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Synthesis, crystal structures, and molecular hyperpolarizabilities of a new Schiff base ligand, and its copper(II), nickel(II), and cobalt(II) metal complexes

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Dedicated to Professor Tobin J. Marks for his outstanding contributions to all aspects of inorganic chemistry

Abstract

A new ligand (HL) obtained from the Schiff base condensation of 4-(diethylamino)salicylaldehyde with 4-nitroaniline is reported, with its nickel(II), copper(II), and cobalt(II) complexes. The crystal structures are reported for the four derivatives. While, Ni^{II}L₂ and Cu^{II}L₂ are centrosymmetric molecules, Co^{II}L₂ exhibits a pseudo-tetrahedral molecular structure. The quadratic hyperpolarizabilities (β) of HL and Co^{II}L₂, measured by electric field induced second harmonic (EFISH) technique, are equal to 66 and 110 × 10⁻³⁰ cm⁵ esu⁻¹, respectively. Beside a geometric effect (pseudo-T_d symmetry), the coordination of the metal center provides an intrinsic enhancement of the NLO response. In addition, an enhancement of the thermal stability of about 60° is found upon metal complexation. © 2004 Elsevier B.V. All rights reserved.

Keywords: Schiff bases complexes; Nonlinear optics; EFISH; Semi-empirical calculations; X-ray diffraction

1. Introduction

Molecular materials with quadratic nonlinear optical (NLO) properties are currently attracting considerable interest [1–8]. The quadratic hyperpolarizability (β) of a chromophore is associated with charge transfers between donor and acceptor substituents linked through π -conjugated pathways. Most NLO chromophores have been found in organic molecules, such as substituted stilbene [9,10], thiophene [4,11], or polyene families [12] but the introduction of a metal center as a donor or acceptor subunit has also led to various novel organometallic [13–15] and inorganic [16–20] molecules with large NLO responses.

In the late 1980s, Professor Tobin Marks was one of the first researchers who became interested in investigating metal-organic structures for NLO purpose. The initial approach was mainly based on a systematic screening of the NLO response of inorganic [21] and organometallic [22] species, within the framework of the emerging INDO/SOS formalism [23,24]. Some synthetic work conducted by Tobin's group came also to implement the initial idea that a metal center can lead to enlarged NLO response [25].

Later on, Tobin et al. investigated the promising class of bis(salicylaldiminato)metal Schiff base complexes [26–29]. In these systems, the metal atom is located at the center of the chromophore, making a better use of the d-hybridation scheme of the metal. It has been observed that varying the nature of the metal could lead to various electronic properties, with enhancement of the NLO response in some cases, the geometry of the rigid bis(salicylaldiminato)-based complex being roughly unaffected. On the occasion of the special issue of *Inorganica Chimica Acta* dedicated to the career of Professor Marks, it seemed interesting to us to bring about the

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field of NLO bis(salicylaldiminato)metal complexes with an additional investigation.

Contrary to the previous reports in which the metal atom was located at the center of rigid square planar tetradentate ligands, the present contribution explores electronic effects obtained upon metal complexation, in alternatives molecular geometries. This can be achieved by changing the nature of the metal and by using a nonrigid Schiff base ligand. 4'-Dimethylamino-1-nitrostilbene (DANS, Scheme 1), which has widely been used as the typical benchmark NLO chromophore along the 1980s offers a useful model skeleton for this investigation. The parent (diethylaminosalicylaldiminato)nitrobenzene (HL, Schemel) derivative, in which a nitrogen atom has been incorporated in the π -conjugated bridge to ensure the coordination of a metal, has been preferred for the present investigation. Our study focuses on the synthesis and crystal structures of HL and its nickel(II), copper(II), and cobalt(II) metal complexes. The electronic properties of the different species are compared in relation to their molecular structures, and the NLO responses are investigated by the electric field induced second harmonic (EFISH) technique [30,31] and within the framework of the INDO/SOS (ZINDO) formalism [23,24].

