516. *Neptunium and Plutonium Trioxide Hydrates.*

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Neptunium trioxide di- and mono-hydrates, $NpO_3,2H_2O$ and NpO_3,H_2O, have been prepared by ozone oxidation of aqueous suspensions of neptunium(v) hydroxide at 18 and 90°, respectively; thermal decomposition of the mono-hydrate above 300° yielded the black pentoxide, Np_2O_5. Oxidation of plutonium(IV) hydroxide under the same conditions yielded $PuO_3,0.8H_2O$; uranium(IV) hydroxide and U_3O_8 behave in a similar manner, both yielding $UO_3,0.8H_2O$.

UNTIL recently the highest recorded oxides of neptunium and plutonium [1] were Np_3O_8 and PuO_2; a trioxide hydrate, $NpO_3,2H_2O$, has now been reported [2] to be formed by the ozone oxidation of neptunium(v) in a molten lithium–potassium nitrate eutectic at 150°, the precipitated product being washed with water. At times, however, the reaction yielded a brown neptunium(v) oxide, whereas in molten lithium perchlorate at 260° the neptunium(v) oxide was said to be the more common product; indeed, the trioxide di-hydrate was formed on only one occasion. However, polyneptunates and polyplutonates also appear to be formed in such media,[3] and the formation of plutonates has occurred by the oxidation of PuO_2 with atmospheric oxygen,[4] and the reaction of PuO_2 with alkaline-earth oxides.[5] Since neptunium(v) and plutonium(IV) hydroxides have a very small, though measurable, solubility in water, it seemed worthwhile to examine their behaviour with ozone in aqueous media.

The ozone oxidation of neptunium(v) hydroxide ($\sim$1 g. scale) suspended in water is slow at 90°; the colour changes from grey-green to chocolate brown after about ten hours, and becomes reddish brown after twenty hours. The final product, of composition NpO_3,H_2O, is sufficiently stable to be dried in an air-oven at 100—105°; the intermediate product appears to be a mixture of the dihydrate with some monohydrate, a mixture which can also be obtained by prolonged ozonisation at room temperature.

A solution of the monohydrate in 1M-perchloric acid gave only the spectrum of neptunium(VI), that of neptunium(v) (980 and 620 mμ) and neptunium(IV) (960 and 720 mμ) being completely absent. The infrared spectrum of the monohydrates shows the OH stretching frequency at 3370 cm.$^{-1}$, and other peaks at 969, 940, 893, and 845 cm.$^{-1}$, but no free-water vibrations were present (1626 cm.$^{-1}$). The spectrum is closely similar to that for UO_3,H_2O,[6] and indicates that the compound is more correctly formulated as $NpO_2(OH)_2$. Its X-ray powder photograph showed it to be isostructural with the orthorhombic II form [7] of UO_3,H_2O. The thermal decomposition of the monohydrate under a vacuum is shown in the Figure, from which it can be seen that there is no evidence for the anhydrous trioxide; the first decomposition product (300°), a black solid, has the composition Np_2O_5. This is stable up to 420° and easily isolated; its solution in 1M-perchloric acid gives only the spectrum of neptunium(v), and the addition of sodium nitrite [to reduce any neptunium(VI) present] did not materially affect the intensity of the neptunium(v) peaks as would be expected if the material were Np_3O_8. The infrared spectrum resembled that of α-U_3O_8, with only a broad band from about 850 to at least 600 cm.$^{-1}$. X-Ray powder photographs showed a structure similar to, but not identical with, Np_3O_8.[8]

