

Quinquevalent Protactinium, Niobium, and Tantalum Nitrates and Nitrato-complexes

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Hexanitratoprotactinates(v), $M^I\text{Pa}(\text{NO}_3)_6$ ($M^I = \text{Cs}$, NMe_4 , and NEt_4), have been prepared by reaction of the hexachloroprotactinates(v) with liquid dinitrogen pentoxide at room temperature. The niobium(v) and tantalum(v) hexachloro-analogues form oxytetranitrato-complexes, $\text{NMe}_4M^V\text{O}(\text{NO}_3)_4$ ($M^V = \text{Nb}$ and Ta), under similar conditions. Protactinium(v) halides react with fuming nitric acid, yielding the hydrated oxynitrate $\text{PaO}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ ($1 < x < 4$) which is probably polymeric. Dinitrogen tetroxide reacts with protactinium(v) halides in anhydrous methyl cyanide to give the dimeric, solvated oxynitrate $\text{Pa}_2\text{O}(\text{NO}_3)_8 \cdot 2\text{MeCN}$, whereas liquid dinitrogen pentoxide converts the pentahalides and freshly prepared hydroxide, but not the pentoxide, into the acid hexanitrate-complex $\text{HPa}(\text{NO}_3)_6$. Some chemical properties and the infrared spectra of the compounds are reported.

SOME unreliable solubility data¹ and results of solvent extraction studies, summarised recently,² have been reported for protactinium(v) in aqueous nitric acid solutions, but, owing to the limited solubility of the hydroxide in aqueous nitric acid and the instability to hydrolysis of the protactinium(v) nitrato-complexes in aqueous solution, little else is known about the protactinium(v) nitrates. The preparation of niobium(v) and tantalum(v) nitrates has, however, been reported; the oxytrinitrates,^{3,4} $M^V\text{O}(\text{NO}_3)_3$, and niobium(v) oxynitrate-methyl cyanide complex,⁴ $\text{Nb}_3\text{O}_6(\text{NO}_3)_3 \cdot 2\text{MeCN}$, have been prepared respectively by the reaction between the appropriate pentachloride and liquid dinitrogen pentoxide and a methyl cyanide-dinitrogen tetroxide mixture. We now report the preparation of hexanitratoprotactinates(v), $M^I\text{Pa}(\text{NO}_3)_6$ ($M^I = \text{Cs}$, NMe_4 , and NEt_4), and tetramethylammonium oxytetranitrato-niobate(v) and -tantalate(v) complexes, $\text{NMe}_4M^V\text{O}(\text{NO}_3)_4$ ($M^V = \text{Nb}$ and Ta), from the reaction between the hexachloro-complexes and liquid dinitrogen pentoxide. A solvated protactinium(v) oxynitrate, $\text{PaO}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ ($1 < x < 4$) has been isolated from fuming nitric acid, $\text{Pa}_2\text{O}(\text{NO}_3)_8 \cdot 2\text{MeCN}$ from methyl cyanide-dinitrogen tetroxide mixtures, and the acid hexanitratoprotactinate(v), $\text{HPa}(\text{NO}_3)_6$, from liquid dinitrogen pentoxide.

The reaction between hexachloroprotactinates(v) and liquid dinitrogen pentoxide at room temperature produces hexanitrate-complexes of the type $M^I\text{Pa}(\text{NO}_3)_6$ which are soluble in dinitrogen pentoxide. The white, moisture-sensitive, caesium, tetramethylammonium, and tetraethylammonium hexanitrate-complexes prepared in this manner and isolated by vacuum evaporation of excess of reagent are the first fully nitrated compounds of a quinquevalent element to be prepared. They are immediately decomposed by water, aqueous ammonia, and dilute acids but can be handled in dry air. Room-temperature hydrolysis with aqueous ammonia proceeds vigorously and low nitrate determinations result unless the compound is "frozen" by dipping it momentarily into liquid nitrogen prior to hydrolysis. The infrared spectra of the complexes (Table) indicate that the nitrate

