



Contribution ID: 702

Type: Poster

## Np(V)-phenanthroline-dicarboxylic acid compounds: Synthesis, structure, spectral studies, complexation in solutions

Tuesday, 15 May 2018 18:30 (15 minutes)

The interest in interaction of actinide “yl” cations with anions of heterocyclic carboxylic acids appreciably increased recently, which is caused by a number of factors. In particular, it became clear that the coordination behavior in the series of hexavalent (U, Np, Pu) and pentavalent (Np, Pu, Am) actinides in some systems significantly varies. For more detailed study of the coordination interaction of f elements with various kinds of ligands, it is necessary to expand the range of the experimentally studied complexes. In this aspect 1,10-phenanthroline-2,9-dicarboxylic acid, C<sub>12</sub>H<sub>6</sub>N<sub>2</sub>(COOH)<sub>2</sub> (H<sub>2</sub>PDA), is of much interest. Its specific feature is the rigid structure determined by the phenanthroline core, with fairly strictly fixed distances between atoms of functional groups. These properties of the PDA<sup>2-</sup> ion allow us to expect increased selectivity of the complexation with metal ions depending on their ionic radius. Therefore, this ion is considered as promising ligand for separation of elements with similar properties. Among complexes of actinyl ions, before this work only one uranyl compound, UO<sub>2</sub>(PDA), has been isolated in the crystalline form and structurally characterized. Here three novel complexes of Np(V) with 1,10-phenanthroline-2,9-dicarboxylic acid, of the compositions [(NpO<sub>2</sub>)<sub>2</sub>(PDA)(H<sub>2</sub>O)<sub>3</sub>]·H<sub>2</sub>O (I), (NH<sub>4</sub>)<sub>2</sub>[NpO<sub>2</sub>(PDA)]<sub>2</sub>·3H<sub>2</sub>O (II), and [C(NH<sub>2</sub>)<sub>3</sub>]<sub>2</sub>[NpO<sub>2</sub>·(PDA)]<sub>2</sub>·4H<sub>2</sub>O (III) were synthesized and structurally characterized by a single crystal diffractometry. All the compounds were synthesized by the hydrothermal procedure. The Np atoms in the crystal lattices of all the compounds have the pentagonal bipyramidal coordination surrounding, with the [C<sub>12</sub>H<sub>6</sub>N<sub>2</sub>(COO)<sub>2</sub>]<sup>2-</sup> anions acting as chelate-bridging N,O-donor ligands. In the structure of I, two crystallographically independent NpO<sub>2</sub><sup>+</sup> dioxocations participate in the cation–cation interaction leading to the formation of tetrameric cation–cation complexes. The nonequivalence of the Np atoms is manifested in splitting of the main absorption band of Np(V) in the electronic spectrum of solid compound I. The structures of II and III are based on dimeric anionic complexes [NpO<sub>2</sub>(C<sub>12</sub>H<sub>6</sub>N<sub>2</sub>(COO)<sub>2</sub>]<sub>2</sub><sup>2-</sup>. Only one kind of complexes, NpO<sub>2</sub>(PDA)<sup>-</sup>, was detected in the solution, and high value of the concentration stability constant β ~ 10<sup>12</sup> L mol<sup>-1</sup>, is due to tetradentate coordination of the ligand.

**Primary authors:** BESSONOV, Alexei A. (A.N. Frumkin Institute of Physical chemistry and Electrochemistry Russian academy of sciences (IPCE RAS)); Prof. FEDOSSEEV, Alexandre M. (A.N. Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences); Dr CHARUSHNIKOVA, Iraida A. (A.N. Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences)

**Presenter:** BESSONOV, Alexei A. (A.N. Frumkin Institute of Physical chemistry and Electrochemistry Russian academy of sciences (IPCE RAS))

**Session Classification:** Poster TAN

**Track Classification:** Chemistry of Actinide and Trans-actinide Elements