The ionic strength dependence for aquation of the triaquo complex is considerably larger than for the first two aquation steps. Here a threefold increase in ionic strength from 0.3 to 1 *M* decreases the rate by *ca.* 40% while similar increases in ionic strength give rate decreases of less than 20% for the previous aquation steps, an effect possibly associated with greater ion pairing of the 3+ substrate. From the temperature dependence of k_3 a linear Arrhenius plot was obtained, with least-square activation parameters $E_a = 27.5 \pm 0.3$ kcal mol^{-1}, $\log PZ(sec^{-1}) = 14.08 \pm 0.17$, and $\Delta S^*_{298} = 4 \pm 1$ cal deg^{-1} mol^{-1}.

The aquation rate parameters of pink $Cr(en)(NH_3)(OH_2)_3^{3+}$ are compared in Table VII with those for the remaining two aquation steps to $Cr(OH_2)_6^{3+}$; in all three aquations Cr–N bonds are ruptured. The activation energies are very similar and substantially different from those for the two preceding steps in which Cr–Br bonds are ruptured. For these aquations involving Cr–N bond rupture, rate differences are chiefly due to differences in ΔS^*.

TABLE VII

RATE PARAMETERS FOR THE AQUATION STEPS FROM PINK $Cr(en)(NH_3)(OH_2)_3^{3+}$ TO $Cr(OH_2)_6^{3+}$ IN 3 *F* $HClO_4$ AT 60°

Substrate	10^6k, sec^{-1}	E_a, kcal mol^{-1}	ΔS^*, cal deg^{-1} mol^{-1}
Pink $Cr(en)(NH_3)(OH_2)_3^{3+}$[a]	133	27.5 ± 0.3	+3 ± 1
$Cr(en)(OH_2)_4^{3+}$[b]	3.0	27.7 ± 1.5	−3 ± 5
$Cr(enH)(OH_2)_5^{4+}$[b]	1.9	25.4 ± 2.3	−11 ± 7

[a] This research. [b] Reference 6.

The evidence for the geometric configuration of pink $Cr(en)(NH_3)(OH_2)_3^{3+}$ is ambiguous. Assuming the correctness of our configuration assignments for the dibromo and monobromo complexes, we would expect the 1,2,6-triaquo complex to be the aquation product of the monobromo complex if there is configuration retention without isomerization. Comparison of the visible absorption bands of pink $Cr(en)(NH_3)(OH_2)_3^{3+}$, namely, 378 ($\epsilon$ 31) and 496 nm (ϵ 41.0), with those[13] of 1,2,3-$Cr(dien)(OH_2)_3^{3+}$, namely, 375 (ϵ 33) and 510 nm (ϵ 66), and 1,2,6-$Cr(dien)(OH_2)_3^{3+}$, namely, 391 (ϵ 45) and 495 nm (ϵ 90), favors a 1,2,6 assignment if based on the wavelength of the lower energy band but a 1,2,3 assignment if based on the intensity of that band and the wavelength and intensity of the higher energy band. Attempts to make a further comparison with the spectra of 1,2,3- and 1,2,6-$Cr(NH_3)_3(OH_2)_3^{3+}$ [3,7] are rendered difficult by the uncertain configuration assignments of the triammine complexes and the fact that their spectra resemble that of 1,2,3-$Cr(dien)(OH_2)_3^{3+}$ more than that of 1,2,6-$Cr(dien)(OH_2)_3^{3+}$. In the absence of positive isolation of the second possible geometric isomer of $Cr(en)(NH_3)(OH_2)_3^{3+}$, we regard the above spectral comparison as ambiguous and prefer to make no configurational assignment for pink $Cr(en)(NH_3)(OH_2)_3^{3+}$ at this time.

The successive steps in the aquation of green $Cr(en)(NH_3)(OH_2)Br_2^{+}$ to $Cr(OH_2)_6^{3+}$ have been shown to be progressively slower, in line with successive aquations of similar bromo- and chlorochromium(III)–amine complexes. The green dibromo complex, which has been confirmed to have a *trans*-dibromo configuration, aquates to magenta $Cr(en)(NH_3)(OH_2)_2Br^{2+}$ without stereochemical change, in agreement with the related *trans*-dibromo isomers of $Cr(en)(OH_2)_2Br_2^{+}$ [4] and $Cr(NH_3)_3(OH_2)Br_2^{+}$ [3] and the *trans*-dichloro isomers of $Cr(en)(OH_2)_2Cl_2^{+}$ [8] and $Cr(NH_3)_3(OH_2)Cl_2^{+}$ [3] and their aquation.

