Preparation and the Crystal and Molecular Structure of $[NEt_4][Ge\{Co_2(CO)_7\}\{Co_2(CO)_6[HgCo(CO)_4]\}]$: † an Anion containing a Mercury-bridged Cobalt–Cobalt Bond

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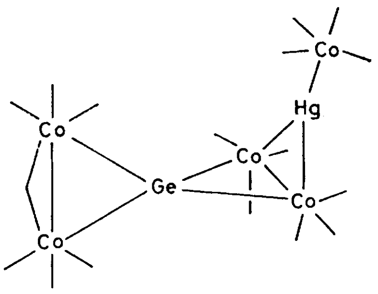
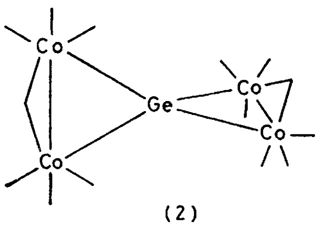
The title compound has been isolated from the reaction of GeI_4 with $Na[Co(CO)_4]$ in the presence of Hg and has been characterised by *X*-ray analysis. Crystals are triclinic, $a = 12.065(1)$, $b = 17.334(2)$, $c = 9.222(1)$ Å, $\alpha = 95.17(3)$, $\beta = 82.72(3)$, $\gamma = 96.95(3)°$, space group $P\bar{1}$, and $Z = 2$. The structure has been solved by direct methods and refined to $R = 0.049$ for 3 136 reflections $[I \geqslant 5\sigma(I)]$. The anion contains a common Ge atom bridging the Co–Co bonds both of a $Co_2(CO)_7$ unit and of a $Co_2(CO)_6$ unit which is also bridged by a $HgCo(CO)_4$ group.

DURING the preparation of $[Ge\{Co_2(CO)_7\}_2]$ (2) it was noted that the benzene–insoluble residue contained an anionic species.[1] This could not be characterised completely by chemical or spectroscopic means so a single-crystal *X*-ray analysis was carried out. This showed that the anion is a novel species of formula $[Ge\{Co_2(CO)_7\}\{Co_2(CO)_6[HgCo(CO)_4]\}]^-$ (1) which is *formally* derived by replacing one μ-CO of (2) by a hypothetical μ-$[HgCo(CO)_4]^-$ group, giving the first example of an Hg-bridged Co–Co bond.



(1)



(2)

EXPERIMENTAL

All reactions were carried out using standard inert-atmosphere techniques. The compounds GeI_4 (Laramie Chemical Co.) and $[Co_2(CO)_8]$ (Pressure Chemicals) were used as received. Infrared spectra were recorded using a Perkin-Elmer model 180 spectrometer and electron-probe analysis using an ORTEC energy-dispersive *X*-ray analyser attached to a JEOL JSM 35 scanning electron microscope.

Preparation of (1).—A solution of $[Co_2(CO)_8]$ (3.4 g, 10 mmol) in tetrahydrofuran (thf) (40 cm^3) was reduced with 1% sodium amalgam. After decantation, the solution of $Na[Co(CO)_4]$ (containing traces of finely suspended amalgam) was evaporated under vacuum. The residue was suspended in benzene–hexane (1 : 2, 60 cm^3) and GeI_4 (1.9 g, 3.6 mmol) was added. After stirring for 3 h at 25 °C the supernatant (containing[1] $[Ge\{Co_2(CO)_7\}_2]$) was removed. The residue was dissolved in Et_2O (15 cm^3) and $[NEt_4]Br$ (1.0 g) was added. After 10 min the mixture was filtered and the filtrate evaporated to give the crude product which contained (1) and various amounts of a Hg-free anion. Pure (1) was obtained as air-sensitive black crystals by fractional crystallisation from CH_2Cl_2–hexane solvent: ν(CO)(CH_2Cl_2) at 2 080w, 2 060m, 2 037m, 2 023vs, 2 004w, 1 970w, and 1 818w,br cm^{-1}. Yields of (1) were low (typically *ca.* 5%) and variable. Electron-probe analysis showed the presence in (1) of Hg : Ge : Co in *ca.* 1 : 1 : 5 ratio and full characterisation was achieved by *X*-ray crystallography.

Structural Determination of (1).—*Data collection.* A single crystal of dimensions 0.33 × 0.14 × 0.08 mm was sealed in a glass capillary. Preliminary precession photographs showed triclinic symmetry. Intensity data were collected on a Hilger and Watts automatic four-circle diffractometer using zirconium-filtered Mo-K_α radiation.

