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Peculiarities of complex formation of hexavalent Np and Pu with tetrahedral XO_4^{2-} oxoanions (X=S, Se, Cr, Mo)

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Abstract

This work was designed for further investigations of coordination compounds of penta- and hexavalent actinides with tetrahedral XO_4^{2-}-anions. Although a high similarity in the structure and properties of AnO_2^{2+} compounds with XO_4^{2-}-anions (where An=Np, Pu) was expected, our data on the behaviour of AnO_2^{2+} compounds in aqueous solutions pointed to marked differences depending on the nature of both actinides and a central X-atom in ligands. © 1998 Elsevier Science S.A.

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1. Introduction

Most actinide(V) and (VI) compounds are known to be derivatives of AnO_2^{+} and AnO_2^{2+} dioxocations. The linear symmetric structure, which is typical for these cations in the free state, can strongly be influenced depending on the ligand surroundings in a crystal lattice, as followed by changes in their spectral characteristics. It is solid AnO_2^{+} and AnO_2^{2+} compounds that are of particular interest. Dioxocations of different actinides in the same oxidation state are often considered as chemical analogs, since, as it is commonly accepted, the strength of the An–O bond decreases slightly in the row U–Am. Furthermore, a question about the influence of the actinide nature on an An–Lig bond is still unsolved now.

Numerous studies of solid Np(V) and Am(V) compounds with XO_4^{2-} ligands pointed to marked differences in their properties [1,2]. In addition to this, significant differences were found in the behaviour of U(VI), Np(VI) and Pu(VI) during hydrolytic polymerization [3]. In such a way, a comparative study on the behaviour of An(VI) during complex formation in various solutions and subsequent formation of crystalline compounds is currently a central problem.

In our studies, Np(VI) and Pu(VI) compounds with XO_4^{2-} anions (where X=S, Se, Cr, Mo) were selected as the object of investigation. Since XO_4^{2-} have a complex formation ability similar to that of H_2O molecules, we assumed the possibility of feasible production of compounds with different compositions of the first coordinational sphere.

Moreover, it was interesting to estimate an influence of the nature of the tetrahedral ligand's central X-atom on the properties of An(VI) compounds, exactly as it was done for Np(V) and U(VI). It should be noted here that physicochemical and spectral characteristics of similar Np(V) with XO_4^{2-}-anion compounds depend on the central atom nature [4,5]. In contrast to this, studies of numerous uranyl complexes allowed the authors [6] to conclude that, in the case of XO_4^{2-}-anions with a fixed charge (X=S, Se, Cr), the nature of the X-atom did not virtually influence the electron-donor power, and a donor-acceptor interaction between uranyl-ion and equatorial ligands was determined only by geometric factors.

2. Materials and methods

Plutonium-239 and Np-237 were purified by ion-exchange method. The solutions containing sulfate, selenate, chromate and molybdate ions were prepared from standard chemically pure reagents. DMSO was of the same purity degree.

Absorption spectra of the studied solid compounds in

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the infra red and visible ranges were recorded on Specord-M80 and Shimadzu-3020 instruments, respectively, with the use of solid molten NaCl matrices by the procedure described in [7].

The single crystal X-ray structural analysis was performed using the equipment of the X-Ray Structural Center of Nesmejanov Institute of Organoelement Compounds of the Russian Academy of Sciences.

3. Results and discussion

To date, very few and contradictory data are available about the complex formation of Np(VI) and Pu(VI) with XO_4^{2-}-anions and isolation of the corresponding solid complexes. Thus, only crystalline $K_2NpO_2(SO_4)_2.2H_2O$ complex could be produced from aqueous Np(VI) solutions in the presence of excess K_2SO_4, whereas two complexes — $Cs_2(NpO_2)_2(SO_4)_3$ and $Cs_2NpO_2(SO_4)_2$ — were formed in the presence of Cs_2SO_4. In a UO_2-Cs_2SO_4-H_2O system only two complexes, similar to neptunyl ones, were formed [9]. In a study by Weigel and Hellman [10], $M_2NpO_2(SO_4)_2.nH_2O$ and $M'_2PuO_2(SO_4)_2.nH_2O$ complexes (M=K, Rb, Cs; M′=K, Cs; n=0.5; 2; 4; 10) were described and parameters of their elementary cells were calculated. While virtually the same methods were used in references [8] and [10] to isolate Np(VI) and Pu(VI) sulfate complexes, it was difficult to understand why one of the disulfate Np complexes was anhydrous, but the other was precipitated as water-enriched hydrates.

