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The preparation and structures of two Ge–Co–Fe anionic clusters; $[GeCoFe_3(CO)_{14}]^-$ and $[Ge_2Co_5Fe_2(CO)_{22}]^-$

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Abstract

Reaction of $[Et_4N]_2[Fe_2(CO)_8]$ with μ_4-$Ge[Co_2(CO)_7]_2$ gives the mixed-metal cluster compound $Et_4N[Ge_2Co_5Fe_2(CO)_{22}]$, the anion of which has $-GeCo_3(CO)_9$ and $-GeCoFe_2(CO)_{10}$ sub-units coordinated *trans* about a planar $Co(CO)_3$ group *via* the germanium atoms. $Et_4N[GeCoFe_3(CO)_{14}]$ was isolated from the reaction of $[Me_2GeFe(CO)_4]_2$ and $Et_4N[Co(CO)_4]$; this anion also contains a $-GeCoFe_2(CO)_{10}$ tetrahedral core, with the germanium atom further bonded to an $Fe(CO)_4$ group.

Introduction

The addition of metal carbonyl anions to metal carbonyl clusters is a well established procedure for increasing the nuclearity of the clusters, although the products are not always predictable [1]. We have previously shown [2,3] that the addition of $[Co(CO)_4]^-$ to μ_4-$Ge[Co_2(CO)_7]_2$, (**1a**), occurs straightforwardly to give $[\mu_5\text{-}GeCo_5(CO)_{19}]^-$, (**2**), which can then be treated with $Co_2(CO)_8$ to give $[\{(OC)_9Co_3Ge\}_2Co(CO)_3]^-$, (**3**). In contrast, the closely-related μ_4-$Si[Co_2(CO)_7]_2$, (**1b**), with $[Co(CO)_4]^-$ gives paramagnetic $[SiCo_9(CO)_{21}]^{2-}$, with an encapsulated Si atom [4]. Under a variety of conditions there was no indication of formation of a silicon analogue of **2** or **3**, nor of a germanium analogue of $[SiCo_9(CO)_{21}]^{2-}$.

We now report the reaction of $[Fe_2(CO)_8]^{2-}$ with **1a**, which we expected might lead to a $GeCo_4Fe_2$ cluster but which instead gave a $Ge_2Co_5Fe_2$ species **4**. We also describe the structure of a cluster **5** which is formed in the reaction of $[Co(CO)_4]^-$ with $[Me_2GeFe(CO)_4]_2$. Both **4** and **5** incorporate a pseudo-tetrahedral $GeCoFe_2(CO)_{10}$ structural unit.

Experimental

Reactions were conducted under nitrogen by standard Schlenk techniques and with redistilled solvents. μ_4-$Ge[Co_2(CO)_7]_2$ [5], $[Me_2GeFe(CO)_4]_2$ [6],

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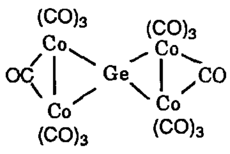
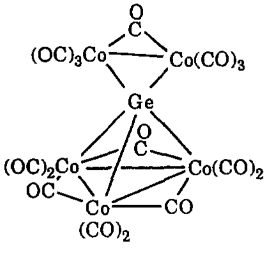


1a. E = Ge
1b. E = Si



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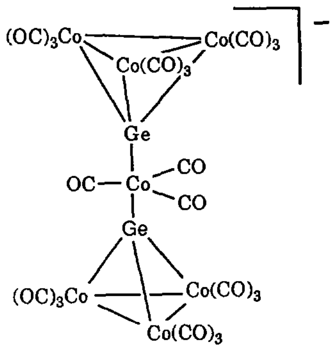

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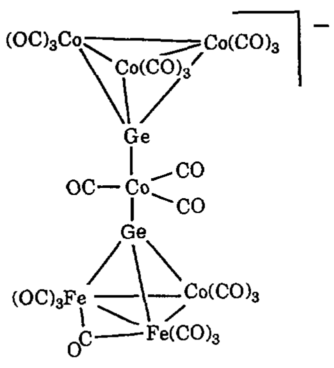

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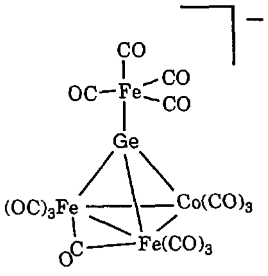

5

$[Et_4N]_2[Fe_2(CO)_8]$ [7] and $Et_4N[Co(CO)_4]$ [8] were synthesised by reported methods.

