64. *The Crystal Structure of Iron Enneacarbonyl.*

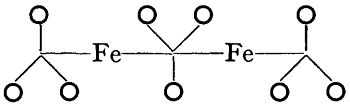
By H. M. POWELL and R. V. G. EWENS.

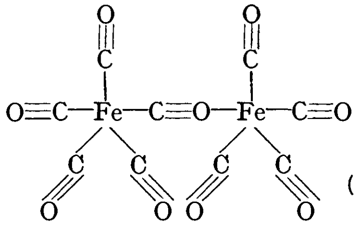
By means of Patterson and Fourier analyses, the crystal structure of iron enneacarbonyl has been determined. The structure differs from those proposed by Brill and by Sidgwick and Bailey. The molecular formula of the compound is $Fe_2(CO)_9$; each iron atom is linked to three terminal carbonyl groups and the two iron atoms are joined by three $>C=O$ bridges. The magnetic properties of the substance are discussed.

THE problem of the structure of the metal carbonyls has been previously attacked by the methods of *X*-ray crystal analysis. Rüdorff and Hoffmann (*Z. physikal. Chem.*, 1935, *B*, **28**, 351) have given details for the hexacarbonyls, and Brill (*Z. Krist.*, 1927, **65**, 89) has published results for iron enneacarbonyl; he did not determine the atomic positions, and the structure (I) which he proposed for the compound does not completely specify the mode of linkage of the atoms in the molecule, since no attempt is made to distinguish carbon and oxygen atoms. Instead, carbonyl groups are represented by the small circles as spherical units. The constitution (II) has been suggested by Sidgwick and Bailey (*Proc. Roy. Soc.*, 1934, *A*, **144**, 521).

The compound $Fe_2(CO)_9$ has now been re-examined, and by means of Patterson and Fourier analyses it has been possible to determine the positions of the atoms in the unit cell and thus to find the correct constitution.

The material was prepared by the method of Dewar and Jones (*ibid.*, 1905, *A*, **76**, 573), *viz.*, through the action of light on iron pentacarbonyl, and was obtained in clusters of very thin, yellow, hexagonal plates from which a few single crystals were separated. They were optically uniaxial with positive double refraction. Oscillation photographs about the *a* and *c* axes were taken, and a zero layer line Weissenberg photograph with rotation about the *a* axis was obtained with a regular hexagonal plate of side 0·2 and thickness 0·02 mm. For these photographs copper radiation from a Philips Metalix tube was used. Owing to the extreme platy form of the crystals, it was impossible to obtain a satisfactory Weissenberg photograph with rotation about the *c* axis.


(I.)


(II.)

The unit cell dimensions deduced were $a = 6{\cdot}45$, $c = 15{\cdot}98$ A., and these, combined with the density 2·08, show that there are two molecules per unit cell. The photographs were indexed by the usual chart methods, and the Weissenberg photograph was used to provide a series of relative F' values for the subsequent Fourier analysis. The relative intensities of the spots on this film were estimated by eye, by comparison with an intensity scale previously prepared by timed exposures to an *X*-ray beam. The results, divided by their appropriate Lorentz and polarisation factors, gave values of F'^2 for the spectra $h0\bar{h}l$, and hence the magnitudes of the F's. In Table I are listed the observed F' values with the calculated values found later. No correction for absorption was made.

TABLE I.