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[13] Unpublished research of D. K. Lin and C. S. Garner, cited by R. G. Hughes, E. A. V. Ebsworth, and C. S. Garner, *Inorg. Chem.*, **7**, 882 (1968).

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Complexes of Molybdenum(V) and Tungsten(V). Far-Infrared Spectra and Some Other Properties

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The far-infrared spectra of tetraalkylammonium complexes of $M(OR)Cl_5^-$ and $M(OR)_2X_4^-$ and of the dimeric species $[W(OR)_2Cl_3]_2$ and $[W(OR)_3Cl_2]_2$ (M = W or Mo; X = Cl or Br; R = CH_3, C_2H_5, or C_3H_7) were recorded in the range 80–650 cm^{-1}. The M–OR stretch has been assigned and several trends which depend on the nature of the alkoxide, halide, and metal are reported. In addition, the preparation and properties of $[(C_2H_5)_4N]M(OR)_2X_4$ (M = W or Mo; X = Cl or Br; R = CH_3 or C_2H_5), $[(C_3H_7)_4N]MoOCl_4$, and $[(C_4H_9)_4N]MoOCl_4$ are given.

The far-infrared spectra of a large number of metal hexahalo complexes have been reported,[1-3] and the work has been extended to mixed hexahalo complexes of the type $MX_4Y_2^{2-}$ (M = Ti or Sn; X = Cl, Br, or I).[4] Other workers have studied the vibrations of oxohalo complexes Nb(V), Mo(V), and W(V).[5] Detailed in-

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[1] R. J. H. Clark, *Spectrochim. Acta*, **21**, 955 (1965), and references therein.

[2] S. M. Horner, R. J. H. Clark, B. Crociani, D. B. Copley, W. H. Horner, F. N. Collier, and S. Y. Tyree, Jr., *Inorg. Chem.*, **7**, 1859 (1968).

[3] J. E. D. Davies and D. A. Long, *J. Chem. Soc.*, *A*, 2560 (1968).

[4] R. J. H. Clark, L. Maresca, and R. J. Puddephatt, *Inorg. Chem.*, **7**, 1603 (1968).

[5] A. Sabatini and I. Bertini, *ibid.*, **5**, 204 (1966).

frared and Raman spectra of chromium(III) alkoxides have also been measured.[6]

Preparations for most of the compounds investigated in the present program were described previously.[7,8] Tungsten(V) bromoalkoxo complexes are of interest for comparison with chloroalkoxo anions. Funk and Schauer described the alcoholysis of WBr_5 and its reactions with phenols and aldehydes to give $WBr_2(OR)_3 \cdot ROH$ and $WBr_2(OH)_3$, respectively.[9]

This study was undertaken to gain information about vibrations, bonding, and sterochemistry of complex ions $W(OR)Cl_5^-$, $W(OR)_2Cl_4^-$, $W(OR)_2Br_4^-$, and $Mo(OR)_2Cl_4^-$ and dimeric compounds $[W(OR)_2Cl_3]_2$ and $[W(OR)_3Cl_2]_2$ ($R = CH_3$, C_2H_5, or C_3H_7).

Experimental Section

Materials.—Commercial chloroform and methylene chloride were dried by distillation in the presence of phosphorus pentoxide. $MoCl_5$ from several commercial sources was purified by fractional sublimation under vacuum. WBr_5 was obtained from Alfa Inorganics. Drying, purification, and sources of other materials were described previously.[7]

Preparation of Compounds.—The tungsten compounds except for $[W(OCH_3)_2Cl_3]_2$, $[W(OC_2H_5)_3Cl_2]_2$, $[(C_2H_5)_4N]WBr_6$, and $[(C_2H_5)_4N][W(OCH_3)_2Br_4]$ were described previously.[7]

$[W(OCH_3)_2Cl_3]_2$.—The compound was prepared after the manner of Funk and Naumann.[10] *Anal.* Calcd for $WCl_3C_2H_6O_2$: W, 52.19; Cl, 30.19; C, 6.82; H, 1.72. Found: W, 52.06; Cl, 30.11; C, 6.73; H, 1.69.

