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SPIN EQUILIBRIUM OF ${}^6A_1 \rightleftharpoons {}^2T_2$ IN TRIS (MONOTHIO- β -DIKETONATO)IRON(III)

J. Akashi, K. Endo and H. Sano

Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Fukasawa, Setagaya, Tokyo 158, Japan

Résumé.- L'équilibre des spins, spin-fort(6A_1) \rightleftharpoons spin-faible (2T_2) a été étudié dans la série des composés de tris (monothio- β -dikétonato)fer(III), FeL_3 ($L = RCSCHCOR'$). On a trouvé que l'équilibre des spins est sensible à la substitution dans les ligands et que l'effet sur l'équilibre des spins dû à la substitution de R est bien différent de celui dû à la substitution de R'. On a aussi trouvé que le déplacement isomérique des composés chélés augmente à mesure que la contribution de l'état de spin-fort s'augmente.

Abstract.- Spin equilibrium of high-spin (6A_1) \rightleftharpoons low-spin (2T_2) has been investigated in a series of compounds of tris-(monothio- β -diketonato)iron(III), FeL_3 ($L = RCSCHCOR'$). It was found that the spin equilibrium is sensitive to the substituent in ligands and that the effect of substitution of R on the spin equilibrium is quite different from that of R'. It was also found that the isomer shift of the chelates roughly increases with increasing contribution of the high-spin state.

Several tris(monothio- β -diketonato)iron(III) compounds have been shown to be spin cross-over complexes /1/. Cox et al. have provided the direct evidence of ${}^6A_1 \rightleftharpoons {}^2T_2$ spin equilibrium for the compounds by using the Mössbauer spectroscopy /2/. However, there have so far been few systematic studies of the effect of substituents in the ligand on the spin equilibrium. In the present work, we prepared some new derivatives of tris(monothio- β -diketonato)iron(III) and studied the effect of the substituents by means of the Mössbauer spectroscopy and magnetic behavior of the compounds.

The compounds no. 1 and 6 listed in table I were prepared according to Chaston et al. /3/. The other new compounds, no. 2, 3, 4 and 5 were prepared by the reaction of anhydrous ferric chloride in absolute ethanol with the ligands which were prepared by the condensation of O-methyl-thiobenzoate or its derivatives with the ketones. The procedures are essentially the same as the methods reported on 1, 3-diphenyl-3-thioloprop-2-ene-1-one by Uhlemann and Müller /4/.

The purity of the ligands was checked by elemental analysis and NMR. The purity of the coordination compounds was confirmed by elemental analysis.

Magnetic susceptibilities were determined by the Faraday method with $Co[Hg(SCN)_4]$ and $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$ as calibrants.

Mössbauer measurements were carried out on powder samples with a constant acceleration mode. The velocity was calibrated with respect to metallic iron. The Mössbauer spectra were fitted for two Lorentzian doublets by the least-squares method. The

area ratio of the high-spin component, S', to the total area, S, was calculated in each spectrum.

The Mössbauer spectra and the effective magnetic moments indicate that all the compounds studied are in the spin equilibrium of high-spin (6A_1) and low-spin (2T_2). Typical Mössbauer spectra of sample 2 were shown in figure 1. Mössbauer parameters obtained are summarized in table I.

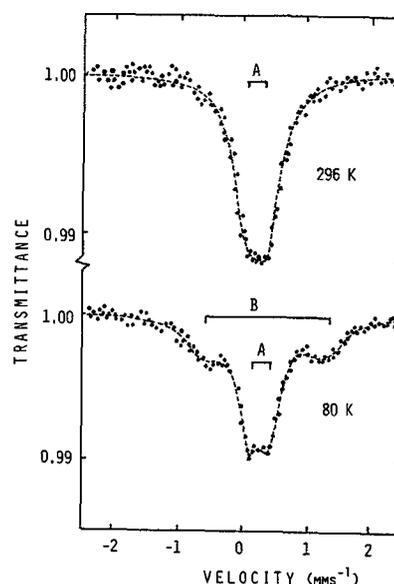


Fig. 1 : Mössbauer spectra of tris(1-(4-methylphenyl)-3-phenyl-3-thioloprop-2-ene-1-onato)iron(III).

Both the components of the spin isomers are found in the Mössbauer spectrum of sample 2 at 80 K ($S'/S = 0.65$), where the inner doublet A is ascribed to the high-spin ($S=5/2$) iron(III) species and the outer doublet B to the low-spin ($S=1/2$) iron(III) species.

Table I :

Mössbauer parameters and effective magnetic moments of tris(monothio- β -diketonato)iron(III) compounds.

