

Preliminary communication

THE USE OF ^{57}Fe MÖSSBAUER SPECTROSCOPY IN ASSIGNING THE TYPES OF IRON CARBONYL UNITS PRESENT IN Fe-CONTAINING CLUSTERS

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Summary

Comparison of the ^{57}Fe Mössbauer spectra of series of related M_3 , M_4 and M_5 clusters has enabled correlations to be made between the Mössbauer parameters δ (isomer shift) and q (quadrupole splitting), and the type of iron site present, viz. $\text{Fe}(\text{CO})_n^t$, $\text{Fe}(\text{CO})_n^t(\text{CO})_m^{\text{br}}$ or $\text{Fe}(\text{CO})_n^t(\text{CO})_m^{\text{br}}\text{H}^{\text{br}}$ (t = terminal, br = bridging ligand).

We have been studying the use of ^{57}Fe Mössbauer spectroscopy to assign the various types of iron carbonyl units found in Fe-containing clusters [1]. In this communication we wish to report the results of some further measurements and to make some general observations for related series of compounds containing three, four, or five metal atoms. Previous work by Knight and Mays [2] had clearly established that Mössbauer spectroscopy could distinguish between $\text{Fe}(\text{CO})_4^t$ and $\text{Fe}(\text{CO})_3^t(\text{CO})_2^{\text{br}}$ sites (t = terminal, br = bridging ligands). In the compounds $[\text{Fe}_3(\text{CO})_{12}]$ (I), $[(\eta^5\text{-C}_5\text{H}_5)\text{CoFe}_2(\text{CO})_9]$ (II), $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})\text{-RhFe}_2(\text{CO})_8]$ (III) the quadrupole splittings (q) for $\text{Fe}(\text{CO})_3^t(\text{CO})_2^{\text{br}}$ units were $\approx 1.0 \text{ mm s}^{-1}$ in all cases, while those for $\text{Fe}(\text{CO})_4^t$ units were much lower, Table 1. This work also established that when iron was bonded to other metals there was little effect on q . Our previous work has suggested a possible correlation between cluster unit and q (and, to a lesser extent, the isomer shift, δ) [1]. In the case of Fe_5 -*nido* clusters, the sequence of q values varied as (highest) $\text{Fe}(\text{CO})_3^t$ apical $\approx \text{Fe}(\text{CO})_2^t(\text{CO})_2^{\text{br}} > \text{Fe}(\text{CO})_2^t(\text{CO})^{\text{br}}\text{H}^{\text{br}} \approx \text{Fe}(\text{CO})_2^t(\text{CO})^{\text{semi-br}} > \text{Fe}(\text{CO})_3^t$ basal $> \text{Fe}(\text{CO})_2^t(\text{CO})^{\text{br}}$. We have now extended this sequence to include M_4 -cluster compounds (IV to VII), Table 1, and the

TABLE 1
 MOSSBAUER PARAMETERS (mm s^{-1})^a

Compound	Assignment	δ Isomer shift	q Quadrupole splitting	Ref.
$\text{Fe}_3(\text{CO})_{12}$ (I)	$\text{Fe}(\text{CO})_3^t(\text{CO})_2^{\text{br}}$	0.30	0.98	2
	$\text{Fe}(\text{CO})_4^t$	0.22	0.0	
$(\eta^5\text{-C}_5\text{H}_5)\text{CoFe}_2(\text{CO})_9$ (II)	$\text{Fe}(\text{CO})_3^t(\text{CO})_2^{\text{br}}$	0.29	0.99	2
	$\text{Fe}(\text{CO})_4^t$	0.21	0.40	
$(\eta^5\text{-C}_5\text{H}_5)(\text{CO})\text{RhFe}_2(\text{CO})_8$ (III)	$\text{Fe}(\text{CO})_3^t(\text{CO})_2^{\text{br}}$	0.25	1.04	2
$\text{FeRu}_3\text{H}(\text{CO})_{12}\text{N}$ (IV)	$\text{Fe}(\text{CO})_3^t\text{H}^{\text{br}}$	0.20	0.99	This work
$\text{Fe}_4\text{H}(\text{CO})_{12}\text{N}$ (V)	$\text{Fe}(\text{CO})_3^t\text{H}^{\text{br}}$	0.15	1.01	This work
	$\text{Fe}(\text{CO})_3^t$	0.42	0.87	This work
$\text{Fe}_4(\text{CO})_{12}\text{N}^-$ (VI)	$\text{Fe}(\text{CO})_3^t$ (b)	0.03	1.12	This work
	$\text{Fe}(\text{CO})_3^t$ (a)	0.39	1.08	
$\text{Fe}_4(\text{CO})_{12}\text{C}^{2-}$ (VII)	$\text{Fe}(\text{CO})_3^t$ (b)	0.22	0.88	This work
	$\text{Fe}(\text{CO})_3^t$ (a)	0.35	0.62	
$\text{Fe}_5(\text{CO})_{14}\text{C}^{2-}$ (VIII)	$\text{Fe}(\text{CO})_3^t$ (apical)	0.28	1.03	This work
	$\text{Fe}(\text{CO})_2^t(\text{CO})_2^{\text{br}}$	0.25	1.18	
	$\text{Fe}(\text{CO})_3^t$ (basal)	0.32	0.43	
	$\text{Fe}(\text{CO})_2^t(\text{CO})_2^{\text{br}}$	0.40	0.31	

