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Theoretical investigations into the Spectrophotometrically Analyzed Niobium (V)-6-Chloro-3-hydroxy-7-methyl-2-(2'-thienyl)-4*H*-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)-4*H*-chromen-4-one (CHMTC) in the ratio of 1:2. The complex is quantitatively extractable into carbon tetrachloride from $HClO_4$ 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, ΔE_{gap} = 3.62 V and for Nb(V)-CHMTC Complex, ΔE_{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)-4*H*-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 iron[3]. Niobium is utilized in the jewelry industry as an alternative to nickel which is hypoallergenic because of its slow atmospheric oxidation[3].

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-section[4–9]. 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 spectrophotometry[12–18]. 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 methods[19–25] 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)-4*H*-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 literature[26–30]. 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 stability[31–34]. 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-