

Abstract

Thirteen new rare-earth compounds could be synthesized and characterized via X-ray-diffraction in the context of the present work. Herein each class of condensation are represented except of layer structures.

New representatives of the $\{ZM_6\}X_{10}^-$ and $\{ZM_6\}X_{12}M$ -structure were synthesized in the class of monomeric clusters. $\{Ru_3Gd_{11}\}Cl_{15}$ is the third compound with trimeric clusters which are condensed via octahedral faces and could be characterized in the class of oligomeric clusters. With the synthesis of $\{Ru_4Gd_{16}\}Br_{24}(GdBr_3)_4$ yet another representative with tetrameric clusters could be characterized. This compound was topologically and electronically compared with $\{Ru_4Gd_{16}\}Br_{23}$ and with the isotypic compounds $\{Os_4Sc_{16}\}Cl_{24}(ScCl_3)_4$ and $\{Ru_4Sc_{16}\}Cl_{24}(ScCl_3)_4$. The substitution of the endohedral atom gave a rise to electronically provoked distortions in the analyzed oligomeric clusters (e. g. $\{Ir_3Gd_{11}\}Cl_{15}$).

The synthesized compounds $\{RhY_3\}I_3$, $\{CoGd_3\}I_3$, $\{RuGd_3\}Br_3$ and $\{OsGd_4\}Cl_4$ are characterized by chains of edgecondensed clusters. Noticeable is the increase of the coordination number for the endohedral atoms from (6+1) (in $\{ZM_3\}X_3$) to 8 (in $\{ZM_4\}X_4$). Chains of edgecondensed tetraedra could be realized via incorporating nonmetal atoms as oxygen and $(\beta\text{-}\{NGd_2\}Cl_3$ and $\{O_4Gd_8\}Cl_{15}$). $\{Ru_2Lu_3\}$ and $\{Rh_4Gd_5\}$ are representatives of the class of formally highest condensation.

The bonding situation of all together 27 compounds were investigated via band structure calculations utilizing TB-LMTO-ASA.

An increase of the metallic interactions in depending of the degree of condensation could be observed. Likewise the "magic" number of cluster based electrons decrease with increasing condensation. Homoatomic interactions increase with growing condensation as well, but are even in high condensed phases less important. Due to the inconvenience to determine the degree of condensation quantitatively it is difficult to analyze the influence of the condensation on the bonding situation. Nevertheless it seems that the condensation has the function to balance the CBE-budget.

Furthermore in some structures there is less correlation between interatomic distances and bonding nature. The shortness of those secondary interatomic contacts seems to be the

consequence of primary bonding interactions (e. g. α -{NGd₂}Cl₃).

The analysis of different compounds of one system Z/M/X exposed various bonding situations without disclosing an electronically preferred structure type.