Preparation of $Et_4N[GeFe_3Co(CO)_{14}]$ (5). To a CH_2Cl_2 solution of $[Me_2GeFe(CO)_4]_2$ (0.79 g, 1.45 mmol) was added $Et_4N[Co(CO)_4]$ (0.25 g, 0.75 mmol). After 24 h stirring no reaction appeared to have taken place, so the CH_2Cl_2 was replaced by tetrahydrofuran (THF) and the mixture was stirred at 45°C for 16 h. After evaporation of the solvent the dark residue was washed with pentane to remove a small amount of unchanged $[Me_2GeFe(CO)_4]_2$. A subsequent extraction with Et_2O/CH_2Cl_2 (5 : 1) dissolved the main product, together with some unchanged $Et_4N[Co(CO)_4]$. Fractional crystallisation from the same solvents gave red-black crystals, identified by X-ray crystallography as $Et_4N[GeFe_3Co(CO)_{14}]$, (0.53 g, 65% based on Fe), $\nu(CO)$ (CH_2Cl_2, cm^{-1}) 2070w, 2016vs, 1944mw, 1910mw, 1810w,br.

Reaction of μ_4-$Ge[Co_2(CO)_7]_2$ with $[Et_4N]_2[Fe_2(CO)_8]$. A mixture of μ_4-$Ge[Co_2(CO)_7]_2$ (0.20 g, 0.29 mmol) and $[Et_4N]_2[Fe_2(CO)_8]$ (0.17 g, 0.29 mmol) in CH_2Cl_2 (15 ml) was stirred at ambient temperature. Monitoring by infrared spectroscopy showed that there was an initial rapid reaction giving rise to $[Co(CO)_4]^-$ ($\nu(CO)$ 1888 cm^{-1}) and probably $[FeCo(CO)_8]^-$ ($\nu(CO)$ 1990 m, 1960 m, 1780 m, cm^{-1}, *cf.* ref 9). A subsequent slower reaction gave increasing amounts of a species with a strong absorption at 2016 cm^{-1}. After 4 hours all μ_4-$Ge[Co_2(CO)_7]_2$ had been consumed. Solvent was removed and an ether extract of the residue dissolved $Co_4(CO)_{12}$ together with the main product, which was identified by X-ray crystallography after recrystallisation from CH_2Cl_2, as red-brown $Et_4N[Ge_2Co_5Fe_2(CO)_{22}]$, ν(CO) 2071w, 2016vs, 1949w, 1913m, 1810w,br cm^{-1}. An electron probe analysis of single crystals showed a Ge : Fe : Co ratio of 2.0 : 2.0 : 4.8 (calc. 2 : 2 : 5).

X-ray crystallography

For both compounds space group and preliminary cell dimensions were determined by precession photography. Accurate cell dimensions and intensity data were obtained on an Enraf Nonius CAD4 (for **4**) or a Nicolet P3 (for **5**) diffractometer, with monochromated Mo-K_α radiation (λ = 0.7107 Å). All calculations were performed using the SHELX programs [10].

Crystal data for 5: $C_{22}H_{20}CoFe_3GeNO_{14}$, M_r = 821.47. Orthorhombic, space group *Pbcn*, *a* 17.459(5), *b* 21.347(6), *c* 16.228(4) Å, *U* 6048(3) Å^3, D_c 1.80 g cm^{-3} for $Z = 8$, $F(000) = 3264$, μ(Mo-K_α) 30 cm^{-1}, *T* 138 K.

