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THE MÖSSBAUER SPECTRA OF IRON CARBONYL-CARBIDE AND -NITRIDE CLUSTER COMPOUNDS

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Summary

The ^{57}Fe Mössbauer spectra of related iron cluster carbides and nitrides were measured at liquid nitrogen temperatures. The isomer shift and quadrupole splitting parameters are reported. A correlation of quadrupole splittings with the known or implicated types of $Fe(CO)_n$ site was attempted. This enabled a systematic analysis of the "completeness" of each $Fe(CO)_n$ in terms of its involvement in cluster bonding to be made.

Introduction

The importance of metal carbonyl cluster compounds as model compounds for catalytic sites on metal surfaces and as catalysts themselves, has been stressed by many researchers recently and has promoted investigations into their electronic structure. Explanations of the electronic origin of cluster compounds have been largely based on the geometrical relationships between many metal clusters and boranes. The work of Wade [1], and Hoffmann et al. [2] has produced the "isolobal, isoelectronic" description of the metallo groups such as $Fe(CO)_3$, $(\eta^5\text{-}C_5H_5)Co$ compared with the BH group, and has led to attempts to explain why many metallaboranes and metal clusters are structurally related. In a number of recent publications [3,4] we have investigated the electronic structure of metallaboranes related to the *nido*-B_5H_9, B_6H_{10} and *closo*-$B_6H_6^{2-}$ systems and the iron cluster $Fe_5(CO)_{15}C$ [4]. This work was theoretical, using Hoffmann's self-consistent charge calculation and was aimed at testing the validity of the "isolobal, isoelectronic" description. For the metallaboranes an experimental check on the calculations is provided by a number of published photoelectron spectra. For metal clusters no such check is available and the calculational method is clearly at the limit of its ability.

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We are presently using a number of spectroscopic techniques to obtain information on the electronic structure of metal clusters and their structural relationships to borane compounds. In this paper we report the results of a series of Mössbauer spectroscopic studies on $Fe_5(CO)_{15}C$ and a number of related compounds. Since beginning this work the Mössbauer spectra of the carbide compounds have been reported, along with their ESCA spectra [5]. The authors of this report summarize the Mössbauer spectra as generally being broad singlets or poorly resolved doublets, and consequently make very few comments on the spectra. Their results are very different to ours. We found generally much more detail in our spectra and can offer a critical analysis of the source of the spectra and their relationships to the cluster structures.

Experimental

The compounds $Fe_5(CO)_{15}C$, $[(C_2H_5)_4N]_2Fe_5(CO)_{14}C$ [6], $Fe_5H(CO)_{14}N$, $[(C_2H_5)_4N]Fe_5(CO)_{14}N$ [7] and $[(C_2H_5)_4N]_2Fe_6(CO)_{16}C$ [8] were all prepared by literature methods. The compounds were identified by microanalysis and infrared spectroscopy and mass spectrometry in the case of $Fe_5(CO)_{15}C$ and $Fe_5H(CO)_{14}N$.

Mössbauer spectra were measured on an apparatus previously described [9] with microcrystalline samples. The spectra were recorded at room and liquid nitrogen temperatures. In all cases the low temperature spectra were better resolved and are the ones shown and discussed. In two cases $Fe_5(CO)_{15}C$, and $[(C_2H_5)_4N]_2$-$Fe_6(CO)_{16}C$, aligned samples were prepared by arranging numerous crystals with their morphology axes parallel. Absorption was typically 3% of incident radiation at the absorption maxima, and spectra were measured to give $\sim 9 \times 10^5$ counts per channel and hence ~ ±5% accuracy for the reported chemical shifts and quadrupole splittings. Collection times were typically 24–30 h. Values of the shift (δ) and quadrupole splitting (q) are all given in units of mm s^{-1} and the former are measured with respect to sodium nitroprusside. The chemical shift and quadrupole splitting parameters for the compounds studied are listed in Table 1.

