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Chemical and Structural Studies of Rhenium(V) Oxyhalide Complexes. II. M[ReX_4O] and M[ReX_4OL] Complexes from $KReO_4$[1]

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By reducing potassium perrhenate with zinc in the presence of excess HX, a new series of compounds with the general formula M[ReX_4O] (where M is a monopositive cation and X is Cl, Br, or I) has been prepared. Physical and chemical studies of these complexes suggest that they contain mononuclear, square-pyramidal [ReX_4O]$^-$ ions, in which there is extensive oxygen-to-rhenium π bonding. As shown by infrared spectroscopy, the reversible addition of acetonitrile to the coordination sphere of the rhenium atom in tetraphenylarsonium oxotetrabromorhenate(V) can occur, with the resultant formation of [$(C_6H_5)_4As$][$ReBr_4O(CH_3CN)$]. Reactions of the M[ReX_4O] compounds indicate their chemical relationship to various other oxyhalide complexes of rhenium(V) previously reported in the literature.

Introduction

In the course of our investigation of the oxidative degradation of the nonabromotrirhenium(III) cluster, a compound was isolated which was shown by X-ray diffraction to contain the novel [$ReBr_4O(H_2O)$]$^-$ anion.[3,4] In order to obtain better chemical and structural information about this and related anions and, particularly, with the hope of developing a more rational and efficient method of preparation, a more extensive study was undertaken.

In this paper, the direct, nearly quantitative preparation of M[ReX_4O] compounds, where M is a univalent cation and X is chlorine, bromine, or iodine, from potassium perrhenate will be described. In addition, the ability of these compounds to form the related M[ReX_4O(solvent)] compounds will be shown. An extensive investigation of the chemical, spectral, and magnetic properties of these rhenium(V) oxyhalide complexes has been carried out, and their chemical relationship to other known rhenium(V) compounds established. A complete three-dimensional X-ray crystal structure analysis of one of these, [$(C_6H_5)_4As$][$ReBr_4O(CH_3CN)$], has also been performed, the results of which will be reported in a later paper in this series.[5]

Experimental Section

All compounds were prepared from reagent grade chemicals. Melting points were taken on a conventional hot-stage microscope and are corrected. Analyses were performed by Galbraith Laboratories, Knoxville, Tenn., except for oxygen, which was determined by neutron activation analysis at General Atomic, San Diego, Calif.

Tetraphenylarsonium Oxotetrabromorhenate(V), [$(C_6H_5)_4As$][$ReBr_4O$].—To a mixture of 75 ml. of concentrated H_2SO_4 (18 *M*) and 75 ml. of methanol were added 2.5 g. of $KReO_4$ and 4 g. of zinc metal (particle size 10 mesh). The mixture was heated on a steam bath (solution temperature *ca.* 90°) for 1 hr. To the hot solution, now deep purple-black in color, a mixture of 50 ml. of methanol and 50 ml. of 48% aqueous HBr was added slowly, over a period of 10 min., with stirring. Hydrogen gas was rapidly generated and the solution color became dark red. After an additional 2 hr. on the steam bath, the solution was cooled to ice temperature and filtered to remove an insoluble white residue, probably $ZnSO_4$. A solution of 4.0 g. of tetraphenylarsonium bromide in 25 ml. of methanol was next added with stirring to the dark red filtrate, now *ca.* 150–155 ml. in volume. A bright coral-red precipitate formed at once and stirring was continued for 1 hr. The product was filtered, washed with one 10-ml. portion of cold 48% HBr, then with diethyl ether until no odor of HBr could be detected above the filter frit. After recrystallization from acetonitrile, the product was dried at 80° under vacuum for 24 hr.; yield, 7 g. of red prisms.

Anal. Calcd. for [$(C_6H_5)_4As$][$ReBr_4O$]: C, 31.84; H, 2.23; As, 8.28; Br, 35.31; O, 1.77. Found: C, 31.4; H, 2.20; As, 8.31; Br, 35.3; O, 1.81. This compound could also be made directly from $K_2[ReBr_6]$ according to the above method, by substituting 6.4 g. of potassium hexabromorhenate(IV) for $KReO_4$. The yields were generally poorer, however.

Solubility.—Soluble in acetone, alcohols, acetonitrile, chloroform, and tetrahydrofuran. Insoluble in hydrocarbons, diethyl ether, 48% HBr. Hydrolyzes instantly in water and slowly in moist air to form a black powder.

Tetra(*n*-butyl)ammonium Oxotetrabromorhenate(V), [$(n\text{-}C_4H_9)_4N$][$ReBr_4O$].—This compound was prepared in a manner analogous to the preparation of [$(C_6H_5)_4As$][$ReBr_4O$]. Here, addition of 2.8 g. of [$(n\text{-}C_4H_9)_4N$]Br in 20 ml. of methanol to the dark red filtrate precipitated a coral-red powder which was filtered, washed with 48% HBr and ether, and then dried under vacuum at 80°; yield, after recrystallization from methanol–2-propanol, 4.6 g.

Anal. Calcd. for [$(C_4H_9)_4N$][$ReBr_4O$]: C, 25.14; H, 4.76; N, 1.83; Br, 41.82; O, 2.10. Found: C, 24.89; H, 4.74; N, 1.84; Br, 40.78; O, 2.28.

Solubility.—Qualitatively identical with that of [$(C_6H_5)_4As$][$ReBr_4O$].

Tetraethylammonium Oxotetrabromoaquorhenate(V), [$(C_2H_5)_4N$][$ReBr_4O(H_2O)_{1/2}$].—A solution containing 20 ml. of H_2O, 20 ml. of concentrated (18 *M*) H_2SO_4, 2.5 g. of zinc (10 mesh particle size), and 1.25 g. of $KReO_4$ was heated on the steam bath for 1 hr. Subsequently, a mixture of 25 ml. of 48% aqueous HBr and 12 ml. of H_2O was added slowly, with stirring, and the resultant mixture kept at the steam bath temperature (*ca.* 90°) for 2 hr. Filtration of the cooled solution gave a dark red filtrate to which was added 4.5 g. of [$(C_2H_5)_4N$]Br with stirring. After 12 hr., orange crystals were filtered, washed with 20% aqueous HBr, then exhaustively with ether, and air dried to give a yield of 2.45 g. Chemical analysis indicated an impure product. Recrystallization from CH_3CN resulted in the formation of a mixture of red, yellow, and black crystals as revealed by examination on the microscope stage (*cf.* ref. 4). Recrystalliza-

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[2] NSF Predoctoral Fellow, 1962–1965.

[3] F. A. Cotton and S. J. Lippard, *Chem. Commun.* (London), 245 (1965).

[4] F. A. Cotton and S. J. Lippard, *Inorg. Chem.*, **4**, 1621 (1965).

[5] F. A. Cotton and S. J. Lippard, to be published as part III of this series.

tion from acetone, however, was successful. In this medium, the yellow and black crystals were insoluble and could be filtered off before evaporation (at *ca.* 11 mm.) of the solvent yielded large, light red plates. These were dried under vacuum at 100° for 24 hr. An infrared spectrum revealed the presence of water.