A total of 2792 unique reflections $5° < 2\theta < 40°$ was collected on a plate shaped crystal (0.30 × 0.20 × 0.10 mm, from Et_2O at −30°C) using ω scans. The data were corrected for Lorentz and polarisation effects but not for absorption. The 1401 reflections with $I > 2\sigma(I)$ were used in all calculations. The structure was solved by direct methods for the metal skeleton and other atoms were located in a subsequent difference map. In the final cycles of full-matrix least-squares refinement metal atoms were assigned anisotropic temperature factors and other atoms were treated isotropically. Hydrogen atoms were not included. Refinement converged with *R* 0.0843, R_w 0.0721 where $w = [\sigma^2(F) + 0.00345F^2]^{-1}$, with no final shifts greater than 0.2 σ and no residual electron density > 0.9 e Å^{-3}.

Crystal data for 4: $C_{30}H_{20}Co_5Fe_2Ge_2NO_{22}$, M_r = 1298.03. Triclinic, space group $P\bar{1}$, *a* 12.397(1), *b* 13.051(3), *c* 16.031(2) Å, α 76.53(5), β 88.14(4), γ 62.51(1)°, *U* 2229 Å^3, D_c 1.93 g cm^{-3} for $Z = 2$, $F(000) = 1268$, μ(Mo-K_α) 37 cm^{-1}, *T* 291 K.

A total of 3245 unique reflections $2° < 2\theta < 42°$ was collected on a small, weakly diffracting crystal (from CH_2Cl_2/hexane) using θ–2θ scans. The data were corrected for Lorentz and polarisation effects, but not for absorption since suitable reflections on which to base azimuthal corrections could not be found. The 1245 reflections with $I > 2\sigma(I)$ were used in all calculations. The structure was solved by direct methods for the metal skeleton and other atoms were located in subsequent difference maps. There are two crystallographically distinct Et_4N^+ cations, each lying on an inversion centre so each was necessarily disordered. They were modelled with four methyl C atoms defining a square about the N, with eight half-carbon atoms at the corners of a cube for the methylene atoms. The equatorial CO ligands on the central Co atom were also partly disordered. All these factors aggravated problems associated with poor crystal quality so that the structure is less precisely defined than usual. In the final cycles of full-matrix least-squares refinement metal atoms were assigned anisotropic temperature factors and other atoms were treated isotropically. H atoms were not included. Refinement converged with *R* 0.0784, R_w 0.0628 where $w = [\sigma^2(F) + 0.0001F^2]^{-1}$,

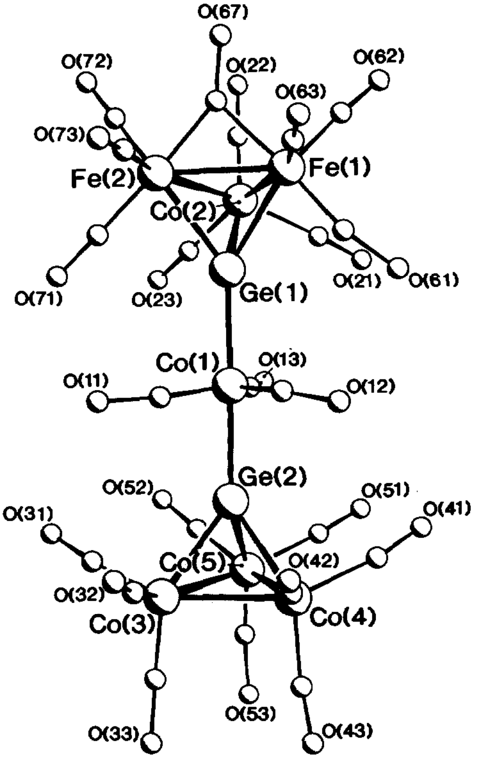

Fig. 1. The structure of the anion $[Ge_2Fe_2Co_5(CO)_{22}]^-$ (4).

