Inorganica Chimica Acta, 35 (1979) 35–41
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

The Coordination Chemistry of Molybdenum and Tungsten.
Part XIV. Dioxomolybdenum(VI) Complexes of Bidentate, Tridentate, and Tetradentate Schiff Bases Containing Oxygen, Nitrogen and Sulphur Donors

W. E. HILL*
Department of Chemistry, Auburn University, Auburn, Ala. 36830, U.S.A.

N. ATABAY, C. A. McAULIFFE*, F. P. McCULLOUGH, and S. M. RAZZOKI
Department of Chemistry, University of Manchester Institute of Science and Technology, Manchester M60 1QD, U.K.

Received October 11, 1978

A large number of bidentate, tridentate, and tetradentate Schiff base ligands containing oxygen, nitrogen, and sulphur donor atoms have been complexed to the cis-MoO_2 *moiety. The structures of the resulting complexes are postulated on the basis of infrared and proton n.m.r. arguments previously developed by Yamada.*

In the case of the complexes of the tetradentate ligands, the nature of the backbone between the imine groups determines which cis *isomer is found.*

Introduction

Chelating Schiff-base ligands have been much studied by inorganic chemists, but the early heavy transition metals have been fairly neglected in these investigations. We have previously published [2, 3] our results on molybdenum(V) complexes of tetradentate Schiff-base ligands (H_2L) and shown that under certain conditions it is possible to produce [MoOLCl] complexes [2], which contain tetradentate dianionic ligands, or [$MoOCl_3(H_2L)$], in which the unusual binding of neutral bidentate ligands *via* the imine donors occurs [3]. We have now extended our investigations to include the binding of potentially bidentate, tridentate and tetradentate Schiff-base ligands, containing a number of different donor atoms, to molybdenum(VI). Two brief studies of this area have previously been published [4, 5], but no conclusive evidence about structure was obtained. In our previous work on molybdenum(V) [2, 3, 6], we were able to use electron paramagnetic resonance spectroscopy to assign structures to the complexes and whilst this technique is not available for studying molybdenum(VI) species, we have been able to use proton n.m.r. to good effect in the work reported here.

We have found that the nature of the backbone between the imino groups in the tetradentate ligands has a marked effect on whether structure *cis*(IV) or *cis*(V) is formed, or whether a mixture of these *cis* structures is obtained.

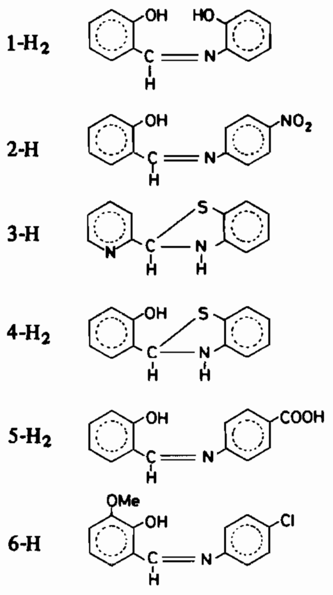


Fig. 1. Ligands used.

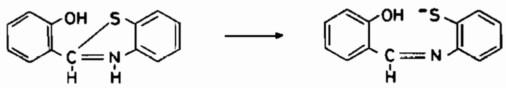


Fig. 2. Conversion of ligands to Schiff-bases.

Results and Discussion

It is convenient to divide the work into two sections, *viz.* that relating to bidentate and tridentate ligands, and that relating to tetradentate ligands.

Potentially Bidentate and Tridentate Ligands

The ligands used are shown in Fig. 1. We have abbreviated them, *e.g.* 1-H_2, 3-H, *etc.*, to indicate the number of possible ionisable protons. Certain ligands are not, strictly speaking, Schiff-base ligands, but can become so on reaction with a metal ion

---

*Authors to whom correspondence should be addressed.

TABLE I. Physical Properties and Analytical Data for the Ligands.

