

Theoretical investigations into the Spectrophotometrically Analyzed Niobium (V)-6-Chloro-3-hydroxy-7-methyl-2-(2'-thienyl)-4H-chromen-4-one Complex

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Pentavalent niobium cation forms a stable yellow-colored binary complex with 6-chloro-3-hydroxy-7-methyl-2-(2'-thienyl)-4H-chromen-4-one (CHMTC) in the ratio of 1:2. The complex is quantitatively extractable into carbon tetrachloride from HClO₄ solution maintained at pH 1.26–1.75 and strictly adheres to Beer's law as verified by the Ringbom plot with an optimized range of determination as 0.385–1.211 ppm of Nb(V). The ligand-metal complex system shows good precision, accuracy, sensitivity, and selectivity and handles satisfactorily the analysis of several samples of varying complexity. The results are highly reproducible as confirmed by statistical data. The stability of the complex is theoretically confirmed with the help of HOMO-LUMO values and the energy gap [for CHMTC, $\Delta E_{\text{gap}} = 3.62$ V and for Nb(V)-CHMTC Complex, $\Delta E_{\text{gap}} = 2.97$ eV]. The reactivity descriptors were calculated for detailed computational study to probe into the chemical behavior of the studied ligand and its complex. Further, mapped electrostatic potential diagrams help in justifying the donor sites of CHMTC ligand which is in accordance with the analytical findings.

Keywords: Niobium; 6-Chloro-3-hydroxy-7-methyl-2-(2'-thienyl)-4H-chromen-4-one; spectrophotometry; DFT; MEP

INTRODUCTION

Niobium (Nb), previously known as columbium (Cb), is a transition element found in minerals pyrochlore and columbite^{1,2}. Furthermore, Niobium has a pale gray color, crystalline structure, and ductile nature, and in its purest form has a Mohs hardness that is comparable to that of pure titanium and a ductility that is analogous to that of iron³. Niobium is utilized in the jewelry industry as an alternative to nickel which is hypoallergenic because of its slow atmospheric oxidation³.

Furthermore, Niobium is one of the three elemental Type II superconductors, along with vanadium and technetium. Niobium is used in nuclear processes where neutron transparent structures are desired because it has a low thermal neutron capture cross-section⁴⁻⁹. In addition, Niobium is not known to have any biological application, but it occupies a valuable place in a variety of industrial applications, such as jewelry, superconducting alloys, the nuclear industry, electronics, optics, and numismatics^{10, 11}.

Therefore, due to its significant commercial usage, a trustworthy analytical technique for its determination is required. Several instrumental research methodologies are utilized to determine the concentration level of metal ions in various fields. The most popular methods are AAS, AES/AFS, ICP-MS, ICP-OES, NAA, XRF, AVS, and UV-VIS spectrophotometry¹²⁻¹⁸. However, the UV-VIS spectrophotometric approach is utilized the most frequently among all because being less expensive and a simpler method of determination. Several similar spectrophotometric techniques have been published in the past employing a wide range of organic or inorganic ligands to determine niobium metal as its complex. Even

if the methods¹⁹⁻²⁵ satisfactorily assisted in the trace determination of the metal in a variety of environmental, biological, and other samples, further development is required to attain better analytical results.

Herein, we report a sensitive and selective approach for determining niobium in its pentavalent state by complexing it with a bidentate benzopyran ligand, 6-chloro-3-hydroxy-7-methyl-2-(2'-thienyl)-4H-chromen-4-one (CHMTC). In addition to analytical investigations, the work contributes to the rationalization of the structural coordination chemistry of CHMTC through the use of density functional theory (DFT) calculations to assess the ability of the reported ligand to donate and accept electrons during complexation as reported in the literature²⁶⁻³⁰. The DFT simulations are used to determine the geometrical, electrical, and thermodynamic attributes of the complex. With the help of HOMO-LUMO values along with global reactivity descriptors and MEP diagrams, which clearly indicated the electron density around various atoms, structural elucidation of the pentavalent niobium complex revealed results in support of its stability³¹⁻³⁴. These results were consistent with analytical results.

EXPERIMENTAL

Instrumentation, Reagents and Solutions

A dual beam UV-Visible spectrophotometer (2375; Electronics India) with 10 mm coordinated quartz cells is used for absorbance calculations and spectral studies. A standard stock solution of one milligram per milliliter and working solutions with concentrations of micrograms per milliliter of the metal ion were prepared as descri-

bed earlier²². The necessary solutions of the other metal ions are produced by dissolving the soluble chemically pure sodium or potassium salts of other metal ions in doubly distilled water or diluted mineral acids to a concentration of up to 10 mg ml⁻¹. The acidic conditions necessary for complex formation are accomplished by using a solution of freshly produced aqueous HClO₄ at a concentration of 8 M. The extraction of the complex from the aqueous layer to the organic layer makes use of carbon tetrachloride (AR, CDH) in its natural state.

6-Chloro-3-hydroxy-7-methyl-2-(2'-thienyl)-4H-chromen-4-one solution [CHMTC] (Fig. 1): The benzopyran, CHMTC, was synthesized using the methods described in^{35, 36}. It was then dissolved in ethanol to a concentration of 0.1% (w/v).

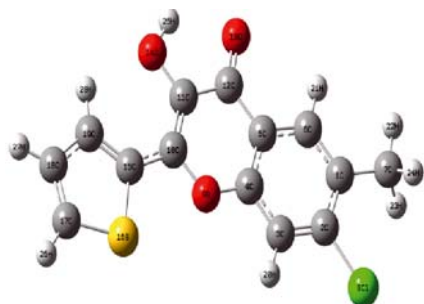


Figure 1. 6-Chloro-3-hydroxy-7-methyl-2-(2'-thienyl)-4H-chromen-4-one solution (CHMTC)

Samples

The viability of the procedure is demonstrated by the successful analysis of the samples listed below.

Synthetic samples: To prepare synthetic samples with different compositions, milligram quantities of niobium (V) are combined with other metal ions in varying compositions (Table 1).

Natural and Industrial samples: Samples of reverberatory flue dust and water (from various sources) were made into suitable solutions by following the procedures described in the literature²². On the other hand, the BCS 261/1 steel sample was formed by gradually heating 0.05 g of the sample in aqua regia over a sand bath. The content was produced to 50 ml net volume carrying strength of 4 M using HClO₄ after being evaporated to dryness and dissolved in 10 ml of deionized water. Thus, the prepared solutions were finally analyzed under optimum conditions (Table 1).

