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.

1. Introduction

Vapour complexation of solid rare-earth halides with gaseous halides of group-IIIA elements such as Al, In or Ga increases their apparent volatility by factors that, depending on the system and on temperature, may reach up to 10^{13}. This property is of crucial importance for a number of technical applications of rare-earth materials [1] and has motivated many experimental studies of the gaseous clusters, ranging from thermodynamic measurements to electronic absorption and fluorescence spectroscopy (see Boghosian and Papatheodorou [2] and references given therein). The so-called hypersensitive *f*-electron transition spectra of lanthanide chlorides, whose intensity increases when the rare-earth is surrounded by a field of lower symmetry, have some structural implications with regard to the role of the countercation in polarizing the chlorines and to temperature-dependent shifts of the chemical equilibrium between the various species. However, these spectroscopic techniques do not give adequate information on the microscopic structure, such as could be derived from diffraction experiments on the vapour or from matrix-isolation infrared and Raman-scattering studies.

In this perspective Boghosian and Papatheodorou [2] have proposed a number of possible structures for vapour complexes described by the chemical formula $M_nRX_{3(n+1)}$, where R is a rare-earth element, M a group-IIIA element, X a halogen, and n can take the values from 1 to 4. For each n they list structures in the shape of highly symmetric rings or clusters and allow for an increase of the rare-earth coordination number in the complex as n increases, from fourfold in MRX_6 to that of solid rare-earth halides (reaching up to nine in a number of compounds). The assumption that the coordination of the lanthanide ion in vapour complexes may increase with the number of available halogens is very reasonable and is consistent with the experimental evidence, as discussed by Boghosian and Papatheodorou [2]. In this view, both eightfold and ninefold coordinations could arise for the first time in M_3RX_{12}. No experimental studies nor theoretical calculations seem to have been carried out to ascertain the various possibilities.

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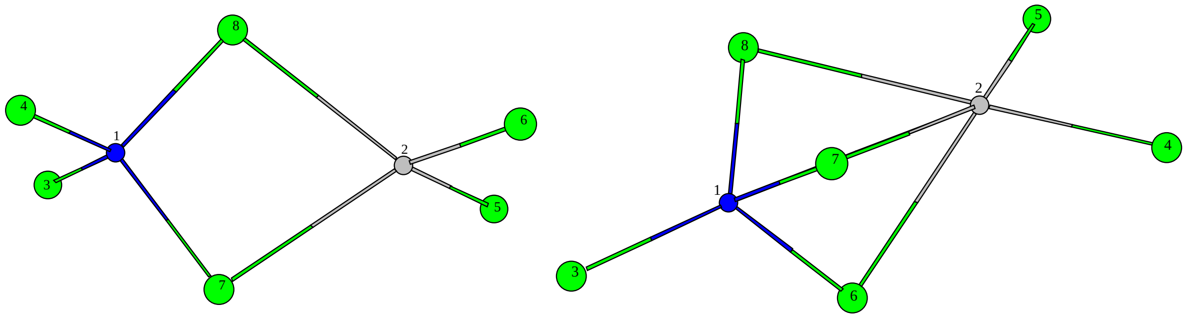

Fig. 1. Ball-and-stick picture of the fourfold (*left*) and fivefold (*right*) configurations of the $MRCl_6$ vapour complex. The group-IIIA ion (M) and the rare-earth ion (R) appear in this and in the following figures as a dark-gray and a light-gray sphere, respectively. The large light-gray spheres represent the chlorines.

In this work we carry out calculations of the structure for a number of these complexes with X = Cl. The cases that we consider were selected so as to allow us to expose the structural trends holding across the whole series of compounds and at the same time to include some compounds which have been of particular experimental interest. In the case of $MRCl_6$ we have considered R = La, Nd, Er or Lu together with M = Al or Ga, in order to assess the role of the ionic radius of the rare-earth ion across the lanthanide series as well as that of the polarizing power of the countercation. The structural trends that are revealed in this calculation are then followed in M_2RCl_9 and M_3RCl_{12} for M = Ga and R = Nd. The main qualitative conclusion is that a relatively high coordination number for the lanthanide ion and the shielding of its Coulomb field are the dominant factors in determining the thermodynamic stability of the ground state taken by a cluster for each value of n, rather than the symmetry of the molecular structure. In all cases the group-IIIA element lies in a distorted tetrahedral configuration.

