Structure of Rare-earth/Group-IIIA Chloride Complexes

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We evaluate the structures taken by vapour complexes of chloride compounds with the chemical formula $M_nRCl_{3(n+1)}$ where R is a selected rare-earth element, M a group-IIIA element, and $n = 1$, 2, or 3. The main predictions that emerge for the most stable structures from our model calculations are as follows: (i) in $MRCl_6$ a fivefold coordination of the rare-earth element (for R = La, Nd, Er, or Lu) is very stable relative to a fourfold one, with the excess binding energy decreasing slightly from La to Lu and being almost the same when M = Al or Ga; (ii) a sixfold coordination of Nd becomes very stable in Ga_2NdCl_9; and (iii) sevenfold and eightfold coordinations of Nd can arise in Ga_3NdCl_{12}, with the latter being more stable. All these structures are obtained from the RCl_3 monomer by substituting n chlorines with n MCl_4^- distorted tetrahedra, which complete the coordination shell of the rare-earth ion *via* edge or face-sharing. This criterion combines high coordination of the rare-earth ion with shielding of its Coulomb field by bonding chlorines in double or triple sets. The possible appearance of the unusual fivefold and sevenfold coordination states in the vapour complexes should provide further motivation for experimental structural studies and for refined quantum-chemical calculations.

Key words: Ionic Clusters; Vapour Complexes; Molten Salts.