Inorg. Chem. **2002**, *41*, 5920–5924

Inorganic Chemistry
Article

Synthesis and Characterization of $K_{38}Nb_7As_{24}$ and $Cs_9Nb_2As_6$: The First Mixed-Valence Transition-Metal Zintl Phases

Franck Gascoin and Slavi C. Sevov*

Department of Chemistry and Biochemistry, University of Notre Dame,
Notre Dame, Indiana 46556

Received April 2, 2002

The two title compounds were prepared by direct reactions of the corresponding elements at high temperature, and their structures were determined from single-crystal X-ray diffraction data. The structure of $K_{38}Nb_7As_{24}$ (orthorhombic; *Cmcm*; $Z = 4$; $a = 10.4974(6)$, $b = 23.915(2)$, $c = 36.046(2)$ Å) comprises isolated tetrahedra of $NbAs_4$ and two types of dimers of edge-sharing tetrahedra: dimers containing only Nb^{V}, $[Nb^{V}2As_6]^{8-}$, and mixed-valence dimers with both Nb^{IV} and Nb^{V}, $[Nb^{IV}Nb^{V}As_6]^{9-}$. The structure of $Cs_9Nb_2As_6$ (orthorhombic; *Pbca*; $Z = 8$; $a = 17.5848(7)$, $b = 16.940(2)$, $c = 18.183(4)$ Å) contains only the latter dimers. Magnetic measurements showed Curie–Weiss paramagnetic behavior for both compounds consistent with one unpaired electron/mixed-valence dimer. $Cs_9Nb_2As_6$ exhibits also an antiferromagnetic transition at about 36 K. The two compounds are the first mixed-valence (of class III) transition-metal Zintl phases.

Introduction

Since Zintl's pioneering work on polar main-group intermetallic compounds that now carry his name, Zintl phases,[1] their number has grown almost exponentially throughout the years.[2] Perhaps the greatest evolution of the Zintl's concept took place when compounds containing transition metals were included in the family. "Admitted" initially were transition-metal phases that were isostructural with known main-group Zintl phases.[3] These included, for example, Na_8TiAs_4 and Na_5HfAs_3 isostructural with A_8SnSb_4 (A = Na, K) and Na_5SnAs_3, respectively.[4] Next came all electronically balanced compounds that contain transition-metal ions with d^0 or d^{10} closed-shell configurations. These involve elements of groups 4−6 as fully oxidized d^0 ions[5] and of groups 10−12 as d^{10} ions.[6] Finally, the view was broadened even further by adding also compounds containing transition-metal ions with partially filled d-orbitals as long as the compounds were electronically balanced. This latter group, however, has only two members so far, both based on manganese. One of the structure types, that of $A_{14}MnPn_{11}$ (A = Ca, Sr, Ba, Eu; Pn = As, Sb, Bi),[3] contains Mn(III), while the other, $Sr_{21}Mn_4Sb_{18}$,[7] involves Mn(II). Thus, despite the large variety of transition metals and numerous feasible combinations with main-group elements, this field has remained quite under-

---

* To whom correspondence should be addressed. E-mail: ssevov@nd.edu.

(1) (a) Zintl, E.; Dullenkopf, W. *Z. Phys. Chem.* **1932**, *B16*, 183. (b) Zintl, E.; Brouer, G. *Z. Phys. Chem.* **1933**, *B20*, 245. (c) Zintl, E. *Angew. Chem.* **1933**, *52*, 1.

(2) (a) Corbett, J. D. In *Chemistry, Structure and Bonding of Zintl Phases and Ions*; Kauzlarich, S. M., Ed.; VCH Publishers: New York, 1996; p 139. (b) Corbett, J. D. *Angew. Chem., Int. Ed.* **2000**, *39*, 670. (c) Eisenmann, B.; Cordier, G. In *Chemistry, Structure and Bonding of Zintl Phases and Ions*; Kauzlarich, S. M., Ed.; VCH Publishers: New York, 1996; p 61. (d) Belin, C.; Tillard-Charbonnel, M. *Prog. Solid State Chem.* **1993**, *22*, 59.

