

Derivatization of the Rhombohedral Rare-Earth-Metal (*R*) Cluster Halides $R_7(Z)X_{12}$: The New $\text{NaLa}_6(\text{Os})\text{I}_{12}$

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The many examples of $R_7(Z)X_{12}$ cluster phases for R = rare-earth metal, Z = interstitial element, X = Cl, Br, I, occur in a characteristic rhombohedral structure $R^{3+}[R_6(Z)X_{12}]$ in which the seventh R atom is situated in a trigonal antiprismatic X' site between halide-interbridged clusters in an anionic network that can be described as $[\text{La}_6(\text{Os})]X_6^i X_6^{i-a} X_6^{a-i}$. The first example of a substituted derivative, $\text{NaLa}_6(\text{Os})\text{I}_{12}$, has been achieved via exploratory synthetic reactions in neat systems near 850°C. The structure has been refined in space group $R\bar{3}$ (No. 148), $a = 16.214(4)$ Å, $c = 11.172(4)$ Å, $R/R_w(F) = 3.5/3.9\%$. The cluster is geometrically very close to an ideal octahedron in shape, showing a trigonal elongation of only 0.026(3) Å and La–Os–La angles of $90 \pm 0.37(4)^\circ$. The La–I and Na–I distances are likewise very similar and substantially ideal. This regularity is unexpected in view of both the cluster's apparent 15-cluster-based electron configuration with an expected nominal f_{10}^i HOMO and the behavior of many other cluster structures with incomplete electronic structures. Furthermore, the phase inexplicably exhibits only a TIP term in magnetic susceptibility, $\sim 3.4 \times 10^{-4}$ emu mol⁻¹, for which no explanation is currently available. © 2001 Academic Press

INTRODUCTION

“Simple” rhombohedral cluster dihalides of zirconium chloride, bromide, and iodide were recognized fairly early in studies of reduced halides of zirconium once superior containers of tantalum were utilized (1–3). However, high and reproducible yields of dimensionally well-defined cluster dihalides followed only after it was demonstrated that these all require an interstitial atom (Z) centered in the clusters for stability (4, 5). The early accidental syntheses, usually in correspondingly low yields, probably originated because of H or C impurities, but $\text{Zr}_6X_{12}Z$ phases were later systematically obtained in high yields with encapsulated B, Be, and even Cr, Mn, as well as C or H interstitials (6–8).

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The electron-poorer rare-earth elements (R) instead form a slightly different version of the same rhombohedral structure in which an additional seventh R atom is bound in an antiprismatic halogen environment between clusters, this evidently serving principally as the source of three electrons for further bonding in the cluster, viz., $R^{3+}(R_6(Z)X_{12}^{3-})$ (1, 9–13). Adventitious carbon was again the probable source of the first discoveries. However, Z in these phases has been found to range over a wide variety of other elements, not only B or N but also an unusual number of transition metals Mn–Ni, Ru–Pd, Re–Au, etc. (14) that center each cluster. The last variations allow appreciable ranges for the number of cluster-based-electrons, 15–20. The range of stability generally appears to be governed mainly by the relative stabilities of alternate R_xZ phases.

A few earlier attempts to achieve a heterocation substitution at the seventh RX_6 position and thence to increase the versatility of the structure were only partially successful with Ca. Compositions up to $\text{Ca}_{0.65}\text{Pr}_{0.35}(\text{Pr}_6\text{I}_{12}\text{Co})$, and less for Ca in $\text{Gd}_7\text{I}_{12}Z$, $Z = \text{Fe}, \text{Co}$, were achieved in a brief exploration (13). Recent unrelated investigations intended to expand the variety of the very novel, evidently metallic layered phases with the $\alpha\text{-K}_4\text{La}_6\text{I}_{14}\text{Os}$ structure (15) have now led us to the discovery of the first quaternary derivative of an $R_7X_{12}Z$ phase, the sodium example $\text{NaLa}_6\text{I}_{12}\text{Os}$, which is reported herein.

EXPERIMENTAL SECTION

Syntheses

Reactions were carried out in welded Nb or Ta containers with reactants La, Pr, LaI_3 , PrI_3 , NaI, KI, and Fe, Pt, Os. The metals La and Pr (R) (Ames Laboratory, 99.99%) and the transition metals (Alfa, 99.95%) were used as received. The alkali-metal iodides (Fisher, 99.95%) were dried under dynamic vacuum and then vacuum sublimed. The triiodides were prepared from the elements and vacuum sublimed as before (11–14). Owing to the air and moisture sensitivity of some of the reagents and all of the products, all operations were carried out in N_2 -filled glove boxes.



