

Compounds with Intermediate Spin. 7. * Influence of the Substituents on the Magnetic Properties of Tris(dithiocarbamato)iron(III) Compounds

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The influence of inductive and cooperative effects, steric interference and electronic factors on the high spin-low spin equilibrium of solid substituted iron(III)dithiocarbamates $[\text{Fe}(\text{S}_2\text{CNRR}')_3]$ has been studied. The discussion is based on $\text{p}K_a$ values of the parent secondary amine ($\text{RR}'\text{NH}$), magnetic susceptibility measurements, accurate structural parameters and ESCA measurements. The inductive and cooperative effects were found to be of minor importance. The most important factor in determining the spin state is the intramolecular steric interference of the substituents (R and R') acting on the ligand bite angle $\text{S}-\text{C}-\text{S}$. Increased steric interference increases the low spin contents. No significant shift between different canonical forms could be observed except when the $\text{RR}'\text{N}$ moiety exhibits aromaticity, making the corresponding $\text{Fe}(\text{S}_2\text{CNRR}')_3$ low spin.

* For part 6 in this series see Ref. 5.

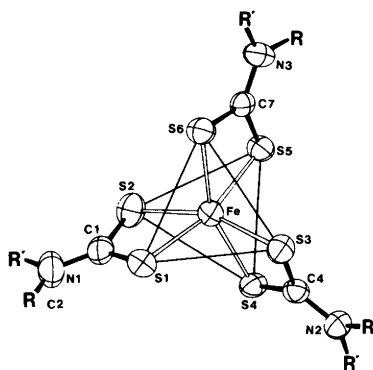


Fig. 1. An $\text{Fe}(\text{dte})_3$ complex viewed along the pseudo threefold axis.

Substituted iron(III)dithiocarbamates $\text{Fe}(\text{dte})_3$ in the solid state has been subject to numerous structural¹⁻¹⁵ and magnetic¹⁶⁻¹⁹ investigations. All known $\text{Fe}(\text{dte})_3$ structures comprise mononuclear van der Waals packed complexes with pseudosymmetry D_3 (Fig. 1). The magnetic properties can be described as a thermal equilibrium between the low spin (LS) and the high spin (HS) forms, giving effective magnetic moments (μ_{eff}) between ~ 2 B.M. (low temperature limit, $S=\frac{1}{2}$) and 5.92 B.M. (high temperature

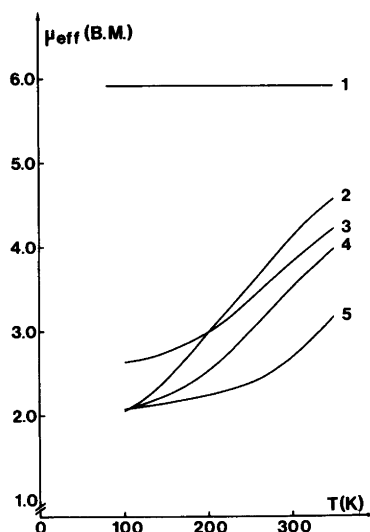


Fig. 2. Effective magnetic moment vs. temperature for $\text{Fe}(\text{dte})_3$ compounds with various substituents; 1. Tetramethylene; 2. Dimethyl; 3. Dipropionitrile; 4. Dibenzyl; 5. Diisopropyl.

limit, $S = \frac{5}{2}$) (Fig. 2). At intermediate μ_{eff} the crystal structure observed is the weighted average of the LS and HS forms ($\mu_{\text{eff}}^2 = x_{\text{HS}}(\mu_{\text{eff}}^{\text{HS}})^2 + (1-x_{\text{HS}})(\mu_{\text{eff}}^{\text{LS}})^2$, where x_{HS} is the HS molar ratio).

The magnetic properties in the interval 80–300 K are strongly dependent on the substituents R and R' and in some cases on solvate molecules in the crystal structure. By varying R and R' it is possible to obtain compounds exhibiting pure HS behaviour, a more or less complete HS–LS transition or almost pure LS behaviour. There are four main effects through which the substituents may influence the magnetic behaviour.

