Heteroatomic Deltahedral Clusters: Synthesis and Structures of *closo*-[Bi₃Ni₄(CO)₆]³⁻, *closo*-[Bi₄Ni₄(CO)₆]²⁻, the Open Cluster [Bi₃Ni₆(CO)₉]³⁻, and the Intermetalloid *closo*-[Niₓ@{Bi₆Ni₆(CO)₈}]⁴⁻

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Abstract: Reactions of ethylenediamine solutions of K_4Bi_5 with $Ni(PPh_3)_2(CO)_2$ yielded four novel hetero-atomic Bi/Ni deltahedral clusters. Three of them, the 7-atom pentagonal bipyramidal $[Bi_3Ni_4(CO)_6]^{3-}$, the 8-atom dodecahedral $[Bi_4Ni_4(CO)_6]^{2-}$, and the Ni-centered or empty 12-atom icosahedral $[Ni_x@\{Bi_6Ni_6(CO)_8\}]^{4-}$, are *closo*-species according to both electron count and shape. The centered icosahedral cluster resembles packing in intermetallic compounds and belongs to the emerging class of *intermetalloid* clusters. The shape of the fourth cluster, $[Bi_3Ni_6(CO)_9]^{3-}$, can be derived from the icosahedral Ni-centered $[Ni@\{Bi_6Ni_6(CO)_8\}]^{4-}$ by removal of three Bi- and one Ni-atoms of two neighboring triangular faces. The clusters were structurally characterized by single-crystal X-ray diffraction in compounds with potassium cations sequestered by 2,2,2-crypt or 18-crown-6 ether. They were also characterized in solution by electrospray mass spectrometry.

Introduction

Heavy main-group elements in negative oxidation states are fascinating species with novel and often unexpected chemical behavior, bonding, and reactivity. Yet to date, the studies carried out in this area of chemistry have been very limited, and the findings are scattered and incomplete. One specific group of species that have attracted much attention in recent years are the nine-atom deltahedral Zintl anions of group 14, $E_9{}^{n-}$ for E = Si, Ge, Sn, Pb and $n = 2, 3, 4$.[1] It has been shown that some of them, particularly those of germanium, can participate in a variety of reactions that lead to their oligomerization,[2−9] polymerization,[10−12] functionalization with a number of main-group organometallic fragments and purely organic ligands,[13−16] centering by transition-metal atoms,[17−26] and capping of trian-

gular or square faces by ligated transition-metal atoms.[24−28] The existence and relative stability of these clusters, including $E_9{}^{4-}$ in the solid-state precursors A_4E_9 and $A_{12}E_{17}$ (A = alkali metal),[29] raised the question as to whether there were similar clusters involving elements of other groups. Such explorations led to the discovery of the heteroatomic species $[In_4Bi_5]^{3-}$ (isoelectronic with $E_9{}^{4-}$) crystallized from ethylenediamine solutions of precursors with the general formula $A_xIn_yBi_z$.[30] Another heteroatomic cluster that was isolated from these

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solutions was tetrahedral $[InBi_3]^{2-}$ isoelectronic and isostructural with P_4 molecules and with the anions E_4^{4-} in the intermetallic compounds A_4E_4.[30a] The most interesting result from these studies, however, was the synthesis of the diatomic dianionic molecule Bi_2^{2-} in $[K-(2,2,2-crypt)]_2Bi_2$ (2,2,2-crypt stands for 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]-hexacosane).[31] The two bismuth atoms are bonded by a double bond, i.e., $[Bi=Bi]^{2-}$ with a distance of 2.838 Å, and the anion is isoelectronic with molecular oxygen. This is only the second anionic species of bismuth characterized in addition to the long-known squares of Bi_4^{2-}, which can be viewed as the product of the oxidative coupling of two Bi_2^{2-} molecules (a pseudo-oxidative cyclization).[32] The same diatomic dianion was later isolated from solutions of more rational precursors such as the newly discovered compounds A_3Bi_2 and A_5Bi_4.[33] The former contains the same Bi_2^{2-} species while the latter exhibits isolated and flat zigzag tetramers of Bi_4^{4-} (A_5Sb_4 and A_5As_4 also exist and are isostructural with A_5Bi_4).[33] Both compounds have an extra cation each, and the additional electron is delocalized over the whole structure making the compounds metallic.

The fact that Bi_2^{2-} molecules can be crystallized even from solutions of A_5Bi_4[33b] combined with the proposed but structurally unconfirmed existence of Bi_3^{3-}, Sb_3^{3-}, and As_3^{3-} in solutions[34] and with the structurally characterized rings of Sb_5^{5-} in compounds crystallized from liquid ammonia[35] suggests that, upon dissolution, the oligomers in A_3Bi_2 and A_5Bi_4 can fragment and recombine to form both shorter and longer species. This was later confirmed by the isolation of the ozone (and allyl) analogue Bi_3^{3-} as a part of the heteroatomic *closo*-clusters $[Bi_3M_2(CO)_6]^{3-}$ (M = Cr, Mo) which are trigonal bipyramids with two equatorial transition-metal atoms.[36] These anions were made by reacting ethylenediamine solutions of K_5Bi_4 with the corresponding arene complexes $ArM(CO)_3$ (Ar = mesitylene, cycloheptatriene). The idea for exploring such reactions came from the successful attachment of the same $M(CO)_3$ fragments to nine-atom clusters of group 14 which resulted in the synthesis of $[E_9M(CO)_3]^{4-}$ for E = Sn, Pb and M = Cr, Mo, W.[27] Similarly, the successful attachment of ZnPh-fragments to the same clusters to form $[E_9Zn-Ph]^{3-}$ for E = Si, Ge, Sn, and Pb[28] inspired reactions of K_5Bi_4 solutions with $ZnPh_2$. These led to the novel heteroatomic cluster $[Zn@(Bi_4Zn_8)Bi_7]^{5-}$, a Zn-centered icosahedron made of four Bi- and eight Zn-atoms that has seven faces capped by an additional seven Bi-atoms.[37] Further expansion on the concept of exploring analogous reactions of successful group 14 experiments lead us to study the reaction of K_5Bi_4 solutions with $Ni(PPh_3)_2(CO)_2$ after the successful addition of Ni(CO) to Ge_9-clusters.[26] Herein we report the synthesis and structures of four Bi–Ni heteroatomic clusters $[Bi_3Ni_4(CO)_6]^{3-}$ (**1**), $[Bi_4Ni_4(CO)_6]^{2-}$ (**2**), $[Ni_x@\{Bi_6Ni_6(CO)_8\}]^{4-}$ (**3**), and $[Bi_3Ni_6(CO)_9]^{3-}$ (**4**) as well as one Sb–Ni cluster, $[Sb_3Ni_4(CO)_6]^{3-}$ (**1a**) isostructural with **1**, that were discovered during these studies

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Experimental Section

All reactions and compounds were handled under argon or nitrogen using standard Schlenk-line and glovebox techniques. Ethylenediamine (Alfa-Aesar, 99%) was distilled over sodium metal and stored in a gastight ampule under nitrogen in the glovebox. Pyridine (anhydrous, Acros, 99.0%) was used as received. The precursor compound K_5Bi_4 was synthesized from stoichiometric mixtures of the elements (K: Strem, 99+%; Bi: Alfa-Aesar, 99.998%) heated at 800 °C over a 2 day period in sealed niobium containers jacketed in evacuated fused silica tubes according to previously reported synthetic procedures.[33b] 2,2,2-crypt (Acros, 98%), 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane, Acros, 99%), and $Ni(PPh_3)_2(CO)_2$ (Strem, 98%) were used as received after carefully drying them under vacuum.

