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MOLECULAR AND CRYSTAL STRUCTURE OF (+)-TETRACARBONYL(METHYL-1-NAPHTHYLPHENYLGERMYL)-COBALT

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Summary

The crystal and molecular structure of (+)-tetracarbonyl(methyl-1-naphthylphenylgermyl)cobalt was solved from three dimensional X-ray diffraction data by Patterson and Fourier syntheses and refined by full-matrix least-squares method to a final unweighted R of 0.047, excluding zeroes. The crystal is monoclinic, space group $P2_1$, with $a = 9.950(4)$, $b = 6.860(3)$, $c = 14.792(6)$ Å, $\beta = 99.89(5)°$, $Z = 2$. 1990 independent reflexions were recorded at room temperature with Ni-filtered Cu-K_α radiation. The determination of absolute configuration confirmed chemical assumptions.

Introduction

Optically active compounds [$Co(CO)_4(Me\text{-}1\text{-}NpPhX)$] with X = Si, Ge were synthesized and crystallized in pentane by Corriu et al. [1,2]. Their rotations respectively were +2.0° for the Si compound and +2.7° for the Ge compound, for the sodium D line at 20°C. They were prepared from octacarbonyldicobalt:

$$Co_2(CO)_8 + R_3XH \rightarrow R_3XCo(CO)_4 + HCo(CO)_4$$

($R = Me, \alpha\text{-}Np, Ph$)

It is usually assumed [3,4] that the X—H bond is replaced with retention of configuration at the asymmetric center, although the reaction mechanism is not known.

In order to check these assumptions, crystalline samples were supplied to determine the absolute configuration by X-ray analysis. The most suitable crystals were those of (+)-tetracarbonyl(methyl-1-naphthylphenylgermyl)cobalt, and we describe here the X-ray study of them.

Experimental

Crystal data. $[Co(CO)_4(Me\text{-}1\text{-}NpPhGe)]$. Molecular weight 462.52; monoclinic, $a = 9.950(4)$, $b = 6.860(3)$, $c = 14.792(6)$ Å, $\beta = 99.89(5)°$, $V = 994.5$ Å^3, $Z = 2$, $D_c = 1.545$. Systematic absences: $0k0$ $k \neq 2n$. Space group: $P2_1/m$ or $P2_1$ ($P2_1$ confirmed by structure analysis). $\mu = 86.3$ cm^{-1} (λ(Cu-K_α) = 1.5418 Å). $F(000) = 464$.

A 0.23 × 0.30 × 0.08 mm crystal shaped as a parallelepiped was selected. Weissenberg photographs were used to determine lattice constants and space group and a preliminary set of visually *hkl* data. 1990 intensities were collected at room temperature up to $\theta = 66°$ on a CAD-3 Enraf—Nonius diffractometer with $\theta - 2\theta$ scan mode, at a rate of 1/6°/sec. Each scan is 0.90° wide at $\theta = 0°$ and an increment, $\Delta(\theta) = 0.35 \times \tan\theta$ is added, to take into account spectral dispersion; background was measured at each end in fixed position with a total counting time equal to the scanning time.

The intensities of two standard reflexions (0 0 14 and 6 0 $\bar{2}$) were alternately measured every 40 reflexions. A linear decay of ca. 10% was observed; data were then corrected.

Standard deviations were calculated from:

$$\sigma(I) = \{I + I_1 + I_2 + [0.02(I - I_1 - I_2)]^2\}^{1/2}$$

where I_1 and I_2 are the background and I the peak counts.

336 reflexions having $I \leqslant 3\sigma(I)$ were considered unobserved and then omitted. The remaining 1654 reflexions were used for solving the structure. Corrections were applied for Lorentz and polarization factors and for absorption, with a modified version of program ORABS [5].

Structure determination

Statistics on normalized structure factors gives the following results:

	experimental	theoretical non-centrosymmetric	theoretical centrosymmetric
$\langle\lvert E^2 - 1\rvert\rangle$	0.8075	0.7360	0.9680
$\langle\lvert E\rvert\rangle$	0.8614	0.8860	0.7980

The structure has then been solved in the non-centrosymmetric space group $P2_1$.

