



# Synthesis, characterization, crystal structure and density functional theory (DFT) calculations of dioxomolybdenum (VI) complexes of an ONS donor ligand derived from benzoylacetone and S-benzyl dithiocarbamate

Manashi Chakraborty<sup>a</sup>, Sathi Roychowdhury<sup>b</sup>, Nikhil Ranjan Pramanik<sup>c</sup>, Tapas Kumar Raychaudhuri<sup>c</sup>, Tapan Kumar Mondal<sup>d</sup>, Subhankar Kundu<sup>d</sup>, Michael G.B. Drew<sup>e</sup>, Saktiprosad Ghosh<sup>c</sup>, Sudhanshu Sekhar Mandal<sup>c,\*</sup>

<sup>a</sup> Department of Chemistry, NITMAS, Jhinga, P.O. Amira, Diamond Harbour Road, District 24 Pgs. (S), West Bengal 743368, India

<sup>b</sup> Sinthi Kasturba Kanya Vidyapith, 1, Kalicharan Ghosh Road, Kolkata 700050, India

<sup>c</sup> Department of Chemistry, University College of Science, 92, Acharya Prafulla Chandra Road, Kolkata 700009, India

<sup>d</sup> Department of Chemistry (Inorganic Section), Jadavpur University, Kolkata 700032, India

<sup>e</sup> Department of Chemistry, The University of Reading, Whiteknights, Reading RG66AD, UK

## ARTICLE INFO

### Article history:

Received 10 July 2012

Accepted 4 December 2012

Available online 20 December 2012

### Keywords:

Dioxomolybdenum (VI) complexes

Chelating ligands

X-ray structures

DFT calculations

## ABSTRACT

A few dioxomolybdenum complexes of the type MoO<sub>2</sub>L and MoO<sub>2</sub>L·B of a new diprotic tridentate ONS chelating ligand, H<sub>2</sub>L, have been synthesized with the aim to examine their potential to behave as models for the active site of an oxidoreductase molybdoenzyme like xanthineoxidase. The MoO<sub>2</sub>L complex produces MoO<sub>2</sub>L·B on treatment with neutral monodentate Lewis bases such as  $\gamma$ -picoline, 2-methylimidazole or 1-allylimidazole, utilizing the vacant sixth coordination site. They have been characterized by spectroscopic and electrochemical techniques. The complexes MoO<sub>2</sub>L (**1**), MoO<sub>2</sub>L( $\gamma$ -pic) (**2**) and MoO<sub>2</sub>L(1-allyl imz) (**4**) were structurally characterized by single crystal X-ray diffraction. The complex Mo<sup>VI</sup>O<sub>2</sub>L exhibits oxotransfer to PPh<sub>3</sub> in acetonitrile medium leading to the formation of Mo<sup>IV</sup>OL, which is reoxidized to Mo<sup>VI</sup>O<sub>2</sub>L on treatment with DMSO or pyridine N-oxide. DFT calculations on the ligand and complexes **1**, **2** and **4** were also carried out.

© 2012 Elsevier Ltd. All rights reserved.

## 1. Introduction

Apart from their versatile behavior in relation to numerous oxidation states (−2 to +6), variable stereochemical and electronic properties [1], and catalytic activity toward some industrially important chemical processes [2,3] in the higher oxidation states, complexes of Mo(V) and Mo(VI) ligated to some NS/ONS donor ligands [4–7] have still retained the attention of coordination chemists and bio-inorganic chemists, especially because of their deep involvement in some important bio-chemical processes occurring in several forms of plants and some lower order animals [8,9].

Attempts to design and synthesize model complexes that contain characteristic features which hold the possibility of forming complexes that may mimic the active center of a molybdoenzyme are still actively being pursued. In this backdrop, we have undertaken the present work. It may be mentioned that for several years we have continuously been involved in this area of molybdenum chemistry [10–15]. In this paper, we report the synthesis of the complexes MoO<sub>2</sub>L and MoO<sub>2</sub>L·B (where B is a neutral monodentate

Lewis base) of a tridentate ONS chelating ligand derived from benzoylacetone and S-benzylthiocarbamate. Characterization by elemental analyses and various spectroscopic (IR, UV–Vis and <sup>1</sup>H NMR) methods are also reported. The crystal and molecular structures of three complexes, MoO<sub>2</sub>L (**1**), MoO<sub>2</sub>L( $\gamma$ -pic) (**2**) and MoO<sub>2</sub>L(1-allyl imz) (**4**), have been determined by single crystal X-ray crystallography. The chemical activity and the electro-chemical behavior of these complexes have been examined.

## 2. Experimental

### 2.1. Materials

Reagent grade solvents were dried and distilled prior to use. All other chemicals used for the preparative work were of reagent grade, available commercially and used without further purification.

### 2.2. Synthesis

#### 2.2.1. Synthesis of the ligand (H<sub>2</sub>L)

A mixture of 10 ml (0.2 mol) hydrazine hydrate and 11.2 g (0.2 mol) KOH in 70 ml of 90% ethanol was cooled down to

\* Corresponding author. Tel.: +91 033 2350 8386; fax: +91 033 2351 9755.

