Electronic Structure of Axially Distorted Molybdenum(v) Complexes; an Absorption Spectral Study

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Electronic absorption spectra of a range of molybdenum(v) complexes and $[WOCl_4(H_2O)]^-$ have been measured in the temperature range 4.2—300 K and in the energy range 4 000—40 000 cm^{-1}. The absorption bands below 18 000 cm^{-1} have been assigned to the one-electron promotion $d_{xy}^* \longrightarrow d_{xz}^*, d_{yz}^*$. Bands in the visible region have been classified as type I ($d_{xy}^* \longrightarrow d_{x^2-y^2}^*$) or type II (in-plane ligand-to-metal charge transfer). Assignments of the absorption spectra of the chromophores MoO^{3+}, VO^{2+}, WO^{3+}, MoN^{2+}, RuN^{3+}, and OsN^{3+} have been compared to produce a self-consistent assignment.

The assignment of the electronic absorption spectra of terminal mono-oxo- and nitrido-complexes of d^1 and d^2 configurations has been the subject of continual study since the initial observations of Jørgensen[1] and the publication of the molecular orbital calculations of Gray and co-workers.[2,3] Many assignments[4—15] have since been proposed and the major controversy in the oxo-systems has been the nature of the absorptions in the visible region of the spectrum. The most detailed studies for MoO^{3+} have been the single-crystal measurements on $[MoOCl_4]^-$,[10] $[MoOCl_4(H_2O)]^-$,[11] and $[MoOCl_3(hmpa)_2]$ [hmpa = $P(NMe_2)_3O$],[16] where different assignments have been proposed for the bands at *ca.* 22 000 cm^{-1}, based on the observed vibrational structure and polarization data. More recently, the successful interpretation[12] of the electronic structure of a range of VO^{2+} complexes prompted a new investigation of the polarized single-crystal spectrum of $[AsPh_4][CrOCl_4]$ which led to a reinterpretation of the visible absorption[17] bands of $[CrOCl_4]^-$. This CrO^{3+} chromophore is now believed to provide a basis for the comparison of the electronic spectra of VO^{2+} and MoO^{3+} moieties. Herein are presented the electronic absorption spectra of several MoO^{3+} complexes and an assignment of each that is in accord with that described[12] for VO^{2+} complexes and subsequently extended[17] to $[CrOCl_4]^-$.

Experimental

Preparation of Compounds and Structural Information.— Pentachloromolybdenum(v), $MoCl_5$ (Alfa), was purified prior to use, by sublimation in an evacuated four-compartment tube using a tube furnace. This sublimation took place over a temperature gradient of 280—30 °C during a period of *ca.* 3 d.

Trichlorooxobis(tetrahydrofuran)molybdenum(v), $[MoOCl_3(thf)_2]$. The contents of an $MoCl_5$ sublimation tube (*ca.* 30 g, 0.1 mol) were dissolved in dry CH_2Cl_2–CCl_4 (500 cm^3, 1:1 v/v) under dinitrogen. Dry, peroxide-free, thf (25 cm^3) was added and the mixture stirred at 0 °C until the solution was bright green. The volume was reduced to *ca.* 50 cm^3 by evaporation under reduced pressure at *ca.* 70 °C. The emerald-green product was collected by filtration under dinitrogen, washed with dry CCl_4, dry hexane, and pumped to dryness at room temperature.

Tetrachlorobis(tetrahydrofuran)molybdenum(IV), $[MoCl_4(thf)_2]$, was prepared from resublimed $MoCl_5$, after the method of Anker *et al.*[18]

Tetraphenylarsonium tetrachlorooxomolybdate(v), $[AsPh_4](MoOCl_4]$, was prepared as described previously.[10] (Found: C, 45.3; H, 3.0; Cl, 22.8; Mo, 15.1. Calc. for $C_{24}H_{20}AsCl_4MoO$; C, 45.2; H, 3.1; Cl, 22.3; Mo, 15.1%). This compound has been shown to crystallize in the *P4/n* space group,[10] with the unique crystal and molecular four-fold axis of symmetry parallel to the elongated direction of the tetragonal block-like crystals. The absorption spectra, at 4.2 K recorded with the electric vector of the incident radiation polarized parallel to the molecular *z* and *xy* axes, are shown in Figure 1(*a*) and the band positions (s = strong, m = medium, w = weak, sh = shoulder, and br = broad) are: *z* polarization, 16 000(vbr)w, 21 650w, 22 032m, 22 430m, 22 740m, 23 100m, 23 460m, 23 800(sh), and 26 480s; *xy* polarization, 12 530(sh), 13 750(br)w, 14 720w, 15 630m, 16 670(sh), 17 680w, 22 160(sh), 22 520m, 22 840m, 23 160m, 23 580w, 23 850w, 24 110(br)(sh), 24 580(br)(sh), 26 380s, 28 230s, 30 850s, and 32 070s cm^{-1}.

Tetraphenylarsonium tetrachloro(methanol)oxomolybdate-(v), $[AsPh_4][MoOCl_4(MeOH)]$, was prepared by the recrystallization of $[AsPh_4][MoOCl_4]$ from dry MeOH, by allowing solvent evaporation in a dry-box. (Found: C, 44.9; H, 3.6; Cl, 21.0; Mo, 14.4. Calc. for $C_{25}H_{24}AsCl_4MoO_2$: C, 44.8; H, 3.6; Cl, 21.2; Mo, 14.3%). This compound also crystallizes in the *P4/n* space group, with *z* and *xy* molecular directions being parallel to the edges of the tetragonal blocks so obtained.[19] The electronic spectra recorded for this compound as a single crystal at 4.2 K are presented in Figure 1(*b*) and the band positions are: *z* polarization 11 740(sh)w, 12 520m, 13 410s, 14 250s, 15 000s, 15 830(sh), 17 140(sh), and 22 600s; *xy* polarization, 11 340(sh), 12 530s, 13 410s, 14 250s, 15 000s, 15 830m, 16 760(sh), 17 660(sh), 21 380(sh), 21 690(sh), 22 030(sh), 22 290m, 22 550m, 22 830w, and 24 550(sh) cm^{-1}.

Tetraphenylarsonium aquatetrabromoxomolybdate(v), $[AsPh_4][MoOBr_4(H_2O)]$, was prepared by precipitation with $[AsPh_4]Cl{\cdot}H_2O$ (1 g, 2.3 mmol in concentrated aqueous HBr) from a concentrated hydrobromic acid solution (20 cm^3) of ammonium paramolybdate $[NH_4]_6[Mo_7O_{24}]{\cdot}4H_2O$ (1 g, 5.66 mmol Mo), following reduction with hydrazine (2 cm^3 of a 40% aqueous solution), according to the procedure of Sabat *et al.*[20] (Found: C, 35.1; H, 2.6; Br, 38.4; Mo, 11.5. Calc. for $C_{24}H_{22}AsBr_4MoO_2$: C, 34.6; H, 2.6; Br, 38.4; Mo, 11.5%).

Although this compound has been crystallographically characterized[21] and the space group shown to be *P4/n*, crystals suitable for a polarization study could not be grown. The mull spectrum at 77 K is reported in Figure 1(*c*) and the band positions are: 10 780(vbr)w, 12 130m, 12 820s, 13 720s, 14 660m, 15 680m, 16 480(sh), 17 650w, 20 380vs, 22 900vs, and 24 870vs cm^{-1}.

