

# Articles

Contribution from the Department of Chemistry,  
Iowa State University, Ames, Iowa 50011

## Rare-Earth-Metal Iodide Clusters Centered by Transition Metals: Synthesis, Structure, and Bonding of $R_7I_{12}M$ Compounds ( $R = \text{Sc, Y, Pr, Gd}$ ; $M = \text{Mn, Fe, Co, Ni}$ )

Timothy Hughbanks<sup>1</sup> and John D. Corbett\*

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The compounds  $R_7I_{12}M$  ( $M = \text{Co, Ni}$  for  $R = \text{Sc}$ ;  $M = \text{Fe, Co}$  for  $R = \text{Y}$ ;  $M = \text{Mn, Fe, Co}$  for  $R = \text{Gd}$ ;  $M = \text{Mn, Fe, Co, Ni}$  for  $R = \text{Pr}$ ) have been synthesized by reactions of  $RI_3$ ,  $MI_2$ , and  $R$  metals at 750–950 °C in sealed Nb or Ta containers. These compounds all adopt the  $\text{Sc}(\text{Sc}_6\text{Cl}_{12}\text{B})$  structure (space group  $R\bar{3}, Z = 3$ ) with a transition metal at the cluster center (in place of boron). The seventh "isolated"  $R^{3+}$  ion can be substituted by  $\text{Ca}^{2+}$  in several of the Pr and Gd cases. The structural details of  $\text{Sc}_7\text{I}_{12}\text{Co}$ ,  $\text{Y}_7\text{I}_{12}\text{Fe}$ , and  $(\text{Ca}_{0.65}\text{Pr}_{0.35})(\text{Pr}_6\text{I}_{12}\text{Co})$  were determined by single-crystal X-ray diffraction methods ( $a = 14.800, 15.351, 15.777$  Å;  $c = 10.202, 10.661, 10.925$  Å;  $R = 3.3, 3.8, 3.4\%$ ;  $R_w = 6.7, 3.3, 3.5\%$ , respectively). The last of these presented twinning difficulties endemic to this structure type, but these were overcome satisfactorily by an approximate separation procedure. R–M distances in the clusters are short; Pr–Co = 2.770, Y–Fe = 2.621, and Sc–Co = 2.431 Å. While MO theory provides some useful guides to these compounds' stability, the true breadth of the chemistry possible remains to be explored.

### Introduction

Cluster halides formed by rare-earth or zirconium metals have demonstrated an astounding proclivity to encapsulate guest atoms at their centers. In nearly all cases, the clusters (or condensed clusters) derive from  $M_6X_{12}$  (6–12) units in which halide (X) bridges all edges of a nominal metal octahedron. The recognition of these compounds as distinct from their early formulation as binary phases led to a fruitful, but eventually circumscribing, view of these compounds as containing "interstitially stabilized" clusters. Thus, workers in our laboratory and others explored the boride, carbide, and nitride chemistry of these clusters through the synthesis of a variety of compounds, viz.,  $\text{Sc}(\text{Sc}_6\text{Cl}_{12}(\text{B,N}))$ ,<sup>2</sup>  $\text{Sc}(\text{Sc}_6\text{I}_{12}(\text{B,C}))$ ,<sup>3</sup>  $\text{Y}_4\text{I}_5\text{C}$ ,<sup>4</sup>  $\text{Gd}_{10}\text{Cl}_{18}(\text{C}_2)_2$ ,<sup>5</sup>  $\text{Gd}_6\text{I}_7(\text{C}_2)_2$ ,<sup>6</sup>  $\text{Sc}_6\text{I}_{11}(\text{C}_2)$ ,<sup>7</sup>  $\text{Zr}_6\text{X}_{12}\text{C}$  ( $X = \text{Cl, Br, I}$ ),<sup>8,9</sup>  $\text{Zr}_6\text{Cl}_{13}\text{B}$ ,<sup>9</sup>  $\text{Zr}_6\text{Cl}_{15}\text{N}$ ,<sup>10</sup>  $\text{CsKZr}_6\text{I}_{15}\text{B}$ ,<sup>11</sup> and many more.

The discovery that larger atoms such as Al, Si, Ge, and P could be bound within zirconium iodide clusters<sup>12,13</sup> made it clear that the role of metal–"interstitial" bonding could be more important than that of metal–metal bonding in stabilizing a cluster phase. However, our appreciation of chemical variations possible with the "interstitial" broadened considerably when metals such as Cr, Mn, Fe, Co,<sup>14,15</sup> and even K<sup>16</sup> were found capable of filling zirconium halide (6–12) clusters in phases such as  $\text{CsZr}_6\text{I}_{14}\text{Mn}$ . The present paper takes up the description of our successes in the

synthesis and characterization of  $R(\text{R}_6\text{X}_{12})$  (7–12) type rare-earth-metal iodide cluster compounds in which 3d transition metals are ensconced. Some of these results were briefly noted in a recent communication.<sup>14</sup>

### Experimental Section

**Materials.** All compounds were manipulated in gloveboxes under a dry nitrogen or argon atmosphere. Scandium metal was prepared in the Ames Laboratory by metallothermic reduction of  $\text{ScF}_3$  with triply distilled calcium followed by sublimation. Typical purity has been cited before.<sup>2</sup> The yttrium, praseodymium, and gadolinium employed were the usual high-purity Ames Laboratory materials.

