

Synthesis, Structure, Spectroscopic Studies and *ab-initio* Calculations on First Hyperpolarizabilities of N,N'-Bis(2-hydroxy-1-naphthyl-methylidene)-1-methyl-1,2-diaminoethane-N,N',O,O'-copper(II)

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N,N'-Bis(2-hydroxy-1-naphthylmethylidene)-1-methyl-1,2-diaminoethane-N,N',O,O'-copper(II) has been synthesized, and characterized by FT-IR and UV/vis spectroscopies. Its crystal structure has been determined by X-ray diffraction analysis. The maximum absorption wavelengths recorded by linear optical experiments are estimated in the UV region to be shorter than 450 nm, showing good optical transparency to the visible light. It may thus possess first hyperpolarizabilities with non-zero values for nonlinear optical (NLO) applications. *Ab-initio* quantum chemical calculations of the electric dipole moments (μ) and the first static hyperpolarizabilities (β) were carried out. The computational results suggest that the complex may indeed have microscopic NLO behavior with non-zero values.

Key words: Copper(II) Complex, UV-visible Spectroscopy, Crystal Structure, First Hyperpolarizability, Electric Dipole Moment

Introduction

In the last decades, nonlinear optics (NLO) has become a key field in the area of photonics and optoelectronics [1–4]. Organic molecules have been intensively studied with respect to their potential applications as NLO media [5–7]. Large optical nonlinearity could be seen in organic conjugated molecules having an electron acceptor group at one end and a donor group at the opposite end [8]. Davydov and co-workers [9] concluded that dipolar aromatic molecules possessing an electron donor group and an electron acceptor group contribute to large optical nonlinearity arising from the intramolecular charge transfer (CT) between the two groups of opposite nature. Organic molecules with π -electron delocalization are currently of wide interest as NLO materials with potential applications in optical switches and other NLO devices [10]. Although a great deal of work has been carried out on the investigation

of the NLO properties for organic materials, the optical nonlinearities of metal complexes have started to be actively studied more recently [5,11]. Compared to organic compounds, metal complexes offer a larger variety of structures, the possibility of high environmental stability, and a diversity of electronic properties by virtue of the coordinated metal center.

The metal complexes are rather important since they are expected to exhibit large molecular hyperpolarizabilities due to the transfer of electron density between the metal atom and the ligands. The encouraging NLO results prompted us to focus our work on the metal complexes. This paper reports the synthesis, FT-IR study, crystal structure with X-ray diffraction analysis and linear optical characterization with UV-visible spectroscopy for the title copper(II) complex (Fig. 1). The main aim of this work is to relate the microscopic NLO mechanism with the structural and linear optical properties. So, we also present here an *ab-initio* study

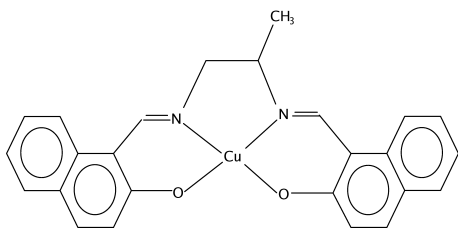


Fig. 1. Chemical structure of the title compound.

utilizing the Finite Field (FF) method on first static hyperpolarizabilities.

Experimental Section

Reagents and techniques

1,2-Diaminopropane, 2-hydroxy-1-naphthaldehyde and copper(II) acetate monohydrate were purchased from Aldrich Chemical Co. Methanol and ethanol were purchased from Riedel. Elemental (C, H, N) analyses were carried out by standard methods. FT-IR spectra were measured with a Perkin-Elmer Model Bx 1600 instrument with the samples as KBr pellets in the 4000–400 cm^{-1} range. UV-visible spectra were measured using a Cary 1-E UV-visible spectrometer with 1.0 cm quartz cells.