ions are covalently bound; with increasing cation size it is seen that the N-O stretching vibration ν_2 and the out of plane rocking vibration ν_6 (assigned after Gatehouse *et al.*⁵) which are sharp, well defined peaks, move to lower wavelengths. The effect of cation size on the symmetric and asymmetric stretching vibrations, ν_1 and ν_4 , respectively, cannot be assessed with reasonable certainty since they appear as strong, rather broad bands. The spectra do not contain ionic nitrate vibrations, and X-ray powder photographs confirm the absence of MNO_3 ($M = \text{Cs}$, NMe_4 , and NEt_4) from the products; the complexes appear to possess low symmetry and their powder photographs have not been interpreted. Oxides of nitrogen are evolved at approximately $90^\circ/10^{-3}$ mm. Hg. Attempts to prepare tetramethylammonium octanitratoprotactinate(v) from $[\text{NMe}_4]_3\text{PaCl}_8$ have been unsuccessful; the product is a mixture of $\text{NMe}_4\text{Pa}(\text{NO}_3)_6$ and NMe_4NO_3 , the latter being identified by its X-ray powder pattern and by the appearance of an ionic nitrate vibration⁶ at 1333 cm^{-1} in the infrared spectrum of the product.

Tetramethylammonium hexachloro-niobate(v) and -tantalate(v) dissolve readily in liquid dinitrogen pentoxide at room temperature but the products obtained on vacuum evaporation of the solvent are oxytetranitrato-complexes, $\text{NMe}_4M^V\text{O}(\text{NO}_3)_4$, not the fully nitrated compounds analogous to those of protactinium(v). The white, moisture-sensitive complexes hydrolyse immediately in aqueous ammonia and water and are soluble in dinitrogen pentoxide and anhydrous methyl cyanide. The action of gaseous dinitrogen tetroxide on tetramethylammonium hexachloroniobate(v) dissolved in anhydrous methyl cyanide provides an alternative route to tetramethylammonium oxytetranitratonibate(v). The last reaction is markedly different from that observed with niobium pentachloride under identical conditions⁴ when the insoluble, polymeric mononitrate complex $\text{Nb}_3\text{O}_6(\text{NO}_3)_3 \cdot 2\text{MeCN}$ is formed. Tetramethylammonium hexachlorotantalate(v) reacts only partially with dinitrogen tetroxide in methyl

¹ R. C. Thompson, 1946, U.S.A.E.C. Reports AECD-1897 and AECD-2488.

² D. Brown and A. G. Maddock, *Quart. Rev.*, 1963, **17**, 289.

³ B. O. Field and C. J. Hardy, *Proc. Chem. Soc.*, 1963, 11.

⁴ K. W. Bagnall, D. Brown, and P. J. Jones, *J. Chem. Soc.*, 1964, 2396.

⁵ B. M. Gatehouse, S. E. Livingstone, and R. S. Nyholm, *J. Chem. Soc.*, 1957, 4222.

⁶ K. W. Bagnall, D. Brown, and J. G. H. du Preez, *J. Chem. Soc.*, 1964, 5523.

cyanide and, even after several hours, unchanged chloro-complex, identified crystallographically, is always found in the product. The infrared spectra of the niobium(v) and tantalum(v) oxytetranitrato-complexes show the nitrate groups to be covalently bonded; in addition to the vibrations listed in the Table a medium-intensity, broad absorption band observed at about 730 cm^{-1} in each spectrum may be the asymmetric bending mode, ν_5 . The Nb=O stretching vibration, 881 cm^{-1} , occurs at a higher wavelength than in niobium oxytrinitrate,³ 906 cm^{-1} , and ν_2 , the N-O stretching vibration, is resolved into two bands in both the niobium(v) and

stable concentrated solutions. The rapid, almost quantitative dissolution of protactinium(v) hydroxide, yielding solutions $\sim 0.5\text{M}$ in Pa^{V} , contrasts markedly with the weak complexing observed in aqueous nitric acid ($< 12\text{M}$) and the instability⁷ of solutions greater than 10^{-5}M Pa^{V} in this solvent. In fact the characteristic low stability of protactinium(v) hydroxide in aqueous nitric acid has allowed us to remove occluded ammonium ion from the freshly precipitated hydroxide by washing with 0.5M or 4.0M -nitric acid before reaction with fuming nitric acid. Less than 5 mg. of freshly precipitated hydroxide was observed to dissolve in

