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Co(II), Cu(II) and Zn(II) complexes of tridentate ONO donor Schiff base ligand: A DFT studies

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ABSTRACT

A series of Cu(II), Co(II), and Zn(II), mononuclear Schiff base complexes were studied and characterized by DFT calculations. The ligand was derived from the experiment of condensing 5-acetyl-4-hydroxy-2H-1,3-thiazine-2,6(3H)-dione with o-phenylenediamine. The Schiff base ligand has coordination sites on phenolic oxygen, azomethine nitrogen, and amino group nitrogen, where it behaves as a monobasic tridentate. All studied structure was constructed based on the ration 1:1 (metal: ligand) stoichiometry. Except for the Cu(II) complex, which exhibited a square planar arrangement, the metal complexes exhibited octahedral geometry. The Orca quantum program's Density Function Theory (DFT) level was used to optimize the structure and several structural parameters of the ligand and its metal complexes, including total energy, HOMO, LUMO, and dipole moment. Correlations were established between the calculated and experimental data.

Introduction

Schiff bases are one of the most significant chelating ligands in coordination chemistry, and they have a wide range of applications. These compounds are used as catalysts, dyes and pigments, intermediates in chemical synthesis, and polymer stabilizers, among other applications.[1]–[4] As a result of their numerous uses, including photophysical, photoluminescence, thermal, and optical characteristics, as well as their varied biological significance. Schiff base metal complexes especially have caught the interest of researchers due to their wide range of applications, which include antimicrobial, anticancer, antitumor, antioxidant, anti-inflammatory, antiviral, and herbicidal activities, as well as catalytic, thermal, and electrochemical properties.[5]–[9] Antibiotics have significantly decreased the frequency of infectious illnesses and saved lives since their discovery. However, researchers concentrated on the creation of antibacterial chemicals in order to circumvent the well-documented resistance to antibiotics[5], [10], [11]. Thus, in pursuit of novel antimicrobial compounds with enhanced activity and/or reduced resistance, various metallic complexes such as vanadium, manganese, chromium, iron, copper, and cobalt have been described in the literature. Because of their antibacterial, antimicobacterial, anticancer, and antitumor properties[12], [13], compounds containing the 1,3-thiazine ring have gotten a lot of attention recently. They have substantial antibacterial, antifungal, anticancer, antimalarial, antineoplastic, and antiviral properties.[14] Due to its significant features such as

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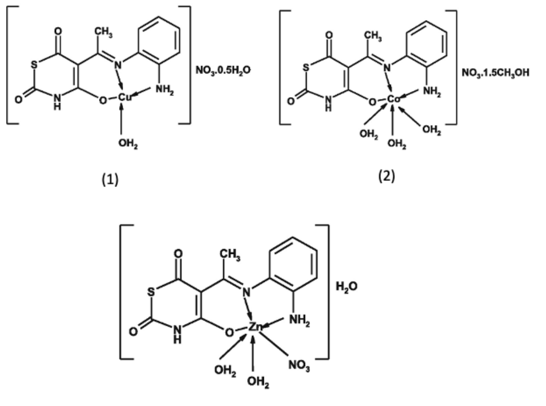
catalytic, magnetic, fluorescent, and electrochemical, transition metal complexes with asymmetrical Schiff base ligands have garnered considerable interest. Tridentate Schiff bases with nitrogen and oxygen donor set atoms enable the coordination of a broad variety of metal ions in a number of ways. Additionally, transition metal complexes of heterocyclic Schiff bases have been extensively investigated due to their widespread application in the biological area. These ligands have been widely employed as polychelator ligands and have demonstrated excellent steric properties and electronic soft tuning of their metal complexes. Chemists construct Schiff bases as polydentate ligands and their complexes, which have found use in a variety of fields of chemistry.[7], [15]–[19]



(1) (2)

(3)

Figure 1: Representative structures of the three metal asymetrical complexes

In this work, we focus on strucral determination of the three assymetrical Schiff base complexes generated by Cu^{2+}, Co^{2+} and Zn^{2+} with the tridendate ligand erived from 5-acetyl-4-hydroxy-2H-1,3-thiazine-2,6(3H)-dione (denoted as STL ligand). The structures of the ligand and its metal complexes were characterized by DFT calculations and the results are correlation with experimental data.

Experimental method

All density functional theory (DFT) calculations were performed using the BP86 functional and the well balanced polarized triple-zeta basis set def2- TZVP basis set along with associated Weigend's "universal" Coulomb fitting (def2/J) as integrated and implemented in Orca 4.2 quantum program[7]. Our preliminary studies structural detemination of such transtition metal complexes have evidenced the high accuracy and predictive power of this methodology for various homogeneously catalysis.[20] The numerical thresholds were systematically increased using the TightSCF, Grid5 and FinalGrid6 options. All the studied structures are verified with no imaginary frequencies.