2. Experimental

2.1. Materials and equipment

4-Nitroaniline, Ni(AcO)₂ · 4H₂O, Cu(AcO)₂ · H₂O, and Co(AcO)₂ · 4H₂O were purchased from Aldrich and used as received, as were DANS (Kodak) and 4-(diethylamino)-salicylaldehyde (Lancaster). Solvents (SDS or Calo Erba) for the spectroscopic studies were used without further purification. The ¹H NMR spectra were recorded on a Bruker AM 250 spectrometer. Elemental analyses were performed by the Service de Microanalyses du LCC-CNRS, Toulouse. Thermal measurements were performed by TG/DTA analysis on a Setaram-TGDTA92 thermoanalyser. The experiments were conducted under nitrogen on 5 mg of sample (rate of heating: 10 °C/min). The decomposition temperature (T_d) was assigned as the intercept of the leading edge of the decomposition endotherm with the baseline of the DTA scan [32].

2.2. Synthesis

HL: In absolute ethanol (40 mL) were successfully added 276 mg (2×10^{-3} mol) of 4-nitroaniline, 386 mg (2×10^{-3} mol) of 4-diethylaminosalicylaldehyde, and one drop of sulfuric acid. The mixture was refluxed for two days. After concentration to 1/3 of the initial volume and cooling down, a red precipitate was filtered, washed with the minimum amount of cold absolute ethanol, and dried under vacuum. Yield: 501 mg, (80%). *Anal.* Calc. for C₁₆H₁₉N₂O₂: C, 65.16; H, 6.11; N, 13.41. Found: C, 64.90; H, 6.22; N, 13.33%. ¹H NMR(CDCl₃): δ = 1.216 (t, 7.1 Hz, 6H), 3.417 (q, 7.1 Hz, 4H), 6.221 (d, 1.8 Hz, 1H), 6.277 (dd, 2.0 and 8.9 Hz, 1H), 7.180 (d, 8.8 Hz, 1H), 7.295 (d, 8.9 Hz, 2H), 8.241 (d, 8.9 Hz, 1H), 8.408 (s, 1H), 13.160 (s, 1H). Single crystals suitable for X-ray studies were obtained by recrystallization in ethanol.

NiL₂: To a solution of 250 mg (8×10^{-4} mol) of HL in 20 mL of hot ethanol was added, a solution of 114 mg (4×10^{-4} mol) of Ni(AcO)₂ · 4H₂O dissolved in 20 mL of hot ethanol, and the resulting solution was refluxed for two days. After concentration to one half of the initial volume and cooling down, an orange precipitate was filtered, washed with ethanol, and dried under vacuum. Yield: 205 mg (75%). *Anal.* Calc. for C₃₄H₃₆N₆NiO₆: C, 59.76; H, 5.31; N, 12.30. Found: C, 59.95; H, 5.02; N, 12.28%. Single crystall suitable for X-ray studies were obtained by recrystallization in ethanol.

CuL₂: Following the same procedure, the use of 80 mg $(4 \times 10^{-4} \text{ mol})$ of Cu(AcO)₂ · H₂O affords 179 mg (65 % yield) of an orange precipitate. *Anal.* Calc. for C₃₄H₃₆CuN₆O₆: C, 59.34; H, 5.21; N, 12.21. Found: C, 59.55; H, 5.40; N, 12.15%. Single crystals suitable for X-ray studies were obtained by recrystallization in ethanol.

CoL₂: Similarly, the use of 100 mg $(4 \times 10^{-4} \text{ mol})$ of Co(AcO)₂ · 4H₂O affords 191 mg (70% yield) of a red precipitate. *Anal.* Calc. for C₃₄H₃₆CoN₆O₆: C, 59.74; H, 5.31; N, 12.29. Found: C, 59.67; H, 5.17; N, 11.97%. Single crystals suitable for X-ray studies were obtained as follows: in one arm of a H-shaped tube, a solution of 8×10^{-4} mol of HL in ethanol was slowly diffused into a solution containing 4×10^{-4} mol of Co(AcO)₂ · 4H₂O in the other arm of the tube. Crystals were obtained over a period of one week.

