ca. 49 Hz; $^3J(^{119}Sn^1H)$ = *ca.* 14 Hz. (0.1 M/C_6D_6; 270 MHz): 0.256 ppm; $<^2J>$ = 44 Hz; $<^3J>$ = 17.6 Hz; 1.261 and 1.253 ppm; 1.947 and 1.885 ppm; $^2J(^1H^1H)$ = 12.7 Hz; 70 eV monoisotopic mass spectrum: 696, 0.5, $Ph_4Me(PhMe_2CCH_2)$-Sn_2; 345, 27, $PhMe(PhMe_2CCH_2)Sn$; 197, 23.4, PhSn.

Reaction of (6) with LiEt₃BH

Reaction of (6) with LiEt₃BH

A 1 M solution LiEt₃BH in THF (2.2 cm³) was added drop-wise to *(6)* (1.40 g, 2 mmole) in THF (10 cm³). After 2 h, the reaction mixture was hydrolyzed with wet Et₂O. A brown precipitate appeared: $[Ph_3P(CO)_3Co]_2$. T.l.c. (SiO₂; 1:4 PhH:p.e.) showed an important spot at R_F = 0.65 which turned brown with AgNO₃, and a small spot at R_F = 0.30 [starting product *(6)*]. No Ph₂MeSnH could be detected in the reaction mixture. The raw product was chromatographed on SiO₂ (elution with 1:2 PhH:p.e.) yielding $(Ph_2MeSn)_2$ (0.45 g, 78%), mp 94–96° (recryst. p.e. 40°); ¹H n.m.r. (0.3 M/C_6D_6): δ(MeSn): 0.67 ppm; $^2J(^{119}Sn^1H)$ = 50 Hz; $<^2J(SnH)>$ = 14.5 Hz; H_{ortho} = 7.6 ppm; $<^3J(SnH)>$ = 46 Hz; $H_{meta} + H_{para}$ = *ca.* 7.2 ppm; 80 eV monoisotopic mass spectrum: 578, 4.1, $(Ph_2MeSn)_2$; 563, 64.1, $Ph_2MeSnSnPh_2$; 351, 59.7, Ph_3Sn; 289, 100, Ph_2MeSn; 212, 97.6, PhMeSn; 197, 97.6, PhSn; 120, 41.4, Sn.

Acknowledgements

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Oxocation Complexes, Part X*. Oxomolybdenum(V) and Dioxomolybdenum(VI) Complexes with Tri- and Tetra-dentate Schiff Bases

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Summary

Many new oxomolybdenum(V) and dioxomolybdenum(VI) complexes have been synthesized with tri- and tetradentate Schiff bases derived by the condensation of salicylaldehyde, thiosalicylaldehyde, *o*-hydroxyacetophenone, 3-carboxy-salicyclaldehyde or acetylacetone with aminoalcohols, polymethylenediamines and *o*-phenylenediamines. Mononuclear oxothiolato Schiff base complexes of molybdenum(V) have been prepared for the first time. Quadridentate Schiff bases derived from salicylaldehyde and substituted salicylaldehydes and *o*-phenylenediamine have also been successfully employed

to isolate dioxomolybdenum(VI) complexes in the solid state, in which two oxygen atoms of the MoO₂ group are *cis*- to each other, similar to the situation observed for other dioxomolybdenum(VI) complexes of salicylaldehyde-polymethylene-diamine Schiff base ligands.

Structures have been determined with the help of elemental analyses, magnetic susceptibilities, molar conductances, i.r., electronic and ¹H n.m.r. spectral data.

Introduction

Despite extensive work on first-row transition metal complexes with Schiff bases[1], there seems to be remarkably little work on the molybdenum complexes with this class of ligands[2].


Recently much attention has been focussed on the molybdenum chelates, since many molybdenum(IV) and molybdenum(V) complexes have been found to act as simple models for biochemical redox[3] and in nitrogenase enzymes[4].

