Preparation and Preliminary Structure Investigation of β-Tetrakis(acetylacetonato)-neptunium(IV)

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Experimental. About 5 mg neptunium dioxide (Radiochemical Centre) was completely dissolved in hot perchloric acid. The radiochemical purity of the neptunium solution was checked, and the disintegration product content was found to be negligible. Sodium hydroxide was added until an acid concentration of 2 M was reached. The neptunium in the solution was reduced to Np(III) with hydrogen (platinum black as catalyst) and oxidised in air to Np(IV). The reduction-oxidation reactions were investigated by absorbance measurements [1] in the wavelength range with acetylacetone purified in the manner 350—750 nm. The solution was saturated described by Rydberg.[2] By slow addition of 1 M sodium hydroxide the pH was increased to 4.5—5.0. The acetylacetonate was extracted with benzene, and the organic phase was examined by absorbance measurements in the range 350—2700 nm. By evaporation of the organic phase, light green needle shaped crystals were formed. The melting point was 175±2°C. The neptunium content determined by α-counting was found to be 38.3±1.4 %. (Theoretically for NpA_4: 37.19 %; A=acetylacetonate).

Preliminary structure investigation. Crystals were mounted in glass capillaries. Rotation around the *c*-axis with Cu*K*α radiation gave preliminary Weissenberg data. The crystals disintegrated after about 6 h of radiation. From Guinier photographs the lattice parameters were determined to be $a=22.055(5)$ Å, $b=8.380(1)$ Å, $c=14.416(1)$ Å, $\beta=116.23(1)°$, $V=2390$ Å^3 and $Z=4$. The space group was $C2/c$. These data indicate that the β-form of the acetylacetonate was obtained (*cf.* Table 1).

Table 1. Lattice parameters of hitherto examined acetylacetonates of tetravalent metals.

Complex	α-form ($P2_1/c$)				β-form ($C2/c$)			
	a (Å)	*b* (Å)	*c* (Å)	β (°)	*a* (Å)	*b* (Å)	*c* (Å)	β (°)
ZrA_4					21.67	8.38	14.14	116.67[3]
HfA_4						+		[3]
CeA_4	11.70	12.64	16.93	112.25[4]	22.01	8.38	14.37	115.78[5]
ThA_4	11.72	12.76	17.02	112.25[4]	21.90	8.52	14.56	115.77[4]
UA_4	11.65	12.68	16.95	112.25[4]	22.02	8.39	14.49	115.72[6]
Np_4					22.06	8.38	14.42	116.23

For the β-form of ZrA_4 and ThA_4 the original lattice parameter values given in the references noted are those relevant to a description of the structure as $I2/c$. The values given in the table have been recalculated from these in order to be consistent with a description of the structure as $C2/c$.

1. Sjöblom, R. and Hindman, J. C. *J. Am. Chem. Soc.* **73** (1951) 1744.
2. Rydberg, J. *Svensk. Kem. Tidskr.* **62** (1950) 179.
3. Silverton, J. V. and Hoard, J. L. *Inorg. Chem.* **2** (1963) 243.
4. Grdenic, D. and Matkovic, B. *Acta Cryst.* **12** (1959) 817.
5. Titze, H. *Acta Chem. Scand.* **23** (1969) 399.
6. Titze, H. *Acta Chem. Scand.* **24** (1970) 405.

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