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Electron Spin Crossover in Iron(III) Dithiocarbamates

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More than 30 years ago, Cambi and his coworkers reported[1] that tris(*N*,*N*-diorganodithiocarbamato)iron(III) complexes exhibited solid and solution magnetic moments which were intermediate between the two values normally observed for iron(III) complexes (high spin, $\mu \simeq 5.9$ BM; low spin, $\mu \simeq 2.0$ BM). Cambi suggested an equilibrium between two "magnetically isomeric" forms of the compound to account for the anomalous behavior. Subsequent workers have indicated that the apparent spin state is sensitive to temperature, pressure, and the nature of the nitrogen substituent in the dithiocarbamate ligand. These properties have been interpreted as those of a system in which the $^6A_1$ and $^2T_2$ states (assuming octahedral symmetry) are in thermal equilibrium.[2-4] Such a system is in spin-crossover equilibrium. Octahedral spin-crossover systems have recently been reviewed by Martin and White.[5]

Ewald, Martin, Sinn, and White[3] have proposed that the principal trend influencing the magnetic behavior of these complexes is an increasing R–N–R bond angle resulting from steric interactions between the nitrogen substituents.

This study, however, indicates that the primary function of the substituent, R, is as an electron-releasing group. Steric interactions appear to be relatively unimportant, except when a secondary carbon is the substituent. Further, in contrast to Ewald, *et al.*,[3] it is maintained that limiting form I (*vide infra*) is the structure having the stronger ligand field and is of greater importance when magnetic moments are low.

Experimental Section

The tris(*N*,*N*-diorganodithiocarbamato)iron(III) complexes were prepared by published methods.[4]

The solution magnetic moments were determined at room temperature in chloroform and, in a few cases, benzene, by the Gouy method.[6] For most of the compounds the measurements were performed at two or more concentrations and, for many, at two field strengths (~8000 and ~5500 G). A ground-joint stoppered Pyrex Gouy tube of the compensating type[6] was used.

Constitutive and diamagnetic corrections[6] were applied to the measured susceptibilities. The reported corrected magnetic moments, μ_{eff}, were obtained from

$$\mu_{\text{eff}} = 2.83\sqrt{\chi_{\text{M}}'T}$$

where χ_{M}' is the corrected molar susceptibility, T is the absolute temperature, and the constant 2.83 was calculated from recent accepted values of the component constants.[7]

The error in the magnetic moment data is estimated on the basis of reproducibility with different samples to be no greater than ±0.1 BM.

Amine basicities not available from the literature were measured by pH determination in aqueous solution or in water–alcohol solutions. Amines were fractionally distilled, and the middle fraction was taken. pK's measured in various percentages of alcohol were extrapolated to aqueous media.[8] The error in pK_a measurements done by us is estimated to average ±0.2 pK_a unit.

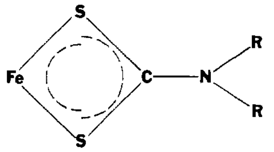
All compounds were subjected to elemental analysis, and, with the exception of the tetrahydroisoquinolinyl and isoamylphenyl derivatives, the results were quite satisfactory. Since the preparation of the foregoing compounds was straightforward and their behavior typical, it is assumed that instability was responsible for the failure of repeated attempts to obtain an acceptable analysis.

Analyses were performed by Galbraith Laboratories, Spang Microanalytical Laboratory, and Crobaugh Laboratories.

Results and Discussion

The solution magnetic moments of 37 tris-(*N*,*N*-disubstituted-dithiocarbamato)iron(III) compounds and the aqueous pK_a of the parent secondary amines are given in Table I. Figure 1 demonstrates, with notable exceptions, an approximately linear relationship between μ_{eff} and pK_a for these compounds.

The dependence of the solution magnetic moment on the pK_a of the parent amine may be explained in terms of the structures



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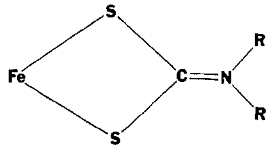

II

In limiting form I, a sulfur electron pair is delocalized within the metal–chelate ring. The multiple character in the iron–sulfur bond is due to interaction of partially filled d orbitals of iron(III) with empty ligand π orbitals, arising from the d orbitals of the sulfur atoms. In limiting form II, the nitrogen lone pair has been donated to the C–N bond, placing a formal positive charge on the nitrogen atom and resulting in a net shift of electron density toward the sulfur atoms. It has been suggested by Cotton and McCleverty[9] that as the sulfur atoms accept electron density from the nitrogen, they are less able to do so from the iron. This diminished covalency would result in a lengthened metal–sulfur bond and a smaller Δ (ligand field splitting parameter) and would favor the high-spin state. The reduction in ligand field strength attendant to increasing metal–ligand bond length has been demonstrated for a series of nickel