Crystal data.‡ $C_{25}H_{20}Co_5GeHgNO_{17}$, $M = 1\,174.28$, Triclinic, space group $P\bar{1}$, $a = 12.065(1)$, $b = 17.334(2)$, $c = 9.222(1)$ Å, $\alpha = 95.17(3)$, $\beta = 82.72(3)$, $\gamma = 96.95(3)°$, $U = 1\,893$ Å^3, $D_m = 1.98$ g cm^{-3} (by flotation), $Z = 2$, $D_c = 2.06$ g cm^{-3}, $F(000) = 1\,120$, μ(Mo-K_α) = 67.6 cm^{-1}, $\lambda = 0.710\,7$ Å, 23 °C.

A total of 5 507 unique reflections for which $2\theta \leqslant 46°$ were collected by the θ—2θ scan technique. Three standard reflections monitored at regular intervals showed no sign of crystal decomposition. The data were corrected for Lorentz and polarisation effects and for absorption. Main programs used were HILGOUT, ABSORB, SHELX76, and ORTEP. Details have been described elsewhere.[1]

Solution and refinement. Initial solution by direct methods (SHELX76) was attempted assuming a metal core of $GeCo_{5-6}$. A network of six metal atoms was revealed but one of these had very high electron density and would not refine as a Co or Ge atom. The suspicion that this was a Hg atom was confirmed by electron-probe analysis

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† Tetraethylammonium [μ-carbonyl-bis(tricarbonylcobaltio)-(*Co–Co*)][μ-tetracarbonylcobaltiomercurio-bis(tricarbonylcobaltio)(*Co–Co*)]germanate(4*Co–Ge*).

‡ Throughout this paper, estimated standard deviations in the least-significant figures are given in parentheses.

(see *Preparation*). Refinement of the $HgGeCo_5$ core followed by a Fourier-difference synthesis revealed all other atoms in the anion and the N and terminal carbons of the NEt_4^+ cation. The ethyl groups were found to be disordered, with different conformations giving two equivalent sites for each of the four methylene C atoms. These were included with site occupancy of 0.5 and refined sensibly. Similar disorder of ethyl groups is well known.[2] To reduce computing time only the 3 136 reflections for which $I \geqslant 5\sigma(I)$ were included in the analysis. Blocked full-matrix least-squares refinement using a model with metal and oxygen atoms anisotropic and all other atoms isotropic converged at $R = 0.049$, $R' = 0.052$ with the 5σ data. A final structure-factor calculation using all 5 507 reflections gave $R = 0.081$ with no significant discrepancies between $|F_o|$ and $|F_c|$.

