



Zirconium (IV)-3-hydroxy-2-tolyl-4*H*-chromen-4-one complex—the analytical and DFT studies

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Abstract

Trace determination of Zr(IV) was carried out by its complexation with a newly synthesized chromone derivative, 3-hydroxy-2-tolyl-4*H*-chromen-4-one (HToC) for the formation of a 1:4 (M:L) yellow-colored complex from the bicarbonate medium maintained at pH 7.90–8.13. The complex was extractable into the non-aqueous organic solvents showing maximum and stable color intensity in dichloromethane in the wavelength range 414–430 nm. The complex obeyed Beer's law showing linearity of calibration curve in the range 0.0–1.1 $\mu\text{g Zr(IV) ml}^{-1}$ with an optimum range of determination as 0.44–1.0 ppm Zr(IV) detected from the Ringbom plot. Molar absorptivity, specific absorptivity, and Sandell's sensitivity of thus prepared complex were ascertained, respectively as $4.1971 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$, $0.4601 \text{ ml g}^{-1} \text{ cm}^{-1}$, and $0.0022 \mu\text{g Zr(IV) cm}^{-2}$ at 420 nm. The linear regression equation being $Y = 0.4485X + 0.0114$ ($Y = \text{absorbance}$, $X = \mu\text{g Zr(IV) ml}^{-1}$) with the correlation coefficient of 0.9977 and detection limit of the procedure as $0.0729 \mu\text{g ml}^{-1}$. Theoretical calculations were used to determine and compare structural and bonding properties of the Zr(IV)-HToC complex along with justification of the donor sites provided by ligand for complexation with respect to the metal. The consequences obtained were highly cogent with standard deviation of ± 0.0021 absorbance unit. The procedure was applied to various synthetic (some analogous to cooperate and nickel zirconium) and technical (reverberatory flue dust and water) samples with satisfactory results.

Keywords Zirconium · 3-hydroxy-2-tolyl-4*H*-chromen-4-one · Extraction · Spectrophotometric determination · DFT

Introduction

Chromones comprise of significant organically transpiring compounds thus building curiosity due to their fruitfulness as biologically active reagents. Chromone subsidiaries incorporate cytotoxic (anticancer), neuroprotective, HIV-inhibitory, antimicrobial, antifungal, and cell reinforcement activities [1]. In addition, these reagents give rise to more deep colored complexes with metal ions including vanadium, both in its trivalent [2] and pentavalent [3] states, molybdenum [4], niobium [5], tungsten [6], palladium [7], thorium [8], cerium [9], and tin [10]. This coloring gives advantage for

its use in analysis of different metal ions and their properties. Thus, research has to expand for the same reason.

In the following manuscript, a new chromone named 3-hydroxy-2-tolyl-4*H*-chromen-4-one (HToC) has been complexed with zirconium(IV) to produce a yellow-colored complex that has been studied for its description via UV–VIS spectrophotometry. The presented system is quiet transitory, reliable, more selective, and sensitive as compared to a number of existing methods of determination of zirconium [11–15] using chromones or other organic reagents and holds a good application in numerous synthetic, technical, and natural samples of analytical interest.

In addition to spectrophotometric analysis, computational methods are found to be of utmost benefit for understanding molecular structure, electron distribution, and chemical reactivity of the transition metal complexes these days [10, 16–20]. Study has been expanded using Density Functional Theory for quantum chemical calculations on the presented Zr(IV)-HToC complex that is effective enough for the determination of chemical behavior of the developed complex and its rationalization thus justifying the stability.

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Methodology

Experimental

Equipments, reagents, and solutions

The UV–VIS spectrophotometer used for absorbance measurements and spectral investigation, the standard stock solution and working solutions of Zr(IV), and the solutions of other metal ions were the same as used in our earlier reported method [21].

Sodium bicarbonate (2 M) was prepared fresh to be used for complexation and analysis. Dichloromethane (DCM; CDH® 'AR') was used as the extraction solvent.

HToC [molecular formula = C₁₆H₁₂O₃, molar mass = 252 g mol⁻¹, melting point = 206 °C] was synthesized by the literature method [22–24] (Fig. 1), and its 0.2% (m/v) fresh solution in ethanol was used for analysis.

Synthetic and technical samples

As depicted in Table 1, Zr(IV)-HToC complex was mixed with diverse composition of metal ions in suitable quantities to form synthetic samples. In addition to this, technical samples like reverberatory flue dust and water (tap and well) were dissolved to appropriate volumes as per prior accounted work [21].

