Infrared Spectra and Configurations of some Molybdenum(VI) Dihalide Dioxide Complexes

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The i.r. spectra of $MoO_2X_2L_2$ and MoO_2X_2L' complexes (X = Cl or Br; L = dmf, dmso, or pyo; L' = bipy or phen) have been compared in order to identify stretching and bending modes involving the molybdenum atom. For $MoO_2Cl_2\cdot2dmf$, assignment of bands has been assisted by calculation of vibration frequencies through normal-co-ordinate analysis. The spectra of all the adducts are consistent with a *cis–trans–cis*-octahedral arrangement of the terminal oxygen atoms (O_t), halogens, and ligand oxygen atoms (O_l), respectively, about the molybdenum. The more weakly bonded O_l atoms are thus co-ordinated *trans* to the strongly bonded O_t. There is a fairly regular relation between ligand donicity and the ν(Mo–O_t) frequency.

THE extensive co-ordination chemistry of molybdenum(VI) with oxo-ligands suggested the need for information on the identification of molybdenum–oxygen vibration frequencies. Mononuclear molybdenum(VI) dihalide dioxide adducts of the type $MoO_2X_2L_2$ [L = O-donor ligand, *e.g. NN*-dimethylformamide (dmf), dimethyl sulphoxide (dmso), and pyridine *N*-oxide (pyo)] have been used for making these i.r. assignments. Also, comparisons have been made with spectra of MoO_2X_2L' derivatives [L' = 2,2'-bipyridyl (bipy) or 1,10-phenanthroline (phen)]. For the adducts $MoO_2Cl_2\cdot2dmf$[1] and $MoO_2Cl_2\cdot2dmso$[2] (similarly $MoO_2Br_2\cdot bipy$[3]) *X*-ray structure determinations have shown a *cis–trans–cis* distorted octahedral arrangement of the O_t, X, and O_l (or N) pairs of atoms (O_t = terminal and O_l = ligand oxygen). As now reported, the spectra of related molybdenum chloride and bromide oxide complexes with a variety of

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[1] L. R. Florian and E. R. Corey, *Inorg. Chem.*, 1968, **7**, 722.
[2] L. R. Florian, *Diss. Abs.*, 1970, **B30**, 3078.
[3] R. H. Fenn, *J. Chem. Soc. (A)*, 1969, 1764.

ligands show a fairly consistent pattern of bands which suggests their structures are all based on the same *cis–trans–cis* arrangement.

RESULTS AND DISCUSSION

In the compounds examined most of the bands above 300 cm^{-1} involving the molybdenum atom were identifiable (in terms of the main vibration component) through intercomparison of the spectra. Using the vibrational pattern for these bands to provide reference points in fitting of force constants, it was possible through normal-co-ordinate analysis to calculate the frequencies of all vibration modes of the group $MoO_2Cl_2(O_l)_2$ within the adduct $MoO_2Cl_2{\cdot}2dmf$ for which the molecular geometry is known. Although the precision of the calculation is reduced by the simplifying assumption that each O_l atom is independent of the ligand molecule, a combination of intercomparison of spectra and normal-co-ordinate analysis [4] enabled identification of all 15 modes for the $MoO_2Cl_2(O_l)_2$ unit of the dmf complex. In this way it was possible to make a more complete assignment of molybdenum co-ordination bands than is available from earlier studies on other $MoO_2X_2L_2$ molecules.[5]

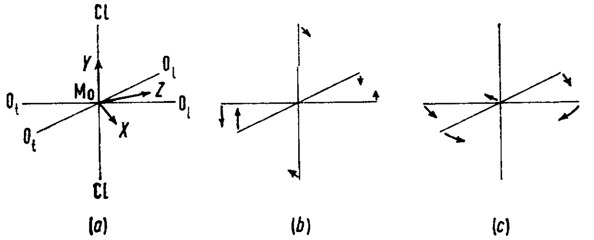

FIGURE 1 (*a*) Positions of the ligand atoms with respect to the co-ordinate axes, taking the *Z* axis as that of two-fold symmetry; (*b*) the twisting mode, $\rho_t(Mo{-}O_t)$ (the chlorine atoms counter-twist in the *XY* plane); (*c*) the in-plane bend, $\delta(O_t{-}Mo{-}O_l)$ (the molybdenum also moves in the *XZ* plane)

