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(2-3:5-6-η-Norbornadiene)propylidyneheptacarbonyltricobalt, Containing the Co_3C Tetrahedral Cluster

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Abstract. $C_2H_5CCo_3(CO)_7(\pi\text{-}C_7H_8)$, $C_{17}H_{13}O_7Co_3$, monoclinic, $P2_1/c$, a = 9·764 (1), b = 9·121 (1), c = 21·859 (3) Å, β = 105·75 (2)°, V = 1873·6 Å^3, M_r = 506·09, D_c = 1·79 g cm^{-3}, Z = 4, μ(Mo $K\alpha$) = 27·64 cm^{-1}. Two of the three Co atoms of a Co_3C tetrahedral cluster are each coordinated by three terminal CO groups (two equatorial and one axial) while for the third Co atom, the two equatorial CO groups have been replaced by a norbornadiene molecule.

Introduction. Samples of $C_2H_5CCo_3(CO)_7(\pi\text{-}C_7H_8)$ were kindly prepared by Dr B. H. Robinson (Elder, Robinson & Simpson, 1975) and supplied as air-stable dark-red crystals. The monoclinic space group $P2_1/c$ was established uniquely from systematic absences observed in photographs. A plate-shaped crystal 0·5 × 0·23 × 0·025 mm was chosen for intensity collection. 1753 reflections were recorded in the range of $0 \leq 2\theta \leq 40°$ on a Hilger & Watts four-circle diffractometer with Zr-filtered Mo $K\alpha$ radiation and θ–2θ scan techniques. Of these, 1008 had $I > 3\sigma(I)$ 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 and transmission factors ranged from 0·57 to 0·94.

The structure was solved by the heavy-atom method, with all three Co atoms, located from the Patterson function, used for phasing. Subsequent least-squares refinement followed by difference syntheses showed all the remaining C and O atoms. Refinement with the three Co atoms anisotropic, the C and O atoms isotropic and H atoms fixed at their calculated positions gave R = 0·072 and, after correction of the data for absorption, convergence was reached with R = 0·053 for all 1008 reflections. In the full-matrix least-squares procedures, the function minimized was $\sum w||F_o| - |F_c||^2$ and the weights w were $4|F_o|^2/(\sigma|F_o^2|)^2$. Scattering factors of Co, C and O were from Cromer & Waber (1965), those for H from Stewart, Davidson & Simpson (1965). Anomalous-dispersion corrections for Co were from Cromer (1965). Positional and thermal parameters of all atoms are listed in Table 1, anisotropic thermal parameters of Co atoms in Table 2. Selected bond distances and angles are given in Tables 3 and 4.*

Table 1. *Atomic coordinates* (×10^3) *and thermal parameters*

	x	y	z	B (Å^2)
Co(1)	−303·8 (2)	214·7 (2)	120·5 (1)	*
Co(2)	−119·9 (2)	165·8 (2)	63·9 (1)	*
Co(3)	−193·6 (2)	420·2 (2)	77·2 (1)	*
C(1)	−114 (2)	273 (2)	138·2 (7)	3·5 (3)
C(2)	3 (2)	290 (2)	200·1 (9)	6·2 (4)
C(3)	131 (4)	238 (4)	209 (2)	16·5 (10)
C(4)	−327 (2)	302 (2)	207·7 (7)	4·2 (4)
C(5)	−462 (2)	274 (2)	167·6 (7)	4·5 (4)
C(6)	−507 (2)	119 (2)	181·0 (8)	5·1 (4)
C(7)	−389 (2)	28 (2)	156·2 (8)	5·4 (4)
C(8)	−261 (2)	56 (2)	195·4 (8)	5·0 (4)
C(9)	−284 (2)	162 (2)	246·3 (8)	5·4 (4)
C(10)	−428 (2)	111 (2)	252·5 (9)	6·4 (5)
C(11)	−447 (2)	196 (2)	50·7 (8)	4·5 (4)
C(21)	−221 (2)	132 (2)	15 (1)	6·2 (4)
C(22)	−94 (2)	−8 (3)	91·2 (9)	6·4 (5)
C(23)	−45 (2)	205 (2)	54·1 (8)	5·5 (4)
C(31)	−299 (2)	446 (2)	−2·1 (9)	5·8 (4)
C(32)	−276 (2)	544 (2)	115·1 (8)	5·4 (4)
C(33)	−39 (2)	519 (2)	80·1 (8)	5·0 (4)
O(11)	−539 (2)	188 (1)	4·5 (6)	6·1 (3)
O(21)	−281 (1)	119 (1)	−68·1 (7)	7·9 (3)
O(22)	−72 (1)	−125 (2)	116·0 (7)	9·3 (4)
O(23)	−157 (1)	233 (1)	46·8 (6)	7·4 (3)
O(31)	−368 (1)	462 (1)	−53·6 (7)	7·1 (3)
O(32)	−332 (1)	631 (1)	138·8 (6)	6·9 (3)
O(33)	−67 (1)	583 (1)	84·3 (6)	6·7 (3)
H(21)	13	399	210	6·0
H(22)	−34	242	234	6·0
H(31)	176	196	255	6·0
H(32)	145	164	179	6·0
H(33)	203	318	200	6·0
H(41)	−269	397	211	6·0
H(51)	−520	346	136	6·0
H(61)	−463	46	157	6·0
H(71)	−419	−36	116	6·0
H(81)	−169	13	193	6·0
H(91)	−193	177	282	6·0
H(101)	−476	171	279	6·0
H(102)	−429	3	268	6·0