Anal. Calcd. for $[(C_2H_5)_4N][ReBr_4O(H_2O)_{\sim 0.53}]$[6]: C, 14.34; H, 3.52; N, 2.04; Br, 47.70; O, 3.64. Found: C, 14.01; H, 3.37; N, 2.08; Br, 47.34; O, 3.73.

Solubility.—Soluble in acetone and acetonitrile to give yellow-orange solutions. Insoluble in hydrocarbons, alcohols, ethers, and chloroform.

Pyridinium Oxotetrabromorhenate(V), $(C_5H_5NH)[ReBr_4O]$.—When 2.0 ml. of pyridine was added to the dark red filtrate obtained from the zinc reduction of perrhenate (see preparation of $[(C_6H_5)_4As][ReBr_4O]$) and the resultant mixture stirred for 12 hr., golden brown crystals formed. These were filtered, washed with diethyl ether, and dried at 80° under vacuum; yield, 0.8 g.

Anal. Calcd. for $(C_5H_5NH)[ReBr_4O]$: C, 9.98; H, 1.01; N, 2.33. Found: C, 10.25; H, 1.10; N, 2.34.

Solubility.—Insoluble in all common organic solvents. Hydrolyzes to form a black residue in water.

Cesium Oxotetrabromorhenate(V), $Cs[ReBr_4O]$.—This compound was prepared in a manner analogous to the preparation of $[(C_6H_5)_4As][ReBr_4O]$; here, addition of a twofold excess (3.7 g.) of solid cesium bromide to the filtrate, followed by 12 hr. of stirring, produced 1.0 g. of orange product. This was washed with a few ml. of 48% HBr, then exhaustively with ether. Recrystallization from 48% HBr at *room temperature* gave red-orange platelets, which were dried at 80° under vacuum.

Anal. Calcd. for $Cs[ReBr_4O]$: Br, 48.85. Found: Br, 48.16.

Solubility.—Soluble only slightly in 48% aqueous HBr. Hydrolyzes instantly in neutral water or moist air to form a black, insoluble residue.

Tetraphenylarsonium Oxotetrachlororhenate(V), $[(C_6H_5)_4As]$-$[ReCl_4O]$.—This compound was prepared both directly from $KReO_4$ (method A) as well as by halogen exchange (method B) with $[(C_3H_5)_4As][ReBrO_4]$.

Method A.—The procedure for synthesizing $[(C_6H_5)_4As]$-$[ReBr_4O]$ was followed except that concentrated HCl (12 *M*) was used instead of 48% HBr. After filtering the white residue ($ZnSO_4$), a light green filtrate remained. To this was added 3.6 g. of $[(C_6H_5)_4As]Cl$ in 25 ml. of methanol. After stirring for 12 hr., a cream-colored precipitate was filtered on a glass frit and washed with 10 ml. of concentrated HCl and several 10-ml. portions of anhydrous ether. To avoid rapid hydrolysis by water vapor in the air, the wet product was then dissolved in anhydrous acetonitrile and washed from the frit into a filter flask. Evaporation of the solvent at *ca.* 11 mm. yielded 0.9 g. of large yellow plates and deep yellow prisms. These were dried for 2 hr. under vacuum at 80° and sealed *in vacuo* until analyzed.

Anal. Calcd. for $[(C_6H_5)_4As][ReCl_4O]$: C, 39.63; H, 2.78; As, 10.30; Cl, 19.50; O, 2.20. Found: C, 39.7; H, 2.78; As, 10.6; Cl, 19.2; O, 2.64.

Solubility.—Qualitatively identical with that of $[(C_6H_5)_4As]$-$[ReBr_4O]$ except much more susceptible to hydrolysis by atmospheric water vapor.

Method B.—$[(C_6H_5)_4As][ReBr_4O]$ (0.39 g.) was dissolved in 4 ml. of acetone and 10 ml. of concentrated HCl added. The orange solution was evaporated on the steam bath (~90°) for 15 min. and filtered. A pale yellow solid was collected, washed with concentrated HCl, and recrystallized from ethanol to yield yellow crystals. These were dried under vacuum at 80°.

Anal. Found: C, 39.7; H, 2.89.

Tetra(*n*-butyl)ammonium Oxotetraiodorhenate(V), $[(n\text{-}C_4H_9)_4N][ReI_4O]$.—The procedure for synthesizing $[(C_6H_5)_4As]$-$[ReBr_4O]$ was followed, except that 55% aqueous HI was used instead of 48% HBr. Upon cooling the reaction mixture, a black residue was filtered off, and 3 g. of purple-black, microcrystalline product was isolated by filtration, washed with diethyl ether (in which the crystals were partly soluble), and dried in air.

Anal. Calcd. for $[(n\text{-}C_4H_9)_4N][ReI_4O]$: C, 20.18; H, 3.82; N, 1.47. Found: C, 19.6; H, 5.55; N, 1.32.

The analytical results for this compound are not entirely satisfactory, probably because of contamination from products of hydrolysis. Attempts to recrystallize the product were unsuccessful.

Solubility.—Soluble in acetone, acetonitrile, ethers.

Dioxotetrapyridinerhenium(V) Bromide Dihydrate, $[Re(C_5H_5N)_4O_2]Br\cdot 2H_2O$.—This compound was first prepared by Johnson, Lock, and Wilkinson[7] and was obtained from $[(C_6H_5)_4As][ReBr_4O]$ in the following manner. Tetraphenylarsonium oxotetrabromorhenate(V), 0.5 g., was refluxed under nitrogen in 20 ml. of pyridine for 2 hr., after which the solution was cooled to 0°, producing a bright orange precipitate. The pyridine had not been rigorously dried. Filtration and recrystallization from chloroform–cyclohexane yielded 0.2 g. of product.

Anal. Calcd. for $[Re(C_5H_5N)_4O_2]Br\cdot 2H_2O$: C, 36.92; H, 3.73; N, 8.61; Br, 12.28. Found: C, 36.6; H, 3.36; N, 8.20; Br, 12.6.

Solubility.—Soluble in water, alcohols, acetone, acetonitrile, pyridine. Insoluble in hydrocarbons, ethers.

As reported by Johnson, *et al.*,[7] the infrared spectrum of this compound has a very strong, sharp band at 822 cm.$^{-1}$ which may be assigned to the linear O–Re–O grouping. Furthermore, we have extended their conductivity study to the solvent acetonitrile in which $[Re(C_5H_5N)_4O_2]Br\cdot 2H_2O$ is a 1:1 electrolyte (molar conductivity, Λ_M = 184 ohm^{-1} cm^2.). In addition, we have measured the ultraviolet–visible absorption spectrum from 8000 to 43,000 cm.$^{-1}$ of this compound in spectral grade acetonitrile, with the following results

ν, cm.$^{-1}$	ϵ_{max}
23,250	Shoulder
29,400	14,500 (sharp)
40,650	15,500 (sharp)

Finally, the addition of silver nitrate to an aqueous solution of $[Re(C_5H_5N)_4O_2]Br\cdot 2H_2O$ produced the expected curdy white precipitate of AgBr, verifying the presence of anionic bromine.