Computational methods

The quantum chemical computation with geometry optimization of the ligand and complex molecules was performed using the B3LYP (Becke's three parameter hybrid functional using the LYP correlation functional) at 6–31 p G(d,p) basis set with Hyperchem Professional 8.0 packet program [25]. For better understanding of chemistry of complexes, quantum chemical parameters have been executed, rooted on the study of electronic parameters of the complex in its most stable conformation. The HOMO/LUMO energies [25] and the band gap energy ($E_{\text{gap}} = E_{\text{HOMO}} - E_{\text{LUMO}}$) [26] had

Table 1 Examination of various synthetic samples

S No	Sample Composition		Zr(IV) found (μg 10 ml ⁻¹)**
	Matrix*	Zr(IV) added (μg 10 ml ⁻¹)	
1	Zn(5), Ca(5), Cr ^{VI} (0.1) ^a	4	4.23 ± 0.03
2	V(0.1), Hg(2), Cd(5) ^b	2	1.99 ± 0.01
3	Mo(0.1), Pb(3), Ni(5) ^c	6	5.94 ± 0.005
4	W(0.1), Bi(0.01), Au(0.5) ^d	10	10.11 ± 0.02
5	Fe ^{III} (0.2), Co(0.5), Se(0.2) ^a	6	6.04 ± 0.016
6	Pd(0.2), Sr(0.5), Al(0.2) ^c	4	4.23 ± 0.016
7	Fe ^{II} (0.5), Nb(0.5), Pt(0.1) ^f	2	2.24 ± 0.010
8	Ti(0.1), Ir(0.5), As(0.5) ^g	6	6.13 ± 0.010
9	Ba(2), Sr(0.5), Se(0.2)	10	10.02 ± 0.016
10	Pd(0.5), La(0.5), Hg(3)	4	4.17 ± 0.026
11	Mg(2), Sn(0.5), Cu(0.5)	8	8.06 ± 0.016
12	Ni(0.07), W(0.123) ^{d,h}	5	5.10 ± 0.012
13	Ni(2.68) ^h	5	5.13 ± 0.0124
14	Water (i) tap water	8	7.96 ± 0.008
	(ii) Well water	4	4.19 ± 0.02
15	Reverberatory flue dust	6	6.06 ± 0.016

*Numbers in parentheses indicates amount of metal ion in mg 10 ml⁻¹. **Average of triplicate analysis ± SD. ^aIn the presence of 100 mg ascorbic acid; ^bIn the presence of 20 mg Disodium 'EDTA'; ^cIn the presence of 1 ml hydrogen peroxide; ^dIn the presence of 100 mg sodium thiocyanate; ^eIn the presence of 100 mg sodium iodide; ^fIn the presence of 50 mg potassium fluoride; ^gIn the presence of 100 mg sulphosalicylic acid; ^hComposition analogous to cooperite and nickel zirconium, respectively

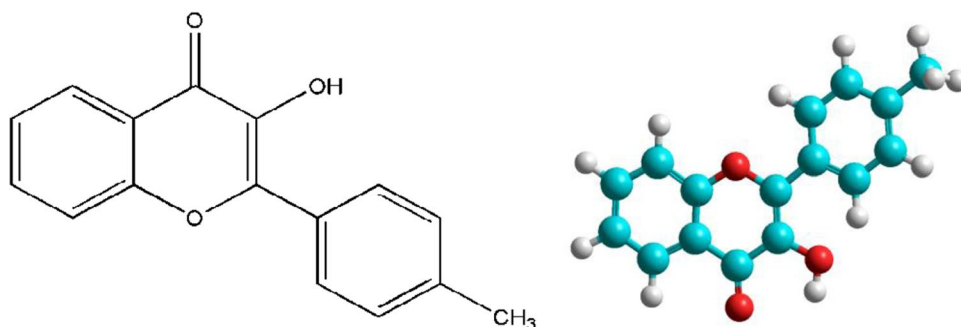
been evaluated and utilized for determination of electronic properties of Zr(IV)-HToC complex such as the ionization energy I , electron affinity A [27], electronegativity (χ), absolute hardness (η), global softness (σ), and work function P_i , as premeditated deploying the following respective equations [28]:

$$I = -E_{\text{HOMO}}; A = -E_{\text{LUMO}};$$

$$\chi = (I + A)/2; \eta = (I - A)/2;$$

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

Fig. 1 Structure of HToC (2D and optimized)



Reactivity of a molecule could be explained with consideration of chemical hardness, which is directly proportional to the HOMO–LUMO energy gap (DEH-L) [29, 30]. Higher chemical hardness or higher DEH-L indicates lower reactivity of molecule.