Tetraphenylarsonium aquatetrachlorooxotungstate(v),

$[AsPh_4][WOCl_4(H_2O)]$, was prepared as pale blue crystals by reduction of WCl_6 (0.91 g, 2.3 mmol) by ethanolic hydrochloric acid (30 cm^3 of a 1 : 10 v/v mixture) in the presence of granulated zinc with the subsequent addition of $[AsPh_4]Cl$ (1 g, 2.3 mmol). A powdered sample of this compound was most conveniently obtained, using standard Schlenk-tube techniques, by dissolving WCl_6 (0.91 g, 2.3 mmol) in absolute ethanol (100 cm^3), saturated with hydrogen chloride, and passing HCl gas into the solution until a light blue colouration was obtained. Addition of $[AsPh_4]Cl$ (1 g, 2.3 mmol), followed by partial removal of solvent under reduced pressure, filtration, and drying *in vacuo* produced a pale blue powder (Found: C, 24.7; H, 3.0; Cl, 18.5; W, 24.7. Calc. for $C_{24}H_{22}AsCl_4O_2W$: C, 24.8; H, 3.0; Cl, 19.1; W, 24.8%).

Crystalline $[AsPh_4][WOCl_4(H_2O)]$ has been shown[22] to be isomorphous with its molybdenum analogue. An attempt was made to record a single-crystal spectrum by polarizing the incident radiation parallel to the extinction directions of the tetragonal block. Unfortunately the crystal proved too small to obtain meaningful spectral data. The mull spectral data obtained at 4.2 K are given in Figure 1(*d*) and the band positions are: 12 400w, 13 380s, 14 590s, 15 500s, 16 550m, 17 430w, 18 260w, and 25 100s cm^{-1}.

Tetraphenylarsonium acetonitriletetrabromooxomolybdate(V), $[AsPh_4][MoOBr_4(MeCN)]$, was prepared by repeated recrystallization of $[AsPh_4][MoOBr_4(H_2O)]$ from dry MeCN *in vacuo*.[22] The crystals were obtained as green plates (Found: C, 36.8; H, 2.8; Br, 37.0; Mo, 10.8. Calc. for $C_{26}H_{23}Br_4MoNO$: C, 36.5; H, 2.7; Br, 37.4; Mo, 11.2%).

The salt $[AsPh_4][ReOBr_4(MeCN)]$ is triclinic[23] and, since several of the molybdenum complexes reported here are isomorphous with the corresponding rhenium analogue,[24–26] it is possible that this extends to these two acetonitrile adducts. However, since the well developed faces of crystals of $[AsPh_4][MoOBr_4(MeCN)]$ did not display colour changes or extinction, when examined under a polarizing microscope, an unpolarized crystal spectrum was obtained at 5 K and the details are presented in Figure 1(*e*). The band positions are: 12 880(sh), 14 440(sh), 15 010(sh), 15 680w, 16 080m, 16 360(sh), 16 600w, 16 950m, 17 210(sh), 17 420(sh), 17 800(sh), 19 860vs, 21 100vs, 23 410vs, and 25 400vs cm^{-1}.

Ammonium pentafluorooxomolybdate(V), $[NH_4]_2[MoOF_5]$. The crystal structure of $K_2[MoOF_5]\cdot H_2O$ has been reported.[27] The compound crystallizes in the monoclinic space group C_2 with the $[MoOF_5]^{2-}$ anions having C_s symmetry. The Mo–O(terminal) bond length is 1.666(26) Å, with a mean in-plane Mo–F distance of 1.88 Å and a Mo–F distance, *trans* to the oxo-group, of 2.028(10) Å. An intense i.r. absorption has been reported at 980 cm^{-1} and assigned as the Mo–O(terminal) stretching frequency. However, the preparation of this compound as one of a number of components from the reduction of Mo^{VI} in aqueous HF is not a suitable method for the studies intended here. Similarly, the procedure for the preparation of $[MoOF_5]^{2-}$ described by Chakravorti and Pandit[28,29] is unsuitable,[30] producing a mixture of products including contamination by 'molybdenum blues.' The solution e.p.r. studies of Garif'yanov *et al.*[31] suggest that a successful preparation of $[MoOF_5]^{2-}$ would yield a product with a *g* value of *ca.* 1.91.

The following method was used to prepare $[NH_4]_2[MoOF_5]$. Ammonium paramolybdate (6.0 g, 34 mmol of Mo) suspended in hydrofluoric acid (60%, 60 cm^3) in a Polythene beaker was treated with hydrazine hydrate (40%, 5 cm^3) and heated on a steam-bath until the effervescence ceased and the solution was blue. Ammonium fluoride was then added to produce a $[NH_4]^+$: Mo ratio of 2 : 1. The solution was purged with purified dinitrogen and a portion of this solution was set aside in the dark to crystallize by slow evaporation of solvent. After several weeks large blue plates which showed no extinctions or polarizations under the polarizing microscope had grown from the reaction medium (Found: H, 3.3; F, 38.8; Mo, 39.2; N, 11.3. Calc. for $H_8F_5MoN_2O$: H, 3.2; F, 39.1; Mo, 39.5; N, 11.5%). A strong i.r. absorption was found at 980 cm^{-1}. The compound was e.s.r. active with $g = 1.904$ for a powder sample at room temperature. An unpolarized crystal spectrum obtained at 4.2 K yielded the results shown in Figure 1(*f*) and the band positions: 12 420m, 25 000(sh), 31 220(sh), 31 660s, 32 220vs, 32 530s, 33 350s, and 34 940(sh) cm^{-1}. Features above 30 000 cm^{-1} were obtained using a very thin crystal (*ca.* 10^{-3} in, *ca.* 2.5×10^{-5} m).

The salt $[NEt_4]_2[MoO(NCS)_5]$ was produced[20] by hydrazine (5 cm^3 of a 40% solution) reduction of ammonium paramolybdate (3 g, 17 mmol of Mo) in concentrated hydrochloric acid (75 cm^3), with subsequent addition of NH_4NCS (7 g, 92 mmol) and NEt_4Br (9 g, 42 mmol). The compound was recrystallized by slow evaporation of a dry acetone solution of the deep red product in a dry-box (Found: C, 37.9; H, 5.9; Mo, 14.7; N, 14.6. Calc. for $C_{21}H_{40}MoN_7OS_5$: C, 38.1; H, 6.0; Mo, 14.4; N, 14.8%). An unpolarized crystal spectrum at 80 K yielded the results shown in Figure 2(*a*). The band positions are: 12 190m, 12 890m, 13 650m, 19 150vs, 20 920vs, 23 150vs, and 24 770s cm^{-1}.

The compound $[MoNCl_2(PPh_3)_2]$ was prepared using the method of Chatt and Dilworth[32] (Found: C, 60.9; H, 4.5; Cl, 10.6; N, 2.1. Calc. for $C_{36}H_{30}Cl_2MoNP_2$: C, 61.1; H, 4.3; Cl, 10.1; N, 2.0%). The electronic absorption spectrum was recorded as a mull in poly(dimethylsiloxane) at 5 K as shown in Figure 2(*b*) with band positions: 24 490(sh), 25 120vs, 25 930s, 26 770s, 27 630s, and 28 470(sh) cm^{-1}. There are no bands between 5 000 and 24 000 cm^{-1}.

The compound $[MoOCl_3(hmpa)_2]$ was prepared as described previously[16] (Found: C, 25.0; H, 6.7; Mo, 16.9; N, 14.5. Calc. for $C_{12}H_{36}Cl_3MoO_3P_2$: C, 25.0; H, 6.3; Mo, 16.6; N, 14.6%). The crystals were obtained as needles with a diamond cross-section. Extinction and polarization directions were apparent under the polarizing microscope, being parallel and perpendicular to the needle axis on one of the four large crystal faces. These directions are parallel to the *b* and c^* crystal axes and are defined[16] as $z(\parallel)$ and $y(\perp)$ directions. The spectra recorded at 4.2 K are given in Figure 2(*c*) with band positions: 'perpendicular' polarization, 11 490(sh), 12 110m, 12 980s, 13 740s, 14 539m, 15 240m, 16 110w, 17 230w, and 22 900s; 'parallel' polarization, 11 370(sh), 12 110w, 12 980m, 13 740m, 14 450m, 15 240w, and 22 900m cm^{-1}.

