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Computational Study of Static and Dynamic Nonlinear Optical Properties of the Zn (II) Complex

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Abstract

The static and dynamic (frequency-dependent) nonlinear optical (NLO) behaviors of a new complex of zinc (II) ion, $[ZnCl_2(peta)_2]$ [peta: 4-Pyridinethioamide] were investigated using the density functional theory (DFT)/B3LYP method with 6-311++G (d, p) basis set. Frontier molecular orbital (FMO) energies, band gap, and global reactivity descriptors were calculated at the same levels using the 6-311++G (d, p) basis set. The relationship between molecular hardness and both the static and dynamic first/second-order hyperpolarizabilities was analyzed using the DFT method. The dynamic NLO parameters of the Zn (II) complex were computed at ω = 532 nm (0.0856 au) laser frequency.

Keywords: *DFT, Energy, FMO, NLO*

1. Introduction

Nonlinear optical (NLO) materials are essential for the advancement of photonic devices, optical data storage, and telecommunications [1]. It is easier for π systems to access delocalized π electrons in compounds with higher-order NLO characteristics. Materials having high values for the NLO characteristic may be processed easily and react quickly, which is crucial for prospective uses in optoelectronics and photonics technologies. Metal complexes, such as those of copper, nickel, and zinc, are highly prized due to their applications in optical and frequency switching, optical modulation, optical communication, and optical focusing [1-9].

Zinc complexes have become an important research area in the development of nonlinear optical (NLO) materials in recent years. The d^{10} electron configuration of the Zn (II) ion provides a stable and predictable electronic structure independent of magnetic interactions, allowing ligand-based tuning of NLO properties. A multitude of investigations have been undertaken on Zn (II) complexes, especially those incorporating π-conjugated ligands, to develop systems exhibiting robust second/third-order nonlinear optical responses [9-12].

In previous work, the crystal structure of the Zn (II) complex was reported using single crystal X-ray diffraction (XRD) and FT-IR spectroscopy [13]. In this study, the static/dynamic nonlinear optical parameters of the Zn (II) complex were calculated using the DFT/B3LYP method. The frontier molecular orbitals (FMOs) energies and energy gap, chemical hardness, softness, and electronegativity of the Zn(II) complex in different media (gas phase, ethanol, and methanol) were computed by the time-dependent DFT (TD-DFT) applying the integral equation formalism-polarised continuum model (IEF-PCM).

2. Computational Details

All calculations were performed using the GAUSSIAN 09W program [14] and visualised using the GaussView05 program [15]. The DFT and TD-DFT method B3LYP [16] hybrid functional with 6-311++G (d, p) basis set were used to calculate the static/dynamic nonlinear optical parameter, energy gap, hardness, softness, and electronegativity.

3. Result and Discussion

3.1. Frontier Molecular Orbitals and Reactivity Descriptors

The optimized geometries of the Zn (II) complex and peta [17] were performed using the DFT/B3LYP method with 6-311++G (d, p) basis set. The structure of the Zn (II) complex obtained as a result of XRD structure analysis [13] and its optimized structure are shown in Figure 1. The HOMO, LUMO, energy gap (ΔE), chemical hardness (η), chemical potential (μ),

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softness (s) and electronegativity (χ) of the Zn(II) complex and peta were calculated using the TD-DFT method with B3LYP/6-311++G (d, p) level in the gas phase, ethanol, and methanol.

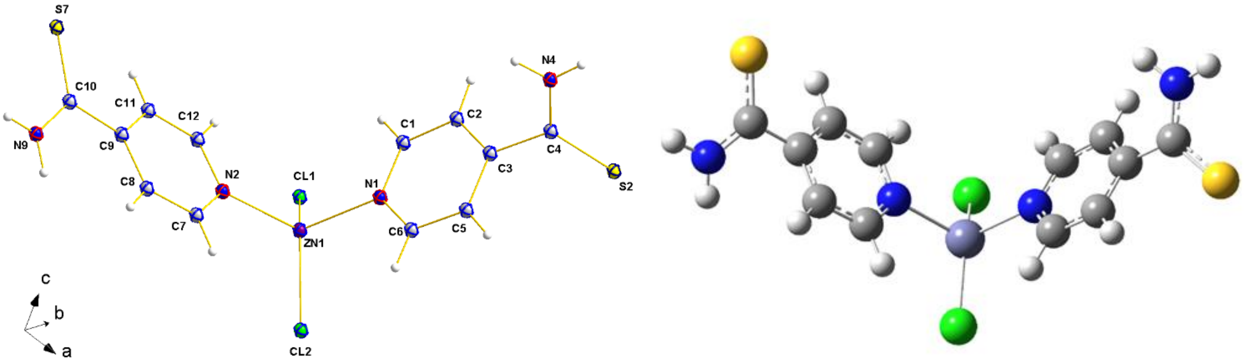

Figure 1. XRD molecular structure and optimized geometric structure of the Zn (II) complex.

