Å for unsubstituted[22] and 1.395(2) and 1.431(6) Å for 1-phenyl[23] and 4-phenyl[24] thiosemicarbazides, respectively, suggests that the N−N bond also has some double-bond character. A similiar shortening of the N−N bond was reported as a weighted average distance of 1.37 Å for some thiosemicarbazones[29] that have an extensively delocalized group attached to the nitrogen N(3) and can be attributable to the inclusion of resonance forms involving the aryl ring.

There are three hydrogen atoms bonded to the nitrogen atoms which could form hydrogen bonds. The intermolecular hydrogen bonds which link the molecules are indicated in the molecular packing shown in Figure 2. There are dimerlike molecules formed by S(1)···H(1Aa)−N(1a) (1 − *x*, 2 − *y*, 1 − *z*) hydrogen bonds. These N−H···S hydrogen bonds are weak since the N···S separation of 3.41 Å is at the upper end of the range of values summarized by Srinivasan.[30] The dimerlike units are linked into a three-dimensional network by S(1)···H(2Ab)−N(2b) (2 − *x*, *y* − 0.5, 0.5 − *z*) with the N···S separation of 3.37 Å. Bond angles around H(1Aa) and H(2Ab) are 173 and 164°, respectively.

Crystal Structures of the Complexes. The coordinates and thermal parameters of the non-hydrogen atoms of complexes **2** and **3** are listed in Tables 4 and 5, respectively. It has been shown[31] that the thiosemicarbazide molecule itself exists in the *trans* configuration and, while complexing in this configuration, it behaves as a monodentate ligand, bonding only through the sulfur atom. Gerbeleu et al.[32] have shown that bonding may also occur through the hydrazine nitrogen and the amide nitrogen, if the sulfur center is substituted. In most of the complexes studied the thiosemicabazone function coordinates to the metal ion in the *cis* configuration,[33] as a bidentate ligand bonding through the thione/thiol sulfur atom and the hydrazine nitrogen atom. And it also postulated that the most common sterochemistries encountered in bidentate thiosemicarbazone complexes are centrosymmetric octahedral and square planar; therefore in order to obtain a noncentrosymmetric complex molecule, it is necessary to control the thiosemicarbazones coordinating as a monodentate sulfur bonding ligand. HSAB considerations dictate that the softer acid characters of Cd(II) and Hg(II) exhibit higher stability constants with this class of sulfur ligands, because of the formation of strong σ-bonds as well as $d_\pi{-}d_\pi$ bonds by donation of a pair of electrons to the ligands. So it can be expected that the cadmium halide complexes **2** and **3** might be S-bonding monodentate.

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Table 3. Selected Bond Lengths (Å) and Angles (deg) for the Free Ligand (L) and Complexes[a]

