Electronic Structure and Chemical Bonding of a Series of Rare Earth Metal Clusters $R_7X_{12}Z$

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The DV–Xα–SCC method was used to study the electronic structure and chemical bonding of a series of rare earth metal clusters, $R_7X_{12}Z$. (R = Sc, Y, Pr; X = Cl; Z = Co, Fe, N) The results show that for the clusters containing a transition metal atom at the center, the number of cluster valence molecular orbitals (CVMOs) is 9; for the empty cluster and the clusters containing a nonmetal element, the number of CVMOs is 7, the same as in $(B_6H_6)^{2-}$. Among the calculated clusters, only in the empty cluster are there RE–RE metal–metal bonds; in the cluster $(Sc_6Cl_{12}N)^{3-}$, there are weak RE–RE bonds; in the interstitial clusters containing a transition metal, the transition metal atom in the octahedral RE skeleton forms covalent bonds with six RE atoms. The main contributions to the RE–TM bonding come from the 5d, 6s orbitals of RE and d, p orbitals of TM. The 4f orbitals of rare earth metal atoms are nonbonding. The bonding of RE–X is mainly ionic in character. The valence electron counting rules for octahedral clusters have been discussed based on molecular orbital analysis.

Introduction

In 1988 Hughbanks, Corbett, et al. successfully synthesized a series of rare earth halide clusters, $R_7I_{12}M$, where R = Sc, Y, Pr, and Gd and M = Mn, Fe, Co, and Ni, determined their crystal structure, and briefly discussed the nature of chemical bonding by EHMO method.[1] Before this, Corbett et al. had synthesized isologous interstitial clusters, $Sc_7X_{12}Z$, where X = Cl and Br and Z = B, C, and N.[2–4] In these clusters, we wish to ask the following questions. Why can different elements, from main group elements to transition metals, be embedded? What is the nature of chemical bonding between interstitial atoms and cluster skeleton atoms? Is there any common ground in electronic structure among these clusters?

In this paper, the electronic structure and chemical bonding of the series of rare earth clusters, $R_7X_{12}Z$ (R = Sc, Pr, Y; Z = Co, Fe, N), are studied by means of the DV–Xα–SCC method. The calculated cluster anions are as follows: $(Sc_6Cl_{12}Co)^{3-}$ (I), $(Pr_6Cl_{12}Co)^{3-}$ (II), $(Y_6Cl_{12}Fe)^{3-}$ (III), $(Sc_6Cl_{12}N)^{3-}$ (IV), and $(Sc_6Cl_{12})^{3-}$ (V) (hypothetical empty cluster). Since the terminal six outer chlorides were thought to be important for simulating the true structure properly,[5,6] a comparative calculation is made for $(Sc_6Cl_{18})^{9-}$ (VI).

Methods and Parameters

The nonrelativistic DV–Xα–SCC method was used. The minimal numerical basis set was used. The approximation of frozen core was adopted. The active valence orbitals are as follows: 4f, 5d, 6s for Pr; 3d, 4s, 4p for Sc, Co, and Fe; 4d, 5s, 5p for Y; 2s, 2p for N and Cl.[7–9] In the results of calculation, the combination coefficients of the MOs are based on AOs translated from group orbitals so as to analyze the bonds between atoms.[10] The exchange parameter of Sc and Y was taken as 0.7 and that of Pr was taken as 0.63.[11]

In order to simplify the calculation, the I atoms of clusters I–III are replaced by Cl atoms. The edge-bridging Sc–Cl bond lengths are taken as 2.58 Å, the mean length of Sc–Cl bonds in $Sc_7Cl_{12}B$ and $Sc_7Cl_{12}N$, and terminal Sc–Cl bond lengths are taken as 2.75 Å. Pr–Cl bond lengths are taken as the sum of covalence radii, 2.82 Å. Y–Cl bond lengths are taken as 2.76 Å, which is the average bond length of Y–Cl in Y_2Cl_3.[12] Such simplification will not affect the main results.

