Application of Magnetic-perturbation Mössbauer Spectroscopy to Binuclear Complexes with Inequivalent Iron Atoms

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^{57}Fe Mössbauer spectra of diamagnetic binuclear iron complexes in applied magnetic fields have been computed for a number of cases of interest. Analysis of the spectra shows that one can deduce the signs of the quadrupole coupling constants at both iron sites, regardless of the complexity of the zero-field spectrum, and in many cases the asymmetry parameters can be evaluated as well. The magnetically perturbed spectra also provide completely unambiguous assignments of the Mössbauer parameters for the two iron atoms.

A LARGE number of iron(0) carbonyl complexes containing two or more inequivalent iron atoms are known, and many have been studied by ^{57}Fe Mössbauer spectroscopy. In general the symmetry at each iron site is lower than cubic and the resultant electric-field gradients (e.f.g.s) split each ^{57}Fe resonance into a doublet. Thus, in the case of two different sites one expects to observe a four-line Mössbauer spectrum, although occasionally similarities in isomer shifts, δ, and/or quadrupole splittings, $|\Delta E_Q|$, for the two sites lead to accidental degeneracy, so that only two or three of the four lines are clearly resolved.

For a di-iron complex which produces a four-line spectrum, there are three possible combinations of pairs of lines. The usual method for deciding amongst these possibilities has been to use an empirical approach and to pick that combination which gives $|\Delta E_Q|$ and δ parameters in close agreement with those obtained from related molecules containing only one iron site. For example, in the monosubstituted sulphido-bridged derivatives [$Fe_2(CO)_5L(SR)_2$] (R = alkyl or aryl; L = tertiary phosphine, arsine, or stibine),[1,2] the line assignment chosen [1] was that which yielded one set of parameters corresponding fairly closely to that for the unsubstituted parent complexes [$Fe_2(CO)_6(SR)_2$], in which the two iron atoms are equivalent. Semi-intuitive arguments based on known crystallographic data [3-5] and predicted effects of ligand variation on the Mössbauer parameters [1,2,4,6,7] have also been employed as aids in assigning the lines in such spectra.

While these approaches generally lead to reasonable isomer-shift and quadrupole-splitting parameters for each site, there has been no conclusive and unequivocal demonstration that a given assignment is unique. Indeed, there are several instances where a clear-cut choice between two or more alternative assignments could not be made.[1,5-7] Furthermore, in no case has the Mössbauer spectrum of any such complex been determined with the sample subjected to an applied magnetic field, so that nothing is known about the signs of the quadrupole splittings or magnitudes of the asymmetry parameters at the two sites.

The purpose of the present paper is two-fold. First, we shall show that although the situation is considerably more complex than for compounds containing only one kind of iron atom, magnetic-perturbation Mössbauer techniques [8] are capable of yielding the sign of the e.f.g. at each site in iron(0) derivatives with two inequivalent iron atoms. This is true whether the zero-field spectrum consists of two, three, or four lines. Secondly, we wish to point out that this technique provides a method for overcoming many of the difficulties associated with assigning the spectral lines for such complexes, since each combination will lead to a distinctive pattern when the sample is placed in a large magnetic field. If the differences in isomer-shift and/or quadrupole-splitting parameters predicted for each of the possible choices are sufficiently great, the spectrum produced under such circumstances will be unique and a definitive assignment of the lines can be made. This method requires no knowledge of the structure or even the stoicheiometry of the complex, nor of the Mössbauer parameters of supposedly related derivatives. The magnetic-perturbation technique has apparently never before been utilized for either purpose.†

COMPUTATION

Theoretical spectra were generated by a program based on one generously supplied by Dr. G. Lang.[11] The value of $g_1\beta_n$ (g_1 = gyromagnetic ratio of the excited state, β_n = nuclear magneton) was taken as $6{\cdot}8 \times 10^{-3}$ mm s^{-1} kG^{-1}, and the value $-1{\cdot}750$ was used for the ratio ($g_0 : g_1$) of the g values of the ground and excited states. The basic program by Lang [11] was employed using as input parameters the magnitude of the applied magnetic field,

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† However, magnetic-perturbation methods have been employed in studies of iron–sulphur proteins containing inequivalent iron sites.[9,10]

[1] J. A. de Beer, R. J. Haines, R. Greatrex, and N. N. Greenwood, *J. Chem. Soc.* (*A*), **1971**, 3271.

[2] J. P. Crow and W. R. Cullen, *Canad. J. Chem.*, 1971, **49**, 2948.

[3] W. R. Cullen, D. A. Harbourne, B. V. Liengme, and J. R. Sams, *J. Amer. Chem. Soc.*, 1968, **90**, 3293.