Compositions such as $\text{Na}_4\text{La}_6\text{I}_{14}\text{Os}$ and $\text{Na}_4\text{Pr}_6\text{I}_{14}\text{Os}$ were first studied primarily in an effort to achieve phases isostructural with $\alpha\text{-K}_4\text{La}_6\text{I}_{14}\text{Os}$ (15,16). The new $\text{NaLa}_6\text{I}_{12}\text{Os}$ was first observed from the corresponding composition that had been heated to 850°C for 650 h and slowly cooled ($5^\circ\text{C}/\text{h}$) to 300°C . Several black crystals were found, and the Guinier powder diffraction pattern showed $> 80\%$ of a powder pattern similar to that of the well-known $\text{La}_7\text{I}_{12}\text{Os}$ type (14,17,18) plus $\sim 10\%$ NaI. The same phase was also found after other reactions, $\text{Na}_4\text{La}_6\text{I}_{14}\text{Os}$ (yield: $\sim 80\%$ $\text{NaLa}_6\text{I}_{12}\text{Os}$, 15% NaI) and $\text{Na}_4\text{La}_7\text{I}_{12}\text{Os}$ (60% $\text{NaLa}_6\text{I}_{12}\text{Os}$, 20% NaI, 20% LaOI), which had been reacted at 870°C for 28 days and at 850°C for 23 days, respectively. A similar reaction loaded as $\text{Na}_4\text{Pr}_6\text{I}_{14}\text{Os}$ resulted in 70% $\text{NaPr}_6\text{I}_{12}\text{Os}$ along with 15% NaI. (A new low angle line was also sometimes seen from some unknown.) Synthesis at the structure-based $\text{NaLa}_6\text{I}_{12}\text{Os}$ composition gave a high yield product ($\sim 90\%$), and the Li–Os and Na–Fe analogues also appear to exist. A target of the potassium salt yielded substantially only $\text{La}_6\text{I}_{10}\text{Os}$ (19) plus KI.

Single-Crystal X-Ray Diffraction

The phase $\text{NaLa}_6\text{I}_{12}\text{Os}$ was initially believed to be the isopointal $\text{La}_7\text{I}_{12}\text{Os}$ because of the close similarity in the powder patterns. However, a structural solution from a small single crystal X-ray data set indicated that the correct constitution was $\sim \text{NaLa}_6\text{I}_{12}\text{Os}$ rather than $\text{La}_7\text{I}_{12}\text{Os}$. Subsequently, a better black plate-like crystal of dimensions $0.08 \times 0.04 \times 0.03$ mm was mounted in a glass capillary, and a total of 2134 reflections was collected on a Rigaku AFC6R diffractometer at room temperature ($2\theta_{\text{max}} = 55^\circ$; $\pm h, k, l$; $\omega - 2\theta$ scans). These gave 1309 unique data of which 782 were observed ($I > 3\sigma_I$) ($R_{\text{INT}}(F^2) = 4.6\%$ for all reflections). The systematic absences for hkl , $-h + k + l = 3n$ for all reflection types, indicated that the correct space group was $R\bar{3}$ (no. 148) or the acentric $R3$ (No. 146), and the former was confirmed by the intensity statistics together with the structural refinement. None of the disorder (10), acentricity (11), or extreme ellipsoids for the seventh metal atom along \bar{c} (9, 10, 12) that have sometimes been encountered earlier with other $R_7X_{12}Z$ samples (20) was found here.

The structure was solved by direct methods (SHELXS (21)). Refinement programs, scattering factors, etc., utilized were those in the TEXSAN (22) package. An empirical absorption correction ($\mu = 219.8 \text{ cm}^{-1}$) was first applied to the full data set with the aid of three scans near $\theta = 90^\circ$ and later, after isotropic refinement, by DIFABS, as recommended (23). The latter step resulted in a reduction of positional and displacement parameter errors by 30 to 50%. Data collection and refinement parameters are given in Table 1.

