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Article

Synthesis and Characterization of Transition-Metal Zintl Phases: $K_{10}NbInAs_6$ and $K_9Nb_2As_6$

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The two title compounds were prepared by direct reactions of the corresponding elements at high temperature. The structures were determined by single-crystal X-ray diffraction: $K_{10}NbInAs_6$, monoclinic, $P2_1/n$, $Z = 2$, $a = 9.107(1)$ Å, $b = 8.2878(8)$ Å, $c = 15.139(1)$ Å, $\beta = 91.112(9)°$; $K_9Nb_2As_6$, monoclinic, $P2_1/c$, $Z = 2$, $a = 9.348(1)$ Å, $b = 9.113(1)$ Å, $c = 12.798(1)$ Å, $\beta = 95.98(1)°$. They contain isolated dimers made of edge-sharing tetrahedra of $[NbAs_4]$ and $[InAs_4]$ in the former, $NbInAs_6^{10-}$, and only $[NbAs_4]$ in the latter, $Nb_2As_6^{9-}$. Magnetic measurements show that $K_{10}NbInAs_6$ is diamagnetic, i.e., a d^0 transition-metal Zintl phase, while $K_9Nb_2As_6$ exhibits a Curie–Weiss behavior consistent with the presence of one unpaired electron. The latter defines $K_9Nb_2As_6$ as a mixed-valence (presumably of type III) transition-metal Zintl phase, only the third example of such phases.

Introduction

Added recently to the large family of Zintl phases were two new compounds, $K_{38}Nb_7As_{24}$ and $Cs_9Nb_2As_6$.[1] They are also the first mixed-valence transition-metal Zintl phases. Both compounds contain dimers of edge-sharing tetrahedra of arsenic centered by mixed-valent Nb(IV/V), $[As_2Nb(\mu\text{-}As)_2NbAs_2]^{9-}$, that are bent around the shared edge. It was shown that, as a result of this bending, the d_{z^2} orbitals of the two niobium atoms overlap and share the unpaired electron. The full delocalization of this electron makes the mixed valence of type III[2] and provides a formal bond order of 0.5 for the Nb−Nb interaction.[1] Such and similar electronic effects could be found not only in mixed-valence but generally in reduced transition-metal Zintl phases.[3] In the known phases of this type, the transition metal is coordinated by the heavy main-group p-element, and the d-orbitals experience extremely weak, almost nonexistent crystal fields generated by such "ligands" of very low electronegativity and overall negative charge. Such systems may have interesting magnetic and transport properties. As a matter of fact, somewhat unexpected magnetic ordering has been already observed for some of them.[1,4]

Our interest has been specifically in systems containing alkali and/or alkaline-earth metal, niobium, and arsenic, systems that have already shown their potential.[1,5] Their further exploration led to the discovery of the two new transition-metal Zintl phases, $K_{10}NbInAs_6$ and $K_9Nb_2As_6$, described here.

Experimental Section

Synthesis. The two title compounds were made from direct reactions of the pure elements used as received: Nb powder (−325 mesh, 99.8%) from Acros; K (98%), In (99.9%), and As (99.5%) from Alfa Aesar. All manipulations were carried out in a glovebox with typical moisture and oxygen levels below 1 ppm (the compounds are air-sensitive). The mixtures were loaded in tubular niobium containers that were already sealed at one end by arc-welding under argon and were then similarly sealed at the other end. These containers were enclosed and sealed in evacuated fused-silica ampules in order to protect niobium from oxidation. $K_{10}NbInAs_6$ was initially made by a reaction intended to produce

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Table 1. Crystallographic Data for $K_9Nb_2As_6$ and $K_{10}NbInAs_6$