Quantum Chemical Comprehension

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 6-311++G (d, p) for ligand and LANL2DZ for complex basis set³⁷. Quantum chemical parameters, based on the analysis of electronic parameters of the Nb (V)-CHMTC complex in its most stable conformation, have been used to better understand the chemistry of the complexes. Electronic properties of the ligand CHMTC, and its complex Nb (V)-CHMTC were calculated using the HOMO/LUMO energies and the band gap energy ($E_{\text{gap}} = E_{\text{HOMO}} - E_{\text{LUMO}}$)³⁸, including the ionization energy (I), electron affinity (A)³⁹, electro-negativity (χ),

Table 1. Analysis of various synthetic, natural, and technical samples

No.	Sample Composition		Nb (V) found (μg /10ml)**
	Matrix*	Nb (V) added (μg/10ml)	
1	Cu(2),Zn(5),Pb(5)	3	3.07±0.0082
2	Hg(5), Ca(2), Ba(5)	5	5.15±0.0081
3	Al(5), Co(5), Mg(5)	7	6.98±0.0047
4	Mn(5), Ce(1), Ru(0.5)	9	8.91±0.0047
5	Cr ^{VI} (0.2), Ir(0.5), V(0.05) ^a	8	8.15±0.0125
6	Mo(0.5), Ni(5), W(0.5)	10	10.10±0.0124
7	Fe ^{III} (0.1), Se(2), Cd(5)	3	3.09±0.0125
8	Ag(0.5), Sn(0.05), Zr(0.1)	5	5.08±0.0047
9	Pd(0.5), As(0.5), Sr(0.5)	7	6.97±0.0169
10	Au(0.5), Pt(0.5), La(0.5)	9	8.93±0.0125
11	Cr ^{III} (0.5), Fe ^{II} (0.5), Ti(0.1) ^b	5	5.16±0.0287
12	Bi(0.5), Mo(0.5), Pd(0.5)	3	3.05±0.0082
13	Water i) Tap Water ii) Ground Water	5 3	5.06±0.0169 2.97±0.0216
14	Reverberatory Flue Dust	9	8.97±0.0163
15	BCS(261/1) ^a	0.91% ^c	0.90±0.0008

*Figure in parentheses indicates amount of metal ion in mg/10 ml.

**Average of triplicate

analyses ± SD. ^aIn presence of 100 mg sodium dithionite;

^bIn presence of 100 mg ascorbic acid.

absolute hardness (η), and global softness (σ) according to the following respective equations⁴⁰:

$$\text{Electronegativity } (\chi) = I + A/2 \quad (\text{i})$$

$$\text{Chemical potential } (\mu) = -(I + A)/2 \quad (\text{ii})$$

$$\text{Chemical hardness } (\eta) = I - A/2 \quad (\text{iii})$$

$$\text{Chemical softness } (\sigma) = 1/2\eta \quad (\text{iv})$$

$$\text{Electrophilicity index } (\omega) = \mu^2/2\eta \quad (\text{v})$$

Chemical hardness, which is inversely correlated with the HOMO-LUMO energy gap, can be used to explain why a molecule is reactive^{41, 42}. Reactivity decreases as chemical hardness increases. The entire electronic density of the molecule is shown by the molecular electrostatic potential (MEP), which is an important descriptor in determining the sites of electrophilic and nucleophilic interactions.

Extractive Spectrophotometric Determination of Nb(V)

In a 125 ml separating funnel, an aliquot of the working solution that contains up to 14 μg of Nb (V) is added. To keep the pH between 1.26–1.75 in a total aqueous volume of 10 ml, a suitable amount of HClO₄ and then 2 ml of 0.1% (w/v) solution of CHMTC in ethanol are added. The aqueous content thus prepared is transferred to the organic phase, equilibrating once with 10 ml of carbon tetrachloride for 30 seconds. One equilibration yields quantitative extraction. Following the completion of the phase separation process, the carbon tetrachloride layer is filtered into a 10 ml volumetric flask using Whatman filter paper No.41. The layer is then diluted with pure carbon tetrachloride until it reaches the mark. With a pair of 10 mm quartz cuvettes, the contents are gently combined, and the absorbance of the yellow extract

is measured at 425 nm in comparison to the similarly prepared blank solution. The calibration curve acquired by the aforementioned technique is used to calculate the amount of niobium.

Modifications for V (V) and Ti (IV): Since V (V) and Ti (IV) were contributing significantly to an already elevated optical density value, adjustments were made to the process to mitigate their impact. Prior to adding the reagent in a 10 ml water phase, 100 mg of sodium dithionite and 100 mg of ascorbic acid effectively cover up to 0.2 mg of V (V) and Ti (IV), respectively.

RESULTS AND DISCUSSION

Spectral Analysis

The capacity of CHMTC to complex niobium in its pentavalent state has been demonstrated. In the HClO_4 medium, this reaction produces a yellow-colored, extremely sensitive ($\epsilon = 5.613 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$), stable binary complex (pH 1.26–1.75). In comparison to the reagent blank, the absorption spectra for the Nb (V)-CHMTC complex are shown in Figure 2 with a maximum and constant absorption plateau in the range of 410–432 nm, using 425 nm as the working wavelength. All readings are referenced to a blank solution, which also absorbs some light in the selected wavelength range.

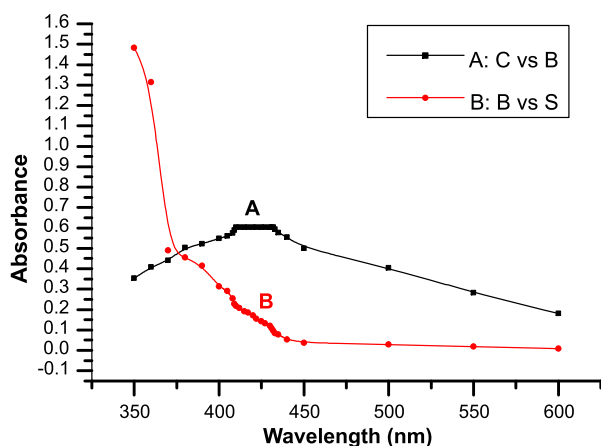


Figure 2. CAbsorption spectra of Nb(V)-CHMTC complex in carbon tetrachloride; A- $1.0 \mu\text{g ml}^{-1}$ Nb (V) measured against reagent blank; B- Reagent blank measured against carbon tetrachloride

Different media were tried out to achieve maximum and constant absorbance of the complex under study with the following observed trend: $\text{Na}_2\text{CO}_3 < \text{NaHCO}_3 < \text{CH}_3\text{COOH} < \text{H}_3\text{PO}_4 < \text{HCl} < \text{H}_2\text{SO}_4 < \text{HClO}_4$. Maximum consistent absorbance was observed using HClO_4 as the complexing medium, hence justifying the choice for further studies.

