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# AN ELECTRON DIFFRACTION DETERMINATION OF THE GAS PHASE STRUCTURE OF GERMYLCOBALT TETRACARBONYL *

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## Summary

The molecular structure of germylcobalt tetracarbonyl in the gas phase has been determined by electron diffraction. Principal parameters ($r_a$) are: $r$(C—O), 112.8(4); $r$(Co—C)(average), 180.0(6); $r$(Co—Ge), 241.6(4) pm. The difference between axial and equatorial Co—C distances is very small. The equatorial carbonyl groups are bent towards the germyl group, with $C_{eq}$—Co—Ge angles of 83.8(3)°.

## Introduction

Although multiple bonding in silyl and germyl transition metal complexes, involving overlap of filled metal *d* orbitals with vacant silicon 3*d* or germanium 4*d* orbitals, is possible on symmetry grounds, there is little experimental evidence for or against it. Study of Si—M and Ge—M bond lengths may provide some such evidence, particularly by showing the effects of changing the metal, or the Group IV atom or its substituents. We have recently studied by electron diffraction the structures of silyl-, trifluorosilyl- and germyl-manganese pentacarbonyl [1,2]. The gas phase structure of silylcobalt carbonyl was studied some years ago [3], but otherwise only solid phase structures have been reported. As part of a series of structural studies of this type of compound, we present here the results of a determination of the gas phase structure of germylcobalt tetracarbonyl, and compare them with those for related compounds.

## Experimental

Germylcobalt tetracarbonyl was prepared by addition of germyl bromide to a solution of sodium cobalt tetracarbonyl in diethyl ether at room tempera-

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* No reprints available.

TABLE 1

WEIGHTING FUNCTIONS, CORRELATION PARAMETERS AND SCALE FACTORS

| Camera height (mm) | $\Delta s$ (nm$^{-1}$) | $s_{min}$ (nm$^{-1}$) | $s_1$ (nm$^{-1}$) | $s_2$ (nm$^{-1}$) | $s_{max}$ (nm$^{-1}$) | $p/h$ | Scale factor |
|---|---|---|---|---|---|---|---|
| 250 | 4 | 76 | 105 | 260 | 300 | 0.4201 | 1.069 ± 0.032 |
| 500 | 2 | 28 | 40 | 120 | 140 | 0.4795 | 1.020 ± 0.026 |
| 1000 | 1 | 10 | 17 | 64 | 72 | 0.4994 | 1.033 ± 0.052 |

ture, and purified by fractional condensation in vacuo [4]. Purity was checked spectroscopically.

Electron diffraction scattering intensities were collected photographically using Ilford N60 plates and a Balzers' KD G2 gas diffraction apparatus, and were obtained in digital form using a Joyce—Loebl microdensitometer. During the exposures the sample was maintained at 313 K and the nozzle at 328 K. Nozzle-to-plate distances of 250, 500 and 1000 mm were used, giving data over a range of the scattering variable, $s$, from 10 to 300 nm$^{-1}$. Calculations were carried out on an ICL 4-75 computer at the Edinburgh Regional Computing Centre using data reduction and least squares refinement programmes previously described [5,6], and the complex scattering factors of Cox and Bonham [7]. Table 1 shows weighting points (used to set up the off-diagonal weight matrix), correlation parameters and scale factors. The electron wavelength of 5.663 pm was determined by direct measurement of the accelerating voltage and from the diffraction pattern of powdered thallous chloride.