Recommended procedure for analysis

To an aliquant holding $\leq 11 \mu\text{g}$ Zr(IV) solution and adjusting its pH 8.01 by adding sodium bicarbonate solution was added 1 ml of 0.2% (m/v) ethanolic solution of HToC and enough doubly deionized water thus raising the final aqueous volume to 10 ml in a 125-ml separating funnel. The complex formed in the aqueous solution was then transferred to non-polar equivolume organic solvent, DCM, by equilibrating once for 30 s with continuous release of pressure through stop cock. As the complex got transferred to organic layer, it was filtered through Whatman filter paper 41 (pre-treated with DCM) in a 10-ml volumetric flask and made upto the mark with pure DCM. A yellow-colored complex extract obtained was measured for absorbance at 420 nm averse to blank HToC prepared in a complimentary manner. The precise amount of zirconium was thus calculated from calibration curve acquired by plotting a graph between varied zirconium amount and the respective absorbance under optimum conditions of the said procedure.

Results and discussion

HToC formed a yellow-colored complex having stability for more than 4 days with Zr(IV) in a sodium bicarbonate medium maintained at pH 7.90–8.13. Absorption spectra for Zr(IV)-HToC complex showed maximum absorption range 414–430 nm in contrast to blank that absorbed very little in the same range (Fig. 2). Hence, all measurements were carried out at 420 nm. The complexation tendency and extraction conduct were explored in several media and solvents respectively and were observed to increase in the following order:

$\text{HCl} < \text{NH}_3 < \text{Na}_2\text{CO}_3 < \text{H}_2\text{SO}_4 < \text{H}_3\text{PO}_4 < \text{CH}_3\text{COOH} < \text{HClO}_4 < \text{NaHCO}_3$

Methyl isobutyl ketone < Carbon tetrachloride < Toluene < Benzene < Cyclohexane < Ethyl acetate < Chloroform < 1,2-Dichloroethane < Isoamyl acetate < Dichloromethane(DCM)

The extraction in DCM was quantitative (100%) showing maximum and stable (more than 4 days) optical density in it and thereby verifying the reason for its choice in this proposed method of analysis.

The impact of varied physical parameters like pH (using sodium bicarbonate), HToC concentration, and equilibration time for Zr(IV)-HToC extraction and determination

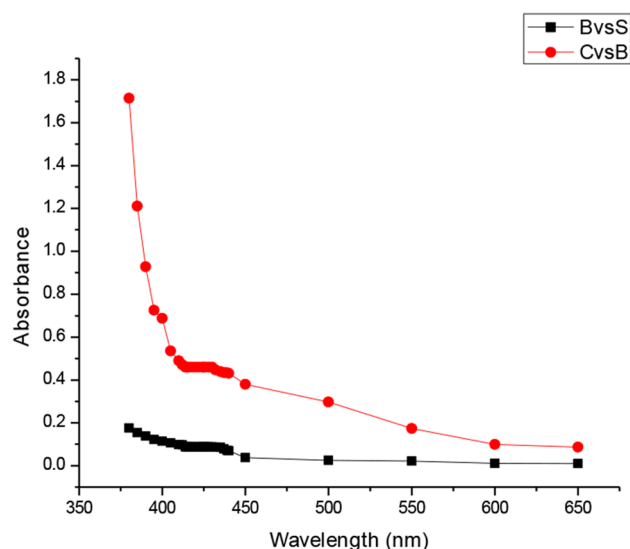


Fig. 2 Absorption spectra of Zr(IV)-HToC complex in dichloromethane; C vs B: $1.0 \mu\text{g ml}^{-1}$ zirconium(IV) measured against reagent blank; B vs S: Reagent blank measured against dichloromethane

process have been summarized in Table 2. Concisely, a yellow-colored Zr(IV)-HToC complex is formed containing $\leq 11 \mu\text{g}$ Zr(IV) in 10 ml of aqueous phase, maintaining a pH 7.90–8.13 by adding sodium bicarbonate followed by addition of 0.6–1.2 ml of 0.2% (m/v) HToC solution in alcohol, in same order and extracting in equi-volume DCM for 10–300 s to show maximum and stable absorbance in the wavelength range 414–430 nm.