Infrared vibrational frequencies (cm^{-1})

	ν_4	ν_1	ν_2	ν_6	ν_3	Metal-oxygen
$\text{HPa}(\text{NO}_3)_6$	1600sh 1563 1536 } s	1299sh 1265 } s	1018m	803sh 796 } m	746m	—
$\text{CsPa}(\text{NO}_3)_6$	1594sh 1558 1527 } s	1290sh 1262 1220sh } s	1015m	799 792 786 } w	751 744 } m	—
$\text{NMe}_4\text{Pa}(\text{NO}_3)_6$	1595sh 1567sh 1543 } s	1266s	1016m	805 799 793 } w	748 743 } m	—
$\text{NEt}_4\text{Pa}(\text{NO}_3)_6$	1597sh 1567 1541 } s	1277 1255 } s	1023m	810 803 799 } w	750 747 } m	—
$\text{PaO}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$	1524s,b	1269s,b	1021m	804m	746m	773s
$\text{Pa}_2\text{O}(\text{NO}_3)_8 \cdot 2\text{CH}_3\text{CN}$	1603sh 1558 } s	1299sh 1256 } s	1016m	803sh 798 } m	749m	721m
$^*\text{NbO}(\text{NO}_3)_3$	1646s 1567w	1299w 1213s	1004m	783 775 770 } s	722w	906s
$\text{NMe}_4\text{NbO}(\text{NO}_3)_4$	1629sh 1598 1563 } s	1276 1249 1226sh } s	1014 1002 } m	806 797 789 } m	772 762 } m	881m,b
$\text{NMe}_4\text{TaO}(\text{NO}_3)_4$	1618 1568 } s	1260s,b	1018 1002 } m	790 780 } m	773 763 } m	877m,b

b, broad; m, medium; s, strong; sh, shoulder; w, weak. * Ref. 3.

tantalum(v) oxytetranitrato-complex. The complexes appear to possess low symmetry and their X-ray powder photographs have not been interpreted. Traces of ionic nitrate, $\sim 1330\text{ cm}^{-1}$, are observed in the infrared spectrum of each of the compounds which appear to be radiation-sensitive since that portion of the mull in the light path becomes brown but elsewhere in the mull the compounds remain white. Also when X-ray samples are sealed in quartz capillaries only lines due to tetramethylammonium nitrate are found on the powder patterns but specimens sealed in Pyrex capillaries exhibit no such decomposition.

Cæsium hexachloro-niobate(v) and -tantalate(v) dissolve in, and react with, liquid dinitrogen pentoxide but the white products, obtained by vacuum evaporation of the excess of pentoxide, contain cæsium nitrate, identified by X-ray diffraction analysis, and are not homogeneous phases.

Protactinium pentoxide, Pa_2O_5 , prepared by ignition of the hydroxide at $500\text{--}750^\circ$, does not react with fuming nitric acid. However, the freshly prepared hydroxide, the pentachloride, pentabromide, and the chloro-complex $\text{SO}[\text{PaCl}_6]_2$ all dissolve readily to give

40 ml. of 4.0M -nitric acid solution during this washing process. Fuming nitric acid solutions of protactinium(v) are reasonably stable and hydrolytic condensation of protactinium(v) was not observed after several days at room temperature. No crystallisation takes place during this time, and on vacuum evaporation the solutions obtained by dissolving protactinium halides initially become colourless (removal of N_2O_4 , NOCl , or NOBr) and finally deposit a white, non-crystalline compound of variable water content; the product invariably has a 3 : 1 nitrate-to-protactinium(v) ratio but the number of water molecules ranges from 1.5 to 4.0. Accordingly the product has been designated $\text{PaO}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$. Attempts to obtain the anhydrous compound by prolonged pumping *in vacuo* at room temperature and by vacuum thermal analysis have been unsuccessful. In the latter instance the hydrated compound starts to decompose at about $50^\circ/10^{-3}\text{ mm. Hg}$ and we have obtained no evidence of stable phases between the hydrated oxytrinitrate and the pentoxide Pa_2O_5 .