Ligand	M.p. °C	Colour	Analysis % Calcd. (Found)		
			C	H	N
1-H_2	186	red-brown	73.2(73.0)	5.1(5.2)	6.6(6.5)
2-H	156	orange	64.5(64.5)	4.1(4.0)	11.6(11.6)
5-H_2	208	orange	69.7(69.5)	4.6(4.6)	5.8(5.7)
3-H	110	cream	67.3(66.8)	4.6(4.5)	13.1(13.1)
6-H	102	orange	64.2(64.2)	4.6(4.6)	5.4(5.4)
4-H_2	138	cream	68.1(68.6)	4.8(4.7)	6.1(6.1)

TABLE II. Infrared Spectra of the Ligands.

Ligand	I.R. Spectra (cm^{-1})		
	ν(OH)	ν(C=C)	ν(C=N)
1-H_2	2700	1615	1630
2-H	2730	1590	1615
5-H_2	2720	1600	1620
3-H	–	1590	1320(C–N)
4-H	2730	1585	1320(C–N)
6-H	2730	1575	1615

(Fig. 2). Such a transformation can easily be monitored by the disappearance of ν(N–H) and the appearance of ν(C=N) in the infrared spectrum. The physical properties of the ligands and some important infrared frequencies are listed in Tables I and II, respectively.

It was reported previously [4] that the reaction of dioxobis (salicylaldehydato)molybdenum(VI) with alkyl- and aryl-amines yielded bis(N-arylsalicylaldiminato) complexes of dioxomolybdenum(VI) including yellow MoO_2 (X-Sal-R)$_2$, red MoO_2(X-Sal-R) and purple Mo_2O_3(H-Sal-R)$_4$. The yellow MoO_2(X-Sal-R)$_2$ complexes are six-coordinate with a *cis*-MoO_2 group. The red MoO_2(X-Sal-R) complexes are considered to be multinuclear molybdenum(V) complexes, whilst the purple Mo_2O_3(H-Sal-R)$_4$ complexes are thought to be binuclear with one oxygen atom as a bridge. This method is not successful for the synthesis of dioxo[bis(salicylaldehyde polymethylenediiminato)]molybdenum(VI) complexes. Yamanouchi and Yamada [5] made use of a new method starting from dioxobis(acetylacetonato)-molybdenum(VI), which was allowed to react with a series of Schiff bases to yield the bis(salicylaldehyde)polymethylenediiminato complexes. In our studies we have used $MoO_2(acac)_2$ as starting material and this was reacted with the Schiff-bases in a 1:2 ratio in tetrahydrofuran. After refluxing for six hours the solid was filtered off and dried. The complexes isolated are listed in Table III and the important vibrational and electronic spectral features are listed in Table IV.

All the ligands bind as monoanionic species, even when the free ligands have potentially two ionisable hydrogens. In two cases, those with ligands 1-H_2 and 5-H_2, despite the reaction stoichiometry Mo:ligand of 1:2, only one ligand binds and the resulting MoO_2 (acac) (ligand anion) clearly contain one acac group (infrared and elemental analyses evidence). All of the complexes exhibit two infrared bonds in the 880–920 cm^{-1} region, indicative of *cis*-MoO_2 groups [4, 7, 8]; the *trans*-MoO_2 configuration would result in a single ν(Mo=O) bond.

We have been able to use proton n.m.r. spectra to help elucidate the structure of the *cis*-MoO_2(ligand

TABLE III. Colour and Analytical Data for Molybdenum(VI) Complexes.

Complex	Colour	Analysis % Calcd. (found)		
		C	H	N
MoO_2(acac)(1-H)	brown	49.0(49.9)	4.0(4.9)	3.0(3.2)
$MoO_2(2)_2$	yellow	51.0(50.5)	3.0(3.1)	9.0(8.7)
MoO_2(acac)(5-H)	yellow	48.7(48.3)	3.85(3.8)	3.0(3.1)
$Mo_4O_{11}(3)_2$	dusty-brown	29.1(30.0)	2.0(2.3)	5.7(5.4)
MoO_2(4-H)$_2$	brown	43.9(43.0)	2.5(2.6)	3.9(3.9)
$MoO_2(6)_2$	orange	52.0(51.8)	3.0(3.5)	4.0(4.4)

TABLE IV. Some Important Infrared and Visible Absorption Frequencies for the Complexes.