TABLE 1

MÖSSBAUER PARAMETERS (mm s^{-1})

Compound	Assignment	Isomer shift (δ)	Quadrupole splitting (q)
$Fe_5(CO)_{15}C$	$Fe(CO)_3$ apical	0.18	0.98
	$Fe(CO)_3$ basal	0.19	0.45
$Fe_5H(CO)_{14}N$	$Fe(CO)_2{}^t(CO)_2{}^b$	0.12	1.19
	$Fe(CO)_2{}^t(CO)^bH^b$	0.22	0.65
$Fe_5(CO)_{14}C^{2-}$	$Fe(CO)_2{}^t(CO)_2{}^b$	0.27	1.14
	$Fe(CO)_2{}^t(CO)^b$	0.39	0.35
$Fe_5(CO)_{14}N^-$	$Fe(CO)_2{}^t(CO)^b(CO)^{semi\text{-}b}$	~ 0.27	~ 0.99
	$Fe(CO)_2{}^t(CO)^{semi\text{-}b}$	0.26	0.65
$Fe_6(CO)_{16}C^{2-}$		0.23	0.56

Results and discussion

The Mössbauer spectrum of an aligned sample of polycrystalline $Fe_5(CO)_{15}C$ is shown in Fig. 1a. This is one case for which the spectrum can be assigned unambiguously. The crystal structure of this compound has been determined [10] and the molecule has a square based pyramidal geometry of iron atoms, with the carbon atom slightly below the centre of the square base, and every iron atom having three terminally bonded carbonyl ligands (Figs. 2 and 3a). The spectrum (Fig. 1a) shows two doublets one with chemical shift δ 0.19 mm s^{-1}, quadrupole splitting q 0.45 mm s^{-1} about four times as intense as one with δ 0.18 mm s^{-1} and q 0.98 mm s^{-1}. Clearly the low intensity doublet corresponds to the apical iron atom of the pyramid, and the high intensity doublet corresponds to the four basal iron atoms. The chemical shifts for the two doublets are virtually identical which is more

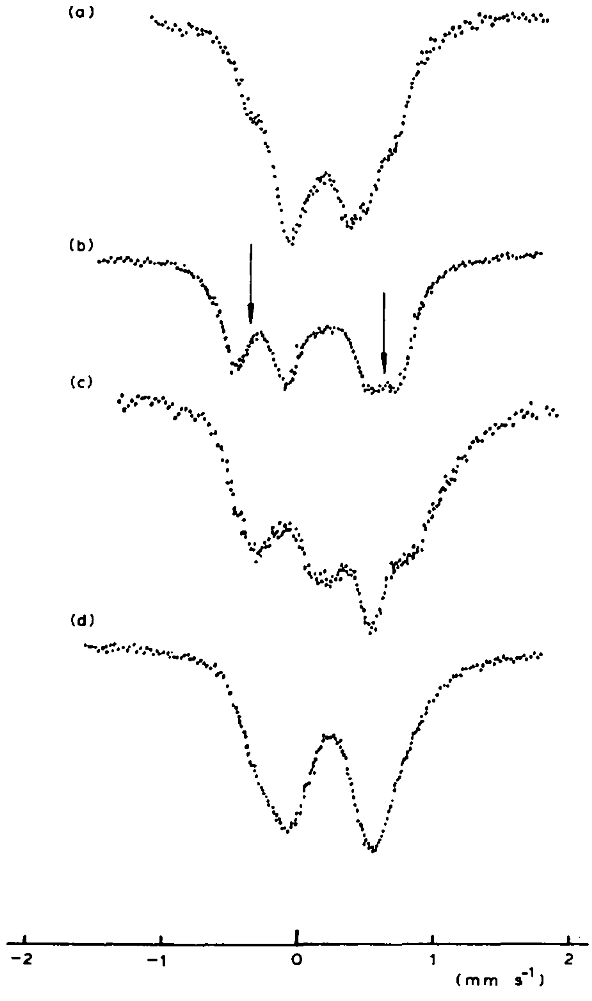

Fig. 1. Mössbauer spectra of Fe_5 clusters.

likely to arise from the same occupation of 4*s* and 3*d* orbitals in the two types of iron site, than from a fortuitous balancing of changes in the two occupations. The large difference in quadrupole splitting must arise from the different arrangement of charges around the two distinct sites in the molecule.

