# Crystal and Molecular Structure of Di-μ-carbonyl-(tricarbonylcobaltio)-carbonyl(π-cyclopentadienyl)iron

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The crystal structure of the title compound has been determined by *X*-ray diffraction methods by use of counter data and refined to *R* 0·055 for 1240 unique reflections by a full-matrix least-squares procedure. The monoclinic unit cell, space group $P2_1/m$, has dimensions $a = 7{\cdot}008 \pm 0{\cdot}009$, $b = 10{\cdot}941 \pm 0{\cdot}107$, $c = 8{\cdot}605 \pm 0{\cdot}016$ Å, $\beta = 104{\cdot}7 \pm 0{\cdot}1°$, for $Z = 2$. The molecule possesses *m* symmetry (a requirement of the space group) and has a non-planar $Fe(CO)_2Co$ bridging system, the angle between the two Fe(CO)Co planes being 143·5°. Fe ··· Co is 2·545(1) Å. The terminal carbonyl groups lying on the mirror plane are in a *cis*-configuration. The metal to bridge-carbon distances are: Fe–C 1·882(7), Co–C 2·036(7) Å. The cobalt is in a square-based pyramidal environment.

INFRA-RED studies of compounds of the type $[(\pi\text{-dienyl})FeCo(CO)_6]$ have shown the presence of carbonyl-bridged species, both in solution and the solid state.[1] The interpretation of the spectra suggested the carbonyl bridges would be non-planar with interplanar bridge angles of *ca.* 140°.[1] The structure of the compound for which the dienyl ligand is indenyl ($C_9H_7$) has been shown to possess a distorted bridging system.[2] The crystal structure of the title compound was undertaken with a view to explaining the distortions observed in the bridging system of the indenyl compound.

## EXPERIMENTAL

*Crystal Data.*—$C_{11}H_5CoFeO_6$ $M = 347{\cdot}9$, Monoclinic, $a = 7{\cdot}008 \pm 0{\cdot}009$, $b = 10{\cdot}941 \pm 0{\cdot}017$, $c = 8{\cdot}605 \pm 0{\cdot}016$ Å, $\beta = 104{\cdot}7 \pm 0{\cdot}1°$, $U = 638{\cdot}3$ Å$^3$, $D_m = 1{\cdot}80$ (by flotation), $Z = 2$, $D_c = 1{\cdot}81$, $F(000) = 344$. Mo-$K_\alpha$ radiation, $\lambda = 0{\cdot}71069$ Å, $\mu(\text{Mo-}K_\alpha) = 24{\cdot}2$ cm$^{-1}$, for cell parameters and intensity measurements. Systematic absences $00k$ for $k = 2n + 1$. Space group $P2_1$ ($C_2^2$, no. 4) or $P2_1/m$ ($C_{2h}^2$, no. 11).

The complex crystallises as dark brown plates lying on the (001) face, elongated along *a*, with pinacoids {100} and {010}. Unit-cell parameters were determined from single-crystal precession photographs by the use of Mo-$K_\alpha$ radiation. Systematic absences indicated the space group to be $P2_1$ or $P2_1/m$. The intensities were collected on a Philips PAILRED diffractometer by use of monochromatised Mo-$K_\alpha$ radiation. Each reflection in the 0—10*kl* layers for $\sin\theta < 0{\cdot}54$ was recorded. 1240 reflections gave counts[3] for which $\sigma(I)/I < 0{\cdot}5$, and these were used for the structure analysis. Intensities were corrected for Lorentz and polarisation effects, but no correction for absorption or extinction was applied.

The scattering factor curves for all atoms were taken from ref. 4, the values for cobalt and iron atoms being corrected for the effects of anomalous dispersion. Calculations were carried out on a PDP 10 computer of the University of Essex using programmes written by one of us (F. S. S.).

