

KNa₃In₉: A Zintl Network Phase Built of Layered Indium Icosahedra and Zigzag Chains. Synthesis, Structure, Bonding, and Properties

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This phase was discovered following direct fusion of the elements in welded Nb tubes at 550 °C and equilibration at 300 °C for 1 week. Single-crystal X-ray diffraction analysis reveals that KNa₃In₉ crystallizes in an orthorhombic system (*Cmca*, *Z* = 8, *a* = 9.960(1) Å, *b* = 16.564(2) Å, *c* = 17.530(2) Å, 23 °C). The structure contains a three-dimensional indium network built of layers of empty In₁₂ icosahedra that are each 12-bonded and interconnected by 4-bonded indium atoms that also form zigzag chains. All cations bridge between cluster faces or edges, and their mixed sizes appear critical to the stability of this particular structure, which does not occur in either binary system. Both empirical electron counting and EHTB band structure calculations on the macroanion indicate that the bonding in this structure is closed-shell, whereas resistivity and magnetic susceptibility measures show that the compound is a moderately poor metal.

Introduction

Exploratory synthetic efforts within the alkali-metal–triel systems, particularly the Ga, In, and Tl family, have revealed a remarkable richness and variety of clusters and cluster frameworks. These have accordingly boosted interest in understanding problems such as stoichiometry, structure, chemical bonding, resistivity, and magnetic susceptibility of these unusual compounds.^{2,3} Compared with the indium systems, gallium forms many more binary and ternary network compounds built of, particularly, interbridged or fused clusters or cluster fragments,^{4,5} whereas thallium has proved to be extremely rich in phases containing individual thallium cluster anions.^{6–8} Most clusters in the indium and thallium systems can be well understood in terms of classical and modern versions of cluster bonding paradigms,^{2,3} whereas

similar successes with gallium systems have been more limited, in part because of their complexity.^{9–11}

Knowledge of the compositions and structures of even binary alkali-metal-indium phases is limited.^{12,13} Up to now, investigations of the K–Na–In system have revealed the existence of only two ternary phases, the K₃Na₂₆In₄₈ family^{14,15} and K_{21–δ}Na_{2+δ}In₃₉ (*δ* = 2.8).¹⁶ The anion in the former can be described as a covalent 3D framework of In₁₂ icosahedral and hexagonal antiprismatic clusters. The latter phase consists of a network of heavily interbonded In₁₂ and In₁₅ clusters. Here we report a new intermediate compound, KNa₃In₉, which crystallizes with a layered In₁₂ icosahedra network interconnected by zigzag indium chains and isolated indium atoms. Use of different sizes of alkali metals has proven to be very effective in opening routes to clusters not known in the binary systems,³ evidently because cations of different sizes lessen cation packing limitations. A number of novel thallium clusters not present in the binary systems have been successfully isolated by size tuning with mixtures

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- (1) This research was supported by the Office of the Basic Energy Sciences, Materials Sciences Division, U.S. Department of Energy. Ames Laboratory is operated for DOE by Iowa State University under contract No. W-7405-Eng-82.
- (2) Corbett, J. D. In *Chemistry, Structure and Bonding of Zintl Phases and Ions*; Kauzlarich S., Ed.; VCH Publishers: New York, 1996; Chapter 3.
- (3) Corbett, J. D. *Angew. Chem., Int. Ed.* **2000**, *39*, 670.
- (4) Belin, C. H. E.; Tillard-Charbonnel, M. *Prog. Solid State Chem.* **1993**, *22*, 59.
- (5) Tillard-Charbonnel, M.; Manteghetti, A.; Belin, C. H. E. *Inorg. Chem.* **2000**, *39*, 1684.
- (6) Dong, Z.-C.; Corbett, J. D. *J. Am. Chem. Soc.* **1994**, *116*, 3429.
- (7) Dong, Z.-C.; Corbett, J. D. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1006.
- (8) Dong, Z.-C.; Corbett, J. D. *J. Am. Chem. Soc.* **1995**, *117*, 6447.

- (9) Belin, C.; Ling, R. G. *J. Solid State Chem.* **1983**, *48*, 40.
- (10) Schäfer, H. *J. Solid State Chem.* **1985**, *57*, 97.
- (11) Burdett, J.; Canadell E. *J. Am. Chem. Soc.* **1990**, *112*, 7207. Burdett, J.; Canadell, E. *Inorg. Chem.* **1991**, *30*, 1991.
- (12) Sevov, S. C.; Corbett, J. D. *Inorg. Chem.* **1992**, *31*, 1895, and references therein.
- (13) Sevov, S. C.; Corbett, J. D. *Inorg. Chem.* **1993**, *32*, 114.
- (14) Sevov, S. C.; Corbett, J. D. *Inorg. Chem.* **1993**, *32*, 1612.
- (15) Carrillo-Cabrera, W.; Caroca-Canales, N.; Peters, K.; von Schnering, H.-G. *Z. Anorg. Allg. Chem.* **1993**, *619*, 1556.
- (16) Carrillo-Cabrera, W.; Caroca-Canales, N.; von Schnering, H.-G. *Z. Anorg. Allg. Chem.* **1994**, *620*, 247.

