Acta Cryst. (1987). C**43**, 2283–2285

Structure of the Tetrahedral Cobalt Cluster [$Co_4(\eta^5\text{-}C_5H_5)_2(CO)_7$]

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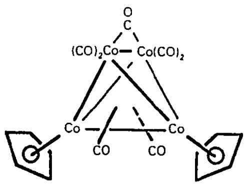
(*Received* 24 *April* 1987; *accepted* 14 *July* 1987)

Abstract. [$Co_4(\eta^5\text{-}C_5H_5)_2(CO)_4(\mu\text{-}CO)(\mu_3\text{-}CO)_2$], μ-carbonyl-di-μ_3-carbonyl-tetracarbonylbis(η^5-cyclopentadienyl)-*tetrahedro*-tetracobalt, $M_r = 562{\cdot}0$, monoclinic, $P2_1/m$, $a = 7{\cdot}862\,(1)$, $b = 12{\cdot}289\,(2)$, $c = 9{\cdot}344\,(1)$ Å, $\beta = 97{\cdot}26\,(1)°$, $V = 895{\cdot}6\,(4)$ Å^3, $Z = 2$, $D_x = 2{\cdot}084$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 36{\cdot}75$ cm^{-1}, $F(000) = 552$, $T = 298$ K, $R = 0{\cdot}033$ for 3328 observed reflections. The molecule lies on a mirror plane. The four Co atoms form an irregular tetrahedron; Co—Co distances range from 2·4171 (4) to 2·4942 (2) Å. The planes of the two cyclopentadienyl rings form a dihedral angle of 48·6 (1)°. A carbonyl ligand is unsymmetrically bound to three Co atoms; Co—C bond lengths vary from 1·942 (1) to 2·019 (1) Å. The doubly bridging carbonyl is tilted towards one of the Co atoms to which it is not bound. A comparison of the title compound with the previously reported structure of the pentamethylcyclopentadienyl analogue, [$Co_4\{\eta^5\text{-}C_5(CH_3)_5\}_2(CO)_4(\mu\text{-}CO)(\mu_3\text{-}CO)_2$] [Cirjak, Ginsburg & Dahl (1979). *J. Chem. Soc. Chem. Commun.* pp. 470–472], shows that Co—C_{Cp} bond lengths are shorter for the title compound; the same trend is found for Co—Co distances. The planes of the two pentamethylcyclopentadienyl rings form a dihedral angle of 52·0° (average of two); the difference is attributable to steric interactions involving the methyl groups. Solution ^{13}C NMR and IR spectra of the title compound show that the solution structure is similar to the solid.

Introduction. The replacement of cyclopentadienyl ligands (Cp) by the bulkier and more electron-donating pentamethylcyclopentadienyl ligand (Cp*) has been shown to cause significant structural changes in some organometallic complexes (Cirjak, Ginsburg & Dahl, 1982; Huang & Dahl, 1983). The tetranuclear cobalt cluster (I) was isolated as a byproduct in the course of the photochemical synthesis of $CoCp(CO)_2$. It appeared of interest to us to solve the crystal structure of (I) and to analyze the structure of (I) relative to its Cp* analogue [$Co_4\{\eta^5\text{-}C_5(CH_3)_5\}_2(CO)_4(\mu\text{-}CO)(\mu_3\text{-}CO)_2$] (II). Recalling the structural variability of the tricobalt cluster, [$CoCp(CO)]_3$ (Bailey, Cotton, Jamerson & Kolthammer, 1982), the solution structure of (I) was studied spectroscopically.



(I)

Experimental. Title compound isolated from photochemical reaction of dicobalt octacarbonyl with cyclopentadiene in hexane at room temperature (King, 1965). Black crystals isolated by slow crystallization from hexane at room temperature. Mass spectrum: molecular ion peak at *m*/*e* 562. The IR spectrum (KBr pellet) sharp peaks at 2043, 2008, 1991, 1844, 1727 and 1705 cm^{-1} show presence of terminal, doubly and triply bridging carbonyl ligands. The ^{1}H NMR (400·1 MHz) and ^{13}C NMR (100·6 MHz, d_8-toluene, 298K) peaks at δ 4·43 (*s*, 10H) and 89·81 (*s*, 10C), respectively, correspond to equivalent protons and carbons in the Cp rings.

