Inorg. Chem. **2003**, *42*, 8768–8772

Inorganic Chemistry
Article

Synthesis and Characterization of the New Cluster Phase $K_{39}In_{80}$. Three K–In Compounds with Remarkably Specific and Transferable Cation Dispositions

Bin Li and John D. Corbett*

Ames Laboratory—DOE[1] and Department of Chemistry, Iowa State University, Ames, Iowa 50011

Received June 20, 2003

The titled compound $K_{39}In_{80}$ (Pearson symbol *hP238*) has been synthesized by fusion of the elements in stoichiometric proportions in Nb containers. The trigonal structure was established by single-crystal X-ray means ($P\bar{3}m1$, $Z = 2$, $a = b = 17.211(2)$ Å, $c = 28.888(6)$ Å). The crystal structure can be described as a three-dimensional indium network composed of five kinds of clusters: three types of empty In_{12} icosahedra with different exo-bonding and symmetry, A (12 exo-bonds, $\bar{3}m$), B (12 exo-bonds, m), and C (6 exo-bonds, $\bar{3}m$); an In_{16} icosioctahedron centered by a tetrahedral In atom (D, $3m$); and a rather open In_{15} spacer (E, $3m$). This new intermediate lies between $K_{17}In_{41}$ and $K_{22}In_{39}$. Remarkably specific and transferable potassium dispositions about each cluster anion occur in the title compound as well as in $K_{17}In_{41}$ and $K_{22}In_{39}$. This characteristic makes it easier to understand the structural relationships among these three compounds, which all exhibit a common K_{136} clathrate-II network of alkali metal atoms that are stuffed by cluster anions. The presence of the regular cation positions is probably decisive for the formation of all three structures. The title compound is metallic.

Introduction

The intermetallic chemistry found in compounds between the alkali metals and group 13 (triel) elements (particularly Ga, In and Tl) exhibits a remarkable richness of clusters and cluster frameworks.[2,3] However, the structures among these always appear to show more differences than similarities. Thallium exhibits the greatest variety of isolated cluster anions,[4−7] whereas indium and gallium tend to form more anionic cluster networks. Compared with indium systems, gallium has been reported to form more binary and ternary network compounds built of interbridged or fused clusters or cluster fragments, but almost always with apparent problems of fractional occupancies of some gallium and cation positions as well as disorder.[8−13] For indium, a few isolated and often hypoelectronic clusters are found, such as the "naked" $In_{11}{}^{7-}$ cluster in K_8In_{11} [14,15] and isolated Z-centered In_{10} clusters of lower symmetry in $K_{10}In_{10}Z$ (Z = Ni, Pd, Pt),[16] as well as isolated distorted In_4 tetrahedra in Na_2In.[17] However, other linkages of clusters into networks via simple exo bonds are frequently observed as well. Examples of the latter are Na-centered *closo*-In_{16} clusters and *nido*-In_{11} units in $Na_{15}In_{27.4}$,[17] *closo*-In_{12} and In-centered *closo*-In_{17} clusters in $K_{17}In_{41}$,[18] *closo*- and *arachno*-In_{12} in $A_3Na_{26}In_{48}$ (A = K, Rb, Cs),[19,20] and *closo*-In_{12} plus an In_{15} spacer in both $K_{18.2}Na_{4.8}In_{39}$ (with some cation intermixing)[21]

---

* To whom correspondence should be addressed. E-mail: jdc@ameslab.gov.

(1) This research was supported by the Office of the Basic Energy Sciences, Materials Sciences Division, U.S. Department of Energy (DOE). The Ames Laboratory is operated for DOE by Iowa State University under Contract 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) Dong, Z.-C.; Corbett, J. D. *J. Cluster Sci.* **1995**, *6*, 187.

(5) Cordier, G.; Muller, V. *Z. Kristallogr*. **1992**, *198*, 281.

(6) Dong, Z.-C.; Corbett, J. D. *J. Am. Chem. Soc*. **1993**, *115*, 11299.

(7) Dong, Z.-C.; Corbett, J. D. *J. Am. Chem. Soc*. **1994**, *116*, 3429.

(8) Belin, C. H. E.; Tillard-Charbonnel, M. *Prog. Solid State Chem.* **1993**, *22*, 59.

