

Synthesis and characterization of dioxidomolybdenum(VI) complexes with thiosemicarbazone ligands

A Dissertation

Submitted in partial fulfillment

FOR THE DEGREE OF

MASTER OF SCIENCE IN CHEMISTRY

Under Academic Autonomy

NATIONAL INSTITUTE OF TECHNOLOGY,

ROURKELA-769008



Affiliated to

Deemed University

By

Shweta

Under the guidance of

Dr. RUPAM DINDA

Department of Chemistry

NATIONAL INSTITUTE OF TECHNOLOGY

ROURKELA-769008 (ODISHA)

INTRODUCTION

The chemistry of thiosemicarbazone complexes of transition metals has been to be the subject of attention, primarily because of overgrowing biological properties [1-8]. Thiosemicarbazones have been investigated as anti-viral, antibacterial and anticancer agents [9-12]. It behaves as an ONS/NNS tridentate or tetradentate chelate towards metal ions. Some thiosemicarbazones, such as marboran or triapine, are already used in medical practice. Recent discovery of the antitumor effects of metal complexes and their potential use in cancer diseases have received increasing attention [13, 14].

Chemistry of nitrogen–sulfur chelating ligands bound to Mo at higher oxidation states is a field of current interest. These studies have been considered even more important after the revelation that several enzymes like DMSO reductase, xanthine oxidase and other oxotransferases in their prosthetic groups contain Mo(IV), Mo(V) or Mo(VI) ions coordinated by nitrogen, oxygen or sulfur donor atoms of a macromolecular ligand system [15-17].

To extend these observations, in this dissertation an attention is focused on the synthesis and characterization of new dioxo-molybdenum(VI) complexes featuring thiosemicarbazone ligands. The ligands and their corresponding molybdenum complexes were successfully characterized by IR, UV-VIS and NMR spectroscopy.

2. EXPERIMENTAL

2.1. *Materials:*

Chemicals were procured from renowned company like Aldrich, E. Merck, obtained from standard commercial sources and used without further purification. HPLC grade DMSO was used for spectroscopic and electrochemical studies and ethanol, methanol, acetic acid were used for synthesis of ligands and metal complexes.

2.2. *Physical Measurements:*

IR spectra were recorded on a Perkin-Elmer Spectrum RXI spectrometer. ^1H NMR and ^{13}C NMR spectra were recorded with a Bruker Ultrashield 400 MHz spectrometer using SiMe_4 as an internal standard. Electronic spectra were recorded on a Lamda25, Perkin Elmer spectrophotometer.

2.3. *Synthesis of ligands:*

The thiosemicabazides were prepared from distilled substituted aniline by a known method reported earlier [18]. The ligands, (H_2L^{1-4}) of salicylaldehyde were prepared in 80-90% yield by stirring equimolar ratio of the substituted thiosemicabazide with salicylaldehyde in methanol medium by standard procedures [19]

2.4 *Synthesis of metal complexes*

All the complexes were prepared following the same procedure. Ethanolic solution of $\text{MoO}_2(\text{acac})_2$ was mixed with 20 ml of hot ethanolic solution of H_2L^{1-4} ligand. The mixture was then refluxed. Red cubic crystals, suitable for X-ray crystallography were obtained by slow evaporation from DMSO.

3. RESULT AND DISSCUSION:

3.1. Spectral Characteristics:

IR spectra

Infrared spectra of all the complexes are similar (Figure 3.1 & 3.2). The ligands exhibit, bands due to two $\nu(\text{N-H})$ and $\nu(\text{O-H})$ moieties in $3321\text{--}2984\text{ cm}^{-1}$ region, however the complexes do not exhibit, $\nu(\text{N-H})$ as well as the $\nu(\text{O-H})$ bands. Thus it reveals that the ligands coordinate to the metal centre in the anionic forms. The sharp band in the range $739\text{--}756\text{ cm}^{-1}$ due to $\nu(\text{C-S})$ stretching in the ligand is shifted by $10\text{--}15\text{ cm}^{-1}$, indicating participation of the thione sulphur in coordination [20, 21]. The characteristic bands at 919 & 901 cm^{-1} in complexes attributes to the presence of dioxo $\nu(\text{Mo=O})$ [22, 23].