Synthesis of [K-(2,2,2-crypt)]$_3$1·en·tol. K_5Bi_4 (50 mg, 0.049 mmol) and 2,2,2-crypt (104 mg, 0.276 mmol) were dissolved in approximately 2 mL of ethylenediamine in a test tube yielding a dark greenish-blue solution. $Ni(PPh_3)_2(CO)_2$ (132 mg, 0.206 mmol) was added to this solution, and the mixture was allowed to stir for approximately 2 h. The resulting dark reddish-brown solution was filtered, the filtrate was layered with toluene, and the test tube was left undisturbed to allow for crystallization. Dark red platelike crystals were obtained after 2 days (22% crystalline yield). IR (en, cm^{-1}): 1998, 1937, 1905, 1871 (ν_{CO}). ES-MS: *m/z* 973 $[Bi_3Ni_4(CO)_4]^-$, 1001 $[Bi_3Ni_4(CO)_5]^-$, 1029 $[Bi_3Ni_4(CO)_6]^-$, 1041 $\{(K^+)([Bi_3Ni_4(CO)_5]^{2-})\}^-$, 1068 $\{(K^+)([Bi_3Ni_4(CO)_6]^{2-})\}^-$, 1417 $\{(K^+\text{-crypt})([Bi_3Ni_4(CO)_5]^{2-})\}^-$, 1444 $\{(K^+\text{-crypt})([Bi_3Ni_4(CO)_6]^{2-})\}^-$. The isostructural compound [K-(2,2,2-crypt)]$_3$-(**1a**)·en·tol was synthesized by an analogous procedure using K_5Sb_4 instead of K_5Bi_4 (the two precursors are isostructural).[33]

Synthesis of [K-(2,2,2-crypt)]$_2$2·0.5tol. A crystalline sample of [K-(2,2,2-crypt)]$_3$1·en·tol (45 mg, 0.018 mmol) was dissolved in a test tube with pyridine (1 mL) yielding a dark reddish-black solution. The solution was filtered to remove any impurities and was subsequently layered with toluene to allow for crystallization. Small black, blocklike crystals were isolated after 1 week (37% crystalline yield). IR (nujol, cm^{-1}) 1902, 1855 (ν_{CO}). ES-MS: *m/z* 1182 $[Bi_4Ni_4(CO)_4]^-$, 1210 $[Bi_4Ni_4(CO)_5]^-$, 1625 $\{(K^+\text{-crypt})([Bi_4Ni_4(CO)_5]^{2-})\}^-$, 1653 $\{(K^+\text{-crypt})([Bi_4Ni_4(CO)_6]^{2-})\}^-$.

Synthesis of [K-(18-crown-6)]$_4$3·3en and [(K-18-crown-6)]$_3$4·en· 0.5tol. K_5Bi_4 (102 mg, 0.099 mmol) and 18-crown-6 (134 mg, 0.507 mmol) were dissolved in approximately 2 mL of ethylenediamine in a test tube yielding a dark greenish-blue solution. $Ni(PPh_3)_2(CO)_2$ (63 mg, 0.099 mmol) was added to this solution, and the mixture was allowed to stir for approximately 2 h. The dark brownish-black suspension was filtered, and the resulting filtrate was layered with toluene to allow for crystallization. Black crystalline needles of [(K-18-crown-6)]$_3$4·en·0.5tol were obtained after a week (34% crystalline yield). IR (nujol, cm^{-1}) 1940, 1905, 1883 (ν_{CO}). ES-MS: *m/z* 1091 $[Bi_3Ni_6(CO)_4]^-$, 1119 $[Bi_3Ni_6(CO)_5]^-$, 1147 $[Bi_3Ni_6(CO)_6]^-$, 1175 $[Bi_3Ni_6(CO)_7]^-$, 1203 $[Bi_3Ni_6(CO)_8]^-$, 1214 $\{(K^+)([Bi_3Ni_6(CO)_7]^{2-})\}^-$, 1242 $\{(K^+)([Bi_3Ni_6(CO)_8]^{2-})\}^-$, 1270 $\{(K^+)([Bi_3Ni_6(CO)_9]^{2-})\}^-$, 1309 $\{(K^+)_2([Bi_3Ni_6(CO)_9]^{3-})\}^-$, 1534 $\{(K^+\text{-crown})(Bi_3Ni_6(CO)_9]^{2-})\}^-$. A few black rods of [K-(18-crown-6)]$_4$3·3en were recovered as a minor side product of this reaction. All attempts to improve the yield of the compound were unsuccessful, but reproducible outcomes yielding [K-(18-crown-6)]$_4$3·3en and (K-18-crown-6)$_3$4·en·0.5tol in similar ratios resulted. ES-MS: *m/z* 1812 $\{(K^+)([Bi_6Ni_6(CO)_6]^{2-})\}^-$, 1898 $\{(K^+)-([Ni@Bi_6Ni_6(CO)_7]^{2-})\}^-$, 1926 $\{(K^+)([Ni@Bi_6Ni_6(CO)_8]^{2-})\}^-$, 2021 $\{(K^+\text{-crown})([Bi_6Ni_6(CO)_4]^{2-})\}^-$.

Mass Spectrometry. Electrospray mass spectra (ES-MS) in negative-ion mode were recorded on a Micromass Quattro-LC triple quadrupole mass spectrometer (100 °C source temperature, 125 °C desolvation temperature, 2.0–2.8 kV capillary voltage, 25–30 V cone voltage). Crystals of each compound were dissolved in DMF, and the solutions were introduced into the spectrometer by direct infusion with a Harvard syringe pump at 10 μL/min.

Table 1. Selected Data Collection and Refinement Parameters for [K-(2,2,2-crypt)]$_3$**1**·en·tol, [K-(2,2,2-crypt)]$_3$(**1a**)·en·tol, [K-(2,2,2-crypt)]$_2$**2**·0.5tol, [K-(18-crown-6)]$_4$**3**·3en, and [K-(18-crown-6)]$_3$**4**·en·0.5tol

chemical formula	[K-(2,2,2-crypt)]$_3$ **1**·en·tol	[K-(2,2,2-crypt)]$_3$ **1a**·en·tol	[K-(2,2,2-crypt)]$_2$ **2**·0.5tol	[K-(18-crown-6)]$_4$ **3**·3en	[K-(18-crown-6)]$_3$ **4**·en·0.5tol
formula weight	2428.84	2167.15	2131.06	3243.55	2247.70
space group, Z	$P2_1/c$, 4	$P2_1/c$, 4	$P2_1/n$, 8	$P\bar{1}$, 1	$P\bar{1}$, 2
a (Å)	21.0795(6)	21.0938(8)	11.7566(18)	13.7111(3)	12.4407(7)
b (Å)	18.9497(5)	18.9442(7)	48.054(7)	14.3075(4)	12.7175(7)
c (Å)	22.5312(5)	22.6611(8)	22.508(3)	15.4124(6)	22.9792(13)
α (deg)				111.699(2)	86.716(2)
β (deg)	99.782(2)	99.628(1)	90.448(2)	91.646(2)	89.544(2)
γ (deg)				118.149(1)	82.269(2)
V (Å^3)	8869.2(4)	8927.9(6)	12715(3)	2399.6(1)	3596.7(3)
radiation, λ (Å)			Mo Kα, 0.710 73		
ρ_{calcd} (g·cm^{-3})	1.819	1.612	2.211	2.245	2.075
μ (mm^{-1})	6.974	1.931	6.192	12.413	9.093
R1/wR2,^{a} $I \geq 2\sigma_I$ (%)	6.70/17.84	6.46/16.67	4.55/9.70	4.64/11.41	5.60/11.20
R1/wR2,^{a} all data (%)	9.84/19.52	11.28/19.27	6.01/10.05	6.27/11.96	10.38/12.29

^{a} R1 = $[\Sigma||F_o| - |F_c||]/\Sigma|F_o|$; wR2 = $\{[\Sigma w[(F_o)^2 - (F_c)^2]^2]/[\Sigma w(F_o^2)^2]\}^{1/2}$; $w = [\sigma^2(F_o)^2 + (AP)^2 + BP]^{-1}$, where $P = [(F_o)^2 + 2(F_c)^2]/3$.