The germanium and cobalt atoms were located from a three-dimensional Patterson synthesis. Since $P2_1$ is a polar space group, the origin point along the b-axis was fixed at $y = 1/4$ for germanium. Unfortunately, both heavy atoms have the same y coordinate and the subsequent Fourier synthesis was not free of spurious symmetry. The electron density map contained peaks for both the true structure and its mirror image. At that time the best resolved molecule was chosen. Repeating the structure factor calculations and Fourier process, all atoms but hydrogen ones were located. The structure was refined isotropically to the conventional R factor of 0.130. The scattering factors were computed

TABLE 1

NON-HYDROGEN ATOMIC COORDINATES ($\times 10^4$) with estimated standard deviations ($\times 10^4$) in parentheses

Atom	*x/a*	*y/b*	*z/c*
Ge	8087(1)	2500	2541(0)
Co	7050(1)	2472(3)	3934(1)
C(1)	8477(10)	3894(17)	4501(6)
O(1)	9364(8)	4806(13)	4880(5)
C(2)	5816(10)	3897(18)	3200(6)
O(2)	5023(8)	4840(14)	2757(5)
C(3)	6057(9)	2255(19)	4851(6)
O(3)	5407(8)	2136(18)	5382(4)
C(4)	7425(10)	−11(14)	3898(6)
O(4)	7639(10)	−1669(12)	3895(6)
C(5)	8116(10)	5166(15)	2062(7)
C(6)	7076(7)	748(13)	1600(5)
C(7)	5902(8)	−159(14)	1765(6)
C(8)	5136(9)	−1394(13)	1095(6)
C(9)	5567(9)	−1698(15)	289(6)
C(10)	7221(10)	−1149(18)	−750(6)
C(11)	8333(12)	−209(20)	−955(7)
C(12)	9091(10)	1020(20)	−314(7)
C(13)	8681(9)	1364(15)	505(6)
C(14)	7527(8)	444(12)	755(5)
C(15)	6757(9)	−863(14)	89(6)
C(16)	9987(7)	1666(13)	2844(5)
C(17)	10385(9)	−209(16)	2632(7)
C(18)	11766(11)	−753(21)	2821(9)
C(19)	12738(10)	577(25)	3242(8)
C(20)	12348(9)	2332(31)	3466(7)
C(21)	10981(9)	2963(16)	3268(6)

from Cromer and Mann tables [6]. The real parts of the anomalous scattering factors of Ge and Co atoms were included [7].

At this stage the absolute configuration was determined. The imaginary part of Ge and Co scattering factors [7] was then introduced in calculations. The structure factors were calculated for both enantiomers and the R factors were $R^+ = 0.129$ and $R^- = 0.091$, indicating that the mirror image has the correct absolute configuration. To confirm it, 518 reflexions were selected for which $|F_o| \geqslant 30.0$ and the magnitude of the computed Bijvoet difference [8] defined as $[F(hkl) - F(\bar{h}\bar{k}\bar{l})]/1/2[F(hkl) + F(\bar{k}\bar{h}\bar{l})]$ was >0.05. The R factors were respectively $R^+ = 0.154$ and $R^- = 0.069$. The visual estimation of some significative observed Bijvoet differences on Weissenberg photographs confirmed these results.

The refinement was continued with the correct configuration taking anomalous dispersion into account. With anisotropic thermal parameters F dropped to 0.060. The 15 hydrogen atoms were located on a difference synthesis at chemically reasonable positions. They were given the isotropic temperature factor of the carbon atom to which they are bonded. Their positional parameters were refined, all other parameters being held constant.

