Synthesis of neptunium(VII) compounds with aluminium and europium in alkaline solutions

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The compounds of actinides (Np and Pu) in an oxidation state of +7 with Al^{III} and rare-earth metals were prepared in aqueous solutions and characterised by IR and UV–VIS spectra.

The studies[1] of the formation of actinide (An) compounds with aluminium(III) in solutions revealed the absence of direct interactions between aluminium ions and neptunium or plutonium in oxidation states of +5 and +6 regardless of pH. At the same time, there is no data on the behaviour of An^{VII} in solutions in the presence of aluminium ions. As for An^{VII} compounds with triply charged cations, well-known $[Co(NH_3)_6]NpO_5$ and $[Pt(NH_3)_6]NpO_5$ complexes and unstable compounds with $[Co(en)_6]^{3+}$ and $[Cr(NH_3)_6]^{3+}$ cations were described.[2] Bulky complex cations, which do not undergo hydrolysis, were chosen to synthesise these compounds. Therefore, it was of interest to prepare a compound of Np^{VII} with the triply charged aluminium cation, which is very small in size and considerably undergoes hydrolysis.

We found that a green precipitate (product **1**) was formed on the slow addition of a 0.1–0.5 M aluminium nitrate solution to a Np^{VII} (~10^{-2} mol dm^{-3}) solution in 0.4–0.5 M NaOH. The precipitation was complete at pH 10–11. The residual Np concentration in the solution was found to be lower than 10^{-5} mol dm^{-3}. The Al:Np molar ratio in the precipitate was close to 1:1. The compound was analysed by a sensitive spectrophotometric technique[6] for determining aluminium in the presence of neptunium with an error of 4.5%. This routine technique was checked by the gravimetric analysis of previously separated neptunium and aluminium. A 100 mg portion of ^{237}Np contained in product **1** was used for gravimetry. The error of the gravimetric determination was 1%. The substance is amorphous to X-rays. The IR spectra are similar to the known spectra[3] of compounds like $Ba_3(NpO_5)_2$. The wide and intense band with a maximum at 730 cm^{-1} is related to the stretching vibrations of –Np–O–Np– chains (Figure 1). The intense bands at 900–1100 and 1250–1450 cm^{-1} result from the deformation vibrations of water molecules and OH groups. The band at 1550–1700 cm^{-1} is characteristic of the deformation vibrations of coordinated water. The intense band with a maximum at 540 cm^{-1} is due to the stretching vibrations of –Al–O–Np– bridges. The IR spectra of all compounds were measured in Vaseline oil because it was found that the grinding of Np^{VII} compounds with KBr promotes the reduction of Np^{VII} to Np^{VI}. Therefore, published spectral data for Np^{VII} compounds in KBr matrices may be incorrect. The electronic absorption spectrum of the freshly prepared precipitate was identical to the spectrum of Np^{VII} anions in alkaline solutions (Figure 2), which exhibits characteristic maximums at 412 and 620 nm.[5] Therefore, it is believed that Np^{VII} occurs as the NpO_5^{3-} anion in the obtained compound, as well as in alkaline solutions.[5] The thermal analysis indicated the presence of a large amount of water ($n_{cryst.}$ ~12) in the test samples. At the same time, these samples did not contain detectable amounts of CO_2. Thus, we can conclude that the synthesised substance has a polymeric structure, which contains large amounts of coordinated and interlayer water and OH groups. The chemical composition of the newly obtained product can be described by the empirical formula $AlNpO_5 \cdot nH_2O$.

The initially green compound $AlNpO_5 \cdot nH_2O$ became black (product **2**) after ageing for several hours either in a dry atmosphere free of CO_2 or in air at room temperature. The electronic absorption and IR spectra and X-ray diffraction data confirmed