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TABLE I

SOLUTION MAGNETIC MOMENTS AND pK_a OF PARENT SECONDARY AMINE OF TRIS(*N*,*N*-DIALKYLDITHIOCARBAMATE)IRON(III) COMPLEXES, $Fe(S_2CNR_2)_3$

Compound	μ_{eff},[a,b] BM	pK_a[c]
Tris(*N*,*N*-di-*sec*-butyldithiocarbamato)iron(III)	2.2	10.91[g]
Tris(*N*,*N*-diisopropyldithiocarbamato)iron(III)	2.41	11.05[f]
Tris(*N*,*N*-dicyclohexyldithiocarbamato)iron(III)	2.55[d]	11.25[g]
Tris(*N*,*N*-diphenyldithiocarbamato)iron(III)	2.9	0.79[k]
Tris(*N*,*N*-dicyclopentyldithiocarbamato)iron(III)	2.97	10.93[g]
Tris(2,6-dimethylpiperidyl-*N*-carbodithioato)iron(III)	3.10	10.99[l]
Tris(*N*-ethyl-*N*-1-naphthyldithiocarbamato)iron(III)	3.38	4.24[h]
Tris(*N*-ethyl-*N*-phenyldithiocarbamato)iron(III)	3.45	5.11[j]
Tris(*N*-methyl-*N*-phenyldithiocarbamato)iron(III)	3.47	4.85[j]
Tris(*N*-methyl-*N*-*p*-tolyldithiocarbamato)iron(III)	3.52	5.33[h]
Tris(*N*-isopentyl-*N*-phenyldithiocarbamato)iron(III)	3.58	5.0[i]
Tris(*N*,*N*-dibenzyldithiocarbamato)iron(III)	3.60	8.52[g]
Tris(*N*-isopropyl-*N*-phenyldithiocarbamato)iron(III)	3.64	5.77[j]
Tris(*N*-ethyl-*N*-*p*-tolyldithiocarbamato)iron(III)	3.65	5.67[h]
Tris(2-methylpiperidyl-*N*-carbodithioato)iron(III)	3.73	10.99[l]
Tris(*N*-propyl-*N*-phenyldithiocarbamato)iron(III)	3.75	5.02[j]
Tris(*N*,*N*-diisobutyldithiocarbamato)iron(III)	3.77 (3.31)[d]	10.50[f]
Tris(morpholinyl-*N*-carbodithioato)iron(III)	4.02	8.49[g]
Tris(1,2,3,4-tetrahydroisoquinolinyl-*N*-carbodithioato)iron(III)	4.05	9.49[i]
Tris(*N*-phenylpiperazinyl-*N*-carbodithioato)iron(III)	4.06	9.0[i]
Tris(*N*-methyl-*N*-benzyldithiocarbamato)iron(III)	4.06	9.58[f]
Tris(piperidyl-*N*-carbodithioato)iron(III)	4.09[e]	11.123[g]
Tris(*N*,*N*-di-*n*-propyldithiocarbamato)iron(III)	4.14	11.00[f]
Tris(*N*,*N*-dimethyldithiocarhamato)iron(III)	4.19	10.732[f]
Tris(*N*-ethyl-*N*-benzyldithiocarbamato)iron(III)	4.22	9.68[f]
Tris(*N*,*N*-di-*n*-heptyldithiocarbamato)iron(III)	4.23 (5.23)[d]	11.0[i]
Tris(*N*-methyl-*N*-butyldithiocarbamato)iron(III)	4.26	10.90[g]
Tris(1,2,3,6-tetrahydropyridyl-*N*-carbodithioato)iron(III)	4.31	10.25[i]
Tris(*N*,*N*-di-*n*-pentyldithiocarbamato)iron(III)	4.32 (3.92)[d]	11.18[h]
Tris(*N*,*N*-diallyldithiocarbamato)iron(III)	4.34[d]	9.29[f]
Tris(*N*,*N*-diisopentyldithiocarbamato)iron(III)	4.37[e]	10.92[g]
Tris(*N*,*N*-diethyldithiocarbamato)iron(III)	4.37	10.93[f]
Tris(*N*,*N*-di-*n*-hexyldithiocarbamato)iron(III)	4.38	11.00[i]
Tris(*N*-ethyl-*N*-butyldithiocarbamato)iron(III)	4.40	11.17[i]
Tris(*N*,*N*-di-*n*-butyldithiocarbamato)iron(III)	4.53 (4.18)[d]	11.25[f]
Tris(3-pyrrolinyl-*N*-carbodithioato)iron(III)	5.41	10.40[i]
Tris(pyrrolidyl-*N*-carbodithioato)iron(III)	5.83	11.11[g]

