

THE CRYSTAL AND MOLECULAR STRUCTURE OF $(\text{BrHg})_2\text{Fe}(\text{CO})_4$ *

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INTRODUCTION

Although mercury derivatives of transition metal carbonyl compounds¹⁻³³ have been known since 1928 when $\text{Fe}(\text{CO})_4\text{Hg}_2\text{Cl}_2$ was first reported¹ and although many proposals have been made concerning their stereochemistry, the structures of none of these compounds have been previously determined by X-ray diffraction. The nature of the iron carbonyl mercury halide derivatives in particular has been a subject of considerable speculation. The reaction of $\text{Fe}(\text{CO})_5$ with excess HgX_2 ($\text{X} = \text{Cl}, \text{Br},$ or I) in aqueous solution yields the compound $\text{Fe}(\text{CO})_4\text{Hg}_2\text{X}_2$, which first was proposed^{1,2} to be either a double salt, $\text{Fe}(\text{CO})_4 \cdot \text{Hg}_2\text{X}_2$, or an addition compound, $\text{HgFe}(\text{CO})_4 \cdot \text{HgX}_2$. The formulation of $\text{Hg}_2\text{Fe}(\text{CO})_4\text{X}_2$ also was suggested³. Sidgwick⁴ postulated that in the presumably related $\text{Fe}(\text{CO})_4(\text{HgCH}_3)_2$, the product of the reaction of $\text{H}_2\text{Fe}(\text{CO})_4$ with CH_3HgOH , each mercury atom is coordinated to a methyl group and to an oxygen atom of a carbonyl group with the four carbonyl carbon atoms arranged tetrahedrally about the iron atom.

The present investigation of $(\text{BrHg})_2\text{Fe}(\text{CO})_4$ has revealed a monomeric octahedral-type structure containing two *cis*-oriented $\text{Fe}-\text{HgX}$ bonds. Subsequent spectroscopic analyses of $(\text{XHg})_2\text{Fe}(\text{CO})_4$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$)⁵⁻⁷ not only have independently established the correct molecular configuration but also have provided insight into the nature of the $\text{Fe}-\text{HgX}$ bonds.

EXPERIMENTAL

X-ray examination of $(\text{IHg})_2\text{Fe}(\text{CO})_4$

Prior to the X-ray study of $(\text{BrHg})_2\text{Fe}(\text{CO})_4$, work was carried out on $(\text{ClHg})_2\text{Fe}(\text{CO})_4$ and $(\text{IHg})_2\text{Fe}(\text{CO})_4$. Samples of these latter two compounds were generously supplied to us by Dr. E. Coffey of E. I. DuPont de Nemours Company (Wilmington, Delaware) and later were prepared in our laboratories by the reaction of iron pentacarbonyl with the corresponding mercuric halide^{1,2}. Recrystallization techniques on the chloride analogue failed to yield single crystals which gave satisfactory X-ray data.

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Crystals of $(\text{IHg})_2\text{Fe}(\text{CO})_4$ were characterized by X-ray photographs to possess an orthorhombic unit cell with $a = 13.17 \pm 0.02 \text{ \AA}$, $b = 13.32 \pm 0.02 \text{ \AA}$, $c = 13.40 \pm 0.02 \text{ \AA}$. The lattice parameter measurements of a and b were determined by the "two-theta" method³⁴ with $\text{CoK}\alpha$ radiation; the c parameter was determined from internally-calibrated precession photographs. Eight $(\text{IHg})_2\text{Fe}(\text{CO})_4$ molecules per unit cell give a calculated density of 4.65 g/cm^3 in excellent agreement with the observed³⁵ density of 4.66 g/cm^3 . Systematic extinctions of $h+1$ odd for $(h0l)$ and k odd for $(0kl)$ indicate the probable space group to be either $Pbn2_1$ or $Pbnm$ [non-standard settings of $Pna2_1$ (C_{2v}^2 , No. 33) and $Pnma$ (D_{2h}^{16} , No. 62), respectively]. The observed peak distribution in the three-dimensional Patterson map indicates the non-centrosymmetric space group $Pbn2_1$, which requires that all atoms be located in general positions such that two $(\text{IHg})_2\text{Fe}(\text{CO})_4$ species comprise the asymmetric part of the unit cell. Three-dimensional intensity data consisting of 540 independent reflections were collected with Zr-filtered $\text{MoK}\alpha$ radiation by the multiple-film, equi-inclination Weissenberg technique for reciprocal levels $hk0$ through $hk8$ and by the timed-exposure precession method for the $0kl$ and $hk0$ zones. The crystal used for the X-ray analysis was a needle crystal of width 0.08 mm and length 0.32 mm. Both three-dimensional "unsharpened" and "sharpened" Patterson functions were calculated, but attempts to interpret these maps for a satisfactory trial model were unsuccessful, possibly due to a disorder and/or twinning phenomena. Consequently, a structural analysis of the bromide derivative was performed.

X-ray data for $(\text{BrHg})_2\text{Fe}(\text{CO})_4$

Yellow single crystals of $(\text{BrHg})_2\text{Fe}(\text{CO})_4$ were prepared by the addition of $\text{Fe}(\text{CO})_5$ to an aqueous solution of mercuric bromide¹. (Found: C, 6.67; H, 0.0; Br, 21.82; Fe, 7.35; Hg, 55.18. $\text{C}_4\text{Br}_2\text{FeHg}_2\text{O}_4$ calcd.: C, 6.59; H, 0.00; Br, 21.93; Fe, 7.66; Hg, 55.04%.)* The crystal used in the X-ray investigation was a fairly regular parallelepiped of length 0.17 mm and of average width 0.06 mm with the long direction approximately parallel with the lattice vector c . The unit cell lengths were determined from $h0l$ and $0kl$ precession photographs which were calibrated with a NaCl crystal. Eleven reciprocal layers of multiple-film equi-inclination Weissenberg data, $hk0$ through $hk10$, together with timed-exposure $h0l$ precession data were obtained with Zr-filtered $\text{MoK}\alpha$ radiation. The intensity of each of the 246 independent maxima recorded was estimated visually by comparison with a calibrated set of standard spots obtained from the same crystal. The intensities were corrected for Lorentz and polarization effects, but no extinction corrections were made. Since the linear absorption coefficient for $\text{MoK}\alpha$ radiation is 428 cm^{-1} , absorption corrections were applied to the Weissenberg data in which the crystal was assumed to approximate a cylinder. The resulting systematic error was further minimized by the determination of separate scale factors for each reciprocal layer by least-squares refinement.

Variable weights were assigned to the observed structure factors (i.e., $I(hkl)_0 \sim F(hkl)_0^2$) according to the following scheme: $I_0 < I_{\min}\sqrt{20}$, then $\sqrt{w} = I_0^2/F_0 I_{\min}^2$; $I_0 \geq I_{\min}\sqrt{20}$, then $\sqrt{w} = 20/F_0$.

