Actinide Structural Studies. Part 2.[1] Crystal and Molecular Structures of Rubidium Tris(nitrato)dioxoneptunate(1−) and Sodium Tris(acetato)dioxoneptunate(1−)

By **Nathaniel W. Alcock** * and **Michael M. Roberts**, Department of Chemistry and Molecular Sciences, University of Warwick, Coventry CV4 7AL
David Brown, Building 220, Chemistry Division, A.E.R.E. Harwell, Didcot, Oxfordshire OX11 0RA

The crystal structures of the title complexes, $Rb[NpO_2(NO_3)_3]$ (1) and $Na[NpO_2(O_2CMe)_3]$ (3), have been determined using *X*-ray diffraction methods. Complex (1) is hexagonal, space group $R\bar{3}c$, with hexagonal-bipyramidal co-ordination about the neptunium atom due to three bidentate nitrate groups. Complex (3) is cubic, space group $P2_13$, with hexagonal-bipyramidal co-ordination of three bidentate acetate groups to the neptunium atom. The neptunium–ligand oxygen distances in (1) and (3) fall in the range 2.46—2.47 Å and in the NpO_2^{2+} group are 1.731(18) Å in (1) and 1.765(7) and 1.786(7) Å in (3). Lattice parameters are: for (1), a = 9.281(2), c = 19.033(4) Å, and Z = 6; for (3), a = 10.638(4) Å and Z = 4. The structures have been refined to R values of (1) 0.067 and (3) 0.046 using, respectively, 305 and 632 observed diffractometer-measured intensities.

THE crystal structures of $Rb[NpO_2(NO_3)_3]$ (1) and $Na[NpO_2(O_2CMe)_3]$ (3) have been determined as part of a study of actinide co-ordination. The lattice parameters of (3) have previously been reported,[2] and the structures of the uranyl(VI) analogues of (1) and (3), $Rb[UO_2(NO_3)_3]$ (2) and $Na[UO_2(O_2CMe)_3]$ (4), have been published.[3,4]

EXPERIMENTAL

Preparation.—Compound (1) was prepared by the addition of rubidium nitrate (18 mmol) to freshly ozonised neptunyl(VI) nitrate [5] (5 mmol) in moderately concentrated nitric acid. Suitable crystals were obtained by evaporation of the resulting solution. Crystals of (3) were grown from an aqueous acetic acid solution containing Np^{VI} (5 mmol) and sodium acetate (5 mmol). Good quality crystals of (1) and (3) were selected, mounted on quartz fibres, and enclosed in Lindemann glass capillaries. These operations were performed in a glove-box to provide protection from the α-active ^{237}Np. For crystal data see Table 1. Mo-K_α radiation (λ = 0.710 69 Å) was used throughout.

Data Collection and Structural Refinement.—Reflection data were collected using a Syntex $P2_1$ automatic four-circle diffractometer. For the study of (1), a crystal of dimensions 0.20 × 0.20 × 0.05 mm was used, which gave transmission factors in the range 0.234—0.497. Accurate cell constants were derived from least-squares calculations based on the positions of 15 reflections. The θ—2θ scan technique was used, at rates varying from 1.0 to 29.3° min^{-1}, depending on the intensity of a 2-s pre-scan. The scan range about both the $K_{\alpha1}$ and $K_{\alpha2}$ positions was ±0.8°. Three standard reflections monitored every 100 reflections showed no appreciable decrease in intensity. Of the 545 reflections collected in the range $3 \leqslant 2\theta \leqslant 60°$, 305 were considered observed $[I/\sigma(I) \geqslant 3.0]$ and used in the refinement.

