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A Novel Structure Type for Isolated Rare-Earth-Metal Clusters Centered by Transition Metals: $Cs_4R_6I_{13}Z$ (R = Ce, Pr; Z = Co, Os)

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Introduction

The rare-earth-metal halides form a remarkable variety of highly reduced phases that contain metal clusters.[1,2] The great majority of these clusters are derived from octahedral metal units R_6 that are bridged over each edge by a halide atom to form R_6X_{12} units and are also centered by an essential interstitial atom Z. Possible interstitial atoms are late transition metals (i.e., group 7 and 8 elements), second-period main-group elements (such as C and N), and even small dimers such as C_2. These provide not only central bonding to the cluster but also additional valence electrons as well that aid in fulfilling certain minimal electron counts necessary for metal−metal bonding of the relatively electron-poor rare-earth metals.

Our research in recent years has focused on the condensation of clusters into dimers, oligomers and chains as well as on the different patterns of connectivity generated by the halide atoms that link the clusters into certain frameworks. Although many stoichiometries and structural varieties are found among the centered zirconium cluster halides, rare-earth-metal clusters that are isolated from each other and centered by transition metals are so far reported for ternary phases only in three different structure types, as follows:

(a) Representatives of the $R_6X_{10}Z$-family[3−5] crystallize triclinic for several rare-earth metals (such as Y, La, and Pr) and with iodine or bromine as possible halides. Only transition metals have been found so far as interstitial atoms, but these include almost all members of groups 7 and 8. The interconnection pattern between cluster and halides can be formulated[1] as $(R_6Z)X^{i}_{2}X^{i-i}_{4/2}X^{i-a}_{6/2}X^{a-i}_{6/2}$.

(b) The rhombohedral $R_7X_{12}Z$-structure type[3,6] is certainly by far the most versatile one with compounds known for many rare-earth-metals with chlorine, bromine, or iodine. Not only can many transition metals occupy the center of the cluster unit, but the main-group elements B, C, C_2, and N can as well.[7,8] Besides a discrete metal−metal bonded R_6Z-cluster, the structure contains a seventh trivalent (R^{III}) metal that is only surrounded by halides and without any metal−metal contacts with the cluster. Therefore, the halide connectivity is $R(R_6Z)X^{i}_{6}X^{i-a}_{6/2}X^{a-i}_{6/2}$.

(c) So far only four $R_6X_{8.5}Z$ compounds ($Pr_{12}I_{17}Fe_2$, $Pr_{12}I_{17}Re_2$,[9] $La_{12}I_{17}Fe_2$, and $Ce_{12}I_{17}Fe_2$[10]) are known. They adopt a complex triclinic structure with the interconnection pattern $[(R_6Z)X^{i-i}_{7/2}X^{i-a}_{4}X^{i-a-a})]_2$ providing the unusual hypostoichiometric (iodine-poor) composition.

The research reported here has been focused on the introduction of alkali-metal atoms into the structures in order to expand the variety of quaternary compounds with discrete rare-earth-metal clusters centered by transition metals. This direction was encouraged by other recent results with isolated clusters centered only by small main-group elements, such as $Cs_4Pr_6I_{13}C_2$ and $Cs_4Sc_6I_{13}C$,[11] and by many examples in the chemistry of reduced zirconium halides.[1]

Experimental Section

Synthesis. The synthetic and sublimation techniques for PrI_3 and the reaction procedures utilizing welded Nb tubing have been described before.[6,12] CsI (Alfa, 99.9%) was dried by slow heating under dynamic high vacuum and then sublimed. Pr metal (Ames Laboratory), Os powder (Alfa, 99.95%), and Cs metal (Johnson-Mathey, 99.98%) were used as received and handled in a glovebox. Initial reactions with an overall stoichiometry $Cs_2Pr_6I_9Os$ were heated at 800 °C for 27 days and slowly cooled at 5 °C/h to 500 °C, and then the furnace was turned off. Besides unreacted praseodymium metal, the products were black crystals of $Cs_4Pr_6I_{13}Os$ (~70%, according to Guinier powder diffraction), 10% PrOI, and an unknown phase that gave few weak lines.

