Structural Characterization of Two Large Bismuth–Cobalt Carbonyl Clusters: $(PPN)_2[Bi_4Co_9(CO)_8(\mu\text{-}CO)_8]\cdot 2THF$ and $(PPN)_2[Bi_8Co_{14}(CO)_{12}(\mu\text{-}CO)_8]\cdot 1.08THF$

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The reaction of $PPN[Bi_2Co_4(CO)_{10}(\mu\text{-}CO)]$ with $Mo(CO)_3$(toluene) in THF yields, after slow oxidation, the large clusters, $(PPN)_2[Bi_4Co_9(CO)_8(\mu\text{-}CO)_8]$ and $(PPN)_2[Bi_8Co_{14}(CO)_{12}(\mu\text{-}CO)_8]$ [PPN = bis(triphenylphosphine)iminium] which exhibit close-packed arrays of main group elements and transition metal atoms.

Transition metal clusters incorporating main group elements have been studied intensely in recent years.[1] Recently, many clusters containing very large frameworks of metal atoms have been synthesized by several groups.[2–4] As these clusters become larger in size, their structures begin to more closely resemble those of solid-state metal phases, and may even serve as convenient precursors to these phases at lower temperatures.

The known anionic cluster $[Bi_2Co_4(CO)_{10}(\mu\text{-}CO)]^-$ arises from the reduction of the *closo* tetrahedral cluster, $[BiCo_3(CO)_6(\mu\text{-}CO)_3]$,[5] and may be viewed as either a *nido* pentagonal bipyramid or an *arachno* dodecahedron. The possibility that the 'missing' vertex in the molecule may be filled by a metal fragment[6] of the appropriate electron count was intriguing and suggested a reaction with $Mo(CO)_3$(toluene) to supply the $Mo(CO)_3$ fragment. This fragment should add no additional electrons to the cluster electron count. The product of the reaction between $PPN[Bi_2Co_4(CO)_{11}]$ and $Mo(CO)_3$(toluene) has a complex IR spectrum and has not been isolated in pure form; however, the slow oxidation of this product in THF with adventitious air over several weeks has produced the bismuth–cobalt cluster, $(PPN)_2[Bi_8Co_{14}(CO)_{20}]$ **2**, in crystalline form. A more rapid oxidation by a deliberate, brief exposure to air produced a related cluster $(PPN)_2[Bi_4Co_9(CO)_{16}]$ **1** as well as a small amount of **2**. Both clusters are produced along with significant amounts of insoluble solids which lack ν-CO bands in the IR. These clusters are insoluble in all common organic solvents and water. An IR spectrum of **2** was recorded, showing a three band spectrum.† The last band at 1837 cm^{-1} is consistent with the presence of bridging carbonyl ligands.

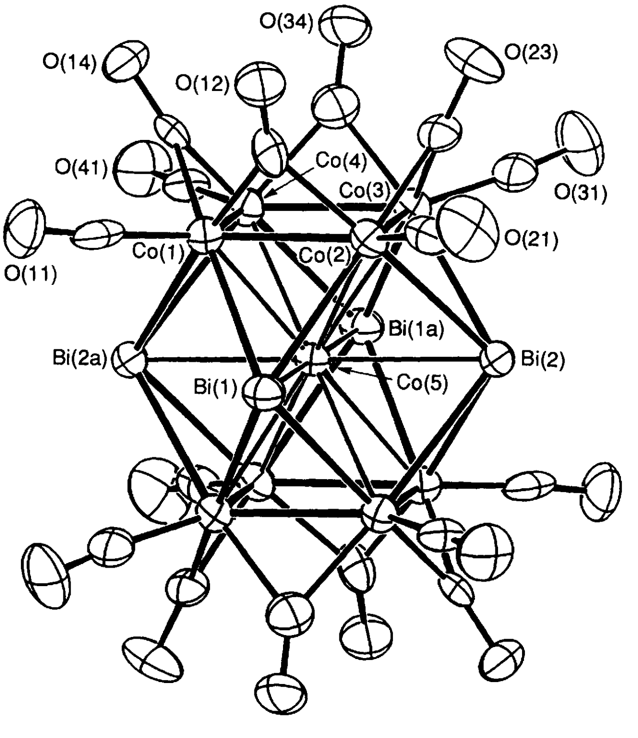

Fig. 1 ORTEP diagram of the anion $[Bi_4Co_9(CO)_8(\mu\text{-}CO)_8]^{2-}$ showing 50% thermal probability ellipsoids and atom labelling

X-Ray analysis‡ shows that the anions both pack in triclinic unit cells, with each of the two asymmetric units containing a crystallographically unique half of the cluster. In **1**, the interstitial Co(5) (Fig. 1) resides at the inversion centre, whereas in **2**, the centre of symmetry lies at the centroid of the ring formed by Co(6), Co(7), Co(6a), and Co(7a) (Fig. 2).

The anion of **1** consists of an interstitial cobalt atom which sits at the centre of a square-planar array of four Bi atoms, with this Bi_4Co moiety sandwiched by two four-membered cobalt rings. Four terminal and four bridging carbonyl ligands are bound to each of the Co_4 rings. The anion of **2** may be viewed as a fusion of two of the anions found in **1** by sharing of a Co_4 face. Here, the central ring of cobalt atoms coordinates only four terminal carbonyl ligands. These anions both have approximate D_{4h} symmetry. The close-packed nature of the bismuth–cobalt arrays is best illustrated in **2**. Connecting the eight bismuth atoms produces a cube in which cobalt atoms Co(5), Co(6), Co(7), and their symmetry related counterparts occupy the face centres.

