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Inorganic Chemistry Article

Cation Substitutional Chemistry in the $R_7X_{12}Z$-Type Structure for Four Lanthanum Iodide Examples

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A series of quaternary lanthanide halide cluster compounds $ALa_6I_{12}Z$ with transition metal interstitials (principally Os) and alkali or alkaline-earth metal cations (A = Na, Mg, Ca, Sr) have been synthesized by high temperature solid state techniques. The compounds were structurally characterized by single crystal and powder X-ray diffraction methods. The new compounds are isotypic ($R\bar{3}$, $Z = 3$) with rhombohedral $R_7X_{12}Z$ (R = Sc, Y, La–Lu; X = Cl, Br, I; Z = transition or main group element) and contain nominally octahedral R_6X_{12} units centered by interstitial Z. Here, the cation (A) rather than the seventh R occupies the isolated position between clusters along *c* as A_xR_{1-x} with $0 < x \leq 1$. The balance of the structure remains essentially unchanged. The refined X-ray crystal structures of $NaLa_6I_{12}Os$, $(Ca_{0.906}La_{0.094})La_6I_{12}Os$, $(Ca_{0.621}La_{0.379})La_6I_{12}Os$, $SrLa_6I_{12}Os$, and $(Sr_{0.526}La_{0.474})La_6I_{12}Os$ are reported, along with results of electrical resistivity and magnetic susceptibility measurements on these and some analogous phases. The phases are generally semiconductors, but the complex paramagnetic properties are not those of simple spin-only systems.

Introduction

Reduced lanthanide halides form only three structures that contain isolated $R_6X_{12}(Z)$-type clusters with R = lanthanide; X = Cl, Br, I; Z = transition metal or other interstitial, namely $R_7X_{12}Z$, $R_6X_{10}Z$- and $R_{12}X_{17}Z$-types. Other reduced lanthanide halides contain bioctahedral clusters, oligomers of four condensed octahedra, or infinite chains or layers of condensed octahedra. The variety of bridging halide modes leads to a vast array of compositions and structures.[1−3]

The rhombohedral $R_7X_{12}Z$ structure is the most versatile example, known for R = Sc, Y, and most of La−Lu with X = Cl, Br, or I, although the bromides have been considerably less well studied. These compounds accept a great variety of interstitial elements, including most of the transition metals in groups 7−11 as well as main group elements (B, C, N, Si, etc.). The structure (Figure 1) consists of R_6 trigonal antiprismatic clusters, only slightly distorted from ideal octahedra, with Z bound in the centers. All 12 edges of each are bridged by one of two crystallographically distinct X atoms. Six X1 atoms bridge the R−R edges of the “top” and “bottom”, the basal faces (as X^i). The other six edges about the cluster waist are bridged by X2 that also form exo bonds to metal vertices of adjacent clusters (X^{i-a}). Reciprocally, the vertices of each cluster are terminally bonded to X2 atoms which bridge R−R waist edges of neighboring clusters (X^{a-i}). The seventh R atom (crystallographically R2) is located halfway between R_6Z clusters along *c* and is surrounded trigonal antiprismatically by six X1 atoms (from the clusters above and below). A detailed formulation of $R_7X_{12}Z$ is $R^{+3}[R_6(Z)(X1^i)_6(X2^{i-a})_{6/2}(X2^{a-i})_{6/2}]^{-3}$.[4,5]

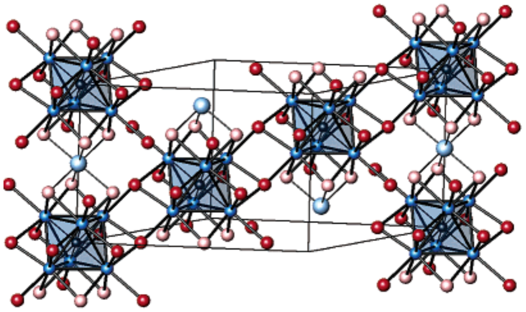

Figure 1. ~[110] section of the rhombohedral unit cell of $NaLa_6I_{12}Os$, showing a portion of the chain of $La_6I_{12}Os$ clusters along *c* (vertical). Black, blue, light blue, pink, and red spheres represent Os, La, Na, I1, and I2, respectively. In the parent compound, $La_7I_{12}Os$, the Na position is occupied by La2.