## Refinements

The molecule was assumed to have $C_3$ symmetry, with all C—O bonds of equal length. The structure was then defined by the distances Co—C$_{ax}$, Co—C$_{eq}$,

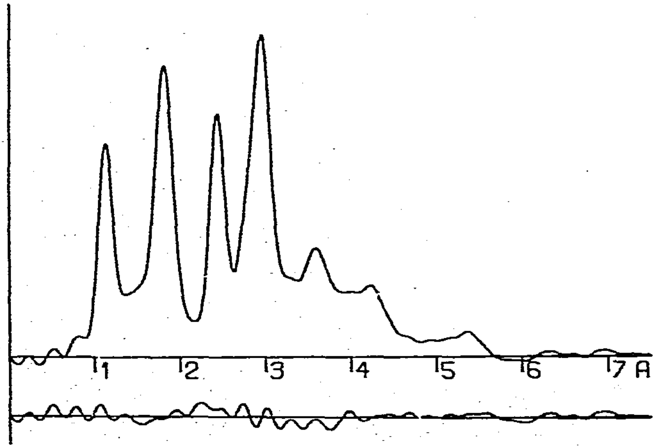

Fig. 1. Radial distribution curve, $P(r)/r$. Before Fourier inversion the data were multiplied by $s \exp(-0.000025\, s^2)/(z_{Co}-f_{Co})(z_O-f_O)$.