Molybdates of hexavalent transuranium elements (TUE) occurred only in the form of simple molybdate and dimolybdate hydrates [11]; whereas no information was found about hexavalent TUE chromates.

Thus, it was interesting to extend our knowledge about the specified compounds and to compare the influence of An(VI) with XO_4^{2-}-anions complex formation on spectra of both dissolved and solid Np(VI) and Pu(VI).

Fig. 1, Fig. 2 and Fig. 3 illustrate a concentration-dependent effect of XO_4^{2-}-anions in solution on AnO_2^{2+} spectra, whose changes were rather complicated and non-monotoneous. Therefore, both neptunyl- and plutonyl-ion were likely to be present in the form of several complexes in the XO_4^{2-}-containing solutions.

Moreover, the absorption peak within a range of 860–830 nm virtually disappeared in a spectrum of 0.7 M molybdate solution of plutonyl: therefore, it may be suggested the formation of a centrosymmetric Pu(VI) complex.

It is difficult to settle the question, which of the coexisting complexes may participate in the crystal lattice formation. To refine some general laws of complex formation of Np(VI) and Pu(VI) with XO_4^{2-}, solid hexavalent TUE complexes with these anions were synthesized.

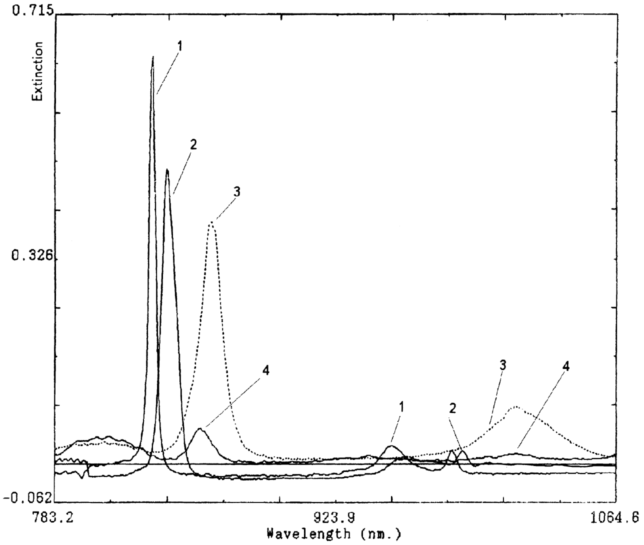

Fig. 1. The absorption spectra of solutions of Pu(VI) in the presence of different XO_4^{2-}-anions. (1) The initial solution, [Pu(VI)]=1.3×10^{-3} mol/l. (2) [Pu(VI)]=1.3×10^{-3} mol/l; [SO_4^{2-}]=0.1 mol/l. (3) [Pu(VI)]=1.3×10^{-3} mol/l; [CrO_4^{2-}]=0.1 mol/l. (4) [Pu(VI)]=1.3×10^{-3} mol/l; [MoO_4^{2-}]=0.1 mol/l.

3.1. Sulfate compounds of An(VI)

We synthesized the following compounds: $K_2NpO_2(SO_4)_2.2H_2O$; $(NH_4)_2NpO_2(SO_4)_2.2H_2O$; $Cs_2NpO_2(SO_4)_2$; $Cs_2PuO_2(SO_4)_2$; $Cs_2(NpO_2)_2(SO_4)_3$, which were isostructural to the corresponding uranyl compounds. We could not produce the compounds similar to those described in [10]. In the general case, the

