

808. *Technetium. Part I. The Preparation and Properties of Potassium Hexahalogenotechnetates.*

By J. DALZIEL, NAIDA S. GILL, R. S. NYHOLM, and R. D. PEACOCK.

Potassium hexa-chloro-, -bromo-, and -iodo-technetates have been prepared. Their magnetic susceptibility, absorption spectra, and crystal structures are very similar to those of the corresponding rhenium compounds.

TECHNETIUM, the middle member of the Group VIIB triad, was first prepared¹ in 1937 but can now be isolated in relatively large amounts from the liquors produced when the slug from nuclear reactors is dissolved in nitric acid for purification. In the past few years elemental technetium has been characterised and its properties investigated;² also the oxides,³ sulphides,⁴ the tetrachloride,⁴ and the heptavalent pertechnetates have been prepared and their magnetic properties examined. Nelson, Boyd, and Smith³ have found that the quadrivalent dipotassium hexachlorotechnetate is isomorphous with the corresponding rhenium compound. They also studied the magnetic behaviour of the crystalline material over a range of temperature.

The position of technetium in the Periodic Table makes the magnetic and structural properties of its compounds of interest. Manganese forms spin-paired complexes with some reluctance whereas rhenium complexes are almost all of this type. From the work to date it appears that technetium bears a closer resemblance to rhenium than to manganese and hence it is to the former that one looks for a guide to its expected chemical behaviour.

All oxidation states of rhenium from -1 to $+7$ are now well established. The properties of many of these, *e.g.* rhenium(III) containing four non-bonding *d* electrons, are of interest in the light of ligand field theory. Unusual stereochemical arrangements are possible and the large spin-orbit coupling constants have interesting spectral and magnetic consequences. Since it falls between manganese, with a low spin-orbit coupling constant,

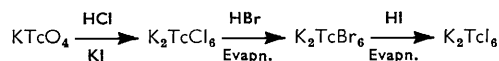
¹ Perrier and Segre, *J. Chem. Phys.*, 1937, **5**, 712; 1939, **7**, 155.

² Cobble, Nelson, Parker, Smith, and Boyd, *J. Amer. Chem. Soc.*, 1952, **74**, 1852.

³ Nelson, Boyd, and Smith, *ibid.*, 1954, **76**, 348; see also *ibid.*, 1952, **74**, 556.

⁴ Knox, Tyree, Srwastava, Norman, Bassett, and Holloway, *ibid.*, 1957, **79**, 3358.

and rhenium with a large constant, technetium should show intermediate behaviour, possibly both magnetic susceptibility and stereochemistry being very sensitive to type of ligand. Since only 15 mg. of technetium as potassium technetate have been available to us, the following scheme of reactions, based on experience with rhenium, was designed to make the maximum use of the material:



In this scheme the conversion of chlorotechnetate through the bromo-compound into iodotechnetate should be quantitative. Comparison of observed and calculated changes in molecular weight could therefore be used to follow the reactions to completion and so avoid the loss of samples to chemical analysis. The atomic weight of ^{99}Tc was estimated from packing-fraction data ⁵ to be about 98.9₀.

Potassium bromo- and iodotechnetates are indistinguishable from their rhenium analogues. Potassium chlorotechnetate shows the greatest divergence, being yellow (the chlororhenate is yellow-green). Purified potassium chlorotechnetate and bromotechnetate crystallise slowly from their strongly acid solutions in large regular octahedral crystals.

The X-ray powder photographs of potassium chlorotechnetate show that it is isomorphous with, but has a slightly smaller unit cell than, potassium chlororhenate. Table I summarises the results of these unit-cell measurements. This does not agree with the earlier work by Nelson, Boyd, and Smith but is in accordance with the expected trend, owing to the lanthanide contraction in this part of the Periodic Table. The lines missing from the powder photograph are such that potassium chlorotechnetate must have a face-centred cubic cell: probably with the same space-group ($0_h^5F_{M3M}$; $Z = 4$) as was derived by Aminoff ⁶ for potassium chlororhenate. Potassium bromotechnetate also has a face-centred cubic lattice with its unit cell slightly smaller than that of potassium bromorhenate. Potassium iodotechnetate has a non-cubic structure. Its powder pattern is almost identical with that of potassium iodorhenate. Morrow ⁷ has reported that the latter has orthorhombic symmetry with four formula weights in the unit cell. Fourteen of the seventeen lines in Guinier powder patterns of dry potassium iodorhenate can be indexed more satisfactorily with respect to a body-centred orthorhombic cell which contains two formula weights. The other three weak lines can be indexed when the related monoclinic cell, containing four formula weights, is used. The details of the body-centred orthorhombic pattern which have been found for potassium iodorhenate are given in Table 2.