Dioxotetrapyridinerhenium(V) Chloride Dihydrate, $[Re(C_5H_5N)_4O_2]Cl\cdot 2H_2O$.—From 0.5 g. of $[(C_6H_5)_4As][ReCl_4O]$, 0.25 g. of orange microcrystalline product was prepared by the method described for the bromo analog (*vide supra*). Recrystallization was carried out in acetonitrile, with the concomitant production of a little green impurity from which the orange product was separated manually and dried in air.

Anal. Calcd. for $[Re(C_5H_5N)_4O_2]Cl\cdot 2H_2O$: C, 39.63; H, 4.00; N, 9.25. Found: C, 38.03; H, 4.08; N, 9.03.

The presence of two waters of hydration is postulated in view of the findings of Johnson, *et al.*[7]

Oxotribromobistriphenylphosphinerhenium(V), $ReBr_3[(C_6H_5)_3P]_2O$.—This compound has been reported previously.[8] $[(C_6H_5)_4As][ReBr_4O]$ (1 g.) was dissolved in 20 ml. of acetonitrile (not rigorously dried) and a twofold excess of triphenylphosphine (0.6 g.) stirred in. After 10 min., the solution was filtered to yield a bright yellow crystalline powder. The solid was washed with diethyl ether and dried in air; yield, 0.5 g.; m.p. 179–182° (lit.[8] 181–183°).

Anal. Calcd. for $ReBr_3[(C_6H_5)_3P]_2O$: C, 44.5; H, 3.06; Br, 24.5. Found: C, 44.4; H, 3.11; Br, 24.2.

Solubility.—Insoluble in all common organic reagents. This compound was further identified by the strong ReO band at 982 cm.$^{-1}$ in its infrared spectrum (see ref. 8). We have also prepared it by the above method using $[(n\text{-}C_4H_9)_4N][ReBr_4O]$ as the starting material.

Oxotrichlorobistriphenylphosphinerhenium(V), $ReCl_3[(C_6H_5)_3$-

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(6) This formula is consistent with the result of the neutron activation analysis for oxygen and will be discussed further. It should be noted that since the analysis is sensitive to O_2 and H_2O absorbed on the sample, the result given is an upper limit.

(7) N. P. Johnson, C. J. L. Lock, and G. Wilkinson, *J. Chem. Soc.*, 1054 (1964).

(8) J. Chatt and G. A. Rowe, *ibid.*, 4019 (1962).

TABLE I

THE [ReX_4O]$^-$ COMPOUNDS AND THEIR PROPERTIES

Compound	Color	Electronic spectra[a]	Λ_M at 25°, ohm^{-1} cm.^{2}		ν(R=O), cm.$^{-1}$
			In CH_3NO_2, ~10^{-3} *M*	In CH_3CN ~10^{-3} *M*	
[$(C_6H_5)_4As$][$ReBr_4O$]	Coral red	In acetone: 8880 (37), 9760 (sh), 12,000 (22), 18,900 (75), 22,500 (68), 26,300 (sh), 37,700 (4000), 37,000 (sh), 38,100–38,200 (4700)[b]	114	163	1000 ± 5
[$(n\text{-}C_4H_9)_4N$][$ReBr_4O$]	Coral red	In chloroform: 8930 (29), 10,000 (sh), 12,000 (20), 19,200 (93), 23,000 (125), 26,400 (sh), 32,300 (sh), 35,700 (4300)	83.5	...	1010
[$(C_2H_5)_4N$][$ReBr_4O(H_2O)_{\sim 0.5}$][c]	Red-orange	In acetonitrile: 8360 (br), ~10,000 (sh), ~14,000 (27), 18,900 (100), 22,200 (sh), 32,200 (sh), 34,500 (4225)	108	145	1004
(C_5H_5NH)[$ReBr_4O$]	Golden brown	...	...	...	1000
Cs[$ReBr_4O$]	Red-orange	...	...	...	955
[$(C_6H_5)_4As$][$ReCl_4O$]	Cream	In acetonitrile[d]: 8440 (~25, br), 12,000 (21, br), 20,800 (35), 23,800 (sh), 27,800 (sh), 38,200 (1100)	93	...	1000 ± 5
[$(n\text{-}C_4H_9)_4N$][ReI_4O]	Purple-black	...	...	...	...

[a] Solvent, followed by positions of maxima in cm.$^{-1}$; molar extinction coefficients are in parentheses; sh = shoulder. It should be noted that the formulas given in the first column of the table do not necessarily correspond to the formulas of the species whose spectra and conductivities in solution are reported. Thus, for example, the sixth compound may exist as [$(C_6H_5)_4As$]$^+$ and [$ReCl_4O(CH_3CN)$]$^-$ ions in solution. [b] A closely spaced doublet of narrow, equally intense bands. [c] See ref. 6. [d] Due to great sensitivity of this compound to traces of H_2O, the ϵ values are subject to uncertainty.

P]$_2$O.—References 8 and 9 contain the first reports of this compound. [$(C_6H_5)_4As$][$ReCl_4O$] (1 g.) was dissolved in 15 ml. of acetonitrile containing two drops of concentrated HCl, and 0.74 g. of $(C_6H_5)_3P$ was stirred in. The solution turned green at once and after several minutes, a yellow-green solid was filtered, washed with diethyl ether, and dried in air; yield, 1.0 g.

Anal. Calcd. for $ReCl_3[(C_6H_5)_3P]_2O$: C, 52.00; H, 3.61; Cl, 12.78. Found: C, 52.0; H, 3.70; Cl, 12.3.

The infrared spectrum of a Nujol mull of this compound revealed a strong band at 970 cm.$^{-1}$ indicative of the ReO group.[8]

Oxotribromobistriphenylarsinerhenium(V), $ReBr_3[(C_6H_5)_3As]_2O$.—This compound has been reported previously.[8] Here, a fourfold excess (0.82 g.) of triphenylarsine was added to a solution of 0.5 g. of [$(n\text{-}C_4H_9)_4N$][$ReBr_4O$] in 25 ml. of acetonitrile. Evaporation of the solvent in air yielded yellow microcrystals which were washed with diethyl ether and dried in air; yield, 0.5 g.

Anal. Calcd. for $ReBr_3[(C_6H_5)_3As]_2O$: C, 40.95; H, 2.85; Br, 22.75. Found: C, 40.5; H, 3.14; Br, 22.4.

From the occurrence of a strong band at 978 cm.$^{-1}$ (969 cm.$^{-1}$ shoulder) in the infrared spectrum of this compound, the presence of the ReO group was detected.

Tetraphenylarsonium Perrhenate, [$(C_6H_5)_4As$]ReO_4. Reaction of [$(C_6H_5)_4As$][$ReBr_4O$] with Diaryl Sulfoxides.—An excess of R_2SO, R = C_6H_5, $C_6H_5CH_2$, or p-$CH_3C_6H_4$, was added to 1.0 g. of [$(C_6H_5)_4As$][$ReBr_4O$] in 20 ml. of acetonitrile, and the resulting solution was evaporated to dryness in air at room temperature. To the residue was added 5 ml. of acetonitrile from which pale yellow tetrahedra were separated by filtration. These were washed with ether and dried in air; yield, *ca.* 0.3 g. From chemical analyses and from the infrared spectra which showed the usual broad band at ~910 cm.$^{-1}$ due to the ReO_4^- group,[10] the product with each of the sulfoxides was shown to be mainly tetraphenylarsonium perrhenate.