E-mail address: [ssmandal2000@gmail.com](mailto:ssmandal2000@gmail.com) (S.S. Mandal).

–10 °C, then 15 ml (0.25 mol) of CS<sub>2</sub> was added dropwise with constant stirring. The yellow oil which formed was separated and dissolved in 60 ml of previously cooled 40% ethanol. To this, 23 ml (0.2 mol) of benzyl chloride was added slowly with vigorous stirring. The white product which formed was collected and after recrystallization from benzene was dissolved in 50 ml of absolute ethanol. To this solution, 32.4 g (0.2 mol) of benzoylacetone in 50 ml ethanol was added. The resulting mixture was stirred for 1 h at room temperature. The crystals which settled down were filtered off, washed with ethanol and dried in vacuo (Scheme 1). Yield: ~80%; M.p.: ~120 °C. *Anal.* Calcd. for C<sub>18</sub>H<sub>18</sub>N<sub>2</sub>S<sub>2</sub>O: C, 63.16; H, 5.26; N, 8.19. Found: C, 62.19; H, 5.53; N, 7.89%. IR (KBr pellet), cm<sup>-1</sup>: ν<sub>(N–H)</sub> 3025 (w), ν<sub>(O–H)</sub> 3357 (s), ν<sub>(C=N)</sub> 1627 (s), ν<sub>(C=S)</sub> 1315 (s); <sup>1</sup>H NMR (dmso-d<sub>6</sub>): (H<sub>3</sub>C–C=N) 2.46 (s, 3H), (–CH<sub>2</sub>–) 4.36 (s, 2H), (–CH) 6.48 (s, 1H), (–NH–) 12.1 (s, 1H), (–OH) 12.26 (s, 1H), (aromatic protons) 7.20–7.33 (m, 10H).

## 2.2.2. Synthesis of the complexes

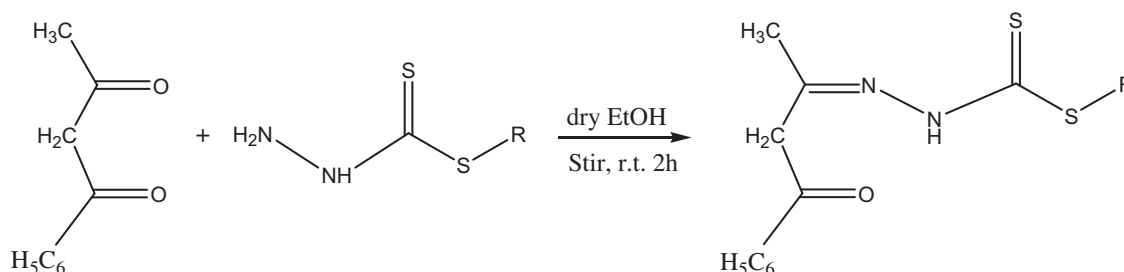
**2.2.2.1. MoO<sub>2</sub>L (1).** To a filtered solution of 0.33 g (1.0 mmol) of MoO<sub>2</sub>(acac)<sub>2</sub> in 20 ml of dry CH<sub>3</sub>OH was added 0.342 g (1.0 mmol) of the ligand H<sub>2</sub>L in 15 ml of dry CH<sub>3</sub>OH. The resulting red solution was stirred at room temperature for 2 h. The crystalline red compound that separated out was filtered, washed with cold CH<sub>3</sub>OH and dried in vacuo over anhydrous CaCl<sub>2</sub>, in a yield of ~80%. The compound was recrystallized from dry CH<sub>3</sub>OH. *Anal.* Calcd. for C<sub>18</sub>H<sub>16</sub>N<sub>2</sub>S<sub>2</sub>O<sub>3</sub>Mo: C, 46.15; H, 3.42; N, 5.98; Mo, 20.51. Found: C, 46.01; H, 3.39; N, 5.25; Mo, 20.02%. IR (KBr pellet), cm<sup>-1</sup>: ν<sub>(C=N)</sub>

1598 (s), ν<sub>(Mo=O)</sub> 905 (vs), 840 (vs), ν<sub>(Mo–N)</sub> 583 (m), ν<sub>(Mo–S)</sub> 471 (w); UV–Vis (CH<sub>2</sub>Cl<sub>2</sub>) [λ<sub>max</sub>/nm (ε/dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>): 258 (5550), 342 (4030), 406 (2750)]; <sup>1</sup>H NMR (dmso-d<sub>6</sub>): (H<sub>3</sub>C–C=N) 2.49 (s, 3H), (–CH<sub>2</sub>–) 4.43 (s, 2H), (–CH) 6.42 (s, 1H), (aromatic protons) 7.27–7.37 (m, 5H), 7.42–7.50 (m, 5H).

