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^{57}Fe MÖSSBAUER SPECTROSCOPIC STUDY OF SOME CLUSTERS RELATED TO $\text{Fe}_3(\text{CO})_{12}$

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Summary

The ^{57}Fe Mössbauer spectra of $\text{Fe}_3(\text{CO})_{12}$ -related clusters $[\text{Fe}_3(\text{CO})_{11}]^{2-}$, $[\text{Fe}_2\text{Ru}(\text{CO})_{12}]$, $[\text{FeRu}_2(\text{CO})_{12}]$, $[\text{Fe}_3(\text{CO})_{11}\text{PPh}_3]$, $[\text{Fe}_3(\text{CO})_{11}\text{PPh}_2\text{Me}]$, $[\text{Fe}_3(\text{CO})_{11}\text{PPhMe}_2]$, $[\text{Fe}_3(\text{CO})_9(\text{PPh}_2\text{Me})_3]$, $[\text{Fe}_2\text{Ru}(\text{CO})_{11}\text{P(OMe)}_3]$, $[\text{FeRu}_2(\text{CO})_{11}\text{PPh}_3]$ and $[\text{FeRu}_2(\text{CO})_{10}(\text{PPh}_3)_2]$ have been recorded at 78 K. The data are compared with published data for other M_3 clusters.

Generally, the isomer shifts (δ) fall within a narrow range, for example with compounds containing Fe or Fe and Ru and four or five CO ligands per metal, all δ values lie between 0.29 and 0.36 mm s^{-1} even though the ligands may be terminal, doubly bridging or triply bridging. Values of quadrupole splitting (Δ) are much more susceptible to changes in the Fe environment, for example the $\text{Fe}(\text{CO})_4$ sites have Δ values from about zero $\{\text{Fe}(\text{CO})_4^{\text{I}}$ in $[\text{Fe}_3(\text{CO})_{12}]\}$ to 1.52 $\{\text{Fe}(\text{CO})_3^{\text{I}}\text{CO}^{\text{Ibr}}$ in $[\text{Fe}_3(\text{CO})_{11}]^{2-}\}$. The quadrupole splitting of the Fe site in $[\text{FeRu}_2(\text{CO})_{12}]$ (0.77 mm s^{-1}) clearly indicates that the structure of this cluster is not exactly similar to that of $[\text{Ru}_3(\text{CO})_{12}]$. Substitution of CO by phosphine in general leads to small changes in δ and Δ if the geometry of the Fe site is unaltered. However, Δ especially can be affected if phosphine substitution causes changes in geometry or if there is multiple substitution.

Introduction

As part of a continuing programme of investigations into iron cluster chemistry [1], we have measured the Mössbauer spectra of a series of Fe_3 -based clusters. The compounds include some phosphine derivatives of $[\text{Fe}_3(\text{CO})_{12}]$, mixed Fe-Ru clusters and some of their phosphine derivatives. Also, we have reassessed the Mössbauer spectrum of $[\text{Fe}_3(\text{CO})_{11}]^{2-}$ since the one published [2] did not appear to be consistent with the known solid state structure of this dianion. All of the systems reported are of the *arachno* three cluster atom type e.g. $[\text{M}_3(\text{CO})_{12}]$. Compounds based on four cluster atoms e.g. $[\text{Fe}_4(\text{CO})_{13}]^{2-}$, $[\text{Fe}_3(\text{O})(\text{CO})_9]^{2-}$, $[\text{Fe}_2\text{Se}_2(\text{CO})_9]$, $[\text{Fe}_4(\text{C})(\text{CO})_{12}]^{2-}$, etc., will be discussed in a later paper. Many of the compounds reported here have been characterised using X-ray crystallography. The structural data obtained by this technique is particularly valuable to the present study where the major objective is to correlate Mössbauer parameters for chemical isomer shift (δ) and quadrupole splitting (Δ) with the ligand environment of each iron site.

Results and discussion

(A) $[\text{Fe}_3(\text{CO})_{12}]$, $[\text{Fe}_3(\text{H})(\text{CO})_{11}]^-$, and $[\text{Fe}_3(\text{CO})_{11}]^{2-}$

The full X-ray crystallographically determined molecular structure of $[\text{Fe}_3(\text{CO})_{12}]$ (Fig. 1) was reported in 1969 [3]. Previously, many attempts had been made to deduce the probable structure from infrared and Mössbauer spectra. In agreement with previous studies [4], the Mössbauer spectrum shows three clear lines (Table 1) which correlate with two different iron sites. The outer pair of lines (δ 0.36, Δ 1.11, Γ 0.23 mm s^{-1}) are due to the CO bridged $\text{Fe}(\text{CO})_3(\text{CO})_2^b$ sites and the inner, broader, line (δ 0.30, Δ 0.08, Γ 0.38 mm s^{-1}) is due to the unique $\text{Fe}(\text{CO})_4^a$ site. The latter has the iron atom in a virtually octahedral environment with the local symmetry approaching C_{2v} . As has been pointed out previously, this is expected to give rise to a small quadrupole splitting [5] i.e. approaching zero. Values of Δ have been variously reported as being between "about zero" to 0.13 mm s^{-1} . The value obtained in the present work was 0.08 mm s^{-1} .

The spectrum of $[\text{Fe}_3(\text{H})(\text{CO})_{11}]^-$, was reported [6] to be very similar to that for $[\text{Fe}_3(\text{CO})_{12}]$ with unique iron site parameters δ 0.30 and Δ 0.13 mm s^{-1} and for the

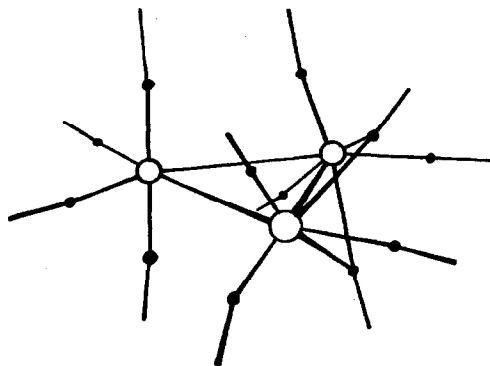


Fig. 1. Molecular structure of $\text{Fe}_3(\text{CO})_{12}$.

