

Die Lanthanoid(III)-Chlorid-Oxoselenate(IV) $MCl[SeO_3]$

($M = Sm - Lu$) im $HoCl[TeO_3]$ - oder B-Typ

The Lanthanoid(III) Chloride Oxoselenates(IV) $MCl[SeO_3]$ ($M = Sm - Lu$) with $HoCl[TeO_3]$ - or B-Type Structure

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The B-type lanthanoid(III) chloride oxoselenates(IV) $MCl[SeO_3]$ ($M = Sm - Lu$) crystallize in the orthorhombic space group *Pnma* (no. 62) with $Z = 4$ in the structure type of $HoCl[TeO_3]$. Their lattice constants are decreasing following the lanthanoid contraction from $a = 730.01(7)$, $b = 707.90(7)$, $c = 895.64(9)$ pm for $SmCl[SeO_3]$ to $a = 714.63(7)$, $b = 681.76(7)$, $c = 864.05(9)$ pm for $LuCl[SeO_3]$. In contrast to $NdCl[SeO_3]$, the only representative of the A-type structure, where the coordination numbers of the Nd^{3+} cations are 7+2 and 8, the B-type structure is dominated by pentagonal bipyramids $[MO_5Cl_2]^{9-}$ ($CN(M^{3+}) = 7$), which are connected *via trans*-oriented $O \cdots O$ edges to ${}_{\infty}^1\{[MO_{4/2}^e O_{1/1}^t Cl_{2/1}^t]^{5-}\}$ chains (e = edge-sharing, t = terminal) running parallel to the [010] direction. Their inclination relative to each other allows for an alternating interconnection of these chains *via* Cl^- and ψ^1 -tetrahedral $[SeO_3]^{2-}$ anions to form a three-dimensional structure. The distances within the $[SeO_3]^{2-}$ groups are in the normal range ($d(Se-O) = 165 - 172$ pm), while those of the O^{2-} and Cl^- anions to the central M^{3+} cation diminish in dependence of the increasing atomic number ($d(M-O) = 226 - 244$ pm / $216 - 232$ pm, $d(M-Cl) = 277 - 278$ pm / $266 - 270$ pm, $M = Sm/Lu$). For the synthesis of the chloride oxoselenates(IV) $MCl[SeO_3]$ the respective lanthanoid sesquioxide (M_2O_3) and selenium dioxide (SeO_2) were reacted with either an eutectic mixture of $RbCl$ and $LiCl$ or with the corresponding lanthanoid trichloride (MCl_3) in evacuated silica ampoules for either five weeks at $500^\circ C$ or one week at $850^\circ C$.

Key words: Lanthanides, Chlorides, Oxoselenates(IV), Crystal Structures