

Molybdenum Complexes of Some N-S Donors: Part I—Syntheses & Reactivity of Mo(VI) Complexes of Some Ring-substituted 4-Phenylthiosemicarbazides

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A number of Mo(VI) complexes with ring-substituted 4-phenylthiosemicarbazides (LH) have been synthesized and characterised. These compounds are either six-coordinated *cis*-dioxo, $[\text{MoO}_2\text{L}_2]$ or seven-coordinated $[\text{MoOL}_2\text{Cl}_2]$ species. In all the complexes the thiosemicarbazides are ligated to the Mo(VI) acceptor centre in the deprotonated enol form. All the compounds have been characterised by elemental analyses, spectral (UV-vis, IR), magnetic susceptibility and conductance studies. Change in the Mo=O stretching frequency as a function of the donor atom situated *trans* to the Mo=O bond and its implication for the probable structure of the complexes have also been discussed. Reactions of $[\text{MoOL}_2\text{Cl}_2]$ with monodentate nucleophiles like pyridine, imidazole and acetate have been examined.

During recent years considerable attention has been focussed on the oxo complexes of Mo(VI) due to their relevance as model systems for Mo-sites in enzymes. Sulphur donors have assumed special importance in this respect because of their presence inside the coordination sphere of Mo in molybdoenzymes¹⁻⁵. Although various dithio-ligands⁶ have been utilised extensively to gain an insight into the chemistry of molybdenum ligated to sulphur donor centres, studies on the interaction of this important metal ion with N, S donor ligands have not received adequate attention so far. In the present paper we report the syntheses, characterisation and reactivity of some molybdenum (VI) complexes of 4-phenyl, 4-(*p*-methylphenyl), 4-(*p*-chlorophenyl), 4-(*m*-chlorophenyl), 4-(*p*-methoxyphenyl) and 4-(*m*-methoxyphenyl) thiosemicarbazides, all of which can exist in keto and enol forms.

Materials and Methods

Reagent grade solvents, distilled and dried by standard methods, were used in all cases. All the other chemicals were of reagent grade and were used without further purification. The thiosemicarbazides were prepared following the standard procedure⁷.

Preparation of $[\text{MoO}_2\text{L}_2]$ type complexes

To a filtered solution of $[\text{MoO}_2(\text{acac})_2]^8$ (0.33 g, 0.001 mol) in methanol (30 ml), a methanolic solution (20 ml) of the ligand (0.002 mol) was added slowly with constant stirring at room temperature. The solution immediately turned deep red from which a maroon coloured microcrystalline compound separated out.

The product was collected by filtration, washed with methanol and dried *in vacuo*; yield ~80%.

Preparation of $[\text{MoOL}_2\text{Cl}_2]$ type complexes

Method 1: To a stirred suspension of $[\text{MoO}_2\text{L}_2]$ (0.0005 mol) in methanol (20 ml), 2.5 ml of 1.8 M HCl in methanol was added dropwise over a period of 15 min. The suspension was stirred at room temperature for 5 hr when the colour of the reaction mixture turned deep red. The solution was evaporated to a small volume when a granular solid separated out. It was filtered, washed with chloroform and dried *in vacuo*; yield ~50%.

Method 2: To a stirred solution of the ligand (0.002 mol) in methanol (30 ml), $(\text{NH}_4)_2[\text{MoOCl}_5]^9$ (0.325 g, 0.001 mol) was added directly when the solution immediately turned deep red. The solution was stirred at room temperature for 3 hr and then the whole solution was evaporated to dryness *in vacuo*. The dark coloured residue was treated with dry acetonitrile (25 ml) and NH_4Cl was filtered off. The solution was concentrated to half its volume when a dark coloured compound separated out. It was filtered, washed with hot benzene and dried *in vacuo*; yield ~70%.

C, H and N were analysed with the help of a Perkin-Elmer 240 C, H, N-analyser. Mo was estimated gravimetrically using oxine as the reagent¹⁰. Sulphur was determined by peroxide fusion of the sample followed by gravimetric estimation as BaSO_4 . Analytical data of the compounds are given in Table 1.

