SECTION A
Inorganic, Physical, and Theoretical Chemistry

Mössbauer Effect in Bis-μ-[oxy(phenyl)carbene-*C,O:C′,O′*]-bis(tricarbonyliron)(Fe–Fe) and related Compounds

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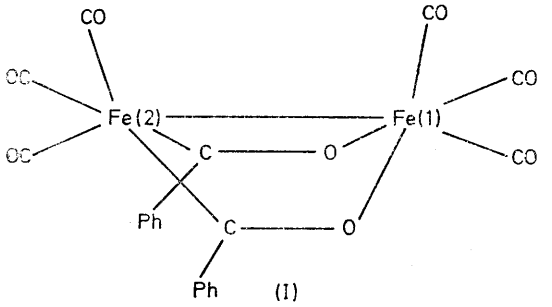
The Mössbauer effect has been used to show that the structure of bis-μ-[oxy(phenyl)carbene]-bis(tricarbonyliron)-(Fe–Fe) is asymmetrical (in agreement with *X*-ray data). Results obtained for related compounds, in which one of the carbonyl or phenyl groups is replaced by a secondary amine, indicate that these have the same basic structure with the carbon atoms of the two bridging carbonyl groups bonding to the same iron atom, and arguments are presented which suggest that it is at this iron atom that the replacement takes place.

We report studies on bis-μ-[oxy(phenyl)carbene-*C,O:C′,O′*]-bis(tricarbonyliron)(Fe–Fe) (I) and related compounds.

The discovery, synthesis, a qualitative description of the Mössbauer spectrum, and the *X*-ray structure of this compound have been reported,[1—3] and it has been shown that the compound is binuclear and is bridged by two carbon monoxide groups, which are both bonded *via* oxygen to one of the iron atoms and by carbon to the other iron atom [structure (I)].



(I)

Similar compounds, where one of the carbonyl and/or the phenyl groups have been replaced by a secondary amine, have been synthesized. We show by means of the Mössbauer effect: (i) that the structure of the compound is asymmetric, *i.e.* that there are two iron atoms with different environments, (ii) that in the substituted compounds this basic unit is maintained, (iii) which iron atom is substituted in substituted complexes, and (iv) which of the alternative descriptions proposed [1,2] is correct, *i.e.* if it is a benzoyl complex or a oxyphenylcarbene complex.

EXPERIMENTAL

Measurements were made with a conventional constant acceleration Mössbauer spectrometer as described elsewhere.[4] A ^{57}Co in Pd source was used (*ca.* 5 mCi). Compounds were transferred in a dry-box to Perspex absorber holders provided with O-rings so as to make them completely leak-tight and minimize the risk of decomposition. The sample holders were firmly attached to the transducer, so as to minimize mechanical vibrations.

In all cases the samples were *ca.* 0·13 mm thick. All measurements were made at room temperature except for compound (I) where spectra were also taken at 80 K.

As reported previously [1] the spectrum found for compound (I) shows four peaks. For the substituted derivatives we have found only three peaks. In all cases the results were fitted by computer, by least-squares. All the spectra were fitted with Lorentzian curves with allowance for admixture of Gaussian curve (typically 10—30%) with four independent peaks; *i.e.* for each peak the position, height, and width were fitted independently. For the substituted compounds the use of four peaks, compared with three independent peaks does not lead to a notable improvement in the value of χ^2. Typical examples of the changes are from 169 to 161 and from 197 to 195, both for *ca.* 190 degrees of freedom. As this occurs for all three of the substituted compounds, it seems unlikely that this is due to accidental superposition of peaks belonging to different doublets.

Table 1 shows the relevant data for some individual runs and Table 2 the results obtained as discussed later and averaged for six runs in each case. Typical spectra of these compounds are shown in Figures 1 and 2.

DISCUSSION

The first Mössbauer spectra of the complex were taken before the analysis of the *X*-ray data was complete and there were still doubts as to whether the compound belonged to the *Pnma* space-group which requires that the molecule has a mirror plane (I) or to the *Pna*2$_1$ group which places no restriction on the molecular shape. The spectrum indicated that the iron atoms had two different environments since Figure 1 clearly shows two quadrupole doublets.