Extraction conduct of Nb (V)-CHMTC complex followed the order: cyclohexane < ethyl acetate < isopentyl acetate < isobutyl methyl ketone < benzene < toluene < 1, 2-dichloroethane < dichloromethane < chloroform < carbon tetrachloride. 100% extraction with maximum absorbance of the complex was noted in carbon tetrachloride and hence was the choice.

The influence of various physical parameters including pH (using HClO_4), CHMTC concentration, and equilibration time on extractive determination of the complex

under investigation had been studied and plotted in Figures 3–5 thus giving the optimum set of conditions required for the formation of Nb(V)-CHMTC complex.

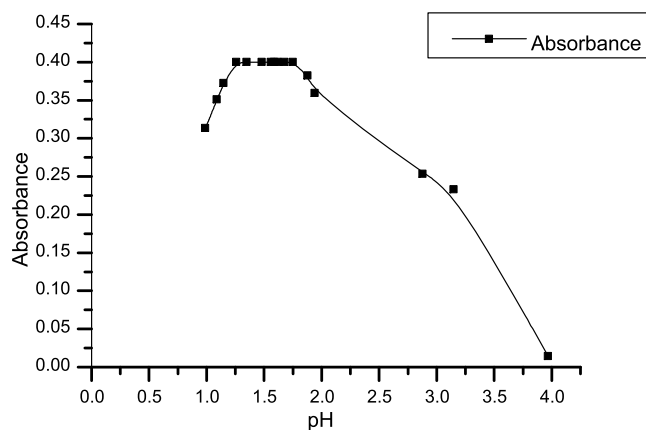


Figure 3. Effect of pH^a on absorbance of Nb (V)-CHMTC complex

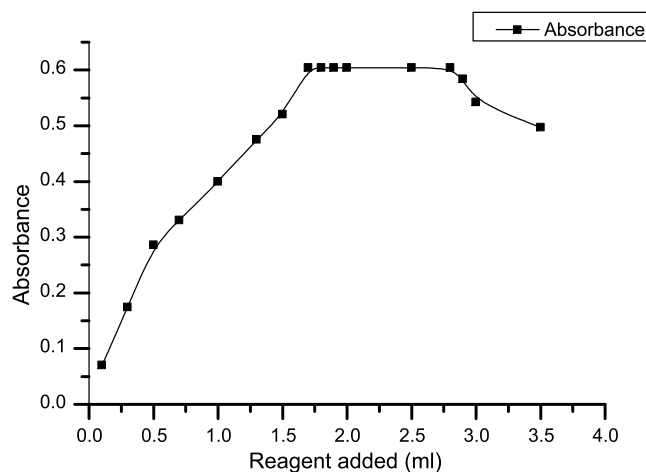


Figure 4. Effect of reagent concentration^b on absorbance of Nb (V)-CHMTC complex

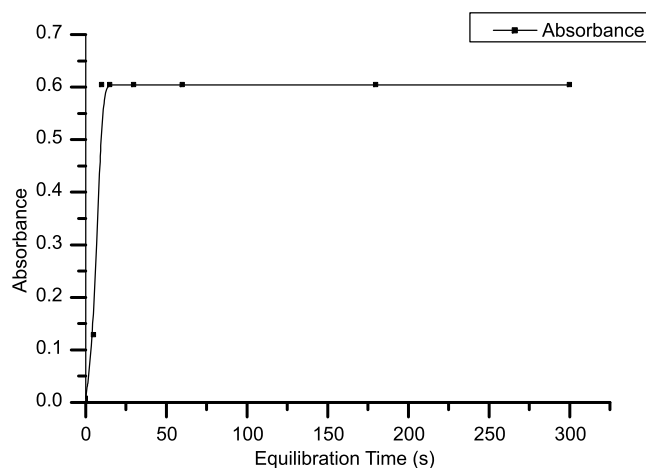


Figure 5. Effect of equilibration time^c on absorbance of Nb (V)-CHMTC complex

Conditions:

^aNb (V) = $10 \mu\text{g}$; pH = variable; CHMTC [0.1% (m/v) in ethanol] = 1 ml; aqueous volume = solvent volume = 10 ml; solvent = carbon tetrachloride; equilibration time = 30 seconds; $\lambda_{\text{max}} = 425 \text{ nm}$

^bpH = 1.48; remaining parameters same as in 'a' excepting variation in CHMTC concentration

$^{\circ}\text{CHMTC}$ [0.1% (m/v) in alcohol] = 2 ml; remaining parameters same as in 'b' excepting variation in equilibration time.

Effect of Anions/Complexing Agents and Cations

Tables 2 and 3 summarize the influence of various ions, including anions/complexing agents and cations, on the selectivity and tolerance limit of the Nb(V)-CHMTC complex, which was conducted by adding the ions into the system (before adding the reagent) under conditions analogous to those in the proposed policy. Only oxalate and hydrazine sulphate (among many others) were shown to cause significant interference even at low concentrations.

Spectrophotometric and statistical specifics

Figures 6 and 7 display the linear response of the Nb(V)-CHMTC complex up to $1.4 \mu\text{g ml}^{-1}$ of Nb(V)

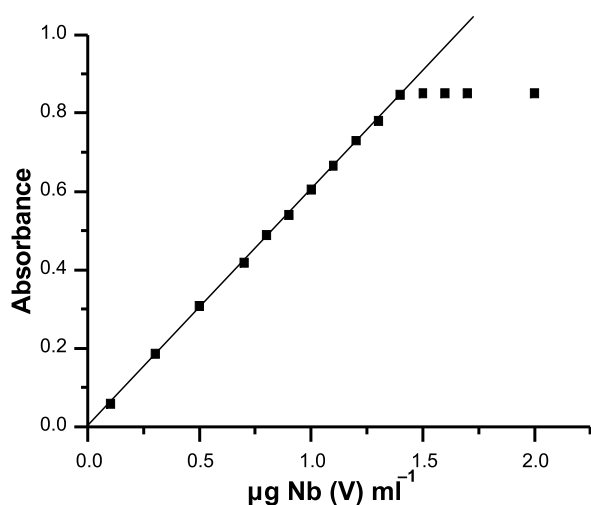


Figure 6. Beer's law range of Nb(V) – CHMTC complex in carbon tetrachloride at 425 nm

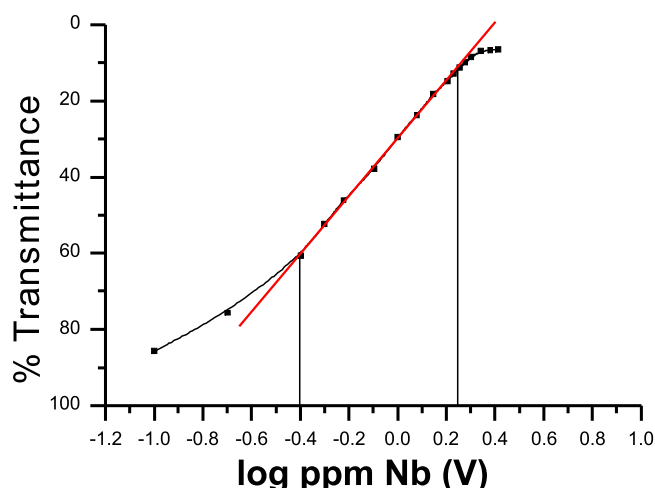


Figure 7. Ringbom plot for Nb(V) – CHMTC complex in carbon tetrachloride at 425 nm

and the optimal range of determination as 0.385–1.211 ppm by Ringbom plot⁴³. The linearity of the process was further corroborated by the high correlation coefficient of 0.9999. Table 4 provides a summary of spectral and statistical characteristics.