TABLE 1

 ^{57}Fe MÖSSBAUER SPECTRA PARAMETERS FOR M_3 CLUSTERS (mm s^{-1})

Compound	Site ^a	Isomer shift (δ)	Quadrupole splitting (Δ)	Peak width at half-height (Γ)
$\text{Fe}_3(\text{CO})_{12}$	$\text{Fe}(\text{CO})_4^{\text{t}}$	0.30	0.08	0.38
	$\text{Fe}(\text{CO})_3^{\text{t}}(\text{CO})_2^{\text{br}}$	0.36	1.11	0.23
$[\text{Fe}(\text{H})(\text{CO})_{11}]^-$	$\text{Fe}(\text{CO})_4^{\text{t}}$	0.30	0.14	0.25
	$\text{Fe}(\text{CO})_3^{\text{t}}(\text{CO})_2^{\text{br}}(\text{H})^{\text{br}}$	0.32	1.36	0.30
$[\text{Fe}_3(\text{CO})_{11}]^{2-}$	$\text{Fe}(\text{CO})_3^{\text{t}}(\text{CO})_2^{\text{tbr}}$	0.30	1.52	0.24
	$\text{Fe}(\text{CO})_3^{\text{t}}(\text{CO})_2^{\text{tbr}}(\text{CO})^{\text{br}}$	0.32	1.12	0.25
$\text{Fe}_2\text{Ru}(\text{CO})_{12}$	—	0.33	1.04	0.25
$\text{FeRu}_2(\text{CO})_{12}$	—	0.29	0.77	0.28
$[\text{Fe}_2\text{Mn}(\text{CO})_{12}]^-$ ^e	—	0.33	0.93	—
$\text{Fe}_3(\text{CO})_{11}\text{PPh}_3$ ^b	$\text{Fe}(\text{CO})_4^{\text{t}}$	0.30	0.0	0.42
	$\text{Fe}(\text{CO})_3^{\text{t}}\text{PPh}_3$	—	—	—
	$\text{Fe}(\text{CO})_3^{\text{t}}(\text{CO})_2^{\text{br}}$	0.38	1.27	0.26
	$\text{Fe}(\text{CO})_2^{\text{t}}\text{PPh}_3(\text{CO})_2^{\text{br}}$	—	—	—
$\text{Fe}_3(\text{CO})_{11}\text{PPh}_2\text{Me}$ ^b	$\text{Fe}(\text{CO})_4^{\text{t}}$	0.30	0.0	0.41
	$\text{Fe}(\text{CO})_3^{\text{t}}\text{PPh}_2\text{Me}$	—	—	—
	$\text{Fe}(\text{CO})_3^{\text{t}}(\text{CO})_2^{\text{br}}$	0.37	1.25	0.25
	$\text{Fe}(\text{CO})_2^{\text{t}}\text{PPh}_2\text{Me}(\text{CO})_2^{\text{br}}$	—	—	—
$\text{Fe}_3(\text{CO})_{11}\text{PMe}_2\text{Ph}$ ^b	$\text{Fe}(\text{CO})_4^{\text{t}}$	0.27	0.0	0.43
	$\text{Fe}(\text{CO})_3^{\text{t}}\text{PMe}_2\text{Ph}$	—	—	—
	$\text{Fe}(\text{CO})_3^{\text{t}}(\text{CO})_2^{\text{br}}$	0.34	1.21	0.29
	$\text{Fe}(\text{CO})_2^{\text{t}}\text{PMe}_2\text{Ph}(\text{CO})_2^{\text{br}}$	—	—	—
$\text{Fe}_3(\text{CO})_9(\text{PPh}_2\text{Me})_3$	$\text{Fe}(\text{CO})_3^{\text{t}}\text{PPh}_2\text{Me}$	0.31	0.38	0.28
	$\text{Fe}(\text{CO})_2^{\text{t}}\text{PPh}_2\text{Me}(\text{CO})_2^{\text{br}}$	0.35	1.09	0.30
$\text{Fe}_3(\text{CO})_9\text{PMe}_2\text{Ph}_3$ ^f	$\text{Fe}(\text{CO})_3^{\text{t}}\text{PMe}_2\text{Ph}$	0.28	0.57	—
	$\text{Fe}(\text{CO})_2^{\text{t}}\text{PMe}_2\text{Ph}(\text{CO})_2^{\text{br}}$	0.30	1.13	—
$\text{Fe}_2\text{Ru}(\text{CO})_{11}\text{P}(\text{OMe})_3$	$\text{Fe}(\text{CO})_3^{\text{t}}(\text{CO})_2^{\text{br}}$	0.27	0.97	0.30
$\text{FeRu}_2(\text{CO})_{11}\text{PPh}_3$ ^c	$\text{Fe}(\text{CO})_4^{\text{t}}$	0.26	0.91	0.31
$\text{FeRu}_2(\text{CO})_{10}(\text{PPh}_3)_2$	$\text{Fe}(\text{CO})_2^{\text{t}}(\text{CO})_2^{\text{br}}$	0.26	0.95	0.28
$[\text{Fe}_2\text{Mn}(\text{CO})_{11}\text{PPh}_3]^-$ ^e	$\text{Fe}(\text{CO})_3^{\text{t}}(\text{CO})_2^{\text{br}}$	0.35	0.81	—
	$\text{Fe}(\text{CO})_2^{\text{t}}\text{PPh}_3(\text{CO})_2^{\text{br}}$	0.34	1.07	—
$\text{Fe}_2\text{Co}(\text{CO})_9(\text{C}_5\text{H}_5)$ ^g	$\text{Fe}(\text{CO})_4^{\text{t}}$	0.27	0.43	—
	$\text{Fe}(\text{CO})_3^{\text{t}}(\text{CO})_2^{\text{br}}$	0.35	1.01	—
$\text{Fe}_2\text{Rh}(\text{CO})_9(\text{C}_5\text{H}_5)$ ^{d,g}	$\text{Fe}(\text{CO})_3^{\text{t}}(\text{CO})_2^{\text{br}}$	0.25	1.04	—
$\text{FeRh}_2(\text{CO})_6(\text{C}_5\text{H}_5)_2$ ^{d,g}	$\text{Fe}(\text{CO})_3^{\text{t}}(\text{CO})_2^{\text{tbr}}$	0.24	1.05	—
$\text{FeNi}_2(\text{CO})_5(\text{C}_5\text{H}_5)_2$ ^h	$\text{Fe}(\text{CO})_3^{\text{t}}(\text{CO})_2^{\text{tbr}}$	0.30	1.10	0.34
$\text{Fe}_3(\text{CO})_{10}(\text{ffars})$ ⁱ	$\text{Fe}(\text{CO})_4^{\text{t}}$	0.28	0.0	0.38
	$\text{Fe}(\text{CO})_2^{\text{t}}(\text{As}')(\text{CO})_2^{\text{br}}$	0.42	1.52	0.23
$\text{Fe}_3(\text{H})(\text{CO})_{10}(\text{CNMe}_2)$ ^j	$\text{Fe}(\text{CO})_4^{\text{t}}$	0.30	0.16	0.24
	$\text{Fe}(\text{CO})_3^{\text{t}}\text{H}^{\text{br}}(\text{CNMe}_2)^{\text{br}}$	0.22	0.94	0.24

