\( \mu \)-Oxodecafluororhenates(IV)

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Received 10 January 1983; revised and accepted 22 March 1984

New \( \mu \)-oxodecafluororhenates(IV), \( \text{M}_4\text{Re}_2\text{OF}_{10} \) (where \( \text{M} = \text{K} \) and Cs) have been prepared and characterised by their chemical analyses, IR and UV data and magnetic and conductivity measurements.

Only one complex fluoro anion of tetravalent rhenium, viz. \( \text{ReF}_5^- \) is known in the form of its salts\(^1\) – 3. A compound of composition, \( \text{K}_2\text{ReF}_6(\text{OH}) \), was suspected\(^2\) to exist in the reaction mixture of potassium hexabromorhenenate(IV) and hydrofluoric acid, but its isolation was unsuccessful. In the course of our studies on fluoronitrosyl complexes of rhenium\(^4\) we have prepared a new oxofluoro complex of rhenium(IV), \( \text{M}_4\text{Re}_2\text{OF}_{10} \), (\( \text{M} = \text{K}, \text{Cs} \)) analogous to the well known\(^5\) \( \text{K}_4\text{Re}_2\text{OCl}_{10} \). The complexes have been characterised by chemical analyses and the study of their physico-chemical properties.

Potassium perrhenate (99.8\% pure, Johnson Matthey) and all other reagents were of appropriate purity; \( \text{KH}_5 \) was of GREM quality. Polythene vessels (for reactions up to 100 \(^\circ\)C) and platinum wares (for higher temperatures) were used. IR spectra in KBr matrix were recorded on a Beckman IR 20 instruments, electronic spectra on a Hilger UVISPEK spectrophotometer and ESR spectra on a Varian E-4 X-band spectrometer. Magnetic susceptibilities were measured on a Gouy balance with a magnetic field strength of 9.1 x 10\(^{-4}\) Oe. Conductances were measured on a Philips’ RCL bridge.

Potassium \( \mu \)-oxodecafluororhenate(IV)

Freshly precipitated rhenium(IV) oxide\(^6\) (300 mg) was taken in a platinum crucible and fused with potassium bifluoride (3 g) and the mixture kept in the molten state for 1 hr on a low flame. The cooled fusate was washed with water (10 ml), the green residue boiled with water (50 ml) and filtered. The filtrate was kept overnight in an ice-chest when a solid product separated out as fine rose-red crystals. These were filtered off, washed with minimum volume of ice-cold water and dried in vacuo over solid \( \text{P}_2\text{O}_5 \) to yield 130 mg of the pure substance.

Cesium \( \mu \)-oxodecafluororhenate(IV)

Cesium carbonate (100 mg) was dissolved in minimum volume of aq HF and the solution added dropwise to an aqueous solution of the above potassium salt (75 mg), till the precipitation was complete. The red crystals were filtered off, washed with water and dried in vacuo (yield 100 mg).

For analysis, a mixture of the compound and anhydrous \( \text{Na}_2\text{CO}_3 \) was taken in a platinum boat and heated under \( \text{H}_2 \) to 500 \(^\circ\)C for 1 hr. After the reaction was over, the residue was extracted with oxygen-free water and fluoride determined in the filtrate by titration with thorium nitrate\(^7\). The residue was dissolved in 2 \( N \) sulphuric acid containing a few drops of hydrogen peroxide and rhenium finally determined by electrolytic deposition on platinum electrode\(^8\).

(i) K-salt (Found: Re, 50.5; F, 25.1; K, 20.7; \( \text{K}_4\text{Re}_2\text{OF}_{10} \) requires Re, 50.7; F, 25.9; K, 21.3\%);
(ii) Cs-salt (Found: Re, 32.9; F, 17.7; Cs, 48.5; \( \text{Cs}_4\text{Re}_2\text{OF}_{10} \) requires Re, 33.6; F, 17.1; Cs, 47.9\%). For the determination of oxidation number of rhenium a known weight of \( \text{K}_4\text{Re}_2\text{OF}_{10} \) was oxidised with a known volume of standard \( \text{K}_2\text{Cr}_2\text{O}_7 \). From the amount of oxidant consumed the oxidation number of the metal was calculated\(^9\) to be 3.87.

\( \text{K}_4\text{Re}_2\text{OF}_{10} \) is a rose-red microcrystalline solid, sparingly soluble in water producing a very stable red solution. On repeated evaporation with 40\% hydrofluoric acid, it is slowly converted into colourless \( \text{K}_2\text{ReF}_6 \) (Found: Re, 50.0; F, 29.8; K, 19.9. Calc for \( \text{K}_2\text{ReF}_6 \): Re, 49.2; F, 30.1; K, 20.7\%); \( \mu_{\text{eff}} \), 3.4 B.M. In contrast to K-salt, the Cs-salt is only slightly soluble in water.