	$K_{10}NbInAs_6$	$K_9Nb_2As_6$
fw	1048.25	987.24
space group, Z	$P2_1/n$, 2	$P2_1/c$, 2
a (Å)	9.107(1)	9.348(1)
b (Å)	8.2878(8)	9.113(1)
c (Å)	15.139(1)	12.798(1)
β (deg)	91.112(9)	95.98(1)
V (Å^3)	1142.4(2)	1084.3(2)
ρ_{calcd} (g/cm^3)	3.047	3.024
radiation, λ (Å)	Mo Kα, 0.71073 Å	
temp (K)	293	
μ (cm^{-1})	119.36	118.47
R1/wR2^a for $I \geq 2\sigma_I$ (%)	5.37/12.96	5.36/9.10
R1/wR2^a for all data (%)	6.63/13.84	10.89/10.71

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR2 = \{[\sum w[(F_o)^2 - (F_c)^2]^2]/[\sum w(F^2{}_o)^2]\}^{1/2}$ for $F_o{}^2 > 2\sigma(F_o{}^2)$, $w = [\sigma^2(F_o)^2 + (AP)^2 + BP]^{-1}$ where $P = [(F_o)^2 + 2(F_c)^2]/3$ and with $A = 0.03$, $B = 6.022$ and $A = 0.0958$, $B = 0.7953$ for $K_9Nb_2As_6$ and $K_{10}NbInAs_6$, respectively.

Table 2. Important Distances (Å) and Angles (deg) in $K_{10}NbInAs_6$ and $K_9Nb_2As_6$

$K_{10}NbInAs_6$		$K_9Nb_2As_6$	
In/Nb−As1	2.570(1)	Nb−As1	2.474(1)
In/Nb−As2	2.582(1)	Nb−As2	2.484(1)
In/Nb−As3	2.653(1)	Nb−As3	2.553(1)
In/Nb−As3	2.657(1)	Nb−As3	2.556(1)
In/Nb−In/Nb	3.521(1)	Nb−Nb	3.408(2)
As1−In/Nb−As2	113.25(5)	As1−Nb−As2	113.09(6)
As1−In/Nb−As3	111.50(5)	As1−Nb−As3	111.40(6)
As2−In/Nb−As3	112.97(5)	As2−Nb−As3	110.98(6)
As1−In/Nb−As3	110.72(5)	As1−Nb−As3	111.96(6)
As2−In/Nb−As3	110.31(5)	As2−Nb−As3	111.94(6)
As3−In/Nb−As3	96.96(4)	As3−Nb−As3	96.32(5)
In/Nb−As3−In/Nb	83.04(4)	Nb−As3−Nb	83.68(5)

$K_6NbInAs_4$ isostructural with the known $K_6NbTlAs_4$, a compound with isolated polyanions of $NbTlAs_4{}^{6-}$ (tetrahedral $NbAs_4$ with one Tl-bridged edge).[5a] It was later synthesized in nearly 100% yield from a stoichiometric mixture heated at 600 °C for a week and cooled slowly. The compound crystallizes as very thin and shiny plates with dark-gray to black color and very smooth surfaces. $K_9Nb_2As_6$, on the other hand, does not form upon slow cooling. Instead, it requires very fast cooling rates that can be achieved by quenching in either icy water or liquid nitrogen. Thus, the synthesis of this compound was carried out at 800 °C for 2 days followed by breaking of the hot quartz ampule under liquid nitrogen. It crystallized as small, gray, and shiny pieces of irregular shape. The compound was discovered while attempting to get higher yields, by quenching, of another compound, $K_{24}Nb_5As_{16}$,[6] which has almost the same composition ($2.5 \times K_9Nb_2As_6 = K_{22.5}Nb_5As_{15}$). Apparently, $K_{24}Nb_5As_{16}$ forms only upon slow cooling while $K_9Nb_2As_6$ is stabilized by the quenching. However, despite their similar compositions, the two phases were never found coexisting in the same product. According to X-ray powder diffraction (Enraf-Nonius Guinier camera with Cu radiation), each compound can be made as a pure phase.