^a t = terminal, br = doubly bridging, tbr = triply bridging. ^b Samples contain two isomers, values of $\Delta = 0.0$ signify the lines are not resolved. ^c Fe site has weakly semibridging CO's. ^d Spectra reported at 293 K. ^e See Ref. 13. ^f See Ref. 15. ^g See Ref. 12. ^h See Ref. 16. ⁱ See Ref. 17. ^j See Ref. 18.

H-bridged sites, δ 0.32 and Δ 1.41 mm s^{-1} . The present study produced corresponding results δ 0.30, Δ 0.14 and δ 0.32, Δ 1.36 mm s^{-1} in very good agreement with the previous data. A comparison of the local environments of the iron atoms in $[\text{Fe}_3(\text{CO})_{12}]$ and $[\text{Fe}_3(\text{H})(\text{CO})_{11}]^-$ (Fig. 2) [7] reveals that although they are basically very similar, there are several differences worthy of comment. For example, the unique iron in $[\text{Fe}_3(\text{CO})_{12}]$ has CO ligands axial to the Fe_3 triangle which make a

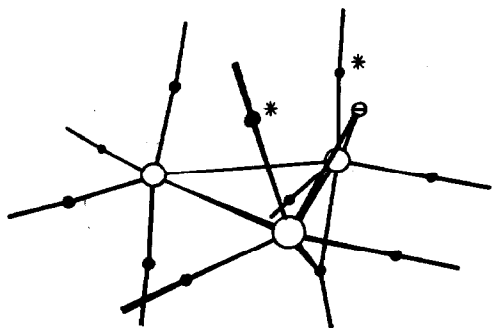


Fig. 2. Molecular structure of $[\text{Fe}_3(\text{H})(\text{CO})_{11}]^-$.

CFeC bond angle of $172.1(7)^\circ$ and corresponding CFeFe angles of $86.6 \pm 3.4^\circ$ [3]. The related values for the $[\text{Fe}_3(\text{H})(\text{CO})_{11}]^-$ compound are a CFeC angle of $167.6(5)^\circ$ and two CFeFe angles, one of $92.6 \pm 1.0^\circ$ for the axial CO ligand *trans* to the bridging H and the other $76.7 \pm 0.4^\circ$ for the CO ligand *trans* to bridging CO. Thus one of the axial CO ligands has tipped slightly ($\sim 10^\circ$) towards the bridged Fe–Fe bond and somewhat reduced the almost octahedral local environment of the unique Fe site. Hence the quadrupole splitting has slightly increased. Likewise there are some minor differences in the geometries of the bridged Fe sites which may be related to the smaller steric requirements of the bridging H ligand compared to μ -CO. For instance the angle $\text{FeFe}_{\text{br}}\text{H}$ is $90.5 \pm 0.5^\circ$ and $\text{FeFe}_{\text{br}}\text{C}$ for the terminal CO ligand which is attached to a bridged Fe site (Fe_{br}) and is nearest H and the unique iron site is $98.1 \pm 0.5^\circ$ whereas in $[\text{Fe}_3(\text{CO})_{12}]$ $\text{FeFe}_{\text{br}}\text{C}_{\text{br}}$ is $87.2 \pm 2.7^\circ$ but $\text{FeFe}_{\text{br}}\text{C}$ for the terminal CO ligand nearest CO bridging and the unique iron site is $81.8 \pm 2.3^\circ$. Thus the terminal CO group nearest H and the unique iron site (CO^* in Fig. 2) has twisted away from the Fe_3 triangle and is closer to the H bridging site compared with the equivalent CO group in $[\text{Fe}_3(\text{CO})_{12}]$. Overall, the numerous subtle changes in the environments of the bridged Fe sites leads to an increase in Δ from 1.11 in $[\text{Fe}_3(\text{CO})_{12}]$ to 1.36 mm s^{-1} in the hydride.