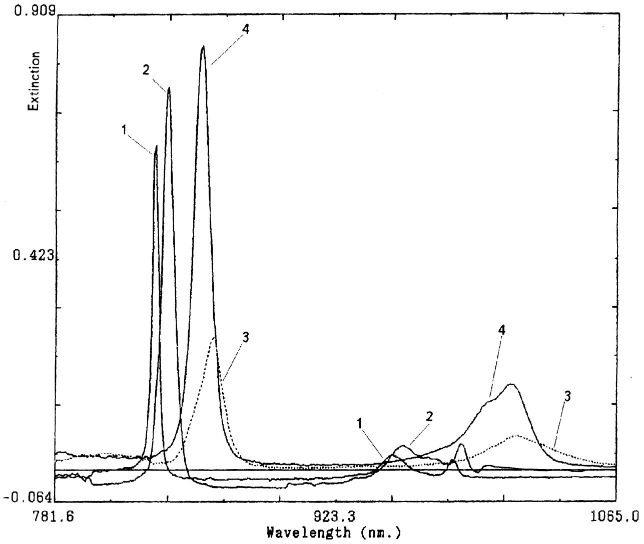

Fig. 2. The absorption spectra of solutions of Pu(VI) in the presence of different XO_4^{2-}-anions. (1) The initial solution, [Pu(VI)]=1.3×10^{-3} mol/l. (2) [Pu(VI)]=1.3×10^{-3} mol/l; [SO_4^{2-}]=0.5 mol/l. (3) [Pu(VI)]=1.3×10^{-3} mol/l; [CrO_4^{2-}]=0.5 mol/l. (4) [Pu(VI)]=1.3×10^{-3} mol/l; [MoO_4^{2-}]=0.5 mol/l.

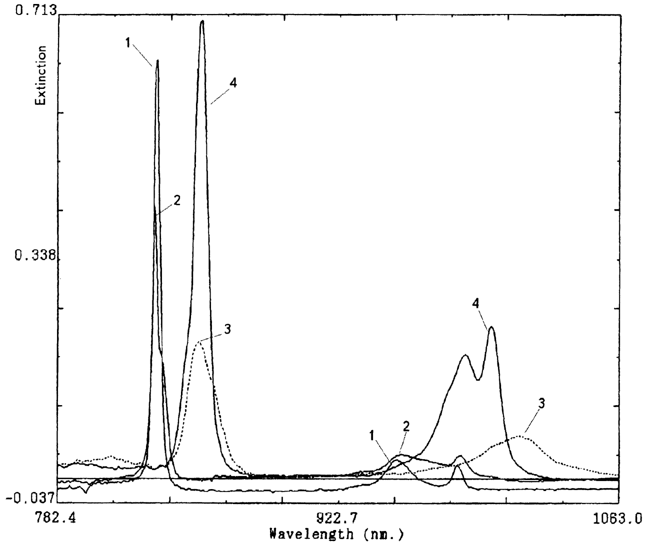

Fig. 3. The absorption spectra of solutions of Pu(VI) in the presence of different XO_4^{2-}-anions. (1) The initial solution, [Pu(VI)]=1.3×10^{-3} mol/l. (2) [Pu(VI)]=1.3×10^{-3} mol/l; [SO_4^{2-}]=1 mol/l. (3) [Pu(VI)]=1.3×10^{-3} mol/l; [CrO_4^{2-}]=1 mol/l. (4) [Pu(VI)]=1.3×10^{-3} mol/l; [MoO_4^{2-}]=1 mol/l.

existence of such hydrates of disulfate complexes of An(VI) with Cs seems to be unlikely. Actually, in a row of the known uranyl complexes $M_2UO_2(SO_4)_2.nH_2O$ (M= Li, Na, K, Rb, Cs) the number of H_2O molecules, *n*, decreases from Li to Cs; therefore, the formation of only anhydrous complexes with cesium is very probable, and may also take place for Np(VI) and Pu(VI).

3.2. Molybdate compounds of An(VI)

The behaviour of Np(VI) and U(VI) in molybdate solutions differed significantly. By adding the neutral solutions of uranyl salts to 1–2 M Na_2MoO_4 solutions, acidified to reach molar Mo:H^+ ratios of 10:1 to 1:1, UO_2^+ concentrated metastable systems were obtained. Several hours (or days) after, a bright-yellow crystal $Na_2UO_2(MoO_4)_2.4H_2O$ product was precipitated from these systems. Note that under different crystallization conditions within the temperature range from 0 to 240°C only this complex with just the same structure was formed.

The addition of 0.01–0.03 M neptunyl(VI) nitrate or perchlorate solutions to 1–2 M Na_2MoO_4 led to the formation of greenish-brown solutions, the spectra of which point to a strong complex formation in such a system. Then, dark-green $Na_2NpO_2(MoO_4)_2.4H_2O$ crystals, as revealed by single-crystal X-ray structural analysis (SCSA) were formed from these solutions, whereas in acidified Na_2MoO_4 solutions the crystals of the other structure were found. The addition of $CsNO_3$ to NpO_2^{2+}-MoO_4^{2-} system resulted in $Cs_2NpO_2(MoO_4)_2.H_2O$ formation, as proved by SCSA.

One of the most interesting compounds isolated from NpO_2^{2+}-MoO_4^{2-} system was a mixed-valence compound with layer structure. Its molar Np(V):Np(VI) ratio was determined by spectrophotometry after dissolving in diluted perchloric acid to be equal to 2:1.