Vibration Modes of the cis–trans–cis-$MoO_2X_2(O_l)_2$ *Group*.—Using the initial simplification that the *cis-trans-cis*-co-ordinated atoms lie on orthogonal axes, they form a point group of C_{2v} symmetry. The 15 vibration modes are then $6A_1 + 2A_2 + 4B_1 + 3B_2$. The A_2 modes would be inactive in the i.r. region, but all would be Raman active. For the actual structure, however, loss of symmetry through bond-angle distortion could be expected to render all modes i.r. active also. For the idealised (octahedral) structure the distribution of modes is: $\nu(Mo{-}O_t)$, $A_1 + B_1$; $\delta(Mo{-}O_t)$, $A_1 + A_2 + B_2$; $\nu(Mo{-}O_l)$, $A_1 + B_1$; $\delta(Mo{-}O_l)$, $A_1 + A_2 + B_2$; $\nu(Mo{-}X)$, $A_1 + B_1$; $\delta(Mo{-}X)$, $A_1 + B_1$; and $\delta(O_t{-}Mo{-}O_l)$, B_1. Two of these vibration modes are represented in Figure 1 (*b*) and (*c*), with the four oxygen atoms lying in the equatorial plane and the axes oriented as shown. These modes are respectively (*i*) the twisting mode, $\rho_t(Mo{-}O_t)$, and (*ii*) $\delta(O_t{-}Mo{-}O_l)$ in which there is in-plane bending of O_t and O_l.

The I.r. Spectrum of $MoO_2Cl_2{\cdot}2dmf$.—Within the spectrum of this adduct there were eleven bands (ν_1—ν_6 and ν_{10}—ν_{14}, Table 1) clearly identifiable (through intercomparison) as relating to the $MoO_2Cl_2(O_l)_2$ group.

TABLE 1

Observed and calculated wavenumbers for $MoO_2Cl_2{\cdot}2dmf$

	Wavenumber/cm^{-1}		Main component of vibration	Symmetry type [a]
	obs.	calc.		
ν_1	940s	940	$\nu_{sym}(Mo{-}O_t)$	A_1
ν_2	905s	905	$\nu_{asym}(Mo{-}O_t)$	B_1
ν_3	416s [b]	417	$\nu_{sym}(Mo{-}O_l)$ [c]	A_1
ν_4	390m	390	$\nu_{asym}(Mo{-}O_l)$	B_1
ν_5	378m	368	$\delta_{sym}(Mo{-}O_t)$ [c] (in-plane)	A_1
ν_6	340s	353	$\nu_{asym}(Mo{-}Cl)$ [d]	B_2
ν_7	310w [e]	310	$\nu_{sym}(Mo{-}Cl)$	A_1
ν_8	278w [e]	271	$\rho_t(Mo{-}O_t)$ [f]	A_2
ν_9	265w [e]	267	$\delta(O_t{-}Mo{-}O_l)$ [g] (in-plane)	B_1
ν_{10}	252s	252	$\rho_r(Mo{-}O_t)$ [d]	B_2
ν_{11}	213m	213	$\delta_{sym}(Mo{-}O_l)$ (in-plane)	A_1
ν_{12}	197m	196	$\rho_r(Mo{-}O_l)$	B_2
ν_{13}	166m	182	$\rho_t(Mo{-}O_l)$ [f]	A_2
ν_{14}	145w	138	$\delta_{sym}(Mo{-}Cl)$	B_1
ν_{15}	133w	133	$\delta_{sym}(Mo{-}Cl)$	A_1

[a] For idealised structure with ligands on orthogonal axes. [b] The $\delta(NCO)$ ligand band at 683 cm^{-1} has been omitted. [c] $\nu_{sym}(Mo{-}O_l)$ and $\delta_{sym}(Mo{-}O_t)$ are strongly coupled. [d] $\nu_{asym}(Mo{-}Cl)$ and $\rho_r(Mo{-}O_t)$ out-of-plane rock are strongly coupled (Figure 2). [e] Approximate values only. [f] Twisting mode [see Figure 1(*b*)]. [g] As in Figure 1(*c*).