Table 1. Some Crystal and Refinement Data for KNa₃In₉

fw	1141.45
system, space group, Z	Orthorhombic, <i>Cmca</i> (No. 64), 8
unit cell dimens ^a (Å, Å ³)	
<i>a</i>	9.960(1)
<i>b</i>	16.564(2)
<i>c</i>	17.530(2)
<i>V</i>	2892.2(6)
<i>d</i> _{calcd} (Mg/m ³)	5.235
μ , cm ⁻¹ (Mo K α)	143.80
R1, wR2 ^b [<i>I</i> > 2 σ (<i>I</i>)]	0.0288, 0.0569

^a Refined from Guinier powder with Si as internal standard, $\lambda = 1.540562$ Å, 23 °C. ^b R1 = $\sum ||F_o| - |F_c|| / \sum |F_o|$; wR2 = $\sum w(|F_o|^2 - |F_c|^2)^2 / \sum w(F_o^2)^{1/2}$.

of alkali metals, such as Na₂K₁₉Tl₂₁,⁶ Na₁₄K₆Tl₁₈Mg,⁷ and Na₄K₆Tl₁₃,⁸ and a remarkable indium network is found in K₂SrIn₇¹⁷ when cation charge is also varied. The title compound nicely illustrates how delicately size factors and electronic requirements can combine to create another unprecedented three-dimensional structure.

Experimental Section

Syntheses. The samples were synthesized from the neat elements (all from Alfa-Aesar) in sealed niobium tubes. The surfaces of the sodium Na chunks (99.9%), indium (99.999%), and potassium (99.95%) were cut clean with a scalpel before use. The general reaction techniques in welded Nb containers sealed within evacuated silica jackets have been described elsewhere.¹⁸ Because both reagents and products are very sensitive to air and moisture, all operations were performed in a N₂- or He-filled glovebox with typical humidity levels less than 0.1 ppm (vol).

No ternary diagrams are available for mixed alkali-metal–indium systems. Following both the binary phase diagrams and experience, reaction mixtures were usually melted at ~550 °C (the highest melting points in the Na–In and K–In systems are about 440 and 478 °C) and annealed at 300 °C. Single crystals were first discovered following reaction of the loaded composition KNa₂In₈ that was first melted at 550 °C, quenched to room temperature, then annealed at 300 °C for 1 week, and finally cooled (3 °C/h) to room temperature. Once the stoichiometry had been established from crystallography, a high-purity ($\geq 95\%$) phase of KNa₃In₉ was obtained (according to a comparison of its Guinier powder pattern and that calculated for the refined structure) from a stoichiometric mixture that was reacted similarly but annealed at 300 °C for 2 weeks. The product from the close-lying composition KNa₄In₉ was only a new unknown phase, whereas a KNa₂In₉ composition gave the present phase with no lattice constant shifts plus some KIn₄. Note that these quantitative synthesis features are powerful evidence for the assigned stoichiometry and against impurity stabilization. The structure is not formed when K is substituted by either Rb or Cs.

X-ray powder patterns for samples mounted between pieces of cellophane were collected with the aid of an Enraf-Nonius Guinier camera, Cu K α radiation ($\lambda = 1.540562$ Å), and NIST silicon as an internal standard. Least-squares refinements of 33 lines indexed on the basis of the refined structural model resulted in the lattice constants given in Table 1. These were also used in the distance calculations.

Structure Determination. A silvery block-shaped crystal of ~0.20 × 0.30 × 0.32 mm was mounted in a glass capillary inside

(17) Chi, L.; Corbett, J. D. *Inorg. Chem.* **2001**, *40*, 3596.

(18) Corbett, J. D. *Inorg. Synth.* **1983**, *22*, 15.

Table 2. Atomic Coordinates ($\times 10^4$) and Isotropic-Equivalent Displacement Parameters ($\text{Å}^2 \times 10^3$) for KNa₃In₉

	multiplicity, symmetry	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} ^a
In1	8 m	0	1037(1)	3616(1)	15(1)
In2	8 m	0	1630(1)	5228(1)	14(1)
In3	16 l	2587(1)	813(1)	4629(1)	15(1)
In4	16 l	8491(1)	9427(1)	3696(1)	14(1)
In5	8 m	0	3262(1)	5854(1)	16(1)
In6	8 2	2500	8380(1)	2500	15(1)
In7	8 m	0	2431(1)	2448(1)	18(1)
K	8 m	0	9661(2)	1585(2)	38(1)
Na1	16 l	6920(3)	7683(2)	4102(2)	28(1)
Na2	8 2	2500	1142(3)	2500	38(1)

^a *U*(eq) is defined as one-third of the trace of the orthogonalized *U*_{ij} tensor.

a glovebox. The crystal was first checked by Laue photography for its singularity and then transferred to a Bruker SMART 1000 CCD-equipped X-ray diffractometer for data collection, which took place at 20 °C with monochromated Mo K α radiation. A total of 1260 frames were collected with an exposure time of 20 s each. The reflection intensities were integrated with the SAINT subprogram in the SMART software package.¹⁹ An orthorhombic unit cell was initially indicated from 200 indexed reflections, and the data collection process yielded a total of 18 030 reflections, out of which 15 430 had intensities greater than 3 σ (*I*) and 1847 were independent. The program SADABS²⁰ was applied for an empirical absorption correction.

