Review Paper:

DFT Studies of Zr(IV) - 3-Hydroxy-2-[2’-(5’-methylthienyl)]-4*H*-chromen-4-one Complex

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Abstract

Various approaches to solve the Schrödinger equation have evolved since the advent of quantum mechanics in 1920s and the introduction of the Schrödinger equation in 1926. The initially impossible solution of Schrödinger equation is made possible by breakthroughs in computing approaches like Density functional theory (DFT). DFT is a useful technique for investigating the molecular characteristics of metal complex systems. It is based on the idea that the exact energy can be calculated using only the electron density over the molecular system.

The goal of this work is to investigate the structural characteristics of zirconium complex using contemporary density functional theory methods. The method has successfully been used to evaluate the metal ligand interactions and chemical reactivity of the complex of zirconium in tetravalent state with 3-hydroxy-2-[2’-(5’-methylthienyl)]-4H-chromen-4-one using reactivity descriptors.

Keywords: Zirconium, 3-Hydroxy-2-[2’-(5’-methylthienyl)]-4*H*-chromen-4-one, DFT, Reactivity descriptors.

Introduction

Transition metal chemistry is known for its vibrant hues and rich excited-state activity. Apart from their fundamental importance, transition metal compounds are increasingly being used as sensitizers-solar energy conversant, phosphorescent dyes for organic light emitting diodes, luminescence-based sensors, in electron or energy transfer assemblies as active constituents, non-linear optical materials and initiators of electron transfer in biomolecules.

The present-day experimental and theoretical researchers are focused on comprehending the structure and dynamics of electronic excited states of the coordination and organometallic compounds[24,25].

Zirconium (Zr), one of the transition metals frequently involved in formation of transition metal complexes, is a lustrous grey white transition element with atomic number 40. However, the human body contains 250 mg of the metal, depending on the nutritional diet with a daily consumption of 4.1mg collectively through food (3.5 mg) and water (0.65 mg). In nature, zirconium is widely distributed and may be found in all biological systems such as whole wheat, brown rice, spinach, eggs and ground beef. Furthermore, the metal is widely employed in lucrative items such as fumigant sticks and aerosol antiperspirants, a subclass of deodorants like aluminium zirconium tetrachlorohydroxies having the potential to clog pores in the skin and preventing sweat from escaping. Zirconium is also used in water filtration to prevent phosphorus pollution[15,20].

Due to the wide commercial applications of zirconium, we need to create a process for micro scale analysis of the element that is reliable, quick, has good sensitivity and selectivity. The target is accomplished using numerous techniques involving first derivative spectrophotometry, graphite furnace atomic absorption spectrometry (GFAAS), inductively coupled plasma atomic emission spectrometry (ICP-AES), laser ablation inductively coupled plasma optical emission spectrometry (LAICP-OES), adsorption inversion voltametry and UV-VIS Spectrophotometry[1-3,6,9,10,12,14,16,18,21-23]. However, the most effective approach satisfying the mentioned requirements is the UV-VIS spectrophotometry[1-3,6,9,10,14,23].

The selected analytical reagent, 3-hydroxy-2-[2'-(5'-methylthienyl)]-4*H*-chromen-4-one (HMTC) was applied to analyse zirconium (IV) spectrophotometrically with commendable results as reported[6]. Extractable into dichloromethane from ammoniacal medium, Zr (IV) is noticed to form a 1:4 (M:L) yellow coloured complex with HMTC at pH 7.05-7.09 and λ_{max} 424-440 nm and obeying Beer's Law up to 0.9 μg Zr (IV) ml^{-1} . Molar absorptivity of the Zr (IV)-HMTC complex was 8.22×10^{4} l $mol^{-1}cm^{-1}$ with a sensitivity of 0.0011 μg Zr (IV) cm^{-2}, the regression equation being Y=0.981X-0.036 with a detection limit of 0.0174 μg ml^{-1}.

The obtained results were highly consistent with the standard deviation(SD) of ±0.0039 a.u. as confirmed by a 0.5 % limit by student's t-test. The proposed method has been tested on a variety of synthetic and industrial samples with great success.