1. Inductive effects.
2. Cooperative effects.
3. Steric interference on the FeS_6 core.
4. Electronic interactions.

This investigation intends to evaluate the influence of these four factors on the magnetic properties of the various $\text{Fe}(\text{dtc})_3$ compounds. The discussion is based on solid state magnetic moments in the interval 80–300 K, accurately determined crystal structures of Fe(III) and some non-Fe dtc compounds, $\text{p}K_{\text{a}}$ values of the parent secondary amine $\text{RR}'\text{NH}$ as a measure of the inductive effects and some ESCA results. The importance of different canonical forms (Fig. 3) will also be discussed. The influence of solvate molecules in the crystal structure on μ_{eff} is discussed elsewhere.⁸ This work is part of a series of investigations aiming at correlating the magnetic behaviour of solid iron(III)dithiocarbamates with their structural features.

EXPERIMENTAL

Preparations. Alkali dtcs were prepared by mixing stoichiometric amounts of CS_2 , $\text{RR}'\text{NH}$ and MOH in aqueous solutions according to eqn. (1).

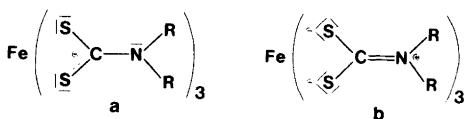
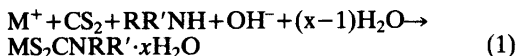


Fig. 3. Proposed canonical forms for $\text{Fe}(\text{dtc})_3$.

The compounds were recrystallized from aqueous solutions under reduced pressure.

$\text{Fe}(\text{dtc})_3$ were prepared by mixing stoichiometric amounts of CS_2 , $\text{RR}'\text{NH}$, FeCl_3 and NaOH in ethanol solutions and recrystallized from chloroform by slow addition of ethanol.

ESCA measurements. The ESCA measurements were made on the sodium tetramethylene dimethyl, diethyl and diisopropyl dithiocarbamate hydrates using an AEI ES 200 Photoelectron spectrometer. The technique of internal standard established by Larsson, Folkesson and Lykvist^{20–22} was used, assuming the Na^+ charge to be exactly +1.0 in all compounds, $E_{\text{b}}(\text{Na } 1s) = 1071.1 \text{ eV}$ is related to $(\text{C}_6\text{H}_5)_4\text{P}^+$ via F^- in $(\text{C}_6\text{H}_5)_4\text{PF}$ and NaF . The dimethyldithiocarbamate spectra was recorded at 273 and 103 K, the others at 273 K.

Susceptibility measurements. The magnetic susceptibility (Figs. 2 and 6) was measured on polycrystalline samples with a microcomputer-controlled Cahn RG electrobalance using the Faraday principle.^{5,23} To investigate the effects of crystal size and perfection the measurements were repeated after careful grinding of the sample with agate mortar and pestle. The magnetic moments did not show any dependence on the magnetic field strength (~ 0.6 and $\sim 0.8 \text{ T}$).

Statistical treatment. Correlations between structural parameters and the magnetic moment have been tested by linear regression (Figs. 7, 9a and b). In Figs. 7 and 9b mean values of the structural parameters have been used. Since it was not possible to give correct relative weights to all observations, due to the different origin of the structural parameters and magnetic moments, equal weights have been used.

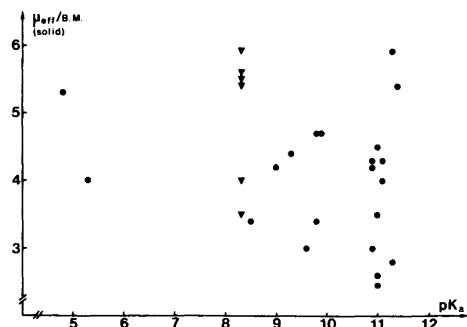


Fig. 4. Effective magnetic moment of some $\text{Fe}(\text{dtc})_3$ ^{1–14,19} vs. $\text{p}K_{\text{a}}$ of the parent secondary amine.^{33,34} The $\text{p}K_{\text{a}}$ value for aromatic amines is corrected according to Ref. 25. ▼ indicates tris(morpholinecarbodithiato)iron(III) with various solvate molecules.