Effect of anions/complexing agents and cations

Effect of diverse ions had been studied by adding respective diverse ions (prior to addition of the reagent) under ideal conditions of the suggested plan to $10 \mu\text{gZr(IV)}$ concentration in 10 ml aqueous volume. For evaluation of selectivity of Zr(IV)-HToC system and to depict its tolerance limit, impact of different anions/complexing agents and cations had been explored as shown in Tables 3 and 4. The tolerance limit was customized as the amount of diverse ion causing an error $\pm 1\%$ in the extracted species. The interfering effect of some of the samples had been studied under the presence of masking/complexing agents to nullify their impact. Of the 22 anions and 32 cations studied (alone/after masking), only oxalate interfered seriously.

Ocular attribution, precision, and accuracy

Zr(IV)-HToC yellow-colored complex following proposed procedure showed a linear response upto $1.1 \mu\text{g ml}^{-1}$ with an optimum range of determination 0.44–1.01 ppm

Table 2 Effect of physical parameters on the absorbance of Zr(IV)-HToC complex

pH ^a	6.81	7.42	7.65	7.80	7.84	7.88	7.90–8.13	8.19	8.24
Absorbance	0.156	0.322	0.379	0.429	0.439	0.445	0.460	0.428	0.380
HToC (ml) ^b	0.1	0.2	0.5	0.6–1.2	1.3	1.4	1.5	2.0	2.5
Absorbance	0.120	0.220	0.430	0.460	0.449	0.440	0.420	0.391	0.357
Equilibration time(s) ^c	0	2	5	10–300					
Absorbance	0.002	0.433	0.438	0.460					

Conditions: ^aZr(IV) = 10 µg; pH = variable; HToC [0.2% (m/v) in alcohol] = 1 ml; aqueous volume = solvent volume = 10 ml; solvent = dichloromethane; equilibration time = 30 s; λ_{\max} = 420 nm

^bpH = 8.01; remaining parameters same as in (a) except for the variation in HToC concentration; HToC = 3-hydroxy-2-tolyl-4H-chromen-4-one

^cHToC [0.2% (m/v) in alcohol] = 1ml; remaining parameters same as in (b) excepting variation in equilibration time

Table 3 Effect of anions or complexing agent on Zr(IV)-HToC complex

S. No	Anion or complexing agent added	Tolerance limit (mg 10 ml ⁻¹)	Absorbance
1	None	-	0.460
2	Sodium chloride, sodium bromide, sodium iodide, sodium nitrate, sodium carbonate, sodium sulfite, potassium thiocyanate, thiourea, sulfosalicylic acid, sodium sulfate, ascorbic acid, hydrazine sulfate	100	0.460
3	Sodium dithionite, sodium nitrite, potassium fluoride	50	0.460
4	'Disodium' EDTA, sodium phosphate	20	0.460
5	Sodium acetate	10	0.460
6	Sodium potassium tartrate	1	0.460
7	Hydrogen peroxide (30%), glycerol	1*	0.460
8	Sodium oxalate**	0.1	0.400

*Amount added in ml; **Seriously interfered

Table 4 Effect of cations on Zr(IV)-HToC complex

S. No	Cation Added	Tolerance limit (mg 10 ml ⁻¹)	Absorbance
1	None	-	0.460
2	Ir(III), Ru(III), Al(III), Zn(II), Pb(II), Hg(II), Ca(II), Ba(II), Co(II) Mg(II), Mn(II), Ce(II), Ni(II), Cd(II), Ag(I)	10	0.460
3	Se(IV)	5	0.460
4	Cr(VI) ^a	2	0.460
5	Pt(IV), Au(III), As(III), Bi(III), Cu(II), Sr(II), Fe(II) ^b	1	0.460
6	Mo(VI) ^c , W(VI) ^d , V(V) ^e , Nb(V), La(III), Fe(III) ^a , Sn(II), Pd(II) ^f	0.5	0.460
7	Ti(IV) ^g	0.2	0.460
8	Cr(III)	0.1	0.460

^aIn the presence of 100 mg ascorbic acid; ^bIn the presence of 50 mg potassium fluoride; ^cIn the presence of 1 ml hydrogen peroxide; ^dIn the presence of 100 mg sodium thiocyanate; ^eIn the presence of 20 mg Disodium 'EDTA'; ^fIn the presence of 100 mg sodium iodide; ^gIn the presence of 100 mg sulfosalicylic acid

as determined via Ringbom plot [31]. The method had a correlation coefficient of 0.9977 further confirming the linearity of calibration curve. Student's *t* test [32] at 10% confidence level divulged that no biasness in the applied method had occurred. Table 5 tabulates spectral and ocular innate.