Preparation of *N,N'*-bis(2-hydroxy-1-naphthylmethylidene)-1-methyl-1,2-diaminoethane-*N,N',O,O'*-copper(II)

The ligand was prepared by reaction of 1,2-diaminopropane (1 mmol) with 2-hydroxy-1-naphthaldehyde (2 mmol) in hot ethanol (100 ml). The yellow compound precipitated from solution on cooling. The title compound was prepared by addition of 1 mmol of copper(II) acetate monohydrate in 40 ml of hot ethanol to 1 mmol of ligand in 80 ml of boiling ethanol. The mixture was stirred, and then cooled to r.t. to give a precipitate, which was collected by suction filtration. Recrystallization from ethanol afforded single crystals suitable for X-ray structure determination. $\text{C}_{25}\text{H}_{20}\text{N}_2\text{O}_2\text{Cu}$: calcd. C 67.63, H 4.54, N 6.31; found: C 67.60, H 4.50, N 6.28. UV/vis (CH_3OH): $\lambda_{\text{max}}(\lg \epsilon) = 250 \text{ nm}$ (0.88), 320 nm (0.35), 375 nm (0.20). IR (KBr, cm^{-1}): $\nu(\text{C}=\text{N})$ 1618, $\nu(\text{C}=\text{C})$ 1503, 1458, $\nu(\text{C}-\text{O})$ 1122, 1181. The chemical structure of the title molecule is given in Fig. 1.

X-ray structure determination

Diffraction measurements were made on three-circle CCD diffractometers using graphite-monochromated $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at r.t. for the compound. The intensity data were integrated using the SAINT [12] program. Absorption, Lorentz and polarisation corrections were applied. The structures were solved by direct meth-

Table 1. Crystal data and structure refinement for the title compound.

Empirical formula	$\text{C}_{25}\text{H}_{20}\text{N}_2\text{O}_2\text{Cu}$
Formula weight	443.97
Temperature	293(2) K
Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell dimensions	$a = 14.0348(11) \text{ \AA}$ $b = 8.4956(10) \text{ \AA}$; $\beta = 112.706(2)^\circ$ $c = 17.4470(13) \text{ \AA}$
Volume	$1919.0(3) \text{ \AA}^3$
Z	4
Density (calculated)	1.537 g cm^{-3}
Absorption coefficient	1.164 mm^{-1}
Reflections collected	12173
θ Range for data collection	2.41 to 27.51°
Index ranges	$-18 \leq h \leq 12$, $-11 \leq k \leq 11$, $-21 \leq l \leq 22$
Independent reflections	4379 [$R_{\text{int}} = 0.1259$]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4379 / 0 / 272
Goodness-of-fit on F^2	$S = 0.969$
R Indices [$I > 2\sigma(I)$]	$R_1 = 0.0649$, $wR_2 = 0.1112$
Largest diff. peak and hole	0.632 and $-0.471 \text{ e \AA}^{-3}$

ods and refined using full-matrix least-squares against F^2 using SHELXTL [12]. All non-hydrogen atoms were assigned anisotropic displacement parameters and refined without positional constraints. Hydrogen atoms were included in idealised positions with isotropic displacement parameters constrained to 1.5 times the U_{equiv} of their attached carbon atoms for methyl hydrogens, and 1.2 times the U_{equiv} of their attached carbon atoms for all others. The crystallographic data used for the intensity data collection and some features of the structure refinement are listed in Table 1. Selected bond lengths and angles are listed in Table 2, and an ORTEP view of the molecular structure is shown in Fig. 2. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-297108 [13].