Subsequent reactions with the appropriate starting materials and the exact stoichiometry yielded also black, microcrystalline samples of $Cs_4Pr_6I_{13}Co$ and $Cs_4Ce_6I_{13}Os$ in high yields (≈90%, besides ca. 10% PrOI or CeOI respectively) under the same reaction conditions. They were only examined by Guinier powder diffraction. Interestingly, several reactions with La instead of Pr and Ce did not give an isostructural product but an unidentified phase. Attempts to obtain $Cs_4Pr_6I_{13}Ru$ yielded Pr_3I_3Ru[13] (60%), CsI (30%), and PrOI (10%). Other interstitials and rare-earth-elements have not been tried.

Single Crystal X-ray Study. Crystals of $Cs_4Pr_6I_{13}Os$ (above) were mounted in thin-walled capillaries in the glovebox, and their quality was checked by Laue and oscillation photographs on Weissenberg cameras. The monoclinic cell parameters and the orientation matrixes were obtained from one crystal with the approximate size $0.05 \times 0.05 \times 0.15$ mm via a least-square refinement of the setting angles of 25 centered reflections collected on a CAD4 diffractometer using graphite-monochromated Mo $K\alpha$ radiation. A total of 2017 reflections were collected ($4° \leq 2\theta \leq 50°$; $+h$, $+k$, $\pm l$; $2\theta-\omega$ scans) at room temperature to give 1559 unique data ($I > 3\sigma_I$, $R_{av} = 0.055$) for the space group $C2/m$ (no. 12) after averaging the redundant data. The structure was solved using direct methods (SHELXS[14]). Programs, scattering factors, etc. utilized were those in the instrument package TEXSAN.[15] An empirical absorption correction was applied to the full data set with the aid of four Ψ-scans and later after isotropic refinement by DIFABS, as recommended[16] (minimum/maximum relative transmission factors: 0.883/1.122, $\mu = 226.3$ cm^{-1}). The residuals after the anisotropic refinement of all atoms (65 variables) were $R(F) = 0.033$ and $R_w = 0.040$. The largest residual peak was 1.75 e/Å^3, 0.84 Å from Os. The Guinier powder pattern calculated for the refined structural model agreed very well with that observed for the bulk product with Si as internal standard. This allowed indexing and a more accurate determination of the lattice constants. Some data collection and refinement parameters are given in Table 1. The final atomic

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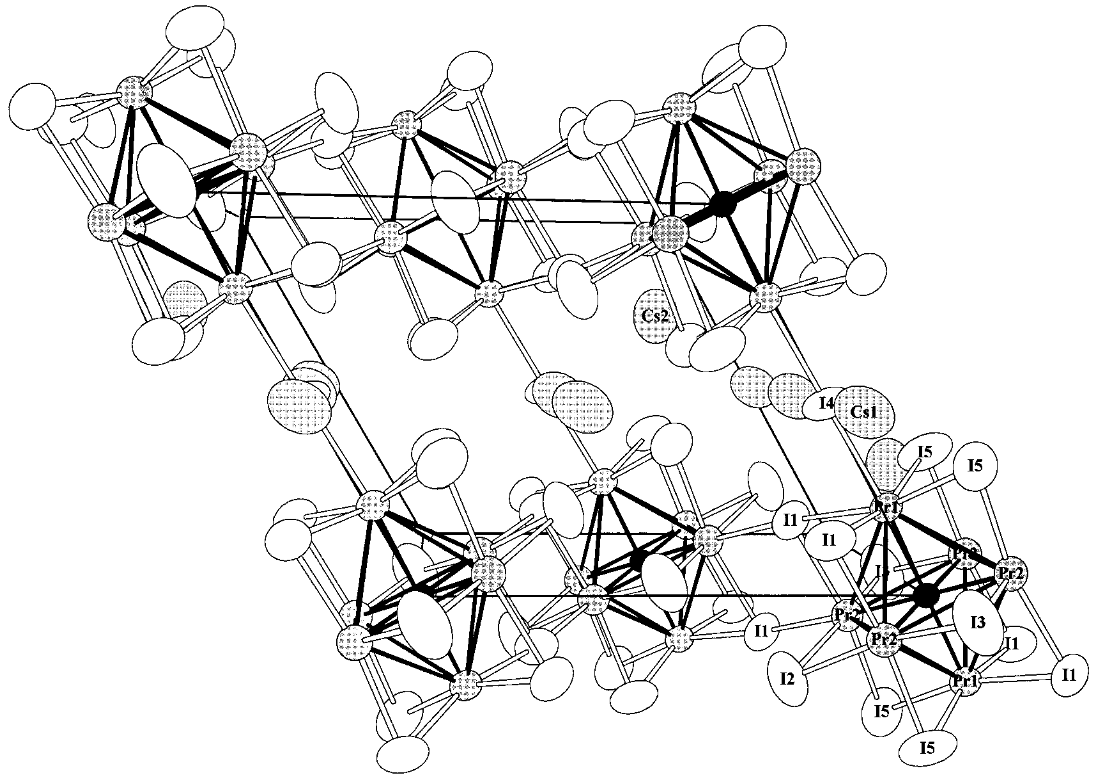