2.3. X-ray data collection and structure determination

The data were collected on a Stoe Imaging Plate Diffraction System (IPDS) equipped with an Oxford cryosystems cooler device, with a tube power of 1.5 kW for HL and Ni^{II}L₂, and 1.8 kW for Cu^{II}L₂ and Co^{II}L₂. The crystal to detector distance was 80 mm for the three complexes and 70 mm for the ligand. For HL, Ni^{II}L₂ and Cu^{II}L₂, the structures were solved by direct methods (SHELXS-86) [33] and refined by least-square procedures. Crystallographic data are summarized in Table 1. The weighting scheme used in the last refinement cycles was $w = w' [1 - (\Delta F / 6\sigma (F_o)^2)]^2$, where $w' = 1/\sum_{1}^{n} A_r T_r(x)$ with coefficients A_r for the Chebyshev polynomial $A_r T_r(x)$, where x was $F_c/F_c(\max)$ having the following values: 1.695, -1.490, 1.523, -0.609 and 0.262 for HL; 1.346, 0.546 and 0.798 for $Ni^{II}L_2$; 5.698, -7.715, 4.870 and -2.342 for Cu^{II}L₂. The calculations were carried out with the CRYSTALS package programs [34] running on a PC. The structure of Co^{II}L₂ was solved by SHELXS-97 [35] and refined using the least-square method on F^2 . The drawings of the molecular structures were obtained with the help of CAMERON [36]. The atomic scattering factors were taken from International Tables for X-ray Crystallography [37]. Crystallographic data (excluding structure

factors) have been deposited with the Cambridge Crystallographic Data Centre.

2.4. Spectroscopy

The UV-visible spectra were recorded on a Hewlett– Packard 8452 A spectrophotometer. The oscillator strengths were extracted from the spectra through the relation [38]:

$$f = 4.315 \times 10^{-9} \int \varepsilon \,\mathrm{d}\nu,\tag{7}$$

where the integration extends over the entire absorption band and v is the wavenumber (cm^{-1}) .

2.5. NLO measurements

The quadratic molecular hyperpolarizabilities (β) were measured by the EFISH technique [30,31]. The light source was a nanosecond (10 ns) Nd-YAG pulsed (10 Hz) laser (B.M. Industries) operating at $\lambda = 1.064$

Table 1 Crystal data, data collection and refinement for HL, Ni^{II}L, Cu^{II}L, and Co^{II}L

	HL	$Ni^{II}L_2$	$Cu^{II}L_2$	$Co^{II}L_2$
Crystal data				
Chemical formula	$C_{17}H_{19}N_3O_3$	C ₁₇ H ₁₈ N ₃ Ni _{0.5} O ₃	$C_{17}H_{18}Cu_{0.5}N_3O_3$	C ₁₇ H ₁₈ Co _{0.5} N ₃ O ₃
Molecular weight	313.36	341.70	344.12	341.81
Crystal size (mm)	0.7 imes 0.4 imes 0.1	0.8 imes 0.55 imes 0.1	0.2 imes 0.1 imes 0.05	$0.2 \times 0.15 \times 0.1$
Crystal system	monoclinic	triclinic	triclinic	monoclinic
Space group	$P2_1/c$	$P\overline{1}$	$P\overline{1}$	C2/c
a (Å)	16.272(2)	7.8106(12)	7.2215(12)	25.763(6)
b (Å)	7.900(1)	9.6823(15)	8.3765(12)	9.931(4)
<i>c</i> (Å)	13.288(1)	10.7656(15)	13.5007(18)	12.657(3)
α (°)	90	84.63(2)	77.88(2)	90
β (°)	114.04(1)	81.65(2)	88.84(2)	96.62(3)
γ (°)	90	86.04(2)	78.94(2)	90
$V(Å^3)$	1559.99	800.7	783.49	3216.6
Ζ	4	2	2	8
F(000)	664.15	358.35	359.33	1428
ρ (calcd.) (Mg/m ³)	1.334	1.417	1.458	1.412
μ (Mo K α) (cm ⁻¹)	0.871	6.597	7.510	5.890
<i>T</i> (K)	180	293	160	293
Data collection				
Radiation (Mo Ka) (Å)	0.71073	0.71073	0.71073	0.71073
Scan mode	ϕ	ϕ	ϕ	ϕ
Scan range	$0 < \phi < 200$	$0 < \phi < 250.5$	$0 < \phi < 250.5$	$0 < \phi < 250.6$
2θ range	$3.3 < 2\theta < 52.1$	$3.8 < 2\theta < 48.2$	$5.1 < 2\theta < 48.3$	$4.40 < 2\theta < 46.5$
Reflections collected	14 594	6459	6433	13077
Reflections unique (R_m)	2969 (0.058)	2382 (0.02)	2364 (0.11)	2484 (0.13)
Reflections observed	$1392[I > 3\sigma(I)]$	$1997[I > 3\sigma(I)]$	$1131[I > 3\sigma(I)]$	$2230[I > 2\sigma(I)]$
Refinement				
Refinement on	F	F	F	F^2
R	0.0324	0.048	0.0616	0.0622
wR	0.0361	0.057	0.0609	0.1494
Number of variables	213	215	215	215
$\Delta \rho_{\rm max}$ (e Å ⁻³)	0.112	0.606	0.599	0.232
$\Delta \rho_{\rm min}$ (e Å ⁻³)	-0.124	-0.306	-0.479	-0.223
Goodness-of-fit	1.02	1.07	1.13	0.90