Complex	I.R. Bands (cm^{-1})		U.v./Visible (10^3 cm^{-1})
	ν(Mo=O)	ν(C=N)	
MoO_2(acac)(1-H)	910 930	1585	23.3, 13.8
$MoO_2(2)_2$	900 920	1615	23.2, 16.9
MoO_2(acac)(5-H)	910 940	1600	22.7, 14.7
$Mo_4O_{11}(3)_2$	905 950	1325 (C–N)	23.8, 15.3
MoO_2(4-H)$_2$	920 930	1285 (C–N)	21.7, 16.1
$MoO_2(6)_2$	900 920	1610	22.2

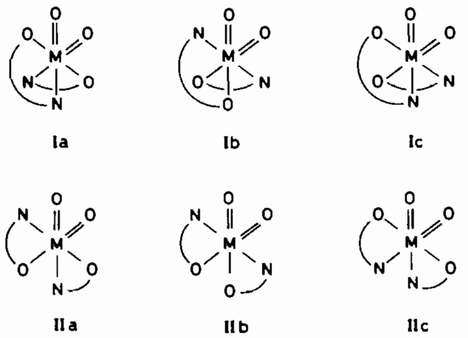


Fig. 3. Possible isomers of *cis*-MoO_2L_2.

anion)$_2$ complexes. Because there is no backbone joining the bidentate ligand donor sets as there is in the case of tetradentate ligands, three isomeric forms each of basic structures (I) and (II) are possible as shown in Fig. 3. Only structures (IIb) and (IIc) possess a C_2 axis of symmetry and would therefore be expected to show only one signal for the methine (N=CH) hydrogen atom in the pmr. The pmr spectra values for these [MoO_2L_2] complexes are listed in Table V. For the complexes where L is 6 and 2, only one signal is observed for the methine hydrogens. Thus these complexes must have either structure (IIb) or (IIc) since the infrared confirmed the presence of the *cis*-MoO_2 groups. In the case of the MoO_2(4-H)$_2$ complex, the large shift in δNH in going from the free ligand to the complexes indicated that the ligand is O,N coordinated rather than O,S coordinated and since only one signal is observed for the N–H proton, this complexes also must be either structure (IIb) or (IIc). The pmr gives no structure information on the complexes [MoO_2(acac)(L)] where L = 1-H or 5-H since only one methine signal is possible regardless of which isomer is present.

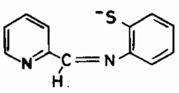


Fig. 4. Ligand (3) in $Mo_4O_{11}(3)_2$.

In the case of the complex $Mo_4O_{11}(3)_2$ little can be said of its structure. Its formulation implies that it is at least tetrameric, and it may even be polymeric. The ligand is present as an anion, as evidenced by the elemental analysis and this would imply coordination as the species shown in Fig. 4. However, there is no ν(C=N) present and the ν(C–N) appears at virtually the same frequency in the complex as it does in the free ligand. This is obviously a most interesting compound but, unfortunately, lack of solubility has hindered structural assignment by spectroscopic means.

Potentially Tetradentate Ligands

The ligands used in this study, and their abbreviations are listed in Figure 5. The analytical and spectroscopic date for the ligands are listed in Table VI. The complexes were synthesised by reacting MoO_2(acac)$_2$ with the free ligand in a 1:1 ratio in

TABLE V. Chemical Shifts in Proton Magnetic Resonance Spectra of Molybdenum(VI) Complexes in $(CD_3)_2SO$.[a]

Compound	N=CH	Ph	OH	OCH_3	CH_3	N–H	N–CH
4-H_2		6.4–7.1	9.69			7.9	7.45[d]
MoO_2(4-H)$_2$		6.8–7.2 7.6–7.8				8.98	8.55[d]
6-H	7.90	6.2–6.8		3.17			
$MoO_2(6)_2$	8.99	6.8–7.5		3.83			
2-H	8.67	6.7–8.4	9.92				
1-H_2	7.98	6.25–7.0	10.3				
MoO_2(acac)(1-H)	9.2	6.75–7.8			1.85(–CH_3)[b] 2.5(C–H)		

[a] δ in ppm downfield from TMS. [b] acac. [d] doublet.