[4] W. R. Cullen, D. A. Harbourne, B. V. Liengme, and J. R. Sams, *Inorg. Chem.*, 1969, **8**, 95.

[5] W. R. Cullen, D. A. Harbourne, B. V. Liengme, and J. R. Sams, *Inorg. Chem.*, 1970, **9**, 702.

[6] J. P. Crow, W. R. Cullen, J. R. Sams, and J. E. H. Ward, *J. Organometallic Chem.*, 1970, **22**, C29.

[7] L. S. Chia, W. R. Cullen, J. R. Sams, and J. E. H. Ward, *Canad. J. Chem.*, 1973, **51**, 3223.

[8] See, for example, R. L. Collins and J. C. Travis in 'Mössbauer Effect Methodology,' ed. I. J. Gruverman, Plenum Press, New York, 1967, vol. 3.

[9] M. C. W. Evans, D. O. Hall, and C. E. Johnson, *Biochem. J.*, 1970, **119**, 289.

[10] H. Frauenfelder, I. C. Gunsalus, and E. Münck in 'Mössbauer Spectroscopy and its Applications,' I.A.E.A., Vienna, 1972, p. 231.

[11] G. Lang, *J. Chem. Soc.* (*A*), 1971, 3245.

the zero-field values of $|\Delta E_Q|$ and linewidth, Γ, and the asymmetry parameter, η, assumed for each of the two sites. Initially, e^2qQ was chosen to be positive and δ to be zero for each site. In the next stage of the computations the output argument lists, with offsets appropriate to the difference in δ values for the two sites, were summed to give the four possible composite spectra resulting from the various permutations of the signs of e^2qQ. The relation employed was that a change in sign of e^2qQ gives an identical spectrum but in reverse order (provided $\delta = 0$). In the present work, the assumption was made that each site contributed equally to the total absorption area of the spectrum. This is tantamount to the assumption that resonance fractions for the two sites are equal. In a large majority of the cases of interest this is probably a good approximation, although it would be a relatively simple matter to weight the two component spectra appropriately for a case of unequal absorption areas.

Binuclear iron(0) carbonyl complexes of the kinds considered here generally exhibit one of three basic types of Mössbauer spectra in zero magnetic field.[1,2,4] In type (I) all four component lines are resolved and have approximately equal areas. If we number the lines (1)—(4) in order of increasing energy and ignore perturbations of the two iron atoms Fe^A and Fe^B, there are three possible ways of assigning the lines: (Ia) lines (1) and (2) to Fe^A, lines (3) and (4) to Fe^B; (Ib) lines (1) and (3) to Fe^A, lines (2) and (4) to Fe^B; and (Ic) lines (2) and (3) to Fe^A, lines (1) and (4) to Fe^B. Spectra of type (II) consist of three lines with areas in the approximate ratio 1 : 1 : 2. There are now but two possible line assignments, depending on whether the high-area line [here denoted (3)] is assumed to be a single unsplit line or to arise from overlap of the high-energy components of two quadrupole doublets: (IIa) lines (1) and (2) to Fe^A, line (3) to Fe^B; (IIb) lines (1) and (3) to Fe^A, lines (2) and (3) to Fe^B. In type (III) spectra only two lines are clearly resolved, although in some instances one or both may be substantially broadened. Again there are two possibilities: (IIIa) each line is unsplit and arises from a different iron atom; (IIIb) the two iron atoms have nearly identical values of both δ and $|\Delta E_Q|$.

For a given type, theoretical spectra were computed for each assignment using all possible combinations for the signs of the e.f.g.s at the two iron atoms, *i.e.* Fe^A+, Fe^B+; Fe^A-, Fe^B+; Fe^A+, Fe^B-; and Fe^A-, Fe^B-. In the initial calculations η was constrained to zero for both iron sites. At this stage one can make an unequivocal choice amongst the possible assignments. In a number of instances we also computed spectra with $\eta \neq 0$ at one or both sites, but only η values of 0, 0·6, and 0·8 were considered. The spectra were not particularly sensitive to values of η less than *ca.* 0·5. Where comparison was made between theoretical and experimental spectra, the extent of agreement was judged visually and no attempt was made to fit the observed spectrum by least-squares techniques.