Data collected from irregular black crystal fragment, 0·44 × 0·50 × 0·36 mm. Enraf–Nonius CAD-4 diffractometer with graphite monochromator. Space group from systematic absences 0*k*0 with *k* odd and successful refinement in the centrosymmetric choice. Cell dimensions and crystal orientation from 25 reflections having $12 \leq \theta \leq 13°$. ω–2θ scans, scan rates varied 0·45–4·0° min^{-1}, designed to yield $I \sim 50\sigma(I)$ for significant data; maximum scan time 120 s. Scan rate determined during a 4° min^{-1} prescan; if $I < 0{\cdot}5\sigma(I)$ during prescan flagged as unobserved. 4073 unique reflections with $1 \leq \theta \leq 35°$, *h,k,l* range 0,0,−15 to 12,19,14; $R_{\rm int} = 0{\cdot}016$. Three standard reflections, 700, 0,10,2, 002, no decrease in intensity. Absorption correction by ψ scans, minimum relative transmission coefficient 81%. 3328 data with $I > 3\sigma(I)$ used in refinement. Co positions from Patterson map; other non-hydrogen atoms from Fourier maps; H atoms visible in ΔF map, positions calculated, C—H 0·95 Å. 143 variables refined by weighted full-matrix least squares based on *F*, $w = 4F_o^2[\sigma^2(I) + (0{\cdot}02F_o^2)^2]^{-1}$.

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Table 1. *Positional parameters and equivalent isotropic thermal parameters*

$B_{eq} = \frac{4}{3}(a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab\beta_{12}\cos\gamma + ac\beta_{13}\cos\beta + bc\beta_{23}\cos\alpha)$.

	x	*y*	*z*	B_{eq}(Å^2)
Co1	0·21117 (3)	0·15166 (2)	0·29396 (3)	2·208 (4)
Co2	0·37237 (4)	0·250	0·12602 (3)	1·806 (5)
Co3	0·48155 (4)	0·250	0·38269 (3)	1·767 (5)
C1	0·0320 (4)	0·250	0·2103 (4)	3·46 (6)
C2	0·4436 (2)	0·1219 (2)	0·2552 (2)	2·30 (3)
C3	0·1728 (3)	0·1170 (2)	0·4720 (2)	3·15 (4)
C4	0·1298 (3)	0·0302 (2)	0·2055 (3)	3·80 (4)
O1	−0·1007 (3)	0·250	0·1418 (4)	5·28 (7)
O2	0·5264 (2)	0·0434 (1)	0·2374 (2)	3·09 (3)
O3	0·1462 (2)	0·0953 (2)	0·5859 (2)	5·14 (4)
O4	0·0843 (3)	−0·0483 (2)	0·1491 (3)	6·50 (5)
C1*A*	0·2353 (4)	0·250	−0·0797 (3)	3·15 (6)
C2*A*	0·3420 (3)	0·1581 (2)	−0·0617 (2)	3·21 (4)
C3*A*	0·5131 (3)	0·1928 (2)	−0·0324 (2)	3·34 (4)
C1*B*	0·5220 (4)	0·250	0·6080 (3)	4·24 (8)
C2*B*	0·5995 (3)	0·1574 (2)	0·5540 (3)	3·95 (5)
C3*B*	0·7228 (3)	0·1925 (2)	0·4665 (3)	3·49 (4)

Non-H atoms refined anisotropically; H-atom positions fixed, isotropic *B*'s refined. Calculations using *SDP* software package (Frenz, 1985). Atomic scattering factors from *International Tables for X-ray Crystallography* (1974), anomalous-dispersion coefficients of Cromer (1965). Secondary-extinction coefficient, $g = 2{\cdot}01\,(5) \times 10^{-6}$, where the correction factor $(1 + gI_c)^{-1}$ was applied to F_c. $wR = 0{\cdot}043$, $R = 0{\cdot}033$, $S = 2{\cdot}431$, $(\Delta/\sigma)_{max} = 0{\cdot}09$. Maximum residual on Fourier map 1·08 e Å^{-3} located 0·85 Å from Co3, minimum −0·754 e Å^{-3}. Atomic parameters are listed in Table 1.*