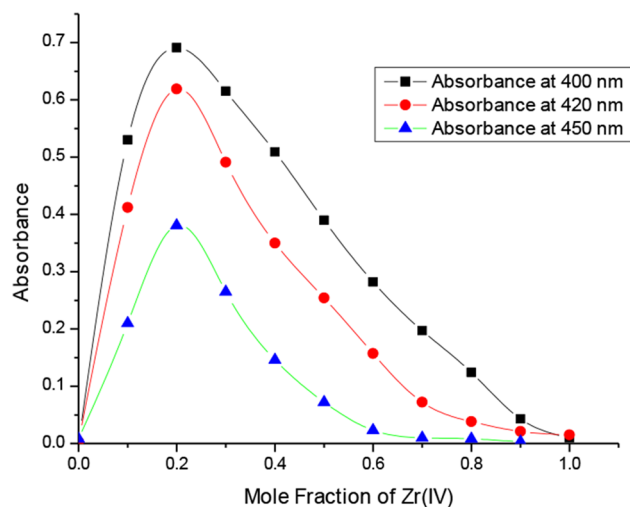
Stoichiometry of Zr(IV)-HToC complex

As confirmed by Job's continuous variation method [33] revised for a two-phase system by Vosburgh and Cooper [34], the complex showed 1:4 (M:L) stoichiometric ratio (Fig. 3). This was also confirmed by mole ratio (Fig. 4) [35] and equilibrium shift methods [36].

Table 5 Spectral characteristics, precision, and accuracy data

S. No	Parameter	Value
1	λ_{\max} (nm)	414–430
2	Beer's law limits ($\mu\text{g ml}^{-1}$)	0–1.1
3	Optimum range of determination (ppm)	0.44–1.01
4	Molar absorptivity ($\text{l mol}^{-1} \text{cm}^{-1}$)	4.1971×10^4
5	Sandell's sensitivity ($\mu\text{g cm}^{-2}$)	0.0022
6	Correlation coefficient (r)	0.9977
7	Regression equation (Y) [*]	$Y = 0.4485X + 0.0114$
8	Slope (b)	0.4485
9	Intercept (a)	0.0114
10	Standard deviation	± 0.0021
11	Relative standard deviation (%)	0.45
12	Limit of detection ($\mu\text{g ml}^{-1}$)	0.0729

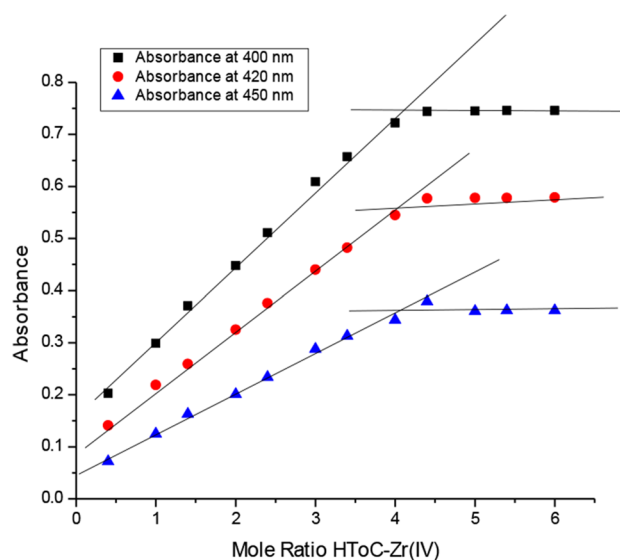
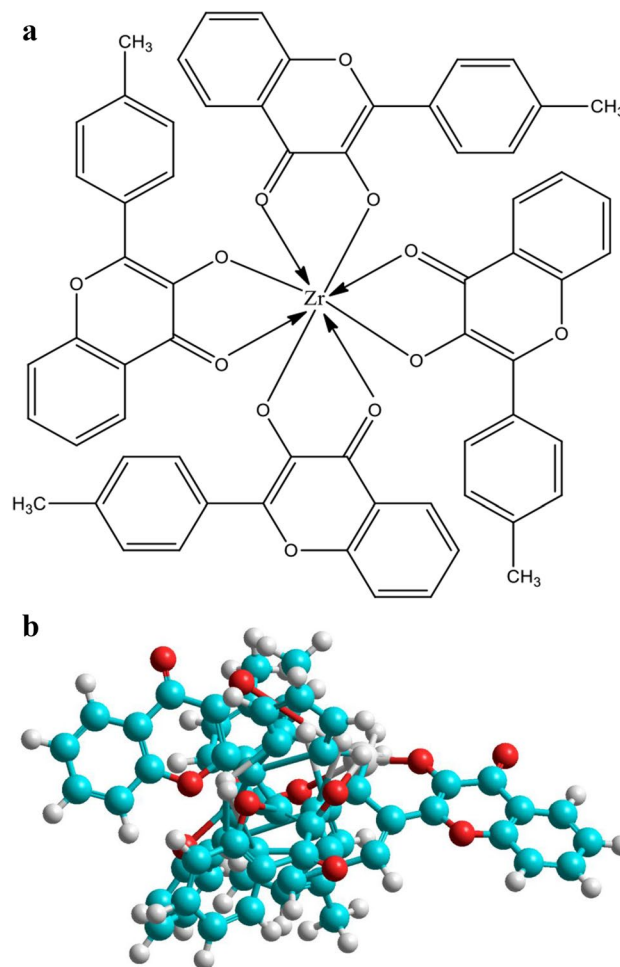
* $Y = 0.4485X + 0.0114$; where Y = absorbance and X = Concentration of Zr(IV) in $\mu\text{g ml}^{-1}$