IR spectra of H_2L^4

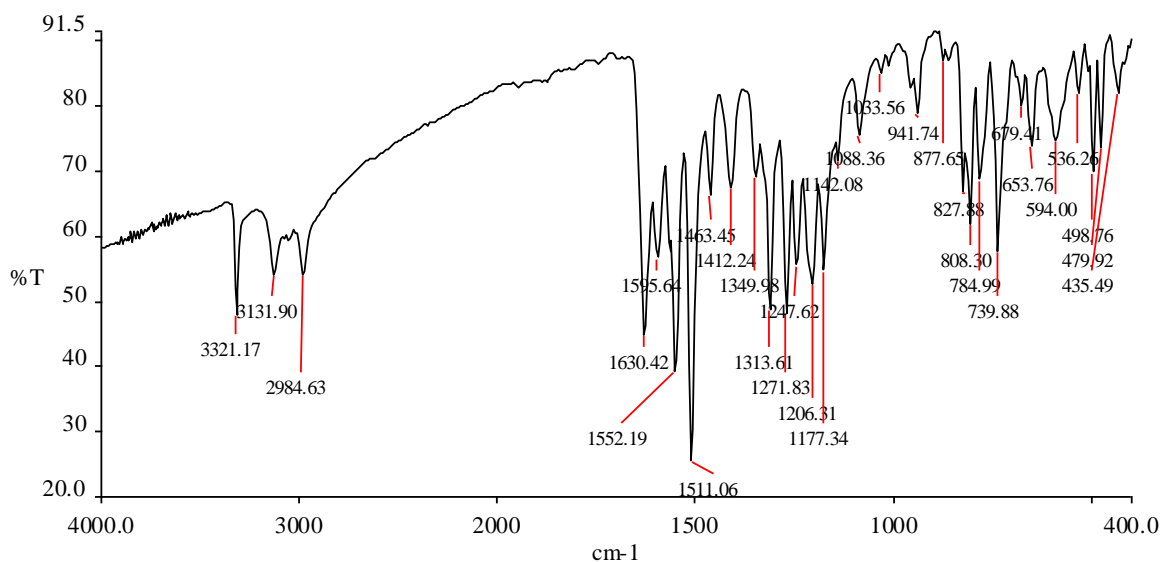


Figure 3.1

IR spectra of Complex **4**: [MoO₂(L⁴)(DMSO)]

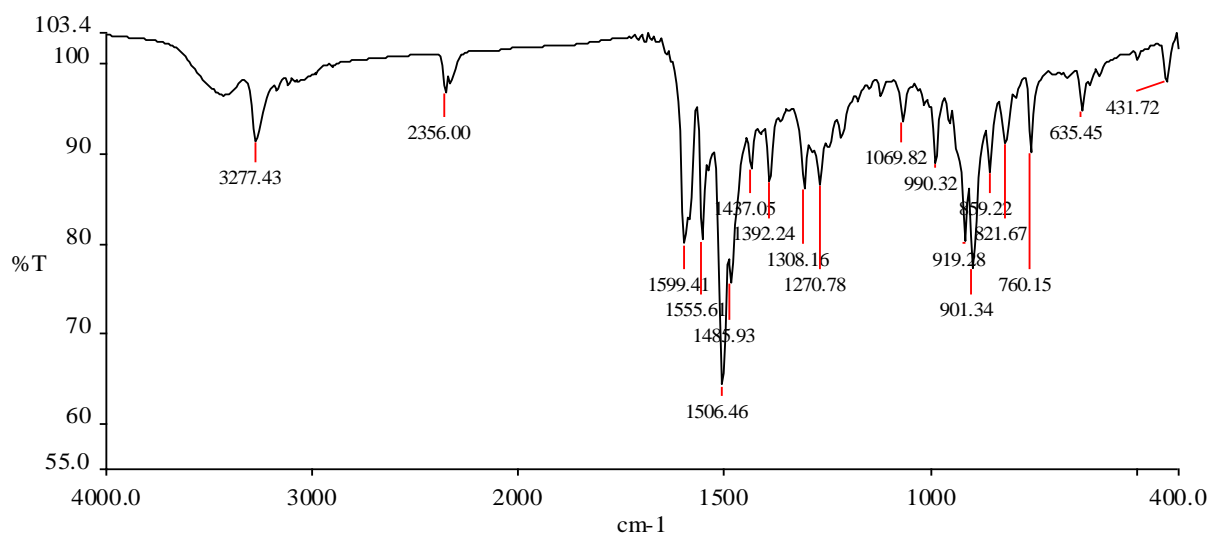


Figure 3.2

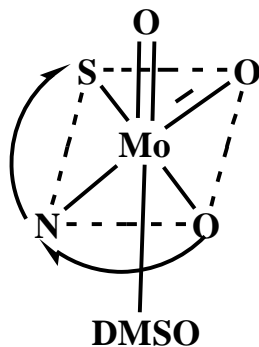
UV-VIS spectra

The electronic absorption spectra (in CH₃CN) of all the complexes (**1–4**) display a shoulder in 400- 440 nm region and two strong absorptions are located in the 260– 320 nm range, which are assignable to L–M(*dπ*) LMCT and intraligand transitions respectively [24]

NMR spectra of the ligands

The ¹H NMR and ¹³C spectral data of the free ligands and its corresponding Mo(VI) were recorded using DMSO-*d*₆. The spectrum of the free ligands exhibit two close but separate singlets in the range 12.00–8.49 ppm due to OH(O-H) and NH (N-H) groups respectively, which are absent in the spectra of complexes indicating coordination of these groups to the metal centre. Signals for aromatic protons found as multiplets in the 8.5–6.02 ppm range [25]. The ¹³C NMR spectra of the ligands showed a sharp singlet appearing at 180–110 ppm.