INDUCTIVE EFFECTS

It has been proposed that the spin cross-over behaviour of the iron(III)dithiocarbamates is influenced by the inductive effect of the substituents.²⁴⁻²⁶ The inductive effect is reflected in the pK_a value of the parent secondary amine, $RR'NH$. As seen from Fig. 4 there is no correlation between the pK_a values and the solid state magnetic moments at room temperature. The lack of influence from the pK_a value on μ_{eff} is especially evident for the morpholinyl substituted $\text{Fe}(\text{dtc})_3$ compounds where μ_{eff} varies between 3.0 and 5.92 B.M. depending on which solvent molecule is present in the crystal structure.

COOPERATIVE EFFECTS

Spin transitions in the solid state are often described as a cooperative phenomenon.²⁷⁻³¹ The number of minority spin complexes is increased by nucleation and growth of small minority spin domains. The nucleation and growth is governed by the temperature and the number of nucleation sites. An increased number of nucleation sites will increase the number of minority spin complexes in the beginning of the transition, but will also hinder the domain growth towards the end of the transition. An increased number of nucleation sites can be attained by careful grinding of the compound. The influence of grinding on the μ_{eff} vs. T curves seems to be dependent on the

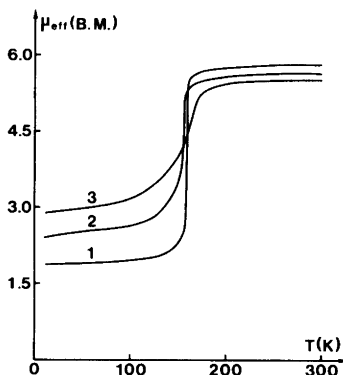


Fig. 5. Effective magnetic moment vs. temperature for $[\text{Fe}(3\text{-OCH}_3\text{-SalEen})_2]\text{PF}_6$.²⁸: 1. Unperturbed microcrystalline solid; 2. Sample ground with mortar and pestle; 3. Sample ground in a ball mill.

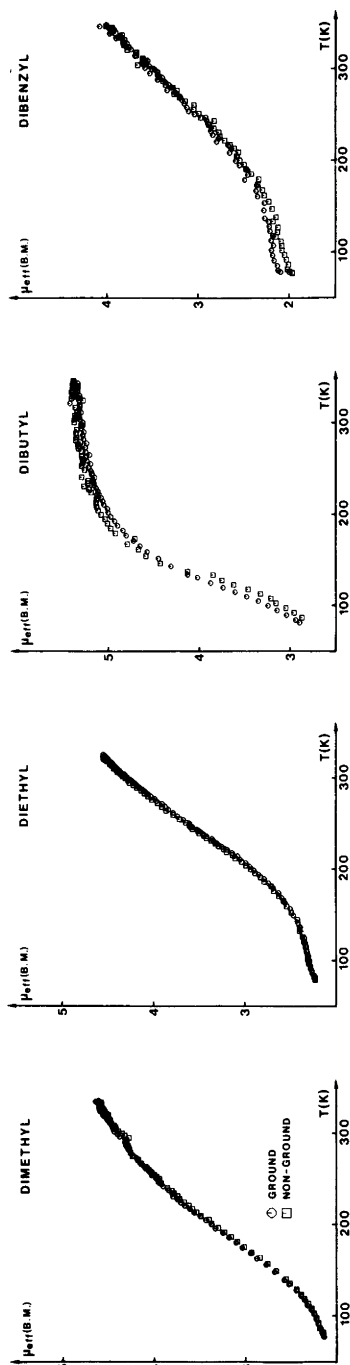


Fig. 6. Effective magnetic moment vs. temperature for some ground and non-ground $\text{Fe}(\text{dtc})_3$ samples crystallizing without solvate molecules.

nature of the spin transition. The effect is typically dramatic when the unperturbed spin transition is dramatic (*i.e.* almost completed within a few K) (Fig. 5).

In the case of $\text{Fe}(\text{dtc})_3$ the spin transitions are always gradual, and in an investigation of the grinding effect on the dimethyl, diethyl, dibutyl and dibenzyl substituted compounds the observed effects were small, (Fig. 6) *i.e.* the coopera-

tive effects on the magnetic behaviour of $\text{Fe}(\text{dtc})_3$ are of minor importance.