$[W(OC_2H_5)_3Cl_2]_2$.—WCl_5 (10.8 g, 0.03 mol) was cooled to −78° before addition to 25 ml of ethanol also at −78°. The yellow-brown solution which was obtained became green when warmed to room temperature. The red-brown precipitate left after vacuum evaporation of the solution formed a deep red suspension upon addition of 40 ml of ethanol. The red precipitate was filtered and washed with ethyl ether and dried under vacuum. *Anal.* Calcd for $WCl_2C_6H_{15}O_3$: W, 47.15; Cl, 18.18; C, 18.48; H, 3.88. Found: W, 46.77; Cl, 18.65; C, 18.35; H, 3.65.

$[(C_2H_5)_4N]WBr_6$.—WBr_5 (8.75 g, 0.015 mol) was added to a solution (at −78°) of 25 ml of ethanol which had been presaturated with HBr at 0°. The deep red solution which formed was warmed to 0° and filtered to remove any residual solids. To the filtrate, a solution of 3.2 g of $(C_2H_5)_4NBr$ (0.015 mol) in 25 ml of ethanol was rapidly added. After the solution was allowed to warm to room temperature, a black precipitate formed which was washed with a 5:1 ether–ethanol mixture. This was followed by washing the compound with ether alone and drying under vacuum. Spang Microanalytical Laboratory, Ann Arbor, Mich., reported difficulty in handling this compound so no C, H, and N analyses were obtained. *Anal.* Calcd for $WBr_6C_8H_{20}N$: W, 23.17; Br, 60.42. Found: W, 22.71; Br, 59.78.

$[(C_2H_5)_4N][W(OCH_3)_2Br_4]$.—Ten grams of $(C_2H_5)_4NWBr_6$ was added to 25 ml of methanol. The suspension was gradually heated until the precipitate changed color from black to yellow-green. The precipitate was washed with a 5:1 ether–methanol solution and then with ethyl ether and was dried under vacuum. *Anal.* Calcd for $WBr_4C_{10}H_{26}NO_2$: W, 26.42; Br, 45.94; C, 17.26; H, 3.77; N, 2.01. Found: W, 25.91; Br, 46.21; C, 17.17; H, 3.61; N, 2.09.

$[(C_2H_5)_4N][Mo(OC_2H_5)_2Cl_4]$.—$MoCl_5$ (4.4 g, 0.015 mol) was added to a solution (−78°) of 20 ml of ethanol which was presaturated with HCl at 25°. The solution was allowed to warm to 0°. A solution of 2.5 g of tetraethylammonium chloride in 20 ml of ethanol was added to it. A yellow-green precipitate was obtained, washed with a 5:1 ether–ethanol solution and then with ether, and was dried under vacuum. *Anal.* Calcd for $MoCl_4C_{12}H_{30}NO_2$: Mo, 20.94; Cl, 30.95. Found: Mo, 21.12; Cl, 31.32.

$[(C_4H_9)_4N]MoOCl_4$.—$MoCl_5$ (4.4 g, 0.0.5 mol) was added to a solution (−78°) of 20 ml of ethanol which had been presaturated with HCl at 0°. A brown suspension formed and to it a solution of 4.2 g of $[(C_4H_9)_4N]Cl$ (0.015 mol) in 20 ml of ethanol was slowly added. A brown-orange precipitate formed. It was filtered, washed with ethyl ether, and dried under vacuum. All manipulations were carried out at −78°. The compound was maintained under vacuum and was then allowed to warm to room temperature. The initial compound changed color from brown-orange to the light green of the final complex, $[(C_4H_9)_4N]MoOCl_4$. *Anal.* Calcd for $MoCl_4C_{16}H_{36}NO$: Mo, 19.33; Cl, 28.58; C, 38.73; H, 7.31; N, 2.82. Found: Mo, 19.47; Cl, 28.83; C, 38.45; H, 7.26; N, 2.72.

$[(C_3H_7)_4N]MoOCl_4$.—The preparation was similar to the previous one with the appropriate substitution of tetraalkylammonium halide. *Anal.* Calcd for $MoCl_4C_{12}H_{28}NO$: Mo, 21.80; Cl, 32.22; C, 32.75; H, 6.56; N, 3.18. Found: Mo, 21.48; Cl, 32.38; C, 32.38; H, 6.70; N, 3.08.

