# Anionic Germanium Polycobalt Carbonyl Clusters. Part 3.† Preparation and Structures of $[NEt_4][Ge_2Co_7(CO)_{21}]$ and $[NEt_4][Ge\{Co_7(CO)_{20}\}]$;‡ Two Large Clusters incorporating Tetrahedral $GeCo_3$ Units

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Reactions of the $[Ge\{Co_5(CO)_{16}\}]^-$ cluster have given rise to two new germanium–polycobalt cluster anions, characterised as their $NEt_4^+$ salts by *X*-ray crystallography. The complex $[NEt_4][Ge_2Co_7(CO)_{21}]$ (1a) forms triclinic crystals, space group $P\bar{1}$, with $a$ = 13.085(2), $b$ = 19.712(7), $c$ = 12.220(8) Å, $\alpha$ = 109.10(3), $\beta$ = 92.60(2), $\gamma$ = 129.32(3)°, and $Z$ = 2. The structure was solved by direct methods and refined to $R = R'$ = 0.046 for 2 076 reflections with $I > 3\sigma(I)$. The anion (1) consists of two $-GeCo_3(CO)_9$ units bonded mutually *trans* about a trigonal planar $Co(CO)_3$ group, giving idealised $C_{3v}$ symmetry. For $[NEt_4][Ge\{Co_7(CO)_{20}\}]$ (2a), crystals are monoclinic, space group $P2_1/c$, with $a$ = 12.761(7), $b$ = 18.415(3), $c$ = 17.675(4) Å, $\beta$ = 102.91(3)°, and $Z$ = 4. The structure was refined to $R$ = 0.077, $R'$ = 0.074, for 1 123 reflections with $I > 2\sigma(I)$. The anion (2) is a derivative of the $C_{3v}$ structure of $[Co_4(CO)_{12}]$ with the axial carbonyl ligand of one basal cobalt replaced by a $-GeCo_3(CO)_9^-$ fragment. The $Co_4$ tetrahedron is disordered.

THERE is current interest in metal carbonyl clusters containing main-group elements as part of their basic core structures.[1,2] Among the main-group 4 elements, carbon is found in conjunction with from three[3] to fifteen transition-metal atoms.[4] However, for the heavier Group 4 elements examples are rather restricted, excluding relatively open species based on simple $M'M_2$ triangular units[5] ($M'$ = Group 4 element; $M$ = transition metal). Established species are (3a) and (3b) with a trigonal bipyramidal $M'_2M_3$ nucleus,[6] $[M'R\{Co_3(CO)_9\}]$ (4) [R = $Co(CO)_4$, Ph, or $CH_3$], containing $M'Co_3$ cores,[7-9] and $[Ge\{Co_5(CO)_{16}\}]^-$ (5) which combines tetrahedral $GeCo_3$ and triangular $GeCo_2$ moieties.[10] As part of our efforts to extend this area of chemistry to higher nuclearity clusters containing heavier Group 4 elements we have used the $[Ge\{Co_5(CO)_{16}\}]^-$ anion (5) which has recently become available[10] to prepare the new anions $[Ge_2Co_7(CO)_{21}]^-$ (1) and $[Ge\{Co_7(CO)_{20}\}]^-$ (2), described herein.

## EXPERIMENTAL

All manipulations were conducted under dry nitrogen using standard Schlenk techniques. Infrared spectra were recorded on a Perkin-Elmer model 180 spectrometer and are accurate to ±1 cm$^{-1}$.

*Preparation of* $[NEt_4][Ge_2Co_7(CO)_{21}]$ (1a).—The compound $[Co_2(CO)_8]$ (0.15 g, 0.4 mmol) was added to a solution of $[NEt_4][Ge\{Co_5(CO)_{16}\}]$ (*ca.* 0.4 mmol, prepared *in situ* from $[Ge\{Co_4(CO)_{16}\}]$ and excess of $[NEt_4][Co(CO)_4]$) in tetrahydrofuran (thf) (20 cm$^3$) and the mixture was heated at 45—50 °C for 8 h. Solvent was removed under vacuum and the residue extracted with diethyl ether (20 cm$^3$). The filtered extract was evaporated to give a solid which was recrystallised from $CH_2Cl_2$–hexane (1 : 1) to give deep red *crystals* of $[NEt_4][Ge_2Co_7(CO)_{21}]$, [ν(CO) ($CH_2Cl_2$) 2 065m, 2 027vs, and 2 004w cm$^{-1}$], characterised by *X*-ray crystallography.

*Preparation of* $[NEt_4][Ge\{Co_7(CO)_{20}\}]$ (2a).—A sample of $[NEt_4][Ge\{Co_5(CO)_{16}\}]$ which had been stored at −30 °C for several months was recrystallised from $CH_2Cl_2$–light petroleum (b.p. 40—60 °C) (1 : 1). The first crystals to form were small black plates of $[NEt_4][Ge\{Co_7(CO)_{20}\}]$ [ν(CO) ($CH_2Cl_2$) 2 054s, 2 033s, 2 028s, 1 990w, and 1 825 m,br cm$^{-1}$].