* Analysis was carried out by Schwarzkopf Microanalytical Laboratory, 37th Avenue, Woodside 77, New York.

Unit cell and space group of $(\text{BrHg})_2\text{Fe}(\text{CO})_4$

The parameters of the orthorhombic unit cell are $a = 24.84 \pm 0.06 \text{ \AA}$, $b = 13.65 \pm 0.03 \text{ \AA}$, and $c = 12.91 \pm 0.03 \text{ \AA}$. The calculated density of 4.43 g/cm^3 based on 16 $(\text{BrHg})_2\text{Fe}(\text{CO})_4$ formula species per unit cell falls between the observed densities of 4.02 and 4.66 g/cm^3 measured for $(\text{ClHg})_2\text{Fe}(\text{CO})_4$ and $(\text{IHg})_2\text{Fe}(\text{CO})_4$, respectively³⁵.

The space group $Fdd2(C_{2v}^{19}$, No. 43) was uniquely defined by the systematic absences of $h+k$, $k+l$, $h+l \neq 2n$ for (hkl) ; $k+l \neq 4n$ for $(0kl)$; and $h+l \neq 4n$ for $(h0l)$. The choice of this non-centrosymmetric space group was confirmed both from the peak concentration in the Patterson synthesis and from the resulting structural determination. The iron atoms were found to be in two sets of 8-fold special positions ($8a$: $0,0,z$; $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}+z$; $+F$ centering) located on twofold axes, while the 16-fold sets of general positions ($16b$: x,y,z ; \bar{x},\bar{y},z ; $\frac{1}{4}-x, \frac{1}{4}+y, \frac{1}{4}+z$; $\frac{1}{4}+x, \frac{1}{4}-y, \frac{1}{4}+z$; $+F$ centering) were found to be occupied by mercury atoms (two sets), bromine atoms (two sets), carbon atoms (four sets), and oxygen atoms (four sets)³⁶. The structural determination, therefore, involved the location of two crystallographically independent half-molecules consisting of two iron, two mercury, two bromine, four carbon, and four oxygen atoms.

Determination of the structure of $(\text{BrHg})_2\text{Fe}(\text{CO})_4$

The interpretation of the three-dimensional Patterson function led to a self-consistent set of coordinates for the two independent mercury atoms which gave discrepancy factors of $R_1 = [\sum ||F_o| - |F_d|| / \sum |F_o|] \times 100 = 22\%$ and $R_2 = [\sum w ||F_o| - |F_d||^2 / \sum w F_o^2]^{1/2} \times 100 = 29\%$. For the calculation of structure factors an isotropic thermal parameter of 2.0 \AA^2 arbitrarily was chosen for the mercury atoms. The first approximation to a three-dimensional electron density map*, phased on the contributions of the mercury atoms (Hg_1 and Hg_2), showed only four prominent peaks (other than those of the two mercury atoms) in the asymmetric part which were attributed to the two iron atoms (Fe_1 and Fe_2) and two bromine atoms (Br_1 and Br_2). Two of these latter peaks were located on the crystallographic twofold axes and were designated as the iron atoms (See Figs. 1-3). Structure factor calculations based only on the mercury and bromine atoms decreased the unweighted discrepancy factor to $R_1 = 17\%$. A further lowering of R_1 to 15% occurred when the iron atoms were included. A three-dimensional difference Fourier synthesis of the form $F_o - F_c$ (Hg, Br, Fe) was calculated, and atomic coordinates were obtained for the four carbonyl groups. For the fourteen independent atoms the R_1 and R_2 values were 14 and 18% , respectively, at this point.

Least-squares refinement³⁹ of the twelve interlayer scale factors and the positional and isotropic thermal parameters of the six heavy atoms was attempted, but the thermal parameter of Fe_2 became nonpositive-definite. Since a three-dimensional difference map revealed some anisotropy in the thermal motion of the mercury atoms, a least-squares heavy-atom anisotropic refinement (with the scale factors held constant) also was attempted but again gave nonpositive-definite thermal param-

* Since both the Sly-Shoemaker Fourier Program³⁷ and the Blount Fourier Program³⁸ do not calculate correctly for symmetries involving diamond glides, the Fourier maps for $Fdd2$ were computed on the basis of the unit cell symmetry of the monoclinic space group $F2$ by inclusion of a second octant of reciprocal space in the input data.

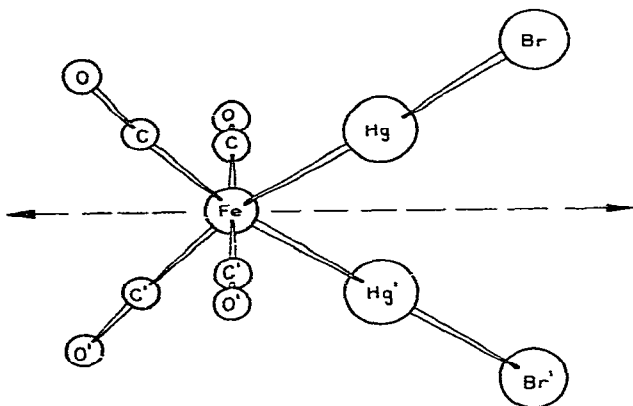


Fig. 1. The molecular configuration of $(\text{BrHg})_2\text{Fe}(\text{CO})_4$.

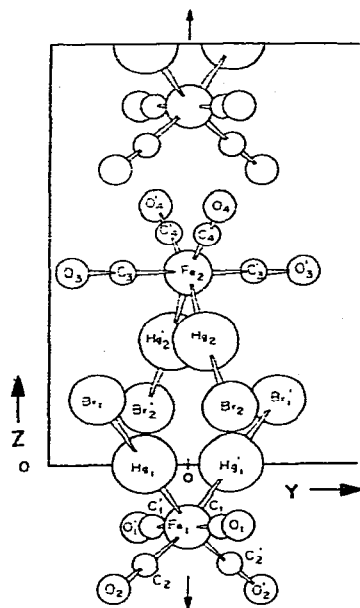


Fig. 2. $[100]$ projection of the row of molecules along the 2_c axis at $x=y=0$.