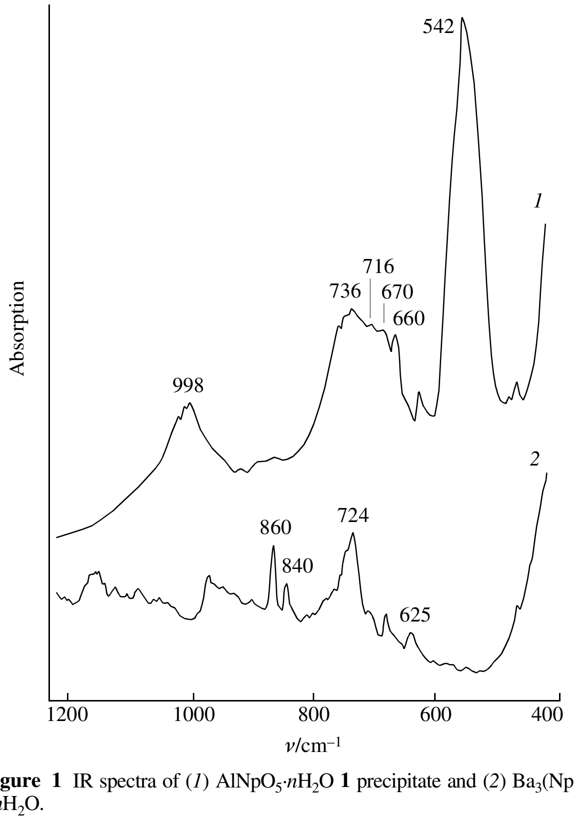

Figure 1 IR spectra of (*1*) $AlNpO_5 \cdot nH_2O$ **1** precipitate and (*2*) $Ba_3(NpO_5)_2 \times nH_2O$.

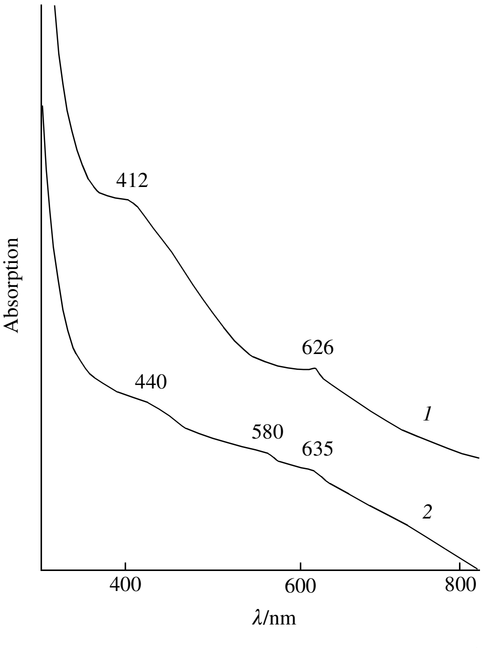

Figure 2 Electronic absorption spectra of (*1*) $AlNpO_5 \cdot nH_2O$ **1** and (*2*) $AlO(NpO_4) \cdot nH_2O$ **2**.

Table 1 X-ray diffraction data for product **2** obtained by the ageing of $AlNpO_5 \cdot nH_2O$ either in a dry atmosphere free of CO_2 or in air at room temperature.

d_{hkl}	I
4.68	strong
4.36	strong
3.02	weak
2.21	weak
1.71	very weak

the identity of both of the aged substances. This fact is also indicative of the absence of active carbonisation of the products, which is known for other Np^{VII} anionic species.[7] X-ray diffraction data also indicate that the substance is much more crystallised than the initial $AlNpO_5 \cdot nH_2O$ (Table 1). However, structural parameters cannot be calculated from these data. Our attempts to obtain better crystallised samples were unsuccessful.