The stretching vibration of the O-H group occurs as a

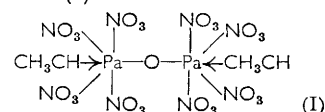
⁷ C. J. Hardy, D. Scargill, and J. M. Fletcher, *J. Inorg. Nuclear Chem.*, 1958, **7**, 257.

broad band at 3206 cm^{-1} (shoulder at 3378) in the infrared spectrum of the hydrated oxytrinitrate but the bending mode of the co-ordinated water, expected around 1630 cm^{-1} , could not be identified with certainty owing to the broad asymmetric stretching vibration, ν_4 , of the covalent nitrate groups. In addition to the characteristic covalent nitrate vibrations (Table) a band is observed at 773 cm^{-1} in the spectrum, and in the light of the position of the Nb=O (906 cm^{-1}) stretching vibration in the oxytrinitrate,³ the stretching vibration observed⁸ at 730 cm^{-1} for Pa_2O_5 and the position of the vibration associated with the oxygen bridge in NbOCl_3 , 767 cm^{-1} , we tentatively attribute this peak at 773 cm^{-1} to the presence of the Pa-O-Pa group. The close agreement with the value for the oxygen bridge in NbOCl_3 is, of course, fortuitous. In the absence of an infrared vibration associated with the Pa=O group it appears that the oxytrinitrate is dimeric or even polymeric. The hydrated oxytrinitrate dissolves readily in the Karl Fischer reagent during the water determinations but, owing to the insolubility of the compound in solvents such as acetone and methylene dichloride, it has not been possible to determine molecular weights. The compound, which is amorphous to X-rays, is immediately decomposed in water and aqueous ammonia. The absence of co-ordinated dinitrogen tetroxide and of the nitronium ion was confirmed by the lack of reaction between the solid, which dissolved, and ceric sulphate in 2M-sulphuric acid solution. In addition vibrations associated with the NO^+ group were absent from the infrared spectrum of the compound.

Vacuum evaporation of the fuming nitric acid solutions in which protactinium(v) hydroxide has been dissolved gives a white, X-ray amorphous solid. Several such products have given Pa , NO_3^- , and H_2O analyses consistent with the trimeric protactinium oxynitrate $\text{Pa}_3\text{O}_4(\text{NO}_3)_7 \cdot 7\text{H}_2\text{O}$ and the infrared spectra of such preparations all contained a band at 774 cm^{-1} in addition to the covalent nitrate vibrations. However the reaction between protactinium(v) hydroxide and fuming nitric acid appears to be irreproducible and we have obtained products with a $\text{Pa} : \text{NO}_3$ ratio ranging between 1:2.2 and 1:3.4. Thus it seems most likely that the product is actually a mixture of hydrated oxynitrates which, unlike $\text{PaO}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$, are insoluble in Karl Fischer reagent, and that the most frequently observed "phase," $\text{Pa}_3\text{O}_4(\text{NO}_3)_7 \cdot 7\text{H}_2\text{O}$, is not a genuine compound. Protactinium(v) hydroxide is less soluble in concentrated nitric acid than in fuming nitric acid and there is always an appreciable quantity of the hydroxide (30–35%) which will not dissolve even on the addition of fresh nitric acid or on warming. Thus we have only been able to prepare 0.033M-protactinium(v) solutions in concentrated nitric acid in this way whereas we have obtained 0.5M solutions in fuming nitric acid; in the latter 90–95% of the hydroxide invariably dissolves in 24 hours at room temperature or within a few minutes on warming.

Protactinium pentachloride and pentabromide react

in anhydrous methyl cyanide with gaseous dinitrogen tetroxide to give a white product, $\text{Pa}_2\text{O}(\text{NO}_3)_8 \cdot 2\text{MeCN}$, which is soluble in methyl cyanide at room temperature. This compound is basically analogous to the previously reported⁹ oxyfluoride Pa_2OF_8 and the oxychloride Pa_2OCl_8 which we have recently isolated¹⁰ during the preparation of the pentachloride by the reaction between chlorine and a mixture of protactinium pentoxide and carbon. In addition to the covalent nitrate vibrations (Table) the infrared spectrum of the compound contains a sharp band at 2278 cm^{-1} and a medium-intensity band at 721 cm^{-1} . The former is assigned to the $\text{C}\equiv\text{N}$ stretching vibration of co-ordinated methyl cyanide since the compound fails to react with ceric sulphate, thereby ruling out the alternative formulation $\text{NO}[\text{PaO}(\text{NO}_3)_4]_x\text{MeCN}$ which could be fitted to the analytical data. The band at 721 cm^{-1} is the only band extra to the covalent nitrate vibrations observed in the other protactinium(v) nitrate compounds and is tentatively assigned to the Pa-O-Pa group in the dimeric compound (I).