RESULTS AND DISCUSSION

The amount of information which can be derived from magnetic-perturbation studies of binuclear iron complexes depends on the type of zero-field spectrum observed, and tends to decrease with increasing superposition and overlap of the spectral lines. The technique is perhaps most helpful when the spectrum is of type (I), since one can obtain unambiguous pairing of spectral lines with iron-atom sites, the signs of e^2qQ at both sites, and usually a fairly reliable estimate of η at both sites. In the least favourable case [type (III)], decision between two single-line absorptions and two overlapping doublets is easily made, and for the latter situation the sign of the e.f.g. at each site can be determined. However, since the two iron atoms must then necessarily have very similar δ and $|\Delta E_Q|$ values, little additional information can be expected in general.

We consider each of the three types of spectra separately. In the case of type (I) we analyse an experimental spectrum in detail, in order to illustrate more clearly the actual procedures involved in the treatment of data. For the other two types we make use of hypothetical spectra, the assumed parameters (δ, $|\Delta E_Q|$, and Γ) being typical of those often encountered.[1,2,12,13]

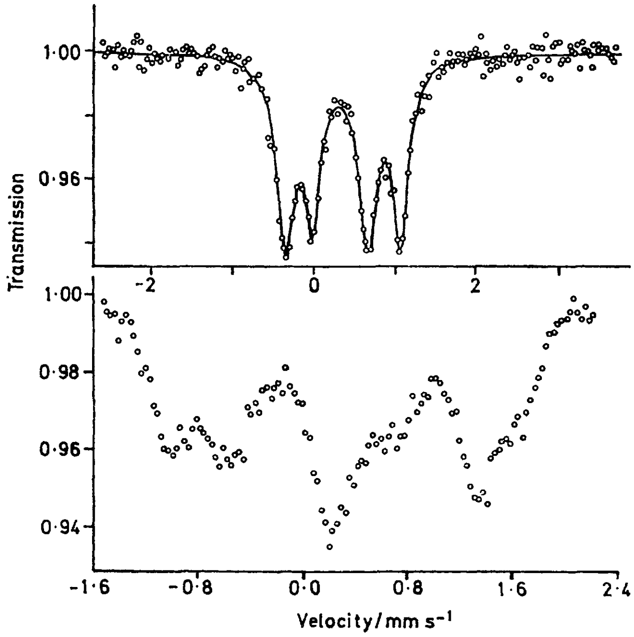

FIGURE 1 Mössbauer spectra of the cyclopent-1-ene complex: (*i*) at 80 K in zero applied field; (*ii*) at 4·2 K in a longitudinal magnetic field of 50 kG

Type (I) *Spectra*.—As an illustration of the present technique we consider the complex $[(OC)_3\overline{Fe(\mu\text{-}L)Fe}(CO)_3]$ [L = 1,2-bis(dimethylarsino)hexafluorocyclopent-1-ene], whose zero-field Mössbauer spectrum at 80 K is shown in Figure 1(*i*). We purposely delay any discussion of the structure of this complex. It is important to note that in order to achieve a correct and unambiguous pairing of lines with sites we require no knowledge of the geometry of the complex nor of the nature of the bonding at either site. For the spectrum in Figure 1(*i*), isomer-shift and quadrupole-splitting values derived from the three possible line assignments are listed in the Table.

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[12] L. S. Chia, W. R. Cullen, J. R. Sams, and J. C. Scott, unpublished work.

[13] J. C. Scott, Ph.D. Thesis, University of British Columbia, 1973.

It can be argued that assignment (Ia) is suspect on the grounds that both isomer-shift values lie outside the range normally observed for diamagnetic iron(0) carbonyl derivatives, but it is not possible to choose between (Ib) and (Ic) on the basis of these parameters in the absence of structural data.

Mössbauer parameters for the cyclopent-1-ene complex at 80 K based on the three possible line assignments

Line assignment and iron atom		Isomer shift (δ/mm s^{-1})	Quadrupole splitting ($\Delta\|E_Q\|$/mm s^{-1})
(1), (2) (A)	(Ia)	−0·20	0·34
(3), (4) (B)		0·83	0·40
(1), (3) (A)	(Ib)	0·13	1·00
(2), (4) (B)		0·50	1·06
(2), (3) (A)	(Ic)	0·30	0·67
(1), (4) (B)		0·33	1·41

Figure 1(*ii*) shows the Mössbauer spectrum of the complex at 4·2 K in a longitudinal magnetic field of 50 kG. Typical spectra which would be produced by this complex for each of the line assignments (Ia)—(Ic) are depicted in Figures 2—4, respectively, where we used all possible combinations of signs for e^2qQ and set $\eta = 0$ throughout. It will be seen that the only theoretical spectrum which is similar to the experimental one of Figure 1(*ii*) is that for assignment (Ic) with e^2qQ negative at Fe^A and positive at Fe^B [Figure 4(*ii*)]. The assumption of non-zero η values for one or both sites altered the detailed shapes of the computed

