Crystal and Molecular Structure of *cis*-Di-μ-carbonyl-bis[carbonyl-(π-cyclohexa-1,3-diene)cobalt]

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The crystal structure of the title compound has been determined by photographic *X*-ray diffraction methods and refined to *R* 0·091 for 690 unique reflections by a full-matrix least-squares procedure. The orthorhombic unit cell, space group *Cmcm*, has dimensions *a* = 10·041, *b* = 7·880, *c* = 18·881 Å, for *Z* = 4. The dimer molecule has symmetry *mm* (a requirement of the space group) with an almost planar $Co(CO)_2Co$ bridging system: Co · · · Co is 2·559 Å. The cyclohexadiene ligands bond to the cobalt atoms *via* butadiene fragments with Co–C(butadiene) 2·04 and 2·13 Å. The C–C distances of the butadiene fragments are equal, mean 1·40 Å.

It has been established by i.r. spectroscopy that *cis–trans* isomerism exists for $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ and many related complexes,[1] and for the isoelectronic and isostructural $[(\pi\text{-diene})Co(CO)_2]_2$ derivatives.[2] The crystal structures of *cis*- and *trans*-$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ [3,4] and of *trans*-$[(\pi\text{-2,3-dimethylbuta-1,3-diene})Co(CO)_2]_2$ [5] have been determined by *X*-ray diffraction techniques. The i.r. spectrum of $[(\pi\text{-cyclohexa-1,3-diene})Co(CO)_2]_2$ suggests that although it exists as a mixture of *cis*- and *trans*-isomers in solution, with the former predominating, only the *cis*-isomer is found in the solid state.[2] The crystal structure analysis of this compound has been undertaken to determine its molecular structure.

EXPERIMENTAL

Crystal Data.—$C_{16}H_{16}O_4Co_2$, $M = 390{\cdot}2$, Orthorhombic, $a = 10{\cdot}041 \pm 0{\cdot}014$, $b = 7{\cdot}880 \pm 0{\cdot}009$, $c = 18{\cdot}881 \pm 0{\cdot}027$ Å, $U = 1493{\cdot}9$ Å^3, $D_m = 1{\cdot}74$ (by flotation), $Z = 4$, $D_c = 1{\cdot}734$, $F(000) = 792$, Mo-K_α radiation, $\lambda = 0{\cdot}71069$ Å; $\mu(\text{Mo-}K_\alpha) = 23{\cdot}2$ cm^{-1}, for cell parameters and intensity measurements. Systematic absences *hkl* if $h + k = 2n + 1$ and *h0l* if $l = 2n + 1$, space group $Cmc2_1$ (No. 36), *C2cm* (No. 40), or *Cmcm* (No. 63), shown to be the last-named by the subsequent successful analysis.

The complex crystallises as golden diamond-shaped plates lying on the (001) face with pinacoids {110} and $\{\bar{1}10\}$. Unit-cell parameters were determined from single-crystal precession photographs by use of Mo-K_α radiation. Intensities were estimated visually from precession photographs for the layers 0—4, 0—3, and 0,2,4 precessing about *a*, *b*, and [110] respectively. 1105 Non-zero reflections were obtained. After Lorentz and polarisation corrections had been applied, the intensities were placed on a common arbitrary scale by internal correlation. No correction for absorption or extinction was made; 690 non-zero unique reflections were obtained.

Wilson's method [6] was used to place the data approximately on an absolute scale. The scattering factor curves for all atoms were taken from ref. 7, the values for the cobalt atom being corrected for anomalous dispersion. All calculations were carried out on the Atlas computer at S.R.C., Chilton, with programmes of Hodgson, Mills, and Stephens.

Structure Determination.—From the systematic absences the space group is $Cmc2_1$, *C2cm*, or *Cmcm*. Statistical analysis of the intensity data [*N*(*Z*) test] and the Patterson map indicated the centric space group *Cmcm* and this was confirmed subsequently by the successful structure analysis. The Patterson map yielded the positions for all non-hydrogen atoms and showed the dimer molecule to possess *mm* symmetry. The structure factors, calculated with the co-ordinates for all atoms and an overall thermal parameter of *B* 3·0 Å^2, gave *R* 0·247.

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 unity for the initial refinement and was calculated from the expression $w = (10{\cdot}0 + 0{\cdot}1|F_o| + 0{\cdot}01|F_o|^2)^{-1}$ for the final refinement. Reflections, for which the calculated structure factors were less than one-third of the observed values, were omitted from the least-squares analysis.