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Experience with other structures has shown that introduction of alkali or alkaline-earth metal cations and the corresponding electrons or halide anions may produce new compounds with more reduced or more open structural frameworks of the metal−halide clusters. The cations mainly fulfill charge requirements, as in the compounds $AR_6I_{10}Z$ (A = K, Cs; R = La, Pr; Z = Mn, Fe, Os),[6] $Cs_4R_6I_{13}Z$ (R = Ce, Pr; Z = Co, Os),[7] and $Cs_2La_{10}I_{17}Co_2$.[8] Earlier attempts to substitute the R2 position in $R_7X_{12}Z$ structures by Ca resulted in only partial substitution in $(Ca_{0.65}Pr_{0.35})Pr_6I_{12}Co$, $(Ca_{1-y}Gd_y)Gd_6I_{12}Fe$, and $(Ca_{1-z}Gd_z)Gd_6I_{12}Co$.[5] Another investigation yielded $CsEr_6I_{12}C$ with a comparable stoichiometry, but with a different cation position and differently connected clusters.[9] More recently, a complete substitution was discovered in $NaLa_6I_{12}Os$[10] during attempts to synthesize analogues of $K_4La_6I_{14}Os$.[11] The present work greatly expands on the $ALa_6I_{12}Z$ series and includes several single crystal X-ray refinements of the cation occupancy and some electrical and magnetic properties.

Experimental Section

The general techniques, including the use of welded Ta containers and Guinier powder diffraction, have been described before.[10,12] All manipulations were carried out within N_2- or He-filled gloveboxes.

Syntheses. Elemental Na (Fisher, 99.9%), Sr (Alfa Aesar, 99.95%), and Os (Alfa Aesar, 99.95%) were stored in a N_2-filled glovebox and used as received. The binary iodides NaI (Mallinckrodt, 99.9%), CaI_2 (Alfa Aesar, 99.5%), and SrI_2 (Aldrich, 99.99%) were dried and sublimed under dynamic vacuum before storage in a N_2-filled glovebox. The rare-earth metal triiodide LaI_3 was prepared by direct reaction of the elements, purified by vacuum sublimation in contact with only Ta,[13] and stored in tightly capped vials in a N_2-filled glovebox. Lanthanum (≥99.99%) was obtained from the Ames Laboratory. The thin cold-rolled sheets were stored within a N_2-filled glovebox, scraped with a scalpel to remove surface films (oxides or "tarnish"), and cut into small pieces immediately before use. Iodine (Fisher, 99.8%) was used as received. Typically, ∼0.25 g of reactants were loaded into Ta tubes that had previously been cleaned, crimped, and welded on one end. Their open ends were then tightly crimped, arc-welded under Ar, and sealed into well-evacuated and baked fused silica jackets before being heated in a furnace. Reactions were generally allowed to take place around 900 °C for one week, although success with Sr and Na was also achieved 100 and 200 °C lower, respectively.

Phases were identified and yields were estimated by both visual examination of Guinier powder diffraction patterns (Enraf-Nonius FR-552) of the products and comparisons with calculated patterns. Positions of the indexed diffraction lines of known phases and those of standard Si (NIST, SRM-640b) as an internal standard were used in the calculation of lattice parameters and standard deviations via least-squares refinements. Reported parameters came from powder patterns composed of at least 90% of $ALa_6I_{12}Z$-type products (as estimated visually) and with 10−37 indexed diffraction lines that were matched on individual patterns. The average number of indexed lines was 19, and over half of the powder patterns examined fell within the range 19 ± 4 lines. When powder pattern data came from two or more reactions with identical loaded compositions, the refinement with the greatest number of matched lines is reported.

The most common impurity observed was LaOI. This phase appeared in almost every powder pattern, usually in ≤10% yield, and presumably arose from adventitious water in the fused silica, oxygen in the Ta tubing, and so forth. Some niobium tubing was much worse in this respect.

During the initial stages of the investigation, various alkali and alkaline-earth metals (A) were loaded in reaction mixtures with stoichiometry $ALa_6I_{12}Z$ in which Z was Os as well as a number of other transition metals. Compounds with rhombohedral $R_7X_{12}Z$-type structures were found in the products of reactions in which A = Li (to be reported in a separate article), Na, Mg, Ca, and Sr but not for A = K, Rb, Cs, or Ba. These usually produced $La_6I_{10}Z$ compounds plus unreacted AI or AI_2 instead.

For $NaLa_6I_{12}Z$ (Z = Os, Ir, Pt, Ru, Fe, Co, or Ni), $MgLa_6I_{12}Os$, $CaLa_6I_{12}Z$ (Z = Os, Ir, Co or Ni), and $SrLa_6I_{12}Z$ (Z = Fe, Ru or Os), the best yields (∼80%) were obtained from stoichiometric reactions run at 900 °C for one week followed by cooling to room temperature at 10 °C/h. Most reactions produced ≤10% LaOI as well. No $NaLa_6I_{12}Z$ compound was obtained for Z = Re, Au, Pd, Cu, Mn; the products included cubic La_3I_3Z,[14] LaI_3, and/or NaI instead. In successful syntheses of $MgLa_6I_{12}Os$, the lattice constants of selected single crystals corresponded to those for triclinic $La_6I_{10}Os$,[15] but this phase was not observed in the powder patterns. Reactions of $CaLa_6I_{12}Z$ that utilized Z = Re, Pt, or Mn did not produce the target compound and gave large percentages of LaI_3 in the products instead. A number of samples were also loaded for mixed cations on the isolated site, namely $(A_xLa_{1-x})La_6I_{12}Os$. The values obtained for the A contents (see later) may of course be affected by errors in measuring alkali or alkaline-earth metal reactants, evaporative losses during the welding process, and/or stoichiometric deviations caused by formation of LaOI during reaction. (This impurity, though usually <10% of the products, effectively sequesters a portion of the loaded La and I.) Reactions loaded to afford half an equivalent of A per formula unit required only about 14 mg of CaI_2 or 4 mg of Sr.

