

indication of the lack of a sufficient difference in the tin share of the electrons of the N-Sn and S-Sn dative bonds and the tin-halogen bonds. The above order and suggested similarities are reasonable, but the relative polarities of donor-atom-to-metal dative bonds and metal-to-halogen bonds have not been clearly established to date.

The large half-width of the absorption for $\text{SnBr}_4 \cdot \text{CH}_3\text{O}(\text{CH}_2)_2\text{OCH}_3$, 1.61 mm/sec (which compares with 1.8 mm/sec for the absorption envelope for the corresponding chloride), strongly suggests an unresolved doublet. This complex and those of dimethyl sulfoxide are the only oxygen-donor complexes that failed to show quadrupole splittings. The infrared spectra of $\text{SnCl}_4 \cdot 2\text{DMSO}$ and $\text{SnBr}_4 \cdot 2\text{DMSO}$ ¹⁵ indicate abnormally high O-Sn and Sn-halogen stretching frequencies. It is evident that a number of line widths do not differ significantly from the value 0.88 mm/sec observed for $[(\text{CH}_3)_4\text{N}]_2\text{SnCl}_6$, for which no appreciable deviation

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from spherical symmetry of the tin electron cloud is expected.

If there are significant differences between the tin share of the electrons of the dative bond and the tin-halogen bonds, larger quadrupole splittings are expected for *trans* than for *cis* complexes. The electric dipole moment of $\text{SnCl}_4 \cdot 2(\text{C}_4\text{H}_9)_3\text{P}$, 2.4 D, indicates that this complex, which shows the largest quadrupole splitting, is chiefly *trans* in solution. The large moments of the triphenylphosphine oxide complexes, Table II, indicate a *cis* configuration, and the large values for $\Delta\epsilon/X_2$ for the partially dissociated tetramethylurea complexes, compared to values of 22 and 50 for solvated SnCl_4 ¹⁶ and SnBr_4 and 19 for tetramethylurea, indicate a *cis* configuration for these complexes. The moment of $\text{SnBr}_4 \cdot 2\text{C}_4\text{H}_9\text{S}$, 8.0 D, indicates a *cis* configuration for this compound in solution, compared to a *trans* configuration reported for the solid from X-ray diffraction studies.¹⁷

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Oxochloro Complexes of Rhenium(VI)

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The magnetic and spectroscopic properties of the oxopentachlororhenate(VI) ion have been examined and compared with the closely related MOCl_5^{2-} d^1 ($M = \text{Mo}$ or W) and d^2 ($M = \text{Re}$) systems. Partial hydrolysis of this ion results in the formation of an oxygen-bridged dimeric rhenium(VI) species, which has also been characterized.

Introduction

The chemistry of rhenium(V) oxohalide complexes has been thoroughly investigated. Thus the ReOX_5^{2-} and ReOX_4^- ions and neutral adducts of rhenium(V) oxotrichloride have been prepared and examined by several groups of workers,¹⁻⁵ and a complete X-ray determination was carried out on $(\text{C}_6\text{H}_5)_4\text{As}[\text{ReOBr}_4 \cdot \text{CH}_3\text{-CN}]$.⁶ However the theoretically more interesting d^1 systems derived from rhenium oxotetrahalides have received scant attention. The magnetic properties of ReOCl_4^7 and ReOF_4^8 have been examined, but little has been reported on the reactions or spectra of these compounds or the related ReOX_5^- ions. Ippolitov and Nikolaev⁹ first prepared the oxofluoride ion ReOF_5^- by partial hydrolysis of octafluororhenate(VI) com-

plexes and reported room-temperature magnetic susceptibilities, and the corresponding complex chloride ion was prepared and briefly reported by the present authors.¹⁰

Here, we report in full the preparation and physical properties as well as some of the reactions of the oxopentachlororhenate(VI) ion and compare this ion with the ReOCl_5^{2-} , MoOCl_5^{2-} , and WOCl_5^{2-} systems.

Experimental Section

Analyses.—Rhenium was determined as tetraphenylarsonium perrhenate after dissolution of the sample in dilute sodium hydroxide solution containing a little hydrogen peroxide. Halogen and oxidation state determinations were carried out as previously described.¹¹

Physical Measurements.—Electronic spectra were recorded on the solid or in solution on an SP500 spectrophotometer in the range 10,000–30,000 cm^{-1} . Cells adapted for vacuum line operation were used for obtaining the solution spectra of air-sensitive compounds.