Scandium and yttrium triiodides were prepared by direct reaction of the elements in a sealed silica apparatus.<sup>17</sup> Cold-rolled metal (15 mil) was cut into small pieces ( $\sim 3 \times 3$  mm) and put into a tungsten crucible. The end of the fused silica enclosure containing the crucible was heated at 850 °C for 3 days while the iodine reservoir was kept at 150 °C. The crude product was sublimed three or more times in a tantalum apparatus to give yellow  $\text{ScI}_3$  or white  $\text{YI}_3$ . The  $\text{PrI}_3$ ,  $\text{GdI}_3$ , and  $\text{DyI}_3$  were available in our laboratory from earlier studies during which they had been prepared and purified similarly. The transition metal diiodides ( $\text{MnI}_2$ ,  $\text{FeI}_2$ ,  $\text{CoI}_2$ ,  $\text{NiI}_2$ ) were all made by direct reaction of the elements in sealed silica tubes that were subjected to temperature gradients sufficiently steep to keep the  $\text{I}_2$  pressure at one end below 1 atm but to give useful reaction rates at the metals in the hotter end. Each of these diiodides was vacuum sublimed two or more times prior to use, except for  $\text{NiI}_2$ , which was sublimed in a sealed tube to avoid decomposition to the elements. Occluded or adsorbed  $\text{I}_2$  was removed from the  $\text{NiI}_2$  at 200 °C under vacuum.

**Syntheses.**  $R_7I_{12}M$  (7–12) compounds were obtained by reaction of stoichiometric ratios of  $RI_3$  ( $R = \text{Sc, Y, Pr, Gd}$ ) and  $MI_2$  ( $M = \text{Mn, Fe, Co, Ni}$ ) with metal strips (Sc, Y) or turnings (Pr, Gd) in 10–15% excess. Reactions intended to yield  $\text{Ca}(\text{R}_6\text{I}_{12}\text{M})$  ( $R = \text{Pr, Gd}$ ;  $M = \text{Fe, Co}$ ) were loaded with stoichiometric ratios of all reactants, distilled Ca metal serving as the source of that element. The reactants were loaded into Ta or Nb tubes and heated at temperatures between 750 and 950 °C for 2–4 weeks. Techniques of sealing and handling reaction containers have been described previously.<sup>17</sup> Temperatures of 850 °C were found to be generally close to optimal for maximizing yields of the  $R_7I_{12}M$  phases, and unless otherwise stated, we refer to reactions run at that temperature. The identities of the products reported herein were established by detailed comparison of calculated powder patterns with those measured with the aid of an Enraf-Nonius (FR-552) Guinier camera.

Yields of the 7–12 compounds varied from fair to quantitative. No impurity phases were detected by Guinier powder diffraction of the  $\text{Sc}_7\text{I}_{12}\text{Co}$ ,  $\text{Y}_7\text{I}_{12}\text{Fe}$ ,  $\text{Pr}_7\text{I}_{12}(\text{Fe,Co,Ni})$ , or  $\text{Gd}_7\text{I}_{12}(\text{Fe,Co})$  products. The

- (1) Present address: Department of Chemistry, Texas A&M University, College Station, TX 77843.
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Table I. Lattice Parameters (Å) of  $R_7I_{12}M$  Phases<sup>a</sup>

comps	params		electron count <sup>b</sup>
	a	c	
Sc <sub>7</sub> I <sub>12</sub> Co	14.800 (1)	10.202 (1)	18
Sc <sub>7</sub> I <sub>12</sub> Ni	14.814 (1)	10.115 (1)	19
Y <sub>7</sub> I <sub>12</sub> Fe	15.351 (1)	10.661 (1)	17
Y <sub>7</sub> I <sub>12</sub> Co	15.332 (1)	10.683 (1)	18
Pr <sub>7</sub> I <sub>12</sub> Mn	15.788 (2)	10.955 (3)	16
Pr <sub>7</sub> I <sub>12</sub> Fe	15.821 (1)	10.787 (1)	17
Pr <sub>7</sub> I <sub>12</sub> Co	15.815 (1)	10.805 (1)	18
Pr <sub>7</sub> I <sub>12</sub> Ni	15.833 (1)	10.734 (1)	19
Gd <sub>7</sub> I <sub>12</sub> Mn	15.502 (1)	10.655 (1)	16
Gd <sub>7</sub> I <sub>12</sub> Fe	15.492 (1)	10.624 (2)	17
Gd <sub>7</sub> I <sub>12</sub> Co	15.458 (1)	10.737 (1)	18
Ca <sub>0.65</sub> Pr <sub>0.35</sub> (Pr <sub>6</sub> I <sub>12</sub> Co)	15.777 (1)	10.925 (1)	17.35
Ca <sub>1-x</sub> Gd <sub>x</sub> (Gd <sub>6</sub> I <sub>12</sub> Fe)	15.478 (2)	10.726 (2)	16 + y
Ca <sub>1-x</sub> Gd <sub>x</sub> (Gd <sub>6</sub> I <sub>12</sub> Co)	15.463 (1)	10.751 (1)	17 + z

<sup>a</sup>Data from Guinier powder diffraction; space group  $R\bar{3}$  (hexagonal setting); Cu K $\alpha$  radiation,  $\lambda = 1.54056 \text{ \AA}$ . <sup>b</sup>Cluster-based electrons.

Sc<sub>7</sub>I<sub>12</sub>Ni was formed in ~90% yield together with unidentified black plate crystals; Pr<sub>7</sub>I<sub>12</sub>Mn and Gd<sub>7</sub>I<sub>12</sub>Mn were obtained in 85 to 90% yield, and in the latter case no sign of the impurity phase could be detected visually. This may imply that further exploration of the last system will turn up new cluster phases. The Y<sub>7</sub>I<sub>12</sub>Co was produced in ~75% yield together with unreacted YI<sub>3</sub> and Y metal; the metal may have been coated with Y<sub>2</sub>Co, a possible diversion product of the CoI<sub>2</sub> reactant. This speculation is bolstered by experience in the Y-Cl-Co system, wherein reactions of Y with CoCl<sub>2</sub> yield YCl<sub>3</sub> as the only apparent product containing chlorine, and no Y<sub>2</sub>Cl<sub>3</sub>. Interestingly, Sc<sub>7</sub>I<sub>12</sub>Fe did not form at all; instead, a mixture of ScI<sub>3</sub>,  $x \sim 2.2$ ,<sup>3</sup> and very thin, unidentified black plates was obtained. At 950 °C, Y<sub>7</sub>I<sub>12</sub>Fe was produced in the form of large (>0.1 mm) and well-faceted black crystals. Under the same conditions, however, crystalline Pr<sub>7</sub>I<sub>12</sub>Fe and Pr<sub>7</sub>I<sub>12</sub>Co were formed only in poor yield; the poorly crystalline products had once been partially molten and gave Guinier powder patterns showing only a few 7-12 lines. Reactions at 750 °C often provided notably lower yields or less well-crystallized products.

