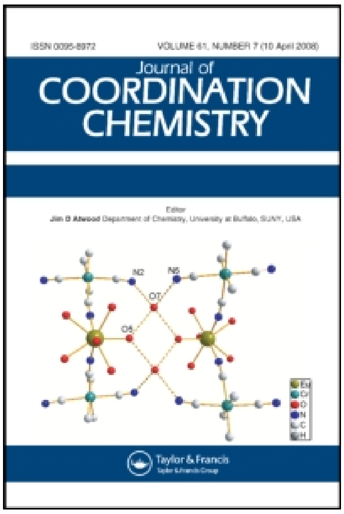

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SYNTHESIS, CRYSTAL STRUCTURE AND THIRD-ORDER NONLINEAR OPTICAL PROPERTIES OF COPPER(II) COMPLEXES WITH SCHIFF-BASE LIGAND DERIVATIVES FROM DITHIOCARBAZATE

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SYNTHESIS, CRYSTAL STRUCTURE AND THIRD-ORDER NONLINEAR OPTICAL PROPERTIES OF COPPER(II) COMPLEXES WITH SCHIFF-BASE LIGAND DERIVATIVES FROM DITHIOCARBAZATE

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The synthesis and spectroscopic characterization of D-M-D type neutral Cu(II) chelates with Schiff base ligands, $R\text{-}C_6H_4CHNNHCSSCH_3$ ($R = -N(CH_3)_2, -CH_3O$) are reported. Spectroscopic data suggest that the Schiff base ligands act as single negatively charged bidentate ligands forming stable neutral metal complexes. Single crystal X-ray structure determinations of the Cu(II) chelates established that the coordination geometry of Cu(II) is square planar with two equivalent Cu-N and Cu-S bonds. The Schiff base ligands lost a proton from their tautomeric thiol form and coordinated to Cu(II) *via* the mercapto sulfur and β-nitrogen as expected. The two phenyl rings and the coordination moieties are almost in one plane forming an extensive electronic delocalization system. Magnetic properties and ESR data support the square-planar coordination geometry for both of the Cu(II) chelates. Nonlinear optical properties were measured using z-scan methods in CH_3CN solution.

Keywords: Copper(II); crystal structures; nonlinear optical properties

INTRODUCTION

Recently, the study of structure property relationships for series of compounds having enhanced optical nonlinearity has increased the

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understanding of molecular level design criteria important for maximizing second-order and third-order optical nonlinearity.[1] It has been postulated that molecules possessing extensively conjugated π-electron systems can exhibit large optical nonlinearities, especially the third-order efficiency described as second-order molecular hyperpolarizability. Transition metal organometallic and coordination complexes have emerged[1–6] as potential building blocks for nonlinear optical (NLO) materials due to the various excited states present in these systems as well as the tailorability of metal–organic ligand interactions. In comparison to organic molecules, metal complexes offer a larger variety of structures, comparable, or in some cases, higher environmental stability and a much greater diversity of tunable electronic properties by virtue of the coordinated metal center. Thio-Schiff base compounds, RCH=NNHCSSR′, are known to coordinate readily with transition metals to give stable complexes, forming a long π-conjugated system by deprotonation as complexes form.[7–9] Thus metal dithiocarbazato complexes might exhibit large second order molecular hyperpolarizability. In our group,[10–12] much effort has been made to find potential metal complexes derived from Schiff-base ligands containing nitrogen and sulphur donors, such as thiosemicarbazone, dithiocarbazate and their derivatives. As part of studies on synthesis and nonlinear optical properties of metal dithiocarbazatos, we report herein the synthesis, crystal structures and optical nonlinearity of two Cu(II) complexes derived from Schiff-base ligands: HL^1, S-methyl-β-N-(4-dimethylaminophenyl)methylenedithiocarbazate; HL^2, S-methyl-β-N-(4-methoxylphenyl)methylenedithiocarbazate.

EXPERIMENTAL

S-methyl-β-N-(4-dimethylaminophenyl)methylenedithiocarbazate,[13] HL^1 and S-methyl-β-N-(4-methoxylphenyl)methylenedithiocarbazate,[14] HL^2 were prepared by literature methods. Other chemicals used were of analytical grade.

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. Electronic spectra were obtained on a Shimadzu UV3100 spectrophotometer in dichloromethane solution. Solid-state electronic spectra were obtained by the reflection technique on a Shimadzu UV240 spectrophotometer using MgO as the reference material. ESR spectra were recorded on a Bruker ER 200-D-SRC spectrometer. Magnetic susceptibility data were collected with a CAHN 2000 magnetobalance and corrected by Pascal constants.