There were also inflexions at *ca*. 310, 278, and 265 cm^{-1} on the sides of strong bands, and weak bands at 135, 100, and near 90 cm^{-1}. All molybdenum complexes of the type $MoO_2X_2L_2$ show a pair of strong bands in the range 890—960 cm^{-1} and a band near 380 cm^{-1}. The present low-frequency study has established a further common band near 250 cm^{-1}. Following earlier $\nu(Mo{-}O_t)$ assignments,[5-10] the two strong bands at 940 and 905 cm^{-1} in $MoO_2Cl_2{\cdot}2dmf$ may be attributed respectively to the symmetric and asymmetric stretching vibrations and the medium band at 378 cm^{-1} to the $\delta_{sym}(Mo{-}O_t)$ in-plane bending vibration. The pair of bands at 416 and 390 cm^{-1}, the positions of whose counterparts in the dmso and pyo derivatives vary with the ligand but not with the halogen (Table 2), could arise from the $\nu_{sym}(Mo{-}O_l)$ and $\nu_{asym}(Mo{-}O_l)$ modes.

The strong i.r. band shown by the dmf adduct at 340 cm^{-1} had a weak Raman counterpart (347 cm^{-1}) and is attributed to the $\nu_{asym}(Mo{-}Cl)$ vibration. On the other hand the weak i.r. absorption at 310 cm^{-1} was strong in the Raman (312 cm^{-1}) and arises from $\nu_{sym}(Mo{-}Cl)$. It will be seen from Tables 2 and 3 that these $\nu(Mo{-}Cl)$ bands from the dmf complex are matched in the spectra of the other chlorides but not in the bromides.

The results of the normal-co-ordinate analysis of the spectrum of $MoO_2Cl_2{\cdot}2dmf$ substantiate these assignments, but add the information that the ν_3 and ν_5

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[4] See, for example, I. Nakagawa and T. Shimanouchi, *Spectrochim. Acta*, 1966, **22**, 759.

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frequencies at 416 and 378 cm^{-1} (Table 1) arise from mixing of the ν_{sym}(Mo–O$_l$) and δ_{sym}(Mo–O$_t$) in-plane modes and that the pair of bands, ν_6 and ν_{10}, at 340 and 252 cm^{-1} involve strong coupling of the ρ_r(Mo–O$_t$) out-of-plane and ν_{asym}(Mo–Cl) vibrations, as shown in Figure 2.

TABLE 2

I.r. spectra of the oxo-complexes (in cm^{-1}) [a]

Assignment \ Complex	MoO_2Cl_2· 2dmf	MoO_2Cl_2· 2dmso	MoO_2Br_2· 2dmso	MoO_2Cl_2· 2pyo	MoO_2Br_2· 2pyo	MoO_2Cl_2· 2thf	MoO_2Br_2· 2thf	MoO_2Cl_2· 2NCMe [b]
ν_{sym}(Mo–O$_t$)	940s	921s	922s	933s	929s	958s	958s	960s
ν_{asym}(Mo–O$_t$)	905s	892s	890s	901s	898s	920s	917s	920s
ν_{sym}(Mo–O$_l$)	416s	454s	453s	478m	472m			
ν_{asym}(Mo–O$_l$)	390m	436s	437s	467m	461m			
δ_{sym}(Mo–O$_t$)	378m	385w	376m	392m	380m	388m	380m	387m
ν_{asym}(Mo–X)	340s	330s	242s [c]	320s	238s [d]	345s	*e*	346s
ν_{sym}(Mo–X)	310w	292m	225m	303w	224m	318 (sh)	*e*	320w
ρ_r(Mo–O$_t$)	252s	256m	252s [c]	250m	249s [d]	260m	261m, br	250m
δ_{sym}(Mo–O$_l$)	213m	225m, 200m	205m	215m	214m	*f*	*f*	*f*
ρ_r(Mo–O$_l$)	197m	180m	170m	182m	185m			
δ_{sym}(Mo–X)	145w, 133w	128w	92w	122w				

[a] Ligand bands are generally weak and have been omitted. [b] MoO_2Cl_2·2NCMe is included for comparison. [c,d] For MoO_2Br_2·2dmso and MoO_2Br_2·2pyo the ν_{asym}(Mo–Br) and ρ_r(Mo–O$_t$) bands cannot be distinguished. [e] Not identified. [f] Spectra were not run below 200 cm^{-1}.