Calcium substitution at the isolated cation site in the  $R(R_6X_{12})$  structure was attempted for iron- and cobalt-centered cluster iodides of praseodymium and gadolinium. Guinier lattice constants are quite clearly altered in the cases of Ca<sub>1-x</sub>Pr<sub>x</sub>(Pr<sub>6</sub>I<sub>12</sub>Co) and Ca<sub>1-x</sub>Gd<sub>x</sub>(Gd<sub>6</sub>I<sub>12</sub>Fe) (Table I). The relative intensities of low-angle diffraction lines also changed as predicted for the substitution of a comparatively light atom at the 0, 0, 1/2 site. The reaction product aimed at "Ca(Gd<sub>6</sub>I<sub>12</sub>Co)" gave lattice parameters that were not very different from those of Gd(Gd<sub>6</sub>I<sub>12</sub>Co), probably indicating limited calcium substitution. The powder pattern obtained for "Ca(Pr<sub>6</sub>I<sub>12</sub>Fe)" may be interpreted as pertaining to a mixture of two 7-12 type phases, one calcium rich and one calcium poor.

Lattice constant values for all the phases considered are listed in Table I. These were all determined by Guinier and least-squares techniques described before<sup>14</sup> and are referenced to NBS Si powder as an internal standard.

**Crystallography.** Single crystals suitable for structure determination were mounted within a drybox into 0.2-mm thin-wall capillaries, where they were held with a small amount of grease. Diffraction data were collected at ambient temperature with a Syntex P2<sub>1</sub> diffractometer equipped with a graphite monochromator. Crystal data are summarized in Table II. Variable scan speeds of 2.0-29.3 min<sup>-1</sup> were used in data collection for Sc<sub>7</sub>I<sub>12</sub>Co and speeds of 1.0-29.3 min<sup>-1</sup> for Y<sub>7</sub>I<sub>12</sub>Fe and Ca<sub>0.64</sub>Pr<sub>0.36</sub>(Pr<sub>6</sub>I<sub>12</sub>Co). Empirical absorption corrections based on azimuthal scans (at two values of  $\theta$  for Sc<sub>7</sub>I<sub>12</sub>Co, four for Y<sub>7</sub>I<sub>12</sub>Fe, and five for Ca<sub>0.65</sub>Pr<sub>0.35</sub>(Pr<sub>6</sub>I<sub>12</sub>Co)) were applied to the data. No detectable decay of any of the crystals occurred during data collection. Programs used in data reduction and in full-matrix least-squares refinement and the source of the scattering factors employed (which included corrections for anomalous dispersion) have been previously referenced.<sup>18</sup>

Since the identity of each phase had been clearly established by powder diffraction, initial atom positions could be taken from earlier refinements of Sc<sub>7</sub>X<sub>12</sub>Z structures containing light interstitial atoms Z.<sup>2</sup> In the case of Sc<sub>7</sub>I<sub>12</sub>Co and Y<sub>7</sub>I<sub>12</sub>Fe, the structural solution consisted of

Table II. Single-Crystal Data Collection and Refinement Parameters<sup>a</sup>

	Sc <sub>7</sub> I <sub>12</sub> Co	Y <sub>7</sub> I <sub>12</sub> Fe	Ca <sub>0.65</sub> Pr <sub>0.35</sub> (Pr <sub>6</sub> I <sub>12</sub> Co)
space group	$R\bar{3}$	$R\bar{3}$	$R\bar{3}$
Z	3	3	3
crystal dimens, mm	0.08	0.12	0.10
	0.08	0.12	0.12
	0.1	0.16	0.15
2 $\theta$ (max), deg	50	55	55
no. of reflns			
measd ( $h, \pm k, \pm l$ )	2405	3523	3802
obsd <sup>b</sup>	1088	2036	2394
indep	405	729	860
R <sub>av</sub> , %	3.9	2.9	5.3
secondary ext coeff (10 <sup>-4</sup> )	4.7 (6)	1.14 (5)	0.31 (3)
abs coeff ( $\mu$ ), cm <sup>-1</sup> (Mo K $\alpha$ )	165	270	219
transmissn coeff range (normalized)	0.84-1.00	0.48-1.00	0.27-1.00
R <sub>c</sub> , %	3.3	3.8	3.4
R <sub>w</sub> , <sup>d</sup> %	6.2	3.3	3.5
no. of variables	33	33	35

<sup>a</sup>Hexagonal setting; lattice constants in Table I. <sup>b</sup> $F_o \geq 3\sigma_F$  and  $I_o > 3\sigma_I$ . <sup>c</sup> $R = \sum(|F_o| - |F_c|) / \sum|F_o|$ . <sup>d</sup> $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$ ,  $w = 1/\sigma_F^2$ .

a straightforward succession of refinement cycles in which positional and thermal parameters were allowed to vary. No problems associated with obverse-reverse or other twinning, which have been characteristic of many compounds with the 7-12 structure type (space group  $R\bar{3}$ ),<sup>3,19</sup> were in evidence in these samples. The isolated R(1) and interstitial M atoms refined to within 2 $\sigma$  of unit occupancy and were therefore fixed at that value. Peaks in the final difference map were  $< \sim 0.4 \text{ e/\AA}^3$  for Sc<sub>7</sub>I<sub>12</sub>Co and  $< \sim 0.5 \text{ e/\AA}^3$  for Y<sub>7</sub>I<sub>12</sub>Fe.