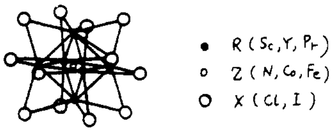

Figure 1. Molecular structure of calculated clusters, $(R_6X_{12}Z)^{3-}$.

The molecular structure and atom labeling for the calculated cluster anions I–V are shown in Figure 1. They all belong to the O_h point group. In order to simulate the effect of positive ions, a sphere shell with positive charge around anion cluster is introduced for each cluster. The center of the sphere is the center of cluster anion. The charge on the sphere shell is +3 for I–V, and +9 for VI. The radii of the sphere are 10.5, 12.0, 11.0, 10.5, 10.5, and 13.0 au for the sequence I–VI, respectively. The number of integral points was 6000 for I–V and 7800 for VI. The self-consistency of charges converges to less than 10^{-3}. All calculations were carried out on VAX-785 computer.

Results and Discussion

Comparison between $(Sc_6Cl_{12})^{3-}$ and $(Sc_6Cl_{18})^{9-}$. The results of DV–Xα–SCC calculation of some α-spin MO energies for V and VI are shown in Figure 2, in which the important R–R bonding orbitals are labeled by symmetry. The inclusion of the six terminal chlorides affects all molecular orbitals, not just the six R–R MOs (a_{1g}, e_g and t_{1u}), and makes them go up about 5 eV evenly. This enhancement of all MO energy levels is probably duo to the additional six negative charges. The gap between HOMO and LUMO for V is 1.51 eV, almost equal to that for VI, 1.50 eV. The number of R–R bonding orbitals for VI is seven, the same as for V. The symmetry of CVMOs for V and VI is also the same, and the composition is similar. Due to too much negative charges on the $(Sc_6Cl_{18})^{9-}$ model, the R–X bonds possess stronger ionic bonding character. Thus, the neglect of six terminal X atoms will not affect much the qualitative results about CVMOs and R–X bonding MOs.

Classification of MOs for $(Pr_6Cl_{12}Co)^{3-}$. This cluster has 69 occupied MOs, which may be classified into three groups according to their composition and bonding character as shown in Table I. Figure 3 is an energy level diagram of some MOs for $(Pr_6Cl_{12}Co)^{3-}$.

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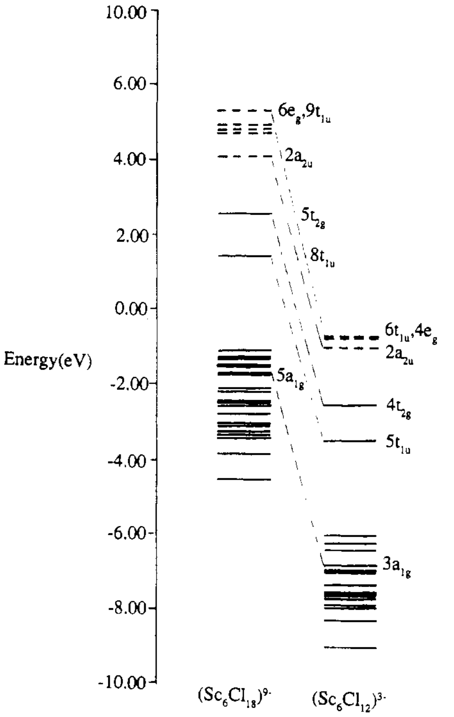

Figure 2. Some α-spin MO energies for $(Sc_6Cl_{12})^{3-}$ and $(Sc_6Cl_{18})^{9-}$. Important R-R bonding orbitals are labeled by symmetry.