TABLE 1
Crystallographic Data for $\text{NaLa}_6\text{I}_{12}\text{Os}$

Formula weight	2569.48
Crystal color, habit	Black, plate-like
Crystal dimensions (mm)	$0.08 \times 0.04 \times 0.03$
Space group, Z	$R\bar{3}$ (no. 148), 3
Lattice parameters, ^a Å	$a = 16.214(4)$ $c = 11.172(4)$ $\gamma = 120^\circ$
V (Å ³)	2544 (1)
Density calc. (g/cm ³)	5.032
μ (MoK α , cm ⁻¹)	219.80
Diffractometer	Rigaku AFC6R
Radiation, λ (Å)	MoK α , 0.70958
Scan type	$\omega - 2\theta$
Octants measured, $2\theta_{\text{max}}$	$\pm h, k, l, 55^\circ$
Measured reflections	2134
Independent reflections, R_{INT}	1309, 4.6%
Obs. reflections, $I > 3\sigma_I$	782
Number of variables	32
Goodness of fit	1.79
Absorption corrections	Empirical, 3θ scans, DIFABS
Relative transmission coeff. range	0.776–1.000
Largest residual peak (e/Å ³)	1.55, 0.78 Å from La
R, R_w^b	3.5, 3.9%

^aFrom Guinier powder data with Si as an internal standard, $\lambda = 1.540562$ Å, 23°C .

^b $R = \sum ||F_o| - |F_c|| / \sum |F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w(F_o)^2]^{1/2}$; $w = \sigma_F^{-2}$.

The structure solution indicated locations for Os at $0, 0, \frac{1}{2}$ (on a $\bar{3}$ center) followed by the lanthanum and two iodine atoms. The origin at $(0, 0, 0, \text{at } \bar{3})$ also showed a high electron density in a Fourier map, and another lanthanum was first placed there in accordance with the known $\text{La}_7\text{I}_{12}\text{Os}$ structure. However, successive least squares refinement cycles of the positional parameters of all atoms and then their isotropic displacement parameters resulted in a very large parameter ($\sim 90 \times 10^{-2} \text{ \AA}^2$) for “lanthanum” at the origin. Refining Na there instead seemed to be the logical step as only $\sim 10\%$ of the Na in the reaction mixture was found as NaI in the powder pattern, and this resulted in a very reasonable isotropic U for Na, $\sim 4.4(7) \times 10^{-2} \text{ \AA}^2$ (Table 2). (A difference Fourier map following least-squares refinement cycles without any atom at $0, 0, 0$ also showed the electron density at the origin roughly expected for a Na atom.) It is equally suitable, but not sensible, to place $1/3$ La at the same position, but the latter possibility can be ruled out by the high yield (90%) obtained for a $\text{NaLa}_6\text{I}_{12}\text{Os}$ composition.

The final (anisotropic) refinement of all of the atoms (32 variables, 782 data in $R\bar{3}$) yielded $R(F)/R_w = 0.035/0.039$. The largest residual peak, 1.55 e/\AA^3 , was 0.78 \AA from La. The Guinier powder pattern calculated with the refined structural model agreed well with that observed for the bulk product. The Guinier-based lattice parameters utilizing

TABLE 2
Positional, Isotropic, and Anisotropic Displacement Parameters
for NaLa₆I₁₂Os

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{iso}^a		
Na	0	0	0	4.4(7)		
Os	0	0	0.5	0.81(4)		
La	0.04443(7)	-0.11639(7)	0.3510(1)	1.63(4)		
I1	0.0996(1)	-0.2543(1)	0.1693(1)	2.56(5)		
I2	0.18126(9)	0.0504(1)	0.1662(1)	2.10(4)		
Atom	U_{11}^b	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Na	0.07(1)	0.07	0.02(1)	0.04	0.03	0.03
Os	0.0103(5)	0.0103	0.0101(8)	0.0052	0.0045	0.0045
La	0.0187(5)	0.0201(6)	0.0215(5)	0.0086(5)	-0.0005(5)	0.0044(5)
I1	0.0318(7)	0.0434(8)	0.0354(8)	0.0287(7)	-0.0093(6)	-0.0161(6)
I2	0.0293(7)	0.0265(7)	0.0239(6)	0.0140(6)	0.0102(6)	0.0037(6)

$$^a U_{iso} = (8\pi^2/3) \sum_i \sum_j U_{ij} \bar{a}_i^* \bar{a}_j^* \bar{a}_i \bar{a}_j, \text{ \AA}^2 \times 10^2.$$

$$^b U_{ij} = \exp \{ -2\pi^2 (U_{11} h^2 a^{*2} + \dots + U_{23} k l b^* c^*) \}$$

NIST Si as an internal standard were used for the distance calculations. (These differed from diffractometer data by up to 0.035 Å or 5σ.) The final atomic coordinates, their displacement parameters, and the estimated standard deviations are listed in Table 2.

