890. *Halide and Oxyhalide Complexes of Molybdenum and Tungsten.*

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Two types of oxyhalide complex, $M^{I}_{2}[M^{V}OX_{5}]$ and $M^{I}[M^{V}OX_{4}]$, have been prepared, the first in aqueous acid (HX) and the second in sulphur dioxide; some compounds of the second type have also been made in aqueous acid. The spectra and magnetic properties of these compounds have been examined under a variety of conditions, and the results are discussed in terms of a recently proposed molecular-orbital scheme. Hexachloromolybdates(IV), $M^{I}_{2}[MoCl_{6}]$, have also been prepared and examined.

Quinquevalent molybdenum and tungsten form two types of oxyhalide complex (i) $M^{I}_{2}[M^{V}OX_{5}]$ and (ii) $M^{I}[M^{V}OX_{4}]$, where M^{I} = univalent cation and X = Cl or Br. Although a number of examples of each type, except $M^{I}[MoOCl_{4}]$, have been reported previously,[1] relatively little was known of their properties until recently. Thus apart from a few isolated magnetic susceptibility measurements [2] at one temperature, no structural work was attempted until 1957 when Jørgensen [3] examined the visible and ultraviolet spectra of the $[MoOCl_{5}]^{2-}$ ion. The present work was initiated several years ago to extend the range of known compounds, to prepare if possible the $M^{I}[MoOCl_{4}]$ type, and to examine the magnetic and spectral properties of the chloride and bromide complexes of both molybdenum and tungsten.[4] Very recently, Gray and his co-workers[5] have published work on the magnetic and spectral properties of the ions $[CrOCl_{5}]^{2-}$ and $[MoOCl_{5}]^{2-}$, including molecular-orbital calculations.

EXPERIMENTAL

Analytical Methods.—Molybdenum, tungsten, nitrogen, chlorine, and bromine were determined as described previously.[6] Rubidium and cæsium were determined gravimetrically as the tetraphenylborates. Valency-state determinations were made by dissolving the compounds in standard cerium(IV) sulphate solution, and titrating the excess of the latter with iron(II) ammonium sulphate.

Preparation of $M^{I}_{2}[M^{V}OCl_{5}]$ *Salts* (M^{I} = univalent cation, and M^{V} = Mo or W).—Molybdenum(V) or tungsten(V) chloride [$K_3WO_2(C_2O_4)_2$ could also be used] and the appropriate metal chloride or amine hydrochloride were dissolved separately in concentrated hydrochloric acid, and mixed in proportions such that the $M^{I} : M^{V}$ ratio was close to 2 : 1. Saturation of the resultant solution with hydrogen chloride gas at 0° precipitated the *salts*; these were filtered off under nitrogen, washed with ether containing 10% of thionyl chloride and then with dry ether, and kept *in vacuo* for some hours before analysis or further investigation. The prescribed washing was essential to avoid hydrolysis.

An attempted preparation of the quinolinium salt gave a brown compound $(C_9H_8N)WOCl_4$ (see Table 2).

The trimethylammonium salt, $(NHMe_3)_2WOCl_5$, was prepared by dissolving tungsten(VI) chloride in anhydrous ethanol saturated with hydrogen chloride and adding ethanolic trimethylammonium chloride. The *product* obtained by partial evaporation of the solution followed by

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[1] (*a*) Klason, *Ber.*, 1901, **34**, 148; Henderson, *Proc. Chem. Soc.*, 1903, 245; (*b*) Weinland and Knöll, *Z. anorg. Chem.*, 1905, **44**, 81; (*c*) Weinland and Fiederer, *Ber.*, 1906, **39**, 4092; 1907, **40**, 2092; (*d*) Collenberg, *Z. anorg. Chem.*, 1918, **102**, 259; (*c*) Foerster and Fricke, *ibid.*, 1923, **36**, 458; (*f*) Collenberg and Guthe, *ibid.*, 1924, **134**, 317; (*g*) James and Wardlaw, *J.*, 1927, 2145; (*h*) Angell, James, and Wardlaw, *J.*, 1929, 2578; (*i*) Von Beck, *Z. anorg. Chem.*, 1931, **196**, 85.

[2] Tjabbes, *Proc. Acad. Sci. Amsterdam*, 1932, **35**, 693; Ray, *J. Indian Chem. Soc.*, 1930, **7**, 741.

