A Correlation between Mössbauer Spectra and Paramagnetic Measurements for High-spin Iron(III) Compounds: the Case of Chlorobispentane-2,4-dionatoiron(III)

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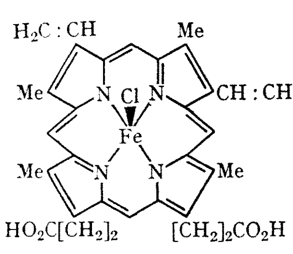
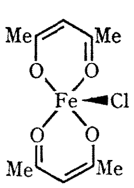
BECAUSE long spin-lattice relaxation times are associated with ^6S electronic ground states, spin–spin relaxation dominates the behaviour of ferric compounds with $S = 5/2$ If these relaxation times are comparable with the Larmor precession times, a broadening of the peaks in the ^{57}Fe Mössbauer spectrum is observed.[1] This broadening is especially noticeable in quadrupole-split spectra because it shows as an asymmetry in peak heights.[2] Ferric chlorohaemin (I) exhibits a room-temperature spectrum of two peaks differing markedly in intensity; a doublet spectrum with about equal components is observed at low temperatures. This increase in relaxation time with increasing temperature has been accounted for[3] on the basis of the Kramers' doublet $M_S = \pm \frac{1}{2}$ lying lowest in energy and relaxing fastest.



(I)



(II)

We have measured the Mössbauer spectrum of Fe acac$_2$Cl[4] (acac = MeCO·CH·COMe) at various temperatures (Figure 1); it exhibits haemin-like behaviour. The peak asymmetry is sufficiently pronounced at 80°K to have caused the weak peak to be overlooked in an earlier study.[5] Fe acac$_2$Cl is essentially magnetically dilute down to 80°K (μ = 5·98 B.M. at 301°K) and the chemical isomeric shift from

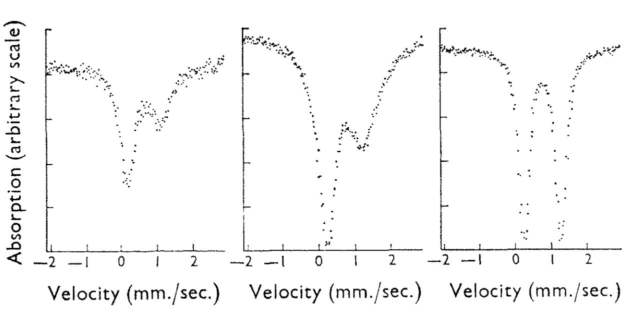


FIGURE 1. *Mössbauer spectra of* Fe acac$_2$Cl *at* (a) *Room temperature,* (b) 80°K *and* (c) 4°K.

$Na_2[Fe(CN)_5NO]$ is *ca.* 0·60 mm. sec.$^{-1}$, which is correct for high-spin ferric complex. The quadrupole splitting of *ca.* 1 mm. sec.$^{-1}$ is consistent with non-cubic symmetry about the iron. These results, together with the similarity of the temperature behaviour to that of haemin, lead us to the conclusion that Fe acac$_2$Cl is also square pyramidal as depicted in (II). It is a further example of pentacoordinate ferric iron, but with $S = 5/2$ rather than $S = 3/2$ as in the $Fe(R_2N{\cdot}CS_2)_2Cl$ [6,7] series. Because the high-energy peak in the spectrum of compound (II) has the lower intensity, it is the $\pm\frac{3}{2} \rightarrow \pm\frac{1}{2}$ transition and V_{zz} is positive. This is reasonable, because a square-pyramidal array of ligands has more negative charge in the XY plane than on the Z-axis and there is no valence contribution to the electric field gradient.[8] V_{zz} is negative in $FeCl_3,6H_2O$.

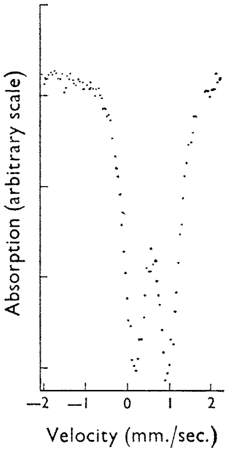


FIGURE 2. *Mössbauer spectrum of* [Fe salen]$_2$O *at* 80°K.

Whilst magnetically dilute ferric complexes with quadrupole splitting show some peak asymmetry, intramolecular antiferromagnets containing a pair of ferric ions, *e.g.*, [Fe salen]$_2$O,[9] [salen = 1,2-di(salicylideneamino)ethane] exhibit no broadening over comparable temperature ranges (see Figure 2). Analogous compounds behave similarly; we conclude that this class of compound undergoes fast spin–spin relaxation at all temperatures. It is reasonable to suppose that this spin-spin interaction is transmitted through the oxygen bridge of [Fe salen]$_2$O. Similar remarks apply to the [phen$_2$ Fe·O·Fe phen$_2$] systems (phen = 1,10-phenanthroline) which also show peaks of equal intensity (Figure 2).

All examples for which Mössbauer and paramagnetic data are available fit into this picture. The magnetically dilute systems include $FeCl_3,6H_2O$,[10] together with haemin[11] and Fe acac$_2$Cl, whilst compounds exhibiting sharp doublets of equal intensity and known to be intramolecular antiferromagnets include [Fe salen]$_2$O,[9] [Fe salenCl]$_2$,[12] and [Fe salenF]$_2$, together with the [phen$_2$Fe·O·Fe phen$_2$]$^{4+}$ family.[13]

Since this communication was submitted, a paper dealing with relaxation in these systems has appeared.[14] The authors of this take the view that the relaxation process in the dimers could be intermolecular, and quote results of dilution studies using unspecified frozen solvents as matrices for the dimers in Mössbauer experiments. Many solvents split the Fe·O·Fe bridges, so such experiments could mislead. We adhere to our present view that the spin–spin relaxation is intramolecular and we are actively seeking suitable diamagnetic diluents to help probe this interesting point further.

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