The SHELXTL software package²¹ was used for the space group determination, from which systematic absences indicated this structure should be C-centered with a *c* glide around a plane perpendicular to the *b* axis and an *a* or *b* glide perpendicular to the *c* axis. The possible space groups would be *C2cb* (No. 41) or *Cmca* (No. 64). The intensity statistics showed a clear indication of a centrosymmetric space group ($\langle E^2 - 1 \rangle = 0.954$), and the centric space group *Cmca* gave satisfactory refinement results.

The structure was solved by direct methods. Seven apparent heavy atom positions were assigned to In atoms on the basis of both bond distances and peak heights, and subsequent least-squares refinements and difference Fourier syntheses quickly gave positions for all four alkali-metal atoms. Once all atoms were located, their occupancies were allowed to vary successively, but refinements did not lead to any significant change from unity in the occupation factors. Refinement, finally with anisotropic thermal parameters and a secondary extinction correction, converged at R1 = 2.9%. The largest residual peak and hole in the ΔF map were 1.15 and -0.89 e/Å⁻³ at distances of 0.84 and 1.54 Å from In1 and In4, respectively. Some crystallographic and refinement details are listed in Table 1. Table 2 gives the atomic positional and isotropic-equivalent displacement parameters. The only faint indication of any problem might be the slightly larger isotropic parameter of K compared with those for Na. The reported isotropic thermal parameters of K in Na₈K₂₃Cd₁₂In₄₈,²² Na₁₂K₃₈Tl₄₈Au₂,²³ and Na₂₃K₉Tl_{15.3}²⁴ are similarly also larger than those for Na. In the present case, the larger *U*_{iso} parameter of K originates with the elongation within potassium's anisotropic ellipsoids (*U*₁₁:*U*₂₂:*U*₃₃ ≈ 1:2.7:4.4). However, a more

(19) SMART; Bruker AXS, Inc.; Madison, WI, 1996.

(20) Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33.

(21) SHELXTL; Bruker AXS, Inc.; Madison, WI, 1997.

(22) Flot, D. M.; Tillard-Charbonnel, M. M.; Belin, C. H. E. *J. Am. Chem. Soc.* **1996**, *118*, 5229.

(23) Huang, D. P.; Dong, Z.-C.; Corbett, J. D. *Inorg. Chem.* **1998**, *137*, 5881.

(24) Dong, Z.-C.; Corbett, J. D. *Inorg. Chem.* **1996**, *35*, 3107.

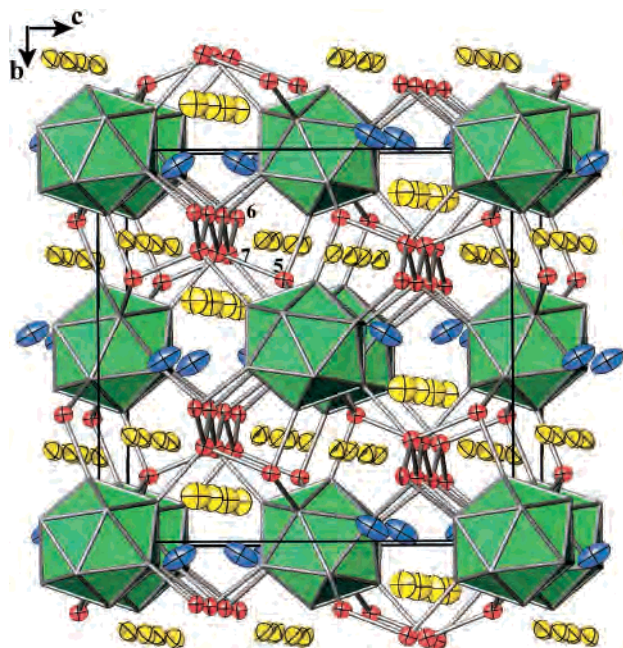


Figure 1. $\sim[100]$ view of the unit cell of orthorhombic KNa_3In_9 . The icosahedral In_{12} units are green, isolated In_5 – In_7 atoms (marked) are red, and the K and Na ellipsoids are blue and yellow, respectively (95% probability).

detailed study of the unusual environment of potassium (below) shows that the large anisotropic displacement of K follows the positions and distances to neighboring atoms. More detailed crystallographic data and the anisotropic displacement parameters are in the Supporting Information. These and the structure factors are also available from J.D.C.