(9) Tillard-Charbonnel, M.; Manteghetti, A.; Belin, C. H. E. *Inorg. Chem.* **2000**, *39*, 1684.

(10) Belin, C.; Ling, R. G. *J. Solid State Chem.* **1983**, *48*, 40.

(11) Schäfer, H. *J. Solid State Chem.* **1985**, *57*, 97.

(12) Burdett, J.; Canadell, E. *J. Am. Chem. Soc.* **1990**, *112*, 7207.

(13) Burdett, J.; Canadell, E. *Inorg. Chem.* **1991**, *30*, 1991.

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

(15) Blase, W.; Cordier, G.; Somer, M. *Z. Kristallogr.* **1991**, *194*, 150.

(16) Sevov, S. C.; Corbett, J. D. *J. Am. Chem. Soc.* **1993**, *115*, 9089.

(17) Sevov, S. C.; Corbett, J. D. *J. Solid State Chem.* **1993**, *103*, 114.

(18) Cordier, G.; Mueller, V. *Z. Kristallogr.* **1993**, *205*, 353.

(19) Sevov, S. C.; Corbett, J. D. *Inorg. Chem.* **1993**, *32*, 1612.

(20) Carrillo-Cabrera, W.; Caroca-Canales, N.; Peters, K.; von Schnering, H.-G. *Z. Anorg. Allg. Chem.* **1993**, *619*, 1556.

10.1021/ic030201e CCC: $25.00

and $K_{22}In_{39}$.[22,23] Recently, only *closo*-In_{12} clusters plus four-bonded (interconnecting) indium atoms were found in KNa_3In_9.[24]

Perhaps because of the "beauty and brilliance" of these triel clusters, the cation sublattices present in these compounds have with a few exceptions[20,21] been neglected or overlooked. In addition, although mixtures of the different sized or charged cations have been observed to be very effective in opening routes to new cluster species,[2,7,19,25−27] the roles and regular geometries of the cations distributed within the three-dimensional anionic network surrounding the clusters have not been extensively studied. Especially the importance of the alkali metal "solvation" environment about the polyanions has not been well considered in understanding the general chemistry of such intermetallic compounds and their interrelationships, mainly because of incomplete exploration among related compounds. During our explorations for new compounds, the present phase $K_{39}In_{80}$ was discovered. According to the K−In phase diagram,[28] there are, in addition to the recently discovered $K_{22}In_{39}$, K_8In_{11}, and $K_{17}In_{41}$, two structurally unknown phases with compositions of about KIn_2 (or K_5In_9) and K_2In_5 (or K_3In_7), according to just the thermal analysis data. The former one is evidently the compound reported here. Close comparisons of its structure with those of the neighboring $K_{22}In_{39}$ and $K_{17}In_{41}$ reveal remarkably specific and transferable potassium dispositions occuring around each of the three types of clusters.

Experimental Section

Syntheses. All reactions were carried out in welded niobium tubes jacketed in a fused silica container by methods and techniques described previously.[6,7,14,25] All materials were handled in N_2- or He-filled gloveboxes that had moisture levels below 0.1 ppm (volume). A single crystal of the title compound was first obtained in an attempt to prepare a closed shell phase K_2LaIn_7 by substituting La for Sr in the hypoelectronic phase K_2SrIn_7.[27] A mixture of K, La, and In in an atomic ratio of 2:1:7 was heated at 1000 °C for 18 h and quenched to room temperature. The sample was then reheated to 600 °C, held there for 166 h, and finally cooled to room temperature at 2 °C/h. Several single crystals with the same structure were also obtained from reactions of $K_4Sr_2In_{11}$ and $K_4Eu_2In_{11}$ compositions under almost the same conditions. Once the structure of $K_{39}In_{80}$ had been established, a single phase sample was obtained after stoichiometric amounts of potassium (Alfa, 99.9%) and indium (Alfa, 99.9995%) had been heated at 700 °C for 12 h, quenched to room temperature, then reheated at 200 °C for two weeks, and finally cooled to room temperature at 3 °C/h. X-ray powder patterns for samples mounted between pieces of cellophane were collected with the aid of an Enraf-Nonius Guinier camera, Cu Kα1 radiation ($\lambda = 1.540562$ Å), and NIST silicon as an internal standard.