(3) Kauzlarich, S. M. In *Chemistry and Bonding of Zintl Phases and Ions*; Kauzlarich, S. M., Ed.; VCH Publishers: New York, 1996; p 245.

(4) (a) Stuhrmann, J.; Adam, A.; Schuster, H. U. *Z. Naturforsch. B* **1993**, *48*, 898. (b) Adam, A.; Schuster, H. U. *Z. Naturforsch. B* **1990**, *45*, 559.

(5) (a) Gascoin, F.; Sevov, S. C. *Angew. Chem., Int. Ed.* **2002**, *41*, 1232. (b) Gascoin, F.; Sevov, S. C. *Inorg. Chem.* **2002**, *41*, 2820. (c) Vidyasagar, K.; Hönle, W.; von Schnering, H. G. *J. Alloys Compd.* **1996**, *236*, 38. (d) Nuss, J.; Hönle, W.; von Schnering, H. G. *Z. Anorg. Allg. Chem.* **1997**, *623*, 1763. (e) Lin, J. H.; Hönle, W.; von Schnering, H. G. *J. Alloys Compd.* **1992**, *183*, 403. (f) Nuss, J.; Hönle, W.; Peters, K.; von Schnering, H. G. *Z. Anorg. Allg. Chem.* **1996**, *622*, 1879. (g) Nuss, J.; Cardoso Gil, R. H.; Hönle, W.; Peters, K.; von Schnering, H. G. *Z. Anorg. Allg. Chem.* **1996**, *622*, 1854. (h) Vidyasagar, K.; Hönle, W.; von Schnering, H. G. *Z. Anorg. Allg. Chem.* **1996**, *622*, 518. (i) Huang, D.; Corbett, J. D. *Inorg. Chem.* **1998**, *37*, 4006.

(6) (a) Somer, M. *Z. Naturforsch. B* **1994**, *49*, 1203. (b) Dong, Z. C.; Henning, R. W.; Corbett, J. D. *Inorg. Chem.* **1997**, *36*, 3559. (c) Sevov, S. C.; Corbett, J. D. *J. Am. Chem. Soc.* **1993**, *115*, 9089. (d) Henning, R. W.; Corbett, J. D. *Inorg. Chem.* **1999**, *38*, 3883. (e) Dhingra, S. S.; Haushalter, R. C. *J. Am. Chem. Soc.* **1994**, *116*, 3651. (f) Zachwieja, U.; Muller, J.; Wlodarski, J. *Z. Anorg. Allg. Chem.* **1998**, *624*, 853. (g) Huang, D. P.; Dong, Z. C.; Corbett, J. D. *Inorg. Chem.* **1998**, *37*, 5881. (h) Todorov, E.; Sevov, S. C. *Angew. Chem., Int. Ed.* **1999**, *38*, 1775. (i) Kaskel, S.; Corbett, J. D. *Inorg. Chem.* **2000**, *39*, 3086. (j) Queneau, V.; Sevov, S. C. *J. Am. Chem. Soc.* **1997**, *119*, 8109.

(7) Hyungrak, K.; Condron, C. L.; Holm, A. P.; Kauzlarich, S. M. *J. Am. Chem. Soc.* **2000**, *122*, 10720.

10.1021/ic020250b CCC: $22.00

developed and unexplored. We have been interested in the solid-state chemistry of the systems alkali metal−niobium−arsenic and have undertaken extensive and systematic studies of these systems. This has led to yet another level of complexity for the Zintl phases: the first mixed-valence (of class III,[8] i.e., with complete electron delocalization) transition-metal Zintl phases by the two title compounds which contain the unprecedented $[Nb^{V}Nb^{IV}As_6]^{9-}$ species (or $Nb^{IV.5}$-$Nb^{IV.5}As_6$).