$[(C_2H_5)_4N][Mo(OCH_3)_2Cl_4]$.—$MoCl_5$ (4.4 g, 0.015 mol) was added to a 20-ml ethanol solution (−78°) which had been presaturated with HCl at 0°. A 2.5-g sample of $[(C_2H_5)_4N]Cl$ dissolved in 20 ml of ethanol was added to the above solution. As the solution warmed, the brown-orange suspension became yellow. The precipitate was immediately filtered, was washed with a 5:1 ether–ethanol solution and then ether, and was dried under vacuum. *Anal.* Calcd for $MoCl_4Cl_{10}H_{26}NO_2$: Mo, 22.30; Cl, 32.97. Found: Mo, 22.04; Cl, 33.34.

Spectra.—Far-infrared spectra were determined in Nujol mulls. CsBr plates were used from 650 to 320 cm^{-1}. Below that, polyethylene disks were used. The spectra were determined with a Perkin-Elmer 301 spectrophotometer. The low solubility in suitable solvents precludes their study in solution. Nuclear magnetic resonance spectra were recorded with a Varian A-60 spectrophotometer.

Experimental Techniques.—Experimental methods, inert-atmosphere techniques, and procedures for visible–ultraviolet spectra, infrared spectra, and magnetic moments have been described.[7]

Analyses.—Mo was determined by precipitation with 8-hydroxyquinoline,[11] C, H, and N were determined by Spang Microanalytical Laboratory, Ann Arbor, Mich., and W, Mo, and Cl, as in the earlier work.

Results and Discussion

We have previously reported the loss of alkyl halide from the anion[7] $W(OR)Cl_5^-$ in the solid state. An attempt was made to prepare the analogous molybdenum monoalkoxide complex. Two compounds, which were prepared and isolated at −78°, changed color from brown-orange to green and evolved ethyl chloride at room temperature. The brown-orange species had a C—O stretch at 1020 cm^{-1} in the ir spectrum whereas the green species had a Mo═O absorption at 990 cm^{-1}. The green products were $[(C_4H_9)_4N]MoOCl_4$ and $[(C_3H_7)_4N]MoOCl_4$. It thus seems the elimination of alkyl halide also occurs with $Mo(OC_2H_5)Cl_5^-$, but in contrast to the tungsten monoalkoxide complexes, the molybdenum compounds rapidly evolved alkyl chloride. Elemental analysis indicated the molybdenum oxyhalide product was pure. In the decomposition of $[(C_2$-

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[6] D. A. Brown, D. Cunningham, and W. K. Glass, *J. Chem. Soc., A*, 1563 (1968).

[7] D. P. Rillema, W. J. Reagen, and C. H. Brubaker, Jr., *Inorg. Chem.*, **8**, 587 (1969).

[8] D. A. McClung, L. R. Dalton, and C. H. Brubaker, Jr., *ibid.*, **5**, 1985 (1966).

[9] H. Funk and H. Schauer, *Z. Anorg. Allgem. Chem.*, **306**, 203 (1960).

[10] H. Funk and J. Naumann, *ibid.*, **343**, 294 (1966).

[11] R. Nierické and W. T. Treadwell, *Helv. Chim. Acta*, **29**, 1472 (1946).

$H_5)_4N][W(OCH_3)Cl_5]$, the vapors released were collected in a vacuum trap. The identities of the alkyl halides obtained in the gases, which were evolved, were verified by vapor pressure measurements on the trapped liquids. Chlorine, hydrogen chloride, and an unknown vapor which gave a single absorption at 1150 cm^{-1} were also obtained.

In a complex, such as $W(OCH_3)Cl_5^-$, which has C_{4v} symmetry there should be (in addition to the C–H vibrations) four A_1 and four (pairs of) E modes which are ir active. The A_1 vibrations include two M–X vibrations, one M–O stretch, and one (O–M–X, X–M–X) deformation. The modes that are bases for the E representations are a pair of M–X stretching modes, two pairs of X–M–X bending modes, and a pair of O–M–X bending vibrations.

