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COORDINATION CHEMISTRY OF SCHIFF BASE COMPLEXES OF MOLYBDENUM

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CONTENTS

ABBREVIATIONS

acacen	deprotonated anion of Schiff base derived from acetylacetone and ethylenediamine
acac	acetylacetonate ($CH_3COCHCOCH_3^-$)
aepy	aminoethylpyridine

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ANA	*o*-aminobenzoic acid
AP	*o*-aminophenol
ATP	*o*-aminothiophenol
bipy	2,2′-bipyridyl
bn	tetramethylenediamine
BHZ	benzoylhydrazide
BTH	2-benzothiazole carbohydrazide
CHZ	*o*-cresotic acid hydrazide
den	3-azapentane-1,5-diamine
DMF	*N*,*N*-dimethylformamide
DMSO	dimethyl sulphoxide
en	ethylenediamine
EA	2-aminoethanol
ETA	2-aminoethanethiol
FHZ	furan-2-carboxylic acid hydrazide
hap	*o*-hydroxyacetophenone
hbp	*o*-hydroxybenzophenone
hexen	hexamethylenediamine
hyd	2-hydroxy-1-naphthaldehyde
im	imidazole
INAHZ	isonicotinic acid hydrazide
Me	methyl
MPH	5-methylpyrazole-3-carbohydrazide
ophen	1,10-phenanthroline
ox	oxalate ($C_2O_4^{2-}$)
OABA	*o*-aminobenzyl alcohol
OHYMBA	*o*-hydroxy(methylbenzyl)amine
OYHBA	*o*-hydroxybenzylamine
phen	*o*-phenylenediamine
pn	propylenediamine
py	pyridine
pyd	pyridoxal
pyNO	pyridine-*N*-oxide
Ph	phenyl
sal	salicylaldehyde
salen	deprotonated anion of Schiff base derived from salicylaldehyde and ethylenediamine
salphen	deprotonated anion of Schiff base derived from salicylaldehyde and *o*-phenylenediamine
salpn	deprotonated anion of Schiff base derived from salicylaldehyde and propylenediamine
saltrien	deprotonated anion of Schiff base derived from salicylaldehyde and trimethylenediamine

SBDT	*S*-benzyldithiocarbazate
SMDT	*S*-methyldithiocarbazate
TCH	thiophene-2-carboxylic acid hydrazide
THF	tetrahydrofuran
TSC	thiosemicarbazide

A. INTRODUCTION

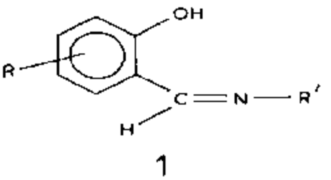
Metal complexes of Schiff bases represent an important and interesting class of coordination compound. Schiff bases containing polyfunctional groups have not only produced stable metal complexes of transition, non-transition, inner-transition and actinide metal ions, but these ligands and their metal complexes have also played a significant role in the domains of stereochemistry, structure, isomerism, magnetism, spectroscopy, kinetics and mechanism of reactions, reaction of coordinated ligands, model systems of biochemical interest, analytical chemistry, catalysis, stabilizers, polymers, pigments and dyes, photography, electro-optical display devices and agriculture. The present review describes the coordination chemistry of Schiff bases with molybdenum in various oxidation states. The enthusiasm shown in the coordination chemistry of molybdenum follows the discovery of molybdenum in a number of redox enzymes [1] such as aldehyde oxidase, sulphite oxidase, xanthine oxidase, nitrate reductase and nitrogenase, the last two enzymes being involved in the nitrogen cycle of plants. Work on molybdenum compounds has also been stimulated by the use of molybdenum compounds as corrosion inhibitors, lubricants and anti-wear additives. The previous reviews on molybdenum include the work published up to 1984 [2–5] but are limited to the general coordination chemistry of molybdenum, and no details have been reported on molybdenum Schiff base complexes.

The arrangement of material in this review is in the order of higher to lower oxidation states and within each oxidation state the increasing order of donor atoms is maintained.

B. MOLYBDENUM(VI) COMPLEXES

(i) Complexes of bidentate Schiff bases

The higher oxidation states of molybdenum are dominated by complexes containing the molybdenum oxo group. Most simple molybdenum(VI) coordination compounds contain the *cis*-dioxo MoO_2^{2+} cation. Zelentsov et al. [6] first reported the synthesis of dioxomolybdenum(VI) complexes of the ON donor Schiff base **1** ($R = H$; $R' = C_6H_5$) derived from salicylaldehyde and aniline. The complex was of the type MoO_2L_2 (where LH = monobasic bidentate Schiff base) and was prepared by the reaction of dioxomolybdenum(VI) dichloride with *N*-phenylsalicylaldimine. Yamanouchi and Yamada [7] prepared the dioxomolybdenum(VI) complexes of the type MoO_2L_2 with the ligands **1** (R = H, 3-OCH_3; R′ = CH_3, C_2H_5, *n*-C_3H_7, *n*-C_4H_9, C_6H_5, *m*-$CH_3C_6H_4$, *p*-$CH_3C_6H_4$, *p*-ClC_6H_4, *p*-BrC_6H_4, *p*-$C_6H_5C_6H_4$ and $CH_2C_6H_5$) by reacting the appropriate amine with $MoO_2(sal)_2$ or MoO_2(3-methoxysal)$_2$ in methanol. The same synthetic procedure was also adopted by Oh and Koo [8–10] to prepare

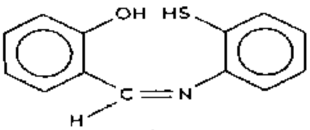


1

R = H, 3-CH_3, 3-OCH_3
R′ = CH_3, C_2H_5, *n*-C_3H_7, *n*-C_4H_9, C_6H_{10}, *n*-C_7H_{15}, C_6H_5, *m*-$CH_3C_6H_4$, *p*-$CH_3C_6H_4$, *p*-ClC_6H_4, *m*-ClC_6H_4, *p*-IC_6H_4, *p*-FC_6H_4, *p*-BrC_6H_4, *p*-$NO_2C_6H_4$, *p*-$OCH_3C_6H_4$, *p*-$C_2H_5C_6H_4$, 3,4-$Cl_2C_6H_3$, *p*-$C_6H_5C_6H_4$, $CH_2C_6H_5$

diamagnetic yellow to orange dioxomolybdenum(VI) complexes of Schiff bases **1** (R = H, 3-CH_3, 3-OCH_3; R′ = C_6H_5, *p*-FC_6H_4, *p*-ClC_6H_4, *m*-ClC_6H_4, *p*-IC_6H_4, *p*-$NO_2C_6H_4$, *p*-$OCH_3C_6H_4$, *p*-OHC_6H_4, *p*-$C_2H_5C_6H_4$, and 3,4-$Cl_2C_6H_3$). $MoO_2(acac)_2$ was also used as the starting material to synthesize MoO_2L_2 (where LH = **1**, R = H, R′ = *n*-C_7H_{15}, C_6H_5, *p*-BrC_6H_4, *p*-$CH_3C_6H_4$ and *p*-$NO_2C_6H_4$) [11], sparingly soluble in methanol, ethanol, chloroform and dichloromethane and fairly stable in the atmosphere at room temperature. The complexes exhibit two IR bands in the region 898–909 and 917–925 cm^{-1} due to the ν_{asym}(O=Mo=O) and ν_{sym}(O=Mo=O) stretches respectively. The IR data are indicative of the presence of a *cis*-MoO_2 group, in the complexes; in the case of a *trans*-MoO_2 group, only one band is expected. Dioxomolybdenum(VI) prefers to form the *cis*-MoO_2 structure for maximum utilization of the $Mo_{d\pi}$–$O_{p\pi}$ orbitals for chemical bonding. The single-crystal X-ray structure analysis of the dioxomolybdenum(VI) complex of **1** (R = H, R′ = *n*-C_3H_7) has confirmed the presence of a *cis*-MoO_2 six-coordinate, octahedral structure in the complex [12,13]. The complexes exhibit intense electronic absorption bands at around 25 800 and 32 400 cm^{-1} due to the ligand → metal charge transfer and intraligand transitions respectively.

Dioxomolybdenum(VI) complexes of the type *cis*-MoO_2L_2 have also been prepared with the Schiff bases derived from hydroxylamine and *o*-hydroxyacetophenone [14] or 2,4-dihydroxyvalerophenone [15]. Hill et al. [16] have described the synthesis of complexes of the type MoO_2L_2 with the Schiff bases **2** and **3** by the reaction of bis(acetylacetonato)dioxomolybdenum(VI) and the Schiff base in THF. The Schiff base **3** yields a tetrameric complex of the type $Mo_4O_{11}L_2$. The ligands **4** and **5** give complexes of the type *cis*-MoO_2(acac)L. Although the ligands are potential tridentates, they behave as ON donor bidentate monobasic and NS donor bidentate monobasic ligands in *cis*-MoO_2L_2 and as a monobasic ligand in $Mo_4O_{11}L_2$. The observation of the only signal due to the methine proton in the NMR spectra of dioxomolybdenum(VI) complexes of **2** and **4** confirms the presence of a *cis*-MoO_2 structure. The ligand **2** undergoes cyclization and is converted to **6** which is in reality coordinated to molybdenum(VI). The observation of a large shift in δNH in going from free ligand (7.9 ppm) to MoO_2L_2 (8.98 ppm) indicates the ON donor behaviour of **6** rather than coordination through oxygen and sulphur atoms. Although NMR spectra identified the complexes to have a *cis*-MoO_2 structure, NMR spectra cannot distinguish between the two possibilities **7** and **8**.



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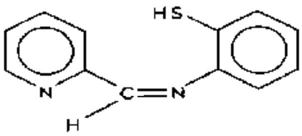

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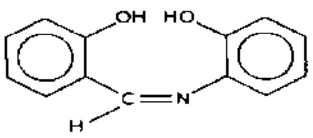

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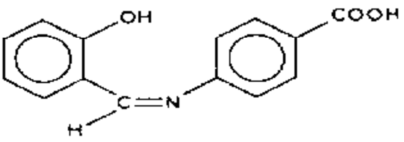

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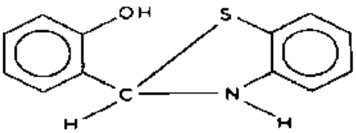

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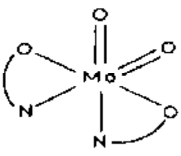

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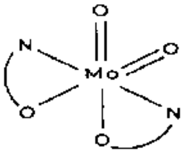

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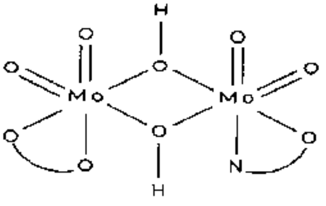
Bis(acetylacetonato)dioxomolybdenum(VI) reacts with aniline or benzidine in a 1 : 1 ratio in methanol [17] to give greenish yellow crystals of (acetylacetonato)dioxomolybdenum(VI)-μ-diol(acetylacetonatoanil)dioxomolybdenum(VI) monohydrate or (acetylacetonato)dioxomolybdenum(VI)-μ-diol(acetylacetonatobenzidine)dioxomolybdenum(VI) (**9**). The Schiff base formation between acetylacetone and benzidine occurs at only one of the two amine groups of benzidine and the Schiff bases behave as ON donor bidentate ligands. The addition of benzidine or aniline to the reaction medium (methanol) raises the pH of the solution and this favours the formation of hydroxo bridges.



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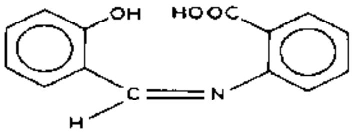
Topich [18] has reported the synthesis of a heterochelate complex $MoO_2(acac)L$ (where LH = Schiff base **10**) by the reaction of $MoO_2(acac)_2$ and **10** in ethanol or ethyl acetate [18]. Only one acetylacetone molecule was displaced under the reaction conditions and the second acetylacetone was not displaced even when the metal-to-ligand ratio was greater than unity. IR data indicate that **10** coordinates through the oxygen atom of the carboxylic acid group and nitrogen atom of azomethine group and not through the phenolic oxygen atom.



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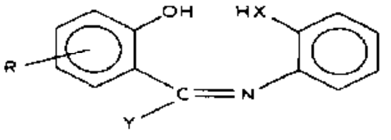
N-Phenylacetylacetoneimine (L) reacts with *cis*-MoO_2Cl_2 in ethyl acetate to give *cis*-$MoO_2Cl_2L_2$ in which L is coordinated through the oxygen atom. The single-crystal X-ray analysis confirms its six-coordinate and octahedral structure [19].

(ii) Complexes of tridentate Schiff bases

Extensive studies have been reported on the synthesis and characterization of dioxomolybdenum(VI) complexes with tridentate Schiff bases. The complexes of the types MoO_2L_2 and $MoO_2L \cdot A$ (where LH_2 = tridentate Schiff base; A = monodentate ligand) have been prepared with the Schiff bases **11** and **12** starting from MoO_2Cl_2, MoO_2Cl_2, $MoO_2(acac)_2$, $MoO_2(sal)_2$, Na_2MoO_4 or $(NH_4)_2MoO$ [18,20–30].



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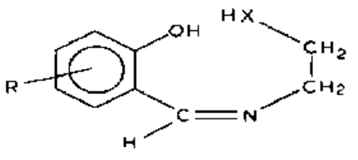

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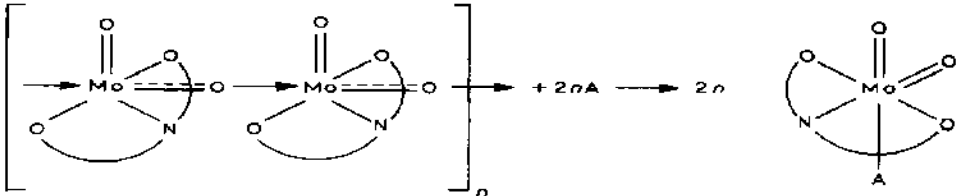
R = H, 5-CH_3, 3-C_4H_9, 5-C_4H_9,
5,6-C_4H_4, 5-NO_2, 5-Br, 5-Cl,
5-OCH_3
X = O, S
Y = H, CH_3

R = H, 5-Cl, 5-Br, 5-NO_2, 5-CH_3,
5-OCH_3, 3-C_4H_9, 5-C_4H_9, 5,6-C_4H_4
X = O, S

Depending on the molybdenum precursor, ligand and reaction conditions, the complexes synthesized are of the type MoO_2L, $MoO_2L \cdot H_2O$ or $MoO_2L \cdot C_2H_5OH$. The complexes $MoO_2L \cdot H_2O$ and $MoO_2L \cdot C_2H_5OH$ are yellow in colour and are monomers. $MoO_2L \cdot C_2H_5OH$ is converted to brown MoO_2L on heating at 100 °C. The $MoO_2L \cdot A$ complexes exhibit two ν(O=Mo=O) vibrations in the region 910–950 (ν_{asym}) and 890–925 (ν_{sym}) cm^{-1} indicating the presence of a *cis*-MoO_2 structure. However, the MoO_2L complexes exhibit only one ν(Mo=O) at 930 cm^{-1} and a strong band at 800 cm^{-1} due to $\cdots$ Mo=O $\cdots$ Mo=O $\cdots$ interaction [21] and IR data suggest the presence of an oligomeric structure (**13**) for MoO_2L. Goh and Lim [25] have suggested a dimetallic structure (**15**) involving phenolic oxygen bridges for the dioxomolybdenum(VI) complex with the Schiff base **12** (R = H; X = S). Although the mass spectrum of the complex shows that the complex can be easily split into two identical units, the authors have not given proof of the dimeric structure from the molecular ion peak in the mass spectrum. The oligomers **13** react with unidentate ligands (A) such as DMSO, DMF etc. by breaking the oligomeric chains, and as a result monomeric complexes (**14**) are formed [21]. In **14** the tridentate Schiff bases occupy the meridional coordination sites about the $[MoO_2]^{2+}$ unit and A occupies the labile coordination site *trans* to an oxo oxygen. The $MoO_2L \cdot A$ complexes undergo substitution reactions [21,22] of the type

$$MoO_2L \cdot A + A' \rightarrow MoO_2L \cdot A' + A \qquad (1)$$

where A and A′ are different unidentate ligands, and a large number of complexes with A′ = methanol, DMSO, DMF, Ph_2SO, pyridine, γ-picoline,



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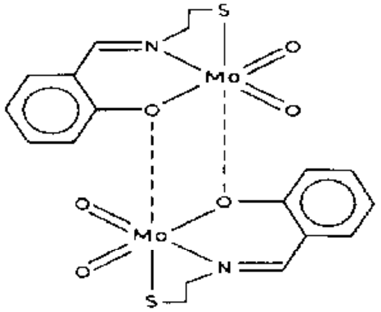

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pyridine-*N*-oxide, methylamine, aniline, triphenylphosphine, triphenylphosphine oxide (tppo), hexamethylphosphonic acid amide, imidazole, substituted imidazoles, acetaldehyde, benzaldehyde and *p*-anisaldehyde have been synthesized by ligand displacement reactions. The order of A′ binding is as follows: $CH_3OH < C_6H_5OH <$ *p*-anisaldehyde < DMF < γ-picoline < DMSO < imidazoles < pyridine-*N*-oxide. The $MoO_2L \cdot A'$ complexes also exhibit two *cis*-MoO_2 stretches in the region 880–950 cm^{-1} and the species with nitrogen donors exhibit $\nu(O{=}Mo{=}O)$ at lower energies than those with oxygen donors. NMR and thermogravimetric data indicate weak bonding of A or A′. The $MoO_2L \cdot A'$ complexes lose A′ on heating and are converted to MoO_2L in a single endothermic step [21]. The temperature at which the loss of A′ occurs depends on the nature of A′, e.g. DMSO, 190 °C; pyridine, 170 °C; DMF, 120 °C. The MoO_2L, $MoO_2L \cdot A$ and $MoO_2L \cdot A'$ complexes are non-electrolytes and diamagnetic as expected for the $4d^0$ system. The electronic spectra of the complexes are dominated by a strong band in the region 22400–28900 cm^{-1} ($\epsilon = 2500$–$15000\ l\ mol^{-1}\ cm^{-1}$) due to a ligand → metal charge transfer transition (LMCT). Topich and Lyon [23] have observed that the energy of this transition shifts to higher energy as the R group in **11** (X = O) becomes more electron withdrawing. The ability of molybdenum to bind to sulphur donors is of great importance in the chemistry of molybdenum. It is this affinity for sulphur which fixes molybdenum in biological systems. Experiments on many more relatively small molecules containing the Mo–S linkage are needed to gain more

TABLE 1

Spectroscopic and electrochemical data for dioxomolybdenum(VI) complexes of tridentate Schiff bases