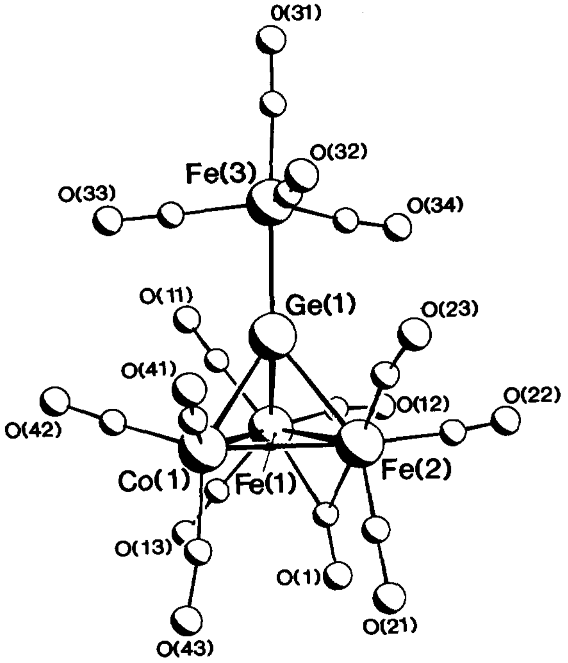

Fig. 2. The structure of the anion $[GeCoFe_3(CO)_{14}]^-$ (5).

Table 1

Final positional parameters for $Et_4N[Ge_2Co_5Fe_2(CO)_{22}]$ (4)

Atom	x	y	z	Atom	x	y	z
Ge(1)	0.1327(5)	0.2506(5)	0.2774(4)	Ge(2)	−0.0768(5)	0.6590(5)	0.1892(4)
Fe(1)	0.3140(7)	0.0782(7)	0.2720(5)	Fe(2)	0.1109(8)	0.0750(7)	0.3144(5)
Co(1)	0.0278(8)	0.4550(7)	0.2263(6)	Co(2)	0.2253(7)	0.1296(7)	0.4173(5)
Co(3)	−0.2693(7)	0.8152(7)	0.1415(5)	Co(4)	−0.0661(7)	0.8196(7)	0.0968(5)
Co(5)	−0.1225(7)	0.8119(7)	0.2543(5)	C(11)	−0.117(7)	0.457(6)	0.191(5)
C(12)	0.091(9)	0.453(8)	0.152(7)	C(13)	0.058(6)	0.476(6)	0.314(5)
C(21)	0.321(7)	0.207(7)	0.423(5)	C(22)	0.289(6)	0.009(7)	0.487(5)
C(23)	0.088(6)	0.219(5)	0.462(4)	C(31)	−0.351(5)	0.756(5)	0.203(4)
C(32)	−0.292(4)	0.773(4)	0.050(3)	C(33)	−0.359(6)	0.965(7)	0.125(4)
C(41)	0.097(6)	0.765(5)	0.122(4)	C(42)	−0.057(5)	0.776(5)	−0.005(4)
C(43)	−0.136(5)	0.975(6)	0.066(4)	C(51)	0.025(7)	0.767(6)	0.301(4)
C(52)	−0.176(5)	0.754(5)	0.348(4)	C(53)	−0.190(7)	0.943(9)	0.257(5)
C(61)	0.342(5)	0.188(6)	0.226(4)	C(62)	0.453(6)	−0.018(6)	0.321(4)
C(63)	0.334(5)	0.036(5)	0.176(4)	C(67)	0.274(5)	−0.048(5)	0.325(3)
C(71)	−0.040(5)	0.180(4)	0.311(3)	C(72)	0.104(5)	−0.034(6)	0.396(4)
C(73)	0.079(5)	0.037(5)	0.223(4)	O(11)	−0.194(6)	0.459(6)	0.179(5)
O(12)	0.171(5)	0.470(4)	0.094(3)	O(13)	0.085(4)	0.480(4)	0.389(3)
O(21)	0.369(4)	0.254(4)	0.430(3)	O(22)	0.345(3)	0.906(4)	0.539(3)
O(23)	0.012(4)	0.276(3)	0.493(2)	O(31)	−0.395(3)	0.713(3)	0.259(3)
O(32)	−0.296(4)	0.731(4)	−0.009(3)	O(33)	−0.421(4)	1.070(4)	0.088(3)
O(41)	0.193(4)	0.719(4)	0.147(3)	O(42)	−0.051(4)	0.739(4)	−0.063(3)
O(43)	−0.171(4)	1.074(4)	0.035(3)	O(51)	0.121(4)	0.729(4)	0.327(3)
O(52)	−0.203(4)	0.699(4)	0.394(3)	O(53)	−0.250(4)	1.064(4)	0.246(3)
O(61)	0.391(3)	0.261(4)	0.211(3)	O(62)	0.557(4)	−0.074(4)	0.363(3)
O(63)	0.353(3)	−0.001(3)	0.113(3)	O(67)	0.335(4)	−0.155(4)	0.343(3)
O(71)	−0.140(4)	0.249(3)	0.323(2)	O(72)	0.093(4)	−0.097(4)	0.455(3)
O(73)	0.055(4)	0.020(4)	0.161(3)	N(1)	0.50	0.50	0.00
N(2)	0.50	0.50	0.50	C(81)	0.526(5)	0.348(5)	−0.084(4)
C(82)	0.540(7)	0.515(7)	0.658(5)	C(83)	0.295(6)	0.527(6)	0.539(4)
C(84)	0.647(6)	0.328(6)	0.130(5)	C(85)	0.45(1)	0.41(1)	0.006(9)
C(86)	0.38(1)	0.63(1)	0.48(1)	C(87)	0.442(9)	0.416(9)	0.541(7)
C(88)	0.35(1)	0.60(1)	−0.048(8)	C(89)	0.56(1)	0.46(1)	−0.072(8)
C(90)	0.506(9)	0.402(9)	0.099(6)	C(91)	0.51(1)	0.42(1)	0.438(8)
C(92)	0.43(1)	0.57(1)	0.39(1)				