µm. The outcoming Stokes-shifted radiation at 1.907 µm generated by Raman effect in a hydrogen cell (1 m long, 50 bar) was used as the fundamental beam for second harmonic generation (SHG). Chloroform was used as a solvent for any EFISH measurement. The centrosymmetry of the solution was broken by dipolar orientation of the chromophores with a high voltage pulse (5 kV) synchronized with the laser pulse. The dipole moments were measured independently by a classic method based on the Guggenheim theory [39]. Further details of the experimental methodology and data analysis are reported elsewhere [40].

2.6. Calculation of NLO response

The all-valence INDO/S (intermediate neglect of differential overlap) method [41,42], in connection with the sum-over-state (SOS) formalism [43], was employed. Details on the computationally efficient INDO-SOSbased method for describing second-order molecular optical nonlinearities have been reported elsewhere [23,24]. The calculation of electronic transitions and molecular hyperpolarizabilities was performed using the commercially available MSI software package INSIGHT II (4.0.0) [44]. In the present approach, the closed-shell restricted Hartree-Fock (RHF) formalism was employed. The monoexcited configuration interaction (MECI) approximation was employed to describe the excited states. The 100 energy transitions between the 10 highest occupied molecular orbitals and the 10 lowest unoccupied ones were chosen to undergo CI mixing. Metrical parameters used for the calculations were taken from the present crystal structure of HL. The structure of DANS was a model obtained from the HL backbone.

3. Results and discussion

3.1. Synthesis and characterization

The HL ligand has been obtained by Schiff base condensation in the presence of a drop of sulfuric acid, a

procedure previously used in the case of weakly reacting amines, such as 4'-nitroaniline [45,46]. The completeness of the reaction can be easily monitored by ¹H NMR spectroscopy to verify the disappearance of the CHO signal located at 9.47 ppm in the starting (diethylamino)salicylaldehyde and the appearance of the imine signal at 8.41 ppm. Metal complexes were obtained by simple mixing of HL with the appropriate metal(II) acetate in ethanol. Contrary to $Ni^{II}L_2$ and $Cu^{II}L_2$, Co^{II}L₂ was found to be very weakly soluble in most common solvents, and no crystals suitable for X-ray experiments were obtained by recrystallization. On the other hand, large single crystals were easily obtained by diffusion. The thermal stability of the chromophores rises from 260 (HL) to 320 °C (Co^{II}L₂) after metal complexation. This observation may deserve some interest, as a good thermal stability has become an important prerequisite for various practical applications.

3.2. Description of the structures

Figs. 1–4 illustrate the atomic numbering scheme employed for molecules HL, Ni^{II}L₂, Cu^{II}L₂, and Co^{II}L₂, respectively. The X-ray structure analysis of HL reveals $P2_1/c$ space group, with one HL entity in the asymmetric unit. Except for the ethyl substituents of the amine, the molecule is nearly planar, with an angle of 10°77 between the two phenyl groups. This value is indicative of significant conjugation of the whole π -system and hence large intramolecular charge transfer upon electron excitation from the amine to the nitrosubstituent.

Ni^{II}L₂ and Cu^{II}L₂ crystallize in the triclinic $P\bar{1}$ space group. The asymmetric unit contains half a metal atom and one L⁻ entity, with the metal atom located at the inversion center, in both cases. Therefore, Ni^{II}L₂ and Cu^{II}L₂ are centrosymmetric molecules, which cannot exhibit any quadratic NLO effect ($\beta = 0$). For symmetry reason, the geometry is strictly planar around the metal centers in both molecules. Centrosymmetry is a natural trend in nickel(II) complexes. By contrast, the geometry of bis-bidentate Schiff base copper(II) complexes can be the result of steric and electronic effects which result in various intermediate geometries between square planar



Fig. 1. Atom labeling scheme and thermal vibration ellipsoids for HL.



Fig. 2. Atom labeling scheme and thermal vibration ellipsoids for Ni^{II}L₂. H atoms are omitted for clarity.