Complex	ν(Mo=O) (cm^{-1})	E_{pc}[a] (V(SCE))	$\nu_{\max} \times 10^3$ (cm^{-1})[b] (ϵ (l mol^{-1} cm^{-1}))	Ref.
MoO_2(sal–AP)	931, 910,	−1.24,		29
	937, 909,	−1.08,		
	815	−1.50,		21
		−1.55		72
MoO_2(sal–AP)·MeOH	928, 903			21
MoO_2(sal–AP)·EtOH	931, 903			21
MoO_2(sal–AP)·tppo	928, 901			21
MoO_2(sal–AP)·PhCHO	927, 902			21
MoO_2(sal–AP)·DMF	924, 900			21
MoO_2(sal–AP)·DMSO	924, 892			21
	943, 910	−1.09	23.7 (3890)	18
MoO_2(sal–AP)·*p*-anisal	921, 905			21
MoO_2(sal–AP)·Ph_2SO	918, 898			21
MoO_2(sal–AP)·pyNO	912, 888			21
MoO_2(sal–AP)·$MeNH_2$	920, 892			21
MoO_2(sal–AP)·py	918, 897			21
MoO_2(sal–AP)·pic	918, 893	−1.085,		
		−1.510		21
MoO_2(sal–AP)·im	917, 901			21
MoO_2(sal–AP)·aniline	915, 890			21
MoO_2(sal–AP)·PPh_3	930, 905			21
MoO_2(5-Clsal–AP)	912, 888	−1.17		29
MoO_2(5-Brsal–AP)	920, 896	−1.17		29
MoO_2(5-Brsal–AP)·DMSO	963, 920	−1.07	23.1 (3981)	18
MoO_2(5-NO_2sal–AP)	945, 923,	−1.11		
	896			29
MoO_2(5-NO_2sal–AP)·DMSO	945, 923	−0.97	23.6 (5248)	18
MoO_2(5-OMesal–AP)	937, 910	−1.25		29
MoO_2(5-OMesal–AP)·DMSO	974, 937	−1.14	22.5 (4266)	18
MoO_2(5-Mesal–AP)	935, 905,			
	815			21
MoO_2(5-Mesal–AP)·DMSO	924, 903			21
MoO_2(5-Mesal–AP)·aniline	915, 885			21
MoO_2(3-t-Butsal–AP)·H_2O	922, 900			21
MoO_2(3-t-Butsal–AP)·pic	918, 896			21
MoO_2(5-t-Butsal–AP)	943, 830	−1.160		21
MoO_2(5-t-Butsal–AP)·DMF	930, 901	−1.165		21
MoO_2(5-t-Butsal–AP)·im	916, 896			21
MoO_2(hyd–AP)	938, 830	−1.040,		
		−1.425		21
MoO_2(hyd–AP)·MeOH	932, 908			21
MoO_2(hyd–AP)·DMSO	910, 890			21
MoO_2(hyd–AP)·aniline	922, 892			21

TABLE 1 (continued)

Complex	ν(Mo=O) (cm^{-1})	E_{pc} [a] (V(SCE))	$\nu_{max} \times 10^3$ (cm^{-1}) [b] (ϵ (l mol^{-1} cm^{-1}))	Ref.
MoO_2(sal–EA)	940, 929, 890	−1.49		29
	900, 815	−1.40		21
MoO_2(sal–EA)·H_2O	940, 929	−1.27	29.1 (2570)	18
MoO_2(sal–EA)·pic	932, 912, 890			21
MoO_2(5-Clsal–EA)	912	−1.48		29
	940, 912	−1.24	28.2 (2570)	18
MoO_2(5-Brsal–EA)	912	−1.48		29
	938, 912	−1.24	28.2 (2570)	18
MoO_2(5-NO_2sal–EA)	915	−1.25		29
MoO_2(5-NO_2sal–EA)·1/2H_2O	915	−1.06	29.7 (16218)	18
MoO_2(5-Mesal–EA)·DMSO	930, 920, 902			21
MoO_2(5-Mesal–EA)·pic	929, 920, 900			21
MoO_2(5-t-Busal–EA)·H_2O	930, 920	−1.490		21
MoO_2(5-t-Busal–EA)·pic	924, 918, 903			21
MoO_2(5-OMesal–EA)	924, 886	−1.53		29
MoO_2(5-OMesal–EA)·H_2O	924	−1.28	26.7 (2691)	18
MoO_2(sal–ATP)	925	−1.11	26.7 (6918), 21.7sh	23
	922, 892	−1.17, −1.445		21
MoO_2(sal–ATP)·tppo	928, 899			21
MoO_2(sal–ATP)·py	921, 890			21
MoO_2(5-Clsal–ATP)	943, 934	−1.06	26.5 (5623), 22.1sh	23
MoO_2(5-Brsal–ATP)	940, 926	−1.05	26.5 (6457), 21.9sh	23
MoO_2(5-OMesal–ATP)	912	−1.13	31.3 (15136), 26.3 (5240), 23.3sh 21.5sh	23
MoO_2(sal–ETA)	947, 902	−1.25	28.9 (4467)	23
MoO_2(5-Clsal–ATP)	918	−1.22	28.7 (4266)	23
MoO_2(5-Brsal–ATP)	922, 914	−1.22	30.3sh, 28.6 (3388)	23
MoO_2(5-OMesal–ATP)	920, 906, 887	−1.27	28.9 (4570)	23
MoO_2(sal–ANA)·acac	941, 914	0.88	27.8 (4266)	18
MoO_2(5-Clsal–ANA)·H_2O	946	0.84	26.9 (3715)	18
MoO_2(5-Brsal–ANA)	946	0.84	26.9 (3162)	18
MoO_2(5-OMesal–ANA)·H_2O	940	−0.92	25.2 (2818)	18

TABLE 1 (continued)

Complex	ν(Mo=O) ($\mathrm{cm^{-1}}$)	E_{pc} [a] (V(SCE))	$\nu_{max} \times 10^3$ ($\mathrm{cm^{-1}}$) [b] (ϵ ($\mathrm{l\ mol^{-1}\ cm^{-1}}$))	Ref.
$\mathrm{MoO_2}$(sal–MPH)·MeOH	940, 910		25.0 (1750)	48
$\mathrm{MoO_2}$(sal–BTH)·MeOH	935, 910		23.5 (8400)	46
$\mathrm{MoO_2}$(hyd–BTH)·MeOH	940, 910		22.2 (8950)	46
$\mathrm{MoO_2}$(sal–SBDT)·MeOH	940, 915		25.7 (7400)	49
$\mathrm{MoO_2}$(sal–SMDT)·MeOH	940, 905		24.4 (8200)	49
$\mathrm{MoO_2}$(sal–TSC)·MeOH	925, 890		27.8 (2700)	49
$\mathrm{MoO_2}$(hyd–SBDT)·MeOH	940, 890		23.8 (8100)	49
$\mathrm{MoO_2}$(hyd–SMDT)·MeOH	955, 910		25.0 (6100)	49
$\mathrm{MoO_2}$(hyd–TSC)·MeOH	925, 880		26.7 (6300)	49
$\mathrm{MoO_2}$(hap–SBDT)·MeOH	925, 880		25.7 (7750)	49
$\mathrm{MoO_2}$(hap–SMDT)·MeOH	930, 885		26.0 (8350)	49
$\mathrm{MoO_2}$(hbp–SBDT)·MeOH	945, 915		25.5 (6800)	49
$\mathrm{MoO_2}$(hbp–SMDT)·MeOH	945, 905		26.3 (5650)	49
$\mathrm{MoO_2}$(pyd–TSC)·MeOH	935, 895		26.7 (4950)	49
$\mathrm{MoO_2}$(sal–CHZ)·$\mathrm{H_2O}$	925, 890		25.3 (4500)	40
$\mathrm{MoO_2}$(sal–CHZ)·THF	925, 905		25.5 (4150)	40
$\mathrm{MoO_2}$(sal–CHZ)·py	915, 900		24.8 (3850)	40
$\mathrm{MoO_2}$(hyd–CHZ)·$\mathrm{H_2O}$	940, 910		23.3 (3520)	40
$\mathrm{MoO_2}$(hyd–CHZ)·THF	935, 910		23.6 (4750)	40
$\mathrm{MoO_2}$(hyd–CHZ)·py	920, 910		24.1 (3510)	40
$\mathrm{MoO_2}$(hap–CHZ)·$\mathrm{H_2O}$	930, 900		25.6 (4200)	40
$\mathrm{MoO_2}$(sal–TCH)·$\mathrm{H_2O}$	940, 910		25.0 (4550)	40
$\mathrm{MoO_2}$(sal–TCH)·THF	930, 905		25.3 (3800)	40
$\mathrm{MoO_2}$(sal–TCH)·py	935, 910		24.7 (3990)	40
$\mathrm{MoO_2}$(hyd–TCH)·$\mathrm{H_2O}$	940, 895		23.8 (3900)	40
$\mathrm{MoO_2}$(hyd–TCH)·THF	930, 895		24.4 (4100)	40
$\mathrm{MoO_2}$(hyd–TCH)·py	920, 900		25.0 (4450)	40
$\mathrm{MoO_2}$(sal–FHZ)·$\mathrm{H_2O}$	940, 900		24.1 (3400)	40
$\mathrm{MoO_2}$(sal–FHZ)·THF	920, 890		25.0 (4550)	40
$\mathrm{MoO_2}$(sal–SHZ)·$\mathrm{H_2O}$	945, 920, 910			35
$\mathrm{MoO_2}$(sal–SHZ)·THF	940, 915, 900			35
$\mathrm{MoO_2}$(sal–SHZ)·en	925, 900			41
$\mathrm{MoO_2}$(sal–SHZ)·tn	925, 900			41
$\mathrm{MoO_2}$(sal–SHZ)·bn	930, 905			41
$\mathrm{MoO_2}$(sal–SHZ)·bipy	910, 880			41
$\mathrm{MoO_2}$(sal–SHZ)·ophen	910, 880			41
$\mathrm{MoO_2}$(5-$\mathrm{NO_2}$sal–SHZ)·$\mathrm{H_2O}$	945, 925, 910			35
$\mathrm{MoO_2}$(5-$\mathrm{NO_2}$sal–SHZ)·THF	945, 925, 915			35
$\mathrm{MoO_2}$(hyd–SHZ)·$\mathrm{H_2O}$	940, 910			35
$\mathrm{MoO_2}$(hyd–SHZ)·THF	935, 915, 900			35

TABLE 1 (continued)

Complex	ν(Mo=O) (cm^{-1})	$E_{pc}{}^{a}$ (V(SCE))	$\nu_{max} \times 10^3$ (cm^{-1}) ^{b} (ϵ ($l\ mol^{-1}\ cm^{-1}$))	Ref.
MoO_2(sal–BHZ)·H_2O	940, 915,. 905			36
MoO_2(sal–BHZ)·en	900, 880			41
MoO_2(sal–BHZ)·bipy	905, 880			41
MoO_2(sal–BHZ)·ophen	905, 880			41
MoO_2(sal–BHZ)·phen	930, 905			41
MoO_2(sal–BHZ)·aepy	930, 905			41
MoO_2(sal–INAHZ)·H_2O	922, 898			38
MoO_2(sal–INAHZ)·DMF	932, 908			38
MoO_2(sal–INAHZ)·PyNO	926, 904			38
MoO_2(sal–INAHZ)·THF	928, 912			38
MoO_2(sal–INAHZ)·DMSO	910, 894			38
MoO_2(hyd–INAHZ)·H_2O	928, 902			38
MoO_2(hyd–INAHZ)·DMF	924, 898			38
MoO_2(hyd–INAHZ)·PyNO	920, 898			38
MoO_2(hyd–INAHZ)·THF	930, 908			38
MoO_2(hyd–INAHZ)·DMSO	918, 900			38
MoO_2(hap–INAHZ)·H_2O	934, 908			38
MoO_2(hap–INAHZ)·DMF	930, 904			38
MoO_2(hap–INAHZ)·PyNO	926, 900			38
MoO_2(hap–INAHZ)·THF	932, 908			38
MoO_2(hap–INAHZ)·DMSO	930, 906			38
MoO_2(hap–BHZ)·H_2O	870, 846			38
MoO_2(hap–BHZ)·DMF	906, 894			38
MoO_2(hap–BHZ)·PyNO	908, 896			38
MoO_2(hap–BHZ)·THF	878, 848			38
MoO_2(hap–BHZ)·DMSO	908, 898			38
MoO_2(hyd–FHZ)·H_2O	940, 910		22.3 (3550)	40
MoO_2(hyd–FHZ)·THF	935, 910		24.4 (3950)	40
MoO_2(5-Clsal–FHZ)·H_2O	940, 915		24.7 (4500)	40
MoO_2(5-Brsal–CHZ)·H_2O	950, 915		24.7 (3800)	40
MoO_2(5-NO_2sal–CHZ)·H_2O	935, 910		25.0 (2400)	40
MoO_2(3-OEtsal–CHZ)·H_2O	940, 900		24.7 (2200)	40
MoO_2(sal–CHZ)·en	900, 880			41
MoO_2(sal–CHZ)·tn	915, 895			41
MoO_2(sal–CHZ)·bn	900, 880			41
MoO_2(sal–CHZ)·bipy	905, 880			41
MoO_2(sal–CHZ)·ophen	905, 880			41
MoO_2(sal–OHYBA)·MeOH	925, 880		27.4 (3880)	50
MoO_2(sal–OHYMBA)·MeOH	910, 880		25.8 (3500)	50
MoO_2(hyd–OHYBA)·MeOH	930, 895		25.6 (3500)	50
MoO_2(hyd–OHYMBA)·MeOH	920, 885		25.7 (4000)	50
MoO_2(hap–OHYMBA)·MeOH	920, 880		25.4 (3400)	50
MoO_2(pyd–AP)·H_2O	920, 890		25.0 (5000)	50
MoO_2(pyd–OABA)·H_2O	935, 895		22.7 (3600)	50

TABLE 1 (continued)

Complex	ν(Mo=O) (cm^{-1})	E_{pc} [a] (V(SCE))	$\nu_{max} \times 10^3$ (cm^{-1}) [b] (ϵ (l mol^{-1} cm^{-1}))	Ref.
MoO_2(pyd–ANA)·H_2O	940, 900		24.9 (4350)	50
MoO_2(sal–OHYBA)·bipy	905, 875		24.4 (3650)	50
MoO_2(sal–OABA)	930		25.9 (4200)	51
MoO_2(sal–OABA)·DMSO	920, 890		25.2 (3850)	51
MoO_2(sal–OABA)·py	920, 900		25.6 (3850)	51
MoO_2(hyd–OABA)	915		26.0 (4260)	51
MoO_2(hyd–OABA)·DMSO	920, 890		27.4 (3880)	51
MoO_2(hyd–OABA)·py	920, 900		25.0 (3900)	51

[a] In DMF or DMSO solution. [b] In DMF, DMSO or CH_3OH solution.

insight into the gross mechanism of enzyme activity.

The cyclic voltammetric behaviour of the dioxomolybdenum(VI) complexes of **11** and **12** has been reported independently by Topich and coworker [18,23,26] and Rajan and Chakravorty [21,27]. Irreversible behaviour has been observed for all the *cis*-dioxomolybdenum(VI) complexes. The cathodic reduction potentials (E_{pc}) of some complexes are given in Table 1. The plot of E_{pc} vs. Hammet parameter, σ_p, indicates that a linear relationship exists between E_{pc} and σ_p for each series of *cis*-dioxomolybdenum(VI) complexes. However, since the peak potential is irreversible such a correlation should be treated with caution. The parameter Δ has been calculated using the relation [23]

$$\Delta = (E_{pc})_{comp} - (E_{pc})_{stand}[MoO_2(\text{sal-AP})]$$

A positive Δ value indicates that the dioxomolybdenum(VI) complex is easier to reduce than the standard. However, a negative Δ value signifies the more difficult reducible nature of the dioxomolybdenum(VI) complex in comparison with the standard. E_{pc} is dependent on (i) the substitution on the salicylaldehyde moiety, (ii) the substitution of a sulphur atom for an oxygen atom in the ligand, and (iii) the degree of ligand π electron delocalization. An electron-withdrawing group withdraws the electron density away from the molybdenum and forces the molybdenum to be more easily reduced. The E_{pc} values are in the order $CH_3OH < H < Cl = Br < NO_2$. The substitution of a sulphur atom in place of an oxygen atom in the ligand lowers the charge on the molybdenum and as a result the molybdenum complexes with sulphur donor ligands are more easily reduced than the molybdenum complexes with oxygen donor ligands. Molybdenum(VI) complexes having extended π delocalized systems, e.g. MoO_2(5-R-sal-ATP), are as expected, easier to reduce than the molybdenum(VI) complexes containing limited π delocalized systems.

Reactions of the dioxomolybdenum(VI) complexes with the Schiff bases **11** and **12** ($X = S$; $R = H$, 5-Cl, 5-Br, 5-OCH_3) with $PEtPh_2$ in DMF lead to the reduction of the dioxomolybdenum(VI) complexes to the oxomolybdenum(IV) complexes, MoOL. A kinetic study of the oxygen transfer reaction

$$MoO_2L + PEtPh_2 \rightarrow MoOL + OPEtPh_2 \tag{2}$$

has been reported by Topich and Lyon [28,29,31]. The reactions are first order with respect to both $PEtPh_2$ and the molybdenum(VI) complex and the rate law follows the equation

$$-d[MoO_2L]/dt = +d[MoOL]/dt = k_1[MoO_2L][PEtPh_2] \tag{3}$$

The reaction proceeds directly from the reactants to products without the formation of any reaction intermediate and no consecutive reaction takes place. The rate of appearance of MoOL is equal to the rate of disappearance of MoO_2L and this indicates that $k_1 \gg k_2$. The electronic spectral studies show that the molybdenum(VI) dimer, $Mo_2O_3L_{2n}$, is not formed via the reaction

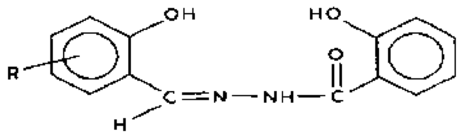
$$MoO_2L_n + MoOL_n \rightarrow Mo_2O_3L_{2n} \tag{4}$$

Although the R substituents are not directly bonded to the metal, their electronic effect is transmitted to the Mo-oxo core through the ligand. k_1 is in the order $Br > Cl > H > OCH_3$. The electron-donating group removes the electron density from the $[MoO_2]^{2+}$ moiety and makes the oxo oxygen atoms the most electrophilic in the series. However, the electron-donating ability of the OCH_3 group makes the oxo-oxygen the least electrophilic of the series. A comparison of the activation enthalpies of these complexes with those of $MoO_2(S_2CNEt_2)_2$ and MoO_2(ethyl-L-cysteinate)$_2$ indicates that the rate of reaction for $MoO_2(S_2CNEt_2)_2$ is two to three orders of magnitude greater than that for MoO_2L and the reactivity of dioxomolybdenum(VI) complexes with $PEtPh_2$ decreases in the order ONO < ONS < NNSS < SSSS (where ONO, ONS, NNSS and SSSS are the donor atoms of the ligands) [29]. A molybdenum(VI) complex with a Schiff base having a sulphur donor atom, an extended π electron system and an effective electron-withdrawing substituent is more effective in oxidizing $PEtPh_2$. A linear dependence exists between the Hammet σ_p parameter for the substituents R in the ligand and $\log(k_{1R}/k_{1H})$, and between k_1 and the cathodic reduction potential (E_{pc}) within each series of complexes.

^{95}Mo NMR spectra of dioxomolybdenum(VI) complexes of Schiff bases **11** ($R = H$; $X = S$, O) and **12** ($R = H$, 5-Cl, 5-Br, 5-NO_2, 5-OCH_3; $X = O$) have been reported [32,33]. The chemical shifts referenced to 2 M Na_2MoO_4 are in the range 26–543 ppm with linewidths ranging from 156 to 1170 Hz. The replacement of an oxygen atom of the Schiff base by a sulphur atom causes deshielding of the ^{95}Mo NMR signal from 34 to 231 ppm [34]. Least shielding occurs in the case of the electron-donating methoxy substituent and as a result the resonance occurs in methoxy-substituted dioxomolybdenum(VI) Schiff base complexes significantly downfield compared with R = H.