TABLE 1

Final positional parameters ($\times 10^4$) for (1) *

Atom	X/a	Y/b	Z/c
Ge	2 613(1)	7 004(1)	1 412(1)
Hg	2 500(1)	8 734(1)	1 075(1)
Co(1)	2 738(2)	6 463(1)	−1 122(2)
Co(2)	2 795(2)	5 638(1)	997(2)
Co(3)	1 395(1)	7 734(1)	2 947(2)
Co(4)	3 702(1)	8 023(1)	2 553(2)
Co(5)	2 111(2)	9 653(1)	−764(3)
C(B)	4 007(13)	6 069(9)	−440(16)
C(11)	1 219(20)	6 467(12)	−1 056(23)
C(12)	3 434(14)	7 360(10)	−1 739(17)
C(13)	2 894(16)	5 811(12)	−2 743(23)
C(21)	3 778(17)	5 607(11)	2 283(22)
C(22)	1 369(18)	5 507(12)	1 825(21)
C(23)	2 717(17)	4 693(13)	12(23)
O(B)	4 930(9)	6 040(8)	−753(16)
O(11)	308(13)	6 404(9)	−1 134(18)
O(12)	3 902(12)	7 914(7)	−2 168(12)
O(13)	3 051(16)	5 411(10)	−3 790(18)
O(21)	4 375(15)	5 509(10)	3 063(19)
O(22)	407(13)	5 435(9)	2 257(19)
O(23)	2 695(15)	4 100(8)	−645(18)
C(31)	1 325(13)	7 064(10)	4 316(19)
C(32)	291(16)	7 589(11)	1 889(20)
C(33)	1 160(15)	8 616(11)	4 080(21)
C(41)	3 910(13)	7 409(9)	3 862(18)
C(42)	4 802(15)	8 102(10)	1 164(19)
C(43)	3 815(16)	8 926(12)	3 685(22)
O(31)	1 217(13)	6 642(9)	5 172(16)
O(32)	−510(12)	7 463(12)	1 292(18)
O(33)	971(14)	9 169(9)	4 822(16)
O(41)	4 092(11)	7 030(8)	4 771(13)
O(42)	5 604(10)	8 159(9)	313(17)
O(43)	3 849(15)	9 457(9)	4 499(17)
C(51)	1 434(18)	10 084(13)	939(24)
C(52)	1 436(16)	8 811(12)	−1 651(21)
C(53)	3 619(24)	9 763(15)	−1 155(28)
C(54)	1 849(21)	10 350(15)	−1 980(28)
O(51)	930(15)	10 326(11)	1 916(21)
O(52)	959(14)	8 253(8)	−2 184(16)
O(53)	4 578(15)	9 784(10)	−1 530(17)
O(54)	1 665(19)	10 807(11)	−2 717(21)
N	7 487(10)	7 375(7)	−3 958(13)
C(1)	8 555(30)	6 968(21)	−4 361(39)
C(1′)	7 182(33)	6 530(23)	−3 810(43)
C(2)	8 300(20)	6 079(14)	−4 165(26)
C(3)	7 055(28)	7 196(20)	−2 299(37)
C(3′)	8 471(25)	7 765(18)	−3 096(33)
C(4)	7 978(20)	7 629(13)	−1 332(26)
C(5)	7 816(25)	8 177(17)	−4 237(33)
C(5′)	6 411(34)	7 841(24)	−3 373(44)
C(6)	6 637(21)	8 669(15)	−3 707(27)
C(7)	6 520(28)	6 917(19)	−4 870(37)
C(7′)	7 879(37)	7 607(25)	−5 538(49)
C(8)	6 916(20)	7 188(13)	−6 555(26)

* Primed atoms refer to disordered atoms, with two equivalent sites, see text.

Final positional parameters, together with the estimated standard deviations from the final cycle of refinement, are listed in Table 1. Selected bond lengths and angles are given in Table 2. A full listing of thermal parameters and tables of observed and calculated structure factors has been deposited as Supplementary Publication No. SUP 22954 (36 pp.).*

TABLE 2

Selected bond lengths (Å) and angles (°) for (1)

Bond lengths

Hg–Co(3)	2.675(2)	Ge–Co(1)	2.432(2)
Hg–Co(4)	2.591(2)	Ge–Co(2)	2.397(2)
Hg–Co(5)	2.551(3)	Ge–Co(3)	2.317(2)
Co(1)–Co(2)	2.536(3)	Ge–Co(4)	2.325(2)
Co(3)–Co(4)	2.751(2)	Co(1)–C(B)	1.95(1)
C(B)–O(B)	1.12(2)	Co(2)–C(B)	1.97(1)

Other Co–C distances are 1.73—1.83 Å (average 1.79 Å)
Other C–O distances are 1.10—1.18 Å (average 1.14 Å)

Non-bonded distances

Hg · · · Ge	3.063(2)	Ge · · · C(B)	2.79

Bond angles

Co(1)–Ge–Co(2)	63.4(1)	Ge–Co(1)–Co(2)	57.7(1)
Co(3)–Ge–Co(4)	72.7(1)	Ge–Co(2)–Co(1)	59.0(1)
Co(3)–Hg–Co(4)	63.0(1)	Ge–Co(3)–Co(4)	53.8(1)
Co(3)–Hg–Co(5)	140.1(1)	Ge–Co(4)–Co(3)	53.5(1)
Co(4)–Hg–Co(5)	157.1(1)		
Ge–Co(3)–Hg	75.3(1)	Ge–Co(4)–Hg	76.9(1)

Dihedral angles

Ge–Co(1)–Co(2)/Co(1)–Co(2)–C(B)	103
Ge–Co(3)–Co(4)/Co(3)–Co(4)–Hg	96
Ge–Co(1)–Co(2)/Ge–Co(3)–Co(4)	92