The presented theoretical study has been performed to get a comprehensive quantum examination of the structural characteristics of the mentioned spectrophotometrically analysed zirconium (IV) metal complex with HMTC using DFT simulations. Experimental data is directly compared to quantum chemical parameters by the thus present study.

Computational Details

The Gaussian09 package was used to perform DFT and theoretical calculations on the ligand (HMTC) and its Zr (IV) complex. The basis set for HMTC is B3LYP, 6-311G, ++, d, p, charge 0 with singlet spin, whereas the optimisation basis set for Zr (IV)-HMTC complex is B3LYP, LanL2DZ, charge 0 with singlet spin[4,8]. For a deeper structural knowledge of HMTC and the complex, quantum mechanical characteristics such as HOMO and LUMO energies and HOMO-LUMO energy gap (E_{gap}) were determined. The various reactivity descriptors like chemical potential (P_i), absolute electronegativities (χ), absolute hardness (η), global electrophilicity (ω), absolute softness (σ) and fractional change of transferred electron (ΔN) to apprehend the direction of electron flow, were evaluated for both HMTC and the complex using HOMO and LUMO energy values and the formulae are given below[5,7,11,13,17,26,28].

$$\chi = -(E_{LUMO} + E_{HOMO})/2; \ \eta = (E_{LUMO} - E_{HOMO})/2$$

$$\sigma = 1/\eta; \ P_i = -\chi$$

$$\omega = P_i^2/2\eta; \ \Delta N = -P_i/\eta$$

Optimisation of HMTC and Zr (IV)-HMTC complex

Frontier Molecular Orbital: Computational studies have opened up a lot of possibilities for designing ideal geometric structures and electrical characteristics for ligands and their complexes. DFT hence has been used to investigate the stability and reactivity of HMTC and its Zr (IV) complex. Figure 1 and 2 show the optimised structures of the ligand, HMTC and its Zr (IV) complex. Figures 3-6 show the distributions of electron density of frontier molecular orbitals (FMOs), that is HOMOs and LUMOs, for HMTC and Zr (IV)-HMTC complex respectively.

E_{HOMO} and E_{LUMO} are generally used as reactivity markers in terms of molecule's willingness to give and receive electrons under favourable conditions. The frontier orbital gap, E_{gap}, the energy difference between HOMO and LUMO is a crucial component in defining the electrical transport characteristic of a molecule. The FMO energies, E_{gap} and dipole moments of the investigated Zr (IV)-HMTC complex are listed in table 1. HMTC is a soft molecule with a small E_{gap} that is highly polarizable carrying a high chemical reactivity and a low kinetic stability indicating that the chelating agent HMTC donates its electron density from its HOMO to the LUMO of the core metal ion for chelation. The complex Zr(IV)-HMTC has larger ΔE_{gap} making it a hard kinetically stable molecule with low polarizability and low chemical reactivity. Thus, highly stable nature of Zr (IV)-HMTC complex (stability > 4 days) as deduced from spectrophotometric examination is supported satisfactorily by DFT studies.

Furthermore, the Zr (IV)-HMTC complex has a large dipole moment, indicating strong dipole dipole interactions. The predicted energy change is provided in table 1 as the energy change that a molecule may achieve for the optimal optimisation of its structure with no negative frequencies for evaluation of the HOMO and LUMO structures of HMTC and Zr (IV) - HMTC along with the achieved values.

Reactivity descriptors: For the Zr (IV)-HMTC complex, a positive high value of electronegativity (χ) indicates that Zr (IV) accepts electrons from its HMTC ligand environment, thus increasing stability of the created complex. Absolute Hardness (η) and Absolute Softness (σ), denoted by high and low E_{gap} respectively showed HMTC as a soft molecule and Zr (IV)-HMTC complex as a hard one, implying more ligand reactivity and hence the development of a stable and soft complex with low reactivity and high ΔE_{gap}.

