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## Caesium Tetrachlorodioxoneptunate(V)

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**Abstract.** Cs<sub>3</sub>[NpCl<sub>4</sub>O<sub>2</sub>], monoclinic, *C2/c*, *a* = 15.468 (9), *b* = 7.275 (4), *c* = 12.757 (6) Å,  $\beta$  = 117.23 (4)°, *U* = 1276.4 (3.0) Å<sup>3</sup>, *Z* = 4, *D<sub>c</sub>* = 4.21 g cm<sup>-3</sup>,  $\mu(\text{Mo } K\alpha)$  = 144.6 cm<sup>-1</sup>, *R* = 0.036 (*R<sub>w</sub>* = 0.033) for 951 reflections. The complex contains [NpCl<sub>4</sub>O<sub>2</sub>]<sup>3-</sup> ions with *trans* oxygen atoms in the linear NpO<sub>2</sub><sup>+</sup> group [Np—O = 1.814 (34) Å]. The Np—Cl distances are 2.752 (13) and 2.760 (19) Å.

**Introduction.** As part of an investigation of the structural chemistry of neptunyl(V) and (VI) the structure of Cs<sub>3</sub>[NpCl<sub>4</sub>O<sub>2</sub>] has been redetermined. The high *R* value, 0.17, reported for the earlier investigation (Vodovatov, Ladygin, Lychev, Mashirov & Suglobov, 1975) suggested that the data would not be sufficiently precise to allow a meaningful comparison with the structure recently determined for NpCl<sub>2</sub>O<sub>2</sub>·2tpo (Alcock, Roberts & Brown, 1982*a*) to identify the effects of the additional *f* electron on bond lengths in the NpO<sub>2</sub><sup>+</sup> groups and those in the equatorial planes around them.

Suitable crystals of Cs<sub>3</sub>[NpCl<sub>4</sub>O<sub>2</sub>] were obtained by allowing Cs<sub>2</sub>[NpCl<sub>4</sub>O<sub>2</sub>] dissolved in an ethanol–water mixture to undergo spontaneous reduction. Turquoise, needle-like crystals grew as the solution slowly evaporated during a three or four day period. Suitable crystals were mounted on quartz fibres and encapsulated in glass capillaries which were then coated with

Araldite. These operations were performed in a glove box to afford protection from the  $\alpha$ -activity associated with <sup>237</sup>Np.

Reflections were collected at 153 K on a Syntex P2<sub>1</sub> automatic four-circle diffractometer with an attached LT-1 low-temperature device, using Mo *K* $\alpha$  radiation ( $\lambda$  = 0.71069 Å). A crystal of dimensions 0.18 × 0.06 × 0.08 mm bounded by faces (110) and ( $\bar{1}$ 10) was used, which gave transmission factors in the range 0.346–0.505.

Accurate cell parameters were obtained by least-squares calculations based on the positions of 15 reflections in the range 25 ≤ 2 $\theta$  ≤ 27°. The  $\theta$ –2 $\theta$  scan technique was used, with scan rates varying from 1.0 to 29.3° min<sup>-1</sup>, depending on the intensity of a 2s pre-scan. The scan range was ±1.0° around both the *K* $\alpha$ <sub>1</sub> and *K* $\alpha$ <sub>2</sub> positions. 1229 reflections were collected in the range 0 ≤ 2 $\theta$  < 50°, of which 951 were considered observed [*I*/ $\sigma$ (*I*) ≥ 3.0] and used in the refinement. Three standard reflections monitored every 100 reflections showed no appreciable decrease in intensity.

The systematic absences *h* + *k* ≠ 2*n* for *hkl* and *l* ≠ 2*n* for *h0l* reflections indicated the space group *C2/c*. The coordinates of the atoms were obtained from the published crystal structure of Cs<sub>3</sub>[NpCl<sub>4</sub>O<sub>2</sub>] in space group *B2/b* (Vodovatov, Ladygin, Lychev, Mashirov & Suglobov, 1975) by an appropriate transformation.

The atoms were refined starting from these coordinates. The weighting scheme  $W = XY$  was applied, where  $X = 1.0$  or  $\sin \theta/0.3$  if  $\sin \theta \leq 0.3$  and  $Y = 1.0$  or  $160.0/F_o$  if  $F_o \geq 160.0$ . After least-squares refinement of all atoms with anisotropic temperature factors, the  $R$  factors converged to the final and weighted values of 0.036 and 0.033, respectively.