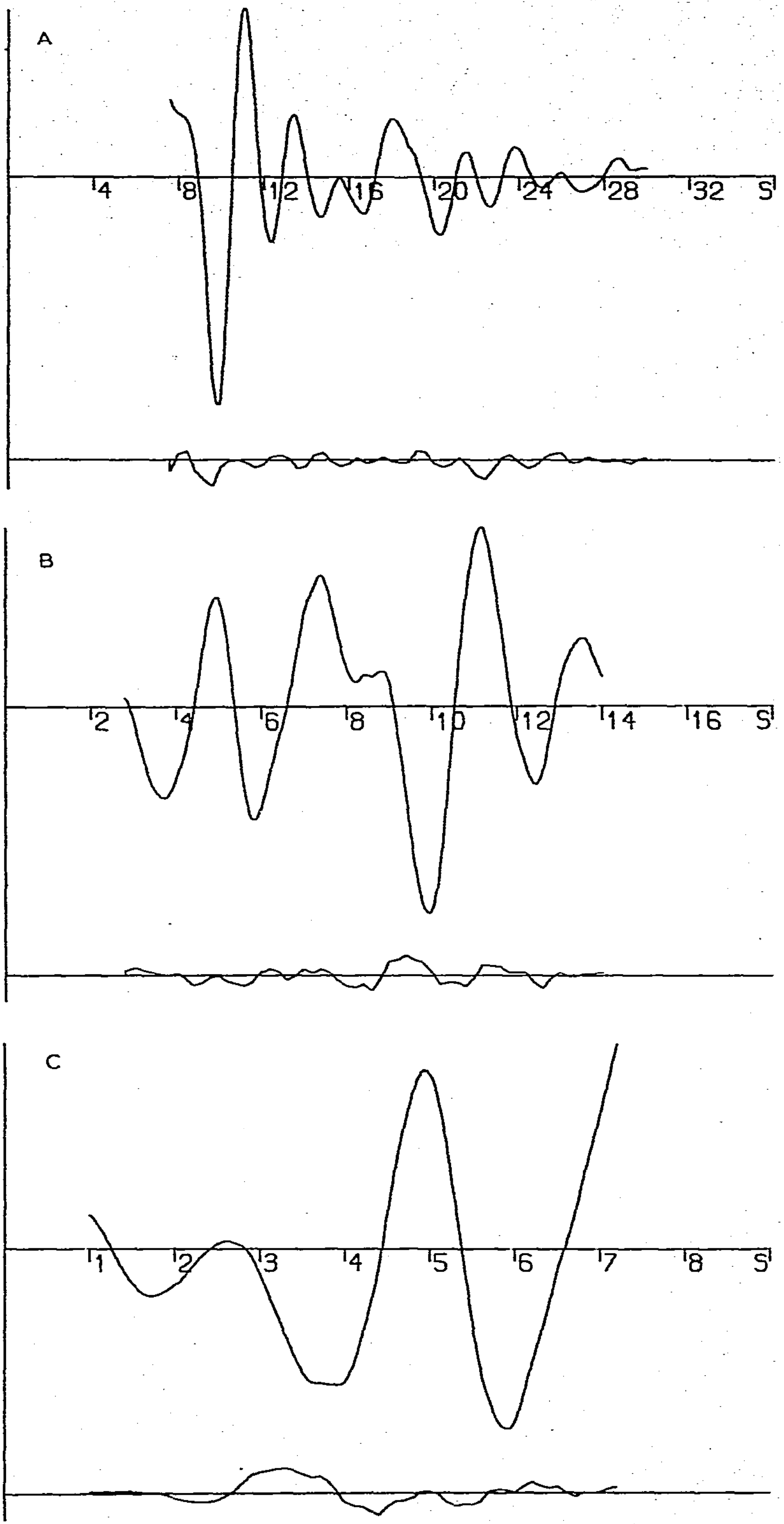

Fig. 2. Observed and final weighted difference molecular scattering intensities for $GeH_3Co(CO)_4$ for data sets obtained with nozzle-to-plate distances of 250, 500 and 1000 mm.

C—O, Co—Ge and Ge—H, the angles $C_{eq}$—Co—Ge, Co—$C_{eq}$—$O_{eq}$ and Co—Ge—H, and the twist angle of the germyl group away from the position in which it was eclipsed with respect to the Co(CO)$_4$ group. Of these, the C—O, Co—C(average) and Co—Ge distances and associated amplitudes of vibration all refined satisfactorily, as did the Co—C—O and C—Co—Ge angles. The dihedral angle was set at the value that was found to give the lowest $R$ factor, but was not included in subsequent refinements. The difference between axial and equatorial Co—C bond lengths was allowed to refine, but the estimated error in the value obtained is greater than the value itself. In any case, electron diffraction is not a good method for determining small deviations from idealised models, and any error in this parameter will be reflected in the amplitude of vibration associated with the Co—C distances.

TABLE 2

MOLECULAR PARAMETERS[a]

*(a). Independent distances and amplitudes (pm)*

| | | | |
|---|---|---|---|
| $r1$ | (Co—C)(mean) | 180.0(6) | |
| $\delta$ | (Co—C)(eq-ax) | −1.0(16) | |
| $r2$ | (C—O) | 112.8(4) | 5.2(7) |
| $r3$ | (Co—Ge) | 241.6(4) | 6.9(5) |
| $r4$ | (Ge—H) | 152.5(fixed) | 10.0(fixed) |

*(b). Dependent distances and amplitudes (pm)*

| | | | |
|---|---|---|---|
| d5 | (Co—$C_{eq}$) | 179.8(8) | 6.1(6) |
| d6 | (Co—$C_{ax}$) | 180.8(15) | 6.1(tied to $u$ 5) |
| d7 | (Co···$O_{eq}$) | 291.7(13) | 6.8(5) |
| d8 | (Co···$O_{ax}$) | 292.8(18) | 6.8(tied to $u$ 7) |
| d9 | ($C_{eq}$···$C_{eq}$) | 308.7(14) | 13.0(18) |
| d10 | ($C_{eq}$···$O_{eq}$) | 408.6(18) | 15.7(tied to $u$ 9) |
| d11 | ($O_{eq}$···$O_{eq}$) | 500.2(25) | 18.6(tied to $u$ 9) |
| d12 | ($C_{ax}$···$C_{eq}$) | 268.3(18) | 14.5(fixed) |
| d13 | ($C_{ax}$···$O_{eq}$) | 361.3(24) | 17.5(fixed) |
| d14 | ($C_{eq}$···$O_{ax}$) | 360.0(23) | 17.5(fixed) |
| d15 | ($O_{ax}$···$O_{eq}$) | 437.4(30) | 21.0(fixed) |
| d16 | (Ge···$C_{ax}$) | 420.3(19) | 10.0(16) |
| d17 | (Ge···$O_{ax}$) | 532.1(23) | 11.0(tied to $u$ 16) |
| d18 | (Ge···$C_{eq}$) | 284.2(6) | 16.5(14) |
| d19 | (Ge···$O_{eq}$) | 355.0(8) | 19.9(tied to $u$ 18) |
| d20 | (Co···H) | 325.1(12) | 15.0(fixed) |
| d21 | (H···$C_{eq}$) | 274.8(8) | 15.0(fixed) |
| d22 | (H···$C_{eq}$) | 379.1(9) | 15.0(fixed) |
| d23 | (H···$C_{eq}$) | 395.1(11) | 15.0(fixed) |
| d24 | (H···$O_{eq}$) | 295.0(8) | 15.0(fixed) |
| d25 | (H···$O_{eq}$) | 445.5(13) | 15.0(fixed) |
| d26 | (H···$O_{eq}$) | 472.7(14) | 15.0(fixed) |
| d27 | (H···$C_{ax}$) | 491.7(22) | 20.0(fixed) |
| d28 | (H···$O_{ax}$) | 599.6(29) | 20.0(fixed) |
| d29 | (H···H) | 248.9(fixed) | 11.0(fixed) |

