Well-resolved Mössbauer Spectra for Spin-isomeric Tris(monothio-β-diketonato)-iron(III) Compounds

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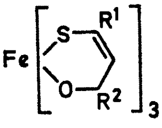
Summary The coexistence of individual spin isomers has been observed in the Mössbauer spectra of tris(monothio-β-diketonato)-iron(III) complexes.

ALTHOUGH the concept of thermal equilibrium between $^6A_1$ and $^2T_2$ spin isomers accounts for the magnetic susceptibility data observed[1,2] for tris-(*NN*-dialkyldithiocarbamato)-iron-(III) complexes, unfavourable relaxation times prevent the detection of the individual isomers using Mössbauer spectroscopy. We have investigated a different system which is more favourable in this respect, specifically tris(monothio-β-diketonato)-iron(III) complexes, (I), for which spin isomerism was discovered by Ho and Livingstone[3] using paramagnetic measurements. We have measured paramagnetic susceptibilities and Mössbauer spectra in the temperature range 80—300°K of four compounds of general formula (I).



(Ia) $R^1 = R^2 = Ph$
(Ib) $R^1 = R^2 = Me$
(Ic) $R^1 = Me, R^2 = Ph$
(Id) $R^1 = Ph, R^2 = Me$

Compound (Ia) has been prepared before.[3] The other compounds are new and were prepared by the reaction of freshly synthesised ligand[4] with anhydrous iron(III) chloride in the presence of triethylamine in suitable solvents. The ligands were prepared by a multistage synthesis[4] which enabled us to prepare geometrical isomers (Ic) and (Id). Preparation of the ligand from the parent β-diketone allows the synthesis of isomer (Ic) only.[5]

The important feature of the Mössbauer study is that both spin-isomers can be seen in the Mössbauer spectrum if present in appreciable amounts. A typical example is provided by compound (Ia) (see Table and Figure 1 and 2).

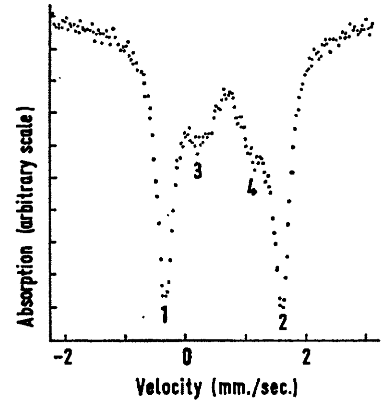


FIGURE 1. *The Mössbauer spectrum at* 80°K *of compound* (Ia).

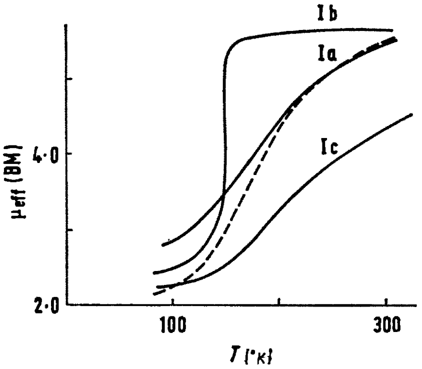


FIGURE 2. *Variation of effective magnetic moment,* μ_{eff}, *with absolute temperature for compounds* (Ia), (Ib), *and* (Ic). *Dashed curve shows previous*[3] *results for compound* (Ia).

Mössbauer parameters for tris(monothio-β-diketonato)-iron*(III) *compounds*

	300°K				80°K			
	High-spin		Low-spin		High-spin		Low-spin	
	ΔE	δ	ΔE	δ	ΔE	δ	ΔE	δ
(Ia)	0·61	0·65	—	—	0·93	0·65	1·90	0·60
(Ib)	0·26	0·75	—	—	—	—	0·24	0·52
(Ic)	0·56	0·60	1·47	0·57	—	—	1·91	0·61
(Id)†	—	—	—	—	0·00	0·85	1·68	0·58

* ΔE is the quadrupole splitting and δ the chemical isomeric shift relative to disodium pentacyanonitrosylferrate(II); † Room temperature spectrum too weak to measure.

Peaks 1 and 2 (Figure 1) are assigned to the low-spin ($^2T_2$) isomer whilst peaks 3 and 4, corresponding to a much lower quadrupole splitting, are due to the high-spin ($^6A_1$) isomer. The observed quadrupole splittings have values similar to those previously obtained for $^2T_2$ and $^6A_1$ iron(III) compounds.[6] Because the ligand field is close to the critical cross-over value, the chemical isomeric shifts are not expected to be much different as is here observed. As can be seen from

Figure 1, the low-spin form predominates at this temperature in agreement with the observed magnetic moment of 2·80 BM, which is somewhat higher than the previously reported value.[3] The magnetic moments at the higher temperatures agree well (Figure 2).

Compound (Ib) shows a sharp transition between the $^6A_1$ and $^2T_2$ states at *ca.* 150°K but the Mössbauer spectra of the two forms are very similar. Neither spin isomer appears to have appreciable quadrupole splitting and we conclude that this is a case where the ferric ion lies at a site of near-cubic symmetry despite the presence of asymmetric chelating ligands. Compound (Ic) behaves similarly to (Ia); no trace of the $^6A_1$ state can be seen in the Mössbauer spectrum at 80°K whilst both are clearly discernible at 300°K in agreement with the magnetic data (Figure 2). Compound (Id) does not give a satisfactory Mössbauer spectrum at 300°K but both spin-isomers can be seen at 80°K and the correlation with the magnetic data is good (μ_{eff} = 5·75 BM at 300°K and 4·95 BM at 87°K).

This is the first observation of spin isomers by Mössbauer spectroscopy in a $^6A_1 \rightleftharpoons {}^2T_2$ cross-over situation. It is reasonable to conclude that the relaxation time to change from one spin-state to another is long compared with the effective quadrupole period in contrast to the behaviour so far reported for the Fe^{III} trisdithiocarbamato-complexes which exhibit time-averaged spectra of only two lines whose separation varies slightly with temperature.

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