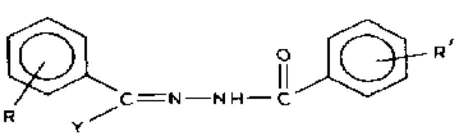
The Schiff bases **11** have been used for the quantitative extraction of molybdenum(VI) from chloride and perchlorate media at pH 4.5 [34(a)]. The reaction of MoO_2(sal-AP) with catechol, naphthalene-2,3-diol or 3,5-di-*tert*-butylcatechol in chloroform leads to the synthesis of six-coordinate heterochelate complexes of the type MoO(sal-AP)(AA) (where AA = bidentate ligand). The complexes exhibit only one ν(Mo=O) band at 930–939 cm^{-1}. The crystal structure of the MoO(sal-AP)(naphthalene-2,3-diol) indicates the distorted octahedral environment about molybdenum(VI) and the Mo=O distance is 1.685 Å. The nitrogen atom of the Schiff base and the terminal oxo ligand occupy the opposite vertices of the octahedron and the four anionic oxygen donors of the bidentate and tridentate ligands are in the equatorial plane. The complexes undergo reversible one-electron reduction at −0.5 to −0.7 V followed by irreversible one-electron reduction at 1.6–1.9 V. The heterochelates exhibit the molecular ion peak in the mass spectra and are monomers. The ^{95}Mo NMR chemical shift of MoO(sal-AP) (naphthalene-2,3-diol) is +385 ppm [34(b)]. The reaction of molybdic acid in 30% H_2O_2 with an acetone solution of **11** (R = H, X = O) at 0 °C leads to the synthesis of a peroxo compound, $MoO(O_2)L$ (LH_2 = **11**) [34(c)].

The Schiff base ligands **16** and **17** produced from salicylaldehyde, substituted salicylaldehyde and salicylhydrazide or benzoylhydrazide are tridentate and form complexes of the form $MoO_2L \cdot X$ (where X = H_2O, THF) [35,36]. The aquo complexes are obtained by reacting a dilute sulphuric acid solution of $(NH_4)_2MoO_4$ with a dilute sodium hydroxide solution of the Schiff base. This is the first report of the synthesis of dioxomolybdenum(VI) complexes of Schiff bases in aqueous medium. For the synthesis of dioxomolybdenum(VI) complexes of Schiff bases a non-aqueous medium is commonly used and starting materials such as MoO_2Cl_2, $MoO_2(acac)_2$ and $MoO_2(sal)_2$ are used, as the Schiff bases are prone to hydrolysis. In the case of Schiff bases which are less susceptible to hydrolysis, the synthesis of



16

R = H, 5-Cl, 5-Br, 5-NO_2, 3-OCH_3, 3-OC_2H_5, 3,5-Cl_2, 5,6-C_4H_4

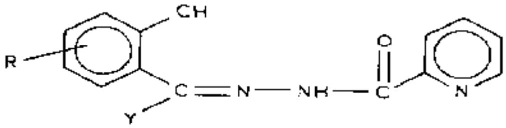


17

R = H, 5-Cl, 5-Br, 5-NO_2, 3-OCH_3, 3-OC_2H_5, 5,6-C_4H_4
R′ = H, 2-NH_2, 4-NH_2
Y = H, CH_3

dioxomolybdenum(VI) complexes can be carried out in aqueous medium. The labile H_2O molecule in aquo complexes $MoO_2L \cdot H_2O$ is easily replaced by THF, resulting in complexes of the type $MoO_2L \cdot THF$ [35,36]. The complexes are orange to yellow in colour, non-electrolytes, monomers and diamagnetic and contain the *cis*-dioxo arrangement. The THF adducts are less stable than the aquo adducts. The complete removal of THF takes place on heating the complexes at 120 °C. Dutta and Pal [17] have also prepared the dioxomolybdenum(VI) complexes with the ligand **17** ($R = H$, 5,6-C_4H_4; $R' = Y = H$) by reacting $MoO_2(acac)_2$ and the ligand in methanol. It is interesting that the aquo adduct and not the methanol adduct is formed under the reaction conditions. However, the crystal structure of the complex $MoO_2L \cdot C_2H_5OH$ (LH_2 = **17**; $R = R' = Y = H$) prepared from Na_2MoO_4 and LH_2 in ethanol confirms the presence of an ethanol adduct [37]. The $MoO_2L \cdot H_2O$ (LH_2 = **17**; $R = R' = Y = H$) exhibits an LMCT band at 23 800 cm^{-1} ($\epsilon = 3750$ l mol^{-1} cm^{-1}). Prabhakaran and Nair [38] have reported the synthesis of dioxomolybdenum(VI) complexes of the Schiff base **17** ($R = R' = H$; $Y = CH_3$) of the type $MoO_2L \cdot X$ ($X = H_2O$, DMF, THF, pyridine-*N*-oxide). The separation between $\nu_{sym}(O{=}Mo{=}O)$ and $\nu_{asym}(O{=}Mo{=}O)$, $\Delta\nu$, is in the order H_2O > DMF > pyridine-*N*-oxide > THF > DMSO and is consistent with the donor power of X. The thermal stability of the complexes is in the order H_2O > pyridine-*N*-oxide > DMSO > DMF > THF.

Complexes of the type *cis*-MoO_2ClL (where LH_2 = **17**; $R = H$; $R' = H$, 2-NH_2, 4-NH_2; $Y = H$) have been prepared by the reaction of diammonium oxopentachloromolybdate(V) with the Schiff base [39]. The complexes exhibit a strong band at 33 000 cm^{-1} due to the LMCT transition. Similar monomeric, non-electrolyte and diamagnetic *cis*-dioxomolybdenum(VI) complexes, $MoO_2L \cdot X$ ($X = H_2O$, THF, DMF, DMSO, pyridine-*N*-oxide; LH_2 = **18**) have been reported [36]. $\Delta\nu$ is dependent on X and is in the order H_2O > DMF > pyridine-*N*-oxide > THF > DMSO and is consistent with the donor strength of X. $\Delta\nu$ also varies as L changes and is in the order **18** ($R = H$; $Y = CH_3$) > **18** ($R = 5,6\text{-}C_4H_4$; $Y = H$) > **18** ($R = Y = H$) > **17** ($R = H$; $Y = CH_3$). The above order has been explained in terms of the

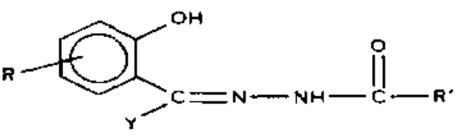


18

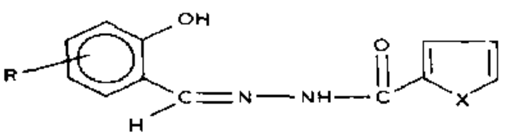
$R = H$, 5,6-C_6H_4
$Y = H$, CH_3

basicity of the ligands and ligand repulsion.

Still other hydrazide Schiff base complexes of dioxomolybdenum(VI) have been synthesized and studied by IR, electronic spectra and molecular weight measurements. The dioxomolybdenum(VI) complexes formed by the tridentate ligands **19** (R = H, 5,6-C_4H_4; R′ = *o*-(OH)$CH_3C_6H_3$; Y = H, CH_3) and **20** (R = H, 5-Cl, 5-Br, 5-NO_2, 5-OC_2H_5, 5,6-C_4H_4; X = O, S) are of the type $MoO_2L \cdot X$ (X = H_2O, pyridine, THF) [40] and are yellow or orange in colour, monomers, non-electrolytes and diamagnetic. The complexes are stable at room temperature but lose mass at 110–150 °C owing to loss of X. The presence of two ν(O=Mo=O) bands in the IR spectra of the complexes in the region 915–940 and 890–910 cm^{-1} indicates their *cis*-$[MoO_2]^{2+}$ structure. $\Delta\nu$ values are in the order H_2O > THF > pyridine and the order is explained on the basis of the donor strength of the X molecule. The electronic spectra of the complexes are dominated by a strong LMCT band at 22250–25600 cm^{-1} (ϵ = 2200–4750 l mol^{-1} cm^{-1}) [40].



19

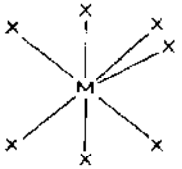


20

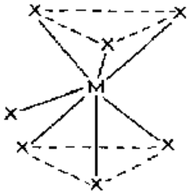
R = H, 5,6-C_4H_4
R′ = *o*-(OH)$CH_3C_6H_3$
Y = H, CH_3

R = H, 5-Cl, 5-Br, 5-NO_2, 5-OC_2H_5
X = O, S

The nitrogen donor bidentate ligands such as ethylenediamine, trimethylenediamine, tetramethylenediamine, *o*-phenanthroline, 2,2′-bipyridine, *o*-phenylenediamine, 2-aminoethylpyridine react with the labile six-coordinate $MoO_2L \cdot H_2O$ (where LH_2 = **16**, R = H; LH_2 = **17**, R = R′ = Y = H and LH_2 = **19**, R = Y = H, R′ = *o*-(OH)$CH_3C_6H_3$) and as a result the seven-coordinate heterochelates [MoO_2L(AA)] are formed [41–43] containing the *cis*-[MoO_2] structure. The lability of $MoO_2L \cdot H_2O$ has been attributed to the long Mo–OH bond distance. The replacement of the aquo molecule in $MoO_2L \cdot H_2O$ by the bidentate ligands is accompanied by an increase in coordination number and by a shift of the ν_{sym}(O=Mo=O) and ν_{asym}(O=Mo=O) stretches to lower energy. These shifts are in accordance with an increase in electron density at molybdenum leading to an increase in repulsive forces with the non-bonding electrons of the Mo–O bond. $\Delta\nu$ values are in the order en ≃ tn ≃ bn < bipy ≃ ophen ≃ aepy ≃ phen and are in line with the weaker donor character of the aliphatic amines compared with the aromatic amines. Three different structures are possible for seven-coordinate complexes: (i) capped octahedron (**21**), (ii) capped trigonal prism (**22**), and (iii) pentagonal bipyramid (**23**). The pentagonal bipyramid is the most regular arrangement of these three structures. The capped octahedron and capped trigonal prism structures are usually observed in coordination compounds containing less rigid unidentate ligands, e.g. **21** in $MoBr_4(PPhMe_2)_3$ [44] and **22** in $[Mo(NCC_5H_{11})_7](PF_6)_2$ [45]. The heterochelates $MoO_2L(AA)$ contain one bidentate ligand and one tridentate ligand which are sterically more rigid in comparison with the unidentate ligands and which can coordinate involving only *cis* positions. A pentagonal bipyramidal structure (**23**) has been suggested for complexes in preference to **21** and **22** [41–43].



21



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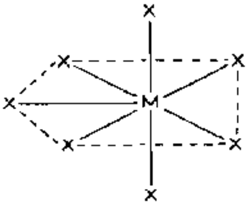
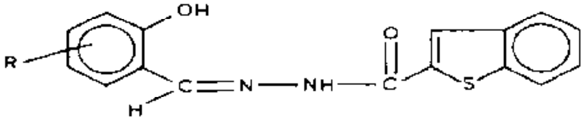


23

The Schiff base **24** (R = H, 5,6-C_4H_4) reacts with $MoO_2(acac)_2$ in methanol and produces diamagnetic *cis*-$MoO_2L \cdot CH_3OH$ (LH_2 = **24**) [46].

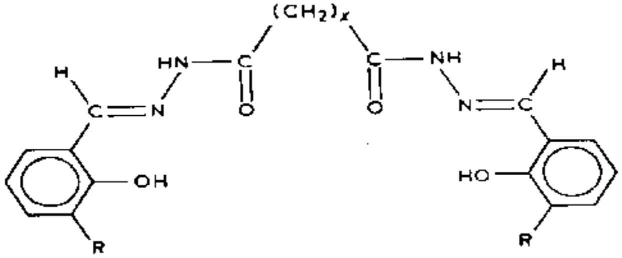


24

R = H, 5,6-C_4H_4

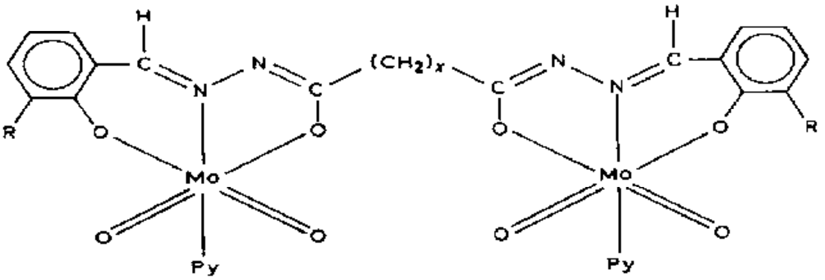
The presence of a new band at 975–1000 cm^{-1} due to the ν(C–O) stretch indicates methanol coordination to the molybdenum. The complexes exhibit three electronic absorption bands in DMF at 25975–25980 cm^{-1} (ϵ = 12000–15900 l mol^{-1} cm^{-1}), 27150–28980 cm^{-1} (ϵ = 15300–17400 l mol^{-1} cm^{-1}) and 22200–23535 cm^{-1} (ϵ = 8400–8950 l mol^{-1} cm^{-1}) due to $n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$, and the LMCT respectively.

Molybdenum(VI) complexes of the hexadentate ligand **25** derived from the condensation of salicylaldehyde or 3-methoxysalicylaldehyde and various dihydrazides have been reported. The complexes are dimetallic and have the composition $[MoO_2LPy]_2$ (where LH = **25**). Two pyridine molecules are lost in the temperature range 150–200 °C. A six-coordinate dimeric octahedral structure **26** has been suggested for the complexes [47].



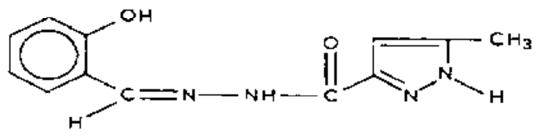
25

R = H, OCH_3
x = 0, 1, 2, 4, 8



26

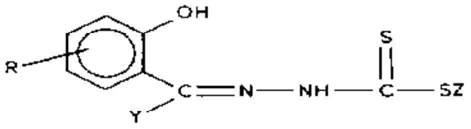
Dioxomolybdenum(VI) complexes of the form $MoO_2L \cdot CH_3OH$ have also been reported with the Schiff base **27** derived from salicylaldehyde and 5-methylpyrazole-3-carbohydrazide [48]. ^1H NMR data indicate the dibasic tridentate nature of the Schiff base. The appearance of a methyl proton signal at 3.12 ppm confirms the methanol coordination. The ligand exhibits three electronic absorption bands in DMF at 30760 cm^{-1} (ϵ = 16880 l



27

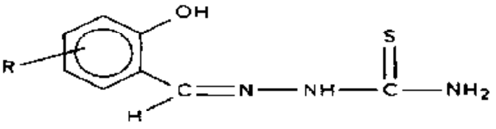
mol^{-1} cm^{-1}), 33 800 cm^{-1} ($\epsilon = 21\,000$ l mol^{-1} cm^{-1}) and 35 100 cm^{-1} ($\epsilon = 20\,370$ l mol^{-1} cm^{-1}) due to the transitions n → π*, π → π* and hydrogen bonding and association respectively. The latter band is absent in the spectrum of the complex, indicating the breaking of the hydrogen bond and association and consequent coordination of the ligand to the molybdenum atom. The bands due to n → π* and π → π* transitions undergo a negative shift to 29 400 cm^{-1} ($\epsilon = 17\,170$ l mol^{-1} cm^{-1}) and 32 250 cm^{-1} ($\epsilon = 19\,200$ l mol^{-1} cm^{-1}) respectively, suggesting the coordination of the Schiff base to the molybdenum atom. The complex exhibits a non-ligand band at 25 000 cm^{-1} ($\epsilon = 1750$ l mol^{-1} cm^{-1}) which is assigned to LMCT transition [48].

Bis(acetylacetonato)dioxomolybdenum(VI) undergoes a ligand exchange reaction with the Schiff bases **28–30** (R = H, 5,6-C_4H_4; Y = H, CH_3; Z = CH_3, C_6H_5) in methanol and complexes of the type $MoO_2L \cdot CH_3OH$ (where LH_2 is a Schiff base) are formed [49]. ^{1}H NMR spectra together with IR data confirm the tridentate dibasic ONS donor nature of the Schiff bases. The Schiff base **30** exhibits the ν(C=N)(ring) and ν(C–O) (alcoholic, pyridoxal) bands at 1595 and 1200 cm^{-1} respectively and these bands remain unaffected in the complex, indicating their non-involvement in coordination.



28

R = H, 5,6-C_4H_4
Y = H, CH_3, C_6H_5
Z = CH_3, C_6H_5



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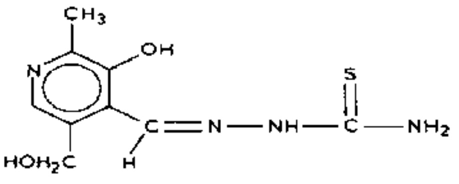
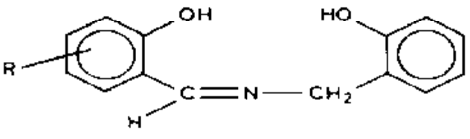
R = H, 5,6-C_4H_4



30

Dioxomolybdenum(VI) complexes of the Schiff bases **31–34** (R = H, 5,6-C_4H_4; Y = H, CH_3; R′ = *o*-C_6H_4OH, *o*-$C_6H_4CH_2OH$, $C_{10}H_6COOH$) have been reported by Syamal and Maurya [50,51]. Depending upon the reaction medium, complexes of the type $MoO_2L \cdot CH_3OH$ (LH_2 = **31** and **32**), $MoO_2L \cdot H_2O$ (LH_2 = **34**) [50] and MoO_2L (LH_2 = **33**) [51] are formed. Although the Schiff bases **31** and **33** are isomeric in nature, they form



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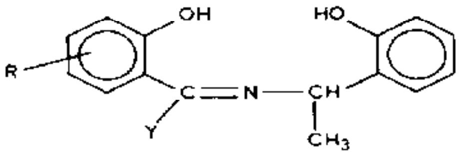
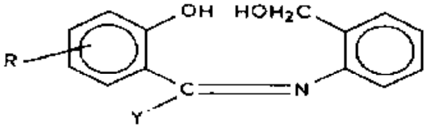


32

R = H, 5,6-C_4H_4

R = H, 5,6-C_4H_4
Y = H, CH_3



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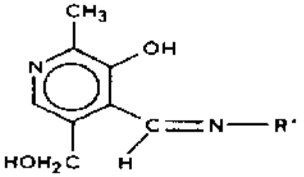


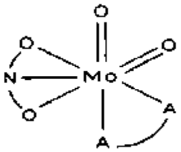
34

R = H, 5,6-C_4H_4
Y = H, CH_3

R′ = *o*-C_6H_4OH, *o*-$C_6H_4CH_2OH$,
$C_{10}H_6COOH$

complexes of different stoichiometry. This may be due to the change in position of the CH_2 group. The absence of a ν(O–H) band in the spectra of the complexes of the Schiff bases **33** supports this formulation. All other complexes show a broad band at ca. 3400 cm^{-1} which confirms the presence of coordinated water or methanol. The water and methanol adducts lose water and methanol at 120 °C and 165 °C respectively, indicating lower thermal stability for the aquo adduct than for the methanol adduct. The complex $MoO_2L \cdot CH_3OH$ (where LH_2 = **31**, R = H) reacts with 2,2′-bipyridine in methanol to produce a seven-coordinate heterochelate, $MoO_2L \cdot$ bipy. The MoO_2L complexes exhibit only one band due to ν(M=O) at ca. 930 cm^{-1} and a strong band at ca. 800 cm^{-1} due to $\cdots Mo{=}O \cdots Mo{=}O \cdots$ interaction while all other complexes exhibit two bands in the region

875–900 and 905–940 cm^{-1} due to the ν_{asym}(O=Mo=O) and ν_{sym}(O=Mo=O) bands respectively. The bands due to ν(C=N)(ring) and ν(C–O)(alcoholic, pyridoxal) of the tridentate binding Schiff base **34** remain unaffected in the complexes, indicating non-participation of the alcoholic oxygen and ring nitrogen atoms of the pyridoxal moiety in coordination. The electronic spectra exhibit an LMCT band in the region 22700–27400 cm^{-1} (ϵ = 3400–5000 l mol^{-1} cm^{-1}). On the basis of the spectral evidence an oligomeric structure **13** for MoO_2L, **14** for $MoO_2L \cdot H_2O$ and $MoO_2L \cdot CH_3OH$, and a seven-coordinate pentagonal bipyramidal structure **35** containing the *cis*-MoO_2 moiety has been suggested for $MoO_2L \cdot AA$ (where AA = bipy) [50,51].