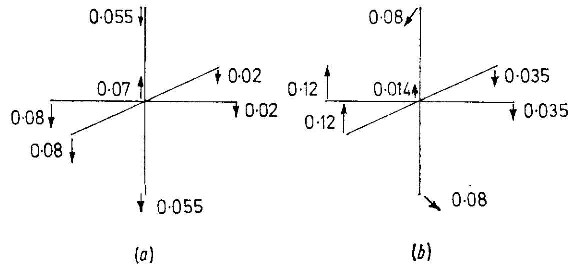
TABLE 3

I.r. spectra of 2,2′-bipyridyl and 1,10-phenanthroline complexes (cm^{-1}) [a]

Assignment \ Complex	MoO_2Cl_2·bipy	MoO_2Br_2·bipy	MoO_2Cl_2·phen	MoO_2Br_2·phen
ν_{sym}(Mo–O$_t$)	938s	934s	938s	936s
ν_{asym}(Mo–O$_t$)	904s	905s	904s	903s
δ_{sym}(Mo–O$_t$) (in-plane)	390m	375m	382w	366w
ν_{asym}(Mo–X)	342s	252s, br [b]	339s, br	257m [c]
ν_{sym}(Mo–X)	318w	218m	310m	216m
ρ_r(Mo–O$_t$)	241m	252s, br [b]	238s	257m [c]
ν(Mo–L)	208m, 192m	192w, 178m	192w, 180w	193w, 178m
δ_{sym}(Mo–X)	145m	*d*	148m [e]	117m

[a] Ligand bands are omitted. [b,c] ν_{asym}(Mo–Br) and ρ_r(Mo–O$_t$) are unresolved. [c] A shoulder at 248 cm^{-1} corresponds to a ligand band. [d] Not identified. [e] A band at 165 cm^{-1} has not been assigned.

To facilitate comparison with the vibration frequencies shown by other compounds (Table 2), these ν_3, ν_5, ν_6, and ν_{10} bands of MoO_2Cl_2·2dmf are designated in terms of their respective main vibration components, ν_{sym}(Mo–O$_l$), δ_{sym}(Mo–O$_t$) in-plane, ν_{asym}(Mo–Cl), and ρ_r(Mo–O$_t$) out-of-plane.



(a) (b)

FIGURE 2 The ν_6 (*a*) and ν_{10} modes (*b*) for MoO_2Cl_2·2dmf which both arise from coupling of the ν_{asym}(Mo–Cl) stretching and the ρ_r(Mo–O$_t$) out-of-plane bending vibrations. Relative vibration amplitudes are shown. Atomic vibrations are largely in the vertical (*Y*) direction, but for the chlorine atoms in (*b*) the vector lies in the *YZ* plane

Calculation of Vibrational Frequencies for MoO_2Cl_2·2dmf.—The force constants and vibrational frequencies were calculated using a program based on the approach of Gwinn.[11] The input co-ordinates for the distorted octahedral grouping $MoO_2Cl_2(O_l)_2$ were taken from the *X*-ray structural data.[1] Output from the computer program allowed simple identification of the vibrations and was especially useful in showing those of mixed type. The later stages of refinement of the force constants were made using a minimum-deviation criterion, *i.e.*

$$\delta\{\Sigma|\bar{\nu}_{calc.} - \bar{\nu}_{exp.}|\} = 0$$

Twelve frequency values were available for calculation of force constants, eleven of them from well resolved bands. The last represented the ν_{sym}(Mo–Cl) mode, already established as lying at 310 cm^{-1}. Initial calculations showed the vibration pattern in the region 380—240 cm^{-1} to be sensitive to the combination of force constants employed, and also that in general stretch–bend interactions were of minor significance as compared with stretch–stretch. The set of constants in Table 4 was found to give a pattern in qualitative accord with the assignments required for the higher-frequency

TABLE 4

Calculated force constants

f	Value	*f*	Value
Mo–O$_t$ [a]	6·82	Mo–O$_t$, Mo–Cl [b]	–0·03
Mo–O$_t$, Mo–O$_t$ [b]	0·47	O$_t$–Mo–O$_t$ [c]	1·32
Mo–O$_l$ [a]	1·23	O$_t$–Mo–Cl [c]	0·85
Mo–O$_l$, Mo–O$_l$ [b]	–0·04	O$_t$–Mo–O$_l$ [c]	0·92
Mo–Cl [a]	1·54	O$_l$–Mo–O$_l$ [c]	0·58
Mo–Cl, Mo–Cl [b]	0·46	O$_l$–Mo–Cl [c]	0·68

[a] Stretch, mdyn Å^{-1}. [b] Stretch–stretch, mdyn Å^{-1}. [c] Bend, mdyn Å rad^{-2}.