Work in our laboratory has shown that bi-, tri-, and tetradentate Schiff bases having O, N, S donor atoms can form complexes with molybdenum in oxidation states (III) to (VI)[5]. This report details our work on the molybdenum (V and VI) complexes with tri- and tetra-dentate Schiff bases. We also include the synthesis of mononuclear oxothiolato Schiff base complexes of molybdenum(V) for the first time. While our work was in progress, some studies in this area have been published[6], but the Schiff base ligands, excepting those shown in Figures 3 and 4 (but not all types) employed by us have never been used for the syntheses of oxomolybdenum complexes. Well characterized oxomolybdenum(V) compounds containing "biologically relevant" ligands are invariably binuclear[7] species and contain the μ-oxo-$[Mo_2O_3]^{4+}$ or bis-μ-oxo-$[Mo_2O_4]^{4+}$ structural units. In this respect our isolation of mononuclear oxothiolato Schiff base complexes of molybdenum(V) is significant. Very recently Boyd, et al.[8] have characterised mononuclear arylthiolato anions $[MoO(SAr)_4]^-$.
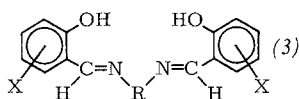
The following abbreviations have been used for the Schiff base ligands employed in the present investigation:
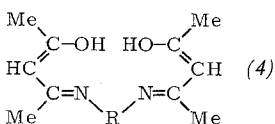

(1)
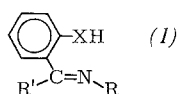
(1 a)	R = o-C$_6$H$_4$OH;	R' = H;	X = O	(SOAP-H$_2$)
(1 b)	R = CH$_2$CH$_2$OH;	R' = H;	X = O	(SALENA-H$_2$)
(1 c)	R = o-C$_6$H$_4$OH;	R' = Me;	X = O	(HAOAP-H$_2$)
(1 d)	R = o-C$_6$H$_4$OH;	R' = H;	X = S	(SOATP-H$_2$)

(2)
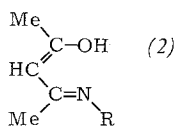
| (2 a) | R = o-C$_6$H$_4$OH | | (ACOAP-H$_2$) |

(3)

(3 a)	X = H;	R = -(CH$_2$)$_2$	(BSEN-H$_2$)
(3 b)	X = H;	R = -(CH$_2$)$_3$	(BSTN-H$_2$)
(3 c)	X = H;	R = -CH$_2$CH(OH)CH$_2$	(BSDA-H$_2$)
(3 d)	X = H;	R = o-C$_6$H$_4$	(BSOP-H$_2$)
(3 e)	X = 3-Me;	R = -(CH$_2$)$_2$	(BMSEN-H$_2$)
(3 f)	X = 3-Me;	R = -(CH$_2$)$_3$	(BMSTN-H$_2$)
(3 g)	X = 3-Me;	R = o-C$_6$H$_4$	(BMSOP-H$_2$)
(3 h)	X = 3-CO$_2$H;	R = -(CH$_2$)$_2$	(BCSEN-H$_4$)
(3 i)	X = 3-CO$_2$H;	R = -(CH$_2$)$_3$	(BCSTN-H$_4$)
(3 j)	X = 3-CO$_2$H;	R = o-C$_6$H$_4$	(BCSOP-H$_4$)

(4)

| (4 a) | R = -(CH$_2$)$_2$ | (BAEN-H$_2$) |
| (4 b) | R = o-C$_6$H$_4$ | (BAOP-H$_2$) |

Experimental

Elemental analyses of Mo, N, S and halides were carried out in our laboratory by conventional methods. C and H microanalyses were made by the C.D.R.I., Lucknow, India and i.r. spectra (KBr phase) were recorded by the same Institute. Conductances were measured with a Mullard conductivity bridge. Electronic spectra were recorded on a Beckman Du-2 or Spectromom spectrophotometers. Magnetic susceptibilities were recorded in a Gouy balance. Solvents and Chemicals were purified and dried by usual procedures.

Oxomolybdenum (V and IV) complexes were prepared in a N_2 atmosphere.

Schiff base ligands were prepared by condensing carbonyl compounds with stoichiometric quantities of amines in the usual way.

Starting materials

Bis(acetylacetonato)dioxomolybdenum(VI), MoO$_2$-(acac)$_2$[9], ammonium oxopentachloromolybdenum(V), (NH$_4$)$_2$[MoOCl$_5$][10], pyridinium hexathiocyanatomolybdenum(IV), (PyH)$_2$[Mo(NCS)$_6$][11] and trichlorooxobis(tetrahydrofuran)molybdenum(V), MoOCl$_3$(THF)$_3$[12] were prepared by literature methods.