Structure Determination. X-ray diffraction data sets of single crystals of [K-(2,2,2-crypt)]$_3$**1**·en·tol, [K-(2,2,2-crypt)]$_3$(**1a**)·en·tol, [K-(2,2,2-crypt)]$_2$**2**·0.5tol, [K-(18-crown-6)]$_4$**3**·3en, and [K-(18-crown-6)]$_4$**4**·en·0.5tol were collected at 100 K on Bruker D8 and X8 diffractometers equipped with APEX-II CCD area detectors using graphite-monochromated Mo Kα radiation. The single crystals were selected under Paratone-N oil, mounted on fibers, and positioned in the cold streams of the diffractometers. The structures were solved by direct methods and refined on F^2 using the SHELXTL V6.21 package.[38] Details of the data collections and refinements are given in Table 1.

Electronic-Structure Calculations. Single-point DFT calculations were carried out on the clusters in order to assess their stability. The calculations employed the Becke three-parameter density functional with the Lee−Yang−Parr correlation (B3LYP) in conjunction with the LanL2DZ basis set[39] and were performed with the Gaussian 98 package, revision A.11.3.[40] The calculated HOMO−LUMO gaps of 1.79, 2.42, 1.54, 2.24, and 2.46 eV for **1**, **1a**, **2**, Ni-centered **3**, empty **3**, and **4**, respectively, confirmed the stability of the clusters.

Results and Discussion

Synthesis. The general synthetic procedure for these and other similar bismuth-based clusters begins with dissolving the intermetallic precursor in ethylenediamine in the presence of a sequestering agent. These solutions are reacted with different amounts of a transition-metal complex and are then layered with toluene for crystallization. Often different species are formed from these reactions (according to mass spectra), but depending on the sequestering agent, only one type is usually crystallized (as with **1** and **4**). The resulting crystalline compounds can be redissolved in a variety of different solvents such as DMF or pyridine. On numerous occasions we have found that certain solvents such as pyridine play a nontrivial role and can further oxidize the clusters present in solution as observed in the formation of **2**. Also, prolonged stirring sometimes leads to inadvertent oxidation and similarly oxidized species (as with **3** found in small amounts cocrystallized with **4**).

The overall oxidation state of each bismuth atom in K$_5$Bi$_4$ is more negative than 1− (assuming complete electron transfer from the potassium atoms) and, therefore, the isolated zigzag tetramers in this precursor have a charge of at least 4−, i.e., Bi$_4^{4-}$. Upon dissolution these tetramers may fragment and rearrange into smaller or larger oligomers, but in the absence of solvent reduction and excessive electron solvation, the overall charge per bismuth atom will remain 1−, i.e., Bi$_n^{n-}$ such as Bi$_2^{2-}$, Bi$_3^{3-}$, Bi$_5^{5-}$, etc., in addition to Bi$_4^{4-}$ (confirmed by the crystallization of Bi$_2^{2-}$ from such solutions[33b]). When reacted with transition-metal complexes, some of these negatively charged oligomers may have the appropriate shape and electron count necessary to replace one or more ligands of the complex or, conversely, to coordinate to one or more metal centers. Thus, the formation of **1** can be represented as

$$Bi_3{}^{3-} + 4Ni(PPh_3)_2(CO)_2 \rightarrow$$
$$[Bi_3Ni_4(CO)_6]^{3-} \ (\mathbf{1}) + 8PPh_3 + 2CO \ (1)$$
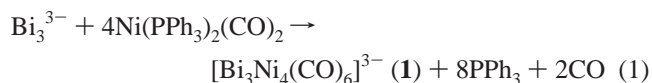
The fact that the same anion forms for antimony, [Sb$_3$Ni$_4$(CO)$_6$]$^{3-}$ (**1a**), suggests that similar small chainlike oligomers Sb$_n^{n-}$ may exist in solutions of K$_5$Sb$_4$. This is supported by the structurally characterized cyclic Sb$_5^{5-}$ in Li$_5$Sb$_5$·16NH$_3$ crystallized from liquid ammonia solution of lithium reacted with elemental antimony.[35] Nonetheless, it seems that for Sb and As the well-known species Sb$_7^{3-}$ and As$_7^{3-}$ are so thermodynamically stable that more reduced oligomers quickly convert to them making it very difficult to isolate said species.

The synthetic procedure used for the isolation of [Ni@{Bi$_6$Ni$_6$(CO)$_8$}]$^{4-}$ (**3**) and [{Bi$_3$Ni$_6$(CO)$_9$}]$^{3-}$ (**4**) is essentially the same as that for **1** except for the agent used to sequester the potassium cations. While 2,2,2-crypt envelops the cations completely and prevents any cation−anion interactions, 18-crown-6 typically caps the cations on one side and leaves a hemisphere available for additional interactions. Although only electrostatic in nature, such interactions are often vital in the stabilization and/or crystallization of particular anionic species. A good example is the stabilization of a tetramer of Ge$_9$-clusters, [(Ge$_9$)$_4$]$^{8-}$, by cation−anion interactions in [Rb-(18-crown-6)]$_8$-(Ge$_9$)$_4$·2en but only a trimer of [(Ge$_9$)$_3$]$^{6-}$ when 2,2,2-crypt is used.[3,4] Similarly, the reactions between Bi-oligomers and Ni(PPh$_3$)$_2$(CO)$_2$ produce the larger clusters **3** and **4** when 2,2,2-

(38) Sheldrick, G. M. *SHELXTL*, version 6.21; Burker-Nonius AXS: Madison, WI, 2001.
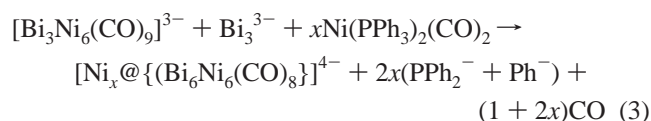(39) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev.* **1988**, *B37*, 785. (c) Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. *Chem. Phys. Lett.* **1989**, *157*, 200. (d) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270. (e) Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 284. (f) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.
(40) Frisch, M. J., et al. *Gaussian98*, revision A.11.3; Gaussian, Inc.: Pittsburgh, PA, 2002.

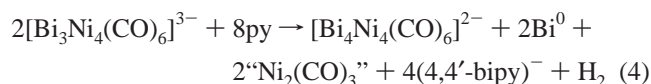crypt is replaced with 18-crown-6 as a sequestering agent. The formation of **4** can be represented as

$$Bi_3^{3-} + 6Ni(PPh_3)_2(CO)_2 \rightarrow$$
$$[Bi_3Ni_6(CO)_9]^{3-} (\mathbf{4}) + 12PPh_3 + 3CO \quad (2)$$
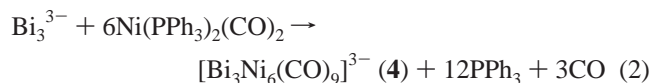
The minor product of $[Ni_x@\{(Bi_6Ni_6(CO)_8)\}]^{4-}$ is obviously the result of some oxidation process (0.67− per Bi-atom in **3** compared to 1− per Bi-atom in **4**), perhaps similar to the one proposed for the formation of **2** from **1** in pyridine (below) but with the difference that it occurs in ethylenediamine and in the presence of 18-crown-6 instead. One possible oxidizing agent is the PPh_3 released from the Ni-reagent. We have shown previously that in warm solutions (50−80 °C) anionic clusters, Ge_9^{4-} for example, can be oxidized by PPh_3, forming PPh_2^- and Ph^- with the latter quickly abstracting a proton from the ethylenediamine to form benzene.[2,14] A possible reaction could be the following:

$$[Bi_3Ni_6(CO)_9]^{3-} + Bi_3^{3-} + xNi(PPh_3)_2(CO)_2 \rightarrow$$
$$[Ni_x@\{(Bi_6Ni_6(CO)_8)\}]^{4-} + 2x(PPh_2^- + Ph^-) +$$
$$(1 + 2x)CO \quad (3)$$

Unfortunately in this case the temperature cannot be raised because CO will be lost at temperatures above 40 °C.[24]

