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Synthesis and Characterization of Transition-Metal Zintl Phases: $Cs_{24}Nb_2In_{12}As_{18}$ and $Cs_{13}Nb_2In_6As_{10}$ with Isolated Complex Anions

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The title compounds were prepared by direct reaction of the corresponding elements at high temperature. Their structures were determined by single-crystal X-ray diffraction ($Cs_{24}Nb_2In_{12}As_{18}$, triclinic, $P\bar{1}$, $Z = 1$, $a = 9.519(4)$, $b = 9.540(5)$, and $c = 25.16(1)$ Å, $\alpha = 86.87(4)$, $\beta = 87.20(4)$, and $\gamma = 63.81(4)°$; $Cs_{13}Nb_2In_6As_{10}$, triclinic, $P\bar{1}$, $Z = 1$, $a = 9.5564(5)$, $b = 9.6288(5)$, and $c = 13.9071(7)$ Å, $\alpha = 83.7911(8)$, $\beta = 80.2973(8)$, and $\gamma = 64.9796(8)°$). $Cs_{24}Nb_2In_{12}As_{18}$ and $Cs_{13}Nb_2In_6As_{10}$ contain isolated anions of $[Nb_2In_{12}As_{18}]^{24-}$ and $[Nb_2In_6As_{10}]^{13-}$, respectively. Each anion includes two cubane-like units made of one niobium, three indium, and four arsenic corners where a fifth arsenic atom completes the tetrahedral coordination at niobium, $[(NbAs)In_3As_4]$. In $Cs_{13}Nb_2In_6As_{10}$ these two units are connected via a direct In–In bond between two indium vertexes of the cubanes. In $Cs_{24}Nb_2In_{12}As_{18}$, on the other hand, the same two units are linked by a dimer made of semicubanes of $[In_3As_4]$, i.e., a cubane with one missing vertex. Magnetic measurements show that $Cs_{24}Nb_2In_{12}As_{18}$ is diamagnetic, i.e., a d^0 transition-metal Zintl phase, while $Cs_{13}Nb_2In_6As_{10}$ exhibits a Curie–Weiss behavior that corresponds to one unpaired electron.

Introduction

A number of novel compounds with diverse structures and interesting structural features have been recently found in the system alkali metal−niobium−arsenic.[1−5] This indicates further potential for rich structural chemistry in this system, most likely associated with tetrahedrally coordinated niobium $[NbAs_4]$. This unit is found in all the compounds and seems to be quite common. It exists as isolated species with a charge of 7−, $[NbAs_4]^{7-}$, in A_7NbAs_4 and $A_5(AE)NbAs_4$, where A = Na, K, Rb, and Cs and AE = Sr and Ba.[5,6] In $K_{38}Nb_7As_{24}$ and $K_{24}Nb_5As_{16}$ the same unit coexist with dimers of itself, i.e., Nb_2As_6 made of two edge-sharing tetrahedra.[2,7] Dimers alone are found in $K_9Nb_2As_6$ and $Cs_9Nb_2As_6$ that represent the first mixed-valence transition metal Zintl phases.[2,4] The tetrahedral unit can serve also as a basic building block around which more complex anions are built. Thus, when an edge of the unit is bridged by various atoms or groups of atoms, the anions that have been obtained include $[NbAs_4(As)]^{6-}$, $[NbAs_4(Tl)]^{6-}$, $[NbAs_4(TtAs)]^{8-}$, and $[NbAs_4(InAs_2)]^{10-}$ with bridging As, Tl, TtAs (Tt = Ge, Sn, Pb), and $InAs_2$, respectively.[1,4,8] The isolated cubane-like anion $[NbIn_3As_5]^{7-}$ found in $Cs_7NbIn_3As_5$ can be considered as made of the same tetrahedral unit $[NbAs_4]$ where three neighboring edges are bridged by indium atoms that are in turn connected to a supplementary arsenic atom.[3] Another way to view this anion is to consider it as made of a semicubane fragment $[In_3As_4]$, i.e., a cubane with one missing vertex, that acts as a tridentate ligand to a niobium center. The tetrahedral coordination of the latter is completed with

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[1] Gascoin, F.; Sevov, S. C. *Inorg. Chem.* **2002**, *41*, 2820.