Experimental Section

Synthesis. The new compounds are as moisture- and air-sensitive as alkali metals are. Thus, all manipulations were carried out in an Ar-filled glovebox with typical moisture level below 1 ppm. The two title compounds were discovered while investigating the systems alkali metal−Nb−As motivated by the recent discovery of $Cs_7NbIn_3As_5$,[5a] A_6NbAs_5 (A = K, Rb and Cs), $K_6NbTlAs_4$, and $K_8NbPbAs_5$[5b] and especially by the fact that niobium readily reacts with arsenic in the presence of alkali metals. The compounds were prepared by direct synthesis from the corresponding elements used as received (Cs, 99.95%, and Nb powder with −325 mesh, 99.8%, from Acros; K, 98%, and As sponge, 99.5%, from Alfa Aesar). The stoichiometric mixtures were loaded in tubular niobium containers that were then sealed by arc-welding under argon. These containers were themselves protected from oxidation by sealing them in fused-silica ampules under vacuum. The assemblies were kept at 850 °C for 1 week and were then slowly cooled to room temperature at a rate of 5 °C/h. The compounds are shiny dark-gray to black, brittle, and exhibit very smooth surfaces. The crystals of $K_{38}Nb_7As_{24}$ are small plates while those of $Cs_9Nb_2As_6$ are quite large and irregular. Both compounds were made as single phases according to their X-ray diffraction powder patterns taken on an Enraf-Nonius Guinier camera with Cu Kα_1 radiation.

Structure Determination. Crystals of the two compounds were mounted in thin-wall class capillaries using a drybox equipped with a microscope. They were inspected for singularity on an Enraf-Nonius CAD4 single-crystal diffractometer (Mo Kα radiation, λ = 0.710 73 Å), and data sets were collected for the best ones (0.16 × 0.16 × 0.08 mm for $K_{38}Nb_7As_{24}$; 0.12 × 0.10 × 0.08 mm for $Cs_9Nb_2As_6$) at room temperature ($2\theta_{max} = 50°$, $\omega-2\theta$ scans). The structures were solved in the orthorhombic space groups *Cmcm* and *Pbca* for $K_{38}Nb_7As_{24}$ and $Cs_9Nb_2As_6$, respectively, and were refined (on F^2) with the aid of the SHELXTL-V5.1 software package. Two of the potassium positions in $K_{38}Nb_7As_{24}$, K15 and K16, were found somewhat too close to each other at 3.17(2) Å, and the thermal displacement parameter of K16 was unusually large while that of K15 was quite elongated and pointing toward K16. When freed to vary, the occupancies of these two positions refined to 49.3% for K16 while K15 stayed fully occupied. This suggested that when K16 is occupied, K15 takes the far extremity of its position and achieves proper distance to K16, while when K16 is empty, then K15 occupies the closest extremity since there is no interference from an atom at K16. The latter relaxation of K15 means that no large holes are created in the structure. Details of the data collection and refinement for the two compounds are given in Table 1 while important distances and angles are listed in Table 2.

Magnetic Measurements. The magnetizations of 25 mg of $K_{38}Nb_7As_{24}$ and 36 mg of $Cs_9Nb_2As_6$ were measured on a Quantum Design SQUID magnetometer at a field of 3 T over the temperature ranges of 2.5−250 K for the former and 10−250 K for the latter. The samples were enclosed between the ends of two rods of fused silica that fit tightly in tubing of the same material, and the ends were flame-sealed. The data were corrected for the holder and for ion-core diamagnetism. When plotted versus the temperature, the resulting molar magnetic susceptibilities indicated Curie−Weiss behavior for both samples. The regions of 2.5−250 K for $K_{38}Nb_7As_{24}$ and 50−250 K for $Cs_9Nb_2As_6$ were fitted with $\chi = C/(T - \Theta) + \chi_0$, where χ_0 is a temperature-independent contribution to the paramagnetism. The accuracies of the two fits were higher than 99.9% with parameters of C = 0.484(3) (emu·K)/mol, Θ = −14.5(1) K, and $\chi_0 = 2.28(3) \times 10^{-3}$ emu/mol for $K_{38}Nb_7As_{24}$. The corresponding numbers for $Cs_9Nb_2As_6$ were 0.364(2), −121(6), and $2.4(4) \times 10^{-3}$, respectively. Antiferromagnetic ordering at 36 K was observed for $Cs_9Nb_2As_6$ while no transition was found for $K_{38}Nb_7As_{24}$ down to 2.5 K. The paramagnetic behavior of the two compounds was also confirmed by electron paramagnetic resonance spectroscopy performed on a Bruker EMX EPR spectrometer at room temperature and at 77 K using polycrystalline samples.