TABLE I. Comparison of unit-cell dimensions of potassium halogeno-technetates and -rhenates (in Å).

K_2TcCl_6	$a_0 = 9.82(\pm 0.01)^a$ $a_0 = 9.89^b$	K_2ReCl_6	$a_0 = 9.82(\pm 0.01)^a$ $a_0 = 9.842^b$ $a_0 = 9.861^c$
K_2TcBr_6	$a_0 = 10.37(\pm 0.02)^a$	K_2ReBr_6	$a_0 = 10.38(\pm 0.02)^a$
K_2TcI_6	$a = 11.22$ $b = 8.00$ $c = 7.84$ } ± 0.03 Å	K_2ReI_6	$a = 11.22$ $b = 8.00$ $c = 7.84$ } ± 0.02 Å $a = 11.07(\pm 0.05)^d$ $b = 13.48(\pm 0.07)^d$ $c = 10.19(\pm 0.05)^d$

^a Present work. ^b Ref. 3. ^c Ref. 6. ^d Ref. 7.

The magnetic moments at room temperature of the halogenotechnetates in the corresponding halogen acid solutions are shown in Table 3. They decrease in the order $\text{K}_2\text{TcI}_6 > \text{K}_2\text{TcCl}_6 < \text{K}_2\text{TcBr}_6$, the discontinuity being just outside the experimental error. For solid hexachlorotechnetate Nelson, Boyd, and Smith report a moment of 4.3 B.M.

⁵ Kaplan, "Nuclear Physics," Addison-Wesley Publ. Co. Inc., New York, 1955, 182.

⁶ Aminoff, *Z. Krist.*, 1936, A, **94**, 246.

⁷ Morrow, *J. Phys. Chem.*, 1956, **60**, 19.

The hexahalogenotechnetates of technetium(IV) have an octahedral d_e^3 configuration. This half-filled d_e shell behaves essentially like an S spectroscopic state, equivalent to a half-filled p shell. The orbital angular momentum L in a cubic field of perfect octahedral symmetry should be effectively zero. As a result the moment should be given by the spin-only value of 3.88 B.M., obtained by putting S (total spin) = $1\frac{1}{2}$ and $L = 0$ in the expression $\mu = [4S(S + 1) + L(L + 1)]^{\frac{1}{2}}$. The values shown in Table 2 are all slightly

TABLE 2. *Indices and approximate intensities of Guinier powder lines for potassium iodorhenate. (Cu-K α radiation.)*

Intensity	Sin ² θ (obs.)	Sin ² θ (calc.)	hkl	Intensity	Sin ² θ (obs.)	Sin ² θ (calc.)	hkl
s	0.0140	{ 0.0141	110	m	0.0742	0.0758	022
		0.0145	101	s	0.0773	0.0773	400
m	0.0190	0.0190	011	w	0.0937	0.0932	031
m	0.0194	0.0193	200	m	0.0963	{ 0.0963	411
w	0.0483	—	—			0.0964	013
mw	0.0516	0.0516	121	w	0.1221	—	—
		0.0528	112, 310	w	0.1261	0.1270	132, 330
m	0.0527	{ 0.0532	301			0.1291	123
		0.0565	220	m	0.1297	{ 0.1301	510
s	0.0569	0.0565	220			0.1532	422
mw	0.0578	0.0581	202	w(b)	0.1509	0.1532	422
w	0.0667	—	—				

s = strong, m = medium, mw = medium weak, w = weak, (b) = broad line.

TABLE 3. *Magnetic moments (μ_{eff}) of potassium halogeno-technetates and -rhenates (in B.M. at 20° unless otherwise indicated; the Curie law is assumed to hold).*

	Chloride	Bromide	Iodide
Tc	4.05 \pm 0.1	3.94 \pm 0.1	4.14 \pm 0.1
Re	3.30 (at 24°)	3.20 (at 22°)	3.57

^a Klemm and Frischmuth, *Z. anorg. Chem.*, 1937, **230**, 220; Jensen, *ibid.*, 1944, **252**, 317.