Cluster **2**, $[Bi_4Ni_4(CO)_6]^{2-}$, has an average charge of 0.5− per bismuth atom. It was obtained by dissolving in pyridine the crystalline compound containing cluster **1**, $[Bi_3Ni_4(CO)_6]^{3-}$, which has an average charge of 1− per bismuth atom. Obviously, the process involves oxidation of **1**, and the oxidizing agent is most likely the solvent which, in turn, is reduced to form 4,4′-bipyridine anion and dihydrogen, i.e., $2C_5H_5N + e^- \rightarrow [NC_4H_4C−CC_4H)_4N]^- + H_2$. We have isolated and structurally characterized this radical anion in numerous occasions, as both $[A-(2,2,2-crypt)]^+$ and $[A-(18-crown-6)]^+$ salts.[41] (Surprisingly, the structure of the anion has never been reported before, although its metrics have been calculated by various *ab initio* computational approaches.[42]) At this stage, it is not clear how the oxidation of **1** proceeds and what other products may be formed. The overall reaction, however, can be written as follows:

$$2[Bi_3Ni_4(CO)_6]^{3-} + 8py \rightarrow [Bi_4Ni_4(CO)_6]^{2-} + 2Bi^0 +$$
$$2\text{"}Ni_2(CO)_3\text{"} + 4(4,4'-bipy)^- + H_2 \quad (4)$$

The conversion of some bismuth to elemental form is often observed either as a precipitate or as a metallic mirror plating the walls of the test tube. The "$Ni_2(CO)_3$" fragments are perhaps solvated by pyridine or fall apart to other species.

Electron Counting Methodology. Before discussing the specifics of each cluster, it will be helpful to briefly review the approaches to electron counting and the Wade−Mingos rules for electron counts in deltahedral clusters. According to these rules a *closo*-deltahedron, i.e., a cluster with triangular faces and no missing vertices, requires a total of $4n + 2$ **c**luster

valence **e**lectrons (cve).[43] Of these, $2n + 2$ are considered necessary for the bonding within the cluster, i.e., they are **c**luster **b**onding **e**lectrons (cbe), while the remaining $2n$ are electrons for exo-bonds and/or lone pairs. The elements of the nickel group behave as main-group elements with zero valence electrons in these and other similar negatively charged heteroatomic clusters.[17−26] Their closed-shell d^{10} configurations behave as a core because the d orbitals are much lower in energy than the s and p orbitals of the participating negatively charged main-group elements such as bismuth or antimony in this case. A carbonyl ligand contributes a pair of electrons while each bismuth and antimony atom provides five electrons.

An alternative electron counting approach focuses on the cluster bonding electrons (cbe) alone. It usually works well for main-group clusters with covalent exo-bonds such as the boranes and the carboranes where the molecular orbitals of the exo-bonds are lower in energy and well separated from the cluster-bonding molecular orbitals. The approach is less applicable for clusters with naked main-group and/or ligated transition-metal atoms because the corresponding lone-pair and ligand-based molecular orbitals are often intermixed with the cluster-bonding molecular orbitals and cannot be clearly assigned as such. Furthermore, following this methodology, the transition-metal fragments need to be converted to their isolobal main-group analogues in order to determine the numbers of electrons contributed for cluster bonding. Thus, using $Ni(CO)_4$ as a tetrahedral 18-electron complex isolobal with CH_4, it is easy to see that the NiCO and $Ni(CO)_2$ fragments are isolobal with CH^{3+} and CH_2^{2+}, respectively, and contribute correspondingly zero and two cbe. Also, in this approach, a bismuth atom provides 3 cbe while its remaining two valence electrons are used for a lone pair pointing radially away from the clusters.

Structures and Electron Counts. $[K-(2,2,2-crypt)]_3\mathbf{1}\cdot en\cdot tol$ and $[K-(2,2,2-crypt)]_3(\mathbf{1a})\cdot en\cdot tol$ are isostructural and contain pentagonal bipyramidal clusters (Figure 1) disordered among two orientations (figures in Supporting Information). This shape corresponds to a classical *closo*-deltahedron. Compared to the recently reported trigonal bipyramidal $[Bi_3M_2(CO)_6]^{3-}$ (Figure 2) for M = Cr (**5a**), Mo (**5b**) synthesized by a similar reaction of Bi-oligomers and $ArM(CO)_3$,[36] this cluster has two more transition-metal vertices inserted in the equatorial plane. Both clusters, however, exhibit the same bent bismuth trimers with a charge of 3−, Bi_3^{3-}, and in both cases the two end atoms of the trimer serve as the axial apexes of the bipyramids. The Bi−Bi distances in **1**, 3.071(3) and 3.039(1) Å (2.979(3) and 3.010(1) Å for the second orientation), are somewhat longer than those in the trigonal bipyramid, 2.956(1) and 2.954(1) Å for **5a** and 2.992(1) and 3.005(1) Å for **5b**. This is quite reasonable considering that (a) there are more Bi−Ni interactions in **1** than Bi−Cr and Bi−Mo interactions in **5a** and **5b**, respectively, and (b) the central ring of the pentagonal bipyramid is larger than that of the trigonal bipyramid. Another effect of the latter is the much smaller Bi−Bi−Bi angle in **1**, 75.32(5)° (75.17(6)° in the second orientation), compared to 92.5° and 96.5° for **5a** and **5b**, respectively. Capping a larger base, while keeping the same distances to the equatorial atoms as observed in a smaller-base pyramid, naturally brings the capping atom closer to the equatorial plane and, therefore, reduces the

(41) The structure of the compound [Na-(2,2,2-crypt)](4,4′-bipy) is provided as Supporting Information. The distances in the flat 4,4′-bipy radical anion are remarkably close to those derived from theoretical calculations.[42]

(42) (a) Ould-Moussa, L.; Poizat, O.; Castella-Ventura, M.; Buntinx, G.; Kassab, E. *J. Phys. Chem.* **1996**, *100*, 2072. (b) Castella-Ventura, M.; Kassab, E. *J. Raman Spectrosc.* **1998**, *29*, 511. (c) Kihara, H.; Gondo, Y. *J. Raman Spectrosc.* **1986**, *17*, 263.

(43) (a) Wade, K. J. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1. (b) Wade, K. *J. Chem. Soc. D* **1971**, 792. (c) Mingos, D. M. P. *Nat. Phys. Sci.* **1972**, *99*, 236. (d) Mingos, D. M. P. *Acc. Chem. Res.* **1984**, *17*, 311.
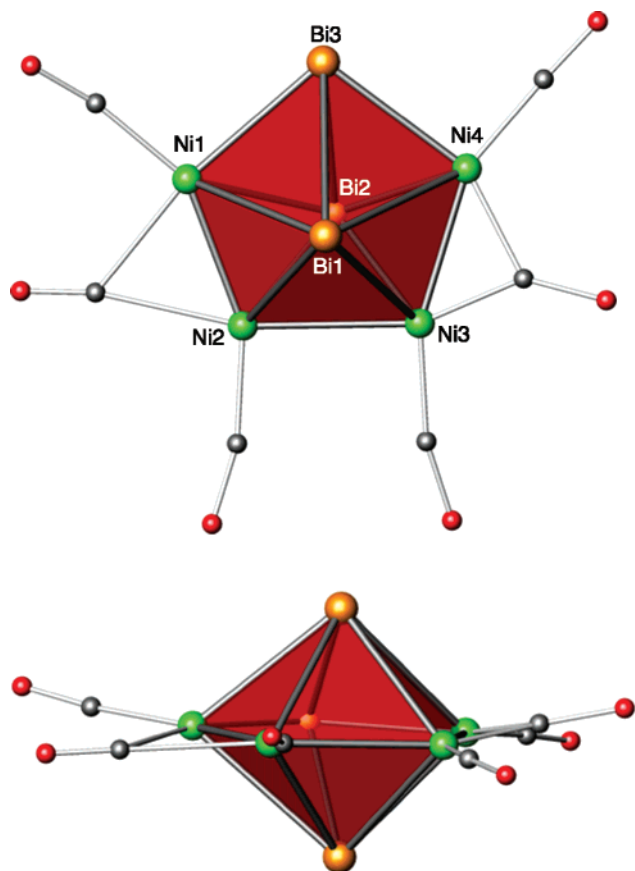
Figure 1. Two views of the pentagonal bipyramidal cluster **1**, $[Bi_3Ni_4(CO)_6]^{3-}$ (the Sb-analogue **1a** is isostructural).
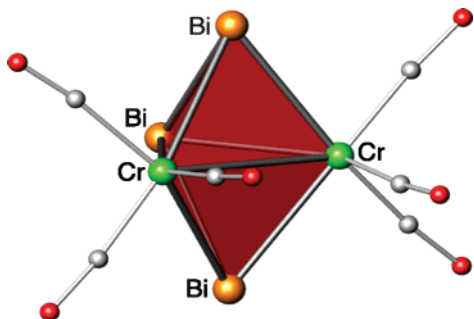

Figure 2. Trigonal bipyramidal cluster $[Bi_3M_2(CO)_6]^{3-}$ (M = Cr, Mo).[36]

$Bi_{ap}-Bi_{eq}-Bi_{ap}$ angle. This effect is also manifested by the much shorter distance between the apical Bi-atoms in **1**, 3.732 Å, compared to 4.287 Å in **5a**.

