1141. *New Compounds in which Technetium has a Low Valency.*

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By reduction of technetium in the quadrivalent state with hydroxylamine, the chloride of a complex cation has been isolated containing bivalent technetium, with hydroxylamine and ammonia as ligands. Reduction with zinc and concentrated hydrochloric acid gave an ill-defined amorphous compound from which yttrium, ammonium, and potassium salts with an anion $[Tc_2Cl_8]^{3-}$ have been prepared. Other reduction products of technetium have also been obtained, and it is suggested that technetium may have a fairly extensive solution chemistry in its lower valency states.

UNTIL 1959, when Nyholm[1] isolated ditertiary arsine complexes of technetium in the +2 and the +3 oxidation state, established solid compounds of technetium were only known in the +4 and the +7 state. On the other hand, reports of solutions containing technetium in lower oxidation states are quite numerous; Tc^+ has been reported[2] in tracer concentration, formed by the radioactive decay of dibenzylmolybdenum-99; Tc^{2+} has been reported by Gerlit[3] as arising on reduction of technetium with zinc and concentrated hydrochloric acid; and evidence for Tc^{3+} has been obtained[4] in electrolytic reduction of technetium solutions.

In the present work, attempts were made to produce solid compounds of technetium in low valency states by reducing technetium, as $[TcCl_6]^{2-}$, with a variety of reducing agents. Sulphur dioxide, hydrazine, tin and hydrochloric acid, zinc and hydrochloric acid, and hydroxylamine gave colour changes indicative of reaction, probably reduction, and solid compounds of technetium have been isolated from the reactions with the last two of these reagents. The starting material was 1 gram of the long-lived ($T\frac{1}{2} = 2{\cdot}1 \times$ 105 years) isotope ^{99}Tc, as ammonium pertechnetate.

Reaction of ammonium hexachlorotechnetate with hydroxylamine hydrochloride solution gave an immediate colour change and some effervescence, indicating reduction of the technetium. It proved difficult to isolate pure solid compounds from the neutralised reaction mixture, not because of instability to water or air, but because several products were formed. One of these, however, was separated as a solid. It contained a complex pink cation of bivalent technetium, and its empirical formula was

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[1] Nyholm, *Nature*, 1959, **183**, 1039.
[2] Baumgartner, Fischer, and Zahn, *Naturwiss.*, 1961, **40**, 478.
[3] Gerlit, Proc. U.N. Conf. on the Peaceful Uses of Atomic Energy, Geneva, 1955, Vol. VII, p. 145.
[4] Thomason, Oakridge National Laboratory, Tennessee, U.S.A., Report No. 2453.

$[Tc(NH_2{\cdot}OH)_2(NH_3)_3]^{2+}2Cl^-$. The 5-co-ordination implied by this formula seems unlikely, and the accuracy of the results is such it cannot be distinguished from

$$[Tc(NH_2OH)_2(NH_3)_3H_2O]^{2+}2Cl^-.$$

In the purification and separation of this compound at least two other compounds of technetium were observed, both intensely purple. One of these moved as a cation in paper electrophoresis; the other did not move and was thus an uncharged species.

The only known compounds of bivalent rhenium and technetium have been the uncharged complexes with o-phenylenebisdimethylarsine (D), $(MD_2Hal_2)^0$, where M = Tc or Re, and Hal = halogen.[1,5] Our work suggests the existence of a series of ammines of bivalent technetium, accessible by normal aqueous-solution methods.

Reaction of ammonium hexachlorotechnetate with zinc and hydrochloric acid gave a mixture from which salts of the acid $H_3Tc_2Cl_8$ have been isolated; full analyses have been carried out on the ammonium salt, $(NH_4)_3[Tc_2Cl_8],2H_2O$ and the yttrium salt, $YTc_2Cl_8,9H_2O$. These were isolated by crystallisation from fairly concentrated hydrochloric acid, in which they are soluble and in which they are oxidised only slowly. In dilute hydrochloric acid or water they decompose rapidly by oxidation and hydrolysis.