The main problem arises in the assignment of the peaks to the two sites. The following facts suggest that peaks 1 and 4, and 2 and 3, respectively, are to be

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[1] E. O. Fischer, V. Kiener, D. St. P. Bunbury, E. Frank, P. F. Lindley, and O. S. Mills, *Chem. Comm.*, 1968, 1378.

[2] P. F. Lindley and O. S. Mills, *J. Chem. Soc.* (*A*), 1969, 1279.

[3] V. Kiener, Dissertation, T.H., Munich, 1969.

[4] E. Frank, *Nuovo Cimento*, 1968, **58***B*, 407.

matched. (i) They show similar (<20% difference) intensities and areas, in pairs at room temperature, which are similar to values found for other organometallic compounds.

(ii) The combination of peaks 1 and 2, and 3 and 4 must be discarded because of the high negative isomer shift and because the change in isomer shift with temperature for both doublets, which should be similar for both doublets, is different.

(iii) The combination 1 and 3, and 2 and 4 must also be discarded for the latter reason.

With this assumption, we have calculated the quadrupole splitting and isomer shift data for compound (I).

The assignment of the parameters to the different iron atoms is not straightforward as the electronic configuration around the iron atoms is not known in detail, but it can be attempted if data for the other three compounds are used.

Table 1 shows that for the substituted compounds two of the three peaks have roughly the same intensities whereas the third is about twice as intense. It is not to be expected that two different sites in the same compound would have *f* factors which differ by nearly 100%, so it is easy to find the Mössbauer parameters for each of the iron atoms without knowing which assignment is correct.

In all three cases the peak at more negative velocities has the largest intensity (*i.e.* quadrupole splitting *ca.* 0).

TABLE 1

Mössbauer data for compounds of the type $[(CO)_3Fe(COR^1)_2Fe(CO)_2R^2]$

R^1	Ph	Ph	Ph	$HNEt_2$
R^2	CO	NHC_5H_{10}	$NHEt_2$	$NHEt_2$
P_1 [a]	−0·754 ± 0·001			
I_1 [b]	1·073 ± 0·015			
Γ_1 [c]	0·230 ± 0·008			
P_2 [a]	−0·505 ± 0·002	−0·507 ± 0·001	−0·481 ± 0·003	−0·416 ± 0·006
I_2 [b]	1·224 ± 0·015	1·922 ± 0·010	1·884 ± 0·031	1·983 ± 0·090
Γ_2 [c]	0·238 ± 0·008	0·323 ± 0·003	0·319 ± 0·006	0·268 ± 0·015
P_3 [a]	−0·207 ± 0·002	−0·173 ± 0·002	−0·196 ± 0·005	−0·227 ± 0·009
I_3 [b]	1·280 ± 0·012	1·067 ± 0·010	1	1
Γ_3 [c]	0·276 ± 0·005	0·299 ± 0·006	0·299 ± 0·012	0·210 ± 0·029
P_4 [a]	0·545 ± 0·002	0·321 ± 0·001	0·307 ± 0·002	0·201 ± 0·005
I_4 [b]	1	1	1·042 ± 0·015	1·025 ± 0·026
Γ_4 [c]	0·262 ± 0·007	0·297 ± 0·004	0·297 ± 0·007	0·247 ± 0·017

[a] *P* refers to the position of the peaks with reference to the cobalt-57–palladium source used in mm/s. [b] *I* refers to the intensities relative to the least intense. [c] Γ Width in mm/s.

TABLE 2

Isomer shift (IS) and quadrupole splitting (QS) for compounds of the type $[(CO)_3Fe(COR^1)_2Fe(CO)_2R^2]$

R^1	R^2	IS_1 *	QS_1 *	IS_2 *	QS_2 *
Ph	CO	0·088 ± 0·004	0·294 ± 0·006	0·338 ± 0·005	1·292 ± 0·010
Ph	HNC_5H_{10}	−0·071 ± 0·005	0	0·516 ± 0·005	0·501 ± 0·006
Ph	$HNEt_2$	−0·034 ± 0·010	0	0·492 ± 0·003	0·507 ± 0·007
$HNEt_2$	$HNEt_2$	0·016 ± 0·011	0	0·430 ± 0·004	0·432 ± 0·007

* In mm/s. The data for isomer shifts are referred to sodium nitroprusside. Labelling of the iron atoms as in ref. 2.