Magnetic susceptibilities were measured at room temperature

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TABLE I
 INFRARED AND MAGNETIC MEASUREMENTS

Compound	μ , BM	$\nu(\text{Re-O})$, cm^{-1}	Far-ir (200–500 cm^{-1} range)
ReOCl_4	1.53 ^a	1033 s, 1016 s	...
$(\text{C}_6\text{H}_5)_4\text{As}[\text{ReOCl}_5]$	1.65	968 s	350 s, b, 328 sh, 270 s, 228 s
$(\text{C}_2\text{H}_5)_4\text{N}[\text{ReOCl}_5]$	1.55	966 s	322 s, b, 257 s, 232 s, 220 s, b
$[(\text{C}_6\text{H}_5)_4\text{As}]_2\text{Re}_2\text{O}_3\text{Cl}_5$	0.60	977 s, 970 sh, 725 m	...
$[(\text{C}_2\text{H}_5)_4\text{N}]_2\text{Re}_2\text{O}_3\text{Cl}_5$	Diamagnetic	977 s, 955 s, 740 m	312 s, 331 s, 340 sh, 361 m, 460 s
$\text{Cs}_2\text{ReOCl}_5$	0.80 ^b	950 s	318 sh, 310 s, b, 227 sh, 214 s

^a Recorded on a 56.2% solution in chloroform. ^b Slightly field-dependent magnetic moment.

 TABLE II
 VISIBLE AND ULTRAVIOLET SPECTRA ($\text{cm}^{-1} \times 10^{-3}$)

Compound	Reflectance (10.0–30.0 range)	Solution (10.0–50.0 range) (ϵ_{max})
ReOCl_4	\sim 12.3 vb, sh, 18.1, 23.9	12.6 vb (80), 17.4 (520), 23.3 (2000), 34.5 sh, 39.0 (5400)
$(\text{C}_6\text{H}_5)_4\text{As}[\text{ReOCl}_5]$	11.8 vb, 18.1, \sim 23.0 b	11.2 (12), 11.7 (13), 12.1 (12), 18.0 (160), 23.0 (1200)
$(\text{C}_2\text{H}_5)_4\text{N}[\text{ReOCl}_5]$	11.8 b, asym, 18.1, 22.2 sh, 24.0	11.6 (15), 12.0 (15), 18.2 (120), 22.2 sh, 24.7 (800), 32.3 (2000), 42.6 (17,000)
$[(\text{C}_6\text{H}_5)_4\text{As}]_2\text{Re}_2\text{O}_3\text{Cl}_5$	11.8, 12.2, 17.1, 18.1, 27.0	...
$[(\text{C}_2\text{H}_5)_4\text{N}]_2\text{Re}_2\text{O}_3\text{Cl}_5$	12.0, 12.3, 17.4, 18.9, 27.0	...
$\text{Cs}_2\text{ReOCl}_5$	10.9, 11.3, 20.6	...

on a Gouy balance. The values reported below have been corrected for diamagnetism.

Conductivity measurements were made on a Wayne-Kerr auto-balance bridge at $20 \pm 1^\circ$.

Infrared spectra in the 4000–650- cm^{-1} region were examined as Nujol mulls unless otherwise stated using a Perkin-Elmer 237 spectrophotometer. Spectra to 200 cm^{-1} were determined on a Grubb-Parsons DM4 spectrophotometer and the spectrum of $(\text{C}_6\text{H}_5)_4\text{As}[\text{ReOCl}_5]$ was recorded from 370 to 20 cm^{-1} using a Grubb-Parsons "Iris" interferometer.

X-Ray diffraction measurements were made using a Debye-Scherrer type of powder camera of 11.46-cm diameter, using nickel-filtered $\text{Cu K}\alpha$ radiation (λ 1.5405 Å). Finely ground samples were loaded into 0.3-mm Lindemann glass capillaries and sealed. Line intensities were judged by eye.

The molecular weight of rhenium oxotetrachloride was determined on a chloroform solution of the compound in an atmosphere of dry nitrogen using a Mechrolab vapor pressure osmometer, but the accuracy of the result was low because of the sensitivity of the oxochloride toward traces of moisture.

Materials.—Solvents used for the preparation of rhenium(VI) complexes and for spectral measurements were purified by several distillations *in vacuo* from fresh phosphorus pentoxide. Tetraethylammonium and tetraphenylarsonium chlorides were recrystallized and pumped *in vacuo* to remove traces of water.

Rhenium oxotetrachloride was prepared by the reaction of sulfuryl chloride on rhenium metal at 400° .¹² *Anal.* Calcd for ReOCl_4 : Re, 54.2; Cl, 41.2; mol wt, 344. Found: Re, 54.2; Cl, 40.8; oxidation state, 6.01; mol wt on a 0.0395 *M* chloroform solution, 392.