Preparation of the Copper(II) Complexes

A solution of Cu(II) acetate (0.5 mmol) in ethanol (20 cm^3) was added to an ethanol solution (20 cm^3) of the ligand (1 mmol). The mixture was refluxed and stirred for 4 h, cooled to room temperature, and the crystals which formed were filtered off, washed with ethanol and dried in *vacuo* over P_2O_5. The prepared chelate complexes with their analytic and spectral data are listed in Table I.

Crystallographic Structure Determination

Information concerning crystallographic data and structure refinement of the Cu(II) complexes are summarized in Table II. The intensities of the compounds were collected at 294K on a Rigaku RAXIS-IIC imaging plate diffractometer using Mo-Kα ($\lambda = 0.71073$ Å) from a rotating-anode generator operating at 50 KV and 90 mA ($2\theta_{max} = 55.2°$); 60 oscillation frames in the range of 0–180°, exposure of 10 min per frame for the two copper complexes, respectively.[15,16] Both of the structures were solved by direct method. All non-hydrogen atoms were refined anistropically 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 SHEXTL-PC program package.[17] Analytical expressions of neutral-atom scattering factor were employed, and anomalous dispersion corrections were incorporated.[18] Supplementary materials available from the Cambridge Crystallographic Data Center comprise complete lists 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 determinated by the z-scan technique.[19] Using a Gaussian laser beam in a

TABLE I Analytical data, relevant IR frequencies (cm^{-1}), data of UV–Vis, ESR and magnetic moment in room temperature for the two ligands and their Cu(II) complexes

Comp	*Found (calcd.)*^{a}%			*IR* (cm^{-1})				*UV–Vis*^{b}	*ESR*^{d}	*Magnetic moment*^{e}
	C	H	N	ν(N–H)	ν(C–N) ν(C=N)	ν(C=S) ν(C–S)	ν(Cu–N) ν(Cu–S)	λ(nm) (log ϵ)	g	μ
HL^{1}	53.3	6.0	16.3	2969	1590	1005				
	(53.2)	(5.9)	(16.6)	3102	1455	951				
HL^{2}	50.2	4.9	11.8	2965	1569	1007				
	(50.0)	(5.0)	(11.7)	3117	1435	962				
CuL$^{1}_{2}$	46.1	4.8	14.1		1473	962	471	448(4.49)	2.06	1.82
	(46.4)	(4.9)	(14.4)				369	788^{C}		
CuL$^{2}_{2}$	44.1	3.9	10.4		1461	944	459	438(427)	2.03	1.75
	(44.3)	(4.1)	(10.3)				354	775^{C}		

[a] Figures in parentheses are the calculated values.
[b] Band maximum in nm (log ϵ).
[c] Spectra in solid.
[d] g value at room temperature.
[e] Room temperature magnetic moments.

TABLE II Crystallographic data for the two Cu(II) complexes

Compound	CuL^1_2	CuL^2_2
Formula	$C_{22}H_{28}CuN_6S_4$	$C_{20}H_{22}CuN_4O_2S_4$
Formula weight	568.3	542.2
Colour/habit	Dark blue prism	Red-brown prism
Size, mm	0.24 × 0.35 × 0.36	0.25 × 0.35 × 0.42
Crystal system	Monoclinic	Triclinic
Space group	c2/c	P-1
a, Å	18.785(1)	8.585(2)
b, Å	17.274(1)	8.901(2)
c, Å	8.344(1)	15.100(3)
α, deg		88.49(3)
β, deg	108.64(1)	84.59(3)
γ, deg		82.36(3)
V, $Å^3$	2565(1)	1138.4(6)
Z	4	1
μ, mm^{-1}	1.200	1.352
d(calcd.), $g\,cm^{-3}$	1.471	1.582
Reflections unique	2430 (Rint = 7.91%)	4285
Reflections observed	1735 ($F > 4.0\sigma(I)$)	2767 ($F > 4.0\sigma(I)$)
R, Rw	0.045, 0.061	0.041, 0.044
w^{-1}	$\sigma^2(F) + 0.0008F$	$\sigma^2(F)$
GOOF	1.11	1.03
$\Delta(\rho)_{max,min}$ e $Å^{-3}$	0.28, −0.34	0.36, −0.63