*Structure Determination.*—From the systematic absences, the space group is $P2_1$ or $P2_1/m$. With two molecules per unit cell, there are no symmetry restrictions on the molecular geometry imposed by the non-centric space group $P2_1$. However, for the centric space group $P2_1/m$, the molecules must possess either a centre of symmetry or a mirror plane. Only the latter is feasible for the present compound. A

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[1] A. R. Manning, *J. Chem. Soc.* (*A*), 1971, 2321.

[2] F. S. Stephens, *J.C.S. Dalton*, 1974, 13.

[3] M. Mack, *Norelco Reporter*, 1965, **12**, 40.

[4] ' International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

statistical analysis of the intensity data [$N(Z)$test] indicated the centric space group.[5] The three-dimensional Patterson synthesis was consistent with this space group, and readily gave the positions of the metal atoms. The centric group was assumed therefore and confirmed subsequently by the successful structure analysis. A series of Fourier and difference syntheses, each phased by an increased number of atoms, gave the positions of all non-hydrogen atoms.

Refinement of the structure was carried out by a full-matrix least-squares procedure in which the function minimised was $\Sigma w\Delta^2$. The weight for each reflection, $w$, was initially unity and in the final refinement given by $w = (5{\cdot}0 - 0{\cdot}1|F_o| + 0{\cdot}004|F_o|^2)^{-1}$. For this latter weighting scheme the average values of $w\Delta^2$ for ranges of increasing $|F_o|$ were almost constant. Reflections for which the calculated structure factors were less than one-third of the observed values were omitted from the least-squares analysis.

Initial refinement used a procedure in which positional and individual isotropic thermal parameters for each atom were refined. A difference synthesis, calculated when the maximum shift in any parameter was of the order of its $\sigma$, showed no unusual features, and gave the approximate positions of all the hydrogen atoms. These were included in subsequent calculations with positions calculated assuming C–H 1·0 Å and thermal parameters of $B$ 6·0 Å$^2$.

Final refinement was carried out with anisotropic thermal parameters for all non-hydrogen atoms. After several cycles the positional parameters of the hydrogen atoms were included in the least-squares matrix. The refinement was terminated when the maximum shift in a parameter was $< 0{\cdot}1\sigma$. 1225 reflections were included in the final cycle of refinement. The final value of $R$, based on 1240 reflections, was 0·055 and for $R'\{= [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}\}$ was 0·057.

Final atomic co-ordinates and thermal parameters are given together with their estimated standard deviations in Tables 1 and 2. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21149 (8 pp., 1 microfiche).*

TABLE 1

Atomic co-ordinates (fractional) with estimated standard deviations in parentheses

| | $x/a$ | $y/b$ | $z/c$ |
|---|---|---|---|
| Co | 0·1496(2) | $\frac{1}{4}$ | 0·4441(1) |
| Fe | 0·1355(2) | $\frac{1}{4}$ | 0·1457(1) |
| O(B1) | 0·0213(13) | 0·4786(6) | 0·2652(8) |
| O(T11) | −0·2115(11) | $\frac{1}{4}$ | 0·5548(10) |
| O(T12) | 0·3964(10) | 0·4406(6) | 0·6281(7) |
| O(T21) | −0·2602(13) | $\frac{1}{4}$ | −0·0556(11) |
| C(B1) | 0·0712(11) | 0·3786(7) | 0·2686l8) |
| C(T11) | −0·0756(13) | $\frac{1}{4}$ | 0·5043(10) |
| C(T12) | 0·3013(10) | 0·3679(7) | 0·5539(7) |
| C(T21) | −0·1077(17) | $\frac{1}{4}$ | 0·0281(12) |
| C(1) | 0·4329(19) | $\frac{1}{4}$ | 0·1832(15) |
| C(2) | 0·3707(22) | 0·3470(11) | 0·1006(20) |
| C(3) | 0·2500(13) | 0·3107(8) | −0·0386(10) |
| H(1) | 0·510(9) | $\frac{1}{4}$ | 0·280(7) |
| H(2) | 0·347(14) | 0·090(9) | 0·088(12) |
| H(3) | 0·177(11) | 0·146(8) | −0·119(10) |

