dihydroxynaphthalene or 3,4-dihydroxybenzoate (extinction of blue fluorescence at $\lambda_{em} = 440$ nm upon oxidation to the quinone). Noradrenaline reacts similarly to adrenaline down to pH 5. Adrenochrome (**2**) is unstable and polymerizes to brown and finally insoluble black products upon prolonged standing in solution.

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Cubane with a Handle: $[\{In_3As_4Nb\}{-}As]^{7-}$ in $Cs_7NbIn_3As_5$**

Franck Gascoin and Slavi C. Sevov*

Compared to the large number of main group Zintl compounds there are only a few that contain transition metals.[1] This is not surprising since the traditional definition of Zintl phases automatically excludes transition metals. However, many such compounds with transition metals can qualify for Zintl phases when a broader definition is used. The latter includes compounds of transition metals with filled or empty d shells, that is the late transition metals of the Ni, Cu, and Zn groups,[2] and the early transition elements of the Ti, V, and Cr groups at maximum formal oxidation states.[3] There are only two Zintl compounds containing a transition metal with partially filled d shell, both based on manganese, $(AE)_{14}MnPn_{11}$ (AE = alkaline-earth metal, Pn = pnictogen) and $Sr_{21}Mn_4Sb_{18}$.[4] Perhaps only they should be called true "transition metal Zintl phases" although the name is contradictory in itself. All but two of the d^0 compounds contain isolated tetrahedra $[MPn_4]^{n-}$ (M = Nb, Ta, W, Ti).[5] The two exceptions are Na_5HfAs_3 with dimers of edge-sharing tetrahedra of $[Hf_2As_6]^{10-}$ and $Rb_5TaAs_4Tl_2$ with $[TaAs_4]$ tetrahedra, where two Tl atoms bridge opposite edges, $(\mu\text{-Tl})[As_2TaAs_2](\mu\text{-Tl})^{5-}$.[6] Here we report a new d^0 transition metal Zintl phase, $Cs_7NbIn_3As_4$, which contains an unprecedented anion, $[\{In_3As_4Nb\}{-}As]^{7-}$, a cubane made of three indium, four arsenic, and one niobium atom and a "handle" composed of an arsenic atom that is multiply bonded to the niobium corner.

The title compound was initially made in an attempt to synthesize the recently reported $Cs_5In_3As_4$ at temperatures higher than the original 500 °C.[7] The reaction was carried out in niobium containers at 800 °C, at which temperature the arsenic apparently attacked the container and formed the quaternary compound $Cs_7NbIn_3As_4$. Later it was synthesized in high yield using the corresponding elements in stoichiometric ratio at the same temperature.[8]

The overall structure of $Cs_7NbIn_3As_5$ is quite simple and unremarkable,[9] an ionic assembly of isolated anions of $[NbIn_3As_5]^{7-}$ immersed in a "sea" of cesium cations that screen them from each other (inter-anion $d_{min} = 5.009(4)$ Å). What is remarkable is the structure and bonding of the anion (Figure 1). Its geometry can be viewed in a few different ways. The more obvious approach is to recognize the cubane shape made of one Nb, three In, and four As atoms, $[NbIn_3As_4]$, and its "handle" of a fifth arsenic atom attached to the niobium

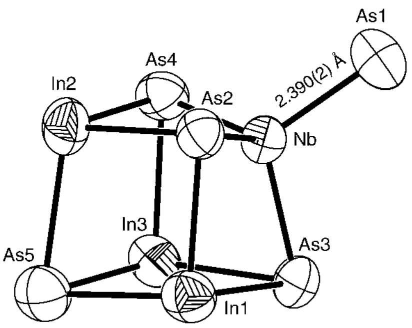

Figure 1. Structure of the cubane with a "handle" $[\{As(InAs)_3\}Nb{=}As]^{7-}$ (ORTEP drawing; thermal ellipsoids at the 95% probability level). The unusually short distance of the handle is shown. The remaining distances [Å] are: Nb-As2 2.484(2), Nb-As3 2.526(2), Nb-As4 2.535(2), In1-As2 2.834(2), In1-As3 2.794(2), In1-As5 2.908(2), In2-As2 2.864(2), In2-As4 2.789(2), In2-As5 2.894(2), In3-As3 2.845(2), In3-As4 2.822(2), In3-As5 2.858(2). The angles [°] at Nb and As5 are in the range 107.26(7)–112.82(7) and 79.32(5)–80.27(5), respectively. The angles around As2, As3, and As4 fall in the range 78.15(6)–82.09(5)°. The angles at the indium atoms that involve As5, 98.34(5)–99.28(6)°, are larger that those that do not, 91.25(5)–92.20(5)°.