TABLE VI. Analytical and Spectroscopic Data for the Ligands.

Ligand	M.p.	Analysis (%) Calc./(found)			I.R. Spectra (cm^{-1})			
		C	H	N	ν(OH)	ν(C=N)	ν(C=C)	ν(C=O)
VantnH_2	98	66.6 (66.4)	6.4 (6.4)	8.1 (8.0)	2690	1625	1583	1370 1160
VanenH_2	165	65.6 (64.7)	6.0 (6.0)	8.59 (8.6)	2680, 2480	1625	1580	1380 1240 1170
SaltnH_2	56	71.8 (72.0)	6.3 (6.4)	9.9 (9.8)	2660 2735	1633	1580	1380 1210
SalphenH_2	170	75.9 (75.6)	5.1 (5.1)	8.8 (8.9)	2700	1610	1560	1375 1275 1190
m-CH_3-SalphenH_2	120	76.1 (76.7)	5.7 (5.4)	8.4 (8.3)	2710	1618	1560	1377 1190
SalhexH_2	102	74.07 (73.9)	7.4 (7.2)	8.64 (8.7)	2700	1630	1580	1375 1280 1360
HapenH_2	196	72.9 (70.9)	6.7 (6.5)	9.4 (9.2)	2720	1605	1570	1380 1240 1160

TABLE VII. Analytical and Spectroscopic Data for Molybdenum(VI) Complexes.

Complex	Analysis % Calcd. (found)			I.R. Bands (cm^{-1})			
	C	H	N	ν(Mo=O)	ν(C=N)	ν(C–O)	Other
MoO_2(vantn)	48.7(47.9)	4.27(4.1)	6.98(5.6)	885, 910	1614, 1635	1550	–
MoO_2(vanen)	47.5(47.3)	3.96(4.3)	6.1(5.9)	875, 903, 925	1605, 1600	1535	–
MoO_2(saltn)	50.(49.3)	3.92(3.9)	6.86(6.9)	870, 910	1608, 1585	1530	–
MoO_2(salphen)	54.2(53.8)	3.2(3.3)	6.3(6.1)	870, 904, 915	1605, 1595	1550	–
MoO_2(*m*-CH_3-salphen)	55.2(53.5)	3.51(3.6)	6.1(6.0)	870, 910	1625, 1610	1550, 1525	–
MoO_2(hapen)	51.4(51.3)	4.26(4.4)	6.6(6.6)	885, 910	1605	1545	–
Mo_2O_5(salhex)	40.4(41.0)	3.8(4.3)	4.7(4.7)	895, 922	1625, 1600	–	722,[a] 628, 420

[a] δ(Mo–O–Mo).

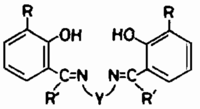
tetrahydrofuran as outlined in the Experimental section. The analytical and spectroscopic data are listed in Table VII.

All of the complexes of type MoO_2L (LH_2 = tetradentate Schiff-base ligand) exhibit two or in some cases three infrared absorption bands due to the MoO_2 group in the range 896–935 cm^{-1}. In the case of MoO_2(Saltn) the complex shows two infrared absorption bands at 911 and 870 cm^{-1}. It may thus be presumed that the two oxygen atoms of the molybdenyl group are *cis* to each other in these complexes [4, 7, 8] and thus structure (III) in Fig. 6 is excluded. No absorptions appeared at lower frequency attributable to Mo–O–Mo bridges in any of the complexes except for Mo_2O_3 (Salhex).