Theoretical Calculations

As the first step of our calculation, the geometry taken from the crystallographic data [13] was optimized in the UHF (unrestricted open-shell Hartree-Fock) level. The geometry is considered converged even if the displacement is larger than the cut-off value when the forces are two orders of magnitude smaller than the cut-off value [14]. This criterion was very important in geometry optimization. The electric dipole moments and the first hyperpolarizability tensor components were calculated by the FF scheme [15]. The

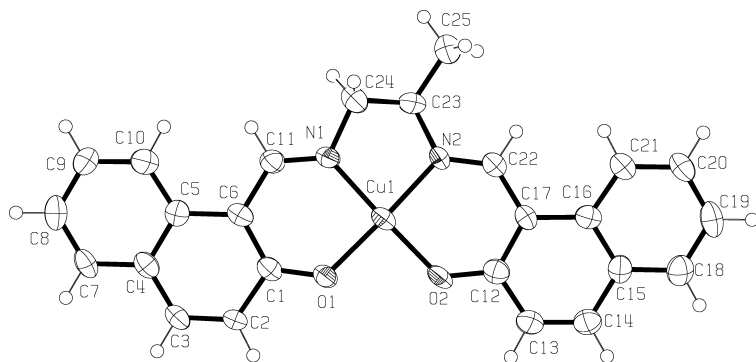


Fig. 2. The molecular structure of the title copper(II) complex. Displacement ellipsoids are plotted at the 50% probability level and H atoms are presented as spheres of arbitrary radii.

Table 2. Some selected bond lengths [Å] and angles [°] for the title compound.

Cu(1)–O(2)	1.887(3)	Cu(1)–O(1)	1.899(3)
Cu(1)–N(1)	1.919(4)	Cu(1)–N(2)	1.923(4)
O(1)–C(1)	1.302(6)	O(2)–C(12)	1.319(6)
N(1)–C(11)	1.290(6)	N(1)–C(24)	1.476(6)
N(2)–C(22)	1.279(6)	N(2)–C(23)	1.476(6)
O(2)–Cu(1)–O(1)	89.48(1)	O(2)–Cu(1)–N(1)	178.06(2)
O(1)–Cu(1)–N(1)	92.46(2)	O(2)–Cu(1)–N(2)	93.09(2)
O(1)–Cu(1)–N(2)	177.32(2)	N(1)–Cu(1)–N(2)	84.97(2)
C(1)–O(1)–Cu(1)	127.7(3)	C(12)–O(2)–Cu(1)	128.2(3)
C(11)–N(1)–C(24)	119.0(4)	C(11)–N(1)–Cu(1)	127.9(4)
C(24)–N(1)–Cu(1)	113.1(3)	C(22)–N(2)–C(23)	122.9(4)
C(22)–N(2)–Cu(1)	125.5(4)	C(23)–N(2)–Cu(1)	110.8(3)

relativistic ECP basis set LanL2mb [16] was employed in all calculations of the complex so that the relativistic effects of heavy atoms on β were taken into account. All μ and β calculations were performed using GAUSSIAN98W [17], on an Intel Pentium IV 1.7 GHz processor with 512 MB RAM and Microsoft windows as the operating system.

The components of the first hyperpolarizability can be calculated using the following equation:

$$\beta_i = \beta_{iii} + 1/3 \sum_{i \neq j} (\beta_{ijj} + \beta_{jij} + \beta_{jji}). \quad (1)$$

Using the x , y and z components, the magnitude of the first hyperpolarizability tensor can be calculated by:

$$\beta_{\text{tot}} = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2}. \quad (2)$$

The complete equation for calculating the magnitude of first hyperpolarizability from the GAUSSIAN98W output is given as follows [18]:

$$\beta_{\text{tot}} = [(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{yzz} + \beta_{yxx})^2 + (\beta_{zzz} + \beta_{zxx} + \beta_{zyy})^2]^{1/2}. \quad (3)$$

Since these β values of the GAUSSIAN98W output are reported in atomic units (a. u.), the calculated β values in this paper have been converted into electrostatic units (esu) ($1 \text{ a. u.} = 8.6393 \times 10^{-33} \text{ esu}$). To calculate all the electric dipole moments and the first hyperpolarizabilities, the origin of the cartesian coordinate system (x, y, z) = (0, 0, 0) has been chosen at the center of mass of the compound in Fig. 1.