The new $K_{39}In_{80}$ is extremely sensitive to traces of air or moisture. According to Guinier X-ray powder diffraction, the patterns of supposedly pure products always contained minor amounts of the KIn_4 pattern with diffusion lines. Annealing at 150 °C for one month gave the same results. Later, it was found that the proportion of KIn_4 in the product increased with an increase in exposure time for powder diffraction. This indicates that $K_{39}In_{80}$ gives KIn_4 at room temperature from reaction with traces of atmospheric moisture, hence the broad lines.

Structure Determination. Several silvery block-shaped crystal were selected and mounted in glass capillaries inside a glovebox. The crystals were first checked by Laue photography for their singularity. The best one (~$0.22 \times 0.28 \times 0.31$ mm^3) was transferred to a Bruker SMART 1000 CCD-equipped diffractometer for data collection, which took place at 23 °C with monochromated Mo Kα radiation. A total of 1260 frames were collected with an exposure time of 20 s each. A trigonal unit cell was initially indicated from 999 indexed reflections. The reflection intensities were integrated with the SAINT subprogram in the SMART software package.[29] The program SADABS[30] was applied for an empirical absorption correction.

The XPREP subprogram in the SHELXTL 6.1 software package[31] was used for the space group determination. No systematic absences for the apparent trigonal space group could be found, and the intensity statistics clearly indicated a centrosymmetric space group ($\langle E^2 - 1\rangle \geq 0.910$). But no matter which space group was chosen, such as $P\bar{3}$, $P\bar{3}m1$, $P6/mmm$, or even some acentric examples, only ~25% of the In atoms could be found and no structural solution. Finally, the presence of merohedral twinning was tested by XPREP subprogram in SHELXTL 6.1, and the correct Laue group $\bar{3}m1$ and the twin law [−1000−10001] were found. Then the structure was successfully solved by direct methods in space group $P\bar{3}m1$ for a fairly large cell (ca. $17 \times 17 \times 29$ Å^3). Seventeen apparent In positions were assigned on the basis of peak heights, and subsequent least-squares refinements and difference Fourier syntheses quickly located the five other indium atoms and all potassium atoms judging from bond distances and peak heights. Then the occupancies of all atoms were allowed to vary successively, but these test refinements did not lead to any significant change from unity in the occupation factors. Refinements, finally with anisotropic displacement parameters, converged at R1 = 3.1%, GOF = 1.046 for 224 variables, and 6664 independent observed reflections ($I \geq 2\sigma_I$). The largest residual peak and hole in the ΔF map were 1.82 and −2.20 e/Å^{-3} at distances of 0.83 and 1.67 Å from K5 and K9, respectively.

Some crystallographic and refinement details are listed in Table 1. Table 2 gives the atomic positional and isotropic-equivalent displacement parameters. More detailed crystallographic and refinement data and the anisotropic displacement parameters are available in Supporting Information. These and the structure factor data are also available from the corresponding author (J.D.C.).

Properties. Electrical resistivities were measured by the electrodeless "Q" method with the aid of a Hewlett-Packard 4342A Q meter.[32] The method is particularly suitable for measurements on highly air-sensitive samples. For this purpose, 87.5 mg of a

---

(21) Carrillo-Cabrera, W.; Caroca-Canales, N.; von Schnering, H.-G. *Z. Anorg. Allg. Chem.* **1994**, *620*, 247.

(22) Sevov, S. C.; Li, B.; Corbett, J. D. Unpublished research.

(23) The last compound was originally reported as trigonal $K_{21.33}In_{39.67}$ with mixed alkali metal and isolated indium atoms on the same position (Cordier, G.; Müller, V. *Z. Kristallogr.* **1992**, *198*, 302), but our single crystal studies have shown that it is the ordered stoichiometric $K_{22}In_{39}$.[22]

(24) Li, B.; Corbett, J. D. *Inorg. Chem.* **2002**, *41*, 3944.

(25) Dong, Z.-C.; Corbett, J. D. *J. Am. Chem. Soc.* **1995**, *117*, 6447.

(26) Dong, Z.-C.; Corbett, J. D. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1006.

(27) Chi, L.; Corbett, J. D. *Inorg. Chem.* **2001**, *40*, 2705.