Results and discussion

The molecular structures were hypothesized based on experimental evidence that the produced compounds exhibited octahedral and square planar conformations. The construction of novel molecular Schiff base ligands and their metal complexes may be recognized via the use of computational chemistry techniques, which provide an efficient method for assessing their stabilities and estimating structural characteristics. The dipole moment and frontier molecular orbitals (FMO), as well as the energies of the highest occupied and lowest unoccupied molecular orbitals (HOMO, LUMO) are included in this table (Table 1). Figure 2, Figure 3, and Figure 4 illustrate the numbering system, and HOMO and LUMO of the ligand and its Cu(II) complex. It is widely recognized that HOMO orbitals are proportional to ionization potential (electron donating), whereas LUMO orbitals are proportional to electron affinity. The E_{gap} indicate how easy the molecule got excited

Table 1: Energy of HOMO (ev), LUMO (ev), energy gap (ev), and dipole moment (Debye) for the ligand and its metal complexes

Complexes	E_{HOMO}	E_{LUMO}	ΔE	μ
Cu-STL	-9.044	-6.231	2.813	12.99
Co-STL	-8.179	-6.857	1.322	13.91
Zn-STL	-5.945	-2.916	3.029	7.99

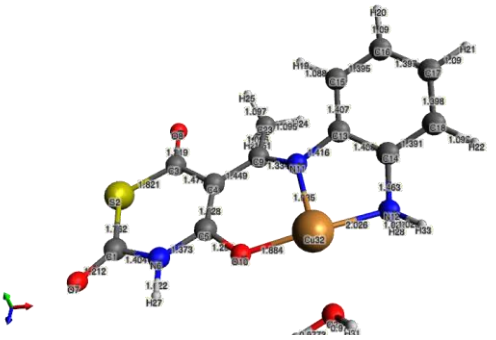


Figure 2: The optimized structure and numbering system of the Cu-STL complex

In the optimized structure of Cu-STL showed astrong distorsion effect since the Cu-N bond length is 2.00 A° while the bondlength of Cu-N is only 1.88A°. The similar partern was observed with Co-STL and Zn-STL complexes. After analysis of the atomic charges in each complexes, there are the strong dipolar effects between the metal center and the N,O atoms in the coordination. It has been reported in literature that binding of drug to a metallo element enhances its activity and in some cases the complex possesses even more healing properties than the parent drug. Metal elements such has cobalt, zinc and copper have small size, higher nuclear charge and thus have a great affinity for coordination.

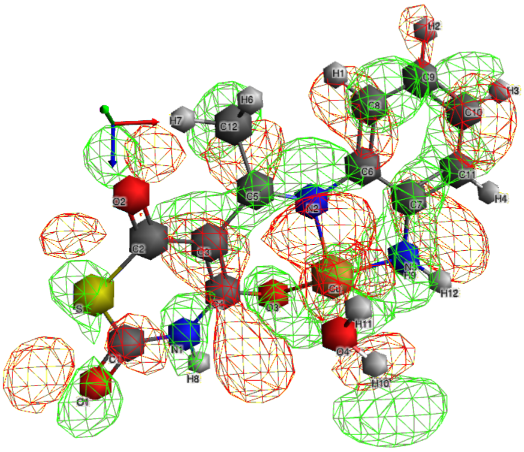


Figure 3: The HOMO of Cu-STL complex

The Figure 2, Figure 3, Figure 4,Figure 5 and Figure 6 illustrate the Frontier Molecular Orbital (FMO) investigation, which revealed that the HOMO is predominantly focused on oxygen (keto groups, OH phenolic), azomethine nitrogen (-Cdouble bondN-), and nitrogen amino group (NH2). However, the LUMO is predominantly focused on the phenyl ring and hetero ring moiety, suggesting that the HOMO-LUMO orbitals are predominantly p-anti-bonding type. The E_{HOMO}, E_{LUMO}, and Egap energy parameters are frequently utilized as reactivity or stability structures [77]. The order of E_{gap}(eV) values indicating the reactivity of the present chemicals is Zn(II) > Cu(II) > Co(II). The anticancer activity of those compounds against the Erlish Ascites Carcinoma cell line is indicated by the decrease in predicted Egap values (Table 1). As a result, the antitumor reactivity is as follows: Zn(II)>Cu(II)>Co(II) complex. The results are in agreement with the experimental values.

The FMOs of Cu(II) complex were assigned to d_{xy} and d_{x2-y2} orbital ($^2B_1$ and $^2B_2$), indicating a square planar geometry. The spin state of value for Cu(II) complex 1 indicate that this complex has a certain magnetic moment, confirming the square planar geometry of the complex. The FMOs of Co(II) complex exhibited the combination of $^4T1g(P)$, $^4T1g(F)$, $^4A_{2g}(F)$ and $^4T_{1g}(F)$ states, recommending octahedral geometry. The FMOs of Zn(II) complexes h might attribute to π , π* or n, π* states, respectively, which is recommended for the octahedral geometry too.