A correlation has been made previously [4,8] between δ and “localised” negative charges in a series of comparable compounds. As the compounds become more reduced e.g. $[\text{Fe}_3(\text{CO})_{12}]$, $[\text{Fe}(\text{H})(\text{CO})_{11}]^-$, $[\text{Fe}_3(\text{CO})_{11}]^{2-}$, the sites most associated with an increase in negative charge would be expected to exhibit a greater reduction in their δ values. Hence, since the bridged sites in $[\text{Fe}_3(\text{H})(\text{CO})_{11}]^-$ show more reduction in δ (0.32 compared with 0.36 mm s^{-1}) than the unique site it can be argued that the negative charge is localised more on the bridged sites.

The dianion $[\text{Fe}_3(\text{CO})_{11}]^{2-}$ contains a very distorted unique iron site compared to either $[\text{Fe}_3(\text{H})(\text{CO})_{11}]^-$ or $[\text{Fe}_3(\text{CO})_{12}]$. An axial CO ligand on the unique iron has tipped so far towards the other iron atoms as to have become a triply bridging CO ligand [9] (Fig. 3). The other three carbonyl ligands remain terminal but the CFeC angles have increased to $\sim 100^\circ$. The doubly bridging CO group is located almost directly below the bridged Fe–Fe bond.

A previously reported spectrum of $[\text{Fe}_3(\text{CO})_{11}]^{2-}$ as the $[\text{Fe}(\text{en})_3]^{2+}$ salt showed two doublets, one due to the cation and the other ($\delta = 0.16$, $\Delta = 2.11 \text{ mm s}^{-1}$) assigned to the anion [2]. This study was completed before the X-ray analysis and it

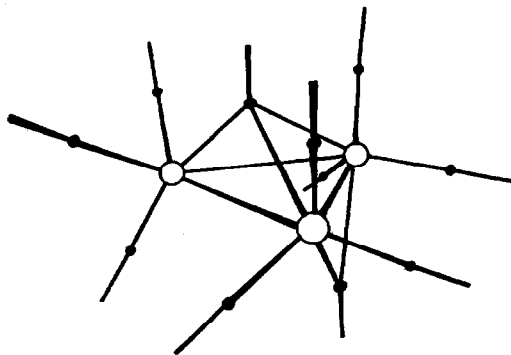


Fig. 3. Molecular structure of $[\text{Fe}_3(\text{CO})_{11}]^{2-}$.

was thought that the dianion contained two triply bridging CO ligands. The present spectrum of the tetraethylammonium salt (Fig. 4) shows a pair of partly resolved doublets in the ratio (1/2)/(2/1). The outer pair (δ 0.30, Δ 1.52 mm s⁻¹) are assigned to the unique iron site and the inner pair (δ 0.32, Δ 1.12 mm s⁻¹) to the two equivalent iron sites. This assignment is consistent with the known structure (Fig. 3) of the $[\text{Et}_4\text{N}]^+$ salt [9], and with the highly distorted unique iron site. From

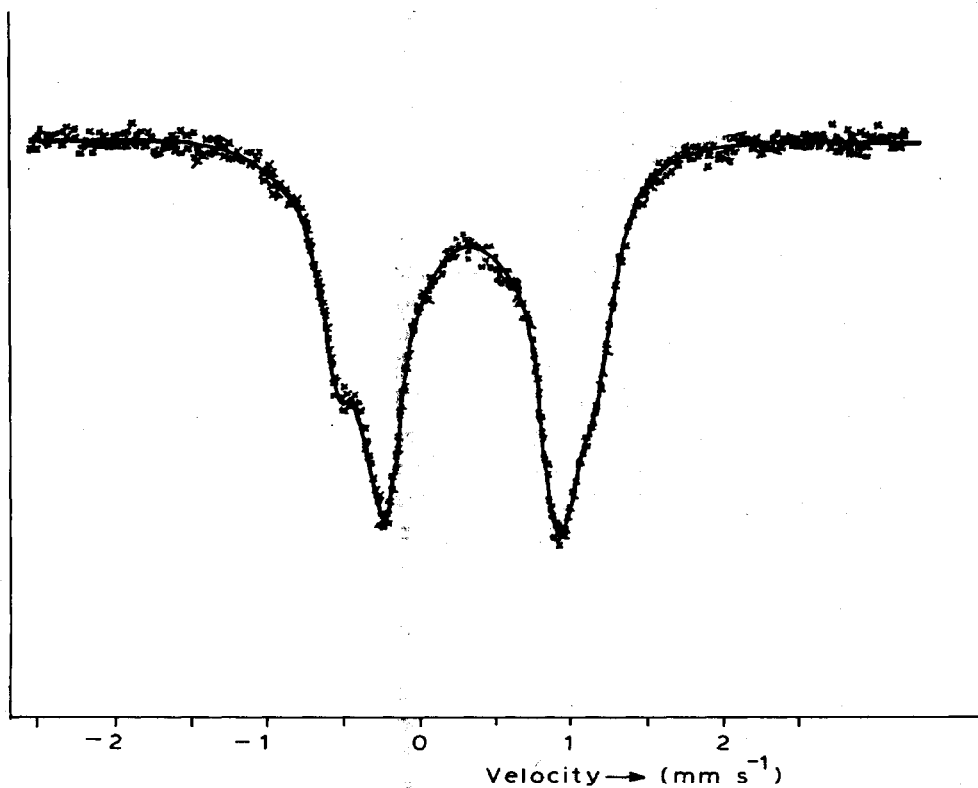


Fig. 4. Mössbauer spectrum of $[\text{Fe}_3(\text{CO})_{11}]^{2-}$.

the data given by Farmery et al. [2] it would seem likely that the spectrum recorded previously as $[\text{Fe}_3(\text{CO})_{11}]^{2-}$ was that of $[\text{Fe}_2(\text{CO})_8]^{2-}$ (δ 0.16, Δ 2.20 mm s⁻¹) rather than the triiron cluster.

