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The Trioxotrichlororhenate(VII) Ion[1]

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The majority of oxygen-containing rhenium(VII) compounds can be considered to be perturbations of the perrhenate ion, ReO_4^-, *e.g.*, ReO_3N^{2-}, ReO_3S^-, ReO_3X (X = F, Cl, Br), and Re_2O_7. Seven-coordinate ReF_7,[2,3] six-coordinate $ReOF_5$,[4] and five-coordinate ReO_2F_3[4] have been described, but no compound of stoichiometry $ReO_3X_3^{2-}$ has been described, although Peacock,[5] when reporting the $ReO_2F_4^-$ ion, considered that $ReO_3F_3^{2-}$ should be capable of existence; both of the isoelectronic ions $WO_3F_3^{3-}$ and $OsO_3F_3^-$ are known.[6,7]

The dissolution of perrhenic acid in concentrated hydrochloric acid saturated with hydrogen chloride produces a yellow solution from which cesium chloride precipitates a pale yellow solid of stoichiometry $Cs_2[ReO_3Cl_3]$. The formation of the ion can be written

$$ReO_4^- + 2H^+ + 3Cl^- \rightleftharpoons ReO_3Cl_3^{2-} + H_2O \qquad (1)$$

The salt dissolves in water or base to give a clear solution without formation of black ReO_2 suggesting that a rhenium(VII) species is present. The salt turns white on exposure to the atmosphere.

The octahedral ion may have two possible geometrical isomers: *cis* (C_{3v}) and *trans* (C_{2v}). Simplified group theory (omitting site symmetry considerations) predicts that the *cis* ion should have 15 normal vibrations of species $4\ A_1 + A_2 + 5\ E$, the 5 E vibrations being doubly degenerate, and that there should be two infrared- and Raman-active metal–oxygen and metal–chlorine stretching modes. Similarly, the *trans* ion should have 15 normal vibrations of species $6\ A_1 + A_2 + 4\ B_1 + 4\ B_2$ with three infrared- and Raman-active metal–oxygen and metal–chlorine stretches.

The infrared spectrum consists of an extremely broad absorption centered around 890 cm^{-1} with a band width of about 100 cm^{-1}. In the 400–250-cm^{-1} region bands were found at 314 (sh), 320 (vs), 334 (m), 360 (sh), and 370 (s) cm^{-1}, but it was not possible to distinguish between Re–Cl stretching bands and O–Re–O deformation modes.

The Raman spectrum of the solid has two sharp bands at 925 (vs) and 895 (s) cm^{-1} in the metal–oxygen stretching region and a series of bands below 400 cm^{-1} at 387 (s), 366 (vs), 297 (s), 220 (vs), 187 (vs), and 154 (s) cm^{-1}. The two sharp bands in the metal–oxygen stretching region is good evidence for a *cis* (C_{3v}) configuration of the $ReO_3Cl_3^{2-}$ ion.

The preparation of the analogous fluoro anion was attempted but without success even when liquid hydrogen fluoride was used as the solvent. (The Raman spectrum of a solution of sodium perrhenate in 15% hydrogen fluoride was that of the unperturbed ReO_4^- ion.) Addition of a solution of cesium fluoride to a solution of perrhenic acid both in concentrated hydrofluoric acid with some additional liquid hydrogen fluoride present did not give an immediate precipitate. If the mixture was kept cool, large white crystals separated out after about 1 week. Analytical, infrared, and X-ray data confirmed that these crystals were cesium perrhenate. Using other cations, $(C_6H_5)_3As^+$ gave an immediate precipitate of the perrhenate, but R_4N^+ and Rb^+ gave no precipitate at all. The two most likely explanations as to why the fluoride cannot be obtained are: (i) the ion is too susceptible to hydrolysis so that an equilibrium such as that of eq 1 is over to the left; (ii) the salts are too soluble relative to the corresponding perrhenate to be obtained in the solid state.

No attempt was made to obtain the bromide or iodide since perrhenic acid partially oxidizes these hydrogen halides and is itself reduced.

Experimental Section

Infrared spectra of Nujol mulls were recorded using Perkin-Elmer 457 and Grubb-Parsons "Spectromaster" instruments; Raman spectra were obtained using a Cary Model 81 spectrometer with an He–Ne laser source.

Dicesium Trioxotrichlororhenate(VII).—Rhenium metal (Johnson, Matthey Ltd. 99.5%) (2 g) was dissolved in 100 vol of aqueous hydrogen peroxide and the solution of perrhenic acid was evaporated to dryness on a hot plate. The residue was dissolved in 10 *M* hydrochloric acid (10 ml) and the solution was saturated with hydrogen chloride. To the resulting yellow solution was added a solution of cesium chloride (4 g) in hydrogen chloride saturated aqueous HCl (10 ml). The mixture was allowed to stand overnight. The yellow crystalline product was collected under an atmosphere of hydrogen chloride, washed with 10 *M* HCl, and dried *in vacuo* over P_4O_{10} (4.15 g, 58%). *Anal.* Calcd for $Cs_2[ReO_3Cl_3]$: Cl, 17.5; Cs, 43.8; O, 7.9; Re, 30.7. Found: Cl, 17.1; Cs, 43.8; O, 7.8; Re, 30.6.

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Fluoro Complexes of Manganese(III) in Acid Perchlorate Solution[1]

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Previous workers[2,3] have noted a doublet in the visible spectrum of Mn(III) in excess fluoride, which has

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