The four nickel atoms, each with a terminal carbonyl group, form two distinct pairs, and each pair is bridged by an additional carbonyl group, i.e., $2[(\mu\text{-CO})(NiCO)_2]$. Exactly the same CO-bridged pairs are also found in clusters **2** and **4**. The Ni–Ni distances within the pairs, 2.387(4) and 2.408(5) Å, are naturally shorter than the distance between them, 2.639(5) Å for Ni2–Ni3 (Figure 1). However, it is important to point out that these and all other distances in the clusters should be viewed in the context of being contacts between vertices in a cluster with delocalized bonding, and conclusions about their strength and/or bond order should not be drawn based solely on their lengths. The Ni–Bi distances at the equatorial bismuth atoms are shorter, 2.653(4) and 2.667(2) Å, compared to those at the
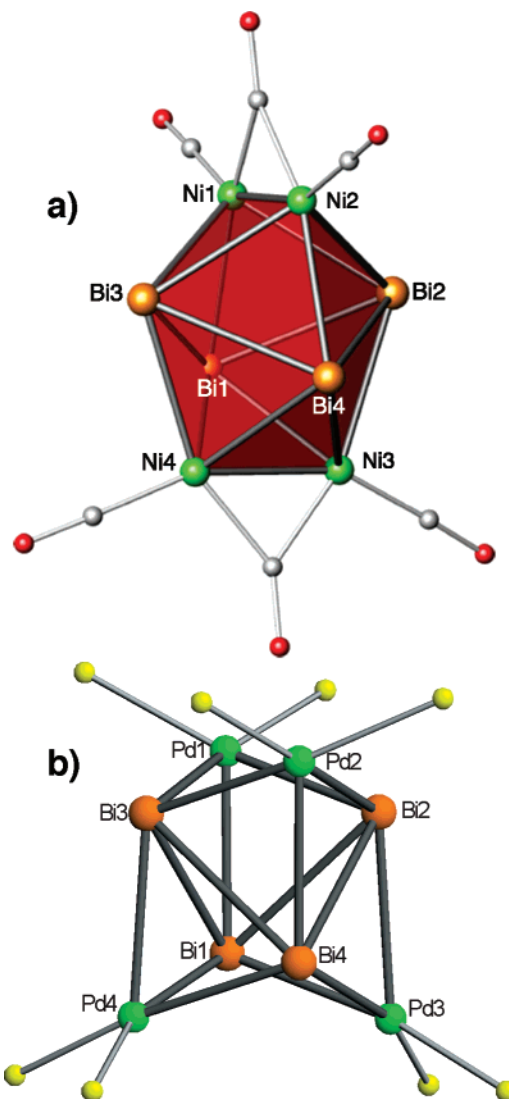

Figure 3. (a) Bisdisphenoidal cluster **2**, $[Bi_4Ni_4(CO)_6]^{2-}$, and (b) $[Bi_4Pd_4(PPh_2Me)_8]^{2+}$ isoelectronic with **2** but with long Pd–Pd distances.[47]

apical atoms, in the range 2.674(3)–2.939(3) Å, due to the lower coordination number of four for the former compared to five for the latter atoms.

Not only the shape of the clusters **1** and **1a** corresponds to a *closo*-deltahedron but also their electron count follows the Wade–Mingos rules for such species.[43] Thus, the cluster has a total of 3×5 (from 3 Bi-atoms) + 6×2 (from 6 CO-groups) + 3 (from the charge) = 30 cluster valence electrons which matches the number of electrons required for bonding in a *closo*-cluster of seven atoms, i.e., $4n + 2 = 30$ where $n = 7$. The available and required cluster bonding electrons in the cluster, 3×3 (from 3 Bi-atoms) + 2×0 (from 2 NiCO fragments) + 2×2 (from 2 $Ni(CO)_2$ fragments) + 3 (from the charge) = 16 and $2n + 2 = 16$ for $n = 7$, respectively, also match.

Cluster **2** (Figure 3a) was characterized in $[K\text{-}(2,2,2\text{-crypt})]_2\mathbf{2}\cdot$ 0.5tol. The structure of the compound contains two crystallographically distinct but otherwise identical clusters and is more properly written as $[K\text{-}(2,2,2\text{-crypt})]_4(\mathbf{2})_2\cdot$tol. This eight-vertex cluster has yet another classical *closo*-deltahedron geometry, that of a dodecahedron known also as a bisdisphenoid, and has the expected cbe and cve counts of $2n + 2 = 18$ and $4n + 2 = $

34, respectively, for a *closo*-cluster (cbe = 4×3 from Bi + 2×0 from 2 NiCO + 2×2 from 2 Ni(CO)$_2$ + 2 from the charge, cve = 4×5 from Bi + 6×2 from CO + 2 from the charge). The cluster exhibits the same pairs of CO-bridged NiCO fragments (Ni−Ni distances within 2.375(1)−2.384(1) Å) that are present in **1**, but the nickel fragments in **2** are well separated. The Bi−Bi and Bi−Ni distances are in the ranges 3.0759(6)− 3.1204(6) and 2.701(1)−2.806(1) Å, respectively.

The bisdisphenoid shape (idealized D_{2d} point-group symmetry) is relatively rare although it seems to tolerate a range of cluster-bonding electron counts. Thus, the classical *closo*-borane and -carborane B$_8$H$_8$$^{2-}$ and C$_2$B$_6$H$_8$ (Me$_2$C$_2$B$_6$H$_6$ in reality),[44] respectively, have the expected 18 cluster-bonding electrons. However, the metallaborane (Cp)$_4$Co$_4$B$_4$H$_4$ and the organometallic (Cp)$_4$Fe$_4$C$_4$H$_4$ are two electrons short for a total of 16 electrons.[45] (CoCp and FeCp are isolobal with BH and BH$^+$, respectively, and provide correspondingly two and one cluster-bonding electrons.) Finally, (Cp)$_4$Ni$_4$B$_4$H$_4$ is two electrons richer than expected and therefore carries 20 cluster-bonding electrons (NiCp is isolobal with CH and provides three electrons), but it also has the bisdisphenoidal shape.[46] At the same time, another species made of bismuth and palladium, [Bi$_4$Pd$_4$(PPh$_2$Me)$_8$]$^{2+}$, carries the "prescribed" 18 electrons as **2**, but its geometry does not correspond to that of the *closo*-deltahedron bisdisphenoid.[47] As shown in Figure 3b, this species is quite open with very long distances of 3.823 and 3.949 Å between the Pd-atoms compared with the Ni−Ni distances of 2.375 and 2.384 Å in **2**. In order to keep reasonable Pd−Bi distances, the four Bi-atoms in [Bi$_4$Pd$_4$(PPh$_2$Me)$_8$]$^{2+}$ are compressed into a shape that is very close to tetrahedral with Bi1−Bi4 and Bi2−Bi3 distances of 3.452 and 3.509 Å, respectively. These distances are much shorter than the distances between the same atoms in **2** (Figure 3a), 4.057 and 4.100 Å, respectively. It is not clear why the two isoelectronic clusters differ so severely in geometry. One possibility is the preference of palladium for square-planar coordination which is practically achieved in [Bi$_4$Pd$_4$-(PPh$_2$Me)$_8$]$^{2+}$ (Figure 3b). The Pd−Bi distances that are vertical in Figure 3b are longer by 0.2−0.3 Å than the remaining Pd−Bi distances, and without them, the Pd-coordination is exactly square-planar. Other possible reasons for the open shape are the bulkiness of the PPh$_2$Me ligands and the subsequent steric inability of the Pd-atoms to get closer to each other and/or the inability of the phosphine ligands to bridge two Pd metal centers.