Physical Properties. The resistivity of the phase was examined by the electrodeless “Q” method with the aid of a Hewlett-Packard 4342A Q meter.²⁵ The method is particularly suitable for measurements on highly air-sensitive samples. For this purpose, 82 mg of a powdered sample with grain diameters between 150 and 250 μm was dispersed with chromatographic alumina and sealed under He in a Pyrex tube. Measurement was made at 34 MHz over the range 120–291 K. The results were reproducible with products of other similar reactions. Magnetic susceptibility data were obtained from a 54.1 mg ground sample of the same product sealed under He in the container type described elsewhere.²⁶ The magnetization was measured over the range 6–300 K on a Quantum Design MPMS SQUID magnetometer. M vs H data were checked at 50 and 200 K to show the absence of significant magnetic impurities.

EHTB Calculations. All the calculations were performed with the CAESAR program package developed by Whangbo and co-workers.²⁷ The atomic orbital energies and exponents for indium employed therein are as follows (H_{ii} = orbital energy (ev), ζ = Slater exponent): 5s, -12.6 , 1.903; 5p, -6.19 , 1.677.²⁸ The densities-of-states were calculated at 516 k-points.

Results and Discussion

Structure and Size Effects. The general $\sim[100]$ view of the unit cell in Figure 1 outlines all In–In separations that

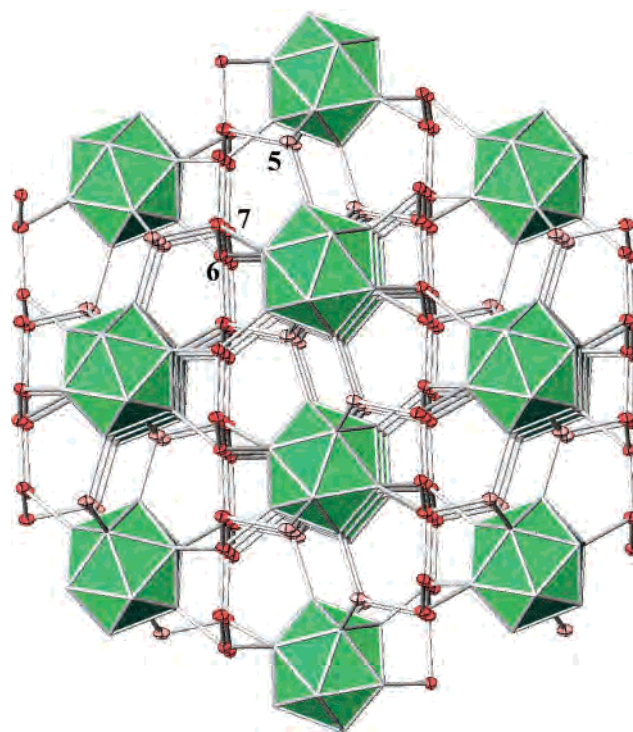


Figure 2. $\sim[110]$ view of the layers of icosahedra connected by the isolated In_5 (orange) and the In_6 and In_7 (red) atoms in zigzag chains (90%).

are less than 3.5 Å, that is, plausible bonds. The structure can be described as a three-dimensional indium network composed of empty, centric 12-bonded icosahedra in an approximate flattened face-centered cube, namely, In_1 – In_4 , which define the cluster, plus more isolated In_5 – In_7 atoms that are 4-bonded to other In. (Further views in the Supporting Information label all atoms.) Within the icosahedra, In–In distances range from 2.9819(7) to 3.1548(6) Å, whereas center-to-vertex distances of 2.72–2.97 Å therein indicate a noticeable distortion from a regular icosahedral geometry, principally a compression along \bar{b} at In_2 . There are no direct bonds between clusters; rather the more isolated indium atoms In_5 , In_6 , and In_7 are bonded to three, two, and one icosahedra, respectively, and at the same time In_6 and In_7 alternate in defining zigzag chains. Distances between the latter atoms are generally shorter (2.897(1)–3.021(1) Å) and typical for single bonds as opposed to the longer ones within electron-deficient clusters with delocalized bonding.^{9–11} This structure also can be viewed along $[110]$, Figure 2, as layers of indium icosahedra that are interconnected by indium zigzag chains along \bar{a} and by separate In_5 atoms more or less along \bar{c} . In fact, a variety of solid-state frameworks have zigzag chains as a structural motif,²⁹ but up to now, none that interconnect icosahedra.

Important distances in KNa_3In_9 are listed in Table 3. The In–In bond lengths as well as the A–In and A–A (A = K, Na) distances are quite similar to those usually found, with the possible exception of the Na_1 – In_6 distance of 3.091(3) Å, which is below a Na–In distance of ~ 3.4 Å generally observed in other intermetallic phases. But this kind of Na–In distance is not unprecedented, as it occurs in several other

(25) Zhao, J. T.; Corbett, J. D. *Inorg. Chem.* **1995**, *34*, 378.

(26) Sevov, S. C.; Corbett, J. D. *Inorg. Chem.* **1991**, *30*, 4875.