TABLE VIII. U.v./vis. and Chemical Shifts in Proton Magnetic Resonance Spectra of Molybdenum(VI) Complexes in (Dimethylsulphoxide)-d_6.[a]

Compound	δN=CH	δPh	δN–CH_2	δOCH_3	δCH_3	U.v./Visible 10^3 cm^{-1}
MoO_2(vantn)	8.55, 8.88 (8.50, 8.77)[c]	6.9–7.3 (6.4–7.5)[c]	3.60, 3.78	3.80, 3.48 (3.82, 3.50)[c]	–	23.255
MoO_2(vanen)	8.46, 8.68, 8.92 (8.74, 8.91)[c]	6.4–7.4 (6.50–7.33)[c]	4.3, 4.2 (4.3, 4.2)[c]	3.87, 3.78, 3.68 (3.84, 3.66)[c]		23.3
MoO_2(saltn)	8.2, 8.49 (8.47, 8.75)[c]	6.5–7.5 (6.40–7.65)[c]	3.4–4.2 (3.65–4.3)[c]			23.2, 21.6 sh.
MoO_2(salphen)	8.57	6.4–7.4	–	–	–	23.148, 20.0
MoO_2(*m*-CH_3-salphen)	8.7	6.7–7.6	–	–	2.13	22.73, 20.4, sh
MoO_2(hapen)	9.37, 9.59	6.5–7.5	3.85, 3.6	–	–	24.6, 22.9
Mo_2O_5(salhex)	8.35	6.5–7.3	3.5–1.9	–	–	23.98
Trans-(Co(salen)$(NH_3)_2ClO_4$[b]	8.13	6.33–7.40	3.86	–	–	–

[a] δ in ppm downfield from TMS. [b] Data taken from ref. 14. [c] Previously reported in ref. 5.



R	*R*[1]	*Y*	*Ligand*
H	H	–$(CH_2)_3$–	saltnH_2
MeO	H	–$(CH_2)_2$–	vanenH_2
MeO	H	–$(CM_2)_2$–	vantnH_2
H	H	–$(CM_2)_6$–	salhexH_2
H	H	-*o*-C_6H_4–	salphenH_2
H	H	-*o*-C_6H_3Me-4	*m*-CH_3-salphenH_2
H	Me	–$(CH_2)_2$–	hapenH_2

Fig. 5. Potentially tetradentate ligands.

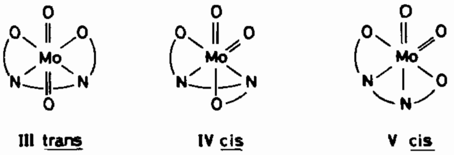


Fig. 6. *Cis* and *trans* structures for dioxo[bis-(salicylaldehyde-polymethylenediiminato]molybdenum(VI).

There is much confusion in the literature about the assignment of the infrared spectra of Schiff base ligands and their metal complexes, due to the complexity of the spectra and the extensive vibrational coupling present. Previous empirical assignments have attributed absorption in the 'double-bond' region of the spectrum to various combinations of ν(C=N), ν(C=C), and ν(C=O) [9–11]. A recent study [12] of ^{15}N-labelled N-arylsalicylideneimines and their metal complexes assigned the three vibrations observed in the range 1550–1600 cm^{-1} to ν(C=N), ν(C=C), and ν(C=O); however, all are extensively coupled. The higher-frequency ν(C=N) vibration is particularly diagnostic of the mode of coordination of the ligands. When co-ordinated as an anionic ligand through both oxygen and nitrogen atoms, the ν(C=N) vibration shifts to lower frequency by ~20 cm^{-1}, whilst coordination as neutral species, through the nitrogen atom only, shifts this band to higher frequency [2, 3, 9, 11–13]. The free ligands also exhibit weak broad absorptions at *ca.* 2700 cm^{-1} assignable to hydrogen-bonded OH groups. In the case of MoO_2(Saltn) complex, for example, the ν(C=N) vibration shifted to lower frequency by ~25 cm^{-1} as shown in Table VII, with a new band at 1608 cm^{-1}. Thus this ligand is co-ordinated as anionic species through the N and O atoms.

