Preparation and Electron Spin Resonance Spectra of Some Molybdenum(V) Complexes of Schiff-Base Ligands and their Oxidation to Molybdenum(VI)

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Trichloro-oxomolybdenum(V) reacts with Schiff bases H_2L in the presence of base, with the dilithium salt Li_2L, or with the bis(trimethylsilyl) derivative $L(SiMe_3)_2$ [L = salen, salpn, salphen, 3-MeO-salen, 3-MeO-salphen, 3-MeO-salpn, or 2,2′-bi(2,3-dihydrobenzothiazolyl) (H_2bzt)] to give the complexes [MoCl(O)L]. E.s.r., and i.r. spectral data suggest that the complex with L = salen[ethylenebis(salicylideneiminato)] exists as a mixture of *cis* and *trans* isomers, but with L = salpn [propane-1,3-diylbis(salicylideneiminato)] or salphen [*o*-phenylenebis(salicylideneiminato)] solely in the *trans* and *cis* configurations, respectively. On heating under reflux in air, the [MoCl(O)L] complexes are oxidised to $[MoO_2L]$.

CHELATING Schiff-base ligands have been the subject of many studies, and in particular complexes with first-row transition metals have been investigated.[1,2] Less information is available on complexes of the early heavy transition-metal ions and we report here some of our work on molybdenum(IV) and molybdenum(V) complexes of such ligands. Previously, reactions of

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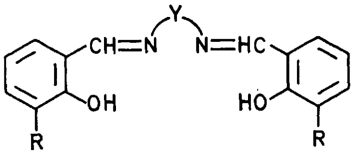
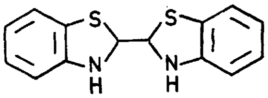
molybdenum hexacarbonyl with bi- and quadri-dentate Schiff bases have produced molybdenum(II)[3] and molybdenum(III)[4] derivatives. van den Bergen *et al.*[5] reported molybdenum(IV) halide derivatives and Yamanouchi and Yamada[6] isolated dioxomolybdenum(VI) complexes of bi- and quadri-dentate Schiff bases derived from salicylaldehyde. These last workers also isolated tetrakis(*N*-methylsalicylideneiminato)trioxomolybdenum(V), the only molybdenum(V) derivative reported prior to this study.

We have investigated the reactions of solvated trichloro-oxomolybdenum(V) with the ligands H_2L, which yield derivatives of the type $[MoCl_3O(H_2L)]$ and $[MoCl(O)L]$. These complexes have subsequently been shown to react with base to give dimeric oxomolybdenum(IV) complexes, $[Mo_2O_3L]$. We have also obtained complexes of the known type[6] $[MoO_2L]$.



R	Y	
H	$[CH_2]_2$	H_2salen
H	$[CH_2]_3$	H_2salpn
H	*o*-C_6H_4	H_2salphen
OMe	$[CH_2]_2$	3MeO-H_2salen
OMe	$[CH_2]_3$	3MeO-H_2salpn
OMe	*o*-C_6H_4	3MeO-H_2salphen



H_2btz

RESULTS AND DISCUSSION

Complexes of the Type $[MCl(O)L]$.—The complexes were obtained by treating $[MoCl_3O(thf)_2]$ (thf = tetrahydrofuran) with (*a*) the free Schiff base H_2L in the presence of triethylamine, (*b*) the dilithium salt of the Schiff base Li_2L, or (*c*) the bis(trimethylsilyl) Schiff base $L(SiMe_3)_2$, the hydroxyl hydrogen being replaced by $SiMe_3$.

When the triethylamine base was omitted for method (*a*) the reactions failed to proceed to completion and mixtures of $[MoCl_3O(H_2L)]$ and $[MoCl_2O(HL)]$ were formed. Similar adducts with Sn^{IV},[7] Ti^{IV},[8] and Mo^{IV} are known.[5] Method (*c*) represents a particularly convenient synthetic route, as the by-product $SiMe_3Cl$ remains in solution. It provides a generally applicable method for the replacement of chloride by anionic chelating ligands and has been used to prepare molybdenum dithiocarbamatonitrido-complexes.[9] However method (*c*) is not applicable to 2,2'-bi(2,3-dihydrobenzothiazolyl), as the $SiMe_3$ derivative cannot be prepared, and here method (*b*) was used.

