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Research paper

A dual approach to study the key features of nickel (II) and copper (II) coordination complexes: Synthesis, crystal structure, optical and nonlinear properties

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ABSTRACT

In the present study, we use a dual approach comprising of experimental and computational techniques to report the syntheses and characterizations of two novel nickel (II) $[Ni(L)_2]$ (**1**) and copper (II) $[Cu(L)_2]$ (**2**) coordination complexes, which are made through the coordination of 1-(*E*-(2, 4-dibromophenylimino) methyl) naphthalene-2-ol (HL) ligand. Several modern techniques including experimental electronic spectroscopy, single crystal X-ray crystallography and quantum computational methods are used to characterize the isolated coordination compounds. Both the complexes display a square planar trans-$[MN_2O_2]$ coordination geometry, whose central M (II) atoms lie on the centre of symmetry. Complexes $[Ni(L)_2]$ (**1**) and $[Cu(L)_2]$ (**2**) crystallize in the monoclinic system of the space groups $P21/c$ with a = 9.307(4)Å, b = 12.242(4)Å, c = 13.823(4)Å, α = 90°, β = 105.262(10)°, γ = 90° and Z = 2 for complex (**1**), a = 9.171(5) Å, b = 12.507(8) Å, c = 13.666(8) Å, α = 90°, β = 103.823(15)°, γ = 90°, and Z = 2 for complex (**2**). The ligand (HL) is coordinated as monobasic bidentate with N and O donor groups suitably oriented for forming two six membered chelate rings. State of the art quantum computations are performed at molecular and bulk levels to get structure-property relationships from molecule to materials. The molecular nonlinear optical (NLO) response properties including third-order polarizability (γ) are calculated using density functional theory (DFT) methods. The calculated γ amplitudes for the synthesized $[Ni(L)_2]$ (**1**) and $[Cu(L)_2]$ (**2**) complexes are found to be 444.09×10^{-36} and 567.03×10^{-36} esu, respectively. These γ amplitudes of $[Ni(L)_2]$ (**1**) and $[Cu(L)_2]$ (**2**) complexes are about 21 and 27 times larger than that of standard *para*-nitroaniline (PNA, a prototype NLO molecule), respectively, which show the potential of these complexes as efficient NLO materials. Additionally, several important optical parameters including dielectric function, reflective index, reflectivity, conductivity and loss function are calculated at bulk level using ab initio methods within periodic boundary conditions (PBC). The obtained results indicate that both coordination complexes has good optical and NLO properties, which may render the above entitled complexes as efficient candidates for optoelectronic and NLO device fabrications.

1. Introduction

The coordination chemistry has emerged as an influential branch of materials science owing to the modern hi-tech applications of Ni(II) and Cu(II) coordination compounds [1]. The basic principles of metal-ligand interactions were first studied among coordination compounds. The synthesis and structural studies of coordination compounds allows the refining of the chemical bonding concept, and it explains influence of bonding on the various physical properties of the compounds. The study of Schiff bases as ligands in metal coordination sphere produces specific functionalities and features, what generates interesting subjects for theoretical studies and practical applications [2]. A large number of

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Ni(II) and Cu(II) coordination compounds with Schiff bases had been reported, and they had been studied extensively as NLO materials [3], model for enzymes active sites [4,5], metallodrugs [6] and some other biological applications [7].These compounds were successfully utilized as sensors [8], fluorescent materials [9,10], as well as they possess catalytic applications in multiple relations of organic synthesis [11,12].

Nonlinear optical materials have been getting significant research interest since the discovery of first functional laser. Recently, many modern hi-tech applications started the utilisation of NLO materials e.g. laser frequency doubling, telecommunications, optical data writing, electro-optical devices, and SHG spectroscopy [13]. There are several classes of materials that exhibit the efficient NLO response properties. Nowadays, quantum chemical methods are effectively used by theoreticians and experimentalists to design efficient optoelectronic materials [14]. Studies spanning over the past several years have highlighted that the organic class of materials has provided many opportunities to design efficient optoelectronic and NLO materials [15–19]. Recently, organic Schiff bases are also highlighted for their potential NLO properties [20,21]. Besides, organic Schiff bases, there are also several reports about metal coordinated Schiff bases for their efficient NLO properties [22–25]. In many contemporary investigations concerning metal Schiff bases, combined experimental and theoretical techniques are used to highlight their several structure-property relationships. Inspired by recent studies on metal coordinated Schiff bases for their efficient NLO properties, we plan to use a dual approach comprising of experimental and computational techniques to synthesise, characterise as well as to study their third-order NLO response properties of Schiff base nickel (II) and copper (II) coordination complexes with 1-(*E*-(2, 4-dibromophenylimino) methyl) naphthalene-2-ol (HL) as Schiff base ligand. Additionally, in view of above reported novel applications and based on our good experience on Schiff base nickel (II) and copper(II) coordination complexes [26–29], in this paper, we propose design strategies for synthesis and characterization of entitled coordination complexes with efficient electro-optical and NLO properties. A solid state structure determination is planned to perform by X-ray analysis. The refined single crystal structures are further subjected to computational studies at molecular and bulk levels using DFT and ab initio methods, respectively. The crystal structure determination also confirmed that the structures of complex $[Ni(L)_2]$ (**1**) and (II) $[Cu(L)_2]$ (**2**) are isostructural. The calculated non-linear optical parameters (NLO) including dielectric function, band gap, reflective index, reflectivity, conductivity, loss function and third-order polarizability (γ) of the studied complexes show promising optical properties. In this regard, unlike the past, the recent developments of hi-speed computing and emerging of several mature algorithms enabled the theoreticians to look into chemical problems beyond certain limits. The quantum computation can provide the insights into structure-property relationship of several materials, which are not possible with conventional characterization instruments due to their intrinsic limitations. Along the similar lines, the computational studies about the coordination compounds has quickly swelled up where it is used with reasonable accuracy to correlate and explain the structural features and functional properties of coordination complexes [30,31]. Thus, we believe that the use of dual approach in present investigation highlights the significance of indigenously synthesised two novel nickel (II) and copper (II) coordination complexes as an efficient NLO materials, which may evoke the interest of scientific community in such efficient optoelectronic and NLO materials for their potential utilization in device applications.