Table 1. Crystallographic Data for $K_{38}Nb_7As_{24}$ and $Cs_9Nb_2As_6$

param	$K_{38}Nb_7As_{24}$	$Cs_9Nb_2As_6$
fw	3934.25	1831.53
space group, Z	*Cmcm*, 4	*Pbca*, 8
a (Å)	10.4974(6)	17.5848(7)
b (Å)	23.915(2)	16.940(2)
c (Å)	36.046(2)	18.183(4)
V (Å^3)	9049(1)	5416(1)
ρ_{calc} (g/cm^3)	2.888	4.492
radiation (λ, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
temp (K)	293	293
μ (cm^{-1})	113.29	200.29
R1/wR2[a]	0.059/0.134	0.056/0.115

[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 $F_o{}^2 > 2\sigma(F_o{}^2)$, and $w = [\sigma^2(F_o)^2 + (AP)^2 + BP]^{-1}$, where $P = [(F_o)^2 + 2(F_c)^2]/3$ and $A = 0.0825$ and $B = 6.2925$ and $A = 0.0575$ and $B = 8.2374$ for $K_{38}Nb_7As_{24}$ and $Cs_9Nb_2As_6$, respectively.

Table 2. Important Distances (Å) and Selected Angles (deg) in $K_{38}Nb_7As_{24}$ and $Cs_9Nb_2As_6$

$K_{38}Nb_7As_{24}$			
$[Nb_2As_6]^{9-}$		$[Nb_2As_6]^{8-}$	
Nb1−As1	2.444(2)	Nb2−As4	2.456(1)
Nb1−As2	2.498(2)	Nb2−As4	2.456(1)
Nb1−As3	2.571(1)	Nb2−As5	2.547(3)
Nb1−As3	2.571(1)	Nb2−As5	2.562(2)
Nb1−Nb1	3.155(3)	Nb2−Nb2	3.527(3)
As3−Nb1−As3	100.29(8)	As5−Nb2−As5	92.67(8)
Nb1−As3−Nb1	75.70(8)	Nb2−As5−Nb2	87.33(8)
dihedral angle around As3⋯As3 = 146.5(1)		dihedral angle around As5⋯As5 = 180	
$[NbAs_4]^{7-}$		$[NbAs_4]^{7-}$	
Nb4−As8	2.530(3)	Nb3−As6	2.555(2)
Nb4−As9	2.472(3)	Nb3−As6	2.555(2)
Nb4−As10	2.528(1)	Nb3−As7	2.490(2)
Nb4−As10	2.528(1)	Nb3−As7	2.490(2)
$Cs_9Nb_2As_6$			
Nb1−As1	2.464(3)	Nb2−As3	2.472(3)
Nb1−As2	2.510(3)	Nb2−As4	2.489(3)
Nb1−As5	2.578(3)	Nb2−As5	2.546(2)
Nb1−As6	2.544(2)	Nb2−As6	2.592(3)
Nb1−Nb2	3.260(2)		
As5−Nb1−As6	98.83(9)	Nb1−As5−Nb2	79.02(8)
As5−Nb2−As6	98.41(9)	Nb1−As6−Nb2	78.79(8)
dihedral angle around As5⋯As6 = 154.1(1)			

---

[8] Demadis, K. D.; Hartshorn, C. M.; Meyer, T. J. *Chem. Rev.* **2001**, *101*, 2655.

