View Article Online / Journal Homepage / Table of Contents for this issue

Some Quinquevalent Fluorotechnetates

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The preparation of the alkali-metal hexafluorotechnetates(V) from technetium hexafluoride is described. The unit cell dimensions, reflectance spectra, and magnetic susceptibilities of the compounds have been measured.

IN a preliminary Communication¹ we reported the formation of sodium and potassium hexafluorotechnetates(v). The properties of these and of other salts of the TcF_6^- ion have now been determined more fully.

EXPERIMENTAL

Technetium Hexafluoride.—Technetium metal, prepared by the reduction of ammonium pertechnetate with hydrogen, was treated with fluorine (4 g./hr.) diluted with an approximately equal volume of nitrogen in a nickel reaction vessel. To minimise contamination the nickel vessel was built inside a Pyrex glass tube whose inner surface was protected from fluorine attack by a slow stream of nitrogen. The reaction commenced at 350° , giving volatile technetium hexafluoride (50° /y yield), which was carried in the nitrogen stream to a cold trap at 75° , and technetium pentafluoride and technetium oxide tetrafluoride, which collected just beyond the reaction vessel.¹ The technetium hexafluoride was purified and was handled under a vacuum by methods similar to those previously described.

¹ A. J. Edwards, D. Hugill, and R. D. Peacock, Nature, 1963, 200, 672.

Iodine Pentafluoride .- This was prepared from the elements by standard procedures.

Quinquevalent Fluorotechnetates.-The preparative method was similar to that described for the fluororhenates(v) and fluoromolybdates(v).² Since technetium hexafluoride is reduced to TcIV by potassium iodide in iodine pentafluoride,¹ the alkali chlorides were used as starting materials.

A quantity of dry, powdered alkali chloride was treated with a slight excess of technetium hexafluoride in the presence of iodine pentafluoride as solvent (5-10 ml. for 0.1 g. of alkali-metal chloride). The volatile fluorides were condensed on the chloride at -75° , and the mixture was allowed to warm to room temperature. The resulting red-brown solution was refluxed at atmospheric pressure for a few minutes to complete the reaction, and was allowed to cool slowly to assist crystallisation of the complex. Excess of reagents was pumped off, and the temperature was raised to 120° to ensure complete removal of traces of TcOF₄ formed during the reaction. The hexafluorotechnetates(v), which were yellow crystalline powders, were handled in completely closed systems (Found: Tc, 41.9. Calc. for NaTcF₆; Tc, 42.0%. Found: K, 15.5; Tc, 39.2; F, 45.4. KTcF₆ requires K, 15.5; Tc, 39.3; F, 45.2%. Found: Tc, 31.8. Calc. for RbTcF₆: Tc, 33.2%. Found: Cs, 37.4; Tc, 27.8; F, 33.5. CsTcF₆ requires Cs, 38.4; Tc, 28.6; F, 33.9%). Confirmation of the identity of the compounds was provided by X-ray powder photography. Considerable difficulty was experienced in the analysis of the rubidium salt, and the result suggests the presence of impurities.

Nitrosonium Hexafluorotechnetate(v).-When technetium hexafluoride was treated with nitric oxide at -45° , an immediate reaction occurred, and a yellow powder was formed. Although analysis showed a composition approaching NOTcF₆ (Found: Tc, 39.7; F, 46.2. Calc. for NOTcF₆: Tc, 40.7; F, 46.9%), X-ray powder photographs showed the presence of more than one phase, and the high magnetic moment ($\mu_{eff}=3{\cdot}32$ B.M. at 25°) indicated the probable presence of TcIV.

Hydrolysis.—During hydrolysis of the fluorotechnetates(v) it was noticed that after the initial precipitate of ${\rm TcO}_2$ had been oxidised to pertechnetate ion by dilute hydrogen peroxide, approximately one half of the technetium in the now colourless solution was not precipitated by nitron acetate reagent. Similarly about half of the fluorine remained "fixed " in solution. These observations suggest the formation of the very stable TcF_{6}^{2-} ion. A sample of KTcF₆ was hydrolysed and the available technetium was estimated in (a) the initial precipitate of TcO_2 , (b) the solution after the TcO_2 had been filtered off, and (c) in the filtrate from (b) after evaporation and alkali fusion. From the results the hydrolysis was found to conform to the schemes:

- (a) $6 \text{TcF}_6^- \longrightarrow 2.87 \text{TcF}_6^{2-} + 0.9 \text{TcO}_2 + 2.21 \text{TcO}_4^ +18F^{-}$
- (b) $3Tc^{V} \rightarrow 1.9Tc^{IV} + 1.1Tc^{VII}$

It is probable that the nearness to a stoicheiometric relationship in scheme (a) is fortuitous.