Figure 1. $Cs_4Pr_6I_{13}Os$: Unit cell along [010] to show the arrangement of the isolated octahedra with their iodine surrounding and the positions of the Cs atoms. The a axis runs horizontal. (Unit cell content between $0 < y < {}^1/_2$; Os atoms are black, other atoms as marked; ellipsoids with 99% probability.)

Table 1. Crystallographic Data for $Cs_4Pr_6I_{13}Os$

fw	3217.10	V (Å^3)	2114(2)
space group; Z	$C2/m$; 2	D_{calc}(g/cm^3)	5.053
lattice constants^a		μ (Mo Kα, cm^{-1})	226.25
a (Å)	14.390(3)	R, $R_w{}^b$	0.033, 0.040
b (Å)	13.641(2)		
c (Å)	12.417(3)		
β(deg)	119.84(2)		

[a] Cell constants from 26 Guinier powder pattern reflections measured with Si as internal standard; $\lambda = 1.540\,562$ Å, 22 °C. [b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o{}^2]^{1/2}$, $w = \sigma_F{}^{-2}$

Table 2. Positional and Isotropic Equivalent Displacement Parameters (Å^2) for $Cs_4Pr_6I_{13}Os$

atom	posn	x	y	z	$U_{eq}{}^a$
Os	2a	0.0	0.0	0.0	0.87(3)
Pr1	4i	0.01090(7)	0.0	0.23097(8)	1.37(3)
Pr2	8j	0.15800(5)	0.14384(5)	0.08410(6)	1.47(2)
Cs1	4h	0.0	0.7123(1)	0.5	3.61(5)
Cs2	4i	0.6743(1)	0.0	0.2877(2)	4.67(7)
I1	8j	0.83325(7)	0.83210(7)	0.17181(8)	2.51(3)
I2	4i	0.3701(1)	0.0	0.2210(1)	3.03(5)
I3	4g	0.0	0.3294(1)	0.0	3.32(5)
I4	2c	0.0	0.0	0.5	2.55(7)
I5	8j	0.18905(8)	0.16615(8)	0.35920(9)	3.61(4)

[a] $U_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i{}^*a_j{}^*\vec{a}_i\vec{a}_j$.

coordinates, isotropic-equivalent temperature factors and their estimated standard deviations^a are listed in Table 2. A larger summary of collection and refinement information as well as anisotropic displacement parameters for all atoms are tabulated in the Supporting Information. These and the structure factor data are also available from J.D.C.

Results and Discussion

The use of the large interstitials Os or Co as well as the large counter atom Cs results in a new structure type for centered cluster iodides with the unusual R_6X_{13} network. $Cs_4Pr_6I_{13}Os$ crystallizes C-centered monoclinic in the space group $C2/m$ with the lattice constants $a = 14.390(3)$, $b = 13.641(2)$, and $c = 12.417(3)$ Å and $\beta = 119.84(2)°$ in the form of black, irregular-shaped crystals. $Cs_4Pr_6I_{13}Co$ ($a = 14.331(8)$, $b = 13.562(6)$, and $c = 12.380(7)$ Å; $\beta = 119.65(5)°$) and $Cs_4Ce_6I_{13}Os$ ($a = 14.450(8)$, $b = 13.709(5)$, and $c = 12.517(9)$ Å; $\beta = 120.18(5)°$) are isostructural according to their powder patterns. The significant structure feature is the octahedral Pr_6 cluster formed by two crystallographically distinct metal atoms and centered by an Os atom that is located on an inversion center (site symmetry $2/m$) in the unit cell (Figure 1). The Pr2 atoms constitute the equatorial plane while Pr1 atoms are the apexes of the nearly regular octahedra. The spread among the four Pr−Pr distances is small ($\Delta = 0.026(3)$ Å), as are correspondingly the Os−Pr separations ($\Delta = 0.010(1)$ Å, Table 3).

