

Crystal structure and third-order nonlinearity of nickel(II) and copper(II) complexes with S-methyl- β -N-(4-nitrobenzal)methylenedithiocarbazate

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Abstract—Ni^{II} and Cu^{II} complexes of general formula ML₂ [HL = S-methyl- β -N-(4-nitrobenzal)methylenedithiocarbazate] have been synthesized and characterized. The Schiff base acts as a single, negatively charged bidentate ligand forming extensive electron delocalization system. Single crystal X-ray diffraction analysis of the copper(II) complex revealed that the ligand lost a proton from its tautomeric thiol form and coordinates to Cu^{II} via mercapto sulfur and β -nitrogen atoms. The geometry of the Cu^{II} ion is square-planar with two equivalent Cu—S and Cu—N bonds. The two nitrobenzal rings and the coordinated moieties are almost in one plane, forming an electronic delocalization system. Third-order response determinations show that the extensive electron delocalization is quite helpful for the complexes exhibit higher second order molecular hyperpolarizability. Crystal structure of the free ligand is also determined for comparison. © 1997 Elsevier Science Ltd

Keywords: Schiff base; third-order; nickel(II); copper(II); crystal structure; S-methyl- β -N-(4-nitrobenzal)methylenedithiocarbazate.

Organic compounds with π electron delocalization are currently receiving much attention [1,2] due to their possible device applications in optical communication and data processing. In contrast to the extensive studies of organic materials for nonlinear optics, transition metal complexes have received little attention [3]. In our laboratory, much effort has been made to find the potential nonlinear optics derived from thiosemicarbazone and dithiocarbazates [4–6]. As part of studies on synthesis and characterization of new metal dithiocarbazates [7,8], this paper describes the preparation, characterization, crystal structure and third-order response of the nickel(II) and copper(II) complexes with Schiff-base ligand, S-methyl- β -N-(4-nitrobenzal)methylenedithiocarbazate.

EXPERIMENTAL

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 4000–400 cm⁻¹ region. The far-IR spectra (500–100 cm⁻¹) were recorded in Nujol mulls between polyethylene sheets. ¹H NMR spectra were made on BRUKER AM-500 spectrometer in CDCl₃ solution using TMS as the internal standard. Electronic spectra were obtained on a Shimadzu UV3100 spectrophotometer in dichloromethane solution. The solid-state electronic spectra were obtained by the reflectance technique on a Shimadzu UV 240 spectrophotometer using MgO as the reflectance material. ESR spectra were recorded on a Bruker ER 200-D-SRC spectrometer. Magnetic susceptibility data were collected with CAHN 2000 magnetobalance and corrected by Pascal constants.

X-ray crystallography and structure solution

Information concerning crystallographic data and structure refinement of the free ligand and the copper(II) complex are summarized in Table 1. The intensities of the compounds were collected at 294 K on a Rigaku RAXIS-IIC imaging plate diffractometer

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Table 1. Crystal data for compound HL and copper complex CuL₂

Compound	HL	CuL ₂
Formula	C ₉ H ₉ N ₃ S ₂ O ₂	C ₁₈ H ₁₆ N ₆ O ₄ S ₄ Cu
Formula weight	255.3	572.1
Crystal colour	yellow	brown
Crystal system	monoclinic	triclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> -1
<i>a</i> (Å)	7.420(1)	5.786(1)
<i>b</i> (Å)	8.886(1)	10.529(1)
<i>c</i> (Å)	17.831(1)	21.639(1)
α (°)		94.09(1)
β (°)	92.80(1)	90.13(1)
γ (°)		105.88(1)
<i>V</i> (Å ³)	1174.3(2)	1264.4(6)
<i>Z</i>	4	2
μ (mm ⁻¹)	0.442	1.229
ρ (g cm ⁻³)	1.444	1.503
reflections unique	2321 (Rint = 0.028)	4673
reflections observed	1640 (<i>F</i> > 4.0 σ (<i>F</i>))	3541 (<i>F</i> > 4.0 σ (<i>F</i>))
<i>R</i> , <i>R</i> _w	0.041, 0.054	0.055, 0.072
	$w^{-1} = \sigma^2(F) + 0.0007F^2$	$w^{-1} = \sigma^2(F) + 0.0005F^2$
GOF	1.07	1.02
$\Delta(\rho)_{\text{max,min}}$ (e Å ⁻³)	0.16, -0.19	0.56, -0.76

using Mo-K α ($\lambda = 0.71073$ Å) from a rotating-anode generator operating at 50 kV and 90 mA ($2\theta_{\text{max}} = 55.2^\circ$); 60 oscillation frames in the range 0–180°, exposure of 8 min and 10 min per frame for the free ligand and copper complex, respectively [9,10]. Both of the two structures were solved by direct method. 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 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 SHELXL-PC program package [11]. Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated [12]. Selected bond lengths and angles for the ligand and copper(II) complex CuL₂ are tabulated in Table 2.