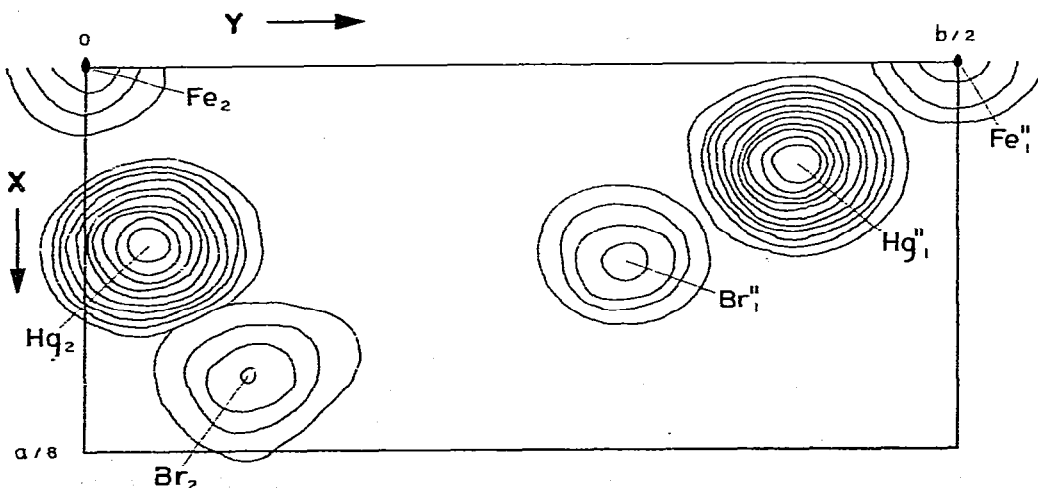


Fig. 3. A composite of a three-dimensional $[001]$ electron density synthesis showing the heavy atoms. Contours are at intervals of $10e/\text{\AA}^3$. The double-primed superscript refers to the symmetry equivalent position: $x, \frac{1}{2}+y, \frac{1}{2}+z$.

eters. The misbehavior of the thermal parameters is attributed mainly to an incomplete correction for the large absorption effects which probably also accounts in part for the difference in the final least-squares and Fourier atomic coordinates (*vide infra*). Consequently, a least-squares refinement of scale factors and the initial coordinates of the heavy atoms obtained from the Fourier maps was begun anew with

only an overall isotropic temperature factor used for further adjustment of the thermal parameters. The third iteration gave parameter shifts which were small compared to the corresponding standard deviations and yielded an R_1 of 14% and an R_2 of 13%. Attempts to refine the carbon and oxygen atoms by least-squares were unsuccessful.

TABLE I

FINAL ATOMIC PARAMETERS^a

Atom		$x(10^4 \sigma_x)$	$y(10^4 \sigma_y)$	$z(10^4 \sigma_z)$	B
Hg ₁	a	0.0356	-0.0917	0.0000	2.1
	b	0.0340(6)	-0.0894(12)	0.0000(—) ^b	2.1
Hg ₂	a	0.0602	0.0365	0.2949	2.1
	b	0.0593(5)	0.0378(11)	0.2966(16)	2.1
Br ₁	a	0.0647	-0.1947	0.1501	5.1
	b	0.0657(18)	-0.1837(41)	0.1454(34)	5.1
Br ₂	a	0.0998	0.1031	0.1356	5.1
	b	0.1027(17)	0.0998(41)	0.1404(34)	5.1
Fe ₁	a	0	0	-0.1467	2.6
	b	0	0	0.4611(62)	2.6
Fe ₂	a	0	0	0.4536	2.6
	b	0	0	0.4611(62)	2.6
C ₁	a	0.075	0.075	-0.150	5.1
O ₁	a	0.125	0.108	-0.150	6.1
C ₂	a	0.021	-0.092	-0.242	5.1
O ₂	a	0.038	-0.158	-0.300	6.1
C ₃	a	0.038	-0.142	0.458	5.1
O ₃	a	0.058	-0.250	0.460	6.1
C ₄	a	0.067	0.042	0.550	5.1
O ₄	a	0.092	0.070	0.617	6.1

^a a: Successive Fourier syntheses b: least-squares refinement with an overall temperature factor. The B's of like atoms have been fixed as equal. ^b Since the symmetry requirements of *Fdd2* do not specify the origin of the unit cell in the *c*-direction, the *z* coordinate of Hg₁ arbitrarily was chosen at 0c and was not varied.

Refinement by successive Fourier and difference Fourier syntheses then was carried out. Within the region of the reciprocal lattice covered (*i.e.*, $\theta < 23^\circ$), 101 reflections were too weak to be recorded; structure factors for these reflections were derived by assignment of intensity values of $\frac{1}{2} I_{\min}$ for a given reciprocal level⁴⁰. Fourier maps were calculated wherein the phase of each structure factor was computed from the contribution of all fourteen atoms. Three-dimensional difference maps of the form $F_0 - F_c$ (Hg, Br, Fe) were used to refine the coordinates of the light atoms. A back-shift correction was made for the last Fourier synthesis to minimize the Fourier series termination errors.

The final parameters for the Fourier and the least-squares refinements are

TABLE 2
OBSERVED AND CALCULATED STRUCTURE FACTORS FROM THE FOURIER REFINEMENT
The symbol x means that the corresponding reflection was unobserved (see text).