[2] Gascoin, F.; Sevov S. C. *Inorg. Chem.* **2002**, *41*, 5920.

[3] Gascoin, F.; Sevov, S. C. *Angew. Chem., Int. Ed.* **2002**, *41*, 1232.

[4] Gascoin, F.; Sevov, S. C. *Inorg. Chem.* **2003**, *42*, 904.

[5] Nuss, J.; Cardoso Gill, R. H.; Hönle, W.; Peters, K.; von Schnering, H. G. *Z. Anorg. Allg. Chem.* **1996**, *622*, 1854.

[6] (a) $Na_5SrNbAs_4$ and $K_5BaNbAs_4$: Vidyasagar, K.; Hönle, W.; von Schnering, H. G. *J. Alloys Compd.* **1996**, *136*, 38. (b) Gascoin, F.; Sevov, S. C. Unpublished results: $Na_3Cs_4NbAs_4$, monoclinic, $C2/c$, $a = 17.702(2)$, $b = 6.991(1)$, and $c = 13.831(2)$ Å, $\beta = 112.539(8)°$; Cs_7NbAs_4, orthorhombic, $Aba2$, $a = 9.936(2)$, $b = 12.983(2)$, and $c = 14.796(2)$ Å; $Cs_5SrNbAs_4$, orthorhombic, $Pca2_1$, $a = 19.479(2)$, $b = 10.973(1)$, and $c = 8.0624(7)$ Å.

[7] Gascoin, F.; Sevov, S. C. Unpublished results: monomers of $[NbAs_4]^{7-}$ and dimers of $[Nb_2As_6]^{8-}$ and $[Nb_2As_6]^{9-}$ coexist in $K_{24}Nb_5As_{16}$ (orthorhombic, $Cmcm$, $a = 10.47(1)$, $b = 24.04(2)$, and $c = 23.76(4)$ Å).

[8] Gascoin, F.; Sevov, S. C. Unpublished results: $K_8NbSnAs_5$ ($a = 31.32(3)$, $b = 9.374(1)$, and $c = 13.362(1)$ Å, $\beta = 95.42(3)°$) and $K_8NbGeAs_5$ ($a = 31.325(8)$, $b = 9.397(2)$, and $c = 13.351(3)$ Å, $\beta = 95.43(2)°$) are isostructural with $K_8NbPbAs_5$.[1]

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an additional arsenic atom to give the formula $[NbIn_3As_5]$. The semicubane tridentate ligand $[In_3As_4]$ can exist on its own as well. It is found in $Cs_5In_3As_4$, where it forms chains and layers by bonding to itself via In−As and In−In bonds.[9] In that regard, it seems that this semicubane unit is yet another stable unit in addition to $NbAs_4$. Hence, the anion $[NbIn_3As_5]^{7-}$ can be described as a result of the condensation of one In_3As_4 and one $NbAs_4$. Here we report two new phases, $Cs_{24}Nb_2In_{12}As_{18}$ (**1**) and $Cs_{13}Nb_2In_6As_{10}$ (**2**), where the same building blocks, combined in different ways, build the anions of the structures.