Results and Discussion

FT-IR study

The FT-IR spectrum of the title compound reveals the bands at $\nu(\text{C}=\text{C})$ 1503, 1458, $\nu(\text{C}-\text{O})$ 1122, 1181 and $\nu(\text{C}=\text{N})$ 1618 cm^{-1} . The IR spectrum of the free Schiff base ligand shows a broad band at 3250–3420 cm^{-1} , which is likely to be a superposition of bands from alcohol-OH and phenol-OH groups. The $\nu(\text{OH})$ band is absent in the IR spectrum of the complex. This indicates that the alcoholic and phenolic protons are lost upon complexation. The $\nu(\text{C}=\text{N})$ band (*ca.* 1636 cm^{-1}) of the free ligand is shifted slightly to lower frequency (*ca.* 1618 cm^{-1}) upon complexation, suggesting that the imino nitrogen atoms are coordinated to the copper ion.

UV-visible spectroscopy

The solution electronic absorption spectral studies regarding potential NLO properties are important for two specific reasons. Firstly, it is necessary to know the transparency region. Secondly, the solvatochromic behavior of the sample is generally considered as indicative of high molecular first hyperpolarizability [19]. The linear optical and NLO properties of donor-acceptor substituted diazabutadienes and hexatrienes have been investigated in a combined

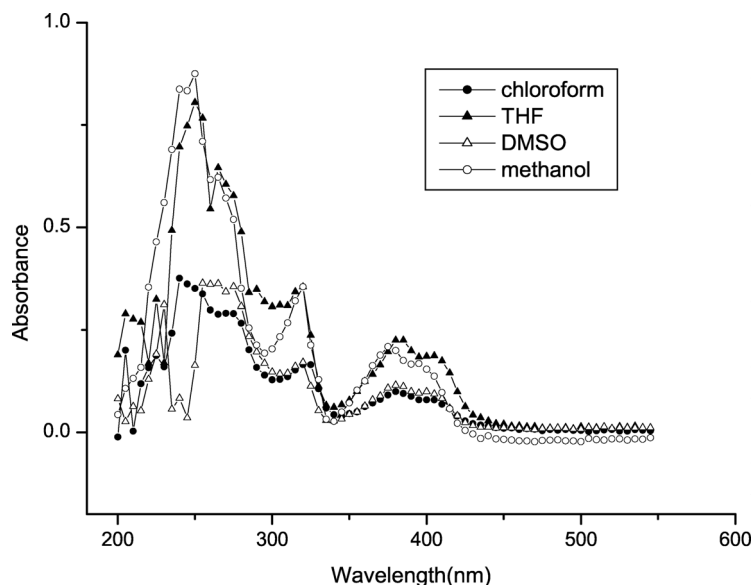


Fig. 3. UV/vis absorption spectra of the title compound in chloroform, THF, DMSO and methanol.

theoretical and experimental study by Dworczak *et al.* [20]. The theoretical calculations lead to a more pronounced bathochromic effect and increased β values. If one considers the azines described by Dworczak *et al.* as polymethine type compounds, replacement of a methine carbon at an even position by an electronegative element should not only lead to a bathochromic shift of the longest wavelength absorption band ($\lambda_{\max} = 394$ nm), but also to an increase in β . Ren *et al.* [21] have shown that all absorption maxima of square-pyramidal zinc complexes are located in the UV region. All of the compounds exhibit solvatochromism, *i.e.* their maximum absorption peaks show hypsochromic or bathochromic shifts. It is well known that solvatochromism can be based on a Two-Level model, which is valid for a large number of organic NLO materials. It is reasonable to say that the solvatochromism of the investigated compound indicates the change of dipole moments in the ground and excited states verifying the existence of intramolecular CT and non-zero NLO responses. The NLO properties and UV-visible studies of push-pull ferrocene complexes containing heteroaromatic rings in the conjugation chain were investigated by Justin Thomas *et al.* [19]. High bathochromic shift has been generally considered as indicative of high β values, and hence potential NLO properties have been observed in dichloromethane.