For the *cis* structure, the two configurations are possible, as shown in the Figure 6. Both of them have an axis symmetry. Calligaris and coworkers [14] have reported the X-ray results of [Co(salen)acac]. It shows that the two methine hydrogens of the salen ligand are not equivalent, as they are in planar complexes. This suggested that n.m.r. spectral analysis could provide useful information about the actual arrangement of the quadridentate ligands. The p.m.r. spectra of the complexes of MoO_2(saltn), MoO_2(vantn), and MoO_2(hapen) have two signals each for the methine, phenyl and polymethylene protons, as may be seen from Table VIII. It is also seen from Table VIII that the methoxy protons in MoO_2(Vantn) and MoO_2(Vanen) exhibit two and three signals respectively, in addition to those mentioned above; and the p.m.r. spectra of MoO_2(salphen), MoO_2(*m*-CH_3-salphen), and Mo_2O_3(salhex), show only one signal for the CH=N resonance. The p.m.r. spectrum of *trans*-[Co(salen)$(NH_3)_2$]ClO_4 in which the ligand Salen assumes planar coordination [15], exhibits a singlet each for the N=CH and N–CH_2 protons, as was reported for other complexes which contain bis(salicylaldehyde)ethylenediiminate with planar geometry [16, 17]. However, the p.m.r.

spectrum for [Co(acac)(salen)], in which Salen assumes non-planar geometry, shows two peaks at δ8.04 and 7.8 for the CH=N resonance [14].

The agreement between the p.m.r. and X-ray results shows that the p.m.r. spectra are useful for deducing reliable conclusions on the overall structure of this type of complex. In comparing the *cis* structures (IV) and (V), structure (V) is more symmetrical than the structure (IV) having a C_2 symmetry axis, which bisects the N–CH_2–CH_2–N chain, and thus two methine hydrogens of the polyethylene ligands are not equivalent in structure (IV), whereas they are in (V) [5]. Thus, the p.m.r. spectra of the complexes MoO_2(Saltn), MoO_2(Hapen) and MoO_2(Vantn) indicate that these compounds have structure (IV); whereas MoO_2(Salphen), and MoO_2(*m*-CH_3-Salphen) exhibit only a singlet for the N=CH protons and therefore have structure (V) since the infrared shows the presence of a *cis* MoO_2 group.

Yamanouchi and Yamada [5] have previously prepared a series of MoO_2L complexes, where L is a dianionic tetradentate Schiff base ligand having a polymethylene backbone similar to those ligands shown in Fig. 5 (where R′=H, OCH_3; R=H; n=2,3,4) and found that all had structure *cis*(IV). We have reprepared the complexes MoO_2L (L=salten, vantn) using tetrahydrofuran as a reaction solvent and isolated complexes, the n.m.r. spectra of which are shown to have structure *cis*(IV), consistent with Yamada's previously reported results [5]. However, in the case of MoO_2 (vanen) we have been able to isolate a material made up of a mixture of structures *cis*(IV) and *cis*(V); this contrasts with the materials consisting entirely of *cis*(IV) which Yamada isolated from methanol. We attribute the presence of both *cis* isomers in our MoO_2(vanen) complex to the effect of the short ethylene ligand backbone between coordinated $N_{(1)}$=C and $N_{(2)}$=C, thus increasing the strain of twisting at $N_{(2)}$=C in structure *cis*(IV). In structure *cis*(V) the twisting strain is balanced between $N_{(1)}$=C and $N_{(2)}$=C causing this structure to be favoured for short polymethylene backbone ligands or rigid backbone ligands, including the *o*-phenylene backbone ligand. It is for this reason that the complexes MoO_2L′ (L′=salphen and M-CH_3-salphen) have structure *cis*(V), where the twisting at the two coordinated azomethines is minimized.

Clearly these results show that the nature of the backbone in complexes of these tetradentate ligands has a marked controlling effect over which *cis* structure is preferred.