[11] W. D. Gwinn, *J. Chem. Phys.*, 1971, **55**, 477.

bands, and to provide satisfactory convergence on refinement. The possibility that any of the observed frequencies might arise from the co-ordinated ligand, rather than the $MoO_2X_2(O_l)_2$ group, was examined. For example, the adducts $SnCl_4$·2dmf and $SnBr_4$·2dmf both show weak i.r. bands at 200 and 180 cm^{-1} (ref. 12) and these may be ligand bands (or may arise from metal–donor bending modes). Since MoO_2Cl_2·2dmf has a band at 197 cm^{-1} the possibility of erroneous assignment was tested by separate calculations which excluded the use of the frequencies at 212, 197, and 166 cm^{-1}, both separately and in pairs. In no case was there more than a small alteration in calculated frequencies. Therefore, although comparison with SnX_4·2dmf suggests that one or two of the bands at 212, 197, and 166 cm^{-1} could arise from ligand vibrations, the calculation confirmed that the $MoO_2Cl_2(O_l)_2$ group itself has vibration frequencies close to these values.

The analysis confirmed the presence of two additional bands (ν_8 and ν_9) in the 300—250 cm^{-1} range, one of which, the twisting mode, ν_8, could be expected to be particularly weak. It also identified the second Mo–Cl bending mode at 133 cm^{-1} (rather than at a lower frequency) and enabled assignment of the Mo–O$_l$ deformation modes ν_{11}, ν_{12}, and ν_{13}, although with ν_{13} agreement between calculated and observed frequencies was not close. Assignments were determined for all the observed bands above 100 cm^{-1}.

Molybdenum Co-ordination Frequencies in Other Adducts.—(i) *Chlorides*. In MoO_2Cl_2·2dmso and MoO_2Cl_2·2pyo the pattern of spectral bands (Table 2) corresponded to that in the dmf adduct. For MoO_2Cl_2·2thf and MoO_2Cl_2·2NCMe (as also MoO_2Br_2·2thf) the pattern differed in showing no identifiable ν(Mo–L) bands above 200 cm^{-1}.* This reflects the generally weaker bonding of these ligands [13,14] associated with their lower donicity values [15] (see below).

(ii) *Bromides*. A medium band at 225 cm^{-1}, as in MoO_2Br_2·2dmso and MoO_2Br_2·2pyo (Table 2), is assigned as ν(Mo–Br). In contrast with the chlorides, the 'ρ_r(Mo–O$_t$)' band was now broadened or resolved into two components. It is inferred that this composite band contains the ν_{asym}(Mo–Br) frequency. The Mo–X bending modes appeared below 150 cm^{-1} for the chlorides and below 125 cm^{-1} for the bromides.

(iii) 2,2'-*Bipyridyl and* 1,10-*phenanthroline complexes*. In these adducts the frequencies of the Mo–O$_t$ and Mo–X modes (Table 3) matched those of the oxo-complexes, but the ν(Mo–L) bands lay at much lower frequency than the ν(Mo–O$_l$), and δ(Mo–L) bending frequencies were not identified.

Ligand Interactions.—A pair of ligands in *cis* positions can interact with all three *d* orbitals of the t_{2g} group, but a *trans* pair with only two. The Mo–O$_t$ bonds have strong π character and for all known structures display a *cis* configuration.[5-10,16] There is much evidence that bonds *trans* to O$_t$ are long and presumably weakened, as for example in the quinolin-8-ol [17] and pentane-2,4-dione [18,19] complexes; it is generally inferred that the atoms in these *trans* positions suffer greater repulsion from the π-bonding charge flowing from O$_t$ into the *d* orbitals of the metal.

In the present compounds, the halogens are *trans* to each other, but mutually *cis* to both the Mo–O$_t$ bands. This configuration may stem from the interplay of a variety of factors. Among these are (*i*) electrostatic interaction between the anionic halides, (*ii*) a preference of the anionic halide for the ('out-of-plane') region which is less enclosed by *d*-orbital charge, and (*iii*) a possible preference of the O$_l$ donor atoms for the (in-plane) co-ordination sites where a greater residual π-bonding potentiality of the molybdenum, through involvement of all three of the t_{2g} orbitals, may still persist.