Comparison of the  $F_c$  data for the yttrium compound calculated on the basis of the refined model with the respective  $F_o$  data for the set of reflections classified as "unobserved" showed no errors in the "unobserved" classification. In only three cases did  $|F_o - F_c|$  exceed 2 $\sigma(F_o)$ , and  $R_w$  with all data increased only modestly (to 3.7%). The relatively larger  $R_w$  value for the scandium phase arises from underestimated errors in the weaker but observed reflections; a reweighting procedure was not deemed worthwhile.

An analogous scheme for structural refinement was attempted for Ca<sub>1-x</sub>Pr<sub>x</sub>(Pr<sub>6</sub>I<sub>12</sub>Co), but it ran into several difficulties associated with the consequences of obverse-reverse twinning. Axial Polaroid photos taken on the diffractometer with extended exposure times showed the layers normal to  $\bar{c}$  (in the hexagonal setting of  $R\bar{3}$ ) clearly and without violations, but oscillation photos about  $\bar{a}$  and  $\bar{b}$  displayed several additional reflections. Despite this, an orientation matrix was obtained that was quite consistent with the rhombohedral cell, and a least-squares refinement of the lattice parameters using 15 intense reflections gave rhombohedral lattice parameters ( $a = 9.795(2) \text{ \AA}$ ,  $b = 9.799(2) \text{ \AA}$ ,  $c = 9.795(2) \text{ \AA}$ ,  $\alpha = 107.02(2)^\circ$ ,  $\beta = 107.07(2)^\circ$ ,  $\gamma = 106.98(2)^\circ$ ,  $V = 782.4(3) \text{ \AA}^3$ ) without 3-fold symmetry being imposed. These are equivalent to hexagonal parameters  $a = 15.752(4) \text{ \AA}$ ,  $c = 10.92(2) \text{ \AA}$ , and  $V = 2347(2) \text{ \AA}^3$ , which show only typical, small deviations from the more accurate Guinier results (Table I). Lacking a crystal without twinning problems, we collected data on this specimen. Any misalignment of domains was not apparent in the profiles of peaks that contain contributions from both orientations (see below), and these were sharp, symmetrical, and well centered.

Attempts to refine the structure ran into difficulties consistent with the twinning model discussed in the sources cited above (see especially Berroth's thesis<sup>19</sup>). In this model, the  $c$  axes of the two twin components are aligned but the hexagonal  $a$  and  $b$  axes are rotated about  $\bar{c}$  relative to each other by an angle  $\delta = 2 \sin^{-1} (3^{1/2}/2(13^{1/2})) \cong 27.796^\circ$ , which is equivalent to twinning through a 180° rotation about [140]. The two reciprocal lattices in every layer normal to  $\bar{c}$  overlap when  $h-3k = 13n$  ( $n = \text{integer}$ ), meaning that 1/13th of the reflections collected on one component of the twin will contain contributions from the other component. The overlapping structures have the characteristics that, for a structural refinement of this compound from data from a twinned crystal, (1) the Co site is filled by iodine in the twin, (2) the isolated Pr cluster atoms become "delocalized" into empty octahedral holes between the iodine layers in the twin, and (3) all the I2 atoms and five-sixths of the

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(19) Berroth, K., Doctoral Dissertation, University of Stuttgart, FRG, 1980.

11 atoms overlap with like atoms in the twin.

These features manifested themselves clearly in the results of the first refinement attempted. With the Co occupancy fixed at unity, the Co thermal parameter did not remain positive, and allowing the Co occupancy to vary gave a value of 118%. This suggests an apparent partial I occupation of this site. The cluster Pr atom occupancies refined to 88% (holding the iodine occupancy at 1.0), with refinement indices for this physically unrealistic case of  $R = 4.0\%$  and  $R_w = 4.0\%$ . If the cluster Pr occupation was fixed at unity, these residuals went to 5.1% and 5.2%, respectively. Electron density maps calculated at this stage showed the Pr peaks to be no larger than those of the I atoms.

When reflections satisfying the  $h - 3k = 13n$  relation were dropped from the refinement (which omits 92 out of 860 independent observed reflections), the refinement indices went to  $R = 3.9\%$  and  $R_w = 3.8\%$  with all occupancies equal to unity except the Ca site (for which a constrained refinement yielded  $\sim 63\%$  Ca and  $37\%$  Pr at this stage). When the multiplicities of the Pr and Co were instead allowed to vary, the former did not move significantly from 1.00 while the latter went to 1.06 (2).

The 92 reflections dropped represent  $1/13$ th of the data out of 1200 total independent reflections (340 unobserved,  $I < 3\sigma(I)$ ). It is notable that none of these 92 reflections was too weak to be observed. Indeed, they were invariably strong because these reflections correspond precisely to those with major contributions from the iodine sublattice. This is to be expected since the twinning involves two components for which the iodine layers superpose. It should be emphasized that unless the twinning model employed is indeed appropriate to the crystal studied, the omission of such a set of precisely measured strong reflections with an otherwise unlikely relationship ( $h - 3k = 13n$ ) would hardly be expected to improve the refinement so dramatically.

