Crystal and Molecular Structure of Bis[dicarbonyl(triethylphosphine)-nitrosylferrio]mercury

By **F. S. Stephens**, Department of Chemistry, University of Essex, Colchester, Essex

The crystal structure of the title compound has been determined by *X*-ray diffraction methods using absorption corrected counter data. Refinement, *R* 0·060 (for 1800 unique reflections), was carried out by a full-matrix least-squares procedure. The monoclinic unit cell, space group $P2_1/n$, has dimensions $a = 7{\cdot}257$, $b = 14{\cdot}178$, $c = 12{\cdot}533$ Å, $\beta = 94°\ 13'$ for $Z = 2$. The crystal is disordered in that the nitrosyl groups could not be distinguished from the carbonyl groups. The two sets of radial ' carbonyl ' groups adopt a staggered configuration as do each set of ethyl groups with respect to its set of ' carbonyl ' groups. The space group imposes a centre of symmetry at the mercury atom but the molecule as a whole approximates to $\bar{3}$ (S_6) symmetry. The mercury–iron distance is 2·534(2) Å.

THE i.r. spectra in solution of the complexes of the type $Hg[Fe(CO)_2(NO)L]_2$ [L = CO, R_3P, $(RO)_3P$, R_3As, and R_3Sb; R = alkyl and aryl] are similar and closely resemble the spectra for the isolectronic complexes $Hg\{Co(CO)_3L\}_2$, from which it has been inferred that the two series are isostructural.[1] The crystal structure of one of these latter complexes $Hg[Co(CO)_3P(C_2H_5)_3]_2$ has shown the molecule to possess a linear P–Co–Hg–Co–P system with trigonal bipyramidal co-ordination about the cobalt atoms.[2] The crystal structure of $Hg[Fe(CO)_2(NO)PEt_3]_2$ has been undertaken to determine its molecular structure and to test the inferences concluded from the i.r. spectral studies.

EXPERIMENTAL

Crystal Data.—$C_{16}H_{30}Fe_2HgN_2O_6P_2$, $M = 720{\cdot}6$, Monoclinic, $a = 7{\cdot}257 \pm 0{\cdot}016$, $b = 14{\cdot}178 \pm 0{\cdot}020$, $c = 12{\cdot}533$

---

[1] M. Casey and A. R. Manning, *J. Chem. Soc.* (*A*), 1970, 2258.

[2] R. F. Bryan and A. R. Manning, *Chem. Comm.*, 1968, 1316.

$\pm$ 0·020 Å, $\beta = 94° 13' \pm 5'$, U = 1280·6 Å^3, D_m = 1·85 (by flotation), Z = 2, D_c = 1·861, $F(000)$ = 728, Mo-K_α radiation, λ = 0·71069 Å; μ(Mo-K_α) = 73·3 cm^{-1}. Space group $P2_1/n$ (C^5_{2h}, No. 14).

The compound crystallises as orange-brown parallelepipeds with pinacoids {011}, {0$\bar{1}$1}, and {10$\bar{1}$}. Unit-cell parameters were determined from single-crystal precession photographs by use of Mo-K_α radiation. These parameters when converted to the equivalent $P2_1/a$ space group (a = 7·257, b = 14·178, c = 14·937 Å, β = 123° 12′) are in good agreement with those found for the isolectronic compound Hg[Co(CO)$_3$PEt$_3$]$_2$.[2] The intensities were collected on a Philips PAILRED diffractometer using monochromatised Mo-K_α radiation. The crystal used for the intensity measurements was 0·27 × 0·27 × 0·20 mm in size. Each reflection in the 0—9kl layers, to a maximum angle of θ = 30°, was recorded. 1800 Unique reflections gave counts for which $\sigma(I)/I < 0·5$ [3] and these were used for the structure analysis. The intensities were corrected for Lorentz and polarisation effects after which they were further corrected for absorption and extinction effects.[4] The programme used for these latter corrections is ABSCOR from the '*X*-ray '63' system.

Wilson's method [5] was used to place the data on approximately absolute scale. The scattering factor curves for all atoms are those given in ref. 6, the values for the mercury, the iron, and the phosphorus atoms being corrected for anomalous dispersion. All structure analysis calculations were carried out on the Atlas computer at S.R.C. Chilton, with programmes of Hodgson, Mills, and Stephens.