Stoichiometry of Nb (V)-CHMTC Complex

The Job's continuous variations method⁴⁴ (revised for a two phase system by Vosburgh and Cooper⁴⁵ (Fig. 8), mole ratio method⁴⁶ (Fig.9) and equilibrium shift methods⁴⁷ (Fig. 10), have all been used to establish and confirm the Nb (V) – CHMTC complex's stoichiometric ratio as 1:2. The results shown in Figure 11 also demonstrate the most probable and optimized structure of the complex.

Table 2. Effect of anions/complexing agents on Nb (V)-CHMTC complex

No.	Anion/complexing agent added	Tolerance limit (mg/10ml)	Absorbance
1	None	–	0.604
2	Sodium Chloride, Sodium Bromide, Potassium Iodide, Sodium Nitrite, Sodium Carbonate, Sodium Dithionite, Thiourea, Sodium Acetate, Ascorbic acid, Potassium Thiocyanate	100	0.604
3	Sodium Sulphite	80	0.604
4	'Disodium' EDTA, Sodium Potassium Tartrate, Sodium Phosphate, Sulfosalicylic acid	50	0.604
5	Sodium Nitrate	20	0.604
6	Potassium Fluoride	10	0.604
7	Sodium Sulphate	1	0.604
8	Glycerol, Hydrogen peroxide (30%),	1*, 0.1*	0.604
9	Sodium Oxalate**, Hydrazine Sulphate**	0.1	0.104, 0.278

*Amount added in ml; **Seriously interfered.

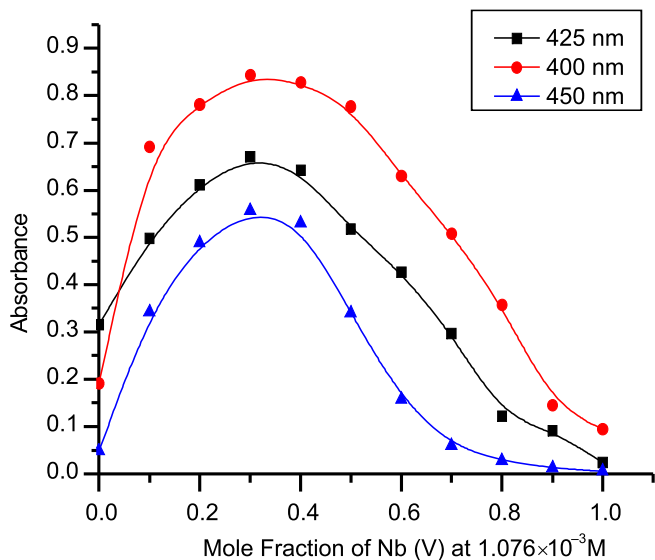
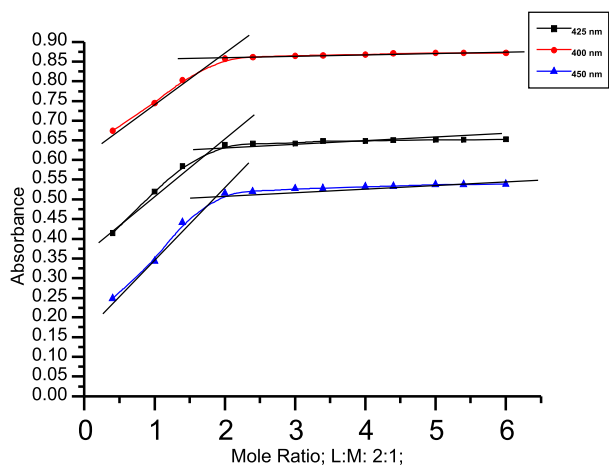
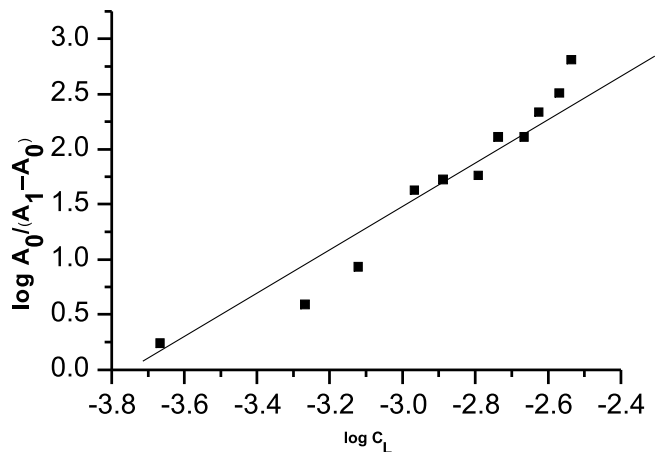
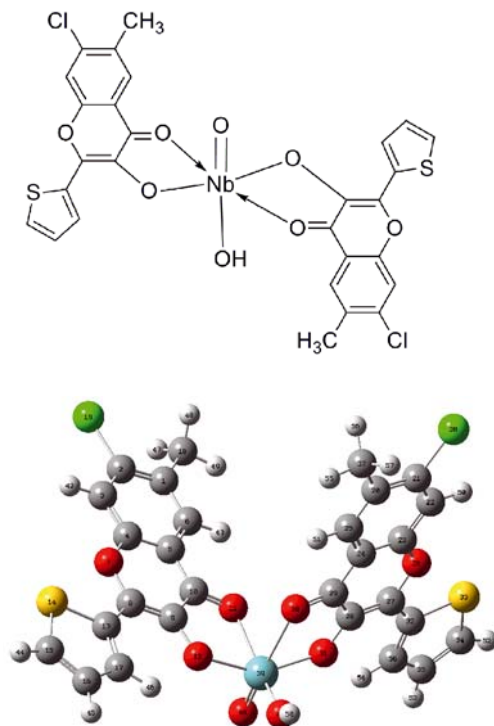
Table 3. Effect of cations on Nb (V)-CHMTC complex