Experimental Section

Synthesis. All manipulations were performed inside an argon-filled glovebox with a moisture level below 1 ppm. The starting materials Cs (99.95%, from Acros), In (99.9%, from Alfa-Aesar), As (99.5%, from Alfa-Aesar), and Nb (−325 mesh, 99.8%, from Acros) were used as received. Mixtures of them were loaded in niobium containers that were then sealed by arc-welding under argon. The containers, easily subject to oxidation when heated in air, were in turn enclosed in fused-silica ampules, which were then flame-sealed under vacuum. These assemblies were heated for 2 days at 650 and 700 °C for **1** and **2**, respectively, and were slowly cooled to room temperature with a rate of 5 °C/h. Compound **1** was made as a pure phase from the corresponding stoichiometric mixture while the nominal composition of the mixture producing compound **2** was "$Cs_{20}Nb_3In_9As_{15}$". Small amounts of compound **1** were found as impurities in the latter synthesis. Both phases are dark-gray to black in color and very brittle. Mixtures of alkali metal and arsenic readily attack the niobium container, and therefore, the latter should be considered as an infinite source of niobium. This makes it difficult to control the amount of niobium in a desired phase. Further complications come from the fact that the known $Cs_5In_3As_4$ (synthesized at lower temperatures) and $Cs_7NbIn_3As_5$ have very similar Cs−In−As compositions with the new phases.

Structure Determination. Crystals of the title compounds were mounted in thin-wall glass capillaries and were checked for singularity on an Enraf-Nonius CAD4 single-crystal diffractometer (Mo Kα radiation, $\lambda = 0.710\ 73$ Å). Data sets were collected on a Bruker APEX diffractometer with a CCD area detector for the best crystals ($Cs_{24}Nb_2In_{12}As_{18}$, black irregular crystal, 0.06 × 0.11 × 0.15 mm; $Cs_{13}Nb_2In_6As_{10}$, dark-gray irregular crystal, 0.20 × 0.14 × 0.06 mm). Both structures were solved in the triclinic space group $P\bar{1}$ and refined (on F^2) with the aid of the SHELXTL-V5.1 software package, after absorption corrections using SADABS.[10] Details of the data collections and refinements are given in Table 1, while important distances are listed in Table 2.

Magnetic Measurements. The magnetizations of 42 mg of $Cs_{24}Nb_2In_{12}As_{18}$ and 10 mg of $Cs_{13}Nb_2In_6As_{10}$ were measured on a Quantum Design MPMS SQUID magnetometer at a field of 3 T over the temperature range 10−250 K. The samples were made by manual selection of large crystals of the corresponding phase from the product. These were then coarsely ground and sealed in fused-silica tubing (i.d. = 3 mm) between two tightly fitting rods of the same material. After corrections for the holder and for ion core diamagnetism $Cs_{24}Nb_2In_{12}As_{18}$ exhibited a negative and temperature-independent magnetic susceptibility varying within $(-0.7$ to $-1.0) \times 10^{-4}$ emu·mol^{-1}. For $Cs_{13}Nb_2In_6As_{10}$ the molar magnetic susceptibility showed a typical Curie−Weiss behavior and was fitted with $\chi = C/(T - \Theta) + \chi_0$, where χ_0 is a temperature-independent contribution (better than 99.3% correlation coefficient for the fit). The following parameters were extracted from the fit: $C = 0.29(2)$ emu·K·mol^{-1}; $\Theta = -24(3)$ K; $\chi_0 = 3.43(1) \times 10^{-3}$ emu·mol^{-1}. This Curie constant corresponds to an effective magnetic moment of 1.52 μ_B and corresponds to one unpaired electron per formula unit. The value somewhat lower than the theoretical 1.73 μ_B is most likely due to small diamagnetic impurities such as traces of $Cs_{24}Nb_2In_{12}As_{18}$ and similar diamagnetic phases in the sample.