*X-Ray Crystallography*.—Single crystals of (1a) and (2a) prepared as described above were sealed in thin-walled glass capillaries. Precession photography was used to establish crystal quality and to assign space groups. Intensity data were collected using a Hilger and Watts four-circle diffractometer for (1a) and an Enraf–Nonius CAD4 diffractometer for (2a). Corrections for Lorentz and polarisation effects and for absorption were executed. Computing details are given elsewhere.[10]

*Crystal data.* (1a), $C_{29}H_{20}Co_7Ge_2NO_{21}$, $M$ = 1 276.19, Triclinic, space group $P\bar{1}$ (no. 2), $a$ = 13.085(2), $b$ = 19.712(7), $c$ = 12.220(8) Å, $\alpha$ = 109.10(3), $\beta$ = 92.60(2), $\gamma$ = 129.32(3)°, $U$ = 2 161 Å$^3$ (23 °C), $D_m$ = 1.96 (flotation), $Z$ = 2, $D_c$ = 1.97 g cm$^{-3}$, $F(000)$ = 1 243, $\mu$(Mo-$K_\alpha$) = 39 cm$^{-1}$, and $\lambda$ = 0.7107 Å. Crystal dimensions 0.4 × 0.2 × 0.15 mm. Of the 3 814 unique reflections with $2\theta < 44°$, 2 076 with $I \geqslant 3\sigma(I)$ were used in the refinement.

(2a), $C_{28}H_{20}Co_7GeNO_{20}$, $M$ = 1 175.48, Monoclinic, space group $P2_1/c$ (no. 14), $a$ = 12.761(7), $b$ = 18.415(3), $c$ = 17.675(4) Å, $\beta$ = 102.91(3)°, $U$ = 4 048 Å$^3$ (25 °C), $D_m$ = 1.95, $Z$ = 4, $D_c$ = 1.93 g cm$^{-3}$, $F(000)$ = 2 303, $\mu$(Mo-$K_\alpha$) = 35 cm$^{-1}$, $\lambda$ = 0.7107 Å. Crystal dimensions 0.11 × 0.07 × 0.03 mm. Of the 2 594 unique reflections with $2\theta < 50°$ that were collected, 1 123 with $I \geqslant 2\sigma(I)$ were used in the refinement.

*Solution and refinement.* The positions of the heavy-metal atoms of (1a) were obtained by direct methods (SHELX). A Fourier synthesis and difference map based on these readily revealed all other non-hydrogen atoms in the asymmetric unit. In the final blocked full-matrix refinement non-hydrogen atoms were assigned anisotropic thermal parameters and hydrogen atoms were included in their calculated positions with a common isotropic thermal parameter. Refinement converged at $R = R'$ = 0.046 for 2 076 reflections with $I \geqslant 3\sigma(I)$, with no positional parameter shifting by more than 0.2 times its estimated standard deviation in the final cycle. A difference map at this stage showed no residual peaks >0.5 e Å$^{-3}$. Positional parameters for (1a) are listed in Table 1.

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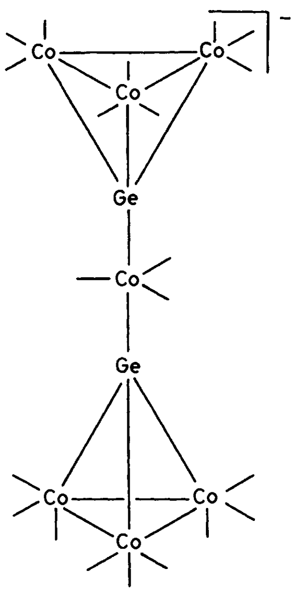
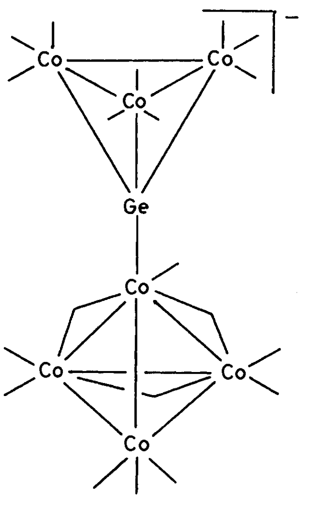
† Part 2 is ref. 10.

‡ Tetraethylammonium tricarbonyl{bis[nonacarbonyl-*triangulo*-tricobaltiogermanio(3 *Co-Ge*)]}cobaltate(2 *Co-Ge*) and tetraethylammonium (nonacarbonyl-*triangulo*-tricobaltio)(1,2;1,4;2,4-tri-μ-carbonyl-1,2,2,3,3,3,4,4-octacarbonyl-*tetrahedro*-tetracobaltio-*Co*$^1$)germanate(4 *Co-Ge*).