[3] Jørgensen, *Acta Chem. Scand.*, 1957, **11**, 73.

[4] Preliminary account: Edwards and Fowles, 7th Internat. Conference on Co-ordination Chemistry, Stockholm, 1962, abstract IF8.

[5] Gray and Hare, *Inorg. Chem.*, 1962, **1**, 363; Hare, Bernal, and Gray, *ibid.*, p. 831.

[6] Edwards and Fowles, *J.*, 1962, 24; Brisdon, Fowles, and Osborne, *J.*, 1962, 1330.

further treatment with hydrogen chloride, was blue, unlike the other oxyhalide complexes, which were green. Table 1 gives the analytical data.

TABLE 1.

Analytical data for $M^I_2M^VOCl_5$ salts.

		Found (%)			Required (%)		
M^I	M^V	M^V	Cl	N	M^V	Cl	N
Rb	Mo	20·8	38·8	—	20·8	38·5	—
Cs	Mo	17·2	32·4	—	17·3	32·0	—
$CH_3{\cdot}NH_3$	Mo	27·0	50·9	8·2	27·2	50·2	8·2
$(CH_3)_2NH_2$	Mo	25·1	46·9	7·3	25·2	46·2	7·35
$(CH_3)_3NH$	Mo	23·3	43·3	6·9	23·4	43·3	6·85
C_5H_6N	Mo	21·4	39·2	6·5	21·4	39·5	6·2
C_9H_8N	Mo	17·8	31·5	5·1	17·5	32·2	5·1
Rb	W	33·7	32·1	—	33·5	32·3	—
Cs	W	28·2	27·5	—	28·6	27·6	—
$(CH_3)_3NH$	W	37·0	35·3	5·7	37·0	35·7	5·65

Preparation of $M^I[MoOCl_4]$ *Salts* (M^I = univalent cation).—These were prepared by treating molybdenum(V) chloride with the metal chloride or amine hydrochloride in liquid sulphur dioxide in sealed ampoules. The precipitated quinolinium and pyridinium salts were filtered off and washed with chloroform. As the diethylammonium salt was completely soluble, the sulphur dioxide was evaporated and the excess of diethylammonium hydrochloride removed by extraction with chloroform.

Analogous reactions with rubidium and cæsium chloride gave two products in each case, one soluble and one insoluble in sulphur dioxide. The insoluble products will be considered in the next section. The soluble products ($M[MoCl_4]$) were obtained by filtration, evaporation of the sulphur dioxide, and washing with chloroform [to remove the excess of molybdenum(V) chloride].

The pyridinium and quinolinium salts were also prepared by treatment of the appropriate $M^I_2MoOCl_5$ salt with sulphur dioxide, decomposition taking place over a period of several days: $M^I_2[MoOCl_5] \longrightarrow M^ICl + M^I[MoOCl_4]$. The methylammonium and anilinium salts did not decompose in this manner.

Preparation of $M^I_2[MoCl_6]$ *salts* (M^I = univalent cation).—The dark green, sulphur dioxide-insoluble products formed in the reactions of molybdenum(V) chloride with rubidium and cæsium chloride were filtered off and washed with sulphur dioxide, concentrated hydrochloric acid,

TABLE 2.

Analytical data for $M^IM^VOCl_4$ salts.

		Found (%)				Required (%)					
M^I	M^V	M^I	M^V	Cl	N	M^I	M^V	Cl	N	Valency state	Colour
Rb	Mo	25·1	29·5	41·6	—	25·2	28·3	41·8	—	4·99	Pale green
Cs	Mo	35·5	24·5	36·8	—	34·4	24·8	36·7	—	4·95	Pale green
C_5H_6N	Mo	—	29·3	41·8	4·2	—	28·8	42·5	4·2	4·97	Yellow
C_9H_8N	Mo	—	25·0	37·0	3·7	—	25·0	37·0	3·65	4·95	Yellow
$(C_2H_5)_2NH_2$	Mo	—	29·8	43·5	4·15	—	29·3	43·3	4·3	5·02	Yellow
C_9H_8N	W	—	39·2	29·4	—	—	39·0	30·1	—	—	Brown

TABLE 3.

Analytical data for $M^I_2[MoCl_6]$ salts.