Preparation of the complexes

Dioxomolybdenum(VI) complexes with tridentate Schiff bases

A solution of Na$_2$MoO$_4$ · 2H$_2$O (0.01 mol) in EtOH (25 cm^3) was mixed with a solution of the Schiff base(s) (0.01 mol) in the same solvent (25 cm^3). The pH of the solution was adjusted to ca. 6 with dilute HCl and the mixture was heated under reflux for 1 h on a steam bath. The crystalline product, obtained on cooling, was filtered off, washed with EtOH and dried in vacuo.

Oxomolybdenum(V) complexes with tridentate Schiff bases

Interaction of EtOH : MeOH solutions of (NH$_4$)$_2$(MoCl$_5$) or (PyH)$_2$Mo(SCN)$_6$ (1 mol) with respective Schiff bases (3 mols) at room temperature yielded these complexes. The precipitated complexes were filtered off, washed with EtOH and dried in vacuo.

Dioxomolybdenum(VI) complexes with tetradentate Schiff bases

An equimolar mixture of MoO$_2$(acac)$_2$ and the Schiff was taken in the mixed 1 : 1 MeOH : THF solvent and boiled under reflux for 3–4 h. The complexes thus obtained was washed with the MeOH : THF mixture and dried in vacuo. A mixed DMF : MeOH solvent system was found to be ideal for isolating complexes with the ligands (3b), (3f) and (3i).

Oxo(chloro)molybdenum(V) derivatives, [ClMoO(TSB)]

Reaction of an equimolar mixture of the ligands (3a) to (3g) with MoOCl$_3$(THF)$_3$ in MeCN in the presence of an excess of Et$_3$N yielded a brown solution which, upon concentration and

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* TSBH$_2$ = dibasic tetradentate Schiff base

chilling, gave a brown powder which was washed with a mixture of MeOH : MeCN and dried in *vacuo*.

Oxo(thiolato)molybdenum(V) derivatives, [MoO(SR)(TSB)] (R = Ph or p-tolyl)

A mixture of [ClMoO(TSB)] (1 mol), RSH (1 mol) and Et$_3$N (1 mol) in MeCN was stirred for 3 h and filtered. The filtrate gave bluish crystalline complexes which were washed with a MeOH : MeCN mixture and dried in *vacuo*.

Results and Discussion

Several oxomolybdenum(V) and dioxomolybdenum(VI) complexes containing different types of tri- and tetradentate Schiff base ligands have been isolated in the solid state and characterized (Tables 1 to 3).

All the molybdenum complexes described in the experimental are new, with the exception of MoO$_2$(BSEN), MoO$_2$(BSTN) and MoO$_2$(BSOP), which were synthesized previously[2d]. The present molybdenum complexes are coloured and stable in air and elemental analyses support their formulations.

As expected, all the dioxomolybdenum(VI) complexes are diamagnetic, while all the oxomolybdenum(V) compexes are paramagnetic with the magnetic moments in the 1.66 to 1.82 B.M. range (room temp.), which indicate that there are no significant interactions between neighbouring oxomolyb-

Table 3. Elemental analyses of some oxomolybdenum(V) complexes of tetradentate Schiff bases.

