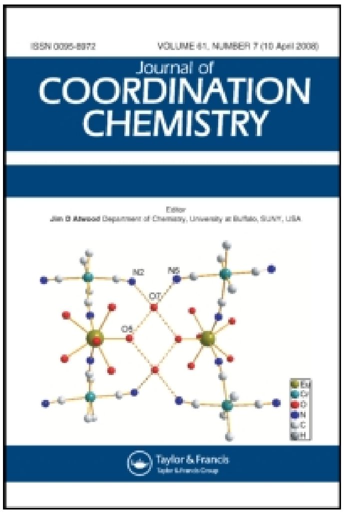

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SYNTHESIS, CRYSTAL STRUCTURE AND NONLINEAR OPTICAL PROPERTIES OF THIOSEMICARBAZONE ZINC COMPLEX

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A new zinc bromide complex of a Schiff-base ligand derived from thiosemicarbazide and 4-methoxylphenyldehyde, which shows *ca* 13 times better SHG efficiency than urea, has been prepared and characterized. Single crystal X-ray diffraction analysis established that the coordination geometry about the zinc atom is tetrahedral with two equivalent Zn–Br and Zn–S bonds. The Schiff-base ligand is coordinated to the Zn(II) via the monodentate mercapto sulfur atom. The polar structure (space group *Aba2*) is stabilized by hydrogen bonds between the oxygen atom and the amino nitrogen atoms N(1).

The complex crystallizes in the orthorhombic space group *Aba2* with cell parameters $a = 11.970(2)$, $b = 21.888(2)$, $c = 9.157(2)$ Å and $Z = 4$. The structure was solved by direct methods and refined by full-matrix least-squares to $R = 0.065$ and $R_w = 0.117$ for the 722 observed reflections with $I > 2\sigma(I)$.

Keywords: Zinc(II); crystal structure; thiosemicarbazone; SHG efficiency

INTRODUCTION

Tremendous efforts have recently been devoted to synthesis of molecular-based materials, organic polymers and organometallic compounds with large second order nonlinear optics[1–3] because of their low cost, fast nonlinear response over a broad frequency range, inherent synthetic flexibility, high optical damage thresholds and intrinsic tailorability.[4–7] However, few

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of them could be used as materials in applications because of the mechanical and thermal instability.

IIB group metal complexes of thiosemicarbazides and thiosemicarbazones are pale in color and quite thermally stable. Some of the cadmium complexes show large SHG efficiency.[8,9] In a continuation of our research in this field,[9-11] we report here the synthesis and crystal structure a new zinc complex of the Schiff base ligand, 4-methoxylphenyldehyde thiosemicarbazone.

EXPERIMENTAL

All chemicals used were of analytical grade and used without purification. Thiosemicarbazide and 4-methoxyphenylaldehyde (Aldrich) were used as received.

Physical Measurements

Elemental analysis data were obtained using a Perkin-Elmer 240 analyser. Infrared spectra were recorded from KBr discs in the range 4000–400 cm^{-1} on a Nicolet FT-IR-170SX instrument. Electronic absorption spectra were obtained on a Shimadzu UV-3100 spectrophotometer in DMF solution (1.0×10^{-4} mol dm^{-3}). Solid-state electronic spectra were obtained by the reflection technique on a Shimadzu UV 240 spectrophotometer using MgO as the reference material, proton NMR spectra (in $CDCl_3$) were measured on a Bruker Cryospec WM 250 (250 MHz) spectrometer.