2. Experimental

2.1. Materials used for synthesis

The chemicals used were of AnalaR grade. 2, 4-dibromobenzenamine; 2-hydroxynaphthalene-1-carbaldehyde; $Ni(OAc)_2{\cdot}4H_2O$ and $Cu(OAc)_2{\cdot}H_2O$ were obtained from Sigma. Used solvent were dried and purified as reported standard method [32,33].

2.2. Synthesis

2.2.1. Synthesis of Schiff base ligand

The Schiff base ligand (HL) was synthesized according to an analogous method reported earlier [26–29]. The HL ligand is a newly prepared compound. The 1-(*E*-(2, 4-dibromophenylimino) methyl) naphthalene-2-ol (HL), a bidentate ligand was synthesized by the refluxing 2, 4-dibromobenzenamine (5.02 g, 20.0 mmol) with 2-hydroxynaphthalene-1-carbaldehyde (3.44 g, 20.0 mmol) in equimolar ratio in dry benzene for 4-5hr. The red crystalline products of Schiff base was obtained which was filtered, washed with ethanol, and stored in a desiccator over $CaCl_2$. The HL gave satisfactory elemental analyses. Isolated yield: 0.380 g (90%). Anal. Calcd. for $C_{17}H_{11}Br_2NO$, HL (%): C, 50.40; H, 2.74; N, 3.46. Found (%): C, 50.42; H, 2.75; N, 3.47. FAB-mass (*m/z*): Obs. (Calcd): 404.91(4 0 5). The ^1H NMR, and ^{13}C NMR spectrum data to support for characterization of Schiff base (HL) was graphically presented in Figs. S1 and S2.

2.2.2. Synthesis of $[Ni(L)_2]$ (1) and $[Cu(L)_2]$ (2)

The Schiff base HL (2.0 mmol, 0.810 g) was dissolved in ethanol (20 mL) in the presence of triethylamine (3.0 mmol, 40 μL) and was combined with $Ni(OAc)_2{\cdot}4H_2O$ (1.0 mmol, 0.249 g)/$Cu(OAc)_2{\cdot}H_2O$ (1.0 mmol, 0.199 g) in constant stirring and heating (60 °C). On cooling the solution to room temperature, green (**1**) and blue (**2**) crystals suitable for single crystal X-ray diffraction were recovered from mother liquor, which were filtered, washed with ethanol and then dried under vacuum. Both coordination complexes gave satisfactory elemental analysis. Isolated yield: 0.670 g (64%) and 0.740 g (70%) for $[Ni(L)_2]$ (**1**) and $[Cu(L)_2]$ (**2**), respectively. Anal. Calcd. for $C_{34}H_{20}Br_4N_2NiO_2$ (**1**), (%): C, 47.11; H, 2.33; N, 3.23. Found (%): C, 47.13; H, 2.34; N, 3.24. FAB-mass (*m/z*):Obs. (Calcd): 866.81(8 6 7). Anal. Calcd. for $C_{34}H_{20}Br_4CuN_2O_2$ (**2**), (%): C, 46.85; H, 2.31; N, 3.21. Found (%): C, 46.87; H, 2.32; N, 3.22. FAB-mass (*m/z*): Obs. (Calcd): 871.6(8 7 2).

2.3. Physical measurement

Elemental analyses were made on an ElementarVario EL III Carlo Erba 1108 analyzer. FAB mass spectra were recorded on a JEOL SX 102/DA 6000 mass spectrometer using xenon (6 kV, 10 mA) as the FAB gas. The accelerating voltage was 10 kV and the spectra were recorded at room temperature (RT) with m-nitro benzoyl alcohol as the matrix. Magnetic susceptibility measurements of powder samples of complexes were made on a Gouy balance using a mercury (II) tetrathiocynatocobaltate (II) as calibrating agent ($\chi_g = 16.44 \times 10^{-6}$ c.g.s. units). All the experimental data were corrected for diamagnetic were estimated from Pascal table and temperature independent Para magnetism (TIP). The molar ion exchange was measured using a systronics digital conductivity meter (TDS-308) using a 10^{-3} M solution in DMSO. UV–Vis spectra were recorded at 25 °C on a Thermo scientific UV–Vis recording spectrophotometer Evolution-3000 in quartz cells. IR spectra were recorded in KBr medium on a Shimadzu IR Affinity -1S Fourier transform infrared spectrophotometer. X-band EPR spectra was recorded with a Varian E-line Century Series spectrometer equipped with a dual cavity and operating at X-band (~9.4 GHz) with 100 kHz modulation frequency at room temperature. Tetracyanoethylene (TCNE) was used as field marker (g = 2.00277). The frozen solution at liquid nitrogen temperature used for EPR spectra was in 3×10^{-3} M in DMSO. Varian quartz tubes were used for measuring EPR spectra of polycrystalline sample and frozen solution. The EPR parameters for copper complex $[Cu(L)_2]$ (**2**) was determined accurately from computer simulation programs such as Monte Carlo, GAMMA, and Easy Spin [34]. All measurements were carried out at 298 K under a nitrogen atmosphere. The solution was deoxygenated by purging nitrogen gas.