Ideally we would like to account for the differences in quadrupole splitting on the basis of data calculated by molecular orbital methods, particularly the self-consistent charge calculations we have previously used. The calculations however show no clear differences between charges on apical and basal iron atoms and carbonyl groups and such small differences as are evident do not correlate across the group of molecules. The differences in quadrupole splitting can be accounted for qualitatively as follows. The quadrupole splitting [11] is given by

$$q=\frac{1}{2}eV_{zz}Q\left[1+1/3\left(\frac{V_{xx}-V_{yy}}{V_{zz}}\right)^2\right]^{1/2}$$

where e is the charge on the proton, Q is the nuclear quadrupole moment, V_{xx}, V_{yy}, V_{zz} are the diagonal elements of the diagonalised electric field gradient tensor, subject to the condition $V_{xx}+V_{yy}+V_{zz}=0$. The squared term is known as the asymmetry parameter, η. For an axially symmetric site such as the apical iron atom, clearly $V_{xx}=V_{yy}=-V_{zz}/2$ thus $\eta=0$, and q is determined only by the V_{zz} term. This reflects the "complete" nature of this cluster site (Fig. 4). Taking the z axis of the basal sites as the direction through the iron atom and the base centred carbon atom, these sites are clearly not axially symmetric, that is they are "incomplete" sites, incomplete compared to the parent *closo* octahedral geometry, to which the apical site is very similar. The effect of this loss of axial symmetry is to displace some of the V_{zz} component into V_{xx} and V_{yy}, increasing η whilst decreasing V_{zz}. For small deviations from axial symmetry, the basal sites still have a conical arrangement of carbonyl ligands and are therefore not drastically perturbed compared to the apex, the latter effect dominates and the reduction in symmetry causes a reduction in quadrupole splitting.

The spectrum of the aligned sample shows that the intensities of the lines in each doublet are not equal, the apical line being weaker at low velocity, the basal one slightly stronger at low velocity. This arises from the alignment of individual molecules with respect to the photon beam and does not occur in an isotropic sample. The asymmetry in intensities depends on the angle the electric field direction through the relevant nucleus makes with the photon beam, and although we cannot quantify the effect as yet it clearly carries further information on the differences between the two sites in the molecule.

The effects discussed above are also evident in the spectrum of the *closo*-anion $Fe_6(CO)_{16}C^{2-}$ (Fig. 5). This compound has an octahedral arrangement of iron atoms with the carbon atom at the centre [12]. One iron atom has three terminal carbonyl ligands, two have two terminal ligands and share equally a bridging carbonyl group. The other three are in a plane, each has two terminal ligands, and the one in the centre of the plane shares bridging ligands with each of the other two. The sharing in this case is unequal, the bridging ligands being closer to the outer two atoms than to the centre one. There are therefore four types of chemically distinct iron sites in the anion. Five iron atoms have three CO ligands and one iron atom has four CO groups bonded to it. However all sites are "complete" cluster sites, having close to axial symmetry with respect to both the cluster and to the carbonyl ligands, and we may expect this to make their quadrupole splittings very similar. The spectrum shows only one well defined doublet δ 0.23, *q* 0.56 mm s^{-1} with lines of near natural linewidth, showing that all four sites have very nearly identical charge environments.

The change in *q* compared to the apical $Fe(CO)_3$ group of $Fe_5(CO)_{15}C$ is probably due to the anionic state of the cluster changing the amount of charge localised on each cluster site. A spectrum of an aligned crystalline sample showed marked asymmetry of the intensities of the doublet. This result is under further investigation.