IR spectra were recorded in KBr on a Perkin-Elmer 783 spectrophotometer. UV-visible spectra were recorded on a Pye-Unicam SP8-150- UV-vis spectrophotometer. Magnetic susceptibilities were

Table 1—Analytical Data of the Complexes

Complex/Formula	Found (Calc.), %					
	C	H	N	Mo	S	Cl
MoO ₂ (4-PhTSC) ₂	36.01	3.56	17.96	20.23	13.01	—
MoC ₁₄ H ₁₆ N ₆ O ₂ S ₂	(36.52)	(3.91)	(18.26)	(20.86)	(13.91)	—
MoO ₂ (<i>p</i> -CH ₃ -4PhTSC) ₂	38.95	4.21	16.97	19.90	12.89	—
MoC ₁₆ H ₂₀ N ₆ O ₂ S ₂	(39.34)	(4.50)	(17.21)	(19.67)	(13.11)	—
MoO ₂ (<i>p</i> -Cl4PhTSC) ₂	31.20	2.89	15.26	18.45	12.35	—
MoC ₁₄ H ₁₄ N ₆ O ₂ S ₂ Cl ₂	(31.75)	(3.02)	(15.88)	(18.14)	(12.10)	—
MoO ₂ (<i>m</i> -Cl4PhTSC) ₂	31.92	3.15	15.45	17.86	11.78	—
MoC ₁₄ H ₁₄ N ₆ O ₂ S ₂ Cl ₂	(31.75)	(3.02)	(15.88)	(18.14)	(12.10)	—
MoO ₂ (<i>p</i> -OCH ₃ 4PhTSC) ₂	36.19	4.01	15.94	18.20	12.15	—
MoC ₁₆ H ₂₀ N ₆ O ₄ S ₂	(36.92)	(4.23)	(16.15)	(18.46)	(12.30)	—
MoO ₂ (<i>m</i> -OCH ₃ 4PhTSC) ₂	36.25	4.35	15.91	18.12	12.08	—
MoC ₁₆ H ₂₀ N ₆ O ₄ S ₂	(36.92)	(4.23)	(16.15)	(18.46)	(12.30)	—
MoO(4-PhTSC) ₂ Cl ₂	32.26	3.42	15.96	18.14		14.31
MoC ₁₄ H ₁₆ N ₆ OS ₂ Cl ₂	(32.62)	(3.49)	(16.31)	(18.64)		(13.78)
MoO(<i>p</i> -CH ₃ 4PhTSC) ₂ Cl ₂	35.92	3.98	15.06	17.98		13.66
MoC ₁₆ H ₂₀ N ₆ OS ₂ Cl ₂	(35.35)	(4.05)	(15.46)	(17.67)		(13.07)
MoO(<i>p</i> -Cl4PhTSC) ₂ Cl ₂	29.21	2.69	13.92	16.01		23.98
MoC ₁₄ H ₁₄ N ₆ OS ₂ Cl ₄	(28.76)	(2.73)	(14.38)	(16.43)		(24.31)
MoO(<i>m</i> -Cl4PhTSC) ₂ Cl ₂	28.99	2.81	14.12	15.96		23.91
MoC ₁₄ H ₁₄ N ₆ OS ₂ Cl ₄	(28.76)	(2.73)	(14.38)	(16.43)		(24.31)
MoO(<i>p</i> -OCH ₃ 4PhTSC) ₂ Cl ₂	32.89	3.70	14.46	16.19		12.08
MoC ₁₆ H ₂₀ N ₆ O ₃ S ₂ Cl ₂	(33.39)	(3.82)	(14.60)	(16.69)		(12.34)
MoO(<i>m</i> -OCH ₃ 4PhTSC) ₂ Cl ₂	33.03	3.65	14.15	16.24		11.98
MoC ₁₆ H ₂₀ N ₆ O ₃ S ₂ Cl ₂	(33.39)	(3.82)	(14.60)	(16.69)		(12.34)

measured with a PAR vibrating magnetometer using Hg[Co(SCN)₄] as the calibrant. Conductivities were measured in acetonitrile solution with a Philips PR-9500 bridge.

Results and Discussion

[MoO₂L₂] complexes are air-stable and have poor solubilities in common organic solvents except acetonitrile, DMF and DMSO. They are non-electrolytes. [MoOL₂Cl₂] complexes are stable in the solid state having good solubility in common organic solvents. All the compounds were recrystallised from dichloromethane and their purities checked by TLC. Conductivity measurements show that they are non-electrolytes in acetonitrile. In the second method employed for the preparation of the [MoOL₂Cl₂], aerial oxidation took place. All the complexes are diamagnetic indicating the presence of *d* Mo(VI) state.

IR spectra

Pertinent IR bands are listed in Tables 2 and 3 along with their most probable assignments. In the IR spectra of complexes δ NH₂ is lowered by 30-40 cm⁻¹ indicating the involvement of the -NH₂ group in coordination. In the case of 4-aryl substituted thiosemicarbazides, the ligand band at ~860 cm⁻¹ is assignable to ν (C-S) which is absent in all their complexes^{12(a),(b),(d)}. Also, the ligand band at ~1300

cm⁻¹ arising from the mixing of ν (C=S), ν (CN) and δ NH₂^{12(c),(d)} modes suffers a negative shift of 10-50 cm⁻¹ in the complexes. These observations along with the nonelectrolytic nature of the complexes indicate that the thiosemicarbazides coordinate exclusively in the enol form via the deprotonated thiol sulphur and the nitrogen atom of the terminal -NH₂ group.