No.	Cations*	Tolerance limit (mg/10 ml)	Absorbance
1	None	–	0.604
2	Al(III), Pb(II), Hg(II), Ca(II), Ba(II), Cu(II), Co(II), Mg(II), Mn(II), Cd(II), Zn(II), Ni(II)	10	0.604
3	Se(IV), Cu(II), Ag(I)	5	0.604
4	Mo(VI), Ce(IV), Pt(IV), Ru(III), Ir(III), Au(III), Cr(III), As(III), Bi(III), La(III), Pd(II), Fe(II)	1	0.604
5	W(VI), Sr(II)	0.8	0.604
5	Cr(VI), Nb(V)	0.5	0.604
6	Zr(IV), Ti(IV) ^a	0.2	0.604
7	V(V) ^b , Fe(III), Sn(II)	0.1	0.604

*Initial oxidation state is shown in parentheses. ^aIn presence of 100 mg ascorbic acid; ^bIn presence of 100 mg sodium dithionite

Table 4. Spectral and Statistical data of Nb(V)-CHMTC complex

Parameter	Value	Parameter	Value
pH	1.26 – 1.75	Limit of detection ($\mu\text{g ml}^{-1}$)	0.0218
Reagent solvent	Ethanol	Correlation coefficient (r)	0.9999
Reagent concentration (0.1% w/v, ml)	1.8–2.8	Regression equation	$Y = 0.602 X + 0.002$
λ_{max} (nm)	410–432	Slope (b)	0.602
Extraction solvent	Carbon tetrachloride	Intercept (a)	0.002
Equilibration time (Seconds)	10–300	Stoichiometry (M:L)	1:2
Beer's law limit ($\mu\text{g ml}^{-1}$)	0.0–1.4	Standard deviation	± 0.0019
Molar absorptivity ($\text{l mol}^{-1} \text{cm}^{-1}$)	5.613×10^4	Relative standard deviation (%)	0.3124
Sandell's sensitivity ($\mu\text{g cm}^{-2}$)	0.0017	Stability	Up to 7 days

**Figure 8.** Job's continuous variations method**Figure 9.** Mole – ratio method**Figure 10.** Equilibrium shift method. Concentration of the metal ion fixed = 5.38×10^{-4} M; Maximum absorbance, $A_0 = 0.653$; Study wavelength = 425 nm; Slope = 1.86**Figure 11.** Nb(V)-CHMTC Complex (Probable and Optimized)

Annotation of CHMTC and Nb(V)-CHMTC using DFT

HOMO – LUMO Analysis and Energy Calculation

DFT helps in determining optimized structure with minimum energy along with the energies of frontier molecular orbitals, the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital)⁴⁸. The frontier orbital gap (HOMO-LUMO gap or ΔE_{gap}) helps to specify the chemical reactivity and kinetic stability of the molecule under study. A molecule with a small frontier orbital gap is more polarizable, is generally associated with a high chemical reactivity and low kinetic stability, and is termed as soft molecule, however, a hard molecule implies a larger frontier orbital gap. The energy gap between HOMO and LUMO is a fundamental parameter to determine molecular electron transport properties. The frontier molecular orbitals give a detailed idea of intending sites of a molecule involved in donor-acceptor correspondence between a ligand and complex as shown in HOMO-LUMO diagrams of bidentate CHMTC ligand and its niobium complex (Fig 12 and Fig. 13). The HOMO of CHMTC is majorly spread over the benzopyran ring, the donor site for the ligand-complex system under study, which is in resonance with the thiophene ring depicted in green color. The evidence supports the stoichiometric ratio as obtained by analytical studies as discussed in the previous section. The orbital

distribution implies transfer of the electron density from HOMO of CHMTC to LUMO of Niobium (V).

As seen in Table 5, the benzopyran derived CHMTC ligand is showing a higher ΔE_{gap} which makes it a hard molecule. However, the lower value of ΔE_{gap} for Nb (V)-CHMTC complex makes it a soft molecule.

Table 5. Quantum chemical parameters

No.	Compound	E_{HOMO} (eV)	E_{LUMO} (eV)	ΔE_{gap} (eV)
1	CHMTC	-6.14	-2.52	3.62
2	Nb(V)-CHMTC	-6.03	-3.06	2.97

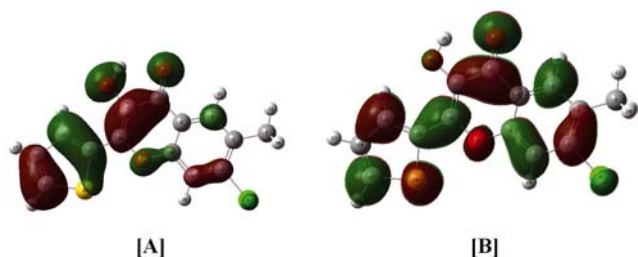


Figure 12. DFT derived HOMO (A) and LUMO (B) of CHMTC

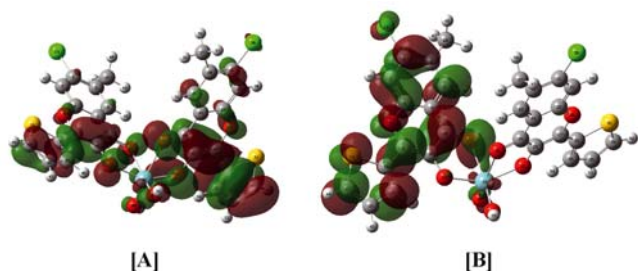


Figure 13. DFT derived HOMO (A) and LUMO (B) of Nb (V)-CHMTC

Reactivity Parameters

To rationalize the reactivity patterns of different molecular systems, global chemical reactivity indicators⁴⁹ (Table 6) have been of great use. The high electronegativity of Nb(V)-CHMTC complex indicates its stability. The electrophilicity index has a positive value for CHMTC also supporting its nucleophilic nature.

MEP Analysis

The MEP plays a unique part in molecular recognition, prediction, and analysis and is frequently useful in proving non-covalent chemical interactions⁵⁰⁻⁵². Spatial regions in molecular structure can be determined where the electrostatic potential is negative or positive by using the ESP surface in a particular color code range. This is important for analyzing electrostatic interactions between the ligand and the core metal cation and for seeing charged areas of a specific molecule. Figures 14 and 15 depict 3D maps of the molecular electrostatic potentials of the examined ligand and complex, describing the size, structure, and charge density of both molecules.