Crystallography. Irregular black crystals or fragments were mounted in thin-walled glass capillaries with a small amount of degassed Apiezon L grease, and Laue photos were used to determine their suitability. Good crystals were found in the products of reactions with loaded composition $Na_4La_9I_{22}Os_3$, $Ca_2La_9I_{22}Os_3$, $Ca_{0.5}La_{6.5}I_{12}Os$, $Sr_2La_6I_{12}Os$, and $Sr_{0.5}La_{6.5}I_{12}Os$. Diffraction data were collected up to $2\theta = 60°$ at room temperature with the aid of graphite-monochromated Mo Kα radiation and a Rigaku AFC6 diffractometer. In all cases, routine indexing and cell reduction readily gave the R-centered hexagonal unit cell. The reflection data were empirically corrected for absorption with the aid of 10 Ψ-scans. Systematic absences indicated two possible space groups: $R\bar{3}$ (No.148) and $R3$ (No. 146). All of the structures were solved by direct methods[16] and refined in the expected centrosymmetric group $R\bar{3}$.

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Table 1. Refined Unit Cell Dimension (Å, Å^3) Constants for Some Rhombohedral $ALa_6I_{12}Z$ Products[a,b]

loaded composition[c]	no. lines	*a*	*c*	*V*
$La_7I_{12}Os$	33	16.146(2)	10.971(3)	2476.9(9)
$NaLa_6I_{12}Ru$	25	16.188(3)	11.108(4)	2421(1)
$NaLa_6I_{12}Os$	27	16.172(2)	11.134(2)	2521.8(8)
$NaLa_6I_{12}Ir$	19	16.206(4)	11.076(4)	2519(2)
$NaLa_6I_{12}Pt$	17	16.058(4)	11.195(7)	2500(2)
$MgLa_6I_{12}Os$	37	16.148(2)	10.971(2)	2477.5(8)
$CaLa_6I_{12}Co$	11	16.06(2)	11.10(2)	2479(8)
$CaLa_6I_{12}Ni$	23	16.026(1)	11.088(1)	2466.2(4)
$CaLa_6I_{12}Os$	23	16.1089(6)	11.1556(7)	2507.0(2)
$SrLa_6I_{12}Os$	31	16.094(1)	11.345(2)	2544.8(5)

[a] Space group $R\bar{3}$ (No. 148), $Z = 3$. [b] Dimensions from least-squares refinement of Guinier powder diffraction patterns with Si as an internal standard; $\lambda = 1.540598$ Å, 23 °C.

Table 2. Refined Unit Cell Parameters (Å, Å^3) for $Na_xLa_6I_{12}Os$[a,b] Reaction Products

loaded composition	no. lines	*a*	*c*	*V*
$Na_{0.25}La_6I_{12}Os$	19	16.152(4)	10.973(4)	2479(2)
$Na_{0.5}La_6I_{12}Os$	23	16.128(3)	11.108(3)	2502(1)
$Na_{1.0}La_6I_{12}Os$	27	16.172(2)	11.134(2)	2521.8(8)
$Na_{2.0}La_6I_{12}Os$	20	16.165(2)	11.162(3)	2525.9(9)

[a] Space group $R\bar{3}$ (No. 148), $Z = 3$. [b] Dimensions from least-squares refinement of Guinier powder diffraction patterns with Si as an internal standard; $\lambda = 1.540598$ Å, 23 °C.

The crystal structures of the following have also been quantified: $Na_{0.887(3)}Pr_{0.113(3)}Pr_6I_{12}Ir$, $Na_{0.954(2)}La_{0.046(2)}La_6I_{12}Fe$, and $Ca_{0.801(1)}La_{0.199(1)}La_6I_{12}Co$.

Energy-dispersive X-ray spectroscopy (EDS) data obtained with the aid of a JEOL system 840A scanning electron microscope equipped with an IXRF X-ray analyzer system were employed to evaluate the elemental compositions of two $A_{0.5}La_6I_{12}Os$ products. A beam of approximately 20 kV and 0.3 mA gave a count rate of about 2500 s^{-1} for typical data collections. Standards of CaI_2, SrI_2, and LaI_3 were used for calibration. The results gave only semiquantitative confirmation of the X-ray refinement results for the same crystals, with σ values of tenths, one, and one in the respective A, La, and I atom coefficients relative to Os.