IR spectra of [MoO₂L₂] complexes in the range 895-975 cm⁻¹ display a two-band pattern characteristic of a *cis*-dioxomolybdenum (VI) centre. The positions of these two *cis* ν (Mo=O) bands in different complexes are found to vary from ligand to ligand indicating that the extent of localisation of electron cloud on Mo orbitals significantly influences the Mo=O bond. In all the [MoOL₂Cl₂] complexes a strong band observed in the region 935-960 cm⁻¹ is assignable to ν Mo=O^{11,14,15}. All these complexes also exhibit a medium broad band at ~330 cm⁻¹ with a weak shoulder at ~310 cm⁻¹ which may be assigned to ν (Mo-Cl)^{16,17} of the *cis*-dichloromolybdenum moiety.

It is known that the metal-oxygen double bond is mostly affected by a change in the donor characteristics of the ligand *trans* to itself¹⁸. Different values of the ν (Mo=O) observed in different complexes indicate that the electron density on the donor atom *trans* to the Mo=O bond changes from ligand to

Table 2—Some Characteristic Infrared and Electronic Spectral Data of the Complexes

Compound	$\delta(\text{NH}_2)$ in the corresponding ligand (cm^{-1})	$\delta(\text{NH}_2)$ in the complex (cm^{-1})	$\nu(\text{Mo}=\text{O})$ <i>cis</i> (cm^{-1})	$\lambda_{\text{max}}/\text{nm}(\epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1})$
$\text{MoO}_2(4\text{-PhTSC})_2$	1630	1610	920,960	425 (6175), 273 (20,182)
$\text{MoO}_2(p\text{-CH}_3\text{4PhTSC})_2$	1620	1590	940,970	450 (10,474), 270(28,848)
$\text{MoO}_2(p\text{-Cl4PhTSC})_2$	1630	1590	940,970	450 (10,559), 270 (27,386)
$\text{MoO}_2(m\text{-Cl4PhTSC})_2$	1620	1590	900,925	445 (11,889), 270(29,517)
$\text{MoO}_2(p\text{-OCH}_3\text{4PhTSC})_2$	1630	1600	895,935	465 (8333), 270(26,016)
$\text{MoO}_2(m\text{-OCH}_3\text{4PhTSC})_2$	1640	1600	950,975	440 (9067), 270(24,107)

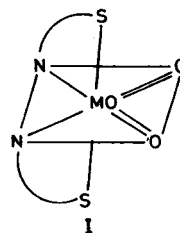
Table 3—Some Characteristic Infrared and Electronic Spectral Data of the Complexes

Compound	$\delta(\text{NH}_2)$ in the complex (cm^{-1})	$\nu(\text{Mo}=\text{O})$ (cm^{-1})	$\nu(\text{Mo}-\text{Cl})$ (cm^{-1})	$\lambda_{\text{max}}/\text{nm}(\epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1})$	
				Solution	Nujol
$\text{MoO}(4\text{-PhTSC})_2\text{Cl}_2$	1600	940(vs)	330,310(sh)	495 (6,221), 400 (4,797), 265 (24,935), 225 (23,636)	530,395
$\text{MoO}(p\text{-CH}_3\text{4PhTSC})_2\text{Cl}_2$	1590	955(vs)	330,310(sh)	495 (6,529), 395 (4,298), 250 (20,286), 235 (20,571), 225 (20,000)	530,400
$\text{MoO}(p\text{-Cl4PhTSC})_2\text{Cl}_2$	1590	938(vs)	335,320(sh)	495 (5,408), 400 (4,367), 270 (30,150), 237 (28,100), 228 (28,600)	525,400
$\text{MoO}(m\text{-Cl4PhTSC})_2\text{Cl}_2$	1585	960(vs)	320,305(sh)	490 (5,767), 395(4,977), 268 (25,710), 240 (23,226), 225 (25,194)	525,400
$\text{MoO}(p\text{-OCH}_3\text{4PhTSC})_2\text{Cl}_2$	1600	955(vs)	330,315(sh)	505 (6,553), 400 (4,251), 255 (31,423), 228(31,867)	535,400
$\text{MoO}(m\text{-OCH}_3\text{4PhTSC})_2\text{Cl}_2$	1610	955(vs)	335,315(sh)	495 (5,144), 400 (3,880), 265 (23,000), 225 (28,103)	530,405

