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Synthesis and Structure of $[Sb_7Ni_3(CO)_3]^{3-}$: A New Structural Type for *nido* 10-Vertex Polyhedral Clusters

Scott Charles,† Bryan W. Eichhorn,*,† and Simon G. Bott‡

Department of Chemistry and Biochemistry
University of Maryland, College Park, Maryland 20742
Department of Chemistry
University of North Texas, Denton, Texas 76203

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Soluble p-block polyanions (Zintl ions) have been known for over 100 years[1] and are still a subject of current interest.[2] The group 14 polyanions of Ge, Sn, and Pb form electron-deficient boron hydride-like polyhedral clusters (*e.g.*, Sn_9^{4-}, Pb_5^{2-}), whereas the group 15 polyanions of P, As, Sb, and Bi adopt polycyclic hydrocarbon-like structures.[2] Insertion of transition metals into Zintl ions sometimes effects structural rearrangements, such as the transformation of the nortricyclic E_7^{3-} ions (**1**) into norbornadiene-like fragments in the $[E_7M(CO)_3]^{3-}$ compounds (E = P, As, Sb; M = Cr, Mo, W)[3,4] or the formation of a cyclooctane-like As_8^{8-} ring in the $[NbAs_8]^{3-}$ ion.[5] Introduction of zero-electron-donor transition-metal fragments [*e.g.*, $Cr(CO)_3$, $Fe(CO)_2$, Ni(CO)] into electron-precise group 15 polyanions should (in theory) transform the clusters into electron-deficient polyhedral structures in accordance with Wade's rules.[6] Herein we report the synthesis of $[Sb_7Ni_3(CO)_3]^{3-}$ (**2**) from Sb_7^{3-} and $Ni(CO)_2(PPh_3)_2$, which represents the first example of this type of transformation. The structure of **2** exhibits a new *nido*-10(iv+iv) cluster type.[7]

Ethylenediamine (en) solutions of K_3Sb_7 react with toluene solutions of $Ni(CO)_2(PPh_3)_2$ in the presence of 2,2,2-crypt[8] (1:1:3 molar ratio, respectively) to give low yields of $[K(2,2,2\text{-crypt})^+]_3[Sb_7Ni_3(CO)_3]^{3-}\cdot$en after 28 h at room temperature.[9] The dark red-brown crystalline compound has been characterized by IR spectroscopy, elemental analysis,[9] and single crystal X-ray diffraction.[10] The formation of the $[Sb_7Ni_3(CO)_3]^{3-}$ ion (**2**) involves the formal insertion of three Ni(CO) fragments into the Sb_7^{3-} cage. A 1:1 ratio of Sb_7^{3-} to $Ni(CO)_2(PPh_3)_2$ reproducibly yields the $[K(2,2,2\text{-crypt})^+]$ salt of **2** in an average 14% crystalline yield (based on Ni); however, the more reasonable 1:3 ratio of reagents does not yield any detectable **2**. The IR spectrum (KBr pellet) of this compound shows three $\nu(CO)$ bands at 1864, 1845, and 1823 cm^{-1}, which is consistent with the solid-state structure.