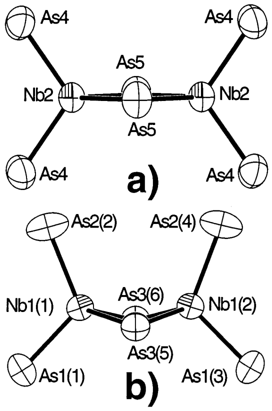

Figure 1. ORTEP drawing (95% probability thermal ellipsoids) of (a) the "flat" and (b) the "bent" dimers in $K_{38}Nb_7As_{24}$. The numbers in parentheses in (b) refer to the numbering of the atoms in the same dimer found in $Cs_9Nb_2As_6$.

Results and Discussion

The overall structures of the two compounds are rather simple. They are ionic made of isolated heteroatomic Nb−As anions that are immersed in seas of alkali metal cations. The anions are well separated and screened by the cations with shortest interanionic distances of 5.248(2) and 5.416(3) Å for $K_{38}Nb_7As_{24}$ (**1**) and $Cs_9Nb_2As_6$ (**2**), respectively (figures of the unit cells are in the Supporting Information). What makes these compounds interesting are the structures and bonding of the anions. There are two types of anionic units in these compounds, both based on niobium centers that are tetrahedrally coordinated by arsenic. These are isolated tetrahedra of $[NbAs_4]$ and dimers made by edge-sharing of the same tetrahedra, $[Nb_2As_6]$. The dimers, however, are not all the same. In some of them the four-membered ring made of the two shared arsenic atoms and the two niobium centers is planar, flat dimers (Figure 1a), while in others this ring is bent around the shared arsenic edge, bent dimers (Figure 1b). Dimers of the first type involving transition metal have been characterized before, for example $[Hf_2As_6]^{10-}$ in Na_5HfAs_3 with d^0 hafnium(IV).[4b]

The structure of $K_{38}Nb_7As_{24}$ contains isolated tetrahedra (crystallographically two different types), flat dimers, and bent dimers in a ratio of 3:1:1, respectively, while the structure of $Cs_9Nb_2As_6$ contains only bent dimers. The Nb−As distances in the tetrahedra, 2.472(2)−2.555(2) Å, compare well with those of the same species found in $Na_5SrNbAs_4$ and $K_5BaNbAs_4$ (2.480(4)−2.503(1) Å),[5c] K_7NbAs_4 and Rb_7NbAs_4 (2.487(2)−2.519(4) Å),[5g] and $Sr_{13}NbAs_{11}$ and $Eu_{13}NbAs_{11}$ (2.508(1)−2.511(2) Å).[5h] There are two types of Nb−As distances in the dimers depending upon whether the arsenic atom is two-bonded or terminal. Those to the terminal atoms are quite shorter, 2.444(2)−2.510(3) Å, compared with the distances to the shared atoms, 2.544(2)−2.592(2) Å. The two sets of distances are quite similar to the corresponding distances to terminal, 2.398(2)−2.483(1) Å, and two-bonded, 2.540(2)−2.616(1) Å, arsenic atoms observed in the recently reported $[NbAs_4As]^{6-}$, where an arsenic atom bridges one edge of the $NbAs_4$ tetrahedron, $[NbAs_4Tl]^{6-}$, where thallium does the same, and $[NbAs_4PbAs]$, where the edge is bridged by a lead atom that is additionally bonded to another arsenic.[5b] The bonding between niobium and arsenic in all these species and the apparent flexibility of the bond length can be attributed to the different degree of π-bonding between the filled p-orbitals of arsenic and the empty d-orbitals of the niobium atoms. In isolated tetrahedra, where all four arsenic atoms are capable of such interactions with the d-orbitals of the central niobium, the "extra bonding" is distributed over all four bonds. The situation is quite different in the dimers where only two arsenic atoms/niobium center, the two terminal ones, can π-interact with the same number of d-orbitals. This results, naturally, in shorter distances to the terminal atoms of the dimers compared to the distances in the isolated tetrahedra. This is in agreement with molecular orbital calculations which indicate bond order of 2.25/bond for the isolated tetrahedron and bond order of 3.00/bond for the two terminal atoms in a tetrahedron where the other two ligands are incapable of π-bonding.[9] Finally, the π-interactions of the bridging arsenic atoms in the dimers are substantially weaker (if at all) and spread among two niobium centers which leads to even longer distances.