Structure Determination. Single crystals of the title compounds were mounted in thin-wall glass capillaries and were inspected for singularity on an Enraf-Nonius CAD4 single-crystal diffractometer (Mo Kα radiation, $\lambda = 0.71073$ Å). Data were collected at room temperature for the best crystals ($K_{10}NbInAs_6$: $0.2 \times 0.1 \times 0.02$ mm, $\omega-2\theta$ scans; $K_9Nb_2As_6$: $0.08 \times 0.04 \times 0.04$ mm, $\omega-\theta$ scans). Both structure were solved and refined (on F^2) with the aid of the SHELXTL-V5.1 software package. More details of the data collections and refinements are given in Table 1 while important distances and angles are listed in Table 2.

One of the potassium positions, K5, in $K_9Nb_2As_6$ was found somewhat too close, at 3.04(1) Å, to its equivalent generated by the inversion center and also close to another potassium, K4, at 3.067(7) Å. Furthermore, the thermal displacement parameter of the same atom, K5, was too large when kept at full occupancy. Also, the thermal ellipsoid of K4, the atom too close to K5, was elongated along the K4−K5 direction. When freed to vary, the occupancy of K5 dropped to 52.2(9)% while K4 stayed fully occupied. All these observations indicated that the occupancy of the K5 position should be kept at 50%. The possibility of having the space group wrong was also explored, and the structure was refined in the noncentrosymmetric $P2_1$ and Pc. The refinement produced good agreement factors, but there were large correlation values for all the atoms that refined well in the centrosymmetric $P2_1/c$. More importantly, two unrelated and close to each other peaks corresponding to potassium with a half occupancy were found at the positions of K5 and its symmetry equivalent in the $P2_1/c$ space group. Thus, for the final refinement, $P2_1/c$ was retained, and K5 was kept as half occupied. Apparently, no voids are created by that half occupancy because when K5 is present K4 takes the farther extreme of its elongated thermal ellipsoid, and it is at the other extreme when K5 is missing.

In $K_{10}NbInAs_6$, the transition-metal position coordinated tetrahedrally by arsenic showed an unreasonably small thermal displacement parameter when refined as niobium. However, when indium was refined at that position (indium is often found in the same coordination by pnictogens), that parameter became too large. When freed to vary, the occupancy of that position became higher than 100% for niobium while the number was 87.7(4)% for indium. In light of the diamagnetic properties of the compound (see following description), the results from elemental analysis (see following description), and charge balance considerations, it was clear that the position was fully occupied but with mixed and equimolar indium/niobium participation. When refined as such, i.e., with the fractions of the two elements freed to vary but restricted to add to a full occupancy, the contributions of niobium and indium refined to 45(1)% and 55(1)%, respectively, i.e., quite close to the ideal 1:1 ratio. Thus, the fractions of the two elements were fixed at 50% each for the final refinement. Such an assignment is also justified by the observed elongation of the thermal ellipsoids of the terminal arsenic atoms toward the mixed niobium/indium position as expected due to the small difference in the Nb−As and In−As distances (see Results and Discussion section). No such phenomenon was observed in $K_9Nb_2As_6$ where the niobium position is occupied by equal fractions of Nb(V) and Nb(IV). Apparently, these two oxidation states do not differ much in size, at least not enough to be noticed in the thermal parameters of the surrounding arsenic atoms.