The systematic absences $hkil(-h + k + l \neq 3n)$ and $h\bar{h}0l$ $(l = 2n)$ indicated the space group $R\bar{3}c$ as for (2); the alternative $R3c$ was not examined. Atom positions were based on those for the corresponding uranium analogue.[3] Anisotropic temperature factors were used for the atoms in successive cycles of least-squares refinement, and a correction for isotropic extinction was made. The weighting scheme $W = X{\cdot}Y$ was applied, where X = 1.0 or (sinθ)/0.3 if sinθ ⩽ 0.3 and Y = 1.0 or $220.0/F_o$ if $F_o \geqslant 220.0$. The final R value was 0.067. The difference-Fourier map showed residual peaks of height ⩽ 2 e Å^{-3} close to Np and ⩽ 1.5 e Å^{-3} elsewhere.

Compound (3) was studied using the LT-1 low-temperature device (−120 °C). The crystal had dimensions 0.15 × 0.18 × 0.33 mm, bounded by faces $[\bar{1}\bar{1}1]$, $[1\bar{1}\bar{1}]$, $[\bar{1}\bar{1}\bar{1}]$, $[0\bar{1}\bar{1}]$, $[011]$, and $[\bar{1}1\bar{1}]$. It gave transmission factors between 0.355 and 0.423. Accurate lattice parameters were obtained from least-squares refinement of the positions of 15 reflections. The scan range used (2θ) about the $K_{\alpha1}$ and $K_{\alpha2}$ positions during the data collection was ±1.2°. The θ—2θ scan technique was used, at rates varying from 2.0 to 29.3° min^{-1}, depending on the intensity of a 2-s pre-scan. The four check reflections monitored at intervals of every 100 reflections showed no significant change in intensity. A total of 1 111 reflections were collected in the range $0 \leqslant 2\theta \leqslant 60°$. Of these, 632 were considered observed $[I/\sigma(I) \geqslant 3.0]$ and used in the refinement.

TABLE 1

Compound	(1) [a]	(2) [b]	(3) [a]	(4) [c]
Formula	$N_3NpO_{11}Rb$	$N_3O_{11}RbU$	$C_6H_9NaNpO_8$	$C_6H_9NaO_8U$
M	540.5	539.5	469.2	468.2
System	Hexagonal	Hexagonal	Cubic	Cubic
Temp., θ_c/°C	16	Room temperature	−120	Room temperature
Space group	$R\bar{3}c$	$R\bar{3}c$	$P2_13$	$P2_13$
a/Å	9.281(2)	9.36(3)	10.638(4)	10.688(2)
c/Å	19.033(4)	18.88(6)		
Z	6	6	4	4
U/Å^3	1 419.8(8)	1 432.5 [d]	1 204.0(8)	1 220.9 [d]
D_c/g cm^{-3}	3.79	3.75	2.59	2.55
μ(Mo-K_α)/cm^{-1}	121.51	Uncorrected	56.62	470 [e]

[a] This work. [b] Ref. 2. [c] Ref. 3. [d] Standard deviations not quoted. [e] With Cu-K_α radiation.

The systematic absences in the $0k0$ ($k \neq 2n$) reflections were compatible with the space group $P2_13$ of the uranium analogue. An attempt to refine the structure based on the atomic positions of $Na[UO_2(O_2CMe)_3]$ was unsuccessful. The neptunium atoms were therefore located from Patterson maps using the heavy-atom technique. The remaining lighter atoms were found through the calculation of successive difference-Fourier maps. The cause of the original difficulty was then seen to lie in a shift of $(-\frac{1}{4}, -\frac{1}{4}, -\frac{1}{4})$ of the co-ordinates of (3) relative to those of (4). This is equivalent to the crystal being of opposite chirality to the specimen of (4) originally studied. (This explanation of the discrepancy was pointed out to us by a referee.)

The weighting scheme $w = X \cdot Y$ was applied, where $X = 1.0$ or $(\sin\theta)/0.27$ for $\sin\theta \leqslant 0.27$ and $Y = 1.0$ or $58.0/F_o$ for $F_o \geqslant 58.0$. Least-squares refinement gave a final R value of 0.046 using anisotropic temperature factors. Refinement of an extinction parameter did not improve R and this was therefore not applied. The final difference-Fourier map showed ripples of 3 e Å^{-3} around the neptunium atom, and peaks $\leqslant 0.7$ e Å^{-3} elsewhere. Some of these were close to the methyl carbons and are possibly due to hydrogen atoms. However, they were not clear enough to be included in the refinement.