*(c). Angles*

| | | |
|---|---|---|
| <1 | (Co—Ge—H) | 109.1(fixed) |
| <2 | ($C_{eq}$—Co—Ge) | 83.8(3) |
| <3 | (twist) | 10.0(see text) |
| <4 | (Co—$C_{eq}$—$O_{eq}$) | 178.3(fixed) |

[a] Distances ($r_a$) are given in pm, and angles in degrees. The angle Co—C—O, fixed in the final refinement, had been included in earlier refinements, in which the quoted value was obtained.

TABLE 3

LEAST SQUARES CORRELATION MATRIX MULTIPLIED BY 100

| $r1$ | $\delta$ | $r2$ | $r3$ | $<2$ | $u3$ | $u4$ | $u5$ | $u7$ | $u9$ | $u16$ | $u18$ | $k1$ | $k2$ | $k3$ | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 100 | −4 | 36 | −4 | −86 | 3 | 11 | 8 | −5 | −15 | −3 | 10 | 17 | 15 | −1 | $r1$ |
| | 100 | 4 | 11 | −2 | 4 | 7 | 17 | 24 | 54 | 32 | −5 | 6 | 15 | 19 | $\delta$ |
| | | 100 | −4 | −67 | 0 | 1 | 7 | −4 | −1 | −3 | −5 | 4 | 3 | −1 | $r2$ |
| | | | 100 | −2 | 0 | 8 | −3 | 7 | −4 | 3 | −17 | 4 | −2 | −9 | $r3$ |
| | | | | 100 | −6 | −12 | −15 | 5 | 12 | 4 | −19 | −30 | −19 | 1 | $<2$ |
| | | | | | 100 | 30 | 28 | 25 | 10 | 8 | 19 | −44 | 30 | 6 | $u3$ |
| | | | | | | 100 | 40 | 30 | 14 | 13 | 25 | 65 | 44 | 5 | $u4$ |
| | | | | | | | 100 | 37 | 22 | 16 | 28 | 62 | 52 | 15 | $u5$ |
| | | | | | | | | 100 | 29 | 21 | −9 | 54 | 42 | 16 | $u7$ |
| | | | | | | | | | 100 | 16 | 15 | 18 | 27 | 26 | $u9$ |
| | | | | | | | | | | 100 | −14 | 39 | 41 | 11 | $u16$ |
| | | | | | | | | | | | 100 | 17 | 16 | 10 | $u18$ |
| | | | | | | | | | | | | 100 | 57 | 12 | $k1$ |
| | | | | | | | | | | | | | 100 | 14 | $k2$ |
| | | | | | | | | | | | | | | 100 | $k3$ |

Owing to the overlapping of peaks in the outer part of the radial distribution curve (Fig. 1) certain groups of amplitudes of vibration were refined together (see Table 2). Apart from those involving the hydrogen atoms, most of these groups refined satisfactorily, the exception being that involving axial···equatorial C···C, C···O and O···O amplitudes of vibration. These non-refining parameters were fixed at typical values. Under these conditions refinement converged to give an $R$ factor ($R_G$) of 0.14. The molecular scattering intensities, and differences calculated using the final refined parameters, are shown in Figure 2.