^a Spectra were recorded at 293 K (ref. 21) and 77 K (this work).

$[\text{Fe}_5(\text{CO})_{14}\text{C}]^{2-}$ cluster VIII has been reassigned based on the recent determination of its crystal structure [3].

Among the M_4 -nitride clusters produced in the work by Muetterties et al. [4] and Gladfelter et al. [5,6] were the isoelectronic series of compounds $[\text{FeRu}_3\text{H}(\text{CO})_{12}\text{N}]$ (IV), $[\text{Fe}_4\text{H}(\text{CO})_{12}\text{N}]$ (V), $[(\text{Ph}_3\text{P}_2\text{N})[\text{Fe}_4(\text{CO})_{12}\text{N}]]$ (VI), and $[\text{CoRu}_3(\text{CO})_{12}\text{N}]$ [6]. The structures of V [4] (Fig. 1), and VI [5] have been determined by X-ray crystallographic analyses and those of IV and $[\text{CoRu}_3(\text{CO})_{12}\text{N}]$ appear to be analogous [5,6]. All the compounds have only terminal CO ligands. The structures of V and VI had the four metal atom skeleton in a "butterfly" arrangement giving two independent metal sites Fe(a), Fe(b). In V the hydride ligand bridges the two Fe(b) sites, Fig. 1. The position of the unique metal atom is unknown in IV and $[\text{CoRu}_3(\text{CO})_{12}\text{N}]$. A comparison of our newly measured Mössbauer spectra of IV and V, Fig. 2, together with the previously reported spectra of M_3 and M_5 compounds now strongly suggests that the iron site in IV is at Fe(b) i.e. is a $\text{Fe}(\text{CO})_3^t\text{H}^{\text{br}}$ unit, and that the compound prepared is a single isomer. In the Fe_5 -clusters the $\text{Fe}(\text{CO})_3^t$ (basal) and $\text{Fe}(\text{CO})_2^t(\text{CO})_2^{\text{br}}$ units had substantially lower q values (0.3 to 0.4 mm s^{-1}) compared to the $\text{Fe}(\text{CO})_2^t(\text{CO})_2^{\text{br}}\text{H}^{\text{br}}$ unit (q 0.65 mm s^{-1}). Likewise one would expect $\text{Fe}(\text{CO})_3^t\text{H}^{\text{br}}$ to have a higher q than $\text{Fe}(\text{CO})_3^t$. Hence we assign the

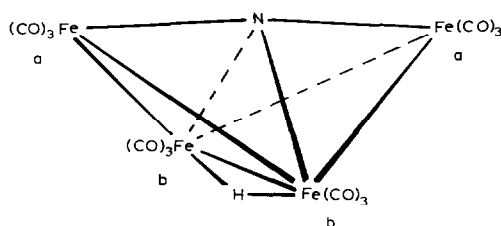


Fig. 1. Structure of $[\text{Fe}_4\text{H}(\text{CO})_{12}\text{N}]$ (V).



Fig. 2. Mössbauer spectra of $[\text{FeRu}_3\text{H}(\text{CO})_{12}\text{N}]$ (IV) upper curve, and $[\text{Fe}_4\text{H}(\text{CO})_{12}\text{N}]$ (V) lower curve.

doublets from V as $\text{Fe}(\text{CO})_3^t\text{H}^{\text{br}}$ (q 1.01 mm s^{-1}) and $\text{Fe}(\text{CO})_3^t$ (q 0.87 mm s^{-1}). The former value is extremely close to that of the doublet from IV (q 0.99 mm s^{-1}) and we conclude that, since the effect of replacing iron atoms by ruthenium atoms can be taken as negligible, this doublet is due to a $\text{Fe}(\text{CO})_3^t\text{H}^{\text{br}}$ unit. Removal of a proton from V gave VI with only $\text{Fe}(\text{CO})_3$ sites [5]. The spectrum of VI shows two doublets with q values much closer than in V, Table 1. We assign the doublet q 1.12 mm s^{-1} as site Fe(b) and that with q 1.08 mm s^{-1} as Fe(a) by comparison of their δ values with those from V. The isoelectronic carbide cluster VII can be assigned similarly, Table 1.