The following weighting scheme was used at the end of refinement:

$$w = (0.00866|F_o|^2 - 0.39692|F_o| + 13.7)^{-1} \text{ for } |F_o| < 72.0 \text{ and}$$

$$w = (0.514|F_o| - 15.32)^{-1} \text{ for } |F_o| \geqslant 72.0.$$

TABLE 2

NON-HYDROGEN THERMAL PARAMETERS ($Å^2 \times 10^4$) IN THE FORM:

$\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})]$

with estimated standard deviations ($\times 10^4$) in parentheses

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ge	300(3)	308(4)	290(3)	−20(3)	27(1)	−14(3)
Co	380(6)	380(6)	318(5)	−16(6)	35(2)	−11(5)
C(1)	538(52)	584(59)	380(43)	−10(25)	85(20)	−3(22)
O(1)	523(37)	780(55)	686(44)	−104(20)	−9(17)	−117(22)
C(2)	459(49)	698(67)	415(47)	−28(25)	86(20)	−45(24)
O(2)	520(40)	938(65)	660(43)	134(23)	−1(17)	92(24)
C(3)	635(49)	471(62)	386(37)	8(26)	73(18)	−13(25)
O(3)	824(47)	1065(85)	610(40)	−76(28)	217(19)	13(26)
C(4)	569(53)	377(52)	327(40)	12(20)	33(17)	27(18)
O(4)	995(61)	464(43)	705(53)	19(22)	13(22)	13(20)
C(5)	534(54)	399(50)	622(57)	−2(21)	100(23)	37(24)
C(6)	246(34)	434(47)	309(36)	15(17)	−7(13)	13(17)
C(7)	357(41)	414(47)	457(45)	−4(19)	30(17)	17(21)
C(8)	408(43)	413(55)	486(50)	−46(20)	−41(18)	−14(20)
C(9)	462(47)	383(42)	530(53)	−31(20)	−80(30)	−22(21)
C(10)	607(59)	729(73)	348(44)	20(27)	−19(20)	−115(24)
C(11)	755(72)	757(80)	463(52)	65(32)	66(24)	−87(28)
C(12)	568(56)	751(72)	459(50)	−2(28)	74(21)	−23(27)
C(13)	447(44)	553(60)	406(44)	−29(22)	20(17)	−58(21)
C(14)	332(27)	292(39)	267(33)	−7(16)	−24(14)	−22(15)
C(15)	469(45)	376(45)	352(40)	26(20)	−23(17)	−53(19)
C(16)	320(36)	418(42)	302(35)	−21(17)	27(15)	2(17)
C(17)	409(46)	468(55)	626(56)	27(20)	44(20)	−28(23)
C(18)	529(60)	739(81)	846(79)	107(30)	63(27)	35(35)
C(19)	334(49)	1047(110)	711(68)	7(30)	59(22)	68(36)
C(20)	349(41)	1149(104)	564(50)	−90(42)	26(18)	48(48)
C(21)	431(45)	712(88)	450(44)	−85(23)	46(18)	−26(23)

TABLE 3

HYDROGEN ATOMIC COORDINATES ($\times 10^3$) with estimated standard deviations ($\times 10^3$) in parentheses
Isotropic temperature factors are in $Å^2$

Atom	x/a	y/b	z/c	B
H1(C5)	876(10)	522(15)	166(7)	3.92
H2(C5)	808(10)	599(18)	255(8)	3.92
H3(C5)	734(11)	570(18)	161(8)	3.92
H(C7)	538(9)	24(15)	225(9)	3.15
H(C8)	447(9)	−206(13)	131(7)	3.57
H(C9)	495(10)	−263(17)	−23(8)	3.62
H(C10)	666(10)	−217(18)	−126(7)	4.32
H(C11)	886(13)	−20(20)	−154(8)	4.83
H(C12)	963(11)	194(20)	−38(7)	4.48
H(C13)	914(9)	218(16)	83(7)	3.39
H(C17)	959(10)	−122(17)	234(8)	4.22
H(C18)	1196(12)	−226(22)	269(10)	5.29
H(C19)	1368(11)	3(26)	303(9)	5.09
H(C20)	1317(10)	326(31)	379(8)	5.36
H(C21)	1071(10)	407(17)	332(7)	3.51

In the last cycles of least-squares refinement the largest parameter shifts were less than 0.01σ for non-hydrogen atoms and 0.15σ for hydrogen atoms. The final R values are:

$$R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.047$$

$$R = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2]^{1/2} = 0.060$$

Positional and thermal parameters are listed in Tables 1, 2 and 3.