SCSA showed that this mixed-valent compound had the composition like $Na_6[(Np^{(V)}O_2)_2(Np^{(VI)}O_2)(MoO_4)_5].13H_2O$.

3.3. An(VI) chromate compounds

A reddish-brown precipitate, containing several crystal products, was gradually formed from 0.05–0.1 M Np(VI)/ 0.5–1.0 M CrO_4^{2-} solutions. One of these products was of $K_2(NpO_2)_2(CrO_4)_3.4H_2O$ composition, as proved by SCSA. Under the same conditions plutonium(VI) was found to form a solid chromate complex $K_2(PuO_2)_2(CrO_4)_3.4H_2O$ isostructural to $K_2(NpO_2)_2(CrO_4)_3.4H_2O$.

Spectra of several solid compounds are given in Fig. 4 and Fig. 5. Obviously, for $Np^{(VI)}O_2^{2+}/Pu^{(VI)}O_2^{2+}$ solid

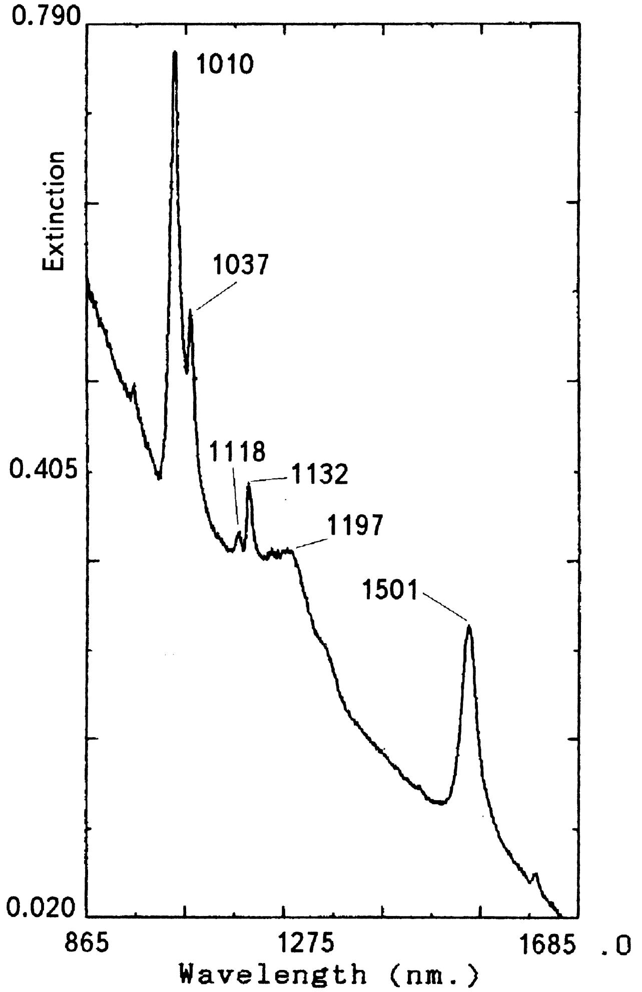

Fig. 4. The absorption spectrum of solid compound $Na_6[(Np^{(V)}O_2)_2(Np^{(VI)}O_2)(MoO_4)_5].13H_2O$ (13 mg) in NaCl-matrix (220 mg).