Property Measurements. Magnetic susceptibility measurements were performed on a Quantum Design MPMS SQUID magnetometer. Unsieved powdered samples (40−70 mg) were loaded into improved fused silica containers[17] in a He-filled glovebox. Magnetizations of the samples at 2 or 5 K were checked as a function of the applied field (0−6 T) to screen for possible magnetic impurities, but none was observed. Magnetic susceptibilities were measured at 1 or 3 T between 5 and 400 K. The data were corrected for the susceptibility of the container as well as for the standard diamagnetic core values. The susceptibility of each sample was fitted to a generalized Curie−Weiss equation with an additional temperature-independent (van Vleck) term.

Bulk electrical resistivities were measured over the temperature range 100−300 K with a Hewlett-Packard 4342A Q-meter operating at ∼34 MHz. The powdered samples (40−60 mg) were sieved to obtain an average particle diameter of 200 μm, diluted with dry chromatographic Al_2O_3 (total volume ∼1 cm^3) to minimize contact between particles, and sealed within an evacuated Pyrex ampule about 5 cm long. Reproducibility was checked for four different samples, and the average deviation in the room temperature resistivity was 7.3%. This method generally gives values correct within a factor of 2 and good temperature dependencies.[18,19]

Results and Discussion

Lattice Dimensions. Unit cell constants of the target products from various loaded $A_1La_6I_{12}Z$ compositions as refined from Guinier powder patterns are listed in Table 1. The dimensions of the compounds do not change much as Z is varied within a period when A is constant, which agrees with previous studies on other reduced halide cluster compounds.[6,20] Possible variations in the actual content of A in these samples were not considered at this point.

When only the nature of the isolated cation A is altered, the lattice constants *a* decrease in the order Na > Mg > Ca > Sr. Likewise, *c* increases in the order Mg < Na < Ca < Sr. The net effect of this is that the unit cell volume of $ALa_6I_{12}Os$ increases with larger A, with changes to the *c* dimension dominating the overall result. This agrees with data from single crystal X-ray studies among examples of $ALa_6I_{12}Os$, which show that only the A−I1 bond distances change significantly, mainly along the *c* direction, whereas the rather fixed dimensions of the La_6Os cluster and the bridging iodine maintain *a* within a 0.08 Å range. The 0.21 Å increase in *c* as the size of the cation A increases (from 3.21 Å for Na^+ to 3.25 Å for Sr^{2+} [20]) accounts for nearly all of the changes in the unit cell volume. The compound with A = Mg is indistinguishable from unsubstituted $La_7I_{12}Os$ on the basis of unit cell dimensions alone, even though the crystal radius of Mg^{2+} is rather less than that of La^{3+} (0.86 and 1.172 Å, respectively, for six coordination[20]). A greater polarizing power of La^{3+} on the six surrounding iodides may explain why $La_7I_{12}Os$ appears smaller than expected on the basis of standard radii alone. The details of the individual distance changes are not available, however. The uniqueness of $MgLa_6I_{12}Os$ was established with the aid of diffraction intensities (described later).

The lattice dimensions of four $Na_xLa_6I_{12}Os$ samples summarized in Table 2 also increase as more Na(*x*) is loaded. The unit cell volumes increase linearly up to $x \simeq 1$ and then become substantially constant, Figure 3. The dimensions of the product when loaded at $x = 0.25$ are nearly the same as those for $La_7I_{12}Os$. In addition, NaI was observed in Guinier powder patterns of the reaction products for $x > 2$, a delayed indication that the cation site was saturated by Na. The only other phase identified in powder patterns of these samples was LaOI (5−10%). Presumably, La^{3+} occupies all of the R2 sites in the parent structure, and when Na is added to the composition, the Na atoms apparently replace La^{3+} in a random way to produce lattice constants intermediate between those of $LaLa_6I_{12}Os$ and $NaLa_6I_{12}Os$. For $x = 1$, Na^+ replaces nearly all of the La^{3+}, and the excess Na^+ must form the next-most-favorable phase, which appears to be NaI under these conditions. This explanation is also generalized with the analyses of the single crystal X-ray data for A =

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Table 3. Crystallographic Data for Rhombohedral $(A_xLa_{1-x})La_6I_{12}Os$[a]

refined cat. comp	Na_1	$Ca_{0.906(1)}La_{0.094(1)}$	$Ca_{0.621(2)}La_{0.379(2)}$	Sr_1	$Sr_{0.526(2)}La_{0.474(2)}$
loaded comp	$Na_{2.7}La_6I_{14.7}Os_2$	$Ca_{1.3}La_6I_{14.7}Os_2$	$Ca_{0.5}La_{6.5}I_{12}Os$	$Sr_2La_6I_{12}Os$	$Sr_{0.5}La_{6.5}I_{12}Os$
fw	2569.5	2595.8	2624	2634.1	2658.4
a, c,[b] Å	16.165(2), 11.162(3)	16.098(3), 11.157(4)	16.118(2), 11.075(4)	16.083(2), 11.366(3)	16.106(2), 11.145(2)
V, Å^3	2526.9(9)	2504(1)	2491.7(7)	2546.1(9)	2503.7(7)
d_{calcd}, g cm^{-3}	5.061	5.153	5.171	5.174	5.241
μ, cm^{-1}	221.67	225.62	226.41	236.54	239.6
R1, wR2[c]	0.057, 0.144	0.037, 0.066	0.053, 0.085	0.051, 0.084	0.058, 0.118