The dialkoxide complexes of Mo(V) have axial symmetry, according to esr measurements, and so should possess D_{4h} symmetry. Of the eleven normal modes only five, the A_{2u} and E_u, are infrared active. The A_{2u} species are an M–O stretching vibration and an O–M–X bending mode. The E_u representations are M–X, X–M–X, and X–M–O bending modes.

Tables I and II contain far-infrared absorptions for monoalkoxo and dialkoxo complexes, respectively.

TABLE I

INFRARED ABSORPTION FREQUENCIES (CM^{-1}) OF $M(OR)Cl_5^-$ IONS (WITH POSSIBLE ASSIGNMENTS)

Assignment	$[(C_2H_5)_4N]$-$[W(OCH_3)Cl_5]$	$[(C_2H_5)_4N]$-$[W(OC_2H_5)Cl_5]$	$[(C_2H_5)_4N]$-$[W(OC_3H_7)Cl_5]$
ν(M–O)	551 m	606 m	613 m
ν(C–C–O)	416 w	412 w	414 w
ν(O–M–X)	354 sh	330 sh	352 sh
ν(M–X)	306 vs	304 vs	306 vs
ν(M–X)	265 vs	283 vs	275 vs
ν(O–M–X)	219 sh	238 sh	250 sh
ν(X–M–X)	174 m	175 m	170 m
ν(X–M–X)	153 m	155 m	155 m

	$[(C_3H_7)_4N]$-$[W(OC_2H_5)Cl_5]$	$[(C_4H_9)_4N]$-$[W(OC_2H_5)Cl_5]$
ν(M–O)	567 m	584 m
	509 w	522 w
ν(C–C–O)	420 m	411 w
ν(O–M–X)	354 sh	354 sh
ν(M–X)	306 vs	306 vs
ν(M–X)	274 vs	281 vs
ν(O–M–X)	214 sh	220 sh
ν(X–M–X)	167 m	169 m
ν(X–M–X)	154 m	152 m

In polymeric chromium alkoxides,[6] M–O was considered to appear at ~500 cm^{-1}. The frequency of bridging Co–Cl in the polymer $CoCl_2 \cdot 2py$ lies about 70 cm^{-1} lower than the terminal frequency of Co–Cl.[1] Therefore, it seems reasonable that the absorption in the 600-cm^{-1} region be assigned as an M–O stretching vibration.

TABLE II

INFRARED ABSORPTION FREQUENCIES (CM^{-1}) OF $M(OR)_2Cl_4^-$ IONS[a] (WITH POSSIBLE ASSIGNMENTS)

Assignment	$[(CH_3)_4N]$-$[W(OCH_3)_2Cl_4]$	$[(CH_3)_4N]$-$[W(OC_2H_5)_2Cl_4]$	$[(C_2H_5)_4N]$-$[W(OC_2H_5)_2Cl_4]$
ν(M–O)	544 s	573 s	584 s
ν(C–C–O)		412 w	412 w
ν(O–M–X)	351 sh	337 sh	
ν(M–X)	290 vs	289 vs	286 vs
ν(O–M–X)	267 sh	233 sh	239 sh
ν(X–M–X)	162 m	160 m	159 m
ν(X–M–X)	139 w	129 w	131 w

	$[(C_2H_5)_4N]$-$[Mo(OCH_3)_2Cl_4]$	$[(C_2H_5)_4N]$-$Mo(OC_2H_5)_2Cl_4]$	$[(C_2H_5)_4N]$-$[W(OCH_3)_2Br_4]$
	625 w		580 w
ν(M–O)	582 s	617 s	542 s
ν(O–M–X)	337 sh, 381 m	331 m, 379 m	311 m, 338 m
ν(M–X)	300 vs	306 vs	198 vs
ν(O–M–X)	262 m	288 vs	373 m
ν(X–M–X)	175 m	164 m	167 sh
ν(C–O)	1060, 1102	1078	1066, 1115

[a] All of the bands attributable to the R_4N^+ ions were also observed. C–O frequencies for $(CH_3)_4N^+$ salts have been reported previously.[7]

The metal–halogen stretching frequencies are approximately the same in monoalkoxo complexes as in the hexachloro compound.[12] Two of three metal–halogen stretching frequencies were found near 300 and 275 cm^{-1} for monoalkoxide complexes. The third probably lies under the other two. In the dialkoxide species, the stretching frequency is almost 20 cm^{-1} lower. The $MoOCl_4^-$ ion gave the highest absorption, ~360 cm^{-1}. Comparison of the M–X stretch of the complexes studied with the results of Sabatini and Bertini[5] leads one to conclude that the following is the order of metal–halogen bond strength: $MOCl_4^- > MOCl_5^{2-} \sim MCl_6^- \sim M(OR)Cl_5^- > M(OR)_2Cl_4^-$ ($M = $ Mo or W; $R = CH_3$, C_2H_5, or C_3H_7).