Magnetic Susceptibilities

Magnetic susceptibilities were measured for a 20-mg sample of ~90% NaLa₆I₁₂Os at 3T on a Quantum Design MPMS machine over the range 6–297 K. The sample was screened for possible ferromagnetic impurities at 50 and 100 K, but none were found (i.e., $M(T) \rightarrow 0$ as $H \rightarrow 0$). The data were corrected for the susceptibility of the container and for the usual diamagnetic core contributions.

Calculations

EHMO calculations were carried out on the isolated cluster La₆(Os)I₁₈⁸⁻ with the observed dimensions and exo-bonded iodines at all metal vertices with the aid of the suite of programs developed by Hoffmann and co-workers (24). The atom parameters were the same as those used for α-K₄La₆I₁₄Os (15).

RESULTS AND DISCUSSION

Synthesis

The introduction of alkali metal cations into the reduced rare-earth metal halide networks has repeatedly shown that it is possible to so alter both the structures and the number of cluster-based electrons. In the K–La–I–Os system, the known phases so far include KLa₆I₁₀Os (isostructural with KPr₆I₁₀Mn (18)), K₂La₆I₁₂Os (25), and two types of

K₄La₆I₁₄Os (15, 16). Experiments carried out in order to synthesize analogous Na₄La₆I₁₄Os from neat La, Os, LaI₃, and NaI near 850°C resulted instead in the new NaLa₆I₁₂Os. Zirconium halides are known to form the same type of rhombohedral network of linked Zr₆(Z)X₁₂ clusters ($X = \text{Cl, Br, I; } Z = \text{H, Be, B, C, or Mn, etc. (7, 8)}$) with the connectivity Zr₆(Z)X₆^{*i*}X_{6/2}^{*i-a*}X_{6/2}^{*a-i*} (*i* = inner edge bridging; *a* = exo-bonded at another cluster vertex) and the evidently essential centered Z. Among the rare-earth metal analogues, the equivalent rhombohedral network of clusters is R₇X₁₂ clusters. The seventh oxidized (R³⁺) metal atom is inserted into the antiprismatic cavity between clusters along the $\bar{3}$ axis, and it so raises the cluster bonding count, for example, from 14 or 15 in the case of R₆(Z)X₁₂, Z = Fe or Co, to 17 or 18. The R₇(Z)X₁₂ phases are known for R = Sc, Y, and several of the lighter lanthanides and with a large range of Z (14). Since attempts to substitute other atom types at that seventh R site have been only partially successful (13), the formation of NaLa₆I₁₂Os is yet another surprise of exploratory solid-state synthesis. The isostructural NaLa₆I₁₂Fe and LiLa₆I₁₂Os have also been identified by powder X-ray diffraction data, whereas other synthetic attempts carried out with K cations or for the purpose of increasing the cluster electron count beyond 15 by substitution of Ni or Pt for Os did not result in isostructural products.

Structure and Properties

The presence of Na as a seventh atom in the R(R₆ZX₁₂) framework, Fig. 1, is rather reasonable according to size alone. The antiprismatic site is known to bind R³⁺ ions in R₇X₁₂Z phases that have crystal radii up to 1.172 Å, and that for Na⁺, 1.13 Å, is quite close (26). The observed Na–I distances, 3.217(2) Å (Table 2), are the same as the sum of crystal radii, 3.22 Å (CN6). The 12 edges of the R₆Os clusters are bridged by two crystallographically distinct iodine atoms. The I2 atoms in each cluster cover the six La–La edges of the basal faces (relative to the $\bar{3}$ axis) as I^{*i*}, whereas the I1 atoms bridge the remaining La–La edges about the waist of the cluster with the functionality I^{*i-a*}, which means all of the latter also form exo bonds (I^{*a-i*}) in a mutually complementary way at vertices in other clusters to interlink the cluster network (Fig. 2). The $\bar{3}$ clusters are thus interlinked by 3-bonded I1 atoms, whereas the edge-bridging I2 atoms are solely neighbors of Na, and the Na and Os atoms lie on inversion centers along the three-fold axis (Fig. 1).

