Oxopentachlororhenate(VI) Complexes

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MANY recent publications[1] have dealt with the problem of interpreting the visible and ultraviolet spectra of distorted octahedral d^1 oxyhalide complexes, MOX_5^{n-}, ($n = 3$ for V; $n = 2$ for Cr, Mo, W). Where $n = 1$ only oxopentafluororhenates(VI) have been briefly reported;[2] consequently we have attempted to characterise oxopentachlororhenate(VI) complexes.

The compounds $B^+ReOCl_5^-$ were obtained by the reaction of chlorides with large organic cations and rhenium oxytetrachloride in chloroform or dichloromethane, in the absence of air or moisture.

Solid, red-brown, crystalline complexes, of satisfactory analyses, slightly soluble in dry chloroform, dichloromethane, and more soluble in nitromethane, were isolated where B = Ph_4As, Et_4N and acridinium. The valence state of the rhenium in the complexes was verified by oxidative titrations with cerium(IV) sulphate and by the ratio of 2 Re^{VII} : 1 Re^{IV} produced on disproportionation in alkali. The complexes decomposed on standing in moist air to give other rhenium(IV) complexes which will be reported later. A 10^{-3}M-solution of the tetraphenylarsonium salt in nitromethane had a molar conductivity of 78 ohm^{-1} cm.^{2} confirming its formulation as a 1 : 1 electrolyte. Infrared measurements on each salt showed strong absorption in the 950—970 cm.$^{-1}$ range, characteristic of a terminal Re–O stretching frequency, with oxygen to rhenium π-bonding, and confirmed the absence of OH or Re–O–Re species.

The absorption-band maxima of the reflectance spectra of all three salts appeared at identical wavelengths which were similar to those of a solution of the tetraphenylarsonium salt in dichloromethane, although in solution the first band was resolved into three peaks. [Solids: 11,800 (br); 18,200; ~23,000 (br); Solution: 11,170 (15); 11,630 (15); 12,050 (15); 18,020 (160); ~23,000 (~1200). Values in cm.$^{-1}$; br = broad; molar extinction coefficients in parentheses]. The resolution of the first ligand-field band into three components at room temperature could be caused by the complete removal of *d*-orbital degeneracy operative through spin–orbit coupling as suggested by Selbin[3] to explain the liquid-nitrogen temperature glass spectrum of the VOF_5^{3-} ion, of the same C_{4v} symmetry. Alternatively the resolution could be of vibronic origin as suggested[4] for the $MoOCl_5^{2-}$ ion.

The magnetic moments of the salts at room temperature are in the range 1·5—1·6B.M. Although rhenium(VI) has a spin–orbit coupling constant of about 4000 cm.$^{-1}$, the axial asymmetry caused by the Re–O bond in these complexes at least reduces the degeneracy of the ligand-field levels and a moment only slightly less than the spin-only value results.

It is of interest to note here that rhenium oxytetrachloride reacts with alkali-metal chlorides in aqueous hydrochloric acid[5] to give $ReOCl_5^{2-}$ complexes of unknown structure, whereas no immediate reaction was observed[6] with rhenium oxytetrachloride and tetra-alkylammonium chlorides in thionyl chloride, but reduction occurred over several days to give hexachlororhenates(IV).

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