Cluster **3**, [Ni$_x$@{Bi$_6$Ni$_6$(CO)$_8$}]$^{4-}$ crystallized with [K-(18-crown-6)]$^+$ countercations, is a 12-vertex *closo*-cluster with the shape of an icosahedron (Figure 4). The cluster has an inversion center, and subsequently, the three unique Bi- and three unique Ni-atoms generate six atoms of each kind. The six bismuth atoms form a cyclohexane-like unit in a chair conformation. The six nickel vertices are split into two groups of three forming two triangles that cap the Bi$_6$-hexagon on both sides. Each Ni-atom has a terminal carbonyl group, and each Ni$_3$-triangle is capped by an additional carbonyl group. The central Ni-atom
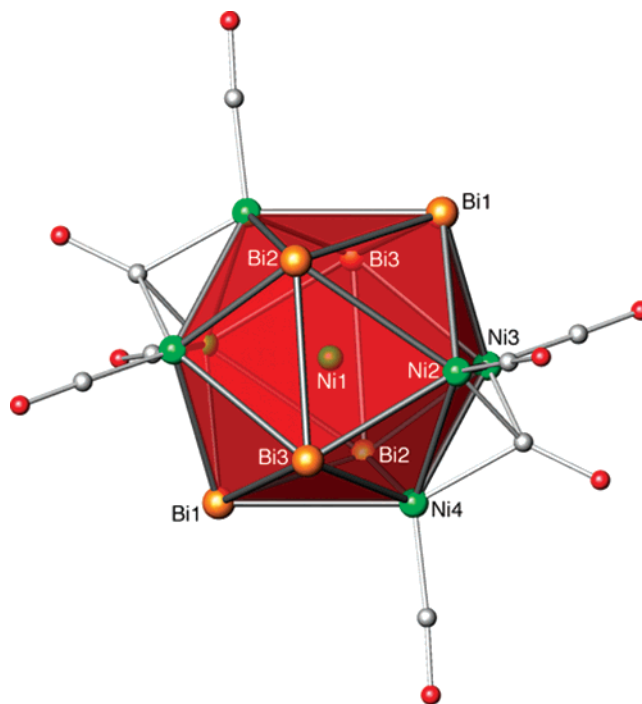
(44) (a) Guggenberger, L. J. *Inorg. Chem.* **1969**, *8*, 2771. (b) Hart, H.; Lipscomb, W. N. *Inorg. Chem.* **1968**, *7*, 1070.
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(46) Bowser, J. R.; Bonny, A.; Pipal, J. R.; Grimes, R. N. *J. Am. Chem. Soc.* **1979**, *101*, 6229.
(47) Stark, J. L.; Harms, B.; Guzman-Jimenez, I.; Whitmire, K. H.; Gautier, R.; Halet, J. F.; Saillard, J. Y. *J. Am. Chem. Soc.* **1999**, *121*, 4409.
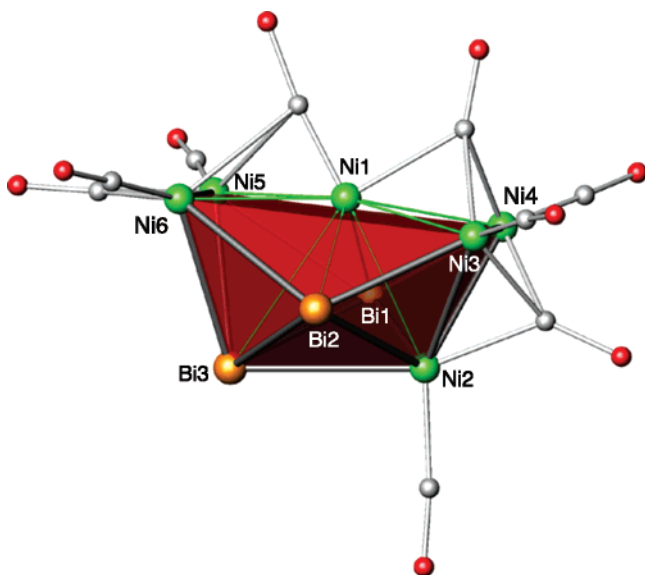
Figure 4. Structure of the icosahedral cluster **3**, [Ni$_x$@{Bi$_6$Ni$_6$(CO)$_8$}]$^{4-}$. The cluster has an inversion center at the central Ni-atom which refines with a partial occupancy of 33.4%.

was refined with a partial occupancy of 33.4(9) %. This means that about two-thirds of the icosahedra are empty [Bi$_6$Ni$_6$(CO)$_8$]$^{4-}$ while the remaining one-third is centered [Ni@{Bi$_6$Ni$_6$(CO)$_8$}]$^{4-}$. The presence of empty and Ni-centered icosahedra was confirmed by electrospray mass spectrometry (below). Similar observations were recently reported for the mass spectra of deltahedral lead clusters which show both empty [Pb$_{10}$]$^-$ (bicapped square antiprism) and [Pb$_{12}$]$^-$ (icosahedron) as well as their Ni-, Pd-, and Pt-centered species [Pd@Pb$_{10}$]$^-$, [Ni@Pb$_{10}$]$^-$, and [Pt@Pb$_{12}$]$^-$.[20] The central atom does not affect the electron count for the cluster because, as already discussed, such d^{10} elements do not contribute cluster-bonding electrons. Thus, independent of whether the cluster is centered or empty, it has $4n + 2 = 50$ total valence electrons provided by 6 Bi-atoms (5 electrons each), the 8 CO-groups (2 electrons each), and the charge (4 additional electrons) needed for a *closo*-cluster. In terms of cluster-bonding electrons the cluster also has the required $2n + 2 = 26$ electrons (6×3 from Bi + 2×0 from 4 NiCO fragments + 2×2 from 2 Ni(CO)$_2$ fragments + 4 from the charge) for such species with 12 vertices.

The presence or absence of the central Ni-atoms seems to be irrelevant also for the overall dimensions of the cluster, and none of the peripheral atoms showed either split positions or radially elongated thermal ellipsoids. This may be the result of a perfect fit of the central atom within the cavity of the empty cluster. The distances from the center of the cluster to the Bi and Ni atoms are in very narrow ranges of 2.7681(4)−2.7875-(4) and 2.525(1)−2.531(1) Å, respectively. The reasons behind such narrow ranges are the very narrow ranges for the Bi−Bi and Ni−Ni distances at the periphery of the cluster, 3.0158-(6)−3.0349(5) and 2.540(1)−2.570(1) Å, respectively. All this suggests that the cyclohexane-like Bi$_6$-unit and the two triangular Ni$_3$-fragments are the primary building units of the icosahedron. In other words, the icosahedron is made of three rigid groups,

Figure 5. Structure of cluster **4**, $[Bi_3Ni_6(CO)_9]^{3-}$, which can be viewed as derived from the icosahedral $[Ni@\{Bi_6Ni_6(CO)_8\}]^{4-}$ (Figure 4) by removal of the top four vertices (3 Bi and 1 Ni) and addition of two CO-groups.

two Ni$_3$-fragments, and one Bi$_6$-fragment, which are stacked on top of each other in a staggered orientation. The resulting Ni−Bi distances are, therefore, defined by the different distances within these rigid groups, i.e., short for Ni$_3$ and much longer for Bi$_6$, and are naturally within a broader range of 2.694(1)−3.029(1) Å.