Complex	Found (Calcd.)%				
	C	H	N	Cl/S	Mo
ClMoO(BSEN)	46.2	3.8	6.9	8.0	23.7
	(46.4)	(3.4)	(6.7)	(8.6)	(23.2)
ClMoO(BSTN)	47.8	3.7	6.5	8.8	22.7
	(47.7)	(3.7)	(6.5)	(8.3)	(22.4)
ClMoO(BSDA)	45.9	3.5	6.6	8.1	21.4
	(46.0)	(3.6)	(6.3)	(8.0)	(21.6)
ClMoO(BSOP)	52.0	3.2	6.2	7.8	20.7
	(52.0)	(3.0)	(6.1)	(7.7)	(20.8)
ClMoO(BMSEN)	49.0	4.1	9.3	8.0	21.8
	(48.9)	(4.1)	(9.0)	(8.0)	(21.7
ClMoO(BMSTN)	50.6	4.4	6.1	7.6	21.1
	(50.0)	(4.4)	(6.1)	(7.8)	(21.1)
ClMoO(BMSOP)	54.0	3.7	5.7	7.3	19.8
	(53.9)	(3.7)	(5.7)	(7.2)	(19.6)
MoO(SC$_6$H$_5$)(BSEN)	54.8	4.0	5.7	6.6	19.9
	(54.2)	(3.9)	(5.7)	(6.6)	(19.7)
MoO(SC$_6$H$_5$)(BSTN)	55.4	4.4	5.8	6.0	19.7
	(55.1)	(4.2)	(5.6)	(6.4)	(19.2)
MoO(SC$_6$H$_5$)(BSOP)	58.8	3.6	5.7	6.0	18.0
	(58.3)	(3.5)	(5.2)	(6.0)	(17.9)
MoO(SC$_6$H$_4$Me-*p*)-(BSEN)	54.9	4.3	5.6	6.7	19.0
	(55.1)	(4.2)	(5.6)	(6.4)	(19.2)
MoO(SC$_6$H$_4$Me-*p*)-(BSOP)	59.1	3.9	5.7	6.0	17.7
	(59.0)	(3.8)	(5.1)	(5.8)	(17.5)

Table 1. Elemental analyses, colours and m.p's of some dioxomolybdenum(VI) complexes with tri- and tetra-dentate Schiff bases.

Complex	Colour	M.p. (dec.) (°)	Found (Calcd.)%			
			C	H	N	Mo
MoO$_2$(SOAP) H$_2$O	white	–	43.5(43.7)	3.0(3.1)	3.8(3.9)	27.0(26.9)
MoO$_2$(SALENA) H$_2$O	grey white	–	34.8(34.9)	3.5(3.6)	4.4(4.5)	31.0(31.1)
MoO$_2$(HAOAP) H$_2$O	grey	–	45.2(45.3)	3.5(3.5)	3.5(3.8)	25.9(25.9)
MoO$_2$(ACOAP) H$_2$O	white	–	39.3(39.4)	3.8(3.9)	4.0(4.2)	28.8(28.7)
MoO$_2$(SOATP) H$_2$O[a]	white	–	41.7(41.8)	2.9(2.9)	3.5(3.7)	25.9(25.7)
MoO$_2$(BSEN)	yellow	250–252	48.5(48.7)	3.5(3.5)	7.0(7.1)	24.2(24.4)
MoO$_2$(BSTN)	yellow orange	262–264	49.8(50.0)	3.9(3.9)	6.6(6.9)	23.2(23.5)
MoO$_2$(BSDA)	light brown	275–276	48.0(48.1)	3.7(3.8)	6.3(6.6)	22.9(22.6)
MoO$_2$(BSOP)	brown	265–267	54.1(54.3)	3.2(3.2)	6.1(6.3)	21.3(21.7)
MoO$_2$(BMSEN)	light yellow	268–270	51.1(51.2)	4.2(4.3)	6.3(6.6)	23.0(22.8)
MoO$_2$(BMSTN)	yellow orange	255–256	52.2(52.3)	4.5(4.6)	6.2(6.4)	22.0(22.0)
MoO$_2$(BMSOP)	light brown	269	56.6(56.2)	3.8(3.8)	5.7(5.9)	20.1(20.4)
MoO$_2$(BCSEN-H$_2$)	yellow orange	275–277	44.7(44.8)	2.9(2.9)	5.5(5.8)	19.5(19.9)
MoO$_2$(BCSTN-H$_2$)	orange	258–260	45.8(45.9)	3.2(3.2)	5.3(5.6)	19.7(19.3)
MoO$_2$(BCSOP-H$_2$)	brown	265–266	49.6(49.8)	2.6(2.6)	5.0(5.3)	18.0(18.1)
MoO$_2$(BAEN)	pale yellow	272–274	41.0(41.1)	5.1(5.1)	7.9(8.0)	27.9(27.4)
MoO$_2$(BAOP)	light brown	267–268	48.1(48.2)	4.5(4.5)	7.2(7.0)	24.0(24.1)

[a] Satisfactory S analysis was obtained.

Table 2. Elemental analyses, colours and magnetic moments of some oxomolybdenum(V) complexes of tridentate Schiff bases.