Table I. α-Spin Occupied MOs of $(Pr_6Cl_{12}Co)^{3-}$

no.	E (eV)	main composition
	Group 1: 48 Ligand Molecular Orbitals (LMOs)	
14–49	−6.96 to −5.43	Cl (3p 69.5–98.9%)
1–12	−17.8 to −17.4	Cl (3s 96.3–99.1%)
	Group 2: 12 4f AOs of Pr Atoms	
58–69	−2.02 to −1.89	Pr (4f 97.3–100%)
	Group 3: 9 CVMOs	
$5t_{1u}$	−3.75	Pr (85.9%) Co (10.5%) Cl (3.6%)
$4e_g$	−4.86	Pr (17.3%) Co (81.6%) Cl (1.0%)
$4t_{2g}$	−5.04	Pr (17.6%) Co (64.4%) Cl (18.0%)
$2a_{1g}$	−7.31	Pr (7.3%) Co (73.8%) Cl (18.9%)

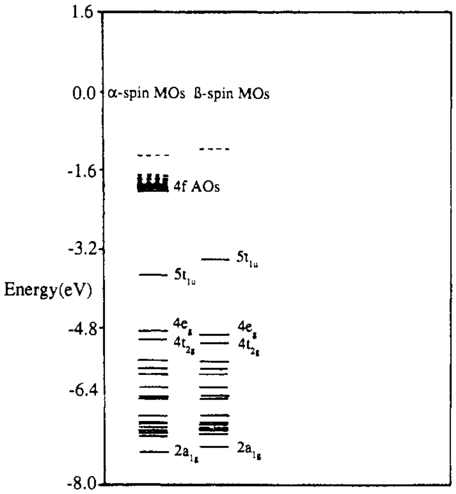

Figure 3. Energy level diagram of some MOs for $(Pr_6Cl_{12}Co)^{3-}$.

Group 1 consists of 48 ligand MOs, which are mainly localized on Cl atoms. According to the sequence of energy levels from low to high, MOs are mainly composed of 3s and 3p AOs of Cl atoms respectively. The MOs of this group correspond to R–Cl bonds and lone pairs of electrons on Cl atoms, however it is difficult to distinguish R–Cl bonds from lone pairs of electrons on Cl atoms based on the composition of MOs. This indicates that the bonding of R–Cl is mainly ionic in character.

Table II. Cluster Valence Molecular Orbitals of $(R_6X_{12}Z)^{3-}$

$(Sc_6Cl_{12}Co)^{3-}$

		composition							
	energy	Sc			Co			Cl	
orbital	(eV)	4s	4p	3d	4s	4p	3d	3s	3p
$5t_{1u}$	−3.78	11.0	10.1	53.2	0.0	18.0	0.0	0.0	8.0
$4t_{2g}$	−5.63	0.0	0.0	12.4	0.0	0.0	74.3	0.0	13.0
$4e_g$	−5.66	2.4	0.0	12.2	0.0	0.0	84.2	0.0	1.0
$3a_{1g}$	−7.24	−5.9	0.8	22.4	41.1	0.0	0.0	0.0	41.5
$2a_{1g}$	−9.40	−4.4	11.8	1.9	41.9	0.0	0.0	3.3	45.5
		LCMO of $3a_{1g}$ and $2a_{1g}$							
$3a_{1g'}$		2.2	0.5	6.3	87.8	0.0	0.0	2.4	0.8
$2a_{1g'}$		1.4	0.4	3.4	7.5	0.0	0.0	5.8	81.5

$(Y_6Cl_{12}Fe)^{3-}$

		composition							
	energy	Y			Fe			Cl	
orbital	(eV)	5s	5p	4d	4s	4p	3d	3s	3p
$5t_{1u}$	−3.98	10.5	5.4	59.6	0.0	18.6	0.0	0.0	6.0
$4e_g$	−4.79	4.2	−1.2	17.5	0.0	0.0	79.2	0.0	0.0
$4t_{2g}$	−5.05	0.0	0.0	23.9	0.0	0.0	64.4	0.0	11.2
$3a_{1g}$	−7.04	−5.3	1.8	30.1	38.6	0.0	0.0	0.0	34.4
$2a_{1g}$	−8.40	0.0	10.0	2.5	32.6	0.0	0.0	2.1	53.5