The neutral molecule $Fe_5H(CO)_{14}N$ is isoelectronic with $Fe_5(CO)_{15}C$ but is known to have a significantly different geometry [13]. Whilst still having a square based pyramid of iron atoms the basal atoms now have two terminal carbonyl ligands each and the four sides of the square base are bridged by three carbonyl groups and an H atom (Fig. 3b). The C_s symmetry of the molecule leads us to expect three doublets in the Mössbauer spectrum, one from the apical atom at half the intensity of ones from each of the symmetry related pairs of basal atoms. The spectrum, shown in Fig. 1b, has four distinct peaks which we assign to the two basal doublets. Potentially four peaks can be arranged as three different pairs of doublets, but we feel that the pairs with δ 0.22, *q* 0.65 and δ 0.12, *q* 1.19 mm s^{-1} are the only viable ones. Any other pairs result in very different δ values for the doublets which are also very different from those of $Fe_5(CO)_{15}C$. We have already seen that δ is fairly insensitive to changes in the local symmetry of the cluster site. It should in fact be sensitive only to 4*s* and 3*d* orbital occupations, and as these also determine the ability of the metallo group to form cluster bonds we do not expect them to change much through this group of molecules.

The absence of the observation of a doublet from the apical iron atom can be explained by assuming this doublet to have similar δ, *q* parameters to that in $Fe_5(CO)_{15}C$. Then the lines of the doublet are expected at the velocities arrowed in Fig. 1b. On the low velocity side the arrow corresponds to a definite broadening of one of the observed lines which could well due to an underlying weak absorption. On the high velocity side the arrow lies directly between the two observed lines and could account for their enhanced intensity, which is not otherwise explicable in an isotropic sample.

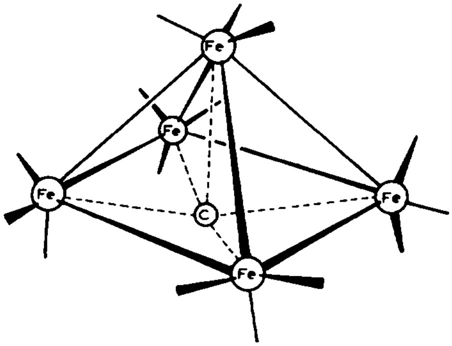

Fig. 2. Solid state structure of $Fe_5(CO)_{15}C$.

There is no information directly from the spectrum that allows assignment of the two doublets to the pairs of basal atoms. However by comparison with $Fe_5(CO)_{15}C$ a tentative assignment can be made. The geometry of $Fe_5H(CO)_{14}N$ has more in common with the related borane B_5H_9 than has that of $Fe_5(CO)_{15}C$. The presence of the bridging ligands around the base of the molecule enhances the axial symmetry of the basal sites as do the bridging hydrogens of B_5H_9. This effect of this enhanced symmetry is to more correctly polarise the available atomic orbitals on the iron (or boron) atom for cluster bonding. Hence we may expect the iron atom sites of $Fe_5H(CO)_{14}N$ with two terminal and two bridging carbonyl ligands to be similar to an apical $Fe(CO)_3$ group. For this reason we tentatively assign the δ 0.12, q 1.19 doublet as due to these sites. The other site with bridging carbonyl and hydride ligands and is less like the apical $Fe(CO)_3$ group sites. This is reflected in the quadrupole splitting which is much smaller than for the other basal site but is quite similar to the basal site in $Fe_5(CO)_{15}C$.

The geometry of the anion $Fe_5(CO)_{14}C^{2-}$ has not been determined crystallographically. The presence of a relatively strong broad bridging carbonyl absorption in the infrared (KBr disc) may be indicative of a solid state structure as in Fig. 3c (i) but the known geometry of the isoelectronic $RhFe_4(CO)_{14}C^-$ [14] has led to a suggested basal geometry shown in Fig. 3c(ii). An alternative structure in which two