Complex	Colour	Found (Calcd.)%					μ$_{eff}$ (B.M.)
		C	H	N	Cl	Mo	
ClMoO(SOAP) H$_2$O	red	41.3(41.4)	2.9(2.9)	3.5(3.7)	9.6(9.4)	25.2(25.5)	1.75
ClMoO(SALENA) H$_2$O	purple	32.8(32.9)	3.3(3.3)	4.1(4.3)	10.6(10.8)	29.4(29.2)	1.68
ClMoO(HAOAP)H$_2$O	purple	43.1(43.0)	3.3(3.3)	3.3(3.6)	9.0(9.1)	24.8(24.6)	1.78
ClMoO(ACOAP) H$_2$O	purple red	37.1(37.2)	3.7(3.7)	3.7(3.9)	10.2(10.0)	27.3(27.1)	1.82
[MoO(SOATP) H$_2$O]$_2$O[a]	light violet	42.5(42.7)	3.0(3.0)	3.6(3.8)		26.0(26.3)	1.32[b]
MoO(SOATP)(H$_2$O)(SCN)[c]	red brown	40.3(40.5)	2.6(2.6)	6.5(6.7)		23.5(23.1)	1.66

[a] Satisfactory S analysis was obtained; [b] μ$_{eff}$ value per Mo atom; [c] Satisfactory S and SCN analyses were obtained.

denum(V) ions in the solid state, analogous to oxomolybdenum(V) and oxovanadium(IV) complexes, which have subnormal magnetic moments[2d, 13]. The only exception in the latter series is [MoO(SOATP)(H₂O)]₂O which exhibits a magnetic moment of 1.32 B.M. at room temperature, thus being well below the spin-only, 1.73 B.M., value usually expected for oxomolybdenum(V) complexes, thus demonstrating some sort of magnetic interaction between the two molybdenum centres. This behaviour is not unknown[14] in oxygen-bridged oxomolybdenum(V) complexes and the reduction of magnetic moments (from 1.73 B.M.) depends on the angle of twist of the two halves of the molecule about the oxygen bridge (the dihedral angle).

The molar conductances of some of the complexes (ca. 10^{-3} M) in solvents such as ethanol, dichloroethane or DMF lie in the 5–10 ohm^{-1} cm² mol^{-1} range, indicating their nonelectrolytic nature in these solvents.

The electronic spectra (Table 4) of dioxomolybdenum(VI) complexes of tridentate Schiff bases show absorption bands of considerably high intensity at ca. 35 000 cm^{-1} and 25 000 cm^{-1} and those of quadridentate Schiff bases at ca. 23 600–24 500 cm^{-1}. These bands may be assigned to ligand-to-metal charge transfer transitions[15], possibly superimposed upon other intraligand transitions. It seems reasonable to assume that characteristic molybdenyl band does not occur in this region[15]. The intensity of the band in the lower energy region, i.e. ca. 23 000 cm^{-1}, seems to be much lower than that associated with ordinary charge transfer bands, and may probably arise from intraligand transitions of semi-forbidden character.

The electronic absorption spectra of the oxomolybdenum(V) complexes with tri- and tetra-dentate Schiff bases are shown in Table 5. The spectra of the complexes with tridentate Schiff bases are similar to each other, thereby suggesting a uniform structure for all of them. The complexes are best considered as octahedral with a strong tetragonal distortion resulting from the molybdenum-oxygen bond. The complexes usually exhibit three distinct absorption bands in the ligand field region. The low intensity absorption peaks in the long wave length region are possibly due to the first crystal field transition $^2B_2 \rightarrow {}^2E$ ($d_{xy} \rightarrow d_{xz}, d_{yz}$). This transition in our complexes are spread over the 13 300–14 280 cm^{-1} region. The second crystal field transition is observed at ca. 19 030–19 450 cm^{-1} and are due to transition $^2B_2 \rightarrow {}^2B_1$ ($d_{xy} \rightarrow d_{x^2-y^2}$). The third peak usually lies at ca. 25 880–22 000 cm^{-1} and is due to the transition $^2B_2 \rightarrow {}^2A_1$ ($d_{xy} \rightarrow d_{z^2}$). In some cases the bands are not well developed and appreared as shoulders (Table 5) and possibly mixed with the ligand transitions.