The stoicheiometry of the $[Tc_2Cl_8]^{3-}$ ion is unusual, and it seems to have no analogues. It may be significant that both analyses indicated enough combined water for the ion to be, in fact, $[Tc_2Cl_8(H_2O)_2]^{3-}$; this would give each technetium atom six ligands in a structure consisting of two octahedra sharing an edge, possibly by halogen bridges as in Al_2Cl_6 and other chlorides. The average valency of technetium in this ion is $2\frac{1}{2}$; it is interesting that ruthenium forms[6,7] an anionic complex, with rather similar ligands, with an average valency of $3\frac{1}{2}$. Fletcher *et al.*[8] assign to this a dinuclear structure in which oxygen and hydroxyl act as bridges between the ruthenium atoms $[Ru_2Cl_6(OH)_2O]^{3-}$. Rhenium is not known to form a halogen complex resembling the $[Tc_2Cl_8]^{3-}$ ion, though salts of the acid $HReX_4$ are known; no halogen complex is known of bivalent rhenium, reduction of perrhenic acid with zinc and 0·2N-hydrochloric acid giving[9] ill-defined hydrated oxides, ReO and Re_2O.

It is thus possible to produce compounds with technetium in a low valency state by using simple inorganic ligands for stabilisation against atmospheric oxidation. In this respect the $[Tc_2Cl_8]^{3-}$ anion is not so stable as the complex cation formed with ammonia and hydroxylamine; the chloro-anion is oxidised slowly in acid solution, but solutions of the pink cation remain apparently unchanged indefinitely.

EXPERIMENTAL

Materials.—To a concentrated solution of ammonium pertechnetate, ammonium chloride was added in slight excess of the stoicheiometric quantity, and then concentrated hydrochloric acid, and the solution was boiled down to a small volume; golden-yellow ammonium hexachlorotechnetate crystallised. It is only sparingly soluble in constant-boiling hydrochloric acid, whereas ammonium chloride is readily soluble, so purification from the excess of ammonium chloride was obtained. The ammonium hexachlorotechnetate was washed with absolute alcohol, then with ether, and dried *in vacuo*. Yields exceeded 90%.

Magnesium hexachlorotechnetate was prepared by similar reduction of magnesium pertechnetate, magnesium pertechnetate being prepared by digestion of ammonium pertechnetate with magnesium oxide.

Analytical Methods.—Technetium was determined by oxidation to ammonium pertechnetate

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[5] Curtis, Fergusson, Nyholm, *Chem. and Ind.*, 1958, 625.

[6] Perry and Cuhrs, *Ber.*, 1929, **62**, 200.

[7] Pshenitsyn and Gintsburg, *Zhur. neorg. Khim.*, 1957, **2**, 112.

[8] Fletcher, Woodhead, Greenfield, and Hardy, AERE R 2577.

[9] Young and Irvine, jun., *J. Amer. Chem. Soc.*, 1937, **59**, 2648.

and solid β-counting against standardised ammonium pertechnetate solution. Chlorine was determined by oxidation of the compounds with alkaline hydrogen peroxide and volumetric determination of chloride by silver nitrate with chromate as indicator. Ammonia was determined by distillation from sodium hydroxide solution into an excess of standard acid and back-titration. Hydroxylamine was determined by reduction to ammonia with Devarda's alloy in alkaline solution, and distillation. Ammonia in the presence of hydroxylamine was determined by distillation from aqueous sodium hydroxide after hydroxylamine had been oxidised to nitrous oxide by heating the solution with an excess of ceric sulphate. Water was determined where possible by Karl Fischer's method, and by determining the loss in weight at 100° *in vacuo*. The oxidation state of the technetium was determined by oxidation to pertechnetate with an excess of ceric sulphate and back-titration with standard oxalate solution. Stabilised alkaline hydrogen peroxide was also used as an oxidising agent; in this case the excess was determined iodometrically. Yttrium was determined by separation of yttrium oxalate, and determination of the oxalate volumetrically with standard ceric sulphate solution.