(28) Morachevskii, A. G.; Bykova, M. A. *Russ. J. Appl. Chem.* **2001**, *74*, 1793.

(29) *SMART*; Bruker AXS, Inc.: Madison, WI, 1996.

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

(31) *SHELXTL*; Bruker AXS, Inc.: Madison, WI, 2000.

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

Table 1. Selected Data Collection and Refinement Parameters for $K_{39}In_{80}$

space group, Z	$P\bar{3}m1$, 2
fw	10710.50
lattice params (Å)	$a = b = 17.211(2)$ Å, $c = 28.888(6)$ Å
V (Å^3)	7411(2)
ρ_{calcd} (g·cm^{-3})	4.800
μ (Mo Kα, cm^{-1})	132.61
R1, wR2[a]	3.10, 7.76

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = \Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w(F^2_o)]^{1/2}$.

Table 2. Atomic Coordinates ($\times 10^4$) and Isotropic Equivalent Displacement Parameters (Å^2 $\times$ 10^3) for $K_{39}In_{80}$

	x	y	z	U_{eq}[a]
In(1)	1581(1)	4918(1)	2408(1)	14(1)
In(2)	2175(1)	4349(1)	1512(1)	16(1)
In(3)	159(1)	3348(1)	2979(1)	15(1)
In(4)	3333	6667	−591(1)	22(1)
In(5)	2171(1)	4342(1)	3316(1)	14(1)
In(6)	173(1)	3347(1)	1869(1)	16(1)
In(7)	1174(1)	2349(1)	1594(1)	15(1)
In(8)	2717(1)	5435(1)	4210(1)	16(1)
In(9)	−1012(1)	1012(1)	4811(1)	16(1)
In(10)	5718(1)	7859(1)	−361(1)	37(1)
In(11)	1009(1)	2019(1)	−181(1)	18(1)
In(12)	1171(1)	2342(1)	3337(1)	14(1)
In(13)	594(1)	1187(1)	4234(1)	14(1)
In(14)	2737(1)	5474(1)	489(1)	36(1)
In(15)	1253(1)	5626(1)	4682(1)	17(1)
In(16)	−1545(1)	3348(1)	1223(1)	36(1)
In(17)	596(1)	1193(1)	758(1)	16(1)
In(18)	4394(1)	5606(1)	−202(1)	36(1)
In(19)	−1427(1)	3369(1)	3520(1)	19(1)
In(20)	1782(1)	1761(1)	2458(1)	14(1)
In(21)	−708(1)	4646(1)	4365(1)	19(1)
In(22)	−3333	3333	1699(1)	42(1)
K(1)	−3333	3333	2947(2)	24(1)
K(2)	3333	6667	3092(2)	13(1)
K(3)	−778(2)	4611(1)	2341(1)	28(1)
K(4)	0	0	1818(2)	15(1)
K(5)	1318(1)	2637(2)	−1333(1)	22(1)
K(6)	6605(2)	9544(2)	585(1)	33(1)
K(7)	453(2)	7133(2)	4304(1)	26(1)
K(8)	−1283(1)	1283(1)	3587(1)	21(1)
K(9)	3333	6667	1626(2)	22(1)
K(10)	0	0	3151(2)	18(1)
K(11)	867(2)	5434(1)	3501(1)	14(1)
K(12)	−2079(1)	2079(1)	2395(1)	28(1)
K(13)	4609(1)	9218(3)	1191(2)	32(1)
K(14)	3333	6667	5680(4)	61(3)
K(15)	2203(1)	4405(2)	5350(1)	22(1)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

powdered sample with grain diameters between 150 and 250 μm was dispersed with chromatographic alumina and sealed under He in a Pyrex tube. Measurements were made at 34 MHz over the range 120−240 K. The measured resistivities of $K_{39}In_{80}$ increase linearly from about 7 to 11.5 $\mu\Omega$·cm (0.30% K^{-1}) over 120−240 K; this change is taken as the defining characteristic of a metal. The extrapolated ρ_{298} is about 14.6 $\mu\Omega$·cm.