In spite of extensive work much controversy exists regarding the assignments of the electronic spectra of oxomolybdenum(V) and oxovanadium(IV) complexes[16-21]. The present assignments are, therefore, extremely tentative. The peak found at ca. 13 000 cm^{-1} is possibly associated with the

$^2B_{2g} \rightarrow {}^2E_g$ transition. The bands observed in the higher energy region are difficult to assign, but may probably arise from charge transfer and intraligand transitions.

The band positions in the binuclear oxomolybdenum(V) [MoO(SOATP)H₂O]₂O complex (Table 5) are similar to those observed in analogous binuclear oxomolybdenum(V) complexes[14] which lends support in favour of oxo-bridged binuclear structure.

The electronic spectrum (Nujol mull) of MoO(SPh)(BSEN) shows a broad band centered at ca. 24 500 cm^{-1} with a prominent shoulder at ca. 17 500 cm^{-1} (Table 5) and this low energy band may be responsible for the blue complex. This broad band may preclude the appeerence of the characteristic bands for mononuclear oxohalomolybdenum(V) species[22].

The low energy transition probably contains a sulphur-to-molybdenum charge-transfer component and is of interest in relation to the presence of an absorption maximum at 580 nm in Xanthine oxidase which has been assigned[23] tentatively to molybdenum. Aqueous solutions of [Mo₂O₄(cysteinyl)₂]²⁻ show similar absorptions[24].

Tables 6 and 7 record the important i.r. spectral bands of the Schiff base SOAP-H₂ and SOATP-H₂ and their complexes with oxomolybdenum(VI) and dioxomolybdenum(V) respectively. Similar data for Na₂MoO₄ · 2H₂O and (NH₄)₂MoOCl₅ are recorded for comparison. The i.r. spectral data of the complexes are typical for coordinated anionic Schiff bases. Other bands may be assigned as earlier[25]. The bands observed for SOATP-H₂ and its complexes are assigned tentatively (Table 7). All other complexes of oxomylbdenum(V) and dioxomolybdenum(VI) with tridentate Schiff bases show analogous i.r. spectral bands. It is thus reasonable to propose that the present oxomolybdenum(V) and dioxomolybdenum(VI) complexes with dibasic tridentate Schiff bases have pseudooctahedrol structure(s) as shown in the (5) and (6)
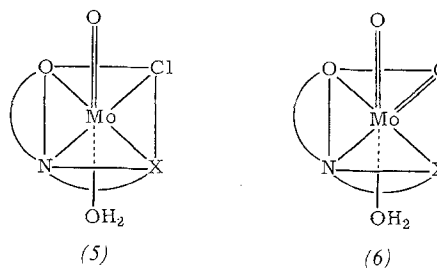

(5)   (6)

where stands for either oxygen or sulphur. The coordinated water in the MoO₂(SOAP)H₂O complex can be substituted by other monodentate ligands stronger than water. For example, recrystallization of the complex from DMSO, DMF and py yielded solvated MoO₂(SOAP) D (D = DMSO, DMF or py) complexes by replacement of water from the coordination site. The cis-MoO₂ stretching vibrations observed for the MoO₂(SOAP)D complex are shifted to lower frequencies as we increase the donor power of D. Based on the cis-MoO₂ stretching frequencies the donor(D) may be arranged (extremely qualitative at present) in order of their increasing basicity: H₂O < DMSO < DMF < py. For the present we only note that N-donors tend to produce lower frequencies than O-donors.

The i.r. spectra of dioxomolybdenum(VI) vomplexes with quadridentate Schiff bases are all alike, indicating that they have probably the similar structures with cis-MoO₂ moiety as supported by the appeerence of two bands in the 870–920 cm^{-1} region[14, 26]. Excepting the complexes MoO₂(BSOP),

Table 4. Electronic spectra of some dioxomolybdenum(VI) complexes with Schiff base ligands.