$h0\bar{h}l$.	Sin θ.	F', obs.	F, calc.	$h0\bar{h}l$.	Sin θ.	F', obs.	F, calc.	$h0\bar{h}l$.	Sin θ.	F', obs.	F, calc.
0002	0·096	52	−62	$10\bar{1}10$	0·497	0	−1	$30\bar{3}3$	0·386	0	−11
0004	0·193	48	−77	$10\bar{1}11$	0·543	0	17	$30\bar{3}4$	0·407	34	−39
0006	0·289	85	−58	$10\bar{1}12$	0·590	0	−21	$30\bar{3}5$	0·432	0	1
0008	0·386	37	−39	$10\bar{1}13$	0·637	50	−56	$30\bar{3}6$	0·460	26	24
00010	0·482	50	−35	$10\bar{1}14$	0·685	0	27	$30\bar{3}7$	0·492	0	− 1
00012	0·578	111	91	$10\bar{1}15$	0·733	0	33	$30\bar{3}8$	0·526	39	−50
00014	0·675	85	−62	$20\bar{2}1$	0·244	83	80	$30\bar{3}9$	0·563	0	6
00016	0·771	41	47	$20\bar{2}2$	0·258	35	24	$30\bar{3}10$	0·592	0	−15
$10\bar{1}0$	0·119	52	−60	$20\bar{2}3$	0·279	0	3	$30\bar{3}11$	0·640	0	− 2
$20\bar{2}0$	0·239	53	−51	$20\bar{2}4$	0·307	0	0	$30\bar{3}12$	0·680	42	55
$30\bar{3}0$	0·358	105	138	$20\bar{2}5$	0·339	20	−13	$40\bar{4}1$	0·479	68	−52
$40\bar{4}0$	0·477	48	−45	$20\bar{2}6$	0·375	22	−24	$40\bar{4}2$	0·487	12	4
$50\bar{5}0$	0·597	43	−58	$20\bar{2}7$	0·413	50	54	$40\bar{4}3$	0·498	0	10
$10\bar{1}1$	0·129	62	−78	$20\bar{2}8$	0·454	26	27	$40\bar{4}4$	0·514	0	24
$10\bar{1}2$	0·153	29	24	$20\bar{2}9$	0·495	0	−10	$40\bar{4}5$	0·534	41	50
$10\bar{1}3$	0·187	0	17	$20\bar{2}10$	0·538	0	15	$40\bar{4}6$	0·558	0	−17
$10\bar{1}4$	0·227	30	23	$20\bar{2}11$	0·581	35	−53	$40\bar{4}7$	0·584	0	−19
$10\bar{1}5$	0·269	75	61	$20\bar{2}12$	0·626	43	−31	$40\bar{4}8$	0·613	0	22
$10\bar{1}6$	0·313	37	−33	$20\bar{2}13$	0·670	53	38	$40\bar{4}9$	0·645	0	2
$10\bar{1}7$	0·358	41	−45	$20\bar{2}14$	0·716	0	− 5	$50\bar{5}1$	0·599	53	75
$10\bar{1}8$	0·404	10	20	$30\bar{3}1$	0·361	0	0	$50\bar{5}2$	0·605	0	18
$10\bar{1}9$	0·450	0	10	$30\bar{3}2$	0·371	33	−29	$50\bar{5}3$	0·614	0	−14

For purposes of comparison the observed relative F's, which were on an arbitrary scale, have been multiplied by a factor so as to give approximate agreement for planes of moderate intensity. Previous investigations have shown that visually estimated intensities are sufficiently accurate for purposes of structure determination by Fourier methods (*e.g.*, Hughes, *J. Chem. Physics*, 1935, **3**, 650).

The only systematic absence attributable to space-group symmetry was that of 000l for l odd, and the space-group may therefore be $C6_3$, $C6_3/m$, or $C6_32$. The space-group $C6/mmc$ —D_{6h} chosen by Brill is incorrect, as shown by the presence on rotation photographs of $hh\overline{2h}l$ with l odd. In the absence of any pyroelectric effect detectable by the liquid-air method or of other evidence of polarity, $C6_3$ was rejected.