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corner of the cube (Figure 1). Cubane is quite a popular shape especially for combinations of four transition metal (M) and four chalcogen (Ch) atoms, M_4Ch_4.[10] Recently reported was also a main group cation with the same geometry, $[Bi_4Te_4]^{4+}$.[11] In all of these systems the two atom types alternate at the cubane corners providing equidistant M–Ch edges. In $[NbIn_3As_4]$, however, the cubane is uneven as one vertex is occupied by a niobium instead of an indium atom (Figure 1). Thus, three of the cubane edges are Nb–As bonds that are shorter ($d_{av} = 2.520$ Å) than the In–As bonds of the remaining nine edges ($d_{av} = 2.842$ Å). This leads to substantial distortion of the cube such that the niobium corner becomes closer to the cubane center than the other corners, and the rest of the cubane is compressed around the Nb–As5 body diagonal (Figure 1). All angles at As5 are, for example, noticeably smaller than 90°, while those at Nb and the As5-In-As angles are larger than 90°. The In–As distances are longer than those of four-bonded indium atoms in $Cs_5In_3As_4$, $K_4In_4As_6$, and Na_3InAs_2 ($d_{av} = 2.70$ Å),[7, 12] but are closer to the distances of similarly three-bonded indium atoms in $Cs_5In_3As_4$ ($d_{av} = 2.90$ Å).[7] The elongation is very likely due to the stronger repulsion between the lone pair at the three-bonded indium and the one or more lone pairs at the arsenic atoms.

exo-Bonded to the cubane at the niobium vertex is the fifth arsenic atom (As1) with a very short distance of 2.390(2) Å. This clearly indicates a multiple Nb–As bond, which, in turn, is the basis for another way to view the anion. It can be described as tetrahedral niobium center coordinated by one tridentate, cagelike ligand of $[As(InAs)_3]$, and one single arsenic atom, $[As(InAs)_3]NbAs$. Such a description is justified by the fact that exactly the same cagelike, semicubane ligands have been already observed in $Cs_5[As(InAs)_3]$, in which they are connected in chains and layers through In–As and In–In *exo*-bonds.[7] When viewed in this way (Figure 2a), the anion resembles known molecules with multiple bonds such as $[\{N(CH_2CH_2(Me_3Si)N)_3\}W{\equiv}As]$ (d(W–As) 2.290(1) Å; Figure 2b),[13] $[(tBu_3SiO)_3Ta{=}As{-}Ph]$ (d(Ta–As) 2.428(2) Å; Figure 2c),[14] and $[(Cp)_2\{H(Tol)[Fe(CO)_4]As\}Nb{=}As(Tol)\{Fe(CO)_4\}]$ (d(Nb–As) 2.516(2) Å; Figure 2d).[15] The multiple bonding in the above compounds and in $[\{As(InAs)_3\}Nb{-}As]^{7-}$ is based on the π interactions between the empty d_{xz} and d_{yz} orbitals on the transition metal and the filled p_π orbitals on the arsenic center. Furthermore, while the two arsenidines $[L_3Ta{=}AsPh]$ and $[L_3Nb{=}AsTol]$ are bent at the arsenic and indicate sp^2 hybridization (maximum bond order of 2), the naked arsenide ligand can be viewed as sp-hybridized where both p_x and p_y orbitals are available for π interactions. This is the only arsenic atom in $[\{As(InAs)_3\}Nb{-}As]^{7-}$ that is capable of π interactions with the Nb d orbitals, since the arsenic atoms of the tridentate ligand are "forced" to be sp^3-hybridized. This results in the very short distance of 2.390(2) Å, and the bonding can be schematically represented as a hybrid of $(\eta^3\text{-L})M{\equiv}As \leftrightarrow (\eta^3\text{-L})M^{+}{=}As^{-} \leftrightarrow (\eta^3\text{-L})M^{2+}{-}As^{2-}$. For comparison, the average Nb–As distance of 2.50 Å in the tetrahedral $[NbAs_4]^{7-}$ ion is longer because all four arsenic atoms are capable of π interactions.[5] According to molecular orbital analysis the bond order for each bond in tetrahedral d^0 species such as the latter is 2.25 (nine available bonding molecular orbitals), while it is 3.00 for tetrahedral species in which only one of the ligands has p_π orbitals such as the single arsenic center in $[\{As(InAs)_3\}Nb{-}As]^{7-}$.[16] Such an interpretation of the bonding is in better agreement with the observed extremely short distance of 2.390(2) Å. Also, when compared to the much longer single Nb–As bond length of 2.720(1) Å in $[Cp_2H_2Nb{-}AsEt_2]$,[17] this short distance corresponds indeed to a triple Nb–As bond.