$(Sc_6Cl_{12}N)^{3-}$

		composition						
	energy	Sc			N		Cl	
orbital	(eV)	4s	4p	3d	2s	2p	3s	3p
$4t_{2g}$	−2.20	0.0	2.8	93.2	0.0	0.0	0.0	4.0
$2t_{1u}$	−9.82	1.0	−1.6	9.3	0.0	81.6	0.5	9.1
$1a_{1g}$	−20.26	0.5	2.2	3.4	92.1	0.0	1.6	0.0

$(Sc_6Cl_{12})^{3-}$

		composition				
	energy	Sc			Cl	
orbital	(eV)	4s	4p	3d	3s	3p
$4t_{2g}$	−2.52	0.0	3.1	91.9	0.0	4.8
$5t_{1u}$	−3.46	15.1	14.9	61.5	0.0	8.7
$3a_{1g}$	−6.84	9.3	24.0	36.0	0.0	30.6
$2a_{1g}$	−9.07	15.4	25.0	0.0	4.0	54.7
		LCMO of $3a_{1g}$ and $2a_{1g}$				
$3a_{1g'}$		16.8	37.5	33.2	12.6	0.0
$2a_{1g'}$		0.0	0.2	7.5	6.6	85.7

Group 2 consists of 12 α-spin occupied 4f orbitals with orbital energy levels between −1.89 and −2.02 eV, which are the highest among the occupied MOs. They are nonbonding orbitals. The 12 4f electrons are spin-parallel; thus, the anion cluster is paramagnetic.

Group 3 consists of nine cluster valence molecular orbitals (CVMOs), which accommodate the six pairs of bonding electrons between the central transition metal atom Co and the six Pr atoms at the vertices of the octahedron, as well as the three lone pairs of d electrons of Co.

Among the three groups of MOs, CVMOs are the most important one for understanding the nature of chemical bonding in clusters. In order to save space, we will concentrate our discussions to the CVMOs of $(R_6X_{12}Z)^{3-}$.

CVMOs of $(R_6X_{12}Z)^{3-}$ Clusters. The composition and energy levels of α-spin cluster valence molecular orbitals for the clusters, $(R_7X_{12}Z)^{3-}$, are listed in Table II and shown in Figure 4 together with those for the well-known $(B_6H_6)^{2-}$ for comparison.

From the results of calculation summarized in Table II, we can draw the following rule about the number of CVMOs for $(R_6X_{12}Z)^{3-}$:

(1) For transition-metal-centered clusters, the number of CVMOs is 9, such as clusters I–III.

(2) For the empty cluster (V) and the non-metal-centered cluster (IV), the number of CVMOs is 7, which obeys Wade's

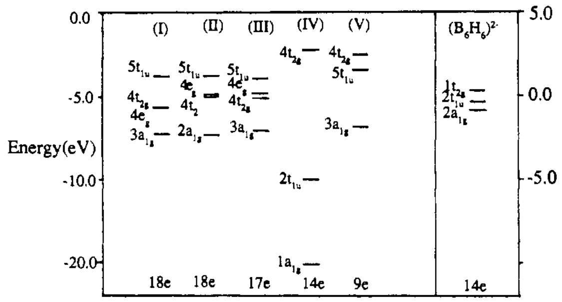

Figure 4. Cluster valence molecular orbitals (CVMOs) of clusters, $(R_6X_{12}Z)^{3-}$ and $(B_6H_6)^{2-}$.