Subsequent to the submission for publication of the work on Fe_5 clusters, the solid state structures of the anions $[\text{Fe}_5(\text{CO})_{14}\text{N}]^-$ and $[\text{Fe}_5(\text{CO})_{14}\text{C}]^{2-}$ were reported by Gourdon and Jeannin [3]. Our analysis of the spectrum of the nitride anion was in accord with its structure but the structural models we took for the analysis of the carbide anion were not correct. In particular we did not consider the possibility of both $\text{Fe}(\text{CO})_3^t$ and $\text{Fe}(\text{CO})_2^t(\text{CO})_2^{\text{br}}$ units being present in the basal geometry. The X-ray diffraction results for VIII showed the presence of one $\text{Fe}(\text{CO})_3^t$ apical, one $\text{Fe}(\text{CO})_3^t$ basal, one $\text{Fe}(\text{CO})_2^t(\text{CO})_2^{\text{br}}$ and two $\text{Fe}(\text{CO})_2(\text{CO})^{\text{br}}$ units. Hence the spectrum could be expected to be very complex. Using the structural data and the results from the other Fe_5 clusters we now reassign the spectrum of VIII to include the apical and basal $\text{Fe}(\text{CO})_3^t$ units as

shown in Table 1. The apical $\text{Fe}(\text{CO})_3^{\text{t}}$ unit has q 1.03 mm s^{-1} , very close to that for the same unit in the $[\text{Fe}_5(\text{CO})_{15}\text{C}]$ compound (q 0.98 mm s^{-1}). The $\text{Fe}(\text{CO})_2^{\text{t}}(\text{CO})_2^{\text{br}}$ unit has q 1.18 mm s^{-1} compared to q 1.19 mm s^{-1} in $[\text{Fe}_5\text{H}(\text{CO})_{14}\text{N}]$. The basal $\text{Fe}(\text{CO})_3^{\text{t}}$ unit which had q 0.45 mm s^{-1} in $[\text{Fe}_5\text{C}(\text{CO})_{15}]$ now has q 0.43 mm s^{-1} in VIII. Finally the two $\text{Fe}(\text{CO})_2^{\text{t}}(\text{CO})^{\text{br}}$ units which may be expected to have q lower than $\text{Fe}(\text{CO})_3^{\text{t}}$ are found to have q 0.31 mm s^{-1} and this is confirmed by the increased intensity associated with these two units compared to the other single units.

In conclusion, this note has suggested consistent assignments of q values for various iron carbonyl units in related series of clusters. Within a series of clusters we find the following factors are of major importance; (i) the number of Fe to metal bonds; the q value is highest for the unit with most Fe—M bonds e.g., in Fe_5 clusters $\text{Fe}(\text{CO})_3^{\text{t}}$ apical with four Fe—Fe bonds has a higher q value than $\text{Fe}(\text{CO})_3^{\text{t}}$ basal which has only 3 Fe—Fe bonds; (ii) the number of ligands (CO or H) attached; units with more ligands attached have higher q values, e.g. in M_3 clusters the $\text{Fe}(\text{CO})_3^{\text{t}}(\text{CO})_2^{\text{br}}$ units have a higher q than $\text{Fe}(\text{CO})_4^{\text{t}}$; (iii) substitution of an Fe atom by another transition metal has little effect on q values.

We are extending our studies to other M_4 and M_5 clusters to test the generality of these observations.

References

- 1 R.P. Brint, K. O'Cuill, T.R. Spalding, and F.A. Deeney, *J. Organomet. Chem.*, 247 (1983) 61.
- 2 J. Knight and M.J. Mays, *J. Chem. Soc. A*, (1970) 654.
- 3 A. Gourdon and Y. Jeannin, *C.R. Acad. Sci. Paris*, 295 (1982) 1101.
- 4 M. Tachikawa, J. Stein, E.L. Muetterties, R.G. Teller, M.A. Beno, E. Gebert, and J.M. Williams, *J. Amer. Chem. Soc.*, 102 (1980) 6648.
- 5 D.E. Fjare and W.L. Gladfelter, *J. Amer. Chem. Soc.*, 103 (1981) 1572.
- 6 D.E. Fjare, D.G. Keyes, and W.L. Gladfelter, *J. Organomet. Chem.*, 250 (1983) 383.