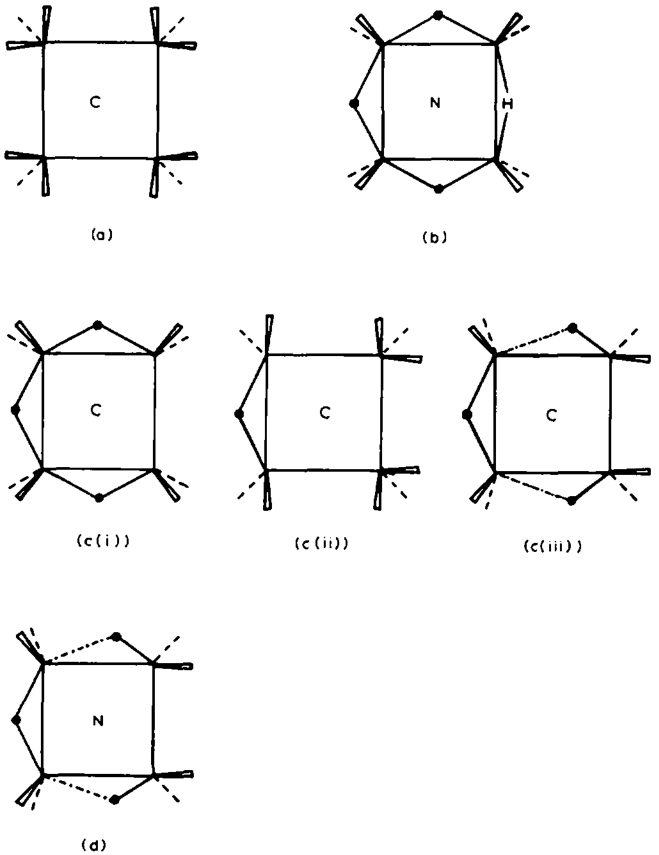

Fig. 3. Geometries of basal sections of Fe_5 clusters.

carbonyl groups are semi-bridging i.e. located nearer one bridged iron than the other, Fig. 3c(iii), is also possible. The Mössbauer spectrum of this anion is shown in Fig. 1c. The spectrum shows two doublets with δ 0.27, q 1.14 and δ 0.39, q 0.35 mm s^{-1}. The C_s symmetry (Fig. 3c) leads to the expectation of three doublets in the spectrum but again there is no direct experimental evidence for the apical doublet. The first of the observed doublets has similar δ and q values as one from $Fe_5H(CO)_{14}N$ which would correlate with this being due to the iron atoms with two terminal and two bridging carbonyl ligands (Fig. 3c(i) or (iii)). The other site (Fig. 3c(i) and (iii)) is less axially symmetric than the corresponding site in $Fe_5H(CO)_{14}N$. This would correlate with the observation of a significant shift in δ value corresponding to the least cluster type environment encountered in this group of molecules and hence a probably significant difference in $3d$ and $4s$ orbital occupations. The q value is also the smallest one encountered which would further correlate with the unsymmetric nature of the site and indicates that structure 3c(ii) is unlikely to be correct. There is evidence for the apical doublet in the low velocity shoulder at ~ -0.50 mm s^{-1} and the high intensity of the band at 0.56 mm s^{-1} which must be explained by an underlying absorption in an isotropic sample. This gives q, δ values for the apical doublet similar to those of $Fe_5(CO)_{15}C$.

