



SYNTHESIS AND CHARACTERISATION OF OXOMOLYBDENUM (V) AND DIOXOMOLYBDENUM (VI) MIXED LIGAND COMPLEXES

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ABSTRACT

Schiff base, 2-(indole-3'-thiocarboxamidyl) iminomethyl furan (ITIF), has been synthesised by the condensation of indole-3-thiocarboxy hydrazide and furfural. Mixed ligand complexes of oxomolybdenum (V) and dioxomolybdenum (VI) have been prepared by the interaction of $\text{MoCl}_5/\text{MoO}_3$ with the Schiff base as primary and 2-hydroxy-5-methyl-2'-carboxyazobenzene (HMCA) as co-ligand. Analytical data suggest the formulae $[\text{Mo}(\text{LL}'\text{H})\text{Cl}](\text{ClO}_4)_2$, $[\text{Mo}(\text{LL}')\text{NO}_3]\text{Cl}$ and $[\text{MoO}(\text{LL}')(\text{NCS})]\text{Cl}$ for MoO (V) and $[\text{MoO}_2(\text{LL}'\text{H})\text{XY}]$ for MoO₂ (VI) complexes (where L = C₁₄ H₁₁ N₃ SO, L'H = C₁₄ H₁₂ N₂ O₃, X = NCS/NO₃ and Y = Cl). The complexes have been characterised by IR spectra electronic spectra, magnetic and conductance studies. An octahedral geometry has been suggested for the mixed ligand complexes. The MoO₂ (VI), complexes have been found to show biocidal activity.

Key words : Oxomolybdenum (V) complex, Dioxomolybdenum (VI)

INTRODUCTION

Molybdenum is one of the most biologically active transition elements and is an essential micronutrient for micro-organisms, plant and animals¹⁻³. Nature has incorporated molybdenum into a number of redox enzymes⁴. The study of molybdenum complexes⁵⁻⁹ achieved prominence recently because of their major role in biological processes and a great variety of oxidation states and coordination number exhibited by molybdenum. Synthesis and spectral studies of MoO (V) and MoO₂ (VI) complexes of 1, 2-dihydro-1, 5-dimethyl-2-phenyl-4-(2, 4-dihydroxy-phenylazo)-3-H-pyrazol-3-one have been carried out¹⁰. The literature survey reveals that no reports are available on the synthesis of MoO (V) and MoO₂ (VI) complexes with 2-(indole-3'-thiocarboxamidyl) iminomethyl furan (ITIF) as primary and 2-hydroxy-5-methyl-2'-carboxyazobenzene (HMCA) as co-ligand. Therefore, it was thought worthwhile to synthesise and characterize mixed ligand complexes of oxomolybdenum (V) and dioxomolybdenum (VI) with these ligands.

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EXPERIMENTAL

3-indole thiocarboxyhydrazide was synthesized by the literature procedure.¹¹ 2-(Indole-3'-thiocarboxamidyl) furan was prepared by refluxing a mixture of furan-2-carboxaldehyde (0.01 mol) and 3-indole thiocarboxyhydrazide (0.0 mol) in ethanol for ~ 2 h at 80–85°C. A few drops of concentrated HCl were added in the mixture. A light yellow product formed was recrystallised from acetone.

2-Hydroxy-5-methyl-2'-carboxyazobenzene was synthesized by the gradual addition of diazotised anthranilic acid to the well cooled p-cresol solution in 10% sodium hydroxide at 0–5°C. Orange crystals of the product separated out. The azo compound was recrystallised from ethanol. MoCl₅ (Aldrich) and MoO₃ (Loba) were used as such.

Preparation of Complexes

(a) **MoO (V) Complexes** : Methanolic solutions of MoO₅ (5 mmol) containing 5–6 drops of 80% perchloric acid and 1.2 g lithium nitrate or ammonium thiocyanate, were mixed with hot ethanolic solution of the synthesized Schiff base and the azo ligand (5 mmol each). The mixture was refluxed on a water bath for ~ 3 h. The solid complexes separated out on cooling at room temperature were filtered through suction, washed properly and dried over anhydrous CaCl₂. Yield ~ 50–52%.

(b) **MoO₂ (VI) Complexes** : 1.2 g Ammonium thiocyanate or lithium nitrate was added to MoO₂ (5 mmol) dissolved in concentrated hydrochloric acid. Hot ethanolic solutions of the synthesised Schiff base and the azo ligand (5 mmol) each were then mixed to it gradually and with continuous stirring magnetically. The mixture was refluxed for ~ 2 h at 70–75°C. The complexes separated out. These were filtered, washed with ethanol and dried over anhydrous CaCl₂. Yield ~ 56%.

RESULTS AND DISCUSSION

The complexes are insoluble in common organic solvents but dissolve in PhNO₂ and DMF. Analytical data reported in Table 1 correspond to 1:1:1 (M–L–L') stoichiometry for all the complexes. Dioxomolybdenum (VI) complexes contain mixed anions. The electrolytic conductance values in DMF (Table 1) at the concentration 10⁻³M suggest 1:2 electrolytic nature of dioxomolybdenum complexes and perchlorate complex of MoO (V) while the other complex of MoO (V) are 1:1 electrolytes.

Magnetic and electronic spectral Studies

The magnetic moments of MoO (V) complexes are in the range 1.66 – 1.71 B. M. at 300 ± 1 K while MoO₂ (VI) complexes are diamagnetic.