DISCUSSION

Preparation.—The reaction between GeI_4 and excess of $Na[Co(CO)_4]$ in hydrocarbon solvent leads to anionic products which can be crystallised as NEt_4^+ salts. The species initially isolated in the present study was found to be $[Ge\{Co_2(CO)_7\}\{Co_2(CO)_6[HgCo(CO)_4]\}]^-$ (1) containing Hg derived from the amalgam used to produce $[Co(CO)_4]^-$ from $[Co_2(CO)_8]$. The overall formation of the anion is summarised in equation (1) but the detailed

$$GeI_4 + 5[Co(CO)_4]^- + Hg \longrightarrow [HgGeCo_5(CO)_{17}]^- + 4I^- + 3CO \quad (1)$$

pathway is obscure. It seems probable that $[Ge\{Co_2(CO)_7\}_2]$ is an intermediate but we have been unable to prove this. As yet an alternative, specific route to (1) has not been found. A different anionic product with a similar i.r. spectrum [ν(CO)(CH_2Cl_2) at 2 078w, 2 048m, 2 022vs, 1 995w, and 1 968br cm^{-1}] but which does not contain Hg can also be isolated from the reaction, the ratio of the anionic products depending on the care taken in freeing the $[Co(CO)_4]^-$ solution from finely suspended amalgam. This second product can also be prepared by reaction of $[NEt_4][Co(CO)_4]$ with $[Ge\{Co_2(CO)_7\}_2]$ in CH_2Cl_2.[3]

Structure of (1).—The crystal consists of discrete anions and cations with no abnormal interionic distances.

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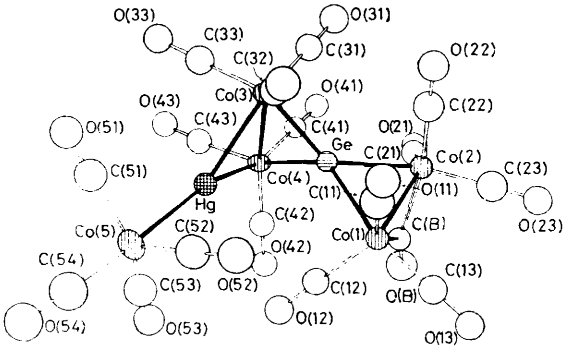
* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

A perspective view of the anion is given in the Figure which also shows the atom-labelling system used.

The anion is formally related [1] to $[Ge\{Co_2(CO)_7\}_2]$ (2) with one of the μ-CO groups replaced by a Hg atom which is further bonded to a $Co(CO)_4$ moiety. The Ge atom acts as a common bridge for two Co–Co bonds giving two mutually perpendicular (dihedral angle 92°) closed $GeCo_2$ triangles with a shared apex. One of the Co–Co bonds is also bridged by the Hg atom to give a $HgCo_2$ triangle. The Hg atom and all three Co atoms bonded to it are strictly coplanar. An electron-counting scheme which rationalises this and gives an 18-electron configuration to each Co atom involves the use of the two valence electrons of the Hg atom to bridge the Co–Co bond (replacing the two-electron donor CO). The Hg atom then accepts a pair of electrons from the Co of the $[Co(CO)_4]^-$ group. In this way the co-ordination about the Hg atom can be related to that found, for example,[4] in $[Co(\eta\text{-}C_5H_5)(CO)_2(HgCl_2)]$.

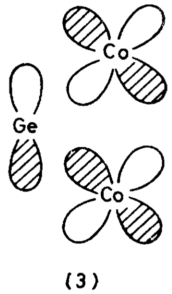


A perspective diagram of (1) showing atom labels

The two Co–Co bonds in the anion are distinctly different. The one bridged by both Ge and CO is similar in length (2.536 Å) to those found in other molecules containing a $Ge[Co_2(CO)_7]$ unit.[1,5,6] In contrast, the Hg-bridged Co–Co bond is unusually long (2.751 Å), presumably to accommodate the large bridging atom; even so the Co(3)–Hg–Co(4) angle is only 63°.