Table III. Valence Charge Distribution and Spin Population of $(R_6X_{12}Z)^{3-}$

	I			II		
	Sc	Co	Cl	Pr	Co	Cl
	Valence Charge Distribution					
f				2.054		
d	1.314	8.292		1.455	8.415	
s	0.264	1.660	1.980	0.194	1.443	1.982
p	0.342	1.049	5.643	0.090	0.671	5.744
tot.	1.920	11.001	7.623	3.793	10.259	7.726
net charge	1.080	−2.001	−0.623	1.207	−1.529	−0.726
	Spin Population					
f				1.980		
d	0.000	0.000		0.117	−0.215	
s	0.000	0.000		0.006	−0.071	−0.001
p	0.000	0.000	0.000	0.009	−0.065	−0.025
tot.	0.000	0.000	0.000	2.119	−0.351	−0.026

	III			IV		
	Y	Fe	Cl	Sc	N	Cl
	Valence Charge Distribution					
d	1.580	7.354		1.564		
s	0.230	1.445	1.980	0.132	1.870	1.982
p	0.188	0.909	5.628	0.154	5.347	5.658
tot.	1.998	9.709	7.608	1.850	7.217	7.640
net charge	1.002	−2.001	−0.608	1.150	−2.217	−0.640
	Spin Population					
d	0.118	−0.073		0.000		
s	0.023	−0.012	−0.001	0.000	0.000	0.000
p	0.014	0.177	−0.001	0.000	0.000	0.000
tot.	0.155	0.092	−0.002	0.000	0.000	0.000

	V			
	valence charge distribn		spin pop.	
	Sc	Cl	Sc	Cl
d	1.423		0.165	
s	0.437	1.973	0.001	0.000
p	0.497	5.599	0.007	−0.003
tot.	2.357	7.572	0.173	−0.003
net charge	0.643	−0.572		

Table IV. Mulliken Orders for $(R_6X_{12}Z)^{3-}$

		I							
		Sc			Co			Cl	
		d	s	p	d	s	p	s	p
Sc	d	0.016	0.018	0.021	0.131	0.054	0.056	0.015	0.112
	s	0.018	−0.005	−0.025	0.030	−0.178	0.270	−0.015	0.045
	p	0.021	−0.025	−0.012	0.031	0.056	−0.195	0.011	0.073
tot.			0.027			0.256		0.241	

		II								
		Pr				Co			Cl	
		f	d	s	p	d	s	p	s	p
Pr	f	0.001	0.002	0.001	0.001	0.009	0.003	0.001	0.001	0.009
	d	0.002	0.039	0.025	0.024	0.155	0.084	0.038	0.013	0.182
	s	0.001	0.025	0.002	−0.022	0.017	−0.177	0.195	−0.007	0.022
	p	0.001	0.024	−0.022	−0.007	0.008	−0.006	−0.177	0.007	0.034
tot.			0.097				0.150		0.261	

		III							
		Y			Fe			Cl	
		d	s	p	d	s	p	s	p
Y	d	0.035	0.019	0.020	0.205	0.072	0.061	0.015	0.155
	s	0.019	−0.014	−0.025	0.036	−0.092	0.196	−0.008	0.042
	p	0.020	−0.025	−0.008	0.019	0.051	−0.191	0.007	0.046
tot.			0.041			0.358		0.257	

		IV						
		Sc			N		Cl	
		d	s	p	s	p	s	p
Sc	d	0.061	0.002	0.017	0.026	0.110	0.009	0.113
	s	0.002	−0.007	−0.003	−0.001	−0.023	0.000	0.063
	p	0.017	−0.003	0.015	0.009	−0.238	0.001	0.051
tot.			0.102		−0.117		0.236	

		V				
		Sc			Cl	
		d	s	p	s	p
Sc	d	0.037	0.043	0.031	0.014	0.127
	s	0.043	0.001	0.034	−0.021	0.025
	p	0.031	0.034	0.024	0.007	0.062
tot.			0.278		0.213	

rule for *closo*-boranes, i.e., for $(B_6H_6)^{3-}$, the number of CVMOs $= n + 1 = 6 + 1 = 7$.

