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Synthesis, molecular structure, spectroscopic studies and second-order nonlinear optical behaviour of N,N'-(2-hydroxy-propane-1,3-diyl)-bis (5-nitrosalicylaldiminato-N,O)-copper(II)

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Abstract

N,N'-(2-Hydroxy-propane-1,3-diyl)-bis(5-nitrosalicylaldiminato-N,O)-copper(II) has been synthesized. The crystal structure has been determined by X-ray diffraction analysis, and linear optical characterization has been determined by UV–vis spectroscopy. It was found that the molecule under investigation has solvatochromic behaviour in the UV region, implying non-zero microscopic first hyperpolarizability. To reveal the microscopic nonlinear optical (NLO) properties, the static first hyperpolarizabilities (β) and the electric dipole moments (μ) were evaluated by using the *ab initio* finite field (FF) method. According to the results of the FF calculations, the synthesized compound exhibits non-zero β values, and it might have microscopic NLO behaviour.
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1. Introduction

Nonlinear optics (NLO) properties of large organic and inorganic molecules have been the subject of extensive theoretical and experimental investigations during the last two decades [1–4]. Significant interest still exists in the design and development of materials exhibiting large second-order NLO response because of the potential application in telecommunications, optical computing and optical signal processing [5–7]. The Schiff base compounds have been under investigation for several years because of their potential application to optical communications and because many of them have NLO behaviour [8,9]. The effect of electron donor–acceptor substituents on the first hyperpolarizability of conjugated systems has received a great deal attention in recent years [10]. Schiff base metal complexes like organic compounds have several advantages as far as their second-order NLO properties are concerned. Organic substituents and transition metal ions with unfilled d-shells influence the nonlinearity through the interaction between the electrons in the substituents and the electrons in the main organic system [11].

Since the calculations of hyperpolarizability values of metal complexes are known to be problematic, the metal complexes have received less attention. The use of semiempirical methods to calculate NLO properties of metal complexes has been less reliable due to parametrization problems in the method of choice. Until now, however, the utilization of *ab initio* methods to calculate the NLO characteristics of metal complexes has been less exploited due to the heavy computational cost in handling these systems. In this paper, we have made an attempt to design a Schiff base metal complex and utilize *ab initio* methods for investigating second-order NLO behaviour. The aim of our study is two-fold: to characterize the newly synthesized Schiff base copper(II) complex (Fig. 1) with FT-IR, UV–vis spectroscopy and X-ray diffraction analysis, and to determine microscopic NLO properties computed by the *ab initio* finite field (FF) method.

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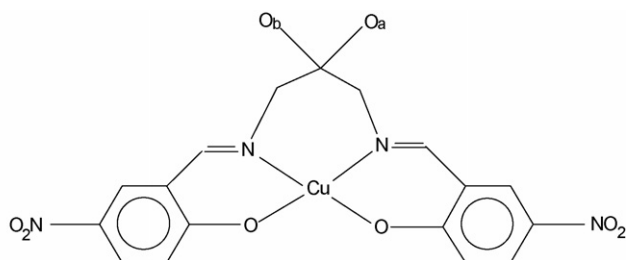 *E-mail address:* hkara@balikesir.edu.tr (H. Kara).

Fig. 1. Chemical structure of the title compound.

2. Experimental section

2.1. Reagent and techniques

1,3-Diamino-2-propanol, 2-hydroxy-5-nitrobenzaldehyde, copper(II) acetate monohydrate, dimethylsulfoxide (DMSO) and ethanol were purchased from Aldrich Chemical Co. Elemental (C, H, N) analyses were carried out by standard methods. FT-IR spectra were obtained using a Perkin-Elmer Model Bx 1600 instrument with the samples presented as KBr pellets and measured in the 4000–400 cm^{-1} range. UV–vis spectra were measured using a Cary 1-E UV–vis Spectrometer with 1.0 cm quartz cells.