Complex	Solvent	v_{max} (10^3 cm^{-1})(log C)
MoO₂(SOAP) H₂O	EtOH	31.5(4.24), 27.4(4.2)
MoO₂(SALENA) H₂O	EtOH	31.7(4.26), 27.8(4.2)
MoO₂(HAOAP) H₂O	EtOH	32.0(4.3), 28.2(4.1)
MoO₂(SOATP) H₂O	EtOH	35.1(4.0), 29.8(3.8)
MoO₂(BSEN)	CH₂Cl₂	24.5(3.46)
MoO₂(BSTN)	DMF	24.3(3.5)
MoO₂(BMSEN)	DMF	23.6(3.2)

Table 5. Characterization data of some oxomolybdenum(V) complexes of tetradentate and tridentate Schiff bases[a].

Complex	μ_{eff} (B.M.)	$\nu(Mo=O)$ (cm^{-1})	$\nu(C=N)$ (cm^{-1})	$\nu(C=O)$ (cm^{-1})	$\nu(Mo–Cl)$ (cm^{-1})	Electronic spectra in DMF (10^3 cm^{-1})[b]
ClMoO(BSEN)	1.78	937	1600	1538	337 280	24.2(2500), 12.7(106)
ClMoO(BSTN)	1.81	928	1610	1543	280	– –
ClMoO(BSOP)	1.72	950	1600	1536	322	19.0(580)
MoO(SC$_6$H$_5$)(BSEN)[c]	1.77	942	1608	1540	–	24.3, 17.5sh
ClMoO(SOAP)H$_2$O[d]	1.75					31.2(4.24), 27.4(4.1), 19.5sh, 13.5(1.5)
ClMoO(HAOAP)H$_2$O[d]	1.78					31.4(4.22), 23.8(3.7), 14.3sh
ClMoO(ACOAP)H$_2$O[d]	1.82					32.5(4.5), 25.8(4.2), 14.1(1.3)
[MoO(SOATP)H$_2$O]$_2$O	1.32					35.1(4.5), 29.8(4.5), 22.0sh, 19.0(1.8), 13.3(1.5)
MoO(SOATP)(SCN)H$_2$O	1.66					37.0(5.3), 30.5(4.8), 22.2sh, 13.8(1.3)

[a] Magnetic moments of the complexes of Table 3 varies between 1.70 to 1.83 B.M. at room temperature; [b] Absorption coefficients (ε/dm^3 mol^{-1} cm^{-1}) are given in parentheses; [c] In mull; [d] Electronic spectra in EtOH.

Table 6. Important i.r. bands of some oxomolybdenum(V) and dioxomolybdenum(VI) complexes of tridentate Schiff bases and their tentative assignments.

Complex	$\nu(C=N)$ (cm^{-1})	$\nu(C–O)$(phenolic) (cm^{-1})	$\nu(Mo=O)$(cis) (cm^{-1})	Other bands (cm^{-1})
SOAP-H$_2$	1615s	1575s	–	725s, 740s, 760s, 900w, 1020w, 1115w, 1140s, 1175s, 1220s, 1310s, 1365w, 1450s, 1480w, 1545w
Na$_2$MoO$_4$ · 2H$_2$O	–	–	800–970s, b	3120–3300s and several w-m bands in the region
(NH$_4$)$_2$MoOCl$_5$	–	–	975s	3150s
MoO$_2$(SOAP) H$_2$O	1605s	1550m	910s, 935s	650s, 735s, 815s, 852s, 880w, 1025s, 1152s, 1250s, 1275s, 1365m, 1455s, 3100–3300s
MoOCl(SOAP) H$_2$O	1600s	1550m	925s	650s, 735s, 815s, 910m, 925s, 1120w, 1250s, 1280s, 1390s, 1475s, 3300s

Table 7. Important i.r. bands of MoO$_2$(SOATP) H$_2$O and [MoO(SOATP) H$_2$O]$_2$O and their tentative assignments.

| SOATP-H$_2$	MoO$_2$(SOATP) H$_2$O	[MoO(SOATP)H$_2$O]$_2$	Tentative assignments
–	3300–3100s, b	3300–3110m, b	$\nu(OH)(H_2O)$
3225	–	–	$\nu(OH)(phenol)$
3040–2600s, b	3000–2750s, b	2980–2850m, b	$\nu(SH)(thiophenol)$
–	2600–2400w, b	2600–2400w, b	$\nu(C–H)$
1630s, 1595s	1613s, 1580s	1620s	Amide I + $\nu C=N$
Several bands: 1450–788s, w	1470, 1030	1480, 1035	Bands of organic ligands
–	975s, 907s, 840w, 782–715m,b	974s	$\nu(Mo=O)$
–	–	817s	$\nu(Mo–O–Mo)$
750s, 735w, 718w	700w	701w	Amide II
–	640, 625s, b	621s, b	Mo–O or Mo–N