FMO research was conducted to examine the electronic characteristics of the peta and its Zn (II) compound, as well as to assess the impact of metal coordination on the ΔE and chemical parameters (see Table 1). The ΔE value for the Zn (II) complex within gas phase, ethanol, and methanol were calculated as 3.59 eV, 3.81 eV, and 3.82 eV, respectively. The ΔE of the Zn (II) complex was calculated to be relatively lower in the gas phase than in solvents (ethanol and methanol). It can be said that the energy gap is slightly increased due to the solvent effect. This parameter of peta ligand within the gas phase, ethanol, and methanol was computed as 3.84 eV, 4.03 eV, and 4.03 eV, respectively. When comparing the Zn (II) complex with peta, it is observed that the band gap decreases. The reduction in the ΔE value indicates that the title compound exhibits more electronic polarizability and possibly improved chemical reactivity relative to the peta, which may be beneficial for NLO applications. The ΔE value calculated in the ethanol and in the methanol is close to each other.

Table 1. The frontier molecular orbital energies and related properties for the Zn (II) complex and peta.

TD-DFT/B3LYP/6-311++G (d, p)	**Gas phase**		**Ethanol**	
Parameters	**Peta**	**Complex**	**Peta**	**Complex**
E_{HOMO} **(eV)**	-6.2531	-6.6292	-6.4706	-6.5666
E_{LUMO} **(eV)**	-2.4147	-3.0367	-2.4389	-2.7559
$\Delta E = E_{LUMO}-E_{HOMO}$ **(eV)**	**3.8384**	**3.5925**	**4.0317**	**3.8107**
Ionization potential [$I = -E_{HOMO}$] **(eV)**	6.2531	6.6292	6.4706	6.5666
Electron affinity [$A = -E_{LUMO}$] **(eV)**	2.4147	3.0367	2.4389	2.7559
Electronegativity [$\chi = (I+A)/2$] **(eV)**	4.3339	4.8329	4.4547	4.6612
Chemical hardness [$\eta = (I-A)/2$] **(eV)**	1.9192	1.7962	2.0158	1.9053
Chemical potential [$\mu=-(I+A)/2$] **(eV)**	-4.3339	-4.8329	-4.4547	-4.6612
Softness [$s = 1/2\eta$] **(eV^{-1})**	0.2605	0.2783	0.2480	0.2624

The η, χ, *and* μ parameters of Zn (II) complex in the gas phase were computed as 1.7962, 4.8329, and -4.8329 eV, respectively. These parameters were calculated as 1.9192, 4.3339, and -4.3339 eV for peta, respectively. The chemical hardness (η) of the Zn (II) complex was determined to be lower than that of the peta, indicating enhanced softness and hence greater reactivity following complex formation. When the calculations made in the gas phase were compared with the calculations made in ethanol, it was seen that the values in the solvent environment increased slightly compared to the gas phase.

3.2. Static Nonlinear Optical (NLO) Properties

The static NLO parameters for the peta and [$ZnCl_2(peta)_2$] compound were computed at the DFT/B3LYP/6-311++G (d, p) method. The dipole moment (μ) increased by nearly 2.2 times upon coordination to the Zn (II) ion, from 3.81 Debye (peta) to 8.49 Debye (the complex). As seen from Table 2, the static polarizability (α) was computed as 4.0660 × 10^{-23} esu for the Zn (II) complex and 1.6055 × 10^{-23} esu for peta.

The *β* (0;0,0) value of the molecule was computed as 3.1342 × 10^{-30} esu, while that of the peta was calculated as 7.3466 × 10^{-30} esu. Coordination-induced electron density redistribution may result in a more localized electronic structure, which would lower β under static conditions [18, 19]. The prototype NLO material, urea, has a β value of 0.32 × 10^{-30} esu, although the Zn (II) complex still has a greater β value [20].