Since the dianion is more "reduced" than either the neutral or monoanionic clusters, a reduction in δ values would be expected although it is not immediately clear which sites would be the more affected. In the event the δ values are the same as those for the monoanion.

From the results on the three compounds so far discussed it would appear that there is a simple trend in Δ values for the unique iron site which increases as the site becomes more distorted from an idealised local octahedral geometry. It was decided to investigate the possible relationship between Δ and the asymmetry parameter η calculated using a simple point charge model [4,5]. Structural data were taken from the published X-ray analyses [3,7,9] and it was assumed as a first approximation that all CO ligands had an equivalent point charge (q_{CO}) and similarly all non-unique iron sites had equivalent point charges (q_{Fe}). For $[\text{Fe}_3(\text{CO})_{12}]$ the calculated η was close to zero but no obvious correlation could be found for the other compounds. Hence the recorded variations of Δ could not be understood in terms of a simple "symmetry effect".

(B) Iron-ruthenium clusters

The compound formed by replacing one Fe atom in $[\text{Fe}_3(\text{CO})_{12}]$ by Ru has been assumed to adopt the $[\text{Fe}_3(\text{CO})_{12}]$ structure with two $\text{Fe}(\text{CO})_3^t(\text{CO})_2^b$ sites [10]. Replacement of two Fe atoms to give $[\text{FeRu}_2(\text{CO})_{12}]$ has been suggested to produce a non-bridged structure like $[\text{Ru}_3(\text{CO})_{12}]$ [10]. Crystallographic disorder precluded a complete X-ray analysis of either of these structures but phosphine substituted compounds have been studied [11]. The Mössbauer spectrum of $[\text{Fe}_2\text{Ru}(\text{CO})_{12}]$ showed one doublet (δ 0.33; Δ 1.04 mm s⁻¹) with parameters close to those for the $\text{Fe}(\text{CO})_3^t(\text{CO})_2^b$ site in $[\text{Fe}_3(\text{CO})_{12}]$. This may be taken as strong supporting evidence for the previously proposed structure for $[\text{Fe}_2\text{Ru}(\text{CO})_{12}]$. The replacement of Fe by Ru would be expected to lead to very small changes in δ and Δ , an effect which has been previously noted in other compounds where Fe was replaced by Co or Rh [12], or Mn [13], (Table 1).

The spectrum of $[\text{FeRu}_2(\text{CO})_{12}]$ showed only one doublet with δ 0.29, Δ 0.77 mm s⁻¹. Although the isomer shift was similar to that for the $\text{Fe}(\text{CO})_4^t$ site in $[\text{Fe}_3(\text{CO})_{12}]$, the quadrupole splitting had increased considerably from the $\text{Fe}(\text{CO})_4^t$ value of 0.08 mm s⁻¹ (Table 1). This suggests that the Fe site in $[\text{FeRu}_2(\text{CO})_{12}]$ is much more distorted from the essentially octahedral environment of $[\text{Fe}_3(\text{CO})_{12}]$. Some evidence in support of this suggestion comes from the X-ray study of the ruthenium substituted phosphine derivative $[\text{FeRu}_2(\text{CO})_{11}(\text{PPh}_3)]$ [11]. In this compound the Fe atom became involved in weak semi-bridging CO interactions with Ru atoms and the $\text{Fe}(\text{CO})_4$ group was twisted so that the equatorial CO ligands on Fe were no longer in the plane containing the Ru_2Fe triangle, (vide infra, Fig. 8). A similar situation may have arisen in the compound $[\text{Fe}_2\text{Co}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_9]$ where one Fe atom was suggested to be $\text{Fe}(\text{CO})_3^t(\text{CO})_2^b$ (δ 0.35; Δ 1.01 mm s⁻¹) but the other iron site (δ 0.27; Δ 0.43 mm s⁻¹) [12], had a Δ value which was much larger than expected (Table 1).

(C) Phosphine and phosphite substituted compounds

For the present study three phosphine substituted derivatives $[\text{Fe}_3(\text{CO})_{11}(\text{PR}_2\text{R}^1)]$

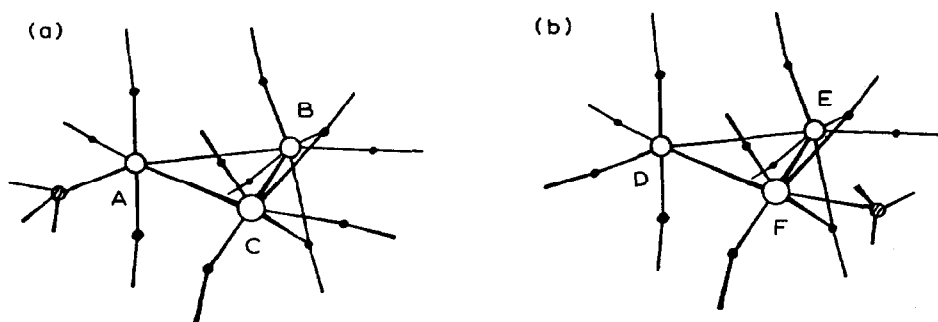


Fig. 5. Molecular structure of $[\text{Fe}_3(\text{CO})_{11}\text{PPh}_3]$. PPh_3 substituted on (a) unique Fe atom and (b) on a bridging Fe atom.