Discussion. The atom-labeling system for (I) and the packing in the unit cell are shown in Figs. 1 and 2. All bond lengths and relevant bond angles are given in Table 2. Compound (I) has *m* (C_s) symmetry. The four Co atoms form an irregular tetrahedron. The single metal–metal bond lengths for the Co atoms range from 2·4171 (4) Å for Co1—Co1′ to 2·4942 (2) Å for Co1—Co3. The carbonyls C2—O2 sitting on the faces of the tetrahedron are unsymmetrically bound to three Co atoms; the difference in distance between C2 and the chemically equivalent Co2 and Co3 is 0·045 (1) Å. Another interesting feature is that the doubly bridging carbonyl C1—O1 is tilted towards Co2. This is apparent from the 102·6 (1)° angle between the planes *P*1 [defined by C1, Co1 and Co1′; O1 lies 0·055 (3) Å from *P*1] and *P*2 (defined by Co1, Co1′ and Co2), while the angle between *P*1 and *P*3 (defined by Co1, Co1′ and Co3) is 171·5 (6)°. The Cp rings are planar with the largest deviation from planarity being 0·003 (3) Å. The rings are in an eclipsed conformation; atoms C1*A*, Co2, Co3 and C1*B* lie in the mirror plane. The angle between the planes of the rings is 48·6 (1)°. The distances from the Co atoms to the centroids of the Cp rings, Co2—Cp*A* and Co3—Cp*B*, are 1·700 and 1·702 Å, respectively. The tilt between the Cp ring normals and the lines defined by Co2—Cp*A* and Co3—Cp*B* are 0·2 and 2·0°, respectively. Steric interactions are found between the carbons of the triply bridging carbonyls and carbons C3*A*, C3*B*, C2*A* and C2*A* in the Cp rings; contact distances are smaller than the sum of the corresponding van der Waals radii. The difference between contact distances for C2—C_{Cp} and the sum of their van der Waals radii varies from 0·806 (3) Å for C2—C3*B* to 0·699 (3) Å for C2—C2*A*. Weaker steric interactions between C1 of the doubly bridging carbonyl and C1*A* of the ring, and C3 of the terminal carbonyl with C1*B* and C2*B* are also present; the difference between contact distances and the sum of their van der Waals radii range from 0·392 (3) Å for C3—C1*B* to 0·318 (3) Å for C3—C2*B*.

The replacement of hydrogens by methyl groups in the Cp rings causes some changes in the molecular structure as seen by comparing the structure of (I) with its Cp* analogue (II). The crystal structure of (II) was reported by Cirjak, Ginsburg & Dahl (1979). Co—Co distances are generally somewhat shorter in (I); the range of Co—Co distances in (II) is 2·386–2·554 Å. The stronger steric interactions in compound (II) are also between the triply bridging carbonyls and the

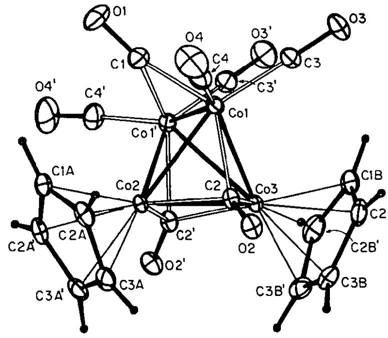

Fig. 1. *ORTEP* diagram (Johnson, 1965) of the title compound showing the atom-labeling scheme. For clarity, H atoms are not labeled.