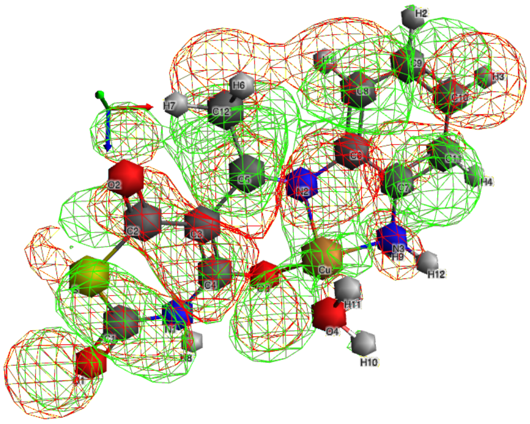


Figure 4: The LUMO of Cu-STL complex

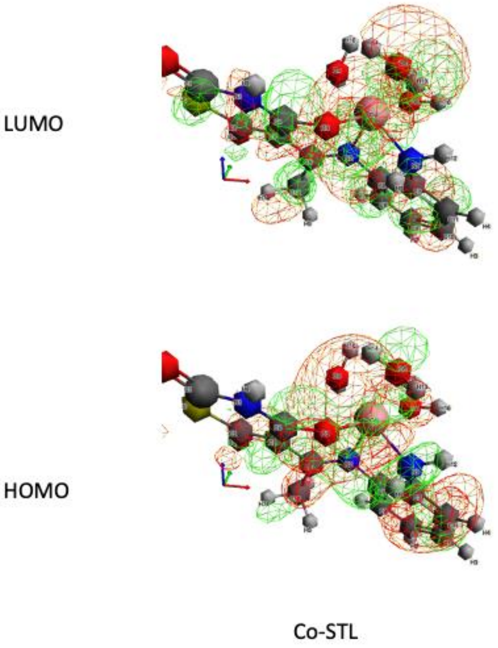


Figure 5: FMOs of Cobalt complexes from theSTL ligand

This explained why the charge in the Zn atom is the highest due to the stabilization between the π bonding with the phenyl ring while π* does not interact with the the π system of the phenyl ring, so the E_{gap} got to the highest value. For the Cu-STL and Co-STL complexes, the bond between metal and three atoms, N and O, has been enhanced by the d_{xy} and d_{x2-y2} which is significantly stabilized by the two phenyl rings. This phenomenon was later verified by the location of molecular orbitals in the two states in the two complexes. Since the metal center is cationic, the particle charge would therefore be dictated by the location of electrons in the bonding between the metal and ligand.

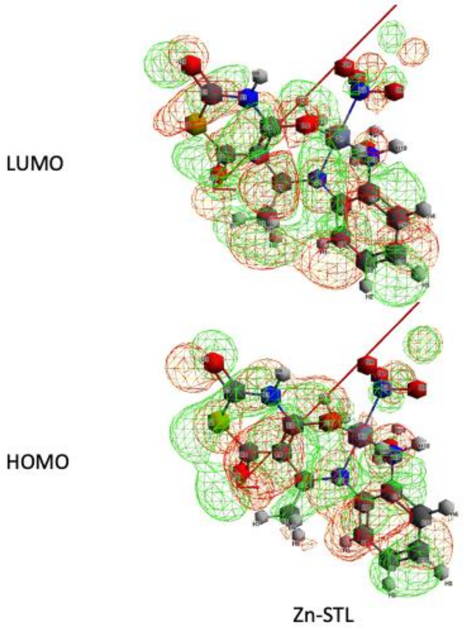


Figure 6: The FMO of Zinc complexes from the STL ligand

Table 2: Muliken atomic charges in each complexes

	Metal	O10	N11	N12
Cu-STL	-0.027	-0.364	0.083	-0.333
Co-STL	-0.174	-0.378	0.060	-0.325
Zn-STL	0.419	-0.417	-0.092	-0.437

Conclusion

This work is devoted to investigate a series of Schiff base complexes a tridentate N2O Schiff base ligand obtained from the combination of 5-acetyl-4-hydroxy-2H-1,3-thiazine-2,6(3H)-dione and o-phenlenediamine. The optimal structures of the ligand and its metal complexes were investigated using Density Functional Theory computations Cu(II), Co(II), Zn(II), metal complexes have been focused to study. The prepared compounds exhibit square planar and octahedral geometries. The ligand and its metal complexes experimentally exhibited antibacterial action and then was verified by the computational results. Calculations and correlations with experimental data have been made for the molecular properties of the ligand and its metal complexes.

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