The $[MCl(O)L]$ complexes (Table 1) are red-brown microcrystalline solids, stable to oxidation when dry. They are insoluble in most organic solvents, but slightly soluble in dichloromethane, thf, and *NN*-dimethylformamide (dmf). The i.r. spectra of the complexes showed absorptions which are typical of co-ordinated anionic Schiff bases. The band occurring in the 1 620—1 650 cm^{-1} region in the free ligand is assigned to $\nu(C=N)$ and moved to lower frequencies on co-ordination.[10] Phenolic $\nu(C-O)$ absorptions were observed in the range 1 535—1 540 cm^{-1} indicating that the Schiff-base ligands do not bridge *via* oxygen in the complexes.[11,12] All the complexes showed a strong absorption in the 930—960 cm^{-1}

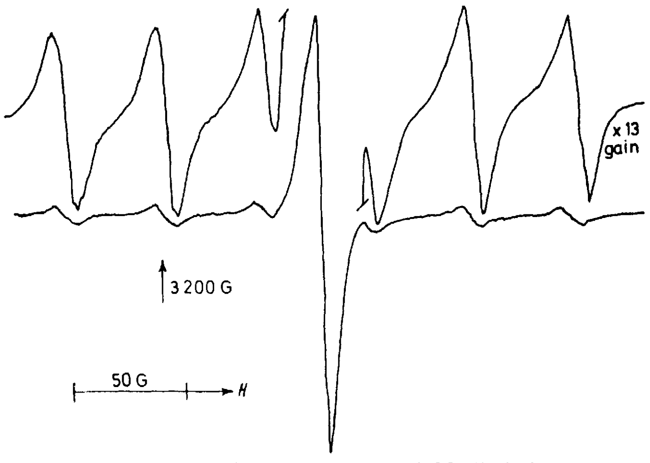


FIGURE 1 *X*-Band e.s.r. spectrum of [MoClO(salphen)] in dichloromethane at room temperature

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TABLE 1

Molybdenum-(V) and -(VI) complexes with quadridentate Schiff bases

Complex	Colour	$\mu_{\text{eff.}}$/B.M.	Analysis (%) [a] C	H	N	Cl	I.r. spectra (cm^{-1}) ν(Mo=O)	ν(C=N)	ν(C=O)	ν(Mo–Cl)	Electronic spectra (10^3 cm^{-1}) [b] In dmf	Solid reflectance
[MoClO(salen)]	Brown	1.68	46.4 (46.7)	3.7 (3.4)	6.9 (6.8)	8.5 (8.6)	939, 930	1 601	1 539	337, 278	24.2 (2 560) 12.1 (106)	22.6, 12.1
[MoClO(salpn)]	Brown	1.67	47.1 (47.4)	3.9 (3.6)	6.3 (6.4)	9.0 (8.5)	926	1 610	1 547	280	20.2 (226) 15.4 (116)	25.9, 23.8, 19.7, 13.8
[MoClO(salphen)]	Red-brown	1.68	52.0 (51.7)	3.0 (3.1)	6.1 (5.9)	7.7 (7.2)	948	1 600	1 535	322	18.9 (531)	26.2, 21.7
[MoClO(3MeO-salen)]	Red-brown	1.66	46.0 (45.6)	4.1 (3.8)	5.6 (5.9)	(7.5)	945, 930 (sh)	1 600	1 535	335, 290	c	26.1
[MoClO(3MeO-salpn)]	Red-brown	1.67	47.1 (46.7)	4.3 (4.1)	5.3 (5.7)	(7.3)	932	1 605	1 537	285	c	23.5
[MoClO(3MeO-salphen)]	Red-brown	1.67	50.1 (50.6)	3.9 (3.5)	5.3 (5.7)	7.0 (6.8)	950	1 601	1 540	330	c	25.1, 20.1 (sh)
[MoClO(bzt)]	Dark brown	1.70	40.2 (39.5)	2.4 (2.7)	6.7 (6.4)	8.5 (7.8)	960	1 610		334	c	
[MoO$_2$(salen)]	Yellow	d	48.9 (48.7)	3.4 (3.6)	6.9 (7.3)		915, 885	1 635	1 535		24.3 (1 580)	22.7
[MoO$_2$(salpn)]	Yellow	d	49.8 (50.0)	4.1 (4.0)	7.2 (6.9)		905, 865	1 630	1 525		24.4 (1 430)	22.7
[MoO$_2$(3MeO-salen)]	Yellow-orange	d	47.3 (47.6)	3.7 (4.0)	6.4 (6.2)		908, 875	1 630	1 535		23.5 (1 190)	22.7, 21.1 (sh)
[MoO$_2$(3MeO-salpn)]	Orange	d	48.4 (48.7)	4.4 (4.3)	5.9 (6.0)		912, 880	1 630	1 530		13.5 (1 220)	22.8

[a] Calculated values are given in parentheses. [b] Absorption coefficients (ε/dm^3 mol^{-1} cm^{-1}) are given in parentheses. [c] Insoluble. [d] Diamagnetic.

region assignable to terminal ν(Mo=O). In some cases this was split into two bands. The ν(Mo–Cl) absorptions occurred in the 250—350 cm^{-1} region and in the cases where two ν(Mo=O) bands were discernible two ν(Mo–Cl) bands also occurred, suggesting that two species are present in these complexes.