Structure Determination.—With Z = 2 in space group $P2_1/n$, the molecule is centrosymmetric with the mercury atom occupying the centre of symmetry. A Fourier synthesis phased by the mercury atom yielded the positions for all non-hydrogen atoms. It was not possible from this map to distinguish the nitrosyl group from the carbonyl groups and thus, it was included as a carbonyl group. Refinement of the structure was carried out by a full-matrix least-squares procedure in which the function minimised was $\Sigma w(|F_o| - |F_c|)^2$. The weight for each reflection, w, was initially unity and in the final refinement given by $w = (100 + 0·4|F_o| + 0·01|F_c|^2)^{-1}$, which gave almost constant average values of $w\Delta^2$ for increasing ranges of $|F_o|$. Reflections, for which the calculated structure factors were less than one-third of the observed values, were omitted from the least-squares analysis.

With individual isotropic thermal parameters for each atom the refinement rapidly reduced R to 0·17 at which stage a difference-Fourier synthesis was calculated. This map showed the structure to be essentially correct and that there was large anisotropic thermal motion associated with the mercury and iron atoms. The refinement was continued with anisotropic thermal parameters for these atoms. When the largest shift in any parameter was of the order of its estimated standard deviation and R was 0·081, a further difference-Fourier synthesis was calculated. This map indicated the approximate positions for six of the fifteen hydrogen atoms. The positions of the methyl-hydrogen atoms could not be obtained, the difference-Fourier map indicating that the methyl groups were probably rotating. The positions of the six hydrogen atoms found were optimised (assuming C–H 1·00 Å) and in subsequent calculations were included with B 7·0 Å^2, but not refined. At this stage it was still not possible to identify the nitrosyl group and refinement was continued assuming three carbonyl groups.

Final refinement was carried out with anisotropic thermal parameters for all non-hydrogen atoms. The refinement was terminated when the maximum shift in any parameter was $<0·1\sigma$. 1790 Reflections were included in the final cycle of refinement. The final values for R, based on 1800 reflections, and R' [$= \Sigma w\Delta^2/\Sigma w|F_o|^2$] were 0·060 and 0·005.

There still remained the problem of which of the carbonyl groups was the nitrosyl group. A like problem existed in the structures of [Mn(CO)$_2$(NO)(PPh$_3$)$_2$] [7] and of [Mn(CO)$_3$(NO)PPh$_3$] [8] and an analysis of the vibration parameters for the carbonyl groups involved clearly showed the nitrosyl group in the former but not in the latter. The analysis of vibration parameters for the three carbonyl groups in the present structure is given in Table 1. There is no significant variation in the results for the three groups, the situation being similar to that found in the last-mentioned manganese complex.[8] It is thus concluded that the disorder is present and that each carbonyl group, on average, represents the contribution from 2/3 CO and 1/3 NO.

TABLE 1

Analysis of the vibration parameters for the carbonyl groups in terms of the root-mean-square displacements (Å) for the atoms corresponding to the thermal parameters given in Table 3

C(1)	0·309	0·262	0·189	O(1)	0·391	0·315	0·252
C(2)	0·257	0·215	0·204	O(2)	0·335	0·316	0·251
C(3)	0·272	0·228	0·173	O(3)	0·342	0·318	0·233