[a] Chloroform solution. [b] All literature values are either in chloroform or benzene. White, *et al.*, have indicated[4] that there is no significant difference in magnetic moments measured in these two solvents. [c] Where multiple literature values were available, the most recent determination is reported. [d] Reference 3. [e] Reference 4. [f] H. K. Hall, Jr., *J. Amer. Chem. Soc.*, 79, 5441 (1957). [g] J. J. Christensen, R. M. Izatt, D. P. Wrothall, and L. D. Hansen, *J. Chem. Soc. A*, 1212 (1969). [h] Reference 5. [i] This work. [j] M. G. Gireault-Vexlearschi, *Bull. Chim. Soc. Fr.*, 589 (1956). [k] M. A. Paul, *J. Amer. Chem. Soc.*, 76, 3236 (1954). [l] H. K. Hall, Jr., *ibid.*, 79, 5444 (1957).

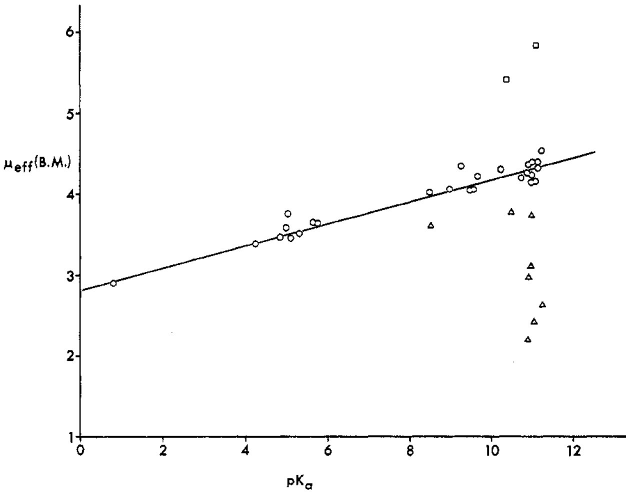

Figure 1.—Dependence of solution magnetic moment (μ_{eff}) on basicity of parent secondary amine for iron(III) dithiocarbamates.

complexes with dithiolate ligands and was rationalized in terms of π-antibonding effects due to differing availability of lone pairs on the sulfur atoms (differing formal charge).[10] In a study of the electronic spectra of dithio complexes, Jørgensen evaluated the relative ligand field strengths of dithio ligands in similar fashion and obtained the order dithiophosphate < dithiocarbamate < xanthate.[11] This is also the direction of increasing bond order within the metal–chelate ring, whether viewed in terms of sulfur π-antibonding effects or iron–sulfur π back-bonding. In any case, the conclusion is that an increase in the charge on the sulfur atoms results in a lengthened metal–sulfur bond and a consequent decrease in the ligand field strength, and we infer, therefore, that limiting form II favors high spin.

Delocalization of the electron pair within the metal–chelate ring, as in limiting form I, would result in greater metal–ligand covalency, shorter Fe–S distance, and a larger Δ favoring the low-spin state.

X-Ray structural determinations,[12–17] nmr studies,[18]

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and infrared spectra[18-20] provide evidence of the importance of limiting form II for this ligand in complex with many metals. Trends in the C–N stretching frequencies of the iron(III) dithiocarbamates are obscured by the complexity of their infrared spectra, however.

The importance of limiting form II will increase as the electron-releasing ability of the $-NR_2$ group increases, which depends on the inductive strength of each substituent R. The aqueous pK_a value, uncorrected, of the parent secondary amine, HNR_2, was taken as a measure of this property.[21] The greater the pK_a of HNR_2, the more available is the nitrogen lone pair to enter into bonding, and the more probable is the formation of a carbon–nitrogen double bond (limiting form II), favoring the high-spin state and a high magnetic moment. This conclusion is in agreement with the results presented in Table I and Figure 1.

