A Paramagnetic Cobalt Carbonyl Cluster Anion with an Encapsulated Silicon Atom; Preparation and Structure of $[\mu_8\text{-SiCo}_9(CO)_{21}]^{2-}$

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Reaction between μ_4-Si[$Co_2(CO)_7$]$_2$ and [$Co(CO)_4$]$^-$ gave the paramagnetic title anion which was isolated as the mixed salt [NEt_4]$_3$[μ_8-$SiCo_9(CO)_{21}$][$Co(CO)_4$]; an *X*-ray structure determination showed the cluster anion to consist of a capped square anti-prismatic array of cobalt atoms encapsulating the silicon atom.

An important sub-group of the expanding field of metal cluster chemistry consists of compounds in which main-group elements are encapsulated within the metal cages. The most numerous examples involve carbon as the interstitial atom,[1] but H, N, P, S, and As are also found.[2] There have been no reports of such clusters incorporating any of the heavier group 4B elements as fully encapsulated atoms, although both [μ_5-$GeCo_5(CO)_{16}$]$^-$ and {μ_4-$GeCo(CO)_4$}$_2$$Co_4(CO)_{11}$ contain a five-co-ordinate germanium atom which could be regarded as 'semi-interstitial'.[3]

We now report that the reaction of μ_4-Si[$Co_2(CO)_7$]$_2$,[4] with an excess of [NEt_4][$Co(CO)_4$] in CH_2Cl_2 at 40 °C gives a deep brown solution which, after filtration and concentration, deposits black crystals on cooling to −30 °C. The isolated, non-optimised yield was *ca.* 12%. The complex exhibited a particularly simple carbonyl-region i.r. spectrum, [ν_{CO} (CH_2Cl_2) 2054w, 2004s br., 1955br. sh, 1888m, 1791w br. cm^{-1}]. An *X*-ray structure determination† has identified the compound as a mixed salt of composition [NEt_4]$_3$[μ_8-$SiCo_9(CO)_{21}$][$Co(CO)_4$]. The cations and the tetrahedral [$Co(CO)_4$]$^-$ anion are unremarkable, but the cluster anion is the first example in which a fully encapsulated silicon atom is found. The identity of the silicon atom rests mainly on the *X*-ray evidence (no alternative element would refine properly) and on the identity of the starting material. Because of the low abundance of silicon in the compound (1.6%) quantitative microanalysis was not practicable; however electron-probe analysis confirmed the presence of silicon in the sample.

The overall geometry of the anion is shown in Figure 1. The nine cobalt atoms define a capped-tetragonal-antiprism, with the silicon atom occupying the cavity within the square-antiprism. There is a crystallographic four-fold axis coincident with the Si–Co(1) vector. The carbonyl ligands fall into three classes; thirteen terminal, four slightly asymmetrically bridging alternate Co(2)–Co(3) edges, and four asymmetrically bridging the Co(1)–Co(2) edges. The overall geometry is therefore very similar to that observed for the [$Rh_9P(CO)_{21}$]$^{2-}$ cluster.[5] However, the two anions are not isoelectronic since [μ_8-$SiCo_9(CO)_{21}$]$^{2-}$ has one electron fewer than the Rh_9P analogue; the consequential paramagnetism is confirmed by a strong, broad [200 G (1 G = 10^{-4} T) peak-to-peak], featureless e.s.r. signal at g = 2.039 in CH_2Cl_2 at 77 K.

