Spin Isomerism in Tris(monothio-β-diketonato)iron(III) Complexes[1]

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Mössbauer spectral parameters and paramagnetic susceptibilities have been measured for four tris(monothio-β-diketonato)iron(III) complexes. The results are interpreted in terms of a thermal equilibrium between sextet and doublet electronic states. In favourable cases, superimposed spectra are observed in which both spin states can be recognised.

DEPENDING upon the strength and symmetry of the crystal field, iron(III) compounds can exist with either sextet ($^6A_1$), quartet (^4A), or doublet ($^2T_2$) electronic ground states. The quartet states are apparently associated with the five-co-ordinate square-pyramidal stereochemistry as in the chlorobis(*NN*-dialkyldithiocarbamato)iron(III) family[2] or in *NN'*-ethylenebis(salicylideneiminato)nitrosyliron(III).[3] The last compound, however, is a spin quartet down to 180 K only; at lower temperatures it crosses over to a doublet state.

These variations in behaviour have been extensively investigated by physical methods. ^{57}Fe Mössbauer spectroscopy has proved to be an effective complement to paramagnetic-susceptibility measurements in these studies because the chemical isomeric shifts and quadrupole splittings serve to characterise each spin state reasonably well. The quadrupole splitting is the more useful parameter in this connection. Tris(chelate)iron(III) compounds generally exhibit quadrupole splitting. This arises from the interaction of the quadrupole moment of the $I = \frac{3}{2}$ nucleus with the electric-field gradient (e.f.g.). This e.f.g. is generated by the iron(III) valence electrons together with any asymmetry of the co-ordination sphere about the iron atom. The quadrupole splitting is given by:

$$\Delta E = \tfrac{1}{2}e^2Qq(1 + \eta^2/3)^{\frac{1}{2}}$$

eq is the principal component of the e.f.g., *Q* is the quadrupole moment of the $I = \frac{3}{2}$ state, and η the asymmetry parameter is given by $\eta = V_{XX} - V_{YY}/V_{ZZ}$.

The e.f.g. in high-spin iron(III) compounds arises from the co-ordination asymmetry only as the valence contribution averages to zero in these $^6A_1$ compounds. For unsymmetrical chelate compounds, the co-ordination asymmetry can be pictured as arising from differences in electronegativity between the six ligand atoms about the ferric atom. If the ligand atoms are identical, as in a symmetrical tris(chelate)iron(III) compound, then a smaller e.f.g. can arise from the constraint imposed by the chelate on the metal-ligand bond distances[4] and small quadrupole splittings, *ca.* 0·5 mm s^{-1}, have been recorded for such symmetrical tris(chelate)iron(III) complexes. In way of contrast, low-spin (^2T) tris(chelate) complexes often show quite appreciable splittings because of a valence contribution to the e.f.g. from the lifting of the three-fold degeneracy of the t_2 manifold by the crystal field. Thus, tris(2,2'-bipyridyl)iron(III) perchlorate shows a splitting of 1·6 mm s^{-1}. Because this does not increase with decreasing temperature, it would appear as if the degeneracy of the t_2 manifold has been raised by energies in excess of kT.[4]

It can be seen that a change from a sextet to a doublet state could be associated by an increase in quadrupole splitting of up to 1 mm s^{-1}. This difference reflects the details of the microsymmetry of the iron atom but it could reasonably be expected to be a feature of many

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[1] Preliminary communication, M. Cox, J. Darken, B. W. Fitzsimmons, A. W. Smith, L. F. Larkworthy, and K. A. Rogers, *Chem. Comm.*, 1970, 105.

[2] H. H. Wickman and A. M. Trozzolo, *Inorg. Chem.*, 1968, **7**, 63.

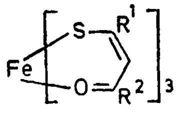
[3] A. Earnshaw, E. A. King, and L. F. Larkworthy, *J. Chem. Soc.* (*A*), 1969, 2459.