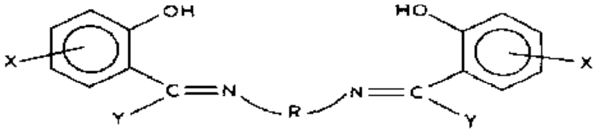


35

The reaction of $MoO_2(acac)_2$ with the Schiff base derived from salicylaldehyde and valine or histidine in a water–methanol (1 : 1 v/v) medium leads to the synthesis of complexes of the type MoO_2L (where LH_2 = Schiff base). The complexes have a six-coordinate oligomeric structure. The Schiff base derived from pyrrole-2-aldehyde and valine gives a monomeric six-coordinate complex, $MoO_2L \cdot H_2O$. The Schiff base derived from pyridine-2-aldehyde and valine produces a monomeric heterochelate complex, $MoO_2L(acac)$. The Schiff base derived from salicylaldehyde and l-histidinol gives a monomeric complex having the formula MoO_2LCl. The MoO_2L complexes are converted to monomeric complexes, $MoO_2L \cdot S$ when dissolved in a solvent (S). The MoO_2 complexes racemize when dissolved in pyridine. The histidinol complex MoO_2LCl however, is optically more stable than MoO_2L and this stability is due to the replacement of the electron-withdrawing carboxylate group at the α-CH position with the hydroxymethylene group. The MoO_2L complexes act as catalysts in the sulphoxidation of organic sulphides and in the epoxidation of 2-phenyl-*E*-cinnamyl alcohol by *tert*-butyl hydroperoxide [51(a)].

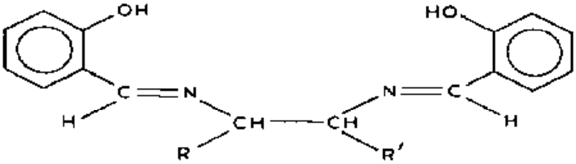
(iii) Complexes of tetradentate Schiff bases

Dioxomolybdenum(VI) complexes of the type *cis*-MoO_2L (where LH_2 is a tetradentate Schiff base **36**) have been synthesized as orange yellow crystals by reacting $MoO_2(acac)_2$ and the Schiff base in methanol [52], THF [16] or THF–methanol (1 : 1 v/v) [24,30]. Dilworth et al. [53] have reported complexes *cis*-MoO_2L with **36** (R = $(CH_2)_2$, $(CH_2)_3$; X = H, 3-OCH_3; Y = H) prepared by reacting the molybdenum(V) complex, $MoOCl_3(THF)_2$ and the Schiff base in dry ethanol in the presence of oxygen. The complexes were also prepared by heating the corresponding oxomolybdenum(V) complex, MoOClL in dry ethanol in the presence of oxygen [53]. These were also synthesized starting from $MoO_2(acac)_2$ [54] and ammonium molybdate [54(a)]. The complexes are insoluble in water, ethanol, ether, *n*-hexane and carbon tetrachloride but are sparingly soluble in methanol, acetone, chloroform, benzene and DMF. Although the complexes are quite stable in air, they are not stable in solution [53]. As is evident from Table 2 the complexes exhibit an intense LMCT band in the region 22700–24500 cm^{-1} (ϵ = 1585–2884 l mol^{-1} cm^{-1}). The complex MoO_2(3-OCH_3–saltrien) exhibits a band at 13500 cm^{-1} (ϵ = 1220 l mol^{-1} cm^{-1}) in DMF and contains the *cis*-[MoO_2] unit [54]. The position of this band at such low energy seems to be unusual for a dioxomolybdenum(VI) complex, and a reinvestigation of the electronic spectral work seems to be in order. The complexes, on refluxing in solution, yield orange to red species which do not exhibit the two IR bands of the *cis*-MoO_2 moiety and are believed to be polymeric species containing Mo^V–O–Mo^V chains [54].



36

X = H, 3-OCH_3
Y = H, CH_3
R = $(CH_2)_2$, $(CH_2)_3$, $(CH_2)_4$, $(CH_2)_6$, $CH(CH_3)CH_2$, $(CH_2)_2NH(CH_2)_2$, *o*-C_6H_4, *o*-$C_6H_3CH_3$, *o*-$C_6H_3(CH_3)_2$, 1,2-cyclohexane, 3-azopentane.



37

R = H, CH_3, C_6H_5
R′ = H, CH_3, C_6H_5

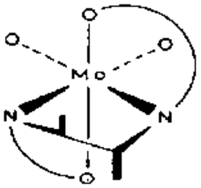
TABLE 2

IR and electronic spectral data for dioxomolybdenum(VI) complexes of tetradentate Schiff bases

Complex	ν(O=Mo=O) (cm^{-1})	Medium ^{a}	$\nu_{max} \times 10^3$ (cm^{-1}) (ϵ (l mol^{-1} cm^{-1}))	Ref.
MoO_2(salen)	920, 885	CH_2Cl_2	24.2 (2884)	52
	915, 885	DMF	24.3 (1580)	53
MoO_2(saltrien)	910, 870	DMF	24.3 (2750)	52
	910, 870	Refl.	23.2, 21.6	16
	905, 865	DMF	24.4 (1430)	53
MoO_2(3-OMesalen)	903, 875	DMF	23.5 (1585)	52
	908, 875	DMF	23.5 (1190), 22.7	53
	925, 903, 875	Refl.	23.3	16
MoO_2(3-OMesaltrien)	914, 882	DMF	23.5 (1585)	52
	912, 880	DMF	22.8, 13.5 (1220)	53
	910, 885	Refl.	23.3	16
MoO_2(salbn)	907, 875	DMF	24.8 (2400)	52
MoO_2(3-OMesalbn)	918, 890	DMF	23.5 (1259)	52
MoO_2(hapen)	910, 885	DMF	25.0 (2884)	52
	910, 885	Refl.	24.6, 22.9	16
MoO_2(salphen)	915, 904, 870	Refl.	23.2, 20.0	16
MoO_2(salhexen)	922, 895	Refl.	24.0	16
MoO_2(acac–BHZ)	940, 900		17	

^{a} Reflectance (Refl.)

The complexes *cis*-MoO_2L can have either structure **38** or **39** in which L adopts a planar or non-planar configuration respectively. The NMR spectra of the complexes of **36** (X = H, 3-OCH_3; Y = H, CH_3, R = $(CH_2)_2$, $(CH_2)_3$) exhibit two signals (Table 3) each for methine and methylene protons [16,52]. The two methine hydrogen atoms of salen are equivalent in **38** and not equivalent in **39**. Thus the complexes with structure **38** which possess a twofold axis would show only one singlet for azomethine protons and for **39** two signals are expected. The NMR data of the molybdenum(VI) complexes with **36** (X = H, 3-OCH_3; Y = H, CH_3; R = $(CH_2)_2$, $(CH_2)_3$) indicate the presence of structure **39** where L has assumed a twisted non-planar geome-



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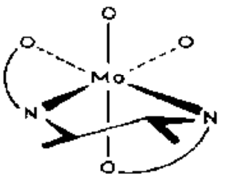

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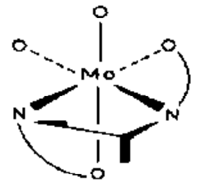
TABLE 3

^{1}H NMR spectral data for dioxomolybdenum(VI) complexes of tetradentate Schiff bases in DMSO-d_6

Complex	δN=CH	δPh	δN–CH$_2$	δOCH$_3$/CH$_3$	Ref.
MoO_2(salen)	8.91, 8.74	6.62–7.73	4.35, 4.23		52
	8.93, 8.78	6.65–7.79	4.38, 4.28		24
MoO_2(3-Omesalen)	8.91, 8.74	6.50–7.33	4.30, 4.20	3.84, 3.66	52
	8.92, 8.68	6.40–7.40	4.30, 4.20	3.87, 3.78	16
MoO_2(3-COOHsalen)	8.91, 8.74	6.69–8.01	4.29, 4.01		24
MoO_2(saltrien)	8.75, 8.47	6.40–7.65	3.65–4.43		52
	8.20, 8.49	6.50–7.50	3.40–4.20		16
MoO_2(3-OMesaltrien)	8.77, 8.50	6.40–7.50		3.82, 3.50	52
	8.55, 8.88	6.90–7.30	3.60, 3.78	3.80, 3.48	16
MoO_2(hapen)	9.37, 9.59	6.50–7.50	3.85, 3.60		16
MoO_2(salhexen)	8.35	6.50–7.30	3.50–1.19		16
MoO_2(salphen)	8.57	6.40–7.40			16
	8.01	7.10–7.40			24
MoO_2(salphenMe-3)	8.70	6.70–7.60		2.13	16

try. The NMR features of these complexes are comparable with the NMR spectrum of [Co(acac)(salen)] (two singlets for the N=CH protons) in which salen is present in a non-planar configuration [55]. The complexes with the ligand **36** (X = Y = H; R = $(CH_2)_6$, *o*-C_6H_4, *o*-$C_6H_3CH_3$-4) exhibit only one singlet for methine protons, indicating the presence of a planar configuration (**38**) of quadridentate ligands. Owing to the presence of the *o*-phenylene backbone, these ligands seem to be incapable of coordination in a non-planar twisted arrangement.

The *cis*-MoO_2 group has been confirmed by the single-crystal X-ray study of dioxomolybdenum(VI) complex of **37** (R = CH_3, R′ = H) [54]. The coordination around the molybdenum is distorted octahedral and the coordinated Schiff base is bent to form a *cis*-MoO_2 structure **40** with the analogous donor atoms (O and O, N and N) of the ligand mutually *cis*. The two Mo–O(oxide) bond distances are 1.71 Å corresponding to a bond order of two. Other bond distances are as follows: Mo–O(ligand), 2.112; Mo–O(ligand), 2.133; Mo–N, 2.133; Mo–N, 2.304 Å. The distorted structure arises from the strain produced by the five-membered chelate ring in the folded quadridentate ligand and from the steric requirements of the $[MoO_2]^{2+}$ group. The diamine chelate ring is in a δ conformation and the six-membered chelate ring (Mo–O–C–C–C–N–) is in a twisted δ conformation. The dioxomolybdenum(VI) complex of a flexible quadridentate ligand propane-1,3-diylbis(salicylideneimine) is of the type (propane-1,3-diylbis(salicylideneiminato)dioxomolybdenum(VI) and also displays a *cis* bent configuration from X-ray analysis of the complex [56].



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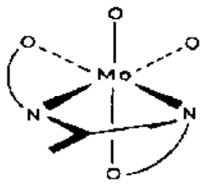

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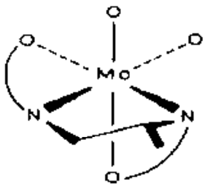

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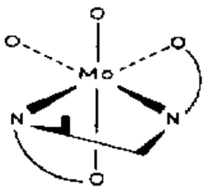

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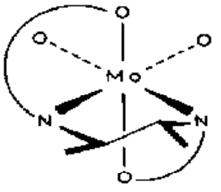
Although only one structure (**39**) and its diastereoisomer are possible for MoO_2(salen), the introduction of one methyl group (**37**, $R = CH_3$, $R' = H$) in the ethylenediamine chelate ring increases the number of possible isomers to two (**41** and **42**) with their diastereoisomers (**40** and **43**). In the solid state only one (**40**) of the possible isomers has been observed. In DMSO solution the complex of **37** ($R = CH_3$, $R' = H$) exhibits four doublets in the region 0.83–1.51 ppm and eight azomethine resonances which have been attributed to four isomers (**40–43**) of the type *cis-β*. The ^{13}C NMR spectrum of the complex of **37** ($R = CH_3$, $R' = H$) confirms the presence of four different methyl groups, and eight azomethine signals occur due to magnetically different azomethine carbon atoms. The circular dichroism (CD) spectrum of the complex of **37** ($R = CH_3$, $R' = H$) consists of a positive–negative doublet at 330 nm due to the exciton splitting of the $\pi \rightarrow \pi^*$ transition of the azomethine groups, and of a Cotton effect at 430 nm. The chirality of the chromophores is opposite and the two chromophores are arranged to form a right-handed helix in the isomers **40** and **43**. This corresponds to a δ conformation of the diamine chelate ring and a Λ configuration of the molecule. The isomers **41** and **42** correspond to the λ-equatorial conformation of the diamine, and these diastereoisomers are observed in solution since the equilibrium $\lambda \rightleftharpoons \delta$ is operative in solution. This isomerization to diastereoisomers is quite fast (although slow on the NMR scale) and attempts to separate the four isomers by chromatography were unsuccessful [54].

The synthesis of the MoO_2L complex with **36** ($R =$ 1,2-cyclohexane, $X = H$, $Y = H$) has been reported by Gulloti et al. [54]. The ^{13}C NMR spectrum of this complex exhibits three azomethine resonances and three signals due to the two CH groups of diamine and is consistent with the



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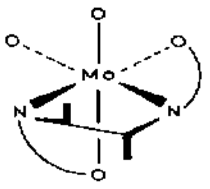
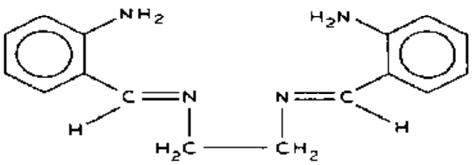


45

presence of a mixture of two isomers (**39** and **44**) in solution. **39** has a Δ configuration and **44** a Λ configuration. The complex of **37** ($R = CH_3$, $R' = CH_3$) exhibits four doublets in the ^1H NMR spectrum and there are two isomers (**39** and **45**) with non-equivalent methyl groups in solution. The isomer ratio (**39**:**45**) is 5:1. However, the complex with **37** (R = Ph, R′ = Ph) exhibits only one azomethine resonance in the ^1H NMR spectrum and has the structure **44** in solution. The relative stability of the isomers is dictated by the substituents at the carbon atoms of the diamine moiety. The complexes with **36** (R = 1,2-cyclohexane) and **37** (R = Ph, R′ = Ph) have symmetric structures (**38** or **44**) while the methyl substituents in **37** ($R = CH_3$, $R' = CH_3$) give rise to a complex having structure **39** or **45**. The mechanism of isomerization in these complexes has not been elucidated and a further study seems to be in order. A twist mechanism [57] involving the flexibility of the ligands seems more likely in these complexes [54].

The complexes MoO_2L (where LH_2 = **46**) have been reported by Kudryavstev and Savich [58], but the spectral data are not available. Dutta and Pal [17] have reported a complex of the type *cis*-MoO_2L with the Schiff base **47**. The complex was prepared by the reaction of $MoO_2(acac)_2$ with benzoylhydrazide in methanol leading to the removal of acetylacetonato groups and the reaction of *cis*-dioxo cores. The authors have suggested the structure **48** for the complex. However, in view of the non-planar twisted



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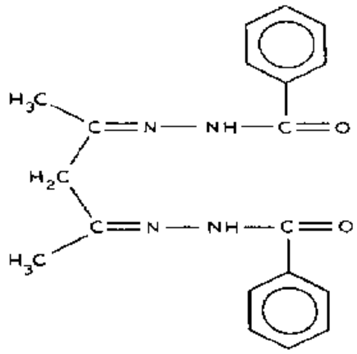
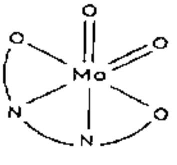


47

configuration of salen in *cis*-MoO_2 (salen), a more plausible structure for the complex is **49**. The NMR spectrum of the complex should be recorded in order to verify its structure.



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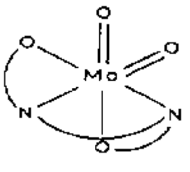
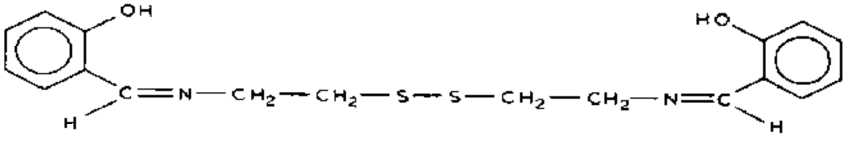


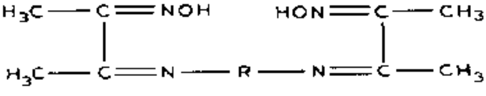
49

Goh and Lim [25] have synthesized dioxomolybdenum(VI) complex with the Schiff base **50** by reacting $MoO_2(acac)_2$ and LH_2 in methanol. The pale yellow complex is remarkably stable in bases and mineral acids. It does not form any adduct with DMSO, pyridine and hexamethylphosphoric acid triamide as the tetradentate ligand has rendered the molybdenum(VI) coordinatively saturated.



50

Reaction between $MoCl_6$ and tetradentate Schiff base **51** leads to the formation of MoO_2L ($LH_2 = $ **51**) in which L is coordinated through two azomethine nitrogen and two deprotonated oxygen atoms [59]. IR and ^1H NMR studies suggest the presence of the *cis*-MoO_2 group and an octahedral structure. The reaction of MoO_2Cl_2 and the Schiff base (**52** and **53**) in absolute alcohol produces complexes of the types MoO_2L, $MoO_3(LH)$ (where LH = **52**). When $MoO_3(LH)$ is refluxed in 2,2-dimethoxypropane $[MoO_2L]_2O$ is formed [60].



