Fluorinated Alkoxides of Chromium(v) and Vanadium(IV)

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Summary The reduction of chromate ion in the presence of perfluoropinacol (PFP) leads to the formation of stable, chelated, alkoxides containing chromium(v) in the ion $[CrO(PFP)_2]^-$, the cations being K^+, Cs^+ or Et_4N^+; the isoelectronic vanadium(IV) complex, $[VO(PFP)_2]_2{}^{2-}$, may be prepared by reaction of PFP with a vanadyl salt.

ALTHOUGH chromium(v) is an uncommon oxidation state for this element, the existence of complexes of the type $[CrOX_4]^-$ and $[CrOX_5]^{2-}$ (X = F,Cl) is now well-established.[1] While chromium(IV) is known to form stable alkoxides[2] and dialkylamides,[3] no alkoxides of chromium(v) have yet been described.

We now report the preparation of a complex ion of the $[CrOX_4]^-$ type† in which the oxochromium(v) ion, CrO^{3+}, is chelated by two doubly ionized molecules of perfluoropinacol, $(CF_3)_2C(OH)C(OH)(CF_3)_2$ (PFP), which we have previously shown to be capable of acting as a bidentate, dinegative, ligand.[4] The complex was prepared by dissolving potassium or caesium chromate and PFP (1:2 molar ratio) in an ethanol–water mixture (30% ethanol v/v), acidified with sulphuric acid, and maintaining at the boiling-point for about 10 minutes. On cooling the resulting deep blue solution, the complex separated as an oil (K^+ salt) or solid (Cs^+ salt) which was purified by removal of solvent and PFP *in vacuo*, followed by recrystallisation from methanol to give $K[CrO(PFP)_2]$ and $Cs[CrO(PFP)_2]$. Reaction of either salt with Et_4NCl in methanol–water precipitated the less soluble $[Et_4N][CrO(PFP)_2]$.

The K^+ and Cs^+ salts were purple solids, with room-temperature magnetic moments of 1·79 and 1·71 B.M. respectively, consistent with the d^1 configuration of Cr^V. The Et_4N^+ salt was blue, with a slightly higher magnetic moment (2·33 B.M.), but the assignment as Cr^V was confirmed by decomposition in concentrated sulphuric acid, when disproportionation occurred and 67% of the total chromium appeared as Cr^{VI}. All three salts were insoluble in water, but dissolved in methanol to give blue solutions. The electronic spectra (Figure) showed in each case a single absorption at 17,400 cm^{-1} (ϵ 171) and a much more intense band, presumably associated with charge transfer, at 32,300 cm^{-1} (ϵ 2800).

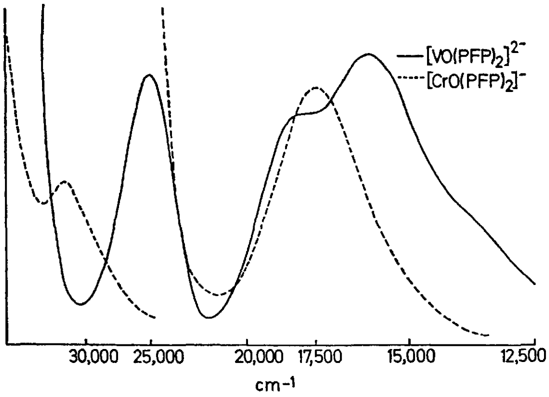

FIGURE. *The electronic spectra (methanol solution) of* $Cs[CrO(PFP)_2]$ *and* $K_2[VO(PFP)_2]$.

The isoelectronic vanadium^{IV} complex, $K_2[VO(PFP)_2]$, was readily prepared by the addition of PFP to aqueous vanadyl sulphate, followed by neutralisation with potassium hydroxide, the procedure we have previously used for ions of first-row transition elements.[4] The compound was blue, soluble in water and methanol, and had a room-temperature magnetic moment of 1·72 B.M. Its electronic spectrum showed three absorptions, at 15,900 (ϵ 35), 18,000 (30), and 25,100 (32) cm^{-1}. This spectrum is typical of vanadyl complexes with chelating ligands, and may be compared with those of $VO(acac)_2$[5] or $[VO(C_2O_4)_2^{2-}]$.[6] However, the reasons for differences between this spectrum and that of

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† Satisfactory analytical data have been obtained for all new compounds.

the isoelectronic chromium(V) complex are not obvious, and the effects of solvent changes are being studied in an attempt to make definite assignments.

In both complexes, an absorption in the i.r. spectrum would be expected in the 900—1000 cm^{-1} region, associated with the metal–oxygen double bond, but the presence in this region of several bands associated with the perfluoropinacol ligand[7] precluded any definite assignment being made.

The remarkable stability of the chromium(V) complex, both to reduction and hydrolysis, is shown by its formation in hot aqueous acid solution in the presence of a reducing agent (ethanol) which, in the absence of PFP, reduces Cr^{VI} into Cr^{III} under these conditions. It is also unusual in forming in strongly acid solution, since VO^{2+} and all other ions we have studied will only interact with PFP when ionization of the weakly acidic ligand has been encouraged by making the solution neutral or basic. Apart from being slightly photosensitive, these salts appear to be the most stable chromium(V) compounds yet reported, and the potential use of PFP for stabilising other metals in high oxidation states is now being investigated.

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