Abstract

In the first part of the present work the performance of already proposed $5f$-*in-core* pseudo-potentials for the trivalent actinides An^{3+} is investigated in calculations for model complexes $An^{3+}L^{n-}$ for three selected actinides ($An^{3+}=Ac^{3+}$, Cm^{3+}, Lr^{3+}) and eight simple ligands with atoms from the first three periods of the table of elements ($L^{n-}=F^-$, Cl^-, OH^-, SH^-, CO, NH_2^-, H_2O, H_2S, NH_3).

Results of Hartree-Fock and coupled cluster with singles, doubles and perturbative triples calculations using basis sets of quadruple-zeta quality are compared to corresponding reference data obtained with scalar-relativistic energy-adjusted $5f$-*in-valence* small-core pseudopotentials.

The inclusion of core-polarization potentials in the $5f$-*in-core* pseudopotential calculations and corrections of the basis set superposition error by the counterpoise correction leads to very good agreement between the $5f$-*in-valence* and $5f$-*in-core* pseudopotential results for bond lengths, bond angles and binding energies.

Results from $5f$-*in-core* and $5f$-*in-valence* pseudopotential calculations using five different density functionals also show reasonable agreement with the more rigorous coupled cluster results. For all three computational methods, two kinds of basis sets were used within the $5f$-*in-valence* calculations: segmented contracted and atomic natural orbital basis.

In the second part density functional theory calculations combined with energy-consistent $5f$-*in-core* pseudopotentials for trivalent f-elements are used to study different complexes of Am^{3+}, Cm^{3+} and Eu^{3+} with bis(2,4,4-trimethylpentyl)dithiophosphinic acid (known as Cyanex 301®, denoted as HL).

The focus lies on the exact geometry, stoichiometry and hence on the coordination number of some postulated complexes ML_3, HML_4, $ML_3(H_2O)$ and $HML_4(H_2O)$. Furthermore, the complex binding energies are calculated considering solvation effects and zero-point vibrational energies. The outlying charge correction within the solvation model, using the COSMO approach, was taken into account, too.

To correct the error within the COSMO model for hydrogen bonds, which occurs in aqueous solutions, a correction term was determined related to different reactions for the formation of water clusters. It is shown that all three cations form the same preferred complex with Cyanex 301®. They have the coordination number six and expose the stoichiometry ML_3.