[a] Space group $R\bar{3}$ (No. 148), $Z = 3$, 23 °C. [b] Lattice constants from refinement of Guinier powder diffraction patterns. [c] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

Table 4. Selected Interatomic Distances for $(A_xLa_{1-x})La_6I_{12}Os$ (Å)

atoms\comp:	$NaLa_6I_{12}Os$	$(Ca_{0.906}La_{0.094})La_6I_{12}Os$	$(Ca_{0.621}La_{0.379})La_6I_{12}Os$	$SrLa_6I_{12}Os$	$(Sr_{0.526}La_{0.474})La_6I_{12}Os$
Os−La1	2.873(1)	2.869(9)	2.867(1)	2.873(1)	2.869(1)
A/La2−I1	3.210(1)	3.1395(9)	3.165(1)	3.2497(9)	3.225(1)
La1−I2[a]	3.253(2)	3.229(1)	3.230(2)	3.229(1)	3.233(2)
La1−I2[a]	3.233(2)	3.234(1)	3.237(2)	3.232(1)	3.235(2)
La1−I2[b]	3.436(2)	3.414(1)	3.417(2)	3.425(1)	3.415(2)
La1−I1	3.224(2)	3.266(1)	3.2746(2)	3.265(1)	3.281(2)
La1−I1	3.232(2)	3.275(1)	3.281(2)	3.277(1)	3.289(2)
La1−La1	4.051(2)	4.049(2)	4.052(2)	4.053(3)	4.053(2)
La1−La1	4.074(2)	4.065(1)	4.057(2)	4.075(2)	4.061(2)
I1−I1[c]	4.427(1)	4.378(1)	4.374(1)	4.360(2)	4.333(2)

[a] Waist bridging iodine. [b] Exo bonding function. [c] Shortest I−I contact.

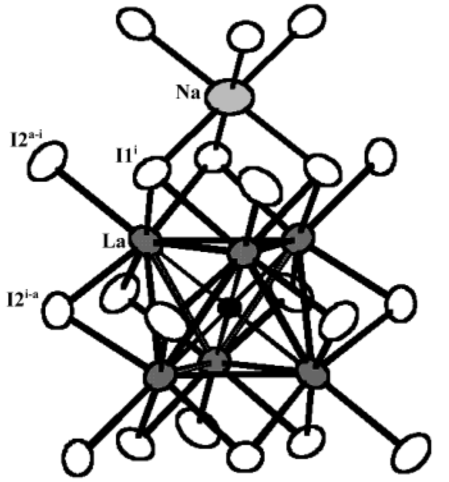

Figure 2. One independent cluster unit in $NaLa_6I_{12}Os$. Black, dark gray, light gray, and white displacement ellipsoids represent Os, La, Na, and I, respectively (90% probability level).

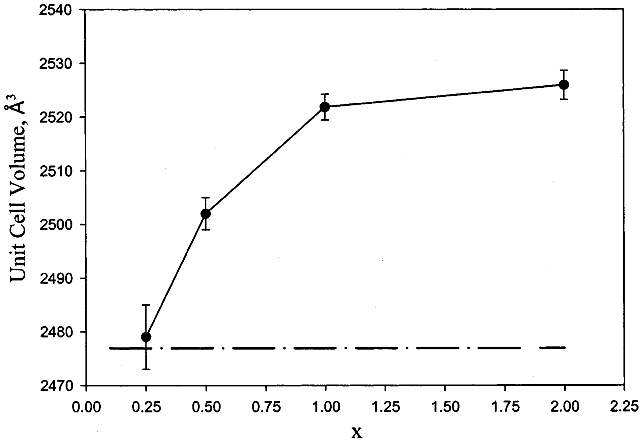

Figure 3. Unit cell volumes as a function of Na content x in a series of reactions loaded as $A_xLa_6I_{12}Os$. Bars mark 3σ error levels.

Ca, Sr (described later), that showed the cation site was occupied by approximately 100% A when loaded at $x \geq 1$, and roughly 50% A and ~50% La when a sample with $x = 0.5$ was loaded. Relative X-ray diffraction intensities support the same general assessment for sodium as well (shown later).

Single Crystal X-ray Diffraction. Figure 2 shows the atom labeling scheme. Some crystallographic parameters and the refined and loaded compositions for the five results reported are given in Table 3, and some important interatomic distances are reported in Table 4. The atom positions, anisotropic displacement and U_{eq} parameters, and interatomic angles are contained in the Supporting Information.

