Asian Journal of Chemistry Vol. 19, No. 6 (2007), 4689-4696

Studies of Some Novel Oxomolybdenum(V) and Dioxomolybdenum(VI) Complexes of Thiophene-2-aldehyde-N(4)-phenylthiosemicarbazone

M.L. HARIKUMARAN NAIR* and K.R. KUMARI NISHA
Department of Chemistry, University College, Thiruvananthapuram-695 034, India
E-mail: drmlhnair@gmail.com

Some novel oxomolybdenum(V) complexes of general formula [MoO(TAPT)XCl_2] and dioxomolybdenum(VI) complexes of general formula [MoO_2(TAPT)XCl] (X = Cl, NO_3, NCS or ClO_4 and TAPT = thiophene-2-aldehyde-N(4)-phenyl thiosemicarbazone) have been synthesized and characterized by elemental analysis, magnetic moment and conductance measurements, IR, ESR, electronic and NMR spectral studies. The thermal behaviour of one of the complexes has also been examined. The ligand and its few metal complexes were screened for their antibacterial activities against gram positive and gram negative bacteria and also screened for their antifungal activity. The molar conductance values of the complexes indicate that the complexes are non electrolytes. The X-band ESR spectra indicate that the pentavalent Mo in the complex [MoO(TAPT)NCS Cl_2] is monomeric in nature. The X-ray diffraction patterns of the complex [MoO_2(TAPT) NO_3Cl] has been examined and found to be orthorhombic with unit cell dimensions such as a= 10.89 Å, b = 8.12 Å and c = 7.03 Å.

Key Words: OxoMo(V), DioxoMo(VI), Complexes, Thiophene-2-aldehyde, N-Phenyl thiosemicarbazide.

INTRODUCTION

Thiosemicarbazones have been found to reduce tissue iron level than the defferoxamine which is used for removing excess of iron accumulated in tissues of patients with cooleys anaemia[1]. In recent years, they have been used for the analytical determination of metals[2]. Of all the metals in 4*d* transition series, molybdenum has aroused considerable interest in recent years in view of its biochemical importance. It is an essential micronutrient for micro organisms, plants and animals[3,4]. The purpose of the present work is to synthesize and characterize some new oxomolybdenum(V) and dioxomolybdenum(VI) complexes of thiophene-2-aldehyde-N (4)-phenyl thiosemicarbazone (TAPT).

EXPERIMENTAL

$MoCl_5$ (Acros organics, Belgium) and MoO_3 (Loba) were used as such. N-Phenyl thiourea, hydrazine hydrate and all other chemicals were of BDH A.R. grade.

Preparation of the ligand thiophene-2-aldehyde-N (4)-phenylthiosemicarbazone

The compound 4-phenylthiosemicarbazide was prepared from N-phenylthiourea and hydrazine hydrate using standard method[5-7]. Thiophene-2-aldehyde-N(4)-phenyl thiosemicarbazone was prepared by refluxing equimolar mixture of N-phenyl thiosemicarbazide and thiophene-2-aldehyde in methanol for *ca.* 3 h. The yellow solid separated was filtered, washed and dried. It was recrystallized from methanol.

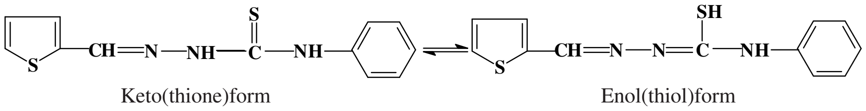

Fig. 1

Preparation of oxomolybdenum(V) complexes

A methanolic solution of $MoCl_5$ (2 mmol) was mixed with a hot methanolic solution of the ligand (2 mmol). It was then refluxed for *ca.* 5 h. The reaction mixture was concentrated, the solid separated was filtered, washed with aqueous methanol and dried over P_4O_{10} *in vacuo*.

The following general method[8] was adopted for the preparation of other oxomolybdenum(V) complexes.

Methanolic solutions of $MoCl_5$ (2 mmol), containing 2-3 drops of $HClO_4$/0.5 g of $LiNO_3$/0.5 g of NH_4NCS as the case may be were mixed with hot methanolic solution of the ligand (2 mmol) and refluxed for *ca.* 5 h. The reaction mixture was concentrated, the complex separated was filtered, washed with aqueous methanol and dried over P_4O_{10} *in vacuo*.