free ligand **1**		complex **2**		complex **3**	
		Cd(1)−Br(1)	2.583(2)	Cd(1)−I(1)	2.748(1)
		Cd(1)−Br(1)	2.599(2)	Cd(1)−I(2)	2.780(1)
		Cd(1)−S(1)	2.541(3)	Cd(1)−S(1)	2.634(2)
		Cd(1)−S(2)	2.526(2)	Cd(1)−S(2)	2.548(3)
				Cd(1)−I(1a)	4.120(8)
S−C(1)	1.690(3)	S(1)−C(1)	1.687(6)	S(1)−C(1)	1.729(5)
N(3)−C(2)	1.270(3)	N(1)−C(1)	1.346(5)	N(1)−C(1)	1.298(5)
N(2)−N(3)	1.368(3)	N(2)−C(1)	1.323(5)	N(2)−C(1)	1.353(6)
N(2)−C(1)	1.344(3)	N(2)−N(3)	1.350(7)	N(2)−N(3)	1.393(6)
N(1)−C(1)	1.322(3)	N(3)−C(2)	1.294(5)	N(3)−C(2)	1.262(6)
		S(2)−C(9)	1.699(6)	S(2)−C(9)	1.708(6)
		N(4)−C(9)	1.346(4)	N(4)−C(9)	1.328(5)
		N(5)−C(9)	1.322(6)	N(5)−C(9)	1.344(6)
		N(5)−N(6)	1.350(6)	N(5)−N(6)	1.387(7)
		N(6)−C(10)	1.292(6)	N(6)−C(10)	1.306(6)
Cl−C(3)	1.735(3)	Cl(1)−C(3)	1.727(5)	Cl(1)−C(3)	1.728(3)
		Cl(2)−C(11)	1.709(4)	Cl(2)−C(11)	1.747(4)
		Br(1)−Cd(1)−Br(1)	116.5(1)	I(1)−Cd(1)−I(2)	115.9(1)
		Br(1)−Cd(1)−S(1)	105.2(1)	I(1a)−Cd(1)−I(1)	85.6(2)
		Br(1)−Cd(1)−S(1)	107.4(1)	I(1)−Cd(1)−S(1)	104.5(1)
		Br(1)−Cd(1)−S(2)	113.5(1)	I(1)−Cd(1)−S(2)	114.9(1)
		Br(1)−Cd(1)−S(2)	102.9(1)	I(1a)−Cd(1)−S(1)	75.3(2)
		S(1)−Cd(1)−S(2)	111.3(1)	S(1)−Cd(1)−S(2)	101.1(1)
				I(2)−Cd(1)−S(2)	117.9(1)
				I(1a)−Cd(1)−I(2)	75.4(2)
				I(2)−Cd(1)−S(1)	98.4(1)
				I(1a)−Cd(1)−S(2)	169.8(2)

[a] Symmetry code: *a*, 1 − *x*, 1 − *y*, 1 − *z*.

Table 4. Atomic Positional and Thermal Parameters for Complex **2**

atom	*x*	*y*	*z*	U_{eq}[a] (Å^2)
Cd(1)	0.5000	0.1763(1)	0.5000	5.8(1)
Br(1)	0.5964(2)	0.1424(1)	0.6171(1)	7.1(1)
Br(2)	0.4352(2)	0.0304(1)	0.4279(1)	6.9(1)
S(1)	0.7363(3)	0.2641(2)	0.4546(2)	7.7(1)
S(2)	0.2376(3)	0.2705(2)	0.4874(2)	6.5(1)
Cl(1)	0.9005(3)	0.6154(2)	0.2029(2)	11.3(1)
Cl(2)	0.6079(3)	0.2851(2)	0.8257(2)	9.2(1)
N(1)	0.5839(3)	0.2186(3)	0.3421(3)	10.7(1)
N(2)	0.7293(3)	0.3525(3)	0.3443(2)	7.3(1)
N(3)	0.6901(3)	0.3659(3)	0.2816(2)	7.1(1)
N(4)	0.1402(3)	0.4155(3)	0.5522(3)	9.7(1)
N(5)	0.3210(3)	0.3202(3)	0.6089(2)	6.4(1)
N(6)	0.3109(3)	0.3779(3)	0.6594(2)	5.9(1)
C(1)	0.6750(3)	0.2810(3)	0.3773(2)	7.0(1)
C(2)	0.7463(3)	0.4380(3)	0.2525(2)	6.6(1)
C(3)	0.7620(3)	0.5444(3)	0.1597(2)	6.8(1)
C(4)	0.7183(3)	0.5698(3)	0.0968(2)	13.2(1)
C(5)	0.6162(3)	0.5077(3)	0.0611(3)	10.8(1)
C(6)	0.5594(3)	0.4251(3)	0.0877(2)	12.8(1)
C(7)	0.5966(3)	0.4051(3)	0.1521(2)	7.7(1)
C(8)	0.7048(3)	0.4628(3)	0.1885(2)	8.4(1)
C(9)	0.2342(3)	0.3375(3)	0.5542(2)	6.2(1)
C(10)	0.4034(3)	0.3601(3)	0.7102(2)	5.6(1)
C(11)	0.4857(3)	0.3831(3)	0.8238(2)	5.6(1)
C(12)	0.4749(3)	0.4372(3)	0.8786(2)	7.1(1)
C(13)	0.3869(3)	0.5214(3)	0.8805(2)	7.5(1)
C(14)	0.2958(3)	0.5457(3)	0.8248(2)	9.1(1)
C(15)	0.2979(3)	0.4907(3)	0.7700(2)	7.1(1)
C(16)	0.3931(3)	0.4092(3)	0.7683(2)	6.6(1)