A program that would correctly separate the intensities of the twin components as a variable of the refinement was lacking. However, the  $M_7X_{12}Z$  structure has been very well established in other studies, and our principal interest at this stage was the metric details of the cluster and an estimate of the distribution in the isolated metal atom position. Therefore, an alternative approximation was devised based on the fact that the problem reflections were of fairly uniform and high intensity. Since  $F_o$ 's for the "twin reflections" are systematically too large by a factor determined by an amount related to the size of the reverse component in the predominantly obverse crystal, these structure factors were reintroduced to the data set after multiplying them by a scale factor equal to the effective fraction,  $f$ , derived for the obverse component. This fraction was determined iteratively as follows: (a) use the structural model to obtain  $F_c$ 's for the "twin reflections"; (b) compute  $f = 1/\sum_{92} F_c/F_o$  where the sum runs over the 92 twin reflections; (c) compute adjusted  $F_o' = fF_o$  values; (d) refine new model by using adjusted  $F_o$ 's and return to step a.

The  $f$  value for the first cycle came from the refinement without the  $h - 3k = 13n$  reflections. Only one additional cycle with the complete "corrected" data set was necessary to get convergent results with  $f = 0.78$  (2). In short, we introduced a single additional scale factor to account for the twinning problem. Because the data used to determine the  $f$  parameter are among the largest in the data set and are therefore precisely measured, this parameter is accurately determined. (Errors from the subdivision of  $F$ , not  $I$ , are thereby also smaller.) The final results ( $R = 3.4\%$ ,  $R_w = 3.5\%$ ) correspond to a calcium occupancy of the isolated R(1) site of 65 (1%). (Even with the approximations involved the answer should at worst be correct within  $\pm 5\%$ , which is sufficient.) A difference map following refinement with this correction contained as the largest residual only a peak of approximately  $1 e/\text{\AA}^3$  near the Co position. Of course, the absorption correction was based on the bulk crystal and will be somewhat in error, which is probably the source of the higher  $R_w$ , Table II. Nonetheless, the thermal ellipsoid parameters show nothing unusual although these are up to about 50% larger than commonly found in related phases.

One of the purposes of carrying through the refinement of the structure of this crystal was to determine the extent to which the "isolated"  $\text{Pr}^{3+}$  in the structure had been replaced by  $\text{Ca}^{2+}$ . In refinement, this site was treated as being populated by either Pr or Ca and being never empty; i.e., the Ca and Pr occupancies were constrained to sum to one. A number of  $\text{Zr}_6\text{X}_{12}\text{Z}$  compounds adopt this structure type with the isolated site completely vacant, but no examples of  $\text{R}_7\text{X}_{12}\text{Z}$  phases are known in which this site is not fully occupied. In addition, the interstitial occupancy in clusters and condensed clusters appear to be complete for all Z that have been tested (except  $Z = \text{H}$ ). Thermal parameters for the Ca and Pr at this site could not be independently varied and so were set equal.

## Results and Discussion

**Syntheses.**  $\text{R}_7\text{I}_{12}\text{M}$  phases are readily synthesized by reaction of  $\text{RI}_3$ ,  $\text{MI}_2$  and excess R metal ( $R = \text{Sc, Y, Pr, Gd}$ ;  $M = \text{Mn, Fe, Co, Ni}$ ).

**Table III.** Positional Parameters for  $\text{R}(\text{R}_6\text{I}_{12}\text{M})$  Phases

	<i>x</i>	<i>y</i>	<i>z</i>
$\text{Sc}_7\text{I}_{12}\text{Co}$			
Sc1	0	0	0.5
Sc <sup>2</sup>	0.1524 (3)	0.0429 (3)	0.1334 (3)
I1	0.3130 (1)	0.2333 (1)	0.0067 (1)
I2	0.1265 (1)	0.1780 (1)	0.3376 (1)
Co	0	0	0
$\text{Y}_7\text{I}_{12}\text{Fe}$			
Y1	0	0	0.5
Y2	0.1576 (1)	0.0436 (1)	0.1387 (1)
I1	0.3167 (1)	0.2369 (1)	0.0065 (1)
I2	0.1306 (1)	0.1819 (1)	0.3340 (1)
Fe	0	0	0
$\text{Ca}_{0.65}\text{Pr}_{0.35}\text{Pr}_6\text{I}_{12}\text{C}$			
(PrCa) <sup>a</sup>	0	0	0.5
Pr2	0.1610 (1)	0.0445 (1)	0.1456 (1)
I1	0.3154 (1)	0.2363 (1)	0.0039 (1)
I2	0.1320 (1)	0.1833 (1)	0.3381 (1)
Co	0	0	0

<sup>a</sup> Refined with equal thermal parameters and with Pr plus Ca occupancies held at unity ( $\sigma \sim 0.01$ ).

**Table IV.** Important Distances ( $\text{\AA}$ ) in  $\text{R}(\text{R}_6\text{I}_{12}\text{M})$  Phases<sup>a</sup>

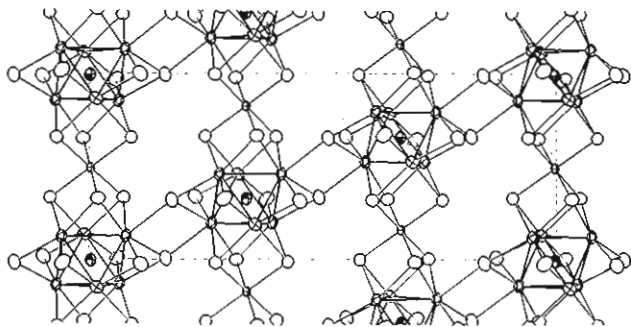
	Sc( $\text{Sc}_6\text{I}_{12}\text{Co}$ )	Y( $\text{Y}_6\text{I}_{12}\text{Fe}$ )	$\text{Ca}_{0.65}\text{Pr}_{0.35}$ - ( $\text{Pr}_6\text{I}_{12}\text{Co}$ )
R(2)-R(2)			
Δ	3.489 (6)	3.747 (2)	3.928 (2)
Δ - Δ	3.386 (6)	3.665 (2)	3.906 (1)
R(1)-R(2)	4.248 (4)	4.417 (1)	4.487 (1)
R(2)-M	2.431 (4)	2.621 (1)	2.770 (1)
R(1)-I(2)	2.874 (1)	3.022 (1)	3.128 (1)
R(2)-I(2) <sup>b</sup>	3.018 (4)	3.171 (1)	3.215 (1)
	3.042 (4)	3.188 (1)	3.227 (1)
R(2)-I(1) <sup>b</sup>	2.927 (4)	3.085 (1)	3.178 (1)
	2.990 (4)	3.127 (1)	3.189 (1)
R(2)-I(1) <sup>a</sup>	3.310 (4)	3.317 (1)	3.350 (1)

<sup>a</sup> The isolated atom is R(1).