$NaLa_6I_{12}Os$. Isotropic refinement of the isolated position at 0, 0, $^1/_2$ as only La resulted in R1, wR2 values of 11.3, 32.8%. On the other hand, isotropic refinement with 100% Na on the site gave R1, wR2 of 10.2, 29.2% and a reasonable U_{eq}. Refinement of a second La atom assigned to share the position with Na (with U_{eq} for both constrained to the same value) failed to converge; therefore, the site occupancy was reset to 100% Na. The anisotropic refinement resulted in final R1, wR2 values of 5.7, 14.4%.

$(Ca_{0.906}La_{0.094})La_6I_{12}Os$. Isotropic refinement of 100% Ca on the site gave R1, wR2 of 10.2, 30.6%. A second La atom (with the same U_{eq}) was assigned to share the position with Ca, and the occupancies refined to 90.6(1)% Ca, 9.4(1)% La2. The U_{eq} value for Ca/La2 was only slightly larger than the average of the other U_{eq}. The anisotropic refinement resulted in final R1, wR2 of 3.7, 7.8%.

$(Ca_{0.621}La_{0.379})La_6I_{12}Os$. A mixed occupancy refined to give 62.1(2)% Ca, 37.9(2)% La2, with a U_{eq} value that was only slightly larger than the average of the others. The anisotropic refinement resulted in final R1, wR2 values of 5.3, 11.2%.

$SrLa_6I_{12}Os$. Isotropic refinement of 100% Sr on the site gave R1, wR2 of 9.8, 27.8% with U_{eq} similar to those of the other atoms. Refinements of either the Sr occupancy (fixed

U_{eq}) or of a second La atom sharing the position failed to converge, so the position was reset to 100% Sr. The final U_{eq} for Sr was comparable to the other atomic U_{eq}. Anisotropic refinement gave final R1, wR2 values of 5.1, 10.3%.

$(Sr_{0.526}La_{0.474})La_6I_{12}Os$. Isotropic refinements of the product of a mixed Sr/La loading starting with 100% Sr on the site gave unsatisfactory results. On the other hand, isotropic refinement with La assigned to share the position resulted in 52.6(2)% Sr, 47.4(2)% La2, and a final U_{eq} comparable to those of the other values. The anisotropic refinement resulted in final R1, wR2 values of 5.8, 15.0%.

The single crystal X-ray diffraction results show that Na, Ca, or Sr atoms will substitute for the isolated lanthanide atom and form, in the limit, $ALa_6I_{12}Os$ phases without destruction of the $R_7X_{12}Z$ structure. Mixed occupancies were also established for the Ca, Sr members when so loaded. Comparison of the interatomic distances, Table 4, reveals that the A−I1 distances increase slightly for larger A cations (3.210(1) vs 3.250(1) Å for $NaLa_6I_{12}Os$ vs $SrLa_6I_{12}Os$, respectively). Also, the Sr−I1 distance increases by 0.025 Å as the Sr content increases from 53% to 100% because Sr appears to be larger than La replaced, but this is complicated by decreases in the opposing Sr/La−I1 distances of −0.014 Å, presumably because the iodine moves away from the more polarizing La^{3+} as it is replaced by Sr^{2+}. On the other hand, an opposite trend appears for the two Ca structures in which the observed A−I1 distances of 3.165(1) and 3.139(1) Å in $(Ca_{0.621}La_{0.379})La_6I_{12}Os$ and $(Ca_{0.906}La_{0.094})La_6I_{12}Os$, respectively, suggest La is effectively larger than Ca. Except for such puzzling changes around A, the La−La, La−Os, and La−I separations remain almost constant throughout the whole series.

The occupancy refinements suggest that essentially all the loaded A substitutes for La2 in the parent structure, but a small balance of La may remain for reactions loaded A_1-$La_6I_{12}Os$, for example, with calcium. Likewise, crystals from reactions loaded with half an equivalent of A per formula unit resulted in refined occupancies close to 50% A, viz., $(Ca_{0.621}La_{0.379})La_6I_{12}Os$ and $(Sr_{0.526}La_{0.474})La_6I_{12}Os$. On the other hand, reactions loaded with excess Na or Sr could be refined only when the A occupancies were held at 100%, although the result is marginal when a $Ca_{1.3}La_6I_{14.7}Os_2$ reaction refined to $(Ca_{0.906}La_{0.094})La_6I_{12}Os$. Roughly 25% LaI_3 and 10% Os were left over for the Na and Ca examples, which were loaded somewhat rich in A, I, and Os. The displacement parameters for the A cations were often 2−5 times larger than those for the other atoms, but this is not unusual for alkali or alkaline-earth metal cations in voids. The sum of crystal radii for six-coordinate A cations and iodide was always within about 0.1 Å of the observed A−I distances. Although nominally isotypic rhombohedral $Zr_6X_{12}Z$ phases are known without the isolated cation,[2] the cation-free lanthanide analogues have never been prepared, probably because of the low electron counts that would result in the clusters.