Preparation of dioxomolybdenum (VI) complexes

MoO_3 (2 mmol) was dissolved in conc. HCl. The solution was added dropwise with stirring to a hot methanolic solution of the ligand (2 mmol). It was then refluxed for *ca.* 6 h. The reaction mixture was concentrated, the complex separated was filtered, washed with aqueous methanol and dried over P_4O_{10} *in vacuo*.

The following general method[8] was adopted for the preparation of other dioxomolybdenum(VI) complexes.

MoO_3 (2 mmol) was dissolved in con. HCl. To this, added 2-3 drops of $HClO_4$/0.5 g of $LiNO_3$/0.5 g of NH_4NCS. This solution was added dropwise with stirring to a hot methanolic solution of the ligand (2 mmol) and refluxed for *ca.* 4 h. The reaction mixture was concentrated, the complex separated was filtered, washed with aqueous methanol and dried over P_4O_{10} *in vacuo*.

Metal and halide in the complexes were estimated by standard methods[9]. Perchlorate was estimated by Kurz's method[10]. Elemental analysis (C, H, N and S) of complexes were carried out at RSIC, CDRI, Lucknow. The IR spectra of the ligand and complexes were recorded in the region 4000-400 cm^{-1} on a Jasco FTIR 430 spectrophotometer, using KBr pellets. The electronic spectra of the ligand and complexes in the solution state (CH_3OH) were recorded on Jasco V-550 UV-Vis spectrophotometer. ESR spectrum of the complex was run on a varian E-112 X-Q band spectrometer with DPPH as reference material. CHNS analysis of the samples were done by microanalytical technique at RSIC, CDRI, Lucknow. ^1H NMR spectra of the ligand and complex were recorded in $CDCl_3$ on a 300 MHz FT NMR instrument using TMS as reference. X-ray powder diffraction patterns of the complexes were recorded using philips X-ray PW 1710 diffractometer. The conductances of the complexes in $C_6H_5NO_2$, CH_3OH and CH_3CN (*ca.* 10^{-3} M) were measured at 300 ± 2 K using an Elico conductivity bridge type CM82T with a dip type cell (ec-03) fitted with platinum electrodes (Cell constant 0.94 cm^{-1}).

RESULTS AND DISCUSSION

The analytical data (Table-1) support that the complexes are of the type $[MoO(TAPT)XCl_2]$ and $[MoO_2(TAPT)XCl]$ where TAPT = thiophene -2-aldehyde-N(4)-phenylthiosemicarbazone and X = Cl, NO_3, NCS, ClO_4. The molar conductances in different solvents show that all the complexes are non-electrolytes.

Infrared spectra

The ligand, TAPT does not display the ν(S–H) mode at about 2600 cm^{-1} indicating that in the solid state, the ligand remains in thioketo form[11]. The two peaks observed at 1290 and 780 cm^{-1} are assigned to ν(C–S) vibrations[12]. The shift of these bands to lower frequencies in the spectra of complexes indicate the coordination of the ligand through thioketo sulphur. The ν(C=N) observed at 1630 cm^{-1} in the spectrum of the ligand show a downward shift by 15-20 cm^{-1} in complexes, suggesting its participation in the coordination[7]. Additionally, ligand exhibits characteristic peaks coresponding to the in-plane and out-of-plane deformation of 2-substituted thiophene at 757 and 575 cm^{-1}, respectively[13,14] which remain in the spectra of the complexes indicating that the thiophene ring sulphur did not coordinate with the metal atom[15,16]. Thus, the ligand TAPT behaves as neutral bidentate chelating agent in these complexes.