For both structures, Lorentz, polarisation, and absorption corrections were applied, the last using the program ABSCOR.[6] The scattering factors used [7] were corrected for anomalous dispersion.[8] Computing was carried out using '*X*-RAY '76' package programs on a B6700 computer.[9] Table 2 lists the final atomic co-ordinates. The observed and calculated structure factors and thermal parameters may be found in Supplementary Publication No. SUP 23171 (11 pp.).*

TABLE 2

Atomic co-ordinates ($\times 10^4$) with standard deviations in parentheses

(*a*) For $Rb[NpO_2(NO_3)_3]$

Atom	*x*	*y*	*z*
Np	0	0	2 500
O(1)	0	0	3 410(9)
O(2)	−4 426(23)	0	2 500
O(3)	−1 729(18)	1 332(18)	2 552(7)
N(1)	−3 134(26)	0	2 500
Rb	0	0	0

(*b*) For $Na[NpO_2(O_2CMe)_3]$

Atom	*x*	*y*	*z*
Np	1 793.5(5)	1 793.5	1 793.5
O(1)	2 752(11)	2 752	2 752
O(2)	824(11)	824	824
O(3)	2 978(11)	2 500(12)	−59(11)
O(4)	3 609(11)	441(13)	1 340(12)
Na	5 775(5)	5 775	5 775
C(1)	3 425(15)	−266(16)	2 281(16)
C(2)	4 324(19)	−1 314(19)	2 579(22)

DISCUSSION

Both rubidium tris(nitrato)dioxoneptunate(1−) (1) and sodium tris(acetato)dioxoneptunate(1−) (3) are isomorphous and isostructural with their uranium analogues (2) and (4), respectively. In each the configuration about the metal atom is a distorted hexagonal bipyramid, with the acetate and nitrate groups coordinating as bidentate ligands (Figures 1 and 2).

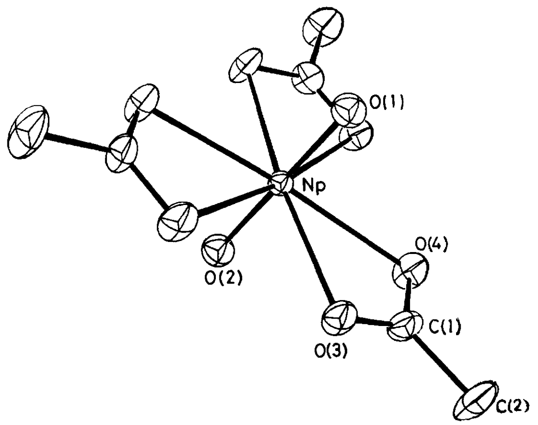

FIGURE 1 The $[NpO_2(O_2CMe)_3]^-$ anion, showing the atomic numbering

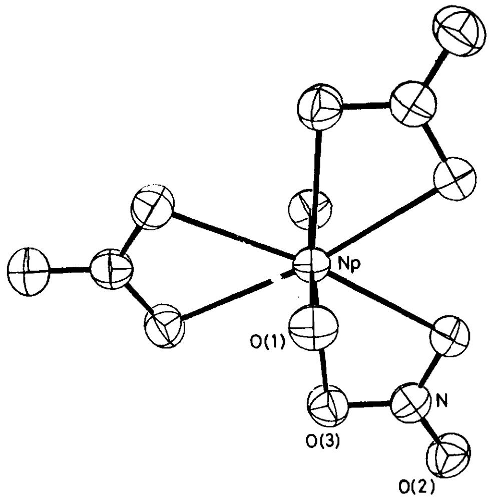

FIGURE 2 The $[NpO_2(NO_3)_3]^-$ anion, showing the atomic numbering

TABLE 3

Bond lengths (Å) and angles (°) for $Rb[NpO_2(NO_3)_3]$ with standard deviations in parentheses