The initial refinement, in which 1105 reflections were used, included individual layer scale-factors together with positional and individual isotropic thermal parameters for each atom. After four cycles of refinement, at which stage the maximum shift in any parameter was $<0{\cdot}5\sigma$ and *R* was 0·125, a difference-Fourier synthesis was calculated. This map showed no unusual features and indicated the approximate positions of the hydrogen atoms. The positions of the hydrogen atoms were optimised, assuming C–H 0·96 Å, and in subsequent refinements were included with an isotropic thermal parameter of *B* 4·0 Å^2, but not refined. After two further cycles of refinement the refined layer-scale factors were used to produce a unique set of reflection data which was used in further refinement.

Final refinement was carried out with anisotropic thermal parameters for all non-hydrogen atoms. The final refinement was terminated when the maximum shift in any parameter was $<0{\cdot}05\sigma$. All reflections were included in the final cycle of refinement. The final values for the residuals, based on 690 reflections, were *R* 0·091 and *R′* 0·015 $[R' = \Sigma w\Delta^2/\Sigma w|F_o|^2]$.

The final atomic co-ordinates and thermal parameters together with their estimated standard deviations are given in Tables 1 and 2 respectively. Observed and calculated structure factors are listed in Supplementary Publication SUP No. 20437 (5 pp., 1 microfiche).*

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* For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. are sent as full size copies).

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[2] P. McArdle and A. R. Manning, *J. Chem. Soc.* (*A*), 1970, 2123.

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[5] P. McArdle, A. R. Manning, and F. S. Stephens, *Chem. Comm.*, 1970, 318; F. S. Stephens, *J. Chem. Soc.* (*A*), 1970, 2745.

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TABLE 1

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

	x/a	y/b	z/c	σ_{rms}(Å)
Co	0	0·2592(2)	0·1822(1)	0·0014
O(1)	0·2599(11)	0·2714(14)	$\frac{1}{4}$	0·011
O(2)	0·1413(13)	0·2670(16)	$\frac{1}{4}$	0·013
C(1)	0	0·6132(14)	0·1368(7)	0·012
C(2)	0	0·4766(16)	0·1553(7)	0·013
C(3)	0·0706(12)	0·0414(11)	0·1375(4)	0·010
C(4)	0·1324(10)	0·1741(13)	0·1018(4)	0·009
C(5)	0·0780(10)	0·2370(11)	0·0311(4)	0·009
H(3)	0·123	−0·049	0·162	
H(4)	0·212	0·199	0·125	
H(51)	0·133	0·334	0·027	
H(52)	0·094	0·176	−0·013	

TABLE 2

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

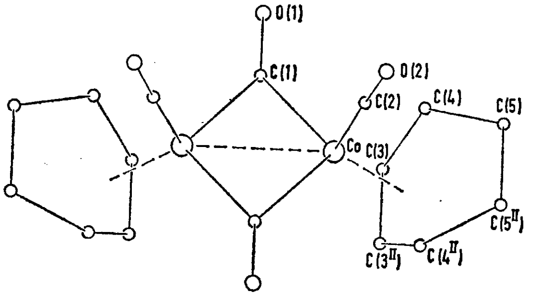
	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Co	50(1)	83(2)	10(0·3)	0	0	2(1)
O(1)	60(9)	230(23)	25(3)	−40(14)	0	0
O(2)	52(10)	118(20)	17(3)	−28(15)	0	0
C(1)	138(17)	138(18)	34(4)	0	0	20(7)
C(2)	66(14)	115(21)	17(3)	0	0	4(6)
C(3)	94(11)	115(14)	15(2)	39(11)	1(5)	−4(4)
C(4)	57(8)	176(17)	14(2)	23(11)	2(4)	−14(5)
C(5)	85(10)	144(15)	13(2)	−6(13)	9(3)	1(5)

For all hydrogen atoms B 4·0 Å^2.

* The anisotropic thermal parameters are given by $\exp[-(h^2b_{11} + k^2b_{22} + l^2b_{33} + 2hkb_{12} + 2hlb_{13} + 2klb_{23})]$.