The electron counts and charges of the isolated tetrahedra and the flat dimers can be easily understood as Nb^V centers coordinated by As^{3-} ligands where two of the ligands in the dimers are bridging, i.e., $[Nb^V(As^{3-})_4]^{7-}$ and $[(As^{3-})_2Nb^V(\mu\text{-}As^{3-})_2Nb^V(As^{3-})_2]^{8-}$, respectively. If one takes into account that a formula unit of $K_{38}Nb_7As_{24}$ contains three isolated tetrahedra $[NbAs_4]^{7-}$ and one flat dimer $[Nb_2As_6]^{8-}$, the charge of the bent dimer is calculated as 9−, i.e., $[Nb_2As_6]^{9-}$, and not 8− as in the flat species. The same is true for the bent dimer in $Cs_9Nb_2As_6$ where nine cesium cations balance its charge. The only way such charge can be achieved is to have one Nb^{IV} and one Nb^V centers. Furthermore, the facts that the two niobium atoms of the bent dimers in **1** are crystallographically equivalent (Nb1), that the coordination arrangements around the niobium atoms of the dimers in compound **2** are virtually identical with sums of Nb−As distances of 10.96 and 10.99 Å around them, and that none of the arsenic atoms of these dimers show any elongation of the thermal ellipsoids along the corresponding Nb−As directions show that the electron exchange between the two oxidation states is without a barrier and the electronic wave functions are no longer time dependent; i.e., this is a mixed-valence state of class III with complete electron delocalization.[8] Perhaps a more appropriate description for the oxidation states in such species is $[As_2Nb^{IV.5}(\mu\text{-}As)_2Nb^{IV.5}As_2]^{9-}$, just like in the first designed mixed-valence complex $[(NH_3)_5Ru^{II.5}(\mu\text{-pyrazine})Ru^{II.5}(NH_3)_5]^{5+}$.[10] The proposed mixed valence for **1** and **2** is in excellent agreement with the magnetic behavior of the two compounds which show Curie−Weiss dependence of the molar susceptibility as a function of the temperature. Furthermore, the magnetic moments derived from the measured Curie constants (see Experimental Section), 1.96 and 1.70 μ_B for **1** and **2**, respectively, correspond to one localized unpaired electron/formula unit, i.e., per one bent dimer. The negative Θ temperatures of −8.1 and −121 for **1** and **2**, respectively,

---

(9) Lin, Z.; Hall, M. B. *Coord. Chem. Rev.* **1993**, *123*, 149.
(10) Creutz, C.; Taube, H. *J. Am. Chem. Soc.* **1969**, *91*, 3988.

indicate that the overall interactions of the spins are antiferromagnetic in both compounds.