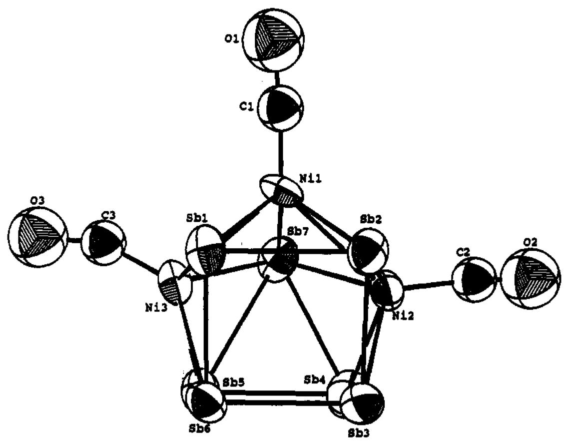

Figure 1. ORTEP drawing of the $[Sb_7Ni_3(CO)_3]^{3-}$ ion. Pertinent bond distances (Å) are: Sb(1)–Sb(2) = 2.917(8), Sb(1)–Sb(6) = 2.877(8), Sb(1)–Ni(1) = 2.57(1), Sb(1)–Ni(3) = 2.52(1), Sb(2)–Sb(3) = 2.873(8), Sb(2)–Ni(1) = 2.59(1), Sb(2)–Ni(2) = 2.50(1), Sb(3)–Sb(4) = 2.915(8), Sb(3)–Sb(6) = 2.842(8), Sb(3)–Ni(2) = 2.62(1), Sb(4)–Sb(5) = 2.846(8), Sb(4)–Sb(7) = 2.935(8), Sb(4)–Ni(2) = 2.51(1), Sb(5)–Sb(6) = 2.810(8), Sb(5)–Sb(7) = 2.977(8), Sb(5)–Ni(3) = 2.51(1), Sb(6)–Ni(3) = 2.71(1), Sb(7)–Ni(1) = 2.54(1), Sb(7)–Ni(2) = 2.65(1), Sb(7)–Ni(3) = 2.61(1), Ni(1)–Ni(2) = 2.79(1), Ni(1)–Ni(3) = 2.68(1), Ni(1)–C(1) = 1.54(7), Ni(2)–C(2) = 1.76(7), Ni(3)–C(3) = 1.62(7).

The structure of $[K(2,2,2\text{-crypt})^+]_3[Sb_7Ni_3(CO)_3]^{3-}\cdot$en was determined by single-crystal X-ray diffraction.[10] The ORTEP drawing of **2** shown in Figure 1 reveals a virtual mirror plane defined by Ni(1), Sb(7), and C(1). The three $[K(2,2,2\text{-crypt})]^+$ ions are well separated from the anion; two are well-behaved crystallographically and one is partially disordered. The en solvate molecule was not located in the X-ray analysis, presumably due to a disorder problem.[3,11]

(**2**) (**3**) (**4**)

The structure of **2** may be viewed as a 10-vertex *nido* cluster with virtual C_s point symmetry. The *nido* architecture is consistent with the 24 cluster electrons in the complex, which is a $2n + 4$ polyhedron according to Wade's rules.[6] However, the structure differs from the other known *nido* complexes (*e.g.*, $B_{10}H_{14}$, $C_2B_8H_{10}^{2-}$)[7,12] that have open six-membered rings [a *nido*-10(vi) structure (**3**)]. The structure of **2** contains two four-membered rings [a *nido*-10(iv+iv) structure][7] fused along a common edge defined by Sb(6)–Sb(3) [bold bond in structure **2**]. An alternative description of the structure involves a 24-electron $[Sb_7Ni(CO)]^{3-}$

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† University of Maryland.

‡ University of North Texas.

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(7) Second moment scaling calculations revealed a well-defined local minimum for the *nido*-10(iv+iv) structure type but was 6 eV less stable than the observed open *nido*-10(vi) structure for $C_2B_8H_{10}^{2-}$. See: Lee, S. *Inorg. Chem.* **1992,** *31,* 3063.

(8) 2,2,2-Crypt is an abbreviation for 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane.

(9) K_3Sb_7 was prepared by fusing a stoichiometric ratio of the elements at ~800 °C in a sealed silica ampule. In a drybox, K_3Sb_7 (88 mg, 0.091 mmol) and 2,2,2-crypt (100 mg, 0.27 mmol) were dissolved in en (~3 mL), forming a gray-brown slurry. In a second vial, $Ni(CO)_2(PPh_3)_2$ (56 mg, 0.088 mmol) was dissolved in warm toluene (~1 mL, 40 °C), producing a light green solution. The toluene solution was added dropwise to the en solution at room temperature, which yielded a red-brown solution. The mixture was stirred for 4 h, concentrated *in vacuo*, and filtered. After 24 h at room temperature, dark red-brown crystals were isolated, washed with toluene, and dried *in vacuo* (crystalline yield, 10.1 mg, 14%). Anal. Calcd for $C_{59}H_{116}N_8O_{21}K_3Ni_3Sb_7$: C, 29.29; H, 4.83; N, 4.63; Ni, 7.28. Found: C, 29.38; H, 5.00; N, 5.23; Ni, 6.39. Formulation includes 1 en solvate molecule.