[4] R. R. Berrett, B. W. Fitzsimmons, and A. A. Owusu, *J. Chem. Soc.* (*A*), 1968, 1575.

of these crossover situations. It is clear that the appearance of the Mössbauer spectrum will critically depend upon this difference. Because of the expected increase in chemical isomeric shift with decreasing temperature, it will be of less use in such studies. There is here the added difficulty of extracting this quantity from complex spectra.

The Mössbauer spectra of well established spin isomers, the tris(*NN*-dialkyldithiocarbamato)iron(III) compounds, have been studied in detail.[5] For these compounds, single-species spectra were always observed and it was proposed that a fast exchange rate between the $^6A_1$ and $^2T_2$ states caused the spectra to be averaged to an apparent single quadrupole doublet. This requires the exchange rate to be faster than the lifetime of the excited state of ^{57}Fe ($1·5 \times 10^{-7}$ s). However, a feature of these spectra is the small apparent quadrupole splitting which we suppose to be due to the symmetrical nature of the dithiocarbamato-ligands coupled with a favourable geometry. But this matter cannot yet be regarded as settled because the crystal-structure determination of tris(*NN*-dibutyldithiocarbamato)iron(III) reveals [6] a non-octahedral arrangement of sulphur atoms.

We wished to study a family of iron(III) complexes that could reasonably be expected to exhibit larger quadrupole splittings and thereby stand a better chance of displaying two pairs of quadrupole-split lines at the appropriate temperatures. It seemed to us that complexes containing unsymmetrical chelates were appropriate. A number of tris(monothio-β-diketonato)iron(III) complexes (I) were prepared from the corresponding monothio-β-diketone after reaction with iron(III) chloride dissolved in a tertiary amine (see Experimental section). Livingstone [7] *et al.*, had already discovered spin isomerism for compound (Ia) by measuring its paramagnetic susceptibility down to 80 K. We also obtained susceptibility data for compound (Ia) as well as for compounds (Ib), (Ic), and (Id), which have not been previously reported. Our susceptibility data are summarised in Table 1. Compound (Ia) has a room-temperature moment of 5·5 B.M.: this falls gradually to 2·8 B.M. at 80 K. Figures 1 and 2 show the Mössbauer spectra at these two temperatures. The two spin isomers are clearly visible in the 80 K spectrum (Figure 2). The outer peaks are due to the low-spin isomer, the inner pair correspond to the high-spin isomer. The relevant Mössbauer parameters for all these compounds are in Table 2. These parameters were computed by fitting the data to Lorent-



(I)

a; $R^1 = R^2 =$ Ph
b; $R^1 = R^2 =$ Me
c; $R^1 =$ Me, $R^2 =$ Ph
d; $R^1 =$ Ph, $R^2 =$ Me

TABLE 1

Magnetic data for compounds (Ia—d)

	Compound (Ia)			
T (K)	300·1	265·3	229·5	193·4
μ_{eff} (B.M.)	5·50	5·28	4·88	3·64
T (K)	157·4	119·5	9·80	89·6
μ_{eff} (B.M.)	3·64	3·04	2·84	2·80
	Compound (Ib)			
T (K)	301	265·5	230·5	194
μ_{eff} (B.M.)	5·66	5·66	5·68	5·60
T (K)	157·5	119·3	98·7	91·2
μ_{eff} (B.M.)	5·58	2·65	2·53	2·66
	Compound (Ic)			
T (K)	300·4	265·4	229·7	193·8
μ_{eff} (B.M.)	4·35	4·03	3·69	3·16
T (K)	157·2	119·6	98·2	89·3
μ_{eff} (B.M.)	2·59	2·34	2·26	2·24
	Compound (Id)			
T (K)	300·5	265·4	229·4	193·0
μ_{eff} (B.M.)	5·75	5·68	5·63	5·60
T (K)	157·0	118·8	97·5	87·0
μ_{eff} (B.M.)	5·38	5·17	5·02	4·95