(*a*) Bond lengths			
(*i*) Around neptunium			
Np–O(1)	1.731(18)	Np–O(3)	2.469(25)
(*ii*) Nitrate groups			
N(1)–O(3)	1.276(17)	N(1)–O(2)	1.199(32)
(*b*) Bond angles			
(*i*) Around neptunium			
O(1)–Np–O(3)	87.7(3), 92.3(3)	O(3)–Np–O(3)	68.7(6), 51.6(6)
O(1)–Np–O(1)	180.0(0)		
(*ii*) Nitrate groups			
O(2)–N(1)–O(3)	122.5(13)		
O(3)–N(1)–O(3)	114.9(24)		
(*c*) Rubidium(1+)–oxygen contact distances (Å)			
Rb ··· O(1)	3.027(18)		
Rb ··· O(2)	3.159(22)		
Rb ··· O(3)	3.262(27)		

The NpO_2^{2+} ion contains a longer Np–O bond in (3) than in (1) (Tables 3 and 4). Also, in the equatorial

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

TABLE 4

Bond lengths (Å) and angles (°) for $Na[NpO_2(O_2CMe)_3]$ with standard deviations in parentheses

(*a*) Bond lengths			
(*i*) Around neptunium			
Np–O(1)	1.765(7)	Np–O(2)	1.786(7)
Np–O(3)	2.457(12)	Np–O(4)	2.456(12)
(*ii*) Acetate groups			
C(1)–O(3)	1.252(20)	C(1)–O(4)	1.267(21)
C(1)–C(2)	1.503(26)		
(*b*) Bond angles			
(*i*) Around neptunium			
O(1)–Np–O(2)	180.0	O(2)–Np–O(3)	90.5(3)
O(1)–Np–O(3)	89.5(3)	O(2)–Np–O(4)	90.1(3)
O(1)–Np–O(4)	89.9(4)	O(3)–Np–O(4)	67.6(4), 52.4(4)
(*ii*) Acetate groups			
O(4)–C(1)–C(2)	120.6(16)	C(2)–C(1)–O(3)	120.4(16)
O(4)–C(1)–O(3)	119.0(15)		
(*c*) Sodium(1+)-oxygen contact distances (Å)			
Na · · · O(3)	2.388(13)		
Na · · · O(4)	2.371(12)		

TABLE 5

Comparison of bond lengths and contact distances

	(1) [a]	(2) [b]	(3) [a]	(4) [c]	(5) [d]	(6) [e]
	$Rb[NpO_2(NO_3)_3]$	$Rb[UO_2(NO_3)_3]$	$Na[NpO_2(O_2CMe)_3]$	$Na[UO_2(O_2CMe)_3]$	$Cs_2[NpO_2(O_2CMe)_3]$	$Ba[NpO_2(O_2CMe)_3]\cdot 2H_2O$
M–O (MO_2^{n+}) ($n = 1$ or 2)	1.731(18)	1.78(1)	1.765(7), 1.786(7)	1.70(4), 1.72(4)	1.834(5)	1.85(2)
M–O (ligand)	2.469(25)	2.48(1)	2.457(12), 2.456(12)	2.47(2), 2.51(2)	2.56—2.67	2.52—2.56
Rb · · · O(1)	3.027(18)	2.94(1)				
Rb · · · O(2)	3.159(22)	3.18(1)				
Rb · · · O(3)	3.262(27)	3.29(1)				
Na · · · O(3)			2.388(13)	2.39(4)		
Na · · · O(4)			2.371(12)	2.36(4)		
O · · · O (same acetate)			2.171(17)	2.21(5)	2.187(6), 2.189(6)	2.17(2), 2.19(3)
O · · · O (adjacent acetates)			2.732(18)	2.76(5)	2.859(6), 2.961(7)	2.85(2), 2.98(3)
O · · · O (same nitrate)	2.151(21)	2.16(1)				
O · · · O (adjacent nitrates)	2.786(20)	2.79(1)				