[1] Katz and Seaborg, " The Chemistry of the Actinides," Methuen, London, 1957, pp. 216 and 281.
[2] Cohen, *Inorg. Chem.*, 1963, **2**, 866.
[3] Carnall, Transplutonium Element Symposium, Argonne National Laboratory, May 1963.
[4] Zastenker, Bedina, Nikolsky, and Pojarskaya, *Radiokhimiya*, 1963, **5**, 141.
[5] Keller, *Nukleonik*, 1962, **4** (No. 7), 271.
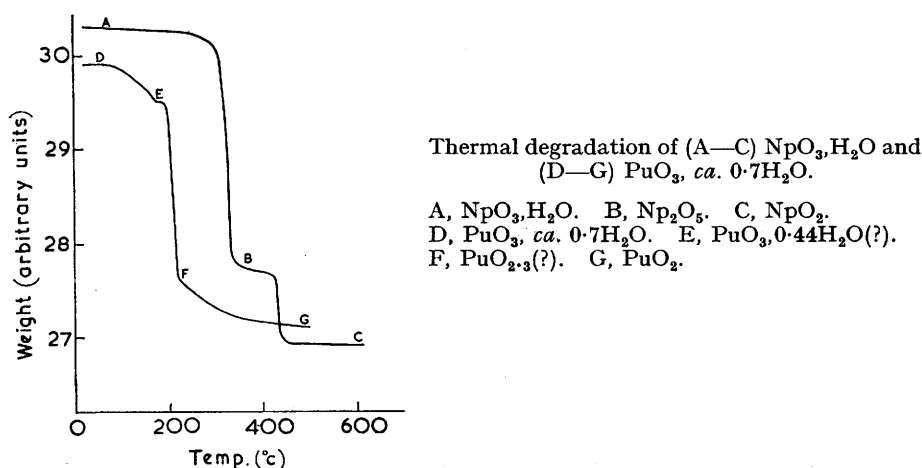[6] Deane, *J. Inorg. Nuclear Chem.*, 1961, **21**, 238.
[7] Dawson, Wait, Alcock, and Chilton, A.E.R.E., unclassified report C/R 1703 (1955).
[8] Roberts and Walter, A.E.R.E., unclassified report R 3624 (1963).

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Ozone oxidation of plutonium(IV) hydroxide (150 mg. scale) for eight hours in water at 90°, yielded reddish gold spangles which had the composition $PuO_3,0\cdot8H_2O$ after vacuum-drying at 130°. The absorption spectrum in 1M-nitric acid showed only the peaks due to sexivalent plutonium (465, 520, 830, and 950 mμ). In the infrared spectrum the OH stretching frequency appeared at 3385 cm.$^{-1}$, with other peaks at 946 and 895 cm.$^{-1}$ and a broad band between 824 and 802 cm.$^{-1}$. On standing in air, the compound took up water until it reached the composition PuO_3,H_2O, and the infrared spectrum then showed the H–O–H bending frequency at 1626 cm.$^{-1}$. The absorbed water could be removed by vacuum-drying at 130°. X-Ray powder photographs showed that the compound is not isostructural with any of the known uranium trioxide hydrates. The Figure shows that thermal decomposition of the compound in a vacuum begins above 200°; there were also breaks in the curve at the approximate compositions, $PuO_3,0\cdot44H_2O$ and $PuO_{2\cdot3}$, but these may be fortuitous since intermediate compounds could not be isolated.

An analogous oxidation of uranium(IV) hydroxide (250 mg. scale) yielded, in one hour, or more slowly with triuranium octaoxide, the yellow $UO_3,0\cdot8H_2O$, shown by its X-ray powder photograph to be the orthorhombic I form.[7] The infrared spectrum was identical with that [6] for $UO_3,0\cdot8H_2O$ apart from a small peak at 1624 cm.$^{-1}$ due to a trace of free water.

X-*Ray Results.*—The observed $\sin^2\theta$ values for neptunium trioxide monohydrate can

Thermal degradation of (A—C) NpO_3,H_2O and
(D—G) PuO_3, *ca.* $0\cdot7H_2O$.

