451.   *Niobium*(v) *and Tantalum*(v) *Nitrates.*

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The reactions of niobium and tantalum pentachlorides with dinitrogen tetroxide in ionising solvents yield solvated nitrato-dioxides, NbO_2NO_3 and TaO_2NO_3, which are probably polymeric. The intermediate compounds in the reaction appear to be complex derivatives of $NbOCl_3$, NbO_2Cl, and TaO_2Cl. Trinitratotantalum oxide, $TaO(NO_3)_3$, has been prepared by the reaction of the pentachloride with dinitrogen pentoxide, which also reacts slowly with freshly precipitated niobium(v) and tantalum(v) hydroxides to give the corresponding trinitrato-compound, but does not react with the anhydrous oxides.

FEW studies of the nitrates of the Group VA metals have been recorded; the nitrato-oxides of vanadium(v), VO_2NO_3 and $VO(NO_3)_3$, are reported to be formed, respectively, by the reaction of vanadium metal with liquid dinitrogen tetroxide–methyl cyanide [1] and of vanadium oxytrichloride (or pentoxide) with dinitrogen pentoxide.[2] More recently,[3] a niobium analogue $NbO(NO_3)_3$, has been prepared by reaction of the pentachloride with dinitrogen pentoxide. Preliminary experiments on the reaction of niobium pentachloride with excess of silver nitrate in dry methyl cyanide solution resulted in the precipitation of all the niobium and all the chlorine as silver chloride, suggesting that the niobium nitrate, if formed, was insoluble. This type of reaction was not pursued further, but it was of interest to examine the reactions of niobium and tantalum in the form of the metals, oxides, hydrated oxides, and pentachlorides, with dinitrogen tetroxide and pentoxide.

[1] Panontin, Fischer, and Heintz, *J. Inorg. Nucl. Chem.*, 1960, **14**, 145.
[2] Schmeisser and Lützow, *Angew. Chem.*, 1954, **66**, 230.
[3] Field and Hardy, *Proc. Chem. Soc.*, 1963, 11.

Liquid dinitrogen tetroxide did not react with niobium pentachloride except in the presence of ionising solvents which increased the self-ionisation of the dinitrogen tetroxide, or with metallic niobium and tantalum and their oxides under any conditions. Addition of liquid dinitrogen tetroxide to niobium pentachloride moistened with methyl cyanide gave rather unsatisfactory products, but saturation of a solution of the pentachloride in that solvent at room temperature with the dry gaseous tetroxide was more promising. After an initial colour change from yellow through brown to red (nitrosyl chloride), the niobium was precipitated quantitatively in 3—5 minutes. The product was a white methyl cyanide complex of nitratoniobium dioxide, $NbO_2NO_3,0\cdot67MeCN$. On standing in moist air, addition of approximately $0\cdot3$ molecule of water occurred initially; this was an additional indication that the complex was trimeric, probably of the form (I), with the entering water molecule co-ordinating to the central niobium atom. The compound is,

(I)   (II)
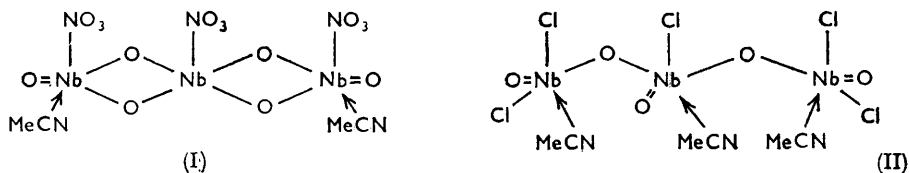
unfortunately, X-ray-amorphous and insoluble in all organic solvents tried, so that the structure and molecular weight could not be obtained; it decomposes slowly above 65° and a thermogravimetric study showed that no definite intermediate compounds are formed before complete decomposition to the pentoxide occurs. The anhydrous compound decomposes slowly on standing in a dry atmosphere (about 5% in 6 months) and is readily hydrolysed by water.