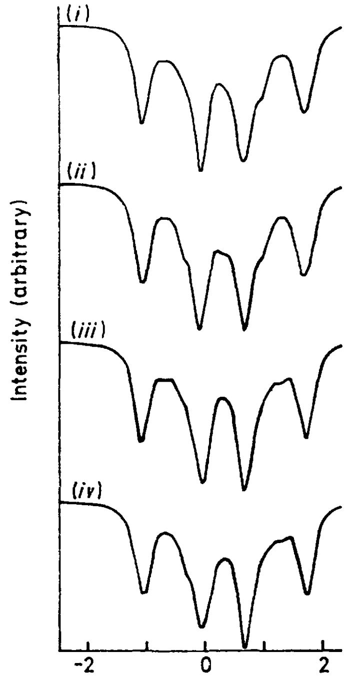


FIGURE 2 Theoretical Mössbauer spectra of the cyclopent-1-ene complex at 4·2 K in a longitudinal magnetic field of 50 kG, based on line assignment (Ia). Isomer-shift and quadrupole-splitting parameters are given in the Table, and for both sites $\eta = 0$ and $\Gamma = 0{\cdot}25$ mm s^{-1}. The assumed signs of e^2qQ at each site are as follows: (*i*) Fe^A+, Fe^B+; (*ii*) Fe^A−, Fe^B+; (*iii*) Fe^A+, Fe^B−; and (*iv*) Fe^A−, Fe^B−

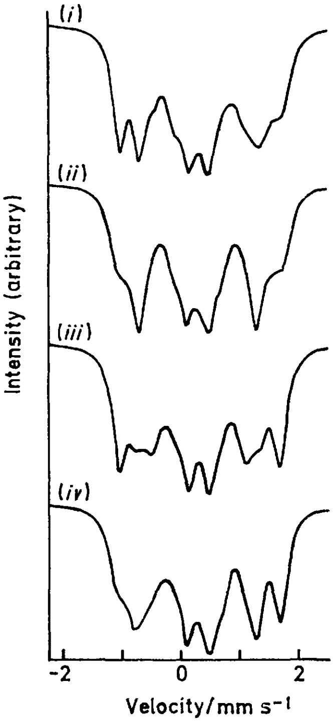


FIGURE 3 Theoretical Mössbauer spectra of the cyclopent-1-ene complex at 4·2 K in a longitudinal magnetic field of 50 kG, based on line assignment (Ib). Parameters are given in the Table, and for both sites $\eta = 0$ and $\Gamma = 0{\cdot}25$ mm s^{-1}. The assumed signs of e^2qQ at each site are as indicated in Figure 2

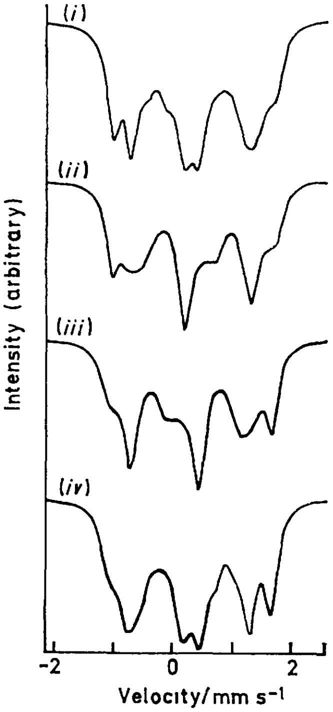


FIGURE 4 Theoretical Mössbauer spectra of the cyclopent-1-ene complex at 4·2 K in a longitudinal magnetic field of 50 kG, based on line assignment (Ic). Parameters are given in the Table, and for both sites $\eta = 0$ and $\Gamma = 0{\cdot}25$ mm s^{-1}. The assumed signs of e^2qQ at each site are as indicated in Figure 2

spectra, but it was not possible using either assignment (Ia) or (Ib) to produce a spectrum which resembled Figure 1(*ii*) in overall appearance. Thus, only assignment (Ic) is consistent with the magnetically perturbed spectrum, and we can state unequivocally that lines (1) and (4) in Figure 1(*i*) arise from one iron atom and lines (2) and (3) from the other. At this point, closer comparison of Figures 1(*ii*) and 4(*ii*) revealed that, although the general shapes of the two spectra were quite similar, the intensities of some of the computed transitions were rather different from those observed. Additional spectra were calculated with $\eta \neq 0$ at one or both iron sites, as outlined above. Best agreement between experimental and theoretical spectra was obtained for $\eta = 0$ at Fe^A and $\eta = 0{\cdot}6$ at Fe^B (see Figure 5). Further refinement of the η values was not attempted.