² G. B. Hargreaves and R. D. Peacock, J. Chem. Soc., 1957, 4212; 1958, 4390; R. D. Peacock, *ibid.*, p. 467.

³ B. Figgis and R. S. Nyholm, J. Chem. Soc., 1959, 331.

Analysis.-The alkali hexafluorotechnetate (0.1 g.) was partially broken down by hydrolysis in dilute alkali. Precipitated TcIV oxide was oxidised to TcVII by dilute hydrogen peroxide, added drop by drop until all the dioxide had dissolved. To destroy the stable TcF_{6}^{2-} ion, the solution was evaporated to dryness, and the residue was fused with excess of sodium hydroxide. The mixture was kept molten for $\frac{1}{2}$ hr. to complete the reaction. Technetium was determined as nitron pertechnetate and fluorine was estimated volumetrically by the Volhard method after precipitation as lead chlorofluoride. Potassium and cæsium were precipitated from the partially hydrolysed solutions and weighed as the tetraphenylboron salts.

Recovery .-- Technetium was obtained from nitron pertechnetate residues by extraction with ammonia-ethyl acetate. Nitron passed into the ethyl acetate layer and the technetium passed into the aqueous layer, from which it was subsequently recovered as ammonium pertechnetate.

Magnetic Measurements.-These were made on a Gouy balance as described previously ³ over the range 290-90° K.

Spectra.--Measurements were made on a Unicam S.P.500 spectrometer fitted with a reflectance attachment.

X-Ray Photographs.-Powder photographs were taken on a 19 cm. powder camera using filtered Cu- K_{α} radiation.

DISCUSSION

The yellow hexafluorotechnetates(v) are not isolated by the action of alkali iodide on technetium hexafluoride in iodine pentafluoride (*i.e.*, $I_2 + IF_4^{-}$),⁴ which apparently results in further reduction to a Tc^{IV} species. Alkali chlorides dissolve in iodine pentafluorides to give chlorine, alkali hexafluoroiodate(v), and iodine trichloride,⁵ and it appears that the last is a sufficiently strong reducing agent in the presence of the alkali hexafluoroiodate(v) (a "base" in iodine pentafluoride solution), to reduce TcF_6 to TcF_6^- .

TABLE 1

Unit cell sizes of fluorotechnetates(v) (all rhombohedral)

	a ₀ (Å)	α		a_0 (Å)	α
Na K	$5.77 \\ 4.97$	55·8° 97·0	Rb Cs	$5.09 \\ 5.25$	$95 \cdot 5^{\circ}$ $96 \cdot 2$

Hydrolysis of the TcF_6^- anion by water or dilute aqueous alkali is incomplete at 25°, as nearly half of the technetium is retained in a form which is resistant to oxidation and is only slowly attacked by concentrated alkali. We believe this intermediate species to be the TcF_{6}^{2-} ion, which has been found by Schwochau and Herr⁶ and by Busey⁷ to be as resistant as $\operatorname{ReF}_{6}^{2-}$ to hydrolysis.

Unlike Schwochau and Herr, who were able to break down potassium hexafluorotechnetate(IV) with concentrated alkali, we found that a hydroxide fusion was required to obtain quantitative results.

4 G. B. Hargreaves and R. D. Peacock, J. Chem. Soc., 1960, 2373.

- ⁶ R. D. Peacock, unpublished observations.
 ⁶ K. Schwochau and W. Herr, Angew. Chem., 1963, 75, 95.
 ⁷ R. H. Busey, Unclassified Document ORNL 3176 (1961).

The unit cells of the complex fluorides fall into the pattern predicted by Kemmitt et al.,8 and the parameters suggest that Tc^{5+} has an ionic radius close to that of Ru⁵⁺. The powder photograph of the impure nitrosonium hexafluorotechnetate(v) showed the chief phase present to have a primitive cubic unit cell of dimension