Our calculations are based on an ionic model that was originally developed for Al chloride molecules and for molecular ions found in Al chloroaluminates [3]. This model was thoroughly tested on the Al chloride complexes against experimental data and by comparisons with the results of first-principles calculations based both on the Hartree-Fock approximation and on density-functional methods. The basic model has already been applied to study a number of other compounds of trivalent and tetravalent metals, and in view of all past experience we believe that the predictions given below are quantitatively reliable (except where explicitly noted). Especially relevant in this context has been our previous work on polymeric structures in Al and Ga halides [4] and on the structure of lanthanide chlorides [5] and of lanthanide-alkali halide compounds [6]. These studies have allowed us to avoid having any disposable parameters in the model interactions that we have used in the present calculations.

Table 1. Ionic radii of selected rare-earth and group-IIIA ions (in Å).

La	Nd	Er	Lu	Al	Ga
1.370	1.346	1.282	1.258	0.95	0.97

For details of the ionic model we refer the reader to the above-mentioned studies [3 - 6]. It suffices to specify here the choice of the main model parameters entering the interionic force laws. For the interactions between chlorine ions and group-IIIA or rare-earth ions we have made use of our results on the molecular dimers Al_2Cl_6 and Ga_2Cl_6 [4] and on the RCl_3 monomers [5], respectively. Our model thus includes an account of the electronic polarizability of the rare-earth ion, in addition to the electronic and short-range overlap polarizabilities of the halogen. In regard to the latter, we have used the parameters from the pure compounds for the terminal chlorines and averages of these parameters for the bonding chlorines.

For the convenience of later discussion, we collect in Table 1 the values of the ionic radii of the metal ions that enter their overlap repulsive interactions with the chlorine ions. The relative magnitudes of these repulsive parameters reflect the relative sizes of the ions [7]. The main trends are (i) a decrease of the rare-earth ionic radius across the lanthanide series by

Table 2. Binding energy E_b of MRCl$_6$ molecules (in eV) in the configurations shown in Fig. 1 left (4f) and right (5f).

	MRCl$_6$ (4f)	MRCl$_6$ (5f)
AlLaCl$_6$	0.34	1.01
AlNdCl$_6$	0.33	0.99
AlErCl$_6$	0.32	0.93
AlLuCl$_6$	0.32	0.90
GaLaCl$_6$	1.28	1.89
GaNdCl$_6$	1.28	1.87
GaErCl$_6$	1.26	1.80
GaLuCl$_6$	1.26	1.77

the well-known *f*-shell contraction effect, and (ii) an increase in ionic radius from Al to Ga.

2. The MRX$_6$ Vapour Complex

Figure 1 shows the two mechanically stable structures that we have found for the MRCl$_6$ molecule. The structure shown on the left, which was proposed by Boghosian and Papatheodorou [2], is formed from two distorted tetrahedra sharing an edge: that is, a rare-earth element in a fourfold-coordination state accompanies the stable fourfold coordination of Al or Ga. However, the structure of deepest energy for the molecule is shown in Fig. 1 (right). It contains the rare-earth element in a fivefold coordination and the binding with the distorted tetrahedron centred on the group-IIIA element is effected by face sharing.

Table 2 reports the values of the binding energy E_b of the vapour complex relative to separated monomers according to the definition

$$M_nRCl_{3(n+1)} \rightarrow RCl_3 + n\,MCl_3 + E_b \tag{1}$$

with $n = 1$ in the present case. The main trend that emerges from these results is that the excess binding energy of the fivefold (5f) configuration of the rare-earth ion relative to the fourfold (4f) one, which is of the order 0.6 eV, decreases somewhat across the lanthanide series. This trend correlates with that shown in Table 1 for the ionic radii, showing that it is yet another example of the general fact that a larger size of the cation favours higher coordination. The trend in the excess binding energy is essentially the same for different countercations (Al *versus* Ga). The absolute magnitude of the binding appears to be stronger in the case of Ga, but this may be an artifact of the choice of model parameters.

Table 3. Predicted bond lengths in some MRCl$_6$ molecules (in Å). The notations Cl^T and Cl^B refer to terminal and bonding chlorines. The number given in parentheses after each bond length is the multiplicity of the bond in the molecule.

