



# A single-crystal X-ray structure determination of neptunium tetrachloride

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## Abstract

The availability of single crystals of neptunium tetrachloride allowed us to carry out a complete structural X-ray investigation of this compound in order to establish precise cell parameters, atomic coordinates and bond distances.  $\text{NpCl}_4$  crystallizes in tetragonal space group  $I4_1/amd$  ( $D_{4h}^{19}$ , No141) with cell dimensions  $a = 8.229(2)$ ,  $c = 7.437(1)$  Å,  $V = 503.62(14)$  Å<sup>3</sup>. There are four molecules in the unit cell. The neptunium atom, with point group symmetry  $-42m$  ( $D_{4h}$ ), is surrounded by eight chlorine atoms; four chlorines are at 2.618(2) Å, and four at 2.867(2) Å from the neptunium atom. The coordination polyhedron may be described as a distorted dodecahedron; the smallest Cl–Cl approach in the polyhedron is 3.110(3) Å. The positional parameters are in agreement with those reported for  $\text{UCl}_4$  and  $\text{ThCl}_4$ . The two sets of Np–Cl distances, 2.618(2) Å and 2.867(2) Å, compare favourably with the values 2.650(3) Å and 2.882(3) Å in  $\text{UCl}_4$  and with the values 2.718(8) Å and 2.903(7) Å in  $\text{ThCl}_4$ . They would indicate, as observed for  $\text{UCl}_4$  in a polarized neutron experiment, a tendency of Np–Cl bonds towards covalency.

**Keywords:** Neptunium tetrachloride; Covalency; Single crystals

## 1. Experimental

### 1.1. Preparation

Neptunium tetrachloride was synthesized as described by Brown [1]: 2 g of neptunium dioxide (provided by Oak Ridge National Laboratory, Tennessee, USA) were treated with carbon tetrachloride and chlorine vapour at 520 °C. After sublimation, neptunium tetrachloride condensed in a cooler zone, forming dark red, air-sensitive single crystals with tetrahedral shape. A selected specimen (0.5 × 0.7 × 0.6 mm), suitable for X-ray analysis, was sealed in a thin-walled glass capillary under an inert atmosphere.

### 1.2. Structural data

The X-ray diffraction data were recorded on a Siemens R3m/V X-ray diffractometer, graphite-monochromated

Mo  $K\alpha$  radiation ( $\lambda = 0.71073$  Å), at room temperature. The unit cell dimensions and standard deviations were determined from the setting angles of 25 reflections in the range  $4^\circ < \theta < 23^\circ$ . The space group was established from systematic absences.  $\text{NpCl}_4$  ( $M_r = 378.8$ ) is tetragonal  $I4_1/amd$  ( $D_{4h}^{19}$ , No. 141), with  $a = 8.229(2)$ ,  $c = 7.437(1)$  Å,  $V = 503.62(14)$  Å<sup>3</sup> and  $Z = 4$ . The origin was chosen at centre  $2/m$ . Other relevant crystal data are:  $D_x = 4.996$  g cm<sup>-3</sup>,  $\mu = 225.66$  cm<sup>-1</sup>,  $F(000) = 644$ .

The intensities of 563 reflections were collected in the range  $2^\circ < \theta < 30^\circ$  ( $h-1 \rightarrow 11$ ,  $k-1 \rightarrow 11$ ,  $l-1 \rightarrow 10$ ) using  $\theta-2\theta$  scans. 209 independent reflections ( $R_{\text{int}} = 0.055$ ) with  $F > 4\sigma(F)$  were used in refinement. Intensities of three standard reflections, measured every 97 reflections, showed no deviations from the mean. The intensities were corrected for Lorentz polarization effects. Semi-empirical absorption corrections, based on a method [2] that used a set of scans of reflections with values close to  $90^\circ$ , gave transmission factors ranging from 56.2 to 98.2%.

The structure was solved by direct methods and refined by full matrix least-squares minimization of  $\sum w(|F_o| - |F_c|)^2$ . The weighting scheme was  $w^{-1} =$

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$\sigma^2(F_o) + 0.0011F_o^2$ . Anisotropic thermal parameters were used in refinement. A secondary-extinction coefficient was refined to a value of  $\chi = 0.0025(3)$  ( $F_c = F_o[1 + 0.002\chi F^2/\sin(2\theta)]^{-1/4}$ ). The final agreement factors were  $R = 0.030$ ,  $wR = 0.047$ ,  $s = 1.01$ . The final shifts/e.s.d.'s were less than 0.02. The data-to-parameter ratio was 20.9:1. The maximum and minimum heights in the final difference Fourier map were +3.78 and  $-3.57 \text{ e } \text{\AA}^{-3}$  (around the Np atom). The atomic scattering factors and anomalous dispersion terms were taken from the *International Tables for X-ray Crystallography* [3]. Calculations were performed with Siemens SHELXTL PLUS package programs.

Atomic coordinates and anisotropic temperature factors are given in Table 1. Bond distances and angles are presented in Table 2. The crystal structure is shown in Fig. 1. Observed and calculated structure factors are available on request from the authors.