h	k	l	FO	FC	AC	RC	h	k	l	FO	FC	AC	RC
0	0	0	785.0	784.8	604.5	604.6	8	0	0	221.2	218.1	-17.4	33.9
0	0	1	126.1	124.2	104.1	104.0	8	0	1	274.0	273.7	-0.3	0.3
0	0	2	102.1	101.8	81.5	81.6	8	0	2	114.9	115.4	-0.5	0.5
0	0	3	43.5	43.5	34.5	34.5	8	0	3	78.3	78.3	0.0	0.0
0	0	4	18.5	18.5	14.5	14.5	8	0	4	49.7	49.7	0.0	0.0
0	0	5	10.5	10.5	8.0	8.0	8	0	5	33.7	33.7	0.0	0.0
0	0	6	6.5	6.5	5.0	5.0	8	0	6	22.7	22.7	0.0	0.0
0	0	7	4.5	4.5	3.5	3.5	8	0	7	15.7	15.7	0.0	0.0
0	1	0	10.5	10.5	8.0	8.0	8	1	0	11.0	11.0	0.0	0.0
0	1	1	10.5	10.5	8.0	8.0	8	1	1	10.5	10.5	0.0	0.0
0	1	2	10.5	10.5	8.0	8.0	8	1	2	10.5	10.5	0.0	0.0
0	1	3	10.5	10.5	8.0	8.0	8	1	3	10.5	10.5	0.0	0.0
0	1	4	10.5	10.5	8.0	8.0	8	1	4	10.5	10.5	0.0	0.0
0	1	5	10.5	10.5	8.0	8.0	8	1	5	10.5	10.5	0.0	0.0
0	1	6	10.5	10.5	8.0	8.0	8	1	6	10.5	10.5	0.0	0.0
0	1	7	10.5	10.5	8.0	8.0	8	1	7	10.5	10.5	0.0	0.0
0	2	0	10.5	10.5	8.0	8.0	8	2	0	10.5	10.5	0.0	0.0
0	2	1	10.5	10.5	8.0	8.0	8	2	1	10.5	10.5	0.0	0.0
0	2	2	10.5	10.5	8.0	8.0	8	2	2	10.5	10.5	0.0	0.0
0	2	3	10.5	10.5	8.0	8.0	8	2	3	10.5	10.5	0.0	0.0
0	2	4	10.5	10.5	8.0	8.0	8	2	4	10.5	10.5	0.0	0.0
0	2	5	10.5	10.5	8.0	8.0	8	2	5	10.5	10.5	0.0	0.0
0	2	6	10.5	10.5	8.0	8.0	8	2	6	10.5	10.5	0.0	0.0
0	2	7	10.5	10.5	8.0	8.0	8	2	7	10.5	10.5	0.0	0.0
0	3	0	10.5	10.5	8.0	8.0	8	3	0	10.5	10.5	0.0	0.0
0	3	1	10.5	10.5	8.0	8.0	8	3	1	10.5	10.5	0.0	0.0
0	3	2	10.5	10.5	8.0	8.0	8	3	2	10.5	10.5	0.0	0.0
0	3	3	10.5	10.5	8.0	8.0	8	3	3	10.5	10.5	0.0	0.0
0	3	4	10.5	10.5	8.0	8.0	8	3	4	10.5	10.5	0.0	0.0
0	3	5	10.5	10.5	8.0	8.0	8	3	5	10.5	10.5	0.0	0.0
0	3	6	10.5	10.5	8.0	8.0	8	3	6	10.5	10.5	0.0	0.0
0	3	7	10.5	10.5	8.0	8.0	8	3	7	10.5	10.5	0.0	0.0
0	4	0	10.5	10.5	8.0	8.0	8	4	0	10.5	10.5	0.0	0.0
0	4	1	10.5	10.5	8.0	8.0	8	4	1	10.5	10.5	0.0	0.0
0	4	2	10.5	10.5	8.0	8.0	8	4	2	10.5	10.5	0.0	0.0
0	4	3	10.5	10.5	8.0	8.0	8	4	3	10.5	10.5	0.0	0.0
0	4	4	10.5	10.5	8.0	8.0	8	4	4	10.5	10.5	0.0	0.0
0	4	5	10.5	10.5	8.0	8.0	8	4	5	10.5	10.5	0.0	0.0
0	4	6	10.5	10.5	8.0	8.0	8	4	6	10.5	10.5	0.0	0.0
0	4	7	10.5	10.5	8.0	8.0	8	4	7	10.5	10.5	0.0	0.0
0	5	0	10.5	10.5	8.0	8.0	8	5	0	10.5	10.5	0.0	0.0
0	5	1	10.5	10.5	8.0	8.0	8	5	1	10.5	10.5	0.0	0.0
0	5	2	10.5	10.5	8.0	8.0	8	5	2	10.5	10.5	0.0	0.0
0	5	3	10.5	10.5	8.0	8.0	8	5	3	10.5	10.5	0.0	0.0
0	5	4	10.5	10.5	8.0	8.0	8	5	4	10.5	10.5	0.0	0.0
0	5	5	10.5	10.5	8.0	8.0	8	5	5	10.5	10.5	0.0	0.0
0	5	6	10.5	10.5	8.0	8.0	8	5	6	10.5	10.5	0.0	0.0
0	5	7	10.5	10.5	8.0	8.0	8	5	7	10.5	10.5	0.0	0.0
0	6	0	10.5	10.5	8.0	8.0	8	6	0	10.5	10.5	0.0	0.0
0	6	1	10.5	10.5	8.0	8.0	8	6	1	10.5	10.5	0.0	0.0
0	6	2	10.5	10.5	8.0	8.0	8	6	2	10.5	10.5	0.0	0.0
0	6	3	10.5	10.5	8.0	8.0	8	6	3	10.5	10.5	0.0	0.0
0	6	4	10.5	10.5	8.0	8.0	8	6	4	10.5	10.5	0.0	0.0
0	6	5	10.5	10.5	8.0	8.0	8	6	5	10.5	10.5	0.0	0.0
0	6	6	10.5	10.5	8.0	8.0	8	6	6	10.5	10.5	0.0	0.0
0	6	7	10.5	10.5	8.0	8.0	8	6	7	10.5	10.5	0.0	0.0
0	7	0	10.5	10.5	8.0	8.0	8	7	0	10.5	10.5	0.0	0.0
0	7	1	10.5	10.5	8.0	8.0	8	7	1	10.5	10.5	0.0	0.0
0	7	2	10.5	10.5	8.0	8.0	8	7	2	10.5	10.5	0.0	0.0
0	7	3	10.5	10.5	8.0	8.0	8	7	3	10.5	10.5	0.0	0.0
0	7	4	10.5	10.5	8.0	8.0	8	7	4	10.5	10.5	0.0	0.0
0	7	5	10.5	10.5	8.0	8.0	8	7	5	10.5	10.5	0.0	0.0
0	7	6	10.5	10.5	8.0	8.0	8	7	6	10.5	10.5	0.0	0.0
0	7	7	10.5	10.5	8.0	8.0	8	7	7	10.5	10.5	0.0	0.0
0	8	0	10.5	10.5	8.0	8.0	8	8	0	10.5	10.5	0.0	0.0
0	8	1	10.5	10.5	8.0	8.0	8	8	1	10.5	10.5	0.0	0.0
0	8	2	10.5	10.5	8.0	8.0	8	8	2	10.5	10.5	0.0	0.0
0	8	3	10.5	10.5	8.0	8.0	8	8	3	10.5	10.5	0.0	0.0
0	8	4	10.5	10.5	8.0	8.0	8	8	4	10.5	10.5	0.0	0.0
0	8	5	10.5	10.5	8.0	8.0	8	8	5	10.5	10.5	0.0	0.0
0	8	6	10.5	10.5	8.0	8.0	8	8	6	10.5	10.5	0.0	0.0
0	8	7	10.5	10.5	8.0	8.0	8	8	7	10.5	10.5	0.0	0.0
0	9	0	10.5	10.5	8.0	8.0	8	9	0	10.5	10.5	0.0	0.0
0	9	1	10.5	10.5	8.0	8.0	8	9	1	10.5	10.5	0.0	0.0
0	9	2	10.5	10.5	8.0	8.0	8	9	2	10.5	10.5	0.0	0.0
0	9	3	10.5	10.5	8.0	8.0	8	9	3	10.5	10.5	0.0	0.0
0	9	4	10.5	10.5	8.0	8.0	8	9	4	10.5	10.5	0.0	0.0
0	9	5	10.5	10.5	8.0	8.0	8	9	5	10.5	10.5	0.0	0.0
0	9	6	10.5	10.5	8.0	8.0	8	9	6	10.5	10.5	0.0	0.0
0	9	7	10.5	10.5	8.0	8.0	8	9	7	10.5	10.5	0.0	0.0
0	10	0	10.5	10.5	8.0	8.0	8	10	0	10.5	10.5	0.0	0.0
0	10	1	10.5	10.5	8.0	8.0	8	10	1	10.5	10.5	0.0	0.0
0	10	2	10.5	10.5	8.0	8.0	8	10	2	10.5	10.5	0.0	0.0
0	10	3	10.5	10.5	8.0	8.0	8	10	3	10.5	10.5	0.0	0.0
0	10	4	10.5	10.5	8.0	8.0	8	10	4	10.5	10.5	0.0	0.0
0	10	5	10.5	10.5	8.0	8.0	8	10	5	10.5	10.5	0.0	0.0
0	10	6	10.5	10.5	8.0	8.0	8	10	6	10.5	10.5	0.0	0.0
0	10	7	10.5	10.5	8.0	8.0	8	10	7	10.5	10.5	0.0	0.0
0	11	0	10.5	10.5	8.0	8.0	8	11	0	10.5	10.5	0.0	0.0
0	11	1	10.5	10.5	8.0	8.0	8	11	1	10.5	10.5	0.0	0.0
0	11	2	10.5	10.5	8.0	8.0	8	11	2	10.5	10.5	0.0	0.0
0	11	3	10.5	10.5	8.0	8.0	8	11	3	10.5	10.5	0.0	0.0
0	11	4	10.5	10.5	8.0	8.0	8	11	4	10.5	10.5	0.0	0.0
0	11	5	10.5	10.5	8.0	8.0	8	11	5	10.5	10.5	0.0	0.0
0	11	6	10.5	10.5	8.0	8.0	8	11	6	10.5	10.5	0.0	0.0
0	11	7	10.5	10.5	8.0	8.0	8	11	7	10.5	10.5	0.0	0.0
0	12	0	10.5	10.5	8.0	8.0	8	12	0	10.5	10.5	0.0	0.0
0	12	1	10.5	10.5	8.0	8.0	8	12	1	10.5	10.5	0.0	0.0
0	12	2	10.5	10.5	8.0	8.0	8	12	2	10.5	10.5	0.0	0.0
0	12	3	10.5	10.5	8.0	8.0	8	12	3	10.5	10.5	0.0	0.0
0	12	4	10.5	10.5	8.0	8.0	8	12	4	10.5	10.5	0.0	0.0
0	12	5	10.5	10.5	8.0	8.0	8	12	5	10.5	10.5	0.0	0.0
0	12	6	10.5	10.5	8.0	8.0	8	12	6	10.5	10.5	0.0	0.0
0	12	7	10.5	10.5	8.0	8.0	8	12	7	10.5	10.5	0.0	0.0
0	13	0	10.5	10.5	8.0	8.0	8	13	0	10.5	10.5	0.0	0.0
0	13	1	10.5	10.5	8.0	8.0	8	13	1	10.5	10.5	0.0	0.0
0	13	2	10.5	10.5	8.0	8.0	8	13	2	10.5	10.5	0.0	0.0
0	13	3	10.5	10.5	8.0	8.0	8	13	3	10.5	10.5	0.0	0.0
0	13	4	10.5	10.5	8.0	8.0	8	13	4	10.5	10.5	0.0	0.0
0	13	5	10.5	10.5	8.0	8.0	8	13	5	10.5	10.5	0.0	0.0
0	1												