The maximum absorption wavelengths (λ) and molar extinction coefficients (ϵ) obtained from

Table 3. The maximum absorption wavelengths and molar extinction coefficients λ , nm (ϵ , $\text{M}^{-1} \text{cm}^{-1}$), respectively, obtained from the UV/vis spectral analysis of the title compound in solvents of different polarity.

Solvents [λ , nm (ϵ , $\text{M}^{-1} \text{cm}^{-1}$)]			
Chloroform	THF	DMSO	Methanol
379.9(9914)	385.0(22559)	400.0(9919)	375.0(20867)
320.2(16510)	319.9(35416)	379.9(11535)	320.0(35295)
239.7(37455)	265.0(64521)	320.0(17109)	249.9(87455)
225.0(18750)	249.9(80510)	275.0(35523)	
205.1(19990)	224.8(32455)	255.2(36324)	
	205.1(28914)	240.0(8316)	
		229.9(31144)	
		210.2(6281)	

the UV/vis spectral analysis in dimethylsulfoxide (DMSO), methanol, tetrahydrofuran (THF) and chloroform, polar solvents of different polarities, are listed in Table 3. Fig. 3 shows the UV/vis absorption spectra in the polar solvents used. The validity of the FF approximation used in all the computations here might be also illustrated by analyzing the relationship between calculated values of β and measured values of λ . The studied Cu(II) complex exhibits solvatochromism (Fig. 3), which is their maximal absorption peaks show bathochromic shifts, implying well molecular first hyperpolarizabilities. There are three bands in the 319–400 nm region involving mainly $\pi \rightarrow \pi^*$ transitions. The two located at lower frequencies have been ascribed to $\pi \rightarrow \pi_1^*$ and $\pi \rightarrow \pi_2^*$ transitions. The additional peak (around 400 nm) found at higher frequencies could correspond to the $\pi \rightarrow \pi_3^*$ transition, where

Table 4. Calculated all static β components and β_{tot} ($\times 10^{-30}$ esu) value of the title complex.

β_{xxx}	β_{xyy}	β_{yyy}	β_{yyy}	β_{xxz}	β_{xyz}	β_{yyz}	β_{xzz}	β_{yzz}	β_{zzz}	β_{tot}
-1316.341	-697.981	2199.862	541.960	-1656.470	-163.587	-2357.107	2598.619	877.558	-1802.508	6817.088

π_3^* is the third unoccupied π molecular orbital. These maximum absorption wavelengths are found shorter than 450 nm, generally considered as indicative of microscopic first hyperpolarizabilities with non-zero values [22, 23].

Description of the crystal structure

The Cu(II) Schiff base complex crystallizes in the monoclinic space group $P2_1/c$ with four molecule per unit cell. The X-ray structure analysis shows that the Cu(II) center is coordinated by four atoms in a near square-planar fashion. The four-coordinate Cu(II) is defined by two nitrogen atoms N(1), N(2) and two oxygen atoms O(1), O(2). In the equatorial plane, the bond distances of Cu(1)-N(1), Cu(1)-N(2), Cu(1)-O(1) and Cu(1)-O(2) are 1.919(4), 1.923(4), 1.899(4) and 1.887(4) Å, respectively. The Cu-O(1) and Cu-O(2) distances are in the ranges of those of related complexes [24–27]. The angles around the copper in five-membered chelate ring are less than the ideal value of 90° [$84.97(2)^\circ$ for N(1)-Cu(1)-N(2)] whereas those in the six-membered rings are greater [$93.46(2)^\circ$ for O(1)-Cu(1)-N(1) and $93.09(2)^\circ$ for O(2)-Cu(1)-N(2)].