The 12 edges of the rare-earth-metal cluster are bridged by four crystallographically different I atoms to form the well-known R_6X_{12} unit common to most rare-earth-metal clusters (Figure 1). Each cluster has four I1 atoms with the functionality I^{i-a}. These bridge a pair of cis Pr1−Pr2 edges and their inversion related pair and also form exo bonds to Pr2 atoms of the four surrounding clusters. Each is naturally opposed by another I1 atom on the latter that links the same clusters as I^{a-i}. All I1 atoms, therefore, connect the tilted clusters into layers along [001]. Two I2 and two I3 atoms cover the four Pr2−Pr2 edges that form the waist of the octahedra as I^i without any bonding to adjacent clusters. Likewise, I5 atoms cover the four remaining Pr1−Pr2 edges as I^i. Finally, two I4 atoms link different layers as I^{a-a} via linear bridges at the Pr1 apexes of each octahedra and afford the 13th halogen in the formula. Therefore, the interconnection pattern of the iodine atoms can be formulated as $(Pr_6Os)I^i{}_8I^{i-a}{}_{4/2}I^{a-i}{}_{4/2}I^{a-a}{}_{2/2}$. The coordination environments of the Pr atoms are slightly distorted octahedra of five I atoms and one Os (Pr1: 2 × I1, I4, 2 × I5, Os. Pr2: 2 × I1, I2, I3, I5, Os).

The Cs atoms occupy iodine-lined cavities between the clusters. Cs1 is surrounded by nine iodine atoms (2 × I1, 2 ×

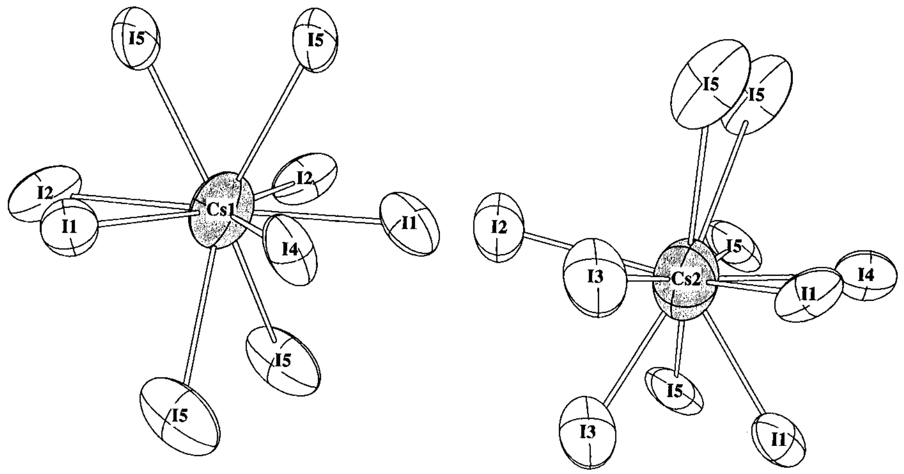

Figure 2. $Cs_4Pr_6I_{13}Os$: Coordination polyhedra of Cs1 (left) and Cs2 (right, ellipsoids 99% probability).

Table 3. Important Interatomic Distances (Å) for $Cs_4Pr_6I_{13}Os$

Os−Pr1	2.793(1)^a	Cs1−I1	3.912(2)^a	I2−Pr2	3.300(1)^a
Os−Pr2	2.7834(8)^b	Cs1−I2	4.176(2)^a	I2−Cs1	4.176(2)^a
		Cs1−I4	3.925(2)	I2−Cs2	4.030(2)
Pr1−Pr2	3.937(1)^a	Cs1−I5	3.961(2)^a		
	3.950(2)^a		4.236(1)^a	I3−Pr2	3.210(1)^a
				I3−Cs2	3.944(2)^a
Pr2−Pr2	3.924(2)	Cs2−I1	3.978(2)^a		
	3.948(2)	Cs2−I2	4.030(2)	I4−Pr1	3.421(1)^a
		Cs2−I3	3.944(2)^a	I4−Cs1	3.935(2)^a
Pr1−I1	3.233(1)^a	Cs2−I4	4.077(2)	I4−Cs2	4.077(2)^a
Pr1−I4	3.421(1)	Cs2−I5	4.433(2)^a		
Pr1−I5	3.191(1)^a		4.624(1)^a	I5−Pr1	3.191(1)
				I5−Pr2	3.231(1)
Pr2−I1	3.259(1)	I1−Pr1	3.233(1)	I5−Cs1	3.961(2)
	3.378(1)	I1−Pr2	3.259(1)		4.236(1)
Pr2−I2	3.300(1)		3.378(1)	I5−Cs2	4.433(2)
Pr2−I3	3.210(1)	I1−Cs1	3.912(2)		4.624(1)
Pr2−I5	3.232(1)	I1−Cs2	3.978(2)		

^{a} Distance occurs twice. ^{b} Distance occurs four times.