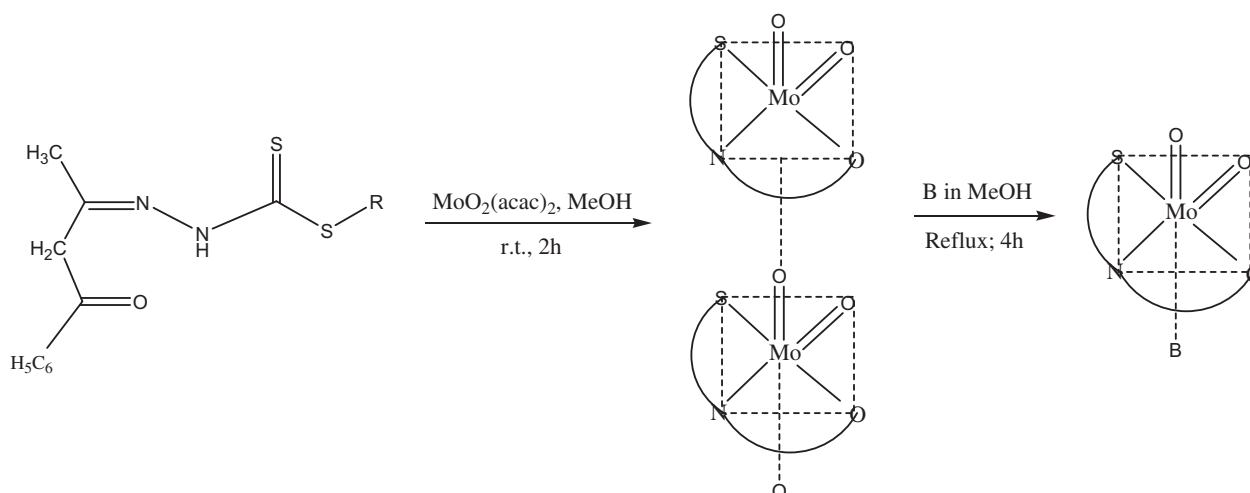
Compounds **2–4**, of the general formula MoO<sub>2</sub>L·B, were prepared by refluxing the parent complex **1** in CH<sub>3</sub>OH with the appropriate monodentate Lewis base (such as γ-picoline, 2-methylimidazole or 1-allylimidazole) in a 1:2 molar ratio for ~4 h (Scheme 2). Red crystalline solids so formed were filtered, washed with dry CH<sub>3</sub>OH and dried in vacuo over anhydrous CaCl<sub>2</sub>, in yields of ~70–75%.

**2.2.2.2. MoO<sub>2</sub>L(γ-pic) (2).** *Anal.* Calcd. for C<sub>24</sub>H<sub>23</sub>N<sub>3</sub>S<sub>2</sub>O<sub>3</sub>Mo: C, 51.33; H, 4.09; N, 7.48; Mo, 17.11. Found: C, 51.05; H, 3.95; N, 7.48; Mo, 16.97%. IR (KBr pellet) cm<sup>-1</sup>: ν<sub>(C=N)</sub> 1598 (s), ν<sub>(Mo=O)</sub> 940 (vs), 840 (vs), ν<sub>(Mo–N)</sub> 581 (m), ν<sub>(Mo–S)</sub>, 471 (w); UV–Vis (CH<sub>2</sub>Cl<sub>2</sub>) [λ<sub>max</sub>/nm (ε/dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>): 256 (22 000), 341 (12 630), 414 (10 330)]; <sup>1</sup>H NMR (dmso-d<sub>6</sub>): (H<sub>3</sub>C–C=N) 2.46 (s, 3H), (–CH<sub>2</sub>–) 4.39 (s, 2H), (–CH) 6.38 (s, 1H), (–CH<sub>3</sub>) 2.42 (s, 3H), (aromatic protons) 7.17–7.33 and 7.38–7.46 (m, 14H).

**2.2.2.3. MoO<sub>2</sub>L(2-meth imz) (3).** *Anal.* Calcd. for C<sub>22</sub>H<sub>22</sub>N<sub>4</sub>S<sub>2</sub>O<sub>3</sub>Mo: C, 48.00; H, 4.00; N, 10.18; Mo, 17.12. Found: C, 47.82; H, 3.90; N, 10.02; Mo, 16.85%. IR (KBr pellet) cm<sup>-1</sup>: ν<sub>(C=N)</sub> 1521 (vs), ν<sub>(Mo=O)</sub> 967 (s), 904 (s), ν<sub>(Mo–N)</sub> 562 (m), ν<sub>(Mo–S)</sub> 480 (w); UV–Vis (CH<sub>2</sub>Cl<sub>2</sub>) [λ<sub>max</sub>/nm (ε/dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>): 265 (3570), 311 (2090), 416



**Scheme 1.** Reaction diagram for the isolation of the ligand (R = –CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>).



(B = γ-picoline, 2-methylimidazole or 1-allylimidazole)

**Scheme 2.** Reaction diagram for the isolation of the Mo (VI) complexes.

Download English Version:

<https://daneshyari.com/en/article/1334688>

Download Persian Version:

<https://daneshyari.com/article/1334688>

[Daneshyari.com](https://daneshyari.com)