TABLE 1

ANALYTICAL AND CONDUCTIVITY DATA OF COMPLEXES

Complex	Analytical % : Found (Calcd.)					Molar conductance (Ω^{-1} cm^2 mol^{-1})					
						$C_6H_5NO_2$		CH_3CN		CH_3OH	
	C	H	N	S	Mo	Conc.× 10^{-3} M	Cond.	Conc.× 10^{-3} M	Cond.	Conc.× 10^{-3} M	Cond.
[MoO(TAPT)Cl_3]	30.08 (30.04)	2.35 (2.29)	8.70 (8.76)	13.38 (13.35)	20.05 (20.01)	1.10	6.2	1.00	10.5	1.00	8.2
[MoO(TAPT)NCSCl_2]	31.14 (31.08)	2.23 (2.19)	11.10 (11.16)	19.18 (19.13)	19.20 (19.11)	1.10	7.8	0.99	30.2	1.10	20.1
[MoO(TAPT)NO_3Cl_2]	28.42 (28.46)	2.08 (2.17)	11.03 (11.07)	12.60 (12.65)	18.55 (18.49)	1.00	8.1	1.00	48.8	0.98	10.5
[MoO(TAPT)ClO_4Cl_2]	26.42 (26.50)	2.09 (2.02)	7.78 (7.73)	11.82 (11.78)	17.60 (17.65)	0.99	6.5	1.00	9.6	1.00	7.8
[MoO_2(TAPT)Cl_2]	31.25 (31.3)	2.44 (2.39)	9.18 (9.13)	13.98 (13.91)	20.80 (20.86)	1.00	2.5	1.10	8.5	1.00	6.5
[MoO_2(TAPT)NCSCl]	32.38 (32.34)	2.30 (2.28)	11.65 (11.61)	19.92 (19.90)	19.94 (19.89)	1.00	2.7	1.00	40.2	1.10	27.1
[MoO_2(TAPT)NO_3Cl]	29.58 (29.60)	2.23 (2.26)	11.58 (11.51)	13.12 (13.16)	19.70 (19.72)	0.99	3.1	1.00	50.8	1.00	8.5
[MoO_2(TAPT)ClO_4Cl]	27.50 (27.48)	2.08 (2.10)	8.07 (8.02)	12.20 (12.22)	18.25 (18.31)	1.00	2.8	1.00	10.5	1.00	17.2

A strong band at 1060 cm^{-1} and a medium intensity band at 617 cm^{-1} observed in the spectrum of the perchlorate complex of Mo(V) are assigned to ν_3 and ν_4, respectively. In the spectrum of $[MoO_2(TAPT)ClO_4Cl]$, two bands (split bands) observed at *ca.*1100 and 1030 cm^{-1} assigned to ν_4 and ν_1 and another set of split bands *ca.* 640 and 625 cm^{-1} assigned to ν_3 and ν_5 vibrations are characteristic of monodentately coordinated perchlorate group. This is supported by the molar conductance data (Table-1). The N-coordinated nature[17] of the thiocyanate group is indicated by ν(C–N) (2050), ν(C–S) (798) and (502 cm^{-1}). The IR spectra of the nitrate complexes are suggestive of monodentate nature of coordinated nitrate groups[18] ($\nu_4 = 1513$, $\nu_1 = 1384$ cm^{-1}).

A very strong band found at 940 cm^{-1} in the spectra of Mo(V) complexes corresponds to ν(Mo=O). Also strong bands exhibited by the dioxomolybdenum(VI) complexes in the region 940-960 and 910 cm^{-1} are attributed to ν_{sym}(O=Mo=O) and ν_{asym}(O=Mo=O), respectively of *cis* -MoO_2 moiety. MoO_2 prefers to form *cis* configuration due to the maximum utilization of the available dπ orbitals for bonding with the oxogroups[19]. The (Mo–N) stretching frequency ν(Mo–N)lies 478 cm^{-1} in the complexes. Medium to weak intensity bands occurring around 450-425 cm^{-1} are attributed to ν(Mo–O) in the complexes[20,21].

^{1}H NMR Spectra: In the ^{1}H NMR Spectra, a strong signal at δ 8.24 due to –CH=N– of ligand undergoes a downfield shift on complexation indicating the participation of azomethine nitrogen in bonding. The aromatic protons of the compound appear as multiplet in the region δ 7.4-7.6. A detailed assignment of the aromatic proton signals are not attempted. The ligand does not show any peak attributable to S–H proton, indicating that it exists in the thioketo form. IR spectral data are also in conformity with these observations.

Electronic spectra: The electronic spectral bands of oxomolybdenum (V) complexes in methanol together with the tentative assignments are discussed[22]. The Mo(V) complexes usually exhibit three distinct absorption bands in the ligand field region at *ca.* 13500-14500, 19000-22000 and 22500-26000 cm^{-1}, assignable to the transitions $^2B_2 \rightarrow {}^2E(d_{xy} \rightarrow d_{xz}, d_{yz})$; $^2B_2 \rightarrow {}^2A, (d_{xy} \rightarrow d_{x2-y2})$ and $^2B_2 \rightarrow {}^2A_2, (d_{xy} \rightarrow d_{z2})$. Usually, the third band is obscured by the more intense charge transfer transition O(π)$\rightarrow$d (Mo) involving the excitation of an electron from the highest filled π-bonding molecular orbital (associated mainly with oxygen) to the *d*-orbitals of molybdenum. All the present Mo(V) complexes show bands in the region 13700-14920 (weak broad), 19610-20000 and *ca.* 25000 cm^{-1}. The electronic spectra thus indicate octahedral environment for all the complexes and are in conformity with the Ballhausen-Gray scheme for an octahedral geometry[22,23]. No bands are observed below 10000 cm^{-1} and hence the possibility of a tetrahedral structure can be ruled out. The complexes can be best considered as octahedral with strong tetragonal distortion (C_{4v} symmetry), resulting from the (Mo=O) multiple bond.