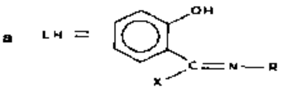
51

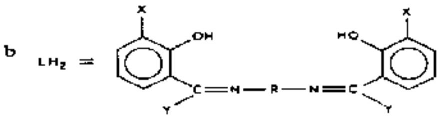
$R = (CH_2)_2, (CH_2)_3, (CH_2)_4, (CH_2)_5, (CH_2)_6$

TABLE 4

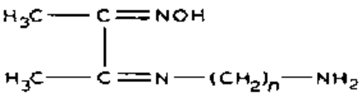
Magnetic and spectroscopic data for molybdenum(V) complexes of bidentate Schiff bases

Compound type			μ_{eff} (BM)	ν(Mo=O) (cm^{-1})	g_{iso} [c]	$A_{iso} \times 10^{-4}$ (cm^{-1})	$\nu_{max} \times 10^3$ (cm^{-1}) [d]
X	Y	R					
$MoOCl_3(LH)_2$ [a] [61]							
H		CH_2CH_3	1.69	950	1.945	46	13.6, 22.5
H		$(CH_2)_3CH_3$	1.61	958	1.940	49	14.0, 22.5
H		C_6H_{11}	1.76	959	1.937	50	14.3, 19.8sh, 23.3
H		o-$CH_3C_6H_4$	1.70	970	1.938	48	13.6, 22.5
H		o-ClC_6H_4	1.68	963	1.941	51	13.2, 19.6sh, 23.1
H		o-OHC_6H_4	1.61	948	1.947	50	13.4, 18.9sh, 22.5
H		$(CH_2)_2OH$	1.61	960	1.941	50	14.3, 19.8sh, 22.8
CH_3		$(CH_2)_2OH$	1.50	978	1.940	47	13.2, 20.0sh, 23.8
$MoOCl_3(LH_2)$ [b] [62]							
H	H	$(CH_2)_2$	1.63	960	1.940	51	13.3, 19.3sh, 24.2
H	H	$(CH_2)_3$	1.66	958	1.946	45	13.4, 19.6sh, 24.3
H	H	$(CH_2)_6$	1.64	958	1.945, 1.936	46	13.5, 19.8sh, 24.0
H	H	o-C_6H_4	1.60	967	1.936	47	13.0, 17.4sh, 24.0
H	H	o-C_6H_3Me-4	1.71	964	1.942, 1.937	50	13.1, 17.2sh, 23.0
H	H	o-$C_6H_2Me_2$-4,5	1.72	972	1.937	44	13.1, 17.1sh, 23.2
MeO	H	$(CH_2)_2$	1.64	945	1.945	48	14.1, 19.0sh, 25.0
MeO	H	$(CH_2)_3$	1.69	948			14.2, 18.5sh, 22.2
MeO	H	o-C_6H_4	1.65	955	1.940	49	13.0, 18.6, 23.0
H	Me	$(CH_2)_2$	1.70	960	1.934	46	13.5, 20.0sh, 24.4
H	Me	$(CH_2)_3$	1.69	973	1.935	50	13.5, 23.8
H	Me	$CH(Me)CH_2$	1.63	960	1.941, 1.935	53	13.2, 20.0sh, 25.0



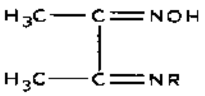


[c] In CH_2Cl_2 solution. [d] Reflectance.



52

$n = 0–6$



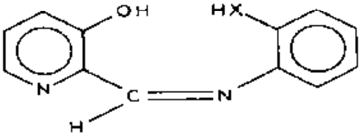
53

R = 2-cyclohexylamine,
2-phenyleneamine,
thiosemicarbazide,
selenosemicarbazide

C. MOLYBDENUM(V) COMPLEXES

(i) Complexes of bidentate Schiff bases

$MoOCl_3(THF)_2$ reacts in a 1 : 2 ratio with a series of Schiff bases **1** (R = H; R′ = C_2H_5, n-C_4H_9, C_2H_4OH, o-C_6H_4OH, C_6H_{11}, o-$CH_3C_6H_4$, o-ClC_6H_4, o-C_6H_4COOH, C_5H_4N), **2** and **54** (X = O, S) containing different donor sites, to give six-coordinate complexes $MoOCl_3(LH)_2$ (LH_2 = Schiff base) [61]. With the Schiff bases **1** (R = H; R′ = o-C_6H_4OH, o-C_6H_4COOH) and **54** (X = 0) the five-coordinate complexes of the type $MoOCl_3(LH)$ have also been isolated by reacting $MoOCl_3(THF)_2$ and the Schiff base in a 1 : 1 ratio [61]. Although the ligands are potentially monobasic bidentate (**1**) and dibasic tridentate (**2** and **54**) ligands, they behave as neutral monodentate ligands coordinating through the azomethine nitrogen. These complexes are very stable and are not converted into monobasic bidentate ligand complexes $MoOClL_2$ even after refluxing in alcohol for several hours. However, the latter have been isolated by reaction of the lithium salt of the Schiff bases and $MoOCl_3(THF)_2$ [61]. All these complexes exhibit magnetic moments in the range 1.61–1.76 BM (Table 4) expected for a d^1 system. The IR spectra are dominated by a strong band at 948–975 cm^{-1} due to the terminal $\nu(Mo{=}O)$. In $MoOClL_2$ complexes this band is observed at ca. 940 cm^{-1} which is lower than that observed for $MoOCl_3(LH)_2$ complexes, and is characteristic of bonding of the ligands as anions. The substitution of R′ affects the $\nu(Mo{=}O)$ frequency which increases in the order $C_2H_5 \simeq n\text{-}C_4H_9 < C_6H_{11} < o\text{-}ClC_6H_4 < o\text{-}CH_3C_6H_4$. This has been explained in terms of increasing π-acceptor behavior of molybdenum towards the oxygen. The complexes exhibit three absorption bands in the regions 12 300–14 900, 16 900–20 000 and 22 000–24 700 cm^{-1} due to the transitions $^2B_2 \rightarrow {}^2E$, $^2B_2 \rightarrow {}^2B_1$ and $^2B_2 \rightarrow {}^2A_1$ respectively. There are three possible structures for the complexes: **55** (*cis-fac*), **56** (*cis-mer*) and **57** (*trans-mer*). The ESR spectrum of $MoOCl_3(LH)_2$ (LH = **2**) exhibits a 1 : 2 : 3 : 3 : 2 : 1 sextet due to the superhyperfine coupling to two non-equivalent nitrogen atoms and a *cis-mer* structure with two non-equivalent N-coordination sites has been suggested for this complex.



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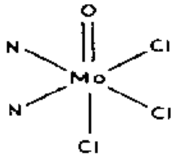
X = O, S



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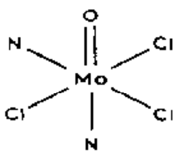

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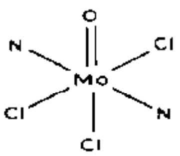
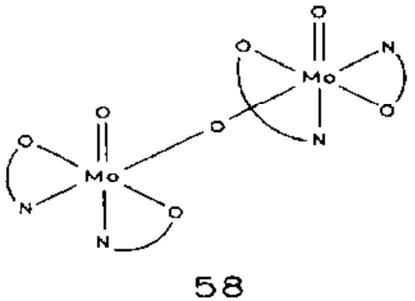


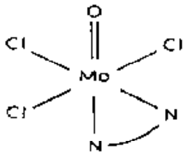
57

Dioxomolybdenum(V) complexes of the type MoO_2L with the Schiff bases **1** (R = H, 3-OCH_3; R′ = CH_3, C_2H_5, *n*-C_3H_7, *n*-C_4H_9, CH_2–C_6H_5) have been reported by Yamanouchi and Yamada [7]; they were prepared by heating a mixture of MoO_2(sal/substituted sal)$_2$ and the appropriate amine at 150 °C in isobutylalcohol or *n*-amylalcohol. In the case of the Schiff base **1** (R = H; R′ = CH_3) red or purple complexes of the type $Mo_2O_3L_4$, stable to strong acids and bases, have also been isolated by reacting a mixture of $MoO_2(sal)_2$ and methylamine in *n*-amylalcohol at 160 °C. The complexes of the type MoO_2L are insoluble in common organic solvents but $Mo_2O_3L_4$ is soluble. The binuclear species exhibit two ν(Mo=O) stretches at around 900–910 and 931–960 cm^{-1} and have magnetic moments close to zero, indicating the presence of a strong Mo–Mo interaction. The electronic spectra of the MoO_2L complexes are dominated by a *d–d* transition of moderate intensity at ca. 20 000 cm^{-1}. The complexes $Mo_2O_3L_4$ showed two bands, one at 14 500 cm^{-1} of moderate intensity due to a *d–d* transition and a high intensity band at 19 300 cm^{-1} due to the oxygen-to-metal charge transfer transition. A binuclear or multinuclear structure for MoO_2L-type complexes and an oxygen-bridged binuclear structure **58** for $Mo_2O_3L_4$ have been suggested [7].



58

Oxomolybdenum(V) complexes of Schiff bases **36** (X = H, 3-OCH_3; Y = H, CH_3; R = $(CH_2)_2$, $(CH_2)_3$, $(CH_2)_6$, $CH(CH_3)CH_2$, $(CH_2)_2NH(CH_2)_2$, *o*-C_6H_4, *o*-$C_6H_3CH_3$-4, *o*-$C_6H_2(CH_3)_2$-4,5) have been reported in which Schiff bases behave as neutral bidentate ligands coordinating through azomethine nitrogen atoms [62], although the Schiff bases are potential tetradentate ligands. All the complexes have been prepared by the reaction of $MoOCl_3(THF)_2$ and an appropriate Schiff base in dichloromethane–toluene. The $MoOCl_3(LH_2)$ complexes obtained are unstable in air as well as in polar solvents and produce acidic solutions in polar solvents. All the complexes exhibit a strong band in the 945–970 cm^{-1} region due to $\nu(Mo{=}O)$ which is slightly higher (10–20 cm^{-1}) than that for the corresponding MoOClL complexes (see text and Table 4). The reflectance spectra of the complexes show a weak low energy band at 12000–14000 cm^{-1} due to the $^2B_2 \rightarrow ^2E$ transition in O_h symmetry and a number of ill-defined absorptions. The isotropic ESR spectra of the complexes (Table 4) exhibit one central line due to ^{96}Mo with $I = 0$ and six weak lines on either side of the central line due to ^{95}Mo and ^{97}Mo ($I = 5/2$). There are two possible structures (**59** and **60**) for the complexes but the isotropic g values cannot distinguish between them. The anisotropic ESR spectra at 123 K favours the less symmetrical structure **59** rather than **60**. The presence of two signals in the complexes with unsymmetrical backbones, e.g. $o\text{-}C_6H_3CH_3\text{-}4$, $CH(CH_3)CH_2$, is due to the presence of a mixture of structures **59** and **60** [62]. The reaction of $MoOCl_2(THF)_2$ and N,N'-ethylenebis(thiophene-2-carbaldimine) in THF gives the complex $MoOCl_3L$ in which the Schiff base behaves as a bidentate NN donor ligand [62(a)].



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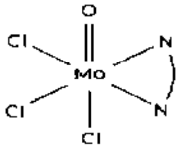

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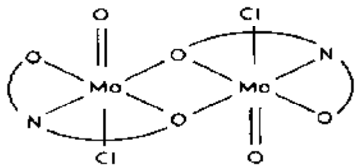
(ii) Complexes of tridentate Schiff bases

Relatively less work has been reported on molybdenum(V) complexes of tridentate Schiff bases in comparison with the work on molybdenum(VI) complexes of tridentate Schiff bases.

Oxomolybdenum(V) complexes of the tridentate dibasic Schiff bases derived from salicylaldehyde, *o*-hydroxyacetophenone, acetylacetone and *o*-aminophenol or 2-aminoethanethiol have been reported by Dey et al. [24]. The complexes are of the types [$MoOClL \cdot H_2O$] (where LH_2 = Schiff base) and [$MoO(SCN)(H_2O)L$] (where LH_2 = Schiff base **11** (R = H; X = S)). The complexes are paramagnetic with magnetic moments in the range 1.66–1.82 BM with no significant magnetic interactions between the neighbouring oxomolybdenum(V) ions, though this is not precluded by the magnetic data. Cryomagnetic, ESR and molecular weight studies of the complexes are necessary in order to authenticate the magnetically dilute nature of the complexes. Syamal et al. [63–66] have reported the complexes MoOClL (where LH_2 = tridentate dibasic Schiff base derived from *o*-hydroxybenzylamine, *o*-aminobenzylalcohol, *o*-aminophenol, 2-aminoethanol, thiosemicarbazide, *S*-benzyldithiocarbazate, furoic acid hydrazide, thiophene-2-carboxylic acid hydrazide and salicylaldehyde, substituted salicylaldehyde or pyridoxal) (**20**, **28**–**34**) using $(NH_4)_2[MoOCl_5]$ or $(pyH)_2[MoOCl_5]$ as starting material. The complexes are dimers with antiferromagnetic exchange ($\mu_{eff} = 0.00$–1.19 BM). In view of this it seems likely that the complexes of the type $MoOClL \cdot H_2O$ are also involved in magnetic exchange. The $-J$ values of the complexes as calculated from the Bleaney–Bowers equation are in the range 621–2193 cm^{-1}. The $MoOClL \cdot H_2O$ complexes exhibit three absorption bands at 13300–14280, 19030–19450 and 22000–25800 cm^{-1} due to the transitions ${}^2B_2 \rightarrow {}^2E$, ${}^2B_2 \rightarrow {}^2B_1$ and ${}^2B_2 \rightarrow {}^2A_1$ respectively while the MoOClL complexes exhibit only the first of two such bands around 14000 and 18000 cm^{-1}, since the third lies underneath a charge transfer (CT) band. Syamal et al. [63,64] indicate that the 19000 cm^{-1} band is not characteristic of dimetallic oxomolybdenum(V) complexes containing the Mo–O–Mo or $\mathrm{Mo}{<}\!\begin{smallmatrix}\mathrm{O}\\ \\ \mathrm{O}\end{smallmatrix}\!{>}\mathrm{Mo}$ bridge since many monometallic oxomolybdenum(V) complexes such as $MoOCl_3(THF)_2$ and $MoOCl_3(CH_3CN)_2$ exhibit a band around 19000 cm^{-1}. Syamal et al. [63,64] have pointed out that in d^9–d^9 and d^1–d^1 systems such as Cu(II)–Cu(II), OV(IV)–OV(IV) and OMo(III)–OMo(III) the electronic spectral bands can be reasonably explained in terms of monometallic MO diagrams. Some MoOClL complexes exhibit a band around 740 cm^{-1} due to $\nu(\mathrm{Mo}\overset{\mathrm{O}}{\diagup\ \diagdown}\mathrm{Mo})$ ligand bridging (**62** and **62**) [63].



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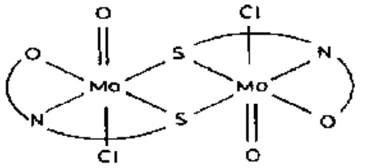
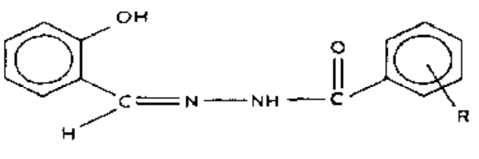


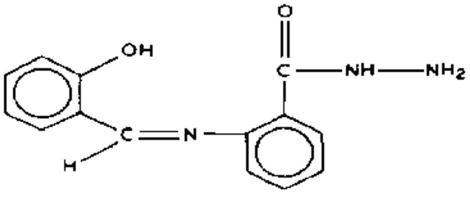
62

Oxomolybdenum(V) complexes of the Schiff bases **63**–**66** derived from various aromatic acid hydrazides and salicylaldehydes or biacetylmonoximes



63

R = H, p-NH$_2$, p-Cl, p-NO$_2$,
o-OH, o-Cl, o-NH$_2$



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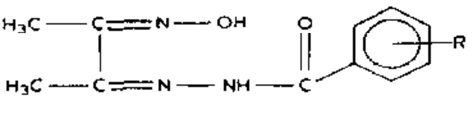
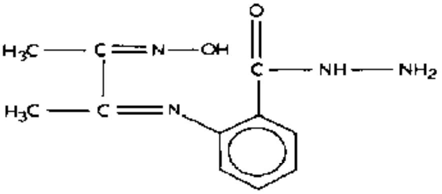


65

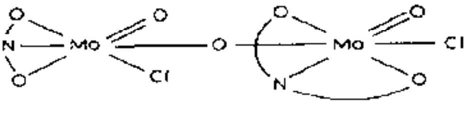
R = H, p-NH$_2$, p-Cl, p-NO$_2$,
o-OH, o-Cl, o-NH$_2$



66

have been reported by Poddar et al. [67]. All the hydrazides undergo condensation via the NH_2 group of the hydrazide while in the case of o-aminobenzoyl hydrazide, condensation takes place via the ring NH_2 group. Reaction of these Schiff bases with $(NH_4)_2[MoOCl_5]$ in dry ethanol resulted in the formation of two types of complexes, $MoOCl_2L$ (with Schiff bases derived from salicylaldehyde) and $Mo_2O_3Cl_2L_2$ (with Schiff bases derived from biacetylmonoxime). The $MoOCl_2L$ complexes are soluble in methanol, show normal magnetic moments (1.54–1.70 BM) and exhibit ν(Mo=O) in the region 950–972 cm^{-1}. The authors report [67] that the $MoOCl_2L$ complexes are monometallic, but, a magnetic moment of 1.54 BM for a d^1 system may be indicative of antiferromagnetic exchange which has not been authenticated from cryomagnetic, molecular weight and ESR studies.

The $Mo_2O_3Cl_2L_2$ complexes are insoluble in methanol and exhibit magnetic moments of less than 0.5 BM, indicating antiferromagnetic exchange and presumably a dinuclear nature in which molybdenum atoms are bridged via oxygen atoms. The presence of a strong band in the region 750–780 cm^{-1} due to ν(Mo–O–Mo) further supports the oxygen-bridged structure **67**



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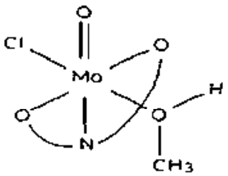
of $Mo_2O_3Cl_2L_2$. The $MoOCl_2L$ complexes show bands in the region 13100–14700 cm^{-1} and 19300–22600 cm^{-1} due to the $^2B_2 \rightarrow {}^2E$ and $^2B_2 \rightarrow {}^2B_1$ transitions respectively. The $Mo_2O_3Cl_2L_2$ complexes exhibit only one band in the region 18200–20400 cm^{-1}. Although Poddar et al. [67] believe that this is a *d–d* band, the present reviewers feel that the origin of this band is charge transfer as the molar extinction coefficient values are in the range 1435–8200 l mol^{-1} cm^{-1}. The monomeric anionic complex, (pyH)[$MoOCl_2$(sal–AP)], has been synthesized by the reaction of the Schiff base with $(pyH)_2[MoOCl_5]$ in methanol and pyridine [68]. When (pyH)[$MoOCl_2$(sal–AP)] is dissolved in methanol, MoOCl(sal–AP) · CH_3OH (**68**) is formed. Other complexes such as [M][$MoOCl_2$(sal–AP)] (where M = $N(C_2H_5)_4$, Ph_4As) have been synthesized from (pyH)[$MoOCl_2$(sal–AP)] by metathetic reaction with tetraethylammonium chloride or tetraphenylarsonium chloride. Ph_4As[$MoOCl_2$(sal–AP)] has a distorted octahedral structure (X-ray) (**69**). The ONO donor tridentate Schiff base occupies the meridional position with the nitrogen atom *trans* to the oxo group. The Mo–O distance is 1.67 Å. The two Mo–Cl bond distances are 2.37 and 2.41 Å and this difference in bond length influences the dissociation of one Cl atom of $MoOCl_2$(sal–AP) in methanol; as a result MoOCl(sal–AP) · CH_3OH is formed.