Additional material is available from the Cambridge Crystallographic Data Center and comprises a complete list of atom coordinates, thermal parameters, bond distances and angles.

Third-order nonlinear optical property measurement

The third-order nonlinear optical (NLO) properties of the compounds were determined by the *z*-scan technique, using a Gaussian laser beam in a tight-focus limiting geometry. Third-order susceptibility $\chi^{(3)}$ can be obtained according to the method we have reported [13]. The third-order nonlinear optical properties of

the compounds were investigated with 200 ps pulse of 532 nm irradiation at a frequency of 5 Hz. CH₃CN solutions of the complexes were placed in a 1 mm quartz cell and used for the optical measurements. The sample is very stable toward air and laser irradiation. The results of calculation from experiments for the ligand, nickel(II) complex NiL₂ and copper(II) complex CuL₂ are $\chi^{(3)} = 6.48 \times 10^{-13}$, 7.35×10^{-13} and 7.03×10^{-13} esu, respectively.

Preparation of the ligand *S*-methyl- β -*N*-(nitrobenzal)-methylenedithiocarbazate HL

An absolute ethanol solution of *S*-methyl-dithiocarbazate (0.12 g, 1 mmol) and *p*-nitrobenzaldehyde (0.15 g, 1 mmol) was refluxed for 2 h. The solid formed was filtered off and washed with ethanol. Yellow pyramid crystals were collected and dried *in vacuo* over P₂O₅, yield 0.20 g (80%). Pale-yellow crystals suitable for X-ray analysis were obtained by slow evaporating an dichloromethane in air. Found: C, 42.6; H, 3.7; N, 16.6; C₉H₉N₃S₂O₂ calcd: C, 42.3; H, 3.5; N, 16.5%. ¹H NMR (chloroform-*d*₁, TMS) δ ppm 2.61 (3H, s, —SCH₃), 8.05–8.35 (4H, m, aromatic), 8.42 (1H, s, CH=N—), 10.21 (1H, br, NH); IR (KBr discs, cm⁻¹), 3144, 2975 (N—H, m), 1565 (C=C), 1525 (C=N, s), 1425 (C—N), 1015 (C=S); Uv–vis, nm (log ϵ), 200 (4.15), 230 (4.20), 278 (4.10), 326 (3.90), 390 (4.70).

Preparation of the metal complexes

An ethanol solution of the metal copper(II) and nickel(II) acetate (0.5 mmol) was added to the ethanol

Table 2. Selected bond lengths (Å) and angles (°) for HL and copper(II) complex

HL		CuL ₂			
		Cu(1)—S(1)	2.177(1)	Cu(2)—S(3)	2.178(1)
		Cu(1)—N(2)	1.936(3)	Cu(2)—N(4)	1.929(3)
S(1)—C(1)	1.661(2)	S(1)—C(1)	1.706(4)	S(3)—C(11)	1.706(4)
C(1)—N(1)	1.343(4)	N(1)—C(1)	1.301(5)	N(4)—C(1)	1.287(6)
N(1)—N(2)	1.367(3)	N(1)—N(2)	1.409(5)	N(4)—N(5)	1.409(6)
N(2)—C(2)	1.265(4)	N(2)—C(2)	1.303(5)	N(5)—C(12)	1.292(5)
		S(1)—Cu(1)—N(2)	85.8(1)	S(3)—Cu(2)—N(5)	85.5(1)
		N(2)—Cu(1)—S(1a)	94.2(1)	N(5)—Cu(2)—S(3b)	94.5(1)
S(1)—C(1)—N(1)	120.2(2)	S(1)—C(1)—N(1)	125.2(3)	S(3)—C(11)—N(4)	124.7(4)
C(1)—N(1)—N(2)	121.2(3)	C(1)—N(1)—N(2)	111.6(3)	C(11)—N(4)—N(5)	112.0(3)
N(1)—N(2)—C(2)	115.7(2)	N(1)—N(2)—C(2)	114.4(3)	N(4)—N(5)—C(12)	114.9(3)