Results and Discussion

Structure Description. The general [100] view of the unit cell in Figure 1 outlines by means of closed polyhedra all In−In separations that are less than 3.5 Å. The overall crystal structure can be described as a three-dimensional indium network composed of three different building blocks: (1) three types of empty In_{12} icosahedra (A, B, and C), (2) In_{17}, an icosioctahedral In_{16} centered by a 4b-In4 atom (D), and (3) a rather open In_{15} spacer (E). The three icosahedra A, B, and C are centered at Wykoff sites 1a, 6i, and 1b in 1:6:1 proportions and with $\bar{3}m$, m, and $\bar{3}m$ symmetries, respectively. (The 12-bonded icosahedron B has the same m symmetry as the 6-bonded icosahedron in $K_{22}In_{39}$, and A and C icosahedra have the same $\bar{3}m$ symmetry as the 12-bonded icosahedra in $K_{22}In_{39}$ and $K_{17}In_{41}$.) Both the icosioctahedron In@In_{16} (D) and the In_{15} spacer (E) are centered on the 3-fold axis in 2d sites with 3m symmetry, the same as In_{17} in $K_{17}In_{41}$ and In_{15} in $K_{22}In_{39}$. The five clusters A, B, C, D, and E are externally 12-, 12-, 6-, 12-, and 15-bonded (<3.60 Å), respectively, to other members via direct intercluster In−In bonds. Thus, only clusters C and D are not bonded to other clusters at all vertices, and there are no isolated indium atoms that interconnect polyhedra. All the inter- and intracluster bond lengths in this structure are comparable to the corresponding bonds in $K_{17}In_{41}$ and $K_{22}In_{39}$. In the present compound, the shortest 2.87 Å bond is In15−In21 in the In_{15} spacer, a little longer than the corresponding 2.81 Å bond in $K_{22}In_{39}$. There are no particularly short bonds. This structure can also be schematically described as an ...abcb... stacking along the c axis (Figure 1) in which the a layer contains icosahedra A plus polyhedra D, b just icosahedra B, and c icosahedra C plus polyhedral spacer E.

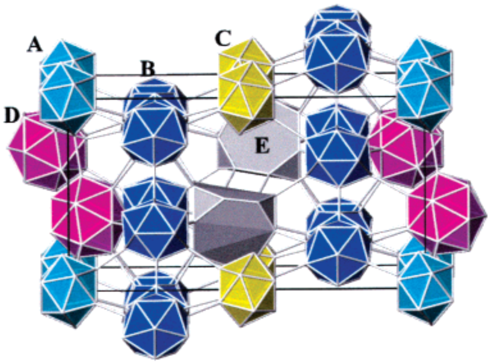

Figure 1. ~(100) overview of the unit cell of $K_{39}In_{80}$ with the indicated different clusters: icosahedra A (turquoise), B (blue), C (yellow); centered icosioctahedron D (red), and In_{15} spacer E (gray). The c-axis is horizontal.

Among 15 types of potassium atoms, all but K1, K14, and K15 cap triangular faces of the polyhedra. These three are all incorporated into the rather open In_{15} spacer; the K14 cation is in the center, and K1 and K15 cap hexagonal and heptagonal faces, respectively. The same type of positions for these alkali metal atoms are found in $(KNa)_{23}In_{39}$ [21] and $K_{22}In_{39}$,[23] and the central atom in the In_{15} spacer, K14 here, always has slight elongation of its displacement ellipsoid. The relationship between the spacer E and the In-centered In_{16} cluster D is shown in Figure 2. The latter (left), broken down as In(In_4In_{12}), can be described as a Friauf 6−3−3 (In_{12}) polyhedron (a truncated tetrahedron) that is centered and In-capped on the four hexagonal faces. As shown, the In_{15} spacer can be derived in a somewhat ad-hoc manner from the In_{17} unit by replacing (a) the three In18 that cap the hexagonal faces in the waist by indium dimers (In15−In21), and (b) the top capping atom (In22), three indium