Oxopentachlororhenate(VI) Salts.—These were prepared *in situ* on the vacuum line by mixing concentrated chloroform or dichloromethane solutions of rhenium oxotetrachloride with solutions of tetraphenylarsonium or tetraethylammonium chloride in the same solvent. The salts precipitated out on standing at room temperature as small red-brown crystals. These were filtered off, washed several times with small portions of dichloromethane or chloroform, and then pumped *in vacuo* to remove excess solvent. *Anal.* Calcd for $(\text{C}_6\text{H}_5)_4\text{As}[\text{ReOCl}_5]$: Re, 24.4;

Cl, 23.3; C, 37.8; H, 2.64. Found: Re, 24.3; Cl, 23.2; C, 38.4; H, 2.64; oxidation state, 6.02; conductivity, 78 $\text{ohm}^{-1} \text{cm}^2$ in 10^{-3} *M* nitromethane. Calcd for $(\text{C}_2\text{H}_5)_4\text{N}[\text{ReOCl}_5]$: Re, 36.5; Cl, 34.8; N, 2.75. Found: Re, 36.6; Cl, 34.6; N, 2.88.

Both compounds were slightly soluble without reaction in dichloromethane and chloroform but insoluble in nonpolar solvents and soluble with subsequent reaction in polar solvents. The tetraethylammonium salt turned mauve on exposure for a short time to atmospheric moisture, whereas the tetraphenylarsonium salt was less sensitive toward hydrolysis.

μ -Oxo-bisoxotetrachlororhenate(VI) Salts.—Salts of this anion were formed on mixing anhydrous chloroform solutions of rhenium oxotetrachloride and the appropriate halide and allowing the red solution to stand in contact with the atmosphere. After a few minutes a deep mauve product precipitated out, was filtered off, washed with chloroform and then ether, and air dried. *Anal.* Calcd for $[(\text{C}_6\text{H}_5)_4\text{As}]_2\text{Re}_2\text{O}_3\text{Cl}_5$: Re, 25.3; Cl, 19.3; C, 39.2; H, 2.74. Found: Re, 24.9; Cl, 18.9; C, 40.4; H, 3.22; oxidation state, 6.01. Calcd for $[(\text{C}_2\text{H}_5)_4\text{N}]_2\text{Re}_2\text{O}_3\text{Cl}_5$: Re, 38.6; Cl, 29.5; N, 2.91. Found: Re, 38.4; Cl, 28.9; N, 2.88; oxidation state, 5.99; conductivity, 124 $\text{ohm}^{-1} \text{cm}^2$ in 10^{-3} *M* methyl cyanide solution.

Both complexes were soluble in methyl cyanide and nitromethane to give mauve solutions which very soon turned colorless. The tetraethylammonium compound decomposed to a pink solid on prolonged exposure to atmospheric moisture.

Cesium Oxopentachlororhenate(V).—This complex was obtained in almost quantitative yield by mixing concentrated hydrochloric acid solutions of rhenium oxotetrachloride and cesium chloride. The fine yellow powder which immediately formed was filtered off and washed with concentrated hydrochloric acid and then ether. *Anal.* Calcd for $\text{Cs}_2\text{ReOCl}_5$: Re, 28.9; Cl, 27.4; Cs, 41.2. Found: Re, 29.1; Cl, 26.9; Cs, 41.1; oxidation state, 5.00.

Results

Table I presents the infrared and room temperature (293°K) magnetic data collected on these compounds. Tables II and III contain details of their visible, ultraviolet, and X-ray diffraction data.

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TABLE III
 X-RAY DIFFRACTION DATA

Cs ₂ ReOCl ₅				(C ₆ H ₅) ₄ AsReOCl ₅	
<i>d</i> _{obsd}	<i>d</i> _{calcd} (for cubic cell, <i>a</i> = 10.25)	<i>I</i> _{obsd}	<i>hkl</i>	<i>d</i> _{obsd}	<i>I</i> _{obsd}
5.92	5.92	8	111	9.46	5
3.63	3.63	10	220	7.47	6
3.08	3.09	4	311	6.71	10
2.946	2.959	4	222	5.87	1
2.563	2.562	7	400	4.97	7
2.356	2.351	2	331	4.67	9
2.087	2.092	7	422	4.42	4
1.974	1.972	4	333, 511	4.21	4
1.811	1.812	6	440	3.98	5
1.731	1.733	3	531	3.60	6
1.621	1.621	5	620	3.32	3
1.564	1.563	1	533	3.15	2
1.545	1.545	3	622	2.969	6
1.479	1.479	4	441	2.776	3
1.437	1.435	3	551, 711	2.629	3
1.370	1.370	6	642	2.498	1
1.336	1.334	2	553, 731	2.446	1
1.283	1.281	2	800	2.347	2
1.209	1.208	3	660, 822	2.276	1
1.147	1.146	3	840	2.219	1
				2.108	3
				2.060	1
				2.025	2
				1.953	1
				1.892	1
				1.845	2
				1.799	1
				1.752	2

