Abstract

The structural variety of compounds consisting of rare-earth metal cluster complexes is almost overwhelming. Compounds being interstitially stabilized by transition metal atoms are a matter of particular interest. A plethora of such cluster-complexes have been known for the elements scandium, yttrium, lanthanum, praseodymium and gadolinium, whereas compounds of terbium and erbium were under-represented. In consequence, the main objective of this work was to synthesize and characterize new compounds with cluster complexes of terbium and erbium resp.. Furthermore, the magnetic behavior should be determined whenever feasible.

A total of 45 compounds could be characterized. Compounds belonging to the formula types $\{ZM_6\}X_{12}M$ and $\{ZM_6\}X_{10}$ (e.g. $\{IrEr_6\}I_{12}Er$ and $\{IrEr_6\}I_{10}$) consist of isolated cluster complexes. The structural relationship between these types of structure can be understood by a kind of shear process. In dependence on the electronic configuration resp. the type of structure distinguishable, deviations of Z-M bond lengths could be observed that are in good agreement with simple MO considerations. Cluster complexes consisting of condensed agglomerates were revealed in $\{Z_4Tb_{16}\}Br_{24}\cdot 4TbBr_3$ (Z = Rh, Ir). At least the internuclear distances Z-Z of the iridium compound give a hint at the occurrence of bonding interactions between these endohedral atoms. The even more condensed, chainlike structure of $\{MnTb_4\}I_6$ shows an incorporation of a transition metal atom for the first time. Higher coordination numbers of endohedral transition metal atoms could be realized in compounds of the formulae $\{ZM_3\}X_3$ (CN 6+1) and $\{ZM_4\}X_4$ (CN 8). In $\{RuTb_3\}Br_3$ and also $\{ZEr_3\}I_3$ (Z =Ru, Ir) cluster complexes are built up by monocapped trigonal prisms sharing common almost square faces. This leads to a chain like constitution of the cluster scaffold incorporating a “zig-zag” chain subunit of the interstitials. Once more the Z-Z distances can be interpreted in terms of bonding interactions. Beyond that, magnetic interactions involving these endohedral atoms seem to be nearly excludable as could be shown by magnetic investigations of $\{RuTb_3\}Br_3$ and $\{RuM_3\}I_3$ (M = Y, Er). In $\{OsEr_4\}Cl_4$ and $\{OsM_4\}Br_4$ (M = Tb, Er) a “zig-zag” chain-like subunit of the interstitials is observed, too. As opposed to the aforementioned type of structure the endohedral atoms reside in distorted chains of face-sharing square anti-prisms. On the basis of $\{OsTb_4\}I_4$ and $\{ZEr_4\}I_4$ (Z = Re, Os) a novel representative of the $\{ZM_4\}X_4$ family with a sinoidal distortion of cluster chains could be established. This sine-wave like modulation that is also found for the interstitial subunit achieves identity after a period of nine cluster-chain links.