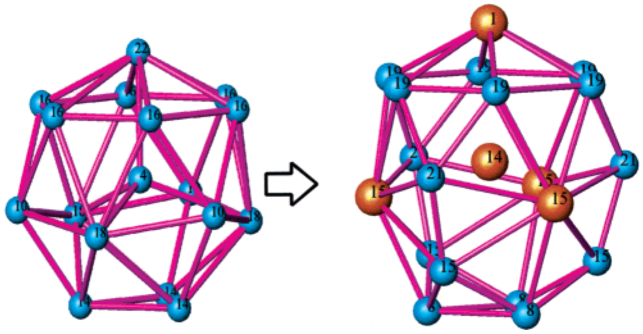

Figure 2. The relationship of In_{17} polyhedron (left) and In_{15} spacer (right) in $K_{39}In_{80}$. The In and K atoms are turquoise and orange, respectively.

atoms (In10) that cap the pentagonal faces, and the centering In4 all by K, giving $K[K_4In_9(In_2)_3]$. Actually, there is a similarity in the genesis of the In_{15} spacer and the In_{17} icosioctahedron as well. The former can be viewed as a tetracapped truncated trigonal prism while the In_{17} icosioctahedron is a tetracapped and centered truncated tetrahedron.

In this structure, two kinds of Samson polyhedra can be found: an icosahedron-centered 104-atom and a icosioctahedron-centered 145-atom polyhedra. Starting from the origin of the cell, the first is constructed of (a) 12 indium atoms in icosahedron A, (b) the 20 potassium atoms that are positioned radially above its triangular faces and form the dual pentagonal dodecahedron, and (c) 12 indium atoms beyond the centers of these pentagonal faces that are exo to the central icosahedron and also cap the 12 inside pentagonal faces of (d) the resulting fullerene-like In_{60} truncated icosahedron. According to the endohedral formalism, this 104-atom polyhedron can also be described in terms of successive onionlike layers as $In_{12}@K_{20}@In_{12}@In_{60}$. Starting from the In4 position, the center of the In_{16} icosioctahedron, there is a 145-atom polyhedron which can be formulated as $In@In_{16}@K_{28}@In_{15}K@In_{84}$. Here one K15 atom and 15 indium atoms form the third sphere as a part of the Samson polyhedra. A similar behavior occurs in the fullerane-like $Na_{96}In_{97}Z_2$ (Z = Ni, Pd, or Pt);[33] here one crystallographic sodium atom Na7 completes a sphere to generate an M_{60}-type fullerene of 48 indium and 12 sodium atoms. The foregoing 104-atom and at 145-atom polyhedra interpenetrate to form the layers (Figure 1) and are connected to the next layers through the 6-bonded icosahedra and the In_{15} spacer. Even when such different ways are used to look at the structure of $K_{39}In_{80}$, the relationship of this kind of complex structure to those of other related compounds, such as $K_{17}In_{41}$ and $K_{22}In_{39}$, is not clear.

Some consideration was given to the possibility that the application of Wade's rules and VEC considerations could allow some conclusions about the electronic requirements of the clusters, the compound, and the observed metallic character. The problem focuses when we consider the appropriate count for the In_{17} cluster for which there are four exo "bonds" at 3.80 Å, beyond a perhaps reasonable cutoff of 3.6 Å. But, EHTB calculations done for the anionic network at only 6k-points gave an overlap populations of 0.144 for the four 3.80 Å separations but −0.052 for the six 3.50 Å "bonds", quite contrary to the usual assumptions for VEC counting. The procedure was not pursued further because of large computing requirements, but the structure suggests heavily delocalized bonding.