Discussion

The structures of several oxotetrahalides have recently been determined,^{13,14} including that of ReOF₄ which is a fluorine-bridged polymer in the solid state.¹³ The crystal structure of ReOCl₄ is as yet unknown, but the oxotetrachloride and -bromide of tungsten occur as oxygen-bridged WOX₄ units in the solid state,¹⁴ so that two oxygen and four halogen atoms form a distorted octahedron around the tungsten atom. The presence of oxygen bridging is also indicated by the infrared spectrum of solid tungsten oxotetrachloride which shows a broad band in the 700–900-cm⁻¹ region.¹⁵ In the presence of a donor solvent, such as methyl cyanide, ether, or carbon disulfide, the solid dissolves and the broad band in the 700–900-cm⁻¹ region is replaced by a strong band around 1000 cm⁻¹, attributable to a terminal W=O stretching mode.

Infrared measurements on rhenium oxotetrachloride dissolved in carbon disulfide show a sharp, strong band at 1030 cm⁻¹,¹² and for a Nujol mull, two bands are observed (1033 and 1016 cm⁻¹) in good agreement with previous observations.¹⁶ The small splitting of the band in Nujol is presumably due to very weak interactions between Re=O groups, but the position of the bands almost certainly precludes a polymer involving Re–O–Re bridges in the solid state. Further evidence for monomeric solid rhenium oxotetrachloride is provided by the physical characteristics of the compound, such as its low melting point and high solubility in most nonpolar organic solvents.

A comparison of visible spectral measurements in

the solid state compared with those of solutions of the oxotetrachloride in chloroform, in which the oxochloride is monomeric, reveals only very small differences in band positions, as would be expected if the absorbing species is unchanged by the phase change. However, the strong Re–O interaction appears to almost exclusively determine the splitting of the d orbitals and hence makes the spectrum relatively insensitive to changes in stereochemistry. Thus, six-coordinate ReOCl₄·CH₃CN, with bands at 12,500, 17,400, and 23,000 cm⁻¹, has a spectrum almost identical with that of five-coordinate rhenium oxotetrachloride in chloroform solution.¹⁷

The room-temperature magnetic moment of a solution of rhenium oxotetrachloride is very similar to the value (1.48 BM) found for the solid at 293°.⁷ Such a value about 0.2 BM below the spin-only value is typical of a d¹ heavy-metal oxo species.

Addition of chloride ions to solutions of rhenium oxotetrachloride in chloroform or dichloromethane results in the formation of the oxopentachlororhenate (VI) ion which provides an interesting comparison with the ReOCl₅²⁻, MoOCl₅²⁻, and WOCl₅²⁻ ions. Some of these relationships are shown in Table IV.

Cs₂ReOCl₅ and (C₆H₅)₄AsReOCl₅ show Re–O stretching frequencies at 950 and 968 cm⁻¹, respectively. Since the cations are different, it is impossible to state with absolute certainty that the increase in frequency is a result of the change in oxidation state of the rhenium, although such a shift might be expected in view of the increasing formal positive charge on the metal which should make it a better π acceptor. However, if we compare the corresponding cesium salts of the WOCl₅²⁻ and ReOCl₅²⁻ ions, we find bands at 957 and 950 cm⁻¹, respectively which give rise to very similar force constants (Table V). The force constants of the M–O bonds in the isoelectronic species WOX₅²⁻ and ReOX₅⁻ increase with increasing atomic number of the metal atom as previously noted for isoelectronic MO₄²⁻ species.¹⁸

The far-infrared bands of the oxopentachlororhenate(V) ion (Figure 1) have been assigned in Table IV by comparison with other such complexes belonging to the point group C_{4v}.¹⁹ In particular the M–Cl stretching and M–O rocking vibrations of this ion occur at frequencies very close to these reported for the WOCl₅²⁻ ions.¹⁹ (C₆H₅)₄As[ReOCl₅] has an M–Cl stretching frequency at 328 cm⁻¹, and the band at 228 cm⁻¹ is in the position expected for an M–O rocking frequency. The M–Cl stretching frequency of the tetraethylammonium salt is about 6 cm⁻¹ lower than that of the tetraphenylarsonium salt, as expected for a smaller cation, but still at a higher frequency than the M–Cl stretch in the oxopentachlororhenate(V) ion.

This leaves unassigned an intense band at 257 cm⁻¹ in the tetraethylammonium salt and the corresponding band at 270 cm⁻¹ in the tetraphenylarsonium salt.