Figure 14 outlines the mapped molecular electrostatic potential (MEP) of Ligand with red color indicating the most negative potential ($-4.663\text{e-}2$ eV) or the

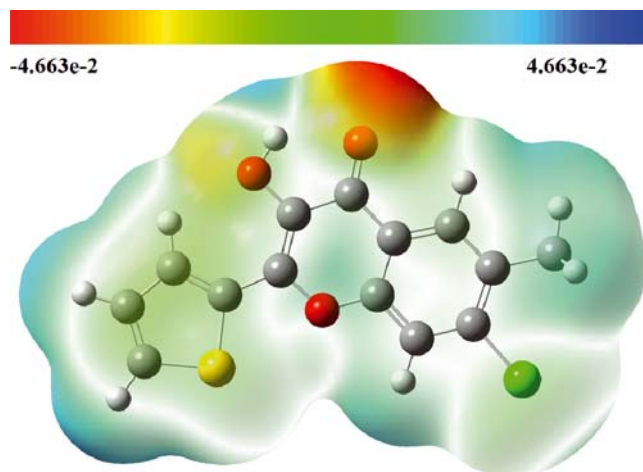


Figure 14. Molecular Electrostatic potential mapped on 3D isosurface of ligand

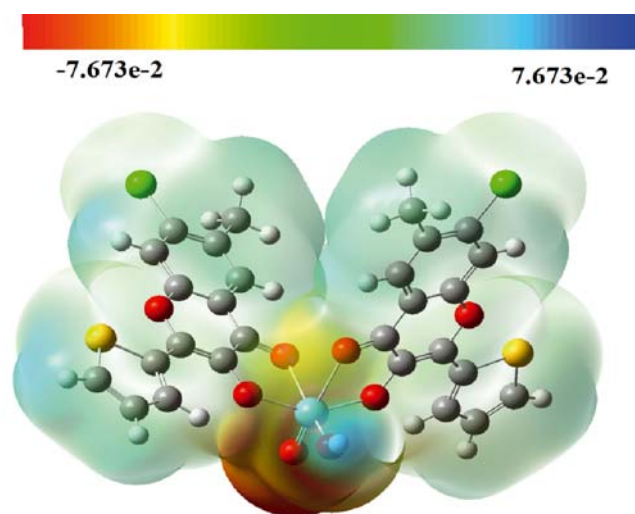


Figure 15. Molecular Electrostatic potential mapped on 3D isosurface of complex

nucleophilic centre, mainly localized over carbonyl and also conjugated double bonds. Green color had been allocated to the most positive potential ($+4.663\text{e-}2$ eV) or the electrophilic centre over thiophene ring.

Figure 15 outlines MEP of the complex with red color indicating the most negative potential ($-7.63\text{e-}2$ eV) or the nucleophilic centre, mainly localized over carbonyl, hydroxyl group and also conjugated double bonds. Green color had been allocated to the most positive potential ($+7.63\text{e-}2$ eV) or the electrophilic centre.

Investigating both the structures it is a comprehensive observation that the results obtained by MEP diagrams of both ligand CHMTC and its pentavalent niobium complex are in great congruence with the precedent analytical detections, implying the fact that HOMO of CHMTC molecule majorly spread over pyran ring, also the nucleophilic centre is responsible for complexation. In the Nb(V)-CHMTC complex, all the red nucleophilic zone is around the core of the molecule, where the niobium metal is forming a chelating ring by the two donor CHMTC moiety.

Table 6. Global chemical reactivity indicators

No.	Compound	Electronegativity, χ (eV)	Chemical hardness, η (eV)	Chemical softness, σ (eV)	Electrophilicity index, ω (eV)
1	CHMTC	4.33	1.81	0.28	5.18
2	Nb(V)-CHMTC	4.54	1.48	0.34	6.98

CONCLUSION

6-Chloro-3-hydroxy-7-methyl-2-(2'-thienyl)-4H-chromen-4-one (CHMTC) has been used as an analytical reagent for the spectrophotometric determination of niobium in pentavalent state in traces. The reagent forms a stable (up to 7 days) yellow 1:2 complex, extractable into carbon tetrachloride from a strongly acidic medium (HClO₄) maintained at pH 1.26–1.75. The complex attains maximum color intensity at 410–432 nm. Beer's law shows its validity between the niobium concentration range of 0.0–1.4 µg ml⁻¹. The sensitivity, versatility and reproducibility of the method are revealed by corresponding values of the acquired spectral and statistical characteristics, including molar absorption coefficient (5.613×10^4 l mol⁻¹ cm⁻¹), Sandell's sensitivity (0.0017 µg cm⁻²), regression coefficient (0.9999) and % RSD (0.3124%). Furthermore, the applicability and commercial adaptability of the method are escalated by its successful application to various synthetic mixtures and technical samples including water, flue dust and steel [BCS (261/1)]. The studied method has a vast tolerance limit for many foreign ions thereby increasing the purview of its application. DFT studies are further incorporated for better understanding of the chemical behavior of ligand as well as its metal complex. The MEP diagrams clearly portray the sites for electrophilic and nucleophilic interactions.

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Data availability

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

References

- Samsonov, G.V. (1968). Mechanical Properties of the Elements, *Handbook of the physicochemical properties of the elements*. New York, USA (pp. 387–446).
- Brian, K. (2002). *Francium to Polonium*: Atlantic Europe Publishing Company 40.
- Standard Atomic Weights: Niobium*: CIAAW (2017).
- Peiniger, M. & Piel, H. (1985). A Superconducting Nb₃Sn Coated Multicell Accelerating Cavity. *IEEE Trans. Nucl. Sci.* 32(5), 3610–3612. DOI: 10.1109/TNS.1985.4334443.
- Moura, H.R.S. & De Moura, L. (2007). *Melting and purification of niobium*. Proceedings of the International Niobium Workshop; Ganapati Rao Myneni, Tadeu Carneiro and Andrew Hutton. AIP Conference Proceedings 927, 30 October – 1 November 2006 (pp. 165–178). Araxa, Brazil. DOI: 10.1063/1.2770689.
- Nowak, I. & Ziolek, M. (1999). *Niobium Compounds: Preparation, Characterization and Application in Heterogeneous Catalysis*. *Chem. Rev.* 99, 3603–3624. DOI: 10.1021/cr9800208.
- Jahnke, L.P., Frank, R.G. & Redden, T.K. (1960). *Columbium Alloys Today*. *Metal. Progr.* 77, 69–74. URL: http://www.osti.gov/energycitations/product.biblio.jsp?osti_id=4183692.