with no final shifts greater than 0.6 σ (involving a disordered atom). Residual electron density was < 0.8 e Å^{-3}.

The geometries of the anions **4** and **5** are illustrated in Figs. 1 and 2 respectively, atom coordinates are given in Tables 1 and 2, and selected bond parameters are listed in Table 3.

Results and discussion

Syntheses

The reaction of μ_4-$Ge[Co_2(CO)_7]_2$ with $[Fe_2(CO)_8]^{2-}$ appears to follow eq. 1, although the detailed stoichiometry has not been established.

$$4\mu_4\text{-Ge}[Co_2(CO)_7]_2\ (\mathbf{1a}) + 2[Fe_2(CO)_8]^{2-} \longrightarrow$$

$$2[Ge_2Fe_2Co_5(CO)_{22}]^-\ (\mathbf{4}) + 2[Co(CO)_4]^- + Co_4(CO)_{12} + 8CO \quad (1)$$

Table 2

Final positional parameters for $Et_4N[GeCoFe_3(CO)_{14}]$ (**5**)

Atom	x	y	z	Atom	x	y	z
Co(1)	0.2036(2)	0.2906(1)	0.0398(2)	Co(1)	0.1985(2)	0.2330(2)	0.1620(2)
Fe(1)	0.0926(2)	0.2256(2)	0.0472(3)	Fe(2)	0.2282(2)	0.1822(2)	0.0170(3)
Fe(3)	0.2366(2)	0.3877(2)	−0.0127(2)	C(1)	0.133(2)	0.141(1)	0.050(2)
O(1)	0.111(1)	0.0883(9)	0.062(1)	C(11)	0.055(2)	0.302(1)	0.056(2)
O(11)	0.025(1)	0.349(1)	0.057(1)	C(12)	0.051(2)	0.217(2)	−0.051(2)
O(12)	0.025(1)	0.2008(9)	−0.116(1)	C(13)	0.020(2)	0.197(1)	0.114(2)
O(13)	−0.026(1)	0.175(1)	0.156(1)	C(21)	0.272(2)	0.119(1)	0.061(2)
O(21)	0.296(1)	0.071(1)	0.091(1)	C(22)	0.219(2)	0.156(1)	−0.087(2)
O(22)	0.210(1)	0.1450(9)	−0.155(1)	C(23)	0.314(2)	0.221(2)	−0.003(2)
O(23)	0.377(1)	0.2381(9)	−0.020(1)	C(31)	0.249(2)	0.459(2)	−0.060(2)
O(31)	0.253(1)	0.510(1)	−0.092(1)	C(32)	0.333(2)	0.375(1)	0.009(2)
O(32)	0.401(1)	0.3749(9)	0.020(1)	C(33)	0.185(2)	0.417(1)	0.075(2)
O(33)	0.157(1)	0.437(1)	0.131(2)	C(34)	0.199(2)	0.353(1)	−0.101(2)
O(34)	0.175(1)	0.333(1)	−0.165(2)	C(41)	0.296(2)	0.254(1)	0.188(2)
O(41)	0.356(1)	0.272(1)	0.196(1)	C(42)	0.144(2)	0.284(1)	0.220(2)
O(42)	0.110(1)	0.321(1)	0.258(2)	C(43)	0.183(2)	0.163(2)	0.210(2)
O(43)	0.172(1)	0.117(1)	0.250(1)	N(1)	0.0	0.035(1)	0.75
C(101)	0.068(2)	0.078(1)	0.727(2)	C(102)	0.141(2)	0.042(1)	0.701(2)
C(103)	−0.020(2)	−0.013(1)	0.680(2)	C(104)	−0.047(2)	0.024(1)	0.601(2)
N(2)	0.50	0.045(2)	0.25	C(201)	0.448(2)	0.086(2)	0.194(3)
C(202)	0.486(3)	0.135(3)	0.151(3)	C(203)	0.432(3)	0.013(3)	0.295(4)
C(204)	0.459(4)	−0.025(3)	0.347(5)				

