# The Anomalous Paramagnetism of Some Iron(III) Complexes of Monothio-β-diketones

By R. K. Y. HO and S. E. LIVINGSTONE*

(*School of Chemistry, University of New South Wales, Kensington, N.S.W.,* 2033, *Australia*)

IRON(III) complexes of some monothio-*β*-diketones, $R^1C(SH):CH \cdot COR^2$ have been prepared and characterized. The complexes were obtained as black or dark-coloured crystals which are stable in dry air and readily soluble in organic solvents but are slowly decomposed by water. They are nonelectrolytes in nitrobenzene and monomeric in toluene, and their analyses agree with their formulation as tris-chelated complexes $Fe(R^1CS{=}CH \cdot COR^2)_3$ analogous to iron(III) acetylacetonate. This is further confirmed by their infrared spectra which display two strong bands at 1600—1510 cm.$^{-1}$ $\nu[(\mathrm{C}\overset{\dots}{-}\mathrm{C})]$ and 1530—1430 cm.$^{-1}$ $[\nu(\mathrm{C}\overset{\dots}{-}\mathrm{O})]$. Assignment of these bands in the spectra of complexes of monothio-*β*-diketones has been discussed.[1]

The room-temperature magnetic moments vary from *ca.* 5·9 to *ca.* 2·2 B.M. depending on the nature of $R^1$ and $R^2$. The iron complex of ethyl thiobenzoylacetate ($R^1$ = Ph, $R^2$ = OEt) obeys the Curie–Weiss Law with $\theta = -8°$ K. The moments of the other complexes are temperature-dependent (see Table) and the plots of $\chi'_M$ against $T$ show broad maxima and minima. This departure from Curie–Weiss behaviour is unlikely to be due to intramolecular antiferromagnetic interaction between iron atoms as in the case of the trinuclear cation $[FeO(MeCO_2)_6]^+$.[2,3] The monomeric nature of the complexes in toluene and their ready solubility in organic solvents suggest that they are not polymeric in the solid state. The possibility of ferromagnetic impurities is excluded by the field-strength independence of the observed magnetic susceptibilities. The analytical data show that the compounds are not mixtures of iron(II) and iron(III) complexes. Our failure to isolate iron(II) complexes of monothio-*β*-diketones further confirms that only iron(III) complexes are present. The anomalous magnetic behaviour is most satisfactorily explained by the postulation of a thermal equilibrium between the nearly equi-energetic spin-paired $(t_{2g}^5)$ and spin-free $(t_{2g}^3 \cdot e_g^2)$ configurations of the iron atom resulting from the approximately equal magnitudes of the ligand field (Δ) and the pairing energy ($\pi$) in these compounds. The nature of the end-groups $R^1$ and $R^2$ of the ligands is apparently able to alter the strength of the ligand field sufficiently to change the magnetic behaviour from spin-free to spin-paired, depending on the temperature. Electron-withdrawing groups such as $CF_3$, Ph, and 4-substituted phenyl, appear to be the most effective in increasing the population of the spin-paired configuration.

TABLE

*Summary of magnetic data of iron*(III) *complexes* $Fe(R^1CS:CH \cdot COR^2)_3$

| $R^1$ | $R^2$ | $\mu$(B.M.) at room temp. | Temp. range (°K) | Range of $\mu$(B.M.) |
|---|---|---|---|---|
| Ph .. .. .. | $CF_3$ | 2·31 | 80—373 | 1·86—3·65 |
| *p*-Bromophenyl .. | $CF_3$ | 3·10 | 80—378 | 2·06—4·45 |
| *p*-Methylphenyl .. | $CF_3$ | 3·45 | 83—378 | 2·11—5·06 |
| *p*-Methoxyphenyl .. | $CF_3$ | 3·44 | 80—375 | 2·70—4·65 |
| 2-Thienyl .. .. | $CF_3$ | 5·49 | 133—368 | 4·13—5·58 |
| 2-Furyl .. .. .. | $CF_3$ | 5·65 | 80—373 | 4·07—5·70 |
| Ph .. .. .. | Ph† | 5·50 | 80—403 | 2·18—5·77 |
| Ph .. .. .. | OEt† | 5·82 | 93—293 | 5·67—5·82 |

† The preparations of these compounds have been previously reported.[1,4]

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