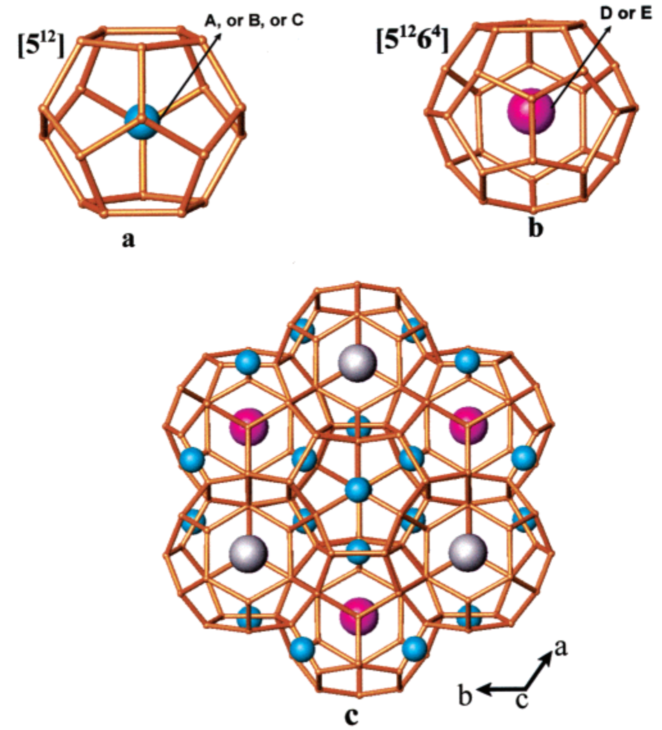

Figure 3. Building units of the $K_{39}In_{88}$ structure: (a) the 20-atom pentagonal dodecahedron $[5^{12}]$ about icosahedra A, B, C (turquoise); (b) the 28-atom hexakaidecahedra $[5^{12}6^4]$ about clusters C and D (red or gray, respectively); (c) the K_{136} clathrate-II network in $K_{39}In_{80}$. The connections among clusters are not shown.

Specific and Transferable Cation Dispositions. It is significant that the title compound $K_{39}In_{80}$ is compositionally precisely intermediate between two neighbors, $K_{17}In_{41}$ [18] and $K_{22}In_{39}$.[22] Even though the three occur in different space groups, cubic $Fd\bar{3}m$, trigonal $P\bar{3}m1$, and rhombohedral $R\bar{3}m$, respectively, they also contain the same or progressively related cluster building blocks. All three contain empty *closo*-In_{12} icosahedra, but different larger indium clusters: *closo*-In_{17} polyhedra in $K_{17}In_{41}$, both *closo*-In_{17} and an In_{15} spacer in the present $K_{39}In_{80}$, and only In_{15} spacers in $K_{22}In_{39}$. But no other deep relationships have been noted among these structures from the usual perspective of just the indium clusters. Perhaps their elegance has overshadowed what are also present, in all three intermetallic phases: a consistent cation substructure. All three can be characterized in terms of an overarching K_{136} clathrate-II type network of alkali metal atoms, a character that has been noted before only in the orthorhombic $Na_{4.8}K_{18.2}In_{39}$.[21] This feature gives a much more complete understanding of these compounds and structures. The K_{136} clathrate-II network is constructed of two polyhedra of different sizes and proportions: a dual 20-atom one that cages the smaller In_{12} icosahedral polyhedron, and a larger 28-atom member that cages the larger In_{17} icosioctahedron, or an In_{15} spacer, or both. Figure 3 shows the clathrate structure of $K_{39}In_{80}$ symbolically with

---

(33) Sevov, S. C.; Corbett, J. D. *Science* **1993**, *262*, 880.

spheres of different colors representing different clusters. According to the formula of a representative clathrate-II structure, $(H_2S)_{16}(CCl_4)_8(H_2O)_{136}$,[34] multiples of these three indium compositions may be reexpressed as the following: $8K_{17}In_{41}$, $[In_{12}]_{16}[In(In_4In_{12})]_8K_{136}$; $4K_{39}In_{80}$, $[In_{12}]_{16}[K(K_4In_{15})]_4[In(In_4In_{12})]_4K_{136}$; $8K_{22}In_{39}$, $[In_{12}]_{16}[K(K_4In_{15})]_8K_{136}$.

All three structures have the same K_{136}-network and empty icosahedra inside the 20-atom cages. The main differences among them are the clusters within the 28-atom cages. The larger cluster $[In(In_4In_{12})]$ inside the 28-atom cage in $K_{17}In_{41}$ is either half or totally substituted by $[K(K_4In_{15})]$ (In_{15} spacer) with decreasing In content from $K_{17}In_{41}$ (70.7 at. %) to $K_{39}In_{80}$ (67.2%) to $K_{22}In_{39}$ (63.9%). To this is added the already noted similarity in the genesis of the In_{17} centered icosioctahedron and the In_{15} spacer. According to the above regularities in cation positions, a larger even more open cluster might be possible inside the 28-atom cage in a K-richer compound. We have already observed an unknown compound (loaded as KIn) with the same potassium “solvation” environment, but a different polyhedron inside the 28-atom cation cage. But the last gives some refinement troubles, perhaps because this cluster may have become too dismantled with increasing K content to be well ordered.