Measurements were made on solid rhenates; solutions of the halogenotechnetates were used: chloro- in 1 : 1-HCl; bromo- in 1 : 1-HBr, iodo- in constant-boiling HI.

in excess of this spin-only value for three unpaired electrons. However, with the limited amount of material available, we have had to carry out our measurements in aqueous solution and at one temperature only. Provided that there is no deviation from the perfect octahedral arrangement then according to Kotani's theory⁸ the magnetic moment of 3.88 B.M. should be independent of temperature, with a Curie constant of zero. In fact, as is apparent with the corresponding rhenium(IV) complexes, some deviation from octahedral symmetry and/or exchange phenomena *via* halogen atoms can occur which affects the moment. With the larger amount of technetium shortly to be available we shall measure μ over a wide range of temperature.

TABLE 4. *Absorption bands (wavelengths in Å) and extinction coefficients (in parentheses) of rhenium and technetium compounds.*

K ₂ TcCl ₆	7000(2.90)	K ₂ ReCl ₆	7100(3.48), 6500(2.79)
K ₂ TcBr ₆	11,300(1.10), 10,600(1.55), 7400(10.6)		
K ₂ ReBr ₆	14,000(17.7), 11,200(23.9), 10,800(25.9), 7500(28.5), ~6700(double, 27.4)		

In Table 4 light-absorption details for chlorides and bromides of technetium and rhenium are compared. The spectrum of potassium chlorotechnetate in 1 : 1 hydrochloric acid is similar to that of potassium chlororhenate⁹ but with a shift of the whole spectrum toward the longer wavelengths. Simple ligand field theory predicts that for an octahedral complex of this type two bands are to be expected in the visible or near-visible region, both corresponding with a transition of an electron from the d_e to the d_g level, *i.e.* the transition

⁸ Kotani, *J. Phys. Soc. Japan*, 1949, **4**, 293.

⁹ Jorgensen, *Acta Chem. Scand.*, 1955, **9**, 7102, and refs. therein.

$d_{\epsilon}^3 \rightarrow d_{\epsilon}^2 d_{\gamma}^1$. (The two-electron transition leading to a $d_{\epsilon}^1 d_{\gamma}^2$ configuration would be at a much higher frequency.) With the complex bromides and iodides the two expected bands are observed at the frequencies and with the extinction coefficients shown in Table 3. However, only one band is observed with the $[\text{TcCl}_6]^{2-}$ ion between 4000—9000 Å. This is puzzling since the corresponding hexachlororhenate does show the expected two bands.

EXPERIMENTAL

Potassium Pertechnetate.—The starting material was 16 mg. of technetium as potassium pertechnetate solution. Potassium pertechnetate (32.2 mg.) was recovered from this by evaporation.

Potassium Chlorotechnetate.—Potassium pertechnetate (32.2 mg.) was dissolved in warm concentrated hydrochloric acid (5 ml.), and powdered potassium iodide (200 mg.) was added to reduce the technetium to the quadrivalent state. The liberated iodine was removed by concentrating the solution under an infrared lamp. After the solution had cooled, the remaining liquid, which contained little technetium, was decanted off. The brownish residue was dissolved in concentrated hydrochloric acid (20 ml.), and the solution allowed to simmer until its colour changed to pure yellow. After concentration of the solution yellow crystals appeared and the solution was allowed to cool. The first crop was practically pure but the second crop was contaminated with potassium chloride. Both crops were washed with acidified (HCl) methanol to remove potassium chloride and dried in a vacuum (yield 59.5 mg.). The yellow potassium chlorotechnetate was recrystallised from 2 ml. of concentrated hydrochloric acid (yield 43.6 mg., *i.e.* about 70%).

Molecular Weight of Potassium Bromotechnetate.—The recrystallised potassium chlorotechnetate (43.6 mg.) was converted into bromotechnetate by successive evaporation to dryness with portions (2 ml.) of concentrated hydrobromic acid ("AnalaR"). [Change in molecular weight: Found, 389.8 to 662.8. Calc., 389.8 to 656.6.]