(27) Ren, J.; Liang, W.; Whangbo, M.-H. *CAESAR for Windows*; Prime-Color Software, Inc.: North Carolina State University: Raleigh, NC, 1998.

(28) Canadell, E.; Eisenstein, O.; Rubio, J. *Organometallics* **1984**, *3*, 759.

(29) Seo, D.-K.; Corbett, J. D. *J. Am. Chem. Soc.* **2000**, *123*, 4512.

Table 3. Bond Lengths (Å) in KNa₃In₉ (<4.0 Å)

In1–In2		2.9925(9)	In6–In4		2.8953(6)
In1–In4	×2	3.0638(7)	In6–In7	×2	2.9456(5)
In1–In7		3.0863(9)	In6–Na1	×2	3.091(3)
In1–In3	×2	3.1516(6)	In6–K	×2	3.6437(18)
In1–Na2	×2	3.1709(5)	In6–Na2		3.707(5)
In1–Na1	×2	3.437(3)	In7–In6	×2	2.9456(5)
In2–In5		2.9171(9)	In7–In5		3.0211(9)
In2–In4	×2	2.9805(7)	In7–Na2	×2	3.282(3)
In2–In3	×2	3.0942(6)	In7–Na1	×2	3.499(3)
In2–Na1	×2	3.254(3)	K–In4	×2	3.5331(8)
In2–Na1	×2	3.477(3)	K–In6	×2	3.644(2)
In3–In5		2.9731(6)	K–In5		3.672(3)
In3–In3		2.9910(8)	K–In3	×2	3.735(2)
In3–In4		3.0158(6)	K–Na2	×2	3.845(4)
In3–In4		3.1516(6)	K–Na1	×2	3.981(4)
In3–Na1		3.299(3)	Na1–In2		3.254(3)
In3–Na1		3.376(3)	Na1–In3		3.299(3)
In3–K		3.735(2)	Na1–In3		3.376(3)
In3–Na2		3.7726(9)	Na1–Na1		3.407(6)
In4–In6		2.8953(6)	Na1–In1		3.437(3)
In4–In2		2.9805(7)	Na1–In5		3.445(3)
In4–In4		3.0061(9)	Na1–In2		3.477(3)
In4–In3		3.0158(6)	Na1–In7		3.499(3)
In4–In1		3.0638(7)	Na1–In5		3.742(3)
In4–In3		3.1516(6)	Na1–Na1		3.824(7)
In4–Na1		3.363(3)	Na2–In1	×2	3.1709(5)
In4–K		3.5331(8)	Na2–In7	×2	3.282(3)
In4–Na2		3.665(4)	Na2–In4	×2	3.665(4)
In5–In3	×2	2.9731(6)	Na2–In6	×2	3.707(5)
In5–In7		3.0211(9)	Na2–In3	×2	3.7726(9)
In5–Na1	×2	3.445(3)	Na2–Na1	×2	3.839(4)
In5–K		3.672(3)	Na2–K		3.845(4)
In5–Na1	×2	3.742(3)			

compounds: Na₇In_{11.8}¹² with $d(\text{In12–Na1}) = 3.06(1)$ Å and $d(\text{Na10–In10}) = 3.12(1)$ Å, Na₄₉In_{80.9}Sn_{9.1}³⁰ with $d(\text{In10–Na4}) = 3.08(2)$ Å, and Na₁₅In_{27.5}¹³ with $d(\text{Na11–In16}) = 3.12(1)$ Å.

The unique role of the sodium atoms in the formation of this phase needs special attention since the most important factor for phase stability appears to be the relative sizes of the cation cavities. As can be found from Table 3, the mean distances of Na1–In and Na2–In are 3.40 Å (7 neighbors, 3.25–3.50 Å) and 3.37 Å, respectively, typical for that pair. (The second $d(\text{Na2–In})$ actually shows a 4 + 6 distribution of distances over 3.17–3.77 Å, and the average given is for the first six.) In other words, the packing is such that the In neighbors define a suitable hole for Na that is naturally too small for K, Rb, or Cs. For comparison, the shortest K–In distances in the present compound and in K₈In₁₁²⁶ are 3.533(1) and 3.619(3) Å, respectively. On the contrary, the K–In distance in the Na₃K₂₆In₄₈ structure¹⁴ is a larger 3.924(1) Å, which makes it possible to substitute this cation by Rb or Cs to form the corresponding isostructural series of compounds Na₃A₂₆In₄₈, A = K–Cs (and mixtures thereof, presumably). Therefore, the formation of the present novel icosahedral cluster structure appears possible only when both small and large cavities are available that discriminate well between Na and K. (There was no sign of mixed cation site occupancies in the refinements.) In general, alkali-metal cation size selectivity and packing limitations can play crucial roles in modeling a structure in addition to the electronic requirements.

(30) Sevov, S. C., Ph.D Dissertation, Iowa State University, 1993; p 280.

