X-Ray Crystal and Molecular Structure of $[Co_8(\mu_6\text{-}As)(\mu_4\text{-}As)(\mu_4\text{-}AsPh)_2(CO)_{16}]_2$

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The compound $[Co_8(\mu_6\text{-}As)(\mu_4\text{-}As)(\mu_4\text{-}AsPh)_2(CO)_{16}]_2$, synthesized from cyclo-$(PhAs)_6$ and $Co_2(CO)_8$ under mild reaction conditions, has been shown by *X*-ray analysis to possess a 'cluster-of-clusters' assemblage of Co_nAs_{4-n} distorted tetrahedral units.

Cobalt carbonyl clusters containing one or more isolobal main-group replacements for $Co(CO)_3$ groups are an increasingly active area of organometallic chemistry. A wide variety of $[Co(CO)_3]_nE_{4-n}$ complexes based upon the parent tetrahedral cobalt carbonyl $[Co(CO)_3]_4$ have been prepared in which E can be CR, SiR, P, As, SR, S, Se, or Te.[1] It has also been shown that in the case of $[Co(CO)_3]_3As$ further condensation can occur *via* carbonyl group displacement to form a cyclic trimer $[AsCo_3(CO)_8]_3$ consisting of three apically associated tetrahedra.[1-4] As a part of our continuing survey of the reactions of metal carbonyls with cyclopolyarsines, we now report the synthesis of $[Co_8(\mu_6\text{-}As)(\mu_4\text{-}As)(\mu_4\text{-}AsPh)_2(CO)_{16}]_2$ (**1**) and its crystal structure.

$$[Co_8(\mu_6\text{-}As)(\mu_4\text{-}As)(\mu_4\text{-}AsPh)_2(CO)_{16}]_2$$

(**1**)

Black crystals of (**1**) were obtained in 21% yield from the reaction of equimolar quantities of $Co_2(CO)_8$ and cyclo-$(AsPh)_6$ in toluene in a sealed tube at 90 °C for 12 h. Complex (**1**) is completely insoluble in all tested solvents and responds poorly to attempts to form mulls (KBr, Nujol, or halocarbon oil). Complex (**1**) has been completely characterized by *X*-ray diffraction techniques.

Crystal Data: (23 °C) for $[Co_8As_4(CO)_{16}(C_6H_5)_2]_2$: monoclinic, space group $P2_1/n$, $a = 11.761(2)$, $b = 16.970(3)$, $c = 19.900(4)$ Å, $\beta = 94.58(1)°$, $U = 3958.9(12)$ Å^3, $Z = 2$. The structure was solved by direct methods (SHELXTL–SOLV) using 3651 unique reflections collected on a R3 Nicolet automated diffractometer using Mo-K_α radiation for $3 \leqslant 2\theta \leqslant 45°$. The final refinement utilized anisotropic thermal parameters for all non-hydrogen atoms, calculated the hydrogen atoms in idealized positions, and converged at a final R value of 0.0437 and R_w of 0.0387, with a goodness of fit of 1.049.†