were prepared ($\text{R} = \text{R}^1 = \text{Ph}$; $\text{R} = \text{Ph}$, $\text{R}^1 = \text{Me}$; $\text{R} = \text{Me}$, $\text{R}^1 = \text{Ph}$). The PPh_3 derivative has been shown to exist as two isomeric forms in the same crystal [14] with the isomers in equal amounts. The basic structures of the isomers are very similar to $[\text{Fe}_3(\text{CO})_{12}]$ with PPh_3 replacing either an equatorial CO on the unique Fe (Fig. 5a) or the terminal CO which was opposite the $\text{Fe}(\text{unique}) - \text{Fe}(\text{equivalent})$ bond (Fig. 5b). Provided the resolution of the spectrum was adequate, six different sites (A to F, Figs. 5a, b) could be anticipated in a sample of $[\text{Fe}_3(\text{CO})_{11}(\text{PPh}_3)]$. However, previous work on phosphine derivatives of $[\text{Fe}(\text{CO})_5]$ has shown that δ and Δ values change only slightly with single substitution [4,5] and hence it was unlikely that these sites would be resolved. The spectrum of $[\text{Fe}_3(\text{CO})_{11}(\text{PPh}_3)]$ resembled that of $[\text{Fe}_3(\text{CO})_{12}]$ but the lines were distinctly broadened. Similar results were obtained with the other phosphine derivatives $[\text{Fe}_3(\text{CO})_{11}(\text{PPh}_2\text{Me})]$ and $[\text{Fe}_3(\text{CO})_{11}(\text{PPhMe}_2)]$ (Table 1). Clearly all three phosphine derivatives are structurally similar to $[\text{Fe}_3(\text{CO})_{12}]$ and the single substitution of CO^t by PR_2R^1 does not appear to alter the Mössbauer parameters of the sites greatly.

The molecular structure and Mössbauer spectrum of $[\text{Fe}_3(\text{CO})_9(\text{PPhMe}_2)_3]$ have been reported by McDonald et al. [15]. The structure (Fig. 6) contains one phosphine ligand per iron with the P atoms approximately in the plane of the Fe_3

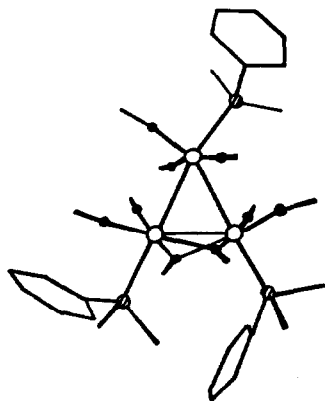


Fig. 6. Molecular structure of $[\text{Fe}_3(\text{CO})_9(\text{PPhMe}_2)_3]$.

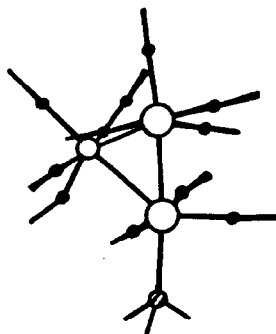


Fig. 7. Molecular structure of $[\text{Fe}_2\text{Ru}(\text{CO})_{11}\text{P}(\text{OMe})_3]$.

triangle. The Mössbauer parameters for the unique iron site and the bridged iron sites were (δ 0.28 and Δ 0.57, and δ 0.30 and Δ 1.13 mm s^{-1}) respectively. Thus the bridged sites were similar to the $\text{Fe}(\text{CO})_3^{\text{I}}(\text{CO})_2^{\text{b}}$ sites in $[\text{Fe}_3(\text{CO})_{12}]$ but the unique site has a much larger quadrupole splitting than the $\text{Fe}(\text{CO})_4^{\text{I}}$ site. To account for this the authors suggested that the unique Fe atom had a more easily distortable charge cloud and was more susceptible to changes in ligand character. In the light of the results for the mono-substituted compounds discussed above, it would appear unlikely that the effects which caused the relatively large increase in quadrupole splitting were solely due to distortion of the charge cloud at the unique Fe site by phosphine substitution at this site alone. There is a clear indication that the increased Δ value was partly caused by changes associated with the di-substitution of the bridged Fe sites.

The tri-substituted compound $[\text{Fe}_3(\text{CO})_9(\text{PPh}_2\text{Me})_3]$ showed a spectrum which was consistent with a structure which was analogous with $[\text{Fe}_3(\text{CO})_9(\text{PPhMe}_2)_3]$, (Table 1). Again the quadrupole splitting (Δ 0.38 mm s^{-1}) for the unique iron site had increased more than that at the bridged sites (Δ 1.09 mm s^{-1}).

Several substituted iron-ruthenium compounds have been reported. X-ray crystallographic studies of $[\text{Fe}_2\text{Ru}(\text{CO})_{11}\{\text{P}(\text{OMe})_3\}]$, $[\text{FeRu}_2(\text{CO})_{11}(\text{PPh}_3)]$, and $[\text{FeRu}_2(\text{CO})_{10}(\text{PPh}_3)_2]$ have shown that substitutions occur only at Ru [11]. The phosphite derivative (Fig. 7) had a similar structure to $[\text{Fe}_3(\text{CO})_{12}]$ and $[\text{Fe}_3(\text{CO})_{11}(\text{PPh}_3)]$. The Mössbauer spectrum showed one doublet (δ 0.27; Δ 0.97 mm s^{-1}) i.e. with parameters close to those for the bridged sites in $[\text{Fe}_3(\text{CO})_{12}]$, and $[\text{Fe}_2\text{Ru}(\text{CO})_{12}]$ (Table 1). The peak width at half height (Γ 0.37 mm s^{-1}) was notably broader than that of the bridged sites in the dodecacarbonyls and this suggests that the sites were in very slightly different environments which gave rise to overlapping spectra. This would correlate with the observed structure where one of the sites is adjacent to the $\text{P}(\text{OMe})_3$ ligand and the other is opposite (Fig. 7).