Magnetic Measurements. The magnetizations of 32 mg of $K_{10}NbInAs_6$ and that of 25 mg of $K_9Nb_2As_6$ were measured on a Quantum Design MPMS SQUID magnetometer at a field of 3 T over the temperature range 10−200 K. Each sample was coarsely ground and sealed in fused silica tubing between two tightly fitting rods of the same material. After correction for the holder and for the core diamagnetism, the molar magnetic susceptibility of $K_{10}NbInAs_6$ was negative and temperature independent, varying within the range (−9.9 to −11.0) $\times 10^{-5}$ emu/mol, while that of $K_9Nb_2As_6$ exhibited Curie−Weiss behavior. The latter dependence was fitted with $\chi = C/(T - \theta) + \chi_0$ where χ_0 is a temperature-

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(6) $K_{24}Nb_5As_{16}$ crystallizes as large bars. Its structure contains isolated tetrahedral units of $[NbAs_4]$ and flat and bent dimers of $[Nb_2As_6]$ in a ratio 1:1:1. Apparently, the structure is intrinsically disordered, and more studies are needed in order to confirm the results.

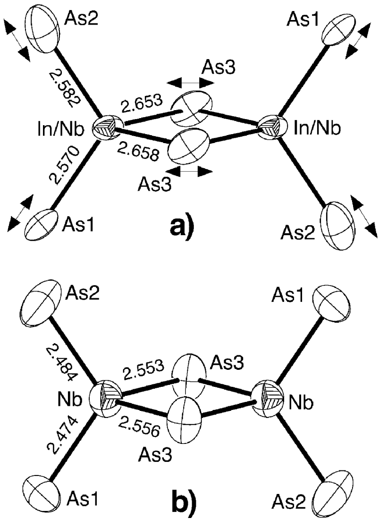

Figure 1. ORTEP drawing (95% probability thermal ellipsoids) of (a) $[NbInAs_6]^{10-}$ in $K_{10}NbInAs_6$ and (b) $[Nb_2As_6]^{9-}$ in $K_9Nb_2As_6$. The elongation of the arsenic thermal ellipsoids is highlighted with arrows.

independent contribution to the paramagnetism. The accuracy of the fit was better than 99.9% with the following parameters: $C = 0.324(7)$ emu·K/mol, $\theta = 2.3(1)$ K, and $\chi_0 = 2.57(9) \times 10^{-3}$ emu/mol. This Curie constant corresponds to an effective magnetic moment of 1.64 μ_B.

Elemental Analysis. The Nb/In ratio of $K_{10}NbInAs_6$ was verified by elemental analysis carried out by ICP on a Perkin-Elmer Plasma 400 emission spectrometer (40 MHz free-running ICP generator and Ar-cooled coil). For that purpose, crystals of the compound were manually selected under microscope and were dissolved in diluted acid (a small quantity of HF is necessary to completely dissolve the niobium). Five “standard” solutions of known concentrations were also prepared for each element using K_2NbF_7 and elemental indium. Multiple measurements for Nb and In were performed and gave an atomic ratio of 1.05 for the two elements.

Results and Discussion

The structures of the two title compounds are very similar and quite simple. They both contain isolated anionic dimers made of two edge-sharing tetrahedra, and the dimers are separated from each other by the potassium cations. The shortest interanionic distances are 5.249(1) and 5.086(2) Å in $K_{10}NbInAs_6$ and $K_9Nb_2As_6$, respectively. The dimers in the two structures (Figure 1) are of the same symmetry, C_i (but very close to C_{2h} with 2-fold axes along As3−As3), and each has three crystallographically different arsenic positions (As1 and 2 are terminal and As3 is bridging) and one position for the atoms centering the tetrahedra. The occupants of the latter position and the overall charge of the dimer (and consequently the number of countercations) is what makes the two structures different. This central position was refined as 50% In and 50% Nb in $K_{10}NbInAs_6$ but as niobium only in $K_9Nb_2As_6$. As already discussed in the Experimental Section, the refinement with mixed occupancy in the former was dictated by different factors. One was the results from the magnetic measurements which clearly indicated that the compound is diamagnetic and, therefore, electronically balanced. This means that the 10 potassium cations per formula unit found in the structure had to be charge-balanced by the charge of the dimer; i.e., the dimer should have a charge of 10−. The six arsenic atoms can be considered as As^{3-} each, and therefore, the sum of the charges of the two central atoms must be 8+. The only way this can be achieved is to have one niobium(V) and one indium(III) at these positions. This assignment is nicely confirmed by the elemental analysis and is in perfect agreement with the crystallographic specifics of the position. The dimers can thus be viewed as made of one Nb(V) and one In(III) coordinated by 6 As^{3-}, leading to $[(As^{3-})_2Nb^{V}(\mu\text{-}As^{3-})_2In^{III}(As^{3-})_2]^{10-}$. A more covalent point of view, usually used for describing the bonding in Zintl phases, would consider 2-center−2-electron bonds for Nb−As and In−As and represent the dimer as $[(As^{2-})_2(Nb^{+})(As^{-})_2(In^{-})(As^{2-})_2]$.