(10) Crystallographic data for $[K(2,2,2\text{-crypt})^+]_3[Sb_7Ni_3(CO)_3]^{3-}\cdot$en: dark red-brown blocks, monoclinic space group $P2_1/n$; $a = 15.169(2)$, $b = 33.608(4)$, and $c = 18.495(1)$ Å, $\beta = 92.862(7)°$, $V = 9417(2)$ Å^3; $Z = 4$, $d_{calcd} = 1.664$ g/cm^3, μ(Mo Kα) = 27.66 cm^{-1}; empirical absorption correction was applied (ψ scans) with max/min transmission factors of 1.09/0.82. Of the 9722 reflections measured (Enraf–Nonius CAD-4, ambient temperature) using ω-scans, 9207 were independent ($R_{merge} = 0.045$), and 2611 having $I \geq 3\sigma(I)$ were used in the solution and refinement of the structure (SHELX-76). The final refinements were carried out in blocks with the Ni and Sb atoms anisotropic and C, N, and O atoms isotropic. The CO ligands and cryptands were given idealized geometries initially which were restrained during refinement. The final residuals were $R = 8.67\%$, $R_w = 9.70\%$, and $S = 1.84$. The largest peak in the final difference map of 1.57 e$^-$/Å^3 was located near an Sb atom.

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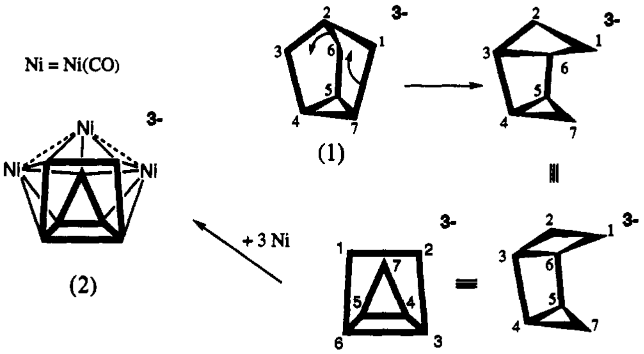
cuneane[13] core (**4**) with an Sb(7)–Ni(1) blade edge. This cuneane core is electron-precise with 12 two-center, two-electron bonds. Two additional Ni(CO) fragments then cap the open faces in **4** to generate **2**.

The Sb–Sb bonds between the four-coordinate Sb atoms in **2** range between 2.810(8) and 2.917(8) Å with longer contacts to the five-coordinate Sb(7) [Sb(7)–Sb(5) = 2.977(8), Sb(7)–Sb(4) = 2.935(8) Å]. These contacts are longer on average than the bonds between two- and three-coordinate Sb atoms in the parent Sb_7^{3-} ion (2.693(4) – 2.880(4) Å)[14] and related $[Sb_7M(CO)_3]^{3-}$ complexes [2.706(2)–2.722(2) Å] where M = Cr, W.[4] The Ni(1)–Ni(3) and Ni(1)–Ni(2) contacts in **2** are 2.68(1) and 2.79(1) Å, respectively, which are similar to the distances found for the intrapentagonal Ni–Ni contacts in $[Ni_{10}(SbPh)_2(CO)_{18}]^{2-}$ (2.680(2)–2.908(4) Å)[15] and related compounds.[16,17] The Ni–Sb contacts in **2**, which range from 2.50(1) to 2.71(1) Å, are also similar to the Ni–Sb bonds in $[Ni_{10}(SbPh)_2(CO)_{18}]^{2-}$ (2.531(2)–2.581(1) Å)[15] and the noninterstitial Ni–Sb contacts in $[Ni_{13}Sb_2(CO)_{24}]^{n-}$ where *n* = 2,3 (2.522(1)–2.770(1) Å).[17]

The formation of **2** from Sb_7^{3-} (**1**) may involve an $[Sb_7Ni(CO)]^{3-}$ intermediate which is electronically equivalent to the structurally characterized $Sb_7M(CO)_3^{3-}$ complexes where M = Cr, Mo, W.[4,18] Formation of **2** from **1** can be accomplished by breaking the bonds between Sb(1)–Sb(7) and Sb(6)–Sb(2), making bonds between Sb(6)–Sb(3) and Sb(6)–Sb(1), and adding three Ni(CO) fragments, as shown in Scheme I. The exact mechanism of this transformation is not known.

Scheme I



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Supplementary Material Available: Complete listings of crystallographic data, bond distances and angles, fractional coordinates, and anisotropic thermal parameters (21 pages); calculated and observed structure factor tables (30 pages). Ordering information is given on any current masthead page.

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