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Synthesis, Characterization and Density Functional Theory (DFT) study on the Zinc Metal Complex for Nonlinear Optical Application

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Abstract

Schiff base metal complexes are well-known for its nonlinear optics (NLO) properties. However, different metals may show different NLO properties. In this study, zinc (Zn) metal, N,N-bis[2-(diphenylphosphino)benzylidene]cyclohexane-1,2-diamine ligand was selected. The ligand was synthesized at room temperature while stirring for 24 hours, using dichloromethane (CH_2Cl_2) as the solvent. Complexation of the selected metals (Zn) was later carried out with the ligand under inert conditions, N_2 gas refluxed for 12 to 24 hours in solvent. The percentage yield of products was 38 %. The types of characterization involved in this study were Fourier transform infrared (FT-IR), and nuclear magnetic resonance (NMR). Computational studies were also performed to optimize the structure of ligand and metal complexes using density functional theory (DFT) method with basis set 6-31G and hybrid functional B3LYP. The data obtained from both experimental and computational methods were compared. To confirm nonlinear optic properties, one can use the HOMO-LUMO energy gap. Our choice of metal complex of zinc with organic ligand was based on the excellent NLO characteristics of transition metal-based organic compounds. Transition metal-based complexes yield impressive results because they offer additional flexibility by offering charge transfer between the metal and the ligand, resulting in a higher NLO response. It was discovered that the zinc complex with the lower band gap of 1.69 eV particularly in comparison with the ligand 2.44 eV. Thus, the lower the band gap, the higher the NLO properties of the compound.

Keywords Nonlinear optics, metal variation, DFT, FTIR, NMR, optimization.

1.0 INTRODUCTION

Nonlinear optics (NLO) is a vibrant and rapidly advancing field with significant implications for both fundamental science and practical applications. Researchers in this field continue to explore new materials, optimize existing nonlinear effects, and develop innovative devices for a wide range of optical and photonic applications. Unlike linear optics, where the response of a material to light is directly proportional to the intensity of the light, nonlinear optics (NLO) involve nonlinear relationships between the input and output light signals. Nonlinear optical (NLO) materials have garnered significant attention in recent years due to their pivotal role in the development of advanced photonic devices and technologies. These materials exhibit nonlinear responses to intense laser light, enabling applications in optical signal processing, frequency conversion, and high-power laser systems. The design and synthesis of novel NLO materials have become a cornerstone in modern materials science, offering the promise of improved efficiency and performance in a wide range of optical applications in medicinal fields like laser surgery, tissue ablation, drug delivery and photothermal therapy [1].

In this context, the exploration of transition metal complexes as potential NLO materials has emerged as a vibrant area of research. Transition metal ions, such as zinc (Zn), are known to exhibit intriguing electronic structures that can give rise to nonlinear optical properties. The rational design and synthesis of metal complexes offer the versatility needed to tailor these properties for specific applications. This study focuses on the synthesis, characterization, and theoretical investigation of a zinc metal complex with the aim of exploring its potential as an NLO material. Zinc, with its variable coordination chemistry and diverse ligand options, presents an ideal platform for the creation of tailored metal complexes with desirable nonlinear optical characteristics.

Transition metal complexes are interesting materials for nonlinear optics as these complexes show large molecular hyperpolarizability. This phenomenon is due to the electron transfer between the complex ligand system and metal atom [2].

A copper(II) complex of (E)-N′-(2-hydroxybenzylidene) acetohydrazide (HL) was studied by Ebrahimipour et al. [3]. The procedure involved in this study includes synthesis, characterization, study of NLO properties as well as DFT calculation. For the preparation of the copper(II) complex, $Cu(OAc)_2 \cdot 4H_2O$ (0.1 mmol, 0.02 g) was added to the ligand (HL) (0.1 mmol, 0.018 g) in solvent ethanol, with sodium hydroxide, NaOH (0.2 mmol, 0.01 g) added later and the solution was refluxed for 10 minutes. The dark-green resulting solution was further added with 1,10-Phenanthroline (0.1 mmol, 0.02 g) and refluxed for approximately 1 hour. The crystal of the compound of interest was acquired by recrystallization from a solution of dichloromethane-methanol and dried in a vacuum desiccator with $CaCl_2$.

In a study carried out by Lacroix et al. [4], a metal complex was synthesized. All the starting materials 4-(diethylamino) salicylaldehyde (0.3865 g, 2 mmol) and diaminomaleonitrile (0.108 g, 3 mmol) were added to $Zn(CH_3COO)_2.2H_2O$ (0.2195 g, 3 mmol) salt in absolute ethanol (50ml) and stirred for 2 days. Dark blue crystals were acquired after 2 days.