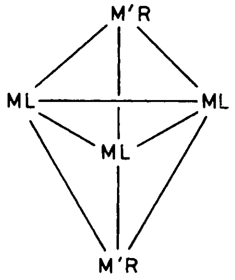
(1) anion

(1a) $NEt_4^+$ salt



(2) anion

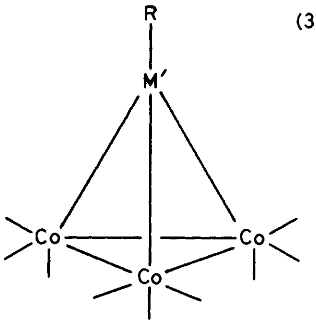
(2a) $NEt_4^+$ salt



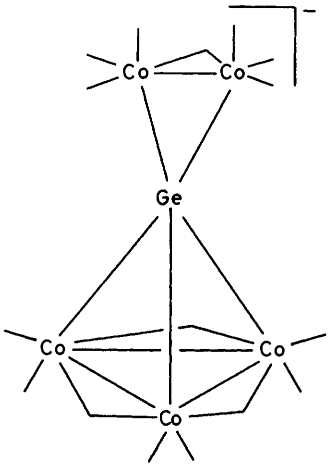
(3a) $M'R = SnCl_3$; ML = Pt(cod)

(3b) $M'R = SnFe(CO)_2(C_5H_5)$; $ML = Fe(CO)_3$

(cod = cyclo-octa-1,5-diene)



| | M' | R |
|---|---|---|
| (4a) | Si | $Co(CO)_4$ |
| (4b) | Ge | $Co(CO)_4$ |
| (4c) | Ge | Ph or $CH_3$ |



(5)

The metal skeleton of (2a) was revealed by direct methods (SHELX). Subsequent cycles of refinement and difference maps gave the positions of the other non-hydrogen atoms. In addition, two peaks in the vicinity of the $Co_4$ unit consistently appeared in chemically unreasonable positions. These apparently arose from disorder of the $Co_4$ tetrahedron and were included in the refinement as Co atoms with partial site-occupancy factors. This was only moderately successful but no further attempts were made to improve the model because of the limited data set available. In the final cycle of full-matrix refinement metal atoms were treated anisotropically and other non-hydrogen atoms were given isotropic thermal parameters. Final agreement indices were $R = 0.077$, $R' = 0.074$ for 1 123 reflections with $I \geqslant 2\sigma(I)$. A difference map revealed several peaks of *ca.* 1 e Å$^{-3}$ in the vicinity of the disordered $Co_4(CO)_{11}$ unit but these were not pursued. Positional parameters for (2a) are listed in Table 2.

Observed and calculated structure factors and thermal parameters of both compounds (1a) and (2a) have been deposited as Supplementary Publication No. SUP 23258 (24 pp.).*

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

TABLE 1

Final atomic positional parameters for $[NEt_4][Ge_2Co_7(CO)_{21}]$ (1a)

($\times$ $10^4$ for heavy-metal atoms, $\times$ $10^3$ for all other atoms)