A, NpO_3,H_2O. B, Np_2O_5. C, NpO_2.
D, PuO_3, *ca.* $0\cdot7H_2O$. E, $PuO_3,0\cdot44H_2O(?)$.
F, $PuO_{2\cdot3}(?)$. G, PuO_2.

be indexed on the basis of an orthorhombic cell with $a = 5\cdot607$, $b = 6\cdot270$, and $c = 9\cdot956$ Å. The agreement between the observed and calculated $\sin^2\theta$ values is good (Table 1). The space group is *Pbca*, with the neptunium atoms in a set of four-fold positions on a face-centred lattice.[7] The weak reflections, (210), (211), (122), (104), and (027), which do not satisfy the conditions $(h + k) = (k + l) = (h + l) = 2n$, are entirely due to oxygen-scattering. The calculated cell volume is 350 Å,^{3} compatible with four molecules per unit cell, giving a calculated density of 5·74 g./cc.

Although the X-ray powder photographs of the neptunium trioxide dihydrate were of poor quality, they were sufficiently clear to leave no doubt about their similarity to those of uranium trioxide dihydrate.

The observed $\sin^2\theta$ values for Np_2O_5 may be compared with those from Np_3O_8 [8] and the recently reported neptunium(V) oxide (Table 2).

Difficulty was experienced in obtaining well-crystalline specimens of plutonium trioxide hydrate for X-ray powder photography; the observed lines (Table 3) could not be indexed on any simple system.

TABLE 1.

X-Ray data for NpO_3,H_2O.

(hkl)	$\sin^2\theta$ (obs.)	$\sin^2\theta$ (calc.)	I (obs.)	(hkl)	$\sin^2\theta$ (obs.)	$\sin^2\theta$ (calc.)	I (obs.)
002	0·0239	0·0239	m	311	0·1909	0·1909	m
111	0·0400	0·0400	vs	133	0·2085	0·2086	m
020	0·0603	0·0604	s	224	0·2318	0·2316	m
200	0·0755	0·0755	m	313	0·2388	0·2388	m
022	0·0842	0·0843	m	040	0·2415	0·2415	m
113	0·0878	0·0878	m	042	0·2655	0·2654	w
210	0·0906	0·0906	vw	026	0·2756	0·2758	w
004	0·0959	0·0958	w	206	0·2906	0·2910	w
211	0·0966	0·0966	vw	135	0·3046	0·3043	w
202	0·0993	0·0994	m	331	0·3116	0·3117	m
122	0·1029	0·1032	w	240	0·3167	0·3170	w
104	0·1146	0·1146	vw	402	0·3264	0·3259	w
220	0·1357	0·1359	m	315	0·3346	0·3346	vw
024	0·1562	0·1561	w	242	0·3407	0·3409	m
222	0·1598	0·1598	s	226	0·3513	0·3513	w
131	0·1606	0·1607	s	027	0·3539	0·3537	w
204	0·1712	0·1713	w	422	0·3861	0·3863	m
115	0·1837	0·1836	w	151	0·4024	0·4022	m

TABLE 2.

X-Ray data for Np_2O_5, Np_3O_8 [8], $Np(v)$ oxide [2]

$\sin^2\theta$ (obs.)	I (obs.)	(hkl)	$\sin^2\theta$	$\sin^2\theta$
0·0340	s	001	0·0339	—
0·0492	vs	110	0·0492	0·0489
0·0548	s	200	0·0547	0·0543
0·0832	s *	111	0·0831	0·0828
0·0888	m	201	0·0887	0·0882
0·1362	w	002	0·1357	—
0·1427	w	020	0·1422	0·1414
0·1590	m	310	0·1587	0·1579
0·1764	w *	021	0·1760	—
0·1850	w *	112	0·1849	—
0·1909	m	202	0·1904	—
0·1929	w	311	0·1926	0·2178
0·1976	w	220	0·1969	0·3318

TABLE 3.

X-Ray data for $PuO_3,0.8H_2O$

$\sin^2\theta$ (obs.)	I (obs.)	$\sin^2\theta$ (obs.)	I (obs.)
0·0219	vw	0·1352	m
0·0256	w	0·1501	m
0·0488	vs	0·1840	m
0·0522	s *	0·1955	m
0·0559	w	0·0246	w
0·0886	w	0·3092	w
0·0947	w	0·3225	vw
0·1070	vw	0·3325	vw
0·1141	vw	0·3460	w

* Diffuse lines.

