

Structural variations of uranium compounds with nitrate anions

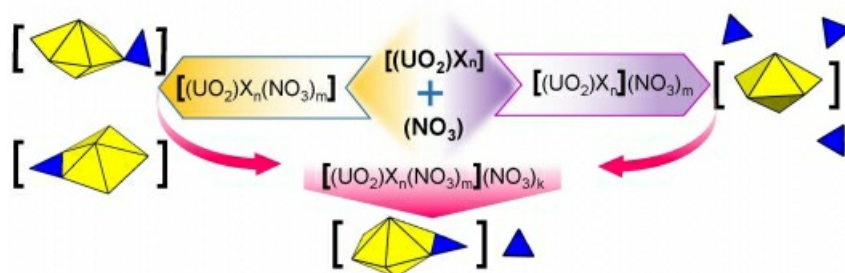
Anastasiya Igorevna Zadova¹, Oleg I. Siidra¹, Evgeniy V. Nazarchuk¹

¹Saint Petersburg State University, Department Of Crystallography, Saint Petersburg, Russian Federation
E-mail: izanastasiia@gmail.com

The nitrate anion, NO_3^- , is known to be widely used in different stages of the PUREX (Plutonium and Uranium Recovery by Extraction) process [1]. By changing nitrate concentration of the initial solution, one may control separation of actinides by various procedures. Three major coordination environments by ligands are observed for linear (UO_2)²⁺ uranyl (Ur) ion in oxocompounds. It is typically coordinated by four, five or six ligands, arranged at the equatorial vertices of UO_4 (square), UO_5 (pentagonal bipyramid) or UO_6 (hexagonal bipyramid), respectively. Nitrate groups in inorganic uranium compounds may either directly coordinate uranyl ion thus forming $[(\text{UO}_2)_n(\text{NO}_3)_m]^{n-2m}$ or being bonded to interstitial cations only with formation of $[(\text{UO}_2)_n\text{X}_m](\text{NO}_3)_n$ complexes, where $\text{X} = \text{O}, \text{Cl}, \text{Br}$. Four new uranyl-nitrate compounds were obtained from aqueous solutions: $(\text{CH}_3)_2(\text{NH}_2)_2[(\text{UO}_2)_2(\text{NO}_3)_2(\text{CrO}_4)_2(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$ (1), $(15\text{-crown-}5)_2[(\text{UO}_2)_2(\text{H}_2\text{O})_4(\text{O}_2)(\text{NO}_3)_2] \cdot (\text{H}_2\text{O})_{3.5}$ (2), $\text{Cs}_2[(\text{UO}_2)_2(\text{NO}_3)_4(\text{OH})_2]$ (3) and $\text{Rb}_3[(\text{UO}_2)_3\text{Cl}_3(\text{NO}_3)](\text{NO}_3)$ (4). The structure of 1 is the first observation of one-dimensional unit (chain) with nitrate groups coordinating UO_6 hexagonal pyramids and formation of $[(\text{UO}_2)_2(\text{NO}_3)_2(\text{CrO}_4)_2(\text{H}_2\text{O})]$. Compound 2 is a rare example of organically templated uranyl compound containing peroxide component with neutral organic and inorganic constituents. Neutral 15-crown-5 and H_2O molecules are packed around $[(\text{UO}_2)_2(\text{H}_2\text{O})_4(\text{O}_2)(\text{NO}_3)_2]$ units providing structural stability exclusively via hydrogen and Van-der-Waals bonding. $[(\text{UO}_2)_2(\text{NO}_3)_4(\text{OH})_2]$ clusters in the structure of 3 were not previously observed in inorganic compounds without organic molecules. And the structure of 4 contains both, NO_3^- directly coordinating uranyl and nitrate bonded to Rb atoms only. The latter is reflected in the structural formula of 4.

This work was supported by the Saint-Petersburg State University internal grant 3.38.238.2015.

[1] Nash K.L. et al., J. Fuger (Eds.) (2006) Chemistry of the Actinide and Transactinide Elements, 4, Springer, The Netherlands, 2644–2666.



Keywords: [nitrates](#), [uranium](#), [clusters](#)