The Zr (IV)-HMTC complex has a bigger negative work function (Pi) indicating greater stability and resistance of the Zr (IV)-HMTC complex to breakdown into its constituent metal ion and ligand. The electrophilicity index (ω) is a measure of a species' proclivity for accepting electrons.

Table 1
Frontial Molecular Orbitals and Energies

	HOMO (eV)	**LUMO (eV)**	**ΔE_{gap} (eV)**	**Dipole moment (Debye)**	**Predicted energy change (Hartree)**
HMTC	-4.93152	-2.26426	2.66726	1.274546	-5.49×10^{-09}
Zr (IV)-HMTC	-6.10297	-2.26371	3.83926	6.332182	-9.83×10^{-09}

Table 2
Reactivity descriptors

S.N.	**Parameter**	**HMTC**	**Zr (IV)-HMTC complex**
1	χ(eV)	3.59789	4.18334
2	η(eV)	1.33363	1.91963
3	σ(eV^{-1})	0.74983	0.52093
4	P_i(eV)	-3.59789	-4.18334
5	ω(eV)	4.85322	4.55825
6	ΔN	2.69782	2.17924

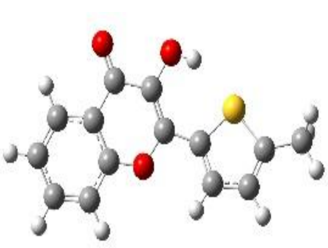

Fig. 1: Structure of HMTC

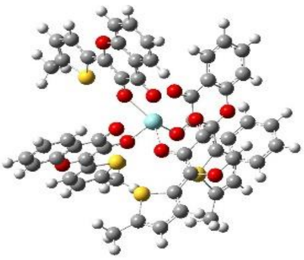

Fig. 2: Optimised geometry of Zr (IV)- HMTC complex

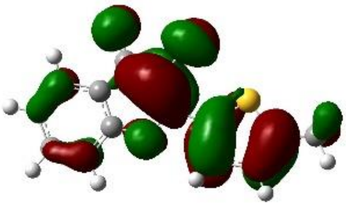

Fig. 3: HOMO of HMTC

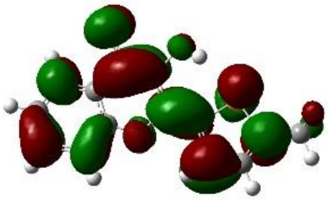

Fig. 4: LUMO of HMTC

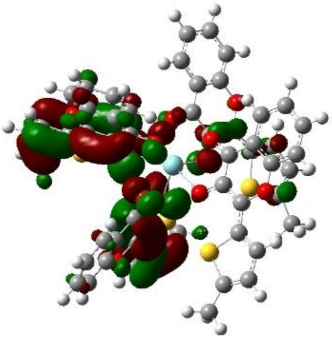

Fig. 5: HOMO of Zr(IV)-HMTC complex

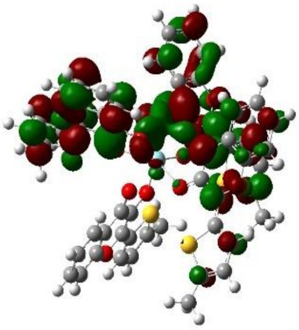

Fig. 6: LUMO of Zr(IV)-HMTC complex

Table 3
Stabilization Energy

1	$\Delta E_{A(B)}$(eV)	-7.76516
2	$\Delta E_{B(A)}$(eV)	-4.55826
3	$\Delta E_{SE(AB)}$(eV)	-12.32342

Compounds with high nucleophilicity and electrophilicity are at opposite extremities of the global scale. An efficiently reactive nucleophile has a lower value of ω; on the other hand, electrophile with a high value of ω is effective. A lower ω value for ligand implies that it is nucleophilic favouring complexation with the positively charged Zr (IV) ion. For HMTC, ΔN, the fraction of electrons transferred, is high, indicating that electron donation/transfer from ligand to tetravalent zirconium metal is feasible. The mentioned descriptors have been shown in table 2.