Fig. 3. Atom labeling scheme and thermal vibration ellipsoids for Cu^{II}L₂. H atoms are omitted for clarity.

and tetrahedral [47–49]. However, no distortion is observed in the coordination sphere of the present $Cu^{II}L_2$, a situation that may tentatively be related to either a modest steric hindrance in the nitrophenyl moieties or a very negative reduction potential in the complex, according to the analysis provided in the previous investigations [47–49].

The coordination spheres of Ni^{II}L₂ and Cu^{II}L₂ (bond lengths and angles) are compared in Table 2, and found rather similar. A slight shortening of the metal–ligand bond lengths is observed on passing from the copper(II) to the nickel(II) derivative. These structural features, which favor steric hindrance between the two L⁻ fragments, can account for the distortion of the ligands in both complexes. Indeed, the angles between the phenyl groups are equal to 72.69° and 52.31°, for $Ni^{II}L_2$ and $Cu^{II}L_2$, respectively. These observations suggest a reduced conjugation, versus that of the free HL ligand.

 $Co^{II}L_2$ crystallizes in the monoclinic C2/c space group. The asymmetric unit contains half a metal atom and one L⁻ entity, with the metal atom located on the twofold axis. By contrast with the previous Ni^{II}L₂ and Cu^{II}L₂ complexes, Co^{II}L₂ reveals a pseudo-tetrahedral coordination sphere, in which the two L⁻ fragments refer to each other by the twofold axis. The angle between the two O(1)–Co(1)–N(1) planes of the molecule is equal to 99.34°. The present geometry strongly reduces the steric hindrance and therefore the conformation of the L⁻ entities is close to that of the free ligand. In particular, the observation of an angle equal to 12.42°



Fig. 4. Atom labeling scheme and thermal vibration ellipsoids for Co^{II}L₂. H atoms are omitted for clarity.

Table 2 Selected bond lengths (A in Å) and angles (B in °) in the coordination sphere of Ni^{II}L₂, Cu^{II}L₂, and Co^{II}L₂

(A)			
Ni(1)–O(1)	1.815(2)		
Ni(1)–N(1)	1.907(3)		
Cu(1)–O(1)	1.859(5)		
Cu(1)–N(1)	2.008(6)		
Co(1)–O(1)	1.859(5)		
Co(1)–N(1)	1.983(6)		
(\mathbf{D})			
	100.0		1160(4)
O(1)-Ni(1)-O(1)#1	180.0	O(1)-Co(1)-O(1)#2	116.9(4)
O(1)-Ni(1)-N(1)	93.1(1)	O(1)-Co(1)-N(1)	96.5(3)
O(1)–Ni(1)–N(1)	86.9(1)	O(1)#2-Co(1)-N(1)	110.1(2)
N(1)-Ni(1)-N(1)#1	180.0	N(1)-Co(1)-N(1)#2	128.2(4)
O(1)-Cu(1)-O(1)#1	180.0		
O(1)–Cu(1)–N(1)	90.9(2)		
O(1)–Cu(1)–N(1)	89.1(2)		
N(1)-Cu(1)-N(1)#1	180.0		

Symmetry transformations used to generate equivalent atoms: #1 2 - x, 1 - y, 2 - z; #2 2 - x, y, 3/2 - z.

between the two phenyl groups favors the conjugation over the whole extent of each ligand, allowing a better use of π -electron system for NLO purpose.

3.3. Optical spectroscopy

The absorption spectra of HL and DANS in dichloromethane are compared in Fig. 5. Both exhibit an intense band at 434 nm ($\varepsilon = 34900 \text{ M}^{-1} \text{ cm}^{-1}$) and 439 nm ($\varepsilon = 26200 \text{ M}^{-1} \text{ cm}^{-1}$), for HL and DANS, respectively. The absorption maxima recorded in non-protic solvents of different polarities are gathered in Fig. 6 versus the Reichardt solvent parameter [50]. It can be observed that both bands exhibit a large positive solvatochromism (red shift in solvent of higher polarity). This behavior is usually associated with changes in dipole moments between the ground (g) and the excited states (e) upon excitation ($\Delta \mu > 0$ in the case of positive solvatochromism), and is indicative of large quadratic hyperpolarizabilities, according to the well known two level description of the NLO response, through the relation [51,52]:

$$\beta = \sum_{i} \frac{3e^{2}\hbar f \Delta \mu}{2m(\Delta E)^{3}} \times \frac{(\Delta E)^{4}}{\left((\Delta E)^{2} - (2\hbar\omega)^{2}\right)\left((\Delta E)^{2} - (\hbar\omega)^{2}\right)},$$
(1)



Fig. 5. Electronic spectra for HL in dichloromethane. DANS (dotted line) is given as a reference.