Preparation of Ammonium Octachloroditechnetate.—To a solution of ammonium hexachlorotechnetate (600 mg.) in concentrated hydrochloric acid (20 ml.) at 100° zinc pellets were added; vigorous reduction occurred. The yellow suspension of hexachlorotechnetate became initially dark green and eventually all the suspended material dissolved. On the continued addition of zinc the solution became brown and a black precipitate was formed. The supernatant liquid and precipitate were then decanted from the residual zinc and the hot solution was centrifuged. The brown supernatant layer was decanted from the black precipitate and kept in a vacuum at room temperature for 24 hr. A brown syrup remained, consisting of a concentrated solution of zinc chloride and reduced technetium species. This syrup was repeatedly extracted with diethyl ether until all the zinc chloride had been removed and a dark brown powder remained. This was dissolved in concentrated hydrochloric acid, giving a reddish-brown solution which rapidly oxidised in air to a turquoise-blue solution. This oxidised solution was evaporated in a vacuum, black shining needles being obtained. These were washed in absolute alcohol, in which they were slightly soluble, then in ether (in which they were insoluble) dried in a vacuum, and weighed. Yields of about 200 mg. of this *compound* were obtained [Found (mean): Tc, 34·5; Cl, 49·6; NH_4, 9·2; H_2O, 6·55. $(NH_4)_3Tc_2Cl_8,2H_2O$ requires Tc, 34·6; Cl, 49·7; NH_4, 9·4; H_2O, 6·3%].

The average valency of the technetium, determined by oxidation with ceric sulphate, was 2·4. Determined by oxidation with alkaline hydrogen peroxide it was 2·45. The compound is oxidised fairly rapidly to hexachlorotechnetate in dilute hydrochloric acid, and slowly in concentrated hydrochloric acid. It is hydrolysed by water to technetium dioxide and hydrochloric acid; by potentiometric titration of the hydrochloric acid against alkali, an acid equivalent weight of the substance was obtained (114·5. 5HCl requires Equiv., 114·4).

Paper electrophoresis with concentrated hydrochloric acid as electrolyte showed the technetium to be in the anionic form; monitoring of the strip, and the migration of the single turquoise band of complex technetium anion showed that there was only one anionic technetium species. The ammonium ion was shown to be the cation in the same experiment by development of the paper strip with sodium hydroxide and Nessler's reagent, showing a brown line migrating to the cathode.

The specific gravity of the compound was measured by flotation, as 2·4 g./cm.^{3}.

Owing to the instability of the substance except in concentrated acid, conductivity measurements in aqueous solution were impossible and *X*-ray measurements proved difficult owing to multiple twinning. Measurement of the optical adsorption spectrum of the compound in concentrated hydrochloric acid showed a maximum in the visible at 615 mμ, to which the colour is due.

Attempts were made to prepare a crystalline iodide complex from the chloride complex. Evaporation of a solution of the chloride complex with hydriodic acid (*d* 1·7) gave an amorphous black powder. Evaporation of solution of the chloride in 50% hydriodic acid gave a crystalline product which, however, on being analysed, was found to be ammonium hexiodotechnetate, a known compound of quadrivalent technetium.

Attempts to prepare other salts of the $[Tc_2Cl_8]^{3-}$ anion from the ammonium salt by double decomposition were unsuccessful, but two were prepared from the magnesium salt as described below.