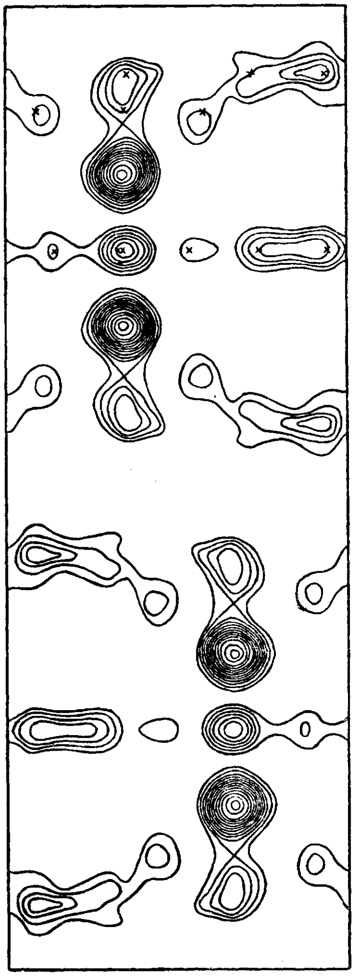
The two space-groups $C6_3/m$ and $C6_32$ have the same two-fold and four-fold positions, in some of which the four iron atoms of the unit cell must be placed. Positions (*c*), (*d*), and (*f*) (nomenclature of International Tables), in which iron atoms would lie on the three-fold symmetry axes in $\frac{1}{3}\frac{2}{3}z$ and $\frac{2}{3}\frac{1}{3}z$, are found to be the only possible ones. These positions have the special additional absence of $hkil$ if $h - k = 3n$ and l is odd, and owing to the relatively large contribution of the iron atoms to the intensities and the small chance of co-operation between the other atoms, spectra of the class mentioned should be very weak. Reference to Table I shows a complete absence of $30\bar{3}l$ when l is odd in agreement with this, and the choice of positions for the iron atoms is therefore limited to the combination (*c*) + (*d*) $\frac{1}{3}\frac{2}{3}\frac{1}{4}$, $\frac{2}{3}\frac{1}{3}\frac{3}{4}$; $\frac{2}{3}\frac{1}{3}\frac{1}{4}$, $\frac{1}{3}\frac{2}{3}\frac{3}{4}$, or (*f*) $\frac{1}{3}\frac{2}{3}z$, $\frac{2}{3}\frac{1}{3}z$, $\frac{2}{3}\frac{1}{3}\frac{1}{2} + z$, $\frac{1}{3}\frac{2}{3}\frac{1}{2} - z$.

The position of the iron atoms was then determined more precisely by means of a Patterson analysis. For this purpose the F'^2s corresponding to the F's given in Table I were used as coefficients in the double Fourier series for P_{xz}. The addition was carried out by the method of Beevers and Lipson. The resulting projection perpendicular to an a axis showed peaks corresponding to iron–iron separations in position (*f*), $\frac{1}{3}\frac{2}{3}z$, etc., with z approximately equal to $\frac{1}{6}$. Since the projection of the structure perpendicular to an a axis belongs to the same plane group whichever of the two possible space groups is assumed, it is possible to proceed with the Fourier analysis without first deciding on the space-group. Relative electron densities were computed by the double Fourier series for ρ_{xz}. The F's of Table I were used as coefficients, and the signs were taken as those of the iron contributions. The resulting electron-density projection, which contained all the essential features of the final projection reproduced in Fig. 1, showed from the disposition of the minor peaks that the carbon and oxygen atoms, concerning the positions of which no assumptions had been made, were located in one twelve-fold and one six-fold position each. The six-fold position with parameter $z = \frac{1}{4}$ can only be (*h*) of the space group $C6_3/m$ with co-ordinates $xy\frac{1}{4}$, etc., where x is approximately $\frac{1}{3}$ for both carbon and oxygen. The presence of the comparatively high peak on the line joining two iron atoms, and attributed to the overlapping of one carbon and one oxygen atom, together with the more or less symmetrical arrangement of the other peaks about this line, cannot be explained if position (*h*), $x\ 2x\ \frac{1}{4}$, of $C6_32$ is assumed. The space-group is therefore $C6_3/m$, and the remaining 12 carbon and 12 oxygen atoms lie in position (*i*), xyz, etc., of this space-group.

From this first projection the iron parameter was re-estimated, and probable parameters for the carbon and oxygen atoms were calculated from consideration of the projection itself and the type of molecule that it indicates for the compound. All the F's were then recalculated, but although there were profound changes in magnitude brought about by the introduction of the carbon and oxygen contributions, very few of the signs were altered. The Fourier summation was repeated with these changes of sign, and the atomic parameters re-estimated. There is necessarily some overlapping of the atoms as seen in the projection (Fig. 1), but this, considered in conjunction with the more complete resolution of the symmetrically related atoms, helps to fix the positions of all the atoms. There are small discrepancies in the positions of peaks corresponding to atoms related by the symmetry, and although there is no doubt as to the structure of the molecule and the approximate lengths of the links, the detail of the projection is subject to some small errors. Apart from any errors due to visual estimation of intensities, a few of the F's are necessarily incorrect owing to the abnormal absorption of the beam along a path in the crystal parallel to the very thin crystal plate, which takes place for one or two reflexions.