* See Table 2.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33370 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Anisotropic thermal parameters* ($\times 10^4$) *for the* Co *atoms* (Å^2)

The expression for the anisotropic thermal ellipsoid is of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co(1)	95 (3)	101 (3)	22 (7)	4 (3)	15 (1)	3 (1)
Co(2)	108 (3)	102 (4)	24 (7)	8 (3)	17 (1)	−4 (1)
Co(3)	123 (3)	94 (3)	24 (7)	−3 (3)	21 (1)	0 (1)

Table 3. *Bond lengths* (Å)

Mean values of bonds assumed to be chemically equivalent are italicized and their associated uncertainties are either r.m.s. deviations from the mean value or the mean of the individual standard deviations, whichever is the larger.

Co(1)–Co(2)	2·483 (3)	C(11)–O(11)	1·16 (2)
Co(1)–Co(3)	2·475 (3)	C(21)–O(21)	1·15 (2)
Co(2)–Co(3)	2·470 (3)	C(31)–O(31)	1·15 (2)
Co(1)–C(1)	1·86 (1)	C(22)–O(22)	1·19 (2)
Co(2)–C(1)	1·88 (2)	C(23)–O(23)	1·18 (2)
Co(3)–C(1)	1·90 (2)	C(32)–O(32)	1·16 (2)
Co–C(apical)	*1·88 (2)*	C(33)–O(33)	1·17 (2)
Co(1)–C(11)	1·78 (2)	C–O	*1·16 (2)*
Co(2)–C(21)	1·77 (2)	C(4)–C(9)	1·52 (2)
Co(3)–C(31)	1·78 (2)	C(5)–C(6)	1·53 (2)
Co–CO(axial)	*1·78 (2)*	C(6)–C(7)	1·62 (2)
Co(2)–C(22)	1·69 (2)	C(6)–C(10)	1·55 (2)
Co(2)–C(23)	1·72 (2)	C(8)–C(9)	1·53 (2)
Co(3)–C(32)	1·72 (2)	C(9)–C(10)	1·52 (2)
Co(3)–C(33)	1·75 (2)	C(4)–C(5)	1·39 (2)
Co–CO(equatorial)	*1·72 (3)*	C(7)–C(8)	1·34 (2)
C(1)–C(2)	1·52 (2)		
C(2)–C(3)	1·30 (3)		

Table 4. *Bond angles* (°)