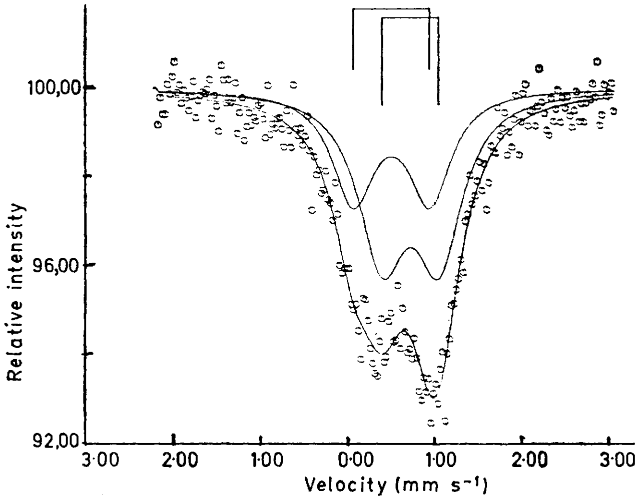


FIGURE 1 Spectrum of compound (Ia) at 300 K

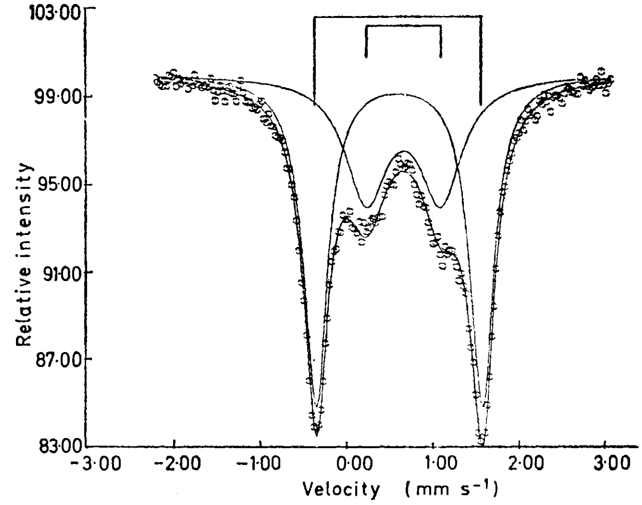


FIGURE 2 Spectrum of compound (Ia) at 80 K

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[5] R. Rickards, C. E. Johnson, and H. A. O. Hill, *J. Chem. Phys.*, 1968, **48**, 5231.

[6] B. F. Hoskins and B. P. Kelly, *Chem. Comm.*, 1968, 1517.

[7] R. K. Y. Ho and S. E. Livingstone, *Austral. J. Chem.*, 1968, **21**, 1987.

zian peaks by means of a least-squares computer program.

The room-temperature spectrum needs further comment. Because the total degeneracies of the $^6A_1$ and $^2T_2$ states are the same, a 1 : 1 mixture is expected to be present at sufficiently high temperatures. In order to find the theoretical effective magnetic moment corresponding to this distribution of spin isomers, knowledge of the magnetic moments corresponding to each isomer is required. Although it is reasonable to associate a magnetic moment of 5·92 B.M. with the $^6A_1$ compound, that of the $^2T_2$ will itself be somewhat temperature dependent and a single unique value cannot be assigned to it. A room-temperature value of 2·3 B.M.[8] is probably good enough for our purposes. The effective magnetic moment of a 1 : 1 mixture is given by $\{\frac{1}{2}(5{\cdot}92)^2 + \frac{1}{2}(2{\cdot}30)^2\}^{\frac{1}{2}} = 4{\cdot}48$ B.M. The observed magnetic moment is 5·50 B.M. from which we calculate that the high-spin isomer is present to the extent of 81%. Qualitatively at least, the Mössbauer spectrum is in good agreement with this in that only the high-spin isomer can be seen and it looks as if the peaks of the low-spin isomer are buried in the wings of the absorption peak. The high-spin isomer exceeds the theoretical 50% maximum for a true Boltzmann distribution between two equi-degenerate energy states and this has been found to be a feature of spin isomerism generally. Reasons for the departure from ideal behaviour have been discussed in detail.[8]