STERIC INTERFERENCE

For 25 accurately determined $\text{Fe}(\text{dtc})_3$ structures¹⁻¹⁴ the linear correlation among 10 mean geometric parameters and μ_{eff} (MY in Fig. 7) has been tested by linear regression. A selection is

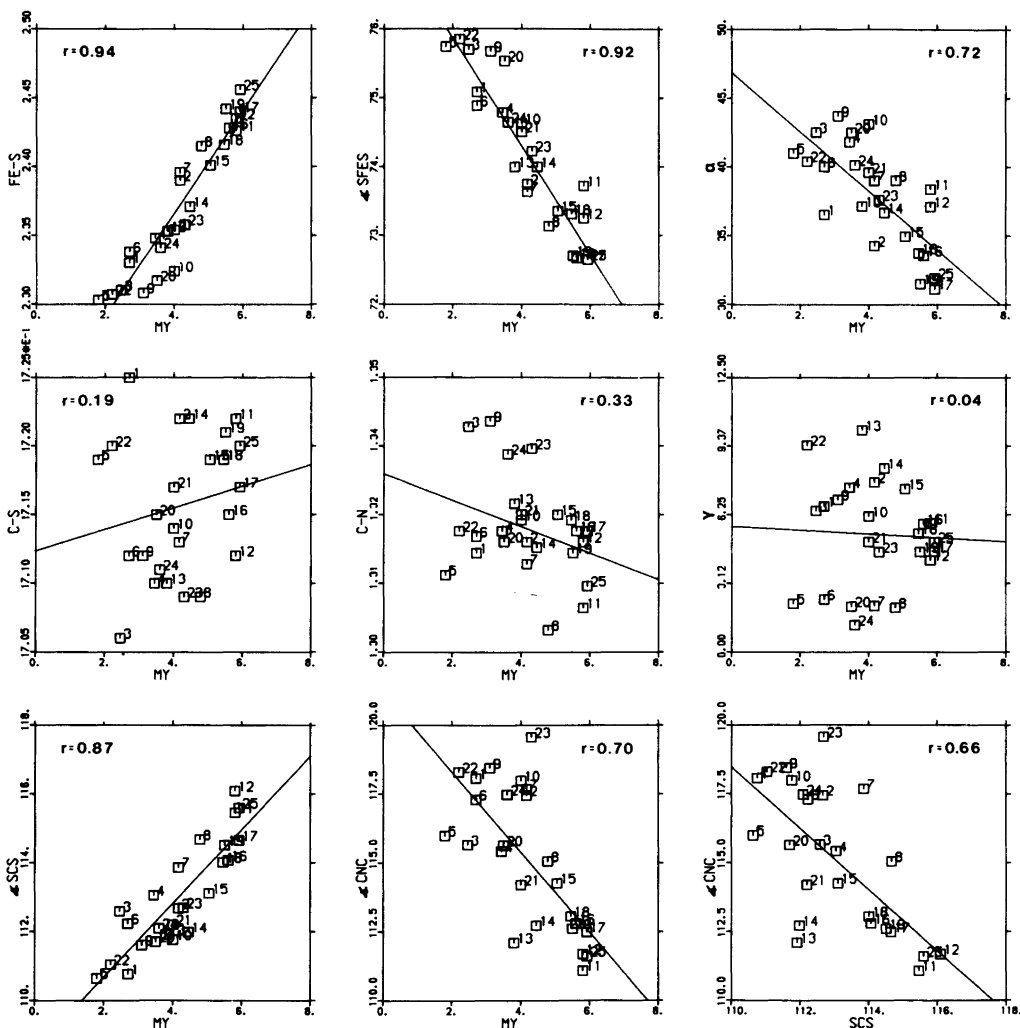


Fig. 7. Correlation between structural parameters and effective magnetic moment (MY) of some substituted $\text{Fe}(\text{dtc})_3$ s. Data about compounds 1-25 are given in Table 3. α is the trigonal twist angle in the FeS_6 polyhedron and γ is the angle between the normal vectors of the S-C-S and C-N-C planes in the ligands. The probability of 25 randomly distributed observations having a correlation coefficient, $r > 0.505$ is 0.005.

Table 1. S-C-S and C-N-C angles in some substituted dithiocarbamates. n is the number of M-S-bonds per ligand.