Anal. Calcd. for [$(C_6H_5)_4As$]ReO_4: C, 46.26; H, 3.56; Br, 0.0. Found for R = C_6H_5: C, 45.73; H, 3.11. Found for R = $C_6H_5CH_2$: C, 45.19; H, 3.28; Br, 0.46. Found for R = p-$CH_3C_6H_4$: C, 45.21; H, 3.20.

As would be expected, the products were 1:1 electrolytes in nitromethane. Thus for the product of the reaction with di(p-tolyl) sulfoxide, Λ_M = 67.7 ohm^{-1} cm.^{2}, and for the product of the reaction with dibenzyl sulfoxide, Λ_M = 80.3 ohm^{-1} cm.^{2}.

Physical Measurements.—Electrolytic conductance measurements were carried out using a standard, commercial Wheatstone bridge with a 30-cc. cell equipped with platinum electrodes, at 25°. Solvents were of spectroscopic grade and the solutions were approximately 10^{-3} *M*. The visible and ultraviolet spectra of solutions were run at concentrations of approximately 10^{-3} to 10^{-4} *M* on a Cary Model 14 recording spectrometer using 1.0-cm. matched quartz cells.

The molar susceptibility of doubly recrystallized, thoroughly dried [$(C_6H_5)_4As$][$ReBr_4O$] was measured by the Gouy method as discussed by Figgis and Lewis,[11] using a Gouy balance described in detail by Meyers.[12] The solid sample was finely pulverized, packed in a tube, and transferred to the balance as quickly as possible to minimize possible air hydrolysis. Several packings in two different Gouy tubes, previously calibrated with Hg[Co(SCN)$_4$] using the data of Figgis and Nyholm,[13] were made, and the results were averaged to give the final value. All measurements were carried out at room temperature.

Infrared spectra and X-ray powder photographs were obtained by the methods previously described.[4]

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[9] C. L. J. Lock and G. Wilkinson, *Chem. Ind.* (London), 40 (1962).

[10] H. H. Claasen and A. J. Zielen, *J. Chem. Phys.*, **22**, 707 (1954).

[11] B. N. Figgis and J. Lewis, Chapter 6 in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience, Publishers, New York, N. Y., 1960, p. 409 ff.

[12] M. D. Meyers, Ph.D. Thesis in Chemistry, Massachusetts Institute of Technology, 1959.

[13] B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 4190 (1958).

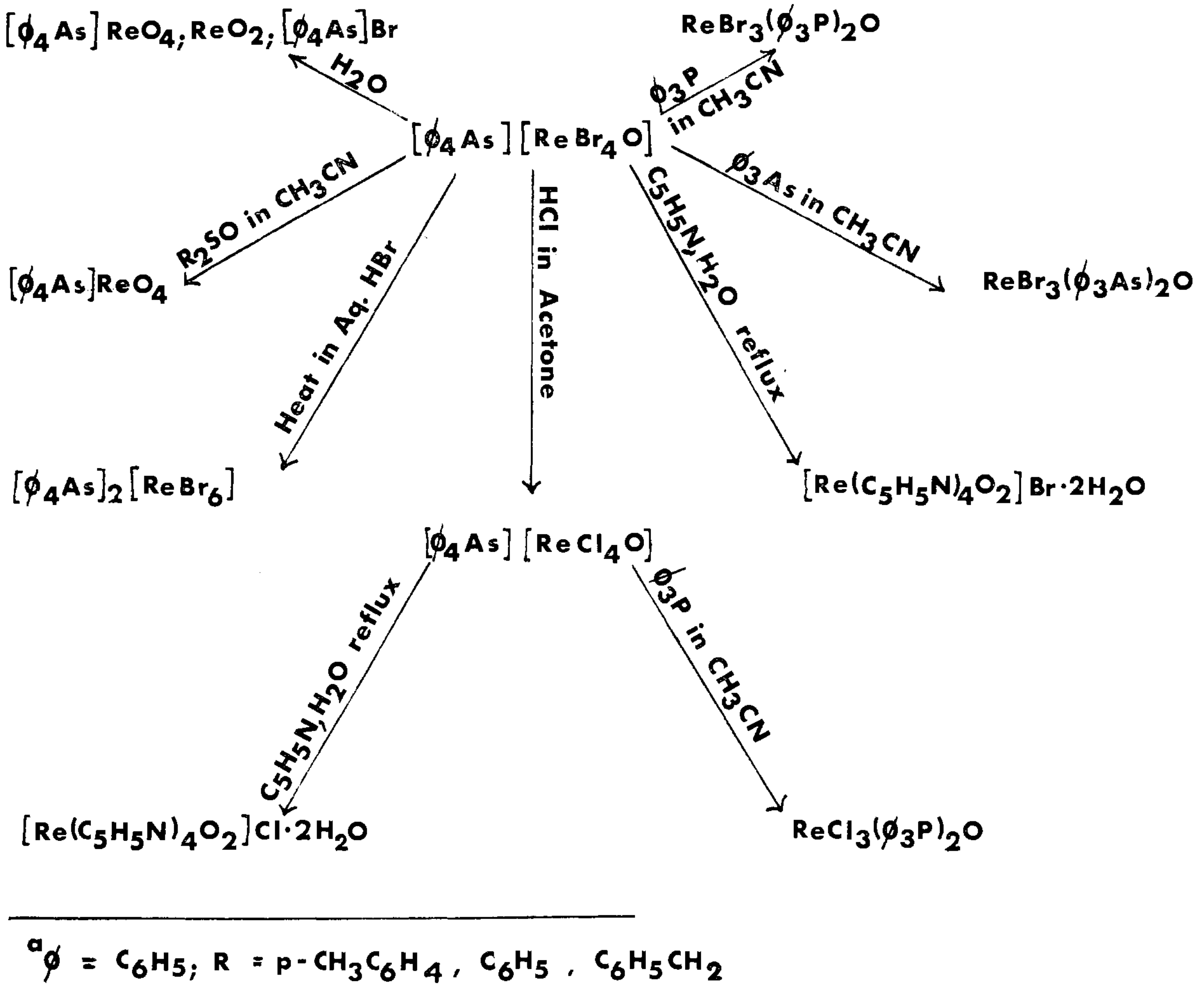

Figure 1.—Diagrammatic representation of the chemistry of M[ReX$_4$O] compounds.