The solid reflectance spectra of the complexes show an intense absorption at *ca.* 23000 cm^{-1} with an ill defined shoulder at lower energy. Taking into consideration studies on electron spectra of molybdenyl complexes, these absorption bands are assigned to ligand-to metal charge transfer transitions (since Mo(VI) has a d^0 configuration no d → d transitions are observed). The complex MoO_2(saltn), for example, shows an intense absorption at 23300 cm^{-1} and two weak low-energy bands at 15900 and 13500 cm^{-1} (Table VIII).

As expected, no electron spin resonance signal was observed for any of these complexes, indicating that no paramagnetic species were formed.

We are unable to suggest any structure for the complex Mo_2O_5 (salhex), but point out that infrared bands are present at 722 and 420 cm^{-1} which can be assigned to –Mo–O–Mo– bridges. It is not surprising that a polynuclear system results from the reaction of a ligand with a hexymethylene link between the imine donors.

Experimental

Reagents

Tetrahydrofuran (THF, C_4H_8O) was dried by refluxing with freshly extruded sodium wire. The dry THF was distilled (b.p. 65 °C) and used immediately.

Absolute ethanol was obtained by predrying 95% ethanol over CaO for 24 hours, decanting and distilling off from Mg and I_2(5g Mg, and 0.1g I_2 per litre of ethanol). The ethanol was distilled and used immediately. Diethylether and cyclohexane were dried with fresh sodium wire (24 hours). Acetonitrile was distilled from P_2O_5. Toluene was distilled from sodium wire and used immediately. The other solvents and reagents used were of the best commercial grade available and were used without further purification.

$MoO_2(acac)_2$ was obtained courtesy of Climax Molybdenum Company and was determined by elemental analysis to be of sufficient purity.

Physical Measurements

Infrared spectra

Routine infrared spectra were obtained in Nujol and hexachlorobutadiene mulls, in the range 4000–400 cm^{-1} on a Perkin Elmer Infracord 735 Spectrophotometer between potassium bromide plates, and on a Perkin Elmer 621 Grating Spectrophotometer in the range 4000–200 cm^{-1} using caesium iodide plates.

Electronic spectra

Solid reflectance spectra were measured on a Beckman Acta M4 Spectrophotometer using magnesium oxide as a dilutant and reference.

Nuclear magnetic resonance spectra (nmr)

Proton magnetic resonance spectra in d_6-dimethylsulphoxide were measured on a Perkin-Elmer Hitachi R20 and also on a Perkin-Elmer R32 high resolution nmr Spectrometer and referenced to TMS (internal).

Microanalyses

Carbon, hydrogen, and nitrogen microanalyses were performed by the Microanalytical Service of this department.

Preparation of Ligands

All of the Schiff base ligands used in this study were prepared by the same general method in freshly distilled ethanol from one of three aldehydes (salicylaldehyde, *o*-hydroxyacetophenone, or pyridine-2-aldehyde) and a diamine in the ratio 1:1 or 2:1, respectively. All products were microcrystalline, precipitating immediately upon addition of the reactants. They were recrystallised from ethanol, cooled, filtered and rinsed with diethyl ether or n-pentane depending on solubility. The Schiff bases range in colour from bright yellow to bright orange and were characterised by infrared and microanalysis. The yields were generally better than 90%. A typical preparation description is given below:

1,3-bis(salicylaldehyde)propylenediimine (saltnH$_2$)

Into a three-necked flask fitted with a magnetic stirrer, reflux condenser, and a dropping funnel, was placed propylenediamine (0.05 mol, 3.7 g) in ~50 ml of freshly distilled ethanol. Salicylaldehyde (0.1 mol, 12.2 g) in ~50 ml of freshly distilled ethanol was added dropwise with vigorous stirring. There was immediate precipitation of product on addition of reactants. The mixture was refluxed by using a water bath for ½ hour, then cooled in an ice bath and filtered. The product was recrystallized by addition of ~50 ml of ethanol. The mixture was cooled in an ice bath, filtered washed with sodium dried diethylether. The Schiff base was then dried *in vacuo* and stored in glass jars, fitted with a screw cap. The yield was approximately 90%.