A list of the structure factors may be obtained from the authors on request.

Results and discussion

The crystal packing is shown in Fig. 1 with atom numbering. The interatomic distances and bond angles are given in Fig. 2 around the Co—Ge bond and in Fig. 3 for the naphthyl and phenyl groups. The average standard deviations are 0.001 Å on Co—Ge, 0.008 Å on Ge—C, 0.009 Å on Co—C, 0.013 Å on C—O and C—C distances; 0.3° on angles around Ge, 0.4° around Co and 0.9° on other angles.

Bonds and angles involving hydrogen atoms are given in Table 4.

Pentacoordinated first transition metal complexes are generally square pyramidal (spy) as $Co(ClO_4)(OAsMePh_2)_4ClO_4$ [9] and $Co(S_2CNMe_2)_2(NO)$ [10] or trigonal bipyramidal (tbp) as $[Co(NCMe)_5]ClO_4$ [11]. An example of the ideal tbp is the pentacarbonyliron $Fe(CO)_5$ [12]. In our case the geometry deviates from the ideal tbp since the C(3)—Co—Ge angle is 170.9° instead of 180°, the equatorial angles being respectively, 113.0°, 112.7° and 130.1°, instead of 120°. The cobalt atom lies 0.21 Å away from the (C(1), C(2), C(4)) plane. Distortions

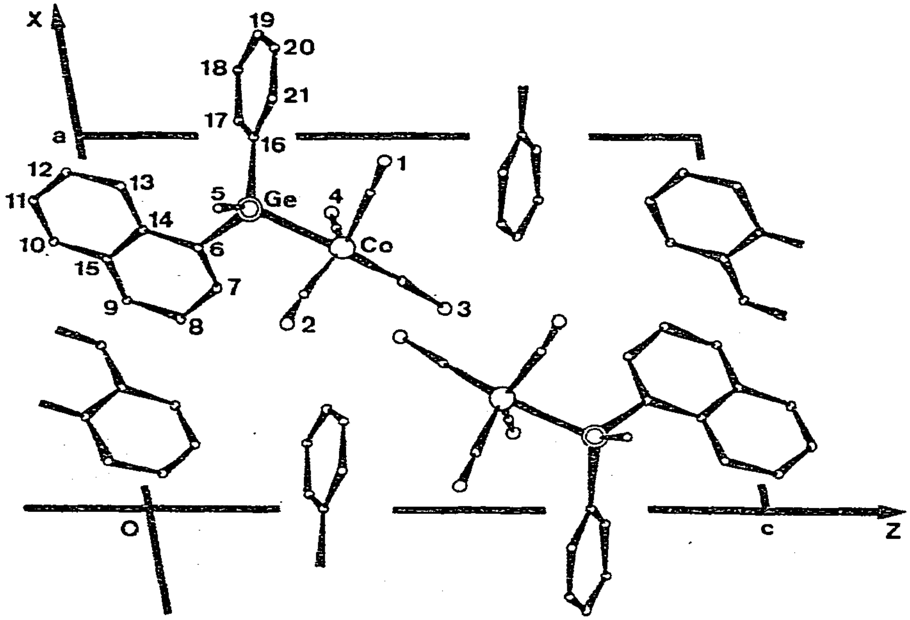

Fig. 1. Projection of the structure in the plane ac.

