Actinide Structural Studies. Part 10.† A Mixed Oxidation State Neptunyl Chloride: Crystal Structure of $Cs_7[Np^{V}O_2][Np^{VI}O_2]_2Cl_{12}$‡

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The crystal structure of $Cs_7[Np^{V}O_2][Np^{VI}O_2]_2Cl_{12}$ has been determined. It is cubic, with a = 15.084(4) Å, space group $I\bar{4}3d$, and R = 0.035 for 1 674 observed $[I/\sigma(I) \geqslant 3.0]$ reflections. Only one neptunium position is found, containing two Np^{VI} and one Np^{V}, substitutionally disordered. They are octahedrally co-ordinated, with Np–O 1.790(15) and Np–Cl 2.685(5) Å, intermediate between the values for Np^{V} and Np^{VI}.

A remarkable mixed-valence neptunium compound of apparent formula $Cs_7[Np^{V}O_2][Np^{VI}O_2]_2Cl_{12}$ was reported by Melkaya *et al.*[1] It was characterised on the basis of analysis, i.r. identification of neptunyl ion absorptions, and u.v. spectra. *X*-Ray powder photography indicated a cubic unit cell. However, the unusual stoicheiometry leaves some residual doubt about the formula, particularly as an isomorphous americium compound was described as $Cs_2AmO_2Cl_4$.[2] Single crystals were prepared in conjunction with optical and i.r. studies[3] for which it was important to determine the crystal structure, both to confirm the proposed stoicheiometry, now shown conclusively to be correct, and to discover the orientation of the neptunyl groups.

Experimental

Preparation.—Crystals of $Cs_7[NpO_2]_3Cl_{12}$ were prepared by dissolving dioxoneptunium(V) hydroxide (0.25 mmol) in ethanol (3 cm^3) containing equimolar quantities of caesium chloride and hydrochloric acid (1.0 mmol). The solvent was evaporated to give a deposit of yellow-green crystals which were washed in ice-cold ethanol and air dried. The thin, plate-like crystal selected was mounted on a quartz fibre and encapsulated in a Lindemann glass capillary.

Crystallography.—*Crystal data.* $Cl_{12}Cs_7Np_3O_6$, M = 2 162.73, cubic, space group $I\bar{4}3d$, a = 15.084(4) Å, U = 3 432.3(1.5) Å^3, Z = 4, D_c = 4.18 g cm^{-3}, $F(000)$ = 3 664, Mo-K_α radiation, λ = 0.710 69 Å, μ(Mo-K_α) = 140.65 cm^{-1}.

Data collection and structural refinement. Reflections were collected with a Syntex $P2_1$ automatic four-circle diffractometer, using a crystal measuring 0.19 × 0.26 × 0.28 mm for which absorption correction by the analytical method[4] gave transmission factors in the range 0.167—0.646. The scan range used was −0.9 to +1.1°(2θ) about the K_{α_1}—K_{α_2} positions. 1 709 Reflections were collected of which 1 674 were deemed to be observed $[I/\sigma(I) \geqslant 3.0]$ and were used in the subsequent refinement. This full orthorhombic data set was merged after absorption correction to give 286 unique observed reflections (R_{merge} = 0.056). Four standards monitored every 100 reflections showed only slight decreases in intensity; the data were rescaled to correct for this. The systematic absences $h + k + l \neq 2n$ for hkl and $2h + l \neq 4n$ for hhl (cyclically permuted) allow only the space group $I\bar{4}3d$. The internal agreement (bearing in mind the very high and variable absorption) confirms the choice of Laue group, and the successful refinement as well as the systematic absences show that the space group has been chosen correctly. A Patterson synthesis located three heavy-atom peaks in the asymmetric unit in special positions 12*a*, 12*b*, and 16*c*. These peaks were initially assigned to three neptunium atoms and refinement was attempted on this basis. The refinement did not produce the expected decrease in the R factor and examination of the thermal parameters suggested that only the identification of the peak in 12*a* was correct and that the peaks in 12*b* and 16*c* corresponded to caesium atoms.