We used this technique to examine a number of other binuclear iron complexes which exhibit type (I) spectra in zero field.[12,13] In no case was there any ambiguity in assigning the lines to the two iron sites, nor did we experience difficulty in determining the signs of the e.f.g.s, even when η was fairly large at both sites. The method thus appears to have general utility for spectra of this type.

A few general observations concerning the spectra in Figures 2—4 should be made. First, it is clear that the four spectra in Figure 2 corresponding to assignment (Ia) are all quite similar, so that for this assignment one might have difficulty in determining with certainty the sign of e^2qQ at each site, especially if $\eta \neq 0$. Fortunately this case is the least probable for a type (I) spectrum.

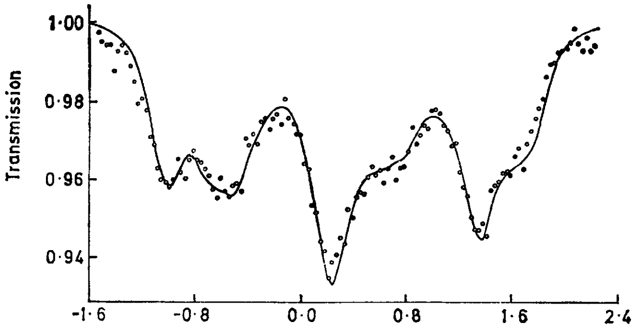
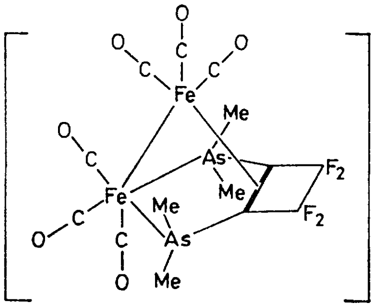


FIGURE 5 Comparison of theoretical and experimental spectra of the cyclopent-1-ene complex in a longitudinal magnetic field of 50 kG. (——), Computed spectrum based on the following parameters: Fe^A $\delta = 0{\cdot}30$, $\Delta E_Q = -0{\cdot}67$ mm s^{-1}, $\Gamma = 0{\cdot}27$ mm s^{-1}, and $\eta = 0{\cdot}0$; Fe^B $\delta = 0{\cdot}33$, $\Delta E_Q = +1{\cdot}41$, $\Gamma = 0{\cdot}26$ mm s^{-1}, and $\eta = 0{\cdot}6$

Secondly, for assignment (Ib) the sign of the e.f.g. at each site is obvious from inspection, at least when η is small. If $e^2qQ > 0$ at Fe^A, the lowest velocity line will be quite intense and well resolved, but this line appears as a weaker shoulder if $e^2qQ < 0$ at Fe^A. Similarly, the highest-velocity line is clearly resolved only when $e^2qQ < 0$ at Fe^B. These considerations will apply in general for assignment (Ib) because of the difference in isomer shifts for the two iron sites. Finally, for the most probable assignment (Ic), the e.f.g. signs are again clear from inspection, and for the latter two cases considerable information can be obtained from the magnetic-perturbation spectra.

The values of the Mössbauer parameters derived for the complex mentioned above are of some interest. The large differences in both $|\Delta E_Q|$ and η for the two iron atoms suggests that the symmetry at Fe^B is considerably lower than that at Fe^A. The structure of this complex is undoubtedly very similar to that found[4,14] for the closely related $[(OC)_3Fe(\mu\text{-}L)Fe(CO)_3]$ [L = 1,2-bis(dimethylarsino)tetrafluorocyclobut-1-ene], the only difference between the two ligands L being the size of the cyclic group. Our results indicate that the arsenic atoms of the cyclopent-1-ene ligand are chelated to Fe^A to provide a distorted octahedral environment at this



site, whilst Fe^B is bonded to the olefin and occupies a site of lower symmetry. Analogous assignments have been suggested[4] for the cyclobut-1-ene ligand and other related complexes on the basis of zero-field Mössbauer data. The fact that the *z* components of the e.f.g. tensors at the two iron atoms in the cyclopent-1-ene complex were of opposite sign is not easily interpreted for a molecule of such low symmetry. It is clear that there is an excess of electron density along the *z* axis at Fe^A and a deficiency of electron density along the *z* axis at Fe^B, but the relative orientation of the molecular axes and the principal axes of the e.f.g. is not known for either site, nor does there appear to be any reason to suppose that the e.f.g. axes at the two sites are collinear.