The compound $[MoOCl_3(tmu)_2]$, (tmu = *N,N,N',N'*-tetramethylurea) was prepared by the reaction of $[MoOCl_3(thf)_2]$ (1 g, 2.76 mmol) with tmu (0.64 g, 5.52 mmol) in dry peroxide-free thf (30 cm^3), partial evaporation of the solvent, and filtration. The pale green solid was washed with dry CCl_4 and dried, *in vacuo*. The preparation was performed in a dry-box. Crystals were grown by slow evaporation of a dry CH_2Cl_2 solution of the complex, *in vacuo* (Found: C, 26.9; H, 5.4; Cl, 24.2; Mo, 21.1; N, 12.0. Calc. for $C_{10}H_{24}Cl_3MoN_4O_3$: C, 26.6; H, 5.3; Cl, 23.6; Mo, 21.3; N, 12.3%).

The crystals were obtained as green needles with a rhomboidal cross-section elongated down two opposite edges. Under the polarizing microscope the two larger needle faces showed polarization (green to yellow-green) and extinction directions. Polarized single-crystal electronic absorption spectra were obtained at 77 K with the electric vector of the incident radiation parallel to these extinction directions. The results obtained, with the electric vector of the incident radiation parallel and perpendicular to the needle axis, close to the molecular *z* and *y* directions, respectively and are shown in Figure 2(*d*) and the band positions are: 'parallel' polarization, 12 500m, 13 700m, 14 460m, 21 800m, and 25 600s; 'perpen-

Table. Comparative electronic absorption band positions,[a] structural and vibrational data for metal(v) (M = Cr, Mo, or W) complexes

Complex	Near-i.r. band/cm^{-1}	Visible band/cm^{-1}	Type	M=O distance[b]/Å	ν(M=O)/cm^{-1}	Ref.
$[MoOCl_4]^-$	16 400	23 000	I	1.610(10)	1 012	10, *c*
$[MoOCl_4(H_2O)]^-$	12 000	23 000	I	1.672(15)	980	11, 16
$[MoOCl_4(MeOH)]^-$	13 000	22 500	I	(isomorphous)	980	19,[c]
$[MoOCl_5]^{2-}$	12 800	22 000	I	*d*	950	22, *c*
$[MoOBr_4(H_2O)]^-$	14 000	20 380	II	1.78(3)	981	21, *c*
$[MoOBr_4(MeCN)]^-$	16 020	19 860	II	—	—	*c*
$[MoOF_5]^{2-}$	12 420	25 000	I	1.666(26)	980	27, *c*
$[MoO(NCS)_5]^{2-}$	13 000	19 150	II	—	946	*c*
$[MoOCl_3(hmpa)_2]$	13 700	22 800	I	1.686(5)	998	11, 16, 45, *c*
$[MoOCl_3(PPh_3O)_2]$	13 000	22 460	I	1.662(13)	996	44
$[MoOCl_3(tmu)_2]$	14 000	22 300	I	1.651(5)	979	45,[c]
$[MoOCl_3(PPh_3S)]$	14 900	22 700	I	1.647(2)	1 008	*e*
$[MoNCl_2(PPh_3)_2]$	—	27 000		—	1 049[f]	*c*
$[CrOCl_4]^-$	14 000	18 000	I	1.519(12)	950	17
$[WOCl_4(H_2O)]^-$	13 500	25 100	I	—	980	*c*

[a] For unresolved spectral features the band position refers to the energy of maximum absorbance. [b] — Indicates data not available. [c] This work. [d] Cl/0 disorder. [e] C. D. Garner, N. C. Howlader, F. E. Mabbs, P. M. Boorman, and T. J. King, *J. Chem. Soc., Dalton Trans.*, 1978, 1350. [f] ν(Mo≡N).

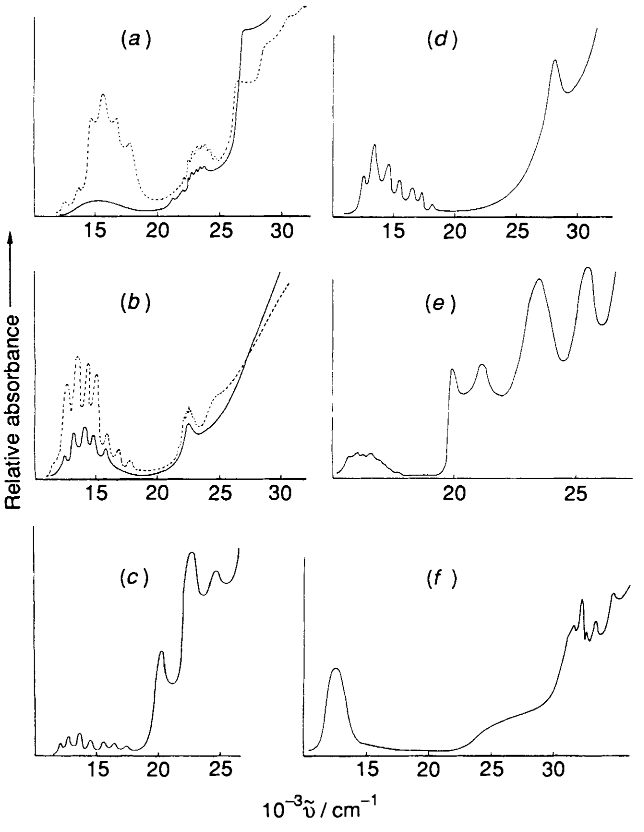

Figure 1. (*a*) Polarized single-crystal electronic absorption spectrum of $[AsPh_4][MoOCl_4]$ at 4.2 K: (*b*) Polarized single-crystal electronic absorption spectrum of $[AsPh_4][MoOCl_4(MeOH)]$ at 4.2 K: (*c*) Electronic absorption spectrum of $[AsPh_4][MoOBr_4(H_2O)]$ mull at 77 K: (*d*) Electronic absorption spectrum of $[AsPh_4][WOCl_4(H_2O)]$ mull at 4.2 K: (*e*) Unpolarized single-crystal electronic absorption spectrum of $[AsPh_4][MoOBr_4(MeCN)]$ at 4.2 K: (*f*) Unpolarized single-crystal electronic absorption spectrum of $[NH_4]_2[MoOF_5]$ at 4.2 K. Polarization: ——, *z*; – – –, *x*,*y*

dicular' polarization, 12 500m, 13 700m, 14 460m, 21 800m, and 25 470s cm^{-1}.

Electronic Spectral Studies.—Absorption spectra (4 000—40 000 cm^{-1}) were recorded between 300 and 4.2 K on a Cary 14 spectrophotometer. Low-temperature spectra were obtained for samples mounted on silica substrates in an Oxford Instruments MD404 immersion Dewar system. Mull spectra were obtained using poly(dimethylsiloxane) as mulling agent.[33] Matched calcite polarizers were used to polarize the radiation. These were mounted such that the non-monochromated i.r. radiation was polarized prior to reaching the sample. The reference beam was attenuated using a Specac saw-tooth attenuator and neutral density screens.

Raman spectra were obtained for powdered samples at room temperature using a Cary 82 spectrometer system.