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

solution (20 cm³) of the ligand (1 mmol). The mixture was refluxed and stirred for 4 h. The crystalline solid formed after cooling to room temperature was collected and washed with ethanol (3 × 10 mL) and dried *in vacuo* over P₂O₅. For NiL₂, Found: C, 38.9; H, 3.0; N, 14.7; C₁₈H₁₆N₆S₄O₄Ni, calcd: C, 39.0; H, 2.8; N, 14.8%. ¹H NMR (chloroform-*d*₁, TMS) δ ppm 2.60 (3H, s, —SCH₃), 8.01–8.45 (4H, m, aromatic), 8.61 (H, s, CH=N—); IR (KBr discs, cm^{−1}), 1565 (C=C), 1471 (C=N, s), 940 (C—S, m), 415 (Ni—N, m), 375 (Ni—S, m); Uv–vis, (nm, log ε), 200 (4.45), 220 (4.50), 295 (4.63), 400 (4.90), 450 (4.34), 660 (solid). For CuL₂: Found: C, 37.6; H, 2.8; N, 14.5; C₁₈H₁₆N₆S₄O₄Cu calcd: C, 37.8; H, 2.8; N, 14.7%. IR (KBr discs, cm^{−1}), 1560 (C=C), 1475 (C=N, s), 935 (C—S, m), 415 (M—N, m), 365 (Cu—S, m); Uv–vis, nm (log ε), 200 (4.42), 225 (4.46), 286 (4.10), 406 (4.70), 453 (4.25), 780 (solid).

RESULTS AND DISCUSSION

Synthesis and characterization of the free ligand HL

The Schiff base ligand was prepared by reaction of S-methyldithiocarbazate with 4-nitrobenzaldehyde in a 1:1 molar ratio. It can be, in principle, exhibited thione–thiole tautomerism, since it contains a thioamide-NH—C=S functional group [14–16]. The IR spectra of the ligand do not display ν(S—H) at *ca* 2570 cm^{−1}, but ν(N—H) at *ca* 3144, 2975 is present, indicating that in the solid state the molecules remain in the thione form. The ¹H NMR in CDCl₃ does not show any peak at δ *ca* 4.0 ppm attributable to the SH proton, suggesting that the thiol tautomeric form is absent even in solution. However, in presence of metal ions, the Schiff base compound is rapidly converted into the thiol tautomeric form to facilitate the formation of metal complexes of the deprotonated ligand.

Structure of compound HL

Figure 1 shows an ORTEP drawing of the molecule of HL with the atom-numbering scheme. Through non-planar as whole, the molecule comprises two planar fragments, namely the nitrobenzal moiety (mean deviation from the plane of 0.004) and dithiocarbazate moiety (mean deviation 0.008) with the dihedral angle of 5.6°. The C—S bond distance (Table 2) of 1.663(2) Å agrees well with those in related compounds, being intermediate between 1.82 Å for a C—S bond and 1.56 Å for a C=S double bond [17]. The corresponding C(1)—N(1) bond is also indicative of some double bond character and the extensive electron delocalization of the whole molecules.

Only the hydrogen atom attached to nitrogen atom N(1) has the potential to form the donor hydrogen bond distance. The intermolecular hydrogen bonds which link the molecules together in the solid state are shown in Fig. 2, featuring a dimeric structure consolidated by hydrogen bonds of the type N(1)—H⋯S(1a) (1−*x*, −*y*, 1−*z*), which is rather weak since the N⋯S separation 3.553 Å is at the upper end of the range summarized by Srinivasan and Chacko [18].

Spectroscopic characterization of the complexes

The spectra of the two complexes do not show any bands at *ca* 2975 and 3150 cm^{−1}, and this suggests that the proton on the α-nitrogen atom is lost upon formation of the complex. A strong band at *ca* 1475 cm^{−1} is assigned as a C—N stretching vibration. The bond is shifted to a higher frequency by about 50 cm^{−1} compared to the corresponding band in the free ligand. This increase of the ν(C—N) on complexation may contribute to an increase of the C—N bond character by conjugation of the —C=N—N=C— group [19], no band at *ca* 1030 cm^{−1} in the IR spectra