| Atom | $X/a$ | $Y/b$ | $Z/c$ |
|---|---|---|---|
| Ge(1) | 9 726(2) | 2 188(1) | 6 959(2) |
| Co(1) | 7 822(2) | 539(2) | 5 539(2) |
| Co(3) | 10 242(2) | 1 683(2) | 5 255(2) |
| Co(5) | 13 752(3) | 5 940(2) | 12 416(2) |
| Co(7) | 10 760(3) | 3 173(2) | 9 043(2) |
| C(11) | 684(2) | 35(1) | 397(2) |
| C(13) | 830(2) | 7(1) | 612(2) |
| C(22) | 746(2) | 206(2) | 582(2) |
| C(31) | 957(2) | 89(1) | 364(2) |
| C(33) | 1 118(2) | 149(2) | 603(2) |
| C(42) | 1 058(2) | 519(2) | 1 188(2) |
| C(51) | 1 481(3) | 695(2) | 1 396(2) |
| C(53) | 1 497(2) | 599(2) | 1 178(2) |
| C(62) | 1 392(2) | 435(2) | 1 232(2) |
| C(71) | 909(2) | 275(2) | 913(2) |
| C(73) | 1 123(2) | 255(1) | 926(2) |
| O(12) | 581(2) | 24(1) | 675(2) |
| O(21) | 720(2) | 97(1) | 253(1) |
| O(23) | 1 074(2) | 409(1) | 573(2) |
| O(32) | 1 274(2) | 360(1) | 558(2) |
| O(41) | 1 235(2) | 630(1) | 1 530(1) |
| O(43) | 872(2) | 303(1) | 1 246(2) |
| O(52) | 1 325(2) | 670(1) | 1 103(2) |
| O(61) | 1 438(2) | 578(1) | 1 558(1) |
| O(63) | 1 061(2) | 252(1) | 1 258(2) |
| O(72) | 1 272(2) | 485(1) | 856(2) |
| N | 597(2) | −147(1) | −98(1) |
| C(1) | 654(2) | −67(2) | −141(2) |
| C(3) | 464(2) | −239(2) | −209(2) |
| C(5) | 698(3) | −158(2) | −68(2) |
| C(7) | 564(2) | −125(2) | 19(2) |
| Ge(2) | 11 817(2) | 4 274(1) | 11 102(2) |
| Co(2) | 8 632(2) | 2 038(2) | 5 228(2) |
| Co(4) | 11 334(3) | 4 916(2) | 12 726(2) |
| Co(6) | 12 863(3) | 4 521(2) | 12 945(2) |
| C(12) | 659(2) | 38(2) | 622(2) |
| C(21) | 777(2) | 138(1) | 358(2) |
| C(23) | 990(2) | 328(2) | 554(2) |
| C(32) | 1 171(2) | 285(2) | 544(2) |
| C(41) | 1 196(2) | 574(2) | 1 431(2) |
| C(43) | 976(3) | 379(2) | 1 256(2) |
| C(52) | 1 340(2) | 638(2) | 1 158(2) |
| C(61) | 1 380(2) | 531(2) | 1 457(2) |
| C(63) | 1 151(2) | 336(2) | 1 278(2) |
| C(72) | 1 190(2) | 417(1) | 871(2) |
| O(11) | 611(1) | −97(1) | 295(1) |
| O(13) | 863(2) | −22(1) | 663(1) |
| O(22) | 667(2) | 207(1) | 620(1) |
| O(31) | 918(1) | 41(1) | 258(1) |
| O(33) | 1 176(2) | 136(1) | 646(2) |
| O(42) | 1 003(2) | 532(2) | 1 138(2) |
| O(51) | 1 544(2) | 757(1) | 1 492(1) |
| O(53) | 1 575(2) | 605(1) | 1 135(2) |
| O(62) | 1 448(2) | 415(1) | 1 188(1) |
| O(71) | 808(2) | 252(1) | 920(2) |
| O(73) | 1 150(2) | 213(1) | 941(2) |
| C(2) | 795(2) | 36(2) | −32(2) |
| C(4) | 373(2) | −330(1) | −188(2) |
| C(6) | 751(3) | −175(2) | −184(2) |
| C(8) | 457(2) | −112(2) | 7(2) |

DISCUSSION

*Preparation of* (1) *and* (2).—Chini and co-workers [11] have shown that the core of a $Co_6C$ cluster could be expanded to $Co_8C$ by reaction with $[Co_4(CO)_{12}]$ [see equation (i)]. Accordingly we attempted to increase the nuclearity of $[Ge\{Co_5(CO)_{16}\}]^-$ by a similar reaction with $[Co_2(CO)_8]$. Mild heating in thf for several hours gave a mixture of products from which only $[Ge_2Co_7(CO)_{21}]^-$ (1) has been isolated in pure form. The deep red crystals of the $NEt_4^+$ salt are stable for short periods in air, although solutions are oxygen-sensitive.

$$2\ [Co_6(CO)_{15}C]^{2-} + [Co_4(CO)_{12}] \xrightarrow[Pr^i_2O]{60\ °C} 2\ [Co_8(CO)_{18}C]^{2-} + 6\ CO \quad (i)$$

The anion (2) was isolated from the attempted recrystallisation of an aged, partly decomposed sample of $[NEt_4][Ge\{Co_5(CO)_{16}\}]$ known to contain $[Co(CO)_4]^-$ and $[Co_4(CO)_{12}]$ among other components. The $[NEt_4]$-

TABLE 2

Final positional parameters ($\times 10^4$) for $[NEt_4][Ge\{Co_7(CO)_{20}\}]$ (2a)