		R-Cl^T	R-Cl^B	M-Cl^T	M-Cl^B
AlLaCl$_6$	(5f)	2.55(2)	3.04(2), 2.91(1)	2.05(1)	2.18(2), 2.22(1)
AlLaCl$_6$	(4f)	2.55(2)	2.83(2)	2.06(2)	2.25(2)
AlLuCl$_6$	(5f)	2.41(2)	2.92(2), 2.76(1)	2.05(1)	2.17(2), 2.23(1)
AlLuCl$_6$	(4f)	2.41(2)	2.69(2)	2.06(2)	2.25(2)
GaNdCl$_6$	(5f)	2.53(2)	2.99(2), 2.85(1)	2.10(1)	2.23(2), 2.29(1)
GaNdCl$_6$	(4f)	2.53(2)	2.78(2)	2.11(2)	2.31(2)
GaErCl$_6$	(5f)	2.45(2)	2.93(2), 2.77(1)	2.10(1)	2.23(2), 2.29(1)
GaErCl$_6$	(4f)	2.45(2)	2.70(2)	2.11(2)	2.31(2)

Table 3 reports an example of the quantitative structural predictions made by the present model in regard to bond lengths, with the notations Cl^T and Cl^B for terminal and bonding chlorines, respectively. The M-Cl^T and R-Cl^T bond lengths are essentially the same in the two different coordination states and are at most by a few hundreds of an Å larger than those in the isolated monomers. The increase in coordination of the rare-earth element from the 4f to the 5f configuration is accompanied by an increase of the R-Cl^B bond lengths, and at the same time the bonding chlorines are allowed to approach the countercation more closely.

In summary, from our calculations the most stable configuration of the MRCl$_6$ complexes is obtained by replacing a Cl$^-$ ion in the RCl$_3$ monomer by a MCl$_4^-$ distorted tetrahedron in a face-sharing configuration. This structure increases the coordination number of the rare-earth ion from three to five and ensures optimal shielding of the R-M Coulomb repulsion.

3. The Ga$_2$NdCl$_9$ and Ga$_3$NdCl$_{12}$ Vapour Complexes

The results reported in Section 2 on MRCl$_6$ vapour complexes illustrate the structural roles played by the rare-earth element and by the group-IIIA element through their ionic radii. In this Section we examine higher complexes formed with Nd and Ga, in order to demonstrate the structural role of the number of chlorines that are available to the rare-earth element.

For Ga$_2$NdCl$_9$ we have found two mechanically stable structures, which are shown in Figure 2. In these structures the Nd ion is in a fivefold (5f) and a sixfold (6f) coordination state, respectively. The binding energies of these two configurations, defined as in (1) with $n = 2$, are 2.53 eV and 3.14 eV. The 6f state is therefore strongly stable relative to the 5f state.

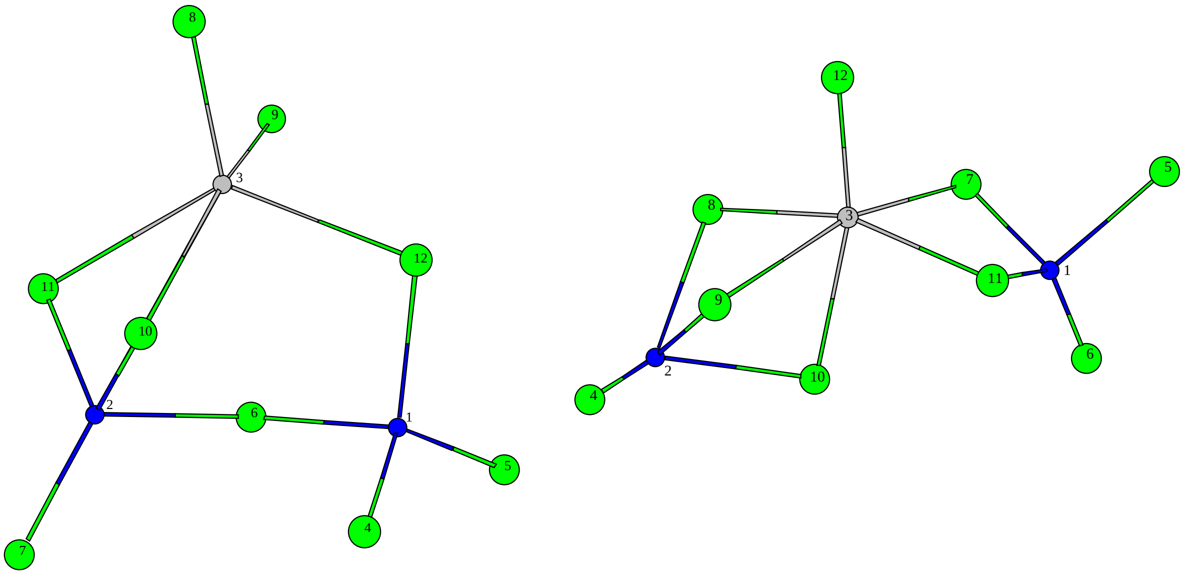

Fig. 2. Ball-and-stick picture of the fivefold (*left*) and sixfold (*right*) configurations of the Ga_2NdCl_9 vapour complex.