The mechanism of formation of this complex could not be investigated spectrophotometrically on account of the broad absorption bands due to the dinitrogen tetroxide present in the solution; attempts were therefore made to isolate intermediates by stopping the reaction after less than one minute (*i.e.*, 2—4 minutes before precipitation of the final product) by rapidly pumping off the dissolved gases. Immediate vacuum evaporation of the resulting rather unstable solution yielded a white solid of composition close to $Nb_3O_5Cl_5,3MeCN$, which might have structure (II), which would suggest that the polymerisation occurs at an early stage, possibly through decomposition of an intermediate nitratochloride, $NbCl_3(NO_3)_2$. The methyl cyanide solution of the intermediate chlorocomplex (II), after removal of the dinitrogen tetroxide, decomposed on warming, so that its molecular weight could not be determined ebullioscopically, and precipitated an X-ray-amorphous material with the composition $NbO_2Cl,MeCN$. The reaction of niobium pentachloride with dinitrogen tetroxide in hot methyl cyanide solution yielded, after 5 minutes, an insoluble white chloro-species, in which the atomic ratio Cl : Nb was approximately $1\cdot32 : 1$. This is probably similar to, or a mixture of, the intermediate chlorides mentioned above.

Electron spin resonance spectra of the anhydrous nitratoniobium dioxide–methyl cyanide complex were taken, and two weak peaks (about 10^{-4} of the intensity of a single unpaired electron) were observed, the one with the higher relaxation time being about 20 gauss in width (*g*-value = $2\cdot01$) and the other about 200 gauss wide (probably due to dinitrogen tetroxide since it could be removed under a vacuum). The changes in the e.s.r. spectrum which occurred on hydration were not reproducible; in some cases the intensity of the narrow peak increased by an order of magnitude during the hydration (7 hours) and then decayed with a half-time of 24 hours; in subsequent cases no change occurred, and in one case hydration quenched the spectrum. Since the chloro-complex precipitated from hot methyl cyanide showed the same e.s.r. spectrum, it may arise from the presence of traces of chemically undetectable impurities rather than from a possible

splitting of the filled $3d^{10}$ level of the middle 5-co-valent niobium atom in structure (I). The hydration phenomena were also followed in the infrared spectrum. Initially the OH stretching frequency of water appeared at 3030 cm.$^{-1}$, indicative of hydrogen bonding, and then moved to 3350 cm.$^{-1}$, a more normal position; the move took place by a broadening of the absorption band rather than by growth and decay of the two peaks. A CH_3 vibration was present at 1010 cm.$^{-1}$ (1030 cm.$^{-1}$ in the $Nb_3O_5Cl_5$ complex), and the C–N stretching frequency, a single sharp peak at 2273 cm.$^{-1}$ for the anhydrous nitrato-compound (and the $Nb_3O_5Cl_5$ complex), appears at 2398—2364 and 2273—2252 cm.$^{-1}$ on hydration and declines in intensity, the splitting not always being clearly discernible. The covalent nitrate frequencies are at 1600, 1560, and 1280—1230 cm.$^{-1}$ for the anhydrous compound, and on hydration the split NO_3 peak at 1600 cm.$^{-1}$ shows, within 5 minutes of exposure to moist air, a marked decrease in intensity relative to the other nitrate peaks, the peaks being at 1613—1616, 1562—1567, and 1286—1311 cm.$^{-1}$. It was not possible to pick out the Nb=O and Nb–O–Nb frequencies [3] (922 and 769 cm.$^{-1}$).

The hydrated nitrato-complex (I) lost one third of its nitrato-groups on standing in moist air for one week, the final ratio of Nb to NO_3^- being 3 : 2·03, which suggests, in conjunction with the infrared results, that the incoming water molecule may first hydrogen-bond to some part of the molecule other than the middle niobium atom, possibly a bridging oxygen atom, and may then re-orientate to present its oxygen atom to the central niobium atom; finally, nitric acid is eliminated from this position, leaving a hydroxyl group.

Tantalum pentachloride reacts with dinitrogen tetroxide in methyl cyanide in the same way as the niobium compound, the precipitated product having a somewhat higher nitrate content (Ta : NO_3^- 1 : 1·2—1·3) and rather variable solvent content; this product is probably a mixture of polymeric species.