From the available structural results it appears to be a general feature of neutral molybdenum(VI) complexes of this type that the anionic groups take up mutually *trans* positions, as in the quinolin-8-ol,[17] 1,3-diphenylpropane-1,3-dione,[20] and uramil-*NN*-diacetic acid [21] derivatives. There is also evidence of a systematic effect of the oxo-ligand on the Mo–O$_t$ and Mo–Cl bonding. The weak co-ordination of thf and MeCN has generally been attributed to the poor electron-donor activity of these molecules, and their donicity values [15] which provide a quantitative measure of this property are found to be low. For the present thf and MeCN adducts the frequencies involving Mo–O$_t$ and Mo–Cl vibrations lie at higher values than for the complexes with stronger ligands. It is of interest, therefore, that for those ligands (L) for which donicity values are available there is a rather close correlation between increasing donicity and reduction in stretching frequencies, ν(Mo–O$_t$), in $MoO_2Cl_2L_2$ molecules (Table 5).

TABLE 5

Dependence of ν(Mo–O$_t$) on ligand donicity in $MoO_2Cl_2L_2$

L	MeCN	EtCN	PrCN	thf	dmf	dmso
Donicity [a]	14·1	16·1	16·6	20·1	26·6	29·8
$\bar{\nu}$(Mo–O$_t$)/cm^{-1}	960	965 [b]	962 [b]	958	942	921
	920	922 [b]	922 [b]	920	907	890

[a] From ref. 15. [b] From ref. 8.

The observed trend in ν(Mo–O$_t$) frequencies with increasing ligand (O$_l$) to metal charge transfer can be

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* thf = Tetrahydrofuran.

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[21] R. J. Butcher and B. R. Penfold, unpublished work.

TABLE 6

Elemental analyses (%), with calculated values in parentheses

Adduct	Method of preparation	Colour	C	H	Halogen [a]	Mo [b]	N
$MoO_2Cl_2{\cdot}2dmf$	(B)	White	20·8 (20·9)	4·1 (4·1)	20·3 (20·6)	27·9 (27·8)	8·3 (8·1)
$MoO_2Cl_2{\cdot}2dmso$	(B)	White	13·8 (13·6)	3·4 (3·4)	19·3 (19·9)	26·9 (27·0)	
$MoO_2Br_2{\cdot}2dmso$	(C)	Yellow	11·0 (10·8)	2·6 (2·7)	36·0 (36·0)	20·8 (21·6)	
$MoO_2Cl_2{\cdot}2pyo$	(A)	White	30·6 (30·9)	2·7 (2·6)			
	(B)		31·2 (30·9)	2·8 (2·6)			7·3 (7·2)
$MoO_2Br_2{\cdot}2pyo$	(A)	Pale yellow	25·5 (25·1)	2·2 (2·2)			
$MoO_2Cl_2{\cdot}2OPPh_3$ [c]	(B)	Yellow	57·3 (57·3)	4·0 (3·8)	9·5 (9·4)	12·7 (12·7)	
$MoO_2Br_2{\cdot}2OPPh_3$ [c]	(C)	Yellow	51·5 (51·3)	3·6 (3·0)	19·3 (18·9)	10·8 (11·4)	
$MoO_2Cl_2{\cdot}2ONMe_3$ [d]	(B)	Pale green [e]	21·3 (20·6)	5·8 (5·2)	20·4 (20·6)	27·2 (27·4)	
$MoO_2Cl_2{\cdot}2OAsMe_3$ [d]	(B)	Pale green [e]	15·2 (15·0)	3·0 (3·8)	14·6 (15·0)	21·1 (20·3)	
$MoO_2Cl_2{\cdot}2thf$	(A)	White	26·1 (28·0)	4·5 (4·35)			
$MoO_2Br_2{\cdot}2thf$	(A)	Yellow	22·1 (22·2)	3·6 (3·7)			
$MoO_2Cl_2{\cdot}2NCMe$	(A)	White	17·0 (17·1)	2·1 (2·1)			
$MoO_2Cl_2{\cdot}bipy$	(C)	White	34·1 (33·9)	2·5 (2·3)			8·0 (7·9)
$MoO_2Br_2{\cdot}bipy$	(C)	Yellow	27·2 (27·1)	2·0 (1·8)			6·4 (6·3)
	(A)		27·2 (27·1)	2·0 (1·8)			
$MoO_2Cl_2{\cdot}phen$	(C)	Pale green [e]	39·3 (38·1)	2·6 (2·2)			7·4 (7·4)
$MoO_2Br_2{\cdot}phen$	(C)	Yellow	30·9 (30·8)	1·8 (1·7)			6·1 (6·0)