As can be seen from Fig. 2 (left), in the 5f case the Nd ion maintains two terminal chlorines at a distance of 2.52 Å and binds a Ga-centred distorted tetrahedron by corner sharing (with an Nd-Cl$^{\mathrm{B}}$ bond length of 2.91 Å) and a second one by edge sharing (with Nd-Cl$^{\mathrm{B}}$ bond lengths of 2.96 and 3.05 Å). The two distorted tetrahedra share a single chlorine and have a pair of terminal chlorines with a Ga-Cl$^{\mathrm{T}}$ bond length of 2.11 Å and a single Ga-Cl$^{\mathrm{T}}$ bond length of 2.09 Å, respectively. Comparison with the bond lengths of the 5f configuration in Table 3 shows that the bond lengths involving terminal chlorines are almost unchanged, while those between the Nd ion and the bonding chlorines are somewhat increased by the addition of a further $GaCl_3$ group. This expansion of the Nd-Cl$^{\mathrm{B}}$ bond lengths is accompanied by a small contraction of the Ga-Cl$^{\mathrm{B}}$ bonds.

The sixfold coordination state of the Nd ion in Fig. 2 (right) is formed by face sharing with a Ga-centred distorted tetrahedron and by edge sharing with the second one, while a single terminal chlorine is preserved for the Nd ion. Again, the bond lengths with the terminal chlorines remain practically the same, while the Nd-Cl$^{\mathrm{B}}$ bond lengths are 2.76 Å in the edge-sharing double bond and 2.85 Å (twice) and 3.04 Å (once) in the face-sharing triple bond.

In summary, the structural changes which are associated with increasing the number of bound counterion monomers, as they emerge from our results on $GaNdCl_6$ and Ga_2NdCl_9, are as follows: (i) increased coordination of the rare-earth ion, accompanied by strong stability of the fourfold coordination for the group-IIIA element; (ii) coexistence of corner and edge-sharing or of edge and face-sharing bonds between the rare-earth coordination shell and the neighbouring distorted tetrahedra, the latter combination being the most stable one; (iii) strong stability of the bond lengths involving terminal chlorines; and (iv) correlations between the expansion (contraction) of the R-Cl$^{\mathrm{B}}$ bonds and the contraction (expansion) of the M-Cl$^{\mathrm{B}}$ bonds.

The same general features are also present in our results for the structure of the Ga_3NdCl_{12} vapour complex. We find in this case that a sevenfold (7f) and an eightfold (8f) coordination state can arise, their binding energies being 4.09 eV and 4.52 eV respectively. The 7f state is shown in Fig. 3 (left) and is formed by constructing the rare-earth coordination shell with a single distorted tetrahedron *via* a face-sharing triple chlorine bond and with two further distorted tetrahedra *via* edge-sharing double chlorine bonds. In the 8f configuration shown in Fig. 3 (right), the rare-earth coordination shell is instead binding the three dis-