2.2. Preparation of N,N'-(2-hydroxy-propane-1,3-diyl)-bis(5-nitrosalicylaldiminato-N,O)-copper(II)

The ligand was prepared by the reaction of 1,3-diamino-2-propanol (1 mmol) with 2-hydroxy-5-nitrobenzaldehyde (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 30 mL of hot DMSO to 1 mmol of ligand in 100 mL of boiling DMSO. The solution was allowed to evaporate at room temperature to give green crystals. Elemental analysis found: C, 45.42%; H, 3.17%; N, 12.48%. The theoretical values for $C_{17}H_{14}N_4O_7Cu$ are C, 45.39%; H, 3.14%; N, 12.45%. UV–vis (CHCl$_3$): λ_{max} (log ε) = 255 nm (0.76), 365 nm (0.78). IR (KBr, cm^{-1}): ν(C=N) 1606, ν(C=C) 1497, 1468, ν(C–O) 1105, ν(NO$_2$ Ar–NO$_2$) 1318. The chemical structure of the title molecule is given in Fig. 1.

2.3. X-ray structure determination

Diffraction measurements for the compound were made on three-circle CCD diffractometers using graphite monochromated Mo Kα radiation (λ = 0.71073 Å) at room temperature. The intensity data were integrated using the SAINT [12] program. Absorption, Lorentz and polarisation corrections were applied. The structures were solved by direct methods and refined using full-matrix least-squares against F^2 using SHELXTL [12]. The O7 atom was split into O7A and O7B. 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

Table 1
Crystal data and structure refinement for the title compound

Empirical formula	$C_{17}H_{14}N_4O_7Cu$
Formula weight	449.86 g mol^{-1}
Temperature	293(2) K
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	a = 7.1228(11) Å, α = 116.215(13)°;
	b = 10.9130(12) Å, β = 100.175(11)°;
	c = 12.3016(15) Å, γ = 90.298(12)°
Volume	840.61(19) Å^3
Z	2
Density (calculated)	1.777 g cm^{-3}
Absorption coefficient	1.354 mm^{-1}
θ range for data collection	2.09–27.48°
Index ranges	$-9 \leq h \leq 9$, $-14 \leq k \leq 14$, $-15 \leq l \leq 15$
Reflections collected	9572
Independent reflections	3821[R_{int} = 0.0192]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3821/2/276
Goodness-of-fit on F^2	S = 1.088
R indices [$I > 2\sigma(I)$]	R_1 = 0.0326, wR_2 = 0.0838
Largest diff. peak and hole	0.382 and -0.255 einstein Å^{-3}

Table 2
Some selected bond lengths (Å) and bond angles (°) for the title compound

Cu(1)–O(1)	1.9223(2)	O(1)–Cu(1)–O(2)	88.82(6)
Cu(1)–O(2)	1.9294(2)	O(1)–Cu(1)–N(2)	168.86(8)
Cu(1)–N(2)	1.9545(2)	O(2)–Cu(1)–N(2)	92.01(7)
Cu(1)–N(1)	1.9624(2)	O(1)–Cu(1)–N(1)	92.12(7)
O(1)–C(7)	1.296(2)	O(2)–Cu(1)–N(1)	169.08(8)
O(2)–C(14)	1.294(2)	N(2)–Cu(1)–N(1)	89.17(8)
O(3)–N(3)	1.230(3)	C(7)–O(1)–Cu(1)	126.11(1)
O(4)–N(3)	1.227(3)	C(14)–O(2)–Cu(1)	126.20(1)
O(5)–N(4)	1.228(3)	C(1)–N(1)–C(15)	118.3(2)
O(6)–N(4)	1.228(3)	C(1)–N(1)–Cu(1)	125.41(2)
O(7B)–C(16)	1.343(4)	C(15)–N(1)–Cu(1)	116.11(2)
O(7A)–C(16)	1.342(4)	C(8)–N(2)–C(17)	118.6(2)
N(1)–C(1)	1.277(3)	C(8)–N(2)–Cu(1)	125.17(2)
N(1)–C(15)	1.477(3)	C(17)–N(2)–Cu(1)	116.06(2)
N(2)–C(8)	1.281(3)		
N(2)–C(17)	1.473(3)		

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, conditions used for the intensity data collection and some features of the structure refinement are listed in Table 1. Selected bond lengths and angles are summarised 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-297107 [13].

3. Theoretical calculations

The theoretical computations in this study involve the determination of dispersion-free first hyperpolarizability tensor components and also electric dipole moments of the title compound using the following method.