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THE CRYSTAL AND MOLECULAR STRUCTURE OF TRICHLOROGERMYLCOBALT TETRACARBONYL, $Cl_3GeCo(CO)_4$

G.C. v d. BERG*, A OSKAM and K. OLIE

Inorganic Chemistry Laboratory, University of Amsterdam, Nieuwe Achtergracht 164—166, Amsterdam (The Netherlands)

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Summary

The crystal and molecular structure of trichlorogermylcobalt tetracarbonyl, $Cl_3GeCo(CO)_4$, has been determined from three-dimensional X-ray data collected by counter methods. The structure has been resolved by vector-analysis and refined by least-squares techniques.

It crystallizes in spacegroup C_c of the monoclinic system, with eight molecules in a cell of dimensions: a = 26.238 (3) Å, b = 6.623 (5), c = 12.969 (2) and β = 106°12′ (2). The final conventional R factor for the 1647 reflections above background is 0.098.

Both molecules in the asymmetric unit exhibit slight, but significant, deviations from C_{3v} symmetry. The coordination of the Co atoms is trigonal bipyramidal, and that of the Ge atoms is tetrahedral. The equatorial carbonyl groups are in a staggered conformation with respect to the chlorine atoms. The corresponding carbonyl—cobalt—germane angles are less than 90°. The average Ge—Co distance of the two molecules in the asymmetric unit is 2.31 Å

Introduction

The metal—metal bond character in $X_3MCo(CO)_4$ compounds has been the subject of several investigations [1—11]. The problem as to what extent metal—metal π-bonding is involved in these complexes has not been satisfactorily clarified. We have carried out valence force-field calculations in order to elucidate this problem, but the complete structures of the compounds, which are essential to an understanding, are known only for a few members of the series.

Robinson et al. [12, 13] have performed X-ray studies on $F_3SiCo(CO)_4$ and $Cl_3SiCo(CO)_4$. An electron-diffraction study was carried out on $H_3SiCo(CO)_4$

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* Author to whom correspondence should be sent

[14]. The differences in geometry for the Si—$Co(CO)_4$ part of the molecules were quite small except for the Si—Co distance in the hydride, which was about 0.15 Å larger than for the other two. As only one Ge—Co distance is recorded in the literature [15], we decided to carry out an X-ray analysis of the $Cl_3GeCo(CO)_4$ complex.

Experimental

A sample of $Cl_3GeCo(CO)_4$ was prepared as described by Patmore and Graham [16]. Small thin needles were grown by subliming the sample under vacuum. Some of the needles were sealed in glass capillaries and mounted on a goniometer head. Weissenberg photographs showed that nearly all the needles were twinned. After many efforts a few suitable non-twinned crystals were obtained.

Systematic absences were observed for hkl, $h + k \neq 2n$ and $h0l$, $l \neq 2n$, indicating the spacegroups C_c or $C_{2/c}$. The choice in favour of the first will be discussed in the next section. Zero-level Weissenberg photographs (Cu-K_α radiation) about [001] and [010] were superimposed with Al-powder lines for calibration. Carefully-measured glancing angles corresponding to $hk0$ and $h0l$ reflections with high θ-values were used to determine the unit-cell dimensions by a least squares procedure (Table 1). The listed errors correspond to three times the estimated standard deviations. The calculated density of 2.14 g cm^{-3} seems reasonable compared with those for F_3Si— and Cl_3Si—$Co(CO)_4$ [12, 13], but no experimental value is available.

The intensities were collected at room temperature with a Nonius automatic three circle diffractometer. Some data: radiation, Cu-K_α; scan, θ—2θ (moving-crystal, moving-counter); scan angle, 2.0°; maximum θ-value, 68.5°; mounting axis of the crystal, [010].

The intensity of the reference reflections was constant during the data collection, indicating that no decomposition of the crystal took place in the X-ray beam. As it was not possible to measure the dimensions of the crystal through the cylindrical capillary wall, no absorption correction could be made.

Solution and refinement of the structure

NOR measurements of the ^{59}Co resonance show two different signals [9, 10]. This indicates the presence of at least two Co atoms in the asymmetric unit.