[a] Equivalent isotropic U_{eq} defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 5. Atomic Positional and Thermal Parameters for Complex **3**

atom	*x*	*y*	*z*	U_{eq}[a] (Å^2)
Cd(1)	0.3509(1)	0.4178(1)	0.2048(1)	4.8(1)
I(1)	0.2966(1)	0.5774(1)	0.3649(1)	5.5(1)
I(2)	0.3366(1)	0.2874(1)	0.3828(1)	5.1(1)
S(1)	0.1384(2)	0.3864(1)	−0.0847(3)	4.8(1)
S(2)	0.5354(2)	0.4060(1)	0.0588(3)	5.7(1)
Cl(1)	0.0368(3)	0.8629(2)	0.0224(3)	8.7(1)
Cl(2)	0.6666(3)	0.0465(2)	0.5894(3)	9.6(1)
N(1)	0.1864(4)	0.4546(3)	−0.3383(4)	6.9(1)
N(2)	0.0958(4)	0.5448(3)	−0.1431(4)	4.7(1)
N(3)	0.0944(3)	0.6086(3)	−0.2413(4)	3.9(1)
N(4)	0.6180(4)	0.2662(4)	−0.1172(4)	8.5(1)
N(5)	0.5984(4)	0.2546(3)	0.1585(4)	4.9(1)
N(6)	0.6295(4)	0.1689(3)	0.1239(4)	5.0(1)
C(1)	0.1427(4)	0.4670(3)	−0.1995(4)	4.4(1)
C(2)	0.0616(4)	0.6824(3)	−0.1796(4)	4.4(1)
C(3)	0.0340(4)	0.8362(3)	−0.2015(4)	5.2(1)
C(4)	0.0210(4)	0.9010(3)	−0.3004(4)	4.8(1)
C(5)	0.0236(4)	0.8824(3)	−0.4740(4)	5.9(1)
C(6)	0.0358(4)	0.7987(3)	−0.5504(4)	6.9(1)
C(7)	0.0518(4)	0.7360(3)	−0.4616(4)	5.4(1)
C(8)	0.0486(4)	0.7515(3)	−0.2812(4)	4.5(1)
C(9)	0.5848(4)	0.3018(3)	0.0290(4)	5.2(1)
C(10)	0.6352(4)	0.1293(3)	0.2569(4)	4.8(1)
C(11)	0.6714(4)	−0.0072(4)	0.3779(4)	5.8(1)
C(12)	0.6885(4)	−0.0937(4)	0.3529(4)	8.4(1)
C(13)	0.6987(4)	−0.1391(4)	0.1919(4)	10.5(1)
C(14)	0.6909(4)	−0.0967(4)	0.0556(4)	9.6(1)
C(15)	0.6726(4)	−0.0085(4)	0.0735(4)	6.7(1)
C(16)	0.6616(4)	0.0381(3)	0.2363(4)	5.2(1)

[a] Equivalent isotropic U_{eq} defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

A crystal of complex **2** consists of individual CdL_2Br_2 neutral molecules (Figure 3). The coordination geometry of the cadmium atom is distorted tetrahedral with the two sulfur atoms from the ligand forming bond angles around the Cd(1) in the range 102.9−116.5°. The thiosemicarbazone ligands are S-bonding neutral monodentate. This can be easily found from the bond lengths of C(1)−S(1) and C(9)−S(2) less than 1.70 Å[34,35] and the same C(1)−N(2) and C(9)−N(5) bonds larger than 1.30 Å.[34,35] The Cd−S bond distances around 2.53 Å of complex **1** are in the range of Cd−S terminal bonds (2.52−