EXPERIMENTAL

Infrared spectra, for mulls in Fluorube or Nujol, were measured on a Hilger H800 spectrophotometer with sodium chloride and cæsium bromide prisms. Other absorption spectra were observed on an Optika CF4/DR recording spectrophotometer and a Unicam S.P. 500 instrument. X-ray power photographs were taken with a 19-cm. Unicam Debye–Scherrer camera and with a Guinier focusing camera, with Cu K_α radiation.

Preparative.—Neptunium trioxide hydrates. A solution of neptunium(v) was prepared by evaporating a stock solution of neptunium-(IV) and -(V) with concentrated nitric acid, diluting this until ~1M in nitric acid, and adding a few milligrams of sodium nitrite to reduce any neptunium(VI). Neptunium(v) hydroxide was precipitated with aqueous ammonia, washed once with water, and redissolved in 1M-nitric acid; the silica was separated by centrifugation, and the hydroxide re-precipitated from the supernatant liquid as before. It was washed repeatedly with water to remove adsorbed ammonia until peptisation occurred. Ozonised oxygen was bubbled through the suspension, at room temperature for the dihydrate and at 90° for the monohydrate, until the colour had changed from grey-green [neptunium(v)] to dark chocolate brown (dihydrate) or reddish brown (monohydrate). On the 1 g. scale, the oxidation to the monohydrate requires about 20 hr. at 90°. The *products* were separated from the colourless, neptunium free, supernatant liquid by centrifugation, and either vacuum-dried (both hydrates) or dried in an air-oven at 100—105° (monohydrate) (Found: Np, 77·9. NpO_3,H_2O requires Np, 78·3%).

Neptunium pentoxide. This *product* was prepared by heating the trioxide monohydrate at 330° under a vacuum until gas ceased to be evolved (Found: Np, 85·5. Np_2O_5 requires Np, 85·6%).

Plutonium trioxide hydrate. A stock solution of plutonium (99·3% [239]Pu) in dilute nitric acid was treated with hydrazine to reduce the plutonium to the tervalent state, and the hydroxide (mauve), which was precipitated with aqueous ammonia, rapidly oxidised to the green quadrivalent hydroxide in a finely divided form, which was washed, as for neptunium, until peptisation occurred. Ozonised oxygen was bubbled through the aqueous suspension at 90° until the colour changed to reddish gold. The supernatant liquid always contained some soluble plutonium(VI) species, but the trioxide hydrate did not dissolve at all on continued washing with water. The *solid* was vacuum-dried at 130° (Found: Pu, 78·7. $PuO_3,0·8H_2O$ requires Pu, 79·1%).

Uranium trioxide hydrate ($UO_3,0·8H_2O$). Freshly precipitated, well-washed uranium(IV) hydroxide, or a suspension in water of fired triuranium octaoxide, was treated as above. The yellow product was dried in an air-oven at 100—105° (Found: U, 79·0. $UO_3,0·8H_2O$ requires U, 79·2%).

Analysis.—Neptunium and plutonium were determined by α-counting aliquots taken from a solution containing a known weight of sample in dilute nitric acid. Both elements were also weighed as dioxides after ignition in air to 700°. Uranium was weighed as triuranium octaoxide after similar ignition. Oxygen determinations were attempted by a carbon monoxide reduction, and estimation of the carbon dioxide produced, but the small amount of water present interfered with the analyses. Water itself could not be detected by the Karl Fischer method in the uranium trioxide hydrate, indicating that the compound should be formulated as a uranyl hydroxide. Insufficient material was available for a water determination on the neptunium and plutonium trioxide hydrates.

Radioactive Handling.—Neptunium, on account of its long half-life ($2·2 \times 10^6$ years), can be handled safely in a fume cupboard, but all plutonium work had to be carried out in a glove-box in order to minimise activity hazards.