**Fig. 3** Job's continuous variations method $[M] + [L] = 1.096 \times 10^{-3}$ M

Obtained from the above stoichiometry, Fig. 5a and b below present the proposed and optimized structure of the Zr(IV)-HToC complex, respectively.

Structural elucidation by DFT

DFT helps in determining the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) energies. The most important orbitals in a molecule are these frontier molecular orbitals, called HOMO and LUMO. The frontier orbital gap helps to specify the chemical reactivity and kinetic stability of the molecule. A molecule with a small frontier orbital gap is more polarizable, is generally associated with a high chemical reactivity

**Fig. 4** Mole ratio method $[M] = 5.48 \times 10^{-4}$ M**Fig. 5** a Proposed structure of Zr(IV)-HToC complex, b Optimized structure of Zr(IV)-HToC complex

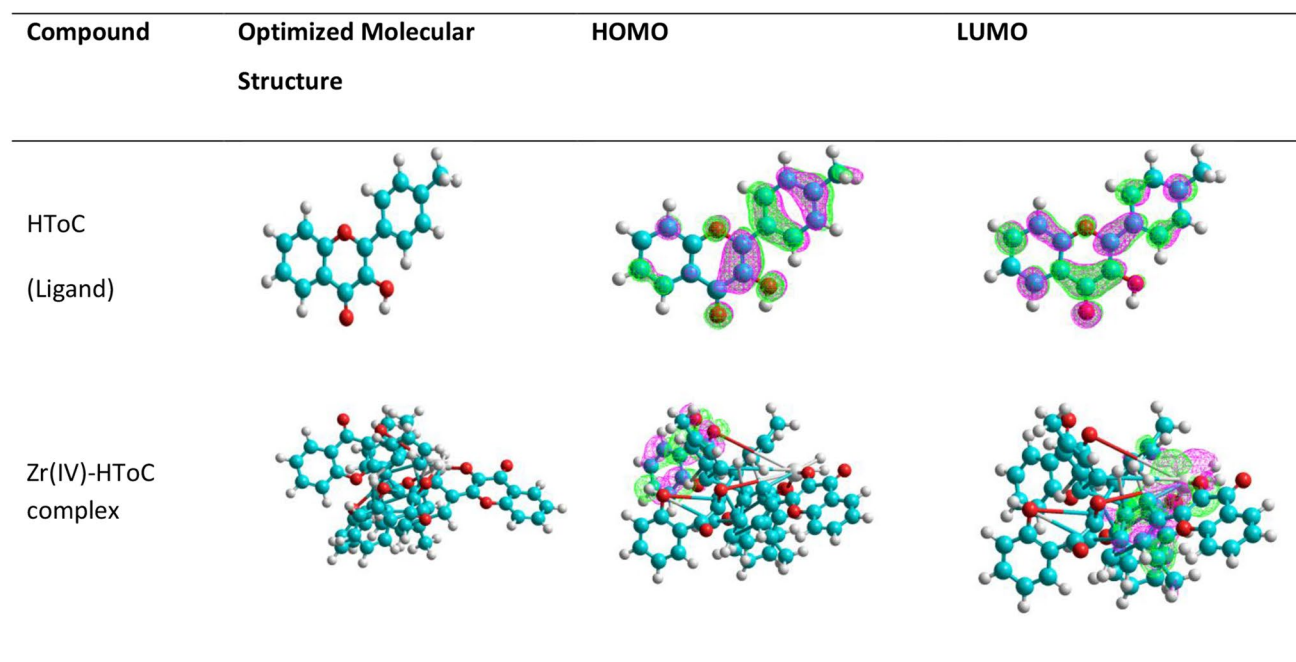


Fig. 6 DFT-derived geometry optimized structures; HOMO and LUMO plot of HToC and Zr(IV)-HToC complex; Green color indicates electrophilic center or most positive potential; and violet color, the nucleophilic center or the most negative potential

and low kinetic stability, and termed as soft molecule [37]. The energy gap between HOMO and LUMO is a fundamental parameter to determine molecular electrical transport properties.