Final parameters are given in Table 2. The estimated standard deviations quoted in the table include the random errors determined in the least squares analysis, and allowances for both systematic errors and any constraints applied during the refinements. The least squares correlation matrix is shown in Table 3.

## Discussion

The bond lengths in some silyl and germyl compounds, listed in Table 4, show that, in general, the difference between distances Ge—X and Si—X depends on the electronegativity of X. This trend is found also for the halides, results for which are not included in the table. The Co—Ge bond length that we have determined [241.4(4) pm] is only 3.3 pm longer than the Co—Si distance in silylcobalt tetracarbonyl [3], and this small difference, compared with 8.0 pm for the manganese pentacarbonyl derivatives [1] may be due to the presence of two more *d* electrons on cobalt than on manganese, making the $Co(CO)_4$ group effectively more electropositive than $Mn(CO)_5$. However, the Co—Si distance also seems long relative to Mn—Si in silylmanganese pentacarbonyl after allowing for the change in radius of the metal, and relative to Co—Si in trifluorosilylcobalt tetracarbonyl (222.5 pm in the solid phase) [8]. Of course, these differences may also reflect the differing electronegativities of the groups involved.

The Co—Ge distance found is considerably longer than that in $GeCl_3Co(CO)_4$

TABLE 4

COMPARISON OF SOME BOND LENGTHS$^a$ INVOLVING SILICON AND GERMANIUM

| Silicon | | | Germanium | | | Ge—Si difference |
|---|---|---|---|---|---|---|
| Compound | Bond length | Ref. | Compound | Bond length | Ref. | |
| $(SiH_3)_2O$ | 163.4(2) | 13 | $(GeH_3)_2O$ | 176.6(4) | 14 | 13.2 |
| $(SiH_3)_3N$ | 173.4(2) | 15 | $(GeH_3)_3N$ | 183.6(5) | 16 | 10.2 |
| $SiH_3Mn(CO)_5$ | 240.7(5) | 1 | $GeH_3Mn(CO)_5$ | 248.7(2) | 1 | 8.0 |
| $SiH_3CH_3$ | 186.7(1)$^b$ | 17 | $GeH_3CH_3$ | 194.5(1)$^b$ | 18 | 7.8 |
| $(SiH_3)_2S$ | 213.6(2) | 19 | $(GeH_3)_2S$ | 220.9(4) | 14 | 7.3 |
| $(SiH_3)_2Se$ | 227.3(4) | 20 | $(GeH_3)_2Se$ | 234.4(3) | 21 | 7.1 |
| $(SiH_3)_3P$ | 224.8(3) | 22 | $(GeH_3)_3P$ | 230.8(3) | 23 | 6.0 |
| $Si_2H_6$ | 233.1(3) | 24 | $Ge_2H_6$ | 240.3(3) | 25 | 7.2/2 = 3.6 |
| $SiH_3Co(CO)_4$ | 238.1(7) | 3 | $GeH_3Co(CO)_4$ | 241.4(4) | | 3.3 |

$^a$ Bond lengths are given in pm, and are $r_a$ values unless stated otherwise. $^b$ $r_s$.

(231.0 pm) [9], but is still some 15 pm shorter than the sum of Co and Ge covalent radii [10,11].

The other structural parameters are much as one would expect. It should be noted that the evidence suggests that the axial Co—C bond is longer than the equatorial ones in germylcobalt tetracarbonyl, whereas the reverse is true in iron pentacarbonyl [12].

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