A closer look at the bent dimers shows that they are quite bent with dihedral angles around the shared As···As edge, 146.5(1) and 154.1(1)° in **1** and **2**, respectively, that are substantially smaller than 180° (Table 2). In addition to this, the angles at the arsenic atoms of the shared edge, 75.70(8)° in **1** and 79.02(8) and 78.79(8)° in **2**, are much smaller than those of the squarelike flat dimer, 87.33(8)°. At the same time the As−Nb−As angles involving the shared arsenic atoms are quite larger in the bent dimers, 100.29(8)° in **1** and 98.83(9) and 98.41(9)° in **2**, than in the flat one, 92.67(8)°. One more parameter in this picture is the length of the shared edge which is quite longer in the bent dimers, 3.947(3) Å in **1** and 3.890(2) Å in **2**, than in the flat species, 3.695(3) Å. (The latter is actually the van der Waals diameter of arsenic.[11]) All these differences indicate that some "force" pulls the two niobium centers toward each other in the bent dimers. This is clearly manifested by the resulting shorter Nb−Nb distances of 3.155(3) and 3.260(2) Å in the bent dimers of **1** and **2**, respectively, compared to the distance of 3.527(3) Å in the flat dimer in **1**. This suggests substantial bonding interactions between the two centers. To assess the degree of bonding, these distances were compared with distances in compounds with Nb−Nb single bonds as well as in niobium metal. Thus, this distance in many coordination compounds is in the range 2.8−3.0 Å, depending upon the type of ligands around the niobium centers,[12] and it is 2.858 Å in elemental niobium.[13] The distances in the bent dimers are longer than these values and, therefore, suggest a bond order of less than 1. Extended Hückel molecular orbital calculations carried out for the bent dimer indicate that the in-phase combination of the d_{z^2} orbitals (see synopsis figure) of the two niobium centers is substantially bonding in the bent dimer. The one d-electron available from the Nb^{IV} ion occupies the resulting molecular orbital and provides a bond order of 0.5. Quite a substantial value of 0.19 was calculated for the bond overlap population for this bond. To put this value in perspective, calculated was also the overlap population for the flat dimer with Nb−Nb distance of 3.53 Å. The resulting number was substantially smaller, 0.07. Also calculated was the overlap population for a dimer artificially bent even further to achieve a Nb−Nb distance of 2.85 Å, a value within the observed range of single-bond distances. The extent of bending is actually limited by the distance between the two terminal arsenic atoms, As2 in **1** (Figure 1b), that get closer to each other upon bending. This distance cannot be shorter than twice the van der Waals radius of arsenic, i.e., 2 × 1.85 Å.[11] At this limit of 3.70 Å the distance between the two niobium centers becomes 2.85 Å (dihedral angle of 115°, Nb−As−Nb angle of 68°). The calculated bond overlap population for Nb−Nb in this model was 0.34, a number that is only about twice larger than the overlap population calculated for the real molecule. This indicates that the interactions between the niobium centers in the latter are indeed very substantial. One more, yet much less precise, measure for the interactions is the multiplicity of the bond estimated from Pauling's relation $d_n = d_1 - 0.6 \log(n)$, where n is the multiplicity and d_n and d_1 are the observed and single-bond distances, respectively.[14] Using $d_1 = 2.9$ Å the bond orders of the bent dimers in **1** and **2** are calculated as 0.38 and 0.25, respectively.

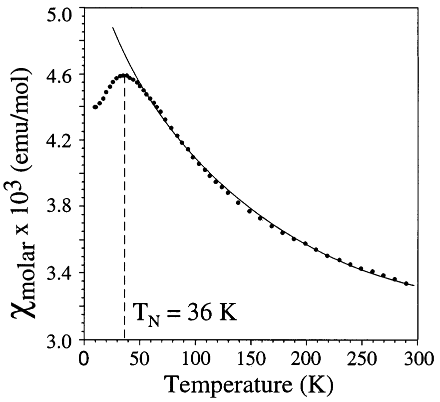

Figure 2. Plot of the magnetic susceptibility of $Cs_9Nb_2As_6$ measured at a field of 3 T as a function of the temperature. The data follow a modified Curie−Weiss law $\chi = C/(T - \Theta) + \chi_0$ above 50 K (solid line) with a Curie constant that corresponds to one unpaired electron/mixed-valence dimer of $[Nb^{IV}Nb^{V}As_6]^{9-}$. The compound undergoes antiferromagnetic ordering with a Néel temperature of 36 K.