The metal–oxygen stretch is also interesting. As the alkoxide increased in size, the metal–oxygen stretch increased in frequency, $OC_3H_7 > OC_2H_5 > OCH_3$. The metal–oxygen stretching frequencies are higher for monoalkoxide than for the analogous dialkoxide complex, $[(C_2H_5)_4N][W(OC_2H_5)Cl_5] > [(C_2H_5)_4N]$-$[W(OC_2H_5)_2Cl_4]$: the stretch occurs at 613 cm^{-1} for $[(C_2H_5)_4N][Mo(OC_2H_5)_2Cl_4]$ compared to 584 cm^{-1} for the tungsten case. The absorption was lowered slightly on changing from chloride to bromide.

The X–M–X modes for monoalkoxo complexes were assigned at ~170 and ~150 cm^{-1} by comparison with WCl_6^{2-} and $MoCl_6^{2-}$ spectra.[13] A broad band began near 90 cm^{-1} but had no maximum above 80 cm^{-1}. Sabatini and Bertini assigned a band in this region to an X–M–X vibration.[5] For dialkoxo and tetrachlorooxo complexes, the X–M–X vibration should be those at ~160 and ~130 cm^{-1}. The degeneracy of the E_u modes is apparently removed in the solid state.

The O–M–X vibrations were assigned by comparison with $[(C_2H_5)_4N][W(OCH_3)_2Br_4]$. Three vibrations are observed in the 300-cm^{-1} region and are probably O–W–Br vibrations. Since X–M–X vibrations are slightly lower (~40 cm^{-1}) for X = Br than X = Cl,[5] one would expect a similar behavior for O–M–X modes. An M–O rocking vibration is observed[5] in oxyhalide compounds.

In addition, a C–C–O bending mode at 370 cm^{-1} was

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(12) K. W. Bagnall, D. Brown, and J. G. H. Du Preeze, *J. Chem. Soc.*, 2603 (1964).

(13) D. M. Adams, H. A. Gebbie, and R. D. Peacock, *Nature*, **199**, 279 (1963).

observed for chromium ethoxide complexes.[6] A band found near 400 cm^{-1} is believed to be this vibration in the molybdenum and tungsten complexes.

The most stable arrangement for dialkoxo complexes is the *trans* as shown by axial symmetry of their esr spectra.[8,14] Further evidence for this structure is found in a shift of 16–20 cm^{-1} to lower energy for M–Cl stretches in dialkoxo complexes compared to that in the similar hexachloro compound and also it is supported by the number of observed vibrations. Five normal modes are required in D_{4h} symmetry whereas thirteen are possible in C_{2v} symmetry. The number of absorptions found for the tetrachlorooxo anion indicate D_{4h} symmetry as was postulated previously.[15]

The far-infrared absorptions of dimeric compounds are given in Table III. The proton nmr absorption spectrum of $[W(OCH_3)_2Cl_3]_2$ in chloroform gave a line absorption at τ 5.6 ± 0.1. This indicates the equivalence of the methyl groups, and, thus, only chloride bridges are possible.

TABLE III

INFRARED ABSORPTION FREQUENCIES (CM^{-1}) OF $MOCl_4^-$ IONS AND DIMERIC TUNGSTEN SPECIES (WITH POSSIBLE ASSIGNMENTS)

Assignment	$[W(OCH_3)_2Cl_3]_2$	$[W(OCH_3)_3Cl_2]_2$	$[W(OC_2H_5)_3Cl_2]_2$
ν(M–O)	567 s	566 s	623 s
ν(M–O)	542 s	520 m	519, 501 m
ν(O–M–O)		455 m	397 m
ν(O–M–X)	357 s	339 w	
ν(M–X)	328 s	318 s	305 s
ν(M–X)	291 s	305 s	288 s
ν(O–M–X)		279 s	247 sh
ν(O–M–X), ν(M–X)	255 s	252 m	218 m
ν(X–M–X)	177 s		
ν(X–M–X)	91 m		
	$[(C_3H_7)_4N]MoOCl_4$	$[(C_4H_9)_4N]MoOCl_4$	
ν(M–O)	990 w	980 w	
ν(M–X)	358 s	354 s	
ν(X–M–X)	162 m	161 m	
ν(X–M–X)	154 m	155 m	