- Nikulina, A.V. (2003). *Zirconium-Niobium Alloys for Core Elements of Pressurized Water Reactors*. *Met. Sci. Heat Treat.* 45, 287–292. DOI: 10.1023/A:1027388503837.
- Behera, A. (2022). Advanced Semiconductor/Conductor Materials. *Adv. Mat.* Springer, Cham. (pp. 557–596). DOI: 10.1007/978-3-030-80359-9_16.
- Vilaplana, J., Romaguera, C., Grimalt, F. & Cornellana, F. (1990). New trends in the use of metals in jewellery. *Contact Derm.* 25, 145–148. DOI: 10.1111/j.1600-0536.1991.tb01819.x.
- Vilaplana, J. & Romaguera, C. (1998). *New developments in jewellery and dental materials*. *Contact Derm.* 39, 55–57. DOI: 10.1111/j.1600-0536.1998.tb05832.x.
- Helaluddin, A.B.M., Khalid, R.S., Alaama, M. & Abbas, S.A. (2016). Main Analytical Techniques Used for Elemental Analysis in Various Matrices. *Trop. J. Pharm. Res.* 15, 427–434. DOI: 10.4314/tjpr.v15i2.29.
- Dong, H.M. & Krivan, V. (2001). Direct solid-sampling electrothermal atomic absorption spectrometry methods for the determination of silicon in oxides of niobium, titanium and zirconium. *Spectrochim. Acta. Part B.* 56, 1645–1656. DOI: 10.1016/S0584-8547(01)00255-5.
- Lu, X.M. & Jin, D.L. (2009). Determination of niobium, silicon and phosphorus in ferrocolumbium by X-ray fluorescence spectrometry using sample preparation technique of centrifugal casting. *Met. Anal.* 29, 16–19.
- Petrova, K.V., Baranovskaya V.B. & Korotkova, N.A. (2022). Direct inductively coupled plasma optical emission spectrometry for analysis of waste samarium-cobalt magnets. *Arab. J. Chem.* 15, 103501. DOI: 10.1016/j.arabjc.2021.103501.
- Faix, W.G., Caletka, R. & Krivan, V. (1981). Radiochemical multielement neutron activation analysis of high-purity niobium with short-lived indicator radionuclides. *Anal. Chem.* 53, 1594–1598. URL: <https://eurekamag.com/research/087/033/087033214.php>
- Ruiz, M.D.C., Rodriguez, M.H., Perino, E. & Olsina, R.A. (2002). Determination of Nb, Ta, Fe and Mn by X-ray fluorescence. *Miner. Engg.* 15, 373–375. DOI: 10.1016/S0892-6875(02)00039-0.
- Yi, W.J., Li, Y., Ran, G., Luo, H.Q. & Li, N.B. (2012). Determination of cadmium (II) by square wave anodic stripping voltammetry using bismuth-antimony film electrode. *Sens. Actua. B: Chem.* 166–167, 544–548. DOI: 10.1016/j.snb.2012.03.005.
- Hamed, M.M., Aglan, R.F. & El-Reefy, S.A. (2015). Normal and second derivative spectrophotometric determination of niobium using solid phase extraction technique. *J. Anal. Chem.* 70, 1103–1110. DOI: 10.1134/S1061934815090075.
- Verdizade, N.A., Zalov, A.Z. & Suleymanova, G.S. (2017). Extraction-spectrophotometric determination of niobium and tantalum. *Azerb. Khim Zh.* 1, 72–76. URL: <https://akj.az/uploads/journal/az/Verdizade.pdf>
- Kutyrev, I.M., Nechepurenko, G.N. & Gaidukova, Yu. A. (2014). Extraction-spectrophotometric determination of niobium in magnetic alloys. *Inorg. Mater.* 50, 1405–1407. DOI: 10.1134/S0020168514140088.
- Agnihotri, N. & Agnihotri, R. (2012). Extractive spectrophotometric determination of niobium (V) using 3-hydroxy-2-(4'-methoxyphenyl)-4-oxo-4H-1-benzopyran as a complexing agent. *Open Anal. Chem. J.* 6, 39–44. DOI: 10.2174/1874065001206010039.
- Tarafder, P.K., Mondal, R.K. & Chattopadhyaya, S. (2009). Extraction and sensitive spectrophotometric determination of niobium in silicate rocks and columbite-tantalite minerals. *Chem. Anal. Warsaw.* 54, 231–246.
- Agnihotri, N., Kamal, R. & Mehta, J.R. (2006). A highly selective spectrophotometric determination of niobium (V) using 3-hydroxy-2-[1'-phenyl-3'-(p-chlorophenyl)-4'-pyrazolyl]-4-oxo-4H-1-benzopyran as a complexing agent. *Ann. Chim. (Rome, Italy).* 96, 479–485. DOI: 10.1002/adich.200690048.
- Agnihotri, N. & Mehta, J.R. (2003). A highly selective spectrophotometric determination of niobium(V) using 6-chlo-

ro-2-(2'-furyl)-3-hydroxy-4-oxo-4H-1-benzopyran as a complexing agent and chloroform as an extractant. *J. Indian Chem. Soc.* 80, 837–840.

26. Uddin, M.A., Sutoanu, B.H., Rub, M.A., Mahbub, S., Alotaibi, M.M., Asiri, A.M. & Kabir, M. (2022). UV-Visible spectroscopic and DFT studies of the binding of ciprofloxacin hydrochloride antibiotic drug with metal ions at numerous temperatures. *Korean J. Chem. Eng.* 39, 664–673. DOI: 10.1007/s11814-021-0924-z.

27. Eroshin, A.V., Otlyotov, A.A., Kuzmin, I.A., Stuzhin, P.A. & Zhabanov, Y.A. (2022). DFT Study of the Molecular and Electronic Structure of Metal-Free Tetrabenzoporphyrin and Its Metal Complexes with Zn, Cd, Al, Ga, In. *Int. J. Mol. Sci.* 23, 939. DOI: 10.3390/ijms23020939.

28. da Silva, T.U., da Silva, E.T., de Carvalho, Pougy, K., da Silva, Lima, C.H. & de Paula, Machado, S. (2022). Molecular modeling of indazole-3-carboxylic acid and its metal complexes (Zn, Ni, Co, Fe and Mn) as NO synthase inhibitors: DFT calculations, docking studies and molecular dynamics simulations. *Inorg. Chem. Commun.* 135, 109120. DOI: 10.1016/j.inoche.2021.109120.

29. Waheeb, A.S., Kyhoiesh, H.A.K., Salman, A.W., Al-Adilee, K.J. & Kadhim, M.M. (2022). Metal Complexes of a new azo Ligand 2-[2'-(5-Nitrothiazolyl) azo]-4-methoxyphenol (NTAMP): Synthesis, Spectral Characterization and Theoretical Calculation. *Inorg. Chem. Commun.* 138, 109267. DOI: 10.1016/j.inoche.2022.109267.

30. Zayed, E.M. & Mohamed, G. (2022). Synthesis, spectroscopic, DFT and docking studies, molecular structure of new Schiff base metal complexes. *Egypt. J. Chem.* 65, 633–644. DOI: 10.21608/ejchem.2021.83871.4116.