Co(1)–Co(2)–Co(3)	60·0 (1)	C(31)–Co(3)–C(32)	99·3 (7)
Co(1)–Co(3)–Co(2)	60·3 (1)	C(31)–Co(3)–C(33)	103·8 (8)
Co(2)–Co(1)–Co(3)	59·8 (1)	C(22)–Co(2)–C(23)	100·7 (9)
Co(1)–C(1)–Co(2)	83·0 (6)	C(32)–Co(3)–C(33)	99·1 (9)
Co(1)–C(1)–Co(3)	82·2 (6)	C(11)–Co(1)–Co(2)	93·4 (5)
Co(2)–C(1)–Co(3)	81·4 (6)	C(11)–Co(1)–Co(3)	93·8 (5)
Co–C(1)–Co	*82·2*	C(21)–Co(2)–Co(1)	103·5 (6)
C(1)–Co(1)–Co(2)	48·9 (4)	C(31)–Co(3)–Co(1)	105·9 (6)
C(1)–Co(1)–Co(3)	49·6 (5)	C(21)–Co(2)–Co(3)	100·1 (6)
C(1)–Co(2)–Co(1)	48·2 (4)	C(31)–Co(3)–Co(2)	96·9 (6)
C(1)–Co(2)–Co(3)	49·6 (4)	C(22)–Co(2)–Co(1)	92·9 (6)
C(1)–Co(3)–Co(1)	48·2 (4)	C(32)–Co(3)–Co(1)	90·2 (6)
C(1)–Co(3)–Co(2)	49·0 (4)	C(23)–Co(2)–Co(3)	97·6 (6)
C(1)–Co–Co	*48·9*	C(33)–Co(3)–Co(2)	102·2 (6)
C(2)–C(1)–Co(1)	132·5 (10)	Co(1)–C(11)–O(11)	177·9 (15)
C(2)–C(1)–Co(2)	131·2 (10)	Co(2)–C(21)–O(21)	174·8 (17)
C(2)–C(1)–Co(3)	128·0 (10)	Co(2)–C(22)–O(22)	174·0 (19)
C(1)–C(2)–C(3)	123·9 (22)	Co(2)–C(23)–O(23)	179·2 (16)
C(22)–Co(2)–C(1)	102·4 (8)	Co(3)–C(31)–O(31)	179·6 (15)
C(23)–Co(2)–C(1)	101·0 (7)	Co(3)–C(32)–O(32)	177·4 (16)
C(32)–Co(3)–C(1)	106·1 (7)	Co(3)–C(33)–O(33)	177·5 (15)
C(33)–Co(3)–C(1)	98·8 (7)	C(5)–C(6)–C(7)	98·3 (12)
C(11)–Co(1)–C(1)	135·3 (7)	C(4)–C(9)–C(8)	101·3 (13)
C(21)–Co(2)–C(1)	144·2 (7)	C(4)–C(9)–C(10)	100·7 (13)
C(31)–Co(3)–C(1)	142·6 (6)	C(8)–C(9)–C(10)	101·1 (14)
C(22)–Co(2)–Co(3)	149·3 (6)	C(5)–C(6)–C(10)	98·7 (13)
C(23)–Co(2)–Co(1)	148·6 (6)	C(7)–C(6)–C(10)	96·2 (13)
C(32)–Co(3)–Co(2)	149·3 (6)	C(4)–C(5)–C(6)	108·6 (14)
C(33)–Co(3)–Co(1)	147·0 (6)	C(5)–C(4)–C(9)	105·4 (14)
C(21)–Co(2)–C(22)	100·0 (9)	C(6)–C(7)–C(8)	108·1 (14)
C(21)–Co(2)–C(23)	101·9 (8)	C(7)–C(8)–C(9)	106·8 (14)
		C(6)–C(10)–C(9)	96·5 (13)

Discussion. Proton NMR studies have shown that methylidyne tricobalt norbornadiene derivatives are non-rigid in solution (Elder, Robinson & Simpson, 1975). The present analysis was undertaken to establish the solid-state structure of $C_2H_5CCo_3(CO)_7(\pi\text{-}C_7H_8)$ and compare it with similar complexes, where CO groups have been substituted by π donors. It had been proposed by Elder & Robinson (1972) that the diene ligand replaces one equatorial and one axial carbonyl to give a structure *cis–trans* with respect to the Co_3C apical C atom.

Figs. 1 and 2 show two different perspective views of $C_2H_5CCo_3(CO)_7(\pi\text{-}C_7H_8)$. Fig. 1 shows the molecule with a view normal to the Co_3 triangle while Fig. 2 presents a second view parallel to the Co_3 triangle with the H atoms of the ethyl group included. The ligand is thus seen to coordinate in a *cis–cis* rather than a *cis–trans* orientation, two equatorial carbonyls attached to one Co atom being replaced. Except for the ethyl group attached to the apical C atom of the Co_3C core, the molecule has an idealized mirror plane through Co(1), C(1), C(6), C(9), C(10), C(11) and O(11).

The norbornadiene molecule is π-bonded to Co(1) *via* its two double bonds, C(4)–C(5) and C(7)–C(8), with a mean Co(1)–C distance of 2·14 (2) Å. This may

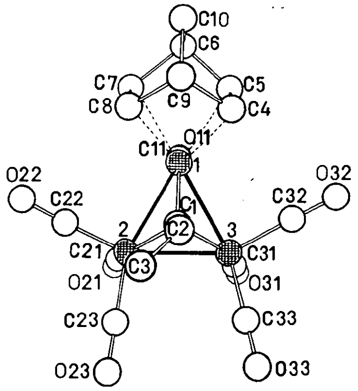

Fig. 1. One molecule of $C_2H_5CCo_3(CO)_7(\pi\text{-}C_7H_8)$ viewed normal to the Co_3 triangle. Co atoms are shown cross-hatched.

