



Research paper

Synthesis, spectroscopy, electrochemistry, crystal structures and *in vitro* cytotoxicity of mononuclear molybdenum(VI) complexes incorporating tridentate ONO donor aroylhydrazone with auxiliary coordination site

T.M. Asha^a, M.R. Prathapachandra Kurup^{a,b,*}^a Department of Applied Chemistry, Cochin University of Science and Technology, Kochi 682 022, Kerala, India^b Department of Chemistry, School of Physical Sciences, Central University of Kerala, Riverside Transit Campus, Nileshevar 671 314, Kerala, India

ARTICLE INFO

Keywords:

Azomethine

Cis-dioxidomolybdenum(VI) complexes

¹H NMR

X-ray diffraction

In vitro cytotoxicity

Lymphoma

ABSTRACT

Four new mononuclear *cis*-dioxidomolybdenum(VI) complexes with the general formula [MoO₂LD], where H₂L = tridentate aroylhydrazone and D = MeOH, pyridine (py), imidazole (im) and 3-picoline (β-pic) have been synthesized by the reaction of bis(acetylacetonato)dioxomolybdenum(VI) with hydrazone derived from 2-hydroxy-3-methoxybenzaldehyde and 3-methoxybenzhydrazide in presence of nitrogen containing bases. The synthesized aroylhydrazone and the complexes were analysed by CHN analysis, electronic and FT-IR spectral studies, molar conductivity measurements, ¹H NMR spectroscopy and cyclic voltammetry. The molecular and crystal structures of all the four complexes were elucidated by single crystal X-ray diffraction analysis. All the complexes adopt a distorted octahedral environment around the molybdenum centre with a *cis* oxo configuration coordinated by the enolized dianionic form of the hydrazone ligand, L²⁻ in a tridentate manner through two deprotonated hydroxyl groups and one azomethine nitrogen atom. The structural analysis also revealed that the molybdenum coordination preferences in conjunction with the ligand donor capabilities offers a supplementary sixth coordination site for all the complexes which could be easily coordinated by competitive ligands such as solvents or *N*-bases by simply modifying the reaction conditions such as solvent, reaction time etc. Furthermore the *in vitro* cytotoxicity of the synthesized aroylhydrazone and all the complexes were assayed against lymphoma ascites cell line.

1. Introduction

Aroyl hydrazones are a good series of versatile organic ligands characterized by the azomethine group and are being capable of binding metal ions, especially transition metal ions leading to metal complexes with intriguing properties. Metal complexes of aroyl hydrazones have played a significant role in the research area of model systems of biochemical interest [1,2], catalysis [3–5], non-linear optics [6], analytical chemistry [7–9] etc. Among the different transition metals, the coordination chemistry of molybdenum has gained substantial attention as it is an essential trace metal of considerable importance in life science owing to its ability to form many complexes with versatile organic ligands. The coordination chemistry of molybdenum has been taken heed of by the scientific community in the last two decades due to its flexibility in possessing stable and accessible oxidation states oscillating between +4 and +6 via a +5 intermediate during turn over [10], as well as being able to form stable complexes

with N, O or S donor atom ligands [11–14]. Molybdenum(VI) ions normally form complexes consisting of two terminal O atoms which commonly exhibit *cis* orientation [15]. The most important role of molybdenum in living organism is as a metal heteroatom at the active site of certain coordinatively unsaturated molybdenum containing enzymes like oxotransfer molybdoenzymes, sulfite and aldehyde oxidase, xanthine oxidase, xanthine dehydrogenase and nitrate reductase [16–18].

In recent years, a number of molybdenum(VI) complexes with aroyl hydrazones of salicylaldehyde derivatives has been reported [19–26]. The investigation of these types of complexes have been stimulated by the fact that, coordination compounds of molybdenum can catalyse a variety of industrially important chemical reactions such as epoxidation and hydroxylation of olefins [27], oxidation of alcohol [28] and oxygen atom transfer reaction [29,30]. Dibasic tridentate ligands together with two terminal oxygen atoms normally form five-coordinate complexes when reacting with the molybdenum(VI) moiety, but the molybdenum

* Corresponding author at: Department of Applied Chemistry, Cochin University of Science and Technology, Kochi 682 022, Kerala, India.

E-mail addresses: mrpcusat@gmail.com, mrp@cukerala.ac.in (M.R.P. Kurup).<https://doi.org/10.1016/j.ica.2018.07.041>

Received 10 January 2018; Received in revised form 24 June 2018; Accepted 25 July 2018

Available online 26 July 2018

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