TABLE 2

Mössbauer spectral parameters * for compounds (Ia—d) at 300 and 80 K

	300 K			80 K			
Compd.	ΔE	δ	Γ	ΔE	δ	Γ	Spin state
(Ia)	0·646	0·714	0·698	0·861	0·675	0·586	$^6A_1$
	0·923	0·521	0·600	1·919	0·610	0·334	$^2T_2$
(Ib)	0·270	0·768	0·456	0·583	0·788	0·610	$^6A_1$
				1·887	0·673	0·296	$^2T_2$
(Ic)	0·617	0·655	0·389				$^6A_1$
	1·452	0·545	0·372	1·930	0·606	0·273	$^2T_2$
(Id)	0·241	0·829	0·441	0·264	0·871	0·516	$^6A_1$
	0·572	0·639	0·532	1·794	0·659	0·224	$^2T_2$

* ΔE, the quadrupole splitting, δ, the chemical isomeric shift and Γ, the full-width at half-maximum, are in mm s^{-1}. δ Is with respect to $Na_2[Fe(CN)_5NO]2H_2O$.

Compound (Ib) behaves similarly to (Ia) except that no low-spin isomer was detected at 300 K.

Compound (Ic) displays a pure two-peak Mössbauer spectrum at 80 K. There is no sign of any high-spin component at this temperature. The magnetic moment at 89·3 K is 2·24 B.M., the lowest attained by any of these compounds. The magnetic moment at 300 K is 4·35 B.M., which corresponds to 46% of the high-spin form. Although the Mössbauer spectrum at this temperature lacks resolution because of the low recoil-free fraction, nevertheless the two components are present in approximately equal amounts. The spectra obtained at 300 and 80 K, together with the computed curves, are shown as Figures 3 and 4 respectively.

Finally, compound (Id) displays a much shallower variation of physical property with temperature than do the others. At 80 K, much high-spin isomer is still present, somewhere around 70%. At 87 K, the moment is 4·95, which corresponds to 60% of the high-spin species. The moment rises to 5·75 B.M. at 300·5 K: the low spin form cannot then be detected. Spectra at 300 and 80 K are shown as Figures 5 and 6 respectively.

It can be seen that compounds (Ia—d) display internally consistent behaviour in that both spin-isomers can be observed in the Mössbauer spectrum when present in significant amounts. As in earlier studies, it is found that the thermal equilibrium is far from ideal in that the theoretical maximum 1 : 1 ratio of isomers is exceeded in some cases. We suspect that the present family of compounds may differ from the dithiocarbamatoiron(III)