On the basis of the composition of MOs for cluster $(Sc_6Cl_{12}Co)^{3-}$, $(Y_6Cl_{12}Fe)^{3-}$ and $(Sc_6Cl_{12})^{3-}$, the orbitals $3a_{1g}$ and $2a_{1g}$ seem to be CVMOs, so the numbers of CVMOs for the three clusters seem to be 10, 10, and 8 rather than 9, 9, and 7. But a linear combination of the MOs of $3a_{1g}$ and $2a_{1g}$, which have the same symmetry and similar energies, gives two equivalent MOs, $3a_{1g'}$ and $2a_{1g'}$. It can be seen that the MO $3a_{1g'}$ is CVMO, while $2a_{1g'}$ is the ligand molecular orbital (LMO).

All seven CVMOs (a_{1g}, t_{1u} and t_{2g}) for the empty cluster are R–R bonding character below a gap of 1.5 eV; the bond orders of these R–Rs are strong. In main-group-centered clusters, the a_{1g} and t_{1u} levels strongly interact with the central atom's $s(a_{1g})$ and $p(t_{1u})$ orbitals to form occupied a_{1g} and t_{1u} levels with R–Z bonding character and antibonding orbitals far above the gap. The occupied a_{1g} and t_{1u} orbitals fall down about 6–13 eV. The cluster-based t_{2g} (d) orbitals are localized on R atoms and are nonbonding. These results are consistent with those obtained by the EHMO method.[2,5,6] However, in the transition-metal-centered clusters, the interaction is different: the cluster-based a_{1g}, t_{2g}, and t_{1u} orbitals all mix respectively with s, d, and p orbitals of the transition metal (TM) to generate nine CVMOs (a_{1g}, t_{2g}, t_{1u}, and e_g) with R–TM bonding character. Although t_{1u} orbitals for I–III almost retain the levels obtained in the empty cluster, they contain a contribution from p orbitals of TM.

Valency Charge Distribution, Spin Population, and Bond Order. The valence charge distribution and spin population calculated by the DV-Xα–SCC method for the clusters $(R_6X_{12}Z)^{3-}$ are listed in Table III. The net charge of R atoms is about +0.6 to +1.2, and the net charge of Cl atoms is about −0.57 to −0.73, while the atom at the center of the octahedron carries a negative charge, reaching about −2.0. For the interstitial transition metal atoms, Co and Fe, electrons are increased on d, p orbitals, and the net charge of Co or Fe reaches about −2.0; this is seldom seen in inorganic compounds.

The electron spins of the clusters are distributed on 4f and 5d AOs of the rare earth atoms.

Table IV gives the Mulliken bond orders calculated for the clusters. The bond orders of R–X bonds in I–V have values ranging from 0.213 to 0.261, indicating that the R–X bonds are rather weak. For the cluster skeleton, there are certain Sc–Sc covalent bonds in the empty cluster (V); in cluster IV centered by N, the covalent bonds among Sc atoms become weaker because of the interstitial N atom, while in clusters I–III, centered by transition metal atoms, the bond orders of R–R are almost equal to zero and the rare earth atoms are combined by bonding with the center atom, Co or Fe.

The bond orders of Sc–Co, Pr–Co, and Y–Fe are 0.256, 0.150, and 0.358. The experimental bond lengths of Sc–Co, Pr–Co, and Y–Fe are 2.431, 2.77, and 2.621 Å, respectively, which are shorter than the sum of covalent radii 2.60, 2.81 and 2.785 Å. These facts indicate that there are considerable strong covalent bonds between the rare earth atoms and the transition metal atoms.

On the basis of the analysis of Mulliken population, it also can be seen that the main contributions to the RE–TM bonding come from the d, s orbitals of RE and d, p orbitals of TM. The 4f orbitals of Pr atoms are nonbonding.