Fig. 6. Solvatochromism versus the Reichardt empirical solvent parameter for HL. The solvatochromism of DANS (white diamond, dotted line) is given as a reference. The slopes are equal to 60, and 73 for HL and DANS, respectively.

in which ΔE is the energy of the $g \rightarrow e(i)$ transition, f its oscillator strength, and $h\omega$ the energy of the incident laser beam. In most push-pull organic chromophores, the summation in Eq. (1) can be restricted to a single and intense low-lying transition. The examination of Fig. 6 may suggest that the $\Delta \mu$ parameter for HL is lower than that of DANS. However, it has to be reminded that the estimation of $\Delta \mu$ by means of solvato-chromism is somewhat ambiguous and not fully reliable in some cases [53,54].

Table 3

Comparison of experimental (in dichloromethane) and INDO spectroscopic data (λ_{max} in nm, ε in M⁻¹ cm⁻¹ and oscillator strength *f*) for HL and DANS

	Expe	rimental		INDO		
	$\lambda_{\rm max}$	f	Solvatochromism ^a	$\lambda_{\rm max}$	f	$\Delta \mu$
HL	434	0.70	60	378	1.35	11.6
DANS	439	0.59	73	397	1.16	18.4

^a Slopes in Fig. 6.



Fig. 7. Electronic spectra in dichloromethane for HL (1) compared with those of $Cu^{II}L_2$ (2), $Ni^{II}L_2$ (3), and $Co^{II}L_2$ (4). The extinction coefficients for the ligand are indicated on the left and for the complexes on the right.

The aforementioned observations can be compared with the INDO-derived spectroscopic properties gathered in Table 3. The INDO data are blue shifted by about 50 nm and the oscillator strengths are overestimated versus the experiment. However, the same trend for higher energy and intensity and reduced solvatochromic shift on passing from DANS to HL is evidenced both experimentally and theoretically. Therefore, we can assume that the calculated spectra roughly fit the experimental data, in order to relate the NLO response and the INDO-based electronic properties.

The absorption spectra of Cu^{II}L₂, Ni^{II}L₂, and Co^{II}L₂ are compared with that of HL in Fig. 7. The copper and nickel derivatives exhibit reduced oscillator strengths (per L⁻ fragment) and blue shifts versus HL with absorption maxima equal to 431 nm ($\varepsilon = 53100$ $M^{-1} \text{ cm}^{-1}$) and 394 nm ($\varepsilon = 40500 \text{ M}^{-1} \text{ cm}^{-1}$), respectively. These modifications can be related to the molecular structures of both complexes. As discussed in the previous section, the planar geometry of the ligands is hampered by steric hindrance in $Ni^{II}L_2$. The resulting lack of conjugation is consistent with the changes observed in the intensity and energy of the charge transfer transition. In Cu^{II}L₂, the ligands are slightly more planar, in relation to longer metal-ligand bond lengths. Therefore, the same qualitative modifications are evidenced in the electronic spectra on passing from HL to Cu^{II}L₂, however to a less extent. In striking contrast with the previous complexes, Co^{II}L₂ exhibits a pseudotetrahedric coordination around the metal center. As a main consequence, no steric hindrance takes place in the ligand, the absorption spectrum of which is therefore closely related to that of HL. Nevertheless, the presence of the metal leads to a slight red shift and increase of the oscillator strength per ligand unit, with $\lambda_{max} = 446$ nm and $\varepsilon = 76150 \text{ M}^{-1} \text{ cm}^{-1}$ (f = 1.55). Both effects suggest a possible β enhancement on passing from HL to

47

b

DANS			
	EFISH data	a	INDO data
	μ (D)	$eta_{1.097~\mu\mathrm{m}}$	$\beta_{1.097~\mu\mathrm{m}}$
DANS ^a	6.6	73	70

66

110

Table 4 Molecular hyperpolarizabilities for HL and $\mathrm{Co}^{\mathrm{II}}L_2$ compared with DANS

^a Ref. [10].

HL

Co^{II}L₂

^bNo data available for open shell chromophores.