It is not possible on the available evidence to rule out the possibility that some or all the covalent nitrate groups are bidentate or even bridging groups. Like the hexanitrate-complexes of protactinium(v) this compound is extremely sensitive to moisture and occasionally the infrared spectra contain weak bands around 3300 cm^{-1} presumably due to the O-H stretching vibration from traces of water picked up during preparation of mulls in the case of the hexanitratoprotactinates(v) or contained in the methyl cyanide used during the preparation of $\text{Pa}_2\text{O}(\text{NO}_3)_8 \cdot 2\text{MeCN}$. Consequently the assignment of a strong, broad band at about 410 cm^{-1} which is observed in the spectrum of $\text{NET}_4\text{Pa}(\text{NO}_3)_6$, the only hexanitrate-complex examined below 660 cm^{-1} , and of $\text{Pa}_2\text{O}(\text{NO}_3)_8 \cdot 2\text{MeCN}$ must be postponed until facilities are available for examining the spectra of radioactive materials down to 170 cm^{-1} . It is hoped that the interpretation of such spectra will be simplified by using a single mull, prepared in paraffin wax, over the region $5000\text{--}175\text{ cm}^{-1}$, thereby enabling us to obtain results on compounds which we are certain contain no trace of water.

In addition to the compounds so far described we have prepared one other protactinium(v) nitrate which, on the basis of the evidence, appears to be the protactinium(v) acid hexanitrate-complex $\text{HPa}(\text{NO}_3)_6$. Vacuum evaporation of a dinitrogen pentoxide solution obtained on dissolution of protactinium(v) hydroxide pentachloride, pentabromide, or the chloro-complex $\text{SO}[\text{PaCl}_6]_2$ yields a white solid which is immediately decomposed by water and aqueous ammonia. Analysis

⁸ L. Stein, personal communication.

⁹ L. Stein, *Inorg. Chem.*, 1964, **3**, 995.

¹⁰ D. Brown and P. J. Jones, to be published.

indicates the presence of six nitrate groups per atom of protactinium(v) and since the dinitrogen pentoxide employed for the preparations is obtained from the reaction between fuming nitric acid and phosphoric oxide, and is therefore likely to contain dinitrogen tetroxide and traces of anhydrous nitric acid, there are several possible formulations for the product. Thus, compounds which will satisfy the analytical results within reasonable limits of error are $\text{HPa}(\text{NO}_3)_6$, $\text{Pa}(\text{NO}_3)_5 \cdot \text{HNO}_3$, $\text{Pa}_2\text{O}(\text{NO}_3)_8 \cdot 2\text{N}_2\text{O}_5$, and, less satisfactorily, $\text{Pa}(\text{NO}_3)_5 \cdot \text{N}_2\text{O}_4$. However, the infrared spectrum of the compound shows only bands associated with covalent nitrate vibrations (Table); no vibration is observed around 900 cm^{-1} (characteristic of anhydrous nitric acid¹¹), 600 cm^{-1} (nitronium ion,¹² NO_2^+), between 1700 and 2400 cm^{-1} (nitrosonium ion,¹³ NO^+). In addition the absence of co-ordinated dinitrogen tetroxide, which would probably show a weak infrared vibration¹⁴ in the region of ν_4 , observed at 1563 cm^{-1} , is confirmed by the lack of reaction of the compound with ceric sulphate. Unfortunately we have been unable to confirm the indications that the compound is $\text{HPa}(\text{NO}_3)_6$ owing to the lack of facilities for proton resonance studies with highly radioactive isotopes such as protactinium-231. The infrared spectrum between 700 and 300 cm^{-1} again contained only one broad, intense band at about 410 cm^{-1} as in the case of $\text{NEt}_4\text{Pa}(\text{NO}_3)_6$ and $\text{Pa}_2\text{O}(\text{NO}_3)_8 \cdot 2\text{MeCN}$, but a weak vibration at 3247 cm^{-1} again suggested the presence of traces of moisture. The compound is insoluble in anhydrous methyl cyanide and methylene dichloride, and does not react with triphenylphosphine oxide dissolved in these solvents.