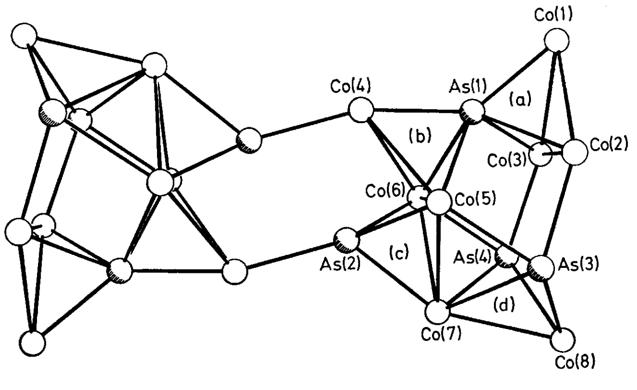

Figure 1. A view of the heavy-atom framework of (**1**) giving the numbering scheme used. The heavy-atom bond distances are: As(1)–Co(1) 2.257(2), As(1)–Co(2) 2.332(2), As(1)–Co(3) 2.316(2), As(1)–Co(4) 2.287(2), As(1)–Co(5) 2.373(2), As(1)–Co(6) 2.352(2), As(2) . . . Co(4) 2.650(1), As(2)–Co(5) 2.240(2), As(2)–Co(6) 2.250(2), As(2)–Co(7) 2.395(2), As(2)–Co(4′) 2.354(2), As(3)–Co(2) 2.344(2), As(3)–Co(5) 2.311(2), As(3)–Co(7) 2.570(2), As(3)–Co(8) 2.377(2), As(4)–Co(3) 2.330(2), As(4)–Co(6) 2.359(2), As(4)–Co(7) 2.501(2), As(4)–Co(8) 2.389(2), As(3) . . . As(4) 3.072(2), As(2) . . . As(2′) 2.828(2), Co(1)–Co(2) 2.634(2), Co(1)–Co(3) 2.651(2), Co(2)–Co(3) 2.582(2), Co(2) . . . Co(5) 2.798(2), Co(3) . . . Co(6) 2.794(2), Co(4)–Co(5) 2.591(2), Co(4)–Co(6) 2.634(2), Co(5)–Co(6) 2.511(2), Co(5)–Co(7) 2.637(2), Co(6)–Co(7) 2.626(2), and Co(7)–Co(8) 2.635(2) Å.

The heavy-atom cluster framework is shown in Figure 1 with pertinent bond distances given in the caption. Although the cluster, *in toto*, possesses no readily assignable molecular geometry, its structure can be decomposed into two, centrosymmetric equivalent fragments (Figure 2) each consisting of four distorted tetrahedra, three of the $AsCo_3$ type and one As_2Co_2, *viz.* (a) As(1)–Co(1)–Co(2)–Co(3), (b) As(1)–Co(4)–Co(5)–Co(6), (c) As(2)–Co(5)–Co(6)–Co(7), and (d) As(3)–As(4)–Co(7)–Co(8) (Figure 1). Thus, the structure may be viewed as a cluster of clusters, or as a macrocluster.

The As(1) atom connects tetrahedra (a) and (b) and this causes it to adopt an extraordinary co-ordination environment for a 'naked' As atom. The rather long Co(2)–Co(5) and Co(3)–Co(6) distances, 2.798(2) and 2.794(2) Å, respectively, may be treated as non-bonding. Tetrahedra (b) and (c) share an edge: Co(5)–Co(6), 2.511(2) Å. The As(2)–Co(5) and As(2)–Co(6) bonds, 2.250(2) and 2.240(2) Å, respectively, are to the best of our knowledge the shortest As–Co bonds known.‡

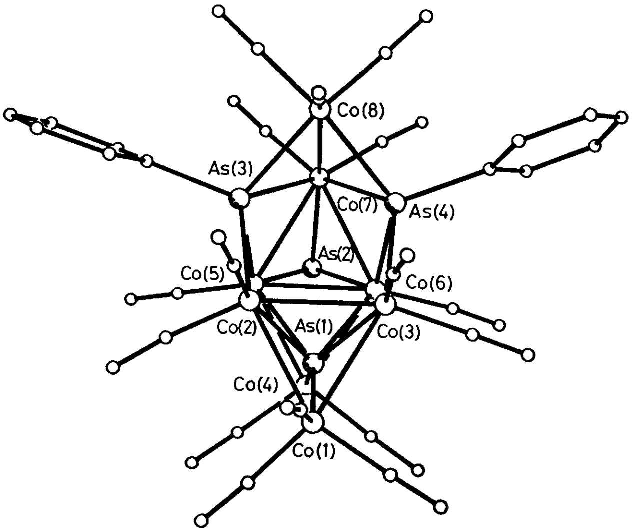

Figure 2. A view of one-half of the complete cluster (**1**) showing the carbonyl and phenyl group substitution.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

‡ Previously reported As–Co distances are in the range, 2.35—2.45 Å. Covalent radius = 2.48 Å.

In contrast, the As(2)–Co(4) bond is long, 2.650(1) Å, and may be non-bonding, but the co-ordination about As(2) is more similar to that about As(1) if this bond is included. [The As(2)–As(2′) distance, 2.828(2) Å, is longer than a normal As–As bonding distance.[5]] Tetrahedra (c) and (d) share a common apex, Co(7), and are further joined by the As(3)–Co(5), 2.311(2) and As(4)–Co(6), 2.359(2) Å bonds. Finally, tetrahedra (a) and (d) are joined by the As(3)–Co(2) and As(4)–Co(3) bonds, 2.344(2) and 2.330(2) Å, respectively. Bond angles, generally, support the concept of an assemblage of tetrahedra. Tetrahedron (d) which lacks an As(3)–As(4) bond, is the most angularly distorted. Loss of the phenyl groups at As(3) and As(4) should lead to the formation of an As–As bond and the angular dimensions in tetrahedron (d) becoming more normal. The identical halves of the macrocluster are connected by a normal As(2)–Co(4′) bond, 2.354(2) Å.

The patterns of CO substitution follow exactly that anticipated by the isolobal substitution principle.

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