In spacegroup $C_{2/c}$ with eight molecules in the unit cell, there is one Co

TABLE 1

CRYSTAL DATA FOR $Cl_3GeCo(CO)_4$

Cell dimensions	a = 26.238 (3) b = 6.623 (5) c = 12.969 (2) Å β = 106°12' (2)
Spacegroup	C_c
Number of molecules per cell	Z = 8
Calculated density	2.14 g cm^{-3}
Absorption coefficient	μ Cu-K_α = 229 cm^{-1}

TABLE 2

ATOMIC COORDINATES AND VIBRATIONAL PARAMETERS (10^{-2} Å^{-2}) FOR $Cl_3GeCo(CO)_4$

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ge_1	0.5608 (0 [a])	0.6275 (6)	0.3982 (0 [a])	2.2 (2)	4.2 (2)	3.1 (2)	0.6 (2)	1.1 (1)	−0.3 (2)
Co_1	0.4909 (2)	0.4704 (8)	0.4599 (5)	2.5 (2)	4.1 (3)	3.3 (2)	1.0 (2)	1.6 (2)	−0.2 (2)
Cl_1	0.6296 (4)	0.7129 (17)	0.5249 (8)	2.6 (4)	7.3 (6)	5.9 (5)	−1.2 (1)	0.1 (3)	1.3 (5)
Cl_2	0.5365 (4)	0.8949 (15)	0.3131 (9)	6.1 (6)	5.1 (5)	7.5 (7)	1.2 (4)	3.1 (5)	3.8 (5)
Cl_3	0.5916 (4)	0.4456 (15)	0.2916 (9)	5.4 (5)	6.0 (6)	7.2 (6)	−0.1 (4)	4.0 (5)	−1.0 (5)
C_1	0.460 (2)	0.443 (5)	0.318 (3)	4.9 (8)					
C_2	0.448 (1)	0.343 (5)	0.505 (3)	4.2 (7)					
C_3	0.487 (1)	0.705 (6)	0.520 (3)	4.7 (8)					
C_4	0.546 (1)	0.292 (6)	0.522 (3)	4.3 (7)					
O_1	0.442 (1)	0.418 (5)	0.229 (3)	7.7 (9)					
O_2	0.416 (1)	0.248 (5)	0.530 (3)	6.5 (8)					
O_3	0.483 (1)	0.856 (6)	0.560 (3)	8.1 (9)					
O_4	0.580 (1)	0.187 (4)	0.568 (2)	5.5 (6)					
Ge_2	0.3101 (2)	0.0402 (5)	0.1415 (4)	1.9 (1)	3.7 (2)	2.8 (2)	−0.1 (1)	1.1 (1)	−0.1 (1)
Co_2	0.2477 (2)	0.2034 (7)	0.2083 (4)	2.4 (2)	3.7 (2)	3.3 (2)	−0.9 (2)	1.8 (2)	−0.3 (2)
Cl_4	0.3803 (4)	−0.0549 (17)	0.2644 (8)	3.7 (4)	7.8 (7)	5.2 (5)	1.8 (4)	1.1 (4)	1.5 (5)
Cl_5	0.3404 (4)	0.2106 (16)	0.0336 (7)	3.7 (4)	7.2 (6)	4.7 (4)	−0.4 (4)	2.1 (4)	1.3 (4)
Cl_6	0.2803 (5)	−0.2321 (16)	0.0554 (10)	6.4 (6)	5.5 (6)	7.7 (7)	−0.9 (5)	3.7 (5)	−2.6 (5)
C_5	0.201 (1)	0.326 (4)	0.268 (2)	3.1 (6)					
C_6	0.215 (1)	0.270 (5)	0.071 (2)	3.4 (6)					
C_7	0.238 (1)	−0.035 (5)	0.255 (2)	3.2 (6)					
C_8	0.303 (1)	0.362 (4)	0.288 (2)	3.0 (6)					
O_5	0.169 (1)	0.414 (5)	0.293 (3)	6.4 (8)					
O_6	0.190 (1)	0.320 (5)	−0.013 (2)	6.4 (7)					
O_7	0.231 (1)	−0.197 (5)	0.289 (3)	6.8 (8)					
O_8	0.337 (1)	0.462 (4)	0.326 (2)	5.7 (7)					

[a] Forced.

atom in the asymmetric unit when the molecule lies in a general position, and two atoms when the Co and Ge are in special positions.

The arrangement with a Co atom in the mirror plane also violates the condition that the Ge atom and one Cl atom lie at 0, y, ¼. This is in agreement with neither the expected molecular configuration nor with the Patterson function, so spacegroup $C_{2/c}$ can be rejected.

Stalick and Ibers [15] had to make the same choice for their compound $Ph_3GeCo(CO)_3PPh_3$. They assumed a disorder of the PPh_3 and $GePh_3$ groups rather than an ordered arrangement in spacegroup C_c because refinement in this group did not give reasonable isotropic thermal parameters of the P and Ge atoms nor a significant reduction of the R_2 value. The existence of a NOR spectrum rejects the possibility of a disordered arrangement, because NOR signals are observed only for ordered systems.