	Found (%)				Required (%)				
M^I	M^I	Mo	Cl	N	M^I	Mo	Cl	N	Valency state
Rb	35·9	20·4	44·1	—	35·6	20·0	44·4	—	4·03
Cs	46·7	16·4	37·6	—	46·3	16·7	37·0	—	3·97
C_5H_6N	—	20·2	45·3	5·8	—	20·5	45·4	6·0	4·03
C_9H_8N	—	16·7	36·9	5·05	—	16·9	37·4	4·9	4·16
$(C_2H_5)_2NH_2$	—	21·4	47·4	5·95	—	21·0	46·6	6·1	4·08

and then ether before analysis. These compounds were much less easily hydrolysed than the oxyhalide complexes.

Tertiary-ammonium hexachloromolybdates(IV) were prepared by reaction of chloroform solutions of the amine hydrochloride and di(propyl cyanide)molybdenum(IV) chloride. The *hexachloromolybdates* (see Table 3) were precipitated from solution as bright yellow solids; they were filtered off and washed with chloroform.

Preparation of $M^I_2[M^VOBr_5]$ *salts* (M^I = univalent cation, M^V = Mo and W).—The procedure was similar to that used for the analogous chloro-complexes, but with 46—48% hydrogen bromide as solvent. The molybdenum source was that part of " molybdenum bromide " (Climax Molybdenum Co.) that dissolved in hydrogen bromide; potassium oxalotungstate(V) was used as the tungsten source. The *products* are recorded in Table 4.

TABLE 4.

Analytical data for $M^I_2[M^VOBr_5]$ salts.

		Found (%)		Required (%)		
M^I	M^V	M^V	Br	M^V	Br	Colour
Rb	Mo	14·0	58·3	14·1	58·6	Brown
Cs	Mo	12·4	51·8	12·3	51·4	Brown
C_5H_6N	Mo	14·3	58·8	14·3	59·5	Brown
Rb	W	23·5	52·2	23·9	51·9	Yellow-brown
Cs	W	21·5	46·4	21·4	46·4	Yellow

Preparation of $M^I[M^VOBr_4]$ *Salts* (M^I = univalent cation and M^V = Mo and W).—The pyridinium, quinolinium, and isoquinolinium *salts* of the tungsten anion were obtained from aqueous hydrogen bromide (see previous section). The pyridinium salt $[C_5H_6N][MoOBr_4]$ was prepared by treating $[C_5H_6N]_2[MoOBr_5]$ with sulphur dioxide (sealed ampoule). Attempts to make the analogous anilinium and tetramethylammonium salts were unsuccessful.

TABLE 5.

Analytical data for $M^IM^VOBr_4$ salts.

		Found (%)			Required (%)			
M^I	M^V	M^V	Br	N	M^V	Br	N	Colour
C_5H_6N	Mo	19·0	64·0	3·0	18·8	62·5	2·7	Orange
C_5H_6N	W	30·9	53·1	—	30·7	53·3	—	Brown
C_9H_8N	W	28·7	49·8	—	28·3	49·2	—	Light brown
iso-C_9H_8N	W	28·4	47·0	—	28·3	49·2	—	Green-brown

Spectral Measurements.—Visible and ultraviolet spectra were measured on a Unicam S.P. 500 spectrophotometer, a diffuse reflectance attachment being used for powdered specimens. The salts $M^I_2[M^VOCl_5]$, $M^I_2[M^VOBr_5]$, and $M^I[M^VOCl_4]$ were sufficiently soluble to be examined as solutions in concentrated aqueous hydrochloric acid, freshly distilled constant-boiling hydrogen bromide, and sulphur dioxide, respectively.

Infrared spectra were measured on Nujol mulls, with Perkin-Elmer Infracord (KBr) and Unicam S.P. 100 spectrophotometers.

Magnetic Susceptibility.—This was measured for solid samples by the Gouy technique occasionally over a temperature range.

RESULTS AND DISCUSSION

Previous workers have prepared these complex salts either by reducing the sexivalent elements directly in aqueous halogen acid (HX) solution, or by preparing a quinquevalent compound and dissolving it in the acid. Addition of the appropriate metal halide or amine hydrohalide then leads to precipitation of the required complex, *e.g.*:

$$MoO_3 \xrightarrow[\text{Electrolytic reduction}]{HCl} [MoOCl_5]^{2-} \xrightarrow{MCl} M_2[MoOCl_5]$$

With simple alkali-metal cations, the salt precipitated was invariably the 2 : 5 complex, $M^I_2[MOX_5]$, but with large pyridinium and quinolinium cations the 1 : 4 complexes

$M^I[MOX_4]$ were usually produced, except when M = Mo and X = Cl. No anhydrous $M^I[MoOCl_4]$ salts have been reported.