The frontier molecular orbitals give us a detailed idea of intending sites of a molecule involved in donor–acceptor correspondence between a ligand (HToC) and complex Zr(IV)-HToC. Figure 6 depicts the optimized structure and HOMO and LUMO electron density distributions of both ligand as well as its Zr(IV) complex. It is quite obvious from the figure that in case of ligand, HOMO electron density has been distributed majorly over pyran ring suggesting its higher electron-donating tendency. In addition to this, structure is an active center for its interaction with zirconium metal as suggested by HOMO and LUMO electron density distribution over hetero atom contained in pyran moiety.

Figure 7 outlines mapped molecular electrostatic potential (MEP) with violet color indicating the most negative potential (-0.140 eV) or the nucleophilic center, mainly localized over hetero oxygen atom, pyran ring, and also conjugated double bonds which further confirmed the dative sites of HToC ligand. Green color had been allocated to the most positive potential ($+0.588$ eV) or the electrophilic center.

Table 6 lists the quantum chemical parameters, and we can infer that higher value of E_{HOMO} for ligand HToC depicts a good chance of electron donation while lower E_{LUMO} value shows better chance of electron acceptance by zirconium

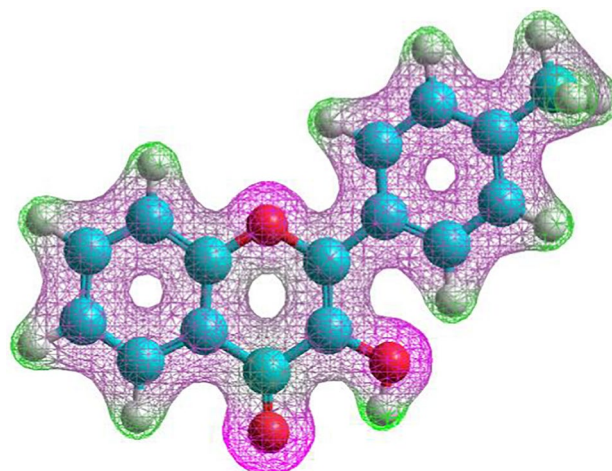


Fig. 7 Electrostatic potential mapped on 3D isosurface of HToC

Table 6 Computed quantum chemical parameters

S. No	Compound	E_{HOMO} (eV)	E_{LUMO} (eV)	ΔE_{gap} (eV)
1	HToC (ligand)	-8.20514	-1.55714	6.64800
2	Zr(IV)-HToC complex	-8.73811	-0.91522	7.82289

Table 7 Global chemical reactivity indicators of HToC and Zr(IV)-HToC

S. No	Compound	χ (eV)	η (eV)	σ	P_i
1	HToC	4.88114	3.32399	0.30084	-4.88114
2	Zr(IV)-HToC complex	4.82666	3.91144	0.25566	-4.82666

χ = electronegativity, η = absolute hardness, σ = global softness, P_i = work function

metal atom respectively. Higher ΔE_{gap} of the complex in comparison to pure ligand also justifies that a stable Zr(IV)-HToC complex is formed. In addition to this, other chemical descriptors like chemical hardness/global hardness (η) which is directly proportional to the HOMO–LUMO energy gap is higher for Zr(IV)-HToC complex in comparison to pure HToC indicating lower reactivity of complex. Global softness η is reciprocal of global hardness representing another parameter for determining low reactivity of the formed stable complex. χ (eV) or P_i indicates further that the complex is highly stable and will not undergo decomposition in its constituent metal atom and ligand (Table 7).

Other properties of Zr(IV)-HToC complex in its unoptimized and optimized states as evaluated by HyperChem software are summarized in Table 8. The properties reveal that optimized structure (Fig. 5b) is the most stable conformation of the complex. Lower binding energy of optimized Zr-HToC complex reflects the stable complex formation. The negative binding energy value reveals that the complex formed is more stable than the reactants, and high amount of energy will be required to split the metal complex into its constituent ligand and metal ion respectively. In general, binding energy is the difference between the total energy of products and individual reactants in DFT calculations.