tight-focus limiting geometry, we measure the transmittance of a nonlinear medium through a finite aperture placed in the far field as a function of the sample position(z) measured with respect to focal plane. We placed the sample ($1.0 \times 10^{-3}\,mol\,dm^{-3}$) having $n_2 > 0$ well in front of the focus (−z).[20] As the sample is moved toward the focus, the increased irradiation leads to a positive lensing effect that tends to collimate the beam, thus decreasing the aperture transmittance. With the sample on the +z side of the focus, the positive lensing effect tends to augment diffraction, and the aperture transmittance is increased. The approximate null at $z = 0$ is analogous to placing a thin lens at the focus that results in a minimal far-field pattern change. For still large +z the irradiation is reduced and the transmittance returns to the original linear value. This value was normalized to unity.

Third order nonlinear optical properties of the compounds were investigated using a M200 high-power Mode-Locked Nd:YAG laser with 200 ps pulse of 532 nm irradiation at a frequency of 5 Hz. CH_3CN solutions of the complexes were placed in a 1 mm quartz cell and used for the optical measurements. The samples are stable toward air and laser irradiation. The NLO properties of the complexes are relatively simple, dominated by nonlinear refraction, as illustrated in Figure 1. The valley-peak pattern of the

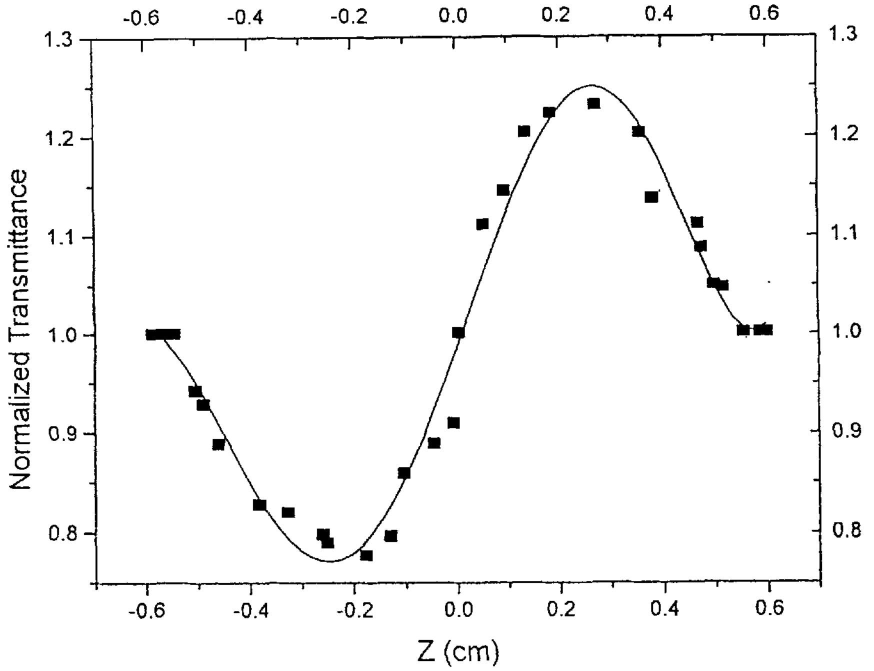

FIGURE 1 Measured z scan of 1-mm thick CuL_2^2 (1.1×10^{-3} M CH_3CN solution) cell at 532 nm with I_0 being 3.26 gw cm^{-2} showing the self-focusing effect.

normalized transmittance curve obtained under a closed aperture configuration shows characteristic self-focusing behavior of the propagating light in the sample.