Table 1

Atomic coordinates ( $\times 10^4$ ) and anisotropic displacements coefficients ( $\text{\AA}^2 \times 10^4$ )<sup>a</sup>

Neptunium			
Position	$x = 0$	$y = 2500$	$z = 8750$
Thermal parameters	$U_{11} = 8(5)$	$U_{22} = 8(5)$	$U_{33} = 64(5)$
	$U(\text{eq}) = 27(5)$		
Chlorine			
Position	$x = 0$	$y = 5610(2)$	$z = 8012(2)$
Thermal parameters	$U_{11} = 296(10)$	$U_{22} = 42(8)$	$U_{33} = 60(7)$
	$U_{23} = 20(5)$		
	$U(\text{eq}) = 133(8)$		

<sup>a</sup>The anisotropic displacement exponent takes the form:

$$-2\pi^2(h^2a^{*2}U_{11} + \dots + 2hka^*b^*U_{12})$$

Equivalent isotropic  $U$  defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

Table 2

Bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) in  $\text{NpCl}_4$  coordination polyhedron. Standard deviations are given in parentheses

Np–Cl (4*) <sup>a</sup>	2.618(2)
Np–Cl* (4*) <sup>b</sup>	2.867(2)
Cl*–Np–Cl* (2*)	65.7(1)
Cl–Np–Cl* (4*)	69.2(1)
Cl–Np–Cl* (8*)	79.9(1)
Cl–Np–Cl (4*)	92.5(1)
Cl*–Np–Cl* (4*)	134.9(1)
Cl–Np–Cl* (4*)	135.0(1)
Cl–Np–Cl (2*)	155.8(1)

<sup>a</sup>(4\*) means four such bonds, Cl referring to chlorines located respectively at:  $0, x, z$ ;  $0, 0.5 - x, z$ ;  $0.75 - x, 0.75, 0.25 - z$ ;  $0.25 + x, 0.75, 0.25 - z$ .

<sup>b</sup>4 such bonds. Cl\* refers to chlorine located respectively at:  $0, -x, -z + 1$ ;  $0, x - 0.5, -z + 1$ ;  $0.25 + x, 0.25, z - 0.25$ ;  $0.75 - x, 0.25, z - 0.25$ .

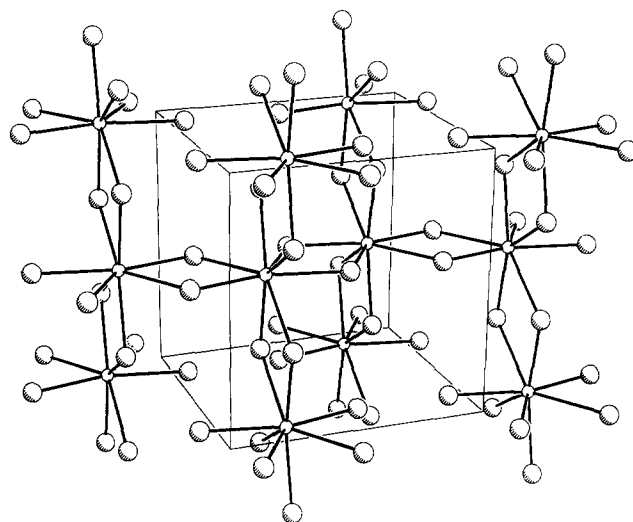


Fig. 1. The crystal structure. The small circles represent neptunium positions; the larger, the chlorine positions.

## 2. Related literature

The earlier X-ray structural investigations reported on  $\text{AnCl}_4$ -type compounds were performed from powder diffraction photographs which showed  $\text{UCl}_4$ ,  $\text{ThCl}_4$ ,  $\text{PaCl}_4$  and  $\text{NpCl}_4$  to be isostructural [4–7]. Mooney [7] established the space group, the unit cell dimensions and deduced the atomic positions in  $\text{UCl}_4$ . The chlorine positions are not accurately determined in this study because of the heavy X-ray scattering by uranium. In 1973, Taylor and Wilson [8] carried out a neutron diffraction powder study on  $\text{UCl}_4$  and confirmed the structures derived in the earlier X-ray powder diffraction study. More accurate cell dimensions were found as well as more accurate and reliable positional parameters for the Cl atoms. Two sets for the U–Cl distances in the coordination dodecahedron were reported: 2.638(4)  $\text{\AA}$  and 2.869(3)  $\text{\AA}$ . A single-crystal X-ray study of  $\text{ThCl}_4$  established the two sets of Th–Cl bonds to be 2.903(7)  $\text{\AA}$  and 2.718(8)  $\text{\AA}$  [9]. Neutron experiments were also performed on single crystals of  $\text{UCl}_4$  at low temperature [10] to study the spatial distribution of the U–Cl bonding electrons. The atomic positions at low temperature were in agreement with the room-temperature positions from the earlier studies. The spin density distribution, determined from a polarized neutrons experiment, showed a small but significant covalent interaction between the U and Cl atoms.

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