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TABLE IV
 SPECTRAL, MAGNETIC, AND UNIT CELL MEASUREMENTS OF SOME MOX_6^{n-} IONS

Compound	$\nu(\text{M-O}),$ cm^{-1}	Magnetic data		Far-ir (500–200 cm^{-1} range)	Reflectance spectra, $\text{cm}^{-1} \times 10^{-3}$	Unit cell type and dimensions, \AA
		$\Delta,$ ^a cm^{-1}	$\lambda,$ ^b cm^{-1}			
$(\text{C}_6\text{H}_5)_4\text{AsReOCl}_5$	968	450–980 ^c	180–280 ^c	350 s, b (cation absorption), 328 s (Re–Cl str), 270 s	11.8 vb, 18.1, ~23.0 b	Noncubic
$\text{Cs}_2\text{ReOCl}_5$	950	318 sh (Re–Cl str), 310 s, b (Re–Cl str), 227s (M–O rock), 214 m (M–O rock)	10.9, 11.3, 20.6	Cubic 10.25 ± 0.02
$\text{Cs}_2\text{MoOCl}_5$	952 ^d	1260–1760 ^e	180–220 ^e	329 s (M–Cl str), ^d 320 sh (M–Cl str), 227 s (M–O rock)	12.8 b, 22.7, 26.7, 30.6 ^e	Cubic ^f 10.24 ± 0.01
Cs_2WOCl_5	957 ^d	333 w (M–Cl str), ^d 309 b (M–Cl str), 230 s (M–O rock)	12.9, 14.7, 25.3 sh, 26.7 ^e	Cubic ^f 10.24 ± 0.01
Rb_2WOCl_5	960 ^d	1000–2100 ^e	400–600 ^e	339 sh (M–Cl str), ^d 317 s (M–Cl str), 229 ms (M–O rock)	13.3, 14.6, 25.5, 27.8 sh ^e	

^a Δ measures the split in the ${}^2T_{2g}$ term under the influence of an axial ligand field component. ^b λ is the spin-orbit coupling constant of the central metal atom. ^c Private communication with D. J. Machin and K. S. Murray. ^d A. Sabatini and I. Bertini, *Inorg. Chem.*, **5**, 204 (1966). ^e B. J. Brisdon, D. A. Edwards, D. J. Machin, K. S. Murray, and R. A. Walton, *J. Chem. Soc., A*, 1825 (1967). ^f D. Brown, *ibid.*, 4944 (1964).

 TABLE V
 FORCE CONSTANTS FOR MOX_6^{n-} IONS AND MOX_4 COMPOUNDS

Compound	Force constant, ^a dyn/\AA
$\text{Cs}_2\text{MoOCl}_5$	7.32
Cs_2WOCl_5	7.86
$\text{Cs}_2\text{ReOCl}_5$	7.83
$(\text{C}_2\text{H}_5)_4\text{N}[\text{ReOCl}_5]$	8.10
$(\text{C}_6\text{H}_5)_4\text{As}[\text{ReOCl}_5]$	8.13
$(\text{C}_6\text{H}_5)_4\text{N}[\text{WOCl}_5]$	8.12 ^a
MoOCl_4	8.23 ^b
WOCl_4	9.20 ^c
ReOCl_4	9.20 ^c

^{a-c} Force constants were calculated from M–O stretching frequencies (solution values where available) given in: (a) G. W. A. Fowles and J. L. Frost, *J. Chem. Soc., A*, 1631 (1966); (b) M. Larson and F. W. Moore, *Inorg. Chem.*, **5**, 801 (1966); (c) ref 12.

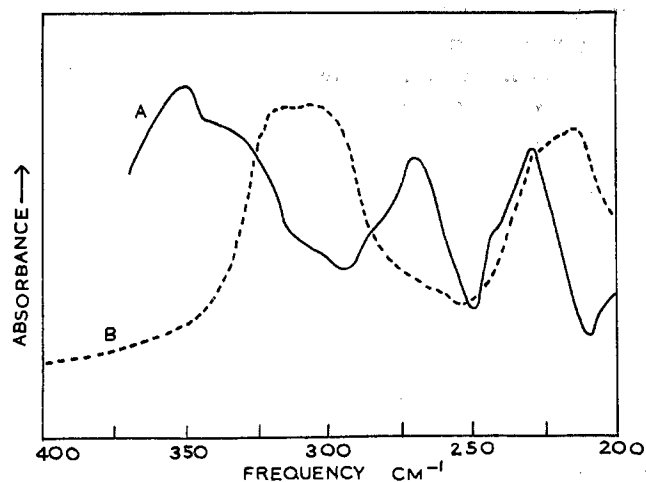


Figure 1.—Far-infrared spectra of (a) $(\text{C}_6\text{H}_5)_4\text{AsReOCl}_5$ and (b) $\text{Cs}_2\text{ReOCl}_5$.