To achieve structure stability, the total change of stabilization energy ($\Delta E_{SE(AB)}$) as a function of reactivity descriptors was computed (Table 3) by using the following equations[19] where the subscript A denotes HMTC molecule and B signifies Zr (IV)-HMTC complex.

$$\Delta E_{A(B)} = \Delta N\,(-\chi_A + \tfrac{1}{2}(\eta_A \Delta N)); \quad \Delta E_{B(A)} = \Delta N\,(-\chi_B + \tfrac{1}{2}(\eta_B \Delta N))$$

$$\Delta E_{SE(AB)} = \Delta E_{A(B)} + \Delta E_{B(A)}$$

Electrostatic surface potential (ESP): Electrostatic surface potential (ESP) method[27,29] further can be used effectively to determine the molecule's reactivity as well as the presence of intermolecular or intramolecular interactions. This presentation also aids in comprehending the molecule's size, reactivity site, shape and charge density delocalization. In the shown ESP diagrams (figures 7 and 8), several hues like yellow, orange, red, bluish green and blue can be utilised to depict the distinct regions of electrical potential that emerged at the surface of molecule HMTC and its Zr (IV) complex.

The figures show a plot of the ESP of HMTC and Zr (IV)-HMTC complex using a colour code ranging from -5.128×10^{-2} to $+5.128\times10^{-2}$. Red represents an electron-rich area or a more negative site whereas blue represents a positive site or the electron deficient area.

In the HMTC molecule,the pyran ring has the maximum electron density as indicated by a great red coloured zone in ESP, justifying donor nature of the site. In Zr (IV)-HMTC complex, further it can be seen that higher electron density is around the pyran ring of the four HMTC ligands and the central metal atom Zr (IV), thus supporting the fact that there is donation of electrons from pyran site of HMTC to Zr (IV) metal ion.This conclusion is in accordance to the chelating linkage between HMTC and the metal ion, the same as proposed by the stoichiometric study in spectrophotometric analysis of the Zr (IV)-HMTC complex.

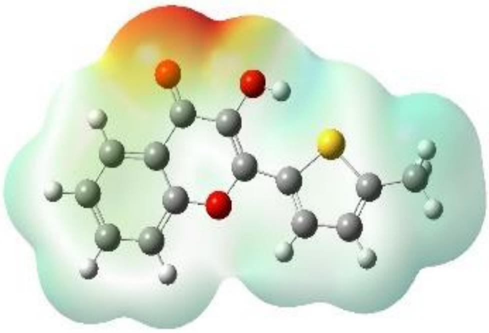

Fig. 7: ESP of HMTC

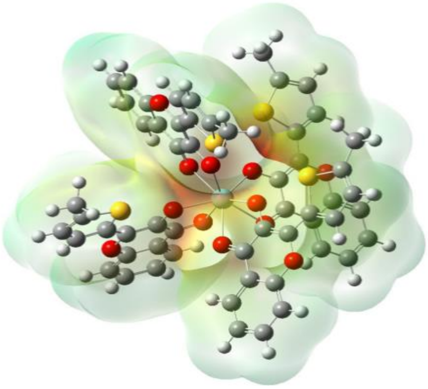

Fig. 8: ESP of Zr (IV)-HMTC Complex

Conclusion

To forecast structural shape and to establish the Zr(IV)-HMTC complex's ultimate stoichiometry, the reported analytical research is successfully extended to DFT calculations. By coordinating the benzopyran ring to metal centre, the calculations not only established an optimum complex structure, but also proved the bidentate ligand's chelating efficiency.

ESP structures for both HMTC and its tetravalent zirconium complex also indicated clearly the presence of electron density around pyran ring in the ligand HMTC and around core metal atom in the complex Zr(IV)-HMTC, thus justifying the coordinating sites. The theoretical study about the respective structures done thereby supported the results obtained by spectrophotometric studies.

Acknowledgement

Thanks go sincerely to the authorities, Maharishi Markandeshwar (Deemed to be University), Mullana for providing facilities to carry out the present work.

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(Received 02nd January 2022, accepted 04th March 2022)