The electronic absorption spectrum of product **2** is much smoother than the spectrum of $AlNpO_5 \cdot nH_2O$. A maximum at 412 nm (Figure 2) is shifted to a long-wave region of 420–460 nm. This fact corresponds to the behaviour of Np^{VII} in solutions as the pH is decreased.[8] If black product **2** was treated with a dilute alkaline solution, the substance became green again and the electronic absorption spectrum became similar to the spectrum of $AlNpO_5 \cdot nH_2O$, which is shown in Figure 2. Note that, after storage for half a day, the compound became irreversibly aged, and the alkaline treatment of the substance did not result in any changes. This can be explained by the formation of a rigid structure as a result of the removal of interlayer water and a part of OH groups during the ageing, which prevents the easy interaction of hydroxyl ions with the aged compound. The X-ray diffraction data for aged product **2** remained almost unchanged, but the signals become more pronounced. Product **2** can also be obtained by the direct interaction of Al^{III} and Np^{VII} in solution. For this purpose, a Np^{VII} solution (10^{-2} mol dm^{-3}) in 0.4–0.5 M NaOH was slowly added to a 0.5 M $Al(NO)_3$ solution to pH 5–6. The X-ray diffraction data confirm the identity of both of the products obtained by ageing of $AlNpO_5 \cdot nH_2O$ in a dry atmosphere or in air and by the direct interaction of the components. The Al:Np molar ratio in product **2** was found to be close to 1:1. The NpO_5^{3-} anion can be transformed into NpO_4^- by decreasing pH of the solution.[9] Therefore, the composition of product **2** can be described by the empirical formula $AlO(NpO_4) \cdot nH_2O$. The IR spectra of the compound retained the bands due to the vibrations of –Np–O–Np– chains (Figure 3). The bands at 900–1100 and 1250–1450 cm^{-1} became less pronounced in comparison with those in the spectrum of $AlNpO_5 \cdot nH_2O$. This can be explained by the dehydration of $AlNpO_5 \cdot nH_2O$ in the course of ageing or by the synthesis at lower pH. Coordinated water is clearly seen in the spectrum of $AlO(NpO_4) \cdot nH_2O$ (a band at 1550–1700 cm^{-1}). It is interesting to note that an intense band at 540 cm^{-1} occurs in the spectrum of $AlNpO_5 \cdot nH_2O$, whereas the IR spectrum of $LiAlO_2$ exhibits a very intense band at 525 cm^{-1}. At the same time, such a band is absent from the IR spectrum of aluminium hydroxide. Therefore, it is believed that the oxygen environments of aluminium atoms in $AlNpO_5 \cdot nH_2O$ and $AlO(NpO_4) \cdot nH_2O$ are similar to the aluminate and hydroxide structures, respectively.

A compound of Np^{VII} with Eu^{III} was synthesised under the same conditions as in the case of $AlNpO_5 \cdot nH_2O$. The IR spectrum of this compound exhibits a broad band at 500–900 cm^{-1}, which is a result of the superposition of the vibrations of Eu–O–Np bridges and Np–O–Np chains. The composition of this compound corresponds to the empirical formula $EuNpO_5 \cdot nH_2O$. It is interesting to note that the obtained compound was not transformed into a species similar to product **2**. Well-known compounds of the $M_3(NpO_5)_2 \cdot nH_2O$ type, where M is an alkaline earth metal, exhibit a similar behaviour. It is likely that this fact can be explained by the much more rigid Eu–O and M–O bonds in the lattices in comparison with Al–O because of the large size of rare earth and alkaline earth metal atoms in comparison with the aluminium atom.

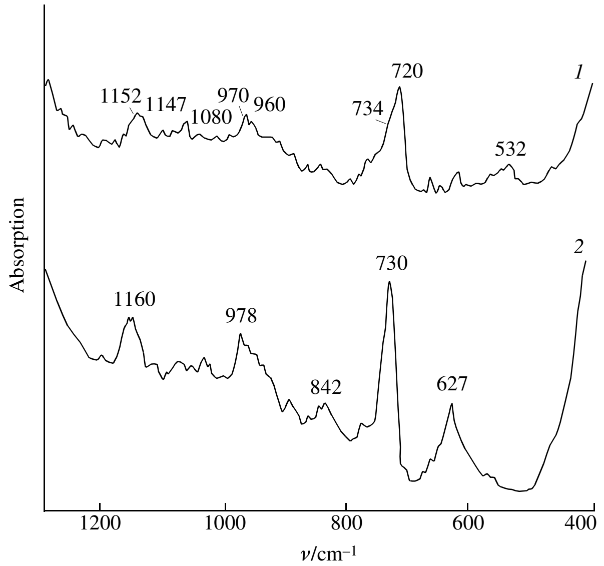

Figure 3 IR spectra of (*1*) $Al(NpO_4) \cdot nH_2O$ **2** and (*2*) $KNpO_4$.

The compounds of Pu^{VII} with Al^{III} and Eu^{III} were obtained under the same conditions as for $AlNpO_5 \cdot nH_2O$. However, the properties of these substances are difficult to study because of the instability of Pu^{VII} resulting from a high redox potential of the pair Pu^{VII}/Pu^{VI} in comparison with the potential of the pair Np^{VII}/Np^{VI}.

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