6.4

7.1

 $Co^{II}L_2$, according to Eq. (1). This will be discussed in the next section.

3.4. NLO properties

Ni^{II}L₂ and Cu^{II}L₂ are centrosymmetric molecules and, therefore, possess strictly vanishing molecular hyperpolarizabilities. By contrast, the β values of HL and Co^{II}L₂ measured by electric field second harmonic (EFISH) technique are compared with that of DANS in Table 4. Before discussing the effect of metal complexation in the NLO response, it is interesting to compare the properties of HL and DANS [10].

Nicoud and Twieg have pointed out that the β values of stilbene analogs change significantly with the incorporation of nitrogen atoms in the π -conjugated bridge. In particular, they have reported that benzylidene nitroanilines exhibit reduced oscillator strengths and blue shifts versus their nitrostilbene analogs, which results in β values divided by 3–4 [55]. Surprisingly, these effects do not take place in the present HL ligand, although the data clearly reveal a slight β reduction, with values equal to 73 and 66×10^{-30} cm⁵ esu⁻¹, for DANS and HL, respectively. At first, the presence of an hydroxy substituent with donating capability in HL might account for this effect.

In order to verify this possibility, the INDO calculated β values are provided in Table 4. Indeed, the calculated data reveal that the β value of HL is only slightly reduced versus that of DANS. Within the framework of

the sum-over-state (SOS) perturbation theory, β is related to all excited states of a molecule [43] and can be partitioned into two contributions, so-called β_{2level} and $\beta_{3\text{level}}$ terms [24]. Analysis of term contributions reveals that in the present case, $\beta_{2\text{level}}$ (Eq. (1)) dominates the nonlinearity, as is usually the case [24]. It can be related to a single HOMO and LUMO-based transition $(1 \rightarrow 4)$, responsible for 85% and 84% of β_{2level} for HL and DANS, respectively (Table 5). Therefore, we can make the assumption that understanding the changes occurring for these transitions on passing from DANS to HL can provide qualitative understanding of the origin of the β differences for both chromophores. The orbitals are compared in Fig. 8. The calculation reveals that the HOMO-LUMO energy gap is enlarged and the charge transfer reduced on passing from DANS to HL, which is consistent with a blue shift, a reduced $\Delta \mu$ factor, and hence a reduced hyperpolarizability. Nevertheless, and contrary to the intuition, the hydroxy substituent seems not to be directly involved in the charge-transfer process in HL.

A direct comparison of the NLO response of HL and $Co^{II}L_2$ raises the important issue of β calculations for open-shell molecules. To the best of our knowledge, the only ones reported with ZINDO are due to Marks and coworkers [27,28]. However, they were restricted to chromophores with spin states equal to 1/2. In Co^{II}L₂, the metal center possesses the d^7 configuration, which in tetrahedric environment corresponds to a spin state S = 3/2. In this case, the β calculation cannot be performed using our ZINDO release. Nevertheless, a theoretical hyperpolarizability of Co^{II}L₂ can be evaluated from the tensorial sum of the individual hyperpolarizability coefficients of the ligands. In this model, no enhancement is expected as compared to the response of the individual ligands. Assuming a one-dimensional character for the NLO tensor of the subunit, β has only one large coefficient along the charge-transfer axis (Ox), namely $\beta_{\text{ligand}} = \beta_{xxx}$. In the C_2 symmetry, this will lead to a complex having the following β tensor component [56]:

Table 5 Energies (λ_{max} in nm), oscillator strengths (*f*), dipole moment changes ($\Delta \mu$ in D), contribution in the β_{2level} , and composition of the transitions for HL and DANS

Transition	λ_{\max}	f	$\Delta \mu$	State (%) ^a	Composition ^b of CI expansion
HL					
$1 \rightarrow 4$	378	1.35	11.6	85	$0.782\chi_{60\to 61} - 0.472\chi_{60\to 62}$
$1 \rightarrow 19$	208	0.53	7.6	3	$-0.577\chi_{54\to 61}+0.415\chi_{60\to 63}$
DANS					
$1 \rightarrow 4$	397	1.16	18.4	84	$0.859\chi_{57\to 58}$
$1 \rightarrow 8$	265	0.21	24.3	5	$-0.748\chi_{56\to 58}-0.412\chi_{57\to 58}$

^a Contribution of the *i*th transition to $\beta_{2\text{level}} \left(\text{state } \% = \frac{\beta_{g \rightarrow e(i)}}{\sum_{i} \beta_{g \rightarrow e(i)}} \right).$

^b Orbital 60 is the HOMO and orbital 61 the LUMO for HL. Orbital 57 is the HOMO and orbital 58 the LUMO for DANS.