The nmr studies of $[W(OC_2H_5)_3Cl_2]_2$ indicate the nonequivalence of the alkoxide groups. Klejnot[16] found a ratio of 2:1 for the proton nmr absorption spectrum of the dimer.

Since there are no observed X–M–X vibrations, if one assumes the proposed structure is correct, then the band at 218 cm^{-1} for $[W(OCH_3)_3Cl_2]_2$ should be the M–X bridging vibration. This band is probably that at 255 cm^{-1} for $[W(OCH_3)_2Cl_3]_2$ and 252 cm^{-1} for $[W(OCH_3)_3Cl_2]_2$. For the latter two species the band probably contains some O–M–X character. The dimeric species also exhibit vibrations at ~520 cm^{-1} which are probably M–O stretches of terminal alkoxide groups in the equatorial plane. The O–M–O vibrations are probably found in the 400-cm^{-1} region by analogy with other results.[6] The other assignments were made in comparison with the other compounds studied.

The infrared, visible, and ultraviolet spectra and magnetic properties of compounds are given in Tables IV and V. Where comparison with earlier work[7,8,17] is possible, agreement is good. The $M(OR)_2Cl_4^-$ both in nitromethane and in an acidic methanol solution, which was prepared by saturating with HCl at 0°, shows two absorptions at ~12 and ~22 × 10^3 cm^{-1}. If the nitromethane solution contains free HCl, the methanol–HCl solution is warmed to 25°, or the methanol is not saturated with HCl, spectra change with time and thus suggest that reactions occur and the species present is no longer $Mo(OR)_2Cl_4^-$. Spectra which were reported previously[8] for $Mo(OR)_2Cl_5^{4-}$ in alcohols were more like those of $MoOCl_4^-$ and the solutions probably had undergone decomposition.

TABLE IV

ELECTRONIC ABSORPTION SPECTRA OF COMPOUNDS

Compound	Medium	$10^3\nu$, cm^{-1} (ϵ_{max})
$[(C_2H_5)_4N][Mo(OCH_3)_2Cl_4]$	Solid	11.9, 21.8, 27.4
	Nitromethane	11.7 (16), 21.8 (27)
	CH_3OH–HCl	11.7 (16), 21.8 (27)
$[(C_2H_5)_4N][Mo(OC_2H_5)_2Cl_4]$	Solid	12.7, 21.3, 26.0
	Nitromethane	12.1 (19), 21.5 (29)
	C_2H_5OH–HCl	12.1 (19), 21.5 (29)
$[(C_2H_5)_4N][W(OCH_3)_2Br_4]$	Solid	11.9, 14.6, 23.5
	Nitromethane	11.9 (17), 14.7 (19)
	Methylene chloride	11.9 (17), 14.7 (19), 23.6 (630), 26.0 (5.0 × 10^3), 350 (3.0 × 10^3), 317 (3.8 × 10^3), 290 (5.9 × 10^3)
$[(C_4H_9)_4N]MoOCl_4$	Solid	14.8, 22.7 sh, 26.3 sh
	Nitromethane	13.6 (18), 22.5 (17)
	Methylene chloride	14.6 (23), 22.7 (19), 26.4 (240), 31.3 (5.1 × 10^3)
$[(C_3H_7)_4N]MoOCl_4$	Solid	14.8, 22.7 sh, 26.7 sh
	Nitromethane	13.6 (14), 22.5 (23)
	Methyl chloride	14.6 (23), 22.6 (30), 26.4 (280), 31.3 (5.1 × 10^3)
	CH_3OH (initially)	14.1 (25), 23.2 (200), 30.8 (2.0 × 10^3), 37.7 sh
	CH_3OH (after 2 hr)	14.1 (25), 23.0 (241), 32.5 (1.7 × 10^3), 37.7 sh