The protactinium(v) nitrates $\text{PaO}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$, $\text{Pa}_2\text{O}(\text{NO}_3)_8 \cdot 2\text{MeCN}$, and $\text{HPa}(\text{NO}_3)_6$ are all thermally unstable, starting to decompose above $50^\circ/10^{-3} \text{ mm. Hg}$ and vacuum thermogravimetric studies have failed to characterise the anhydrous compounds $\text{PaO}(\text{NO}_3)_3$ or $\text{Pa}_2\text{O}(\text{NO}_3)_8$ or to furnish any reproducible indication of stable nitrates intermediate between the starting compounds and protactinium pentoxide.

EXPERIMENTAL

Protactinium was handled in glove-boxes on account of the radioactive hazards associated with weighable amounts of protactinium-231, the isotope used. Preparations involved approximately 100 mg. of ^{231}Pa and the moisture-sensitive compounds were handled in a dry-atmosphere box after isolation. Infrared spectra were measured in the region $2\text{--}35 \mu$ for mulls in Nujol using a Hilger H800 spectrometer with sodium chloride and caesium bromide optics. Samples were mounted between silver chloride or polythene plates and mulls in hexachlorobutadiene were examined between 6 and 8μ , the region where ionic

nitrate vibrations are masked by absorption due to Nujol. X-Ray powder photographs were taken with the samples mounted in thin-walled Pyrex capillaries using a Debye-Scherrer 19 cm. camera and filtered $\text{Cu-K}\alpha$ radiation ($\lambda = 1.54051 \text{ \AA}$). Thermogravimetric measurements were performed with a conventional quartz-fibre thermobalance described previously;¹⁵ the temperature was increased at $0.6^\circ/\text{min.}$ A dry-box was erected around the lower part of the instrument to facilitate the mounting of the radioactive samples and to afford protection from atmospheric moisture during this operation.

Analyses.—Protactinium, niobium, and tantalum were weighed as the oxide, M_2O_5 , after ignition of the hydroxide obtained by treatment of the compounds with aqueous ammonia, or after ignition of the compounds themselves, in air at 750° . Nitrate was weighed^{16a} as nitron nitrate which was formed in acid solution after removal of the protactinium, niobium, or tantalum as hydroxide. Chloride was determined by titration against standard silver nitrate solution and water was determined^{16b} by the Karl Fischer method.

Materials.—The protactinium-231 was part of the batch recently isolated from ethereal sludge residues.² Frequent purifications were carried out in order to recover and re-use the available material; these involved bisulphate fusion to solubilise intractable residues, solvent extraction from hydrochloric acid and sulphuric-hydrochloric acid mixture by di-isobutyl ketone and di-isobutyl carbinol respectively and removal of niobium as described previously.¹⁷ Protactinium pentachloride^{10,18} and pentabromide¹⁹ and the hexachloroprotactinates(v)¹⁸ were prepared as described elsewhere. Protactinium(v) hydroxide was precipitated from 0.5M -hydrofluoric acid and washed with 0.5 or 4M -nitric acid to remove occluded fluoride and ammonium ion and finally vacuum-dried at room temperature after being washed with acetone. AnalaR fuming nitric acid was used as delivered; dinitrogen pentoxide and tetroxide were prepared and used as described previously.⁴ Methylene dichloride and methyl cyanide were dried as described elsewhere⁴ and stored in contact with molecular sieves.