Substituents	Cation	S-C-S	C-N-C	\bar{n}	Ref.
Diisopropyl (S ₂ CN(CH(CH ₃) ₂) ₂) ₂	Na ⁺	118.3(3)	113.8(5)	0	43
	NH ₂ [CH(CH ₃) ₂] ₂ ⁺	117.7(2)	113.8(2)	0	44
	Li ⁺	117.5(3)	114.5(5)	0	45
	Zn ²⁺	115.5(1)	114.6(1)	2-3	46
	Cu ²⁺	111.4(2)	115.9(4)	2	47
	Ni ²⁺	109.3(5)	117.3(8)	2	48
Diethyl S ₂ CN(C ₂ H ₅) ₂	Na ⁺	120.4(4)	114.3(5)	1	49
	NH ₂ (C ₂ H ₅) ₂ ⁺	120.6(1)	115.2(2)	0	50
	Li ⁺	119.1(2)	114.4(3)	0	51
	Zn ²⁺	117.7(6)	116.1(8)	2	52
	Cu ²⁺	113.6(5)	117.1(6)	2	53
	Ni ²⁺	110.6(6)	116.9(1.2)	2	54
Dimethyl S ₂ CN(CH ₃) ₂	Na ⁺	120.9(1)	114.2(3)	1	55
	NH ₂ (CH ₃) ₂ ⁺	119.7(1)	114.7(3)	0	56
	Li ⁺	118.8(1)	115.4(3)	0	57
	Zn ²⁺	118.8(8)	116.9(1.3)	2	58
	Cu ²⁺	113.4(5)	115.3(9)	2	59
	Ni ²⁺	109.9(4)	118.4(5)	2	60
Tetramethylene S ₂ CN(CH ₂) ₄	Na ⁺	122.3(1)	110.8(2)	1	61, 62
	NH ₂ (CH ₂) ₄ ⁺	121.7(1)	110.6(2)	0	63
	Li ⁺	120.2(1)	110.8(1)	0	64
	Zn ²⁺	119.5(3)	111.7(5)	2-3	65
	Cu ²⁺	115.8(4)	113.5(8)	2	66
	Ni ²⁺	111.4(5)	112.0(7)	2	66

Table 2. Effective charges on the atoms in the four Na⁺-dithiocarbamates. Two separate measurements were made for each compound.

	q_S	q_N	q_C
NaS ₂ CN(CH ₂) ₄ · 2H ₂ O	-0.46(3)	-0.24(2)	0.05(1)
	-0.46(3)	-0.24(2)	0.05(1)
NaS ₂ CN(CH ₃) ₂ · 2H ₂ O	-0.43(3)	-0.21(2)	0.07(1)
	-0.43(3)	-0.21(2)	0.07(1)
NaS ₂ CN(C ₂ H ₅) ₂ · 3H ₂ O	-0.43(3)	-0.21(2)	0.06(1)
	-0.43(3)	-0.21(2)	0.07(1)
NaS ₂ CN(CH(CH ₃) ₂) ₂ · 5H ₂ O	-0.31(3)	-0.27(2)	0.03(1)
	-0.34(3)	-0.28(2)	0.03(1)

shown in Fig. 7 and Table 3. Since the spin state is dependent on the ligand field strength, a strong correlation is observed between parameters of the FeS₆ core and μ_{eff} .³² Within the ligands the only parameters significantly correlated to μ_{eff} are the S-C-S and C-N-C angles. Consequently also S-C-S and C-N-C are correlated to each

other (Fig. 7). This correlation can be deduced from steric interference within the ligands (Fig. 8). Steric crowding between the substituents is propagated to the S-atoms through a variable number of C-H...S interactions. This steric interference is balanced by an increased repulsion between the S-atoms. A convincing way to

Table 3. The 25 iron(III) dithiocarbamates of Fig. 7.

No.	Substituents	Solvate	Temp. (K)	Ref.
1	Dihydroxyethyl	—	175	1
2	Dihydroxyethyl	—	295	1
3	Dibenzyl	—	175	2
4	Dibenzyl	—	295	2
5	Dimethyl	—	25	3
6	Dimethyl	—	175	4
7	Dimethyl	—	295	4
8	Dimethyl	—	400	3
9	Dipropionitrile	$\frac{1}{2}\text{CHCl}_3$	178	5
10	Dipropionitrile	$\frac{1}{2}\text{CHCl}_3$	298	5
11	Tetramethylene	$\frac{1}{2}\text{C}_6\text{H}_6$	175	6
12	Tetramethylene	$\frac{1}{2}\text{C}_6\text{H}_6$	295	6
13	Morpholinyl	CH_2Cl_2	20	7
14	Morpholinyl	CH_2Cl_2	110	7
15	Morpholinyl	CH_2Cl_2	178	7
16	Morpholinyl	CH_2Cl_2	293	7
17	Morpholinyl	CH_2Cl_2	293	8
18	Morpholinyl	CHCl_3	300	9
19	Morpholinyl	H_2O	300	9
20	Morpholinyl	$2\text{C}_6\text{H}_6$	300	10
21	Morpholinyl	$\text{C}_6\text{H}_5\text{NO}_2$	300	11
22	Diethyl	—	79	12
23	Diethyl	—	297	12
24	Dibutyl	C_6H_6	295	13
25	Tetramethylene	—	295	14