The hierarchical structural relationships of these compounds to the clathrate and other families is a very useful organizing feature in many solid state systems, there obviously being certain preferred ways in which solids organize, whether these involve molecules, ions, or charged and even interconnected clusters. The term was evidently first generalized in the discussion of the orthorhombic (*Pnma*) $Na_{4.8}K_{18.2}In_{39}$ structure[21] which contains two kinds of interconnected In_{12} clusters each surrounded by a dual dodecahedral A_{28} (K + Na) cation polyhedron plus a rather dismantled In_{15} spacer within $K(Na_{4.8}K_{0.2}In_{15})$ units. The result is most similar to the constitution of $K_{22}In_{39}$ except that one K in the present $K(K_4In_{15})$ units has been replaced by a pair of Na, and all other sites have mixed Na−K occupancies. We have also found other versions of the spacer and cage that occur in $Na_{4.8}K_{18.2}In_{39}$, namely in $Na_{12}K_{10}In_{39}$ and $KNa_{20}In_{39}$.[35] Approximate relationships to a number of other structures, often with gallium, have also been noted.[21] A similar hierachical relationship between the clathrate-I structure type and that of K_3Na_{26} In_{48} has also been described.[20]

Hierarchial relationships have been applied probably more often to just the replacement of atoms in a particular structure type by clusters, viz., the foregoing cluster arrangements are those of the atoms in the Laves phase $MgCu_2$, that in $A_3Na_{26}In_{28}$ (A = K, Rb, Cs) parallels that of the A15 (Cr_3Si) structure,[19] and the clusters in $Na_{12}Ge_{17}$ mirror the $MgZn_2$ Laves phase.[36]

Conclusion

The numerous intermetallic compounds between the alkali metals and group 13 elements Tr (particularly Ga, In, and Tl) and their attractive structural relationships continue to please and amaze us with their details. Although cluster anions define the structure building blocks, their significant polarizabilities appear to give rise to further specific interactions of these with the cations, which usually bridge between two or more clusters. Thus it should be remembered that Madelung energies between the cations and the anionic clusters as well as some parallel covalency must also be significant components of the overall phase stability.[3] The discovery of the new intermediate compound $K_{39}In_{80}$ clearly shows how remarkably specific and transferable these cation dispositions are relative to the neighboring $K_{17}In_{41}$ and $K_{22}In_{39}$, a helpful aid to further understanding and organization. According to this ideal, more members of the related compounds must exist. The cation(s) in these kinds of regular dispositions may also be sodium, as in $Na_{22}Ga_{39}$ [37] and $Na_{35}Cd_{24}Ga_{56}$,[38] or an often specific mixture of sodium and potassium (or other) as found in $K_{18.2}Na_{4.8}In_{39}$ [21] and $Na_{12}K_{18}In_{53}Tl_7$.[39] The presence of regular cation positions is probably decisive for the formation of a given structure because these not only fill space more efficiently but also keep the clusters apart. Presumably, direct interactions between polyanions lead first to interbridging or then condensation where they come in contact. The persistence of specific cation interactions with polyatomic anions and the related advantages of the use of mixed cations in exploratory synthesis have also been noted for other systems.[3]

Supporting Information Available: Tables of additional crystallographic and refinement parameters, anisotropic displacement parameters, a list of distances, and electrical resistivity data for $K_{39}In_{80}$. This material is available free of charge via the Internet at http://pubs.acs.org.

IC030201E

---

(34) Claussen, W. F. *J. Chem. Phys.* **1951**, *19*, 1425.
(35) Li, B.; Corbett, J. D. Unpublished research.
(36) Carrillo-Cabrera, W.; Gil, R.; Cardoso, R. C.; Somer, M.; Persil, O.; von Schnering, H.-G. *Z. Anorg. Allg. Chem.* **2003**, *629*, 601.
(37) Ling, R. G.; Belin, C. *Acta Crystallogr*. **1982**, *B38*, 1101.
(38) Tillard-Charbonnel, M.; Berlin, C. *Mater. Res. Bull.* **1992**, *27*, 1277
(39) Flot, D.; Tillard-Charbonnel, M.; Berlin, C. *New J. Chem.* **1998**, *22*, 591.