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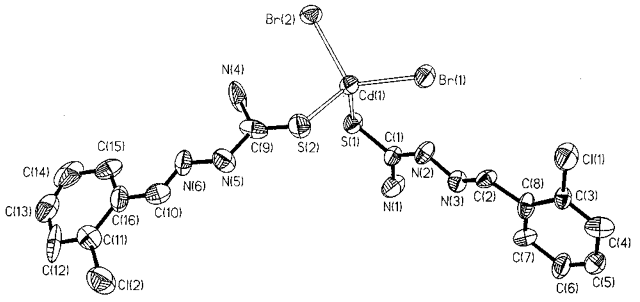

Figure 3. Molecular structure and atom numbering of $[CdL_2Br_2]$, **2**. The thermal ellipsoids are drawn at the 30% probability level.

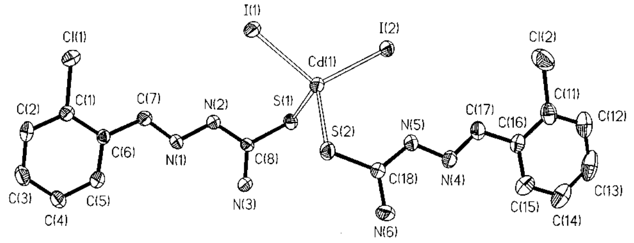

Figure 4. Molecular structure and atom numbering of $[CdL_2I_2]$, **3**. The thermal ellipsoids are drawn at the 30% probability level.

2.79 Å). They are shorter than those found in cadmium complexes of S and N chelates.[36,37] Least-squares planarity analyses indicated that the ligands are planar with the mean deviations from the plane being 0.042 and 0.023 Å for the ligands containing the S(1) and S(2) atoms, respectively; the dihedral angle between the planes is 65.4°.

A crystal of complex **3** also consists of individual CdL_2I_2 neutral molecules (Figure 4). The coordination geometry of the cadmium atom is distorted tetrahedral with the two terminal bromine atoms and the two sulfur atoms from the ligand, where the bond angles around the Cd(1) are in the range 98.4−117.9°. The Cd(1) atom is positioned 0.53 Å above the plane of I(1), I(2), and S(2). Analyses of the intermolecular contacts indicated that there is a very weak contact from I(1a) (4.120(8) Å) of the centrosymmetric relative molecule $(1 - x, 1 - y, 1 - z)$. If the contact is considered as the fifth coordination bond, the complex **3** might be considered as discrete centrosymmetric dimers bridged by the two iodide atoms as shown in Figure 5 and the cadmium ion has an approximate trigonal bipyramid environment. Sulfur S(2) and the two iodide atoms I(1) and I(2) coordinate in the equatorial plane, while S(1) and the I(1a) occupy the axial positions to form the centrosymmetric dimer. This fifth contact is very weak but it is very important in **3**, which crystallizes in a centrosymmetric space group; thus, the complex cannot show any SHG efficiency, even if the molecule might have a quite large β value. It is very interesting to find that the two thiosemicarbazone planes are almost parallel (the dihedral angle is only 1.1°), although the two ligands themselves are much less planar, the dihedral angles between the phenyl plane and the thiosemicarbazone plane being 20.2 and 11.7° for the two ligands containing S(1) and S(2), respectively. As mentioned below, the planarity of the two thiosemicarbazones will decrease the dipole moment and might decrease the β value of the molecule. The bond distances of Cd−S, C−S, and C−N are quite similar to that in complex **2** which indicates that the thiosemicarbazone ligand is coordinated as a neutral S-bonding monodentate species, and this also indicates that the main factor to influence the two complexes crystallizing in difference space groups might be the intermolecular contact of the fifth weak coordinate bond.