Potassium Bromotechnetate.—The bromotechnetate, together with all the rejected chlorotechnetate solutions, was evaporated to dryness repeatedly with portions (3 ml.) of concentrated hydrobromic acid. The solution was finally concentrated to small bulk; reddish-brown crystals of potassium bromotechnetate then appeared. Next day the supernatant solution which contained only a little technetium was siphoned off and the potassium bromotechnetate recrystallised from the minimum of concentrated hydrobromic acid [yield 90.7 mg., *i.e.* about 87%].

Molecular Weight of Iodotechnetate.—Recrystallised potassium bromotechnetate (90.7 mg.) was evaporated to dryness with successive portions (1 ml.) of redistilled "AnalaR" hydriodic acid. After two evaporations the weight became constant. [Change in molecular weight: Found, 656.6 to 943.2. Calc., 656.6 to 938.6].

Potassium Iodotechnetate.—The iodotechnetate was combined with bromotechnetate recovered from residual solutions and evaporated to dryness with redistilled hydriodic acid (2×3 ml.). The product was dried and stored in a vacuum desiccator to avoid hydrolysis or oxidation [yield 124.7 mg., *i.e.* about 84%].

Rhenium Compounds.—An analogous set of molecular-weight determinations was carried out, ammonium chlororhenate being used as starting material. [Changes in molecular weight: Found, 435.3 to 702. Calc. for $(\text{NH}_4)_2\text{ReCl}_6$ to $(\text{NH}_4)_2\text{ReBr}_6$, 435.3 to 712.3. Found, 712.3 to 974. Calculated for $(\text{NH}_4)_2\text{ReBr}_6$ to $(\text{NH}_4)_2\text{ReI}_6$, 712.3 to 984.3.] Specimens of potassium halogenorhenates for X-ray measurements were prepared by standard methods.

X-Ray Photographs.—To avoid loss of material, and in the interests of safety, the vacuum-dried specimen was ground under dry benzene. The suspension was transferred by dropper to a wide-mouthed Pyrex capillary which was already filled with benzene. When the powdered specimen had settled the benzene was allowed to evaporate away. This method of preparing X-ray specimens also minimised possible hydrolysis or oxidation, especially of the iodotechnetate and iodorhenate. Photographs of the potassium halogenotechnetates were taken in 9-cm. cameras (Unicam Instruments Ltd.), cobalt radiation filtered through iron being used. A nickel screen was used next to the film in the camera to minimise the effects of β -radiation from the technetium.

Photographs of potassium iodorhenate were also taken in a Guinier-type camera ("Nonius," Delft), reflected cooper radiations being used. The method of sample mounting made this camera unsuitable for work with technetium.

Magnetic Susceptibilities.—These were determined by the Gouy method, approximately

4 ml. of 0.02—0.08M-solution being used. The column was 6.0 cm. long and the field strength 7000 gauss. The acid concentrations were: hydrochloric approx. 5N; hydrobromic approx. 5N; hydriodic approx. 8N. Owing to the high dilution, moments are considered correct to ± 0.1 B.M.

Absorption Spectrum of Potassium Chlorotechnetate.—Measurements were made with a Perkin-Elmer self-recording Spectracord Type 4000. Solutions of chlororhenate and chlorotechnate were made up in 5—6N-hydrochloric acid. The corresponding bromo-compounds were made up in concentrated hydrobromic acid.

Health Precautions.—The manipulation of technetium on the milligram scale did not present a serious health hazard since ^{99}Tc is only a soft β emitter (0.3 Mev) with a specific activity, calculated from its half life of 2.1×10^5 years,¹⁰ of about 17 microcuries/mg.

Care was taken during the evaporation of strongly acid solutions of technetium, since there was possibility that some heptoxide might volatilise. Solutions were evaporated under infra-red lamps in a well-ventilated fume cupboard. The solution and its container were covered with a beaker which was removed and monitored from time to time.

The grinding of dry technetium compounds under benzene, to prevent their hydrolysis, has already been described. This method had the further advantage that it minimised the hazard from radioactive dust.

We are indebted to the Atomic Energy Research Establishment, Harwell, for the loan of the technetium used and to the University of London for a Turner and Newall Fellowship (to N. S. G.). The authors thank Mr. T. Dunn for helpful discussions.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY, LONDON, S.W.7.
WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES,
UNIVERSITY COLLEGE, LONDON, W.C.1.

[Received, April 28th, 1958.]

¹⁰ Fried, Yaffey, Hall, and Blendenin, *Phys. Rev.*, 1951, **81**, 741.
