Complexation of UO_2^{2+} by 1,10-phenantroline-2,9-dicarboxamides

S. V. Gutorova[1], E. A. Konopkina[1], P. I. Matveev[1], A. L. Trigub[1,2], P. S. Lemport[1], S.N. Kalmykov [1], K.O. Kvashnina[1,3,4]

[1]Department of Chemistry, Lomonosov Moscow State University, 119991 Moscow, Russia;
svetlana.gutorova@chemistry.msu.ru (S.V.G.); konopkina.kate@gmail.com (E.A.K.); petr.i.matveev@gmail.com (P.I.M.); alexander.trigub@gmail.com (A.L.T.); lemport.pavel@yandex.ru (P.S.L.); stepan_5@hotmail.com (S.N.K.); kristina.kvashnina@esrf.fr (K.O.K.)
[2]National Research Centre “Kurchatov institute”, 1 Akademika Kurchatova pl., 123182 Moscow Russia
[3]The Rossendorf Beamline at ESRF – The European Synchrotron, CS40220, 38043 Grenoble CEDEX 9, France
[4]Helmoltz-Zentrum Dresden-Rossendorf (HZDR), Institute of Resource Ecology, P.O. Box 510119, 01314 Dresden, Germany

The process of complexation of organic ligands with actinides is the basis of nuclear technologies used for spent nuclear fuel processing. Worldwide, new solvent extraction systems for the separation of the transuranium elements from spent nuclear fuel are under development. A family of 1,10-phenanthroline-2,9-dicarboxamides is promising for group separation of actinides. One of their interesting features is the influence of substituents at the amide nitrogen atom on their extraction properties [1]. Understanding coordination structures of actinide ions in the organic solution can shine light on extraction mechanisms. In the present work we investigated differences between coordination of organic ligands with UO_2^{2+} in solid-state and in the organic phase and the influence of substituents on such coordination. Therefore, selected 1,10-phenanthroline-2,9-dicarboxamides (Fig. 1) differ by substituents at the amide nitrogen atom: alkyl-alkyl (**1**), alkyl-aromatic (**2**), and two cyclic substituents – six- (**3**) and five- (**4**) membered rings.

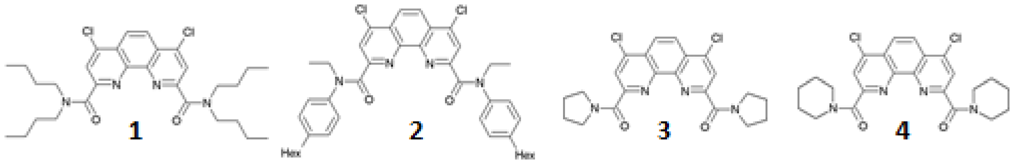

Figure 1. 1,10-phenanthroline-2,9-dicarboxamides studied in this research

Extended X-ray absorption spectroscopy (EXAFS) was performed for four complexes of uranyl ion with ligands **1**-**4** in 1-nitro-3-(trifluoromethyl)benzene solution. Also, monocrystal of **4** with UO_2^{2+} was investigated by x-ray diffraction (XRD) and EXAFS. The conventional method of EXAFS spectra approximation showed that the substituent group does not change the coordination structure of UO_2^{2+} complexes, which confirms results by Zhang X. et al [1]. For further study of complexation specifics, we employed a reverse Monte-Carlo (RMC) method using EvAX code [2]. Based on atomic coordinates derived from RMC optimization radial distribution function (RDF) curves were built for coordination centers (Fig. 2). The RMC-EXAFS method confirmed previous results and showed that NO_3^--group has a stronger bond with UO_2^{2+} in solution than in crystal and amide oxygens (-C=O) are unsymmetrical in solution compared to crystal (for complex **4**).

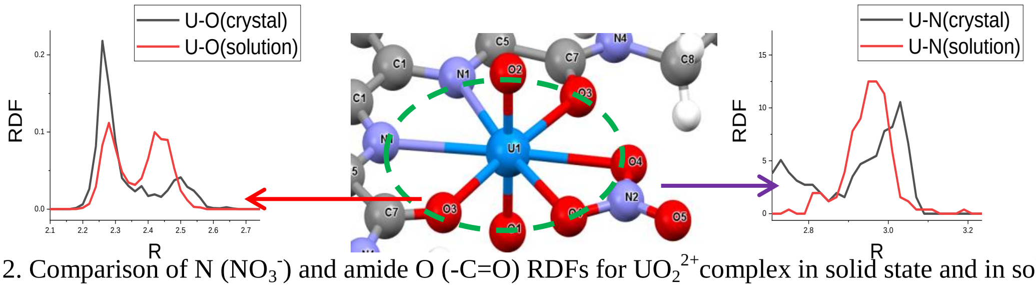

Figure 2. Comparison of N (NO_3^-) and amide O (-C=O) RDFs for UO_2^{2+}complex in solid state and in solution.

References

[1] – Zhang X., Yuan L., Chai Z., Shi W. // Sci China Chem. 2018. V. 61. P. 1285–1292
[2] – Timoshenko J., Kuzmin A., Purans J. // J. Phys. Condens. Matter. 2014. V. 26. 055401.