study the variation in steric interference for different substituents is to use space filling precision molecular models (*e.g.* CPK Precision Molecular Models, The Ealing Corporation, Mass).

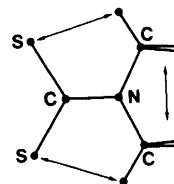


Fig. 8. Steric interference (indicated by arrows) in a dtc ion.

To provide further evidence on the steric interference, some dtc ligands with cations other than Fe(III) were studied (Table 1). For one and the same ligand chelate formation with cations decreases the S-C-S angle and consequently the C-N-C angle increases. As expected, C-N-C in a strained pyrrolidine ring is rather invariant in tetramethylenedithiocarbamate, and the S-C-S to C-N-C correlation increases as the substituents become bulkier, tetramethylene < dimethyl ~ diethyl < diisopropyl (Table 1). For these four ligand types the shortest intramolecular S...H distances increase in the reverse order from about 2.4 Å for diisopropyl to about 2.9 Å for tetramethylene.

The geometry of the dtc ion in compounds with weakly attached cations (Li, Na, NH_2R_2 , Table 1) may be approximated to that in non-bonded dtcs, where S-C-S is solely determined by the steric interference from the substituents. The fact that μ_{eff} of the corresponding $\text{Fe}(\text{dtc})_3$ is strongly correlated to S-C-S in the three "non-bonded" ligands (Fig. 9a) gives further evidence of the importance of the steric interaction in determining μ_{eff} in the iron(III)dithiocarbamates. Fig. 9b

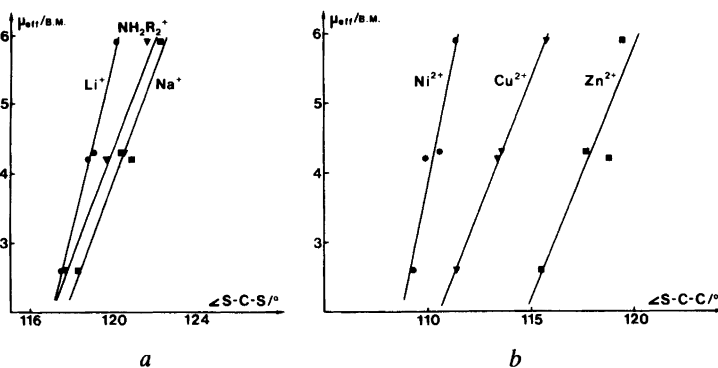


Fig. 9. Effective magnetic moment of some substituted $\text{Fe}(\text{dtc})_3$ s vs. S-C-S angle in the corresponding $\text{M}(\text{dtc})_n$. The substituents are from top to bottom tetramethylene, diethyl, dimethyl, diisopropyl. (a) "Non-bonded" ligands, (b) "Bonded" ligands.

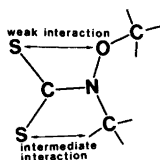


Fig. 10. The weak steric interference in the methylmethoxy substituted dtc giving a high spin $\text{Fe}(\text{dtc})_3$.

shows the same general feature as Fig. 9a but does also illustrate the strong cation influence on S-C-S, S-C-S decreases as the cation-ligand bond strength increases.

To conclude, weak steric interference (e.g. in tetramethylene dtc) results in ligand bites producing a weak ligand field³² and Fe(III) remains high spin. When the steric interference is strong (e.g. in diisopropyl or other di-sec-alkyl dtcs) the resulting smaller ligand bite produces a strong ligand field and Fe(III) becomes low spin. Finally, when the steric interference is intermediate (e.g. in dimethyl-, diethyl- or other di-prim-alkyl dtcs) the ligand bite and ligand field is interme-

diated and the corresponding iron(III) complex will exhibit spin cross-over behaviour.