The La₆ cluster is remarkably symmetric; the La–La distances of 4.040(2) Å within the basal faces and 4.066(2) Å between them together with the six equal La–Os distances, 2.866 Å (Table 3), describe a virtually ideal octahedron with La–Os–La angles of 89.63(4)° to 90.37(4)° (although the iodine disposition is of lower $\bar{3}$ symmetry). The interconnection pattern can be described as (La₆Os)I₆^{*i*}I_{6/2}^{*i-a*}I_{6/2}^{*a-i*}. The pairs

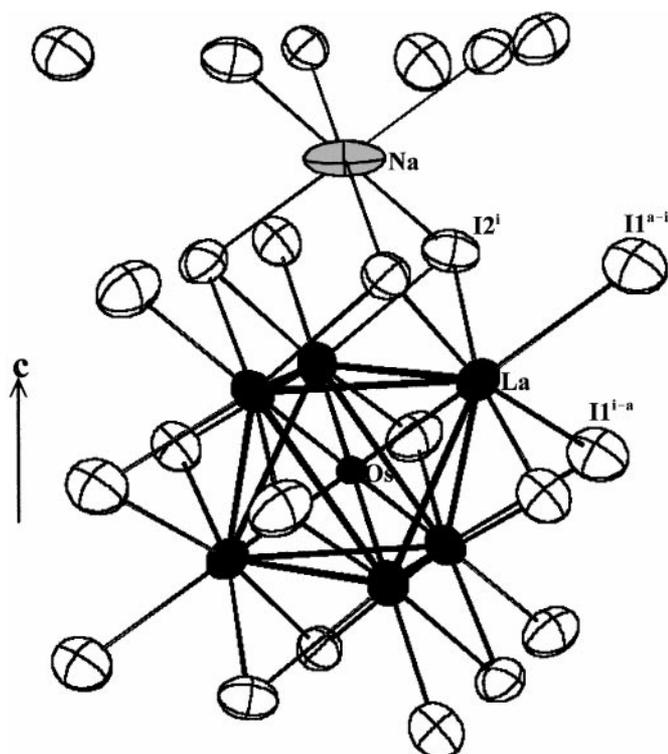


FIG. 1. The local environment about $\text{NaLa}_6(\text{Os})\text{I}_{12}$ with (black) La, Os, (gray) Na, and (open) I as (90%) ellipsoids with the designated functionalities.

of La–I1 and La–I2 distances are highly uniform as well ($3.23\text{--}3.26\text{ \AA}$), whereas the outer La–I1^a bonds are longer (3.45 \AA), as is usual (Table 3). The metal vertices are withdrawn within the square of surrounding Iⁱ, with *trans*-

angles I–La–I of 167.30 and 167.05 (5°), a common matrix effect originating with the large sizes of the anions. The structure is unrelated to two others with similar formulas, $\text{K}_2\text{La}_6(\text{Os})\text{I}_{12}$ (25) with a very different linkage, and $\text{CsEr}_6(\text{C})\text{I}_{12}$ (27), which also occurs in $R\bar{3}$ with similar intercluster bridging and cluster-cation stacking along \bar{c} . However, the two relative lattice dimension lengths are roughly reversed to accommodate the 12-coordinate cesium in a large cavity, which is now well removed from the $\text{Er}(\text{C})\text{I}_{12}$ unit.

This $R_6(\text{Os})\text{I}_{12}$ structural network is a persistent feature in the variety of zirconium halide and the rare-earth metal clusters with a wide range of interstitials (17). The uniqueness of the present structure is the insertion of sodium for the odd rare-earth-metal ion in the antiprismatic site. The high symmetry of the 15-electron lanthanum cluster in $\text{NaLa}_6\text{I}_{12}\text{Os}$, with only a minor trigonal elongation of $0.026(3)\text{ \AA}$, is particularly unusual in comparison with many other clusters that have fewer than the optimal 18 cluster-based electrons. The most noteworthy are the families in which M_6X_{12} -type clusters centered by a transition element have principal four-fold axes, or nearly so, and exhibit sizeable distortions, e.g., the $R_6\text{I}_{10}\text{Z}$ members (14, 19, 28) and $\text{K}_2\text{La}_6\text{I}_{14}\text{Os}$ (25). Among $R_7X_{12}\text{Z}$ examples, the early lanthanide iodides with transition metal interstitials likewise exhibit modest distortions of the antiprisms, $\pm 0.025\text{ \AA}$, whereas only the Sc and Y iodide examples with $3d$ metals for Z distort compressively by as much as 0.08 to 0.10 \AA (19). The older scandium chlorides with second period Z show -0.025 to 0.056 \AA values (9, 11). These metric details appear to depend mainly on relative size effects as both the cluster (Fig. 1) and the lattice (Fig. 2) in effect

