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On the origin of selectivity of bis-triazinyl bipyridine ligands for complexation of americium(III) over lanthanides. Quantum mechanical analysis of M–N bonds

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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, followed by their transmutation into short-lived and stable nuclides 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), the tetra-N-dentate lipophilic ligands which selectively extract trivalent actinides (An) over lanthanide fission products (Ln) from nitric acid solutions (modeling PUREX raffinate) to organic solvents (SANEX process), have been considered the most promising species for partitioning the minor actinides from high-level nuclear waste.

Recent theoretical studies, 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) [J. Narbutt, W.P. Oziminski, Dalton Trans. 41, 14416 (2012)], have shown that greater thermodynamic stability (in water) of the Am-L complexes than that of the analogous Eu species, caused by greater covalencies of the Am–N than Eu–N bonds, is the main reason of BTBP selectivity in the separation of these metal ions.

Theoretical analysis of Am–N and Eu–N bonds in the BTBP complexes was carried out in this work, with the use of one-component Zeroth Order Regular Approximation (ZORA) Hamiltonian and Kohn-Sham density functional theory. Kohn-Sham orbitals were analyzed with Natural Population Analysis (NPA), Mulliken Population Analysis, Second Order Perturbation Theory (SOPT) implemented for Natural Bond Orbitals (NBO) and Symmetrized Fragments Orbitals (SFO) with overlap populations density-of-states (OPDOS). Electron density was analyzed with The Quantum Theory of Atoms in Molecules (QTAIM). The QTAIM analysis for the bond critical points (BCP) confirms mostly ionic character of M–N bonds with slightly bigger covalent contribution for the Am–N than Eu–N bonds. This is due to a bigger charge transfer from the ligand to the Am than Eu ion, in particular to the 6d(Am) and 5d(Eu) orbitals. The results of the SOPT method show that the greater shift of electron density on the 6d(Am) orbitals is due to the large overlap integrals of 6d(Am) with the ligand donor orbitals, not to the smaller energy gap. This is in line with the calculated greater radial expansion of the 6d(Am) than 5d(Eu). The OPDOS coupled with the SFOs has shown that outermost occupied MOs as well as inner MOs are involved in the M–N interactions.

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