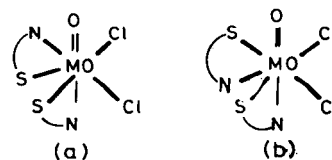
ligand. Such an observation suggests that none of the two chloride ions, ligated to the Mo-centre in $[\text{MoOL}_2\text{Cl}_2]$ occupies the position *trans* to the $\text{Mo}=\text{O}$ bond. Hence, either sulphur atom or the terminal nitrogen atom of the thiosemicarbazide chain should occupy the position *trans* to the $\text{Mo}=\text{O}$ bond. From the structural studies and electron density calculations on 4-phenyl thiosemicarbazide and the corresponding *p*-chloro derivative¹⁹ it has been found that due to the introduction of an electron releasing substituent in the *p*-position of the phenyl ring, significant electron localisation occurs on the nitrogen atom of the terminal $-\text{NH}_2$ group leaving the thiocarbonyl sulphur almost unaffected. Thus, the nitrogen atom of the $-\text{NH}_2$ group occupies the position *trans* to the $\text{Mo}=\text{O}$ bond.

Probable structures of the complexes

With the positioning of the two oxygens of the MoO_2^{2+} moiety *cis* to each other and the coordinated nitrogens *trans* to the two $\text{Mo}=\text{O}$ bonds, the two deprotonated thiol-sulphur atoms can take up positions only *trans* to each other. Hence, the $[\text{MoO}_2\text{L}_2]$ complexes may be represented by the octahedral structure (I).



For the seven coordinated $[\text{MoOL}_2\text{Cl}_2]$ complexes, three structures—capped octahedron, capped trigonal prism and pentagonal bipyramid—are possible. Of these three, the pentagonal bipyramid is much more common and has been reported by previous workers for related type of complexes^{1,16,20}. With two chlorides in *cis* positions and one of the two coordinated nitrogen atoms *trans* to the $\text{Mo}=\text{O}$ bond, two possible seven coordinated pentagonal bipyramid structures are IIa and IIb.



II

Electronic spectra

For the $[\text{MoO}_2\text{L}_2]$ complexes the absorption bands (Table 2) appearing below 300 nm probably arise from internal ligand transitions. The lowest energy band observed in the region 425-465 nm may be assigned to a ligand-to-metal charge transfer (LMCT) transition, due to the promotion of an electron from the highest occupied molecular orbital of S to the lowest unoccupied Mo orbital²¹.

In the electronic spectra of $[\text{MoOL}_2\text{Cl}_2]$ complexes (Table 3) the S→Mo LMCT band is located at ~530 nm. An interesting feature observed in the spectra of these complexes is the shift of the $\text{S}(\pi) \rightarrow \text{Mo}(d\pi)$ charge transfer band by about 30-40 nm towards higher energy in going from solid state ($\lambda_{\text{max}} \sim 530$ nm) to solution ($\lambda_{\text{max}} \sim 495$ nm) which may be ascribed to the change in conformation in the Mo site symmetry on going from solid state to solution^{1,11}. The higher energy band at ~400 nm in the $[\text{MoOL}_2\text{Cl}_2]$ is assignable to a chloride-to-metal charge transfer. This assignment receives support from the observation that this particular band completely disappears when both the chlorides are displaced from the coordination sphere of Mo by monodentate donors like imidazole, pyridine and acetate (*vide infra*).

Reactions of $[\text{MoOL}_2\text{Cl}_2]$ complexes with monodentate nucleophiles

Contrary to the general observation²², the reactions of the Mo(VI) complexes reported in this work are not very fast and we have been able to follow them spectrophotometrically. When $[\text{MoOL}_2\text{Cl}_2]$ is reacted with monodentate donors like pyridine, imidazole and acetate ion, the lowest energy band of the parent compound (~500 nm) is shifted to higher energy by 20-30 nm while the band (~400 nm) arising from chloride-to-molybdenum(VI) charge transfer is gradually diminished in intensity and finally vanishes completely on completion of the reactions. It has been noted that in the reaction of these complexes with imidazole, one of the chloride ions is replaced very quickly by one imidazole, while the second chloride is displaced quite slowly, which is confirmed by conductance measurements. The non-electrolyte $[\text{MoOL}_2\text{Cl}_2]$ becomes 1:1 electrolyte immediately after the addition of imidazole and the intensity of the band around 400 nm diminishes. When this band completely vanishes after 8-10 hr, conductance of the resultant complex

corresponds to a 1:2 electrolyte. This observation allows us to conclude that substitution of the chloride ions by imidazole ligand occurs in two distinct steps. The reactions with acetic acid and pyridine are comparatively slow. Detailed kinetic study of the reactions of these complexes with imidazole, pyridine, acetate, etc. will be reported later.

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