Fig. 8. Frontier orbitals with their related energies for HL (left) and DANS (right). The electron densitities (%) are indicated on the dominant fragments.

$$\beta_{ZYY(\text{complex})} = 2\beta_{xxx}\cos\theta\sin^2\theta,\tag{2}$$

$$\beta_{ZZZ(\text{complex})} = 2\beta_{xxx}\cos^3\theta \tag{3}$$

all other components of the tensor are weak (θ is defined as the angle between the charge-transfer axis (Ox) of the subunit and the twofold axis (OZ) of the metal complex, according to Fig. 9). Within the framework of the EFISH method, the measured β value is the projection of the hyperpolarizability along the dipole moment (C^2 axis in Fig. 9). Therefore, $\beta = \beta_Z$. With a laser operating at 1.907 µm, one can assume that no absorption takes place in the materials. Therefore, the Kleinman conditions can be applied [57,58]:

$$\beta_Z = \beta_{ZXX} + \beta_{ZYY} + \beta_{ZZZ},\tag{4}$$

which leads to

$$\beta_Z = 2\beta_{xxx}\cos^3\theta + 2\beta_{xxx}\cos\theta\sin^2\theta.$$
 (5)



Fig. 9. Model geometry for the $Co^{II}L_2$ chromophore.

With the assumption that the NLO response of Co^{II}L_2 is the sum of the contributions of the ligand subunits in C_2 symmetry (Fig. 9), the charge-transfer axis is the same for HL and for the organic subunits in Co^{II}L_2 . Therefore, the ZINDO calculated β for HL and the crystal data for Co^{II}L_2 lead to $\theta = 43^\circ$. This provides the following relationship:

$$\beta_{\text{(complex)}} = 1.46 \times \beta_{\text{(ligand)}}.$$
 (6)

This expression has to be compared to the experimental data (Table 3), which indicates $\beta_{\text{(complex)}} = 1.67\beta_{\text{(ligand)}}$. Within the approximation of this model, a β enhancement of 14% can be inferred upon metal complexation. It is interesting to compare this β enhancement with those previously reported in other Schiff base complexes. Several reports of metal salen-based NLO chromophores have pointed out that large β enhancements (more than twice the hyperpolarizabilities of the free ligands in some cases) can be obtained in planar geometries [29,45,59]. In these previous investigations, the enhancements were not related to geometric effects but to electronic effects, only. By contrast, the present β enhancement $(\beta_{(complex)} = 1.67\beta_{(ligand)})$ arises from a combination of geometric and, to a lesser extent, electronic effects. These observations seems to indicate that tetrahedral geometry in bis(salicylaldiminato)metal Schiff base complexes can provide an alternative route towards efficient enhancements of the NLO response at the microscopic level.

4. Conclusion

A Schiff base ligand has been presented with several of its metal(II) complexes. Depending on the nature of the metal center, the geometry of the resulting molecule can be tuned from square planar to pseudo-tetrahedral. While the nickel(II) and copper(II) derivatives are centrosymmetric, and therefore exhibit vanishing hyperpolarizabilities, the experimental data indicate that $\beta_{(complex)}$ is equal to $1.67\beta_{(ligand)}$ for Co^{II}L₂. Beside the effect of the coordination on the overall charge-transfer geometry, a β enhancement of 14% is evidenced, related to the electronic effect induced by the metal center, while the thermal stability rises from 260 to 320 °C.

Several bis(salicylaldiminato) metal complexes with quadratic NLO properties have been appeared in the literature [18,19]. It has previously been reported that the metal can lead to β enhancement by use of the d orbitals [45] and β modulation by magnetic transition occurring at the metal center [60]. The present study suggests that cobalt(II) metal complexes, which exhibit a trend towards tetrahedral geometry, can lead to extended chromophores with noncentrosymmetric molecular geometry and high thermal stability. These structural features could also provide a route towards

extended NLO architectures, or chromophores with octupolar geometries [61].

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 231301 (HL), 231302 (Ni^{II}L₂), 231303 (Cu^{II}L₂), and 231304 (Co^{II}L₂). Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1E2, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc. cam.ac.uk, or www:http://www.ccdc.cam.ac.uk).

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