There appears to be an initial rapid reaction in which $[Co(CO)_4]^-$ is formed, consistent with a reaction in which $[Fe_2(CO)_8]^{2-}$ displaces the cobalt anion from **1a**. It is not clear whether this occurs by an addition/elimination sequence, or by an electron transfer process; $[Fe_2(CO)_8]^{2-}$ will be a strong reducing agent, and electrochemical studies show **1a** is irreversibly reduced, with $[Co(CO)_4]^-$ a probable product [11]. The displacement of $[Co(CO)_4]^-$ by $[Fe(CO)_4]^{2-}$ is well-established in simpler systems involving bonds to Group 14 elements [12], but this is the first observation of this type for $[Fe_2(CO)_8]^{2-}$. A subsequent, slower reaction leads to the formation of the complex anion **4**. By comparison with the proposed routes to **3** and to $[(OC)_9Co_3GeCo_4(CO)_{11}]^-$ [3], a reasonable sequence would involve the initial formation of a $[\mu_3\text{-}GeFe_2Co(CO)_{10}]^-$ group which, acting as a Lewis base *via* the lone pair of electrons on the Ge atom, could displace a CO group on the terminal cobalt atom of $(OC)_4CoGeCo_3(CO)_9$ (a known condensation product of **1a** [4]). This would give **4**. However these cluster expansion reactions are seldom straightforward so mechanistic suggestions must remain speculative. Nevertheless, in this system the reaction is quite specific; **4** is the only complex anionic species formed in any quantity, as judged by the infrared spectrum of the crude product.

The ratio of Ge : Fe : Co in single crystals of **4** was indicated by electron probe analysis as being 2 : 2 : 5, within the accuracy of the technique. An infrared spectrum was rather featureless, with one major, broad band as is often found for cluster anions, and with a weak bridging CO peak at 1810 cm^{-1}. The exact identity of **4** was ultimately established by an X-ray crystal structure determination (see below).