From the vector map the positions of the Co, Ge and Cl atoms were determined. A Fourier analysis yielded the positions of the C and O atoms. Thereafter, three cycles of least-squares refinement with individual isotropic temperature factors were followed by three cycles with anisotropic temperature parameters for Ge, Co and Cl. This resulted in an R value of 10.4%. The atomic scattering factors used were those given in the international tables. Finally, four cycles using the values of $\Delta f'$ and $\Delta f''$ for Co and Ge as tabulated in the International Tables were calcualted. This resulted in a final R value of 9.8%. The highest peak on the final difference Fourier map was 2.1 e Å^{-3}.

The positional and vibrational parameters are listed in Table 2.

Discussion of the structure

The molecular configuration is illustrated in Fig. 1, and a few selected intra- and inter-molecular distances and angles are shown in Table 3.

The structure consists of well separated monomeric $Cl_3GeCo(CO)_4$ units; the shortest Co···Co distance is 6.50 Å. The shortest intermolecular distances all

TABLE 3

SELECTED INTERATOMIC DISTANCES (Å) AND BOND ANGLES [a]

Atoms	Distance	Atoms	Angle
Intramolecular			
Ge—CO	2.310 (7) Å		
Co—C(E) [b]	1.79 (3)	∠ Co—C_{ax}—O_{ax}	173° (1)
C—O(E)	1.15(4)	∠ Co—C_{eq}—O_{eq}	174.5° (1)
Co—C(A)	1.79 (3)	∠ C_{eq}—Co—C_{ax}	93° (1)
C—O(A)	1.17 (4)	∠ Cl—Ge—Cl	104.5° (0.2)
Ge—Cl	2.138 (10)		
Intermolecular distances (shortest of each type)			
Co—Co	6.50 Å		
O—O	3.18		
O—Cl	3.55		
Cl—Cl	3.88		

[a] A more complete list is available on request. [b] A parenthetic E indicates an average distance or angle for the equatorial groups; a parenthetic A indicates an axial distance. All distances and angles are averaged for the two molecules in the asymmetric unit.

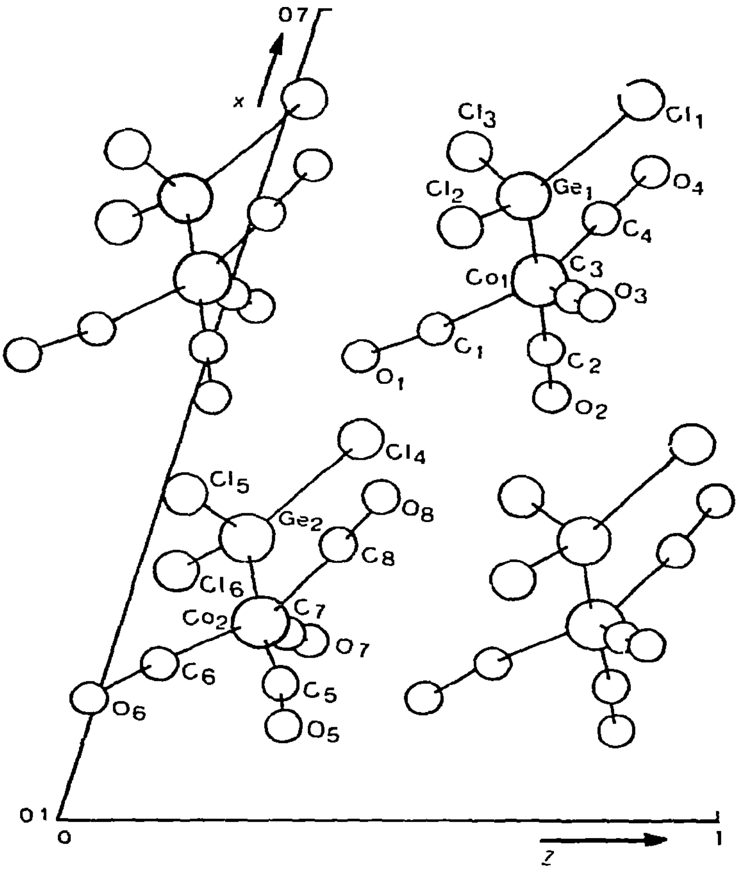

Fig. 1. Perspective view of $Cl_3GeCo(CO)_4$ along the y-axis.

exceed the sums of the appropriate van der Waals radii. From the data it is apparent that the entire molecule possesses approximate C_{3v} symmetry, as in the $Cl_3SiCo(CO)_4$ and $F_3SiCo(CO)_4$ compounds. The equatorial carbonyls and the chlorine atoms are in a staggered conformation. The configuration around the Co atom is trigonal bipyramidal, with slight deviations, especially in the Co—C—O angles. The equatorial carbonyl groups are bent away from the axial one making C_{eq}—Co—C_{ax} angles of 95°. The Co—Ge distance is 2.31 Å. If the covalent radius of Co is taken to be 1.34 Å [17, 18] and that of Ge as 1.22 Å [19], then a single Co—Ge bond length should be approximately 2.56 Å. The observed shortening of 0.25 Å is consistent with a degree of Co—Ge multiple bonding, in agreement with our force-field calculations [11].