These bands occur at lower frequencies than is normal for heavy-metal-chlorine stretches but higher than an M–O rocking frequency. One possible explanation involves the band being produced by the stretch of a

long Re–Cl bond in the position *trans* to the oxygen atom. Crystallographic evidence has shown that the closely related d^1 ion $[\text{MoOBr}_4]^-$ will loosely hold a water molecule in the sixth position,²⁰ and esr measurements on MOBr_5^{2-} species (where M = Mo or W) can be accounted for in terms of in-plane halogen–metal π bonding.²¹ With an increase in the formal oxidation state of the central metal atom, such π bonding should become more important and may cause the ligand *trans* to the strong metal–oxygen bond to become relatively weakly bonded. In an attempt to provide further information on this problem, the infrared spectrum of $(\text{C}_6\text{H}_5)_4\text{As}[\text{ReOCl}_5]$ was recorded down to 20 cm^{-1} in order to compare the Cl–M–Cl deformation modes with those of the WOCl_5^{2-} ion (177–174, 164, and 84–85 cm^{-1}).¹⁹ Only two bands were observed in the rhenium(VI) complex, one at 173 (vs) cm^{-1} and the other at 113 (m) cm^{-1} , which suggests a halogen arrangement different from that in the WOCl_5^{2-} ion.

Magnetic and Spectral Data.—Magnetic studies on $(\text{C}_6\text{H}_5)_4\text{As}[\text{ReOCl}_5]$ ²² show that the spin-orbit coupling constant (λ) of rhenium is reduced considerably from the free-ion value of $\sim 4000 \text{ cm}^{-1}$ by the multiple bonding between the rhenium and oxygen. Δ , which is a measure of the split of the ${}^2T_{2g}$ term under the influence of an axial ligand field component, is positive, indicating that the singly orbitally degenerate level (B_{2g}) lies lowest after the effects of the tetragonal ligand field as was the case for the molybdenum and tungsten oxyhalide complexes²³ and that the splitting (450–980 cm^{-1}) is less than in these complexes. Figgis and Lewis²⁴ suggest that an increase in spin-orbit coupling

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constant in going from MoOCl_5^{2-} to ReOCl_5^- would tend to nullify the effect of the asymmetric field due to the MO^{n+} unit. We find that λ does increase slightly from Mo(V) to Re(VI) in these complexes, but in both cases it is greatly reduced from its free-ion value owing to the multiple bonding discussed above.

Much has been written about the spectra of d^1 MOX_5^n- ions;²⁵⁻²⁸ however, no general agreement about the interpretation of such measurements has been reached.

Gray and Hare²⁵ adapted the molecular orbital scheme proposed by Ballhausen and Gray²⁹ for the vanadyl ion, to explain the spectrum of the MOCl_5^{2-} ions ($M = \text{Cr}$ or Mo). They assigned the two lowest energy bands of the MoOCl_5^{2-} ion at $\sim 14,000$ and $\sim 23,000 \text{ cm}^{-1}$ to the essentially d-d transitions ${}^2B_2 \rightarrow {}^2E$ and ${}^2B_2 \rightarrow {}^2B_1$ and considered the band at $\sim 27,000 \text{ cm}^{-1}$ to be the first charge-transfer band involving the excitation of an electron from the metal-oxygen π -bonding orbital into metal atom orbitals. However, this scheme which included no halogen-metal π bonding could not account for the analogous bromide of molybdenum, nor the tungsten analogs.

On the basis of electron spin resonance studies of several oxoanions of this type, Kon and Sharpless²¹ suggested that very strong metal-oxygen π bonding may cause the e_π levels to fall below the metal-ligand σ bonding orbital (b_1), and then the first charge-transfer band would correspond to the forbidden $b_1 \rightarrow b_2$ transition. They also showed that the bromine hyperfine structures observed in the esr spectrum of the oxobromides of molybdenum and tungsten can be explained in terms of in-plane π bonding between the four halogens in the xy plane and the central metal atom. Further evidence that metal-halogen interactions cannot be neglected has been provided by Horner and Tyree.²⁷