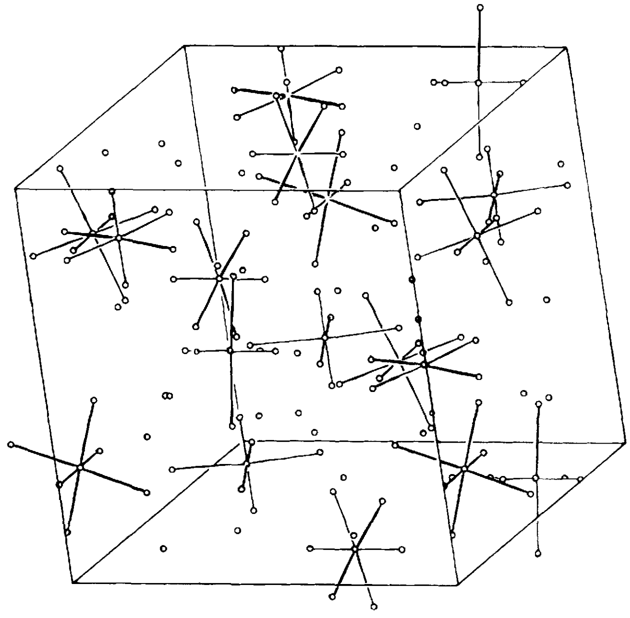

Figure 1. Oblique view of the unit cell of $Cs_7[Np^{V}O_2][Np^{VI}O_2]_2Cl_{12}$

The remaining atoms were found from Fourier syntheses and refined by least-squares methods. All co-ordinates of the neptunium atom and caesium atom (2) are fixed (special positions 12*a* and 12*b* respectively), and caesium atom (1) in special position 16*c*, co-ordinates *x*,*x*,*x*. The oxygen atom has co-ordinates *x*,0.5,0.25 (position 24*d*). The chlorine atom is in a general position. Refinement with anisotropic thermal parameters for all the atoms gave a final R value of 0.035 (for 22 parameters; maximum shift/error ratio on the final cycle 0.001). A weighting scheme of the form $w = 1/[\sigma^2(F) + gF^2]$ with g = 0.000 69 was applied and shown to be satisfactory by a weight analysis. The final Fourier difference synthesis showed ripples of

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† Part 9, N. W. Alcock, D. J. Flanders, K. W. Bagnall, and I. Ahmed, *Acta Crystallogr., Sect. C*, in the press.

‡ *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

Table 1. Atomic co-ordinates ($\times 10^4$) and anisotropic thermal parameters ($Å^2 \times 10^3$)† (with standard deviations in parentheses) for $Cs_7[Np^VO_2][Np^{VI}O_2]_2Cl_{12}$

	Co-ordinates			Thermal parameters					
Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Np	1 250	5 000	2 500	23(1)	36(1)	36(1)	0	0	0
O(1)	2 346(10)	5 000	2 500	17(6)	62(10)	78(14)	49(14)	0	0
Cl(1)	1 304(4)	5 598(3)	824(3)	80(4)	57(3)	38(2)	−3(2)	1(2)	23(3)
Cs(1)	1 020(1)	1 020(1)	1 020(1)	53(1)	53(1)	53(1)	13(1)	13(1)	13(1)
Cs(2)	8 750	5 000	7 500	40(1)	39(1)	39(1)	0	0	0

† The anisotropic thermal parameters exponent takes the form: $-2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + \cdots + 2hka^*b^*U_{12})$.