Table 3

Selected bond parameters for **4** and **5**

Bond lengths (Å) for ***4***					
Ge(1)–Fe(1)	2.35(1)	Ge(1)–Fe(2)	2.37(1)	Ge(1)–Co(1)	2 31(1)
Ge(1)–Co(2)	2.38(1)	Ge(2)–Co(1)	2.29(1)	Ge(2)–Co(3)	2.310(9)
Ge(2)–Co(4)	2.324(9)	Ge(2)–Co(5)	2.298(9)	Fe(1)–Fe(2)	2.60(1)
Fe(1)–Co(2)	2.64(1)	Fe(2)–Co(2)	2.62(1)	Co(3)–Co(4)	2.62(1)
Co(3)–Co(5)	2.59(1)	Co(4)–Co(5)	2.59(1)		
Bond angles (°) for ***4***					
Fe(1)–Ge(1)–Fe(2)	66.9(3)	Fe(1)–Ge(1)–Co(1)	144.5(4)		
Fe(1)–Ge(1)–Co(2)	67.7(3)	Fe(2)–Ge(1)–Co(1)	143.9(4)		
Fe(2)–Ge(1)–Co(2)	67.0(3)	Co(1)–Ge(1)–Co(2)	131.0(4)		
Co(1)–Ge(2)–Co(3)	141.5(4)	Co(1)–Ge(2)–Co(4)	139.5(4)		
Co(1)–Ge(2)–Co(5)	137.4(4)	Co(3)–Ge(2)–Co(4)	68.8(3)		
Co(3)–Ge(2)–Co(5)	68 3(3)	Co(4)–Ge(2)–Co(5)	68.2(3)		
Ge(1)–Fe(1)–Fe(2)	56.8(3)	Ge(1)–Fe(1)–Co(2)	56.7(3)		
Fe(2)–Fe(1)–Co(2)	60.0(3)	Ge(2)–Fe(2)–Fe(1)	56.2(3)		
Ge(1)–Fe(2)–Co(2)	56.8(3)	Fe(1)–Fe(2)–Co(2)	60.7(3)		
Ge(2)–Co(4)–Co(3)	55.3(3)	Ge(2)–Co(4)–Co(5)	55.4(3)		
Co(3)–Co(4)–Co(5)	59.5(3)	Ge(1)–Co(1)–Ge(2)	174.5(5)		
Ge(1)–Co(2)–Fe(1)	55.6(3)	Ge(1)–Co(2)–Fe(2)	56.2(3)		
Fe(1)–Co(2)–Fe(2)	59.3(3)	Ge(2)–Co(3)–Co(4)	55 8(3)		
Ge(2)–Co(3)–Co(5)	55.6(3)	Co(4)–Co(3)–Co(5)	59.7(3)		
Ge(2)–Co(5)–Co(4)	56.4(3)	Ge(2)–Co(5)–Co(3)	56.1(3)		
Co(3)–Co(5)–Co(4)	60.8(3)				
Bond lengths (Å) for ***5***					
Ge(1)–Co(1)	2.334(5)	Ge(1)–Fe(1)	2.387(5)	Ge(1)–Fe(2)	2.382(5)
Ge(1)–Fe(3)	2.316(5)	Co(1)–Fe(1)	2.630(6)	Co(1)–Fe(2)	2.643(6)
Fe(1)–Fe(2)	2.590(5)	Fe(1)–C(1)	1.96(3)	Fe(2)–C(1)	1.96(3)
Bond angles (°) for ***5***					
Co(1)–Ge(1)–Fe(1)	67.7(2)	Co(1)–Ge(1)–Fe(2)	68.1(2)		
Co(1)–Ge(1)–Fe(3)	142.5(2)	Fe(1)–Ge(1)–Fe(2)	65.8(2)		
Fe(1)–Ge(1)–Fe(3)	137.8(2)	Fe(2)–Ge(1)–Fe(3)	140.2(2)		
Ge(1)–Co(1)–Fe(1)	57.1(1)	Ge(1)–Co(1)–Fe(2)	56.8(1)		
Fe(1)–Co(1)–Fe(2)	58.9(1)	Ge(1)–Fe(1)–Co(1)	55.2(1)		
Ge(1)–Fe(1)–Fe(2)	57.0(1)	Co(1)–Fe(1)–Fe(2)	60.8(2)		
Ge(1)–Fe(2)–Co(1)	55.1(1)	Co(1)–Fe(2)–Fe(1)	60.3(2)		
Ge(1)–Fe(2)–Fe(1)	57.2(1)				

The other anion described in this paper was prepared by the reaction of $[Me_2GeFe(CO)_4]_2$ with $Et_4N[Co(CO)_4]$, brought about in THF. The major product, anion **5**, was unexpected since the metal ratio does not reflect the reaction stoichiometry, and the reaction must involve cleavage of Ge–Me bonds which is rare, although not completely unprecedented [13], under these mild conditions. The reaction may involve the base-stabilised germylene $Me_2(THF)GeFe(CO)_4$, since species of this type are known to be generated from $[R_2GeFe(CO)_4]_2$ dimers in THF [14]. Characterisation of **5** was by X-ray crystallography.

Structures

For both **4** and **5** only crystals of rather poor quality for single-crystal X-ray crystallography were obtained, so the structural determinations are of lower accuracy than usual. However the overall features are unambiguous.