## DISCUSSION

Figure 1 shows a perspective drawing of the molecule and the labelling of the atoms.[6] Figure 2 shows the packing of the molecules in the crystal.[6] The molecules

TABLE 2

Thermal parameters ($\times 10^4$),* with estimated standard deviations in parentheses

| | $b_{11}$ | $b_{22}$ | $b_{33}$ | $b_{12}$ | $b_{13}$ | $b_{23}$ |
|---|---|---|---|---|---|---|
| Co | 246(3) | 95(1) | 98(1) | 0 | 52(2) | 0 |
| Fe | 234(3) | 113(1) | 87(1) | 0 | 39(2) | 0 |
| O(B1) | 107(36) | 161(7) | 293(12) | 277(14) | 261(17) | 85(8) |
| O(T11) | 362(20) | 268(13) | 269(15) | 0 | 154(14) | 0 |
| O(T12) | 699(26) | 215(9) | 281(12) | 199(13) | 143(14) | 95(9) |
| O(T21) | 262(21) | 751(38) | 221(16) | 0 | 19(15) | 0 |
| C(B1) | 447(22) | 140(9) | 177(10) | 87(11) | 119(12) | 16(8) |
| C(T11) | 257(21) | 160(12) | 143(12) | 0 | 56(13) | 0 |
| C(T12) | 386(19) | 134(8) | 144(8) | 58(10) | 80(10) | 26(7) |
| C(T21) | 295(28) | 355(26) | 157(15) | 0 | 84(17) | 0 |
| C(1) | 204(24) | 733(76) | 135(15) | 0 | 47(16) | 0 |
| C(2) | 701(51) | 199(17) | 563(38) | 233(27) | 469(39) | 209(23) |
| C(3) | 456(24) | 186(11) | 226(13) | −79(13) | 189(15) | −105(10) |

For all hydrogen atoms $B$ 6·0 Å$^2$.

* Anisotropic thermal parameters in the form: $\exp-(h^2b_{11} + k^2b_{22} + l^2b_{33} + 2hkb_{12} + 2hlb_{13} + 2klb_{23})$.

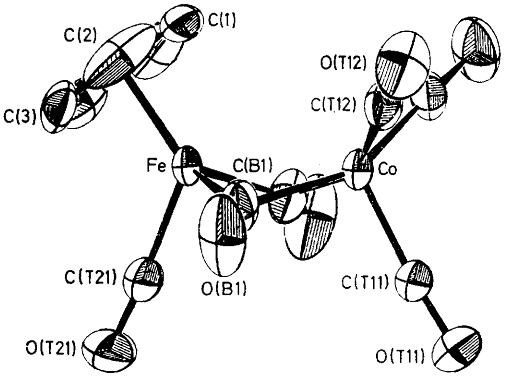

FIGURE 1 A perspective drawing of the molecule and the labelling of the atoms. Thermal ellipsoids are scaled to include 30% probability

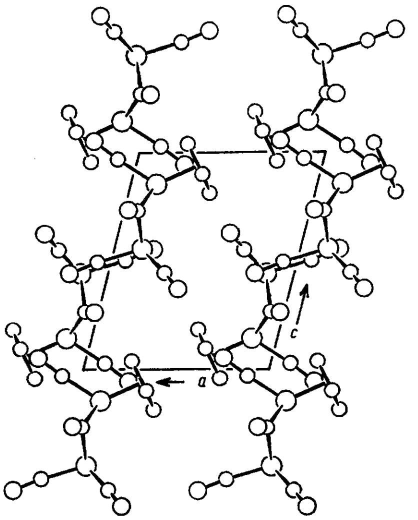

FIGURE 2 The packing of the molecules in the crystal. As a consequence of the mirror plane, only the labelled atoms of Figure 1 are included in the diagram (*i.e.* mirror images are omitted)

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue (items less than 10 pp. are supplied as full size copies).