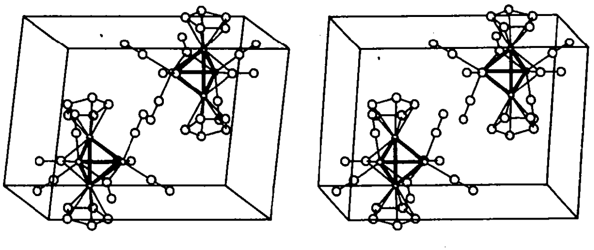

Fig. 2. Stereoview of the unit cell, viewed approximately along the *a* axis, with *b* horizontal.

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* Lists of H-atom coordinates and thermal parameters, anisotropic thermal parameters, and structure-factor amplitudes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44244 (36 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond distances* (Å) *and relevant bond angles* (°) *with e.s.d.'s in parentheses*

Co1–Co1′	2·4171 (4)	Co3–C1*B*	2·089 (2)
Co1–Co2	2·4560 (2)	Co3–C2*B*	2·084 (1)
Co1–Co3	2·4942 (2)	Co3–C3*B*	2·082 (1)
Co1–C1	1·944 (2)	C1–O1	1·153 (3)
Co1–C2	1·942 (1)	C2–O2	1·187 (2)
Co1–C3	1·780 (1)	C3–O3	1·142 (2)
Co1–C4	1·785 (2)	C4–O4	1·136 (2)
Co2–Co3	2·4431 (3)	C1*A*–C2*A*	1·404 (2)
Co2–C2	2·019 (1)	C2*A*–C3*A*	1·405 (2)
Co2–C1*A*	2·082 (2)	C3*A*–C3*A*′	1·407 (4)
Co2–C2*A*	2·075 (1)	C1*B*–C2*B*	1·413 (2)
Co2–C3*A*	2·079 (1)	C2*B*–C3*B*	1·413 (2)
Co3–C2	1·974 (1)	C3*B*–C3*B*′	1·414 (4)

Co1′–Co1–Co2	60·523 (5)	Co1–Co3–C2′	97·37 (4)
Co1′–Co1–Co3	61·017 (5)	Co1–Co3–Cp*B*	138·52
Co1′–Co1–C2	100·86 (4)	Co2–Co3–C2	53·13 (3)
Co1′–Co1–C3	103·84 (6)	Co2–Co3–Cp*B*	156·36
Co1′–Co1–C4	146·74 (6)	C2–Co3–C2′	105·78 (7)
Co1′–Co1–C1	51·55 (4)	C2–Co3–Cp*B*	121·62
Co2–Co1–Co3	59·140 (7)	Co1–C2–Co2	76·61 (5)
Co2–Co1–C2	53·12 (4)	Co1–C2–Co3	79·12 (5)
Co2–Co1–C3	151·30 (5)	Co1–C2–O2	136·5 (1)
Co2–Co1–C4	107·42 (5)	Co2–C2–Co3	75·43 (4)
Co2–Co1–C1	80·98 (6)	Co2–C2–O2	131·7 (1)
Co3–Co1–C2	51·01 (4)	Co3–C2–O2	133·5 (1)
Co3–Co1–C3	92·47 (5)	Co1–C3–O3	179·2 (1)
Co3–Co1–C4	143·09 (6)	Co1–C4–O4	177·4 (2)
Co3–Co1–C1	112·10 (4)	Co2–C2*A*–C1*A*	70·52 (9)
C2–Co1–C3	113·83 (6)	Co2–C2*A*–C3*A*	70·41 (8)
C2–Co1–C4	92·68 (7)	C1*A*–C2*A*–C3*A*	108·8 (1)
C2–Co1–C1	133·88 (7)	Co3–C1*B*–C2*B*	70·0 (1)
C3–Co1–C4	98·03 (7)	C2*B*–C1*B*–C2*B*′	107·2 (2)
C3–Co1–C1	108·97 (8)	Co2–C1*A*–C2*A*	69·99 (9)
C4–Co1–C1	97·73 (7)	C2*A*–C1*A*–C2*A*′	107·1 (2)
Co1–Co2–Co1′	58·95 (1)	Co1–C1–Co1′	76·90 (8)
Co1–Co2–Co3	61·208 (7)	Co1–C1–O1	141·47 (4)
Co1–Co2–C2	50·27 (4)	Co3–C3*B*–C3*B*′	70·15 (5)
Co1–Co2–C2′	97·36 (4)	Co3–C3*B*–C2*B*	70·23 (8)
Co1–Co2–Cp*A*	137·85	C3*B*′–C3*B*–C2*B*	107·7 (1)
Co3–Co2–C2	51·45 (3)	Co3–C2*B*–C1*B*	70·4 (1)
Co3–Co2–Cp*A*	155·20	Co3–C2*B*–C3*B*	70·11 (8)
C2–Co2–C2′	102·45 (7)	C1*B*–C2*B*–C3*B*	108·6 (2)
C2–Co2–Cp*A*	122·68	Co2–C3*A*–C2*A*	70·06 (7)
Co1–Co3–Co1′	57·966 (9)	Co2–C3*A*–C3*A*′	70·22 (5)
Co1–Co3–Co2	59·652 (7)	C2*A*–C3*A*–C3*A*′	107·66 (9)
Co1–Co3–C2	49·87 (4)		