Type (II) *Spectra*.—For spectra of this type it is often possible to decide with a fair degree of certainty between assignments (IIa) and (IIb) in the absence of magnetic-perturbation measurements, since if the line at highest energy is assumed to be a singlet its isomer shift may be unrealistically high. However, we shall see that in an applied magnetic field there is no question as to which assignment is correct.

For the hypothetical type (II) spectrum in zero field we assumed the three lines (all with $\Gamma = 0{\cdot}25$ mm s^{-1}) to be centred at $-0{\cdot}20$, $+0{\cdot}20$, and $+0{\cdot}80$ mm s^{-1}, respectively [relative to disodium pentacyanonitrosylferrate(III)], with the third line having twice the intensity of the other two. Assignment (IIa) then led to δ values of 0·00 and 0·80 mm s^{-1}, and $|\Delta E_Q|$ values of 0·40 and

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[14] F. W. B. Einstein and J. Trotter, *J. Chem. Soc.* (*A*), 1967, 824.

0·00 mm s^{-1}, respectively for Fe^A and Fe^B, whilst for assignment (IIb) the corresponding parameters were δ = 0·30 and 0·50 mm s^{-1} and $|\Delta E_Q|$ = 1·00 and 0·60 mm s^{-1}, respectively. It is clear from Figure 6 that these two alternatives are easily distinguished in a magnetic-perturbation experiment.

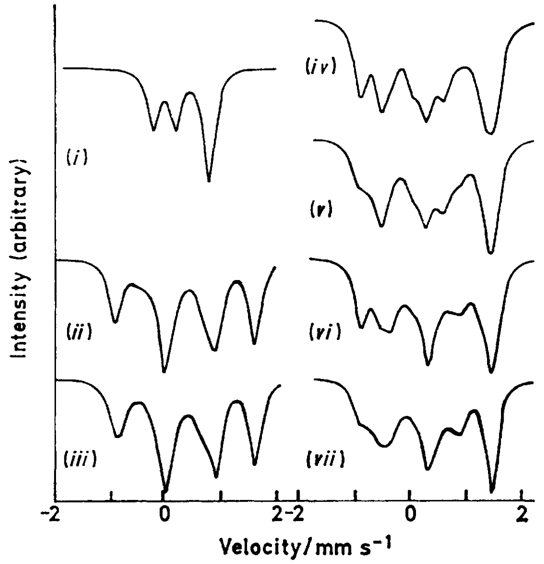

FIGURE 6 Type (II) spectra. In (*i*) there is no applied field and the lines are centred at $-$0·20, +0·20, and +0·80 mm s^{-1}, all with Γ = 0·25 mm s^{-1}. The other spectra are computed for a longitudinal magnetic field of 50 kG with $\eta = 0$. Spectra (*ii*) (Fe^A+, Fe^B0) and (*iii*) (Fe^A-, Fe^B0) correspond to assignment (IIa) with parameters: Fe^A δ = 0·00 and $|\Delta E_Q|$ = 0·40 mm s^{-1}; Fe^B δ = 0·80 and $|\Delta E_Q|$ = 0·00 mm s^{-1}. Spectra (*iv*)—(*vii*) (Fe^A+, Fe^B+; Fe^A-, Fe^B+; Fe^A+, Fe^B-; Fe^A-, Fe^B-) correspond to assignment (IIb), for which the parameters are: Fe^A δ = 0·30 and $|\Delta E_Q|$ = 1·00 mm s^{-1}; Fe^B δ = 0·50 and $|\Delta E_Q|$ = 0·60 mm s^{-1}

The spectra which result from assignment (IIa) showed only small changes on reversing the sign of e^2qQ at Fe^A, the most pronounced differences being in the widths of the two bands at *ca.* $-$0·9 and +0·9 mm s^{-1}. This is because the shape of the spectrum is dominated by lines which result from Zeeman splitting of the intense high-velocity singlet in the zero-field spectrum. In a longitudinal magnetic field this line splits into a quartet with intensity ratio 3 : 1 : 1 : 3. (For a transverse field one obtains a sextet with intensity ratio 3 : 4 : 1 : 1 : 4 : 3.) Superimposed on this is the weaker triplet–doublet pattern from the Fe^A lines. Because of the large difference in δ^A and δ^B, the lowest-velocity line in the spectrum results only from the Fe^A splitting. If $e^2qQ > 0$ this line is narrow since it is one branch of the triplet, but if $e^2qQ < 0$ the line is one branch of the broadened doublet. In the former case the central line of the triplet was also seen as a weak shoulder at *ca.* $-$0·5 mm s^{-1} in Figure 6 (*ii*). The appearance of these two spectra suggests that with data of high quality one could probably determine the sign of e^2qQ at Fe^A if η is small, but it is unlikely that this could be done otherwise.