The γ(0;0,0,0) value markedly increases from 20.8 x 10^{-36} esu (peta) to 72 x 10^{-36} esu (Zn (II) complex), demonstrating that metal coordination substantially boosts third-order nonlinear optical characteristics. The γ value of the Zn (II) compound was significantly elevated in comparison to pNA (γ = 15 × 10^{-36} esu) and urea (γ = 7 × 10^{-36} esu) [20, 21].

Table 2. The static NLO parameters of the peta and Zn (II) complex using DFT/B3LYP/6-311++G (d, p) method.

Parameter	Peta (esu)	Zn (II) Complex (esu)
μ	3.8135 Debye	8.4910 Debye
α (0;0)	1.6055 ×10^{-23}	4.0660 ×10^{-23}
Δα (0;0)	3.7875 ×10^{-23}	7.6288 ×10^{-23}
β (0;0.0)	7.3466 ×10^{-30}	3.1342 ×10^{-30}
γ (0;0.0.0)	20.8 ×10^{-36}	72 ×10^{-36}

3.3. Frequency-Dependent NLO

The polarizability α (-ω; ω) of the Zn (II) complex (4.5243×10^{-23} esu) is more than twice that of the peta (1.7607×10^{-23} esu) at an incident wavelength of 532 nm (Table 3). The first-order frequency-dependent hyperpolarizability *β* (-ω; ω, 0) of the Zn (II) complex (27.536×10^{-30} esu) was calculated to be approximately 9 times the static value, and this value was also found to be approximately 9 times the *β* (-ω; ω, 0) value of the peta.

The β(-2ω;ω,ω), corresponding to the second harmonic generation processes, increases spectacularly from 18.818 ×10^{-30} esu (peta) to 120.450 ×10^{-30} esu (Zn (II) complex), possibly indicating more efficient intramolecular charge transfer in the complex under excitation by an external electric field.

Table 3. Frequency-dependent NLO parameters of the peta ligand and the Zn (II) complex using DFT/B3LYP/6-311++G (d,p) method.

Parameter	Peta (esu)	Zn (II) Complex (esu)
α (-ω; ω)	1.7607 ×10^{-23}	4.5243 ×10^{-23}
Δα (-ω; ω)	1.0808 ×10^{-23}	0.6042 ×10^{-23}
β(-ω;ω,0)	3.125 ×10^{-30}	27.536 ×10^{-30}
β(-2ω;ω,ω)	18.818 ×10^{-30}	120.450 ×10^{-30}
γ (-ω;ω,0,0)	47.361 ×10^{-36}	393.253 ×10^{-36}
γ (-2ω;ω,ω,0)	702.919 ×10^{-36}	4836.585 ×10^{-36}

The second-order hyperpolarizability γ(-ω;ω,0,0) of the Zn (II) complex (393.253 ×10^{-36} esu) was computed to be approximately 5 times the static value, and this value was also found to be approximately 8 times the γ(-ω;ω,0,0) value of the peta. The γ (-2ω;ω,ω,0) value of the Zn(II) complex was calculated as 4836.585×10^{-36} esu. It is seen that the γ (-2ω;ω,ω,0) value of the Zn(II) complex increases approximately 7-fold compared to the γ(-2ω;ω,ω,0) value of the peta. As a result, the static and dynamic NLO properties of the Zn(II) complex were increased compared to the peta ligand, and the NLO properties were significantly more remarkable compared to the literature for similar structures [22, 23].

4. Conclusions

In the present paper, the static and dynamic (frequency-dependent) NLO properties, FMO energies, and global reactivity descriptors of the Zn(II) complex have been investigated by using the DFT method. The ΔE of the Zn (II) complex was relatively smaller than that of the peta ligand and similar complexes. It was also observed that the use of solvent (ethanol and methanol) affected this energy gap, albeit slightly. The low energy gap between FMOs suggests that charge transfer may occur within the Zn (II) complex. The static and dynamic NLO parameters of the Zn (II) complex were calculated to be higher than those of the peta. At the same time, the dynamic NLO properties of the Zn (II) complex appear to be greater than those in the static case. As a result, considering these interesting properties of the Zn (II) complex, it can be said that it may have many areas of use in the future.

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