3.2. Expected Structure of $[MoO_2(L^{1-4})(DMSO)]$



4. CONCLUSION

In this dissertation four 4-(p-X-phenyl) thiosemicarbazone of salicylaldehyde {X=F, Cl Br, OMe} and their corresponding Mo(VI) complexes have been synthesized. The ligands and their metal complexes have been characterized by IR, UV-VIS and NMR spectroscopy. Full characterization of all the complexes has not been possible due to shortage of time.

REFERENCES

- [1] S. Datta, D. K. Seth, R. J. Butcher, S. Bhattacharya, *Inorg. Chim. Acta* 377 (2011)120-128.
- [2] D.X. West, A.E. Liberta, S.B. Padhye, R.C. Chikate, P.B. Sonawane, A.S. Kumbhar, R.G. Yerande, *Coord. Chem. Rev.* 123 (1993) 49-71.
- [3] J.S. Casas, M.S. Garcia-Tasende, J. Sordo, *Coord. Chem. Rev.* 209 (2000) 197-216.
- [4] D.R. Smith, *Coord. Chem. Rev.* 164 (1997) 575-666.
- [5] E.W. Ainscough, A.M. Brodie, J.D. Ransford, J.M. Waters, *Dalton Trans.* (1997) 1251-1255.
- [6] M.A. Ali, A.H. Mirza, A.M.S. Hossain, M. Nazimuddin, *Polyhedron* 20 (2001) 1045-1052.
- [7] M. Baldini, M.B. Ferrari, F. Bisceglie, G. Pelosi, S. Pinelli, P. Tarasconi, *Inorg. Chem.* 42 (2003) 2049-2055.
- [8] M.B. Ferrari, F. Bisceglie, G. Pelosi, P. Tarasconi, R. Albertini, G.G. Fava, S. Pinelli, *J. Inorg. Biochem.* 89 (2002) 36-44.
- [9] M.B. Ferrari, F. Bisceglie, G. Pelosi, P. Albertini, P.P. Dall'Aglio, A. Bergamo, G. Sava, S. Pinelli, *J. Inorg. Biochem.* 98 (2004) 301-312.
- [10] M.J.M. Campbell, *Coord. Chem. Rev.* 15 (1975) 279-319.
- [11] S.B. Padhye, G.B. Kauffman, *Coord. Chem. Rev.* 63 (1985) 127-60.
- [12] D.L. Klayman, J.P. Scovill, J.F. Bartosevich, J. Bruce, *J. Med. Chem.* 26 (1983) 39-42.
- [13] D.B. Lovejoy, D.R. Richardson, *Blood* 100 (2002) 666–676.
- [14] N. Farrell, *Coord. Chem. Rev.* 232 (2002) 1–4.

- [15] S.K. Dutta, D.B. McConville, W.J. Youngs, M. Chaudhury, *Inorg. Chem.* 36 (1997) 2517.
- [16] R. Hahn, U. Küsthardt, W. Scherer, *Inorg. Chim. Acta* 210 (1993) 177.
- [17] R. Dinda, P. Sengupta, S. Ghosh, W.S. Sheldrick, *Eur. J. Inorg. Chem.* (2003) 363.
- [18] Part 1: S.Ghosh, S.Purohit, *Indian J. Chem.* 26A (1987) 131.
- [19] S. Purohit, A.P. Koley, L.S. Prasad, P.T. Manoharan and S. Ghosh, *Inorg. Chem.* 28 (1989) 3735.
- [20] S.K. Chattopadhyay, D. Chattopadhyay, T. Banerjee, R. Kuroda and S. Ghosh, *Polyhedron* 16 (1997) 1925-1930.
- [21] A. Pérez-Rebolledo, I.C. Mendes, N.L. Speziali, P. Bertani, J.M. Resende, A.F.de Carvalho Alcôntara, H. Beraldo, *Polyhedron* 26 (2007) 1449–1458.
- [22] R. Dinda, S. Ghosh, L.R. Falvello, M. Tomás, T.C.W. Mak, *Polyhedron* 25 (2006) 2375–2382.
- [23] R. Dinda, P. Sengupta, M. Sutradhar, T.C.W. Mak, S. Ghosh, *Inorg. Chem.* 47 (2008) 5634.
- [24] R. Dinda, P. Sengupta, S. Ghosh, T.C. W. Mak., *Inorg. Chem.* 41 (2002) 1684.
- [25] S. Naskar, D. Mishra, R.J. Butcher, S.K. Chattopadhyay, *Polyhedron* 26 (2007) 3703.