

Actinide Complexes with Unsaturated Heteropolyanions: Structural Data

M.S. Grigoriev, A.M.Fedosseev

Institute of Physical Chemistry, RAS: 31 Leninsky prosp., Moscow, 119991 Russia

M.Yu. Antipin

Institute of Organoelement Compounds, RAS: 28 Vavilova str., Moscow, 119991 Russia

Ch. Den Auwer, Ph. Moisy

CEA Marcoule, DEN/DRCP/SCPS: BP 17171, F-30207 Bagnols sur Cèze Cedex, France

E-mail: grigoriev@ipc.rssi.ru

Abstract – the complexes of Np(IV) and U(IV) with unsaturated heteropolyanion $\text{SiW}_{11}\text{O}_{39}^{8-}$ have been prepared in single crystal form, their structures have been determined by X-ray structural analysis. Actinide atoms in $[\text{An}(\text{SiW}_{11}\text{O}_{39})_2]^{12-}$ complex anions are eight-coordinated. Their coordination polyhedra can be described as distorted square antiprisms. The main distortion of the coordination polyhedron in both complexes is twisting of one base of the square antiprism from its ideal position by about 9° around the fourfold inversion axis.

INTRODUCTION

Unsaturated heteropolyanions (HPA) $\text{MW}_{11}\text{O}_{39}^{n-}$ ($\text{M} = \text{Ge}, \text{Si}, \text{P}$) or $\text{X}_2\text{W}_{17}\text{O}_{61}^{10-}$ ($\text{X} = \text{P}, \text{As}$) are known to stabilize actinides in the oxidation state (IV). The major part of the studies of such complexes was carried out in solutions, the data on their crystal structures are very limited [1]. Here we present the results of X-ray structural study of two complexes of An(IV) with $\text{SiW}_{11}\text{O}_{39}^{8-}$.

EXPERIMENTAL

Synthesis

The complexes $\text{K}_4[(\text{CH}_3)_4\text{N}]_8[\text{Np}(\text{SiW}_{11}\text{O}_{39})_2] \cdot n\text{H}_2\text{O}$ (**I**) and $\text{K}_{12}[\text{U}(\text{SiW}_{11}\text{O}_{39})_2] \cdot 25.5\text{H}_2\text{O}$ (**II**) have been prepared in the following way:

Solution of HPA was prepared using 0.05 M $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ by adding 1 M KHCO_3 up to pH about 6. Obtained solution was saturated at heating ($\sim 50^\circ\text{C}$) and stirring with $\text{Np}(\text{C}_2\text{O}_4)_2 \cdot 6\text{H}_2\text{O}$ or $\text{U}(\text{SO}_4)_2 \cdot 8\text{H}_2\text{O}$. Complexes **I** and **II** were isolated by adding solid tetramethylammonium nitrate or potassium chloride respectively to neptunium- and uranium-containing solutions up to beginning of complexes crystallization. Crystals of suitable quality were obtained after storage of reaction mixture at temperature not higher than 18°C for several hours. The composition of the complexes has been determined by X-ray structural analysis.

X-Ray Structural Analysis

The experiments were carried out on a Bruker AXS SMART 1000 CCD area-detector diffractometer (MoK_α -radiation, graphite monochromator) at 140 K for **I** and 120 K for **II**. The crystals were sealed in glass capillaries. A hemisphere of the reciprocal space has been measured for **I** and the full sphere for **II**. Absorption correction was made using SADABS procedure [2-3]. The structures were solved by direct method (SHELXS86 [4]) and refined on F^2 with the full-matrix least-squares procedure (SHELXL93 [5]) using all reflections. In **I** not all C atoms of tetramethylammonium cations and O atoms of crystallization water molecules have been located. C, N and O atoms in **I** were refined isotropically. In **II** only O atoms of crystallization water molecules were refined isotropically.

Crystal Data

I – monoclinic, space group $C2/c$, $a = 48.578(12)$, $b = 12.750(3)$, $c = 56.770(14)$ Å, $\beta = 109.860(4)^\circ$, $Z = 12$; $R_1 = 0.0657$, $wR_2 = 0.1046$ [for reflections with $I > 2\sigma(I)$].

II – triclinic, space group $P-1$, $a = 12.638(2)$, $b = 16.534(3)$, $c = 23.090(4)$ Å, $\alpha = 95.639(4)$, $\beta = 100.595(4)$, $\gamma = 91.957(4)^\circ$, $Z = 2$; $R_1 = 0.0555$, $wR_2 = 0.1045$ [for reflections with $I > 2\sigma(I)$].

RESULTS AND DISCUSSION

The structure **I** contains two crystallographically independent $[\text{Np}(\text{SiW}_{11}\text{O}_{39})_2]^{12-}$ complex anions (Fig. 1). One of them is in general position, the other – in special one: Np(2) atom is on the twofold axis. In both anions Np atoms have coordination number 8, coordination polyhedron (CP) of Np atom is distorted square antiprism (Fig. 2). The precision of the determination of Np-O distances is 5 times higher than in literature data for $[\text{U}(\text{GeW}_{11}\text{O}_{39})_2]^{12-}$ complex [1]. The Np-O distances range from 2.28(2) to 2.392(18) Å (Table I), the average values being 2.36(1) and 2.34(2) Å for Np(1) and Np(2) respectively.