Discussed next is the magnetic behavior of $Cs_9Nb_2As_6$ and, specifically, the antiferromagnetic ordering observed below 36 K (Figure 2). Such a transition is quite unexpected for an electronically balanced compound with very "diluted" magnetic centers as in **2** where the shortest distance between niobium atoms of two different dimers is 7.2 Å. This, however, is not without a precedent. Many of the electron-balanced compounds $(AE)_{14}MnPn_{11}$ with Pn = Sb or Bi have shown magnetic ordering despite the separation of about 10 Å between the Mn^{III} ions.[3,15] This has been explained by possible overlap between the valence and conduction bands (confirmed by the observed metallic conductivity) and the resulting delocalized electrons which, according to the RKKY theory,[16] can provide the means for "magnetic communication" between the localized spins. Similar interpretation, however, does not seem likely for the interactions in compound **2** as it appears to be nonmetallic according to many factors: black color; Curie−Weiss paramagnetism; increasing resistance upon cooling. The latter was measured with two electrodes positioned 3 mm apart on a pressed pellet inside the glovebox. The resistance grew nearly linearly from

---

(11) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

(12) See for example: (a) Cotton, F. A.; Diebold, M. P.; Roth, W. J. *Inorg. Chem.* **1987**, *26*, 3319. (b) Cotton, F. A.; Duraj, S. A.; Roth, W. J. *Inorg. Chem.* **1984**, *23*, 3592. (c) Lemenovskii, D. A.; Fedin, V. P.; Slovokhotov, Y. L.; Struchkov, Y. T. *J. Organomet. Chem.* **1982**, *228*, 153. (d) Scheper, J. T.; Jayaratne, K. C.;.Liable-Sands, L. M.; Yap, G. P. A.; Rheingold, A. L.; Winter, C. H. *Inorg. Chem.* **1999**, *38*, 4354.

(13) Wells, A. F. *Structural Inorganic Chemistry*; Clarendon Press: Oxford, U.K., 1984.

(14) Pauling, L. *Nature of the chemical bond*, 3rd ed; Cornell University Press: Ithaca, NY, 1960; p 239.

(15) (a) Rehr, A.; Kuromoto, T. Y.; Kauzlarich, S. M.; Del Castillo, J.; Webb, D. J. *Chem. Mater.* **1994**, *6*, 93. (b) Siemens, D. P.; Del Castillo, J.; Potter. W.; Webb, D. J.; Kuromoto, T. Y.; Kauzlarich, S. M. *Solid State Commun.* **1992**, *84*, 1029.

(16) Kittel, C. *Solid State Phys.* **1968**, *22*, 1.

17 to 29 kΩ upon cooling from −14 to −42 °C (in Supporting Information). This clearly indicates nonmetallic behavior and also clarifies the character of the observed substantial temperature-independent paramagnetic contribution of 2.4×10^{-3} emu/mol (see Experimental Section) to the molar magnetic susceptibility. Possible sources for such a term are van Vleck and Pauli paramagnetisms. However, the latter should be excluded as it is due to delocalized electrons in metals and is inconsistent with nonmetals. Thus, at this stage, no mechanism can be suggested for the antiferromagnetic transition at 36 K, and more measurements, such as detailed four-probe conductivity at lower temperatures and in magnetic fields, are needed in order to clarify this.

The two compounds described here, $K_{38}Nb_7As_{24}$ and $Cs_9Nb_2As_6$, appear to be the first mixed-valence transition metal Zintl phases. They, together with $Cs_7NbIn_3As_5$, A_6NbAs_5 (A = K, Rb, Cs), $K_6NbTlAs_4$, and $K_8NbPbAs_5$, belong to a new class of ternary and quaternary niobium−arsenides of the alkali metals, a class that seems to be structurally quite promising for new compounds with novel structural and bonding features and, perhaps, properties.

Acknowledgment. We thank the National Science Foundation (Grant CHE-0098004) for the financial support of this research.

Supporting Information Available: An X-ray crystallographic file in CIF format, two figures of the two structures showing the unit cells, and a plot of the two-probe resistance of $Cs_9Nb_2As_6$. This material is available free of charge via the Internet at http://pubs.acs.org.

IC020250B