ESR Spectra: The ESR spectrum of the complex [MoO(TAPT) $NCSCl_2$] which was recorded in polycrystalline form at room temperature, exhibited a single line only. The ESR parameters were found to be $g_{||}$ = 1.9859, $g\perp_r$ = 1.9125 and g_{av} = 1.9370. The g_{av} value indicates that the pentavalent Mo in the complex is monomeric in nature[24].

Thermogravimetric analysis: Thermogravimetric curves of the complex [MoO_2(TAPT)NO_3Cl] was recorded in the temperature range from room temperature to 1000°C. The complex shows first a weight loss of 53.66 % around 250°C. This corresponds to the elimination of ligand molecule. The second weight loss of 7.29 % at 495°C was observed corresponding to the loss of chlorine atom. The third weight loss of 12.75 % at 560°C was observed corresponding to the loss of nitrate group. The residual mass is about 26.30 % which indicate that the decomposition[25] product is MoO_3.

X-ray analysis: The complex [MoO_2(TAAP)NO_3Cl] was found to be orthorhombic by X-ray powder diffraction method and was indexed by Hesse and Lipson's procedure[26-28]. The unit cell dimensions a, b and c for the complex was found to be 10.889, 8.117 and 7.029 Å, respectively.

Biological activity

The ligand TAPT and the complexes [MoO(TAPT)$NCSCl_2$] and [MoO_2 (TAPT)NCSCl] were screened for their possible antibacterial activities[15] against the gram positive bacteria *Staphylococcus aureus* ATCC 25923 and gram negative bacteria *Escherichia coli* ATCC 25922 at concentrations 10, 20, 40, 80 and 100 μg/disc tested. But they do not exhibited any antibacterial activities.

The ligand TAPT and complexes [MoO(TAPT)$NCSCl_2$] and [MoO_2 (TAPT) NCSCl] were screened for their antifungal activities using poisoned food technique[29]. The ligand and the complexes were found to be active against *Fusarium oxysporum* species which is a common plant pathogen. Test solutions have been prepared by dissolving appropriate amounts of complexes in ethanol. The test solution in the desired concentration was taken and appropriate volume mixed with molten potato agar medium to have a resultant concentration of 100 ppm. This chemical amended medium was poured into 9 cm petriplates. Mycelial discs of actively growing fusarium culture was cut with cork borer and placed at the centre of petriplates. In control sets, appropriate quantities of ethanol were incorporated in place of test solution. 3 Plates were kept for each sample. The fungal growth was measured in every 24 h, at 2 points along the diameter of the colony. The growth of the colony in control sets was compared with that of the various treatments and percentage inhibition was calculated.

$$\%\ \text{Inhibition} = \frac{\text{Growth in control} - \text{Growth in sample}}{\text{Growth in control}} \times 100$$

TABLE-2
EFFECT OF TAPT AND COMPLEXES ON MYCELIAL GROWTH OF *Fusarium oxysporum*

Samples taken	Mycelial growth (cm)	Inhibition (%)
Control	9.0	–
TAPT	5.2	42.22
[MoO(TAPT)NCS Cl_2]	1.5	83.33
[MoO_2(TAPT)NCS Cl]	2.0	77.77

Results show that the complexes exhibited significant antifungal profile and more activity than the ligand.

On the basis of all the above evidences, a distorted octahedral geometry is suggested for the complexes (Figs. 2 and 3).