In a study carried out by Zhang, et al. [5], chiral cobalt(II) complex which functions as a catalyst for enantioselective hydrogenation of ketones was synthesized. A chiral tetradentate aminophosphine ligand and $CoCl_2.6H_2O$ were used as the starting material. Two reactions were carried out. When refluxed and reacted under an inert condition with N_2 gas for 20 hours, using acetonitrile as the solvent, diaminidiphosphine (PNNP) type ligand with direct connection to phosphorus atom number 2 (denoted as P3) is formed. When carried out in normal atmospheric conditions, oxygen is bonded between the cobalt atom and the phosphorus atom (Co-O-P). A bond length of 2.6340 Å and 2.5256 Å were observed for Co-P2 and Co-P3, respectively. Several studies have been conducted on the variation of metal while retaining the same ligand in a complex.

One of the studies done by Lacroix et al. [4] shows that while the ligand (2,3-bis[[(2-hydroxy-4-(diethylamino)phenyl)(methylene)]amino] 2-butenedinitrile) remains the same, zinc complex shows better NLO property compared to Cu and Ni in the same study due to the presence of d^{10} electronic configuration of zinc atom. The orbitals in zinc atoms act like a bridge which helps in the charge transfer of electrons from metal-to-ligand bonds.

Computational chemistry is a crucial tool in the analysis and interpretation of experimental data in chemical research. Marzzacco et al. [6] computational methods help to save time, reduce cost by preventing material wastage and serve as a comparison set between the real experiment and the data acquired from the simulation. There are predominantly three types of computational methods involved in the field of chemistry, ab initio, semi-empirical and density functional theory [7]. DFT seems to be especially well adapted to the modelling and investigation of massive transition metal-containing systems, whereas time-dependent DFT may be used to evaluate electronic excitation spectra and response characteristics (TD-DFT) [8]. The NLO characteristics of small to medium-sized (mostly organic) molecules have been studied, and it has been shown that TD-DFT calculations are typically accurate and exhibit good agreement with experimental findings [9].

2.0 EXPERIMENTAL

2.1 Materials

(Diphenylphosphino)benzylidene] cyclohexane-1,2-diamine, and transition metal salts were purchased from Sigma Aldrich along with the solvents ethanol, dichloromethane, acetonitrile and tetrahydrofuran.

2.2 Preparation of materials

2.2.1 Synthesis of N,N-bis[2-(diphenylphosphino)benzylidene]cyclohexane-1,2-diamine (Ligand A)

Ligand A was prepared from the reaction of (S,S)-1,2-diaminocyclohexane (0.35 g, 3.0 mmol), 2-(diphenylphosphino)benzaldehyde (1.74 g, 6.0 mmol) and anhydrous Na_2SO_4 in dichloromethane (CH_2Cl_2) (20 ml) as a solvent. The mixture was stirred for 24 hours. A pale-orange solution was obtained. The resulting solution was filtered and placed in a rotary vacuum evaporator to reduce the volume up to ~5 ml. 20 ml of ethanol was added to the resulting liquid and kept at -18°C to obtain a yellow solid. The final product was washed with CH_2Cl_2 and filtered to remove impurities.

2.2.2 Synthesis of Zinc Complex

Synthesis of the complex was done by the zinc salt, zinc chloride and the ligand, N,N-bis[2-(diphenylphosphino)benzylidene]cyclohexane-1,2-diamine in a tetrahydrofuran (20 ml). This reaction was modified by the previous procedure [10]. The ligand and $ZnCl_2$ were dissolved in THF (15 ml) and stirred with reflux for 12 hours. A yellow solution was observed. The crystal of zinc complex was obtained by drying under reduced pressure.

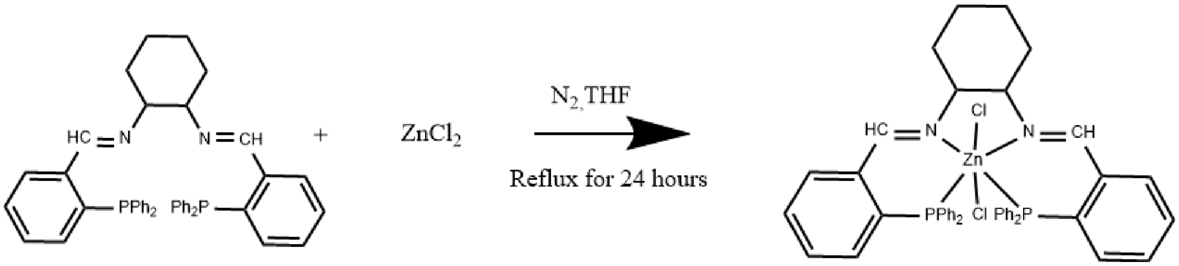

Figure 1 Synthesis of the Zinc complex.