We have found that these 1 : 4 salts can be prepared readily by reaction in liquid sulphur dioxide of molybdenum(V) chloride and the metal chloride or amine hydrochloride. The molybdenum(V) chloride is presumably first solvolysed to give oxychloride, $MoOCl_3$, which then takes up a chloride ion [see (i) below]. It is interesting that, although this reaction is quantitative when the cation is a substituted ammonium ion, there is an appreciable side reaction in the presence of rubidium and cæsium chlorides, with reduction of molybdenum to the quadrivalent state and formation of the hexachloromolybdate(IV) salts, $M^I_2MoCl_6$. There are evidently competitive reactions, one solvolytic (i) and the other redox (ii):

$$\text{(i)}\ MoCl_5 + SO_2 \longrightarrow MoOCl_3 + SOCl_2$$

$$MoOCl_3 + Cl^- \longrightarrow [MoOCl_4]^-$$

$$\text{(ii)}\ MoCl_5 + 2Cl^- \longrightarrow [MoCl_6]^{2-} + \tfrac{1}{2}Cl_2$$

The mechanism of the redox reaction is unknown, but it seems likely that some chlorine is taken up by the solvent with the formation of sulphuryl chloride. It is not clear why the redox reaction should take place only in the presence of rubidium and cæsium ions, although it may result from the low solubility of salts of these ions in sulphur dioxide. An analogous reduction of molybdenum(VI) fluoride to the hexafluoromolybdate(IV) anion in sulphur dioxide has been observed,[7] although in this instance the iodide ion had to be present. Very recently,[8] hexachloromolybdates(IV) have been prepared by the reaction of molybdenum(V) chloride with various alkali-metal chlorides in iodine monochloride, and molybdenum(III) bromide and a metal bromide have been shown to react in iodine monobromide to give the hexabromomolybdate(IV) salts.

Table 6 summarises the various types of complex halides that are known and lists those salts that have been prepared; the reported hydrated salts are not included, since these may be hydrolysed.

TABLE 6.

Known salts of the complex halides of molybdenum and tungsten.

Type	M^I	Ref.
$M^I_2[MoOCl_5]$	NH_4, K, Rb, Cs*, C_5H_6N, C_9H_8N*, $(CH_3)_3NH$, $(CH_3)_2NH_2$*, $CH_3{\cdot}NH_3$	1*a*, *b*, *e*, *g*
$M^I[MoOCl_4]$	Rb*, Cs,* C_5H_6N*, C_9H_8N*, $(C_2H_5)_2NH_2$*	—
$M^I_2[MoOBr_5]$	NH_4, K, Rb, Cs, C_5H_6N, C_9H_8N	1*b*, *h*
$M^I[MoOBr_4]$	C_5H_6N, C_9H_8N	1*h*
$M^I_2[WOCl_5]$	NH_4, Rb, Cs, C_9H_8N, $C_6H_5{\cdot}NH_3$, $(CH_3)_3NH$*	1*d*, 1*f*
$M^I[WOCl_4]$	C_5H_6N, C_9H_8N	1*d*
$M^I_2[WOBr_5]$	NH_4, Rb, Cs	1*i*
$M^I[WOBr_4]$	C_5H_6N, C_9H_8N*, iso-C_9H_8N *	1*i*
$M^I_2[MoCl_6]$	K, Rb, Cs, Tl, C_5H_6N*, C_9H_8N*, $(C_2H_5)_2NH_2$ *	8 †
$M^I_2[MoBr_6]$	Rb, Cs	8

* Reported for the first time in this paper. † Also Allen, Edwards, and Fowles, *Chem. and Ind.*, 1962, 1026.

The $[MOX_5]^{2-}$ anions are monomeric and octahedral. The infrared spectra of salts of the $[MoOCl_5]^{2-}$ and $[CrOCl_5]^{2-}$ anions have been measured[9] and show M=O stretching frequencies at 967 and 952 cm.$^{-1}$, respectively. We have found a similar peak at 970 cm.$^{-1}$ for $Rb_2[WOCl_5]$, which shows that the multiple bonding between the metal and oxygen is much the same throughout the series.