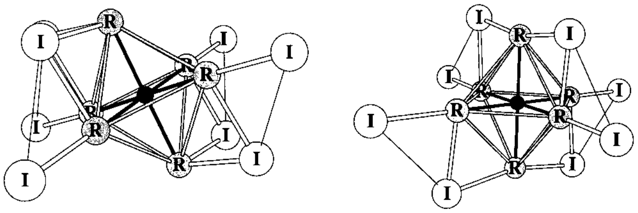

Figure 3. Comparison of the arrangement of I^{i-a} and I^{a-i} around the octahedra in the structures of $Cs_4Pr_6I_{13}Os$ (left) and $Cs_4Sc_6I_{13}C$ (right, with the tetragonal *c*-axis vertical). The thin lines between the I^{i-a} and I^{a-i} atoms symbolize the relative positions of adjacent R_6 octahedra.

I2, I4 and 4 × I5), while Cs2 has 10 iodine atoms as nearest neighbors over a longer range of distances (2 × I1, I2, 2 × I3, I4, and 4 × I5). The coordination polyhedra of both cesium atoms are rather irregular (Figure 2).

The comparison of the formula $Cs_4Pr_6I_{13}Os$ with those of $Cs_4Pr_6I_{13}C_2$ and $Cs_4Sc_6I_{13}C$[11] suggests similar or even isotypic structures. Indeed, the interconnection formulation of the iodine atoms is the same. However, the structure of the osmium and cobalt compounds described here is significantly distinct from those of the carbon representatives. This is reflected by a different arrangement of the four I^{i-a} atoms that link the clusters, which are I1 and I4 for the respective compounds. In $Cs_4Pr_6I_{13}Os$, the two I1 atoms above the waist of each octahedron bridge cis edges and are, because of the inversion center, also reproduced on the opposite side of the cluster (Figure 3 left). The connection of the clusters, therefore, is two dimensional parallel to (110). Contrarily, in $Cs_4Pr_6I_{13}C_2$ and $Cs_4Sc_6I_{13}C$, the two I4 atoms above the waist bridge trans edges and are, reflecting a 4_1-screw axis, rotated by 90° to those below the equatorial plane of the octahedra (Figure 3 right). Hence, they link the clusters into a three dimensional network, with Cs atoms in suitable holes. The only factors that differ between the present compounds with Co and Os and the earlier carbides are sizes of the components, principally the interstitials in the two sets but also the tetragonal elongation of the clusters in $Cs_4Pr_6I_{13}C_2$ because the acetylide interstitial and the smaller host metal as well in $Cs_4Sc_6I_{13}C$. Disregarding the different interstitial species, the relation of the two sets of compounds may be described as polymorphic with the common formula $Cs_4Pr_6I_{13}Z$.

This new structure brings to three the structure types with the uncommon $M_6X_{13}Z$ composition and different bridging modes. Zirconium examples are the earlier orthorhombic $Zr_6Cl_{13}B$ and $KZr_6Cl_{13}Be$ as well as its more recent tetragonal aristotype $Zr_6Cl_{11.5}I_{1.5}B$.[17] They both feature the unusual functionalities Cl^{i-i} and Cl^{a-a-a}.

The synthesis of the three new compounds shows also that the introduction of alkali metals can play an important role in the chemistry of "reduced" cluster compounds stabilized by transition metals. This process, essentially four CsI plus "R_6I_9Z", allows access to structures with higher I:R ratios. In addition this leads to more open structures in order to accommodate the alkali-metal cations. Indeed, the phases discussed here have the highest I:R ratio reported for the relatively electron-poor halide clusters of the rare-earth metals.[18] This seems to be a promising way to novel structures.

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Supporting Information Available: Tables of crystallographic details and anisotropic displacement parameters (2 pages). Ordering information is given on any current masthead page.

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