2.3 Characterization of materials

All samples were characterized using Fourier Transform Infrared (FTIR) Spectroscopy, nuclear magnetic resonance (NMR) spectroscopy and computational DFT methods. FT-IR (Fourier Transform Infrared) Spectrometer was used for structural analysis. About 1-2 mg of sample was placed on the sample area. The FTIR spectrum was then recorded using OMNIC software in the range of 4000 to 650 cm^{-1} to record the spectrum using the ATR technique. With the use of the sampling method known as attenuated total reflection (ATR), materials can be studied immediately in their solid or liquid states without the need for any additional preparation. Samples were characterized then using phosphorous ^{31}PNMR and proton ^{1}HNMR to observe the peaks. Computational DFT characterizations were done using Gaussian software.

3.0 RESULTS AND DISCUSSION

3.1 Characterization of the Ligand and Complexes

3.1.1 Synthesis of the ligand and Zn complex

Figure 2 Image of ligand A sample.

The yield obtained for ligand A was 345 mg (0.5237 mmol), resulting in a percentage yield of 60.83%. The product obtained was an off-white solid as seen in Figure 2. ATR (cm^{-1}): 3257 m υ (CH-Ar), 3052 s υ(CH=N), 2927 s υ(C-H), 2854 s υ(C-H), 1638 s υ(C=N), 1476 s υ(C=C). ^{31}P NMR ($CDCl_3$/ppm): δ -13.769.

Figure 3 Zinc complex.

The yield obtained for zinc complex was 0.045 g, resulting in a percentage yield of 38%. The product obtained was a pale-yellow solid as seen in Figure 3. ATR (cm^{-1}): 3230 w υ(C-H aromatic), 1674 m υ(C=N), 1433 m υ(C=C aromatic). ^{31}P NMR ($CDCl_3$/ppm): δ 30.926, -11.676.

3.1.1 Infrared Spectroscopy (IR)

Table 1 summarizes the IR spectra peak assignment of ligand and complex. The experimental band observed for (C=N) for the ligand is 1635.67 cm^{-1}, medium peak. Due to the presence of intramolecular hydrogen bonding interactions between a nitrogen atom and a hydrogen atom, this value deviates somewhat from the range of 1640 - 1690 cm^{-1}. The observed value of the calculated wavenumber is 1623.55 cm^{-1}, which is also barely lower than the value in the literature [10]. The wavenumber's percentage deviation for the condition (C=N) is 12.12%.

Table 1 Comparison of summary of ATR Spectra for ligand, zinc, copper, and cobalt metal complex.

Compound		C=N	CH=N	C-H aromatic	C=C aromatic
Ligand A	Experimental (cm^{-1})	1635.67	3051.06	-	1433.06
	Computational (cm^{-1})	1623.55	3045.07	3214.77	1438.52
	Percentage deviation	12.12	5.99	-	5.46
Zinc Complex	Experimental (cm^{-1})	1674.21	-	3230.92	1433.13

3.1.2 Geometry Optimization using DFT Methods

The method used for the ligand was DFT/B3LYP/6-31G method using Gaussian software under zero charge and single spin multiplicity. The metal complex Zn was optimized using DFT/B3LYP/GEN in Gaussian software. From the results, it can be observed that the metal complex tends to have lower energy compared to the ligand (-2492.47 a.u. > -3479.12 a.u.). The presence of a metal centre stabilizes the complex by forming back bonding, which allows for the delocalization of electrons and the lowering of the overall energy. The molecular energy attained is summarized in **Table 2**.

Table 2 Comparison of energy between ligand and metal (zinc) complex.

Compound	Energy (a.u.)
Ligand A	-2492.47
Zn complex	-3479.12

3.2 Frontier Molecular Orbital Calculation (HOMO/LUMO) for NLO application

The determination of the HOMO and LUMO of a structure was based on structures that have been optimized to acquire a more accurate geometry in which bond angle and bond length are considered. The HOMO is defined as the molecular orbital with the highest energy level that is occupied by electrons, while the LUMO corresponds to the molecular orbital with the lowest energy level that remains unoccupied. Bandgap (eV) of a molecule can be interpreted as the energy difference between HOMO and LUMO. To evaluate the value of bandgap, the value of LUMO is used to subtract HOMO. The formula of bandgap (eV) is given as such:

$$\text{Bandgap (eV)} = \text{LUMO} - \text{HOMO}$$

Table 3 findings showed that the bandgaps (eV) of ligand A and zinc complex were 2.44 eV and 1.69 eV, respectively. The zinc complex had a smaller bandgap as compared to ligand A because of the addition of the metal. New molecular orbitals, referred to as metal-ligand orbitals, were created due to this interaction. There was a distinct energy distribution in these metal-ligand orbitals and energy levels changed when compared to the solitary ligand orbitals. This metal-ligand charge transfer (MLCT) interaction caused the bandgap to shorten the redistribution of electronic states and changed the HOMO and LUMO's energy levels.