The anion $Fe_5(CO)_{14}N^-$ might be expected to have a similar arrangement of basal ligands as $Fe_5(CO)_{14}C^{2-}$. The structure has not been determined, however the infrared spectrum in KBr disc form shows only a weak absorption in the bridging carbonyl region. The Mössbauer spectrum of the anion is shown in Fig. 1d and differs from the previous two examples, and hence a different basal geometry probably applies in this case. The spectrum shows only three distinct features, however the areas under the curve either side of 0.26 mm s^{-1} are close to equal implying that there are in fact two features on the high velocity side of which only one is resolved. The only evidence for the unresolved feature is a change in slope of the high velocity tail at ~ 0.72 suggesting a minimum at 0.60–0.70 mm s^{-1} and explaining the enhanced intensity of the observed absorption. This would give two doublets with δ 0.26, q 0.65 and $\delta \sim 0.27$, $q \sim 0.99$ mm s^{-1}. The parameter values for the first doublet are comparable with the basal sites of $Fe_5(CO)_{15}C$ and the H bridged sites in $Fe_5H(CO)_{14}N$ whilst those of the second are similar to those of the carbonyl bridged sites of $Fe_5(CO)_{14}C^{2-}$ and $Fe_5H(CO)_{14}N$. One possible geometry that agrees with this assignment is shown in Fig. 3d. The two semi-bridged iron sites are basically $Fe(CO)_3$ groups with one of the terminal carbonyls forming an asymmetric bridge to the other two sites which are $Fe(CO)_2$ groups sharing a bridging carbonyl. This would also explain the broadness of this spectrum as this geometry would probably be subject to small perturbations due to crystal packing effects causing the iron atoms to absorb at slightly different velocities. This effect undoubtably applies in the $Fe_5(CO)_{15}C$ spectrum which is also fairly broad but whose crystal structure shows that all four basal iron atoms have slightly different bonding environments.

The Mössbauer spectra of this group of isoelectronic compounds has been assigned in self-consistent way. No other set of assignments provides consistent values for the chemical shifts and values for the quadrupole splitting that are similar for sites with similar local environments.

Hoffmann et al. [2] have previously drawn attention to the importance of a conical arrangement of ligands on the cluster bonded metal atoms. This arrangement

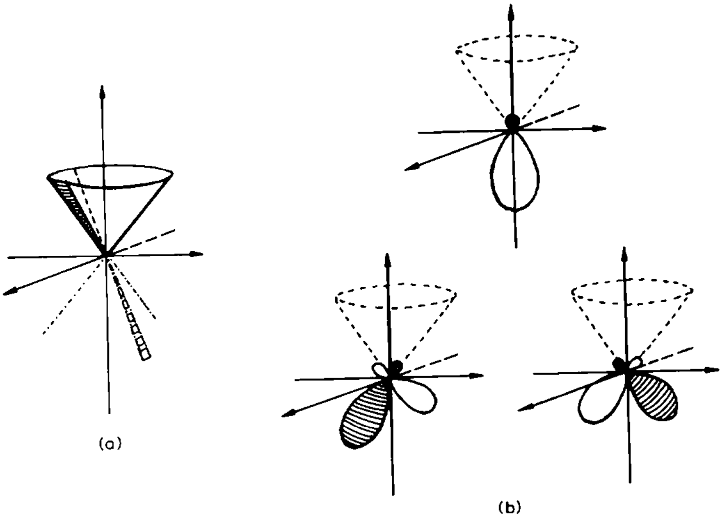

Fig. 4. The axially symmetric apical Fe(CO)$_3$ site: (a) the conical Fe(CO)$_3$ section; (b) the three cluster bonding orbitals from Fe(CO)$_3$ to the rest of the cluster.

produces the correct directional polarisation of available orbitals on the metallo group to encourage cluster bonding (Fig. 4). It is logical that a conical arrangement of the cluster atoms to which the metal is bonded is desirable to maximise the use of these available orbitals. From this we can envisage a range of cluster sites and note the importance of axial symmetry of the metal atom environment. According to Hoffmann et al. the isolated basal Fe(CO)$_3$ groups of Fe$_5$(CO)$_{15}$C are as capable of forming cluster bonds as the apical group. From the geometry it is obvious that some of the available orbitals are not being used in the basal sites, but it is impossible to determine from studies on individual metallo groups if this "incompleteness" causes a significant weakening of the cluster bonding or to what extent the basal groups differ from the axially symmetric apical environment. Also the studies of Hoffmann et al. did not take into account the effect which rearranging the