TABLE 2

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

	x/a	y/b	z/c	σ_{rms}/Å
Hg	0	0	0	
Fe	−0·1065(3)	0·0787(2)	0·1662(1)	0·002
P	−0·2257(4)	0·1482(2)	0·3044(2)	0·003
O(1)	−0·4562(20)	−0·0151(10)	0·1154(10)	0·014
O(2)	0·1790(17)	−0·0192(9)	0·2935(10)	0·013
O(3)	−0·0182(18)	0·2539(9)	0·0658(9)	0·013
C(1)	−0·3135(23)	0·0218(11)	0·1316(10)	0·016
C(2)	0·0684(20)	0·0190(8)	0·2412(10)	0·013
C(3)	−0·0559(17)	0·1821(10)	0·1041(9)	0·013
C(11)	−0·2234(26)	0·0767(15)	0·4276(11)	0·018
C(12)	−0·3044(26)	−0·0210(10)	0·4144(13)	0·017
C(21)	−0·1105(28)	0·2547(15)	0·3549(16)	0·021
C(22)	0·0949(25)	0·2530(15)	0·3764(16)	0·020
C(31)	−0·4625(23)	0·1838(15)	0·2821(14)	0·019
C(32)	−0·5144(25)	0·2413(15)	0·1823(15)	0·019
H(11)	−0·089	0·073	0·461	
H(12)	−0·285	0·114	0·485	
H(21)	−0·142	0·311	0·304	
H(22)	−0·167	0·280	0·421	
H(31)	−0·508	0·219	0·348	
H(32)	−0·551	0·125	0·282	

The final atomic co-ordinates and thermal parameters together with their estimated standard deviations are given in Tables 2 and 3, respectively. Observed and calculated

---

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

[4] J. De Meulenaer and H. Tompa, *Acta Cryst.*, 1965, **19**, 1014.

[5] A. J. C. Wilson, *Nature*, 1942, **150**, 152.

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

[7] J. H. Enemark and J. A. Ibers, *Inorg. Chem.*, 1967, **6**, 1575.

[8] J. H. Enemark and J. A. Ibers, *Inorg. Chem.*, 1968, **7**, 2339.

TABLE 3

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

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Hg	325(2)	64(1)	44(1)	11(1)	44(1)	−16(1)
Fe	266(5)	68(1)	48(1)	4(2)	41(2)	−17(1)
P	172(6)	49(2)	39(2)	5(3)	14(3)	−4(1)
O(1)	428(39)	119(12)	99(10)	−65(18)	−27(16)	−7(8)
O(2)	319(30)	90(10)	123(11)	45(13)	2(15)	8(8)
O(3)	403(35)	84(9)	104(10)	−16(14)	59(15)	22(7)
C(1)	275(35)	83(12)	52(8)	−30(16)	−16(14)	−6(7)
C(2)	233(29)	45(8)	59(8)	17(11)	13(13)	1(5)
C(3)	172(26)	71(9)	50(8)	10(13)	28(11)	−8(7)
C(11)	386(48)	114(14)	61(10)	35(23)	54(18)	14(10)
C(12)	429(51)	45(10)	93(12)	−8(15)	57(20)	5(7)
C(21)	381(54)	115(16)	132(18)	−7(23)	65(25)	−75(14)
C(22)	267(40)	122(16)	116(16)	1(22)	−2(21)	−31(13)
C(31)	259(39)	128(16)	102(14)	82(21)	34(19)	−11(12)
C(32)	292(42)	128(17)	110(15)	72(22)	7(21)	52(13)

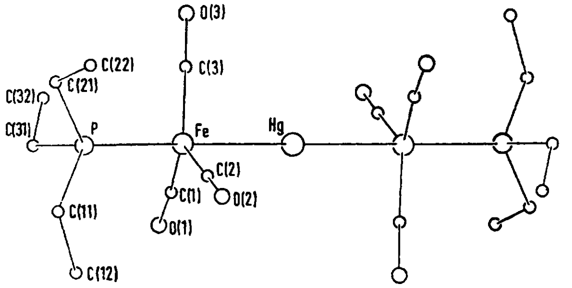
For all hydrogen atoms $B = 7{\cdot}0$ Å^2

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

structure factors are listed in Supplementary Publication No. SUP 20480 (11 pp., 1 microfiche).†

DISCUSSION

The Figure shows a perspective drawing of the complex 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 4. The molecule is isostructural with the cobalt anologue [2] and possesses an approximately linear P–Fe–Hg–Fe–P system with trigonal bipyramidal co-ordination about the iron atoms. The two sets of radial ' carbonyl ' groups adopt a staggered configuration as do each set of ethyl groups with respect to its set of ' carbonyl ' groups. The space group imposes a centre of symmetry at the mercury atom but the molecule as a whole approximates to $\bar{3}$ (S_6) symmetry. The solution i.r. studies [1] of the complex indicate that the nitrosyl groups adopt a *gauche* staggered configuration. This arrangement is not possible if the molecule possesses a centre of symmetry however, since the nitrosyl groups could not be distinguished from the carbonyl groups disorder in the crystal of misaligned *gauche* configurations would seem reasonable. The solid-state i.r. spectrum of the complex [9] shows at least three carbonyl stretching frequencies and two nitrosyl stretching frequencies. This supports the existence of the non-centric arrangements rather than the centric although some contribution from the latter cannot be ruled out.