Results and Discussion

The major structural parameters and electronic absorption band maxima in the solid state at low temperature for the compounds discussed herein are presented, for comparison, in the Table. Using the same model as for previous interpretations of the electronic structure of the MoO^{3+} moiety and, in common with that of VO^{2+} and the recently reinvestigated CrO^{3+} oxycation, an electronic ground state with a single unpaired electron in a d_{xy} in-plane antibonding molecular orbital, which is predominantly metal in character, has again been established. The appropriate selection rules for electric dipole transitions derived for this model may be found in ref. 17.

High-symmetry Complexes.—$[MoOCl_4]^-$, $[MoOCl_4(MeOH)]^-$, $[MoOBr_4(H_2O)]^-$, and $[WOCl_4(H_2O)]^-$. A $^2B_2$ ground state has been assumed. The spectral data for the chloro-complexes [Figure 1(*a*) and (*b*)] show two band envelopes, one in the near-i.r. and one, less intense, in the visible region of the spectrum. In contrast the bromo-compound [Figure 1(*c*)] demonstrates three features in the visible region of a much greater intensity and markedly different profile than the structured near-i.r. band. The two structured envelopes of $[MoOCl_4]^-$ are both more intense in *xy* than in *z* polarization, the band at *ca.* 16 000 cm^{-1} being more intense than that centred at *ca.* 23 000 cm^{-1}. A vibrational progression of *ca.* 960 cm^{-1} was seen on the near-i.r. band whilst the visible band displayed a progression of *ca.* 345 cm^{-1} in both polarizations, although the features do not occupy a common position in each. There are two sharp origins at 26 480 and 26 380 cm^{-1} in the *z*- and *xy*-polarized spectra, respectively, which appear, by comparison with $[CrOCl_4]^-$ [17] to be distorted due to crystal thickness.

The methanol adduct of the $[MoOCl_4]^-$ complex [Figure

1(*b*)] showed a much better defined progression on its i.r. band in both polarizations than those observed for the parent complex or [MoOCl$_4$L]$^{n-}$ (L = Cl[22] or H$_2$O[16]), with an average splitting of *ca.* 850 cm^{-1}, the features being at the same energy in both polarizations. The visible band of [MoOCl$_4$(MeOH)]$^-$ showed vibrational structure only in *xy* polarization, with an average separation of *ca.* 300 cm^{-1}. Also, there was no sharp increase in absorbance at *ca.* 26 000 cm^{-1} as displayed by [MoOCl$_4$]$^-$. The near-i.r. band was more intense than the visible band in *xy* polarization implying that by comparison with VO^{2+} systems the former transition is orbitally allowed and the latter forbidden.

The electronic spectrum of [MoOBr$_4$(H$_2$O)]$^-$ exhibited a progression with a spacing of *ca.* 870 cm^{-1} on its i.r. feature but no band of comparable intensity was seen in the visible region of the spectrum. Indeed the absorbance of the first visible spectral feature at 20 380 cm^{-1} was nearly six times that of the most prominent near-i.r. band member. It is therefore appropriate, in view of this and spectra to be presented later, to classify the absorption bands of these bromo-complexes (and subsequently others) into two types: type I being relatively broad, usually structured, and weak (intensity comparable to that of the i.r. band); type II, sharp, unstructured, and intense.

Assignments. (*a*) *Bands in the near-i.r. region.* In common with previous assignments[10,11] the i.r. band of these MoO^{3+} complexes is assigned to the one-electron promotion $4d_{xy}^* \longrightarrow 4d_{xz}^*, 4d_{yz}^*$ (equivalent to band II for the VO^{2+} [12] and CrO^{3+} [17] spectral studies). The greater intensity in *xy* as compared to *z* polarization for C_{4v} symmetry is consistent with the selection rules.[17] The well resolved vibrational progressions of *ca.* 960, 850, and 870 cm^{-1} for [MoOCl$_4$]$^-$, [MoOCl$_4$(MeOH)]$^-$, and [MoOBr$_4$(H$_2$O)]$^-$, respectively, reinforce this assignment. These quanta are attributable to the totally symmetric Mo–O(terminal) stretching vibration in the excited state. A reduction in the frequency of this excited-state vibration relative to that in the ground state (see Table) is anticipated for an electron promotion into $4d_{xz}^*$, $4d_{yz}^*$ orbitals. The finite intensity in *z* polarization is best discussed with reference to [AsPh$_4$][MoOCl$_4$(MeOH)] for which the best resolved data were obtained. In the absence of spin–orbit coupling, the *xy*- and *z*-polarized band envelopes should not be superimposable since in *z* polarization the features would need to be displaced by the value of an excited-state *E* vibrational mode. One possibility for such a mode would be the Mo-Cl stretching mode which for [MoOCl$_4$(H$_2$O)]$^-$ would lie[34] between 400 and 140 cm^{-1}. No displacement of the strong features is apparent between the two polarizations. Similarly a consideration of spin–orbit coupling would also suggest that the band positions should be different in the two polarizations, because the orbitally degenerate ^2E state is split into the two components Γ_6 and Γ_7[35] with Γ_6 lying below Γ_7.[16,36] Transitions from the $^2B_2$ (Γ_7) ground state to both Γ_6 and Γ_7 are allowed in *xy* polarization, but only to Γ_7 in *z* polarization. However, no displacement of the strong features was observed between the two polarizations. A possible explanation for this is that the intensity of the $\Gamma_7 \longrightarrow \Gamma_7$ transitions is much greater than that of the $\Gamma_7 \longrightarrow \Gamma_6$ transition. However at present there is no entirely satisfactory explanation for the coincidence of the absorption in each polarization or for the weak features which have been observed before the onset of the strong absorption.

(*b*) *Bands in the visible region.* Bands of type I will be considered first. The best resolution was obtained for [AsPh$_4$][MoOCl$_4$]. Here, in agreement with previous work,[10] the individual features are displaced by *ca.* 100 cm^{-1} between the two polarizations. No sharp band origin is seen for this system; for analogous VO^{2+} [12] and OsN^{3+} [14] complexes a broad band envelope of this type was usually indicative of an orbitally forbidden transition. This band broadening may account for the identification of a weak feature in *z* polarization at *ca.* 500 cm^{-1} to lower energy than observed for *xy* polarization [see Figure 1(*a*)]. Many assignments have been suggested for this absorption band envelope (see refs. 10, 11, and 16), but in view of the successful estimation of 10*Dq* for chloride of *ca.* 12 000 and *ca.* 26 000 cm^{-1}, for VO^{2+} [12] and OsN^{3+},[14] respectively, a value of *ca.* 22 000 cm^{-1} would not be unreasonable for MoO^{3+}. This transition is orbitally forbidden in C_{4v} symmetry but allowed in both polarizations in C_{4v}' symmetry. Hence, for this assignment to be correct, the selection rules must not solely be relaxed by spin–orbit coupling. The lower intensity of this band compared with that of the band attributed to the orbitally allowed $4d_{xy}^* \longrightarrow 4d_{xy}^*, 4d_{yz}^*$ transition is also consistent with such an assignment. The absence of an A_2 vibrational mode for [MoOCl$_4$]$^-$ suggests that the intensity in *z* polarization is due to spin–orbit coupling and that an allowing vibration of *E* symmetry is mainly responsible for the *xy* intensity. A Mo–Cl *E* vibrational mode[34] of 114 cm^{-1} is present in the ground state of [AsPh$_4$][MoOCl$_4$], thus allowing the features in *xy* polarization to be displaced to higher energy than the *z*-polarized features.

