

Bis(η -cyclopentadienyl)(methylmethinyl)tetracarbonyltricobalt Containing the Co₃C Tetrahedral Cluster

BY R. S. MCCALLUM AND B. R. PENFOLD

Chemistry Department, University of Canterbury, Christchurch 1, New Zealand

(Received 9 December 1977; accepted 6 January 1978)

Abstract. CH₃CCo₃(CO)₄(η -C₅H₅)₂, C₁₆H₁₃O₄Co₃, tetragonal, $P4_2/n$, $a = 20.471$ (3), $c = 7.781$ (1) Å, $V = 3260.8$ Å³, $M_r = 446.1$, $Z = 8$, $D_m = 1.79$ (2), $D_c = 1.82$ g cm⁻³, $\mu(\text{Mo } K\alpha) = 31.47$ cm⁻¹. One cyclopentadienyl group is bonded to each of two Co atoms of the CCo₃ unit, equatorially with respect to the Co₃ plane. These two Co atoms are also bridged by one carbonyl group in an axial orientation and the third Co atom has three terminal carbonyl groups.

Introduction. Samples of CH₃CCo₃(CO)₄(Cp)₂ (Cp = cyclopentadienyl) were prepared by Dr B. H. Robinson (Elder, Robinson & Simpson, 1975) and supplied as air-stable maroon needles. Laue symmetry $4/m$ and the systematic absences ($hk0$: $h + k = 2n + 1$ and $00l$: $l = 2n + 1$) established the space group uniquely. Intensities were obtained from a crystal, 0.25 mm long and mean cross-section 0.05 mm, with a Hilger & Watts four-circle diffractometer and Zr-filtered Mo K radiation ($\lambda = 0.7107$ Å). The reciprocal lattice was explored to $2\theta = 40^\circ$, yielding 1522 independent reflections. Of these, 905 had $I > 2\sigma(I)$ and were used in the structure determination and refinement. The detailed procedures for data collection and assignment of errors were as described by Countryman & Penfold (1972). Absorption corrections (calculated by Gaussian integration) were applied; transmission factors ranged from 0.740 to 0.798.

The structure was solved by the heavy-atom method with all three Co atoms, located from the Patterson function, used for phasing. Difference maps indicated that anisotropic motion was slight and all atoms were assigned individual isotropic thermal parameters in the full-matrix least-squares refinement. The function minimized was $\sum w||F_o| - |F_c||^2$, where $w = 4|F_o|^2/(\sigma|F_o|^2)^2$. Most H atoms (including one from the CH₃ group) were located from a difference map and before the last refinement cycle all were included in calculated positions with a thermal parameter, B , of 6 Å². Scattering factors of Co, C and O were from Cromer & Waber (1965), those of H from Stewart, Davidson & Simpson (1965); anomalous-dispersion corrections for Co only were from Cromer (1965). The