Preparation of the Mo(VI) Complexes

All of the complexes used in this study were prepared by the same general method. They were prepared in freshly distilled tetrahydrofuran (THF) from MoO$_2$(acac)$_2$ and one of the ligands in the ratio 1:1. All products were microcrystalline-precipitating upon refluxing for 2–3 hr. The precipitates were cooled, filtered and rinsed with n-pentane. The complexes range in colour from orange to reddish-brown and were characterized by infrared microanalysis nmr and u.v./vis. The yield was generally about 40%. Two typical preparations description are given below.

Preparation of dioxo[1,3-bis(salicylaldehyde)propylenediiminato]molybdenum(VI)

Into a three-necked flask fitted with a magnetic stirrer, reflux condenser and a dropping funnel, was placed MoO$_2$(acac)$_2$ (1g) in ~15 ml of freshly distilled tetrahydrofuran (THF). The 1,3-bis(salicylaldehyde)propylenediimine (0.95 g) in ~15 ml of freshly distilled THF was added dropwise with vigorous stirring. The mixture was refluxed for 3 hours. It was cooled in an ice bath, filtered and washed with dry THF. The complex was then dried *in vacuo* and stored in a glass vial.

Dioxobis(salicylaldehyde-3-nitrobenzeneimino)-molybdenum(VI)

Salicylaldehyde 3-nitrobenzeneimino (1.64 g, 6.8 mmol) in 25 ml of freshly distilled THF in a funnel fitted to a three necked flask with a condenser was added with stirring to flask, containing (1 g, 3.4 mmol) dioxobis(acetylacetonate)Mo(VI), dissolved in 25 ml of freshly distilled THF. The solution was heated for 6 hours. A yellow precipitate was produced then cooled, filtered and rinsed with n-pentane (2 X 15 ml) and the compound was dried *in vacuo* and stored in an air tight vial. The yield was 30%.

References

1 Part XIII: C. A. McAuliffe and B. J. Sayle, *Inorg. Chim. Acta*, in press.
2 J. R. Dilworth, C. A. McAuliffe and B. J. Sayle, *J. Chem. Soc. Dalton*, 849 (1977).
3 C. A. McAuliffe, F. P. McCullough, M. J. Parrott, C. A. Rice, B. J. Sayle and W. Levason, *J. Chem. Soc. Dalton*, 1762 (1977).
4 K. Yamanouchi and S. Yamada, *Inorg. Chim. Acta, 9* 83 (1974).
5 K. Yamanouchi and S. Yamada, *Inorg. Chim. Acta, 9,* 161 (1974).
6 C. A. McAuliffe, F. P. McCullough and A. Werfalli, *Inorg. Chim. Acta, 29* 57 (1978), and refs. therein.
7 P. C. H. Mitchell, *Quart. Rev., 20,* 103 (1966).
8 K. Nakamoto, 'Infrared Spectra of Inorganic and Coordination Compounds', Wiley, New York, p. 77 (1963).
9 K. Yamanouchi and S. Yamada, *Inorg. Chim. Acta, 12,* 9 (1975).
10 A. Van den Bergen, R. J. Cozens and K. S. Murray, *J. Chem. Soc. A*, 3060 (1970).
11 V. A. Kogan, O. A. Dripov, V. I. Minkin and V. P. Sodolov, *Russ J. Inorg. Chem., 10,* 45 (1965).
12 G. C. Percy and D. A. Thornton, *J. Inorg. Nucl. Chem.*, 34, 3357 (1972).
13 A. Van den Bergen, K. S. Murray and B. O. West, *Aust. J. Chem., 25* 105 (1975).
14 M. Calligaris, G. Manzini, G. Nardin and L. Randaccio, *J. Chem. Soc. Dalton*, 543 (1972).
15 S. Yamada, H. Nishikawa and E. Yoshida, *Proc. Japan Acad., 40,* 211 (1964).
16 C. Floriani, M. Puppis and F. Calderazzo, *J. Organomet. Chem., 12,* 209 (1968).
17 H. A. O. Hill, K. G. Morallee, G. Pellizer, G. Mestroni and G. Costa, *J. Organomet. Chem., 11,* 167 (1968).