[a] By Volhard titration. [b] As oxinate. [c] Spectra not analysed. [d] For spectral assignments see ref. 5. [e] The colour of these samples may arise from slight contamination by molybdenum(V).

interpreted in terms of a progressive reduction in the transfer of π-bonding charge from O_t to molybdenum [6,9,16] with consequent reduction in π-bond order. At the same time the results do not exclude the possibility of limited π-bonding interaction between the O_l and molybdenum atoms.

EXPERIMENTAL

I.r. Spectra.—These were run on Nujol mulls, using Perkin-Elmer 337, Grubb–Parsons DM4, and RIIC Fourier FS-720 spectrophotometers over the respective ranges 4 000—400, 500—200, and 360—40 cm^{-1}.

Preparation of Adducts.—Three preparative routes were used (see Table 6). Several chlorides and bromides were obtained directly from the dihalide dioxides [22] [method (A)]. Other chlorides were obtained from lead molybdate and acetyl chloride, following Krauss and Huber [23] [method (B)]. Bromides were prepared from molybdic acid and hydrobromic acid [method (C)], as an extension of the procedure of Kergoat and Guerchais.[24] The testing of the applicability of the preparative methods covered several adducts additional to those used in the spectral analysis.

Method (*A*). For the preparation of the tetrahydrofuran (thf) and acetonitrile derivatives solutions of the halide oxides in the liquid ligand were evaporated under vacuum. With pyridine *N*-oxide (pyo) and 2,2′-bipyridyl (bipy) the ligand and halide oxide were mixed in dichloromethane solution.

Method (*B*). A slight excess of the ligand, dissolved if necessary in the minimum quantity of dichloromethane, was added to a solution of lead molybdate in acetyl chloride. Yields were in the range 30—60%. With trimethylamine oxide and pyridine *N*-oxide, ligand hydrochloride also separated making it necessary to recrystallise the complex.

Method (*C*). This procedure readily gave the pure bromide complexes of dimethyl sulphoxide and triphenylphosphine oxide. Complexes of more basic ligands were also obtained by this method, but ligand hydrobromide formed at the same time had to be removed by recrystallisation from acetone.

All samples were pumped free from solvent under high vacuum. Analytical data are given in Table 6. Apart from the thf, MeCN, and trimethylarsine oxide derivatives for which dry-box handling was essential, the adducts were not noticeably affected by limited exposure to air. Examples of specific preparations by methods (B) and (C) are given.

Dichlorodioxomolybdenum–(NN-*dimethylformamide*) (1/2), *method* (*B*). Lead molybdate (5 g) was moistened with dichloromethane (5 cm^3) and acetyl chloride (15 cm^3) added. The mixture was stirred for 30 min, filtered, and the residue washed with a little dichloromethane. Addition of dmf (1·9 cm^3) to the brown filtrate gave a green solution from which pale green crystals separated at 0 °C. The white *product* was recrystallised from dichloromethane and washed with light petroleum.

Dichlorodioxomolybdenum–pyridine N-*oxide* (1/2), *method* (*B*). The filtrate from the lead molybdate–acetyl chloride reaction was obtained as above. Anhydrous (vacuum-distilled) pyridine *N*-oxide (2·6 g) in dichloromethane (7 cm^3) was added. The green product which separated was twice extracted into acetone to eliminate ligand hydrochloride, giving white *crystals* of the complex.

Dibromodioxomolybdenum–dimethyl sulphoxide (1/2), *method* (*C*). Molybdic acid ($H_2MoO_4{\cdot}H_2O$, 5 g) was dissolved with warming in the minimum volume (*ca.* 25 cm^3) of concentrated (46%) hydrobromic acid. Addition of dmso (4·0 cm^3) led to separation of yellow-green crystals of the complex. The product was washed with ethanol and recrystallised as yellow *needles* (5 g) from acetone.

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