Fe, Co, Ni). Although all of the transition metals do not insert equally readily in all the rare-earth-metal clusters tried, praseodymium clusters seem especially avid in taking up the entire range of metals that might be expected to bond (below). Most reactions were run at 850 °C, and no attempts were made below 750 °C. Judging by the lack of sharpness of lines in powder diffraction patterns, the crystallinity of compounds made at 750 °C was clearly poorer. Lower temperatures might be feasible with extended reaction times, but the volatility of the rare-earth-metal triiodide reactant becomes a limiting factor in reaction rates. A complete list of  $\text{R}_7\text{I}_{12}\text{M}$  compounds synthesized, their lattice parameters, and their cluster electron counts is given in Table I.

We presume that these 7-12 compounds represent the thermodynamically stable products at the temperature and compositions used in synthesis. Therefore, the reactants need not have taken the form used, at least in principle. For example, we might have supplied the transition metals as the elemental powders. The preparation of the diiodides seems worthwhile since they appear to facilitate transport of the transition metal<sup>15</sup> and can be more accurately weighed (i.e., with a smaller relative error), and the sublimation step eliminates undesirable oxides that lead to ROI formation. A route we have not yet explored for the 3d transition metals is the utilization of intermetallic phases as precursors (e.g.,  $3\text{Y} + \text{Co} \rightarrow \text{Y}_3\text{Co}$ ;  $\text{Y}_3\text{Co} + 4\text{YI}_3 \rightarrow \text{Y}_7\text{I}_{12}\text{Co}$ ), although this approach has provided interesting consequences in other systems. The role that intermetallic phases may play in the course of the synthetic reactions reported here is not well studied.

**Crystal Structures.** Structures of the three compounds  $\text{Sc}_7\text{I}_{12}\text{Co}$ ,  $\text{Y}_7\text{I}_{12}\text{Fe}$ , and  $\text{Ca}_{0.65}\text{Pr}_{0.35}\text{Pr}_6\text{I}_{12}\text{Co}$  were determined in order to establish the compositions, structural details and dimensional information. Positional parameters for the three are listed in Table III, and some important distances are given in Table IV, while



**Figure 1.** [110] section of  $\text{Sc}(\text{Sc}_6\text{I}_{12}\text{Co})$  and the intercluster connections (hexagonal setting,  $c$  axis vertical). The crossed ellipsoids with heavier interconnections define scandium clusters, and the cobalt interstitials are shaded (90% probability thermal ellipsoids).

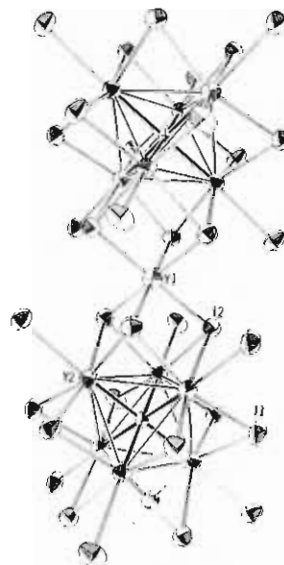
the anisotropic thermal parameter and structure factor data are available as supplementary material.

The  $\text{R}_7\text{X}_{12}$ -type structure originally determined for  $\text{Sc}_7\text{Cl}_{12}^{20}$  (viz.,  $\text{Sc}_7\text{Cl}_{12}(\text{B},\text{N})^2$ ) consists of layers of cubic-close-packed clusters of the  $\text{R}_6\text{X}_{12}$ -type that are oriented with their  $\bar{3}$  axes normal to the layers. For the trivalent elements, an additional R atom occurs in trigonal-antiprismatic halide interstices between these layers while the seventh metal atom is missing in closely related zirconium halide phases such as  $\text{Zr}_6\text{I}_{12}\text{C}$ .<sup>8</sup> A [110] projection of the  $\text{Sc}_7\text{I}_{12}\text{Co}$  result is shown in Figure 1. It can be seen that the scandium clusters centered by cobalt have all edges bridged by "inner" iodides ( $\text{I}^i$ ) and that these are further interconnected at metal vertices by long  $\text{Sc}-\text{I}^a$  bridges in which the "outer"  $\text{I}^a$  atoms are inner, edge-bridging  $\text{I}(2)^i$  atoms around the waists in other clusters, and vice versa. The presence of a  $\bar{3}$  operation at the cobalt atom in the cluster center (0, 0, 0) (Figure 1) generates a cubic-close-packed arrangement of clusters so interconnected.

The structure can also be described in terms of slightly puckered, cubic-close-packed iodine layers in which every 13th iodine is replaced by the interstitial atom; R atoms "clustered" in the six neighboring octahedral  $\text{I}_6$  sites about this point then produce the clusters. The trigonal-antiprismatic site at 0, 0,  $1/2$  that is formed by the  $\text{I}(1)^i$  atoms between two such clusters is the location of the seventh, isolated R atom. The local structure in  $\text{Y}_7\text{I}_{12}\text{Fe}$  is shown in Figure 2. The simple description  $\text{Y}^{3+}(\text{Y}_6\text{I}_{12}\text{Fe}^{3-})$  is apropos if Y-I interactions between these units are neglected.