compounds	T (K)	H. S. (S=5/2)		L. S. (S=1/2)		S'/S	μ_{eff}^* (B. M.)
		I. S. (mm/s)	Q. S. (mm/s)	I. S. (mm/s)	Q. S. (mm/s)		
1 R=C ₆ H ₅ , R'=C ₆ H ₅ tris(1, 3-diphenyl-3-thiolo- prop-2-ene-1-onato) iron(III)	80 296	0.48 0.27	0.52 0.45	0.38 —	1.95 —	0.51 0.95	4.45 5.91
2 R=C ₆ H ₅ , R'=p-CH ₃ C ₆ H ₄ tris(1-(4-methylphenyl)-3- phenyl-3-thiolo-prop-2-ene-1- onato) iron(III)	80 296	0.31 0.26	0.32 0.30	0.38 —	1.85 —	0.65 1.00	5.14 5.57
3 R=C ₆ H ₅ , R'=p-ClC ₆ H ₄ tris(1-(4-chlorophenyl)-3- phenyl-3-thiolo-prop-2-ene-1- onato) iron(III)	80 296	0.36 0.23	0.39 0.22	0.49 —	1.72 —	0.79 1.00	4.96 5.54
4 R=C ₆ H ₅ , R'=C ₄ H ₃ S tris(1-(2-thienyl)-3- phenyl-3-thiolo-prop-2-ene- 1-onato) iron(III)	80 296	0.25* 0.10	0.25* 0.16	0.25* 0.19	1.96* 0.96	* 0.92	3.85 4.47
5 R=p-ClC ₆ H ₄ , R'=C ₆ H ₅ tris(1-phenyl-3-(4-chloro- phenyl)-3-thiolo-prop-2-ene-1- onato) iron(III)	80 296	* 0.28*	* 0.10*	* *	* *	* *	3.21 3.61
6 R=CH ₃ , R'=C ₆ H ₅ tris(1-phenyl-3-thiolo-but- 2-ene-1-onato) iron(III)	80 296	0.38 0.38	0.44 0.62	0.38 0.35	1.79 1.31	0.43 0.96	2.92 4.09

*failed to converge

On the other hand, only one component due to the high-spin isomer was observed in the spectrum at room temperature. The spectra of sample 3 are similar to the spectra of sample 2, although there is a larger contribution of the high-spin component to the spectrum ($S'/S = 0.79$ at 80 K). The higher ratios of S'/S in the samples 2 and 3 than in the ratio ($S'/S = 0.51$ at 80 K) in the sample 1 suggest that the ligands having a para-substituted phenyl group for R' are effective to increase the high-spin component compared with the ligands having phenyl group for R'.

Concerning the effect of substitution of R in the ligands, the reversed change in the magnetic behavior is observed when the phenyl group in R is replaced with para-chloro phenyl group. The effective magnetic moment of sample 5 is 3.61 B. M. even at room temperature, which is the lowest among the values obtained in the present study, whereas sample 3 shows the values of 5.54 B. M. and 4.96 B. M. at room temperature and 80 K, respectively. The significance

of the substitution in R and R' groups suggests that the electrostatic effect through π -system of the ligand is not predominant on the spin equilibrium of iron(III), because it is known that the phenyl groups are not in coplaner with the rest of the structure of the chelate /5/.

The Mössbauer spectrum of sample 4 shows that the low-spin component remains even at room temperature ($S'/S = 0.92$). The effective magnetic moment for this sample is found to be 4.47 B. M. at room temperature. These results indicate that the low-spin state contributes to the equilibrium in sample 4 more than in samples 1, 2 and 3.

Ho and Livingstone reported that the magnetic moment, 5.49 B. M. for the compound $\text{FeL}_3(\text{R}=\text{C}_4\text{H}_3\text{S}, \text{R}'=\text{CF}_3)$ is higher than that of $\text{FeL}_3(\text{R}=\text{C}_6\text{H}_5, \text{R}'=\text{CF}_3)$, 2.31 B.M. both at room temperature /1/. On the contrary to the trend of $\text{C}_4\text{H}_3\text{S}$ group in their studies, the comparison of the data for sample 1 and 4 shows that the substitution of phenyl group with $\text{C}_4\text{H}_3\text{S}$ for R' in the ligands tends to increase the contribution

of the low-spin state, although they tried to explain the increase of the low-spin state by the effect of electron-withdrawing groups both in the positions R and R'. The results obtained in the present studies including those reported by Ho and Livingstone are reasonably explained by assuming that the electron-withdrawing group substituted in R position increases the contribution of the high-spin state, whereas the electron-withdrawing group in R' increases the contribution of the low-spin state. The results indicate that there are large different electrostatic effects of substituents R and R' on the spin equilibrium of these compounds. The different extent of effect of substituents in the ligand may be ascribed to the different bond length of iron-sulphur which is known to be longer than that of iron-oxygen /5/, and also to the different bond character between them because the iron-oxygen bond is more ionic than the iron-sulphur bond. However, the considerable difference between sample 1 and 2 or 3 suggests that there should be some additional effects on the spin equilibrium, such as the intermolecular packing effect in solid.

It was found that the isomer shift of the chelates roughly increased with increasing contribution of the high-spin state as in the case reported for tris(dithiocarbamato)iron(III) compounds /6/. The enhancement of the low-spin component is explained either by the increasing character of π -acceptance or by the increasing character of σ -donation of the ligand molecules. Both the factors may decrease the isomer shift of the Fe(III) species.

The linear relationship was also observed between isomer shift and quadrupole splitting for the high-spin component in the compounds. If the configurations of all tris(monothio- β -diketonato)iron(III) compounds are cis-facial, as shown by X-ray diffraction study for the analogous compounds /5/, no large quadrupole splitting can be expected for the high-spin species which has essentially no EFG because of the spherical distribution of $3d^5$ ($S = 5/2$) electrons. The quadrupole splitting of this series of compounds may be ascribed to the distortion of the molecule.

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