This model also explains the high spin behaviour when the substituents are methyl and methoxy groups²⁵ (Fig. 10).

ELECTRONIC INTERACTIONS

The theory of intramolecular steric interference is not applicable to tris(pyrrolecarbo-dithiato)iron(III) (Fig. 11d). In this compound the S-C-S angles are a bit larger than those expected for a low-spin $\text{Fe}(\text{dtc})_3$ compound, the C-N-C angles are confined to $\sim 108^\circ$ and the S...H distances indicate weak intramolecular S...H interactions.¹⁵ The ligand, however, is somewhat special in having an aromatic pyrrole ring directly bonded to the S_2C -moiety. The aromaticity of the pyrrole ring prevents the lone pair on the N-atom taking part in the $\text{S}_2\text{C}-\pi$ -system. As a result the electronic structure is that of Fig. 11d, corresponding to canonical form *a* in Fig. 3. From a comparison between different Fe(III)dithio compounds (Fig. 11) it is seen that

				Ref.
a		HS		35
b		HS	S-C: 1.737 C-C: 1.381	36,37
c		HS,LS	S-C: 1.706-1.725 C-N: 1.303-1.344	1-14
d		LS	S-C: 1.686 C-N: 1.365	15
e		LS	S-C: 1.693 C-S: 1.713	38,39
f		LS	S-C: 1.684 C-O: 1.328	19,40
g		LS	S-C: 1.678 C-C: 1.527	41,42

Fig. 11. Dominant canonical forms of various dithio ligands and the spin state of the corresponding $\text{Fe}(\text{ligand})_3$. The distances in *b* and *g* are from non-iron compounds.

canonical form *a* in Fig. 3 with low sulfur charges favours the LS state and canonical form *b* with higher sulfur charges favours the HS state of iron(III). The geometric parameter in common to compounds c–g in Fig. 11, which gives a good correlation to μ_{eff} is the S...S distance. The somewhat larger S–C–S angle in compounds d–g is compensated for by the shorter, partly double bonded S–C bond.

The charge distribution of some sodium-dithiocarbamate hydrates have been studied with ESCA and the results are given in Table 2. The difference in the charge on the S-atoms between the diisopropyl compound, –0.31, and the others –0.43–0.46, is highly significant. The ESCA peaks for the S-atoms were symmetric with half-widths of 2.6 eV for all compounds, indicating equal charges on the two S-atoms in each compound. No significant differences between the 273 and 103 K spectra were observed for the dimethyl compound. The significance in the charge difference was tested by a measurement on a mixed diisopropyl and tetramethylene sample. As expected, the half-widths of the S- and N-atoms increased by approximately 0.15 eV, indicating overlapping peaks. Since the diisopropyldithiocarbamate forms an LS Fe(III) compound and the tetramethylenedithiocarbamate forms HS Fe(III) compounds the ESCA results support the above observation that high sulfur charge favours the HS and low sulfur charge favours the LS state of iron(III) in dithio compounds. The variation in charge on the S atoms might be explained by simple electrostatic arguments. A decrease in S–C–S angle increases the electrostatic repulsion between the two S atoms and thus favours canonical form *a* in Fig. 3.

The S–C and C–N distances are not significantly correlated to μ_{eff} (Fig. 6). The observed scatter in S–C and C–N distances is with a probability of >0.9995 and 0.96, respectively, expected from a random distribution (from χ^2 tests). According to Pauling's equation³⁹ the difference in S–C distance between the pure canonical forms (*i.e.* with S–C bond order of 1.5 and 1.0) is 0.14 Å, while the largest difference observed is 0.02 Å. It is thus concluded that for Fe(dtc)₃s the variation in the contribution from the two canonical forms is well below 15 %.

An earlier attempt has been made to explain the influence of the substituents on μ_{eff} in solution in terms of intramolecular steric

interference.¹⁹ In this earlier explanation the bulkier substituents were expected to increase the C–N–C angle, favouring an sp² hybridized nitrogen and thereby canonical form *b* in Fig. 3. Canonical form *b* was therefore postulated to dominate in an LS complex, in contradiction to the results presented above.

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