4-Methoxyphenylaldehyde Thiosemicarbazone(HL)

Five drops of acetic acid were added to a mixture of thiosemicarbazide (0.91 g, 10 mmol) and 4-methoxyphenylaldehyde (1.36 g, 10 mmol) in refluxing ethanol. The solution was further refluxed for 2 h and on cooling a white solid formed. The white solid was recrystallized from methanol and dried *in vacuo* over P_2O_5; yield 1.50 g (72%). Anal. calcd. for HL ($C_9H_{11}N_3OS$): C, 51.7; H, 5.2; N, 20.1%. Found: C, 51.3; H, 4.9; N, 20.5%. IR data (KBr, cm^{-1}) 3385, 3290, 3153 (N–H, m), 1611, 1540 (C=C, C=N, s), 960 (C=S, s). Electronic spectra (nm), (DMF, log ε): λ_{max} 326 (3.48). ^{1}H NMR: δ ppm, 10.93 (br, 1H), 8.60 (s, 1H), 7.22 (d, 2H) 7.63 (br, 2H) 7.05 (d, 2H), 3.65 (s, 3H).

Preparation of the Complex

Ethanol solutions of thiosemicarbazone (0.42 g, 2 mmol) and zinc bromide (0.45 g, 2 mmol) were mixed. The colorless crystalline solid formed after refluxing for 4 h was isolated and dried in *vacuo* over P_2O_5; yield 0.52 g (60%). Crystals suitable for X-ray structure analysis were obtained by slowly evaporating a methanol solution in air. Anal. calcd. for $ZnBr_2(C_9H_{11}N_3OS)_2$: C, 33.5; H, 3.4; N, 13.0. Found: C, 34.0; H, 3.2; N, 12.8%. IR data (cm^{-1}) 3382, 3278, 3158 (N–H, m), 1607, 1535 (C=C, C=N, s), 980 (C=S, s). Electronic spectra nm, (DMF, log ε): 326 (3.27), 420 (solid). ^1H NMR: δ ppm, 10.87 (br, 1H), 8.58 (s, 1H), 7.45 (br, 2H), 7.08 (d, 2H), 3.65 (s, 3H).

Crystallographic Structure Determination

A single crystal with dimensions 0.32 × 0.20 × 0.18 mm was mounted on a Siemens P4 diffractometer using graphite-monochromated MoK_α ($\lambda = 0.71073$ Å) radiation.[12] The data were collected using the $\omega/2\theta$ scan mode with variable scan speeds of 4.0–60.0° min^{-1} in ω and were corrected for Lorentz and polarization effects as well as absorption during data reduction using XSCANS.[12] 1252 independent reflections were collected in the range $3° < 2\theta < 50°$, 722 reflections were considered as observed ($I > 2\ \sigma(I)$). The complex is orthorhombic space group *Aba2*. $Fw = 643.73$, cell parameters $a = 11.970(2)$, $b = 21.888(2)$, $c = 9.157(2)$ Å and $Z = 4$, $D_{calc} = 1.782\ gcm^{-3}$, $F(000) = 1280$, $\mu = 4.556\ mm^{-1}$.

The structure was solved by directed methods. All non-hydrogen atoms were refined anisotropically by full-matrix least squares. Hydrogen atoms were placed in their calculated positions with C–H = 0.96 Å, assigned fixed isotropic thermal parameters (1.2 times that of the atom to which they are attached), and allowed to ride on their respective parent atoms. The contributions of these hydrogen atoms were included in the structure-factor calculations. All the computations were carried out on a PC 586 using SHELXTL.[13] The final R and R_w ($w = 1/\sigma^2$) were 0.065 and 0.117, respectively. The maximum shift/esd and largest peak in the final difference Fourier map were 0.000 and 0.882 $eÅ^{-3}$.