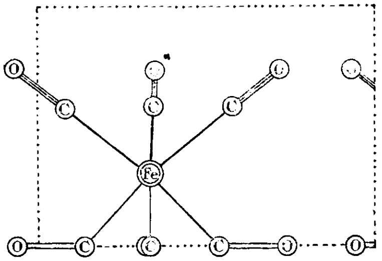
The complete list of parameters is given in Table II. The values of z and z_3 may be found with considerable accuracy direct from the projection. It is clear from the projection that the parts of the molecule are nearly symmetrical about a plane perpendicular to it and passing through the two iron atoms. There is, however, some indication that the molecule is rotated slightly out of this position, and a rotation of 3° about the three-fold symmetry axis agrees well with the results and improves somewhat the intermolecular distances. Also the terminal Fe—C≡O arrangement of atoms appears linear, as would be expected; by assuming this to be strictly so, and inserting the most probable directions of lines joining these atoms, x_2, y_2, x_3, and y_3 were found. The parameters x, x_1, y, y_1 may also be estimated from the projection by making allowance for the slight rotation of the molecule.

FIG. 1.



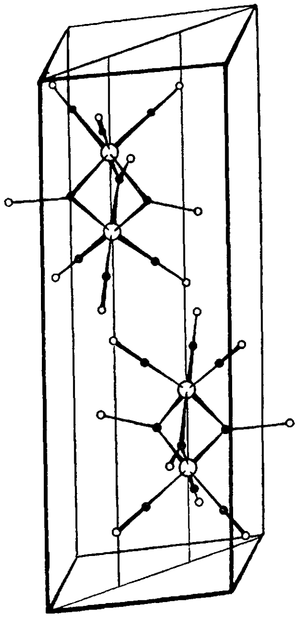
Relative electron density projected perpendicular to an a *axis. Contours are drawn at arbitrary equal intervals, the lowest contours being omitted. The positions of the lighter atoms are marked by crosses in upper part of figure.*

FIG. 2.



Atomic positions to correspond with crosses in Fig. 1.

FIG. 3.



General view of structure of $Fe_2(CO)_9$. *Large circles,* Fe; *small open circles,* O; *small full circles,* C.

The centres of atoms corresponding with these parameters are indicated by crosses in the upper part of Fig. 1. This should be compared with Fig. 2, which shows one half of the molecule drawn to correspond with these crosses.

In Table I are given calculated values of $F_{h0\bar{h}l}$ based on the parameters of Table II. They are in good general agreement with the observed relative F's.

TABLE II.

Table of Parameters.

4 Fe in (*f*) : $\frac{1}{3}\frac{2}{3}z$; $\frac{2}{3}\frac{1}{3}\bar{z}$; $\frac{2}{3}\frac{1}{3}\ \frac{1}{2}+z$; $\frac{1}{3}\frac{2}{3}\ \frac{1}{2}-z$.
6 C in (*h*) : $xy\frac{1}{4}$; $\bar{y}, x-y, \frac{1}{4}$; $y-x, \bar{x}, \frac{1}{4}$; $\bar{x}\bar{y}\frac{3}{4}$; $y, y-x, \frac{3}{4}$; $x-y, x, \frac{3}{4}$.
6 O in (*h*) : $x_1y_1\frac{1}{4}$, etc.
12 C in (*i*) : $x_2y_2z_2$; $\bar{y}_2, x_2-y_2, z_2$; $y_2-x_2, \bar{x}_2, z_2$; $\bar{x}_2\bar{y}_2\bar{z}_2$; $y_2, y_2-x_2, \bar{z}_2$; $x_2-y_2, x_2, \bar{z}_2$; $\bar{x}_2\bar{y}_2, \frac{1}{2}+z_2$; $y_2, y_2-x_2, \frac{1}{2}+z_2$; $x_2-y_2, x_2, \frac{1}{2}+z_2$; $x_2y_2\frac{1}{2}-z_2$; $\bar{y}_2, x_2-y_2, \frac{1}{2}-z_2$; $y_2-x_2, \bar{x}_2, \frac{1}{2}-z_2$.
12 O in (*i*) : $x_3y_3z_3$, etc.

$z = 0{\cdot}173$; $x = 0{\cdot}32$, $y = 0{\cdot}86$; $x_1 = 0{\cdot}315$, $y_1 = 0{\cdot}055$; $x_2 = 0{\cdot}35$, $y_2 = 0{\cdot}43$, $z_2 = 0{\cdot}11$; $x_3 = 0{\cdot}36$, $y_3 = 0{\cdot}285$, $z_3 = 0{\cdot}07$.