Table 2. Bond lengths (Å) and angles (°) (with standard deviations in parentheses) for the neptunyl ions in $Cs_7[Np^VO_2][Np^{VI}O_2]_2Cl_{12}$. Primed atoms are related to unprimed by a two-fold axis; double primed atoms are related to unprimed by a four-fold axis

Np–O(1)	1.790(15)	O(1)–Np–O(1′)	180.0
Np–Cl(1)	2.685(5)	O(1)–Np–Cl(1)	88.3(1)
		O(1)–Np–Cl(1″)	91.7(1)
		Cl(1)–Np–Cl(1′)	176.5(3)

0.9 e $Å^{-3}$ around the neptunium atoms and $\leqslant 1.2$ e $Å^{-3}$ near the caesium atoms. Scattering factors with anomalous dispersion corrections were taken from ref. 5. Computing was done with SHELXTL[6] on a Data General NOVA 3 computer and with X-RAY 76[7] on a Burroughs B6800 computer. The final atomic co-ordinates and thermal parameters are listed in Table 1, bond lengths and angles in Table 2. An oblique view of the cell showing the positions of the ions is given in Figure 1.

Discussion

The overall stoicheiometry is confirmed as $Cs_7[NpO_2]_3Cl_{12}$, requiring two Np^{VI} and one Np^V for electrical neutrality. It consists of Cs^+ cations and isolated $[NpO_2Cl_4]^{n-}$ anions with octahedral geometry. Since the three neptunium atoms are in the special positions 12*a* they are crystallographically identical and it is impossible to distinguish the one Np^V and the two Np^{VI}. The stabilisation of this unusual mixed-valence species can be attributed to exceptionally good packing in the high-symmetry cubic unit cell. The site symmetry of the neptunyl-(v) and -(vi) ions requires them to be linear and at right angles to the mean equatorial plane. Alternate Cl atoms are 0.080 Å above and below the mean equatorial plane, producing a mild puckering of the square plane of Cl atoms [O(1)–Np–Cl(1) 88.3(1) and Cl(1)–Np–Cl(1′) 176.5(3)°].

The Np–O bond length [1.790(15) Å] is intermediate between the values for NpO_2^+ and NpO_2^{2+} reported recently: 1.814(34) Å for Np^V in $Cs_3NpO_2Cl_4$[8] and 1.721(16) and 1.751(18) Å for Np^{VI} in $NpO_2Cl_2{\cdot}2PPh_3O$.[9] The Np–Cl bonds show the same intermediate length [2.685(5) Å] when compared with the neptunyl(v) [2.752(13) and 2.760(19) Å] and neptunyl(vi) [2.622(14) and 2.645(13) Å] bonds in these compounds. The thermal ellipsoids of the chloride and oxygen ligands might be expected to show abnormal elongations because of the disorder, but this is not seen (Figure 2); the greatest elongation is at right angles to the bonds rather than parallel to them. Presumably the expected 0.05—0.15 Å differences in Np–X distances are swamped by the normal thermal motion. The Cs(1) cation is nine-co-ordinate, positioned on a three-fold axis at the centre of a tricapped trigonal prism. Co-ordination to the oxygen and chlorine atoms gives Cs–O contact distances of 3.17(1) Å and Cs–Cl contact distances of 3.73(1) and 3.74(1) Å. Atom Cs(2) is eight-co-ordinate with $\bar{4}$ symmetry at the centre of a dodecahedron of chlorine atoms with Cs–Cl contact distances of 3.54(1) Å.

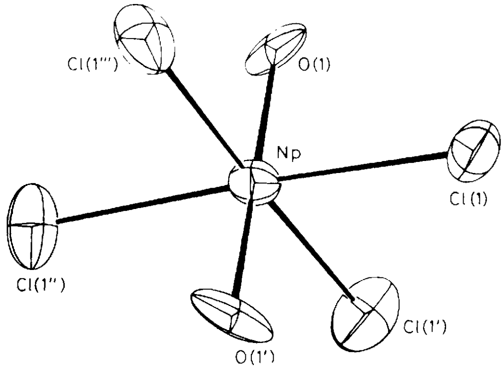

Figure 2. Co-ordination around Np in the NpO_2 ions; thermal ellipsoids drawn at the 50% level

The confirmation of the stoicheiometry for this cubic neptunyl chloride makes it highly likely that the proposed revision to the formula of the cubic americium chloride originally formulated as $Cs_2AmO_2Cl_4$ is also correct.

Acknowledgements

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