The visible and ultraviolet spectra of the 2 : 5 salts in solutions in the appropriate aqueous acid, and with selected examples the diffuse reflectance spectra, have been measured. In every case the spectrum is characteristic of the oxyhalide anion $[MOX_5]^{2-}$ and independent of the cation; when dissolved in aqueous acid, the $M^I[MOX_4]$ salts have

[7] Edwards and Peacock, *Chem. and Ind.*, 1960, 1441.

[8] Edwards, Peacock, and Said, *J.*, 1962, 4643.

[9] Barraclough, Lewis, and Nyholm, *J.*, 1959, 3552.

the same spectra as the $M^I_2[MOX_5]$ salts, showing that the $[MOX_4]^-$ anion readily takes up an X^- ion in solution. All the $M^I[MoOCl_4]$ salts are at least slightly soluble in sulphur dioxide, and the visible spectra have accordingly been measured in this solvent; the spectra are independent of the cation. The spectra for the oxyhalide complexes are summarised in Table 7.

TABLE 7.

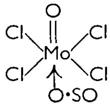
Visible and ultraviolet spectra of the oxyhalide complexes.

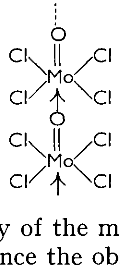
Complex	Conditions	Peak positions (cm.$^{-1}$) (molar extinction coeff. in parentheses)
$M^I_2[MoOCl_5]$	Aqueous HCl	14,100(11); 22,420(10); 28,010(570); 32,260(5300); 40,000(3600)
$M^I[MoOCl_4]$	Liquid SO_2	14,700; 22,730
	Diffuse reflectance	12,050; 22,730
$M^I[MoOBr_4]$	Liquid SO_2	14,810; 22,730
$M^I_2[MoOBr_5]$	Aqueous HBr	14,290(7); 21,280(560); 24,100(3200); 26,530(2500)
	Diffuse reflectance	14,080; 21,300
$M^I_2[WOCl_5]$	Aqueous HCl	14,200(29); 25,190(16); 32,790(500); 37,170(2700); 44,440(3000)
	Diffuse reflectance	13,510; 24,690
$M_2{}^I[WOBr_5]$	Aqueous HBr	14,290(25); 25,640(200)

The oxychloro-complexes of molybdenum and tungsten, $M^I_2[M^VOCl_5]$, both show two weak bands in the visible region, but only one such band is found for the analogous bromo-compounds. All these bands are clearly ligand-field bands and can be readily assigned on the basis that the anions are octahedral with a strong asymmetry in the z-axis resulting from the metal–oxygen bond. As Ballhausen and Gray[10] pointed out, this π-bonding between the metal and oxygen dominates the energy diagram, so that there is considerable further splitting of both the ^2E_g and $^2T_{2g}$ levels. The position of the band that is found near 14,000 cm.$^{-1}$, which is due to the $^2B_{2g} \longrightarrow {}^2E_g$ transition, is almost the same for all the $[MOX_5]^{2-}$ ions. This is to be expected since the splitting of the $^2T_{2g}$ level is brought about by the multiple metal–oxygen band, which is the same for molybdenum and tungsten and independent of the other ligands (chlorine or bromine). The second ligand-field band observed for the chloro-complexes corresponds to the $^2B_{2g} \longrightarrow {}^2B_{1g}$ transition, and its position does depend on the metal, being at an appreciably higher wave-number for tungsten. This, again, is to be expected, because for a particular oxidation state and a given ligand environment, third-row elements always show a bigger splitting of the d levels than do second-row elements. This second band is not observed for the bromide complexes, because it is obscured by charge-transfer bands. Before the latter bands are discussed, the ligand-field bands of the $[MoOCl_4]^-$ anion will be accounted for.