| Atom | $X/a$ | $Y/b$ | $Z/c$ |
|---|---|---|---|
| Ge | 2 389(4) | 6 572(3) | 1 796(3) |
| Co(1) | 2 435(9) | 9 156(4) | 1 492(7) |
| Co(2) | 2 439(8) | 7 783(4) | 1 565(6) |
| Co(3) | 894(7) | 8 463(5) | 1 776(6) |
| Co(4) | 2 439(9) | 8 532(5) | 2 687(6) |
| Co(5) | 2 158(6) | 5 681(4) | 2 661(4) |
| Co(6) | 3 511(5) | 5 558(4) | 1 782(4) |
| Co(7) | 1 455(5) | 5 561(4) | 1 189(4) |
| C(11) | 3 932(52) | 9 166(30) | 1 466(33) |
| O(11) | 4 729(38) | 9 294(23) | 1 327(25) |
| C(12) | 2 120(53) | 10 056(36) | 1 638(41) |
| O(12) | 2 018(37) | 10 624(29) | 1 686(28) |
| C(13) | 2 119(88) | 9 170(54) | 211(70) |
| O(13) | 1 678(39) | 9 161(24) | −258(29) |
| C(21) | 3 142(37) | 7 721(24) | 925(28) |
| O(21) | 3 625(25) | 7 547(17) | 450(20) |
| C(31) | 33(62) | 9 083(39) | 1 189(46) |
| O(31) | 568(38) | 4 243(23) | 4 323(27) |
| C(32) | −52(40) | 7 932(27) | 2 137(30) |
| O(32) | −695(33) | 7 628(21) | 2 421(23) |
| C(41) | 3 535(57) | 9 251(37) | 3 154(42) |
| O(41) | 3 877(35) | 9 568(25) | 3 542(26) |
| C(42) | 2 343(41) | 7 884(29) | 3 476(34) |
| O(42) | 2 076(41) | 7 583(29) | 3 876(32) |
| C(51) | 2 070(46) | 4 806(32) | 2 857(35) |
| O(51) | 1 987(24) | 4 150(17) | 2 991(18) |
| C(52) | 1 036(43) | 5 965(25) | 2 880(30) |
| O(52) | 324(31) | 6 288(19) | 3 105(23) |
| C(53) | 3 131(50) | 5 931(30) | 3 390(37) |
| O(53) | 3 717(35) | 6 215(23) | 4 001(29) |
| C(61) | 3 573(47) | 4 611(35) | 1 858(37) |
| O(61) | 3 716(29) | 3 992(20) | 1 926(23) |
| C(62) | 4 591(58) | 5 856(33) | 2 399(38) |
| O(62) | 5 361(32) | 6 051(18) | 2 836(24) |
| C(63) | 3 848(43) | 5 757(30) | 858(34) |
| O(63) | 4 228(32) | 5 876(21) | 354(25) |
| C(71) | 1 239(40) | 4 589(30) | 1 137(32) |
| O(71) | 1 083(27) | 3 998(18) | 1 072(21) |
| C(72) | 290(46) | 5 920(27) | 1 192(32) |
| O(72) | −609(32) | 6 158(19) | 1 131(22) |
| C(73) | 1 501(47) | 5 777(34) | 260(40) |
| O(73) | 1 696(39) | 5 911(24) | −344(29) |
| C(B23) | 1 109(51) | 7 793(34) | 879(36) |
| O(B23) | 490(32) | 7 527(20) | 260(24) |
| C(B24) | 3 215(37) | 7 855(26) | 2 253(29) |
| O(B24) | 4 450(28) | 7 713(17) | 2 662(19) |
| C(B34) | 1 117(42) | 9 127(31) | 2 561(32) |
| O(B34) | 819(30) | 9 615(21) | 2 909(22) |
| Co(3′) | 1 644(21) | 8 364(16) | 827(16) |
| Co(4′) | 3 470(52) | 8 504(39) | 1 882(41) |
| N | 3 201(28) | 2 424(19) | −106(23) |
| C(1) | 2 224(36) | 2 357(23) | 301(29) |
| C(2) | 2 460(35) | 2 373(23) | 1 194(26) |
| C(3) | 4 026(37) | 1 826(24) | 190(28) |
| C(4) | 3 553(38) | 1 071(24) | 14(28) |
| C(5) | 2 810(35) | 2 406(24) | −905(29) |
| C(6) | 3 657(35) | 2 433(23) | −1 449(27) |
| C(7) | 3 869(37) | 3 103(24) | 156(29) |
| C(8) | 3 319(37) | 3 826(25) | −97(29) |

$[Ge\{Co_7(CO)_{20}\}]$ formed as small, black crystals in rather low yield.

The actual routes to the new anions are not clear, however the formation of both can be rationalised if it is assumed that $[GeCo_3(OC)_9]^-$ is formed on fragmentation of $[Ge\{Co_5(CO)_{16}\}]^-$, and that this can act as a Lewis base substituting for CO in $[(OC)_4CoGeCo_3(CO)_9]$ (4b) or $[Co_4(CO)_{12}]$ [see equations (ii)—(iv)]. Whether or not $[GeCo_3(CO)_9]^-$ exists as such is uncertain. Nevertheless it is apparent that the $[GeCo_3(CO)_9]^-$ fragment, which features in several germanium–polycobalt derivatives, is a particularly favoured one, as indeed are other $[MCo_3(CO)_9]$ species.[2]

$$[Ge\{Co_5(CO)_{16}\}]^- \longrightarrow [GeCo_3(CO)_9]^- + [Co_4(CO)_{12}] + [Co(CO)_4]^- \quad \text{(ii)}$$

$$[GeCo_3(CO)_9]^- + [(OC)_4CoGeCo_3(CO)_9] \longrightarrow \underset{(1)}{[(OC)_9Co_3GeCo(CO)_3GeCo_3(CO)_9]^-} \quad \text{(iii)}$$

$$[GeCo_3(CO)_9]^- + [Co_4(CO)_{12}] \longrightarrow \underset{(2)}{[(OC)_9Co_3GeCo_4(CO)_{11}]^-} \quad \text{(iv)}$$