Table 1. Atomic coordinates ($\times 10^3$) and thermal parameters

	x	y	z	B (Å ²)
Co(1)	382.8 (1)	501.3 (1)	533.2 (3)	3.36 (6)
Co(2)	280.9 (1)	562.9 (1)	592.0 (3)	2.83 (6)
Co(3)	272.6 (1)	456.7 (1)	473.4 (3)	2.96 (6)
C(11)	420.0 (9)	428 (1)	571 (3)	4.4 (5)
O(11)	445.3 (7)	377.1 (7)	603 (2)	5.5 (3)
C(12)	424 (1)	557 (1)	665 (3)	4.3 (5)
O(12)	453.4 (8)	591.4 (8)	753 (2)	6.8 (4)
C(13)	410 (1)	522 (1)	323 (3)	5.8 (6)
O(13)	428.4 (8)	533.1 (8)	182 (2)	7.2 (4)
C(1)	275.9 (9)	538.1 (9)	368 (3)	3.4 (5)
O(1)	267.7 (6)	559.9 (7)	225 (2)	5.2 (3)
C(2)	310.2 (9)	485.5 (9)	674 (3)	3.5 (4)
C(3)	307.7 (9)	456.1 (9)	856 (2)	4.3 (5)
C(21)	275.4 (9)	617.8 (9)	816 (2)	3.7 (4)
C(22)	214 (1)	597.6 (9)	771 (3)	4.0 (5)
C(23)	201 (1)	623 (1)	610 (3)	5.1 (5)
C(24)	252.8 (9)	660.7 (8)	552 (2)	3.5 (4)
C(25)	301.7 (9)	656.9 (9)	684 (2)	3.5 (4)
C(31)	221 (1)	376.7 (9)	559 (3)	4.9 (5)
C(32)	179.1 (9)	416.3 (9)	452 (3)	4.3 (5)
C(33)	207 (1)	417 (1)	297 (3)	5.3 (5)
C(34)	265 (1)	382 (1)	293 (3)	5.3 (6)
C(35)	273.7 (9)	356.7 (9)	460 (3)	4.6 (5)
H(1)	342	492	936	6.0
H(2)	328	405	860	6.0
H(3)	258	455	909	6.0
H(21)	301	605	936	6.0
H(22)	182	566	847	6.0
H(23)	155	616	537	6.0
H(24)	257	688	430	6.0
H(25)	349	682	683	6.0
H(31)	213	365	693	6.0
H(32)	134	440	492	6.0
H(33)	186	441	183	6.0
H(34)	297	374	183	6.0
H(35)	316	327	506	6.0

final R for the 905 reflections was 0.067. Final atomic parameters, with their standard deviations in parentheses, are given in Table 1.*

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33307 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Discussion. A general view of one molecule with all atoms labelled is shown in Fig. 1. The molecules are well separated; the closest intermolecular contact not involving H is 3.4 Å. Bond lengths and angles are given in Table 2.

The compound is one of a series of general composition $YCo_3(CO)_4(Cp)_2$ ($Y = \text{alkyl, aryl or F}$) prepared in the course of a study of the reactivity of dienes towards methylidyne tricobalt enneacarbonyls (Elder, Robinson & Simpson, 1975). The solution spectroscopic data from that study suggested a structure in which there were three terminal and one bridging carbonyl groups associated with the Co_3 triangular cluster – a configuration that this structure determination confirms for the solid state. In the first report of the structure (Penfold & Robinson, 1973) it was noted that the bridging carbonyl was oriented axially with respect to the Co_3 triangle [the angle between the Co_3 plane and the plane $Co(2), Co(3), O(1)$ is 84°], a hitherto unknown conformation for tetrahedral or triangular cluster carbonyls. Were the bridging carbonyl to occupy the more usual equatorial (or basal) orientation, this would result in a prohibitive non-bonded interaction between CO and the C_5H_5 ring. The unusually low stretching frequency associated with the bridging carbonyl in the axial orientation has been commented upon by Elder, Robinson & Simpson (1975). More recently Cotton & Jamerson (1976) have reported the structure of $[CpCo(CO)]_3$ which contains two axially oriented carbonyls which form unsymmetrical bridges across two edges of a Co_3 triangle. Cotton (1977) has also determined the structure of $CH_3CCo_3(CO)_4(C_5Me_5)_2$ which is closely analogous to the present structure.

The C_5H_5 rings are oriented approximately at right angles to the Co_3 plane (dihedral angles are both 84°) and make an angle of 54° with each other. The mean $Co-C(Cp)$ distance of 2.08 (2) Å agrees closely with the value of 2.07 Å observed by Uchtman & Dahl

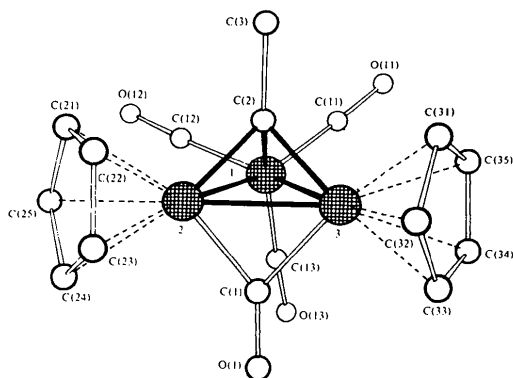


Fig. 1. One molecule of $CH_3CCo_3(CO)_4(\eta-C_5H_5)_2$ viewed approximately parallel to the Co_3 triangle, showing all atoms labelled.