Centered icosahedral clusters resemble the close packing in extended metal structures and can be viewed as small excisions from the solid state. For this reason such species are called metalloid clusters when made of a single metal.[48] When the cluster is made up of different atoms as in $[Ni@\{Bi_6Ni_6(CO)_8\}]^{4-}$, the name *intermetalloid* cluster is more appropriate. This new class of clusters has only a few members so far, all of them discovered in the past few years: $[Zn@(Zn_8Bi_4)@Bi_7]^{5-}$,[27] $[Pd_2@Ge_{18}]^{4-}$,[23] $[Ni_2Sn_{17}]^{4-}$,[21] $[M@Pb_{10}]^{2-}$ and $[M@Pb_{12}]^{2-}$ (M = Ni, Pd, Pt),[18−20] $[As@Ni_{12}@As_{20}]^{3-}$,[49] $[Pd_7As_{16}]^{4-}$,[50] and $[Ni_5Sb_{17}]^{4-}$.[51]

Cluster **4**, $[Bi_3Ni_6(CO)_9]^{3-}$ structurally characterized in $[K-(18-crown-6)]_3$**4**·en·0.5tol, is the only one of these new species that is not a *closo*-cluster (Figure 5). Its shape puzzled us initially until we realized that it can be related to and viewed as derived from an icosahedron. In coming to this realization we were greatly helped by being aware of the existence of two

intermetallic compounds with a similar formation. The isolated cluster in these cases is Tl_9^{9-} found in $Na_2K_{21}Tl_{19}$ and $Na_{12}K_{38}Tl_{48}Au_2$,[52] and its overall shape is virtually identical to that of **4**. One additional similarity between the two systems is the fact that the corresponding icosahedral Tl-centered Tl_{12}-cluster is also known, $[Tl@Tl_{12}]^{11-}$ in $Na_3K_8Tl_{13}$.[53] Thus, similar to the relation between Tl_9^{9-} and $[Tl@Tl_{12}]^{11-}$, cluster **4** can be viewed as derived from the icosahedral Ni-centered cluster **3**, $[Ni@\{Bi_6Ni_6(CO)_8\}]^{4-}$, by the removal of four neighboring vertices of which three are bismuth atoms and one is a NiCO-fragment (figure in Supporting Information). The missing atoms are replaced by two additional carbonyl groups that cap two newly exposed Ni$_3$ triangular faces (top two CO-groups in Figure 5). This is not to imply that this is how such species are chemically related in solution but simply to show the structural relationship between the icosahedron and the lacunary species.

Electronically, cluster **4** provides an even more interesting story. According to Wade−Mingos rules, the removal of one or two vertices from a *closo*-cluster which generates *nido*- and *arachno*-species, respectively, preserves the cbe as the parent *closo*-species but reduces the cve by 2 and 4, respectively. The removal of these vertices does not change the number of bonding molecular orbitals within the cluster although it destabilizes many of them, especially when two neighboring vertices are removed. What changes is the number of electrons for either exo-bonds or lone pairs since the removal of each vertex removes the pair of such electrons associated with it. However, it has been shown by Burdett and Canadell that removal of three neighboring vertices opens up the cluster too greatly, and the missing overlap with orbitals from the removed vertices destabilizes three cluster-bonding MOs to such a degree that they become empty antibonding orbitals.[54] Thus, the total valence electrons required for such a cluster is reduced not by just six electrons for exo-bonding but by an additional six for the missing cluster-bonding orbitals, equaling a total of 12 electrons. Exactly the same effect is observed when four vertices from two neighboring triangular faces are removed. In this case the total valence electrons are reduced by 14 electrons which can potentially be partitioned as 6 cluster-bonding electrons and 8 exo-electrons. This means that the 50 cve required for the bonding of an icosahedron are reduced to 36 (50 − 14 = 36) cve for cluster **4**. This number matches the number of available electrons from 3 Bi-atoms (5 electrons each), 9 CO-groups (2 electrons each), and the charge (additional 3 electrons). The attempt to count cbe using the simplistic approach of breaking the cluster into 3 Bi-atoms (3 electrons each), 3 NiCO-fragments (0 electrons each), 3 Ni(CO)$_2$-fragments (2 electrons each), and charge results in 18 which is 8 electrons short from the 26 for an icosahedron. This would mean that the exo-bonding electrons are reduced by only 6 which may be also a reasonable supposition when taking into account the fact that Ni1 which centers the icosahedron is a peripheral atom in **4** and has two exo-bonded carbonyl groups.

The overall dimensions of cluster **4** are similar to those observed in **3**. One of the Ni$_3$ triangles from the icosahedron is preserved (Ni2, Ni3, Ni4), and the distances are within 2.466-

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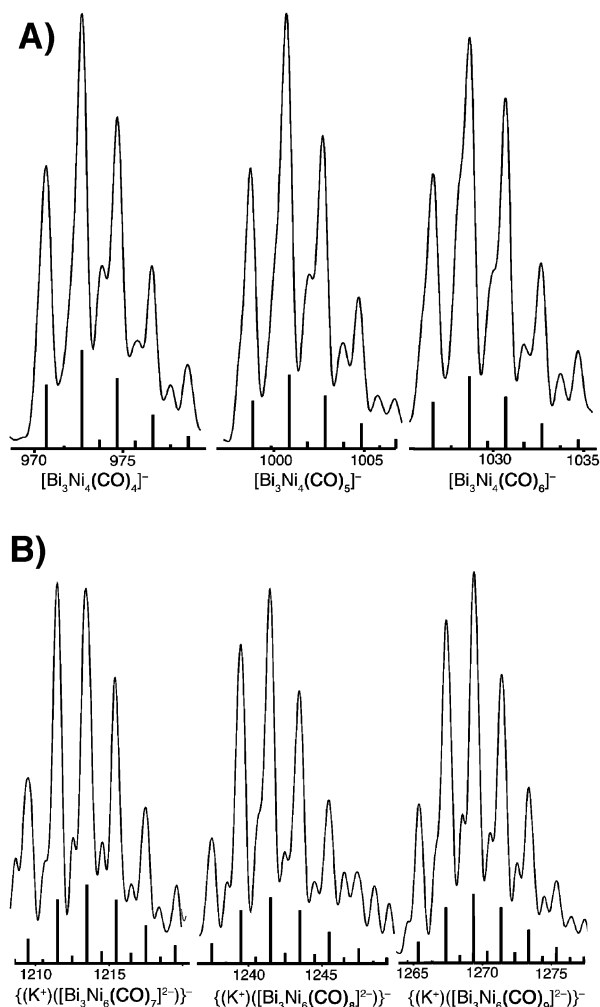(54) Burdett, J. K.; Canadell, E. *Inorg. Chem.* **1991**, *30*, 1991.

A)

$[Bi_3Ni_4(CO)_4]^-$ $[Bi_3Ni_4(CO)_5]^-$ $[Bi_3Ni_4(CO)_6]^-$

B)

$\{(K^+)([Bi_3Ni_6(CO)_7]^{2-})\}^-$ $\{(K^+)([Bi_3Ni_6(CO)_8]^{2-})\}^-$ $\{(K^+)([Bi_3Ni_6(CO)_9]^{2-})\}^-$

Figure 6. Segments of the electrospray mass-spectra in negative-ion mode of [K-(2,2,2-crypt)]₃**1**·en·tol (A) and [K-(18-crown-6)]₃**4**·en·0.5tol (B) dissolved in DMF. The peaks and the theoretical isotope distributions correspond to cluster **1** and cluster **4** (ion-paired with K⁺), respectively, and their derivatives missing one and two carbonyl groups. The loss of CO occurs during the electrospray experiment.

a)   **b)**   **c)**

Figure 7. Segments of the electrospray mass spectrum in negative-ion mode of [K-(18-crown-6)]₄**3**·3en in DMF: (a) $\{(K^+)([Bi_6Ni_6(CO)_6]^{2-})\}^-$, (b) $\{(K^+)(\{Ni@[Bi_6Ni_6(CO)_8]\}^{2-})\}^-$, and (c) $\{(K^+\text{-crown})([Bi_6Ni_6(CO)_4]^{2-})\}^-$.