*Structure of* $[Ge_2Co_7(CO)_{21}]^-$ (1).—The crystal consists of individual $NEt_4^+$ and $[Ge_2Co_7(CO)_{21}]^-$ ions. Selected bond lengths and angles for the anion are given in Table 3. The overall structure is illustrated in Figure 1. The anion consists of two equivalent $GeCo_3(CO)_9$ groups bonded through the Ge atoms to a planar $Co(CO)_3$ moiety in a mutually *trans* configuration; the Ge(1)–Co(7)–Ge(2) angle (174°) is only slightly non-linear. Looking along the three-fold axis of the anion the two $GeCo_3$ groups are staggered with respect to each other and the central $Co(CO)_3$ carbonyl groups lie above the Co atoms of one cluster unit but point between the Co atoms of the other (Figure 1). This gives approximate $C_{3v}$ symmetry overall, reduced from $D_{3h}$ by rotation of one of the $GeCo_4$ groups by 60° about the Co(7)–Ge axis.

TABLE 3

Selected bond lengths (Å) and angles (°) for $[Ge_2Co_7(CO)_{21}]^-$ (1)

| | | | |
|---|---|---|---|
| Bond lengths | | | |
| Ge(1)–Co(1) | 2.332(2) | Ge(2)–Co(4) | 2.328(4) |
| Ge(1)–Co(2) | 2.321(4) | Ge(2)–Co(5) | 2.327(4) |
| Ge(1)–Co(3) | 2.324(4) | Ge(2)–Co(6) | 2.311(4) |
| Ge(1)–Co(7) | 2.282(3) | Ge(2)–Co(7) | 2.294(3) |
| Co(1)–Co(2) | 2.608(5) | Co(4)–Co(5) | 2.597(4) |
| Co(1)–Co(3) | 2.606(4) | Co(4)–Co(6) | 2.596(6) |
| Co(2)–Co(3) | 2.609(6) | Co(5)–Co(6) | 2.592(5) |
| Co–C | 1.74—1.82 (mean 1.77) | C–O | 1.10—1.20 (mean 1.15) |
| Bond angles | | | |
| Ge(1)–Co(7)–Ge(2) | 174.4(2) | | |
| Co–Ge–Co | 68.2 ± 0.1 (over both cluster units) | | |
| Co–Co–Co | 60.0 ± 0.1 (over both cluster units) | | |
| Ge(1)–Co(7)–C(71) | 89.6(5) | Ge(2)–Co(7)–C(71) | 89.6(5) |
| Ge(1)–Co(7)–C(72) | 86.4(5) | Ge(2)–Co(7)–C(72) | 89.2(6) |
| Ge(1)–Co(7)–C(73) | 92.7(5) | Ge(2)–Co(7)–C(73) | 92.5(5) |
| Non-bonded distances | | | |
| O(71) ··· O(12) | 3.39 | O(72) ··· O(52) | 3.50 |
| O(71) ··· O(22) | 3.57 | O(72) ··· O(53) | 3.24 |
| O(71) ··· O(42) | 3.99 | O(73) ··· O(13) | 3.69 |
| O(71) ··· O(43) | 3.69 | O(73) ··· O(33) | 3.55 |
| O(72) ··· O(23) | 3.43 | O(73) ··· O(62) | 3.40 |
| O(72) ··· O(32) | 3.68 | O(73) ··· O(63) | 4.08 |