TABLE 2

Magnetic susceptibility of TcF₆⁻ salts

NaTcF ₆			KTcF ₆		
Т (°к)	10 ⁶ χ _A	μeff	<u>Т</u> (°к)	10 ⁶ χ _A	μeff
288	2201	$2 \cdot 26$	298	2620	2.51
284	2218	2.25	265	2743	$2 \cdot 42$
254	2340	$2 \cdot 19$	252	2848	$2 \cdot 41$
224	2553	$2 \cdot 15$	224	3083	2.36
198	2742	2.09	192	3474	$2 \cdot 32$
163	3077	2.01	163	3868	$2 \cdot 26$
132	3471	1.92	130	4321	$2 \cdot 13$
107	3949	1.85	99	5083	$2 \cdot 02$
91	4301	1.78	90	5407	1.98
	$\theta = 80^{\circ}.$			$\theta = 90^{\circ}.$	
	RbTcF ₆			CsTcF ₆	
Т (°к)	10 ⁶ XA	μ _{eff}	<i>Т</i> (°к)	10 ⁶ χ _A	μ _{eff}
291	2154	2.25	293	2184	2.27
290	2148	2.24	289	2178	$2 \cdot 25$
270	2227	2.20	269	2253	$2 \cdot 21$
250	2344	2.17	247	2346	$2 \cdot 16$
224	2495	$2 \cdot 12$	224	2485	$2 \cdot 12$
185	2796	2.04	189	2756	$2 \cdot 05$
157	3065	1.97	165	2982	1.99
142	3277	1.94	140	3282	1.99
142	3277	1.94	140	3282	1.93
119	3629	1.87	120	3606	1.87
99	4025	1.80	94	4155	1.78
9 0	4215	1.75	90	4247	1.76
	$\theta \Rightarrow 80^{\circ}$.			$\theta = 80^{\circ}$.	

 $a_0 = 10.09$ Å, which is close to the value of 10.16 Å reported for NOPtF₆.9

The reflectance spectrum of $KTcF_6$ shows clearly recognisable peaks at 13,600, 17,800, and 23,000 cm.⁻¹, and a very strong absorption at 32,000 cm.⁻¹.

⁸ R. D. W. Kemmitt, D. R. Russell, and D. W. A. Sharp, J. Chem. Soc., 1963, 4408. 9 N. Bartlett and N. K. Jha, Chem. in Canada, August 1963,

¹⁰ J. S. Griffith, "Theory of Transition-Metal Ions," Cambridge Univ. Press, 1961, p. 261.

Interpretation of the absorption peaks using the Tanabe-Sugano diagrams given by Griffith 10 and Dunn¹¹ indicates that the band at 32,000 cm.⁻¹ is the candidate of lowest energy for the ${}^{3}T_{1} \longrightarrow {}^{3}T_{2}$ transition $(\Delta \text{ for TcF}_6^{2-} \text{ is } 28,400 \text{ cm}.^{-1}).^{12}$ On this basis the peak at 17,800 cm.⁻¹, which is rather narrow, is likely to be the ${}^{3}T_{1} \longrightarrow {}^{1}A_{1}$ transition, (hence $\Delta = 34,600$ cm.⁻¹; B =520 cm.⁻¹) but the other peaks remain unexplained except by assuming the presence of impurities or of splitting due to symmetry effects or spin-orbit coupling.

The magnetic susceptibility (Table 2) scarcely approximates to the Kotani¹³ scheme, and as with the hexafluororhenates(v), the moment of the potassium salt is high. For an undistorted octahedral TcF_{6} ion the magnetic moment on the Kotani theory is given by the expression $\mu^2_{\text{eff}} = 1.5 + 9kT/\zeta_{4d}$ when ζ_{4d} is the spin-orbit coupling constant. The value of ζ_{4d} derived from the present results is about 600 cm.⁻¹, which is much less than that estimated by Figgis and Lewis¹⁴ for Tc^v (1200 cm.⁻¹). In the absence of complete structural data it is not of much value to speculate on this difference, but the TcF_6^- ion could be sufficiently distorted to make the Kotani assumptions inapplicable, or possibly magnetic exchange processes could be taking place (cf. the suggestion of Figgis and Lewis for the fluororhenates(v) ¹⁴]; the large values of θ would suggest the latter point.

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¹¹ T. M. Dunn, in "Modern Co-ordination Chemistry," ed. J.

Lewis and R. G. Wilkins, Interscience, London, 1960, p. 248. ¹² C. K. Jørgensen and K. Schwochau, Z. Naturforsch., 1965, 20a, 65.

 ¹³ M. Kotani, J. Phys. Soc. Japan, 1959, 4, 293.
 ¹⁴ B. N. Figgis and J. Lewis, in "Progress in Inorganic Chemistry," ed. F. A. Cotton, vol. VI, Interscience, London, 1964, p. 142.