Although the spectrum of the $[MoOCl_4]^-$ anion shows two bands in the visible region, the position of the lower-energy band differs somewhat from that found for the $[MoOCl_5]^{2-}$ anion, and it also depends markedly upon whether the spectrum is measured on the solid or in sulphur dioxide solution. We account for the variations by supposing that there is solvation in sulphur dioxide (i), and interaction between neighbouring anions in the solid (ii), *e.g.*:

(i)





(ii)

Interactions of type (ii) would reduce the multiplicity of the molybdenum–oxygen bond, and result in a smaller splitting of the $^2T_{2g}$ level; hence the observed peak shows a considerable red shift. Solvation by a molecule of sulphur dioxide would not change the

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[10] Ballhausen and Gray, *Inorg. Chem.*, 1962, **1**, 111.

multiplicity of the molybdenum–oxygen bond but might cause a somewhat greater asymmetry in the z-axis, giving a small blue shift in the peak position.

Some evidence for the interaction of the anions in the solid state is provided by the infrared spectra which show that the Mo=O stretching frequency is now a doublet. With the rubidium and cæsium salts, for example, these spectra show a very strong band at 1000 and a rather weaker band around 960 cm.$^{-1}$; the amine salts show a similar splitting of the Mo=O stretching frequency.

The other ligand-field band (at 22,730 cm.$^{-1}$) observed for the $[MoOCl_4]^-$ anion, occurs at the same position in the solid as in solution and differs little from that found for the $[MoOCl_5]^{2-}$ ion. Horner and Tyree [11] have found that the position of this band is not effected very much if some of the chlorine ligands are replaced by donors such as dimethyl sulphoxide and triphenylarsine oxide.

To account for the full spectra (visible and ultraviolet) of the $[MOCl_5]^{2-}$ anions of chromium and molybdenum, Gray and Hare [5] devised a molecular-orbital scheme based on that suggested [10] for the vanadyl ion, $[VO]^{2+}$. The two ligand-field bands ($^2B_{2g} \longrightarrow {}^2E_g$ and $^2B_{2g} \longrightarrow {}^2B_{1g}$) are described as before, but it is now possible to assign the three charge-transfer bands. In preparing the energy diagram for molecular orbitals it was assumed that there was multiple bonding between molybdenum (or chromium) and oxygen, but none between the metal and the chlorine atoms; indeed, the inclusion of π-bonding from the chlorine gave poorer quantitative results.

The three bands in the ultraviolet region were assigned to transitions involving transfer of an electron from a bonding π orbital (e_π) which is largely associated with the oxygen atom, to either non-bonding or antibonding orbitals which are essentially *d* in character.

The band at 28,010 cm.$^{-1}$, which has a relatively low extinction coefficient, is produced by the transfer of an e_π electron to the non-bonding b_2 orbital (d_{xy}), and is described as resulting from the transition $^2B_2 \longrightarrow {}^2E(11)$. The 32,260 cm.$^{-1}$ band [transition $^2B_2 \longrightarrow {}^2B_2(1)$] arises when the e_π electron is transferred to an antibonding $e_\pi{}^*$ orbital (originating from the d_{xz} or d_{yz} orbital). For the third band, at 40,000 cm.$^{-1}$ [transition $^2B_2 \longrightarrow {}^2E(111)$], the e_π electron is transferred to an antibonding σ orbital, $b_1{}^*$ ($d_{x^2-y^2}$).

The $[WOCl_5]^{2-}$ anion also shows three ultraviolet peaks, with extinction coefficients comparable with those found for the $[MoOCl_5]^{2-}$ bands, but the peaks now show a blue shift of some 4000—5000 cm.$^{-1}$. Since the transitions involve an increase in electron density on the metal atom (*i.e.*, reduction), we should on general chemical grounds expect this to occur less readily with tungsten than with molybdenum, and a blue shift would be predicted. If we use the same molecular-orbital scheme in a qualitative manner, it is, however, not obvious why all three bands should show this blue shift. Thus we have seen already that the ligand-field band associated with the transition $^2B_{2g} \longrightarrow {}^2E_g$ occurs at the same position for the molybdenum and the tungsten complexes, and we have argued that the splitting of the triplet level is the same for each ion; hence the difference in energy between the antibonding $e_\pi{}^*$ and non-bonding b_2 orbitals is constant. We should not, therefore, except the difference $b_2 - e_\pi$ to change. Hence the first two charge-transfer bands ($e_\pi \longrightarrow b_2$ and $e_\pi \longrightarrow e_\pi{}^*$) should not show a blue shift. The third band ($e_\pi \longrightarrow b_1{}^*$) should show this shift, because of the bigger *d*-level splitting produced by tungsten.