Table 1. Selected Data Collection and Refinement Parameters for $Cs_{24}Nb_2In_{12}As_{18}$ and $Cs_{13}Nb_2In_6As_{10}$

param	$Cs_{24}Nb_2In_{12}As_{18}$	$Cs_{13}Nb_2In_6As_{10}$
fw	6102.06	3351.77
space group, Z	$P\bar{1}$, 1	$P\bar{1}$, 1
a, Å	9.519(4)	9.5564(5)
b, Å	9.540(5)	9.6288(5)
c, Å	25.16(1)	13.9071(7)
α, deg	86.87(4)	83.7911(8)
β, degf	87.20(4)	80.2973(8)
γ, deg	63.81(4)	64.9796(8)
V, Å^3	2046(1)	1142.0(1)
radiation; λ, Å	Mo Kα; 0.710 73	Mo Kα; 0.710 73
temp, °C	20	20
abs coeff, cm^{-1}	213.34	208.56
density (calcd), g/cm^3	4.952	4.874
R1/wR2 ($I > 2\sigma_I$),[a] %	3.29/3.77	4.04/10.34
R1/wR2 (all data), %	7.82/8.03	4.69/10.67

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR2 = \{[\sum w[(F_o)^2 - (F_c)^2]^2]/[\sum w(F_o^2)^2]\}^{1/2}$ for $F_o^2 > 2\sigma(F_o^2)$, $w = [\sigma^2(F_o)^2 + (AP)^2 + BP]^{-1}$, where $P = [(F_o)^2 + 2(F_c)^2]/3$ with $A = 0.0272$ and $B = 30.9846$ for $Cs_{24}NbIn_{12}As_{18}$ and $A = 0.0466$ and $B = 23.9213$ for $Cs_{13}Nb_2In_6As_{10}$.

Table 2. Selected Bond Distances (Å) in $Cs_{24}Nb_2In_{12}As_{18}$ and $Cs_{13}Nb_2In_6As_{10}$

$Cs_{24}Nb_2In_{12}As_{18}$				$Cs_{13}Nb_2In_6As_{10}$	
Nb−As1	2.348(1)	As1−Nb	2.348(1)	Nb−As1	2.357(1)
Nb−As2	2.554(1)	As2−Nb	2.554(1)	Nb−As2	2.565(1)
Nb−As3	2.539(1)	As2−In1	2.783(1)	Nb−As3	2.542(1)
Nb−As4	2.545(1)	As2−In2	2.849(2)	Nb−As4	2.539(1)
In1−As2	2.783(1)	As3−Nb	2.539(1)	In1−As2	2.734(1)
In1−As3	2.813(1)	As3−In1	2.813(1)	In1−As3	2.761(1)
In1−As5	2.773(1)	As3−In3	2.834(2)	In1−As5	2.734(1)
In1−In4	3.006(1)	As4−Nb	2.545(1)	In1−In1	2.878(1)
In2−As2	2.849(2)	As4−In2	2.850(1)	In2−As2	2.844(1)
In2−As4	2.850(1)	As4−In3	2.834(2)	In2−As4	2.843(1)
In2−As5	2.847(2)	As5−In1	2.783(1)	In2−As5	2.881(1)
In3−As3	2.834(2)	As5−In2	2.847(2)	In2−As3	2.864(1)
In3−As4	2.808(1)	As5−In3	2.847(2)	In3−As4	2.833(1)
In3−As5	2.847(2)	As6−In4	2.764(1)	In3−As5	2.918(1)
In4−As6	2.764(1)	As6−In5	2.949(1)	As1−Nb	2.357(1)
In4−As7	2.718(1)	As6−In6	2.754(1)	As2−Nb	2.565(1)
In4−As8	2.669(1)	As7−In4	2.718(1)	As2−In1	2.734(1)
In4−In1	3.006(1)	As8−In4	2.669(1)	As2−In2	2.844(1)
In5−As6	2.949(1)	As8−In5	2.833(1)	As3−Nb	2.542(1)
In5−As8	2.833(1)	As9−In5	2.946(1)	As3−In1	2.761(1)
In5−As9	2.946(1)	As9−In6	2.701(1)	As3−In3	2.864(1)
In6−As6	2.754(1)	As9−In6	2.718(1)	As4−Nb	2.539(1)
In6−As7	2.706(2)			As4−In2	2.843(1)
In6−As9	2.701(1)			As4−In3	2.833(1)
In6−As9	2.718(1)			As5−In1	2.734(1)
				As5−In2	2.881(1)
				As5−In3	2.918(1)