Valence Electron Counting Rules. On the basis of the CVMO analysis, we can better understand why different elements can be embedded by the cluster structure, and we may predict some other centered clusters with similar structures. The valence MOs and valence electrons of octahedral clusters may be counted as follows.

A. Comparison with *closo*-Boranes and Transition Metal Clusters.

$$\text{CVMO} = \text{cluster valence MOs} = n + 1$$

$$\text{LMO} = \text{ligand MOs} = n \text{ or } 6n$$

$$\text{VO} = \text{total valence orbitals} = 2n + 1 \text{ or } 7n + 1$$

$$\text{VE} = \text{total valence electrons} = 4n + 2 \text{ or } 14n + 2$$

Example 1: $(B_6H_6)^{2-}$, CVMO = $n + 1 = 7$, VE = $4n + 2 = 26$ (Wade's Rule).[14,15]

Example 2: $[Os_6(CO)_{18}]^{2-}$, CVMO = $n + 1 = 7$, VE = $14n + 2 = 86$.

B. Octahedral Rare Earth Clusters, $(R_6X_{12}Z)^{3-}$ (R = Rare Earths Metals; X = I, Br, Cl; Z = Main Group Elements or Vacant).

$$\text{CVMO} = n + 1;\ \text{LMO} = 4(2n) = 8n$$

$$\text{VO} = \text{CVMO} + \text{LMO} + (\text{VO})_{4f} = 9n + 1 + (\text{VO})_{4f}$$
$$= (\text{VO})_{\uparrow\downarrow} + (\text{VO})_{\uparrow} + (\text{VO})_{\text{vacant}}$$

$$\text{VE} = 2(\text{VO})_{\uparrow\downarrow} + (\text{VO})_{\uparrow}$$

Examples: $(Sc_6Cl_{12})^{3-}$, VO = $9n + 1 = 55$, VE = $2 \times 52 + 1 = 105$; $(Sc_6Cl_{12}B)^{3-}$, VO = $9n + 1 = 55$, VE = $2 \times 53 + 2 = 108$; $(Sc_6Cl_{12}C)^{3-}$, VO = $9n + 1 = 55$, VE = $2 \times 54 + 1 = 109$; $(Sc_6Cl_{12}N)^{3-}$, VO = $9n + 1 = 55$, VE = $2 \times 55 = 110$.

Prediction 1: $(Pr_6I_{12}P)^{3-}$ or $(Pr_6I_{12}As)^{3-}$

$$\text{VO} = 9n + 1 + (\text{VO})_{4f} = 55 + 6 \times 2 = 67$$

$$\text{VE} = 2 \times 55 + 12 = 122$$

$$N_s = \text{number of spin-unpaired electrons} = (\text{VO}) = (\text{VO})_{4f} = 12$$

Possible method of synthesis:

$$4PrI_3 + (1/4)P_4 + 3Pr \rightarrow Pr_7I_{12}P$$

Seal in Ta crucible and heat to about 850 °C for several weeks.

Prediction 2:

$$Sc^{3+}[Sc_6Cl_{12}N]^{3-} \text{ (known)} \rightarrow Ca^{2+}[Sc_6Cl_{12}O]^{2-} \text{ (unknown)}$$
$$\rightarrow [Gd_6Cl_{12}C_2]^0 \text{ (unknown)}$$
$$\rightarrow [La_6I_{12}Si_2]^0 \text{ (unknown)}$$

C. Octahedral Rare Earth Clusters, $(R_6X_{12}Z)^{3-}$ (R = Rare Earths, X = I, Z = Transition Metals such as Mn, Fe, Co, Ni).

$$\text{CVMO} = 9 \text{ (18e rule)},\ \text{LMO} = 8n$$

$$\text{VO} = 8n + 9 + (\text{VO})_{4f}$$

$$\text{VE} = 2(\text{VO})_{\uparrow\downarrow} + (\text{VO})_{\uparrow}$$

Example 1: $(Pr_6I_{12}Co)^{3-}$, VO = $8n + 9 + (\text{VO})_{4f} = 57 + 12$, VE = $2 \times 57 + 12$, $N_s = (\text{VO}) = (\text{VO})_{4f} = 12$.