[a] This work. [b] Ref. 2. [c] Ref. 3. [d] Ref. 11. [e] Ref. 12.

planes of (1) and (3), the acetate groups bond more closely to neptunium than do the nitrate groups. The differences in each case are small but consistent, although they are only marginally significant statistically. Such a lengthening of the actinyl(VI) M–O distances as the equatorial M–O distance decreases has been noted previously for uranyl(VI) complexes.[10]

Comparison of (1) and (3) with their uranium analogues shows inconsistencies in the MO_2^{2+} group: in the $Rb[MO_2(NO_3)_3]$ species, U–O (UO_2^{2+}) is longer than Np–O (NpO_2^{2+}), yet in the $Na[MO_2(O_2CMe)_3]$ species, Np–O is apparently longer. However, this is probably not a genuine effect, in view of the relatively large estimated standard deviations for (4). The overall contraction between (1) and (2) of 0.049 Å is larger than observed in our previous work (0.025 Å average),[1] but the difference is not statistically reliable. The equatorial shrinkages are 0.011 Å for $Rb[MO_2(NO_3)_3]$, and 0.013—0.054 Å for the $Na[MO_2(O_2CMe)_3]$ complexes. The smaller value with nitrate complexing has been noticed previously,[1] and may be due to the greater interligand repulsion in these complexes.

A substantial lengthening of both the equatorial and axial Np–O bonds occurs when Np^{VI} is replaced by Np^{V}, as in $Cs_2[NpO_2(O_2CMe)_3]$ [11] (5) and $Ba[NpO_2(O_2CMe)_3]\cdot 2H_2O$ (6),[12] which contain the NpO_2^+ cation (Table 5). Compared to (3), the changes in bond length are 0.05—0.11 and 0.05—0.12 Å for the equatorial and axial directions respectively.

The uniformity of this enlargement indicates that the extra *f* electron is in a non-bonding orbital, which may be that along the axis of the bond (δ_u) proposed by Burns and Musikas.[12] The overall enlargement can then be seen as a consequence of the general reduction in electrostatic attraction following the replacement of NpO_2^{2+} by NpO_2^+.

The environment of the alkali-metal cations and the packing has been discussed in earlier papers for (2) and (4),[3,4] and this applies with the necessary changes to (1) and (3).

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REFERENCES

[1] Part 1, N. W. Alcock, M. M. Roberts, and D. Brown, preceding paper.

[2] W. H. Zachariasen, *Acta Crystallogr.*, 1949, **2**, 388.

[3] G. A. Barclay, T. M. Sabine, and T. C. Taylor, *Acta Crystallogr.*, 1965, **19**, 205.

[4] W. H. Zachariasen and H. A. Plettinger, *Acta Crystallogr.*, 1959, **12**, 526.

[5] J. B. Laidler, *J. Chem. Soc. A*, 1966, 780.

[6] N. W. Alcock in ' Crystallographic Computing,' ed. F. R. Ahmed, Munksgaard, Copenhagen, 1970, pp. 271—278.

[7] D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, 1968, **24**, 321.

[8] 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.

[9] J. M. Stewart, The *X*-RAY '76 System, Technical Report TR–446, Computer Science Center, University of Maryland, U.S.A., 1976.

[10] N. W. Alcock, *J. Chem. Soc., Dalton Trans.*, 1973, 1616.

[11] A. A. Lycher, L. G. Mashirov, Yu. I. Smolin, D. N. Suglobov, and Yu. F. Shepelev, *Sov. Radiochem.* (*Engl. Trans.*), 1980, **22**, 27.

[12] J. H. Burns and C. Musikas, *Inorg. Chem.*, 1977, **16**, 1619.