$$\Delta Tv\text{-}p = 0.406\ (1 - S)^{0.25}|\Delta\Phi_0| \qquad (1)$$

$$\Delta Tv\text{-}p = 0.371|\Delta\Phi_0| \qquad (2)$$

$$\Delta\Phi_0 = 2\pi I_0[1 - \exp(-\alpha L)]n_2/(\lambda\alpha_0) \qquad (3)$$

$$n_2 = \Delta\Phi_0\lambda L/(2\pi I_0) \qquad (4)$$

$$\chi^{(3)} = \chi^{(93)}_{Re} = cn_0^2 n_2/(80\pi) \qquad (5)$$

The difference between normalized transmittance values at valley and peak positions, $\Delta Tv\text{-}p$ is related to the nonlinear refractive index n_2 (m^2W^{-1}) by eq. (**1**) and eq. (**4**), where $\Delta\Phi_0$ and I_0 are the on-axis phase shift and on-axis irradiation, both at focus respectively. α_0 and L are the linear absorption coefficient and optical path of the sample. In our experiment, $S = 0.3$, $L = 1.0 \times 10^{-3}$ m and $I_0 = 3.26$ Gw cm^{-2} for all the compounds. Nonlinear absorptions of these complexes are small (α_0 *ca.* 1.0 m^{-1}) and always negligible. The parameters ΔTv-p is measured *ca.* 0.48 (Figure 1) for $CuL_2{}^2$ and 0.83 for CuL_2^1. The n_2 value was calculated to be 0.34×10^{-17} m^2 W^{-1} and 0.58×10^{-17} m^2 W^{-1}. Experiments with varied I_0 show that n_2 is indeed induced independent of I_0, consistent with the notion that $n = n_0 + n_2 I$ and the observed NLO phenomenon is third-order in nature. Since the transparency region of n_2 in the wavelength range 0.5–1 μm is expected to be negligible if we ignore the contribution of NLO absorption, the third-order NLO susceptibility $\chi^{(3)}$ of the title compound can be calculated from the n_2 value by using equations. The results of calculations for the two Cu(II) complexes CuL_2^1 and CuL_2^2 are $\chi^{(3)} = 1.25 \times 10^{-11}$ esu, $\chi^{(3)} = 7.33 \times 10^{-12}$ esu, respectively.

RESULTS AND DISCUSSION

Synthesis and Characterization of the Free Ligand

The Schiff-base ligands were prepared by reaction of S-benzaldithiocarbazate with the corresponding phenylaldehyde in a 1 : 1 molar ratio. It can, in principle, exhibit thione-thiole tautomerism, since it contains a thioamide-NH–C=S functional group.[21] The IR spectra of the ligands do not display ν(S–H) at *ca.* 2570 cm^{-1}, but ν(N–H) at *ca.* 3150, 2970 cm^{-1} is present, indicating that in the solid state the molecules remain in the thione form. A single crystal structure of HL^2 exhibits two kind of C–S bonds (C=S of 1.670 and C–S of 1.746 Å) supporting the suggestion. 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 depronated ligand.

Spectroscopic Characterization of the Complexes

The spectra of the CuL_2^1 and CuL_2^2 do not show any band at *ca.* 2975 or 3140 cm^{-1}, indicating that the proton on the α-nitrogen is lost upon complex formation. A strong band at *ca.* 1475 cm^{-1} is assigned as the C–N stretching vibration. The bond is shifted to higher frequency by about 50 cm^{-1} compared to the corresponding band in the free ligand. This increase of the ν(C–N) on complex formation may be attributed to an increase of the C–N bond character by conjugation of the –C = N–N = C– group.[22] There is no band at *ca.* 1030 cm^{-1} in the IR spectra of the complexes also indicating that the C=S band might be changed to a C–S band. The far IR spectra (100–500 cm^{-1}) of the complexes display a medium band at *ca.* 375 cm^{-1} which may be assigned to the metal-sulphur stretching frequencies.[23,24] A band at higher frequencies in the range 450–470 cm^{-1} can be assigned as the metal-nitrogen stretching vibrations.[25]

The room-temperature magnetic moments of the Cu(II) chelate complexes CuL^1_2 (1.82 BM) and CuL^2_2 (1.75 BM) are expected for a square-planar d^9 ion. Room-temperature ESR spectra give the g value at *ca.* 2.06 and 2.03, respectively, which is also in accordance with square-planar configuration for the Cu(II) complex. The electronic spectrum of the Cu(II) chelates CuL^1_2 and CuL^2_2 in a Nujol mull shows a broad band with a maximum at *ca.* 750 and 760 nm, respectively. This band may be assigned to the *d-d* transition of a square-planar Cu(II) species.[26]

Description of the Structure of the Copper(II) Complexes

Figures 2 and 3 show the ORTEP drawing of the complexes CuL^1_2 and CuL^2_2 with the numbering scheme. The coordination geometry about the Cu(II) ion is squareplanar with crystallographically imposed $\bar{1}$ symmetry. The Schiff-base loses a proton from the tautomeric thiol form and acts as a single-charged, bidentate ligand coordinating to Cu(II) *via* the mercapto sulphur and β-nitrogen atoms. In complex CuL^1_2, the dimethylaminephenyl moiety is completely planar (mean deviation from the best plane is 0.010 Å) and forms a dihedral angle of 4.5° with the chelate ring defined by Cu(1), S(1), C(1), N(1) and N(2) atoms (mean deviations from the best plane is 0.029 Å). The very small dihedral angle indicates the high delocalization of electrons in the π system of the two Schiff-base ligands and Cu(II) ion. In complex CuL^2_2, the methyloxylphenyl moiety is planar (mean deviation from the best plane is 0.010 Å on the average) and forms a dihedral angle of 9.5° on the average with the coordinate chelate ring defined by Cu(1), S(1), C(1), N(1) and N(2) atoms (mean deviation from the best plane is 0.020 Å).