The isolated metal atoms in the previously refined examples of the centric  $\text{R}_7\text{X}_{12}\text{Z}$  structure,  $\text{Sc}_7\text{Cl}_{12}(\text{B},\text{N})$ ,<sup>2</sup> exhibit thermal ellipsoids that are characteristically elongated along  $\bar{c}$ , with  $B_{33}/B_{11}$  ratios in the range of 3.7–7.5. This may arise because of the oversized cavity generated by the cluster network.<sup>2</sup> The use of larger halides provides an increased restriction on the minimum size of the metal cluster because of longer halogen-halogen contact distances (matrix effect), and this together with the demands of a small interstitial (Z) for good R-Z bonding may be responsible for severe distortion of the clusters to the  $\text{C}_{3v}$  symmetry (in space group  $\text{R}\bar{3}$ ) in  $\text{Sc}_7\text{X}_{12}\text{C}$  ( $\text{X} = \text{Br}, \text{I}$ ).<sup>3</sup> Bonding of larger transition metals within the clusters apparently eliminates both problems in that a centric structure with well-behaved thermal ellipsoids for the isolated R(1) atoms are now found ( $B_{33}/B_{11} = 1.4, 1.1,$  and  $2.3$  for the scandium, yttrium, and praseodymium compounds, respectively). Crystals with mixed orientations via obverse-reverse twinning as encountered here for  $\text{Ca}_{0.65}\text{Pr}_{0.35}(\text{Pr}_6\text{I}_{12}\text{Co})$  (Experimental Section) have also been found in other studies of  $\text{R}_7\text{I}_{12}$  phases ( $\text{R} = \text{La}, \text{Tb}, \text{Er}$ ).<sup>19</sup>

Distances found in the present 7–12 structures are highly regular with respect to metal-iodine separations and scale fairly well with crystal radii of R. On the other hand, only a slow increase in the intercluster bridging  $\text{R}-\text{I}^a$  distances occurs with increasing size of R (Table IV), reflecting the outward movement of the rare-



**Figure 2.** Structure of  $\text{Y}(\text{Y}_6\text{I}_{12}\text{Fe})$  showing two clusters and the intervening Y1. The Y-Fe bonding is emphasized (90% ellipsoids).

earth-metal atoms with respect to the surrounding sheath of inner iodine atoms that allows for less restrictive  $\text{I}^a-\text{I}^i$  contacts. A remarkable effect in  $\text{Sc}-\text{I}^a$  distances is found when one makes the extreme comparison of the cobalt and carbon derivatives: the  $\text{Sc}-\text{I}^a$  distance in the cobalt compound is actually  $0.13 \text{ \AA}$  less because the greatly expanded  $\text{Sc}_6$  unit has vertices closer to the plane of the surrounding four  $\text{I}^i$  atoms. The vertex still falls short of planarity with the neighboring  $\text{I}^i$  atoms even in  $\text{Y}_7\text{I}_{12}\text{Fe}$ , as can be at the lower right vertex in Figure 2.

The metal cluster-interstitial (R-M) separations in Table IV are another matter. Although it is not to be expected that these separations could be reproduced by some set of metallic or other radii, the rate of change from  $\text{Sc}-\text{Co}$  to  $\text{Y}-\text{Fe}$  is scaled fairly well by the use of either metallic radii for both elements or the crystal radius for  $\text{R}^{3+}$  and the metallic radius for M. However, the observed values for these two cases are still  $\sim 0.2 \text{ \AA}$  less than predicted with the aid of single-bond metallic radii. Moreover, the observed  $\text{Sc}-\text{Co}$  distance in  $\text{Sc}_7\text{I}_{12}\text{Co}$ ,  $2.431(4) \text{ \AA}$  ( $\times 6$ ), is strikingly less than the  $2.724 \text{ \AA}$  value in  $\text{ScCo}$  ( $\text{CsCl}$  type),<sup>21</sup> a  $2.742 \text{ \AA}$  distance in  $\text{Sc}_2\text{Co}$  ( $\text{Al}_2\text{Cu}$ ,  $\text{CN}8$ ),<sup>22</sup> and the  $2.616 \text{ \AA}$  average within the  $\text{Sc}$  trigonal prism in  $\text{Sc}_3\text{Co}$  ( $2.72 \text{ \AA}$  for eight neighbors).<sup>23</sup> Comparable differences between cluster and intermetallic separations have also been noted for  $\text{Zr}-\text{Mn}$  and  $\text{Zr}-\text{Fe}$  clusters.<sup>15</sup>

On the other hand, the size of the  $\text{Pr}-\text{Co}$  separation in  $\text{Ca}_{0.65}\text{Pr}_{0.35}(\text{Pr}_6\text{I}_{12}\text{Co})$  is surprisingly large,  $0.1-0.15 \text{ \AA}$  greater than expected on the basis of the  $\text{Sc}-\text{Co}$  and  $\text{Y}-\text{Fe}$  compounds when scaled by either metallic or crystal radii for changes expected for the component elements. No obvious explanation is at hand. More data and experience on this sort of system seem necessary.

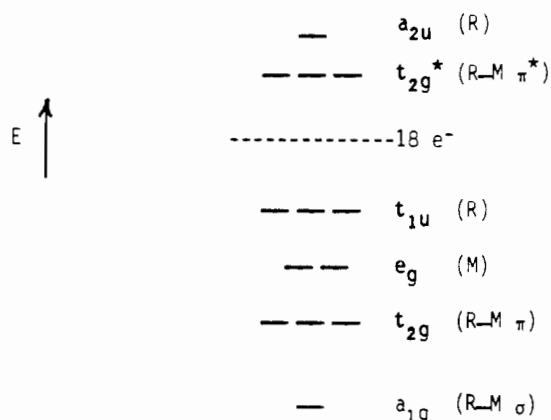
**Electronic Factors.** The role of either main-group or transition elements in bonding within and stabilizing both the rare-earth-metal<sup>2</sup> and zirconium<sup>8,12,15</sup> clusters of this type has been considered before on the basis of extended Hückel molecular orbital calculations. The interstitial provides both electrons and orbitals for the formation of strong bonds with d orbitals of the skeletal metal. The relevant MO's for a 3d interstitial element scale are about as follows:<sup>15</sup>

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The cluster bonding orbitals  $a_{1g}$  and  $t_{2g}$  originate largely from d orbitals on the cluster metal R and the 4s and 3d AO's on the interstitial M, respectively. The  $t_{1u}$  and  $a_{2u}$  MO's are marked R as they have important contributions only on the  $R_6I_{12}$  unit, and just the former shows significant cluster bonding. The  $e_g$  (M) level is largely nonbonding and localized on the transition-metal interstitial.