Table 2. Bond lengths (Å) and angles ($^\circ$)

Mean values of chemically-similar lengths and angles are italicized. The uncertainties in parentheses for mean values are r.m.s. deviations from the mean.

Co(1)–Co(2)	2.480 (3)	C(2)–C(3)	1.55 (3)
Co(1)–Co(3)	2.477 (4)	C(1)–O(1)	1.21 (2)
Co(2)–Co(3)	2.368 (3)	C(11)–O(11)	1.18 (2)
Co(1)–C(2)	1.88 (2)	C(12)–O(12)	1.15 (2)
Co(2)–C(2)	1.82 (2)	C(13)–O(13)	1.19 (3)
Co(3)–C(2)	1.84 (2)	Co–C(Cp)	2.08 (2)
Co–C(apical)	1.85 (2)	(range 2.05 to 2.11)	
Co(1)–C(11)	1.71 (2)		
Co(1)–C(12)	1.76 (2)	C–C(Cp)	1.39 (3)
Co(1)–C(13)	1.77 (3)	(range 1.33 to 1.43)	
Co–CO(terminal)	1.74 (3)		
Co(2)–C(1)	1.82 (2)		
Co(3)–C(1)	1.86 (2)		
Co(2)–Co(1)–Co(3)	57.1 (1)	C(1)–Co(3)–Co(2)	49.1 (6)
Co(1)–Co(2)–Co(3)	61.4 (1)	C(1)–Co(2)–Co(3)	50.7 (9)
Co(1)–Co(3)–Co(2)	61.5 (1)	C(1)–Co(3)–Co(1)	73.7 (6)
C(2)–Co(2)–Co(3)	50.7 (6)	C(1)–Co(2)–Co(1)	74.2 (6)
C(2)–Co(1)–Co(2)	46.8 (6)	Co(1)–C(11)–O(11)	178 (2)
C(2)–Co(1)–Co(3)	47.6 (6)	Co(1)–C(12)–O(12)	176 (2)
C(12)–Co(1)–Co(2)	87.9 (7)	Co(1)–C(13)–O(13)	177 (2)
C(11)–Co(1)–Co(3)	96.7 (7)	Co(2)–C(1)–O(1)	142 (2)
C(13)–Co(1)–Co(2)	108.3 (8)	Co(3)–C(1)–O(1)	137 (4)
C(13)–Co(1)–Co(3)	101.7 (7)	Co(2)–C(1)–Co(3)	80.2 (8)
C(11)–Co(1)–C(12)	105 (1)	Co(1)–C(2)–C(3)	129 (1)
		Co(2)–C(2)–C(3)	131 (1)
		Co(3)–C(2)–C(3)	130 (1)
		C–C–C (Cp ring)	108 (2)
		(range 106 to 112)	

(1969) in $(Cp)_3Co_3(\mu_3-CO)(\mu_3-O)$. The unique $Co(2)–Co(3)$ bond associated with the carbonyl bridge is 0.111 (5) Å shorter than the mean of the remaining two chemically-equivalent $Co–Co$ bonds.

We are grateful to Dr B. H. Robinson, University of Otago, for suggesting this problem and for supplying samples, and to the Research Committee of the New Zealand Universities Grants Committee for grants for equipment.

References

- COTTON, F. A. (1977). Personal communication.
 COTTON, F. A. & JAMERSON, J. D. (1976). *J. Am. Chem. Soc.* **98**, 1273–1274.
 COUNTRYMAN, R. & PENFOLD, B. R. (1972). *J. Cryst. Mol. Struct.* **2**, 281–290.
 CROMER, D. T. (1965). *Acta Cryst.* **18**, 17–23.
 CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104–109.
 ELDER, P. A., ROBINSON, B. H. & SIMPSON, J. (1975). *J. Chem. Soc. Dalton Trans.* pp. 1771–1778.
 PENFOLD, B. R. & ROBINSON, B. H. (1973). *Acc. Chem. Res.* **6**, 73–80.
 STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
 UCHTMAN, V. A. & DAHL, L. F. (1969). *J. Am. Chem. Soc.* **91**, 3763–3769.