$[(C_2H_5)_4N]WBr_6$ was prepared in saturated HBr–alcohol solutions. Conditions similar to those for the preparation of $W(OR)Cl_5^-$ from WCl_6^- lead to the formation of $W(OR)_2Br_4^-$ from WBr_6^-. The W–Br bond is weaker than the W–Cl bond and may account

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TABLE V

MEASURED MAGNETIC SUSCEPTIBILITIES AND MAGNETIC MOMENTS

Compound	Temp, °C	$10^6\chi_m'$, cgsu	μ_{eff}, BM	θ, °K
$[(C_2H_5)_4N][Mo(OCH_3)_2Cl_4]$	297	1226	1.71	2
	195	1885	1.72	
	77	4747	1.72	
$[(C_2H_5)_4N][Mo(OC_2H_5)_2Cl_4]$	297	1252	1.73	4
	195	1915	1.74	
	77	4956	1.75	
$[(C_2H_5)_4N][W(OCH_3)_2Br_4]$	297	1067	1.60	−1
	195	1605	1.59	
	77	4080	1.60	
$[(C_3H_7)_4N]MoOCl_4$	297	1216	1.71	2
	195	1837	1.70	
	77	4628	1.70	
$[(C_4H_9)_4N]MoOCl_4$	297	1224	1.72	4
	195	1912	1.73	
	77	4841	1.73	

for the previous different product observation. Properties of $[(C_2H_5)_4N]WBr_6$ agreed with those previously reported.[18]

The release of an alkyl group by monoalkoxide complexes tends to confirm the expected greater stability of a complete double bond in M=O compared to the partial π-bond character for oxygen in M—O—R. The far-infrared data (Table I) also probably indicate that the bond *trans* to the metal–oxygen is weakened. The low-frequency M–X band is probably the M–X stretch *trans* to the alkoxide group. The greater instability of the molybdenum compound compared to the tungsten complex ought to be due to better overlap of the oxygen p orbitals with the t_{2g} orbitals of the molybdenum in forming Mo–O. Thus, a weaker metal–halogen bond *trans* to the alkoxide group is the result. Although the frequency of the metal–oxygen bond *trans* to the alkoxide increases as the size of the alkyl group increases, the rate of alkyl halide evolution decreases.[7] It is conceivable that the rearrangement in the solid state is hampered by the larger alkyl group.

The elimination of alkyl halide is viewed as a concerted process that involves an axial chloride from one ion with the alkyl group from a neighbor. Evidence points to an intermolecular process since the rate of alkyl halide evolution decreased as the size of the cation increased. The driving force is the formation of the more stable metal–oxygen double bond.

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Absorption and Circular Dichroic Spectral Studies of Europium(III) Complexes with Sugar Acids and Amino Acids, with Remarks on "Hypersensitivity"[1]

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Chelate complexes of Eu(III) with sugar acids, both in the acid and neutral pH ranges, are demonstrated. Complexing takes place through the carboxylate group and the γ-hydroxyl, revealed by the CD relations of the gluconic and galactonic acid complexes. In addition to chelate complexes of the α-amino acids in the neutral to alkaline pH range, monodentate complexes with the zwitterionic form are demonstrated. Besides the known "hypersensitive" behavior of the $^7F_0 \rightarrow {}^5D_2$ transition in the absorption spectrum, hypersensitivity is also indicated for the $^7F_0 \rightarrow {}^5D_0$ and $^7F_1 \rightarrow {}^5D_1$ transitions and perhaps in others which share the relation $|\Delta J| = 0, 2$. A requirement seems to be binding of an anion, which may include reduction of symmetry. Some potentially revealing characteristics of the CD spectra are pointed out.

The absorption spectra of the trivalent rare earth ions are relatively unaffected by varied chemical environments and ligands, certainly in comparison with the more familiar 3d series of transition elements. This is commonly attributed to the "buried" or shielded nature of the 4f orbitals, presumably lying at shorter radii than others in the atomic complement. For the tripositive ions retaining three or more f electrons (or equivalent holes), however, one or a few transitions out of the whole spectrum show marked enhancement of intensity when water in the coordination sphere is replaced by certain other ligands. These transitions have received the designation "hypersensitive," and several theoretical suggestions have been offered for the orgin of the phenomenon.[2-4]

We have shown that chelating ligands (hydroxy acids and amino acids) markedly alter rare earth ab-

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