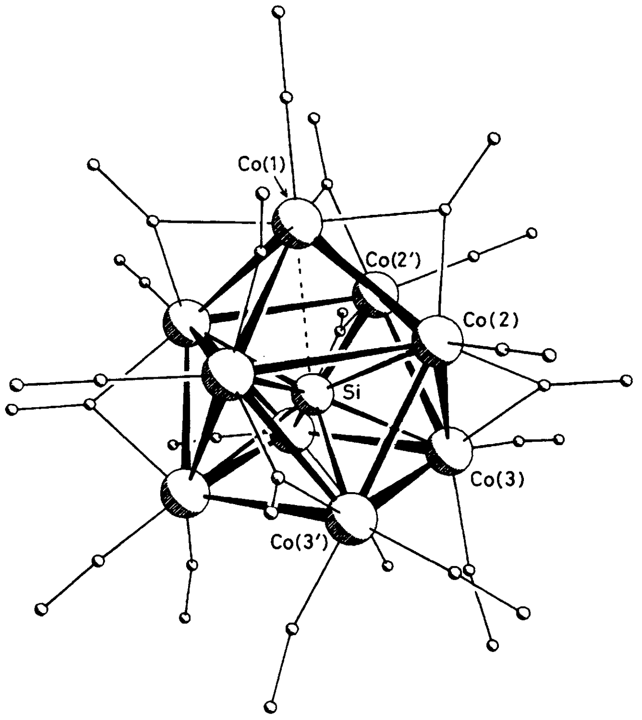

Figure 1. A view of the [$Co_9Si(CO)_{21}$]$^{2-}$ anion. The Si–Co(1) vector is a crystallographic tetrad. Important distances (Å) are: Co(1)–Co(2) 2.613(1), Co(2)–Co(2') 2.940(1), Co(2)–Co(3) 2.688(1), Co(2)–Co(3') 2.593(1), Co(3)–Co(3') 2.808(1), Si · · · Co(1) 2.527(4), Si–Co(2) 2.283(2), Si–Co(3) 2.314(2).

The encapsulated silicon lies virtually in the centre of the eight cage cobalt atoms, with Si–Co distances [average 2.299(2) Å] within the normal ranges found for these bonds in simpler compounds. The Si–Co(1) distance is much longer at 2.527(4) Å and can be regarded as only a weak interaction. The Co–Co distances involving the apical Co(1), and the Co(2)–Co(3) interplanar distances are normal for carbonyl-bridged bonds (*ca.* 2.6 Å). However the Co(3)–Co(3') bonds, 2.808(1) Å, are markedly longer than in other clusters, while the Co(2)–Co(2') bonds, 2.940(1) Å, are quite exceptional. This indicates that there is a significant expansion of the cage to accommodate the silicon atom. The cavity formed by a regular square-antiprism of cobalt atoms (r = 1.35 Å) has a radius[6] of *ca.* 0.85 Å, which is significantly smaller than a silicon atom, r = 1.12 Å. It is therefore not surprising that the equivalent reaction involving germanium, r = 1.22 Å, does not lead to the corresponding encapsulation of the group 4 atom.[3] A comparison with the square-antiprismatic core of [$Co_8C(CO)_{18}$]$^{2-}$ shows that the smaller carbon atom can be

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† *Crystal data:* [NEt_4]$_3$[$SiCo_9(CO)_{21}$][$Co(CO)_4$], $C_{49}H_{60}Co_{10}N_3O_{25}Si$, M = 1708.45, tetragonal, space group $P4/ncc$, a = 16.340(2), c = 24.246(3) Å, U = 6473.5 Å^3, Z = 4, D_c = 1.75 g cm^{-3}, F(000) = 3436, μ(Mo-K_α) = 26.9 cm^{-1}. The intensities of 2295 unique reflections were collected on an Enraf-Nonius CAD4 diffractometer for $0<\theta<25°$ using monochromated Mo radiation and an ω–2θ scan technique. The structure was solved by direct methods and refined by full-matrix least-squares, with all non-hydrogen atoms anisotropic, to converge with R = R_w = 0.039 for 1417 absorption-corrected reflections with $I>2\sigma(I)$. The atomic co-ordinates for this work are available from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

accommodated in the cage with Co–Co distances of 2.47—2.59 Å.[7] Similarly, a significant increase in cage size was found for the encapsulated P or As atoms in $[Rh_9P(CO)_{21}]^{2-}$ and $[Rh_{10}M'(CO)_{22}]^{3-}$, M′ = P, As.[2,5] It is interesting that an expansion of the eight-atom cage is found for all these examples, rather than a rearrangement to a cubic core which has a larger interstitial cavity than a square-antiprism; presumably the greater number of M–M bonds in the latter core is the dominating factor.

The $[Co_9Si(CO)_{21}]^{2-}$ anion is a rare example of a kinetically-stable paramagnetic cluster, and has only 129 valence electrons, rather than the 130 expected for a capped square-antiprism.[8] Interestingly, the only other paramagnetic clusters of this type, namely $[Co_6C(CO)_{14}]^-$ and $[Co_{13}C_2(CO)_{24}]^{4-}$, have one electron in *excess* of those expected for the respective geometries; in these the extra electron is assumed to expand the cage by occupying an appropriate anti-bonding level.[9] The reasons for the electron deficiency in the Co_9Si core are not apparent; further discussion must await more detailed electrochemical studies.

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