Isotropic extinction and absorption corrections were applied, the last using the program *ABSCOR* (Alcock, 1970). The scattering factors used were corrected for anomalous dispersion (*International Tables for X-ray Crystallography*, 1974). Computing was performed using the XRAY 76 system (Stewart, 1976) on a Burroughs B6700 computer. The final difference Fourier map showed only peaks  $\leq 1.5 \text{ e } \text{\AA}^{-3}$ .

The final atomic coordinates and temperature factors are listed in Table 1; bond lengths and angles are included in Table 2.\*

**Discussion.** The structure of  $\text{Cs}_3[\text{NpCl}_4\text{O}_2]$  consists of  $\text{Cs}^+$  ions and isolated  $[\text{NpCl}_4\text{O}_2]^{3-}$  ions with distorted

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36705 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic temperature factors ( $\text{\AA}^2 \times 10^4$ ) with standard deviations in parentheses

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$U_{eq}$
Np	2500	2500	0	119
Cs(1)	0	848 (6)	2500	214
Cs(2)	3487 (3)	1875 (5)	3701 (3)	292
Cl(1)	964 (10)	1793 (21)	481 (14)	391
Cl(2)	1541 (11)	4477 (19)	3683 (11)	324
O(1)	3037 (24)	3922 (50)	1312 (29)	233

Table 2. Bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) in  $\text{Cs}_3[\text{NpCl}_4\text{O}_2]$  with standard deviations in parentheses

(a) Bond lengths

Np—Cl(1)	2.760 (19)
Np—Cl(2)	2.752 (13)
Np—O(1)	1.814 (34)

(b) Bond angles

Cl(1)—Np—O(1)	88.8 (14), 91.2 (14)
Cl(1)—Np—Cl(2)	89.6 (5), 90.4 (5)
O(1)—Np—Cl(2)	89.9 (11), 90.1 (11)

(c) Caesium—oxygen contact distances

Cs(1)—O(1)	3.04 (3) (twice)
Cs(2)—O(1)	3.17 (4), 3.18 (4)

(d) Caesium—chloride contact distances

Cs(1)—Cl(1)	3.584 (20), 3.896 (16) (twice)
Cs(1)—Cl(2)	3.412 (14), 3.497 (17) (twice)
Cs(2)—Cl(1)	3.580 (13), 3.715 (15), 3.830 (15)
Cs(2)—Cl(2)	3.490 (16), 3.546 (17)

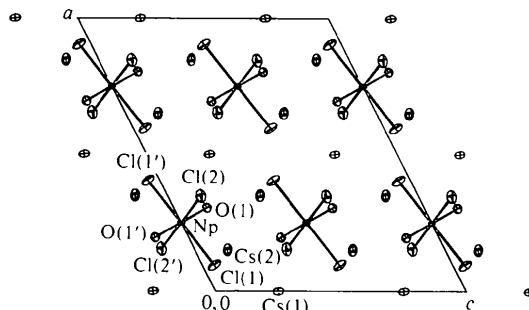


Fig. 1. View of the unit cell of  $\text{Cs}_3[\text{NpCl}_4\text{O}_2]$  down  $b$ .

octahedral geometry. The Np atoms, in the special positions 4(c), have a site symmetry of  $\bar{1}$ . The Np and Cl atoms define a plane that makes an angle of  $87.8(11)^\circ$  with the neptunyl(V) group, which is required to be linear by the same symmetry element. The  $[\text{NpCl}_4\text{O}_2]^{3-}$  octahedra are separated in the crystal by planes of  $\text{Cs}^+$  ions (Fig. 1).

As expected the Np—O(NpO $_2^+$ ) bond length [1.814 (34)  $\text{\AA}$ ] is longer than those in the neptunyl(VI) compound  $\text{NpCl}_2\text{O}_2 \cdot 2\text{tppo}$  [1.721 (16) and 1.751 (18)  $\text{\AA}$ ; Alcock, Roberts & Brown, 1982a]. The Np—Cl bond lengths [2.752 (13) and 2.760 (19)  $\text{\AA}$ ] show the same trend [ $\text{NpCl}_2\text{O}_2 \cdot 2\text{tppo}$ : 2.622 (14) and 2.645 (13)  $\text{\AA}$ ].

These differences in bond lengths are similar to those identified recently for Np $^V$  and Np $^{VI}$  acetato complexes (Alcock, Roberts & Brown, 1982b). The lengthening suggests that the extra  $f$  electron in the Np $^V$  compounds is in a non-bonding orbital, possibly that along the axis of the bond ( $\delta_u$ ) as suggested by Burns & Musikas (1977), resulting in a general reduction in electrostatic attraction relative to that in Np $^{VI}$  compounds.

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