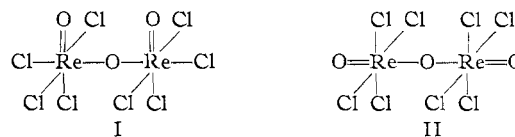
A recent study on the magnetic properties of the MOX_5^{2-} ions ($M = \text{Mo}$ or W , $X = \text{Cl}$ or Br)²³ has shown that the splitting of the ${}^2T_{2g}$ term under the influence of an axial ligand field component is not more than 2100 cm^{-1} for the cesium and rubidium salts of the MoOCl_5^{2-} and WOCl_5^{2-} ions, respectively. Also the free-ion spin-orbit coupling constant is reduced to 220 cm^{-1} or less for the molybdenum complex and is between 400 and 600 cm^{-1} for the tungsten complex. Thus the magnetic evidence suggests a very much smaller split of the ${}^2T_{2g}$ term than the spectral data as assigned by Gray and Hare.²⁵ If the first observed d-d band in these compounds at $\sim 13,000 \text{ cm}^{-1}$ is not due to the ${}^2B_2 \rightarrow {}^2E$ transition, then we may assign this band to the ${}^2B_2 \rightarrow {}^2B_1$ transition, and the second weak band in the $23,000$ – $25,000\text{-cm}^{-1}$ region may be assigned to the ${}^2B_2 \rightarrow {}^2A_1$ transition.

$(b_2 \rightarrow a_1^*) - (b_2 \rightarrow b_1) = x$ then gives a measure of the excited-state splittings, which in turn should re-

fect the M-O bond order, if we assume that the degree of M-O π bonding largely determines the $b_1^*-a_1^*$ separation in these MOX_5^{2-} ions. For the two WOCl_5^{2-} salts listed in Table IV, $x \approx 11,500 \text{ cm}^{-1}$ and for the MoOCl_5^{2-} salt, $x \approx 9900 \text{ cm}^{-1}$, thus reflecting the stronger W-O bond. Further correlations using the Mo- and WOBr_5^{2-} ions are not possible since it seems likely from their extinction coefficients that the bands in the $20,000$ – $25,000\text{-cm}^{-1}$ region are charge transfer in nature rather than d-d.

The solution spectrum of the ReOCl_5^- ion shows only one band centered at $11,700 \text{ cm}^{-1}$ with a low enough extinction coefficient to consider it as a d-d band. By comparison with the WOCl_5^{2-} ion, we assign this band to the $b_2 \rightarrow b_1^*$ transition. It can be resolved into two or three components of separation 300 – 500 cm^{-1} , and this fine structure we suggest is vibronic in origin. The band at $\sim 18,100 \text{ cm}^{-1}$ has a rather high extinction coefficient for a d-d transition and hence is regarded as a halogen $\pi \rightarrow b_2$ or $b_1 \rightarrow b_2$ transition, each of which is forbidden and expected to occur with relatively low extinction coefficients. This band is at rather low frequency for a charge-transfer band, but the high formal oxidation state of the rhenium must make a "reduction" transition of this type relatively easy.

Hydrolysis Products.—The reaction of rhenium oxotetrachloride with tetraphenylarsonium or tetraethylammonium chloride in the presence of atmospheric moisture yields a mauve product in both cases. These solids are weakly paramagnetic and diamagnetic, respectively, although oxidation-state determinations show that the rhenium remains in the hexivalent state. The infrared spectra of these salts exhibit two main M-O bands, a doublet at about 970 cm^{-1} , in the range found for terminal M-O bonds, and another band at about 730 cm^{-1} which suggests M-O-M bonding. This evidence together with the analytical data suggests the formulation $(R_4M)_2\text{Re}_2\text{O}_3\text{Cl}_8$ and two possible structures, one with *cis* oxygen atoms (I) and the other with *trans* oxygens (II). The M-O-M bridge may be linear or bent, but the greatest degree of M-O π bonding will occur in a linear system.



Support for these formulations is provided by the conductivity of the tetraethylammonium salt in dry methyl cyanide, which has a value typical of a 2:1 electrolyte in this solvent, and also by the greatly reduced magnetic susceptibilities of both compounds compared with the ReOCl_5^- ion. Similar reduced susceptibility values have been found for a number of linear oxygen-bridged ions of the heavier transition elements.^{30,31} On the present evidence it is difficult to decide whether the oxygen atoms are *cis* or *trans*; how-

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ever, Cotton, *et al.*,³² have suggested that for a linear arrangement of oxygen atoms in a similar bridged system, the electron-withdrawing effect of the terminal M–O groups should result in a relative weakening of the bridging Re–O bonds and hence a reduction in the frequency of this mode to 675–710 cm^{-1} in the case of $\text{Re}_2\text{O}_3(\text{py})_4\text{Cl}_4$. The antisymmetric stretching mode of structure I might be expected in the more general range of frequencies found for oxygen-bridged systems of halo complexes, *i.e.*, 800–950 cm^{-1} , and consequently structure II seems preferred.

The reflectance spectrum of the $\text{Re}_2\text{O}_3\text{Cl}_3^{2-}$ ion is very similar to that of the ReOCl_5^- ion at long wavelengths, but at shorter wavelengths considerable differences occur. Unfortunately neither sample was sufficiently soluble in a solvent with which it did not react for extinction coefficients to be determined, so no comments can be made on the nature of the bands.