Gray and Hare's scheme is still less successful when applied to the oxybromide anions, because although these show three charge-transfer bands there is a very big red shift. It is reasonable to suppose that in these ions the π-electrons of the bromine atoms are involved in at least some of the transitions.

The magnetic susceptibilities of these oxyhalide complexes have been examined, and the results are summarised in Table 8. The $\chi_M{}'$ and μ values are given for room temperature (294—300°K) but with some compounds measurements have been made at a few temperatures (usually five) over the range 90—300°K. In every case a plot of $1/\chi_M{}'$ against temperature gave a straight line; the θ values are given in Table 8.

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[11] Horner and Tyree, personal communication.

TABLE 8.

Magnetic susceptibilities of oxyhalide complexes.

	M^I	$10^6\chi_M'$	μ (B.M.)	θ (°K)		M^I	$10^6\chi_M'$	μ (B.M.)	θ (°K)
$M^I_2[MoOCl_5]$:	Rb	1205	1·69 *	16	$M^I_2[WOCl_5]$:	Rb	1019	1·55 *	20
	Cs	1216	1·72	—		Cs	942	1·49 *	16
	C_9H_8N	1204	1·70	—		$(CH_3)_3NH$	772	1·35 *	4
	$(CH_3)NH_3$	1277	1·74	—					
	$(CH_3)_2NH_2$	1244	1·72	—	$M^I[WOCl_4]$:	C_9H_8N	852	1·41 *	6
$M^I[MoOCl_4]$:	Rb	1270	1·74	—	$M^I_2[WOBr_5]$:	Rb	807	1·37	—
	Cs	1106	1·63	—		Cs	1096	1·55 *	17
	C_5H_6N	1268	1·73	—					
	C_9H_8N	1267	1·73	—	$M^I[WOBr_4]$:	C_5H_6N	869	1·43	—
	$(C_2H_5),NH_2$	1279	1·74 *	2		C_9H_8N	833	1·40	—
						iso-C_9H_8N	790	1·37	—
$M^I_2[MoOBr_5]$:	Rb	1265	1·73	—					
	Cs	1260	1·73	—					
	C_5H_6N	1173	1·67	—					

* Measured over the range 90—300°K.

The magnetic moments of all the molybdenum compounds are very close to the spin-only value. This is expected since the strong multiple bonding between molybdenum and oxygen atoms reduces the spin–orbit coupling constant from 1030 to 240 cm.$^{-1}$.[5]

The magnetic susceptibilities of the salts $Rb_2[MoOCl_5]$ and $[(C_2H_5)_2NH_2]$ $[MoOCl_4]$ were measured over a temperature range, and in both cases the Curie–Weiss relation was obeyed, with a very small value of θ. Hare *et al.*[5] recently obtained similar results for $(NH_4)_2[MoOCl_5]$, θ being 15°.

The magnetic moments of the analogous tungsten compounds are appreciably less than the spin-only value, and fall within the range 1·35—1·55 B.M. Once again, magnetic susceptibility values obtained over a temperature range give a straight line ($1/\chi_M'$ against °K), with small values of θ. It is apparent that spin–orbit coupling is now more important and responsible for lowering the magnetic moment below the spin-only value. The reduction in the magnetic moment, however, is relatively small because of the axial asymmetry caused by the tungsten–oxygen bond.[12]

The hexahalogenomolybdates(IV) are interesting because few 6-co-ordinate complexes of quadrivalent molybdenum have been reported. Alkali-metal hexachloromolybdates(IV) have now been prepared either from sulphur dioxide or iodine monochloride [8] solutions, and the amine salts have been made by mixing chloroform solutions of the amine hydrochloride with di(propyl cyanide)molybdenum(IV) chloride: $MoCl_4,2PrCN + 2A_2HCl \longrightarrow (AH)_2[MoCl_6] + 2PrCN$. Horner and Tyree [11] have prepared the tetramethylammonium salt by the direct reaction of tetramethylammonium chloride with molybdenum(V) chloride, using either methyl cyanide or methylene dichloride as solvent, but the product contained about a half mole of solvent. Since molybdenum(V) chloride is reduced by methyl cyanide [13] to $MoCl_4,2MeCN$, it is evidently this adduct that reacts with the tetramethylammonium chloride.