Computational results and discussion

Quantum chemistry calculations have been shown to be useful in the description of the relationship among the electronic structure of the systems and their NLO response [28]. To help in the design of new compounds, selecting the directions which the time consuming synthetic work should follow, we have performed *ab-initio* calculations using the FF approach to compute the electric dipole moments and the first static hyperpolarizability tensor components of the synthesized complex. Indeed, for such complexes containing fourth row elements of the Periodical Table the calculated nonlinear coefficients are strongly dependent on the level of theoretical treatment. It is known that for metal complexes the relativistic contributions to β would likely be very important [29]. So, we have performed the calculations on static β values by the FF approach with the ECP basis set LanL2mb. The com-

Table 5. The *ab-initio* calculated electric dipole moment μ (Debye) and dipole moment components for the title complex.

μ_x	μ_y	μ_z	μ
-1.093	2.355	-2.056	3.312

ponents of static β and final β_{tot} values are shown in Table 4. The *ab-initio* non-zero μ values in Table 5 show that the title complex might have microscopic first static hyperpolarizabilities with non-zero values as numerical derivatives of the dipole moments. FF technique allows the calculations of all appropriate tensor components of β for large molecules at the price of moderate computational effort.

The higher dipole moment values are associated, in general, with even larger projection of β_{tot} quantities [30]. The dipoles may oppose or enhance one another, or at least bring the dipoles into the required or out of the required net alignment necessary for NLO properties such as β_{tot} values. The connection between the electric dipole moments of an organic molecule having donor-acceptor substituents and the first hyperpolarizability is widely recognized in the literature [31, 32]. Several research groups have tried to identify molecules with potentially optimal nonlinearities through the Two-Level model. For example, Marder *et al.* [33] used a four-site Hückel model to examine how each of the Two-Level parameters varies with the electron donating and electron accepting abilities of appended substituents. The β responses derived from this model were not optimized with maximal electronic asymmetry unique to a given bridge structure. The maximum was due to the behavior of a non-zero μ value. One of the conclusions obtained from their work is that a non-zero μ value might permit to find a non-zero β value. The *ab-initio* calculated non-zero μ value shows that the title compound might have microscopic first static hyperpolarizabilities with non-zero values as obtained by the numerical second-derivative of the electric dipole moment according to the applied field strength. In this study, where the first hyperpolarizabilities have been computed by the numerical second-derivatives of the electric dipole moments according to the applied field strength in FF approach, there are rather strong relationship among the

calculated μ and β_{tot} values. Therefore, the μ values in Table 5 may be responsible for enhancing and decreasing the β_{tot} value in Table 4. It is also important to stress that, in this β_{tot} investigation, we do not take into account the effect of the field on the nuclear positions, *i. e.* we evaluate only the electronic component of β_{tot} .

The central metal atom in metal complexes can readily coordinate to conjugated ligands and undergo π orbital overlap facilitating effective electronic communication and CT transitions leading to large dipole moment changes. The frontier molecular orbitals (MOs) in Cu(II) complex studied here consist of π orbitals having C=N and O_{2py} contributions, admixed to varying extents with metal $3d$ orbitals of appropriate symmetry. In particular, the low energy CT feature may be characterized as principally $\pi \rightarrow \pi^*$ in character, essentially involving the metal $d_{xy} + O_{2py}$ and the C=N orbitals, and is mainly responsible for the NLO response. The calculated hyperpolarizabil-

ities can be related to the metal electronic configuration, d^9 . Introduction of transition metals with a partially filled d -shell is known to affect a number of CT mechanisms like metal-ligand charge transfer (MLCT), ligand-metal charge transfer (LMCT) and d - d charge transfer [34]. Copper is a transition metal ion with partially filled d -shell which also favors higher value of β_{tot} . The methyl group is an effective donor for enhancing the intrinsic molecular second-order optical nonlinearity. This donor ($-\text{CH}_3$) group in the studied molecule might affect the microscopic second-order NLO behavior.

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