E.s.r. spectra. The e.s.r. spectra were recorded at room temperature in dichloromethane or dmf and were similar in both solvents.

The spectrum of [MoClO(salphen)] (Table 2, Figure 1) consisted of one strong line due to Mo with no nuclear spin and this was flanked by six satellites, the hyperfine structure being due to the interaction of the unpaired electron with Mo with nuclear spin $I = 5$. The $g_{\text{av.}}$ value is 1.938 and the molybdenum isotropic hyperfine coupling constant $A_{\text{iso.}}$(Mo) is 46 G.* The spectrum of [MoClO(salen)] (Table 2, Figure 2) was more complicated and two paramagnetic species (A and B) were clearly present. Each species gives a spectrum consisting of one main line and six satellite lines, and a superimposition of these two lines comprises the observed spectrum. From

TABLE 2

E.s.r. data

Complex	$g_{\text{av.}}$ (A)	$A_{\text{iso.}}$(Mo) (A)/G	$g_{\text{av.}}$ (B)	$A_{\text{iso.}}$(Mo) (B)/G
[MoClO(salen)]	1.938	46	1.948	46
[MoClO(salpn)]			1.944	44
[MoClO(salphen)]	1.938	46		
[MoClO(3MeO-salen)]	1.934	48	1.946	46
[MoClO(3MeO-salpn)]	1.936 *	48	1.948	46
[MoClO(3MeO-salphen)]	1.934	50		
[MoClO(bzt)]	1.967	22		

* Very weak signal.

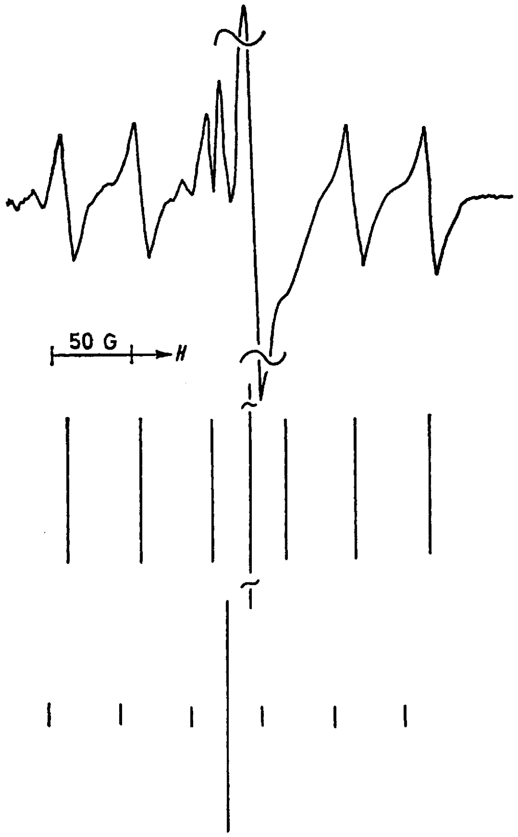

FIGURE 2 X-Band e.s.r. spectrum of [MoClO(salen)] in dichloromethane at room temperature

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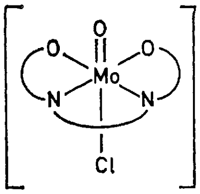
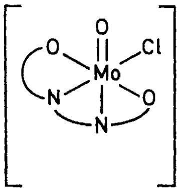
* Throughout this paper: 1 G = 10^{-4} T; 1 mmHg ≈ 13.6 × 9.8 Pa; 1 B.M. ≈ 9.27 × 10^{-24} A m^2.

the relative intensities of these lines species A is present to a larger extent than B.

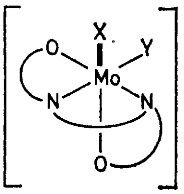
With the complexes of salen and salpn various isomers are possible because of the ability of these ligands to chelate in a non-planar fashion. The most probable isomers are (1)—(3) (X = O, Y = Cl; X = Cl, Y = O). However, salphen is quite rigid due to the *o*-phenylene backbone and all the four donor atoms must co-ordinate in a plane. Thus, for [MoClO(salphen)] only structure (1) is possible and indeed only one species was present in the e.s.r. spectrum.