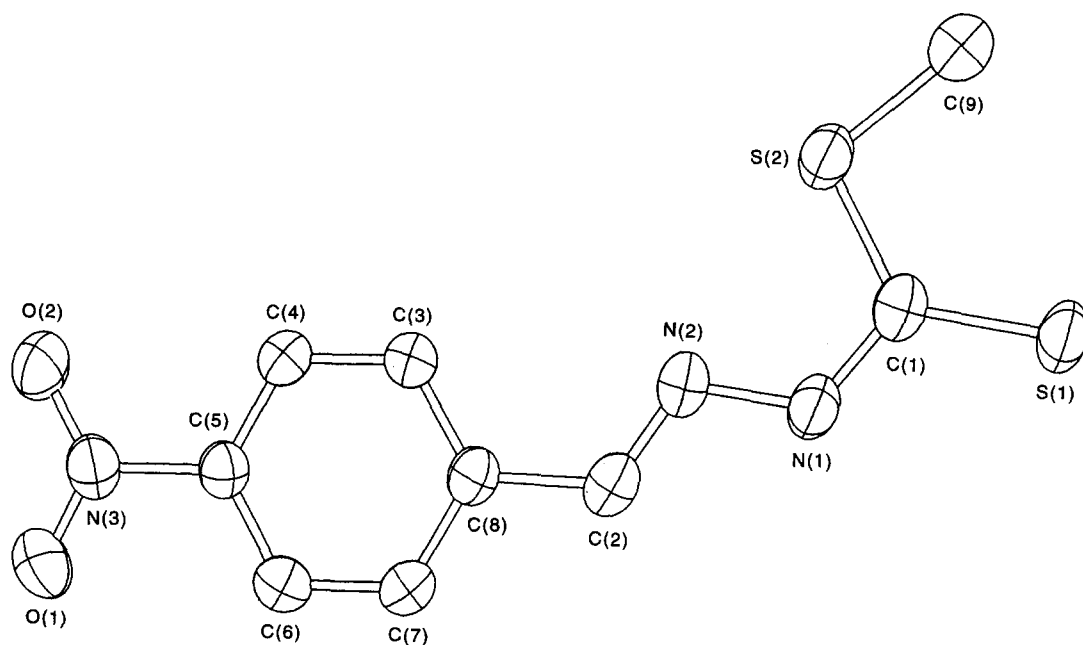


Fig. 1. Molecular structure with atom numbering of the ligand HL. Thermal ellipsoids are drawn at the 30% probability level.

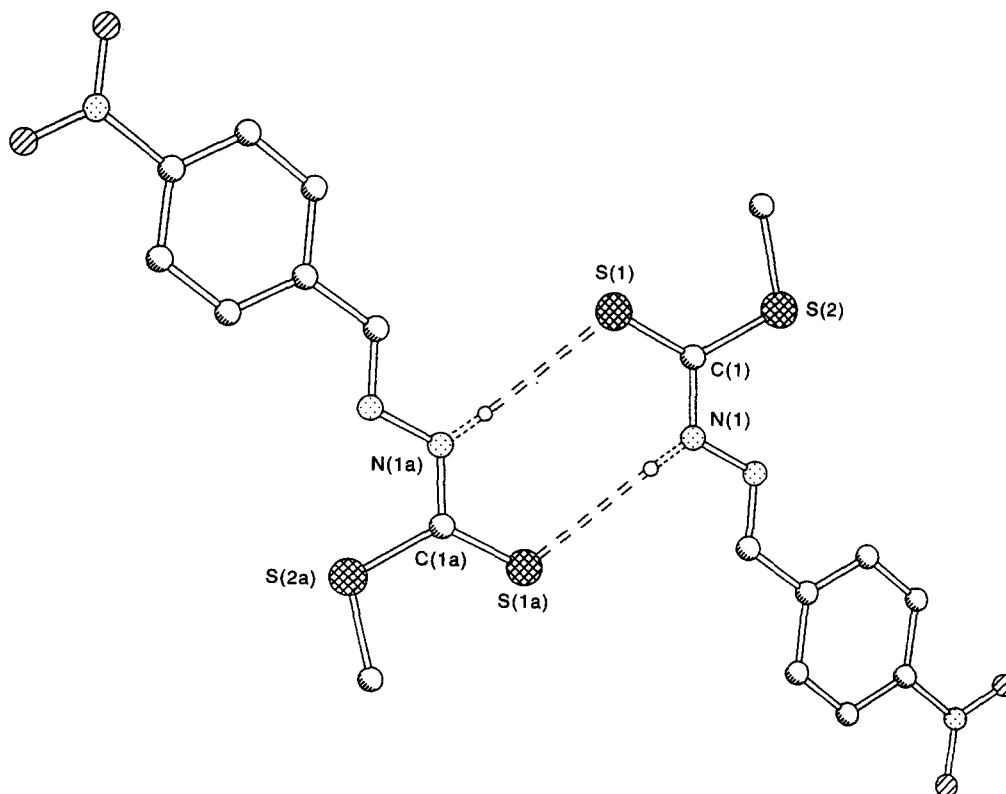


Fig. 2. Hydrogen-bonding scheme showing a dimeric configuration in the crystal of HL. Symmetry code; $a: 1-x, -y, 1-z$.