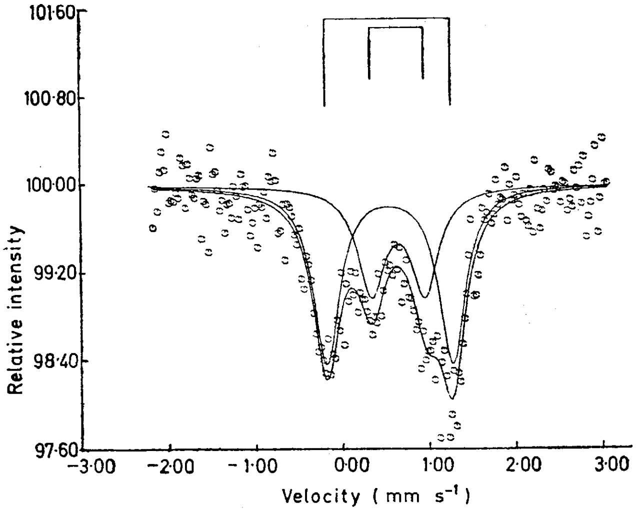

FIGURE 3 Spectrum of compound (Ic) at 300 K

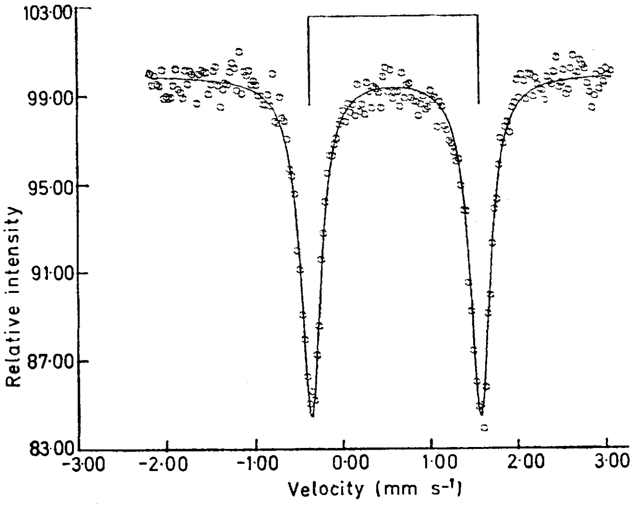

FIGURE 4 Spectrum of compound (Ic) at 80 K

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[8] R. L. Martin and A. H. White, ' Transition Metal Chemistry,' ed. R. L. Carlin, Marcel Dekker Inc., New York, 1968, p. 113.

complexes only in a favourably appreciable quadrupole-splitting difference between the two spin states. It may be this factor which permits the detection of both spin isomers by Mössbauer spectroscopy rather than a slow exchange rate but both factors have to be favourable before the individual spin-isomers can be observed by Mössbauer spectroscopy.

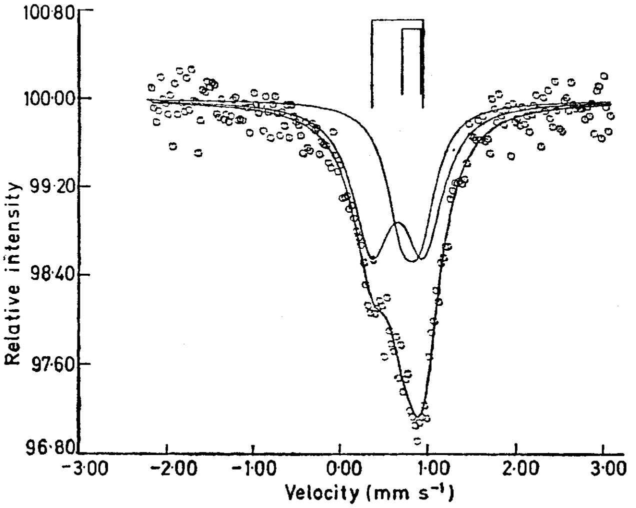

FIGURE 5 Spectrum of compound (Id) at 300 K

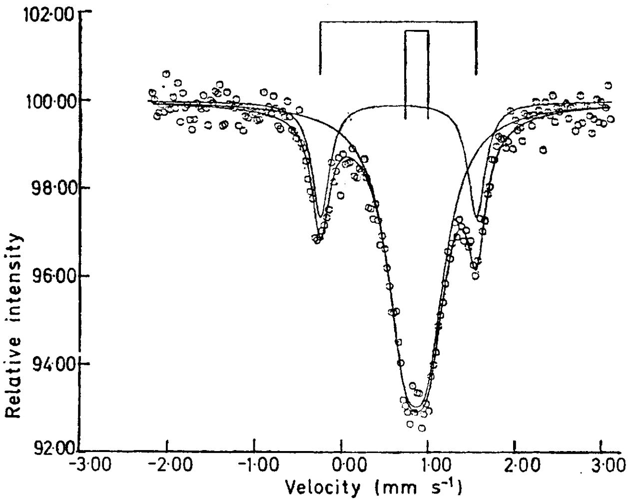

FIGURE 6 Spectrum of compound (Id) at 80 K

EXPERIMENTAL

Tris(3-thioxo-1,3-diphenylprop-2-en-1-onato)iron(III) Fe-($C_6H_5COCHCSC_6H_5)_3$.—A solution of anhydrous iron(III) chloride (0·5 g, 3·1 mmol) in water (20 ml) was added during 1 min to a rapidly stirred solution of monothiodibenzoylmethane (2·30 g, 9·5 mmol) and triethylamine (1·5 g, 15·0 mmol) in acetonitrile (20 ml). The reaction mixture immediately became dark green and a dark oil or solid was deposited. Continued rapid stirring caused the oil to crystallise. The very dark green product was filtered off, washed well with water, and dried *in vacuo* (2·0 g, 83%), m.p. 152° (lit. 152—154). The product could be recrystallised from acetone–light petroleum (b.p. 60—80°) [Found: C, 70·5; H, 4·3; Fe, 7·2. Calc. for $Fe(C_6H_5COCHCSC_6H_5)_3$: C, 69·5; H, 4·3; Fe, 7·2%].