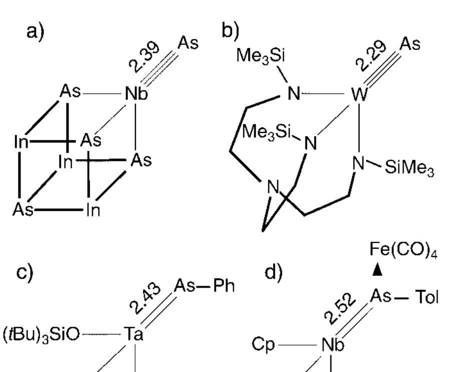

Figure 2. Species with similar coordination around the transition metal: a) $[\{As(InAs)_3\}Nb{\equiv}As]^{7-}$, b) $[\{N[CH_2CH_2(Me_3Si)N]_3\}W{\equiv}As]$; c) $[\{(tBu_3SiO)_3\}Ta{=}As{-}Ph]$, and d), $[(Cp)_2\{H(Tol)[Fe(CO)_4]As\}Nb{=}As(Tol)\{Fe(CO)_4\}]$.

The electron count and the charge of the anion can be accounted for by utilizing Zintl's approach in which atoms achieve an octet by bonding or by additional negative charge. Thus, the cagelike tridentate ligand $[As(InAs)_3]$ has a formal charge of 9 – made of three three-bonded In^{2-} (3b-In^{2-}), and one three-bonded As^0 (3b-As^0) and three two-bonded As^- (2b-As^-) atoms. Of course, these formal charges are assigned for the sole purpose of electron counting, and do not represent the real charges accumulated on the atoms. The cage and the isolated As^{3-} ion are coordinated to a Nb^V center to produce the resulting cubane with a handle $[(3b\text{-}As^0)(3b\text{-}In^{2-})_3(2b\text{-}As^-)_3]Nb^V(As^{3-})$. Conversely, one can apply a different formalism in which the indium atoms are In^I and all arsenic atoms are As^{3-}. This gives the same overall charge of 7 – for the anion. This charge is neutralized by the seven cesium cations of the formula, and, therefore, the compound is electronically balanced, a Zintl phase. This was confirmed by the magnetic measurements which indicated a diamagnetic, saltlike compound.[18]

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[8] All manipulations were performed inside a nitrogen-filled glove box with moisture level below 1 ppm. A stoichiometric mixture of the elements was loaded in a tubular niobium container sealed at one end by arc-welding and then the other end was also arc-welded. The container was enclosed in a fused-silica ampule which was, in turn, flame-sealed under vacuum. The assembly was heated at 800 and 500 °C for three days at each temperature, and was then slowly cooled to room temperature at a rate of 5 °C per hour. The crystals are black, irregular, relatively large (up to several millimeters), and with smooth, coal-like surfaces.

[9] Selected crystals of the compound were mounted in glass capillaries (inside a dry box) and checked for singularity on a Bruker-APEX single crystal diffractometer with a CCD area detector ($\mathrm{Mo}_{K\alpha}$ radiation, $\lambda = 0.71073$ Å). Data were collected on the best one (irregular, $0.39 \times 0.37 \times 0.20$ mm) at room temperature ($2\theta\mathrm{max} = 50°$), and were corrected for absorption (SADABS). The structure was solved in the triclinic space group $P\bar{1}$ and refined (on F^2) with the aid of the SHELXTL-V5.1 software package. Crystal data: triclinic, $P\bar{1}$, $a = 8.8101(9)$, $b = 9.664(1)$, $c = 14.748(2)$ Å; $\alpha = 85.421(2)$, $\beta = 85.961(2)$, $\gamma = 86.421(2)°$, $V = 1246.5(2)$ Å^3; $Z = 2$; $\mu = 198.28\ \mathrm{cm}^{-1}$; $\rho_{\mathrm{calcd}} = 4.642\ \mathrm{g\,cm}^{-3}$. The refinement converged at $R1/wR2 = 0.0546/0.1409$ for 3424 observed reflections ($I > 2\sigma_I$) and 145 variables. Further details of the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldschafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata @fiz-karlsruhe.de) on quoting the depository number CSD-412274.

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[18] The magnetization of $\mathrm{Cs_7NbIn_3As_6}$ was measured on a quantum Design SQUID magnetometer at a field of 3 T over the temperature range 10–250 K. Selected crystals of the compound were ground to a powder (35 mg) which was then sealed in a fused-silica tubing between two tightly fitting rods of the same material. After corrections for the holder and for the ion-core diamagnetism the molar magnetic susceptibility was negative and temperature-independent varying between -1.4×10^{-4} and -1.7×10^{-4} emu mol^{-1}.