It is interesting to compare the reactions of rhenium oxotetrachloride described above with those previously reported. Bagnall, Brown, and Colton¹⁶ were unable to isolate rhenium(VI) complexes by the addition of tetraalkylammonium chlorides to solutions of rhenium oxotetrachloride in thionyl chloride. Reduction occurred in this system and hexachlororhenate(IV) complexes were finally formed. It has been claimed³³ that the reaction of ReOCl_4 with potassium chloride in concentrated hydrochloric acid yielded the rhenium(VI) oxochloro complex K_2ReOCl_6 ; but other workers³⁴ using cesium chloride suggested the product was a mixture of CsReO_4 and Cs_2ReCl_6 . More recently the isolation of ReOCl_6^{2-} salts from concentrated hydrochloric acid solutions of rhenium pentachloride oxidized by atmospheric oxygen has been claimed.³⁵ Wilkinson, *et al.*,⁴ were, however, unable to repeat this work, and, even when ozone was used as an oxidant, only ReOCl_5^{2-} salts were isolated. Even starting with a rhenium(VI) species (ReOCl_4) in concentrated hydrochloric acid, we have been unable to isolate a rhenium(VI) complex. The oxotetrachloride dissolves immediately in ice-cold concentrated hydrochloric acid (11 *M*) with the evolution of chlorine gas, and the addition of cesium chloride merely produces $\text{Cs}_2\text{ReOCl}_5$. Thus it appears that Re(VI) is capable of oxidizing HCl to chlorine and is itself reduced to Re(V). Colton³⁵ found that $\text{Cs}_2\text{ReOCl}_5$ was paramagnetic with a "spin-only" value for the magnetic moment, but as for the $\text{Cs}_2\text{ReOCl}_5$ sample prepared by

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one of the routes of Wilkinson,⁴ we find a much reduced moment which is slightly field dependent. The reflectance spectrum of $\text{Cs}_2\text{ReOCl}_5$ in the range 10,000–30,000 cm^{-1} (Figure 2) is quite different from the solution spectra previously recorded for rhenium(V) in various concentrations of aqueous hydrochloric acid.⁴

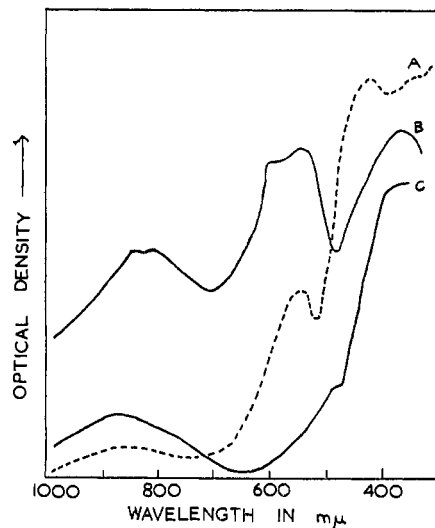


Figure 2.—Diffuse reflectance spectra of (a) $(\text{C}_6\text{H}_5)_4\text{AsReOCl}_5$, (b) $(\text{C}_6\text{H}_5)_4\text{As}_2\text{Re}_2\text{O}_3\text{Cl}_8$, and (c) $\text{Cs}_2\text{ReOCl}_5$.

The X-ray powder pattern of $\text{Cs}_2\text{ReOCl}_5$ could be indexed on the basis of a face-centered cubic lattice and it seemed probable that it was isostructural with K_2PtCl_6 , having the anti-fluorite structure (space group no. 225, $\text{Fm}\bar{3}\text{m}$, O_h^5). The lattice parameter, a_0 , was found to be $10.25 \pm 0.02 \text{ \AA}$ and the observed and calculated d values are listed in Table III. These data show $\text{Cs}_2\text{ReOCl}_5$ as having a similar lattice parameter and as being isostructural with the group Cs_2MOCl_5 (where $\text{M} = \text{Cr}, \text{Nb}, \text{Mo}, \text{or W}$) which is known^{36,37} to have the K_2PtCl_6 structure. Thus the ReOCl_5^{2-} ions will be at the corners and centers of the faces of a cubic unit cell, surrounded by eight Cs^+ ions at the corners of the cube.

The powder pattern of $(\text{C}_6\text{H}_5)_4\text{AsReOCl}_5$ has also been examined but is obviously of much lower symmetry and has not been indexed at this time; the observed d values and visually estimated intensities are given in Table III.

Acknowledgment.—We wish to thank Dr. R. A. Walton for measuring the spectra in the 200–500- cm^{-1} region and Drs. D. J. Machin and K. S. Murray for providing the results of magnetic studies on $(\text{C}_6\text{H}_5)_4\text{As}[\text{ReOCl}_5]$.

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