Considering the bands classified as type II, the intense absorptions of [MoOBr$_4$(H$_2$O)]$^-$ are separated by *ca.* 2 000 cm^{-1} and probably correspond to separate electronic transitions. These may be bromine-to-metal charge-transfer transitions. Lack of definitive polarization data prevents the symmetries of the states involved to be ascertained. A Raman spectrum of [AsPh$_4$][MoOBr$_4$(H$_2$O)] using 5 154 Å (19 436 cm^{-1}) exciting radiation, which falls within the absorption band envelope of the first type II feature of this complex at room temperature, allows the resonance enhancement to be observed. A three-membered progression with average spacing at 190 cm^{-1} originating at 228 cm^{-1} from the exciting line is indicative of a metal–bromide vibration. Excitation away from this absorption band envelope ($\nu_{\text{max.}}$ 20 380 cm^{-1}) revealed two prominent features in the conventional Raman spectrum at 195 and 980 cm^{-1}. Since no feature corresponding to a $\nu(\text{Mo=O})_{\text{str}}$ is observed in the resonance-enhanced spectrum these observations tend to support the view that at least the first of these type II absorption bands is bromide-to-metal charge transfer in nature.

An absorption classified as type II does not appear for [MoOCl$_4$]$^-$ since the band intensity of the feature at 26 000 cm^{-1} does not allow it to be classified as such. Rather the resemblance of this spectrum to that recorded between 20 000 and 26 000 cm^{-1} for a thick [AsPh$_4$][CrOCl$_4$] crystal,[17] and the lack of such a band for [AsPh$_4$][MoOCl$_4$(MeOH)], implies that the absorption is due to the one-electron promotion $4d_{xy}^* \longrightarrow 4d_{z^2}^*$. This is consistent with the situation for VO^{2+} where co-ordination of a ligand *trans* to the terminal oxygen resulted in a shift of the band origin of the $^2B_2 \longrightarrow {}^2A_1$ transition to higher energy.[12]

The spectrum of [WOCl$_4$(H$_2$O)]$^-$ possesses two bands, one in the region at *ca.* 15 000 cm^{-1} and showing some vibrational fine structure, and the second, a single feature, in the visible region at 25 100 cm^{-1}, apparently devoid of any vibrational fine structure [see Figure 1(*d*)]. The first two features of the i.r. band are split by 900 cm^{-1} and the second and third by 1 200 cm^{-1}, followed by splittings of 900, 950, 880, and 830 cm^{-1}. This band may be assigned, by comparison with the oxomolybdenum(V) series, to the transition $5d_{xy}^* \longrightarrow 5d_{xy}^*, 5d_{yz}^*$. Since it has been noted for [OsNCl$_4$]$^-$ that a mull spectrum displays primarily the most intense features of the combined polarizations,[13,14] a value for the spin–orbit coupling constant of W$^{\text{V}}$ may be deduced by assuming that the mull displays the characteristics of *xy* polarization. The splitting of 900 cm^{-1} is taken to be indicative of the W–O(terminal) stretch in the excited state, reduced from its ground-state value (980 cm^{-1}) by the $d_{xy}^* \longrightarrow d_{xz,yz}^*$ promotion. An increased separation of 1 200 cm^{-1}

between the second and third members of the sequence indicates a discontinuity in the vibrational fine structure and so may be assigned to the second spin–orbit component of the excited-state doublet. Hence, the identification of the electronic origins at 12 400 and 14 590 cm^{-1} to the Γ_6 and Γ_7 spin–orbit components of ^2E respectively leads to an estimate of 2 200 cm^{-1} for the spin–orbit coupling constant of W^V in this complex. This is reduced from the estimated[35] free-ion value of 2 700 cm^{-1}. Using the free-ion value[35] of 900 cm^{-1} for Mo^V this suggests on the basis of the same proportional reduction that the spin–orbit coupling constant in the oxomolybdenum(V) chloro-complexes may be *ca.* 750 cm^{-1}, similar to the excited-state vibrational Mo–O(oxo) stretching frequency. The lack of polarization and/or detailed vibrational fine structure makes the assignment of the visible band of $[WOCl_4(H_2O)]^-$ difficult. Evidence that this band is due to the one-electron promotion $5d_{xy}^* \longrightarrow 5d_{x^2-y^2}^*$ comes from the data of Allen *et al.*[5] These workers reported an absorption of 21 600 cm^{-1} for the bromo-analogue of this compound in the solid state. The relative intensity of this band was not reported, but an absorption at this energy is consistent with the expected trends upon changing the ligand-field strength in the square plane of these complexes.

Low-symmetry Molybdenum Complexes.—These complexes do not have C_{4v} site symmetry at the metal centre although in certain instances polarization data can be obtained relating to the *z*- and *xy*-axis systems of the C_{4v} complexes.

$[AsPh_4][MoOBr_4(MeCN)]$. The spectrum recorded for the sample at 5 K displayed a weak, poorly resolved band envelope centred around 16 000 cm^{-1}, with the two most prominent features being at 16 080 and 16 950 cm^{-1} [see Figure 1(*e*)]. This separation is typical of the frequency in the excited state of the Mo–O(terminal) stretching mode. This band system may be assigned to the one-electron promotion $4d_{xy}^* \longrightarrow 4d_{xz}^*, 4d_{yz}^*$ by comparison with the complexes above, and in common with previous interpretations.[10,11,16] The remaining vibrational fine structure was poorly resolved and a detailed assignment of the vibrational features of this band system, in common with others presented in this work, is not yet possible. From these data it is not possible to estimate the degree of spin–orbit interaction for this molybdenum(V) compound. However, a larger spin–orbit coupling constant value may be anticipated for bromo-complexes of MoO^{3+} *versus* chloro-complexes, since the spin–orbit coupling constant for chlorine[37] (587 cm^{-1}) is significantly lower than for bromine[38] (2 460 cm^{-1}). A previous polarization study[22] of $[MoOBr_4(H_2O)]^-$ implied a $\Gamma_6 - \Gamma_7$ separation of *ca.* 1 600 cm^{-1}.

The four very strong bands in the visible region of the spectrum may be classified as type II. Their positions do not correspond with these similar features displayed by the $[MoOBr_4(H_2O)]^-$ chromophore and indeed the MeCN complex showed one extra feature in this region. This difference may be due to sample quality (*i.e.* a crystal usually shows better transmission characteristics than a mull) giving enhanced definition of spectral bands. Alternatively, a charge-transfer feature from MeCN to metal could arise {NB $[MoCl_4(MeCN)_2]$ is dark brown, but $[MoCl_4(thf)_2]$ is orange}. Whilst a detailed assignment of this spectrum is not possible, the two studies on bromo-complexes suggest that the 'visible band' of MoO^{3+} complexes is not necessarily invariant to change in the in-plane ligand as has been suggested,[39] nor to change in the ligand *trans* to the terminal oxo group.