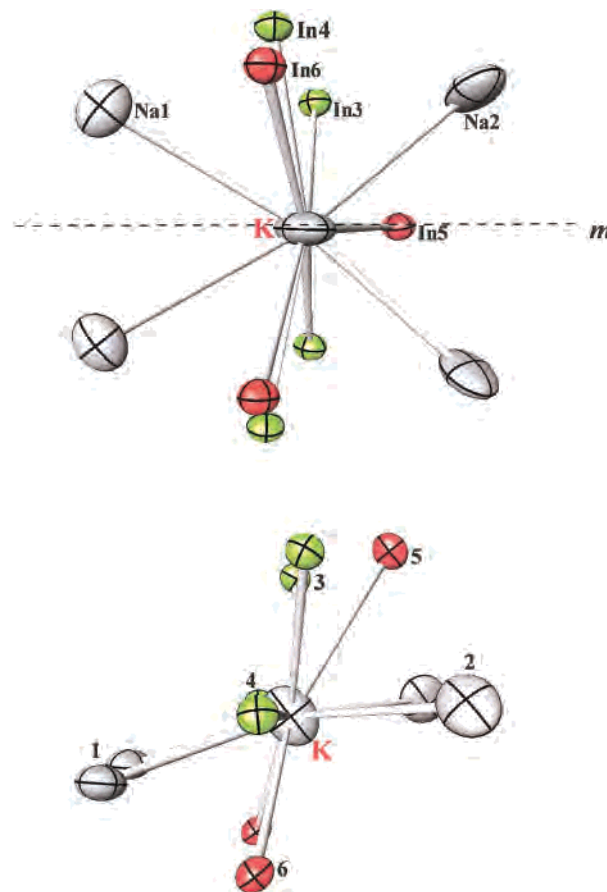


Figure 3. Unusual distribution of nearest neighbors about the central potassium ion (a) with the mirror plane containing K and In5 lying horizontal and normal to the paper and (b) with the mirror plane in the plane of the page. Cations are gray, and the indium are color-coded as in Figure 1 (90%).

The Potassium Cavity. We have observed before that the larger cations in many compounds containing M_6X_{12} -type clusters, either isolated or in networks (M = rare earth metal, Zr, etc.), may be situated in particularly irregular or misshapen cavities.^{31–34} These usually involve Cs^+ or Rb^+ , but the present case shows an extreme example for potassium. Figure 3 shows all neighboring atoms within 4.0 Å of potassium in two views: (a) with the horizontal mirror plane through K normal to the figure and (b) when the same plane lies in the page. Six of the seven In neighbors at 3.533–3.735 Å, all relatively fixed by intercluster bonding, lie in a narrow approximately vertical band, whereas the seventh (In5, m) is off at an angle on one side at 3.672 Å. These interactions are assumed to be principally Coulombic. Surprisingly, the ends of the elongated (90%) displacement polyhedron for potassium are more or less defined by *repulsive* interactions with four sodium neighbors at 3.845–3.981 Å. Thus, the refined ellipsoid for K (which is defined as centric) appears to reflect the shape and distributions in this odd arrangement in some sort of “make-do” response.

(31) Corbett, J. D. In *Modern Perspectives in Inorganic Crystal Chemistry*; Parthé, E., Ed.; (NATO ASI) Kluwer Academic Publishers: Dordrecht, 1992; pp 27–56.

(32) Corbett, J. D. *J. Alloys Comp.* **1995**, 229, 10.

(33) Lulei, M.; Corbett, J. D. *Z. Anorg. Allg. Chem.* **1996**, 622, 1677.

(34) Qi, R.-Y.; Corbett, J. D. *Inorg. Chem.* **1995**, 34, 1646.

Table 4. Electron-Counting Scheme for the Unit Cell of Na_3KIn_9 [$(\text{In}^-)_3\text{In}_6^-$, $Z = 8$]

In_{12} : skeletal electrons ($2n + 2$)	$26 \times 4 =$	104
In_{12} : exo-bonding σ electrons	$12 \times 4 =$	48
electrons for 4-bonded In (σ)	$3 \times 4 \times 8 =$	96
total In bonding electrons per cell		248
total valence electrons available	$8 [3 + 1 + 3(9)] =$	248

This is the first such odd, mixed environment for a cation that we have noted.

Chemical Bonding and Electronic Requirements. Simply counting of electrons in main-group systems in which clusters are the principal building blocks has proven to be a very useful, even elegant, method for rationalizing observed cluster geometries and interpreting the frameworks.^{2,9,10} Overall, the alkali metals occupy structure voids or are encapsulated inside larger clusters in these compounds. According to the Zintl–Klemm concept, it is assumed that the alkali (or other active) metals donate their electrons (and become solvating cations) and provide an essential Coulombic component to the stability of the anionic lattice of the more electronegative elements.^{35,36} Accordingly, it has often become a simple matter either to apply octet rules or, with clusters, to judge their generally well-delineated electron counts according to either empirical “Wade’s rules”³⁷ or routine MO calculations.