Results

Chemical and Other Properties of M[ReX$_4$O] Compounds.—The formulas and various physical data for the M[ReX$_4$O] compounds are summarized in Table I. Figure 1 contains a diagrammatic representation of their chemistry.[14] Included in the figure is the result of an investigation of the hydrolysis of [(C$_6$H$_5$)$_4$As][ReBr$_4$O]. A small amount of finely powdered sample, 0.504 g., was weighed out and heated at 80° in the presence of moist air. The black residue which formed was then heated 30 min. longer under vacuum, cooled to room temperature, and weighed (final weight 0.382 g.). Assuming the hydrolysis to proceed according to the equation

$$3[(C_6H_5)_4As][ReBr_4O] + 5H_2O \longrightarrow [(C_6H_5)_4As]ReO_4(s) + 2ReO_2(s) + 2[(C_6H_5)_4As]Br(s) + 10HBr(g)$$

the expected weight loss would be 0.132 g. This is within 8% of the observed value, 0.122 g. It is interesting to note that [(C$_6$H$_5$)$_4$As][ReBr$_4$O] which has been recrystallized from acetonitrile and dried in air at room temperature is far less susceptible to hydrolytic decomposition. As will be shown, the increased stability results from the inclusion of a molecule of acetonitrile in the coordination sphere of the rhenium atom to form the [(C$_6$H$_5$)$_4$As][ReBr$_4$O(CH$_3$CN)] complex.

Infrared Spectra.—The infrared spectra of each compound was recorded and compared with the spectrum of the corresponding free ligand or cation. The results for many of the compounds appearing in Figure 1 have already been reported in the detailed description of their preparation (*vide supra*). Table I includes the ReO stretching frequencies for compounds of the type M[ReBr$_4$O]. For several of these, it was quite difficult to discern the ReO band, the 1000 cm.$^{-1}$ region being obscured by one or more intense cation absorptions. Careful matching of the positions and relative intensities of the free cation bands against the oxotetrahalorhenate(V) bands, however, revealed the likely position of the ReO stretching frequency in every case.

Of particular interest is the apparently anomalous ReO stretching frequency in Cs[ReBr$_4$O], 955 cm.$^{-1}$ *vs.* 1000 ± 10 cm.$^{-1}$ for the other compounds of Table I. A small amount of the cesium salt was dissolved in 48% aqueous HBr and tetraphenylarsonium bromide added. Tetraphenylarsonium oxotetrabromorhenate(V) precipitated at once; this was filtered, dried, and mulled in Nujol to give an infrared spectrum in which the ReO band had shifted to 1000 cm.$^{-1}$. This striking result is depicted in Figure 2, where, for comparison pur-

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(14) The reduction of [(C$_6$H$_5$)$_4$As][ReBr$_4$O] to [(C$_6$H$_5$)$_4$As]$_2$[ReBr$_6$] included in the figure was qualitatively observed; the ability of 48% HBr to reduce M[ReBr$_4$O] has already been well documented.[4]

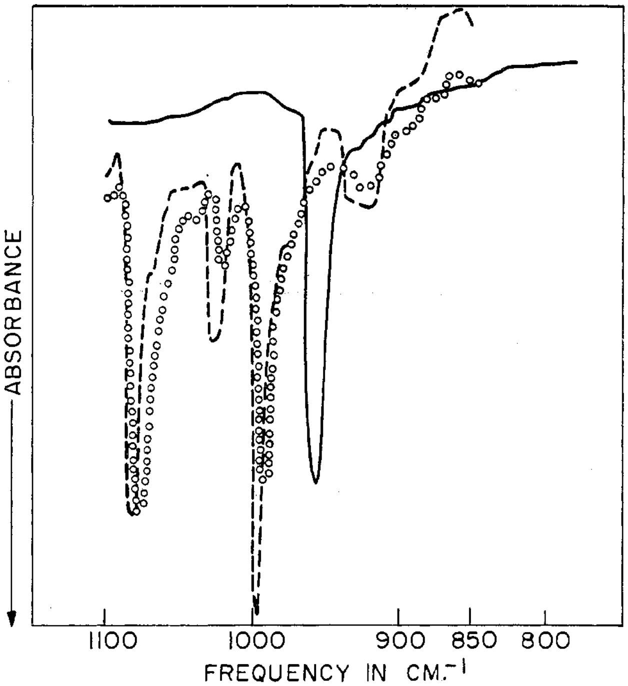

Figure 2.—Infrared spectra results for the Cs[ReBr$_4$O] to [(C$_6$H$_5$)$_4$As][ReBr$_4$O] conversion in the ReO stretching frequency region: Cs[ReBr$_4$O] (———); [(C$_6$H$_5$)$_4$As][ReBr$_4$O] (---------); [(C$_6$H$_5$)$_4$As]Br (oooo).

poses, the spectrum of [(C$_6$H$_5$)$_4$As]Br is also shown. From Figure 2 it is clear that the tetraphenylarsonium band which occurs at *ca.* 1000 cm.$^{-1}$ in the free cation has been enlarged in the [(C$_6$H$_5$)$_4$As][ReBr$_4$O] complex, presumably by the underlying ReO absorption (*cf.* also ref. 4 for a similar result in the tetraethylammonium oxotetrabromoaquorhenate(V) complex).

In the course of preparing single crystals of [(C$_6$H$_5$)$_4$As][ReBr$_4$O] by recrystallization from acetonitrile for X-ray studies,[5] the presence of two sharp, relatively weak bands at 2280 and 2305 cm.$^{-1}$ in the infrared spectrum of a sample which had been dried in air at room temperature was detected. Normally, all M[ReX$_4$O] complexes were dried at 80–100° under vacuum after recrystallization, and when this procedure was applied here, the new infrared bands disappeared. As will be shown, these bands are characteristic of acetonitrile which has entered the coordination sphere of the rhenium atom with the resultant formation of a new complex, [(C$_6$H$_5$)$_4$As][ReBr$_4$O(CH$_3$CN)]. This reversible addition of acetonitrile, although it raises the coordination number of the rhenium atom from five to six, changes neither the position nor the intensity of the ReO infrared band and apparently has no effect on the chemical properties of the complex, except to increase its resistance to hydrolysis (*vide supra*). All further physical measurements reported in this paper were made on [(C$_6$H$_5$)$_4$As][ReBr$_4$O] which had been thoroughly dried.

Visible and Ultraviolet Spectra.—Table I presents the results obtained for compounds containing the [ReX$_4$O]$^-$ ion, where X is bromine or chlorine, dissolved in an appropriate solvent. Solutions of Cs[ReBr$_4$O] and (C$_5$H$_5$NH)[ReBr$_4$O] could not be obtained and, consequently, their spectra were not measured. A typical spectrum, for the case of tetraphenylarsonium oxotetrabromorhenate(V) in acetone, is shown in Figure 3.

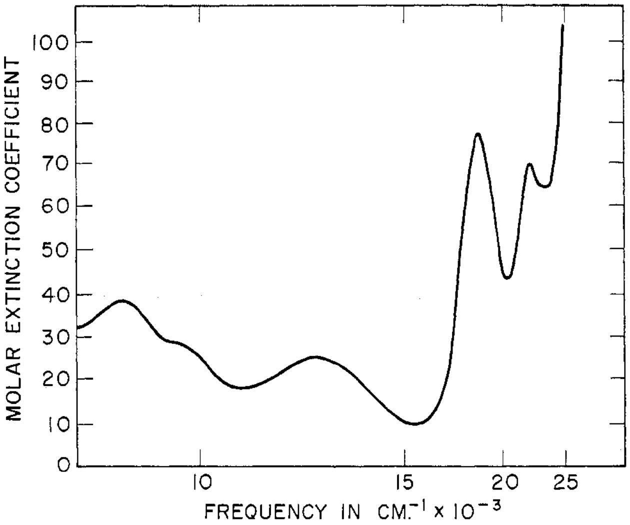

Figure 3.—Electronic spectrum of [(C$_6$H$_5$)$_4$As][ReBr$_4$O] in acetone.