[5] E. R. Howells, D. C. Phillips, and D. Rogers, *Acta Cryst.*, 1950, **3**, 210.

[6] C. K. Johnson, 1965, ORTEP, A Fortran Thermal Ellipsoid Plot Program for Crystal Structure Illustrations, Report ORNL 3794, Revised 1971, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

are held in the crystal by van der Waals forces. The closest intermolecular contacts are O(T12) $\cdots$ O(T12) at $1 - x, y, 1 - z$ (3·21 Å), O(B1) $\cdots$ C(3) at $-x, -y, -z$ (3·29 Å) and O(T21) $\cdots$ C(1) at $-1 + x, y, z$ (3·33 Å). All other non-hydrogen contacts are >3·37 Å. Bond distances and angles, together with their estimated standard deviations derived directly from the least-squares inverse matrix, are given in Table 3. The C–H distances are appreciably shorter than accepted values,[7] but this is realistic since the hydrogen positions obtained are those of electron-density maxima rather than nuclei.

TABLE 3

Bond lengths (Å) and angles (°), with estimated standard deviations in parentheses

(*a*) Distances

| | | | |
|---|---|---|---|
| Fe $\cdots$ Co | 2·545(1) | Co–C(B1) | 2·036(7) |
| Fe–C(B1) | 1·882(7) | Co–C(T11) | 1·781(9) |
| Fe–C(T21) | 1·748(12) | Co–C(T12) | 1·783(7) |
| Fe–cp * | 1·729(11) | C(T11)–O(T11) | 1·142(10) |
| C(B1)–O(B1) | 1·147(8) | C(T12)–O(T12) | 1·127(8) |
| C(T2)–O(T21) | 1·128(12) | C(1)–C(2) | 1·290(18) |
| Fe–C(1) | 2·027(13) | C(2)–C(3) | 1·340(16) |
| Fe–C(2) | 2·078(10) | C(3)–C(3′) | 1·327(17) |
| Fe–C(3) | 2·060(6) | C(2)–H(2) | 0·71(10) |
| C(1)–H(1) | 0·87(6) | C(3)–H(3) | 0·88(8) |

(*b*) Angles

| | | | |
|---|---|---|---|
| Co–Fe–C(B1) | 52·2(2) | Fe–Co–C(B1) | 46·9(2) |
| C(B1)–Fe–C(B1′) | 96·8(3) | C(B1)–Co–C(B1′) | 87·5(3) |
| C(B1)–Fe–cp * | 124·7(3) | C(B1)–Co–C(T11) | 97·1(3) |
| C(B1)–Fe–C(T21) | 89·3(3) | C(B1)–Co–C(T12) | 155·0(3) |
| C(T21)–Fe–cp * | 122·0(3) | C(T11)–Co–C(T12) | 107·4(3) |
| Fe–C(B1)–Co | 80·9(3) | C(T12)–Co–C(T12′) | 92·7(3) |
| Fe–C(B1)–O(B1) | 144·5(6) | Co–C(T11)–O(T11) | 174·8(8) |
| Co–C(B1)–O(B1) | 134·6(6) | Co–C(T12)–O(T12) | 177·6(6) |
| C(2′)–C(1)–C(2) | 110·7(5) | Fe–C(T21)–O(T21) | 175·9(10) |
| C(2)–C(1)–H(1) | 124·7(7) | C(1)–C(2)–C(3) | 107·3(10) |
| C(2)–C(3)–C(3′) | 107·3(5) | C(1)–C(2)–H(2) | 156(9) |
| C(2)–C(3)–H(3) | 130(6) | C(3)–C(2)–H(2) | 95(9) |
| C(3′)–C(3)–H(3) | 122(6) | | |

Primed atoms refer to the equivalent position at $x, \frac{1}{2} - y, z$, relative to atoms at $x, y, z$.

* cp is the centroid of the cyclopentadienyl ring.