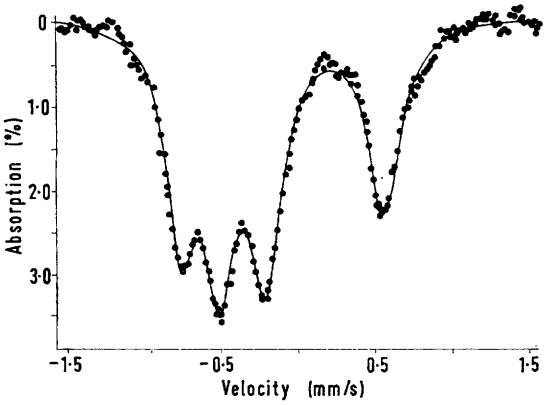


FIGURE 1 Mössbauer spectrum of compound (I) at room temperature, referred to the cobalt-57–palladium sourced used

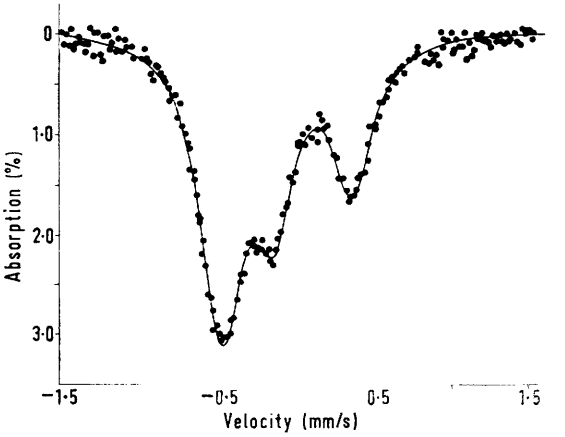
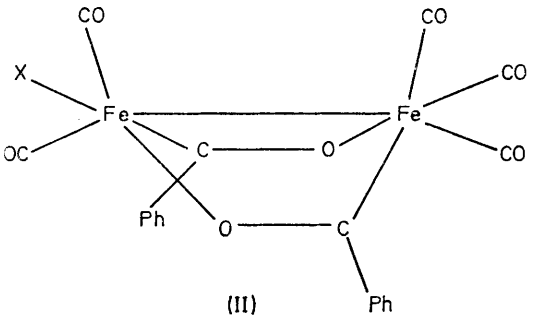


FIGURE 2 Mössbauer spectrum of $[(CO)_3Fe(COPh)_2Fe(CO)_2NHEt_2]$

This, together with the fact that the parameters differ only slightly from one compound to another, shows that the structure of these three compounds is the same.

However, it is not clear whether or not the structure of the three substituted compounds is the same as in compound (I), as a structure like (II) would produce two different superimposed Mössbauer spectra as well, since the environments are different because of the introduction of the new ligand.



We believe that the Mössbauer data suggest that the basic structure has not changed. If the structure of the unsubstituted compound had the form shown (II; X = CO), since the two iron atoms would be indistinguishable, we would expect an isomer shift value intermediate between the two values found for compound (I) (if the rest of the structure remained unchanged), *i.e.* *ca.* 0·2 mm/s.

It is well established [5-8] that in iron complexes two main mechanisms affect the isomer shift: (*a*) in high-spin complexes where the *s* electron density in the 4*s* orbital is most important, *i.e.* the *s* electron density decreases with increasing tendency of the ligands to withdraw electrons from the iron atom, the isomer shift is increased and (*b*) in low-spin complexes, the main factor is the strength of the π-bonding between the central atom and the ligands. Strong π-bonding decreases the electron density in the metal *d* orbitals and hence the screening of the *s* electrons, which lowers the isomer shift. Simultaneously with this effect, there is a contribution to σ-bonding from the ligands, which has the opposite effect; withdrawal of electrons increases the isomer shift. We suppose, therefore, that replacement of carbon monoxide, a strong π-acceptor ligand, by ethylamine would have roughly the same effect as the replacement of nitrous oxide by ammonia in disodium pentacyanonitrosylferrate, which changes the isomer shift from 0 to 0·012 mm/s or as the change from trisodium hexacyanoferrate to trisodium pentacyanotriphenylphosphineferrate, where the change is from 0·136 to 0·235 mm/s.

