New Rhenium(v) Oxyhalide Complexes

By F. A. COTTON and S. J. LIPPARD

(*Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts, 02139, U.S.A.*)

WE report the systematic preparation and characterization of compounds containing the ions $[ReCl_4O]^-$, $[ReBr_4O]^-$, and $[ReI_4O]^-$. The new work requires that the previously reported[1] $[ReBr_4(H_2O)_2]^-$ and $[ReBr_4]^-$ compounds be reformulated as $[ReBr_4O]^-$ derivatives. The preparative method consists in reduction of ReO_4^- by zinc in a mixture of methanol and concentrated sulphuric acid.

The correct identities and structures of the compounds $M[ReX_4O]$ and $M[ReX_4OL]$, in which M may be one of many large cations (R_4N, R_4As, pyridinium, etc.) and L a solvent molecule (H_2O or CH_3CN), have been demonstrated by various physical measurements. Direct proof of the presence of oxygen has been obtained by neutron-activation analysis. Three-dimensional X-ray-diffraction studies of $[(C_2H_5)_4N][ReBr_4O(H_2O)]$ and $[(C_6H_5)_4As][ReBr_4O(CH_3CN)]$ have been carried out. The virtual symmetry of the anions in these compounds is C_{4v} (see Figure) with a rhenium to (oxo) oxygen distance of 17.2 ± 0.02 Å. This rather short Re–O bond length, compared with the value (~ 1.80 Å) found[2] in other rhenium(v) oxo-complexes, suggests the existence of extensive π-bonding from oxygen to rhenium.

In accord with this is the fact that the metal–oxygen stretching frequencies observed in the infrared spectra of both the $M[ReX_4O]$ and $M[ReX_4OL]$ compounds fall in the 1000 ± 10 cm.$^{-1}$ range (*cf.* ref. 3 for a report of other

[1] F. A. Cotton, N. P. Curtis, C. B. Harris, B. F. G. Johnson, S. J. Lippard, J. T. Mague, W. R. Robinson, and J. S. Wood, *Science*, 1964, **145**, 1305.

[2] For a discussion, see: H. W. W. Ehrlich and P. G. Owston, *J. Chem. Soc.*, 1963, 4368.

[3] J. Chatt and G. A. Rowe, *J. Chem. Soc.*, 1962, 4019.

rhenium(v) oxo-complexes in which the Re–O stretching frequencies all occur at lower energies). Only in Cs[ReBr$_4$O] does the Re–O band occur at 955 cm.$^{-1}$, and we suggest partial interionic bonding between the Cs$^+$ ion and the oxygen atom of the [ReBr$_4$O]$^-$ anion to account for this shift to a lower frequency.

The bond between the rhenium atom and solvent molecule L (see Figure) in both compounds whose crystal structures were investigated is relatively weak, as indicated by the Re–L bond length of
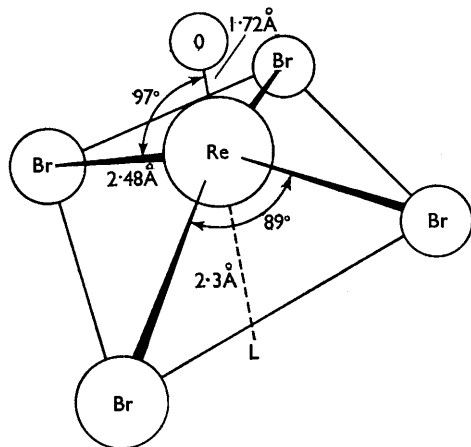
Sketch of the [ReBr$_4$OL]$^-$ *ion,* L = H$_2$O *or* CH$_3$CN.
The dimensions are averages of the crystallographically observed ones for the two compounds investigated.

2·3 Å. This distance is considerably longer than the value of about 2·0 Å reported for other aquo[4] and methyl cyanide[5] transition-metal complexes. Presumably, the basic square-pyramidal (ReBr$_4$O) structural unit also exists in the unsolvated M[ReX$_4$O] compounds. In support of this assumption, the diamagnetic susceptibility of [(C$_6$H$_5$)$_4$As][ReBr$_4$O] was found to be -350×10^{-6} CG mole^{-1}; the value calculated from Pascal's constants is approximately -385×10^{-6} CG mole^{-1}. This diamagnetism is to be expected from simple crystal-field theory for a d^2 metal ion in a square pyramidal environment, since both metal electrons would occupy a low-lying d_{xy} orbital.[6]

The results of conductivity measurements of the M[ReX$_4$O] compounds in nitromethane and acetonitrile are consistent with values found for other 1 : 1 electrolytes. X-Ray powder patterns, using Cu–K_α radiation, of [(C$_6$H$_5$)$_4$As][ReBr$_4$O] and [(C$_6$H$_5$)$_4$As][ReCl$_4$O] were recorded and indicate that these two compounds are isomorphous.

The chemistry of the M[ReX$_4$O] compounds relates them to other rhenium(v) oxyhalides previously reported. Thus, ReCl$_3$[(C$_6$H$_5$)$_3$P]$_2$O,[3,7] ReBr$_3$[(C$_6$H$_5$)$_3$P]$_2$O,[3] ReBr$_3$[(C$_6$H$_5$)$_3$As]$_2$O,[3] and [Re(C$_5$H$_5$N)$_4$O$_2$]Cl,2H$_2$O,[8] have all been prepared in good yields simply by reacting solutions of M[ReX$_4$O] with excess of ligand. A full report of the chemical, physical, and structural properties of these new rhenium(v) oxyhalide complexes is in preparation.

(Received, May 3rd, 1965.)

[4] A. F. Wells, "Structural Inorganic Chemistry," 3rd ed., Clarendon Press, Oxford, 1962, pp. 588–93.
[5] R. D. Willett and R. E. Rundle, *J. Chem. Phys.*, 1964, **3**, 838.
[6] B. N. Figgis and J. Lewis, Chapter 6 in J. Lewis and R. G. Wilkins, eds., "Modern Co-ordination Chemistry," Interscience, New York, 1960, p. 422.
[7] C. J. L. Lock and G. Wilkinson, *Chem. and Ind.*, 1962, 40.
[8] N. P. Johnson, C. J. L. Lock, and G. Wilkinson, *J. Chem. Soc.*, 1964, 1054.