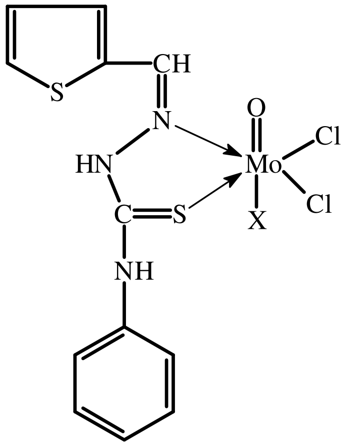

Fig. 2. [MoO[TAPT)XCl_2]
(X = Cl, NCS, NO_3, ClO_4)

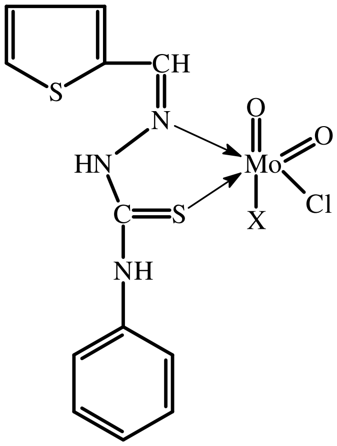

Fig. 3. [MoO_2[TAPT)XCl]
(X = Cl, NCS, NO_3, ClO_4)

ACKNOWLEDGEMENTS

The authors are thankful to Biomedical Technology Wing, SCMIST, Thiruvananthapuram, RRL, Thiruvananthapuram, Bharathiar University, Coimbatore, CDRI, Lucknow and College of Agriculture, Vellayani, Thiruvananthapuram for the facilities.

REFERENCES

1. A.W. Nienhius, *J. Am. Med. Assoc.*, **237**, 1926, (1977).
2. H. Nishioka, T. Kumajai and T. Nagahiro, *Microchem. J.*, **50**, 80 (1994).
3. E.I. Steifel, *Prog. Inorg. Chem.*, **22**, 1 (1977)
4. M.R. Maurya and C. Gopinathan, *Indian J. Chem.*, **35A**, 701 (1996).
5. A.I. Vogel, Text Book of Practical Organic Chemistry, Longmans, London, edn. 3 (1956).
6. P. Bindu and M.R.P. Kurup, *Indian J. Chem.*, **38A**, 388 (1999).
7. P. Bindu and M.R.P. Kurup, *Indian J. Chem.*, **36A**, 1094 (1997).
8. M.L.H. Nair and C.P. Prabhakaran, *Indian J. Chem.*, **35A**, 771 (1996).
9. A.I. Vogel, A Text Book of Quantitative Inorganic Analysis, Wiley, New York, edn. 3 (1963).
10. G. Kurz, Kober and M. Beri, *Analyst. Chem.*, **30**, 1983 (1958).
11. M. Yildiz, B. Dulger, S.V. Koyanai and B.M. Yapier, *J. Indian Chem. Soc.*, **81**, 7 (2004).
12. S.D. Dhumward, K.B. Gudasi and T.R. Goudar, *Indian J. Chem.*, **33A**, 32 (1994).
13. K. Nakanishi and P.H. Solomon, Infrared Absorption Spectroscopy, Holdenday, Inc. Sanfransisco, edn. 2 (1977).
14. V.M. Parikh, Absorption Spectroscopy of Organic Molecules, Addison-Wesley Publishing Company, London (1974).
15. S. Burman and D.N. Sathyanarayana, *Indian J. Chem.*, **20A**, 57 (1981).
16. M.R. Rosenthal, *J. Chem. Edu.*, **50**, 331 (1973).
17. A. Sabatini and I. Bertini, *Inorg. Chem.*, **5**, 204 (1960).
18. C.C. Addison and G. House, *J. Chem. Soc.*, 613 (1960).
19. C.P. Prabhakaran and M.L.H. Nair, *Indian J. Chem.*, **39A**, 989 (2000).
20. O.A. Rajan and A. Chakravorty, *Inorg. Chem.*, **20**, 660 (1981).
21. A. Syamal and M.M. Singh, *Indian J. Chem.*, **32A**, 861 (1993).
22. C.J. Ballhausen and H.B. Gray, *Inorg. Chem.*, **1**, 111 (1962).
23. C.R. Hare, I. Bernal and H.B. Gray, *Inorg. Chem.*, **2**, 568 (1963).
24. M. Gordy, Theory and Applications of Electron Spin Resonance, John Wiley, New York (1980).
25. W.W. Wendlandt, Thermal Analysis, Wiley and Sons, Newyork, edn. 3 (1986).
26. R. Hesse, *Acta Crystallogr.*, **1**, 200 (1948).
27. H. Lipson, *Acta Cryatallogr.*, **2**, 43 (1949).
28. N.F.M. Henry, H. Lipson and W.A. Wooster, The Interpretation of X-ray Diffraction Photographs, Mc.Millan, London (1951).
29. G.A. Zentmyer, *Phytopathology*, **45**, 398(1955).

(*Received*: 19 July 2006; *Accepted*: 24 April 2007) AJC-5610