Magnetic and Mössbauer Investigations of *NN*-Disubstituted Dithiocarbamato-iron(II) Complexes

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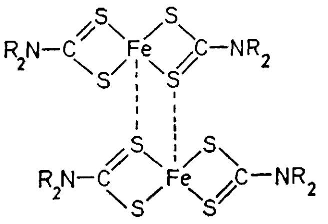
Summary Magnetic susceptibility and Mössbauer measurements show the air-sensitive iron(II) compounds, Fe(R_2NCS_2)$_2$, to be of two different structural types: intramolecular anti-ferromagnetic dimers, *e.g.*, [Fe(Et_2NCS_2)$_2$]$_2$, involving five-co-ordinate iron, and antiferromagnetic polymers, *e.g.*, [Fe(Me_2NCS_2)$_2$]$_n$, believed to involve octahedral co-ordination about the metal.

COMPLEXES of transition metals with the *NN*-disubstituted dithiocarbamate ion ($R_2NCS_2^-$) exhibit a variety[1] of chemical behaviour, but little is known of iron(II) complexes. Recently, some of these reactive, air-sensitive chelates have been converted into interesting iron(III)–mixed ligand complexes by the oxidative addition[2] of bis-(perfluoromethyl)-1,2-dithieten, or by reaction[3] with disodium dicyanoethylenedithiolate followed by oxidation. The iron(II) chelates were used without isolation or definite identification. The Mössbauer parameters of Fe(Et_2NCS_2)$_2$ have been reported,[4] but the complex was found to be too air-sensitive to carry out magnetic susceptibility determinations or record diffuse reflectance spectra.[2,4] This was unfortunate as the number of unpaired electrons could not be deduced and calculations to explain the exceptionally large quadrupole splitting, ΔE, (4·16 mm s^{-1}) of Fe(Et_2NCS_2)$_2$ had to be carried out assuming either two ($S = 1$) or four unpaired electrons ($S = 2$).

Using modifications of apparatus described earlier,[5] we have obtained a series of iron(II)–dithiocarbamato-complexes, Fe(R_2NCS_2)$_2$, (I; R = Me, Et, Pr^n, Bu^n; R_2 = C_4H_8), with satisfactory analyses. Their reflectance spectra were dominated by charge-transfer bands but all contained either one very broad absorption at about 10,000 cm^{-1} (R = Et, Pr^n, Bu^n) or two absorptions at about 8500 and 6250 cm^{-1} (R = Me, R_2 = [C_4H_8]) in the region expected for high-spin iron(II).[6] The magnetic moments, μ_{eff} of the solids at 295 K were close to the spin-only value (4·90 B.M.) for high-spin iron(II) compounds, *e.g.* R = Me and Et, μ_{eff} = 4·84 and 4·42 B.M. respectively, well above that for two unpaired electrons. The temperature variation of the magnetic moments was not that expected for spin isomerism as found in iron(III) dithiocarbamates,[7] but suggested that antiferromagnetic interactions were present; these caused small reductions below 4·90 B.M. of the room-temperature moments of several compounds. With compounds (I; R = Et, Pr^n, and Bu^n), Néel points occurred at 110 K, 185 K, and apparently just below 85 K, the limit of the measurements, but when R = Me or R_2 = [C_4H_8], Curie–Weiss behaviour was observed over the available temperature range, the Curie–Weiss constants θ being 78° and 38° respectively. The different magnetic behaviour was paralleled by the Mössbauer spectra. All compounds had clean two-peak spectra showing that no oxidation had taken place before measurement. The chemical isomeric shifts were as expected for high-spin iron(II) species at room and liquid-nitrogen temperatures which also excludes spin isomerism, *e.g.*, R = Et, isomer shift δ (at liquid nitrogen temperature with respect to natural iron) = 0·875 mm s^{-1}; R = Me, δ = 1·00 mm s^{-1}. Compounds (I; R = Et, Pr^n, and Bu^n) form a series with quadrupole splittings ΔE *ca.* 4·2 mm s^{-1}. We have confirmed from their *X*-ray powder patterns[8] that Fe(Et_2NCS_2)$_2$ and the sulphur-bridged dimer[9] Cu(Et_2NCS_2)$_2$ are isomorphous. It is therefore reasonable to conclude that all three compounds involve the axially bridged five-co-ordinate structure (II)



(II)

These compounds exhibited clean quadrupole doublets at 4·2 K consistent with diamagnetic ground states, and therefore with the dimeric structure. Confirmation of their diamagnetic nature, at sufficiently low temperature where $kT << 2J$ (J is the exchange integral) was obtained from the spectra in an applied magnetic field at 4·2 K which were typical of diamagnetic compounds, having the doublet triplet pattern indicative of low asymmetry with e^2Qq and V_{zz} positive.

The Curie–Weiss behaviour and the low quadrupole splitting of the remaining compounds (I; R = Me and R_2 = [C_4H_8], (ΔE = 2·56 and 2·27 mm s^{-1} respectively) indicate structures substantially different from those of the dimers. Also in contrast to the dimers, at 4·2 K in zero field, complex magnetic hyperfine spectra were observed for both compounds. To produce this effect the structure must lead to a paramagnetic ground state, but since anti-ferromagnetism is present monomeric structures are excluded and a polymeric rather than a dimeric structure is proposed.

(*Received*, 16*th August* 1973; *Com.* 1185(.

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[1] D. Coucouvanis, *Progr. Inorg. Chem.*, 1970, **11**, 233.
[2] L. H. Pignolet, R. A. Lewis, and R. H. Holm, *J. Amer. Chem. Soc.*, 1971, **93**, 360.
[3] L. H. Pignolet, R. A. Lewis, and R. H. Holm, *Inorg. Chem.*, 1972, **11**, 99.
[4] J. L. K. F. de Vries, C. P. Keijzers, and E. de Boer, *Inorg. Chem.*, 1972, **11**, 1343.
[5] L. F. Larkworthy, *J. Chem. Soc.*, 1961, 4025.
[6] A. B. P. Lever, 'Inorganic Electronic Spectroscopy,' Elsevier, Amsterdam, 1968.
[7] R. L. Martin and A. H. White, *Transition Metal Chem.*, 1968, **4**, 113.
[8] J. P. Fackler and D. G. Holah, *Inorg. Nuclear Chem. Letters*, 1966, **2**, 251.
[9] M. Bonamico, G. Dessy, A. Mugnoli, A. Vaciago, and L. Zambonelli, *Acta Cryst.*, 1965, **19**, 886.