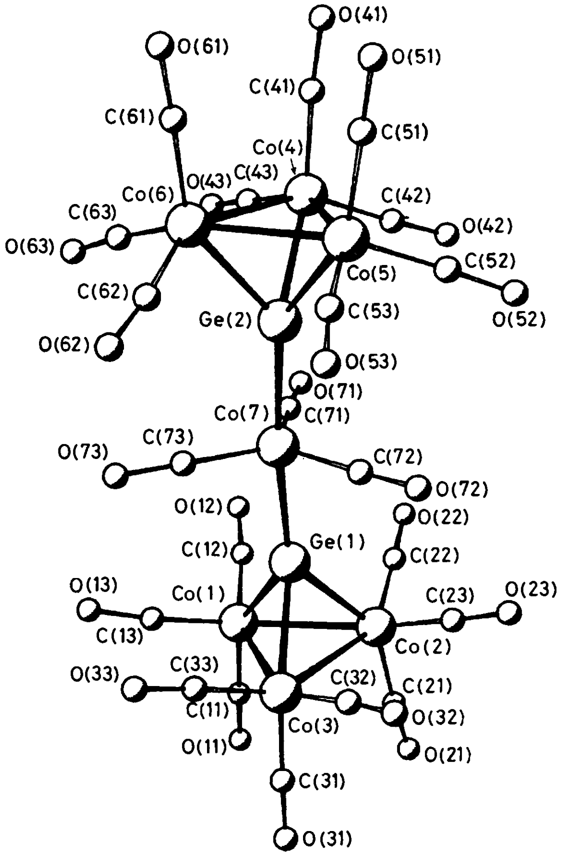


FIGURE 1 A perspective view of the anion $[Ge_2Co_7(CO)_{21}]^-$ (1), showing the atom-labelling scheme

There would be little energy difference between the $C_{3v}$ and $D_{3h}$ forms since the equatorial carbonyl groups on each $GeCo_3(CO)_9$ unit, which incline towards the central $Co(CO)_3$, give an approximately hexagonal array of oxygen atoms so that non-bonded interactions between the central carbonyl groups and those on the $GeCo_3$ clusters are similar in both conformations. The $C_{3v}$ form must be dictated by packing forces which are obviously strong enough to prevent disordering of the $Co(CO)_3$ carbonyls. [A high symmetry form is also indicated for (1) in solution, since the carbonyl-stretching pattern is particularly simple, with only three resolved bands from the 21 carbonyl groups.]

The *exo*-cluster Ge(1) or (2)–Co(7) bond lengths (average 2.288 Å) are exceptionally short, being significantly less than the equivalent bond for $[(OC)_4Co–GeCo_3(CO)_9]$ (4b) (2.35 Å)[7] or for other non-bridged Ge–Co [*e.g.* $H_3Ge–Co(CO)_4$, 2.42 Å; $Cl_3Ge–Co(CO)_4$, 2.31 Å].[12,13] This is apparently because in (1) the Ge–Co bonds are not opposite a CO ligand which exhibits a strong *trans* lengthening effect in this type of compound. For comparison [14] the Si–Mn bond shortens on going from $[Me_3SiMn(CO)_5]$ (2.50 Å) to $[Me_3SiMn(CO)_4(PPh_3)]$ (2.45 Å) as the *trans* CO is replaced by the weaker $\pi$ acceptor/stronger $\sigma$ donor $PPh_3$; similar trends are found for other Group 4 derivatives of transition-metal carbonyls.[15] Hence the short Ge–Co bonds found for (1) indicate that the $[(OC)_9Co_3Ge]^-$ 'ligand' acts as a strong $\sigma$ donor, similar to phosphine bases.

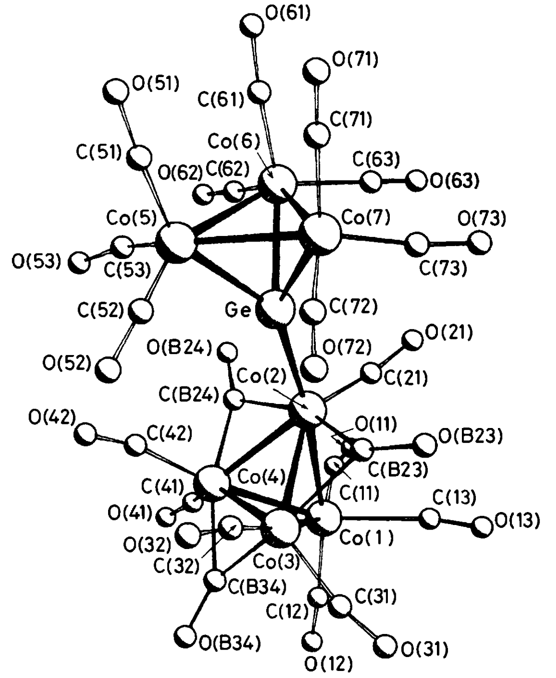


FIGURE 2 The structure of the anion $[Ge\{Co_7(CO)_{20}\}]^-$ (2), showing the atom-labelling scheme

Within the cluster units of (1) the Ge–Co bonds (mean 2.32 Å) are longer, and the Co–Co bond lengths (mean 2.60 Å) slightly shorter, than those in $[(OC)_4CoGeCo_3(CO)_9]$ (Ge–Co 2.28, Co–Co 2.61 Å).[7] Reasons for this are not obvious; there are certainly no unusual steric interactions involved. Other bond lengths and angles in the anion, and the structure of the $NEt_4^+$ cation, are unremarkable.