Results and Discussions

The structures of $Cs_{24}Nb_2In_{12}As_{18}$ and $Cs_{13}Nb_2In_6As_{10}$ contain isolated polyatomic anions, $[Nb_2In_{12}As_{18}]^{24-}$ and $[Nb_2In_6As_{10}]^{13-}$, respectively, and cesium countercations (Figures 1 and 2). As in many similar structures, the latter can be viewed as positively charged continuum that separates and isolates the embedded anions (interanion $d_{min} = 4.989(8)$

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(9) Gascoin, F.; Sevov, S. C. *Inorg. Chem.* **2001**, *40*, 6254.

(10) *SADABS and SHELXTL*, version 5.1; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 1997.

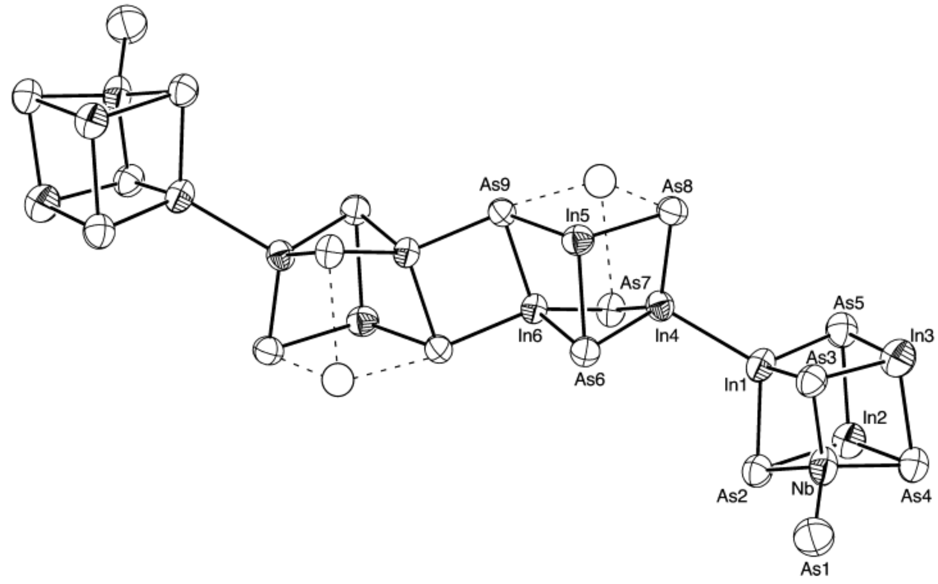

Figure 1. ORTEP drawing of the anion in $Cs_{24}Nb_2In_{12}As_{18}$ (thermal ellipsoids at the 90% probability level): In and Nb, full ellipsoids; As, crossed ellipsoids. In the middle is the dimer of semicubanes of $[In_3As_4]$. The missing corners for full cubanes are shown as open circles and are connected with broken lines. Two cubanes with handles $[NbIn_3As_5]$ are connected via In−In bonds to two indium vertexes of the dimer.

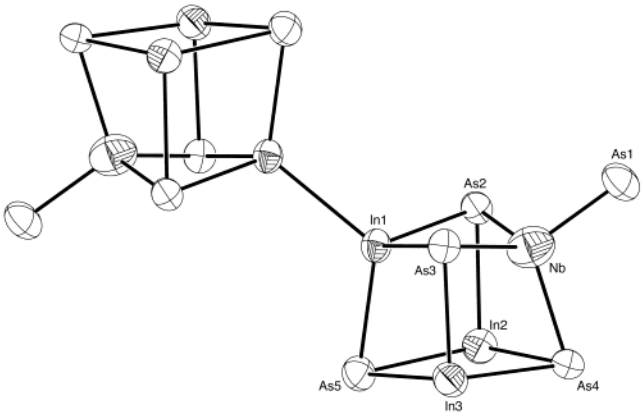

Figure 2. ORTEP drawing of the anion in $Cs_{13}Nb_2In_6As_{10}$ (thermal ellipsoids at the 90% probability level): In and Nb, full ellipsoids; As, crossed ellipsoids. The dimer of cubanes with handles $[NbIn_3As_5]$ is formed by an exo-bond between two indium vertexes.