TABLE II

X-RAY POWDER DATA FOR [(C$_6$H$_5$)$_4$As][ReX$_4$O]

X = Cl		X = Br	
d, Å.[a]	I/I_0	d, Å.[a]	I/I_0
9.19 (0.03)	80	9.24 (0.04)	80
7.82 (0.02)	70	8.06 (0.03)	70
7.44 (0.02)	15		
6.70 (0.02)	90	6.86 (0.02)	100
6.47 (0.01)	90	6.49 (0.02)	90
4.96 (0.01)	50	5.05 (0.01)	40
4.64 (0.01)	100	4.72 (0.01)	90
4.15 (0.01)	15		
4.07 (0.01)	20		
3.94 (0.01)	70	3.99 (0.01)	50
3.736 (0.005)	30	3.83 (0.01)	50
3.584 (0.005)	50	3.67 (0.01)	45
3.233 (0.004)	30	3.285 (0.004)	50
3.049 (0.003)	10	3.057 (0.004)	10
2.901 (0.003)	50	2.911 (0.003)	40
Weak lines, not well resolved		Weak lines, not well resolved	
2.441 (0.002)	50	2.469 (0.002)	60
2.396 (0.002)	5		
2.314 (0.002)	5		
2.282 (0.002)	35	2.306 (0.002)	20
2.117 (0.002)	60	2.165 (0.002)	50
2.038 (0.001)	65	2.058 (0.002)	40

[a] Values in parentheses refer only to the precision of the measurement as calculated by the program DIFFQ (see ref. 15).

The electronic spectrum of one other compound mentioned in this paper, *viz.*, [Re(C$_5$H$_5$N)$_4$O$_2$]Br·2H$_2$O, has already been included in the detailed description of its preparation.

X-Ray Powder Photographs.—These were recorded with a Debye–Scherrer rotating-sample camera, using Cu Kα radiation. The d spacings for [(C$_6$H$_5$)$_4$As][ReX$_4$O], X = Cl, Br, calculated with the aid of DIFFQ,[15] are presented in Table II. The two compounds are isomorphous.

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(15) R. M. Wing, "DIFFQ-Computer Program to Assist in the Measurement of d-spacings," Massachusetts Institute of Technology, 1964.

Magnetic Measurements.—The molar susceptibility of $[(C_6H_5)_4As][ReBr_4O]$ at 25° was found to be $-360 \pm 10 \times 10^{-6}$ c.g.s. mole^{-1} independent of field strength. From Pascal's constants,[16] we estimate the diamagnetic susceptibility to be about -380×10^{-6} c.g.s. mole^{-1}.

Discussion

From the results just presented and from previous findings,[4] it is apparent that rhenium is capable of forming monomeric oxotetrahalorhenate(V) complexes of the type $M[ReX_4O]$ and $M[ReX_4OL]$, where L is a solvent molecule, water or acetonitrile. The compound for which M is tetraethylammonium, X is bromine, and L is water has been prepared both from rhenium(III) bromide and by the zinc reduction of perrhenate. X-Ray powder patterns of both products appear by visual inspection to be identical. Nevertheless, the result of the neutron activation analysis for oxygen in material prepared from $KReO_4$ (*cf.* Table I) indicates the presence of only $\sim$0.5 H_2O per $(ReBr_4O)$ unit,[17] whereas the compound prepared from $(ReBr_3)_3$ contains one water molecule per formula unit (*cf.* single crystal X-ray structure analysis[4]). This discrepancy, which would not be revealed in the powder patterns if the basic structures of the two compounds were alike, may be accounted for by recalling that, in the preparation from $KReO_4$, the product was obtained from a solution whose water content had been diminished by concentrated H_2SO_4 and methanol and, in addition, was recrystallized from acetone. Previously[4] we have seen that the (aquo) oxygen-to-rhenium bond distance of 2.32 Å. in $[(C_2H_5)_4N][ReBr_4O(H_2O)]$ is rather large for coordinated water, and, presumably, it is rather easy to break this bond in solution. It therefore is not too surprising that, under the preparative conditions used here, not all of the rhenium atoms retain their coordinated water, and a compound of composition $[(C_2H_5)_4N][ReBr_4O(H_2O)_{\sim 0.5}]$ forms.

Assuming, then, that the structure of $[(C_2H_5)_4][ReBr_4O(H_2O)_{\sim 0.5}]$ contains the square-pyramidal $(ReBr_4O)$ unit found previously,[4] it seems likely that the rest of the compounds of Table I have the same basic unit. This assumption will be further justified in a later paper[5] when the X-ray crystal structure of $[(C_6H_5)_4As][ReBr_4O(CH_3CN)]$ is presented. At this time, however, we shall attempt to show that the other physical and chemical data found for the unsolvated $M[ReX_4O]$ complexes are consistent with the presence of mononuclear, square-pyramidal $[ReX_4O]^-$ anions.

Nature of the Reduction.—Evidently, when $KReO_4$ is reduced with zinc in the complex reaction mixture containing methanol, sulfuric acid, and HX, the conditions have fortuitously been optimized for the formation of the $[ReX_4O]^-$ ions. The isolation of $[ReX_5O]^-$,[18,19] $[ReX_4O_2]^{-2}$,[19-21] $[ReX_6]^{-2}$,[22] and $[(ReX_4)_2]^{-2}$,[23] ions from reducing solutions containing perrhenate and HX has been previously reported, but in no case was a $[ReX_4O]^-$ species mentioned. The mechanism or rationale behind each of the various routes to Re(V), Re(IV), and Re(III) complexes is at present obscure and remains a subject for further investigation.

Evidence for Oxygen.—As discussed previously,[4] the presence of (oxo) oxygen in the $[ReBr_4O(H_2O)]^-$ anion was at first difficult to detect. Definite proof was provided for the unsolvated compounds described here by the neutron activation analyses. In addition, a careful examination of the infrared spectra of all compounds revealed the ReO stretching frequency at 1000 ± 10 cm.$^{-1}$ (except $Cs[ReBr_4O]$, *vide infra*). The fact that relatively strong ReO stretching bands do exist, albeit obscured by the absorption of the complex cations, is of considerable practical significance. It means that, so far as we know, there is still no exception to the general rule that M=O groups in transition metal complexes give rise to strong, sharp infrared absorption bands in the range 850–1050 cm.$^{-1}$.