For the more likely assignment (IIb), the overall appearances of the various spectra were sufficiently different that no difficulty is to be expected in determining the signs of e^2qQ and approximate magnitudes of η at both sites. We note that for $\eta = 0$ the sign of the e.f.g. at the iron site with the larger splitting (Fe^A) will be obvious from visual inspection of a magnetic-perturbation spectrum. The lowest-velocity line was well resolved only when $e^2qQ > 0$ at this site, otherwise it appeared as a weaker shoulder. This will be true when lines (1) and (2) in the zero-field spectrum are clearly separated. A change in the sign of the e.f.g. at Fe^B from positive to negative was reflected mainly in a broadening of the band centred at *ca.* $-$0·6 mm s^{-1}, with concomitant narrowing and lessening of complexity of the absorption envelope centred at *ca.* +0·3 mm s^{-1}. Of course the exact details of these changes will depend on the differences in δ and $|\Delta E_Q|$ at the two iron atoms, but the values we assumed for these differences were quite ' normal ' compared to those for many complexes showing a type (II) spectrum. Thus, we expect our conclusions to be fairly general.

Type (III) *Spectra.*—In the case of diamagnetic iron(0) complexes a spectrum of this type probably will result only if both iron atoms have very similar δ and $|\Delta E_Q|$ values, due either to nearly identical environments or to accidental degeneracy. The alternative assignment would require each iron atom to be at a site of high symmetry but for the two atoms to have very different isomer shifts, an unlikely situation. However, for completeness we consider both cases. In the most common type (III) spectra the lines are unsymmetrically broadened, and we chose to analyse a spectrum of this kind as shown in Figure 7(*i*).

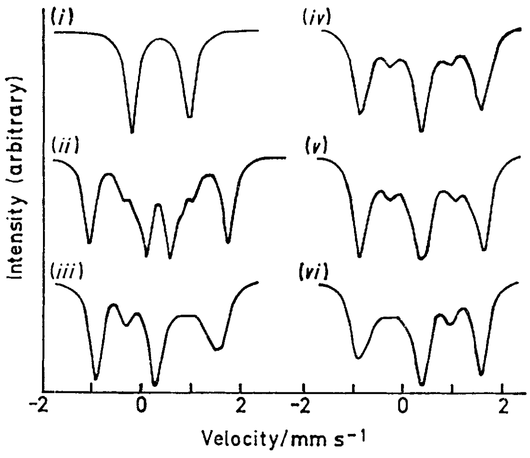

FIGURE 7 Type (III) spectra. In (*i*) the parameters are: Fe^A δ = 0·30 and $|\Delta E_Q|$ = 1·10 mm s^{-1}; Fe^B δ = 0·35 and $|\Delta E_Q|$ = 1·20 mm s^{-1}. For both sites, Γ = 0·25 mm s^{-1}, $\eta = 0$, and $H = 0$. The same parameters were used for spectra (*iii*)—(*vi*) (Fe^A+, Fe^B+; Fe^A-, Fe^B+; Fe^A+, Fe^B-; Fe^A-, Fe^B-), except in these cases $H_{\parallel}$ = 50 kG. Spectrum (*ii*) is that which would be observed for $H_{\parallel}$ = 50 kG if each of the two lines of (*i*) arose from different iron sites

For assignment (IIIa), in which the two lines arise from different iron sites, application of a longitudinal magnetic field splits each line into a quartet with 3 : 1 : 1 : 3 intensity ratio. If the field is sufficiently large these two quartets will overlap as in Figure 7(*ii*), but regardless of the extent of overlap a very symmetrical pattern will result. Indeed, if the two lines in zero field have the same widths and intensities, the applied-field spectrum will have mirror symmetry about a velocity corresponding to the mean isomer shift for the two sites.

Assignment (IIIb) led to spectra which were very different in appearance from those for (IIIa), so that the two cases can be easily distinguished. When the η values were small and the e.f.g. had the same sign at both sites, the familiar [8] triplet–doublet pattern resulted, the triplet lying to lower energy if $e^2qQ > 0$ and to higher energy if $e^2qQ < 0$. Since in general the two iron atoms will have slightly different values of δ and $|\Delta E_Q|$, there will be some line broadening, and for the 50 kG field assumed in our calculations the inner branches of the doublet and triplet overlapped [see Figure 7(*iii*)]. When the e.f.g. was opposite in sign at the two sites, the spectrum was fairly symmetrical, as in Figures 7(*iv*) and (*v*). It is to be noted that for the particular case illustrated there are sufficient differences in the detailed features of the spectra so that one can determine which e.f.g. sign goes with which $|\Delta E_Q|$ value. If the zero-field spectrum is more symmetrical, however, this may no longer be true.