and 4.882(3) Å in **1** and **2**, respectively). The nature of these anions and the way they are built are novel and make the compounds highly interesting. Both anions are made of two “prefabricated” building blocks already known in other compounds but assembled in different ways. The two units are the cubane with a handle $[NbIn_3As_5]$ known from $Cs_7NbIn_3As_5$, where it exists as isolated species,[3] and the dimer of semicubanes $[In_6As_8]$ known from $Cs_5In_3As_4$, where it forms layers by bonding to itself via In−In bonds.[9] Thus, the anion in **1** is made of a dimer of semicubanes that is bonded to two cubanes via In−In bonds (Figure 1). The anions of **2**, on the other hand, are made of two cubanes connected directly to each other via such a bond (Figure 2). Although the building units are the same as in previously known compounds, they are bonded differently in **1** and **2**. While the cubane is isolated in $Cs_7NbIn_3As_5$ and all indium atoms are three-bonded and pyramidal, it is one-bonded in **1** and **2** and one of the indium atoms is tetrahedrally coordinated. Similarly, the dimer of semicubanes is four-bonded via In−In bonds in the layers of $Cs_5In_3As_4$ but is only two-bonded via similar bonds in **1**. This results in two three-bonded pyramidal and two tetrahedral indium atoms in the latter. As already discussed, these building units are in fact secondary building blocks because they can be further decomposed into smaller primary building blocks of tetrahedral $[NbAs_4]$ and a semicubane of $[In_3As_4]$.

In accordance with the description of the anions as made of building blocks their bonding can be also considered formally as primary and secondary, i.e., within the building units and between them, respectively. Thus, primary are all Nb−As and In−As bonds while secondary are the In−In bonds. Nb−As distances are found only in the cubanes and are of two types: a very short distance of 2.348(1) Å for **1** and 2.357(1) Å for **2** within the handle of the cubane; the three longer distances along the edges of the cubane, 2.539(1)−2.565(1) Å. It should be pointed out that while the former are to terminal arsenic atoms the latter are to three-bonded arsenic atoms. The short distances, together with 2.390(2) Å observed for the handle of the cubane in $Cs_7NbIn_3As_5$, are the shortest distances observed between these two elements. This bond can be viewed as triple when considering the d_π−p_π interactions between the two empty d_π orbitals on niobium (d_{xz}, d_{yz}) and the two filled arsenic p_π orbitals (p_x, p_y). As a result of the additional bonding of the three-bonded arsenic atoms they have only very limited capabilities for π interactions. This means that the niobium d_π orbitals are fully available for π interactions with the terminal arsenic atom only. For comparison, in the isolated tetrahedra of $[NbAs_4]^{7-}$, where the π interactions are spread over all four arsenic atoms, the average Nb−As distance is 2.50 Å; i.e., it is longer than the cubane handle but shorter than the edges of the cubane. According to molecular orbital analysis the maximum possible bond order in tetrahedral d^0 species such as $[NbAs_4]$ is 2.25 (nine available bonding molecular orbitals, $4\sigma + 5\pi$ combinations).[11] On the other hand, for tetrahedral species in which only one of the ligands has p_π orbitals such as the terminal arsenic in the cubane, the bond order to this atom becomes 3.00 (total of $4\sigma + 2\pi$ bonding molecular orbitals where the 2π orbitals interact with the terminal atom only).[11] Such an interpretation of the bonding brings better understanding of the distances in the cubane and their relations to the much longer single-bond length of 2.720(1) Å observed in $[Cp_2H_2Nb{-}AsEt_2]$[12] and to various other distances of tetrahedral niobium coordinated by combinations of differently bonded arsenic atoms: 2.46−2.59 Å for the dimers of edge-bridging tetrahedra in $K_{38}Nb_7As_{24}$,[2] $Cs_9Nb_2As_6$,[2] and $K_9Nb_2As_6$[4] and 2.45−2.62 Å for the tetrahedra bridged by a third atom in K_6NbAs_5, $K_6NbTlAs_4$, and $K_8NbPbAs_5$.[1]