Table 1. Analytical, conductance and magnetic moment data of complexes

Complex	Elemental analysis Found (Calc) %							Λ_m ($\text{Ohm}^{-1}\text{cm}^2$ mol^{-1})	μ_{eff} (B.M.)
	Mo	C	H	N	S	Anion			
[MoO ₂ LL'H (Cl)] (ClO ₄) ₂	10.93 (11.01)	38.78 (38.56)	2.64 (2.63)	8.09 (8.03)	3.64 (3.67)	4.02 (4.06)	22.67 (22.82)	134.5	
[MoO ₂ LL'H] (NO ₃)Cl	13.17 (13.08)	45.62 (45.81)	2.98 (2.99)	11.37 (11.45)	4.33 (4.36)	4.80 (4.83)		78.2	
[MoO ₂ LL'H] (NCS)Cl	13.08 (13.15)	46.40 (46.07)	3.0 (3.01)	9.52 (9.59)	4.39 (4.38)	7.90 (7.95)	4.83 (4.86)	76.0	
[MoO ₂ LL'H] (NCS) (Cl)	12.93 (12.85)	44.70 (45.01)	3.06 (3.08)	9.32 (9.37)	4.30 (4.28)	7.72 (7.77)	4.71 (4.74)	136.5	
[MoO ₂ LL'H] (NO ₃) (Cl)	12.87 (12.78)	44.49 (44.78)	3.04 (3.06)	11.09 (11.19)	4.22 (4.26)	4.70 (4.72)		137.4	

L = C₁₄H₁₁N₃SO, L' H = C₁₄H₁₂N₂O₃

The MoO (V) mixed ligand complexes in solution, under study, show bands in the region 13600–14700, 19250–21400 and 24500–25300 cm^{-1} . The observed electronic spectral bands suggest octahedral environment for these complexes and correspond to the Ballhausen–Gray scheme for octahedral geometry^{12,13}.

IR Spectra

The band, characteristic of ν C=N observed at 1630 cm^{-1} in the Schiff base (ITIF), gets shifted to a lower frequency band (1615 – 1605 cm^{-1}) in the spectra of complexes showing the participation of azomethine nitrogen in complexation. In the ir spectra of the present mixed ligand complexes, thioamide bands I and II (existing at 1545 and 1300 cm^{-1} in the Schiff base) show a + ve shift of $\sim 40 \text{ cm}^{-1}$ while band IV (830 cm^{-1}) gets shifted to a low frequency band appearing at $\sim 810 \text{ cm}^{-1}$. These changes in the band positions suggest that the Schiff base ligand coordinates through thione sulphur in the complexes. The characteristic absorption bands for indole–ring in the ligand appearing at 1600 – 1575 and 1450 cm^{-1} are located at the same position in the spectra of complexes indicating that NH group of indole does not participate in complexation.

A bathochromic shift of the $-\text{N}=\text{N}$ band,¹⁴ located at 1400 cm^{-1} in the azo ligand (HMCA), is observed at 1385 – 1380 cm^{-1} in the mixed ligand complexes which shows the link of metal with the azo nitrogen. A broad band noticed at 3475 cm^{-1} in the spectrum of azo ligand assigned to ν OH (phenolic) is, however, not traceable in the spectra of nitrate and thiocyanato complexes of MoO (V). Further, ν sym (C–O) observed at 1350 cm^{-1} in the azo ligand gets shifted to a higher frequency band at 1385–1390 cm^{-1} in the these complexes, suggesting a bonding with the oxygen atom of the deprotonated phenolic group. In the rest of the complexes, 3475 cm^{-1} band gets shifted to a lower frequency band (3400 – 3430 cm^{-1}) showing that phenolic oxygen atom is involved in coordination without deprotonation.

Some non–ligand bands have been found in the far ir region in the range 470 – 480, 500 – 515 and 325 – 340 cm^{-1} , which may be assigned to ν (M–N), ν (M–O) and ν (M–S) vibrations, respectively.

A very strong band found at 940 cm^{-1} in the spectra of Mo (V) complexes corresponds to ν Mo = O. Further, strong bands seen in the spectra of MoO₂ (VI) complexes in the region 930 – 935 cm^{-1} are attributed to ν_s O=Mo=O and ν_{as} O=Mo=O, respectively.

The N–coordinated nature of NCS group is shown by ν C–N, ν C–S and δ NCS observed at 2080, 785 and 505 cm^{-1} in the spectrum of [MoOOLL' (NCS)]Cl. The spectral bands (ν_4 at 1510 and ν_1 1385 cm^{-1}) present in the spectrum of nitrate complex of MoO (V)

show monodentate nature of nitrate group. A band at $\sim 220 \text{ cm}^{-1}$ is also seen in the spectrum of $[\text{MoOLL'H}(\text{CL})](\text{ClO}_4)_2$ which may be due to $\nu \text{ M-Cl}$ vibration.

Thermal behaviour

In the complexes of MoO (V), decomposition starts at $200 - 220^\circ\text{C}$ and is completed at $\sim 570 - 590^\circ\text{C}$. The total weight loss corresponds to loss of chlorine and ligands. The experimental residual weight is in good agreement with the values calculated for MoO_3 . MoO_2 (VI) complexes decompose initially in $270 - 300^\circ\text{C}$ temperature range and at $600 - 630^\circ\text{C}$, both the ligands are completely lost forming MoO_3 as residual mass.

Biocidal activity

The Schiff base and azo ligands and their MoO_2 (VI) complexes, under study, were screened for fungicidal activity against the fungus : *Aspergillus niger*, *Fusarium oxysporium* and *Helminthosporiumoryzae* at 100, 200 and 300 ppm concentrations by the method described in the literature¹⁵. The experiments were carried out at $302 \pm 1^\circ \text{K}$. It has been observed that the activity of the complexes was greater as compared to ligands. The increased activity of the complexes may be due to the increased liophilic nature of the central atom arising due to chelation.¹⁶

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Accepted : 21.7.04