Abstract

The intention of this work was the synthesis and characterization of new dysprosium and holmiumcluster halides. Magnetic measurements were used to analyse the magnetic properties of some compounds. Clustercomplexes oft the rare-earth-elements R are in almost all cases stabilized by an endohedral atom Z. They can be described by the formula $\{Z_aR_b\}X_c$ ligand atoms are represented by X. The endohedral atom may be a non-metal (Z = E) or a transition-metal (Z = T). For synthesis a combination of metallothermic reduction and conproportionation routes was used. Single crystal and powder X-ray diffraction was utilized for characterization. So far, there were neither known any cluster complexes for the systems T/Dy/X nor Z/Ho/Br. Therefore, the experiments were focused on these systems.

Further examples of isolated cluster complexes of the $\{TR_6\}X_{12}R$ type are $\{THo_6\}Br_{12}Ho$ (T = Co, Ni), $\{THo_6\}I_{12}Ho$ (T = Co, Os) and $\{TDy_6\}I_{12}Dy$ (T = Co, Ru, Os and *Ir*). Based on the number of the valence electrons of the endohedral atom distances within the cluster change because the number of (anti-) bonding interactions is dependent upon the electron count.

In $\{(C_2)_2Ho_{10}\}Br_{18}$, $\{(C_2)_2O_2Ho_{14}\}I_{24}$, $\{Ru_4Ho_{16}\}Br_{20}$, $\{Ir_4Ho_{16}\}Br_{24}(HoBr_3)_4$ and $\{Ru_4Dy_{16}\}I_{20}\{\square Dy_4\}I_8$ the cluster complexes are built by oligomeric units. Additional octahedral $[HoBr_{6/2}]$ chains or $\{\square Dy_4\}I_8$ tetrahedra completes the structures of the latter two compounds. All three cluster complexes in $\{Ru_4Ho_{16}\}Br_{20}$, $\{Ir_4Ho_{16}\}Br_{24}(HoBr_3)_4$ and $\{Ru_4Dy_{16}\}I_{20}\{\square Dy_4\}I_8$ exhibit transition metal stabilized tetramers. The distances in the metallic framework vary with the endohedral transition metal, the rare-eart metal and the crystal system as well.

Chain structures are observed in $\{(C_2)Ho_4\}I_6$, $\{RuHo_3\}I_3$, $\{OsHo_4\}X_4$ (X = Cl, Br and I), $\{IrR_4\}Br_4$ (R = Dy and *Ho*) and $\{ReHo_4\}Cl_4$. C_2-intercalated octahedra connect via *trans*-edges in $\{(C_2)Ho_4\}I_6$. The chains in $\{RuHo_3\}I_3$ are built by face condensed monocapped trigonal holmium prisms, which are stabilized by endohedral ruthenium atoms. An increase of the coordination number oft he endohedral atom is realized in compounds with the composition $\{TR_4\}X_4$. The endohedral transition metals are coordinated by eight rare-earth atoms, which build face-sharing square antiprisms. The chains of the monoclinic structure

type $\{ZR_4\}X_4$ with X = Cl and Br are stronger connected via ligands and are arranged in the fashion of a tetragonal packing. In case of X = I $\{TR_4\}X_4$-compounds crystallize in the orthorhombic system in a hexagonal arrangement.