DISCUSSION.

The general character of the structure and the form of the molecule of formula $\mathrm{Fe_2(CO)_9}$ may be seen from Figs. 2 and 3. It does not seem to have been realised that the molecular weight of this compound has never been measured, it being rather insoluble in solvents with which it does not react. Throughout the literature, however, it has been assumed that the above formula, and not a multiple of it, is the correct one. Since in this structure determination the only chemical assumption made is that the empirical formula is $\mathrm{Fe_2(CO)_9}$, the emergence of a molecule containing only two iron atoms is equivalent to a molecular-weight determination.

There is a horizontal plane of symmetry through the molecule, and the two iron atoms are equivalent in every way. On the other hand, the carbon and oxygen atoms fall into two chemically and crystallographically distinct groups. The ends of the molecules are formed by three CO groups co-ordinated to each iron atom so that $\mathrm{Fe} \leftarrow \mathrm{C} \overset{\leftarrow}{=} \mathrm{O}$ is linear. The remaining three CO radicals are not co-ordinated $\mathrm{C} \overset{\leftarrow}{=} \mathrm{O}$ groups but lie in a plane between the two iron atoms which are linked through each of the three carbon atoms. Since each central carbon atom is attached to two iron atoms, Fe, C, and O cannot be linear in this case, and the carbon must be attached to its oxygen by a double bond (Fig. 2). The relative heights of the peaks in the Fourier projection show that in both kinds of CO group it is the carbon atom that is linked to the metal. It has been assumed for some time that the CO groups in the metallic carbonyls are linked through the carbon atoms, but hitherto there has been no experimental evidence for it.

The interatomic distances found are recorded in Table III.

TABLE III.

Fe to Fe	2·46	Intermolecular distances :		Angle between (OC)→Fe bonds	94°
Fe–C in $\mathrm{C{\equiv}O}$	1·9	O to O in terminal $\mathrm{C{\equiv}O}$ groups	3·2 3·65 3·3 3·1	Angle between Fe–C bonds	78°
Fe–C in $\mathrm{C{=}O}$	1·8	O to O between $\mathrm{>C{=}O}$ groups	3·25 3·65	Angle between bonds of $\mathrm{>C{=}O}$	87°
$\mathrm{C{\equiv}O}$	1·15				
$\mathrm{C{=}O}$	1·3				

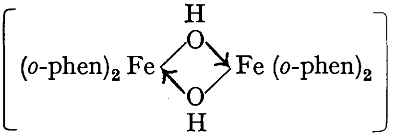
(The interatomic and intermolecular distances are correct to the nearest 0·05 A., and the bond angles are probably correct to ± 4°.)

The iron atoms appear to be six-covalent, having three co-ordinate links from donor $\mathrm{C{\equiv}O}$ groups and three covalencies with carbon atoms, and are formally in the ferric state. The six bonds are slightly distorted from a regular octahedral configuration. Between the three links of Fe to $\mathrm{C{\equiv}O}$ the angle is 94°, and between the links to the central carbon atoms it is 78°. The angle between two bonds of a central carbon atom is 87°. These last two angles represent a compromise between an iron angle of 90° and a tetrahedral carbon angle. If the iron angle is increased beyond 78°, the carbon angle is decreased still further from the tetrahedral, whereas any increase of the carbon angle would compel a great decrease in the iron angle. Although great accuracy cannot be claimed for interatomic distances involving the lighter atoms, it will be seen that the interpretation given to the Fourier projection does lead to distances in accordance with expectation for the constitution proposed. Thus $\mathrm{C{\equiv}O}$ and $\mathrm{C{=}O}$ are found respectively to be 1·15 and 1·3 A. The

Fe–C distances 1·8 and 1·9 appear somewhat short, but they are in fair agreement with the Fe–C distance, 1·84 A., found by electron-diffraction measurements on iron pentacarbonyl (Ewens and Lister, unpublished). Similar metal-to-carbon distances, in every case less than the sums of the appropriate normal single-bond covalent radii, have been found in all the metal carbonyls of the transition elements so far examined (Brockway and Cross, *J. Chem. Physics*, 1935, **3**, 828; Brockway and Anderson, *Trans. Faraday Soc.*, 1937, **33**, 1233; Brockway, Ewens, and Lister, *ibid.*, 1938, **34**, 1350).