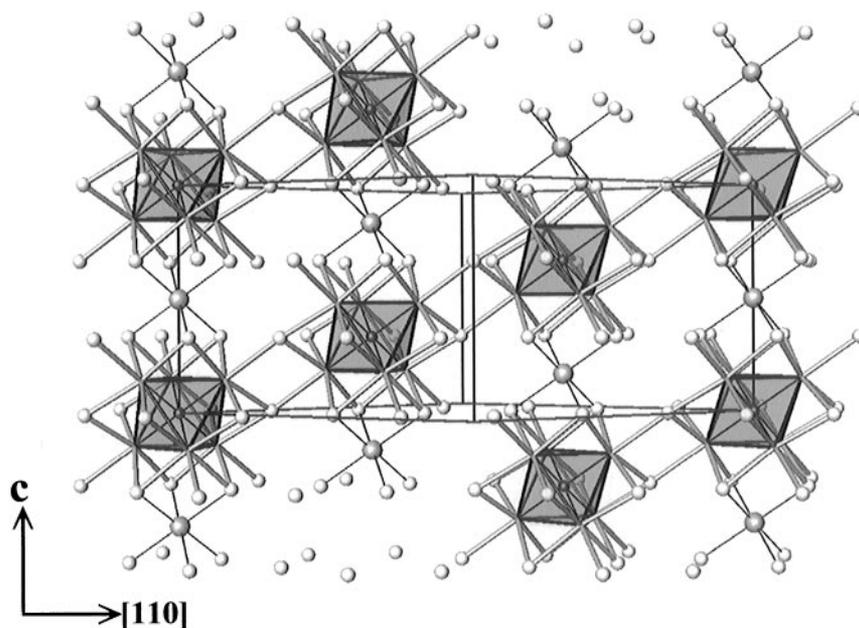


FIG. 2. A $[110]$ section of the structure of $\text{NaLa}_6(\text{Os})\text{I}_{12}$ illustrating the intercluster bridging. Legend of the drawing is as in Fig. 1.

TABLE 3
Important Interatomic Distances (Å) and Angles (deg.)
in NaLa₆I₁₂Os

Os–La	× 6	2.866(1)	La–I2 ⁱ	3.234(2)
La–La	× 2	4.040(2) ^a	La–I2 ⁱ	3.240(2)
La–La	× 2	4.066(2)	Na–I2	× 6 3.217(2)
La–I1 ^{i-a}		3.256(2)	I1–La–I2	167.30(5)
La–I1 ^{i-a}	× 2	3.262(2)	I1–La–I2	167.05(5)
La–I1 ^{a-i}		3.453(2)	La–Os–La	89.63(4)

^aIn basal faces of antiprism.

“breathe” rather than distort for clear reasons of unpaired electrons. In the octahedral description, the 15 bonding electrons in NaLa₆(Os)I₁₂ span the *R*–*Z* bonding MO's *a*_{1g}² and *t*_{2g}⁶, the nominally nonbonding *e*_g⁴ on *Z*, and the *R*–*R* bonding HOMO *t*_{1u}³. However, the splitting of the *t* sets in the present nearby symmetry is very small.

Remarkably, magnetic susceptibility measurements on NaLa₆(Os)I₁₂ reveal basically only a temperature-independent paramagnetism, increasing after core correction from 3.30 to 3.52 (10⁻⁴ emu/mol) over 297 to 100 K and slowly therebeyond (7.8 × 10⁻⁴ at 6 K). Magnetization data secured at 50 and 100 K showed no evidence of ferromagnetic impurities. It does not seem likely that this compound represents another case of a delocalized HOMO in a truly metallic phase, as for K₄La₆(Os)I₁₄ in *D*_{4h} symmetry with its nets of planar I^{i-a} bridges (15). Further investigations will continue on both this strange behavior and other possible rhombohedral AR₆(Z)X₁₂ examples.

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