The In−As distances also depend on the number of bonds to the corresponding atoms. Thus, longest are the distances between 3-bonded indium and 3- or 2-bonded arsenic, 2.83−2.95 Å, and next are those between 4-bonded indium and 3-bonded arsenic, 2.70−2.81 Å, while the shortest are between 4-bonded indium and 2-bonded arsenic, 2.67−2.72 Å. This trend is consistent throughout similar In−As compounds and is most likely a result of various phenomena such as repulsion between lone pairs on indium and arsenic and possible π-interactions with the empty d orbitals on indium.

Finally, each anion has one type of In−In distance, 3.002(6) Å between the dimer of semicubanes and the cubanes in **1** and 2.878(1) Å between the cubanes in **2**. Clearly these are substantially different distances. For comparison, the In−In distance of 3.032(1) Å between the dimers of semicubanes forming a layer in $Cs_5In_3As_4$ is also different.[9] These differences come as a secondary effect of the different coordination numbers of the arsenic atoms to which indium is bonded. Thus, the two In−In bonded indium atoms in **2** are coordinated to six arsenic atoms that are all 3-bonded. On the other hand, two of the neighbors of one of the indium atoms in **1** are 2-bonded. As already mentioned, the In−As distances are longer to 3-bonded than to 2-bonded arsenic. As a result of this, more electron density remains for In−In bonding in **2** than in **1**. The distance in $Cs_5In_3As_4$ is even longer because three of the six arsenic atoms are 2-bonded.[9]

Although the isolated cubane in $Cs_7NbIn_3As_5$ and the exo-bonded cubanes in **1** and **2** are overall very similar, there are some differences in the distances. For example, the Nb−As distances to the terminal arsenic atom are somewhat shorter in **1** and **2** than in the isolated species. This is very likely related to the presence of an exo-bond at one indium corner in **1** and **2**. This indium atom does not carry a lone pair in this case and, consequently, forms shorter bonds to the three arsenic corners of the cubane ($d_{av} = 2.771$ vs 2.825 Å). Two of these arsenic atoms are bonded to the niobium corner, and as a result of their shorter bonds to indium, they form somewhat longer bonds to niobium ($d_{av} = 2.551$ vs 2.515 Å). This, in turn, shortens the distance to the terminal arsenic atom, 2.348(1) Å in **1**, 2.357(1) Å in **2**, and 2.390(2) Å in the isolated cubane.[3] The absence of a lone pair of electrons at the four-bonded indium atom is also visible in the large As−In−As angles in **1** and **2**, 96.0−104.3°, compared to those of the isolated cubane, 92.2−99.3°.[9]

The magnetic measurements of compound **1** show that it is diamagnetic. This means that all niobium atoms are d^0, i.e., Nb^V, and that the compound is electronically balanced; i.e., the number of electrons provided by the cations equals the number of electrons necessary for the bonding of the anion. Compound **2**, on the other hand, shows Curie−Weiss behavior with one unpaired spin/anion. This can only mean that one of the niobium atoms is d^1, i.e., Nb^{IV}. However, the anion is centrosymmetric and the two niobium centers are equivalent positions related by the inversion center. This structural equivalence could be real or artificial. The latter can be achieved by dimers of localized Nb^V and Nb^{IV} centers (Nb^V/Nb^{IV}) where the two different centers are distributed evenly among the dimers, i.e., $(Nb^V/Nb^{IV}):(Nb^{IV}/Nb^V) = 1:1$. It is nearly impossible to distinguish such a distribution from dimers that are with a delocalized electron, i.e., from dimers where each Nb should be assigned as $Nb^{IV.5}$. Nevertheless, it is hard to imagine how such a delocalization can occur in the present system with a predominant σ-character of the bonding and where the two niobium centers are quite far apart. Thus, the mixed-valency in this case seems to be of type I but with statistical disorder of the dimers.