$[NH_4]_2[MoOF_5]$. An unpolarized single-crystal electronic absorption spectrum at 4.2 K was obtained and the results are given in Figure 1(*f*). A fairly broad band centred at 12 420 cm^{-1} was observed which exhibited no vibrational fine structure. No absorption band maximum was apparent at *ca.* 22 000 cm^{-1}, rather a prominent shoulder was identified at around 25 000 cm^{-1}. Finally, a series of fairly sharp intense features were observed at *ca.* 32 000 cm^{-1}. The near-i.r. band may be assigned as $4d_{xy}^* \longrightarrow 4d_{xz}^*, 4d_{yz}^*$ by comparison with the previous data presented here and elsewhere.[10,11,16,22] The shift in the visible band from 22 000 cm^{-1} for $[MoOCl_4]^-$ and related complexes to 25 000 cm^{-1} for $[MoOF_5]^{2-}$ is significant. If this band were to be assigned to a charge-transfer process[40] localized within the MoO group little change would be expected on substituting different in-plane ligands. Similarly an in-plane ligand-to-metal charge transfer is ruled out as a shift of only *ca.* 3 000 cm^{-1} from chloride to fluoride is considered too small.[41] The tentative assignment[16] proposed for this type of transition for MoO^{3+} complexes, $e(O_{2px,y}$, Mo–O $\pi) \longrightarrow b_2^*[4d_{xy}^*$, Mo–L(*cis*) $\pi^*]$ may not be definitely precluded. However, any change in the energy of the e(Mo–O $\pi) \longrightarrow b_2^*$ transition between $[MoOCl_5]^{2-}$ [22] and $[MoOF_5]^{2-}$ may be expected to be reflected as a change in the $b_2^* \longrightarrow e^*$(Mo–O π^*) transition. Since both halogeno-complexes exhibit band envelopes showing maxima around 12 500 cm^{-1} the assignment of the bands near 25 000 cm^{-1} to $e \longrightarrow b_2^*$ may be called into question.

By comparison with the data[12] for VO^{2+} systems the 10*Dq* transition for $[NEt_4]_2[VOCl_4]$ and $[NH_4]_2[VOF_5]$ occurs at 11 600 and 15 500 cm^{-1}, respectively. Also values of $10Dq(VO^{2+})$ for bromide and thiocyanate can be estimated at 11 000 and 17 700 cm^{-1}, respectively. Thus, it seems likely that if the visible band of the MoO^{3+}-containing chromophores is due to the one-electron promotion of $4d_{xy}^* \longrightarrow 4d_{x^2-y^2}^*$, the band envelope would shift to higher energy on replacing four in-plane chloride ligands by fluorides. An attempt was made to estimate the 10*Dq* values of Br^- and NCS^- ligands for MoO^{3+} complexes from a knowledge of the VO^{2+} data. Using a straight-line plot of unit slope passing through the origin a graph of energy (ordinate) *versus* ligand was obtained (not shown). Thus the 10*Dq* values on the straight line allowed the ligand positions on the abscissa to be determined. Using the 10*Dq* values for F^- and Cl^- for MoO^{3+} a straight line between these points was also of unit slope and gave estimated 10*Dq* values for Br^- and NCS^- of 21 000 and 27 500 cm^{-1}, respectively. Hence the 10*Dq* transitions of $[MoOBr_4(H_2O)]^-$ and $[MoOBr_4(MeCN)]^-$ would be masked by the intense type II absorption bands. By comparison with the VO^{2+} series these intense absorptions would also mask the $d_{xy}^* \longrightarrow d_{z^2}^*$ transition estimated at *ca.* 26 000 cm^{-1} for five-co-ordinate MoO^{3+} systems and shifted to higher energy upon six-co-ordination.

Assignment of the sharp features around 32 000 cm^{-1} for $[MoOF_5]^{2-}$ is unclear. These may have the same origin as the type II bands of $[MoOBr_4(H_2O)]^-$, $[MoOBr_4(MeCN)]^-$, and $[MoO(NCS)_5]^{2-}$ (see below). However, as these spectra do not agree with the dilution studies of Wentworth and Piper[42] more experimental work in this region of the spectrum is necessary before detailed discussion is worthwhile.

$[NEt_4]_2[MoO(NCS)_5]$. The three-membered vibrational progression of spacing *ca.* 730 cm^{-1} evident on the near-i.r. band envelope is consistent with the assignment $4d_{xy}^* \longrightarrow 4d_{xz,yz}^*$. This follows the general pattern established for these complexes, where the vibrational frequency is reduced from its ground-state value (946 cm^{-1}) by promotion of an electron into the Mo–O π^* orbital. The bands displayed by $[MoO(NCS)_5]^{2-}$ in the visible region of the spectrum may be classified as type II. The anions $[MoOF_5]^{2-}$, $[MoOCl_4(H_2O)]^-$,[11] $[MoOBr_4(H_2O)]^-$, and $[MoO(NCS)_5]^{2-}$ have the first member of a sequence of type II bands at 31 220, 27 300, 20 380, and 19 150 cm^{-1}, respectively, suggesting that as the ligand becomes more reducing the absorption moves to lower energy. Therefore, at least some of these type II bands are probably due to an in-plane ligand-to-metal charge-transfer process. In order to discover the exact nature of the states or orbitals involved a polarization study is necessary, but the high intensity of the absorptions would

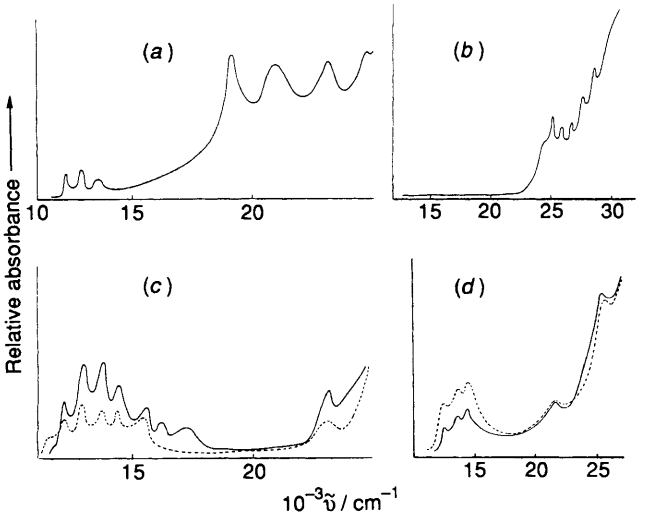

Figure 2. (*a*) Unpolarized single-crystal electronic absorption spectrum of $[NEt_4]_2[MoO(NCS)_5]$ at 4.2 K: (*b*) Electronic absorption spectrum of $[MoNCl_2(PPh_3)_2]$ mull at 4.2 K: (*c*) Polarized single-crystal electronic absorption spectrum of $[MoOCl_3(hmpa)_2]$ at 4.2 K: (*d*) Polarized single-crystal electronic absorption spectrum of $[MoOCl_3(tmu)_2]$ at 77 K

necessitate the use of a suitable diluent host lattice. Indeed, the inherent intensity suggests that these absorptions are charge transfer in nature.[41] Also the optical electronegativity of Jørgensen[41] has been used[43] to give calculated lowest charge-transfer bands for $[MoOCl_4]^-$ and $[MoOBr_4]^-$ at 27 000 and 19 000 cm^{-1} in good agreement with the observed values of 27 300 and 20 380 cm^{-1} for the aqua adducts of these tetrahalogeno-complexes. It would appear that a number of closely spaced ligand orbitals derived from the equatorial plane are involved and shift together as a group as the donor atom is changed. Using the optical electronegativities of ref. 41 for *N*CS$^-$, F$^-$, and O^{2-} and substituting the values in the equations of So and Pope,[43] the first ligand-to-metal charge-transfer bands for these ligands are: F$^-$, 54 000; O^{2-}, 33 000; and *N*CS$^-$, 16 000 cm^{-1}. These calculations suggest that the absorption bands at 19 150 cm^{-1} for $[MoO(NCS)_5]^{2-}$ may also be attributed to an in-plane ligand-to-metal charge-transfer process, but a band system at *ca.* 32 000 cm^{-1} may represent the first charge-transfer band within the MoO^{3+} moiety.