Solutions of niobium pentachloride in ethyl acetate became dark brown in 2—3 hours in a dry atmosphere, but the original paler yellowish brown colour was restored when dry air, nitrogen, oxygen, or dinitrogen tetroxide was passed through the solution; no marked changes appeared in the absorption spectrum. The niobium did not precipitate after saturation of the solution with dinitrogen tetroxide, but did so when dry nitrogen was passed through such a solution after standing for a minimum of two hours; it could also be recovered when such solutions were evaporated to dryness under a vacuum. The white product obtained in both cases had the correct analysis for NbO_2NO_3 with a very variable amount of solvent present as well as traces of chloride; this product decomposed rapidly in moist air. Nitrobenzene, in which niobium pentachloride is only slightly soluble, was unsatisfactory as a reaction medium and no clearly defined product was obtained. Niobium pentachloride is very soluble in *NN*-dimethylacetamide (DMA) but no niobium nitrates were precipitated when solutions of the pentachloride in this medium were saturated with dinitrogen tetroxide gas; on vacuum evaporation of such a solution to small bulk, and subsequent treatment with ethyl acetate and isopentane, a white solid was obtained which had the correct analysis for $Nb_5O_9(NO_3)_7$,7DMA; this is either a reproducible mixture of lower polymers or an oxygen-bridged pentamer. The infrared spectrum showed the absence of water and ethyl acetate, whilst the covalent nitrate peaks were present as before, and the DMA spectrum was similar to that in the uranium tetra-chloride–DMA complex.[4]

NN-Dimethylacetamide exhibited an interesting series of colour changes on saturation with dinitrogen tetroxide gas; the solution first becomes pale blue, turning to very dark bluish green through stages of yellow and yellow-green. On vacuum evaporation the sequence of colour changes is reversed, and addition of a solution of niobium pentachloride in dimethylacetamide to the dark bluish green solution immediately gives the red color-ation due to nitrosyl chloride. The bluish colorations may be due to dinitrogen trioxide.

[4] Bagnall, Deane, Markin, Robinson, and Stewart, *J.*, 1961, 1611.

Niobium and tantalum pentachlorides in nitromethane solution give precipitates with gaseous dinitrogen tetroxide after two minutes, which appear to be solvated NbO_2Cl and TaO_2Cl. They redissolve after further passage of dinitrogen tetroxide, then set to a gel which, when vacuum dried, yields a yellowish white solid of composition $Nb(Ta)O_2NO_3$ with varying degrees of solvation (up to 0·5 molecule of solvent per metal atom). It was observed that the minimum solvation occurred with freshly prepared solutions of the pentachlorides, and the maximum with the most aged solutions (15 days). More highly nitrated species, but of very variable composition [Nb(or Ta)/NO_3^- = 1·5 to 1·8], were obtained by the addition of liquid dinitrogen tetroxide to solutions of the pentachlorides in nitromethane. All these nitrato-species show covalent nitrate peaks in the infrared spectrum, but it was again not possible to identify the M=O or M−O−M frequencies (M = metal).

Tantalum pentachloride reacts readily with, and dissolves in, liquid dinitrogen pentoxide, the off-white trinitrato-compound, $TaO(NO_3)_3$, being easily recovered from the solution by vacuum evaporation. It decomposes slowly above 50° and is insoluble in methyl cyanide, NN-dimethylacetamide, or ethyl acetate. Unlike its niobium analogue[3] it appears to be X-ray-amorphous. Freshly precipitated and vacuum-dried niobium(v) and tantalum(v) hydroxides also react slowly with dinitrogen pentoxide, the former almost completely and the latter to 75% completion in 5—6 days, vacuum evaporation of the filtrate from the reaction yielding the trinitrato-compound in each case. The residue from the reaction with niobium(v) hydroxide is the trinitrato-compound, whereas that from tantalum(v) hydroxide is the pentoxide; the oxides do not react in either case. The niobium compound gave the same X-ray pattern as that already reported.[3]

The infrared spectrum of trinitratotantalum oxide from several preparations was examined, but it was possible to distinguish only two nitrate frequencies, both bands being very broad and centred around 1613 (v_4) and 1220 cm.$^{-1}$ (v_1); it was impossible to distinguish peak positions below 1000 cm.$^{-1}$ satisfactorily, in contrast to the spectra observed for the niobium analogue.[3]

EXPERIMENTAL

X-Ray powder photographs were taken with a Unicam 19 cm. Debye–Scherrer camera using filtered Cu-K_α radiation; all compounds other than trinitratoniobium oxide were X-ray-amorphous. Infrared spectra were taken as mulls in Fluorube or Nujol on a Hilger H800 spectrophotometer; samples for spectra in the range 2—15 μ were mounted between silver chloride plates.