The structure of $[\text{FeRu}_2(\text{CO})_{11}(\text{PPh}_3)]$ (Fig. 8) showed that the four carbonyl ligands attached to Fe were not strictly axial or equatorial like those found in the $\text{Fe}(\text{CO})_4^{\text{I}}$ unit of $[\text{Fe}_3(\text{CO})_{12}]$. Instead, the $\text{Fe}(\text{CO})_4$ unit had been twisted with respect to the plane containing the FeRu_2 triangle. Furthermore the observed bending of several of the CO ligands towards the Ru atoms suggested a tendency to the formation of weak semi-bridging CO ligands [11]. Therefore the $\text{Fe}(\text{CO})_4$ group was in a more distorted environment in $[\text{FeRu}_2(\text{CO})_{11}(\text{PPh}_3)]$ than in $[\text{Fe}_3(\text{CO})_{12}]$.

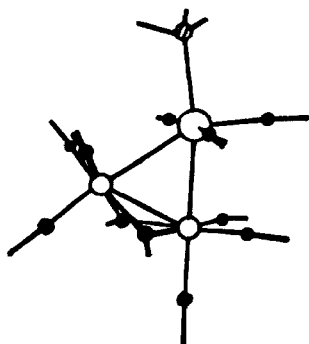


Fig. 8. Molecular structure of $[\text{FeRu}_2(\text{CO})_{11}\text{PPh}_3]$.

and this was confirmed by the Mössbauer spectrum (δ 0.26; Δ 0.91 mm s^{-1}). In the series $[\text{Fe}_3(\text{CO})_{12}]$, $[\text{FeRu}_2(\text{CO})_{12}]$ and $[\text{FeRu}_2(\text{CO})_{11}(\text{PPh}_3)]$ there is an increasing distortion at the $\text{Fe}(\text{CO})_4$ site as demonstrated in the Δ values (0.08, 0.77, 0.91 mm s^{-1}) and the solid state structures are clearly not exactly the same.

Substitution of two carbonyls of $[\text{FeRu}_2(\text{CO})_{12}]$ to give $[\text{FeRu}_2(\text{CO})_{10}(\text{PPh}_3)_2]$ changes the $\text{Fe}(\text{CO})_4$ -site structure considerably (Fig. 9). The iron atom becomes bonded to the Ru atoms via two unsymmetrical CO bridging ligands. The Mössbauer parameters for the $\text{Fe}(\text{CO})_2'(\text{CO})_2''$ site are (δ 0.26; Δ 0.95 mm s^{-1}), close to those for the mono-substituted compound. However, other aspects of the structure of $[\text{FeRu}_2(\text{CO})_{10}(\text{PPh}_3)_2]$ lead to the conclusion that the phosphine disubstitution has considerably changed the electronic environments of all the metal atoms. For example the Ru-Fe bond length increased by 0.12 Å and the Ru-Ru bond contracted by 0.03 Å compared with the value for the mono-substituted compound [11]. Unfortunately it is therefore not possible to offer any further analysis of the factors affecting the quadrupole splitting without recourse to a reliable and accurate molecular calculation for these compounds.

Conclusions

The relative insensitivity of δ to Fe site geometry, type and number of ligands is noteworthy. The range of δ values for all the compounds in Table 1 is 0.22 to 0.42 mm s^{-1} and indeed these particular limiting values were the ones previously

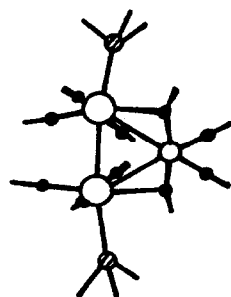


Fig. 9. Molecular structure of $[\text{FeRu}_2(\text{CO})_{10}(\text{PPh}_3)_2]$.

observed for the bridged Fe sites in $[\text{Fe}_3(\text{H})(\text{CO})_{10}(\text{CNMe}_2)]$ and $[\text{Fe}_3(\text{CO})_{10}(\text{ffars})]$ respectively [4]. For compounds containing CO or phosphine ligands only, the range of δ values is 0.26 to 0.38 mm s^{-1} whilst for iron or iron-ruthenium cluster with only CO ligands the range is 0.29 to 0.36 mm s^{-1} .

The quadrupole splitting parameter Δ can show considerable variation with Fe site geometry. This is particularly the case for $\text{Fe}(\text{CO})_4$ sites where the geometry around the Fe atom changes from close to octahedral in $[\text{Fe}_3(\text{CO})_{12}]$ (0.08 mm s^{-1}) through slightly distorted octahedral in $[\text{Fe}_3(\text{H})(\text{CO})_{11}]^-$ (0.14 mm s^{-1}) and an out of M_3 -plane "twisted" $\text{Fe}(\text{CO})_4^t$ (with some weak semi-bridging) in $[\text{FeRu}_2(\text{CO})_{11}\text{PPh}_3]$ (0.91 mm s^{-1}) to a $\text{Fe}(\text{CO})_2^t(\text{CO})_2^{\text{br}}$ site in $[\text{FeRu}_2(\text{CO})_{10}(\text{PPh}_3)_2]$ (0.95 mm s^{-1}) and finally a $\text{Fe}(\text{CO})_3^t(\text{CO})_2^{\text{br}}$ site in $[\text{Fe}_3(\text{CO})_{11}]^{2-}$ (1.52 mm s^{-1}). On the other hand the variation in Δ for $\text{Fe}(\text{CO})_3^t(\text{CO})_2^b$ sites is much less being from 0.81 mm s^{-1} in $[\text{Fe}_2\text{Mn}(\text{CO})_{11}\text{PPh}_3]^-$ to about 1.27 mm s^{-1} in $[\text{Fe}_3(\text{CO})_{11}\text{PPh}_3]$. Furthermore even replacing the doubly bridging CO ligands by H, CNMe_2 or a triply bridging CO group appears to have only a relatively minor effect on these sites. Clearly the possible variations in the geometries of the bridged Fe site are more limited compared to the unique Fe sites and hence the Δ values are more restricted.

