

In Search of Covalency Measure of Gd(III)-Ligand Interactions

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Streszczenie

Experimental electron density distribution of the $[\text{C}(\text{NH}_2)_3]_3[\text{Gd}(\text{EDTA})\text{F}_2] \cdot \text{H}_2\text{O}$ crystal was determined. The derived experimental and theoretical (DFT) topological parameters such as $\nabla^2\rho_c$, ρ_c , bond degree (BD), kinetics, and potential energy were used to study the nature of Gd–O, Gd–F, and Gd–N interactions. The natural charge of the Gd is 1.86; the natural configuration of the cation is $[\text{Xe}]6s^{0.13}4f^{7.10}5d^{0.83}$, and the covalency of the Gd–L bond is mainly connected with the transfer of charge from the sp^x ligand orbitals onto the 5d orbitals of the Gd cation. Simultaneously, the donation of charge onto the 6s and 4f orbitals occurs to a lesser extent. Moreover it was found that the donation of the ligand charges onto the Gd(III) is larger for compounds with a lower coordination number. The obtained topological parameters were analyzed in the context of the Gd(III) f–f transition properties, i.e., energy of the excited $^2S+1L_J$ states, Judd–Ofelt intensity parameters, and luminescence lifetimes, of 18 Gd(III) compounds with various O, N, and F donor ligands (DOTA, EDTA, CDTA, DTPA, NTA, EGTA, ODA, F^- , H_2O , and CO_3^{2-}). The calculated nephelauxetic β parameter may reflect the penetration degree of electron lone pairs of ligands inside the metal basin. Finally, it was found for the first time that the sum of the Gd(III)–L bond energy ($\sum E_{\text{GdL}}$) is correlated with the position of the gravity center of the $^8S_{7/2} \rightarrow ^2S+1L_J$ transitions and increase of covalency of the Gd(III)–L bonds is associated with decrease of their bond energy. The obtained results may shed light on chemical bonding in systems containing f-elements. Such subtle differences in the covalent contribution to the Ln–L or An–L bond may tune the selectivity of the partitioning processes of lanthanides and actinides.

Słowa kluczowe

Cations, Crystals, Electron Density, Ligands

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