$[MoNCl_2(PPh_3)_2]$. A possible assignment which has not been eliminated by any of the previous considerations is that the near-i.r. band envelope contains both the one-electron promotions from d_{xy}* to d_{xz}*, d_{yz}*, and $d_{x^2-y^2}$*, as demonstrated in the VO^{2+} series.[12] This would require a minimal effect on the $10Dq$ transition on going from a $3d$ to a $4d$ metal. Thus, for the system discussed so far, the well developed Mo–O(terminal) stretching progression of the absorption band assigned $d_{xy}^* \longrightarrow d_{xz}^*, d_{yz}^*$ centred around 12 000 cm^{-1} may mask the $d_{xy}^* \longrightarrow d_{x^2-y^2}^*$ transition, the former being orbitally allowed and the latter forbidden. Whilst large changes in ligand-field strength in the equatorial plane (*viz.* Br$^-$, NCS$^-$) may have been expected to shift such a transition away from the $d_{xy}^* \longrightarrow d_{xz}^*, d_{yz}^*$ transition as was observed[12] in the case of $[VO(NCS)_4]^{2-}$, this may not have occurred. The replacement of the terminal oxo-group by a nitrido-ligand would be expected to shift the $d_{xy}^* \longrightarrow d_{xz}^*, d_{yz}^*$ transition to higher energy and leave the $10Dq$ transition relatively unchanged. The compound $[MoNCl_2(PPh_3)_2]$ was chosen since the $[MoNCl_4]^{2-}$ complex could not be prepared. Also attempts to prepare $[MoNCl_2L_2]$ (L = PPh_3O or hmpa), which would have given a better comparison, have yielded $[MoCl_4(PPh_3O)(PPh_3N)]$.

The compound $[MoNCl_2(PPh_3)_2]$ showed no absorptions in the region of the typical MoO^{3+} near-i.r. band envelopes. Therefore it would appear that there is no absorption other than that due to the '*d–d*' $b_2^* \longrightarrow e^*$ transition present in the first band envelope of the MoO^{3+} complexes. It is, however, possible that the PPh_3 ligand could have shifted the $d_{xy}^* \longrightarrow d_{x^2-y^2}^*$ transition to higher energy.

In the visible region of the spectrum a vibrational progression of average spacing 840 cm^{-1} was observed originating at 25 120 cm^{-1}, with a well developed shoulder at *ca.* 24 500 cm^{-1}. This vibrational coupling may be assigned to the ν(Mo–N) stretching frequency in the excited state, in an analogous manner to that discussed for the MoO^{3+} complexes. Thus the electronic transition is considered to be the $4d_{xy}^* \longrightarrow 4d_{xz}^*, 4d_{yz}^*$ promotion which, by comparison with the oxo-complexes, has been shifted to higher energy due to the greater degree of π bonding for N^{3-} as compared to O^{2-}, formally triple and double bonds, respectively. A tentative proposal for the absorption at 24 500 cm^{-1} is the $4d_{xy}^* \longrightarrow 4d_{x^2-y^2}^*$ promotion. Taking $10Dq$ for chloride as 22 100 cm^{-1} (see above), the average environment of $[MoNCl_2(PPh_3)_2]$ gives a $10Dq$ value for PPh_3 of 26 900 cm^{-1}. Unfortunately, it has not been possible to make an immediate comparison with the oxo-complexes, since attempts to prepare $[MoOCl_3(PPh_3)_2]$ have invariably yielded the well characterized compound $[MoOCl_3(PPh_3O)_2]$.[44] Similarly, $[VOCl_2(PPh_3O)_2]$ has been obtained by equivalent reactions with vanadyl complexes.[30]

$[MoOCl_3(hmpa)_2]$. The polarized single-crystal electronic absorption spectrum of this compound at 40 K has been reported[16] with crystals mounted on a glass substrate. For the reasons outlined for the CrO^{3+} chromophore previously,[17] these measurements were repeated at 4.2 K on a silica substrate. These spectra are in good general agreement with those previously reported. The attainment of a lower temperature has sharpened the profile of the band at 22 900 cm^{-1}, but no vibrational structure was observed. Similarly, enhanced resolution was obtained for the near-i.r. band; a major seven-membered progression in perpendicular polarization of average spacing 870 cm^{-1} originating at 12 110 cm^{-1} was observed. The parallel polarized spectrum has five members originating at 12 110 cm^{-1} in common with the other polarization. Both bands originate with weak shoulders at *ca.* 11 400 cm^{-1}.

The parallel and perpendicular crystal directions correspond to alignment along and perpendicular to the O(hmpa)–Mo–Cl molecular axis. This spectrum has been assigned in C_{4v} point symmetry.[16] Since the major features are in an identical position in both polarizations a situation analogous to that observed for $[AsPh_4][MoOCl_4(MeOH)]$ exists. Hence this absorption band may be assigned to the one-electron promotion $4d_{xy}^* \longrightarrow 4d_{xz}^*, 4d_{yz}^*$ by comparison with previous data obtained for MoO^{3+} systems. However, the band intensity in $z(\parallel)$ polarization, which is orbitally forbidden, may be due to lowering the symmetry (approximately C_s but strictly C_1) or to spin–orbit coupling, for which there is as yet no satisfactory explanation (see above). With the lack of vibrational fine structure on the 'visible band' the assignment to the '*d–d*' transition $b_2^* \longrightarrow b_1^*$ is made by comparison with similar MoO^{3+} chloro-complexes.

$[MoOCl_3(tmu)_2]$. The extraordinary vibrational fine structure displayed[12] by $[VOX_2(tmu)_2]$ suggested that co-ordination of the substituted urea ligand tmu to $MoOCl_3$ might prove useful in enhancing the vibrational coupling of the MoO^{3+} moiety.

In contrast to $[VOCl_2(tmu)_2]$, crystals[45] of $[MoOCl_3(tmu)_2]$ showed relatively poor resolution at low temperature. As anticipated, the spectrum comprised a near-i.r. band, showing a three-membered vibrational progression, a visible band envelope at 21 800 cm^{-1} (type I), and a third feature at *ca.* 25 500 cm^{-1} (type II). By analogy with the previous discussions of

MoO^{3+} chloro-complexes, the first two absorptions may be assigned to the $b_2^* \longrightarrow e^*$ and $b_2^* \longrightarrow b_1^*$ promotions; the third feature may derive from a charge-transfer process although this is to lower energy than that noted for $[MoOCl_4(H_2O)]^-$ [11] at 27 300 cm^{-1}.

Conclusion

It has been possible in this and preceding[12,14,17,46] work to assign the electronic spectra of a diverse range of chromophores using basically the Ballhausen and Gray[2] model. The assignments of the d^1 Group 6 complexes have relied upon the results achieved for the VO^{2+} series, whilst the d^2 spectra of the osmium[14] and ruthenium[46] nitrido-complexes were assigned with recourse to a parameterized ligand-field calculation.

The assignment of the electronic absorption spectra[12] of the VO^{2+} compounds showed that the two types of complex studied, (*a*) five-co-ordinate and (*b*) six-co-ordinate, gave rise to two different types of spectra. For group (*a*) all *d–d* transitions were found to lie below 30 000 cm^{-1}. The relative energies of the *d*-orbital set were found to depend on the ligand field exerted in the equatorial plane of the square-pyramidal complexes. Thus $d_{xy}^* < d_{xz}^*, d_{yz}^* < d_{z^2}^*$ was found to be the ordering of the orbitals with $d_{x^2-y^2}^*$ positioned between d_{xy}^* and $d_{z^2}^*$, but variable relative to the d_{xz}^*, d_{yz}^* orbital doublet. The proposition that the $3d_{xy}^* \longrightarrow 3d_{z^2}^*$ transition lies above 30 000 cm^{-1} appears valid for group (*b*), the six-co-ordinate complexes, for which no absorption band, showing a vibrational progression of *ca.* 800 cm^{-1}, was observed in the region 21 000—25 000 cm^{-1}.