DISCUSSION

The Figure shows a perspective drawing of the molecule and the labelling of the atoms. The bond distances and angles together with their estimated standard deviations derived directly from the least-squares inverse matrix are given in Table 3. The molecule possesses *mm* (C_{2v}) symmetry which is space-group imposed. The overall features of the structure are as predicted on the basis of spectroscopic studies.[2] The $Co_2(CO)_4$ moiety has a *cis*-bridged conformation. The diene ligands are bonded to the cobalt atom with C(3)–C(3^{II}) perpendicular to the Co–Co axis, and with their central carbon atoms C(3) and C(3^{II}) closer to the other cobalt atom than are the terminal carbon atoms C(4) and C(4^{II}) of the butadiene fragments. The non-bonded atoms C(5) and C(5^{II}) are even further away. For a given cobalt atom the central carbon atoms of the butadiene fragment are significantly closer to the cobalt atom [Co–C(3) 2·040(9) Å] than are the terminal carbon atoms [Co–C(4) 2·127(9) Å). The butadiene fragments are planar. (The equations of some planes through the molecule are shown in Table 4.) The dihedral angle between the plane of a butadiene fragment and the plane of the Co(CO)$_2$Co bridge is 57·2° which is comparable with the corresponding value of 61·1° found in *trans*-[Co(π-CH$_2$·CMe·CMe·CH$_2$)(CO)$_2$]$_2$.[5] The cyclohexadiene ring is folded about the C(4)–C(4^{II}) axis and the angle between the two planes is 143·2°. The dimensions and bond angles within the molecule are identical with those for the corresponding 2,3-dimethylbuta-1,3-diene complex[5] within the limitations imposed by the *cis*-stereochemistry of the cyclohexadiene complex and the *trans*-nature of the dimethylbutadiene complex. The distances of interest in the present compound are: Co ··· Co 2·559, Co–C(bridge) 1·91, Co–C(terminal) 1·79, and C–C(butadiene) 1·40 Å.



A perspective drawing of the molecule showing the labelling of the atoms

TABLE 3

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

(*a*) Distances

Co ··· Co^{I}	2·559(3)	Co–C(3)	2·040(9)
Co–C(1)	1·911(10)	Co–C(4)	2·127(9)
Co–C(2)	1·787(13)	C(3)–C(3^{II})	1·417(19)
C(1)–O(1)	1·192(17)	C(3)–C(4)	1·391(14)
C(2)–O(2)	1·132(16)	C(4)–C(5)	1·526(12)
		C(5)–C(5^{II})	1·566(17)

(*b*) Angles

C(1)–Co–C(1^{II})	95·8(6)	Co–C(1)–Co^{I}	84·1(5)
C(1)–Co–C(2)	99·6(4)	Co–C(1)–O(1)	138·0(3)
Co^{I}–Co–C(2)	106·5(4)	Co–C(2)–O(2)	178·6(13)
C(3^{II})–C(3)–C(4)	116·5(9)	C(4)–C(5)–C(5^{II})	111·0(7)
C(3)–C(4)–C(5)	120·6(9)		

Roman numerals as superscripts refer to the following equivalent positions relative to atoms at x, y, z:

I $x, y, \frac{1}{2} - z$ II $-x, y, z$

TABLE 4

Least-squares planes and their equations given by $lX + mY + nZ - p = 0$ where X, Y, Z are the atomic co-ordinates in Å. The deviations (Å) of the most relevant atoms from the planes are given in square brackets. Roman numeral superscripts are as defined in Table 3

	l	m	n	p
Plane (1): Co, Co^{I}, C(1) [O(1) −0·016, C(1^{II}) 0·12, O(1^{II}) 0·21]	−0·0430	0·9991	0·0000	2·0408
Plane (2): C(4^{II}), C(3^{II}), C(3), C(4) [C(5) −0·85]	0·0000	0·5419	0·8405	2·3590
Plane (3): C(4^{II}), C(5^{II}), C(5), C(4)	0·0000	0·9374	0·3482	1·9552

The structure of the molecule is similar to that of the isoelectronic complex, *cis*-[(π-C$_5$H$_5$)Fe(CO)$_2$]$_2$.[3] However, in the present compound the M(CO)$_2$M bridging system is almost planar whereas in the iron complex it is puckered, the angle between the two M(CO)M plane being 175·1° for the former and 164° for the latter.[3] The planarity of the bridge in the present compound is difficult to understand particularly as the compound is a derivative of octacarbonyldicobalt in which the corresponding angle is 127°.[8] This angle is clearly a function of the ligands co-ordinated to the metal atoms, and replacement of two carbonyl groups per cobalt atom by a conjugate diene causes it to increase. It could be suggested that as the terminal carbonyl groups are replaced by weaker π-acceptors, the bridge angle increases towards 180° or alternatively that a large bridge angle results in a decrease of the non-bonding interactions within the molecule. However, the structures of other diene derivatives are required before this problem can be clarified.

The dimer molecules are held in the crystal by van der Waals forces. The closest approach of two oxygen atoms is 3·45 Å [O(1) $\cdots$ O(2) at $\frac{1}{2} + x$, $y - \frac{1}{2}$, z] and of an oxygen atom and a carbon atom is 3·45 Å [O(2) $\cdots$ C(3) at $\bar{x}$, $1 + y$, z]. All carbon–carbon atom contacts are $>$3·6 Å.

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