*Structure of* $[Ge\{Co_7(CO)_{20}\}]^-$ (2).—Again an ionic structure is observed with discrete $NEt_4^+$ and $[Ge\{Co_7(CO)_{20}\}]^-$. A perspective view of the anion is shown in Figure 2 and some structural parameters in Table 4.

The anion can be regarded as a derivative of the $C_{3v}$ form of $[Co_4(CO)_{12}]$ with one terminal carbonyl group displaced by the $[GeCo_3(CO)_9]^-$. The metal core therefore consists of two separate tetrahedra, $GeCo_3$ and $Co_4$, connected by a Ge–Co bond. A similar core has recently been reported [16] for $[Ir_8(CO)_{22}]^{2-}$.

As is often found for $[M_3(CO)_{12}]$ or $[M_4(CO)_{12}]$ and their derivatives,[17,18] the $Co_4(CO)_{11}$ part of the structure of (2) was disordered. This took the form of a rotation of the $Co_4$ unit by *ca.* 45° about the Ge–Co(2)–Co(1) vector to place Co(4) at the Co(3) position and to move Co(3) to a triply bridging site (Co′) above the main Co(1)Co(2)Co(3) face, structure (6). The equivalent −45° rotation also took place to generate Co″. The disorder was compensated for by including partial occupancy of Co sites (*ca.* 13 and 7% for Co′ and Co″ respectively) but this was not completely successful as evidenced by some unreasonable bond lengths and angles arising in the refinement. Nevertheless, the overall structure is unambiguous.

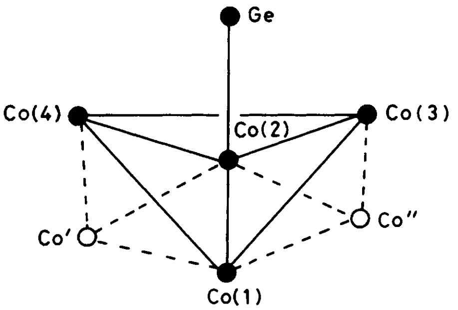
TABLE 4

Selected bond lengths (Å) and angle * (°) for $[Ge\{Co_7(CO)_{20}\}]^-$ (2)

| | | | |
|---|---|---|---|
| Ge–Co(5) | 2.31(1) | Co(5)–Co(6) | 2.58(1) |
| Ge–Co(6) | 3.16(1) | Co(5)–Co(7) | 2.56(1) |
| Ge–Co(7) | 2.34(1) | Co(6)–Co(7) | 2.60(1) |
| Ge–Co(2) | 2.27(1) | Co(1)–Co(4) | 2.40(1) |
| Co(1)–Co(2) | 2.53(1) | Co(2)–Co(4) | 2.42(1) |
| Co(2)–Co(3) | 2.43(1) | Co(3)–Co(4) | 2.25(1) |
| Co(1)–Co(3) | 2.49(1) | | |
| Ge–Co(2)–Co(1) | 172(1) | | |

* Parameters are probably less accurate than e.s.d.s suggest, because of disorder. The Co(3)–Co(4) bond in particular is unrealistically short.

Two other monosubstituted derivatives of $[Co_4(CO)_{12}]$, namely $[Co_4(CO)_{11}I]^-$ and $[Co_4(CO)_{11}(PPh_3)]$, have had structures reported [18,19] and a number of related $[Rh_4(CO)_{12}]$ and $[Ir_4(CO)_{12}]$ derivatives are available.[18] In most examples, these species contain three bridging CO ligands about a basal triangle, as in the $C_{3v}$ $[Co_4(CO)_{12}]$ structure,[18] with substitution occurring at a terminal site of one or more of the basal cobalt atoms. The exception is $[Co_4(CO)_{11}I]^-$ where the iodine is bonded to the unique, *apical* cobalt atom, although a small amount of the more usual isomer is apparently present in the crystal.[18] In $[(OC)_9Co_3GeCo_4(CO)_{11}]^-$ (2) substitution by $[GeCo_3(CO)_9]^-$ has occurred at the axial site of a basal Co atom, exhibiting the 'normal' pattern, as found in the $PPh_3$ derivative.[19] It appears therefore that it is the higher electronegativity of iodine that favours apical substitution in $[Co_4(CO)_{11}I]^-$ (*cf.* ref. 18), whereas the strong $\sigma$ donors $PPh_3$ and $[GeCo_3(CO)_9]^-$ co-ordinate to a bridged cobalt where excess of charge can be distributed *via* the bridging CO ligands.



(6)

The bond lengths and angles in $[Ge\{Co_7(CO)_{20}\}]^-$ are not very reliable in view of the disorder problems, so are not discussed in detail. Suffice it to comment that the Ge–Co and Co–Co bond lengths apparently fall within the ranges reported for other [$Co_4(CO)_{11}$] and [Ge{$Co_3(CO)_9$}] derivatives.

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