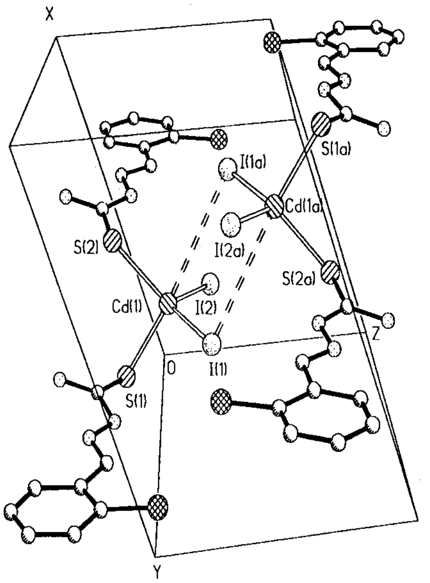

Figure 5. View of the intermolecular contacts of complex **3** parallel to the $a-c$ plane with the intermolecular contacts displayed as broken double lines.

The thiosemicarbazone moiety in the two complexes also shows an *E* configuration about both C(2)−N(3), C(1)−N(2) and C(9)−N(5), C(10)−N(6) with the N(1) and N(4) atoms held away from the cadmium atoms. The data in Table 2 show that all the bond distances in the side chain of the thiosemicarbazones are intermediate between formal single and double bonds, pointing to extensive electron delocation over the entire moiety. As mentioned below, this electron delocation is very important for the optical nonlinearities of those complexes.

Nonlinear Optical Properties Calculation. On the basis of the MNDO Hamiltonian[38] and PM3 parametrization[39] with the MOPAC program package,[40] the molecular hyperpolarizability values, β_μ, the vector components along the dipole moment direction, of the organic ligand and its cadmium complexes are calculated to be -7.2×10^{-30}, -10.8×10^{-30}, and -17.4×10^{-30} esu, respectively. The molecular hyperpolarizabilities β_μ of the organic ligand and its cadmium complexes are comparable with that of *p*-nitroaniline (PNA, 6.3×10^{-30} esu). The absolute values are much greater than that of urea (0.14×10^{-30} esu, qualitatively consistent with the above SHG efficiency experiment). The negative sign of β_μ can be explained by the smaller dipole moment of the lowest excited state compared to that of ground one. The difference in magnitude of β_μ between the ligand and its cadmium complex is small. The similarity of β_μ values can be understood by their similar contributions from a low-energy transition. However, the β value of the CdL_2Br_2 complex is larger than that of the ligand by more than two times. The large molecular hyperpolarizability of the CdL_2I_2 complex is attributed to the relatively greater conjugation between the two ligands of the CdL_2I_2 complex compared to that of the CdL_2Br_2 complex, since the two ligands in the CdL_2I_2 complex are parallel to each other while those in the CdL_2Br_2 complex are distorted by about 56.9°, resulting in poor conjugation. The linear absorption spectrum

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of the ligand and cadmium complex in a solution of DMF exhibits one intense band (log $\epsilon = 4.48, 4.45, 4.78$) near 326 nm. The PM3 electronic spectrum calculation for the ligand and its cadmium complex gives a strong electron transition near 330 nm with oscillator strength 0.91, consistent with the above linear absorption spectra. The optical transition associated with this band is mainly the contribution of a $\pi^* \leftarrow \pi$ or $\pi^* \leftarrow$ n transition of nonbonding electron pairs of N and S atoms according to the analysis of molecular orbital components for the ligand and cadmium complexes, which is the excitation mainly responsible for the NLO response.

It should be noted that the free ligand molecule has a large β value while its crystal fails to exhibit an SHG response due to the centrosymmetric space group in crystallization ($P2_1/c$). However, we obtained a noncentrosymmetric crystal of the cadmium complex arising from the nonplanarity of the two ligand molecules and hydrogen bonds. Additionally, the features of the complexes such as being colorless (transparent), easier to form crystals, and mechanically and thermally stable make them potential optical materials for use in photonic devices.

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Supporting Information Available: Tables of all bond lengths and angles, all atoms introduced at calculated coordinates, and anisotropic thermal parameters in the form of U_{ij}'s for the free ligand **1** and the two cadmium complexes **2** and **3** (Tables S1−S9) (8 pages). Ordering information is given on any current masthead page.

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