The ratio of the alkali metal-rhenium-fluorine is 2: 1: 5 and the anion could easily and quantitatively be converted into \( \text{ReF}_5^- \). Two alternative formulations, viz. \( \text{Re}^{IV}\text{F}_5(\text{OH})^- \) or \( \text{Re}^{V}\text{OF}_4^- \) are possible for the anion with marginal difference in elemental analyses data. Absence of bands at 3600 and 1600 cm\(^{-1}\) in the IR spectrum indicates the absence of OH group and water. The monomeric formula \( \text{ReF}_5(\text{OH})^- \) is, therefore, ruled out. The molar conductance value for the potassium salt in aqueous medium is around 500 ohm\(^{-1}\) cm\(^2\) which is in the range of values for 4:1 electrolytes. This supports the formulation as \( \text{K}_2\text{Re}_2\text{OF}_{10} \). The solubility of the compound is, however, too low to apply Feltham’s test\(^10\).

The IR spectrum of \( \text{K}_4\text{Re}_2\text{OF}_{10} \) exhibits four bands at 900, 735, 525 and 475 cm\(^{-1}\) (Fig. 1). The IR spectra of some of the intermediate mixtures obtained by evaporating \( \text{K}_4\text{Re}_2\text{OF}_{10} \) solutions in aq HF to dryness have also been recorded. The IR spectrum of the ultimate white product, i.e. \( \text{K}_4\text{ReF}_6 \) exhibits only two bands at 735 and 480 cm\(^{-1}\). It is observed that as...
K₄Re₂OF₁₀ gets converted into K₂ReF₆ in increasing amounts. The bands at 900 and 525 cm⁻¹ gradually diminish in intensity and finally vanish (Fig. 1). The bands at 735 and 475 cm⁻¹, on the other hand, get gradually intensified with slight shift in the position of the latter band. The assignment of the bands in K₄Re₂OF₁₀ gets converted into K₂ReF₆ in increasing amounts. The bands at 900 and 525 cm⁻¹ gradually diminish in intensity and finally vanish (Fig. 1). The bands at 735 and 475 cm⁻¹, on the other hand, get gradually intensified with slight shift in the position of the latter band. The assignment of the bands in K₄Re₂OF₁₀ has been done by considering that only two IR active F₁₈ modes should be present in octahedral ReF₆²⁻ ion, one for ν(Re-F) and another for δ(F-Re-F). The band at 735 cm⁻¹ is assigned to ν(Re-F) and that at 475 cm⁻¹ to δ(F-Re-F). In fluoronitrosyl complexes these bands occur at 740 and 480 cm⁻¹ respectively. Contrary to earlier claim, no band appears at 541 cm⁻¹ in pure K₂ReF₆.

The assignment of IR bands of K₄Re₂OF₁₀ is based on a linear arrangement of Re-O-Re in the complex (cf. K₄Ru₂OCl₁₀)¹³. The νₕ(Re-O-Re) appears at 900 cm⁻¹ in K₂Re₂OF₁₀ and the corresponding symmetric vibration is forbidden.¹⁴ The local symmetry of rhenium is C₄ᵥ, for which two ν(Re-F) of A₁ and E modes and two δ(F-Re-F) also of A₁ and E modes are expected. Based on assignment of bands in K₂ReF₆, the band at 735 cm⁻¹ has been assigned to ν(Re-F) and that at 480 cm⁻¹ to δ(F-Re-F). However, the band at 525 cm⁻¹ cannot be assigned with certainty.

The proximity of the νₕ(Re-O-Re) band in K₄Re₂OF₁₀ to that of ν(Re = O) in ReO₄ ion¹⁵ might be due to the effect of the coordinated fluoride ions. The νₕ(Re-O-Re) occurs at 850 cm⁻¹ in the chloro complex, K₄Re₂OCl₁₀, where back donation of electrons from chloride to the metal is possible resulting in the weakening of Re-O-Re bond. In the fluoro complex, however, the absence of any π-bond between rhenium and fluoride makes the rhenium atom relatively more positive. This stabilises the Re-O-Re bond causing an increase in the frequency value. This frequency (900 cm⁻¹) should not, therefore, be taken as ν(Re = O).

The magnetic moment value (1.22 B.M. at 303 K) of K₄Re₂OF₁₀ is unusually low for a simple tetravalent rhenium ion with d⁴-electronic configuration [cf. oxygen-bridged binuclear complexes of Cr(III), Ru(IV) and Re(IV)]. The MO description proposed by Dunitz and Orgel¹⁹ and other workers²⁰ to explain the anomalous magnetic properties of binuclear complexes may well be applied in the present case. No ESR signal could be obtained for the compound even at liquid nitrogen temperature.

The absorption spectrum of K₄Re₂OF₁₀ in water in matched perspex cells (against water) shows two bands in the visible region at 11.6(£37) and 19.8(£98) kK. The former may be due to a d-d transition but that at 19.8 kK obviously originates from charge transfer involving Re and O giving rise to the rose-red colour of the complex ion.

References