Example 2: $(Y_6I_{12}Fe)^{3-}$, VO = $8n + 9 + (\text{VO})_{4f} = 57$, VE = $2 \times 57 + 1 = 113$, $N_s = (\text{VO}) = 1$ (HOMO is singly occupied).

D. Extension of $(R_6X_{12}Z)^{3-}$. We have observed the compound $Y^{3+}[Y_6I_{12}Fe]^{3-}$. Substituting Y^{3+} by Th^{4+} and I^- by Br^-, we have $[Th_6Br_{12}Fe]^{3+}[Br_3]^{3-}$ or $[Th_6Br_{15}Fe]$.[16] $Th_6Br_{15}Co$ had been obtained by Simon et al. recently.[17]

CVMO = 9, LMO = $4(2.5n) = 10n$, VO = $10n + 9 = 69$, VE = $2 \times 68 + 1 = 137$. The HOMO is singly occupied.

Prediction: $Zr_6Br_{15}Co$, VE = 138; $U_6Br_{15}Co$, VE = 138 + 12, $N_s = 12$ (5f).

E. Condensation of Octahedrons. Starting from known compound $Sc^{3+}[Sc_6Cl_{12}N]^{3-}$, and substituting N^{3-} by C_2 and Sc by Gd, we have $Gd_6Cl_{12}C_2$. This neutral cluster fits the electron counting rule VE = $18n + 2 + N_{4f} = 110 + 42$, and it is possible to synthesize it.

Condense two $Gd_6Cl_{12}C_2$ octahedrons by sharing one edge, thus eliminating Gd_2Cl_6 and forming cluster $Gd_{10}Cl_{18}C_4$.[18,19]

Condensation of m octahedrons:

$$m(R_6X_{12}C_2) - (m - 1)R_2X_6 \rightarrow R_{4m+2}X_{6m+6}C_{2m}$$

$$\text{CVMO} = 7m;\ \text{LMO} = 4 \times 6(m + 1) = 24(m + 1)$$

$$\text{VO} = 31m + 24 + (\text{VO})_{4f};\ \text{VE} = 62m + 48 + N_{4f}$$

When R = Gd, $m = 2$, $Gd_{10}Cl_{18}C_4$, VE = 172 + 70; $m = 3$, $Gd_{14}Cl_{24}C_6$, VE = 234 + 98; and $m = 4$, $Gd_{18}Cl_{30}C_8$, VE = 296 + 126.

Conclusions

(1) Because of the embedding of the transition metal, considerable strong RE–TM metal–metal bonds are formed in the series of anion clusters, while the bonding among skeleton R atoms are weakened. The main contributions to the RE–TM bonding come from the d, s orbitals of RE and d, p orbitals of TM; the 4f orbitals of RE atoms are nonbonding. The clusters centered by transition metals are more stable than the clusters centered by main group elements or vacant.

(2) In these clusters, the distribution of electrons presents very strong localization. The R–X bonds in the outer sphere of the octahedral clusters are mainly ionic in character. The R–Z bonds are covalent with some ionic character.

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(3) For the clusters containing a transition metal at the center, the number of CVMOs is 9; for the empty cluster and the clusters centered by main group elements, the number of CVMOs is 7, the same as in $(B_6H_6)^{2-}$. By substitution of molecular fragments or condensation of octahedrons, some new clusters may be predicted.

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Supplementary Material Available: Table of the Cartesian coordinate and atomic basis set for calculated clusters and tables of detailed composition of molecular orbitals for $R_7X_{12}Z$ (5 pages). Ordering information is given on any current masthead page.