Applications

Tables 1, 3, 4, and 5 summarized the application part of Zr(IV)-HToC complex system depicting its rapidity, sensitivity, reproducibility, and selectivity. The proposed method had been successfully used for examining various samples (some of them resembling to the alloys of cooperite and nickel zirconium), natural (water from different sources), and technical (reverberatory flue dust) samples. Proposed method had also been compared with the existing methods of zirconium determination and was found to surpass the latter as mentioned is visualized in Table 9.

Table 8 Optimized properties of Zr(IV)-HToC complex

S. No	Properties	Zr(IV)-HToC (unoptimized)	Zr(IV)-HToC (optimized)
1	Total energy (kcal mol ⁻¹)	540,775.2218	-273,460.2305
2	Binding energy (kcal mol ⁻¹)	800,237.5538	-13,997.8985

Table 9 Collation table of proposed method compared with reported methods

S. No	Aqueous conditions	λ_{max} (nm), solvent	Molar absorptivity (l mol ⁻¹ cm ⁻¹)	Interference	Reference
1	Zr(IV), 2-(2'-furyl)-3-hydroxy-4-oxo-4H-1-benzopyran, pH 6.7–7.3	420, Benzene	1.04×10^5	Pb(II), Zn(II), disodium EDTA, phosphate, and H ₂ O ₂	[11]
2	Zr(IV), 5,7-dibromo-8-hydroxyquinolin in the presence of thiocyanate	416, Chloroform	1.055×10^4	Oxalate, EDTA disodium salt, fluoride	[12]
3	Zr(IV), 2-hydroxynaphthaldehyde-p-hydroxybenzoic hydrozone, pH 1.0, acidic medium, heating for 15 min at 60 °C	415, -	9.86×10^3	-	[13]
4	Zr(IV), 6-chloro-3-hydroxy-2-phenyl-4H-chromen-4-one, In HCl medium	415, Dichloromethane	5.930×10^5	Oxalate, phosphate, EDTA 'disodium'	[14]
5	Zr(IV), 6-chloro-3-hydroxy-2-(2'-hydroxyphenyl)-4-oxo-4H-1-benzopyran	400, Propane-1-ol-H ₂ O	1.78×10^4	EDTA'disodium, tartrate, oxalate, phosphate, Nb(V) and Pb(II)	[15]
6	Zr(IV), 3-hydroxy-2-tolyl-4H-chromen-4-one, pH 7.90–8.13	420, Dichloromethane	4.1971×10^4	Oxalate	Proposed Method

Conclusion

A new binary liquid–liquid extraction system for trace spectrophotometric determination of Zr(IV) involving 3-hydroxy-2-tolyl-4*H*-chromen-4-one (HToC) is established. Optimum conditions for formation of 1:4 (M:L) Zr(IV)-HToC complex are studied. The formed complex is yellow in color and permits in a simple and economical way, the micro level determination of Zr(IV). The procedure is rapid, sensitive ($\epsilon = 4.1971 \times 10^4 \text{ mol}^{-1} \text{ cm}^{-1}$) and selective (21 anions/complexing agents and 32 cations do not interfere). A good linearity is observed upto 1.1 $\mu\text{g Zr(IV) ml}^{-1}$ ($r = 0.9977$). The method is highly reproducible with satisfactory accuracy and precision (RSD = 0.45%). Application of the method can be expanded to the analysis of zirconium in several samples (synthetic, natural, and technical). The analytical study is extended further to DFT calculations successfully to predict the structural geometry and confirm the final stoichiometry of the complex. The calculations not only provided an optimized structure of the complex but also validated the chelating efficiency of bidentate ligand through $\text{C}=\text{O}$ and -OH groups of the benzopyran ring coordinated to the metal center. The complex is entirely soluble and extractable into polar solvents leading to the increasing interest on its catalytic activities.

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Author contribution Chetna Dhonchak: Experimental and writing; Akshay Kumar: DFT and writing; Nivedita Agnihotri: Conceiving the problem, discussion, final reviewing, and editing.

Data availability All the desired analytical and computational data analyzed or generated are included in this study.

Code availability DFT studies were done using Hyperchem Professional 8.0 packet program.

Declarations

Ethics approval and consent to participate NA.

Consent for publication NA.

Conflict of interest The authors declare no competing interests.

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