The data in Table III show that all the bond distances in the side chain are intermediate between formal single bonds and double bonds, also pointing to extensive electron delocalization over the entire moiety. Examination of the structural data for the dithiocarbazate ligands and their Cu(II) complexes show that the C(1)–S(1) bonds in L$^-$ are longer than those in the neutral form HL (1.73 *vs.* 1.67 Å on average, respectively) whereas the

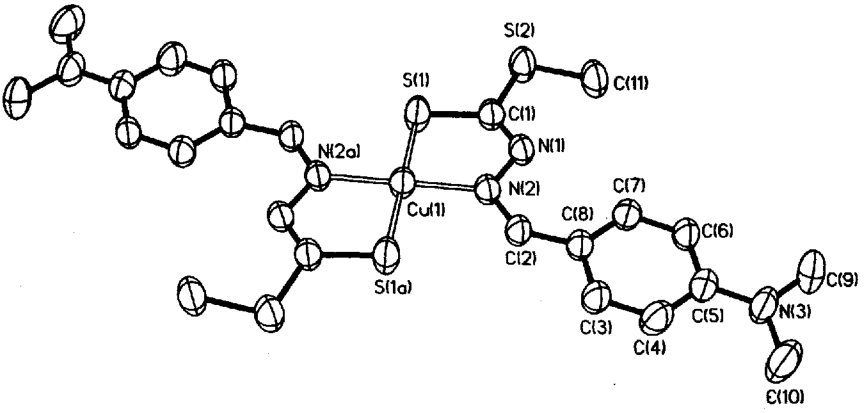

FIGURE 2 Molecular structure and atom numbering of the copper complex CuL^1_2. The thermal ellipsoids are drawn at the 50% probability level.

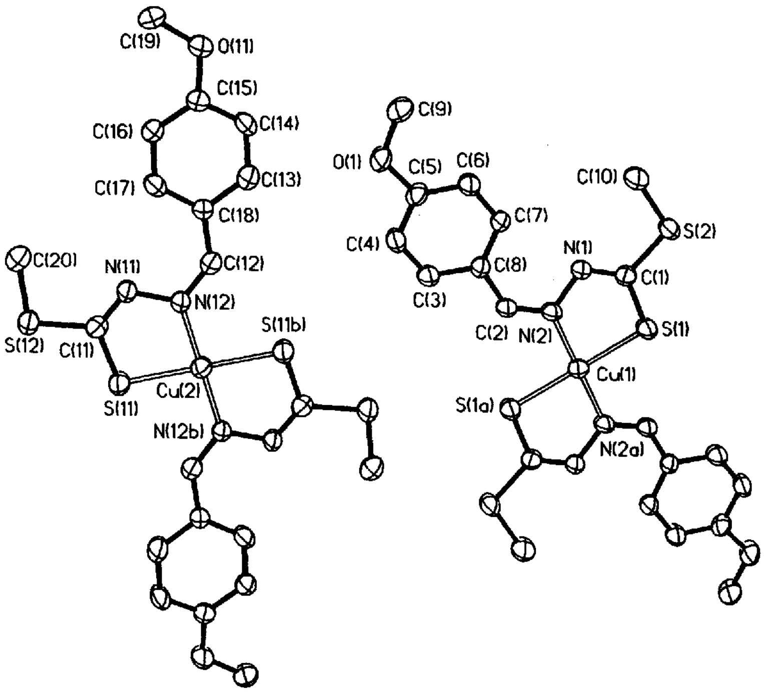

FIGURE 3 Molecular structure and atom numbering of the copper complex CuL^2_2. The thermal ellipsoids are drawn at the 50% probability level.