The reason for presence of niobium atoms of mixed-valency in **2** is not clear. As in the other mixed-valence transition-metal Zintl phases that were discovered recently as well as in many metallic Zintl phases with one or more delocalized "extra" electrons, the most likely reason is packing requirements. Thus, an extra cation is perhaps required for the crystallization of compound **2** with well-packed and well-separated anions. Similarly, extra cations might be required for the formation of the metallic Zintl phases with the difference that the extra electron there cannot localize on one atom since these phases are made of main-group elements only. The only choice is an electron delocalized over the whole structure, both on cations as well as the antibonding orbitals of the anions.

The formal charges of the anions can be rationalized following the octet rule for the main group elements and the corresponding oxidation state for niobium, i.e., Nb^{V+} and Nb^{IV+}. Thus, 4- and 3-bonded indium atoms are In^{III+} and In^{I+} (because of the remaining lone pair), respectively, while an indium dimer is $(In^{II+})_2$. All arsenic atoms are As^{III-}. Consequently, the anions can be written as $[Nb^{V+}{}_2In^{III+}{}_2(In^{II+})_4In^{I+}{}_6As^{III-}{}_{18}]$ and $[Nb^{V+}Nb^{IV+}(In^{II+})_2In^{I+}{}_4As^{III-}{}_{10}]$.

The recent discoveries of many phases in the system alkali metal−niobium−arsenic, along with the possibility to further incorporate supplementary p-block elements such as In, Tl, Si, Ge, Sn, and Pb, and the capabilities to utilize mixtures of cations (alkali and/or alkaline-earth metals) clearly indicate the potential richness of this class of niobium-based transition metal Zintl phases. The possible combinations are indeed endless, but the emergence and recognition of the building blocks $[NbAs_4]$ and $[In_3As_4]$ will definitely facilitate the

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(11) Lin, Z.; Hall, M. B. *Coord. Chem. Rev.* **1993**, *123*, 149.

(12) Nikonov, G. I.; Lorberth, J.; Harms, K.; Lemenovskii, D. A. *Inorg. Chem.* **1995**, *34*, 2461.

studies of these compositionally complex compounds, at least from a structural point of view. The idea of "using" building blocks is very old but also very elusive goal in high-temperature solid-state chemistry. Nevertheless, the particular system A−Nb−In−As (A = alkali metal) may present such an opportunity. It is very likely that various primary and secondary building units such as [$NbAs_4$], [In_3As_4], [$NbIn_3As_5$], [In_6As_8], etc., coexist in the reaction mixture at various temperatures and compositions. Upon cooling, they form different anions and crystallize as the corresponding compounds such as $Cs_5In_3As_4$,[9] $Cs_7NbIn_3As_5$,[3] $Cs_{24}Nb_2In_{12}As_{18}$, and $Cs_{13}Nb_2In_6As_{13}$. This series of compounds extends even further by yet another compound in this system. Although its structure has not been determined well yet, it seems to contain both the isolated cubane with a handle [$NbIn_3As_5$] and its corresponding dimer [$Nb_2In_6As_{10}$].[13] The knowledge of the stable building blocks in a system can be used as a guide in the search for other compounds in that system, and the potential targets would be limited only by one's imagination. One of the drawbacks, however, is that the corresponding phases often have very similar compositions and their syntheses in pure forms are either impossible or very difficult.

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Supporting Information Available: General views of the two structures, a plot of the temperature dependence of the molar magnetic susceptibility of compound **2**, and an X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) Gascoin, F.; Sevov, S. C. Unpublished results.