(1)



(2)



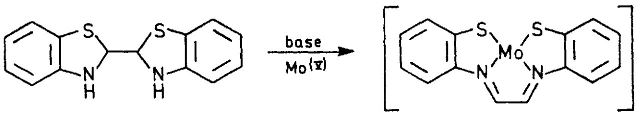
(3)

With [MoClO(salen)] structures (1)—(3) are all possible and we propose that the two species seen in the e.s.r. spectrum of this complex are isomers (1) (Cl *trans* to Mo=O) and a *cis* form [(2) and/or (3)]. Species A has $g_{av.}$ 1.938 and $A_{iso.}$(Mo) 46 G, identical to the values for [MoClO(salphen)], and species B has $g_{av.}$ 1.948 and $A_{iso.}$ (Mo) 46 G. The solid-state i.r. spectrum for [MoClO(salphen)] showed one ν(Mo=O) band at 948 cm^{-1} and a single ν(Mo–Cl) at 322 cm^{-1} and these bands can be assigned to the *trans* structure (1). The spectrum of [MoClO(salen)] showed two ν(Mo=O) bonds at 939 and 930 cm^{-1}, and two ν(Mo–Cl) at 337 and 278 cm^{-1}. We assign the bands at 939 and 337 cm^{-1} to *trans*-O=Mo–Cl [structure (1)] by analogy with [MoClO(salphen)] and the bands at 930 and 278 cm^{-1} to the complex with a *cis*-O=Mo–Cl group [structure (2) and/or (3)]. Rather surprisingly the e.s.r. spectrum of [MoClO(salpn)] showed that only one species is present with $g_{av.}$ 1.944 and $A_{iso.}$ (Mo) 44 G. The i.r. spectrum showed only a single ν(Mo=O) band at 926 cm^{-1} and a single ν(Mo–Cl) at 280 cm^{-1}. These values suggest that only one species is present, similar to one of the species present in [MoClO(salen)] with structure (2) or (3).

Thus, with the salphen ligand the rigidity of the *o*-phenylene backbone ensures that the ligand remains planar on co-ordination and so a *trans*-O=Mo–Cl arrangement results. The salen ligand provides a mixture of these structures, and thus it can be concluded that the *cis* and *trans* structures are of approximately equal stability, and where only one isomer is formed this results from peculiar steric needs of the ligand.

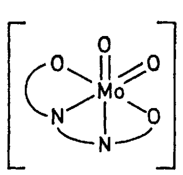
The 3MeO derivatives exhibited e.s.r. spectra similar to their unsubstituted analogues, with two species present for [MoClO(3MeO-salen)] and only one present for [MoClO(3MeO-salphen)]. The $g_{av.}$ and $A_{iso.}$ values indicate that these species are similar to those obtained for the salen and salphen ligands. There is, however, a difference in behaviour between salpn and 3MeO-salpn, because, whereas the former only forms a complex with a *cis* structure, the latter exhibited a spectrum containing a small amount of the *trans* structure (1) in addition to the predominant *cis* isomer.

The [MoClO(bzt)] complex exhibited an e.s.r. spectrum showing only the presence of one species, $g_{av.}$ 1.967 and $A_{iso.}$ (Mo) 22 G. The $g_{av.}$ value is much higher than for the N,O chelates and is consistent with e.s.r. data obtained for molybdenum(V) complexes with S donors.[13] The increase in *g* and reduction in hyperfine splitting can be interpreted in terms of delocalisation of the unpaired electron into sulphur-ligand orbitals. The bzt ligand exists as the 2,3-dihydrobenzothiazolyl compound in the free state and its i.r. spectrum showed no ν(S–H) or ν(C=N) absorptions, but did show a band assignable to ν(N–H). On co-ordination this ν(N–H) band disappeared and a band at 1 610 cm^{-1} due to ν(C=N) appeared. This is consistent with breaking of the C–S bond and co-ordination to molybdenum through S and N donors in the Schiff-base form. Because of the rigidity of the chelate backbone on complex formation the ligand is certainly planar and gives rise to structure (1).



Complexes of the Type [MoO$_2$L].—By treating [MoCl$_3$O(thf)$_2$] with some of the Schiff bases in dry ethanol in the presence of oxygen, yellow or orange crystalline solids were obtained which are quite stable in air. Similar complexes were obtained when the complexes [MoCl(O)L] were heated under reflux in dry ethanol in the presence of oxygen. Only the Schiff bases H$_2$salen, H$_2$salpn, and their 3MeO derivatives gave isolable products.