The iron-to-iron separation in the molecule is only 2·46 A., a distance roughly twice the covalent radius of iron which, for ferric iron, may be slightly less than 1·23 A., the value given for ferrous iron (Pauling and Huggins, *Z. Krist.*, 1934, **87**, 205), but if, as this might suggest, there were a bond between the metal atoms, the iron would have to be quadrivalent. Short interatomic distances are, however, inevitable in polynuclear compounds of this type and have, in fact, been observed in a number of other cases. For example, in the tetrameric triethylarsinecuprous iodide (Wells, *Z. Krist.*, 1936, **94**, 447), 4-covalent copper atoms linked through iodine fall at the corners of a tetrahedron of side 2·6 A., separated therefore by a distance 0·1 A. less than twice the covalent radius (1·35) for tetrahedral copper. The assumption that nearness of approach alone implies a chemical bond would lead in this case to the highly improbable view that copper formed three additional bonds in an awkward configuration. In the complex ion $Tl_2Cl_9^{-3}$ (Hoard and Goldstein, *J. Chem. Physics*, 1935, **3**, 199; Powell and Wells, J., 1935, 1008), which has a configuration closely resembling that proposed for iron enneacarbonyl, the thallium-to-thallium distance is 3·6 A., little more than twice the covalent radius (1·7). It appears, therefore, that atoms in the same molecule, not, however, linked by an ordinary bond, may in some circumstances approach to within a distance as little as twice the covalent radius. The examples quoted all involve metal atoms, and in no instance is the distance appreciably less than either twice the covalent radius or the distance apart of the atoms in the free metal.

This close approach of the iron atoms may provide a clue to the magnetic properties of the enneacarbonyl. The substance is observed to be diamagnetic (Freundlich and Cuy, *Ber.*, 1923, **56**, 2264; Berkmann and Zocker, *Z. physikal. Chem.*, 1926, **124**, 318); on the above structure, both iron atoms are in the ferric state, so there should be one unpaired electron on each, and the substance might be expected to show a paramagnetic moment corresponding to two unpaired electrons. In the chloride of *o*-phenanthrolineferric diol (I) (Gaines, Hammett, and Walden, *J. Amer. Chem. Soc.*, 1936, **58**, 1668), each iron atom



(I.)

has an effective atomic number of 35 (as in the enneacarbonyl), and for one unpaired electron on each, this should correspond to a magnetic moment, for spin only, of 1·73 Bohr magnetons per iron atom. The observed paramagnetic moment is 1·4 Bohr magnetons. In this case the iron atoms are probably about 2·7 A. apart, and the diminution of the moment must be attributed to this close approach. The still closer approach in the enneacarbonyl may well account for the total disappearance of the paramagnetic moment due to the complete coupling of the electron spins. The pairing of the electron spins does not necessarily mean bond formation. Thus thiobenzophenone and tetramethyl-*pp*′-diaminothiobenzophenone have properties characteristic of free radicals, and have been formulated as biradicals, $R{-}\dot{C}{-}\dot{S}$ (Bergmann, Magat, and Wagenberg, *Ber.*, 1930, **63**, 2576; Hunter and Partington, J., 1933, 87), but they are diamagnetic in solution (Allen and Sugden, J., 1936, 440), which suggests that in the biradical form the odd electrons have their spins paired.

Intermolecular distances found in the structure are as a whole satisfactory. The separation between different pairs of the terminal triply-bound oxygen atoms is 3·1, 3·2, 3·3, or 3·65 A., and for the central oxygen atoms, 3·25 or 3·65 A. A separation of 3·1 is somewhat short, but values as low as this have been observed elsewhere, *e.g.*, in cyanuric triazide (Knaggs, *Proc. Roy. Soc.*, 1935, *A*, **150**, 576) the terminal triply-bound nitrogen atoms in the N_3 groups are 3·1 A. apart. Any attempt to increase the distance between the nearest oxygen atoms in the structure now described by further rotation of the $Fe_2(CO)_9$ molecule about the trigonal axis leads to short distances between other oxygen atoms.

In view of the results for iron enneacarbonyl, it follows that the arguments by which Sidgwick and Bailey (*loc. cit.*) assigned structures to the polymetallic carbonyls are inadequate, and further structure determinations on these compounds are clearly necessary.

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