The shortest Co–Co distances are found within the square Co_4 faces in both **1** and **2** [**1**: 2.461(2)–2.480(2); **2** 2.482(5)–

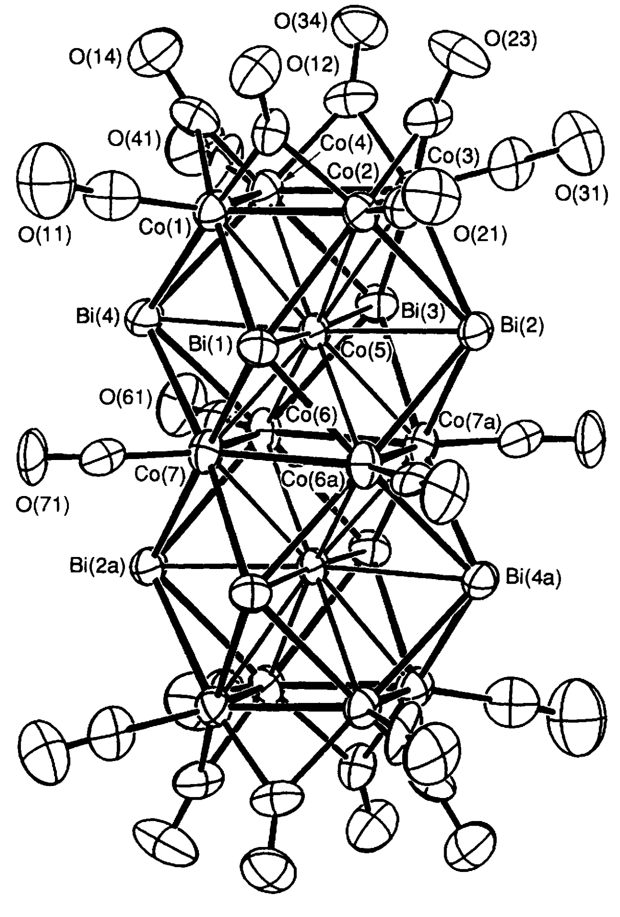

Fig. 2 ORTEP diagram of the anion $[Bi_8Co_{14}(CO)_{12}(\mu\text{-}CO)_8]^{2-}$ showing 50% thermal probability ellipsoids and atom labelling

2.493(4) Å], reflecting the shortening effect imposed by the bridging carbonyl ligands. The average Co–Co bond distance of 2.52(1) Å in $BiCo_3(CO)_9$[7] [2.550(2) Å[5]], which has μ-CO ligands, is comparable to those described above. In addition, the Co–Co bond distance in $[Bi_2Co_4(CO)_{11}]^-$ for the bond bridged by a carbonyl ligand is comparable at 2.54(1) Å[6] [2.538(3) Å[5]]. An interesting comparison of these distances may be made to those of the waist Co_4 unit of **2**, where the distances are *ca.* 0.15 Å longer [2.622(5)–2.654(4) Å]. This is attributed primarily to the lack of bridging carbonyls by comparison to the Co–Co distances in $[Bi_2Co_4(CO)_{11}]^-$ for the bonds which are not bridged by carbonyls of 2.716(9) Å[6] [2.737(4) Å[5]]. The distances from the cobalt atoms in the square arrays of the end units to the interstitial cobalt atom in both anions are only slightly longer on average than the corresponding distances to the interstitial cobalt atoms from the waist cobalt atoms in **2** [**1** 2.615; **2** 2.649 *vs.* 2.589 Å]. The other bond parameters for the two anions are quite similar.

These clusters bear strong structural resemblance to large clusters reported by Fenske *et al.*[2] Two arsenic-containing clusters in particular, $[Ni_9(\mu_4\text{-}As)_6(PPh_3)_5Cl_3]$ and $[Ni_9(\mu_4\text{-}As)_6(PPh_3)_6Cl_2]$,[2a] are similar in terms of the structure of the metal core, with the exception that the M_8 cubes are capped on all faces by arsenic atoms. The total electron count of 127 e^- for **1** makes it quite electron rich in comparison to the two nickel–arsenic clusters listed above, which have 121 and 122 electrons, respectively. These compounds extend the range of electron-counting configurations possible for this class of coupound. The relationship of **1** to **2** clearly suggests the possibility of even larger compounds with additional Co_4 and Bi_4Co layers, leading ultimately to an infinite one-dimensional network. Molecular orbital calculations are currently under way for both of these new clusters.[§]

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Footnotes

[†] IR ν-CO stretching frequencies for **2**: 1972s br, 1890ms, 1837m cm^{-1}.

[‡] *Crystal data* for $(PPN)_2[Bi_4Co_9(CO)_{16}]\cdot 2THF$, triclinic, space group $P\bar{1}$, $a = 13.560(5)$, $b = 15.893(5)$, $c = 11.884(4)$ Å, $\alpha = 105.26(2)$, $\beta = 98.25(3)$, $\gamma = 83.25(3)°$, $Z = 1$, $U = 2437(1)$ Å^3. Refinement converged with $R = 0.033$ and $R_w = 0.035$ for 3709 observations, 397 parameters, and $I > 3\sigma(I)$. For $(PPN)_2[Bi_8Co_{14}(CO)_{20}]\cdot 1.08THF$, triclinic, space group $P\bar{1}$, $a = 17.445(5)$, $b = 18.234(3)$, $c = 9.033(3)$ Å, $\alpha = 92.74(2)$, $\beta = 102.59(3)$, $\gamma = 78.52(2)°$, $Z = 1$, $U = 2748(1)$ Å^3. Refinement converged with $R = 0.037$ and $R_w = 0.041$ for 3547 observations, 458 parameters, and $I > 3\sigma(I)$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

[§] A theoretical study is underway in collaboration with Dr Jean-Yves Saillard at Université de Rennes 1.

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