The frequency 1000 ± 10 cm.$^{-1}$ is among the highest known for rhenium–oxygen bonds[8] and may be taken to indicate a bond order substantially greater than two. Assuming the hybridization of the rhenium atom to be $d_{x^2-y^2}sp^3$, two empty d_{xz} and d_{yz} orbitals would then be available for π bonding with oxygen, in addition to the σ bond formed along the C_4 axis. In the case of $Cs[ReBr_4O]$, where the ReO band appears at 955 cm.$^{-1}$, the cesium ion is probably weakly bound to the oxygen atom in the lattice, thus removing electron density from the ReO system and lowering the absorption frequency (see Figure 2). This is consistent with the fact that of all the cations employed, only cesium is unimpeded by bulky organic side chains, a feature which, from a stereochemical viewpoint, seems necessary for interionic bonding to the oxygen atom in the lattice.

Characteristic Properties of the $[ReX_4O]^-$ Ions.—From the measured magnetic susceptibility of $[(C_6H_5)_4As][ReBr_4O]$, we conclude that the compounds are essentially diamagnetic. The observed diamagnetism is perfectly consistent with that expected from simple crystal field theory for a d^2 complex in a square-pyramidal ligand environment.[11] Presumably, the d_{xy} orbital is lowest in energy and contains the pair of rhenium electrons, leaving the d_{yz} and d_{xz} orbitals available for strong π bonding to the oxygen atom (*cf.* also discussion of infrared data above).

In addition to being diamagnetic, the $M[ReX_4O]$ compounds are 1:1 electrolytes in solution (see Table I). The values reported for the molar conductivity in acetonitrile range from 145 to 163 ohm^{-1} cm.^{2}, well

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(16) P. W. Selwood, "Magnetochemistry," 2nd Ed., Interscience Publishers, New York, N. Y., 1956, p. 93; see also ref. 11, p. 403.

(17) In the following discussion, the existence of a compound of the formula $[(C_2H_5)_4N][ReBr_4O(H_2O)_{0.5}]$ is implied, although this formula may indicate that a mixture of the anhydrous and aquo forms, *viz.*, $[(C_2H_5)_4][ReBr_4O]$ and $[(C_2H_5)_4N][ReBr_4O(H_2O)]$, has been obtained. The neutron activation analysis cannot, of course, distinguish between these two possibilities. In any event, the ensuing discussion is applicable to either formulation.

(18) A. A. Woolf, *Quart. Rev.* (London), **15**, 378 (1961).

(19) V. V. Lebedinskii and B. N. Ivanov-Emin, *Zh. Neorgan. Khim.*, **4**, 1762 (1959).

(20) D. I. Ryabchikov and I. I. Nazarenki, *ibid.*, **7**, 931 (1962).

(21) D. I. Ryabchikov and I. I. Nazarenki, *ibid.*, **6**, 641 (1961).

(22) F. Kraus and H. Steinfeld, *Ber.*, **64**, 2552 (1931).

(23) F. A. Cotton, N. F. Curtis, B. F. G. Johnson, and W. R. Robinson, *Inorg. Chem.*, **4**, 326 (1965).

within that expected[24] for uni-univalent electrolytes. In nitromethane, the molar electrolytic conductances fall in the range 83–114 ohm^{-1} $cm.^2$, slightly high compared to the values reported[24] for other 1:1 salts. Possibly, there is partial ionization of the $[ReX_4O]^-$ ion in this solvent.

From X-ray powder data, the isomorphism of $[(C_6H_5)_4As][ReBr_4O]$ and $[(C_6H_5)_4As][ReCl_4O]$ has been established. In general, there is a 1:1 correspondence of position and intensities of powder lines for these two compounds (Table II). The chloro compound has a few more lines that its bromo analog, but since these are all very weak, they may well be due to an impurity. The fact that the bromo compound had *d* spacings which are uniformly larger than the chloro compound is to be expected from the relative sizes of the halogen atoms.

Finally, we have the electronic spectra of several M[ReX_4O] complexes as summarized in Table I. For present purposes, these spectra serve to illustrate further the similarity of one more physical property of these compounds, and we shall not attempt to assign the bands at this time. Figure 3 shows the variability in the band widths, as observed in the spectrum of an acetone solution of tetraphenylarsonium oxotetrabromorhenate(V), which is typical.

Infrared Evidence for Acetonitrile in $[(C_6H_5)_4As][ReBr_4O(CH_3CN)]$.—As mentioned earlier, we now possess direct structural proof for the existence of a rhenium(V) methyl cyanide complex (*viz.*, $[(C_6H_5)_4As][ReBr_4O(CH_3N)]$).[5] It will be shown here that the infrared results are consistent with the X-ray data.

The infrared spectrum of free acetonitrile in the 2000–2400 $cm.^{-1}$ region[25] has two bands, at 2254 and 2293 $cm.^{-1}$. The first was assigned[25] to the CN stretching frequency and the second to a combination band resulting from the coupling of the symmetric CH_3 deformation (ν_3) and C–C stretching (ν_4) frequencies.[25] Fermi resonance presumably enhances the intensity of the latter. In complexes this pair of bands is characteristically altered[26–28] so that the "CN stretch" is found in the range 2270–2285 $cm.^{-1}$ and the combination band is found at 2290–2310 $cm.^{-1}$. The observation of bands at 2280 and 2305 $cm.^{-1}$ in $[(C_6H_5)_4As][ReBr_4O(CH_3CN)]$ is thus consistent with the presence of the coordinated CH_3CN.

Reactions with Neutral Ligands.—The reactions of $[(C_6H_5)_4As][ReBr_4O]$ and $[(C_6H_5)_4As][ReCl_4O]$ with triphenylphosphine, triphenylarsine, and pyridine have been carefully investigated as described in the Experimental Section and summarized in Figure 1. The tetra(*n*-butyl)ammonium oxotetraiodorhenate(V) complex gave qualitatively similar results, but no attempt was made to isolate or purify the products because of the dubious purity of the starting material. In each case, the reaction proceeded rapidly in good yield and may be recommended as a preparative route to the desired rhenium(V) compound. Since all of the products had been reported and characterized before in the literature, our success in obtaining them simply by mixing the ligand with M[ReX_4O] in an appropriate solvent was an excellent chemical verification of the oxidation state of the rhenium atom.

The reaction with pyridine was quite complex, but excess ligand inevitably yielded $[Re(C_5H_5N)_4O_2]X\cdot 2H_2O$, regardless of the solvent. Difficulties were encountered in removing traces of pyridine from the final product and, generally, a fair amount of MX, where M is the cation in the $[ReX_4O]^-$ salt used, was also present. When a triphenylphosphine–M[ReX_4O]–acetonitrile solution was refluxed under nitrogen, some evidence for reduction of the rhenium was obtained. In particular, evaporation of the solvent from the bright orange reaction mixture gave a final product which consisted of orange platelets (rather than the bright yellow-green $ReX_3[(C_6H_5)_3P]_2O$ complex) and which did not show an ReO band at *ca.* 980 $cm.^{-1}$.[8] There was insufficient sample for chemical analysis, however, and attempts to repeat the reaction gave only oils when the solvent was evaporated. Apparently, further preparative work can be done with this system and may yield some interesting results.

