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## ORAL PRESENTATION - Selectivity of bis-triazinyl bipyridine ligands for americium(III) in Am/Eu separation by solvent extraction. Quantum mechanical study

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Selective separation of actinide elements from highly radioactive nuclear waste is the key issue for modern technologies of nuclear waste reprocessing. Partitioning of long-lived minor actinides, in particular americium, and their subsequent transmutation into short-lived radionuclides would lead to a significant reduction of long-term environmental hazard from this radiotoxic waste, and contribute to the development of safe nuclear power. Derivatives of 6,6'-bis([1,2,4]-triazin-3-yl)-2,2'-bipyridine (BTBP), tetra-N-dentate lipophilic ligands which selectively extract trivalent actinides (An) over lanthanide fission products (Ln) from nitric acid solutions to organic solvents (SANEX process), have been considered the most promising species for hydrometallurgical recovering (partitioning) the minor actinides from high-level radioactive waste.

Theoretical studies were carried out on two pairs of americium and europium complexes formed by the BTBP ligands, neutral  $[ML(NO_3)_3]$  and cationic  $[ML_2]^{3+}$  where  $M = Am(III)$  or  $Eu(III)$ , and  $L = 6,6'$ -bis-(5,6-diethyl-1,2,4-triazin-3-yl)-2,2'-bipyridine (C2-BTBP). Molecular structures of the complexes have been optimised and total energies of the complexes in various media calculated using the DFT method (Gaussian 09). Selectivity in solvent extraction separation of two metal ions is a co-operative function of contributions from all extractable metal complexes. The individual contributions depend on physico-chemical properties of the complexes and on their relative amounts in the system. Semi-quantitative analysis of BTBP selectivity in the Am/Eu separation process has been carried out, based on the contributions from the two pairs of Am(III) and Eu(III) complexes. To calculate the energy of Am/Eu separation, a model of extraction process was used, consisting of complex formation in water and transfer of the formed complex to the organic phase. The greater thermodynamic stability (in water) of the Am-BTBP complexes, as compared with the analogous Eu species, caused by greater covalencies of the Am-N than Eu-N bonds, is most likely the main reason of BTBP selectivity in the separation of the two metal ions. The other potential reason, i.e. differences in lipophilic properties of the analogous complexes of Am and Eu, is less important with regards to this selectivity.

Analysis of Am-BTBP and Eu-BTBP bonding in the complexes studied, performed with the use of theoretical methods: QTAIM, CMO and NBO, allows us to conclude that the origin of the selectivity of BTBP ligands for Am over Eu is due to different contributions into bonding from various atomic orbitals of the Am(III) and Eu(III) ions.

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