Preparation of the Yttrium Salt, $YTc_2Cl_8,9H_2O$.—Magnesium hexachlorotechnetate was prepared from magnesium pertechnetate (300 mg. of Tc), as described previously. Reduction with zinc and hydrochloric acid and subsequent operations were as for the preparation of the ammonium salt. The product, after drying with ether, was a blue-grey, deliquescent substance of ill-defined crystalline form. It was dissolved in concentrated hydrochloric acid (5 ml.), giving an intensely turquoise-blue solution; solid yttrium chloride was added a little at a time and the solution agitated. Fine, blue crystals were obtained and gradually almost all the technetium was removed from solution, leaving only a pale blue liquid. The precipitate was centrifuged off, washed with concentrated hydrochloric acid and absolute alcohol, residual yttrium chloride (readily soluble in alcohol) being removed. The blue precipitate was then dissolved in 6N-hydrochloric acid and recrystallised by evaporation in a vacuum; larger black crystals of the *salt* were obtained (450 mg.), which appeared dark red by transmitted light (Found: Y, 11·85; Cl, 37·4; Tc, 27·0; H_2O, 22·5. $YTc_2Cl_8,9H_2O$ requires Y, 12·1; Cl, 38·8; Tc, 27·0; H_2O, 22·1%).

Of the water found, 7·1% was removed in a vacuum at 100°. This corresponds to $3H_2O$. The remainder was more tightly bound; total water was determined by the Karl Fischer method.

The oxidation state of the technetium, determined by oxidation with ceric sulphate, was 2·6. Determined by alkaline peroxide it was 2·53. The acid equivalent of the substance was determined as for the ammonium salt. Measurement was complicated by the precipitation of yttrium hydroxide during the titration but a value of 137·5 was obtained, in fair agreement with the theoretical value of 146·6 based on a molecular weight of 733. The molar extinction coefficient at 615 mμ was 185; a similar measurement on the ammonium salt gave a value of 188.

By addition of potassium chloride to a concentrated hydrochloric acid solution of the magnesium salt of octachloroditechnetate, a potassium salt was precipitated having the same crystalline form as the ammonium salt. Addition of sodium chloride, however, did not precipitate the sodium salt.

Other Products of Reduction of Hexachlorotechnetate by Zinc–Hydrochloric Acid.—Analysis of the brown substance described above as an intermediate in the preparation of the $[Tc_2Cl_8]^{3-}$ ion showed ammonia, chlorine, and technetium to be present. Results, however, varied considerably and the material appeared to be unstable, becoming black on storage, even in a vacuum-desiccator. From a number of determinations on fresh samples, it appeared that the technetium present was bivalent, but the results were not conclusive.

Analysis of different samples of the black precipitate, which occurred as a by-product of the $[Tc_2Cl_8]^{3-}$ preparation gave 87—92% of technetium. The valency of the technetium in each sample, determined by ceric sulphate, was zero, and the material is believed to be impure metallic technetium.

Reduction of Hexachlorotechnetate with Zinc Amalgam and Concentrated Hydrochloric Acid.—If mercury is present during the reduction with zinc and hydrochloric acid, the black precipitate is not formed, and the mercury becomes highly radioactive. This is presumably due to formation of technetium amalgam.[8] It is possible to remove all technetium from solution into the mercury by continued reduction under these conditions.

Reduction of Hexachlorotechnetate with Tin and Concentrated Hydrochloric Acid.—Reduction of ammonium hexachlorotechnetate with tin and hydrochloric acid was carried out as for zinc and hydrochloric acid. A brown compound was produced from which, however, no clearly defined crystalline compound could be obtained. No black precipitate was formed in the reduction.