TABLE III Selected bond lengths (Å) and angles (°) for the two complexes

CuL_2^1		*CuL_2^2*			
atom–atom	distance	atom–atom	distance	atom–atom	distance
Cu(1)-S(1)	2.174(1)	Cu(1)-S(1)	2.176(1)	Cu(2)-S(11)	2.173(1)
Cu(1)-N(2)	1.932(3)	Cu(1)-N(2)	1.935(3)	Cu(2)-N(12)	1.927(3)
S(1)-C(1)	1.733(4)	S(1)-C(1)	1.723(4)	S(11)-C(11)	1.741(4)
N(1)-C(1)	1.274(4)	C(1)-N(1)	1.291(6)	C(11)-N(12)	1.266(6)
N(1)-N(2)	1.409(4)	N(1)-N(2)	1.405(5)	N(11)-N(12)	1.403(5)
N(2)-C(2)	1.298(4)	N(2)-C(2)	1.298(6)	N(12)-C(12)	1.290(6)
atom–atom–atom	angle	atom–atom–atom	angle	atom–atom–atom	angle
S(1)-Cu(1)-N(2)	85.9(1)	S(1)-Cu(1)-N(2)	86.3(1)	S(11)-Cu(2)-N(12)	85.8(1)
N(2)-Cu(1)-S(1a)	94.1(1)	N(2)-Cu(1)-S(1a)	93.7(1)	N(12)-Cu(2)-S(11b)	94.2(1)
S(1)-C(1)-N(1)	124.4(3)	S(1)-C(1)-N(1)	124.5(4)	S(11)-C(11)-N(11)	124.3(3)
N(2)-N(1)-C(1)	112.9(3)	N(2)-N(1)-C(1)	113.0(3)	N(12)-N(11)-C(11)	112.9(3)
N(1)-N(2)-C(2)	113.8(3)	N(1)-N(2)-C(2)	114.4(3)	N(11)-N(12)-C(12)	114.0(3)
symmary code; a: 0.5−x, 05−y, −z		symmary code; a: 1−x, −y, −z; b: 2−x, 1−y, 1−z.			

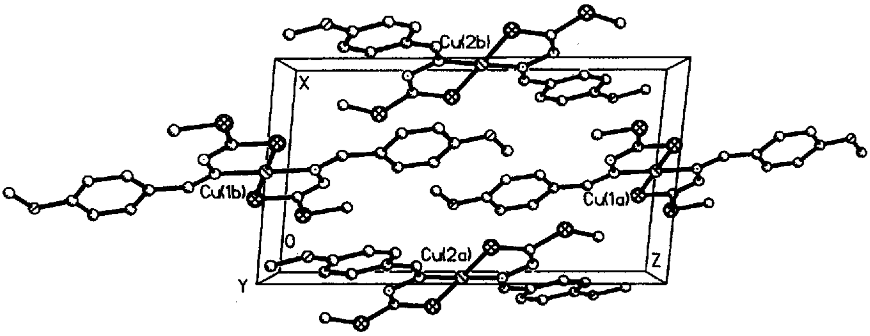

FIGURE 4 Molecular pack diagram view down to the b axis of the CuL_2^2 complex.

N(1)–C(1) bond is shorter than that in HL (1.28 *vs.* 1.34 Å on average). These results, together with the spectroscopic characterization of the complexes indicate the presence of the C-S-MCuL group, formed by enolisation of –NH–C=S in the free ligand to –N=C–SH coordination of the metal through sulphur after deprotonation. This tendency is so strong that there is no metal complex known containing the neutral ligand which coordinates by the thioketo sulphur atom.

In the complex CuL_2^2, there are two independent molecules in an asymmetric unit (Figure 4). The two molecules are almost parallel to each other (the two coordination chelate rings form a dihedral angle of 5.7°). Since the two Cu(II) ions are both on special positions Cu(1), we also tried the monoclinic C lattices to solve the structure, however, the space group *P*-1 is the only space group giving a satisfactory solution. Deprontonation and coordination of the ligands to the metal ion makes the configuration of the ligand quite different. In crystals of the free ligands, the α-nitrogen atom N(2) and the thioketo S atom form intermolecular hydrogen-bonded dimers[13,14] and thus the β-nitrogen atom and the thioketo S atom are in a *trans*-configuration. In the metal complexes, 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 optical susceptibility $\chi^{(3)}$ for the ligands and their copper complexes were measured in acetonitrile solution using the z-scan method. When the substituent group is a strong electron donor, such as $N(CH_3)_2$, the copper complex exhibits a large third-order molecular NLO response, while a moderate electron donor ($-OCH_3$) as the substituent gives a lower third-order NLO response. Third-order optical susceptibility $\chi^{(3)}$ for the ligands shows no obvious third order NLO response.

Supplementary Material

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

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