Nine of the thirty-seven dithiocarbamatoiron(III) complexes do not conform to the overall trend. Of these nine, seven (di-*sec*-butyl, diisopropyl, dicyclohexyl, dicyclopentyl, diisobutyl, 2-methylpiperidyl, and 2,6-dimethylpiperidyl derivatives) have a common feature: the amino groups in these complexes have a secondary carbon, in most cases attached directly to the nitrogen but in no case further than one carbon atom away.

In order to account for the points below the line in Figure 1, then, the apparent importance of limiting form I for these compounds must be explained. One might expect limiting form II to be preferred for those complexes with sterically hindered $-NR_2$ groups, as did Ewald, *et al.*,[3] since the trigonally hybridized nitrogen would permit lessening of these interactions. However, limiting form II requires coplanarity of the atoms S_2CNC_2, and if unfavorable steric interactions between the R groups and the sulfur atoms prevent the S_2CNC_2 system from approaching a planar configuration, limiting form II is sterically inhibited. The contribution of limiting form II to the electronic structure of the ligand will then be considerably less than expected on the basis of the pK_a for these complexes.

Examination of molecular models indicates that for the di-*sec*-butyl, diisopropyl, dicyclopentyl, dicyclohexyl, and diisobutyl derivatives, the opening of the R–N–R bond angle from the tetrahedral configuration does reduce R–R steric repulsions, but steric interactions are minimized, including those between the R groups and the sulfur atoms, if the planes defined by the atoms CS_2 and NC_2 are perpendicular, not coincident. Thus, limiting form II is disfavored for these complexes, accounting for their unexpectedly low magnetic moments.

In order to test this interpretation, compounds were prepared in which there was the possibility of steric interference between R groups and the sulfur atoms but no possibility of such interaction between the substituents on nitrogen (2-methylpiperidyl and 2,6-dimethylpiperidyl derivatives). Therefore, limiting form II could not be sterically favored and in fact is sterically disfavored, enabling a determination of the relative ligand field strengths of the two limiting forms. Both exhibit anomalously low magnetic moments, confirming that limiting form I possesses the stronger ligand field.

Further indication of the likelihood of steric inhibition of resonance form II is provided by nmr studies of restricted rotation about the C–N bond in a series of amides[22] which found that, as one increases the size of either the nitrogen or carbon substituents, the rate of rotation about the C–N bond increases, indicating a sterically forced decrease in multiple-bond character by prevention of the required extensive coplanarity.

The two complexes which have five-member ring amino groups (pyrrolidyl and 3-pyrrolinyl derivatives) both possess magnetic moments which are considerably higher than the value expected in view of their basicities. This apparent preference for limiting form II (possessing the weaker ligand field) is at first puzzling.

A molecular model of the ligand indicates that, in these complexes, there is severe steric interaction between the α hydrogens and the sulfurs in a configuration corresponding to limiting form I; such interaction is absent in limiting form II. Attempts were made to prepare and study the magnetic properties of complexes in which there are similar five-member cyclic amino groups but in which such hydrogen–sulfur interactions are absent. These included the pyrrole, indole, carbazole, imidazole, succinimide, and indoline derivatives, but, due in part to the low basicity of these amines, only the indoline complex could be prepared, and this complex was insufficiently soluble to obtain a valid solution measurement. The Mössbauer isomer shift for the indoline derivative, however, indicates it is not high spin.[23]

The relationship between the solid-phase magnetic moments and pK_a of the parent secondary amines for the iron(III) dithiocarbamates is substantially complicated by solid-state interactions and a plot of such data gives a scatter.

The conclusion of Ewald, *et al.*,[3] that form II would possess a stronger ligand field, resulting in a lower complex magnetic moment, is contradicted by the dependence observed by the present authors, indicating that inductive factors are the primary influence on the properties of the dithiocarbamate ligand and that limiting form I possesses the stronger ligand field.

It is emphasized that it is principally a trend in π bonding which is being described in this work. It is assumed that σ donation is relatively unchanged in the series of iron(III) dithiocarbamates, as was held by Jørgensen for a series of dithio ligands.[11]

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[21] The aqueous pK_a value is not simply a function of inductive effects but also to a significant degree of solvation and steric effects. However, it is assumed that inductive effects predominate, an assumption which is supported by the general additivity of substituent inductive effects in calculation of dissociation constants of organic acids and bases, including a variety of amines: H. K. Hall, Jr., *J. Amer. Chem. Soc.*, **79**, 5441 (1957).

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