MoO$_2$(BMSOP) and MoO$_2$(BCSOP-H$_2$), all other complexes of dioxomolybdenum(VI) with quadridentate Schiff bases might attain a structure *(7a)* where the quadridentate Schiff bases assume nonplanar geometry. The high tendency of the group MoO$_2$ to assume a *cis*-configuration forced the essentially planar ligands to occupy non-planar geometry. This is in line with earlier views[2d, 27]. ^{1}H n.m.r. spectral data (Table 8) of the complexes MoO$_2$(BSEN) and MoO$_2$(BCSEN-Na$_2$) support this view, which has been thoroughly interpreted in recent publications[2d, 27–29]. However, we are doubtful whether this generalization accounts for the structure of MoO$_2$(BSOP),

MoO$_2$(BMSOP) and MoO$_2$(BCSOP-H$_2$), as the distortion from planarity *(7a)* will be comparatively difficult in these systems compared to other complexes discussed above, due to the presence of the *o*-phenylene-diamine backbone. However, these latter complexes might attain the structure depiceted in *(7b)*, as the ^{1}H n.m.r. spectral data (Table 8) show a single (broad) band at 8.01 δ p.p.m. due to N=CH protons, while phenyl protons absorb at 7.10–7.40 δ p.p.m. range with the correct integration. These results support the contention that the ligand [BSOP]$^{2-}$ assumes an approximately planar configuration, thus supporting the structure *(7b)*.

Table 8. Chemical shifts in ^1H n.m.r. spectra of $MoO_2(BSEN)$ and $MoO_2(BCSEN-H_2)$ in $(CD_3)_2SO$ [a].

Complex	N=CH	C_6H_5 [b]	$N-CH_2$
$BSEN-H_2$	8.62	6.75–7.57	3.95
$[Co(BSEN)(NH_3)_2]^+$ [c]	8.13	6.33–7.40	3.85
$Co(BSEN)(acac)$ [d]	8.01, 7.80	6.39–7.34	3.73, 3.94
$MoO_2(BSEN)$	8.93, 8.78	6.65–7.79	4.34, 4.28 [b]
$MoO_2(BCSEN-H_2)$	8.91, 8.74	6.69–8.01	4.29, 4.01 [b]
$MoO_2(BSOP)$ [e]	8.01 [b]	7.10–7.40	–

[a] δ (p.p.m.) downfield from TMS; [b] Broad; [c] Taken from the ref. (2d); [d] Taken from the ref. (28a); [e] In $(CD_3)_2CO$.
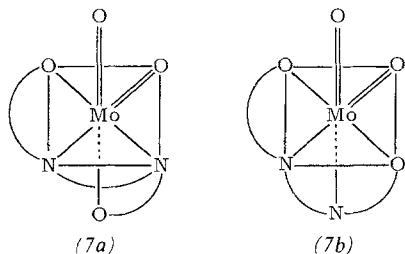
(7a)   (7b)

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TMC 588

Equilibria in Complexes of N-Heterocyclic Ligands. Part 33. Ruthenium(II) Complex Ions with Chelating Pyridyl-imidazoles

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Summary

The complex salts $[RuL_3](ClO_4)_2 \cdot nH_2O$ have been made, where L = 2-(2-pyridyl)imidazole and n = 2 or 2-(2-pyridyl)-benzimidazole, n = 3. Spectra are discussed, including circular dichroism (the complex ions having resulted from asymmetric syntheses).

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Introduction

The strong chelating ability of 1,10-phenanthroline and 2,2'-bipyridyl has been ascribed[1] to the fact that, apart from being good σ-donors, these ligands also function as electron acceptors *via* the delocalised π-orbitals associated with their aromatic ring systems. Similarly, imidazole is of considerable interest as a ligand, in that its presence in many biological systems (*e.g.* in the histidyl residue of proteins) provides a potential binding