of the complexes also indicates that the C=S band might be changed to C—S band after formation of the complexes. For IR spectra ($100\text{--}500\text{ cm}^{-1}$) of the complexes display a medium band at *ca* 375 cm^{-1}

which may be assigned to the metal–sulfur stretching frequencies [20]. A band at higher frequencies in the range $450\text{--}470\text{ cm}^{-1}$ can be assigned as the metal–nitrogen stretching vibrations [21].

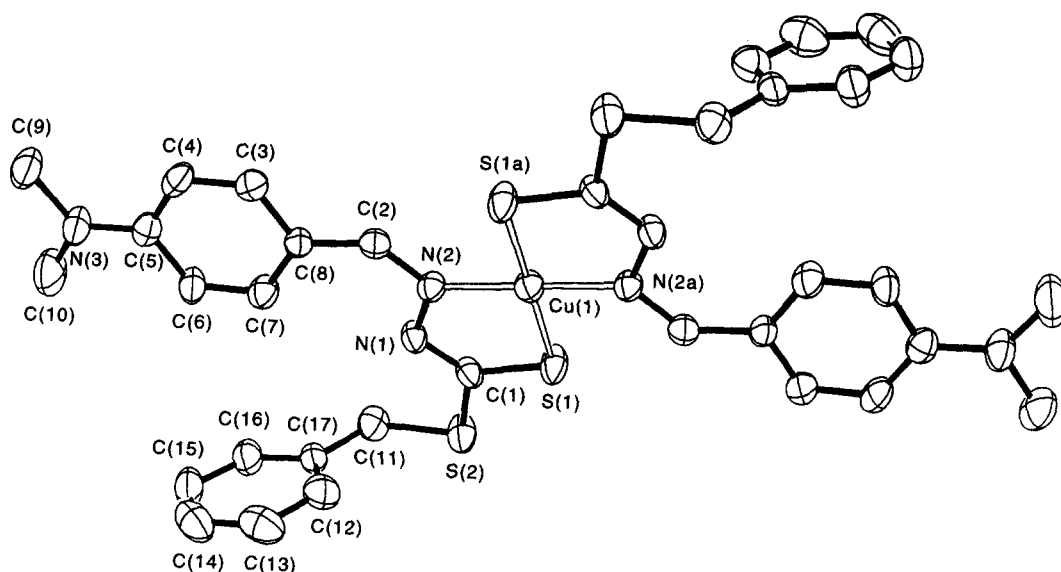


Fig. 3. Molecular structure with atom numbering of the copper complex CuL₂. Thermal ellipsoids are drawn at the 30% probability level.

The room-temperature magnetic moment measurements of the nickel(II) complex suggest that it is essentially diamagnetic in nature. For the d^8 electronic configuration, diamagnetism generally implies that the metal ion has a four-coordinate square-planar configuration. Only the one band at *ca* 650 nm which is assigned as the $^1A_{1g} \rightarrow ^1A_{2g}$ transition, also indicates that octahedral or tetrahedral structures are absent [22].

The room-temperature magnetic moments of the copper(II) chelate (1.85 BM) are expected for a square-planar d^9 ion. Room-temperature ESR spectra give the *g* value at *ca* 2.06, which is also in accordance with the square-planar configuration for the copper(II) complex. The electronic spectrum of the copper(II) chelate in a Nujol mull shows a broad band with a maximum at *ca* 780 nm. This band may be also assigned to the $d-d$ transition of a square-planar copper(II) species [23].

Crystal structure of copper(II) complexes

Figure 3 shows an ORTEP drawing of the complex with the numbering scheme. The structure contains two independent centro symmetric molecules and they are slightly different. In both of them, the copper atom is coordinated in a square-planar configuration with two equivalent Cu—S and Cu—N bonds. The free ligand lost a proton from its tautomeric thiol form and acts as single negatively charge bidentate ligand coordinating to nickel ion *via* the mercapto sulfur and β -nitrogen atoms forming an extensive electron delocalization π system.