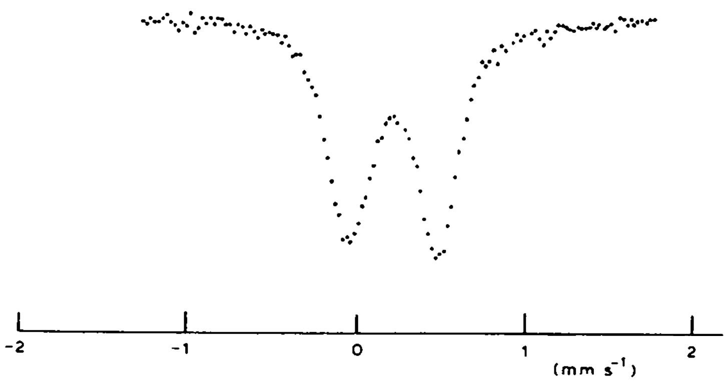

Fig. 5. Mössbauer spectrum of [Fe$_6$(CO)$_{16}$C]$^{2-}$.

ligands to bridging or partially bridging geometries would have on the cluster bonding ability of the group. The Mössbauer spectra may provide a measure of these changes and effects and show that the order of ability to form cluster bonds in a closely related series is $Fe(CO)_3{}^t$ apical $\approx$ $Fe(CO)_2{}^t(CO)_2{}^b$ basal > $Fe(CO)_2{}^t(CO)^bH^b \approx Fe(CO)_2{}^t(CO)^{semi\text{-}b}$ > $Fe(CO)_3$ basal > $Fe(CO)_2{}^t(CO)^b$. This order comes from the correlation between quadrupole splitting and the approach of the iron site to axial symmetry. The larger the deviation from axial symmetry the smaller the quadrupole splitting. In very asymmetric sites the increase in the asymmetry parameter may dominate the reduction in the V_{zz} term and the quadrupole splitting will increase again. However for sites where the deviation from axial symmetry is small the correlation will apply. From a geometric viewpoint a number of the sites discussed above appear to be highly asymmetric but from the quadrupole splittings this is not the case. The reason for this apparent discrepancy is that the distribution of charges, and hence the electrostatic field through the iron atom is dominated by the central carbon or nitrogen atom and the axially arranged carbonyl ligands. The carbonyl ligands carry charge delocalised from the iron atom and the central atom also has a large negative charge according to our calculations. All changes in the charge distribution of this axis will be small compared to this axial charge distribution. This is applicable to all sites.

The chemical shifts apparently provide no particular information relevant to the cluster bonding of the iron atoms, except perhaps for the basal site of $Fe_5(CO)_{14}C^{2-}$ discussed above. However the δ values of the basal sites of various Fe_5 compounds do show a logical progression, those of the neutral molecules being less than the monoanion Fe_5N^- which are less than the dianion Fe_5C^{2-}. This does not correlate with the δ values of the Fe_6C^{2-} anion. The iron sites of the Fe_6 anion are symmetrically and chemically more comparable with the apical sites of the other compounds, but as noted above the q values do not compare. The reason is almost certainly due to the distribution of the ionic charge. The charge of the Fe_6C^{2-} ion is undoubtably evenly distributed over the six iron sites as these are all very similar. In the Fe_5 anions our calculations show that the ionic charge is strongly localised on the unbridged basal bond, the charge apparently attempting to fill the role of the missing ligand. This will result in much the same charge being localised on the iron atoms in all the Fe_5 compounds, but this is quite different to the charge localised on the iron atoms of the Fe_6C^{2-} cluster, and hence the difference in q, δ values for the two types of cluster.

Conclusion

The measurement of Mössbauer spectra of some Fe_5- and Fe_6-iron carbonyl cluster compounds provides a method for determining the suitability of individual iron atom environments for cluster bonding. In the particular group of molecules studied the spectra also appear to show whether the arrangement of basal ligands is related in different compounds. The most obvious extension of this work will be to mixed metal clusters. To test the sensitivity of cluster bonding to changes in the metal atoms involved. Whereas the results from self-consistent charge calculations are subject to reservations as to their accuracy, the application of a more accurate calculational method, e.g. X_α, could be of great value in interpreting Mössbauer results. We are pursuing both these lines of investigation.

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