Reactions Involving a Change in Oxidation State.—The hydrolysis of the M[ReX_4O] compounds to form $ReO_2.n(H_2O)$ and ReO_4^- may be compared to the characteristic disproportionation of other rhenium(V) halides and oxyhalides in water recognized several years ago.[29] The tendency for the $[ReCl_4O]^-$ species to decompose in air is very great, and particular care was taken to recrystallize the crude product from acetonitrile as soon as it was filtered. As with the corresponding bromo compound, undried tetraphenylarsonium oxotetrachlororhenate(V) was more stable to hydrolysis after recrystallization, presumably because of the formation of the analogous $[(C_6H_5)_4As][ReCl_4O(CH_3CN)]$ complex.

The oxidation of $[(C_6H_5)_4As][ReBr_4O]$ to $[(C_6H_5)_4As]ReO_4$ by a diaryl sulfoxide in acetonitrile was somewhat surprising, especially since we were attempting to prepare sulfoxide complexes analogous to those of the other neutral ligands (*vide supra*). The inability of diaryl sulfoxides to oxidize rhenium(III) bromide to perrhenate under similar conditions[30] reflects the greater stability of the Re_3Br_9 group. Apparently, the sulfoxide is the actual oxidizing agent here, since recrystallization of tetraphenylarsonium oxotetrabromorhenate(V) in air from CH_3CN yields (after drying) 100% of the starting material. No other product could be isolated from the sulfoxide reaction mixture.

Comparison with Other Work.—It has recently been reported[31] that by treating $[Re(en)_2O_2]^+$ with excess

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[24] See, for example, F. A. Cotton, B. F. G. Johnson, and R. M. Wing, *Inorg. Chem.*, **4**, 502 (1965), and references contained therein.

[25] P. Venkatesarlu, *J. Chem. Phys.*, **19**, 293 (1951).

[26] B. J. Hathaway and D. G. Holah, *J. Chem. Soc.*, 2400 (1964).

[27] B. J. Hathaway and D. G. Holah, *ibid.*, 2408 (1964).

[28] B. J. Hathaway and D. G. Holah, *ibid.*, 537 (1965).

[29] N. V. Sidgwick, "The Chemical Elements and Their Compounds," Clarendon Press, Oxford, 1950, p. 1305.

[30] F. A. Cotton, S. J. Lippard, and J. T. Mague, *Inorg. Chem.*, **4**, 508 (1965).

[31] J. H. Beard, J. Casey, and R. K. Murmann, *ibid.*, **4**, 797 (1965).

concentrated HCl and adding Cs^+ or $[(C_6H_5)_4As]^+$, the compounds $Cs[ReCl_4(OH)_2]$ and $[(C_6H_5)_4As][ReCl_4(OH)_2]$ can be isolated. The tetraphenylarsonium salt was shown to be essentially diamagnetic and the infrared spectrum of the yellow-orange cesium salt showed a strong band at 960 cm.$^{-1}$. This band was assigned to the Re–O–H group and, in addition, the authors noted the presence of "OH stretching bands at 3500 and 1600 cm.$^{-1}$." Finally, the electronic spectra of these two "$M[ReCl_4(OH)_2]$" compounds were reported as having absorption maxima at 820 mμ (ε 23.8), 480 mμ (ε 27.3), and 408 mμ (ε 33.2).

In view of the results reported in this paper, the formulas and the interpretation of the infrared spectra suggested by Beard, *et al.*,[31] seem to us to be incorrect. First, with regard to the assignment of the infrared spectra of the solid compounds prepared by these authors, we wish to point out that there is no "OH stretching band at 1600 cm.$^{-1}$," while a band at about this frequency is provided by the bending mode of H_2O. In addition, their assignment of the 960 cm.$^{-1}$ band in the cesium salt to an Re–O–H deformation mode, made by analogy to Griffith's work[32] on hydroxy complexes of Os(V) which absorb in the 1050–1090 cm.$^{-1}$ region, is not the only possibility. For, as noted by the authors themselves, the tendency for Re=O bonds to give rise to strong absorptions in the 960 cm.$^{-1}$ region has been well documented.[8] It therefore appears to us that the anionic complex ion in the crystalline compounds is, on the basis of the infrared data alone, probably *trans*-$[ReCl_4O(H_2O)]$. Finally, we wish to point out that the electronic spectra *in concentrated acid solution* of these "$[ReCl_4(OH)_2]$" ions are quite similar to the spectra of the $[ReX_4O]^-$ ions in nonaqueous solvents reported herein. While this is by no means conclusive evidence, we believe that it is very probable that the ion obtained by addition of excess concentrated HCl to $[Re(en)_2O_2]^+$ is $[ReCl_4O(H_2O)]^-$, and not $[ReCl_4(OH)_2]^-$ as reported.

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[32] W. P. Griffith, *J. Chem. Soc.*, 245 (1964).

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Raman Study of Complex Cyanides of Copper(I)[1]

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A Raman study of cyanide complexes of copper(I) in aqueous solution has been carried out. No evidence was found for the formation of mixed complexes of copper(I) cyanides with either halide ions or various organic molecules as potential ligands. The reaction of either cuprous cyanide or the complex cyanides with hydrogen halides leads to the formation of the anion $Cu(CN)_3^{2-}$ and not the mixed complexes. The results are discussed in terms of the stereochemistry of the ions in solution. There is evidence for the importance of π bonding from the abnormal intensity of the C–N vibration frequency.

The interest in ligand–ligand interactions arising from the *trans* effect[2] has led to a number of investigations of bonding in square-planar mixed complexes by vibrational spectroscopy.[3–5] Vibrational frequencies may be particularly informative when polyatomic ligands are studied, as there exists the possibility that ligand–ligand interactions may be observed by changes in the frequencies of the ligands as well as in the metal–ligand frequencies. A study of such interactions in mixed cyanide–halide complexes of trivalent gold has shown that the effect of changing the halide group in these square-planar complexes is observable by a change in the frequency and the intensity of the carbon–nitrogen stretching vibration. Changing the halide atom was found to influence both the metal–carbon σ bond and the metal–carbon π bond from force constant and intensity data.[5] As part of an investigation of ligand–ligand interactions in mixed complexes of different stereochemistries, the formation of mixed cyanide–halide complexes of copper(I) has been investigated to ascertain whether a similar effect was observable in a tetrahedral complex, and the results are presented here.

Copper(I), along with other transition metals, forms complexes with varying numbers of cyanide groups. A number of early studies[6] differ as to the formulation of the species present in solution, but more recent work has clearly demonstrated the value of spectroscopic methods. Both Raman[7] and infrared[8] investigations demonstrated the presence of the ions $Cu(CN)_4^{3-}$ and

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[5] L. H. Jones, *ibid.*, **3**, 1581 (1964); S. M. Smith, L. M. Jones, I. K. Kressin, and R. A. Penneman, *ibid.*, **4**, 369 (1965).

[6] C. Calmar and M. Costa, *Compt. rend.*, **243**, 56 (1958); T. F. Young and A. C. Jones, *Ann. Rev. Phys. Chem.*, **3**, 275 (1952).

[7] G. W. Chantry and R. A. Plane, *J. Chem. Phys.*, **33**, 736 (1960).

[8] R. A. Penneman and L. H. Jones, *ibid.*, **24**, 293 (1956).