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Karbala International Journal of Modern Science 3 (2017) 212–223
http://www.journals.elsevier.com/karbala-international-journal-of-modern-science/

Corrosion resistance and thermal behavior of acetylacetonato-oxoperoxomolybdenum(VI) complex of maltol: Experimental and DFT studies

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Received 2 June 2017; revised 29 August 2017; accepted 29 August 2017
Available online 5 October 2017

Abstract

Corrosion and thermo-chemistry is a prominent discipline of physical science. In the conspicuous fascination to design potent durable materials herein, we report the synthesis of an oxoperoxomolybdenum(VI) complex containing maltol and acetylacetone as co-ligands. Magnetic susceptibility measurements, FAB mass spectrometry, FT-IR spectroscopy and thermal analysis are the main characterization techniques that have been used to arrive at the proposed structure of the compound. Experimental data have been compared with density functional theory (DFT) based theoretical outcomes by applying B3LYP functional, and basis set LanL2DZ for Mo and 6311 + G for all other atoms. A close agreement has been found between computed data and the experimental results. From the overall study, it can be found that the complex bears hepta-coordinate pseudo-pentagonal bipyramidal geometry. Based on combined experimental-DFT calculations, the possible role of the complex in designing smart materials has been evaluated. In addition to satisfactory anticorrosive potential, thermo-gravimetry based excellent heat resistance has been shown by the complex. The article also focuses on the calculation of various thermodynamic and kinetic parameters of the respective pyrolysis (TG curve).

Keywords: Oxoperoxomolybdenum(VI); DFT; HOMO; LUMO; MESP

1. Introduction

Molybdenum is involved in the structure of certain bio-catalysts carrying out redox reactions [1,2]. Many compounds of this metal are applicable in the treatment of Wilson's disease [3], controlling diabetes [4] and also exhibit marvelous anti-carcinogenic properties [5]. The polyoxomolybdenum scaffolds represent excellent catalysts applicable in solid-state technology [6–9]. In order to design materials having thermal resistance and anti-corrosive properties, recently molybdenum oxo-derivatives have attained considerable attention [10–13]. Fabrication of new compounds of this framework having fascinating structural properties is a preferential focus in the modern era [14–16].

Metal complexes of maltol have been shown to possess diversified applications [17–21]. Diketonic compounds, like acetylacetone is referred as a class of potent metal-anchoring ligands that has widened the

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Peer review under responsibility of University of Kerbala.

http://dx.doi.org/10.1016/j.kijoms.2017.08.006

scope of coordination chemistry [22]. Their fluorescent, herbicidal and anticancer implications [23] are among other interesting features.

In the current times, quantum chemical aided structural evaluation is a satisfactory and reliable technique. For the compounds where X-ray crystal growth fails, density functional theory (DFT) is the means that serves better to validate experimental observations. The description of molecules ranging from micro to macro-molecules, implying various chemical fronts, saves both time and labor to arrive at best-fit results. Hence, DFT is described as a powerful tool to predict the geometry of molybdenum complexes [24]. Theoretical investigations have been of great use to fetch the molecular, electronic and binding energies of the molybdenum complexes at a relevant level of the theory [24,25]. Such studies have brought new insights into organomolybdenum chemistry [26].

Motivated towards synthesis and characterization of durable polyoxomolybdenum complexes, the present study encompasses comparative experimental and theoretical study of oxo-peroxomolybdenum complex containing maltol and acetylacetone as co-ligands. Experimental-DFT anti-corrosive potential and thermal behavior of the complex represent main goal of the work.

2. Experimental

2.1. Materials

Molybdenum trioxide (99%) (Sisco Chem. Industries, Bombay), 30% hydrogen peroxide (E. Merck, India Ltd., (Bombay), 3-hydroxy-2-methyl-4-pyrone (maltol) (Lancaster, Alfa Aesar, England), acetylacetone and DMF (Tomas Baker Chemical Ltd., Mumbai) and ethanol (Bengal Chemical and Pharmaceuticals Ltd., Kolkata) were used as received. All the chemicals were of analytical reagent (A.R.) grade.

2.2. Preparation of the mixed ligand complex

The mixed-ligand oxoperoxomolybdenum(VI) complex described in this article was prepared by following a procedure reported by Maurya *et al* [26]. Analysis: Empirical formula: $C_{11}H_{12}MoO_8$,Yield, (78%), Elemental analysis (%); Calctd.: C, 35.8; H, 3.29, Found: C, 35.6; H, 3.18.

3. Analysis

Carbon and hydrogen were determined by micro-analyzer facilitated by CDRI Lucknow. The percentage content of molybdenum was found by gravimetric estimation. Perkin–Elmer model 1620 FT-IR spectrophotometer was used to record infrared spectral data (KBr pellet). For conductance measurement, Toshniwal Conductivity Bridge using dip type cell with a smooth platinum electrode of a cell constant 1.02 was used. Magnetic susceptibility of the model complex was determined by applying Gouy's method using mercury(II) tetrathiocyanatocobaltate(II) as calibrant. Fast Atomic Bombardment (FAB) mass spectrometry recorded on a JEOL SX 102/DA-6000 mass spectrometer/data system using xenon/argon (6 kV, 10 mA) as the FAB gas in the *m/z* range 94.36–508.17, was employed to arrive at the proposed molecular formula of the compound. A BASI Epsilon Electrochemical Analyzer was employed to obtain Linear Sweep Voltammogram (LSV) using DMSO solution of the complex containing tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte.

Density functional theory (DFT) based theoretical calculations were carried out with Becke3–Lee–Yang–Parr (B3LYP) functional, 6-311 + G basis set for all atoms except Mo, wherein LanL2DZ was used [27–30]. Computed vibrations were visualized for each bond using animation programme of Gaussview5.0, which is used to identify the shape of vibrational modes [31,32]. In addition to geometry optimization, frontier orbital analysis, zero point energy calculation and surface potential isosurface were used for finding the charge transfer existence [34].

4. Results and discussion

Synthesis of the mixed-ligand oxoperoxomolybdenum(VI) complex described in the work may be represented as shown in Scheme 1.

Measurement of molar conductance has shown that the complex is a non-electrolyte. A 10^{-3} M DMF solution of the compound was taken to record conductance and 12.5 Ω^{-1} cm^2 mol^{-1} conductivity was observed, which can be expected due to the solvent used. Moreover, the magnetic moment (~0 BM) justifies the diamagnetic behavior of the molybdenum(VI) complex under investigation. Both the non-electrolytic and diamagnetic behavior of the complex under question is comparable to the same type of metallic systems reported elsewhere [26].

FT-IR spectroscopy is a versatile technique which is used to identify different functional groups of a compound. As per maltol ligand, two donor sites are mentionable, i.e., the carbonyl oxygen and the