In the unit cell of KNa_3In_9 ($Z = 8$), there are four empty 12-bonded icosahedra and 24 isolated (4-bonded) indium atoms, or half an icosahedron per formula unit. According to Wade’s rules, an isolated closo-icosahedron In_{12} requires 26 ($2n + 2$) delocalized skeletal electrons, whereas those bonds to and between the isolated In atoms are all considered to be normal two-electron–two-center types. (The free electron pairs in isolated naked clusters play the same role after oxidation as the exo-bonding electrons.) The resulting electron count within the unit cell of KNa_3In_9 is so summarized in Table 4. The total bonding electron count for the complete bonding of the indium network (248) is seen to be perfectly balanced by the total number of valence electrons for the In, K, and Na atoms in the cell; that is, the bonding appears to be closed-shell structurally.³⁸ Thus, the complex cluster framework can be considered as a three-dimensional macroanion in a Zintl phase. In alternate terms, all vertexes of the icosahedron are involved in exo-bonding, and the skeletal electron count of $2n + 2 = 26 e^-$ for the isolated In_{12}^{14-} unit is reduced to In_{12}^{2-} by a formal one-electron oxidation at each vertex to form an exo bond with another In. In the same manner, each 4-bonded indium atom is assigned a -1 formal charge in order to achieve tetrahedral σ -bonding in the network. The empirical electronic formula is thus described as $[(\text{K}^+)_2(\text{Na}^+)_6(\text{In}_{12}^{2-})(\text{In}^-)_6]$, closed-shell, and ideally a semiconductor.

To have a more detailed understanding of this configuration, we have also performed an extended Hückel band

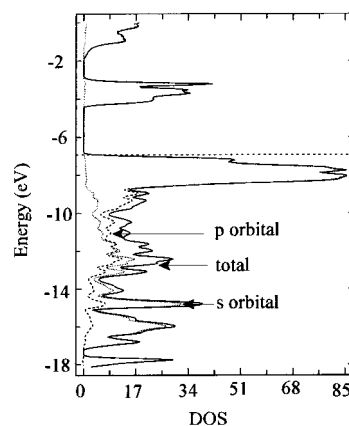


Figure 4. Densities-of-states (DOS) vs energy for the anion network of In_9^{4-} in KNa_3In_9 . The solid, dotted, and dashed lines mark total and In s and 5p projections, respectively. The Fermi level (-6.92 eV) is indicated for 248 electrons per cell ($Z = 8$).

calculation on just the indium framework. Of necessity, sodium and potassium atoms had to be considered only as electron donors and not included in the calculations because workable orbital parameters are not available. The densities-of-states (DOS) result is shown in Figure 4 as both the total (solid line) and the partial projections for In s and In p orbital contributions (dotted and dashed). The latter show that states above ~ 9 eV in the valence band predominantly originate with the In p orbitals. In accord with the above empirical treatment alone, the calculations show that the valence states are completely filled, and the Fermi level occurs at the energy gap. However, this gap is not particularly reliable because the supposed conduction band here is made up of only antibonding In states, and the essential cation components are not included. Moreover, the EHTB method is known to not be very reliable as concerns such excited states.

Properties. “Zintl phase” assignments have commonly been made only on a structural basis,³⁸ as has been done for KNa_3In_9 up to this point. In contrast, over the years additional property measurements (or higher level band calculations) designed to confirm this feature, via properties such as semiconductivity or diamagnetic susceptibility for example, have been pursued much less often, particularly when the main group components come from the tetrel (silicon family) or later groups. In fact, we have found that property investigations among the newer triel examples have frequently shown that structural assessments of many as Zintl (closed-shell) phases are often wrong.^{2,39} (Some recent exceptions to this are $\text{K}_8\text{Tl}_{10}\text{Zn}$,⁴⁰ $\text{Na}_{10}\text{Ga}_{10}\text{Ni}$, and K_2Ga_3 .⁴¹) The same applies to KNa_3In_9 despite the ease with which its precise valence assessment was reached.

Figure 5 (top) shows resistivity data for a single-phase sample of KNa_3In_9 measured by the “Q” method. These are characteristic of a moderately poor metal, with $\rho_{298} \sim 49.4 \mu\Omega\cdot\text{cm}$ and a mean temperature dependence of $0.46\% \text{ K}^{-1}$, the latter being taken as the defining characteristic of a metal.

(35) Klemm, W.; Busmann, E. *Z. Anorg. Allg. Chem.* **1963**, *319*, 297.

(36) Schafer, H.; Eisenmann, B.; Müller, W. *Angew. Chem., Int. Ed. Engl.* **1973**, *121*, 694.

(37) Wade, K. *Inorg. Chem., Radiochem.* **1976**, *18*, 1.

(38) Hughbanks, T. R. In *Inorganometallic Chemistry*; Fehlner, T., Ed.; Plenum Press: New York, 1992; p 291.