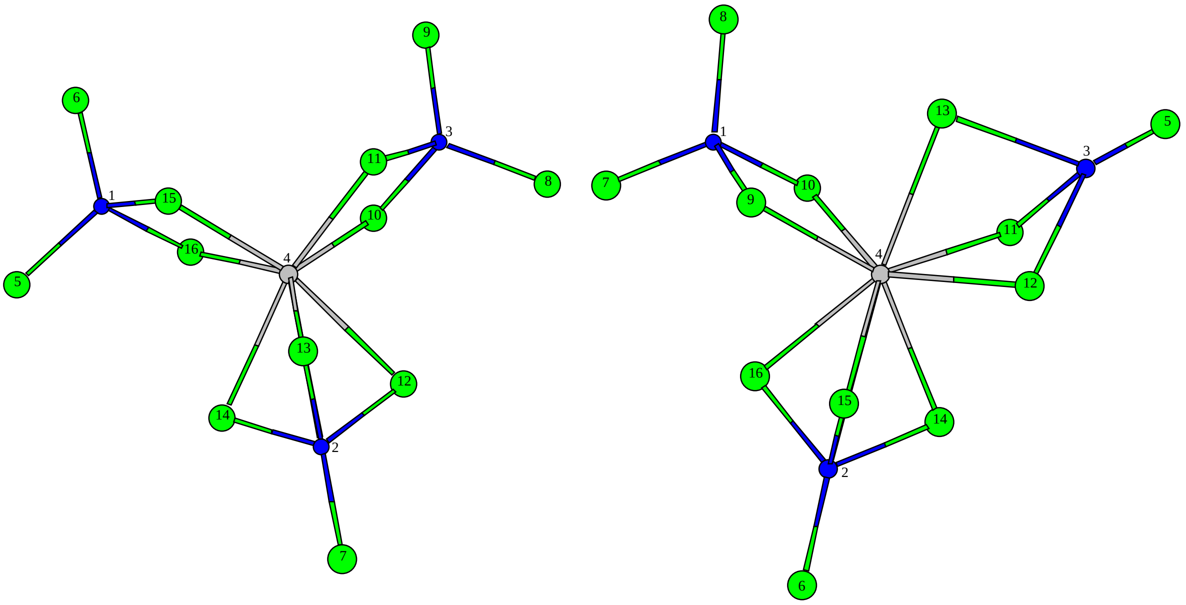

Fig. 3. Ball-and-stick picture of the sevenfold (*left*) and eightfold (*right*) configurations of the Ga_3NdCl_{12} vapour complex.

torted tetrahedra by two face-sharing triple bonds and one edge-sharing double bond. This is the most stable structure for the Ga_3NdCl_{12} cluster, according to our calculations.

In searching for the possible configurations taken by the Ga_3NdCl_{12} vapour complex we have met with three further mechanically stable structures, in which the rare-earth ion is in a state of sixfold coordination. Specifically, we have found (i) a beautifully symmetric structure where the sixfold chlorine shell of Nd binds three distorted tetrahedra by edge-sharing double chlorine bonds, as was included among the proposals made by Boghosian and Papatheodorou [2]; (ii) a chain structure formed from the Ga_2NdCl_9 complex in Fig. 2 (right) by adding a further distorted tetrahedron to one of its tails; and (iii) a ring structure obtained from the Ga_2NdCl_9 complex in Fig. 2 (left) by bringing a third distorted tetrahedron up to the coordination shell of the rare-earth ion. The binding energy of these sixfold coordinated clusters is, however, only about 3.5 - 3.6 eV, so that they are strongly unfavoured relatively to the sevenfold and eightfold coordination states.

We have also searched for a ninefold-coordinated Ga_3NdCl_{12} complex, as would be formed by constructing the coordination shell of the Nd ion by face-sharing with three tetrahedra centered on the Ga ion. However, we have found that such a structure, when artificially created, is mechanically unstable (*i. e.*, its vibrational spectrum contains at least one imaginary frequency) and transforms into the sevenfold or eightfold ones as described above.

4. Summary

In summary, we have evaluated the structures taken by the first coordination shell of chlorines around a rare-earth ion in the presence of n countercations from group-IIIA elements. All the most stable structures that we have found can be realized by replacing n chlorines in the rare-earth trichloride monomer with $n\,MCl_4^-$ tetrahedra and by subsequently allowing the cluster to relax to equilibrium through distortions of the tetrahedra and through changes in the bond lengths between the metal ions and the bonding chlorines. The factors governing the structural stability of these rare-earth vapour complexes are, therefore, the preferred high coordination of the lanthanide ions and the energy gain from shielding their strong Coulomb repulsions with the other metal ions by intercalating double or triple chlorine bonds. States of fivefold or sevenfold coordination for trivalent metal ions and the coexistence of edge and face sharing, which are consequences of the above structural criteria, are rather unusual and are worthy of further studies by experimental or more refined theoretical techniques.

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[1] G. N. Papatheodorou, in “Current Topics in Materials Science”, Vol. 10, ed. E. Kaldis, North-Holland, Amsterdam 1982, p. 249.

[2] S. Boghosian and G. N. Papatheodorou, in “Handbook on the Physics and Chemistry of Rare Earths”, Vol. 23, ed. K. A. Gschneidner, Jr. and L. Eyring, Elsevier, Amsterdam 1996, Chapter 157.

[3] Z. Akdeniz and M. P. Tosi, Z. Naturforsch. **54a**, 180 (1999).

[4] Z. Akdeniz, M. Çaliskan, Z. Çiçek, and M. P. Tosi, Z. Naturforsch. **55a**, 575 (2000).

[5] Z. Akdeniz, Z. Çiçek, and M. P. Tosi, Z. Naturforsch. **55a**, 861 (2000).

[6] Z. Akdeniz, Z. Çiçek Önem, and M. P. Tosi, Z. Naturforsch. **56a**, 721 (2001).

[7] F. G. Fumi and M. P. Tosi, J. Phys. Chem. Solids **25**, 31 (1964).