TABLE 3
INTRAMOLECULAR AND INTERMOLECULAR DISTANCES

Atoms	Fourier refinement	Least-squares refinement	Estimated std. dev. (lower limit)
$\text{Hg}_1 \dots \text{Hg}'_1$	3.07 Å	2.97	0.03
$\text{Hg}_2 \dots \text{Hg}'_2$	3.15	3.12	0.03
$\text{Hg}_1\text{-Br}_1$	2.50	2.41	0.05
$\text{Hg}_2\text{-Br}_2$	2.45	2.44	0.05
$\text{Hg}_1\text{-Fe}_1$	2.44	2.28	0.07
$\text{Hg}_2\text{-Fe}_2$	2.59	2.64	0.07
$\text{Fe}_1\text{-C}_1$	2.13		0.12
$\text{Fe}_1\text{-C}_2$	1.83		0.12
$\text{Fe}_2\text{-C}_3$	2.15		0.12
$\text{Fe}_2\text{-C}_4$	2.15		0.12
$\text{C}_1\text{-O}_1$	1.33		0.15
$\text{C}_2\text{-O}_2$	1.26		0.15
$\text{C}_3\text{-O}_3$	1.57		0.15
$\text{C}_4\text{-O}_4$	1.13		0.15
$\text{Hg}_1 \dots \text{Hg}_2$	4.23	4.25	0.03
$\text{Hg}_1 \dots \text{Br}_2$	3.56	3.59	0.05
$\text{Hg}_1 \dots \text{Br}'_2$	3.79	3.85	0.05
$\text{Hg}_2 \dots \text{Br}_1$	3.67	3.60	0.05
$\text{Hg}_2 \dots \text{Br}'_1$	4.22	4.17	0.05
$\text{Br}_1 \dots \text{Br}_2$	4.16	3.98	0.06
$\text{Br}_1 \dots \text{Br}'_2$	4.28	4.34	0.06
$\text{Br}_1 \dots \text{Br}'_1$	6.21	5.98	0.07
$\text{Br}_2 \dots \text{Br}'_2$	5.70	5.78	0.07
$\text{Hg}_2 \dots \text{Br}_1^a$	3.40	3.38	0.06
$\text{Hg}_1^a \dots \text{Br}_2$	3.29	3.26	0.06

^a Refers to position $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}+z$.

given in Table 1. Table 2 lists the observed and calculated structure factors from the Fourier refinement. Tables 3 and 4 give the distances and bond angles, respectively. Estimated standard deviations of the interatomic distances and angles involving only the heavy atoms were obtained from the least-squares full inverse matrix⁴¹, whereas the estimated standard deviations for the molecular parameters involving both heavy and light atoms were obtained from the variance matrix corresponding to no parameter correlation between atoms. The standard deviations of the positional parameters utilized in this diagonal matrix were taken from the least-squares refinement for the heavy atoms; for each of the light atoms the standard deviation of a positional parameter was assigned from the difference Fourier refinement to be 0.10 Å. The standard deviations calculated in this way for the molecular parameters involving only the heavy atoms agreed closely with the corresponding values from the full inverse least-squares matrix. These estimated uncertainties are based on the inherent assumption of no systematic error and hence in this case represent only the lower limits of the actual errors.