Materials.—Commercially available pentachlorides (New Metals and Chemicals, Ltd.) were used as delivered; for some experiments the material was re-sublimed under a vacuum, and in others " Specpure " material (Johnson Matthey Ltd.), also re-sublimed, was used. All gave the same products.

Methyl cyanide was refluxed over phosphorus pentoxide, fractionated (b. p. 80—81°), and passed down a column of No. 4A molecular sieves which had been vacuum dried at 120°. NN-Dimethylacetamide was dried ($MgSO_4$) (16 hr.) and fractionated (b. p. 163—165°). Nitromethane was fractionated (b. p. 100—101°), and nitrobenzene was subjected to three fractionations, the middle fraction being taken in each case. Ethyl acetate was distilled from phosphorus pentoxide, and the middle fraction redistilled. The final water content was less than 0·01% (Karl Fischer determination) in all cases except nitrobenzene (0·04%). Isopentane of reagent quality (water content 0·02%) was used as delivered. Dinitrogen tetroxide was prepared by heating lead nitrate, and dried (P_2O_5); oxygen was not removed. Dinitrogen pentoxide was obtained by dehydration of fuming nitric acid with phosphorus pentoxide; the tetroxide was not removed.

Preparations.—Solutions of the pentachlorides were made up in the dried solvents in a dry-box into which dry gaseous dinitrogen tetroxide could be admitted directly; all other reagents, etc., were brought into the box by a polyvinyl chloride bag-sealing technique. The products were filtered off and vacuum dried *in situ.* Niobium(v) and tantalum(v) hydroxides

were precipitated from fluoride solution with ammonia, washed with dilute nitric acid and acetone, and vacuum dried. Dinitrogen pentoxide was then condensed on to the solids, which were then left for 5—6 days; filtration, and evaporation of the filtrate to dryness under a vacuum, yielded the products, which were also vacuum dried.

Analysis.—Niobium and tantalum were weighed as the pentoxides, after air ignition of the nitrato-compounds which had been moistened with water to prevent violent deflagration, or of niobic or tantalic acid obtained by treating the compounds with dilute aqueous ammonia. Nitrate was weighed as nitron nitrate.[5a] Organic nitrogen and total nitrogen were determined by Kjeldahl digestion;[5b] other solvents were determined by difference. Water was determined by the Karl Fischer method.[5c]

(1) $NbO_2NO_3,0.67MeCN$. Found: Nb, 43·35; NO_3^-, 28·8; total N, 10·0. $NbO_2NO_3,0.67MeCN$ requires Nb, 43·35; NO_3^-, 28·95; total N, 10·9%. (2) $Nb_3O_5Cl_5,3MeCN$. The amount of solvent was variable but the ratio Nb : Cl was 3 : 5·2. (3) $NbO_2Cl,MeCN$. The amounts of chloride and solvent were variable; the ratio Nb : Cl^- : MeCN was 1 : 0·91—1·1 : 0·98. (4) $Nb_5O_9(NO_3)_7,7DMA$. Found: Nb, 28·1; NO_3^-, 26·4; total N, 11·0. $Nb_5O_9(NO_3)_7,7DMA$ requires Nb, 28·1; NO_3^-, 26·3; total N, 11·9%. (5) $TaO(NO_3)_3$. Found: Ta, 47·2; NO_3^-, 47·7. $TaO(NO_3)_3$ requires Ta, 47·2; NO_3^-, 48·6%.

[5] Vogel, " A Text-book of Quantitative Inorganic Analysis," Longmans, London, 1953, (*a*) p. 505; (*b*) p. 248; (*c*) p. 698.