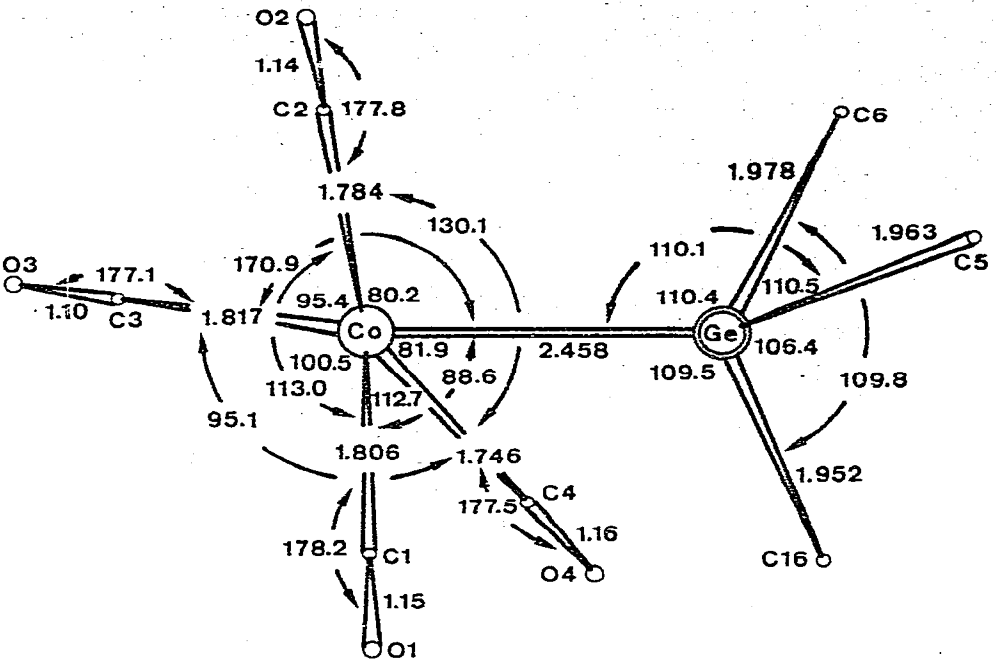

Fig. 2. Interatomic distances (Å) and angles (°) around the Co—Ge bond.

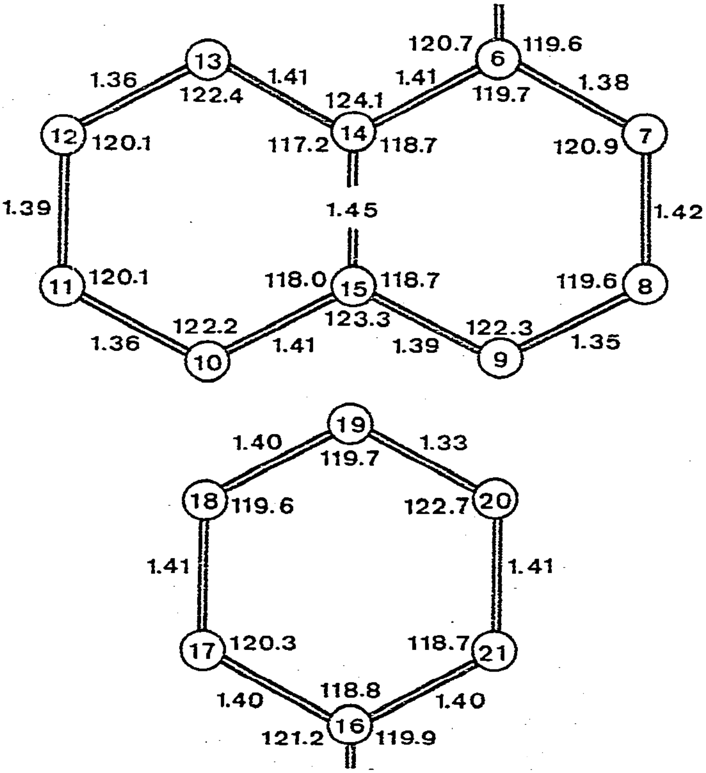

Fig. 3. Bond lengths (Å) and angles (°) in naphthyl and phenyl groups. Largest deviations from least-squares planes are respectively 0.03 Å and 0.02 Å.