The terminal Hg–Co(5) distance (2.55 Å) is apparently normal, being equal to the sum of Pauling's single-bond metallic radii [7] and similar to those found in other cobalt–mercury compounds,[4] although longer than that [8] in $Hg[Co(CO)_4]_2$ (2.50 Å). The Hg–Co bonds within the triangular unit are significantly longer (2.59 and 2.67 Å). The non-bonded distance between the Hg and Ge is only 3.06 Å, well within the sum of the van der Waals radii, so presumably the long Hg–Co edge bonds, and the acute angle at Hg, are required to minimise this Hg · · · Ge interaction. Severe Ge · · · Hg repulsion is not indicated by the $GeCo_2/Co_2Hg$ dihedral angle of 96° which is, if anything, smaller than expected by comparison with related molecules.[5]

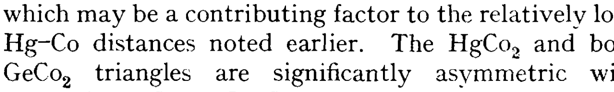
A comparison of the two $GeCo_2$ triangles shows an interesting variation in the Ge–Co bond lengths. Those in the carbonyl-bridged half of the anion (average 2.40 Å) are significantly longer than those in the same units [1] of $[Ge\{Co_2(CO)_7\}_2]$, while the Ge–Co distances in the Hg-bridged half are exceptionally short (2.32 Å). A comparison of the Ge–Co and Co–Co bonds in the two different $GeCo_2$ triangles of (1), together with those in the same units [1,6] in $[Ge\{Co_2(CO)_7\}_2]$ (Ge–Co 2.36, Co–Co 2.56 Å) and $[GePh\{Co(CO)_4\}\{Co_2(CO)_7\}]$ (Ge–Co 2.38, Co–Co 2.55 Å), shows that there is a tendency for decreasing Ge–Co bond lengths with increasing Co–Co distances. This relationship can be qualitatively understood by a consideration of the bonding within the $GeCo_2$ unit.[5] We may expect [9] the highest occupied molecular orbital (h.o.m.o.) of the triangle to have the form (3) which is Co–Co antibonding but Ge–Co bonding. As the Co–Co distance increases, overlap with the Ge orbital becomes more efficient, leading to stronger Ge–Co bonding.



(3)

A similar bonding diagram can be proposed for the $HgCo_2$ triangle; again the main orbital overlap will not be directed along the Hg–Co vectors but will have centrally and peripherally directed components (*cf.* refs. 5 and 9). In this case the large Hg atom will participate poorly in overlap of the type depicted in (3) which may be a contributing factor to the relatively long Hg–Co distances noted earlier. The $HgCo_2$ and both $GeCo_2$ triangles are significantly asymmetric with unequal Hg–Co or Ge–Co bonds. As noted previously, this is a common feature in such units [1,5] and can be explained in the present example by the relief of non-bonded interaction between atoms bridging the same Co–Co bond [Hg and Ge or Ge and C(B)] when they move towards opposite Co atoms.

General.—The most novel feature of (1) is the bridging of a Co–Co bond by a Hg atom. Usually the interaction of Hg with a M–M bond results in an insertion to give a linear M–Hg–M grouping.[10] It is possible that the first step in the insertion reaction involves a Hg-bridged intermediate, similar to the one found here, which then rearranges to give the final product [equation (2)]. In this connection it is noteworthy that insertion reactions in general occur more readily with dimers such as $[Co_2(CO)_8]$ or $[\{Fe(\eta\text{-}C_5H_5)(CO)_2\}_2]$, which favour bridging, than with those such as $[Mn_2(CO)_{10}]$ which have less tendency to form bridged M–M bonds.[10] For (1) the final step of insertion will not be favoured because this



$$L_nM{-}ML_n + Hg \longrightarrow L_nM\overset{Hg}{\text{—}}ML_n \longrightarrow L_nM{-}Hg{-}ML_n \quad (2)$$

would necessitate the breakdown of the $GeCo_2$ unit. At this stage we are unable to state definitely whether the third, terminal, group on the Hg atom is necessary to stabilise the $HgCo_2$ triangle. Superficially there is no reason why a $d^{10}s^2$ Hg atom cannot replace a μ-CO using the s^2 pair of electrons, although a Hg atom is likely to be a very weak base. On the other hand, the bridging unit can be considered as the formally d^{10} $HgCo(CO)_4^+$ which would provide an analogy with the recently reported d^{10} Ag^+ acting as a Lewis acid by interaction with electron-rich metal carbonyls to give an $AgFe_2$ triangle,[11] structurally and electronically similar to the $HgCo_2$ units described herein. This formalism would imply that the third group on the Hg is a necessary feature, and would suggest that other HgR^+ species could act as bridging ligands.

Further work aimed at determining the mechanism of formation of the Hg bridge in (1) and extension to other systems is in progress.

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