The complexes showed the usual ν(C=N) and ν(C=O) absorptions of co-ordinated Schiff bases and showed two bands in the 865—915 cm^{-1} region characteristic of the *cis*-MoO$_2$ group.[14] The complexes appear to be identical to those obtained by Yamanouchi and Yamada[6] who treated the Schiff bases with [MoO$_2$(pd)$_2$] (pd = pentane-2,4-dionate) to yield the molybdenum(VI) derivatives. From n.m.r. measurements they concluded that the complexes have the *cis* structure. This explains why we could obtain no reaction with salphen and 3MeO-salphen, as these ligands appear to be incapable of complexing in a non-planar arrangement.



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[14] K. Nakamoto, 'Infrared Spectra of Inorganic and Co-ordination Compounds,' Wiley, New York, 1963, p. 77.

EXPERIMENTAL

All the manipulations were carried out under dinitrogen, using freshly distilled dry solvents. E.s.r. spectra were obtained as previously described,[15] and other physical measurements as noted previously.[16] The Schiff-base ligands were prepared by the addition of the diamine (1 equivalent) to the appropriate salicylaldehyde derivative (2 equivalents) in ethanol. The reaction mixture was heated under reflux for 0.5 h, cooled, and the resulting yellow Schiff base filtered off, washed with ethanol, and dried *in vacuo*. 2,2′-Bi(2,3-dihydrobenzothiazolyl) was prepared according to a modification of the method of Fernando and his co-workers:[17] *o*-aminobenzenethiol (18.8 g, 0.15 mol) was placed in a flask (200 cm^3) and MeCN (50 cm^3) was added. The mixture was heated under reflux for 1 h. The compound $(CHO)_2{\cdot}H_2O$ (3.9 g, 0.05 mol) was dissolved in water (13 cm^3), and the solution was slowly added to the refluxing mixture while stirring. Gentle refluxing was continued for 15 min, whereupon the mixture was filtered, washed with MeOH (2 × 10 cm^3), and pumped dry over P_4O_{10}. Molybdenum trichloride oxide was obtained from commercial sources.

Preparation of the Complexes [MoCl(O)L].—*Method* (*a*). The appropriate Schiff base (0.005 mol) was dissolved in dry ethanol (20 cm^3) and added to a freshly prepared solution of lithium ethoxide (0.01 mol) in ethanol (20 cm^3), giving an immediate white or pale yellow precipitate of the dilithium salt. Trichloro-oxobis(tetrahydrofuran)molybdenum(v) (1.81 g, 0.005 mol) was dissolved in dry ethanol (50 cm^3) and this solution was added dropwise to the suspension of the dilithium salt, giving an immediate red-brown precipitate of the complex. The reaction mixture was heated under reflux for 0.5 h, cooled, filtered, and the product was washed with ethanol (2 × 10 cm^3) and diethyl ether (2 × 10 cm^3) and dried *in vacuo*.

Method (*b*). Triethylamine (2.02 g, 0.02 mol) was added to $[MoCl_3O(thf)_2]$ (3.62 g, 0.01 mol) and the appropriate Schiff base (0.01 mol) in acetonitrile (100 cm^3) and the mixture was heated under reflux for 0.5 h. The resulting brown solution was filtered hot and brown crystals of the complex appeared on cooling.

Method (*c*). The appropriate Schiff base (0.01 mol) was heated under reflux in hexamethyldisilazane (0.02 mol) until ammonia evolution ceased (*ca.* 1 h). The excess of hexamethyldisilazane was removed by distillation at 30 mmHg and the residue was distilled at 10^{-2} mmHg to give 85–95% yields of the bis(trimethylsilyl)Schiff base. Trichloro-oxomolybdenum(v) (1.1 g, 0.005 mol) was dissolved in acetonitrile (40 cm^3) and the bis(trimethylsilyl) derivative of the appropriate Schiff base (0.006 mol) was added dropwise. The complex precipitated after stirring for 0.5 h and was filtered off, washed with acetonitrile (20 cm^3) and diethyl ether (20 cm^3), and dried *in vacuo*.

Complexes of the Type $[MoO_2L]$.—The preparation was carried out as in method (*a*) above, but the final heating under reflux was carried out in air, giving the complexes as yellow or orange crystalline solids which were washed with ethanol (10 cm^3) and diethyl ether (10 cm^3) and dried *in vacuo*.

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