TABLE 4
BOND ANGLES

Atoms	Fourier refinement	Least-squares refinement	Estimated std. dev. (lower limit)
Hg ₁ -Fe ₁ -Hg ₁ '	78.0°	81.1°	2.5°
Hg ₂ -Fe ₂ -Hg ₂ '	75.1	72.6	2.3
Fe ₁ -Hg ₁ -Br ₁	174.9	177.3	1.3
Fe ₂ -Hg ₂ -Br ₂	165.3	169.0	1.4
Br ₁ -Hg ₁ -Hg ₁ '	128.8	128.7	1.2
Br ₂ -Hg ₂ -Hg ₂ '	119.8	122.1	1.1
C ₁ -Fe ₁ -Hg ₁	86.8		3.2
C ₂ -Fe ₁ -Hg ₁	93.9		3.3
C ₁ -Fe ₁ -C ₂	93.9		4.5
C ₂ -Fe ₁ -C ₂	95.7		7.4
C ₃ -Fe ₂ -Hg ₂	86.9		3.1
C ₄ -Fe ₂ -Hg ₂	87.8		2.8
C ₃ -Fe ₂ -C ₄	83.6		4.0
C ₄ -Fe ₂ -C ₄	109.2		6.4
C ₁ -Fe ₁ -C ₁	177.7		7.0
C ₃ -Fe ₂ -C ₃	176.8		6.9
Fe ₁ -C ₁ -O ₁	171.2		8.3
Fe ₁ -C ₂ -O ₂	174.0		9.1
Fe ₂ -C ₃ -O ₃	173.4		7.3
Fe ₂ -C ₄ -O ₄	162.9		9.3

The atomic scattering factors used in this entire analysis were those of Thomas and Umeda⁴² for mercury, bromine, and iron and those of Berghuis *et al.*⁴³ for carbon and oxygen. Corrections for anomalous dispersion effects⁴⁴ were made in the least-squares refinements.

In order to provide further verification of the structure, the three-dimensional Patterson map was checked against the vectors due to the heavy atoms. With the Fourier atomic coordinates the peak height distribution of all significant Patterson peaks except two moderately sized ones could be satisfactorily explained on the basis of the heavy atom vector sets. The distances of the intramolecular vectors agreed within experimental error with those from both refinements. The heavy atom peaks are clearly revealed in Fig. 3, which is a superposition of the appropriate electron density contours projected onto the (001) plane taken from the final three-dimensional Fourier synthesis. Fig. 4 illustrates the composite electron density contour sections parallel to the (001) plane for the four independent carbonyl groups of the two molecules which are obtained from the final difference Fourier synthesis. The resolution of these carbon and oxygen atoms obtained in this heavy atom problem is good even though the atomic coordinates are not accurately known. Besides these light atom peaks, the final difference Fourier map did not reveal any peaks of significant height other than those involving anisotropy of the heavy atoms. The insensitivity of the carbon and oxygen atoms to a least-squares refinement of the photographic data is not surprising in this case, especially since they comprise less than two percent of the total scattering power.

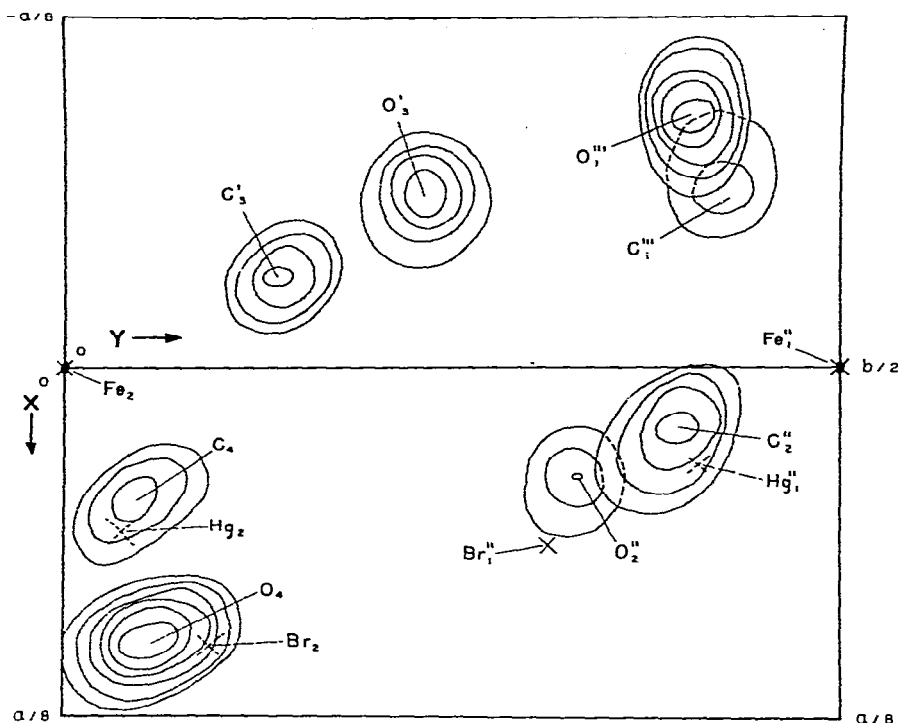


Fig. 4. A composite of a three-dimensional $[001]$ partial-difference electron density synthesis showing the carbonyl groups. Contours are at every $1 e/\text{\AA}^3$ with lowest contour at $2 e/\text{\AA}^3$. The single-, double-, and triple-primed superscripts refer to the positions \bar{x}, \bar{y}, z ; $x, \frac{1}{2}+y, \frac{1}{2}+z$; and $\bar{x}, \frac{1}{2}-y, \frac{1}{2}+z$, respectively. The positions of the heavy atoms which are subtracted out are indicated.

DISCUSSION

Solid $(\text{BrHg})_2\text{Fe}(\text{CO})_4$ exists as discrete molecules of idealized symmetry $C_{2v}-2mm$ in which each central iron atom is approximately octahedrally coordinated to four carbonyl groups and to two *cis*-HgBr ligands as shown in Fig. 1. The large estimated standard deviations reflect that the determined molecular parameters are not as precise as one would desire. Nevertheless, despite the large inaccuracies of the light atom coordinates, the carbon and oxygen atoms are clearly apparent in the composite density difference map (Fig. 4). Consequently, this X-ray investigation unambiguously gives the overall molecular configuration with the first direct proof for the existence of transition metal-mercury bonds. Since the distances and angles from the Fourier refinement show more internal consistency than those from the least-squares refinement, the molecular parameters based on the Fourier refinement are utilized in this discussion.