In agreement with previous studies we find that the replacement of Fe by another metal (Ru) has little effect on the Mössbauer parameters for analogous sites. In the case of $[\text{Fe}_2\text{Ru}(\text{CO})_{12}]$ the Mössbauer spectrum supports the suggestion that the structure is like that of $[\text{Fe}_3(\text{CO})_{12}]$. Whereas the data for $[\text{FeRu}_2(\text{CO})_{12}]$ strongly suggests a structure unlike $[\text{Ru}_3(\text{CO})_{12}]$ but with either weak semibridging CO ligands attached to Fe or with a $\text{Fe}(\text{CO})_n$ unit twisted out of the plane containing the FeRu_2 atoms. Both effects have been reported in $[\text{FeRu}_2(\text{CO})_{11}\text{PPh}_3]$ [11].

The effects of replacing CO ligands by phosphines which are much weaker π acceptors are often complex and depend on the number of CO groups substituted. However, substitutions generally cause only minor changes in δ and Δ unless there are major changes in the other cluster ligand positions. This is illustrated by comparison of the data for $[\text{FeRu}_2(\text{CO})_{11}\text{PPh}_3]$ (δ 0.26, Δ 0.91 mm s^{-1}) and $[\text{FeRu}_2(\text{CO})_{10}(\text{PPh}_3)_2]$ (δ 0.26, Δ 0.95 mm s^{-1}) with the parameters of the unique Fe site in $[\text{Fe}_3(\text{CO})_{12}]$ (δ 0.30, Δ 0.08 mm s^{-1}).

Experimental

Mössbauer spectra. All spectra were recorded for polycrystalline powders at liquid nitrogen temperature (78 K) on a machine which has been described previously [19]. Data were recorded with a Canberra System 40 multichannel analyser and processed on Dec VAX 11/780 computer. Mössbauer parameters are referred to sodium nitroprusside as standard.

Preparation of clusters. The compounds $[\text{Fe}_3(\text{CO})_{12}]$ [20], $[\text{Fe}_2\text{Ru}(\text{CO})_{12}]$, and $[\text{FeRu}_2(\text{CO})_{12}]$ [10], $[\text{Fe}_3(\text{CO})_{11}]^{2-}$ [9], $[\text{Fe}_2\text{Ru}(\text{CO})_{11}\text{P}(\text{OMe})_3]$, $[\text{FeRu}_2(\text{CO})_{11}\text{PPh}_3]$ and $[\text{FeRu}_2(\text{CO})_{10}(\text{PPh}_3)_2]$ [11] were prepared according to literature methods. A sample of $[\text{Et}_4\text{N}][\text{Fe}_3(\text{H})(\text{CO})_{11}]$ was obtained from Alpha-Ventron Ltd. and used without further purification.

The phosphine substituted compounds $[\text{Fe}_3(\text{CO})_{11}\text{PPh}_3]$, $[\text{Fe}_3(\text{CO})_{11}\text{PPh}_2\text{Me}]$, and $[\text{Fe}_3(\text{CO})_{11}\text{PPhMe}_2]$ were prepared by the reaction of equimolar amounts of $[\text{Fe}_3(\text{CO})_{12}]$ and the phosphine in THF for 20 min at room temperature with a catalytic amount of a THF sodium diphenylketyl added [21]. The products were

separated by preparative TLC (silica, hexane/dichloromethane; 9/1) and identified by elemental analysis (C, H, Fe) and spectroscopy (MS and IR):

$[Fe_3(CO)_{11}PPh_3]$. Found: C, 47.43; H, 2.23; Fe, 22.40; calcd.: C, 47.20; H, 2.03; Fe, 22.70%. MS showed M^+ at m/z 754 [$^{56}Fe_3^{31}P^{16}O_{11}^{12}C_{29}^1H_{15}$]. IR (THF) 2090m, 2040, 2015vs, 1970sh, 1940m, 1830sh, 1785m.

$[Fe_3(CO)_{11}PPh_2Me]$. Found: C, 43.01; H, 2.22; Fe, 24.56; calcd.: C, 42.64; H, 1.91; Fe, 24.81%. MS showed M^+ at m/z 676 [$^{56}Fe_3^{31}P^{16}O_{11}^{12}C_{24}^1H_{13}$]. IR (THF) 2090m, 2040s, 2015vs, 1970sh, 1940sh, 1780s, 1730m.

$[Fe_3(CO)_{11}PPhMe_2]$. Found: C, 37.69; H, 2.19; Fe, 27.81; calcd.: C, 37.16; H, 1.83; Fe, 27.32%. MS showed M^+ at m/z 630 [$^{56}Fe_3^{31}P^{16}O_{11}^{12}C_{19}^1H_{11}$]. IR (THF) 2090m, 2040s, 2015vs, 1965sh, 1940m, 1830sh, 1780m.

The trisubstituted compound $[Fe_3(CO)_9(PPh_2Me)_3]$ was prepared in 1% yield from the reaction of $[Fe_3(CO)_{12}]$ and PPh_2Me in a 1/3 molar ratio as described above for $[Fe_3(CO)_{11}PPh_2Me]$. It was identified spectroscopically (IR and Mössbauer) by comparison with $[Fe_3(CO)_9(PPhMe_2)_3]$ [15]; IR (THF) 2049m, 1990s, 1935s, 1815m, 1775m.

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