The absence of Mo=O impurities was shown from the infrared spectra of the salts, which had no absorptions in the 900—1000 cm.$^{-1}$ region. The amine salts showed the usual peaks of the amine. Unfortunately, only diffuse reflectance spectra could be measured, because of the insolubility of the salts in solvents with which they did not react. The Figure shows a typical spectrum, for the pyridinium salt, $[C_5H_6N]_2[MoCl_6]$. The other salts had similar spectra, except that the two peaks at higher wave-numbers were found as a single broad peak for the alkali-metal salts. Table 9 summarises the peak positions and provisional assignments.

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[12] Figgis, *Trans. Faraday Soc.*, 1961, **57**, 198.

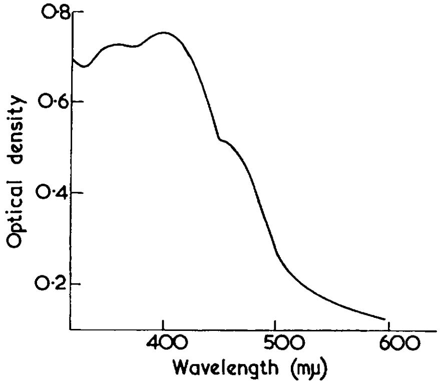
[13] Allen and Fowles, unpublished observations.

Horner and Tyree,[1] who examined their compound in a potassium chloride disc obtained a spectrum showing two peaks at 22,200 and 25,800 cm.$^{-1}$, which agree reasonably with our values. Edwards *et al.*[8] made measurements further into the ultraviolet region, but they comment that because Nujol mulls were used the peak positions are probably inaccurate; the peaks observed were at 24,100, 27,780, 32,750, 35,710, and 40,820 cm.$^{-1}$. Since our first peak appears only as a strong shoulder it is likely that this was not observed by Edwards *et al.* They did not make any assignments, but considered that all the bands were likely to be charge-transfer in type because " rough calculations " indicated extinction coefficients of the order of 2000. We have made tentative assignments on the basis of assignments made by Low[14] for the V^{3+} ion in an octahedral environment. The third assignment, $^3T_{1g} \longrightarrow {}^3A_{2g}$, is somewhat questionable in that it involves a two-electron excitation and should be forbidden, although Ballhausen[15] has suggested that intensity may be borrowed from the $^3T_{1g} \longrightarrow {}^3T_{1g}(P)$ transition in a trigonal field. A further doubt about the third assignment is raised by the fact that the peak is at a lower wave-number than it is for the corresponding transition of the V^{3+} ion. The peak could be analogous to one or other of the weak bands observed by Low and considered to involve spin-forbidden transitions.

TABLE 9.

Visible and ultraviolet spectra of $[MoCl_6]^{2-}$ salts.

Peak positions (cm.$^{-1}$)	21,510	25,640	27,780
Assignment	$^3T_{1g} \longrightarrow {}^3T_{2g}$	$^3T_{1g} \longrightarrow {}^3T_{1g}$ (P)	$^3T_{1g} \longrightarrow {}^3A_{2g}$



Spectrum of pyridinium hexachloromolybdate(IV) in hydrochloric acid.

The magnetic susceptibility has been measured for all five salts at room temperature, and for the rubidium salt over a temperature range (cf. Table 10); the rubidium values gave a straight-line Curie–Weiss plot, with $\theta = 180°$.

TABLE 10.

Magnetic susceptibility of $M^I_2MoCl_6$ salts.

M^I in salt	$10^6\chi_M'$	μ (B.M.)	θ (°K)
Rb	1920	2·13	180
Cs..................	2075	2·22	—
C_5H_6N	2387	2·36	—
C_9H_8N	2272	2·30	
Et_2NH_2.........................	2272	2·30	

Values for the rubidium and cæsium salts agree with those obtained by Edwards *et al.*,[8] who showed that the Kotani theory[16] could be applied reasonably well. They

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[14] Low, *Z. phys. Chem.* (*Frankfurt*), 1957, **13**, 107.
[15] Ballhausen, *Z. phys. Chem.* (*Frankfurt*), 1958, **17**, 246.
[16] Kotani, *J. Phys. Soc. Japan*, 1949, **4**, 293.

obtained appreciably higher values for the thallium and potassium salts and thought this might be caused by small amounts of tervalent molybdenum. We have found higher values for the three amine salts, although valency-state determinations show that tervalent molybdenum is not present.

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