The molecules lie on crystallographic twofold axes, and therefore the independent part of the unit cell is made up of two halves of two symmetry-unrelated molecules both located on a given twofold axis (Fig. 2). The packing then can be described in terms of these two molecules stacked in rows along the *c* direction about each of the eight twofold axes of the unit cell. Only the heavy atoms in the unit cell

are shown in the [001] projection (Fig. 5). The heavy atom framework of this bimolecular unit (of idealized symmetry S_4-4) is approximately that obtained by placing the four bromine atoms at the corners of an equatorial plane of a distorted octahedron and positioning the iron atoms at the apices. The mercury atoms are placed along

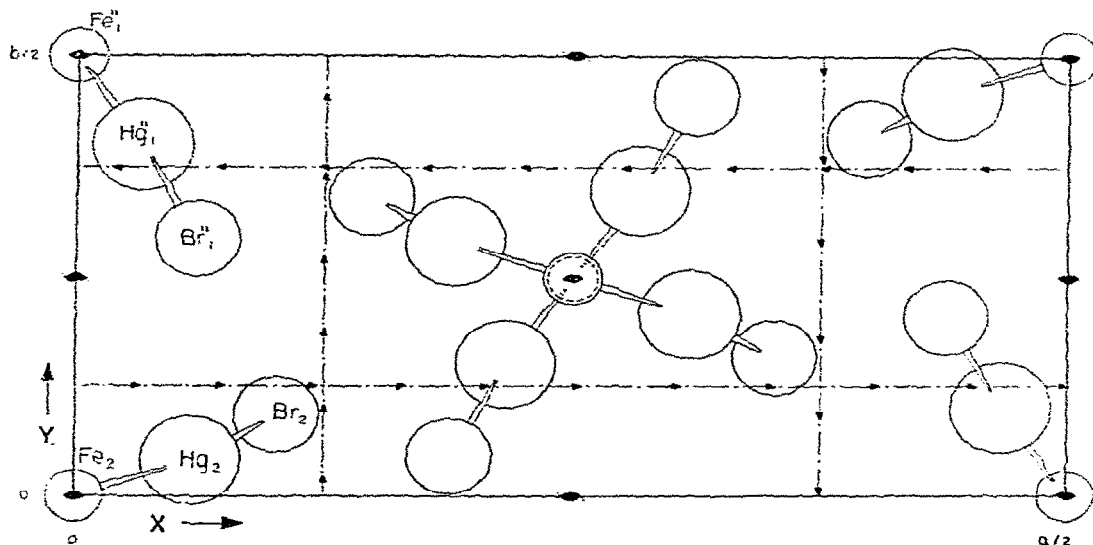


Fig. 5. [001] projection of the heavy atoms. The double-primed superscript refers to $x, \frac{1}{2} + y, \frac{1}{2} + z$.

four of the apex-to-equatorial-plane edges; one set of two *trans* edges are occupied by two mercury atoms below the equatorial plane, while the alternate set of two *trans* edges are occupied by two mercury atoms above the plane. The overall idealized S_4 symmetry of the bimolecular unit is retained with the addition of four carbonyl groups to each iron atom.

As expected, the mercury coordination in $(\text{BrHg})_2\text{Fe}(\text{CO})_4$ is digonal with no significant departure of the Fe–Hg–Br skeleton from linearity. The average intramolecular Hg . . . Hg distance of 3.1 Å compares favorably to the estimated Van der Waals Hg . . . Hg contact distance of 3.0 Å (Cf. ref. 45). The mean value of 2.47 Å for the Hg–Br bond distance in $(\text{BrHg})_2\text{Fe}(\text{CO})_4$ is in agreement with the most recently reported Hg–Br bond lengths in HgBr_2 (2.40⁴⁶ and 2.44⁴⁷ Å from electron diffraction of the vapor phase and 2.48^{48,49} Å from X-ray diffraction of the solid), CH_2HgBr (2.406 Å from microwave spectroscopy of the vapor⁵⁰), and solid Hg_2Br_2 (2.45 Å from X-ray diffraction⁵¹).

Each mercury atom formally can be considered to be in the +1 oxidation state with a $d^{10}s^1$ configuration, and hence each –HgBr group functions as a one-electron donating pseudo-halogen thereby enabling the central iron atom in the diamagnetic $(\text{BrHg})_2\text{Fe}(\text{CO})_4$ to achieve a closed-shell electronic configuration. It should be noted that a large number of transition metal complexes with post-transition atoms including –HgX groups recently have been prepared and characterized by Nyholm, Lewis, and co-workers^{5,6,8,9,52,53,54}. From spectroscopic studies they have suggested that the interaction of the highly polarizing –HgX ligand with such moieties as $\text{Fe}(\text{CO})_4$ also involves some π -back-bonding from the filled d_π -orbitals of the

central metal (*e.g.*, iron) to the vacant orbitals of the $-\text{HgX}$ entity thereby giving partial double-bond character to the Fe–Hg bond. Consistent with their view is that some double-bond character has been inferred from stereochemical considerations for Hg–O and Hg–CN bonds in several non-transition metal complexes^{4,5}.

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SUMMARY

The crystal and molecular structure of $(\text{BrHg})_2\text{Fe}(\text{CO})_4$ has been determined from a three-dimensional X-ray diffraction study. This compound crystallizes with 16 formula species in an orthorhombic unit cell with space group symmetry $Fdd2$ - (C_{2v}^{19}) and lattice parameters $a = 24.84 \text{ \AA}$, $b = 13.65 \text{ \AA}$, and $c = 12.91 \text{ \AA}$. The structure consists of discrete molecules of $(\text{BrHg})_2\text{Fe}(\text{CO})_4$ of idealized C_{2v} symmetry with the central iron atom in an approximately octahedral environment of four carbonyl groups and two *cis*-HgBr ligands. This X-ray study represents the first direct evidence for the existence of an iron-mercury bond. Crystallographic data show the isostructural molecular analogue $(\text{IHg})_2\text{Fe}(\text{CO})_4$ not to be isomorphous in the solid state with $(\text{BrHg})_2\text{Fe}(\text{CO})_4$. Crystals of $(\text{IHg})_2\text{Fe}(\text{CO})_4$ are orthorhombic with 8 formula species in a unit cell of symmetry $Pbn2_1$ (C_{2v}^9) and of lattice parameters $a = 13.17 \text{ \AA}$, $b = 13.32 \text{ \AA}$, and $c = 13.40 \text{ \AA}$.