(39) Klem, M. T.; Vaughey, J. T.; Harp, J. G.; Corbett, J. D. *Inorg. Chem.* **2001**, *40*, 7020.

(40) Dong, Z.-C.; Henning, R. W.; Corbett, J. D. *Inorg. Chem.* **1997**, *36*, 3559.

(41) Henning, R. W.; Corbett, J. D. *Inorg. Chem.* **1999**, *38*, 3883.

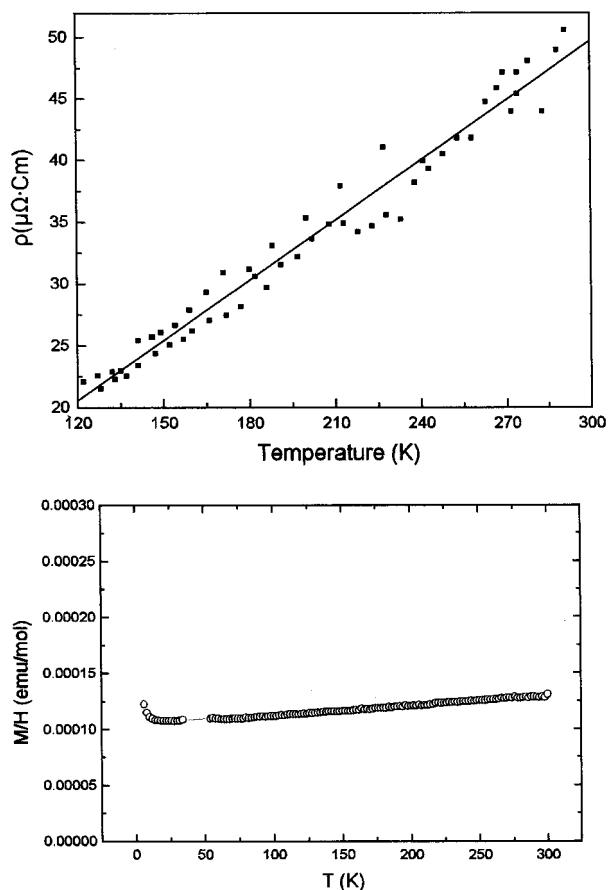


Figure 5. Properties of KNa₃In₉ as a function of temperature (K). Specific resistivities (top) and molar magnetic susceptibilities (bottom).

Likewise, Figure 5 (bottom) shows contradictory magnetic susceptibility results for KNa₃In₉. These are almost temperature-independent, $-(3.66-3.86) \times 10^{-4}$ emu/mol, over 6–300 K after only container correction. Two types of diamagnetic corrections have been subtracted from this number, as before.^{6,12,26} The first, for the ion cores, totals -1.99×10^{-4} emu/mol.⁴² The second is an additional diamagnetic correction χ_L for the Larmor precession of the valence electron pairs in the large orbitals of each cluster.⁴³ We appropriately averaged the distances to the In–In edges

on its surface to gain r_{av} , assuming no significant further delocalization onto the cations, to obtain, $\chi_L = -5.94 \times 10^{-4}$ emu/mol-cluster. Based on the 0.5 proportion of the cluster in the formula unit, the total Larmor correction per mole of KNa₃In₉ becomes -2.97×10^{-4} emu/mol, and the net molar susceptibility is about $(1.1-1.3) \times 10^{-4}$ emu/mol. This is suggestive of a small Pauli paramagnetism. The diamagnetic corrections must be viewed as approximate; valence electrons in bonds between clusters and the isolated indium atoms have not been included and should increase the end result a little.

Reasons for the contradictions between simple valence ideas or band calculations and experimental evidence for a metallic characteristic of triel phases have been detailed before.² These characteristics of course pertain to the least-bound electrons in the compound, whereas the chemically important structure we see is a manifestation of the more tightly held valence electrons. Metallicity of course would arise from the lack of a direct or indirect gap for the early triel elements for which the electron affinities (or $-H_{ii}$ values) are decreasing (or increasing) relative to the later, better behaved tetralide, pnictide, etc., examples of Zintl phases. The magnetic susceptibility characteristics are less definitive because of extra diamagnetic effects for the heavy elements In, Tl, Pb, etc., which in themselves are diamagnetic. A number of related but less extreme triel cluster examples are in fact diamagnetic but metallic.²

The findings of this study further illustrate the remarkable ability of the triel elements to form novel cluster frameworks and to organize these within various structural families, depending on subtle balances between atomic sizes, electron counts, packing contingencies, and valence energy differences.

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Supporting Information Available: Tables of additional crystallographic and refinement parameters, the anisotropic atom displacement parameters, figures of the atom connectivities, and the resistivity and magnetic susceptibility data for KNa₃In₉. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(42) Selwood, P. W. *Magnetochemistry*, 2nd ed.; Interscience Publishers: New York, 1956; p 70.

(43) Ashcroft, N. W.; Mermin, D. N. *Solid State Physics*; Holt, Rinehart and Winston: Philadelphia, PA, 1976; p 649.