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

TABLE 4

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

(*a*) Distances

Hg–Fe	2·534(2)	Fe–P	2·223(3)
Fe–C(1)	1·732(16)	C(1)–O(1)	1·165(18)
Fe–C(2)	1·742(14)	C(2)–O(2)	1·136(16)
Fe–C(3)	1·713(15)	C(3)–O(3)	1·166(16)
P–C(11)	1·845(16)	C(11)–C(12)	1·510(26)
P–C(21)	1·817(19)	C(21)–C(22)	1·495(26)
P–C(31)	1·793(16)	C(31)–C(32)	1·518(24)

(*b*) Angles

Hg–Fe–P	174·8(1)	Fe–P–C(11)	115·4(6)
Hg–Fe–C(1)	84·3(5)	Fe–P–C(21)	116·4(6)
Hg–Fe–C(2)	88·6(4)	Fe–P–C(31)	115·3(6)
Hg–Fe–C(3)	85·1(4)	C(11)–P–C(21)	100·9(10)
P–Fe–C(1)	91·2(5)	C(11)–P–C(31)	103·6(8)
P–Fe–C(2)	96·0(4)	C(21)–P–C(31)	103·4(10)
P–Fe–C(3)	94·8(4)	P–C(11)–C(12)	115·7(12)
C(1)–Fe–C(2)	119·5(7)	P–C(21)–C(22)	118·4(14)
C(1)–Fe–C(3)	119·7(7)	P–C(31)–C(32)	117·2(13)
C(2)–Fe–C(3)	119·3(6)	Fe–C(2)–O(2)	177·4(12)
Fe–C(1)–O(1)	175·3(13)	Fe–C(3)–O(3)	177·2(12)

The Hg–Fe distance of 2·534 Å lies between the values of 2·49 Å found in $(C_5H_5)(OC)_2Fe{\cdot}Hg{\cdot}Co(CO)_4$ [10] and of 2·59 Å found in $(BrHg)_2Fe(CO)_4$,[11] and is in accord with that of 2·499 Å found in the cobalt analogue.[2] The other distances of interest in this compound are in accord with those found in the cobalt analogue [2] and other carbonyl-(phosphine)iron complexes [12] Fe–P 2·223, mean Fe–C 1·73, mean C–O 1·16, mean P–C 1·82, and mean C–C 1·51 Å. The mean Hg–Fe–C angle of 86° is the same as that observed in the cobalt analogue.[2]

The molecules are held in the crystal by van der Waals forces. The closest approach of two oxygen atoms is 2·95 Å [O(1) · · · O(1) ($-1 - x, \bar{y}, \bar{z}$)] and of an oxygen atom and a carbon atom 3·32 Å [O(1) · · · C(21) ($-\tfrac{1}{2} - x,\ y - \tfrac{1}{2},\ \tfrac{1}{2} - z$)]. All carbon–carbon atom contacts are >3·7 Å.

I thank Dr. A. R. Manning for supplying a sample of the complex.

[2/349 *Received, 17th February,* 1972]

---

† For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20.

[9] J. R. Miller and F. S. Stephens, unpublished results.

[10] R. F. Bryan and H. P. Weber, *Acta Cryst.*, 1966, **A21**, 138.

[11] H. W. Baird and L. F. Dahl, *J. Organometallic Chem.*, 1967, **7**, 503.

[12] D. J. Dahm and R. A. Jackson, *Chem. Comm.*, 1966, 496; R. E. Davis, *ibid.*, 1968, 248; W. S. McDonald, J. R. Moss, G. Raper, B. L. Shaw, R. Greatrex, and N. N. Greenwood, *ibid.*, 1969, 1295.