31. Dege, N., Gökce, H., Doğan, O.E., Alpaslan, G., Açar, T., Muthu, S. & Sert, Y. (2022). Quantum computational, Spectroscopic Investigations on N-(2-((2-chloro-4,5-dicyanophenyl)amino)ethyl)-4-methylbenzenesulfonamide by DFT/TD-DFT with Different Solvents, Molecular Docking and Drug-Likeness Researches. *Coll. Sur: Physicochem. Engg. Aspect.* 638, 128311. DOI: <https://newsletter.x-mol.com/paper-Redirect/1482122577481203712>.

32. Kansız, S., Tolan A., Azam M., Dege N., Alam M., Sert Y., Al-Resayes S. & İğbudak H. (2022). Acesulfame based Co(II) complex: Synthesis, Structural investigations, Solvatochromism, Hirshfeld surface analysis and Molecular docking studies. *Polyhedron*. 218, 115762. DOI: 10.1016/j.poly.2022.115762.

33. Mahmudov, I., Demir, Y., Sert, Y., Abdullayev, Y., Sujayev, A., Alwasel, S.H. & Gulcin, I. (2022). Synthesis and Inhibition Profiles of N-Benzyl- and N-Allyl Aniline Derivatives against Carbonic Anhydrase and Acetylcholinesterase – A Molecular Docking Study. *Arab. J. Chem.* 15, 103645. DOI: 10.1016/j.arabjc.2021.103645.

34. Abdulridha, A., Albo Hay Allah, M.A., Makki, A.Q., Sert, Y., Salman, H. & Balakit, A. (2020). Corrosion inhibition of carbon steel in 1 M H₂SO₄ using new Azo Schiff compound: Electrochemical, gravimetric, adsorption, surface and DFT studies. *J. Mol. Liq.* 315, 113690. DOI: 10.1016/j.molliq.2020.113690.

35. Algar J. & Flynn J.P. (1934). A new method for the synthesis of flavonols. *Proc. Roy. Irish Acad.* 42B, 1-7.

36. Oyamada, T. (1934). A new general method for the synthesis of the derivatives of flavonol. *J. Chem. Soc. Jpn.* 55, 1256–1261.

37. Kumar, A., Trivedi, M., Bhaskaran, S.R.K. & Singh, G. (2017). Synthetic, spectral and structural studies of a Schiff base

and its anticorrosive activity on mild steel in H₂SO₄. *New J. Chem.* 41, 8459–8468. DOI: 10.1039/C7NJ00896A.

38. Muscat, J., Wander, A. & Harrison, N.M. (2001). On the prediction of band gaps from hybrid functional theory. *Chem. Phys. Lett.* 342, 397–401. DOI: 10.1016/S0009-2614(01)00616-9.

39. Rienstra-Kiracofe, J.C., Barden, C.J., Brown, S.T. & Schaefer, H.F. (2001). Electron affinities of polycyclic aromatic hydrocarbons. *J. Phys. Chem.* 105, 524–528. DOI: 10.1021/jp003196y.

40. Vektariene, A., Vektaris, G. & Svoboda, J. (2009). A theoretical approach to the nucleophilic behaviour of benzo fused thieno [3,2-b] furans using DFT and HF based reactivity descriptors. *ARKIVOC*. 7, 311–329. DOI: 10.3998/ark.5550190.0010.730.

41. Arab, A., Gobal, F., Nahali, N. & Nahali, M. (2013). Electronic and structural properties of neutral, anionic and cationic Rh_xCu_{4-x} (x= 0–4) small clusters: a DFT study. *J. Clust. Sci.* 24, 273–287. DOI: 10.1007/s2F510876-013-0550-y.

42. Arab, A. & Habibzadeh, M. (2016). Theoretical study of geometry, stability and properties of Al and Al Si nanoclusters. *J. Nanostruct. Chem.* 6, 111–119. DOI: 10.1007/s40097-015-0185-7.

43. Ringbom, A. (1938). On the accuracy of colorimetric analytical methods. *Anal. Chem.* 115, 332–343.

44. Job, P. (1928). Formation and stability of inorganic complexes in solution. *Ann. di Chim.* 9, 113–203.

45. Vosburgh, W.C. & Cooper, G.R. (1941). Complex ions. I. The identification of complex ion in solution by spectrophotometric measurements. *J. Am. Chem. Soc.* 63, 437–442. DOI: 10.1021/ja01847a025.

46. Yoe, J.H. & Jones, A.L. (1944). Colorimetric determination of iron with disodium-1,2-dihydroxybenzene-3,5-disulfonate. *Ind. Eng. Chem. (Anal. Ed.)*. 16, 111–115. DOI: 10.1021/i560126a015.

47. Tarasiewicz, H.P., Grudniewska, A. & Tarasiewicz, M. (1977). An examination of chlorpromazine hydrochloride as indicator and spectrophotometric reagent for the determination of molybdenum (V). *Anal. Chim. Acta.* 94, 435–442. DOI: 10.1016/S0003-2670(01)84546-3.

48. Verma, V.K., Guin, M., Solanki, B. & Singh, R.C. (2022). Molecular structure, HOMO and LUMO studies of Di (Hydroxybenzyl) diselenide by quantum chemical investigations. *Mater. Today Proc.* 49, 3200–3204. DOI: 10.1016/j.matpr.2020.11.887.

49. Üstün, E., Düşünceli, S.D. & Özdemir, I. (2019). Theoretical analysis of frontier orbitals, electronic transitions and global reactivity descriptors of M(CO)₄L₂ type metal carbonyl complexes: a DFT/TDDFT study. *Struct. Chem.* 30, 769–775. DOI: 10.1007/s11224-018-1231-0.

50. Dhonchak, C., Agnihotri, N. & Kumar, A. (2021). Zirconium (IV)-3-hydroxy-2-tolyl-4H-chromen-4-one complex-the analytical and DFT studies. *J. Mol. Model.* 27, 336. DOI: 10.1007/s00894-021-04949-0.

51. Sowrirajan, S., Elangovan, N., Ajithkumar, G. & Manoj, K.P. (2022). (E)-4-((4-Bromobenzylidene) Amino)-N-(Pyrimidin-2-yl) Benzene sulfonamide from 4-Bromobenzaldehyde and Sulfadiazine, Synthesis, Spectral (FTIR, UV-Vis), Computational (DFT, HOMO–LUMO, MEP, NBO, NPA, ELF, LOL, RDG) and Molecular Docking Studies. *Polycyc. Arom. Compd.* 1–16. DOI: 10.1080/10406638.2021.2006245.

52. Luque, F.J., Lopez, J.M., Orozco, M., Muray, J.S. & Sen, K. (2000). Perspective on electrostatic interactions of a solute with a continuum. A direct utilization of ab initio molecular potentials for the prevision of solvent effects. *Theor. Chem. Acc.* 103, 343–345. DOI: 10.1007/s002149900013.