Cp*A* and Cp*B* are the centroids of cyclopentadienyl rings *A* and *B* respectively.

carbons in the backbone of the ring, but the presence of methyl groups in (II) introduces new steric interactions of comparable strength not present in (I). These interactions are between the carbons of the terminal, doubly and triply bridging carbonyls with the methyl groups; the differences between the OC–(Me) distances and the sum of their van der Waals radii vary from 0·53 to 0·31 Å. These new steric interactions seem to be the cause of the greater distances between the Co atoms and the Cp* ligands for (II). The average Co–C_{Cp} and Co–C_{Cp^*} distances are 2·082 and 2·115 Å; the ranges for Co–C_{Cp} and Co–C_{Cp^*} distances are 2·075 (1)–2·089 (2) and 2·100–2·145 Å, respectively. If electronic effects were dominating, the opposite trend would be expected. There is a change of the angle formed by the planes of the rings in (I) to a value of 52·0° (average of two independent molecules) for the corresponding planes in (II). Also in (II) the doubly bridging carbonyl is tilted further away from the cobalt atom analogous to Co2 in (I). This can be judged by the change in the angles between planes *P*1 and *P*2 from 102·6° in (I) to 105·9° for similar planes in (II). The Cp* rings are almost eclipsed; the torsion angles for the two independent molecules in (II), analogous to C1*A*–Co2–Co3–C1*B* in (I), are −16·1 and 0·3°. To within 0·01 Å the Co–CO and the C–O bond lengths remain the same in (I) as in (II). Hence, there is no significant evidence of an increase in back-donation caused by replacing the Cp rings with the more electron-donating Cp* ligands.

An attempt was made to compare the crystal structure of (I) with its structure in solution. ^{13}C NMR spectra were obtained for a solution of (I) in CD_2Cl_2. At room temperature the 100·6 MHz ^{13}C NMR spectrum (natural abundance sample) of the region corresponding to the Cp peak shows only one resonance at 90·3 p.p.m. (relative to TMS). In order to observe the carbonyl region, a low-temperature ^{13}C NMR study was required (resonances of carbonyls bound to a ^{59}Co nucleus are not often seen at room temperature). In the temperature range 188–298 K, weak peaks at 257 and 206 p.p.m. were observed; these are the characteristic resonance frequencies for terminal and doubly bridging carbonyls (Cohen, Kidd & Brown, 1975). Above 273 K no carbonyl resonances were observed nor were resonances seen for the triply bridging carbons at any temperature studied; both observations may be due to T_1 effects. The IR spectrum of (I) in CH_2Cl_2 at room temperature shows peaks at 2045, 2022, 1995, 1867 (broad), 1736 (shoulder) and 1725 cm^{-1}. This spectrum is comparable to its KBr spectrum which proves the presence of three different types of carbonyls both in solution and in the solid state.

Based on the IR data and despite the fact that the triply bridging carbonyl could not be detected by ^{13}C NMR, we conclude that the solution structure of (I) is similar to that of the solid reported here.

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