Reaction of Ammonium Hexachlorotechnetate with Hydroxylamine Hydrochloride.—Ammonium hexachlorotechnetate (350 mg.) was dissolved in the minimum amount (~12 ml.) of 2M-hydroxylamine hydrochloride. Some effervescence occurred as the hexachlorotechnetate slowly dissolved. A golden solution was obtained which darkened to brownish-purple. This solution had a maximum absorption in the visible region at 510 mμ, and a plot of the growth of this adsorption peak against time after dissolution showed that the reaction stops after about 30 min. The solution was set aside for an hour, then ammonia solution was run in slowly with stirring until the solution was neutral. Slow effervescence occurred when the pH was 5·5—7·0. The solution was then allowed to evaporate in a fume cupboard overnight. The purple solid obtained was dissolved in the minimum amount of water and absolute ethanol added, giving a purple precipitate. This was centrifuged off, dissolved in the minimum amount of water, reprecipitated with ethanol, washed with ethanol and ether, dried, and weighed (yields ~100 mg.). Analysis of this substance showed ammonia, hydroxylamine, technetium and chlorine to be present but each sample prepared gave different results, so showing that either the substance contained impurities or there was more than one technetium compound present. Paper electrophoresis showed that the chlorine was anionic, that some of the technetium was cationic, and that the ammonia was not ionic and was therefore not present as impurity (ammonium chloride).

The following procedure gave a well-defined crystalline compound. A solution of ammonium hexachlorotechnetate (600 mg.) in a minimum of 2M-hydroxylamine hydrochloride was evaporated to dryness overnight in a fume cupboard at room temperature. The crystals obtained were dried in a vacuum-desiccator and then extracted three times with diethyl ether. The ether extract was bright yellow. The residual solid was dissolved in the minimum amount of water and evaporated to dryness as before. The solid was then re-extracted three times with ether and dissolved in the minimum amount of water, and ammonia was added until the pH was 7·0. The solution was evaporated at room temperature; the solid was obtained was a pink mass of technetium compound, ammonium chloride, and hydroxylamine. This was dissolved in the minimum amount of water, and absolute ethanol was added, giving a pink microcrystalline precipitate. This product was centrifuged off, washed with absolute ethanol, dissolved in the minimum amount of water, reprecipitated with alcohol, washed with alcohol and ether, dried, and weighed (yields ~80 mg.) {Found: Tc, 33·0; $NH_2\cdot OH$, 23·7; NH_3,17·2; Cl, 24·4; H_2O (by difference), 1·7. Calc. for $[Tc(NH_2\cdot OH)_2(NH_3)_3]2Cl$: Tc, 34·5; $NH_2\cdot OH$, 23·0; NH_3, 17·8; Cl, 24·7. Calc. for $[Tc(NH_2\cdot OH)_2(NH_3)_3H_2O]2Cl$: Tc, 32·5; $NH_2\cdot OH$, 21·6; NH_3, 16·7; Cl, 23·3; H_2O, 5·9%}.

Oxidation of these technetium compounds with ceric sulphate would oxidise the Tc^{2+} to Tc^{7+}, and the hydroxylamine to nitrous oxide: $2NH_2\cdot OH + 4Ce(SO_4)_2 \longrightarrow N_2O + 2Ce_2(SO_4)_3 + H_2O + 2H_2SO_4$. Hence the change in oxidation number for the molecule determined by ceric sulphate would be 5 for the technetium and 4 for the hydroxylamine, a change of 9. A figure of 9·1 was obtained by experiment. The compound was stable in water and the molar conductivity at infinite dilution was 238, on a molecular weight of 287 (theor. for a salt MX_2, ~240). Paper electrophoresis showed the chlorine to be anionic and the pink technetium species to be cationic. It also showed that about 5% of the product consisted of another coloured technetium cationic species, present as impurity. No loss in weight occurred in a vacuum at 100°, and as the substance was insoluble in methyl alcohol no Karl Fischer water determination was possible.

The yellow ether extract obtained during the preparation of the above compound yielded a violet precipitate when dry ammonia was passed into the extract. This material dissolved in water to give a stable violet solution which under electrophoresis appeared to be uncharged. If the ether extract was evaporated, the solid residue dissolved up in water, and the solution made alkaline with ammonia, the solution darkened and gradually gave a black precipitate believed to be technetium dioxide. If, however, some hydroxylamine hydrochloride was added before basification, a deep purple solution was obtained containing cationic technetium

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