Protactinium Oxynitrates.—Protactinium pentachloride or pentabromide ($0.1\text{--}0.15 \text{ g.}$) were dissolved in fuming nitric acid (3 ml.) and vacuum evaporation of the resulting solutions deposited the *nitrate* $\text{PaO}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ [Found, for the product containing the least water: Pa, 50.3 ; NO_3^- , 41.4 ; H_2O , 6.0 . $\text{PaO}(\text{NO}_3)_3 \cdot 1.5\text{H}_2\text{O}$ requires Pa, 50.2 ; NO_3^- , 40.44 ; H_2O , 5.86%]. Protactinium pentachloride or pentabromide (0.15 g.) was dissolved in anhydrous methyl cyanide and dinitrogen tetroxide gas bubbled through the solution for 10 min. Vacuum evaporation of the clear solution gave initially an oil which on prolonged pumping and occasional grinding was converted into a white *solid* [Found: Pa, 43.1 ; NO_3^- , 45.9 . $\text{Pa}_2\text{O}(\text{NO}_3)_8 \cdot 2\text{MeCN}$ requires Pa, 43.75% ; NO_3^- , 46.96%].

Hexanitratoprotactinates(v).—Caesium, tetramethylammonium, or tetraethylammonium hexachloroprotactinate(v) (0.015 g.) was dissolved in liquid dinitrogen pentoxide and the white *hexanitrate-complexes* were obtained by

¹¹ R. A. Marcus and J. M. Fresco, *J. Chem. Phys.*, 1958, **27**, 564.
¹² J. C. Evans, H. W. Rinn, S. J. Kuhl, and G. A. Olah, *Inorg. Chem.*, 1964, **3**, 857.

¹³ J. Lewis, R. J. Irving, and G. Wilkinson, *J. Inorg. Nuclear Chem.*, 1958, **7**, 32.

¹⁴ C. C. Addison, personal communication.

¹⁵ K. W. Bagnall, A. M. Deane, T. L. Markin, P. S. Robinson, and M. A. A. Stewart, *J. Chem. Soc.*, 1961, 1611.

¹⁶ A. I. Vogel, "A Textbook of Quantitative Inorganic Analysis," 2nd edn., Longmans, London, 1951, (a) p. 505; (b) p. 701.

¹⁷ D. Brown and P. J. Jones, *J. Inorg. Nuclear Chem.*, 1964, **26**, 2296.

¹⁸ K. W. Bagnall and D. Brown, *J. Chem. Soc.*, 1964, 3021.

¹⁹ D. Brown and P. J. Jones, *J. Chem. Soc. (A)*, 1966, 262.

removal of excess of solvent *in vacuo*. Alternatively, an equimolar mixture of $\text{SO}[\text{PaCl}_6]_2$ and the appropriate chloride were treated as above [Found: Pa, 30.4; NO_3^- , 51.0. $\text{CsPa}(\text{NO}_3)_6$ requires Pa, 31.4; NO_3^- , 50.55. Found: Pa, 34.26; NO_3^- , 55.0. $\text{NMe}_4\text{Pa}(\text{NO}_3)_6$ requires Pa, 34.1; NO_3^- , 55.0. Found: Pa, 30.7; NO_3^- , 51.7. $\text{NEt}_4\text{Pa}(\text{NO}_3)_6$ requires Pa, 31.5; NO_3^- , 50.7%]. Protactinium(v) hydroxide, $\text{SO}[\text{PaCl}_6]_2$, or the pentahalides treated in the above manner all gave *hydrogen hexanitratoprotactinate(v)* [Found: Pa, 37.85; NO_3^- , 62.0. $\text{HPa}(\text{NO}_3)_6$ requires Pa, 38.3; NO_3^- , 61.6%].

Tetramethylammonium Oxytetranitrato-niobate(v) and -tantalate(v).—These complexes were prepared in the same

way as the hexanitratoprotactinates(v). [Found: Nb, 21.9; NO_3^- , 57.8. $\text{NMe}_4\text{NbO}(\text{NO}_3)$ requires Nb, 21.60; NO_3^- , 57.55. Found: Ta, 34.80; NO_3^- , 47.2. $\text{NMe}_4\text{TaO}(\text{NO}_3)$ requires Ta, 34.85; NO_3^- , 47.8%]. The niobium(v) complex was also obtained by passing dinitrogen tetroxide through a methyl cyanide solution of $\text{NMe}_4\text{NbCl}_6$. The complex, which was soluble in methyl cyanide and liquid dinitrogen pentoxide, separated on vacuum evaporation of the solvent.

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