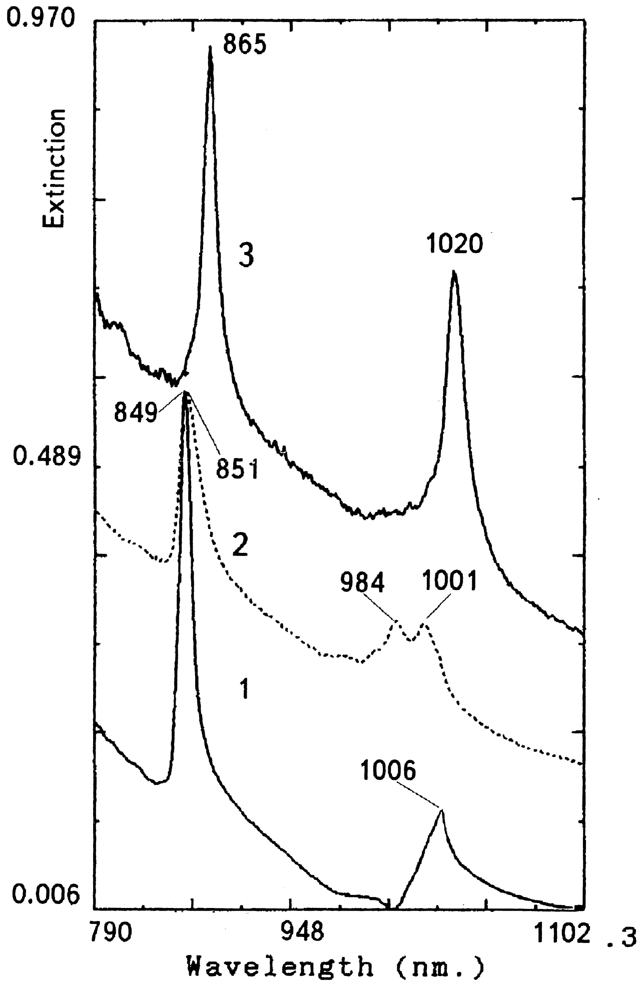

Fig. 5. The absorption spectra of solid Pu(VI) compounds in NaCl-matrix (220 mg). (1) $PuO_2SO_4.2DMSO.H_2O$ (5.03 mg); (2) $PuO_2SeO_4.2DMSO.H_2O$ (10.8 mg); (3) $PuO_2CrO_4.2DMSO.H_2O$ (6.73 mg).

complexes with XO_4^{2-} anions the formation of specific crystal lattice was strongly dependent on the complex preceding formation in solutions.

It follows from the aforementioned data on the complex formation and isolation of solid An(VI) complexes with XO_4^{2-} anions, that isostructural compounds with different XO_4^{2-}-anions could not be produced even for the same AnO_2^{2+}-ion. This fact points to a dependence of complex formation processes on the nature of the actinide and X atom of the anions.

However, we were able to synthesize some complex compounds, like $AnO_2XO_4.2DMSO.H_2O$ (An=Np, Pu; X=S, Se, Cr), which were similar to the known $UO_2SO_4.2DMSO.H_2O$ [12]. According to SCSA data, a coordination AnO_2^{2+} polyhedron in this type of compound was a pentagonal bipyramid, while two of five oxygen atoms located in the equatorial plane of the actinyl(VI) ion, belonged to DMSO molecules. Suggesting this type of AnO_2^{2+} complexes was found earlier for Np(V) compounds [13–15], one could expect an appearance of Laporte-forbidden ff-transition absorption bands similar to those of hydrated AnO_2^{2+} ions.

Table 1
The maxima of absorption bands of Pu(VI) and Np(VI) solid compounds

Compound	λ, nm	Compound	λ, nm
$PuO_2SO_4.2DMSO.H_2O$	849	$NpO_2SO_4.2DMSO.H_2O$	1172
$PuO_2SeO_4.2DMSO.H_2O$	851	$NpO_2SeO_4.2DMSO.H_2O$	1184
$PuO_2CrO_4.2DMSO.H_2O$	865	$NpO_2CrO_4.2DMSO.H_2O$	1165

Maxima of the major Np(VI) and Pu(VI) absorption bands are shown in Table 1.

Thus, the nature of the oxoanion strongly influences the spectral characteristics of AnO_2^{2+} ions, and the extent of such an influence does not correlate with X–O distances in a row SO_4^{2-}–SeO_4^{2-}–CrO_4^{2-} (1.47; 1.63 and 1.61 Å, respectively).

4. Conclusion

This work is the first stage in investigations of physicochemical and spectral properties of hexavalent TUE complexes with various ligands. Our data shows that the properties of solid AnO_2^{2+} compounds with tetrahedral doubly-charged oxoanions are non-monotoneously dependent on the nature of anion and actinide element. Therefore, UO_2^{2+}, NpO_2^{2+} and PuO_2^{2+} ions could not be considered as chemical analogs in systems AnO_2^{2+}-XO_4^{2-} (X=S, Se, Mo, Cr) and it is impossible to predict Np(VI) and Pu(VI) behaviour based only on the data obtained for UO_2^{2+}. It should be stressed that more simple approaches to study on a relationship between complexation in solutions and crystalline complex formation in them are now used by many researchers. For example, using a method of a stepwise substitution of H_2O molecules for XO_4^{2-} ions, at increasing concentrations of the latter [6], is unable to predict the formation of fractional stoichiometry complexes $[(AnO_2)_2(SO_4)_3]^{2-}$, which are rather typical for AnO_2^{2+}.

We believe that the processes which take place in complex formation in solutions and are competitive in crystal lattice formation, are much more sophisticated than can be drawn in the most complete scheme.

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