The gap illustrated leads to the expectation that a stable configuration will pertain for a  $t_{1u}^6$  HOMO, viz., 18 electrons in the cluster-based orbitals  $a_{1g}^2$ ,  $t_{2g}^6$ ,  $e_g^4$ , and  $t_{1u}^6$  after lower lying iodine nonbonding and R-I bonding orbitals are filled. Such a situation would pertain, for example, to  $Sc_7I_{12}Co$  with  $7 \cdot 3 - 12 \cdot 1 + 9 = 18$  electrons. This 18-electron boundary appears to be relatively important with  $Zr_6I_{12}M$  clusters where it has proven difficult experimentally to achieve clusters with other than 18 or 19 cluster-based electrons; in fact, no examples are known with the lower 17-electron count. Experience with Zr-Cl-M systems indicate that the 18-electron preference is, if anything, even more important.<sup>24</sup> On the other hand, the relative ease with which we have been able to synthesize rare-earth-metal examples with 16 or 17 electrons (Table I) indicates that full occupancy of the  $t_{1u}$  level on the  $R_6$  cluster is not so important in these cases, perhaps because of the relatively higher lying AO's for the more electropositive rare-earth elements.

The interesting persistence of the isolated cation in the  $R_7X_{12}$  structures and its absence in the nominally isostructural  $Zr_6X_{12}Z$  version have in the past led to a variety of unsuccessful experiments designed to insert a heterocation into either. The persistence of the seventh metal in  $R_7X_{12}Z$  examples is of course related to the paucity of electrons otherwise present in a  $R_6X_{12}Z$  cluster and the evident impracticality of achieving a 14- (or 18-) electron count in a  $R_6X_{12}Z$  phase with a realistic main-group (or transition-metal) interstitial, where Ar (or Zn?) would in fact be required to furnish something approaching 8 (or 12?) valence electrons for this purpose.

Reduction of the charge on the isolated cation in  $R_7X_{12}Z$  is a more reasonable experiment. This led us to the attempted stoichiometric synthesis of the 17-electron  $CaPr_6I_{12}Co$  and the achievement of only partial replacement, namely  $Ca_{0.65}Pr_{0.35}$

( $Pr_6I_{12}Co$ ) in which the average cluster has about 17.35 electrons. The nickel analogue with 18 electrons might be a slightly more favorable candidate for complete exchange but, as noted above, the 18-electron count factor does not appear to be of paramount importance here. Size should not be a serious factor either since  $Ca^{2+}$  and  $Pr^{3+}$  have virtually the same crystal radii.<sup>25</sup> The larger and somewhat elongated (average) thermal ellipsoids deduced for the isolated (Ca, Pr) atom in this structure may suggest unrecognized problems. However, the method utilized in the twin refinement (see Experimental Section) and the fact that the absorption correction applied to the entire crystal, not just to the refined oververse component, may in fact be responsible for such an artifact. This type of substitution chemistry needs further study.

The lanthanide elements with nominal  $4f^{n-1}$  distributions may achieve oxidation states lower than +3 by one of two strategies: adoption of an f-shell configuration with more electrons than the usual  $f^{n-1}$  or involvement of their bonding orbitals (5d, 6s, (6p)) in strong metal-metal bonds to provide a place for additional electrons or both. While gadolinium and praseodymium choose the latter course in the  $R_7I_{12}M$  phases, similar reactions designed to produce the analogous dysprosium compounds containing iron or cobalt yielded  $DyI_2$  instead. This phase<sup>26</sup> has been shown to occur in the  $CdCl_2$ -type structure and to possess the classic  $4f^{10}$  configuration for the  $Dy^{2+}$  state.<sup>27</sup> For the same reason, we expect it may be difficult to prepare comparable cluster phases for R = Sm, Eu, Tm, Yb, and possibly Nd. Obviously the existence of the metallic  $PrI_2$  ( $MoSi_2$  and other type structures<sup>28</sup>) does not preclude cluster formation.

Other of our results defy any easy explanation. Why, for example, can  $Sc_7I_{12}Co$  be made quantitatively while we find no evidence for the 17-electron iron analogue? On the other hand,  $Y_7I_{12}Fe$  appears to be quite stable; in fact, yields of  $Y_7I_{12}Fe$  are better than those for  $Y_7I_{12}Co$ . There are many factors at work here, and it is not clear that the size of the "interstitial" alone or the strength of the R-R bonding (via  $t_{1u}$  especially) matter at all relative to other factors, especially those related to the strengths of the R-M bonds formed. Of course, this question ultimately comes back to the stability of the alternative R-M intermetallic phases. Distance comparisons alone (above) suggest these clusters exhibit especially tight R-M bonding, for whatever reason.

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**Supplementary Material Available:** A table of anisotropic thermal parameters for  $Sc_7I_{12}Co$ ,  $Y_7I_{12}Fe$ , and  $Ca_{0.65}Pr_{0.35}(Pr_6I_{12}Co)$  (1 page); tables of observed and calculated structure factors for the same compounds (7 pages). Ordering information is given on any current masthead page.

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