The extention of this model to $[CrOCl_4]^-$ [17] has suggested that the origins of all three *d–d* transitions are again seen below 25 000 cm^{-1}, with the $d_{xy}^* \longrightarrow d_{x^2-y^2}^*$ transition for chloride ligands in the equatorial plane having been moved to higher energy compared to $[VOCl_4]^{2-}$. The range of compounds used to assign the VO^{2+} series of spectra with a great degree of certainty was not possible for the CrO^{3+} case,[17] although the detailed vibronic coupling and band-polarization arguments were tenable.

For the MoO^{3+} chromophore the absorption bands observed below 25 000 cm^{-1} have been classified according to their characteristics. The lower-energy band in the near-i.r. region of the spectrum was compared with the visible band envelope. A type I band was defined as being weak (comparable to the near-i.r. band in intensity), broad, and structured, whilst a type II band in the visible region of the spectrum was intense, sharp, and unstructured. The near-i.r. band was assigned as $(d_{xy}^*)^1 \longrightarrow (d_{xz}^*, d_{yz}^*)^1$ in common with previous work.[10] Relaxation of the selection rules seems to be primarily by spin–orbit coupling rather than vibrational coupling as observed for this transition in the VO^{2+} series.[12] The common position of the vibrational bands in each polarization suggested that only the $\Gamma_7 \longrightarrow \Gamma_7$ transition was observed. As yet there is no definitive explanation for this observation.

The nature of the electronic transition responsible for the absorption at *ca.* 22 000 cm^{-1} for the chloro-complexes, defined as type I, is less straightforward. The various possibilities[16] were: (*i*) $4d_{xy}^* \longrightarrow 4d_{x^2-y^2}^*$; (*ii*) $O_{2p} \longrightarrow 4d_{xy}^*$ or $4d_{x^2-y^2}^*$ or $4d_{z^2}^*$ or $4d_{xz}^*$, $4d_{yz}^*$; (*iii*) $Cl_{3p} \longrightarrow 4d^*$. The relative intensity of this band *versus* the near-i.r. band suggested that this is forbidden in *x,y* polarization, *i.e.* is not $B_2 \longrightarrow E$ in nature. Since the associated vibrational progression is not concerned with the totally symmetric Mo–O(terminal) stretching vibration this suggested that oxometal orbitals are not involved in the transition to any major extent. This idea is confirmed by consideration of the absorption bands of the VO^{2+} [12] and OsN^{3+} [14] complexes, where the states derived from d_{xz}^*, d_{yz}^*, and $d_{z^2}^*$ orbitals usually have an associated ν_1 stretching vibration. These results also show that the energy of this transition is not essentially invariant to changes in nature of the ligands *cis* to the oxo-group. This leaves an in-plane ligand-to-metal charge transfer or the *d–d* transition $d_{xy}^* \longrightarrow d_{x^2-y^2}^*$ as the most likely source of the absorption. An orbitally forbidden charge-transfer process could arise from the molecular orbital occupations: $(4d_{x^2-y^2})^2(4d_{xy}^*)^1 \longrightarrow (4d_{x^2-y^2})^1(4d_{xy}^*)^2$ and $(a_2)^2(4d_{xy}^*)^1 \longrightarrow (a_2)^1(4d_{xy}^*)^2$ where a_2 is an in-plane ligand orbital. It is thought unlikely that the band is a charge-transfer type for the following reasons.

(1) The observed stretching frequency of *ca.* 350 cm^{-1} of the absorption band of $[AsPh_4][MoOCl_4]$ is to be compared with the ground-state totally symmetric metal in-plane ligand vibration[10] of 354 cm^{-1}. By comparison with the 4 500 Å band system[14] of $[OsNCl_4]^-$ where the assigned vibrational frequency is also not markedly reduced in the excited state, this is consistent with a change in the antibonding orbital population only. Thus, removal of an electron from an in-plane bonding molecular orbital or addition of an electron only into an in-plane antibonding molecular orbital would be expected to have a greater effect on the observed vibrational frequency.

(2) Since fluoride ligands would not be expected to take part in charge-transfer processes only *ca.* 3 000 cm^{-1} to higher energy[41] compared with the analogous chloro-complexes, the absorption band at 25 000 cm^{-1} of $[MoOF_5]^{2-}$ is probably not fluoride-to-metal in character.

(3) The definition and characterization of type II absorption bands and their probable charge-transfer nature using the optical electronegativity of Jørgensen.[41]

(4) The change in the equatorial ligand field[16] of $[MoOCl_3(hmpa)_2]$ *versus* $[MoOCl_4]^-$ when compared with that of $[VOCl_2(hmpa)_2]$ *versus* $[VOCl_4]^{2-}$ of 11 760 and 11 600 cm^{-1}, respectively, shows that little change in band position would be anticipated for $d_{xy}^* \longrightarrow d_{x^2-y^2}^*$.

(5) The tentative assignment of the feature at *ca.* 26 400 cm^{-1} of $[AsPh_4][MoOCl_4]$ to the one-electron promotion $(4d_{xy}^*)^1 \longrightarrow (4d_{z^2}^*)^1$ would place an upper limit to the '*d–d*' transitions of these complexes by comparison with VO^{2+} and CrO^{3+} chromophores.[12,17]

(6) The successful assignment of the $d_{xy}^* \longrightarrow d_{x^2-y^2}^*$ one-electron transition for four equatorial chloride ligands around VO^{2+} and OsN^{3+} at *ca.* 12 000 and *ca.* 26 000 cm^{-1}, respectively would place 10*Dq*, for chlorides around MoO^{3+}, between these two values.

For these reasons it is suggested that the visible band at *ca.* 22 000 cm^{-1} of MoO^{3+} chloro-complexes is attributable to the one-electron promotion $4d_{xy}^* \longrightarrow 4d_{x^2-y^2}^*$. The mull spectrum of $[WOCl_4(H_2O)]^-$ is assigned with respect to the MoO^{3+} series and a spin–orbit coupling constant of 2 200 cm^{-1} is estimated for the complex.

The d^2 nitrido-complexes of RuN^{3+} [46] and OsN^{3+} [14] produced a self-consistent assignment scheme for the series $[MNX_4]^-$ (X = Cl, Br, or I; M = Ru or Os). The detailed description of the electronic structure was based on the *d*-orbital ordering $d_{xy}^* < d_{x^2-y^2}^* < d_{xz}^*, d_{yz}^* < d_{z^2}^*$ and the use of a parameterized ligand-field model adequately accounted for the observed spectral features.

From the compounds studied here general trends[35,47] anticipated by ligand-field theory in cubic symmetry appear to be valid with extensive axial π bonding. Thus a spectrochemical series for ligands has been derived from the complexes containing VO^{2+}, where in order of increasing 10*Dq*, $Br^- < Cl^- <$ tmu, $PPh_3O <$ hmpa $< Me_2SO < F^- < H_2O <$ *N*$CS^- < CN^-$, and a similar series for metals using their chloride complexes can be obtained: $VO^{2+} < CrO^{3+} < MoO^{3+} < WO^{3+} < RuN^{3+} < OsN^{3+}$. These are the orderings which may have been expected.[35,47]

However, the major conclusion reached is that for *d* transition-metal complexes containing the MO (or N)$^{n+}$ chromophore the low-energy low-intensity electronic absorption spectral bands can be described by *d–d* transitions using the basic model of Ballhausen and Gray.[2] So that except for oxomolybdenum(V) centres with bromo- or thiocyanato-ligands *cis* to the terminal oxo-group there is no need to invoke a charge-transfer description for the absorption bands below *ca.* 25 000 cm^{-1} for the complexes studied here.

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