However,[9] the change from pentacarbonyliron to pentacarbonyltriphenylphosphineiron changes the isomer shift (at 78 K) from 0·17 to 0·14 mm/s suggesting that forward co-ordination of σ electrons is more important, in this case, than back donation, as has already been suggested for $[Fe(CO)_4X]$ derivatives by Collins and Pettit.[9]

We expect, then, that a structure similar to (II) would have isomer shift values which do not differ by more than 0·100—0·150 mm/s from the mean value of 0·200, *i.e.* in the range 0·050—0·350 mm/s. The fact that the values found are outside this range suggests that the basic asymmetric structure found for compound (II) has not been altered by the substitution. The data for compounds with diethylamino-substituents (Table 2) show that replacement of the phenyl group by a diethylamino-group is much more important than the replacement of diethylamine by piperidine in spite of the fact that the former are second-order neighbours to the iron atom. From this consideration and from the fact that the spectra of the two different iron atoms are differently affected by the changes, and, with the hypothesis that the more strongly affected doublet is the one corresponding to the iron atom where the substitution takes place, we conclude that replacement takes place at the site at which the amine is substituted for the phenyl group, *i.e.* the iron atom bonded to the two carbon atoms of the carbon monoxide groups. In consequence in structure (I) and Table 2 we have adopted for the iron atoms (and hence the isomer shift and quadrupole splitting) the same notation as in ref. 2.

CONCLUSIONS

(i) Our argument is based on the fact that we know where the substitution of the amino- for phenyl group takes place, *i.e.* information which does not originate from Mössbauer effect data.

(ii) It can be argued that the variation in the isomer shift values for the two iron atoms when passing from the diethylamino-(phenyl) to the bis(diethylamino)-derivative is not large enough to decide which atom has been affected. In this case the variation of the quadrupole splitting is of help, as there is a significant difference in behaviour.

(iii) There seems to be an anomaly in the data, because when passing from the diethylamino(phenyl)-compound to the phenyl-piperidyl compound the change in isomer shift is apparently larger for the iron atom where we suppose that substitution has not taken place. Nevertheless, the fact that this discrepancy is in the range of experimental error and that the quadrupole splitting values are substantially the same, suggest that our interpretation is correct.

(iv) The data of Table 2 show that the values of the parameters of both iron atoms are highly affected by the different substitution. This should not be surprising because of the iron–iron bond which undoubtedly exists in these compounds which arises through the overlapping of *d* orbitals.

(v) It is surprising that an increase in isomer shift at

[5] V. I. Goldanskii and R. H. Herber, Chemical Applications of Mössbauer Spectroscopy, Academic Press, London, 1968.
[6] J. Danon, Technical Reports Series No. 50, International Atomic Energy Agency, Vienna, 1966.
[7] E. Konig, S. Hufner, E. Steichele, and K. Madeja, *Z. Naturforsch.*, 1967, **22a**, 1543.
[8] I. F. Duncan and R. M. Golding, *Quart. Rev.*, 1965, **19**, 36.
[9] R. L. Collins and R. Pettit, *J. Chem. Phys.*, 1963, **39**, 3433.

one site is paralleled by a decrease at the other site. The replacement of carbon monoxide by diethylamine implies that the *d* electron density around Fe(2) increases, which delocalizes through the π-system to the carbon monoxide ligands on the other iron atom. To maintain the electrical balance, σ-bonding increases so that the isomer shift of the Fe(1) atom is lowered.

(vi) One might have expected on the basis of the *X*-ray data that substitution would have taken place at the Fe(1) atom, with a displacement of the axial carbon monoxide, which lies at a significantly larger distance from the iron atom and thus is bonded in a weaker way.

(vii) From the isomer shift values we favour the description as a benzoyl complex because the description as a oxyphenylcarbene complex implies a more ionic description of the Fe(1) atom which would tend to have a value closer to those for Fe^{2+} compounds and not be located in the lower range of the whole isomer shift scale.

(viii) We are aware of the controversial nature of parts of the present discussion, but in the light of the present knowledge of the systematics of Mössbauer effect data, this is the only way to tackle the problem with Mössbauer effect data alone.

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