REFERENCES

- 1 H. HOCK AND H. STUHLMANN, *Ber.*, 61 (1928) 2097.
- 2 H. HOCK AND H. STUHLMANN, *Ber.*, 62 (1929) 431.
- 3 H. HOCK AND H. STUHLMANN, *Ber.*, 62 (1929) 2690.
- 4 N. V. SIDGWICK, *The Chemical Elements and Their Compounds*, Vol. II, Oxford University Press, London, 1950, p. 1372.
- 5 R. S. NYHOLM, *Abstr. Papers, 151st Natl. Meeting Am. Chem. Soc.*, Pittsburgh, Pennsylvania, March 1966, H-17.
- 6 J. LEWIS, *Abstr. Papers, 151st Natl. Meeting Am. Chem. Soc.*, Pittsburgh, Pennsylvania, March 1966, H-19.
- 7 D. M. ADAMS, D. J. COOK AND R. D. W. KEMMITT, *Nature*, 205 (1965) 589.
- 8 R. S. NYHOLM AND K. VRIEZE, *J. Chem. Soc.*, (1965) 5331; *Proc. Chem. Soc.*, (1963) 138.
- 9 R. S. NYHOLM AND K. VRIEZE, *J. Chem. Soc.*, (1965) 5337; *Chem. Ind. (London)*, (1964) 318.
- 10 K. A. KEBLYS AND M. DUBECK, *Inorg. Chem.*, 3 (1964) 1646.
- 11 E. O. FISCHER, W. HAFNER AND H. O. STAHL, *Z. Anorg. Allgem. Chem.*, 282 (1955) 47; E. O. FISCHER AND R. BÖTTCHER, *Z. Naturforsch.*, 10b (1955) 600.
- 12 M. C. GANGKAR AND M. H. B. STIDDARD, *Chem. Commun.*, (1965) 22.

- 13 W. HIEBER AND W. SCHROPP, JR., *Chem. Ber.*, 93 (1960) 455.
- 14 R. B. KING, *J. Inorg. Nucl. Chem.*, 25 (1963) 1296.
- 15 W. HIEBER AND G. BADER, *Z. Anorg. Allgem. Chem.*, 190 (1930) 193.
- 16 F. HEIN AND E. HEUSER, *Z. Anorg. Allgem. Chem.*, 249 (1942) 293.
- 17 W. HIEBER AND H. BEUTNER, *Z. Anorg. Allgem. Chem.*, 320 (1963) 101.
- 18 W. HIEBER AND W. KLINGSHIRN, *Z. Anorg. Allgem. Chem.*, 323 (1963) 292.
- 19 R. B. KING, *Inorg. Chem.*, 2 (1963) 1275.
- 20 D. M. ADAMS, D. J. COOK AND R. D. W. KEMMITT, *Chem. Commun.*, (1966) 103.
- 21 W. HIEBER AND U. TELLER, *Z. Anorg. Allgem. Chem.*, 249 (1942) 43.
- 22 W. HIEBER AND H. SCHULTEN, *Z. Anorg. Allgem. Chem.*, 232 (1937) 17.
- 23 W. HIEBER, E. O. FISCHER AND E. BÖCKLY, *Z. Anorg. Allgem. Chem.*, 269 (1952) 308.
- 24 S. V. DIGHE AND M. ORCHIN, *Inorg. Chem.*, 1 (1962) 965.
- 25 G. BOR AND L. MARKÓ, *Spectrochim. Acta*, 16 (1960) 1105.
- 26 H. STAMMREICH, K. KAWAI, O. SALA AND P. KRUMHOLZ, *J. Chem. Phys.*, 35 (1961) 2175.
- 27 W. HIEBER AND R. BREU, *Chem. Ber.*, 90 (1957) 1259.
- 28 W. HIEBER AND W. FREYER, *Chem. Ber.*, 91 (1958) 1230.
- 29 E. O. FISCHER AND R. JIRA, *Z. Naturforsch.*, 8b (1953) 1.
- 30 E. WEISS AND W. HÜBEL, *J. Inorg. Nucl. Chem.*, 11 (1959) 42.
- 31 U. KRÜERKE AND W. HÜBEL, *Chem. Ber.*, 94 (1961) 2829.
- 32 J. S. ANDERSON, *Quart. Rev. (London)*, 1 (1947) 331.
- 33 J. W. CABLE AND R. K. SHELIN, *Chem. Rev.*, 56 (1956) 1.
- 34 O. WEISZ, W. COCHRAN AND W. F. COLE, *Acta Cryst.*, 1 (1948) 83.
- 35 W. HIEBER, K. RIES AND G. BADER, *Z. Anorg. Allgem. Chem.*, 190 (1930) 215.
- 36 *International Tables for X-Ray Crystallography*, Vol. I, Kynoch Press, Birmingham, England, 1952, p. 129.
- 37 W. G. SLY AND D. P. SHOEMAKER, *Two- and Three-Dimensional Crystallographic Fourier Summation Program for the IBM 704*, MIFR1, M.I.T., 1960.
- 38 J. F. BLOUNT, *A Three-Dimensional Crystallographic Fourier Summation Program for the CDC 1604 Computer*, Ph. D. Thesis (Appendix), University of Wisconsin, 1965.
- 39 W. R. BUSING AND H. A. LEVY, *A Crystallographic Least-Squares Refinement Program for the IBM 704*, ORNL 59-4-37, Oak Ridge National Laboratory, 1959.
- 40 M. J. BUEGER, *Crystal Structure Analysis*, Wiley, New York, 1960, p. 619.
- 41 W. R. BUSING AND H. A. LEVY, *A Crystallographic Function and Error Program for the IBM 704*, ORNL 59-12-3, Oak Ridge National Laboratory, 1959.
- 42 L. H. THOMAS AND K. UMEDA, *J. Chem. Phys.*, 26 (1957) 293.
- 43 J. BERGHUIS, L. J. M. HAANAPPEL, M. POTTERS, B. O. LOOPSTRA, C. H. MACGILLAVRY AND A. L. VEENENDAAL, *Acta Cryst.*, 8 (1955) 478.
- 44 C. H. DAUBEN AND D. H. TEMPLETON, *Acta Cryst.*, 8 (1955) 841.
- 45 D. GRDENIĆ, *Quart. Rev.*, 19 (1965) 303.
- 46 H. BRAUNE AND S. KNOKE, *Z. Phys. Chem.*, B23 (1933) 163.
- 47 A. H. GREGG, G. C. HAMPSON, G. I. JENKINS, P. L. F. JONES AND L. E. SUTTON, *Trans. Faraday Soc.*, 33 (1937) 852.
- 48 H. J. VERWEEL AND J. M. BIJVOET, *Z. Krist.*, 77 (1931) 122.
- 49 H. BRAEKKEN, *Z. Krist.*, 81 (1932) 152.
- 50 W. GORDY AND J. SHERIDAN, *J. Chem. Phys.*, 22 (1954) 92.
- 51 N. V. BELOV AND V. I. MOKEEVA, *Tr. Inst. Kristallogr., Akad. Nauk SSSR*, 5 (1949) 57.
- 52 C. E. COFFEY, J. LEWIS AND R. S. NYHOLM, *J. Chem. Soc.*, (1964) 1741.
- 53 A. S. KASENALLY, J. LEWIS, A. R. MANNING, J. R. MILLER, R. S. NYHOLM AND M. H. B. STIDDARD, *J. Chem. Soc.*, (1965) 3407.
- 54 A. S. KASENALLY, R. S. NYHOLM AND M. H. B. STIDDARD, *J. Chem. Soc.*, (1965) 5343.