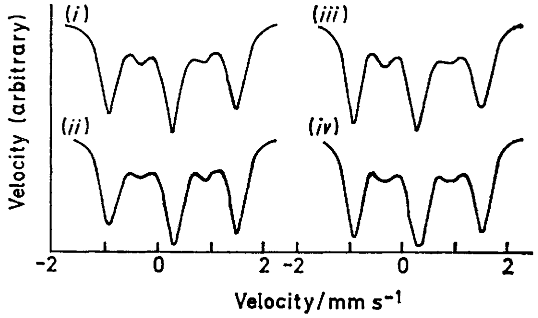

FIGURE 8 The effect of non-zero η-values on a magnetically perturbed type (III) spectrum in which e^2qQ has opposite signs at the two iron sites. For all four spectra there is a 50 kG longitudinal magnetic field, and the other parameters are the same as those used for Figure 7(*iv*). The η values for the two sites are: (*i*) $\eta^A = \eta^B = 0{\cdot}0$; (*ii*) $\eta^A = 0{\cdot}0$, $\eta^B = 0{\cdot}8$; (*iii*) $\eta^A = 0{\cdot}8$, $\eta^B = 0{\cdot}0$; and (*iv*) $\eta^A = \eta^B = 0{\cdot}8$

When $\eta \neq 0$ at one or both sites it becomes more difficult to determine the parameters with certainty, the worst cases being those in which the two e.f.g.s have different signs. This is illustrated by Figure 8, from which it is clear that only rather subtle differences in the spectra are produced by quite large η values. Only with experimental data of exceptionally high quality is it likely that one will be able to deduce η values of even moderate accuracy from type (III) spectra. On the other hand, the sign of e^2qQ at each site can probably be determined in most instances that one is likely to encounter.

Application to ^{119}Sn *Spectra*.—Although most useful for binuclear iron derivatives, the general techniques outlined in this paper would also be applicable to tin compounds with two inequivalent tin atoms. There will, of course, be significant differences in detail owing to the different nuclear parameters for ^{57}Fe and ^{119}Sn. We also anticipate that it will be more difficult to extract the desired information from a magnetically perturbed ^{119}Sn Mössbauer spectrum.

However, a recent paper by Di Salvo *et al.*[15] leads us to suggest at least one potential application of these techniques to ^{119}Sn Mössbauer spectroscopy. These authors reported the intercalation of Sn into TaS_2, a layered transition-metal compound, one of the products obtained having the stoicheiometry $Sn_{1{\cdot}0}TaS_2$. The Mössbauer spectrum of this compound consists of two lines with approximately equal intensities at $-0{\cdot}07$ and $+1{\cdot}07$ mm s^{-1} (relative to α-Sn). There are thus either two electronically different but roughly equally populated sites for the tin atoms, or one site with a substantial quadrupole interaction. No decision between these alternatives could be reached from the available data.[15] In this particular instance a magnetic-perturbation experiment would provide an unambiguous answer, since the two possibilities will produce very dissimilar spectra.

EXPERIMENTAL

The complex $[(OC)_3\overline{Fe(\mu\text{-}L)Fe}(CO)_3]$ [L = 1,2-bis(dimethylarsino)hexafluorocyclopent-1-ene] was prepared and characterized by L. S. Chia of this Department. Its ^{57}Fe Mössbauer spectrum in zero applied magnetic field was recorded with a 10 mCi ^{57}Co(Cu) source at room temperature and the finely powdered absorber at 80 K in transmission geometry, using a spectrometer previously described.[4] The data were least-squares fitted to Lorentzian components using a program which imposed no constraints on the fitting parameters. Isomer shifts are quoted relative to the centroid of the disodium pentacyanonitrosylferrate(III) spectrum.

Magnetic-perturbation measurements were carried out in a Janis model 11MDT helium cryostat fitted with a Westinghouse superconducting solenoid capable of generating magnetic fields of up to 50 kG. The sample was contained in a brass cell, with Mylar windows, located at the centre of the applied field. The vertically mounted ^{57}Co(Cu) source was driven, *via* a thin-walled stainless-steel drive rod, by an Austin Science Associates K-3 linear motor located in the common vacuum space with the absorber. Care was taken to ensure that the source was outside the fringing field of the magnet. With this geometry, the directions of the applied field and of the γ-ray beam were collinear. A zero-field spectrum was also recorded at liquid-helium temperature as a check, and no significant differences in parameters were observed between spectra obtained at 4·2 and 80 K.

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