It will be recalled that the Guinier lattice constants and unit cell volume results did not allow any distinction to be made between $Mg(La_6I_{12}Os)$ and $La(La_6I_{12}Os)$, and no adequate monocrystal of the former could be found for X-ray diffraction. Therefore, changes expected in relative powder pattern intensities for such a substitution were considered instead. The (101) and (110) reflections are the most responsive stronger lines for this purpose. Table 5 summarizes these data for five systems loaded for full occupancy of the seventh cation site (La, Na, Mg, Ca, Sr), three synthesized with excess A (Na, Ca, Sr), and two with a $A_{0.5}La_6$ stoichiometry (Na, Ca). These data alone are generally consistent and supportive of the syntheses and the refined compositions from several single crystal X-ray studies. Observed intensity ratios for four of the five samples loaded for full occupancy are regularly a little larger than calculated, as might result from some preferred orientation in the powdered samples. Ratios from samples prepared with excess A are slightly (Na) to somewhat (Ca, Sr) higher than for on-stoichiometry results, as if La displacements were not complete for stoichiometric loading for the latter pair. Finally, a fractional loading of only 0.5 A (Na, Ca) gives the reduction of the ratio expected for a greater La content. There is no doubt that the designed $MgLa_6I_{12}Os$ product is distinctive from $La(La_6I_{12}Os)$ by this measure, despite the very similar lattice parameters.

Table 5. Ratio of (101) and (110) Reflection Intensities in Guinier Patterns for Various Loaded Compositions

	$I(101)/I(110)$		
loaded composition	obsd	calcd	(cation)
$La_7I_{12}Os$	0.58	0.36	(La)
$NaLa_6I_{12}Os$	1.46	1.31	(Na)
$Na_2La_6I_{12}Os$	1.48		
$Na_{0.5}La_6I_{12}Os$	0.89		
$MgLa_6I_{12}Os$	1.43	1.22	(Mg)
$CaLa_6I_{12}Os$	1.00	1.02	(Ca)
$Ca_2La_6I_{12}Os$	1.26		
$Ca_{0.5}La_6I_{12}Os$	1.01		
$SrLa_6I_{12}Os$	0.82	0.64	(Sr)
$Sr_2La_6I_{12}Os$	0.94		

Properties. Few properties were measured during much of the early development of the interstitial cluster halide chemistry, in part because the necessary equipment was not available. Instead, electron distributions were usually assumed to be those expected on the basis of electron counts and a simple MO model.[22] Likewise, the isolated characteristics of the cluster units have led to the general assumption of isolated spin systems and probable semiconduction. The latter expectation was challenged with the recent discovery of a metallic cluster halide $K_4R_6I_{14}Os$ (R = La, Pr) even though the clusters are separated by bridging iodides.[11] We have therefore taken the opportunity to examine these two properties of a number of the $ALa_6I_{12}Z$ compounds, especially because iodide might be expected to further anomalous behaviors.

Bulk resistivities of six synthetic products have been measured by the "Q-method", namely, $La_7I_{12}Os$, $NaLa_6I_{12}Os$, $NaLa_6I_{12}Ir$, $Na_2La_6I_{12}Os$, $CaLa_6I_{12}Os$, and $SrLa_6I_{12}Os$. All of the samples showed decreasing resistivity with increasing temperature, indicative of semiconducting behavior, for

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Table 6. Magnetic Data Fitting Parameters and Effective Magnetic Moments for Some (A)$La_6I_{12}Z$ Compounds

loaded composition	field, T	T, K	χ_0, 10^{-4} emu/mol	C emu·K/mol	θ, K	μ_{eff} (μ_B)	χ_{300}, 10^{-4} emu/mol
$NaLa_6I_{12}Os$	3	6−300	11.94(3)	0.0323(3)	−5.2(1)	0.508	13.00(3)
$NaLa_6I_{12}Ir$	3	6−300	6.7(1)	0.039(1)	−7.6(6)	0.556	8.0(1)
$Ca_2La_6I_{12}Os$	1	2−350	9.19(4)	0.0284(3)	−2.86(6)	0.477	10.40(4)
$CaLa_6I_{12}Os$	1	2−350	9.60(9)	0.0218(7)	−2.8(1)	0.504	10.10(9)
$SrLa_6I_{12}Os$	1	2−350	5.8(1)	0.0176(3)	−2.14(9)	0.375	6.7(1)
$SrLa_6I_{12}Os$	1	2−350	6.93(8)	0.026(2)	−1.50(3)	0.455	7.58(8)

example, −0.52(2) $\mu\Omega$·cm K^{-1} for $NaLa_{12}I_{12}Os$ (Supporting Information). The resistivity values of the samples at room temperature fell between 126 and 184 $\mu\Omega$·cm for the Na and La extremes, respectively, and with good reproducibility. Although comparable data for the most noncondensed ternary and quaternary lanthanide halide compounds have not been reported earlier, the few known members have nearly always been insulators or poor semiconductors (e.g., $La_{12}I_{17}Fe_2$[23]). In the anomalous α-$K_4R_6I_{14}Os$ (R = La, Pr),[10] octahedral clusters interconnected by planar bridging I^{i-a} into two-dimensional networks give rise to a Pauli paramagnetic property plus low and substantially temperature-independent resistivities of ~120 and ~240 $\mu\Omega$·cm, in the range of poor metals.[20] In the present cases, the metal clusters are linked to adjacent clusters three-dimensionally by nonplanar iodine bridges, and the metal cations are also isolated from the clusters as well as from each other. Given the contrasting structure of the present compounds, there seems to be little reason to expect other than semiconducting properties.