For **5**, the asymmetric unit consists of discrete $[(OC)_4FeGeCoFe_2(CO)_{10}]^-$ anions (Fig. 1), and two half-cations with the two independent Et_4N^+ groups lying on sites of two-fold symmetry; one of these shows partial disorder. Within the cluster there is a $GeCoFe_2$ tetrahedral core, with a further $Fe(CO)_4$ group attached to the germanium atom. It is essentially isostructural with $[(OC)_4FePFe_3(CO)_{10}]^-$ [15], and has the same metal framework as the isoelectronic $[(OC)_4FeGeFe_3(CO)_{10}]^{2-}$ [16], although for this last example the tenth CO ligand is triply-bridging the Fe_3 triangle rather than edge-bridging as in **5** and in the $FePFe_3$ example. The anion **5** can also be related to $(OC)_4CoGeCo_3(CO)_9$ [17] by replacing two $Co(CO)_3$ groups by an $Fe_2(CO)_7$ group, maintaining the electron count for the tetrahedral unit, and replacing the apical $Co(CO)_4$ by an $Fe(CO)_4$ together with an overall negative charge. Clusters incorporating tetrahedral units EM_3 (E = Main Group, M = transition element) are common [18], but **5** is the first structurally-characterised mixed $ECoFe_2$ example with E from Group 14 (other than E = C [19]), although examples with E from Groups 15 or 16 are established [20].

Within the tetrahedral core the Ge–Fe distances (2.385 Å) are longer than the Ge–Co distance (2.334 Å), possibly reflecting the increased steric constraints at the Fe atoms arising from the extra CO ligand. The bridged Fe–Fe bond (2.590 Å) is shorter than the unbridged Fe–Co bonds (2.636 Å), as expected. The Ge–Fe bond to the apical $Fe(CO)_4$ group (2.316 Å) is noticeably short, much less than the Ge–Fe bonds within the cluster unit (2.384 Å). This is the same trend as in $[(OC)_4FeGeFe_3(CO)_{14}]^{2-}$ [16] but the reverse of that in $(OC)_4CoGeCo_3(CO)_9$ where the external Ge–Co bond was found to be *longer* than the Ge–Co distances within the tetrahedral unit [17]. For $[(OC)_4FePFe_3(CO)_{10}]^-$ the apical P–Fe is similar to the cluster P–Fe bonds in length [15].

For **4** the unit cell contains $[Ge_2Fe_2Co_5(CO)_{22}]^-$ anions (illustrated in Fig. 2) and two independent Et_4N^+ cations at crystallographic inversion centres; these are necessarily disordered. The anion is closely related to $[\{(OC)_9Co_3Ge\}_2Co(CO)_3]^-$ (**3**), with two of the $Co(CO)_3$ groups of one unit replaced by an $Fe_2(CO)_7$ group [3]. Alternatively, it can be viewed as a *trans*-$L_2Co(CO)_3$ species with $-GeCo_3(CO)_9$ and $-GeCoFe_2(CO)_{10}$ groups coordinated to the planar $Co(CO)_3$ unit *va* the germanium atoms. A comparison of the $GeCoFe_2(CO)_{10}$ unit of **4** with the same group of **5** gives complete agreement of structural parameters within the accuracy of the determinations, while the $GeCo_3(CO)_9$ unit corresponds closely to that in $(OC)_4CoGeCo_3(CO)_9$, although the Ge–Co bonds appear slightly longer in **4**. The Ge–Co bonds to the central Co(1) are 2.30 Å, similar to those of **3**, and much shorter than the equivalent, external Ge–Co bond in $(OC)_4CoGeCo_3(CO)_9$. It is now a general observation that E–Co bonds *trans* to another ER_3 group are shorter than E–Co bonds *trans* to CO ligands (E = Ge, Sn), and possible reasons for this have been discussed in more detail elsewhere [21].

The characterisation of **4** and **5** establishes $-GeCoFe_2(CO)_{10}$ as equivalent to the common $-GeCo_3(CO)_9$ as a building unit for clusters; more examples can be expected from reactions of Ge–Co species with iron carbonyl anions or from Ge–Fe substrates with $[Co(CO)_4]^-$.

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