These considerations assume that each dimer is made of one $[InAs_4]$ and one $[NbAs_4]$ tetrahedral units that share an edge. However, a model where half of the dimers in the structure are with two indium centers, $[As_2In(\mu\text{-}As)_2InAs_2]$, and the other half are with two niobium centers, $[As_2Nb(\mu\text{-}As)_2NbAs_2]$, should be also considered. Nevertheless, there are two arguments against this model. The first one is that it provides two very differently charged dimers with charges of 12− and 8− for the indium- and niobium-centered species, respectively. In most structures with coexisting and differently charged anions, these charges do not differ by much. It is very unlikely for species with charges that differ by four, as suggested by this model, to coexist in the same structure.

The second argument against different dimers is found in the shapes of the thermal ellipsoids of the arsenic atoms and their relation to the difference in the Nb−As and In−As distances. These distances need to be discussed first. The only known species with bonds between four-bonded indium atoms and terminal arsenic atoms are found in KBa_2InAs_3 with very similar isolated dimers of $[In_2As_7]^{13-}$ (one of the four terminal arsenics is additionally exo-bonded to another arsenic).[7] Three different In−As distances are observed in these dimers: 2.597(4), 2.657(4), and 2.718(4) Å. The distances to the two bridging arsenic atoms in the same dimers are 2.671(3) and 2.694(4) Å. The ranges for the corresponding niobium distances to terminal and to bridging arsenic atoms are 2.444(1)−2.510(3) and 2.544(2)−2.592(3) Å, respectively. These values are taken from $K_{38}Nb_7As_{24}$ and $Cs_9Nb_2As_6$ which contain the same dimers of $[As_2Nb(\mu\text{-}As)_2NbAs_2]$ as those in $K_9Nb_2As_6$.[1] The corresponding distances of the dimer in the latter, 2.484(1) and 2.474(1) Å to the terminal and 2.553(1) and 2.556(1) Å to the bridging arsenic atoms, fall also in these ranges. Clearly, the In−As distances are longer than the corresponding Nb−As distances by about 0.1−0.2 Å. The distances in the dimers in $K_{10}NbInAs_6$, 2.570(1) and 2.582(1) Å to the terminal and 2.653(1) and 2.658(1) Å to the bridging arsenic atoms, are between the Nb−As and In−As values as expected for mixed occupancy. However, they are not real distances but rather averages of two different distances that correspond to Nb and In occupation of the site. These small differences in bond

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distances should, in turn, influence the shape of the thermal ellipsoids of the arsenic atoms. Thus, independent of whether the dimers are mixed In/Nb or only In and only Nb, the terminal arsenic atoms should be elongated along the bond to the central atom. This is exactly what is observed for the shapes of As1 and As2, an elongation toward the central mixed In/Nb position (shown with arrows in Figure 1a).