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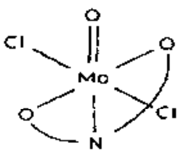

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The syntheses of polymer-anchored molybdenum(V) Schiff base complexes using H_2sal–AP or 5-nitro–H_2sal–AP and chloromethylated polystyrene cross-linked with divinylbenzene have been reported by Topich [69]. The complexes are represented as [P]-X–sal–AP–MoOCl (where X = H, NO_2; [P] is the polymer backbone). Molybdenum atoms are placed on phenyl rings (of the polymer) which are 8–10 styrene units apart in the polymer chain. This results in a magnetically dilute situation for each molybdenum atom because the pathway for molybdenum(V) dimer formation is blocked. However, as the polymer is cross-linked with polymer chains overlapped and twisted, some of the reactive groups come near to one another and as a result some dimerization takes place. The ESR measurements have indicated that the amount of monomeric molybdenum is 60 ± 10% of the total molybdenum present in the polymer. The ESR spectra of the polymer-anchored complexes exhibit a central line originating from the non-magnetic molybdenum isotope ($^{96}M_0$, $I = 0$) and six lines due to the ^{95}Mo and ^{97}Mo isotopes. The smaller hyperfine splitting constant ($A_{\parallel}^{Mo}$) for [P]–nitrosal–AP–MoOCl in comparison with that for [P]–sal–AP–MoOCl indicates that in the former complex the electron-withdrawing effect is transmitted to the molybdenum through the delocalized ligand system, and electron density is effectively reduced at the molybdenum. The ESR spectra of MoOCl(sal–AP) · CH_3OH, $Et_4N[MoOCl_2$(sal–AP)] and [P]–X–sal–AP–MoOCl are identical [69,70]. The ESR results indicate that the electronic structure and stereochemistry of the polymer-anchored oxomolybdenum(V) complex are essentially identical with those of the polymer-free molybdenum(V) complex. The polymer-anchored oxomolybdenum(V) complexes, [P]–X–sal–AP–MoOCl, are oxidized by NO_3^- with complete loss of the molybdenum(V) ESR signal. Work on magnetically dilute polymer-anchored molybdenum(V) complexes is of biochemical importance in the context that molybdenum-containing enzymes such as aldehyde oxidase, sulphite oxidase, xanthine oxidase and nitrate reductase exhibit ESR signals arising from a monomeric molybdenum(V) centre [1].

The cyclic voltammogram of the complex *trans*-$(C_2H_5)_4N[MoOCl_2$(sal–AP)] has been recorded in dry DMF using tetraethylammonium chloride as electrolyte [71]. The E_{pc} value is −1.055 V vs. the standard calomel electrode (SCE). The controlled potential coulometric data ($E_{redn} = -1.250$ V, n (electrons/molecule) $= 1.74 \pm 0.09$) in DMF show that the complex is reduced in a two-electron step to a molybdenum(III) species. The low value of n has been explained in terms of the slow reaction of the complex with traces of water present in the solvent during the course of the coulometric determination. In the anionic complex $[(C_2H_5)_4N]$[MoOCl(sal–AP)], the two-electron reduction is expected because of the presence of charge on the complex. The one-electron reduction peak shifts to a more negative potential owing to the charge and overlaps with a second reduction peak for reduction to the molybdenum(III) state. The complex is not oxidizable to molybdenum(VI) in the range 0.50–2.50 V (SCE) [71].

The reaction of *trans*-MoOCl(sal–AP) · CH_3OH with NO_3^- in DMF leads to oxidation to the dioxomolybdenum(VI) complex, MoO_2(sal–AP)/MoO_2(sal–AP) · DMF, and the reduction of NO_3^- to NO_2 (eqn. (5)) in a one-electron step [72].

$$\mathrm{MoOCl(sal{-}AP)\cdot CH_3OH + NO_3^- \rightarrow MoO_2(sal{-}AP) + NO_2 + Cl^- + CH_3OH} \qquad (5)$$

In the presence of excess NO_3^-, the plots of ln (absorbance A) vs. time t show significant departure from linearity, but the rate increases linearly with increasing NO_3^- concentration and the rate law follows the equation

$$-\mathrm{d}[\mathrm{Mo(V)}]/\mathrm{d}t = k_{obs}[\mathrm{Mo(VI)}][\mathrm{NO_3^-}]/[\mathrm{Cl^-}] \qquad (6)$$

As the chloride concentration was not constant during the reaction and was cited in the denominator (eqn. (5)), this was responsible for the deviation from linearity of the plots of ln A vs. t. It is interesting to note that the complex [MoOCl(sal–AP) · CH_3OH] reduces NO_3^- more rapidly than the other molybdenum(V) complexes such as $MoOCl_3$(dipy), $MoOCl_3$(ophen), $MoOCl(ox)_2$ etc. The presence of a weakly bonded CH_3OH *cis* to the oxo group influences the complex to react rapidly with NO_3^- forming an intermediate complex MoOCl(NO_3^-)(sal–AP) which finally produces NO_2 and MoO_2(sal–AP) [72].

(iii) Complexes of tetradentate Schiff bases

Molybdenum(V) complexes of tetradentate Schiff bases were first reported by Dilworth et al. [53]. Complexes of the type MoOClL (where LH_2 = **36**; X = H, 5-OCH_3; Y = H; R = $(CH_2)_2$, $(CH_2)_3$, *o*-C_6H_4) were synthesized by reacting $MoOCl_3(THF)_2$ and the dilithium salt of the Schiff base in dry ethanol. The complexes have also been prepared by the reaction of $MoOCl_3$ and the bis(trimethylsilyl) derivative of the appropriate Schiff base. Chen et al. [73] have prepared these complexes by the reaction of $MoOCl(acac)_2$ and the respective Schiff base. Dey et al. [24] have synthesized the molybdenum(V) complexes MoOClL with **31** and also the Schiff bases derived from ethylenediamine, *o*-phenylenediamine and acetylacetone by reacting $MoOCl_3(THF)_2$ and the respective Schiff base in acetonitrile in the presence of an excess of $(C_2H_5)_3N$. However, Gheller et al. [74] were unable to prepare the complexes MoOClL (where LH_2 = salen, saltrien, salphen) by following the method of Dilworth et al. [53]. Gheller et al. [74] have synthesized brown or red-brown MoOCl(saltrien) and [MoOL(CH_3OH)]Br (where LH_2 = salen, saltrien and salphen) by reacting $(pyH)_2[MoOCl_5]$ or $(pyH)_2[MoOBr_4]$ and the respective Schiff base in the presence of $NaOCH_3$. The IR spectra of the complexes show strong absorption in the 930–960 cm^{-1} and 350 cm^{-1} regions due to the ν(Mo=O) and ν(Mo–Cl) respectively. The complexes [MoOL(CH_3OH)]Br show a broad band in the region 3000–3300 cm^{-1} due to the ν(O–H) of coordinated methanol. The methanol is not lost in [MoOL(CH_3OH)]Br even after recrystallization from DMF–isopropylalcohol. A thermal study shows the loss of methanol in the temperature range 140–160 °C. The electronic spectra of the complexes exhibit bands at around 12 100–14 290, 15 400–20 300 and 22 600–24 400 cm^{-1} due to the $^2B_2 \rightarrow {}^2E$ ($d_{xy} \rightarrow d_{xz}, d_{yz}$), $^2B_2 \rightarrow {}^2B_1$ ($d_{xy} \rightarrow d_{x^2-y^2}$) and $^2B_2 \rightarrow {}^2A_1$ ($d_{xy} \rightarrow d_{z^2}$) transitions respectively (Table 5). The complexes exhibit magnetic moments in the range 1.66–1.81 BM. The cryomagnetic study of [MoO(salen)(CH_3OH)]Br shows Curie–Weiss behaviour in the temperature range 43–298 K and the absence of magnetic exchange.

TABLE 5

Magnetic moment and spectral data for oxomolybdenum(V) complexes of tetradentate Schiff bases

Complex	μ_{eff} (BM)	ν(Mo=O) (cm^{-1})	Medium	$\nu_{max} \times 10^3$ (cm^{-1}) (ϵ ($l\ mol^{-1}\ cm^{-1}$))	Ref.
MoOCl(salen)	1.68	939,	DMF	24.2 (2560), 12.1 (106)	53
		930	CH_2Cl_2	23.6 (2310)	73
			Refl.	22.6, 12.1	53
MoOCl(3-OMesalen)	1.66	945,	DMF	Insoluble	53
		930sh	Refl.	26.1	53
MoOCl(saltrien)	1.67	926	DMF	20.2 (226), 15.4 (116)	53
			CH_2Cl_2	20.3 (1970)	73
			Refl.	25.9, 23.8, 19.7	53
MoOCl(3-OMesaltrien)	1.67	932	DMF	Insoluble	53
			Refl.	23.5	53
MoOCl(salphen)	1.68	948	DMF	18.9 (531)	53
			CH_2Cl_2	23.6 (4000)	73
			Refl.	26.2, 21.7	53
MoOCl(3-OMesalphen)	1.67	950	DMF	Insoluble	53
			Refl.	24.3, 17.5sh	53
$[MoO(salen)(MeOH)]^+$	1.73	960	DMF	18.8 (436), 24.4 (2074)	74
$[MoO(saltrien)(MeOH)]^+$	1.73	962, 968	DMF	19.9 (777), 27.4 (5005)	74
$[MoO(salphen)(MeOH)]^+$	1.69	963	DMF	23.2 (7007)	74
$[MoO(salen)(SC_6H_5)]$	1.77	942	Nujol	24.3, 17.5	24
$[MoO(salen)_2]O$	Diamagnetic	955	Refl.	14.29, 19.05, 26.62	77

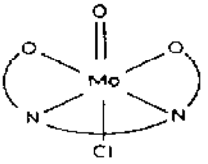
TABLE 6

ESR data for oxomolybdenum(V) complexes of tetradentate Schiff bases [a]

Complex	g_{av}	$A_{iso} \times 10^{-4}$ (cm^{-1})	g_{av}	$A_{iso} \times 10^{-4}$ (cm^{-1})	Ref.
MoOCl(salen)	1.938	46.0	1.948	46.0	53
MoOCl(3-OMesalen)	1.934	48.0	1.946	46.0	53
MoOCl(saltrien)	1.944	44.0			53
	1.943	39.2			75
MoO(OMesaltrien)	1.936	48.0	1.948	46.0	53
MoOCl(salphen)	1.938	46.0			53
	1.940	44.1			70
MoOCl(3-OMesalphen)	1.934	50.0			53
$[MoO(salen)(CH_3OH)]Br$	1.942	42.0			75
$[MoO(saltrien)(CH_3OH)]Br$	1.943	39.6			75
$[MoO(saphen)(CH_3OH)]Br$	1.944	43.7			75

[a] Two g_{av} values are due to two isomers.

The ESR spectra of MoOCl(saltrien) and MoOCl(salphen) in CH_2Cl_2 or DMF at ambient temperature exhibit one strong line due to ^{96}Mo ($I = 0$) and six weak lines on either side of the central line arising from ^{95}Mo and ^{97}Mo ($I = 5/2$) (Table 6) [53]. MoOCl(salen) exhibits two ESR signals ($g = 1.938, 1.948$) with an intensity ratio of 10 : 1 due to the presence of two isomers of the complex. Three structures (**70**–**72**) are possible for the complexes of salen and saltrien owing to the non-planar coordination of these ligands. Because of the rigid configuration of the *o*-phenylene moiety, only the structure **70** with a planar coordination of salphen is possible for MoOCl(salphen). The ESR spectrum of MoOCl(salphen) shows one signal with $g_0 = 1.938$ and $A_0 = 46 \times 10^{-4}$ cm^{-1} due to the presence of a single species. However, Scullane et al. [70] have claimed the presence of two species with similar g_0 and A_0 values, possibly due to a mixture of MoOCl(salphen) and [MoO(salphen)(DMF)]$^+$. They obtained one signal with $g_0 = 1.940$ and $A_0 = 44.1 \times 10^{-4}$ cm^{-1}, after addition of an excess of $[(C_2H_5)_4N]Cl$, due to the presence of a single species, MoOCl(salphen). The presence of two ESR-active species in the complexes [MoO(salphen)(CH_3OH)]Br and MoOCl(saltrien) in CH_3CN or CH_2Cl_2 has also been observed by Bradbury et al. [75]. However, in DMF solution containing 0.1 M $[(C_2H_5)_4N]PF_6$ they observed only a single species for [MoOL(CH_3OH)]Br (LH_2 = saltrien, salphen) and the relative concentration of the second species was less than 4% in [MoO(salen)(CH_3OH)]Br and MoOCl(saltrien). The species of MoOCl(salen) with comparable g_0 value (1.938) for MoOCl(salphen) evidently has the structure **70**. The other species has the structure **71** and/or **72**. The complex MoOCl(saltrien) has the structure **71** or **72** with $g_0 = 1.944$. The presence of one ν(Mo–Cl) at 322 cm^{-1} and one ν(Mo=O) at 948 cm^{-1} in MoOCl(salphen) has been assigned to the structure **70**. MoOCl(salen) exhibits two ν(Mo=O) bands at 939 and 930 cm^{-1} and two ν(Mo–Cl) bands at 337 and 278 cm^{-1}. The higher energy band positions at 939 and 337 cm^{-1} have been attributed to structure **70** by comparing these bands with those of MoOCl(salphen), and the lower energy bands at 930 and 278 cm^{-1} have been attributed to structure **71** and/or **72**. The observation of one ν(Mo=O) at 926 cm^{-1} and one ν(Mo–Cl) at 280 cm^{-1} in MoOCl(saltrien) indicates the presence of structure **70**.



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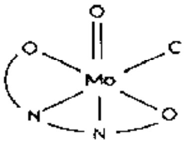

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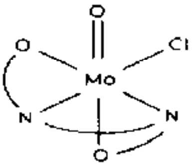

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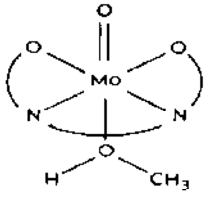
The crystal structure of $[MoO(salen)(CH_3OH)]Br$ [74] shows the molybdenum atom to be six-coordinate with the four ligand atoms ONNO occupying four equatorial positions; the methanol oxygen is *trans* to the Mo=O oxygen (**73**). The Mo=O bond length is 1.666 Å while Mo–O (methanol) is 2.338 Å. The molybdenum atom is displaced 0.37 Å from the basal plane defined by the salen ligand atoms. The complexes $[MoOL(CH_3OH)]Br$ (LH_2 = saltrien, salphen) have the same structure (**73**).



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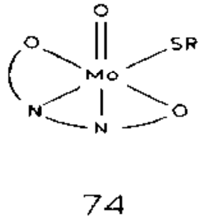
MoOClL (where LH_2 = salen, saltrien, salphen) reacts with thiophenols (SC_6H_4–X, where X = H, p-CH_3) in acetonitrile to give blue complexes of the type $MoOL(SC_6H_4–X)$ [24,76]. $[MoOL(SC_6H_5)]$ exhibits a magnetic moment of 1.77 BM. The IR spectrum of $[MoO(salen)(SC_6H_5)]$ shows a sharp band at 942 cm^{-1} due to ν(M=O). $[MoO(salen)(SC_6H_5)]$ exhibits a *d–d* band at 17500 cm^{-1} and a broad band at 24500 cm^{-1} due to charge transfer. $[MoO(saltrien)(SC_6H_5)]$ and $[MoO(salphen)(SC_6H_5)]$ exhibit a weak *d–d* band at ca. 24000 cm^{-1} and a charge transfer band at 17000 cm^{-1}. MoO(salphen)(SR) (where R = C_6H_5, p-$CH_3C_6H_4$) shows weak bands at 25000 cm^{-1} and 16000 cm^{-1} due to the transitions $^2B_2 \rightarrow {}^2A_1$ and $^2B_2 \rightarrow {}^2E$ respectively and an intense charge transfer band at ca. 17000 cm^{-1}.

The ESR spectra of $[MoO(salen)(SC_6H_5)]$ and $[MoO(saltrien)(SC_6H_5)]$ in CH_2Cl_2 at room temperature are characteristic of the presence of two isomers (**74** and **75**) and the ESR spectrum of [MoO(salphen)(SR)] indicates the presence of the *trans* isomer (**76**) [76]. The ESR parameters for these



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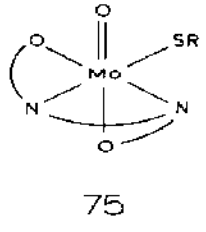
R = C_6H_5, p-$CH_3C_6H_4$



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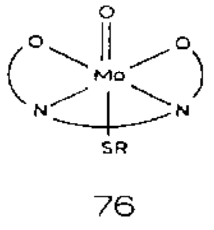
R = C_6H_5, p-$CH_3C_6H_4$



76

R = C_6H_5, p-$CH_3C_6H_4$

TABLE 7

ESR parameters for MoO(ONNO)(SC_6H_4–X)-type complexes [76]

Complex	g_0	$g_{\parallel}$	$g_{\perp}$	A_0 [a]	$A_{\parallel}$ [a]	$A_{\perp}$ [a]
MoO(saltrien)(SC_6H_5)	1.9847	2.0162	1.9689	35.0	55.4	25.0
MoO(saltrien)(SC_6H_4Me-*p*)	1.9844	2.0160	1.9688	35.3	55.6	25.3
MoO(salphen)(SC_6H_5)	1.9784	1.9892	1.9730	38.6	60.5	27.8
MoO(salphen)(SC_6H_4Me-*p*)	1.9781	1.9892	1.9728	38.8	60.8	27.9

[a] Units: $\times 10^{-4}$ cm^{-1}.

complexes are given in Table 7. The $g_{\parallel}$ and $g_{\perp}$ values are in the range 1.9892–2.0162 and 1.9688–1.9730 respectively. The g values of these complexes have been used to distinguish between the *cis* and *trans* isomers. The g value observed for [MoO(saltrien)(SC_6H_5)], higher than the free electron value of 2.0023, indicates the *cis* structure, while the g value lower than the free electron value indicates the presence of a *trans* isomer in [MoO(salphen)(SR)]. The electronic spectral behaviour of the *cis* and *trans* complexes is also different. Al-Mowali [76] has calculated K, the isotropic Fermi contact parameter; β_2, the in-plane π-bonding coefficients; β_1 the in-plane σ-bonding coefficient; and α_2, the out-of-plane π-bonding coefficient from the ESR and electronic spectral data (Table 8). The β_1 values are indicative of the presence of strong covalent metal–ligand bonding in both the *cis* and *trans* complexes. The lower value (see Table 8) of β_2 in the *cis* complexes is due to the presence of a good π-bonding ligand (SR) in the basal plane. The β_2 values also indicate that the unpaired electron in the d_{xy} orbital is delocalized to a greater extent in the *cis* than in the *trans* complexes.