TABLE 4

BONDS (Å) AND ANGLES (°) INVOLVING HYDROGEN ATOMS (average standard deviations are 0.15 Å and 10°)

C(5)—H1(C5)	0.95	Ge—C(5)—H1(C5)	109		
C(5)—H2(C5)	0.92	Ge—C(5)—H2(C5)	106		
C(5)—H3(C5)	1.00	Ge—C(5)—H3(C5)	122	H1(C5)—C(5)—H3(C5)	96
		H1(C5)—C(5)—H2(C5)	126	H2(C5)—C(5)—H3(C5)	100
C(7)—H(C7)	1.00	C(6)—C(7)—H(C7)	124	C(8)—C(7)—H(C7)	113
C(8)—H(C8)	0.91	C(7)—C(8)—H(C8)	114	C(9)—C(8)—H(C8)	126
C(9)—H(C9)	1.10	C(8)—C(9)—H(C9)	119	C(15)—C(9)—H(C9)	119
C(10)—H(C10)	1.11	C(11)—C(10)—H(C10)	119	C(15)—C(10)—H(C10)	119
C(11)—H(C11)	1.09	C(10)—C(11)—H(C11)	135	C(12)—C(11)—H(C11)	105
C(12)—H(C12)	0.85	C(11)—C(12)—H(C12)	131	C(13)—C(12)—H(C12)	106
C(13)—H(C13)	0.82	C(12)—C(13)—H(C13)	115	C(14)—C(13)—H(C13)	123
C(17)—H(C17)	1.09	C(16)—C(17)—H(C17)	118	C(18)—C(17)—H(C17)	122
C(18)—H(C18)	1.08	C(17)—C(18)—H(C18)	115	C(19)—C(18)—H(C18)	125
C(19)—H(C19)	1.11	C(18)—C(19)—H(C19)	102	C(20)—C(19)—H(C19)	133
C(20)—H(C20)	1.08	C(19)—C(20)—H(C30)	115	C(21)—C(20)—H(C20)	123
C(21)—H(C21)	0.82	C(16)—C(21)—H(C21)	114	C(20)—C(21)—H(C21)	126

from the two regular geometries, spy and tbp, are indeed, usual rather than exceptional [13].

The Co—C bond lengths (1.806 Å, 1.748 Å, 1.817 Å and 1.746 Å) indicate a significant double-bond character, although the observed C—O distances (1.15 Å, 1.14 Å, 1.10 Å and 1.16 Å) are close to triple bonds. The Co—C—O angles (178.2°, 177.8°, 177.1° and 177.5°) do not deviate from linearity within the limits of error.

Most transition metals form σ-bonds to one or other of the Group IV elements [14]. The Co—Ge bond, *trans* to a carbonyl C atom (Co—C(3) = 1.817 Å) has a length of 2.458 Å. The first determination of the Co—Ge bond distance, possibly providing evidence for π-bonding, was reported for (triphenylgermyl)-tricarbonyl(triphenylphosphine)cobalt(I) [15], where the Co—Ge bond, *trans* to the P atom, is 2.34 Å (the Co—Ge single bond being taken as 2.56 Å). In the X-ray structure of (PNP)Cr(CO)$_3$ [16] the Cr—C bonds approximately *trans* to

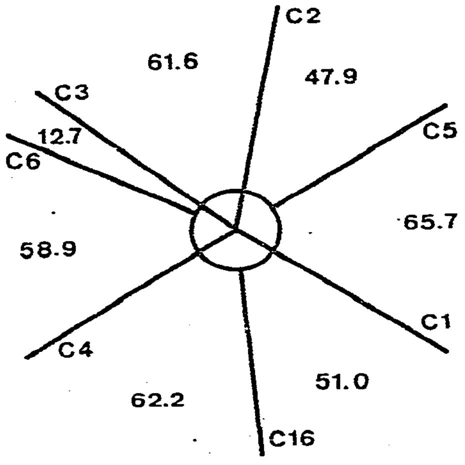

Fig. 4. Newman projection along Co—Ge bond, with Ge atom behind Co atom.

the P atoms are longer (1.822 Å and 1.832 Å) than that approximately *trans* to the N atom (1.804 Å).

It is probable that in the [Co(CO)$_4$(Me-1-NpPhGe)] compound there is some double-bond character involving *d* orbital overlap [17], but there is no sufficient evidence to rule out other explanations for the Co—Ge bond lengths.

Figure 4 shows the Newman projection along the Co—Ge bond. The absolute configuration confirms that the electrophilic substitution by which the complex was made involves retention of configuration at germanium.

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