The expected shapes of the bridging atoms, on the other hand, depend on the type of the dimer. Clearly the In/Nb position is well fixed and immobile, i.e., the thermal ellipsoid is small and quite spherical indicating that there is no statistical deviation from the center (Figure 1a). Therefore, the differences in the In−As and Nb−As distances should be reflected in the ellipsoids of the bridging arsenics. Thus, if the dimers are a statistical mixture of In-only and Nb-only dimers, we should see the two bridging As3 atoms elongated along the line connecting them (the shared edge), i.e., radially to the central square. This particular elongation is expected because the arsenic atoms should be closer to the center of the dimer in order to achieve shorter distances to the two tetrahedral centers when they are niobium atoms, and should be further out when they are indium atoms. That is the only way to accommodate two different distances. On the other hand, the same bridging atoms should be elongated tangentially to the central square if the dimers have one indium and one niobium atoms. Thus, if the left tetrahedron in Figure 1a is centered by niobium, the bridging arsenic atoms will be shifted to the left in order to satisfy the shorter distance to niobium and the longer distance to the right center which is occupied by indium. The other 50% of the dimers will have this situation reversed, and this should result in the described elongation. As can be seen from Figure 1a, this is exactly the shape of the bridging arsenic atoms, and therefore, this model seems to be the correct one.

The purely niobium dimers $[As_2Nb(\mu\text{-}As)_2NbAs_2]$ found in $K_9Nb_2As_6$ are the third type of dimers with this composition but different shape or charge (Figure 1b). The first two types, a flat dimer of $[Nb_2{}^{V}As_6]^{8-}$ and a bent dimer of $[Nb^{IV}Nb^{V}As_6]^{9-}$, were observed in $K_{38}Nb_7As_{24}$ and $Cs_9Nb_2As_6$, respectively.[1] The shape of the dimer in $K_9Nb_2As_6$ is the same as the former but with the charge of the latter, 9−. This charge assignment is confirmed clearly by the magnetic measurements which indicated a Curie−Weiss behavior and an effective magnetic moment of 1.64 μ_B, i.e., one unpaired electron per dimer. This means that a mixed-valence state should be assigned for niobium, Nb(IV/V). The two extreme types of mixed-valence are defined as the following: (a) with an electron that is fully localized at one of the two centers (type I) and the two niobium atoms are distinctively Nb^{IV} and Nb^{V}, and (b) with an electron that is completely delocalized between the two centers (type III) and both niobiums are $Nb^{IV.5}$.[2] The latter case is observed in the bent dimers of $[Nb_2As_6]^{9-}$ in $Cs_9Nb_2As_6$ where a nonzero overlap occurs between the d_{z^2}-orbitals of the two niobium atoms and the unpaired electron is shared between them. Such an overlap is possible due to the following: (a) the shorter Nb−Nb distance and (b) the availability of the orbitals, both possible because of the bending. The dimers in $K_9Nb_2As_6$, on the other hand, are flat but with the same charge of 9−. It should be pointed out that the only difference between the two stoichiometries, $Cs_9Nb_2As_6$ and $K_9Nb_2As_6$, is the cation. Apparently, the different sizes cause the differences in the dimers, perhaps due to packing requirements.

The dimer in $K_9Nb_2As_6$ has only one Nb-position, and all thermal ellipsoids are quite spherical (Figure 1b). This suggests that the unpaired electron in this dimer is also delocalized, just as in the bent dimer in the Cs-analogue. Had it been localized, the small differences in the radii of Nb^{V} and Nb^{IV} would have resulted in slightly elongated ellipsoids.

The two compounds presented here and the few other alkali-metal niobium arsenides discovered recently are an attestation for the opportunities that exist in the solid-state chemistry of transition metals coordinated by heavier main-group elements. Among these Nb−As compounds there are already examples that show magnetic ordering at low temperatures, with Nb−Nb bonding, and with mixed-valence Nb.[4] Adding a second main-group element, as in $K_{10}NbInAs_6$, $K_6TlNbAs_4$, and $K_8PbNbAs_5$,[5] extends these possibilities even further.

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Supporting Information Available: Plot of the temperature dependence of the magnetic susceptibilities of the two compounds, general views of the two structures, 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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