Nonlinear Optical Property Measurement

The second order nonlinear optical intensities were estimated by measuring powder of 76–154 μm in diameter as a pellet. The thickness of the pellet was about 0.8 mm. 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 selection of the wavelength, the laser beam is split into two parts, one to generate the second harmonic signal in the sample while the other generates the second harmonic signal in the reference (urea pellet). According to the principle proposed by Kurtz and Perry,[14] SHG efficiency can be estimated as 13.0 times that of urea. The reflectance spectra show that the zinc complex has a new absorption band from 400 to 450 nm which is absent in the free ligand. The new absorption band is assigned to metal to ligand or ligand to metal charge transfer, which may be associated with large second-order optical nonlinearities.[15]

RESULTS AND DISCUSSION

Synthesis and Characterization

The new Schiff base ligand L was prepared by the reaction of thiosemicarbazide with 4-methoxyphenylaldehyde in a 1 : 1 molar ratio. It has been shown[16] 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.*[17] have shown that bonding may also occur through the hydrazine and amide nitrogens, if the sulfur atom is substituted. However, in most cases, the thiosemicabazone group coordinates to the metal ion in the *cis* configuration,[18] as a bidentate ligand bonding through the *thione/thiol* sulfur atom and the hydrazine nitrogen atom. HSAB considerations dictate that the softer acids of Zn(II), Cd(II) and Hg(II) exhibit higher stability constants with this class of sulfur ligands, because of formation of strong π-bonds as well as dπ–dπ bonds by donation of a pair of electrons to the ligands. It can be expected that the zinc bromide complex might be monodentate with the ligand binding through sulfur was supported by the IR and Uv-vis spectra well as the ^{1}H-NMR spectrum of the zinc complex which is quite similar to that of the corresponding ligand HL, especially with ν(N–H) at *ca* 3150 cm^{-1}.

Crystal Structure Description of Zinc Complex

An ORTEP drawing of the zinc complex with atomic-numbering is shown in Figure 1. Atomic coordinates for non-hydrogen atoms are listed in Table I and selected bond lengths and angles are given in Table II. The coordination

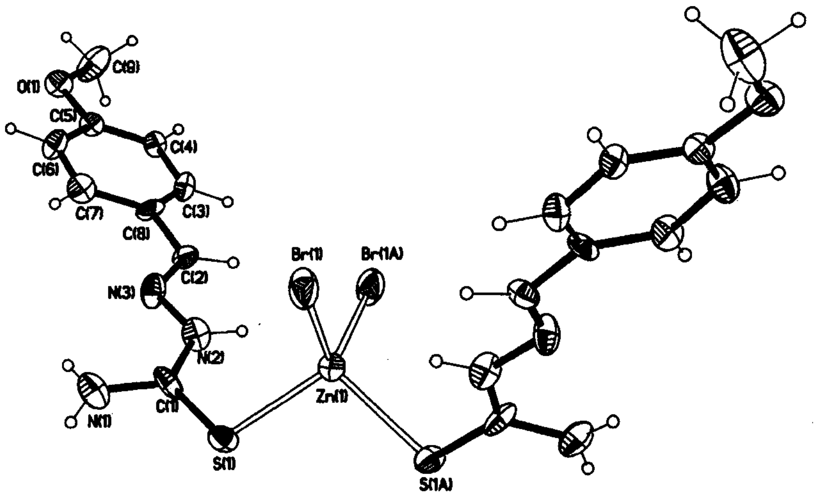

FIGURE 1 ORTEP drawing of $ZnBr_2L_2$ with the atomic numbering scheme. The displacement ellipsoids at the 50% probability level. Symmetry code: A: $1-x$, $2-y$, z.

TABLE I Atomic coordinates and equivalent isotropic displacement parameters (Å²) $U_{eq} = \frac{1}{3}\sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$