Magnetic susceptibility data were measured for nine different compositions, and each set was fitted to a modified Curie−Weiss equation to include temperature-independent paramagnetism (van Vleck, χ_0). The parameters and the effective magnetic moments (μ_{eff}) are collected in Table 6. According to the ideal trigonal antiprismatic MO description,[22] all should be 16-electron examples, two short of the closed shell 18 e^-, except that the sodium phase should have 15 e^- (t_{2g}^3 in O_h). Although the results for $NaLa_6I_{12}Os$ appear to be fit fairly well with the modified Curie−Weiss description, most showed significant deviations which appeared in plots of $1/\chi$ versus T as regions of markedly higher or lower slope, especially at higher temperatures (100 K and above). (Examples are shown in Supporting Information.) The results do not depend either on the particular elements or the formal cluster electron count. Because all of the samples were made from reactions with high yields (95−100%), and none showed evidence of ferromagnetic impurities, the possibility of deviations arising from sample contamination seems low. More importantly, none of the effective magnetic moments calculated from the $1/\chi$ versus T data is anywhere near the classical spin-only value; rather, all are in the range 0.38−0.56 $\mu\Omega$, which would correspond in a simple way to about $^1/_5$−$^1/_3$ unpaired electron per cluster. A spin-only description seems inappropriate for these systems.

In the past, a few other compounds with isolated M_6I_{12}-type clusters and supposedly a single unpaired electron have given μ_{eff} values much closer to simple expectations, including $Zr_6I_{12}Mn$[24] (1.84(7) μ_B), $Sc_6I_{11}C_2$[25] (1.8(1) μ_B), $Sc_7I_{12}C$[3] (isostructural with the $ALa_6I_{12}Z$ series, 1.7 μ_B), $CsZr_6I_{14}C$[26] (1.48 μ_B), and $La_{12}I_{17}Fe_2$[27] (1.11(2) μB), but not α-$K_4La_6I_{14}Os$[10] (0.77 μ_B). Likewise, $CsLa_6I_{10}Z$[2] with Z = Fe or Mn should have one or two unpaired electrons, and these both gave reasonable μ_{eff} values of 1.4 and 2.9 μ_B, respectively. None of these had temperature-dependent deviations in the magnetic susceptibility data comparable to those found for the present $ALa_6I_{12}Z$ compounds, except isostructural $Sc_7I_{12}C$ for which a small flattening at ~300 K was attributed to "thermal population of neighboring levels".[4]

Mixing of a Curie−Weiss paramagnetic ground state with one or more excited states under the influence of an external magnetic field could be one explanation for the observed irregularities. It is also possible that the heavy elements in the present compound, notably osmium and lanthanum, could exhibit extensive spin−orbit coupling and contribute to nonideal behavior.[2] Magnetic susceptibility data have not been reported for any other $R_7X_{12}Z$ compounds except $Sc_7I_{12}C$. Measurements on some $ALa_6I_{12}Z$ compounds with lighter transition metal Z for comparison would be useful.

Conclusions

The quaternary lanthanide halide cluster compounds $ALa_6I_{12}Z$ with transition metal interstitials (Z) and alkali or alkaline-earth metal cations (A) have been synthesized by high temperature solid state techniques in the rhombohedral structure type known for numerous $R(R_6X_{12}Z)$ phases. Powder diffraction data and refinement of lattice constants refined therefrom indicate that the compounds with A = Na, Mg, Ca, Sr in the place of the seventh La can be prepared with various Z, whereas a heavier alkali or alkaline-earth metal A does not form analogous compounds. Single crystals of $ALa_6I_{12}Z$, A = Na, Ca, Sr, were structurally characterized to show that A occupies the R2 position halfway between R_6Z clusters along c. The occupancy of that site occurs as A_xLa_{1-x}, $x \leq 1$, according to the amount of A loaded. All of these compounds are semiconductors, judging from bulk electrical resistivity measurements. The magnetic susceptibility data of these compounds are not regular, giving low μ_{eff} values and, often, appreciable deviations therefrom above ~100 K, possibly because of spin−orbit coupling of the heavy transition metals La or Z and/or mixing of the ground magnetic state with one or more excited states.

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Supporting Information Available: Tables of crystal, positional, ellipsoidal, and angle data for five structures; magnetic susceptibility data for six compounds, and illustrations of resistivity and magnetic susceptibility results. This material is available free of charge via the Internet at http://pubs.acs.org.

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