It is interesting to compare the structure of the ligand in the free state and in the copper complex. The large difference may be due to the distance around

atom C(1). In the free ligand, the bond distances C(1)—N(1) 1.343(4) and C(1)—S(1), 1.661(3) Å suggest that C(1)—N(1) as the single bond and C(1)—S(1) the double bond, while in the complex, the bond distances C(1)—N(1), 1.301(4) and C(1)—S(1), 1.706(4) Å show that C(1)—N(1) is the double bond and C(1)—S(1) the single bond. These results together with the spectra characterization of the copper complex indicate the presence of the C—S—M, formed by the elongation of —NH—C=S group in the free ligand to N=C—SH, and the ligand coordinates of the metal through the sulfur after deprotonation.

Deprotonation and the formation of the metal complex makes the configuration of the ligand quite different. In crystals of the free ligand, the α -nitrogen atom N(2) and the thioketo S atom form intermolecular hydrogen bonded dimers, thus the β -nitrogen atom and the thioketo S atom are in the *trans*-configuration. On the other hand, in the complex the presence of the metal ion makes the Schiff base coordinate as a bidentate ligand, and the thio S and β -nitrogen atoms are *cis* to each other.

Nonlinear optical properties

Third-order nonlinear optical susceptibility $\chi^{(3)}$ for the compound was measured in DMF solution using the *z*-scan method. The third-order optical properties of the ligand is shown in Fig. 4. The calculated methods and related theory have been reported previously [24,25]. The ligand, having a strong electron acceptor, —NO₂, can be expected to show an obvious third-order response. Recently, it has been postulated that an electron-accepting substituent on the π -system of A—A organic compounds can enhance third-order response by an order of magnitude [26]. This pos-

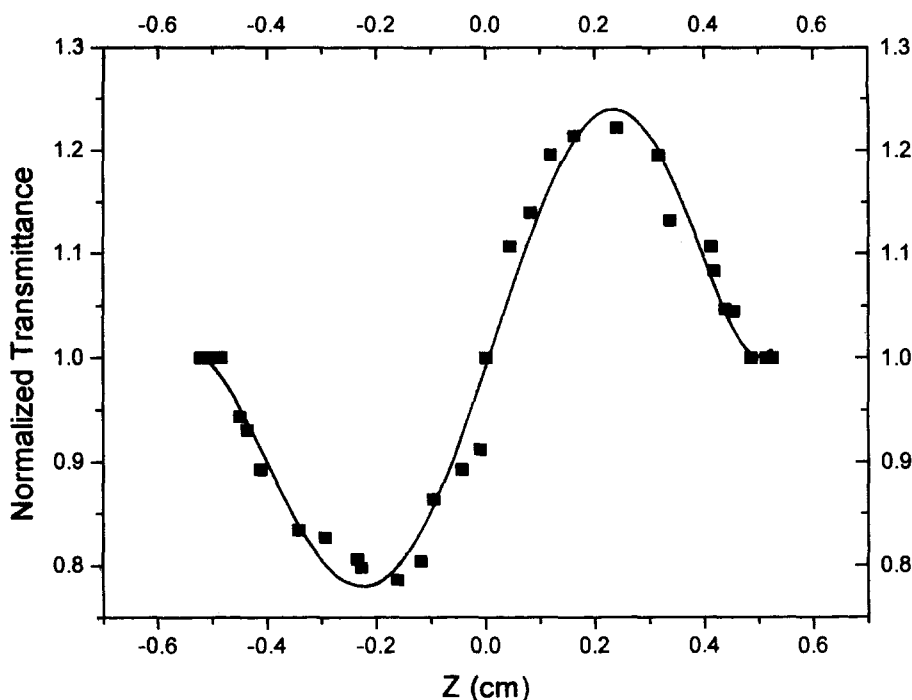


Fig. 4. The z-scan data 4×10^{-3} M of the ligand HL at 532 nm with I_0 being 3.26 gwcm^{-2} .

tulation is also supported by the observation of the A–A paring in the diphenyl poly series being much more effective in enhancing third-order response than that of the D–D paring. So, it also might be expected that the A–M–A (A = acceptor, M = metal) type of metal complex formed by a single negatively charged bidentate ligand with a strong electron acceptor group, $-\text{NO}_2$, might show larger third-order responses than the free ligand. Experimental studies support the expectation as 6.48×10^{-13} , 7.35×10^{-13} and 7.03×10^{-13} esu is observed for the free ligand, the nickel(II) complex NiL_2 and the copper(II) complex CuL_2 , respectively. These results are comparable to the value of the transition metal dithiolenes (7.16×10^{-14} – 3.8×10^{-11} esu) [26].

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