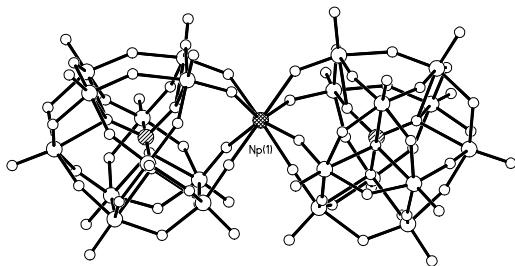


Fig. 1. One of two crystallographically independent $[\text{Np}(\text{SiW}_{11}\text{O}_{39})_2]^{12-}$ complex anions in the structure **I**.

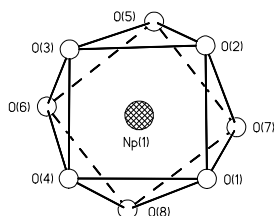


Fig. 2. Coordination polyhedron of Np(1) atom in the structure **I**.

The deviations of O atoms of two square bases of Np(1) CP from their least-squares planes are ± 0.014 and ± 0.007 Å, the dihedral angle between these planes is 3° . At the same time, one can see in Fig. 2 that the CP is slightly twisted around its fourfold inversion axis. The angles between diagonals of the two different bases (i.e., the lines O(1)-O(3) and O(8)-O(5); O(2)-O(4) and O(7)-O(6)) are 55 and 50° , the ideal value being 45° . The angles between two diagonals of the same base (O(1)-O(3) and O(2)-O(4); O(5)-O(8) and O(6)-O(7)) are 89 and 87° .

TABLE I. Interatomic distances in the first coordination sphere of Np atoms in the structure **I**.

Bond	Distance, Å
Np(1)-O(1)	2.34(2)
Np(1)-O(2)	2.39(2)
Np(1)-O(3)	2.392(18)
Np(1)-O(4)	2.35(2)
Np(1)-O(5)	2.358(19)
Np(1)-O(6)	2.36(2)
Np(1)-O(7)	2.36(2)
Np(1)-O(8)	2.30(2)
Np(2)-O(79)	2.28(2)
Np(2)-O(80)	2.380(19)
Np(2)-O(81)	2.36(2)
Np(2)-O(82)	2.33(2)

The structure of the second crystallographically independent complex anion in **I** is almost the same. The fitting of the positions of metal atoms in the two anions gives root-mean-square deviation of 0.176 Å. The deviations of O atoms of the square base of Np(2) CP (this CP has only one crystallographically independent base) from their least-squares plane are ± 0.015 Å, the dihedral angle between the bases is 1° . The angles between diagonals of the two different bases are 54 and 56° , whereas the angle between two diagonals of the base is 89° .

The structure **II** contains only one crystallographically independent complex anion in general position. Its structure is very close to that found in **I**. The U-O distances range from $2.318(11)$ to $2.411(12)$ Å (Table II), the average value being $2.354(12)$ Å.

TABLE II. Interatomic distances in the first coordination sphere of U atom in the structure **II**.

Bond	Distance, Å
U-O(1)	2.375(12)
U-O(2)	2.411(12)
U-O(3)	2.362(11)
U-O(4)	2.320(12)
U-O(5)	2.318(11)
U-O(6)	2.365(11)
U-O(7)	2.331(11)
U-O(8)	2.348(11)

The deviations of O atoms of both square bases of U CP from their least-squares planes are ± 0.004 Å, the dihedral angle between the bases is 4° . The angles between diagonals of the two different bases are 52 and 54° , whereas the angles between two diagonals of the bases are 90 and 91° . Thus, the main distortion in all CP in the studied complexes is twisting of one base of

the square antiprism from its ideal position by about 9° . It seems that such distortion lies in the nature of the complexes.

It is interesting to note that these complex anions are significantly nonlinear. This is the consequence of the noncentrosymmetric structure of Keggin-type HPA. In **I** the angles W...Np...W for W atoms with the longest Np...W distances are 164 and 160° for Np(1) and Np(2) respectively. The corresponding value for **II** is 165° .

An attempt has been made also to prepare a similar complex with Th(IV). The complex anion in Th complex with guanidinium cations has the same structure as in Np and U compounds but the disorder of one of the two HPA makes difficult to obtain precise interatomic distances and to locate organic cations. The crystal data for this complex (at 120 K): $a = 12.210(2)$, $b = 12.212(2)$, $c = 37.630(6)$ Å, $\alpha = 80.987(4)$, $\beta = 81.618(4)$, $\gamma = 64.263(4)^\circ$, $Z = 2$.

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