The bandgap value could have an impact on NLO properties in NLO applications. A reduced HOMO-LUMO energy gap promotes charge flow within the material and facilitates effective electronic transitions. As a result, the charge transfer is improved, which causes the polarizability to increase and the NLO response to be amplified.

Table 3 HOMO, LUMO energy and band gap of the compounds of interest.

Compound	HOMO (eV)	LUMO (eV)	Band Gap (eV)
Ligand A	-8.19	-5.75	2.44
Zinc complex	-7.36	-5.68	1.69

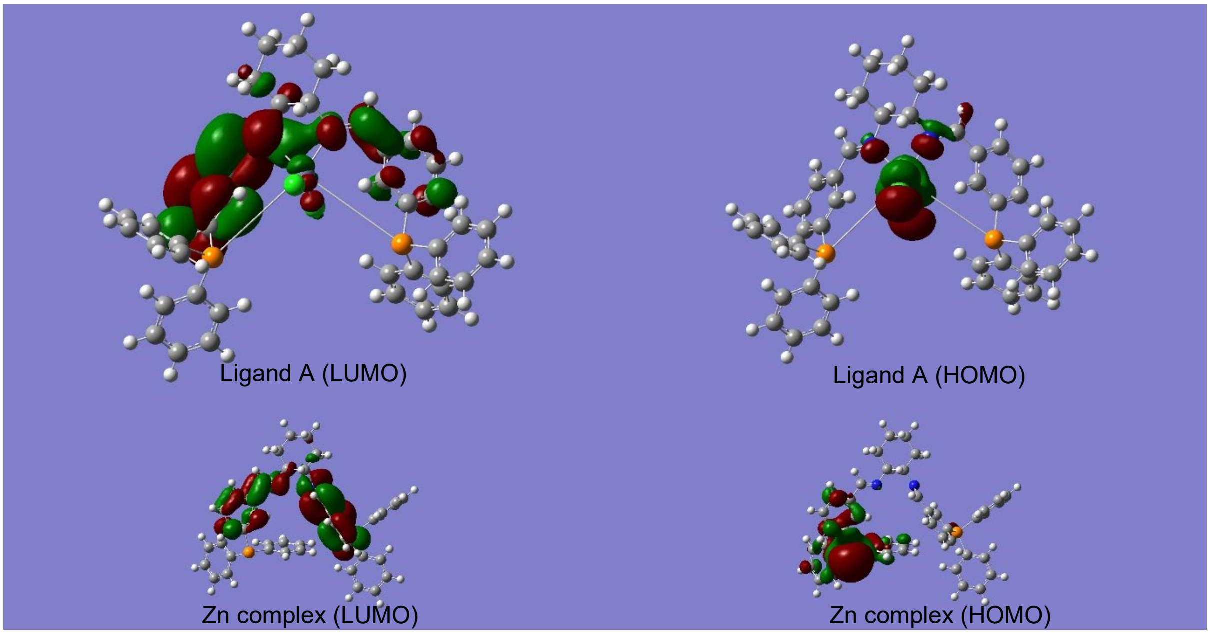

Figure 5: The HOMO LUMO diagram of zinc complex and ligand A

4.0 CONCLUSION

Experimental synthesis and characterization of *N,N-bis*[2-(diphenylphosphino)benzylidene]cyclohexane-1,2-diamine and its respective metal complex (Zn) was successfully synthesized. The computational work on the ligand and zinc complex was done. For the ligand, particular peaks (C=C aromatic), (-C=N), (-C-H aromatic) and (-H-C=N) were present in the IR spectra to confirm the functional groups. The presence of a peak at -11.658 ppm in ^{31}P NMR spectra shows that the ligand has been synthesized. As for the metal complex, the zinc complex showed a chemical shift in ^{31}P NMR spectra at ~30 ppm, which shows its possible formation. Upon comparison of energies and band gap of zinc metal complex and the ligand, it is found that the metal complex is more stable because of the lower energy in terms of optimization and band gap, due to charge transfer between the metal and the ligand making it more stable for NLO application.

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