In this previous article on force-field calculations we used structural parameters fixed throughout the whole series of molecules, because these parameters were not available for each individual molecule, and for the metal—metal and M—X distances we used estimated values. Hence we reconstructed the *G* matrix with the new values found for $Cl_3GeCo(CO)_4$, and recalculated the vibrational frequencies using the previously determined force field.

As can be seen from Table 4, even a change of the Ge—Co bondlength from 2.40 to 2.34 Å does not lead to any great differences in the frequencies. Thus the

TABLE 4

COMPARISON OF VIBRATIONAL FREQUENCIES (cm^{-1})

	$\nu_{\mathrm{exp.}}$	$\nu_{\mathrm{calc.}}$	
		old	new
$\nu(\mathrm{CO})A_1$	2124	2124	2124
$\nu(\mathrm{CO})A_1$	2071	2069	2069
$\nu(\mathrm{CO})E$	2052	2050	2050
$\delta(\mathrm{CoCO_{out}})E$	557	558	552
$\delta(\mathrm{CoCO_{out}})A_1$	548	551	545
$\delta(\mathrm{CoCO_{ax}}) + \nu(\mathrm{CoC_{eq}})E$	488	485	485
$\nu(\mathrm{CoC_{eq}}) + \delta(\mathrm{CoCO_{ax}})E$	464	469	465
$\nu(\mathrm{CoC_{ax}})A_1$	443	452	451
$\nu(\mathrm{CoC_{eq}})A_1$	416	411	412
$\delta(\mathrm{CoCO_{in}})E$	370	368	364
$\nu(\mathrm{Ge{-}Cl})E$	407	408	407
$\nu(\mathrm{Ge{-}Cl})A_1$	392	394	396
$\nu(\mathrm{Ge{-}Co})A_1$	242	244	242
$\delta(\mathrm{GeCl_3})E$	162	165	177
$\delta(\mathrm{GeCl_3})A_1$	162	152	151
$\delta(\mathrm{CCoC})E$	123	126	127
$\delta(\mathrm{CCoC})E$	108	104	105
$\delta(\mathrm{CCoC})A_1$	81	86	85
$\delta(\mathrm{ClGeCo})E$	90	97	97
$\delta(\mathrm{GeCoC})E$	58	53	53

force-field calculations and the conclusions drawn from them are unaffected by small changes in the molecular geometry.

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References

1 G.C. v.d. Berg, A. Oskam and K. Vrieze, J. Organometal. Chem., 57 (1973) 329.
2 G.C. v.d. Berg, A. Oskam and K. Vrieze, J. Organometal. Chem., 69 (1974) 169.
3 K.L. Watters, Ph.D. Thesis, Brown Univeristy, 1970.
4 R.D. George, K.M. Mackay and S.R. Stobart, J. Chem. Soc. Dalton Trans., (1972) 974.
5 B.J. Aylett and J.M. Campbell, J. Chem. Soc. A, (1969) 1910.
6 A P Hagen and A.G. MacDiarmid, Inorg. Chem., 6 (1967) 686.
7 E.E. Saalfeld, M V. McDowell and A.G. MacDiarmid, J. Amer. Chem. Soc., 92 (1970) 2324.
8 H.W. Spiess and R.K Sheline, J. Chem. Phys., 53 (1970) 3036.
9 T L. Brown, P.A. Edwards, C.B. Harris and J.L. Kirsch, Inorg. Chem., 8 (1969) 763.
10 D.D. Spencer, J L. Kirsch and T.L. Brown, Inorg. Chem., 9 (1970) 235.
11 G.C v d. Berg and A. Oskam, to be published.
12 W.T. Robinson and J.A. Ibers, Inorg. Chem., 6 (1967) 1209.
13 K. Emerson, P.R. Ireland and W.T. Robinson, Inorg. Chem., 9 (1970) 436.
14 A.G. Robiette, G.M. Sheldrick, R.W.F. Simpson, B.J. Aylett and J A. Campbell, J. Organometal. Chem., 14 (1968) 279.
15 J.K. Stalick and J.A. Ibers, J. Organometal. Chem., 22 (1970) 213.
16 D.J. Patmore and W.A.G. Graham, Inorg Chem., 7 (1968) 771.
17 F.A. Cotton, T.G. Dunne, B.F.G. Johnson and J.S Wood, Proc. Chem Soc., (1964) 175.
18 J.A. Ibers, J. Organometal. Chem., 14 (1968) 423.
19 L. Pauling, The Nature of the Chemical Bond, Cornell University Press, Ithaca, 3rd ed., 1960.