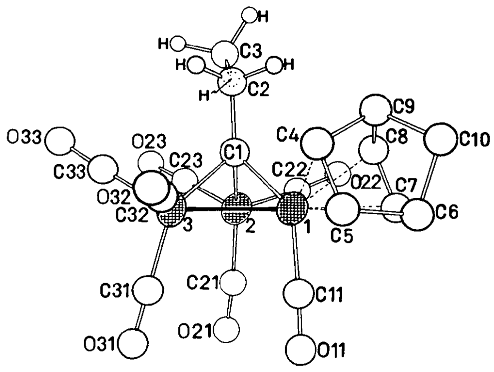

Fig. 2. The molecule viewed parallel to the Co_3 triangle to illustrate the interaction between Co(1) and the norbornadiene ligand.

be compared with the 2·14 (2) Å for the corresponding distances in $PhCCo_3(CO)_6(\pi\text{-}C_6H_3Me_3)$ (Dellaca & Penfold, 1972) where all three carbonyls from a single Co atom have been replaced by a six-electron donor. The structures of these two compounds may be contrasted with those of $PhCCo_3(CO)_6(\pi\text{-}C_8H_8)$ (Brice, Dellaca, Penfold & Spencer, 1971) and $PhCCo_3(CO)_6$-$(\pi\text{-}C_7H_8)$ (Holloway & Penfold, 1977) in each of which a polyene ligand has replaced the axial carbonyls of three different Co atoms while still leaving the basic Co_3C core and the remaining terminal carbonyls unchanged.

While the lengths of the coordinated double bonds of norbornadiene [mean 1·36 (2) Å] do not differ significantly (1·5σ) from the value of 1·333 Å observed in the free ligand (Wilcox, Winstein & McMillan, 1960), the observed lengthening is certainly expected (Stephens, 1972). Corresponding values for the coordinated double bonds in other Co carbonyl norbornadiene complexes, *e.g.* $Co_2(CO)_5(\pi\text{-}C_7H_8)$, $Ph_2Sn[Co(CO)_2(\pi\text{-}C_7H_8)]_2$ and $Cl_2Sn[Co(CO)_2(\pi\text{-}C_7H_8)]_2$, are 1·37 (1), 1·40 (2) and 1·40 (1) Å with Co—C distances of 2·16, 2·18 and 2·17 Å respectively (Stephens, 1972; Boer & Flynn, 1971).

The orientation of the norbornadiene molecule may be conveniently described in terms of the planar group C(4)C(5)C(7)C(8) which makes an angle of 67·5° with the Co_3 plane. An alternative description is in terms of the orientation of the π bonds to Co(1); there is an angle of 22·7° between the Co_3 plane and the Co(1)-C(4–5)C(7–8) plane, where C(4–5) and C(7–8) are the mid-points of the double bonds C(4)—C(5) and C(7)—C(8). This is to be compared with angles of 31·2 and 32·7° between the Co_3 plane and planes formed by Co(2)C(22)C(23) and Co(3)C(32)C(33) respectively. This orientation of the norbornadiene achieves a balance between non-bonded repulsions with the apical C atom [minimum C(1)···C(4)/C(8) = 2·91 Å] and the axial carbonyl bonded to Co(1) [minimum C(11)···C(5)/C(7) = 2·70 Å].

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Two Crystal Structures of Polymorphic Bis(glycine)manganese(II) Bromide Dihydrate

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Abstract. Two crystal structures of the polymorphic compound $[Mn(^{-}OOCCH_2NH_3^{+})_2(OH_2)_2]Br_2$ (M_r = 400·9) have been determined: (I) monoclinic, $P2_1/c$, $Z = 2$, a = 11·943 (3), b = 6·060 (2), c = 8·979 (2) Å, β = 111·65 (3)°, V = 604·06 Å^3, D_m = 2·21, D_x = 2·20 g cm^{-3}, μ(Cu $K\alpha$) = 182·1 cm^{-1}; (II) orthorhombic, $Pbca$, Z = 8, a = 21·613 (5), b = 12·649 (3), c = 8·990 (2) Å, V = 2457·7 Å^3, D_m = 2·15, D_x = 2·17 g cm^{-3}, μ(Cu $K\alpha$) = 197·0 cm^{-1}. All measurements were made on a computer-controlled four-circle diffractometer with Cu $K\alpha$ radiation. The final R_1 values for 722 (I) and 1398 (II) reflections were 0·040 and 0·047