(2)−2.540(2) Å. The second triangle with a capping CO-group is now reduced to a Ni₂ dimer with a distance of 2.367(2) Å, and the capping carbonyl group has become bridging for the dimer. This dimer, with its very short Ni−Ni distance, is exactly the same as those observed in clusters **1** and **2**. The nickel dimer and triangle are connected to what used to be a central Ni atom of the icosahedron, Ni1, and form two additional Ni₃ triangular faces that are capped by two carbonyl groups. Due to this capping the distances from Ni1 to the corresponding atoms Ni3, Ni4, Ni5, and Ni6 are quite a bit shorter, 2.466(2)−2.548(3) Å, than the Ni1−Ni2 distance of 2.732(2) Å. The two Bi−Bi distances, 2.9844(8) and 3.0196(7) Å, are close to those in **3**. Similarly, as in **3** the Bi−Ni distances are within a very broad range of 2.603(1)−3.030(1) Å.

Solution Studies. The existence of all of the reported clusters as stable species in solution was confirmed by electrospray mass spectrometry of the corresponding crystalline samples dissolved in DMF. Most spectra were collected in negative-ion mode; however, cluster **2** was also characterized as an ion-paired species in positive-ion mode. The specific isotope patterns of the multiple bismuth and nickel atoms in these clusters provide very distinct mass envelopes that make the ion identification
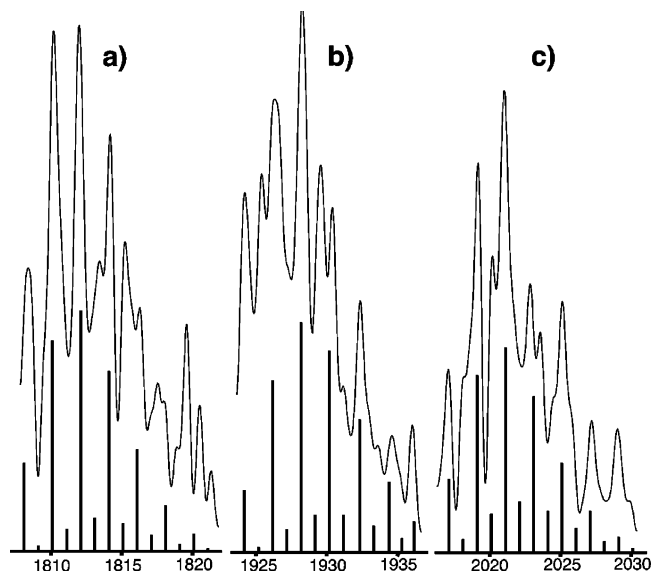
unequivocal. Negative-ion mode electrospray mass spectrometry carried out at relatively high cone voltages, such as 25−30 V as is the case here, has the tendency to oxidize redox active species such as these highly reduced clusters, lowering their overall negative charges. This oxidation ultimately makes observable almost exclusively species with a charge of 1. Lowering the cone voltages could potentially preserve higher-charged anions and prevent fragmentation, but the resulting spectra were very noisy and could not be interpreted. Observation of higher-charged anions is possible, but they are invariably coupled with one or more cations. The high cone voltage also often causes the loss of one or more ligands, carbonyl groups in our case, and the observation of a series of species with the same core but with a different number of ligands becomes possible. These effects are illustrated in Figure 6 with the parent monoanion of cluster **1**, $[Bi_3Ni_4(CO)_6]^-$, and the parent dianion of cluster **4** coupled with a potassium cation, $\{(K^+)([Bi_3Ni_6(CO)_9]^{2-})\}^-$, where species missing one and two carbonyl groups are observed as well, i.e., $[Bi_3Ni_4(CO)_5]^-$ and $[Bi_3Ni_4(CO)_4]^-$ for **1** and $\{(K^+)([Bi_3Ni_6(CO)_8]^{2-})\}^-$ and $\{(K^+)([Bi_3Ni_6(CO)_7]^{2-})\}^-$ for **4**. Cluster **2** was characterized both in negative-ion mode as the ion pair $\{(K^+)([Bi_4Ni_4(CO)_5]^{2-})\}^-$ with one missing carbonyl group) and in positive-ion mode combined with three cryptated potassium cations, $\{(K\text{-crypt}^+)_3\text{-}([Bi_4Ni_4(CO)_6]^{2-})\}^+$ (figure in Supporting Information).

As discussed in the previous section, the position of the central Ni-atom in cluster **3**, $[Ni_x@\{Bi_6Ni_6(CO)_8\}]^{4-}$, was structurally refined as partially occupied. This means that in the crystal structure some clusters are empty and some are filled; however, the X-ray diffraction "sees" the average overall structure. Mass spectrometry, on the other hand, can readily distinguish the two species. This is exactly what was observed in the electrospray mass spectrum which exhibited peaks corresponding to the empty $[Bi_6Ni_6(CO)_8]^{4-}$ and Ni-centered $[Ni@\{Bi_6Ni_6(CO)_8\}]^{4-}$ as well as their derivatives after losing carbonyl groups. As is often the case, many such species were also found ion-paired with naked and/or sequestered cations. Some of these peaks are shown in Figure 7: (a) the empty

species with two carbonyl groups missing and paired with a potassium cation, $\{(K^+)([Bi_6Ni_6(CO)_6]^{2-})\}^-$; (b) the Ni-centered species paired with a potassium cation, $\{(K^+)(\{Ni@[Bi_6Ni_6(CO)_8]\}^{2-})\}^-$; and (c) the empty species with four carbonyl groups missing and paired with a potassium cation sequestered by 18-crown-6, $\{(K^+\text{-crown})([Bi_6Ni_6(CO)_4]^{2-})\}^-$. The presence of mass envelopes corresponding to all of the reported cluster species is indicative of their relative robustness, a fact which is mirrored by the overall stable electron configurations as calculated by theoretical methods.

Conclusions

We have shown that a variety Bi−Ni clusters can be stabilized by reactions of Bi_n^{n-} oligomers with $Ni(CO)_2(PPh_3)_2$. Furthermore, these clusters can undergo mild oxidation leading to their rearrangement into larger species. We believe that further oxidation could lead to even larger nanometric species or to similar cluster geometries with different charges associated with them, including potentially neutral species. These possibilities are a part of our future research plan which will include detailed electrochemistry studies of the anions herein reported. In fact, some preliminary results suggest that the Ni-centered icosahedra may undergo one-electron oxidation to form the radical species $[Ni@\{Bi_6Ni_6(CO)_8\}]^{3-}$. Such species and their cyclic voltametry are of great interest for our future studies.

The existence of the reported here four Bi−Ni heteroatomic clusters with different shapes and sizes as well as the previously reported Bi−Cr, Bi−Mo, and Bi−Zn species attest to the highly versatile chemistry associated with negatively charged bismuth oligomers. It is very promising that these oligomers can coordinate to a number of different transition metals, four thus far, with the possibility for many more to come. The expanding field of heteroatomic main-group/transition-metal cluster chemistry and, more specifically, the emerging subfield of intermetalloid clusters, i.e., clusters that resemble the packing in alloys and intermetallic compounds, may have great impact on many areas of science and engineering such as the nanosciences (as heterometallic nanoparticles), catalysis (as deposited on high surface area materials), composite materials (as grafted on surfaces or self-assembled), and metallurgy (as precursors to metastable alloys). Furthermore, these species are also of interest from a fundamental viewpoint as they complement the existing work done on transition-metal and carborane cluster chemistry thus completing the picture of what happens on a molecular scale when dimensions characteristic of extended solids are approached.

Supporting Information Available: X-ray crystallographic file in CIF format (five structures), ORTEP figures of the compound [Na-(2,2,2-crypt)](4,4′-bipy) and the four clusters with anisotropic thermal ellipsoids (including the disorder of cluster **1** and the two independent clusters **2**), a schematic representation of the relation between clusters **3** and **4**, parts of the electrospray mass spectra of **2** in negative- and positive-ion mode, and complete ref 40. This material is available free of charge via the Internet at http://pubs.acs.org.

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