Cyclic voltammetric and controlled-potential coulometric studies of MoOCl(salphen) [71] show that the complex is reduced by one-electron to a molybdenum(IV) species. The complex is not oxidizable to molybdenum(VI) at +0.50 to −2.50 V (SCE) and dimerizes slowly in DMF on standing to give the oxo-bridged molybdenum(V) dimers. The complex MoOCl(salphen) does not reduce NO_3^- owing to its planar structure in which chloride is

TABLE 8

K and molecular orbital coefficients for MoO(ONNO)(SC_6H_4–X)-type complexes [76]

Complex	K	β_2	β_1	ϵ
MoO(saltrien)(SC_6H_5)	0.62	0.78	0.84	0.82
MoO(saltrien)(SC_6H_4Me-*p*)	0.62	0.79	0.84	0.83
MoO(salphen)(SC_6H_5)	0.67	0.86	0.88	0.80
MoO(salphen)(SC_6H_4Me-*p*)	0.68	0.87	0.89	0.80

coordinated at the *trans* position [72]. The rigidity of the *o*-phenylene backbone precludes the rearrangement of chloride to the *cis* position and thus prevents the coordination of NO_3^- in a position *cis* to the oxo group.

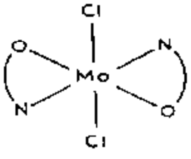
The reaction of $Mo(CO)_6$ and salenH_2 in DMF leads to the formation of insoluble purple crystals of $[MoO(salen)]_2O$ [77]. The complex is diamagnetic due to the complete antiferromagnetic exchange coupling of the two $S = \frac{1}{2}$ spins. The electronic spectra are reported in Table 5. Although Yamanouchi et al. believe that the origin of the 19050 cm^{-1} band is due to a dimetallic structure [68], the present reviewers disagree as argued above. $[MoO(salen)]_2O$ exhibits one ν(Mo=O) at 955 cm^{-1} and two ν(Mo–O–Mo) bands at 750 and 430 cm^{-1}.

The reaction of $MoCl_5$ and thiosemicarbazone or selenosemicarbazone Schiff base (LH_2 = **53**) in boiling ethanol gives the complexes of the type $[MoL]_2O$. The reduction of molybdenum(VI) complex, MoO_2L, with $NaBH_4$ also gives $[MoL]_2O$ [60].

D. MOLYBDENUM(IV) COMPLEXES

Although molybdenum(IV) complexes can act as a simple model for biochemical redox reactions, very few reports are available on molybdenum(IV) complexes of Schiff bases in comparison with those of molybdenum(V) and molybdenum(VI).

Van Den Bergen et al. [77] have provided details about the starting materials used for the synthesis of molybdenum(IV) complexes and reported complexes of the general formula MoX_2L_2 (where LH = **1**; R = CH_3, C_2H_5, *n*-C_4H_9, *i*-C_4H_9, C_6H_5, *p*-ClC_6H_4, *p*-$CH_3C_6H_4$, $CH_2C_6H_5$; X = Cl, Br) and $MoCl_2L$ (LH_2 = Schiff base derived from ethylenediamine and salicylaldehyde or acetylacetone). These purple complexes were prepared either by oxidative substitution of $MoCl_3(py)_3$/$MoBr_3(py)_3$ or by direct substitution of chlorine in $MoCl_4 \cdot 2CH_3CN$ by the Schiff base in acetonitrile in the presence of triethylamine. In the case of *N*-arylsalicylaldimines, brown adducts of the type $MoCl_4(LH)_2$ are formed together with $MoCl_2L_2$ when the synthesis was carried out from $MoCl_4 \cdot 2CH_3CN$ in the absence of triethylamine. The mechanism for this halogen replacement reaction involves initial coordination by two ligand nitrogen atoms followed by halogen elimination and concomitant oxygen coordination. Kan [82] has prepared complexes of the type $MoCl_2L_2$ (where LH = **1**; R = C_6H_5, *o*-ClC_6H_4, *m*-ClC_6H_4, *p*-ClC_6H_4, *m*-FC_6H_4, *p*-FC_6H_4, *p*-$NO_2C_6H_4$, *o*-$CH_3C_6H_4$, *m*-$CH_3C_6H_4$, *p*-$CH_3C_6H_4$, *o*-$OCH_3C_6H_4$, *m*-$OCH_3C_6H_4$, and *p*-$OCH_3C_6H_4$) by the method given by Van Den Bergen et al. [77] and by the reaction of $MoCl_2(acac)_2$ and the respective Schiff base in acetonitrile. All the complexes are stable to oxidation and hydrolysis in the solid state. The complexes MoX_2L_2 are moderately soluble in acetone but dissolve with decomposition in acetonitrile, ethanol and DMF. The $MoCl_2L$ complexes are insoluble in all common solvents but are partially soluble in DMF and methoxyethanol with decomposition. Molecular weight determinations in CH_2Cl_2 or by mass spectroscopy show their monomeric nature. The complexes show two ν(Mo–Cl) bands in the region ca. 310 and 300 cm^{-1}. All these complexes exhibit magnetic moments in the range 2.58–2.80 BM expected for octahedral d^2 complexes. The magnetic susceptibilities of $Mo(sal{-}NC_2H_5)_2Cl_2$ and $Mo(sal{-}N{-}p{-}CH_3C_6H_4)_2Cl_2$ have been measured over the temperature range 90–300 K, and Curie–Weiss plots gave a straight line with θ values of 10 K and 15 K respectively. The $^3T_{1g}$ ground term in octahedral molybdenum(IV) complexes is perturbed simultaneously by spin–orbit coupling and a non-cubic crystal field component. The effective magnetic moment value increases from the predicted value of 1.83 BM in octahedral symmetry towards the spin-only value of 2.83 BM as the magnitude of the distortion increases [77]. Electronic spectra of these *trans* complexes (**77**) show a broad band at ca. 18000 cm^{-1} and an ill-defined shoulder at 22000–26000 cm^{-1} [77,78]. The assignments of these bands as *d–d* transitions, $^3T_{1g} \rightarrow {}^3T_{2g}$ and $^3T_{1g} \rightarrow {}^3T_{1g}(P)$ respectively, are questionable due to their high intensities, although available data summarized by Lever [79] indicate that the bands below 29000 cm^{-1} can be assigned to *d–d* transitions. The complexes **77** are *trans* [80,81]. The single-crystal X-ray structure determination of *trans*-$MoCl_2L_2$ (LH = **1**, R = CH_3) indicates that the Mo–O, Mo–N and Mo–Cl distances are 1.95 Å, 2.14 Å and 2.39 Å respectively and the bond angles about the molybdenum atom are close to 90° [78]. *cis*-MoX_2L_2 and *cis*-MoX_2L complexes have not been identified.



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The polarographic behaviour of the molybdenum(IV) complexes $MoOCl_2L_2$ has been reported in DMF using $[NBu_4][BF_4]$ as supporting electrolyte [82]. Values of the reversible oxidation potential $E^{ox}_{1/2}$ and i^{red}_p/i^{ox}_p of some of the complexes are given in Table 9. The electrochemical data show a typical one-electron reversible process for molybdenum(IV) → molybdenum(V) couples. No further oxidation to molybdenum(VI) species was observed. The oxidation potential depends on the substitution on the aryl moiety of the amine. The oxidation potential decreases with substitution of an electron-donating group such as p-OCH_3 and m-OCH_3 and increases with electron-withdrawing substituents such as p-NO_2 [82].

TABLE 9

Magnetic moments, IR and electrochemical data for some molybdenum(IV) complexes

Complex $[Mo(sal–NR–X)_2Cl_2]$	μ_{eff} (BM)	$E^{ox}_{1/2}$ (V)	i_p^{red}/i_p^{ox}	ν(Mo–Cl) (cm^{-1})	Ref.
$Mo(sal–NC_2H_5)_2Cl_2$	2.74				77
$Mo(sal–NC_4H_9\text{-}n)_2Cl_2$	2.54				77
$Mo(sal–NC_6H_5)_2Cl_2$	2.58	−0.28	1.01	315, 313sh	82
$Mo(sal–NC_6H_4Me\text{-}o)_2Cl_2$	2.60	−0.31	1.10	325, 323sh	82
$Mo(sal–NC_6H_4Me\text{-}m)_2Cl_2$	2.64	−0.30	1.00	325, 323sh	82
$Mo(sal–NC_6H_4Me\text{-}p)_2Cl_2$	2.66				77
	2.64	−0.24	1.10	312, 310sh	82
$Mo(sal–NC_6H_4MeO\text{-}o)_2Cl_2$	2.61	−0.35	1.01	328, 326sh	82
$Mo(sal–NC_6H_4MeO\text{-}m)_2Cl_2$	2.70	−0.28	1.01	325, 323sh	82
$Mo(sal–NC_6H_4MeO\text{-}p)_2Cl_2$	2.65	−0.30	1.05	310, 312sh	82
$Mo(sal–NC_6H_4NO_2\text{-}p)_2Cl_2$	2.80	−0.15	1.02	315, 312sh	82
$Mo(sal–C_6H_4Cl\text{-}o)_2Cl_2$	2.69	−0.27	1.04	325, 323sh	82
$Mo(sal–NC_6H_4Cl\text{-}m)_2Cl_2$	2.65	−0.19	1.03	320, 317sh	82
$Mo(sal–NC_6H_4Cl\text{-}p)_2Cl_2$	2.60	−0.21	1.05	315, 313sh	82
$Mo(sal–NC_6H_4F\text{-}m)_2Cl_2$	2.60	−0.20	1.10	320, 318sh	82
$Mo(sal–NC_6H_4F\text{-}p)_2Cl_2$	2.58	−0.25	1.06	320, 322sh	82

Molybdenum(IV) complexes of the type $Mo(LH)_2Cl_4 \cdot C_7H_7$ and $Mo(LH_2)Cl_4 \cdot C_7H_7$ (where LH = **1** and **2**, R = $o\text{-}CH_3C_6H_4$; LH_2 = **36**, X = H, 5-OCH_3; Y = H, CH_3; R = $(CH_2)_2$, $(CH_2)_3$, CH_3CHCH_2, $o\text{-}C_6H_4$, $m\text{-}CH_3C_6H_4$) in which ligands behave as neutral monodentate (former) and neutral bidentate (latter) have been reported by McAuliffe et al. [83]. The complexes were synthesized by the reaction of tetrachlorobis(butyronitrile) molybdenum(IV) and the respective Schiff base in toluene under nitrogen. The complexes are green or purple in colour and do not lose solvent even after drying under vacuum for several days. The observed magnetic moments are in the region of ca. 2.60 BM expected for a d^2 system. All the complexes neither exhibit bands in the 900–1000 cm^{-1} region due to ν(Mo=O) nor show any EPR signal which precludes the oxidation of complexes to molybdenum(V). The electronic spectra are dominated by two bands at 17000 and 23000 cm^{-1} which have been assigned to the $^3T_{1g} \rightarrow {}^3T_{2g}$ and $^3T_{1g} \rightarrow {}^3T_{1g}(P)$ transitions, respectively.

An interesting series of oxomolybdenum(IV) complexes of the type MoOL · DMF and MoOL · AA (where LH_2 = Schiff base H_2sal–AP and H_2sal–ATP; AA = 2,2′-bipyridyl, o-phenanthroline) have been reported by Boyd and Spence [84]. The complexes MoOL · DMF were prepared either by the reduction of $Mo^{VI}O_2L$ with $PEtPh_2$ or by the reaction of $MoOCl_4$, $MoOCl_2(PMePh_2)_3$ or $MoOCl_2(bipy)(PMePh_2)$ with the respective Schiff base. MoOL · AA-type complexes were prepared by the reaction of MoO_2L with the respective bidentate ligand in the presence of $PEtPh_2$. MoO(sal–ATP) · bipy has also been prepared by the reaction of $MoOCl_2$(bipy)($PMePh_2$) and H_2sal–ATP in the presence of triethylamine in acetonitrile. All the complexes exhibit a sharp band in the region 920–960 cm^{-1} due to ν(Mo=O). It is interesting to note that the ν(Mo=O) frequency occurs at a higher energy in five-coordinate molybdenum(IV) complexes, MoOL · DMF, than in the corresponding six-coordinate molybdenum(V) complexes, $[Et_4N][MoOCl_2L]$ (see text). However, the substitution of DMF by the bidentate ligands shifts the ν(Mo=O) to lower energy. Boyd and Spence believe that this anomalous result may be due to a difference in structure [84]. The cyclic voltammograms of these complexes have been recorded in DMF using $[Et_4N]Cl$ as supporting electrolyte [84]. Electrochemical data are presented in Table 10. The cyclic voltammogram of MoOL · DMF exhibits oxidation and reduction peaks at essentially the same potentials observed in $[Et_4N][MoOCl_2L]$ (LH_2 = H_2sal–AP and H_2sal–ATP). The species formed by the one-electron reduction is attributed to molybdenum(III), which is the same species obtained by the two-electron reduction of molybdenum(V) complexes, $[Et_4N][MoOCl_2L]$. The results indicate that the complexes MoOL · DMF are electrochemically oxidized to $[Et_4N][MoOCl_2L]$ in the presence of $[Et_4N]Cl$. Similarly MoOL · AA complexes are oxidized to $[MoOCl_2L]^-$ on the coulometric time scale according to the equation

$$\text{MoOL}\cdot\text{AA} + 2\text{Cl}^- = [\text{MoOCl}_2\text{L}]^- + \text{AA} + \text{e}^- \qquad (7)$$

Molybdenum(IV) complexes were formed during the electrochemical reduction of oxomolybdenum(V) complexes, MoOCl(salphen) and $(C_2H_5)_4NMoOCl_2$(sal–AP) [71]. Although solid complexes of molybdenum (IV) have not been isolated, Taylor et al. believe that the products are pentacoordinate oxo complexes. The molybdenum(IV) species have distinc-

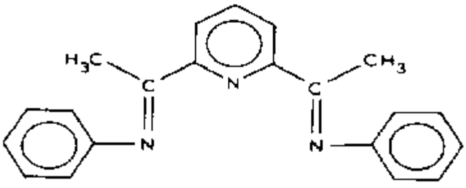
TABLE 10

Spectral and electrochemical data for some oxomolybdenum(IV) complexes [84]

Complex	ν(Mo=O) (cm^{-1})	E_{pa} [ab] (V) (oxidation)	n	E_{pc} [a] (V) (reduction)	n
MoO(sal–AP)·DMF	950	−0.17	1.05	−1.17 (−0.86)	0.96
MoO(sal–AP)·ophen	929	−0.13 (−1.15)	0.73	−1.29 (−1.19)	1.07
MoO(sal–ATP)·DMF	957	+0.11	0.81	−0.96 (−0.41)	0.97
MoO(sal–ATP)·ophen	923	+0.11 (−0.93)	0.79	−1.36 (−0.51)	
MoO(sal–ATP)·bipy	921	+0.06 (−0.97)	0.98	−1.32 (−0.48)	0.99

[a] Values in parentheses are coupled oxidation peaks observed with complete CVA cycle.
[b] In DMF solution.

tive electronic spectra which differ from those of the original molybdenum(V) complexes. The molybdenum(IV) products are sensitive to traces of oxygen or water and are instantly oxidized to the parent complex when they come in contact with air. They slowly undergo oxidation to molybdenum(V) on standing for prolonged periods in DMF under nitrogen [71].



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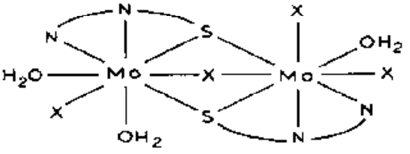
The Schiff base (**78**) derived from 2,6-diacetylpyridine and aniline reactions with $MoX_3 \cdot 3H_2O$ (X = Cl, Br) to form blue-indigo, air sensitive complexes of the type $MoOLX_2$ (where L = Schiff base and X = Cl or Br) in which the Schiff base behaves as a tridentate neutral NNN donor ligand [85]. $MoOLCl_2$ is isomorphous with the corresponding oxovanadium(IV) complexes $VOLCl_2$. The complexes exhibit magnetic moment values in the range 0.7–0.8 BM at 298 K, which has been attributed to temperature-independent paramagnetism. Although the molecular weights have not been reported, the complexes were considered monometallic on the basis of the close resemblance between the diffraction powder patterns of $MoOLCl_2$ and $VOLCl_2$, the latter being a monomer in dichloromethane. In the absence of a dimetallic oxygen-bridged structure, the complexes have been regarded as octahedral low spin d^2 complexes. The low spin nature of the complexes is indicative of very significant distortion from octahedral symmetry towards pentacoordination and X-ray structural proof has not been obtained. The complexes exhibit three electronic spectral bands in the range 8000–8300 cm^{-1} (*d–d*) (ϵ = 700–790 l mol^{-1} cm^{-1}), 16130–16800 cm^{-1} (ϵ = 5770–6450 l mol^{-1} cm^{-1}) and 27500–28500 cm^{-1} (CT) (ϵ = 7700–8100 l mol^{-1} cm^{-1}). ν(M–O) occurs at 950 cm^{-1} [85].

E. MOLYBDENUM(III) COMPLEXES

The reaction of hexacarbonyl molybdenum(0) with *N*-methylsalicylideneimine results in the displacement of all the carbonyl groups and the synthesis of the red-brown tris(*N*-methylsalicylideneiminato)molybdenum (III) [86]. The complex is sensitive to air and soluble in toluene. The complex absorbs oxygen in toluene yielding a violet solution. The complex does not show any band at ca. 2200 cm^{-1} due to the carbonyl groups. The magnetic moment of the octahedral complex is 3.71 BM at 295 K which is slightly lower than the spin-only value of 3.88 BM expected for a d^3 system. The dark brown octahedral complex MoO(LH)L (where LH_2 = Schiff base derived from salicylaldehyde and thiosemicarbazide) was prepared by the reaction of ammonium hexathiocyanato molybdate(III) and the Schiff base [87]. The electronic spectrum is mainly dominated by two absorption maxima at 20 408 and 23 810 cm^{-1} due to the $^4A_{2g} \rightarrow {}^4T_{2g}$ and $^4A_{2g} \rightarrow {}^4T_{1g}$ transitions respectively. IR data indicate that the ligand is coordinated through phenolic oxygen, azomethine nitrogen and sulphur atoms.

The Schiff base ligand **3** produced from pyridine-2-aldehyde and *ortho*-aminothiol forms dark brown complexes of the form $MoLX_2 \cdot H_2O$ (where LH = Schiff base **3**; X = Cl, Br) which have been prepared starting from lithium hexachloromolybdate(III) enneahydrate. The complexes exhibit low magnetic moments (0.7–1.2 BM) [88] due to antiferromagnetic exchange. A dimetallic structure (**79**) involving thiol and halide bridges has been tentatively suggested but single-crystal X-ray structure determinations have not been reported. The bromo complexes are less stable than the chloro complexes and this has been attributed to the difference in polarizabilities of Cl and Br. The complexes are eight coordinate.