TABLE 4

Least-squares planes and their equations given by $lX' + mY' + nZ' - p = 0$ where $X'$, $Y'$, and $Z'$ are orthogonal co-ordinates related to the atomic co-ordinates $X$, $Y$, and $Z$ by $X' = X \sin \beta$, $Y' = Y$, $Z' = Z + X \cos \beta$. The deviations (Å) of the most relevant atoms from the planes are given in square brackets.

| | *l* | *m* | *n* | *p* |
|---|---|---|---|---|
| Plane (1) | | | | |
| C(1), C(2), C(3), C(3′), C(2′) | 0·7816 | 0 | −0·6237 | 1·8154 |
| [C(1) −0·025, C(2) 0·020, C(3) −0·007] | | | | |
| Plane (2) | | | | |
| Fe, Co, C(B1), O(B1) | 0·9491 | 0·3130 | −0·0360 | 1·6886 |
| [Fe 0·003, Co 0·002, C(B1) −0·012, O(B1) 0·007] | | | | |
| Plane (3) | | | | |
| C(B1), C(B1′), C(T12), C(T12′) | −0·7953 | 0 | 0·6062 | 0·9406 |
| [Co 0·408] | | | | |

The molecules possess *m* ($C_s$) symmetry, which is space-group imposed, and has the expected $Fe(CO)_2Co$ bridging system, with the cyclopentadienyl ligand $\pi$-bonded to the iron atom. The terminal carbonyl groups lying on the mirror plane are in a *cis*-configuration with respect to the bridging system. The cyclopentadienyl ring is planar (Table 4) with equal C–C distances round the ring (mean 1·32 Å). The iron to ring-carbon distances are 2·03—2·08 Å, mean value 2·06 Å. The iron atom is 1·73 Å from the ring centroid, and the angle between this direction and the Fe $\cdots$ Co direction is 126·5°.

The centroids of the cyclopentadienyl system and of the bridging carbonyl groups lie on opposite sides of the line Fe $\cdots$ Co, and the angle between the two Fe(CO)Co planes is 143·5° (Table 4). This agrees well with that predicted from the spectral study [1] and also with that of 148° observed in the related indenyl compound $[(\pi\text{-}C_9H_7)\text{-}FeCo(CO)_6]$.[2] This value is intermediate between that of 164° observed [8] in the iron parent compound *cis*-$[\{(\pi\text{-}C_5H_5)Fe(CO)_2\}_2]$, and that of 127° in $Co_2(CO)_8$.[9]

A comparison of the metal to bridge-carbon distances with those of the parent compounds *cis*-$[\{(\pi\text{-}C_5H_5)Fe(CO)_2\}_2]$ [8] and $Co_2(CO)_8$ [9] shows an apparent movement of the bridge-carbon atoms towards the iron atom. The FeC(br) (br = bridge) distance is reduced from 1·92 to 1·88 Å, while the Co–C(br) bond has lengthened from 1·92 to 2·04 Å. This is accompanied by an opening of the Fe–C(B1)–O(B1) angle, the planar environment of C(B1) being maintained by an equivalent closure of the Co–C(B1)–O(B1) angle. A similar geometry has been observed for one of the carbonyl bridges of the related indenyl compound.[2]

The geometrical environment about the cobalt atom can be described in terms of a square-based pyramid with the apical direction defined by the Co–C(T11) direction. The angle between this direction and the normal to the plane of the carbon atoms in the basal plane is 6·4°. The cobalt atom lies 0·41 Å from this plane (Table 4). This contrasts with the analogous indenyl compound in which the cobalt atom environment is intermediate between the square-based pyramidal and trigonal bipyramidal.[2]

Observations from the present compound suggest that the distortion in the bridging system of the indenyl compound [2] involves the bridge carbon atom which is directed over the benzene fragment of the indenyl ligand. It is probable that the short intramolecular contacts involving this carbonyl group are responsible for this distortion, and may account at least in part for the intermediate geometry about the cobalt atom.

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[9] G. G. Sumner, H. P. Klug, and L. E. Alexander, *Acta Cryst.*, 1964, **17**, 732.