Atom	x	y	z	U_{eq}
Br(1)	0.5618(1)	0.9186(1)	0.3215(1)	7.4(1)
Zn(1)	0.5000	1.0000	0.4750(1)	4.0(1)
S(1)	0.6495(1)	1.0271(1)	0.6321(2)	4.4(1)
O(1)	0.9487(3)	1.3549(2)	−0.0615(4)	4.7(1)
N(1)	0.8460(4)	1.0738(2)	0.5649(5)	5.2(2)
N(2)	0.6970(3)	1.1153(2)	0.4449(5)	4.6(2)
N(3)	0.7667(3)	1.1544(2)	0.3666(6)	5.2(2)
C(1)	0.7348(5)	1.0727(2)	0.5386(6)	4.5(2)
C(2)	0.7189(4)	1.1947(2)	0.2949(6)	4.0(2)
C(3)	0.7256(4)	1.2905(3)	0.1476(7)	4.6(2)
C(4)	0.7798(4)	1.3307(2)	0.0577(6)	3.4(2)
C(5)	0.8876(4)	1.3215(2)	0.0254(6)	3.4(2)
C(6)	0.9430(5)	1.2707(3)	0.0774(6)	5.1(2)
C(7)	0.8930(4)	1.2283(2)	0.1678(7)	4.4(2)
C(8)	0.7803(4)	1.2380(3)	0.2021(6)	4.1(2)
C(9)	0.8952(5)	1.4128(3)	−0.1171(8)	7.1(3)

geometry of the zinc atom is distorted tetrahedral with two equivalent Zn–Br, and Zn–S bonds forming bond angles around the Zn(II) atom in the range 105.7–114.0°. The C–S bond distance (Table II) of 1.665(6) Å agrees very well with those in related compounds, intermediate between 1.82 Å for a C–S single bond and 1.56 Å for a C=S double-bond.[19] The corresponding

TABLE II Selected geometric parameters (Å, °)

Br(1)–Zn(1)	2.387(1)	N(1)–C(1)	1.353(7)
Zn(1)–S(1)	2.371(2)	N(2)–C(1)	1.346(7)
S(1)–C(1)	1.665(6)	N(2)–N(3)	1.392(6)
S(1)–Zn(1)–S(1A)	105.29(9)	C(1)–N(2)–N(3)	123.54
S(1)–Zn(1)–Br(1A)	113.87(4)	N(2)–C(1)–N(1)	115.6(5)
S(1)–Zn(1)–Br(1)	108.06(4)	N(2)–C(1)–S(1)	122.5(4)
Br(1)–Zn(1)–Br(1A)	107.84(6)	N(1)–C(1)–S(1)	121.5(4)

Symmetry code: $1-x, 2-y, z$.

C(1)–N(2) and C(1)–N(1) [1.346(7), 1.353(7)] bond distances are indicative of some double-bond character, pointing to extensive electron delocalization over the entire moiety.[20] Analysis of lease-square planes indicated that the whole ligand (except the amino atom N(1) and the methoxy group) is almost planar (the mean deviations from the best plane being 0.058 Å); the zinc atom is 1.935(4) Å from the best plane. The dihedral angle between the two ligand planes is 77.37(7)°.

The polar structure is further stabilized by a hydrogen bond, N(1)–H(1B)···O(1B) ($2-x, 2.5-y, 0.5+z$) with N···O separations of 3.085(6) Å and an N–H···O angle of 155.54(14)°. The H(2B)···Br(1A) distance of 2.600(4) Å, which is less than a normal van der Waals contact,[20] suggests a possible intramolecular hydrogen bond and both the N–H···Br angle of 151.5(1)° and H–N···Br angle of 21.5(1)° support this hypothesis. The Br···N separation is 3.381(4) Å.

A polar crystal for the zinc bromide complex serves to hold the molecules in the head-to-tail fashion which give rise to a dipolar orientation for second-order harmonic generation. This is supported by the powder SHG studies of the complex which has 13 times the SHG efficiency of urea.

Based on MNDO Hamiltonian[21] and PM3 parametrization[22] with the MOPAC program package[23] the molecular hyperpolarizability, β_μ, the vector component along the dipole moment direction, is calculated to be -6.2×10^{-30} esu for the complex. The absolute values are much larger than that of urea (0.14×10^{-30} esu). This result is consistent with the SHG experiment.

SUPPLEMENTARY MATERIALS

Tables of hydrogen atoms coordinates, thermal parameters, bond distances and angles, and observed and calculated structure factors are available from the authors on request.

Acknowledgments

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