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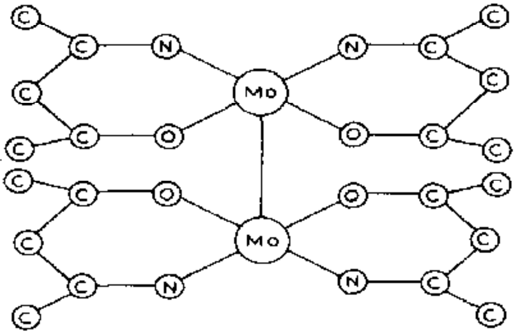
X = Cl, Br

F. MOLYBDENUM(II) COMPLEXES

A red dimeric Schiff base complex containing an Mo–Mo quadrupole bond which is not supported by any bridging ligand was prepared by the reduction of dichloro-*N*,*N*′-ethylenebis(acetylacetoneiminato)molybdenum (IV) with sodium in the presence of diphenylacetylene [89]. The red complex has the formula $[Mo(acacen)]_2$ and is diamagnetic with a tightly bound Mo_2^{4+} unit. Four bonds, viz. one σ bond, one δ bond and two π bonds, are expected from eight electrons involved in the Mo–Mo bonding. The quadrupole bond is in excellent agreement with the very short Mo–Mo bond length of 2.1678 Å present in the complex. The complex is very sensitive to air in solution but is moderately stable to air in the solid state. The structure of $[Mo(acacen)]_2$ was solved by Pennesi et al. [89] and the result is shown in **80**; acacen behaves as a quadridentate ligand and the coordination geometry is roughly square pyramidal. The N_2O_2 donor sets are planar and molybdenum is out of plane by 0.469 Å. The two Mo(acacen) units are bent away from the Mo–Mo fragment, adopting an umbrella conformation. The two ligands (acacen) are in an eclipsed conformation. The Mo–O and M–N



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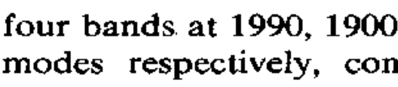
distances are 2.089 Å and 2.116 Å respectively. These distances are significantly longer than those in the corresponding molybdenum(IV) complexes, $[\{Mo(acacen)Cl\}_2(\mu\text{-}O)]$ (Mo–O, 2.026 Å; Mo–N, 2.089 Å) and $[Mo(acacen)Cl_2]$ (Mo–O, 1.988 Å; Mo–N, 2.074 Å) [89].

G. CARBONYL AND ORGANOMOLYBDENUM COMPLEXES

Molybdenum(0) carbonyl complexes of the type $Mo(CO)_4L$ (L = **81**) have been synthesized by the reaction of hexacarbonyl molybdenum(0) with the bidentate ligand **81** (R = C_6H_5, *o*-C_6H_4OH, C_4H_3O; R′ = H, CH_3) [90]. The diamagnetic very soluble complexes are not stable in air. The presence of

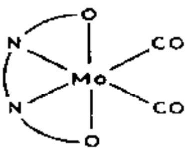


81

$R = C_6H_5$, *o*-C_6H_4OH, C_4H_3O
$R' = H, CH_3$

four bands at 1990, 1900, 1850 and 1800 cm^{-1}, due to $A_1^{(1)}$, B_1, $A_1^{(2)}$ and B_2 modes respectively, confirms the C_{2v} symmetry of the molecules. The stretching force constants for the CO groups *trans* and *cis* to the thio Schiff bases, i.e. k_1 and k_2 and the CO–CO interaction constant, k_i lie in the ranges 13.30–13.90 mdynes Å^{-1}, 15.0–15.20 mdynes Å^{-1} and 0.30–0.40 mdynes Å^{-1} respectively [90].

The treatment of hexacarbonyl molybdenum(0) with tetradentate Schiff bases H_2salen and H_2saltrien produces complexes of the type $[Mo(CO)_2L'] \cdot X$HCl (where $L'H_2$ = hydrogenated Schiff base; $X = 0$ or 1) in which azomethine groups are hydrogenated [91]. During the reaction the zerovalent molybdenum acts as a catalyst and activates the hydrogen atom removed from –OH (of salen) for transfer towards carbon or nitrogen leading to hydrogenation and subsequent coordination. The complex obtained from



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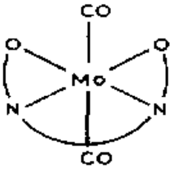

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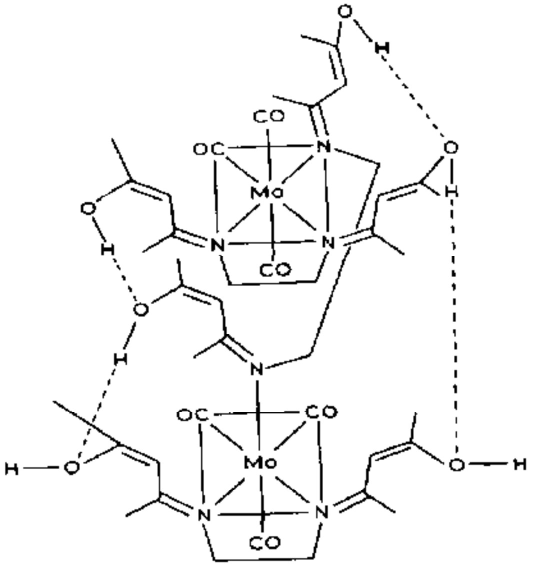
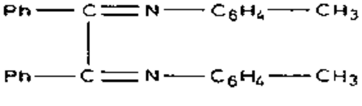
salen is a mixture of *cis* and *trans* complexes (**82** and **83**). Mo(CO)$_2$(hydrogenated saltrien) has the *cis* structure (**83**). Van Den Bergen et al. [77] have claimed the formation of MoO(salen) when hexacarbonyl molybdenum(0) reacts with H$_2$salen in DMF. The reaction of Mo(CO)$_6$ with H$_2$acacen yields [Mo$_2$(CO)$_6$(acacen)] (**84**) [91] in which H$_2$acacen coordinates only through the azomethine nitrogen atoms and behaves as a bidentate neutral ligand.



84

The reactions of Schiff bases *N*,*N*′-ethylenebisbenzalideneimine, *N*,*N*′-ethylenebis(*p*-anisideneimine), *N*,*N*′-ethylenebis(methylphenylketeimine) and *N*,*N*′-ethylenebis(diphenylketeimine) with molybdenum hexacarbonyl lead to the synthesis of *cis*-[Mo(LL)(CO)$_4$] (where LL = Schiff base) [92]. The reaction of the bidentate ligand ophen or bipy with *cis*-[MoLL(CO)$_4$] leads to the expulsion of the Schiff base from the coordination zone, and as a result complexes of the type [Mo(AA)(CO)$_4$] (where AA = ophen or bipy) are formed. Ph$_3$P and Ph$_3$As displace LL easily from *cis*-[Mo(LL)(CO)$_4$] to give *cis*-[Mo(Ph$_3$P/Ph$_3$As)$_2$(CO)$_4$]. These ligand exchange reactions are indicative of the reduced donor ability of LL in comparison with AA, Ph$_3$P and Ph_3As. Bromination and iodination of six-coordinate *cis*-$[Mo(LL)(CO)_4]$ at 25 °C gives seven-coordinate complexes of the type $[Mo(LL)(CO)_3X_2]$ (where X = Br or I). Nitric oxide reacts with *cis*-$[Mo(LL)(CO)_4]$ at room temperature in benzene to give a mixture of $[Mo(LL)(NO)_2(NO_2)_2]$ and $[Mo(LL)(CO)_2(NO)(NO_2)]$; the former is insoluble in benzene and the latter soluble. The reactions of $Mo(Ph_3E)(CO)_5$ (where E = P or As) with *N,N′*-ethylenebis(*p*-anisylideneimine) or *N,N′*-ethylenebis(diphenylketeimine) produces a dimetallic complex $(CO)_4(Ph_3E)Mo$-μ-$(LL)Mo(Ph_3E)(CO)_4$ [92].

The sodium salt of the Schiff base benzil-1,4′-dimethyldianil (**85**) reacts



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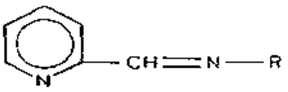

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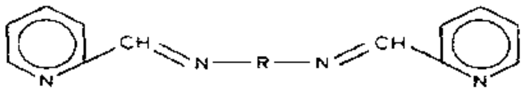
$R = CH_3, C_2H_5, C_6H_{17}, C_{10}H_7, C_6H_5, C_6H_5CH_3$

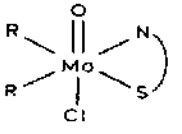


87

$R = CH_3, C_2H_5, C_6H_{17}, C_6H_5$

with molybdenum hexacarbonyl in THF to give $Na_2[Mo(CO)_4L]$ (where L = **85**) which on washing with *n*-hexane is converted to $Mo(CO)_4LH_2$. The latter complex is diamagnetic and monomeric in benzene. $Mo(CO)_4LH_2$ exhibits two electronic spectral bands at 370 nm ($\epsilon = 5927$ l mol^{-1} cm^{-1}) (*d–d*) and 579 nm ($\epsilon = 15\,805$ l mol^{-1} cm^{-1}) (CT) [93]. The present reviewers feel that the origin of both these bands is charge transfer due to their high molar extinction coefficients. Several monometallic and bimetallic molybdenum(0) carbonyl complexes with bidentate and tetradentate Schiff bases (**86** and **87**) have been synthesized by Walther [94] using $Mo(CO)_6$ as starting material. The complexes are of the types $Mo(CO)_4L$, $Mo(Ph_3P)(CO)_3L'Mo(Ph_3P)(CO)_3$ and $Mo(CO)_4L'Mo(CO)_4$ (where L = **86**, L′ = **87**). $Mo(CO)_4L$ reacts with PX_3 to give complexes of the type $Mo(CO)_3(PX_3)L$ (where X = C_6H_5, C_6H_{11}, C_4H_9, or C_2H_5O). These complexes exhibit strong negative solvatochromic effects in organic solutions and in polymers [94].

Bis π-cyclopentadienyl dichlorooxomolybdenum(VI) and bis π-indenyldichlorooxomolybdenum(VI) react with LH (LH = **81**; R = C_6H_5; R′ = H, CH_3, C_6H_5) and L′H (L′H = **81**; R = *o*-C_6H_4OH, *o*-$C_{10}H_6OH$; R′ = H, CH_3) in dry benzene to produce diamagnetic complexes of the formula $R_2MoOClL$ and R_2MoOL' (R = π-C_5H_5, π-C_9H_7) in which the ligands behave as if they were monobasic bidentate and dibasic tridentate respectively [95]. The presence of a sharp band at ca. 980 cm^{-1} confirms the presence of the Mo=O group. The complexes $R_2MoOClL$ and R_2MoOL' have been assigned structures **88** and **89**, respectively ($R = \pi$-C_5H_5) [95].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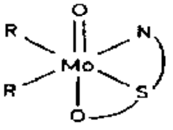
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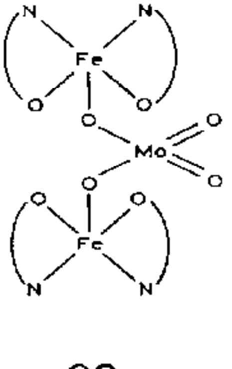
H. HETEROMETALLIC COMPLEXES

The molybdate-bridged iron(III) complexes of Schiff bases **36** (X = Y = H; R = $(CH_2)_2$, $(CH_2)_2NH(CH_2)_2$, *o*-C_6H_4) have been synthesized by adding an aqueous solution of sodium molybdate to the methanol–water solution of the corresponding iron(III) oxo-bridged Schiff base complex (**36**; X = Y = H; R = $(CH_2)_2$) [96]. The complexes are of the types $[Fe(salen)]_2MoO_4$ (**90**), $[Fe(salen)]_2Mo_2O_7$ (**91**), $[Fe(salphen)]_2Mo_2O_7$ (**91**) and $[Fe(saliden)]_2MoO_4$ (**92**). In the case of salphen, the complex MoO_2(salphen) is also formed along with $[Fe(salphen)]_2Mo_2O_7$ under the reaction conditions. Qian et al. [97] also reported the synthesis of the complex $[FeL]_2MoO_4$ (LH_2 = **36**; X = 5,6-C_4H_4; Y = H; R = $(CH_2)_2$). The presence of four new bands in $[Fe(salen)]_2MoO_4$ and $[Fe(saliden)]_2MoO_4$ in the 790–900 cm^{-1} region due to ν(Mo=O) (ν_1, ν_2, ν_6 and ν_8) identify the presence of bridging through two oxygen atoms as only three bands (due to ν_1, ν_2 and ν_4) are expected when molybdenum is involved in bridging through one oxygen atom. The magnetic moment values of all the complexes except $[Fe(salen)]_2Mo_2O_7$ are in the range 5.60–5.90 BM and correspond to high spin iron(III) ($S = 5/2$).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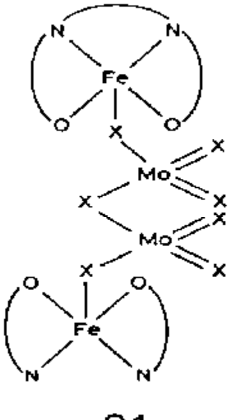
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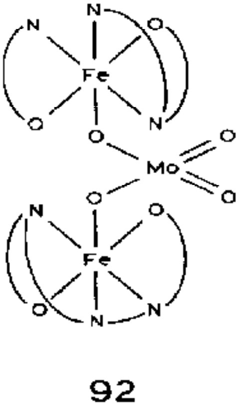
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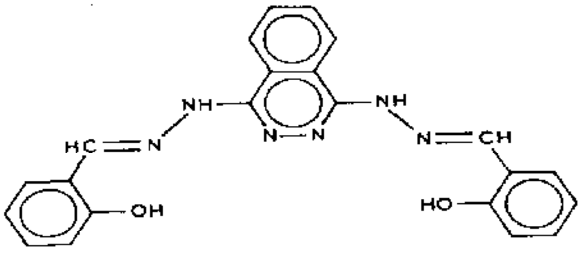
$[Fe(salen)]_2Mo_2O_7$ shows a magnetic moment of 4.50 BM corresponding to $S = 3/2$ and the moment decreases slowly with decrease in temperature owing to antiferromagnetic interaction. The Mössbauer spectrum of $[Fe(salen)]_2Mo_2O_7$ is significantly different from the spectra of the other complexes. A shoulder at ca. 0.48 mm s^{-1} on the main absorption peak relative to pure iron for the complex $[Fe(salen)]_2Mo_2O_7$ supports the presence of the $S = 3/2$ spin state in the complex while in the other complexes the values are observed in the range 0.3–0.4 mm s^{-1}, characteristic of the $S = 5/2$ spin state [97].

Pentachloromolybdenum(V) reacts with $[Fe(salen)]_2O$ and produces $\{[Fe(salen)]_2O(MoOCl_3)_2\}$ in which the molybdenum of the $MoOCl_3$ units are coordinated to the oxygen atoms of salen [98]. The complex shows a sharp band at 856 cm^{-1} due to $\nu(Mo{=}O)$ of $MoOCl_3$. The observed magnetic moment value of 6.50 BM is higher than the expected value of 5.26 BM and this was explained in terms of an increase in bond distances between Fe–O–Fe resulting in the reduction of the paramagnetic interaction between the two iron(III) ions. A polarographic study of $\{[Fe(salen)]_2O(MoOCl_3)_2\}$ in DMF indicates that the two metal reduction waves of $[Fe(salen)]_2O$ shift to more negative potentials in $\{[Fe(salen)]_2O(MoOCl_3)_2\}$. The first wave potential shifts from -0.69 to -0.98 V and the second from -1.28 to -1.38 V. This is expected due to the delocalization of electrons towards the iron(III) centres in the adduct.

I. MISCELLANEOUS MOLYBDENUM COMPLEXES

The potential hexadentate N_4O_2 ligand **93** on reaction with $MoO_2(acac)_2$ in ethanol produces $MoO_2L(H_2O) \cdot 2H_2O$ in which the ligand is coordinated through only two nitrogen atoms and one oxygen atom as shown in structure **94** [99]. Attempts to introduce another molybdenum ion of oxidation state six in **94** were unsuccessful. The reaction of the complex with $(NH_4)_2[MoOCl_5]$ leads to the formation of a molybdenum(V) complex $MoO(LH)Cl_2$ (where $LH_2 = \mathbf{93}$) by completely knocking out the MoO_2 species. The complex $[MoO_2L(H_2O)] \cdot 2H_2O$ reacts easily with other metal



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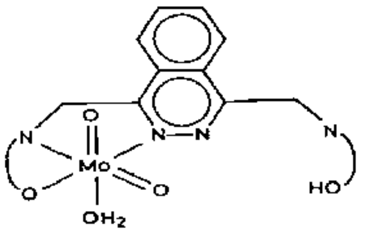

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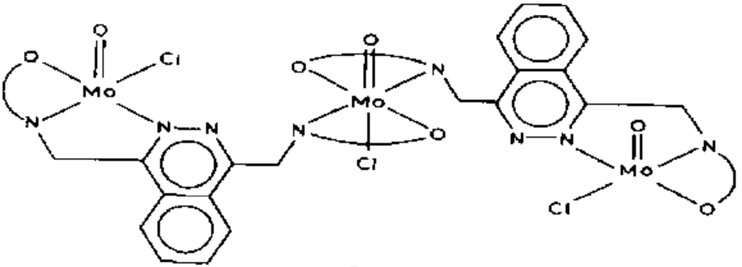
ions such as iron or copper to give the corresponding heterobinuclear compounds. $[MoO_2L(H_2O)] \cdot 2H_2O$ loses all three water molecules on heating at 85 °C under vacuum and is converted to air-stable MoO_2L under vacuum. Recrystallization from acetone yields $[MoO_2L \cdot H_2O] \cdot CH_3COCH_3$ whose X-ray structure shows the presence of a *cis*-$[MoO_2]^{2+}$ group and a distorted octahedral structure. The bond distances within the MoO_2 group are 1.700 and 1.694 Å. The other bond distances are as follows: Mo–N(azomethine), 2.237 Å; Mo–N(ring), 2.079 Å and Mo–O(water), 2.366 Å. These molybdenum(VI) complexes are diamagnetic and exhibit two charge transfer bands in the regions 16100–18200 and 27000–27400 cm^{-1}. LH_2 (LH_2 = **93**) reacts with $(NH_4)_2[MoOCl_5]$ in ethanol in the presence of lithium metal to produce a mixed-valence complex $[Mo^VOCl(Mo^{IV}OLCl)_2]$ (**95**). The complex exhibits $\nu(Mo^V{-}O)$ at 970 cm^{-1} and $\nu(Mo^{IV}{-}O)$ at 946 cm^{-1} [99]. The reduction of this compound with thiophenol gives the binuclear molybdenum(IV) complex $[Mo_2O_2L(OEt)Cl]$ a bimetallic structure with a bridging ethoxide group. The complex exhibits $\nu(Mo{-}O)$ at 946 cm^{-1} and $\nu_{as}(MoOEtMo)$ at 620 cm^{-1}, with a magnetic moment of 0.48 BM due to temperature-independent paramagnetism, and is a low spin complex. The low spin nature is indicative of very significant distortion from octahedral symmetry towards pentacoordination and X-ray structural proof is missing. $[MoO(LH)Cl_2]$ and $[Mo^VOCl(Mo^{IV}OLCl)_2]$ exhibit magnetic moments of 1.64 and 1.01 BM respectively. The ESR spectrum of $[Mo^VOCl(Mo^{IV}OLCl)_2]$



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(**95**) is identical to that of the mononuclear molybdenum(V) complex $[MoO(LH)Cl_2]$, suggesting that the two molybdenum(IV) ions in **95** are present in similar environments and are not involved in a magnetic exchange interaction. An X-ray photoelectron study confirms the presence of localized oxidation states IV and V in $[Mo^VOCl(Mo^{IV}OLCl)_2]$.

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