Tris(4-thioxo-4-phenylbut-3-ene-2-onato)iron(III) $Fe(C_6H_5CSCHCOCH_3)_3$.—Addition of a solution of anhydrous iron(III) chloride (1·0 g, 6·2 mmol) in ethanol (20 ml) to a stirred solution of thiobenzoylacetone (3·3 g, 19·2 mmol) and triethylamine (2·0 g, 20 mmol) also in ethanol (60 ml) immediately gave a dark green solution. A very dark precipitate was formed which was filtered off, washed well with water, and dried *in vacuo* (2·85 g, 78%) m.p. 129°. Recrystallisation from organic solvents resulted in deterioration of the product with formation of the disulphide (Found: C, 61·3; H, 4·4: Fe, 9·5. $C_{30}H_{27}O_3S_3Fe$ requires: C, 61·3; N, 4·6; Fe, 9·5%).

Tris(3-thioxo-1-phenylbut-2-ene-1-onato)iron(III) $Fe(C_6H_5COCHCSCH_3)_3$.—This complex was prepared by the method used in the previous preparation, as a very dark green solid (3·06 g, 84%), m.p. 125—126°. Recrystallisation from organic solvents resulted in deterioration of the product (Found: C, 61·3; H, 4·5; Fe, 9·5. $C_{30}H_{27}O_3S_3Fe$ requires: C, 61·3; H, 4·6; Fe, 9·5%).

Tris(4-thioxopent-3-ene-2-onato)iron(III) $Fe(CH_3CSCHCOCH_3)_3$.—A filtered solution of anhydrous iron(III) chloride (0·5 g, 3·1 mmol) in sodium-dried ether (10 ml) was added rapidly to a shaken solution of *freshly prepared* monothioacetylacetone (1·16 g, 10·0 mmol) and triethylamine (1·0 g, 10·0 mmol) in sodium-dried ether (15 ml). A vigorous reaction occurred and the mixture became dark green. The reaction vessel was stoppered and cooled to −20° for 1 h. The solid products were filtered off and washed well with cold water to remove triethylamine hydrochloride. The resultant black crystalline product was dried *in vacuo*. The compound was not very stable, decomposition occurring slowly even when sealed *in vacuo* (0·6, 48%), m.p. 95°(d). (Found: C, 44·9; H, 5·5; Fe, 13·7. $C_{15}H_{21}O_3S_3Fe$ requires C, 44·9; H, 5·3; Fe, 13·9%).

The ligands were synthesised according to Uhlemann [9-11] and Tanaka.[12]

Magnetic Susceptibility Measurements.—These measurements were carried out by the Gouy method over the temperature range 80—300 K.

Mössbauer Spectra.—Spectra at 80 K were measured in an all-metal liquid-nitrogen cryostat of conventional design. The spectrometer employed counting equipment as in reference 4 but the drive unit was a Centronic Mössbauer Effect Analyser (20th Century Electronics) and an Intertechnic SA 41 400 channel analyser. Data were processed using standard least-squares fitting programs on the London University CDC 6600 computer.

[1/203 *Received, 2nd March*, 1971]

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[9] E. Uhlemann and H. Müller, *Angew. Chem. Internat. Edn.*, 1965, 154.

[10] E. Uhlemann and P. Thomas, *J. prakt. Chem.*, 1966, **34**, 180.

[11] E. Uhlemann and P. Thomas, *Z. Naturforsch.*, 1968, **23b**, 275.

[12] A. Yokoyama, S. Kawanishi, M. Guikuma, and H. Tanaka, *Chem. Pharm. Bull. (Japan)*, 1967, **15**, 540.