

Abstract

Especially the investigation of a looming relationship between rare-earth cluster complexes with endohedral transition metal atoms and corresponding intermetallic phases lies in focus of the present work. Cluster complexes of the rare-earth elements (R) are stabilized by interstitial atoms in almost all known cases. If a transition metal (T) is incorporated, the included $\{T_nR_m\}$ units can be described as cut-outs of the crystal structure of binary intermetallics, which are separated from each other by surrounding halide ligands (X). This view could be verified by investigations on the crystal structure, electronic structure and the physical properties. To characterize the obtained compounds, data from single crystal X-ray diffraction (SCXRD), theoretical calculations based on DFT- or *ab-initio*-methods and magnetic measurements for appropriate samples were used. In that way a trend of a structural and electronic approach of interstitially stabilized cluster complexes to intermetallics by an increasing cluster condensation could be proved. The description of the bonding within both classes of compounds in the sense of polar intermetallics has been verified through bandstructure calculations.

As part of the experimental work the structural diversity of cluster complexes within the systems Pr/T/X (X = Cl, Br, I; T = Fe, Co, Ir, Os, Pt, Rh, Ru) and Tb/Ir/Cl was increased successfully, using the comproportionation route. Thereby three different structure types could be obtained, all containing isolated, octahedral $\{TR_6\}$ cluster units. In the case of the compounds $\{TPr_6\}Br_{10}$ (T = Fe, Os), crystallizing in the $\{TR_6\}X_{10}$ type of structure, a connection between an occurring structural distortion and the electronic structures was explored in more detail. With the compounds $\{TPr_6\}I_{12}Pr$ (T = Rh, Pt) two further examples of the $\{TR_6\}X_{12}R$ type of structure were characterized, utilizing SCXRD. In this connection again an interplay between certain interatomic distances, that means structural factors, and electronic relations could be explained through bandstructure calculations. Both new examples of $\{TPr_6\}Cl_{41}$ (T = Co, Ir) show that the $\{TR_6\}X_{41}$ type can be considered as a third, frequently occurring type of structure of isolated cluster complexes.

Oligomeric cluster complexes of the rare-earth elements could be expanded by the new type of structure of $\{Os_3Pr_{11}\}Cl_{16}Pr$. This compound shows trimeric $\{Os_3Pr_{11}\}$ cluster units, which till now have only been observed for cluster complexes of gadolinium. It contains additional, discrete Pr atoms that are missing in the corresponding well-known Gd compounds. In addition, a further example of tetrameric cluster complexes, containing a capped *Friauf*-polyhedron like cluster units and additional, discrete Tb atoms, was obtained with the compound $\{Ir_4Tb_{16}\}Cl_{24}(TbCl_3)_4$. Both oligomeric cluster compounds show a concerted distortion, whose connection to the electronic structures could be verified by bandstructure calculations.

The cluster complexes of the cubic $\{TR_3\}X_3$ type of structure form three-dimensional networks of helical, interpenetrating cluster chains. Three further examples, $\{TPr_3\}Br_3$ (T = Os, Rh, Pt), were char-

acterized through single crystal X-ray diffraction measurements. In particular, for comparison with corresponding intermetallics, bandstructure calculations were carried out on these and other chain like cluster complexes with eight-coordinate interstitial atoms.

Intermetallic compounds were obtained within the systems T/Pr (T = Co, Ni, Pt), T/Tb (T = Au, Pd, Rh, Ru), and T/Er (T = Rh, Pd) utilizing the *flux-growth*-route. Due to the ratio of $R/T \geq 1$ a structural description using coordination polyhedra of R atoms surrounding a central transition metal atom is useful. Thus, a new type of structure was obtained with the compound Pt_3Pr_4 , which can be described as a layered structure of $\{PtPr_n\}$ polyhedra. Similar but different versions of stackings of layers have been observed within the crystal structures of the compounds $AuTb_2$, Ni_3Pr_7 , T_3Tb_7 (T = Rh, Pd) and Ru_2Tb_5 . However, the compounds Co_7Pr_{17} and Pd_7Er_{17} show a complex structure of differently oriented clusters of polyhedra. Additionally, with the synthesis of Rh_2Er_3 a compound showing chains of face-sharing $\{RhEr_3\}$ cubes and square antiprisms, has been obtained. In particular this one is very conducive for a comparison with cluster complexes of the rare-earth elements, as similar chain structures are also known for this class of compounds, giving the chance to clarify present similarities in a special way.

Furthermore, four cluster complexes containing endohedral non-metal atoms (E) were obtained, which on the one hand represent two new examples of known ($\{N_4Pr_9\}Br_{16}$ and $\{NTb_2\}Cl_3$) and, on the other hand, of two hitherto unknown types of structure, $\{N_4Pr_{10}\}Cl_{20}Pr$ and $\{O_4Tb_8\}Cl_{15}$.