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Magnetism of Tris(dithiocarbamato)iron(III) Complexes Derived from Cyclic Amines

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The magnetic susceptibilities of a large number of tris(N,N-disubstituted dithiocarbamato)iron(III) complexes, $[Fe(RR'NCS_2)_3]$ (or, in general, $[Fe(RR'dtc)_3]$), have been reported in the literature [1]. These complexes exist as thermal equilibrium mixtures of low-spin ($S = 1/2$) and high-spin ($S = 5/2$) iron(III) ions, with magnetic moments which range from about 2.2 B.M. (the pyrrole derivative [2]) to 5.9 B.M. (the pyrrolidyl derivative [3–5]) at room temperature, and which usually are very temperature dependent. Ståhl and Ymén have recently shown that the solid-state magnetic moments of a wide variety of $[Fe(RR'NCS_2)_3]$ complexes correlate very well with the Fe–S bond lengths, and the SFeS, SCS and CNC angles, but there is no correlation with C–S and C–N bond lengths, nor with the pK_a of the parent amine [6].

Some time ago we measured the temperature dependence of the magnetism and Mössbauer behavior of a series of ferric dithiocarbamates derived from cyclic amines with varying ring sizes and basicities. The magnetic data are given in this paper.

Experimental

The tris(dithiocarbamato)iron(III) complexes were prepared by treating a mixture of excess freshly precipitated ferric hydroxide and the secondary amine in absolute ethanol with carbon disulfide. After stirring for 1 to 2 h, the thick reaction mixture was filtered and the filter cake extracted with benzene. The complex was precipitated from the benzene solution by the addition of anhydrous ethanol. All complexes were crystallized at least three times from benzene, then dried in vacuum at 80 °C. All gave satisfactory analyses for C, H, N and S (Alfred Bernardt) and were unsolvated, except for the hexamethyleneimine derivative which contained 1/2 mole benzene per mole of complex.

Abbreviations used for the parent amines: Me_2pyrr, 2,5-dimethyl-3-pyrroline (Aldrich; mixture of *cis* and *trans* isomers); Me_2pyr, 2,5-dimethylpyrrolidine (Aldrich; mixture of *cis* and *trans* isomers); Me_2pip, 2,6-dimethylpiperidine (Fisher; exclusively the *cis* isomer); Thiaz, thiazolidine (Aldrich); Hex, hexamethyleneimine (Aldrich); Octa, octamethyleneimine (Aldrich), and Dhcbz, dodecahydrocarbazole (Baker). The dodecahydrocarbazole can theoretically exist in a total of six *cis*, *trans*, *syn* and *anti* forms; it is not known which of these was the actual form of the amine used in this investigation; most likely it was a mixture of isomers.

Magnetic measurements in the temperature range 2.7–300 K were made on a Faraday-type balance, with an external magnetic field of 1.8 T. Diamagnetic corrections were calculated from Pascal's constants. Estimated error limits on μ_{eff} = ±0.05 B.M.

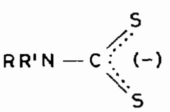
Results

The corrected magnetic moments in the temperature range 5–300 K for seven tris(dithiocarbamato)iron(III) complexes are given in Table 1. There is an essentially linear dependence of μ_{eff} on temperature over the following temperature ranges: $[Fe(Me_2pyrr\ dtc)_3]$, 10–240 K; $[Fe(Me_2pyr\ dtc)_3]$, 30–200 K; $[Fe(Dchbz\ dtc)_3]$, 30–200 K; $[Fe(Me_2pip\ dtc)_3]$, 100–300 K; $[Fe(Thiaz\ dtc)_3]$, 30–300 K; $[Fe(Hexa\ dtc)_3]$, 10–100 K and 120–260 K; $[Fe(Octa\ dtc)_3]$, 40–160 K and 160–260 K.

The magnetic moment of $[Fe(Me_2pip\ dtc)_3]$ reaches a constant value of 2.40 ± 0.05 B.M. by ~100 K.** The only lower value of μ_{eff} reported in the literature is 2.19 B.M. for the pyrrole derivative at room temperature; complexes derived from diphenylamine, diisopropylamine and dicyclohexylamine all have higher moments at room temperature (2.52 B.M. [4], 2.62 B.M. [3, 4] and 2.75 B.M. [3, 4], respectively).

Discussion

There are two canonical forms which contribute to the overall structure of the dithiocarbamate ligand: form **I**, herein called the 'thione' form, and form **II**, herein called the 'thiolate' form:



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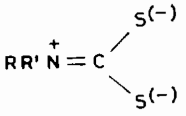

II

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**A room temperature value of 2.46 B.M. was reported in ref. 7.

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TABLE 1. Magnetic Moments (B.M.) of [Fe(RR'dtc)$_3$] Complexes

Temperature (K)	RR'						
	Me$_2$pyrr	Me$_2$pyr	Dhcbz	Me$_2$pip	Thiaz	Hexa	Octa
5	2.30	3.14	2.69		3.50	2.52	1.84
10	2.37	3.25	2.75		4.61	2.84	1.90
30	2.53	3.59	2.78	1.99	5.82	3.04	2.19
40	2.62	3.67	2.96	2.03	5.86	3.10	2.23
60	2.76	3.83	3.12	2.13	6.01	3.16	2.27
80	2.89	4.06	3.37	2.26		3.26	2.28
100	3.05	4.23	3.54	2.33		3.41	
120	3.20	4.40	3.84	2.33		3.48	
140	3.36	4.59	4.11	2.35		3.61	2.33
160	3.55	4.73	4.35	2.39		3.75	2.38
180	3.73	4.90	4.57	2.39		3.92	2.44
200	3.90	5.00	4.70	2.40		4.08	2.56
220	4.05	5.12	4.87	2.43	6.00	4.25	2.66
240	4.21	5.21	5.05	2.40		4.39	2.76
260	4.34	5.25	5.11	2.43	5.94	4.50	2.89
280	4.47	5.31	5.13	2.48	5.95	4.64	3.03
300		5.40		2.51		4.66	

The extent to which each contributes depends strongly upon the nitrogen substituents R,R', which exert both steric and electronic effects. Although the thiolate form should be the stronger σ-bonding form, it favors high-spin iron(III) (as first suggested by Cambi and Szegõ some 57 years ago [8]) because of its strong π-antibonding (π-base) properties [9].

Based on an examination of molecular models, Eley *et al.* [10] concluded that large R,R' groups disfavored the thiolate form, because of steric interactions with the sulfur atoms. Solvent molecules in Fe(RR'NCS$_2$)$_3$] crystal lattices are also known to exert significant steric effects. In most cases it appears that the inductive (electronic) effects of R,R' are of only minor importance, compared to the steric factors, in determining the magnetic moment of the complex. The only exceptions are pyrrole *N*-carbodithioate, where the thiolate form disrupts ring aromaticity, and perhaps the hydroxylamine derivative $CH_3ON(CH_3)CS_2^-$ [7], for which the thiolate form is favored since it removes electron density from the very electron rich >N–O– grouping (but see ref. 6 for a discussion of the steric effects of this ligand).

Room temperature magnetic moments of the cyclic dithiocarbamates given in Table 1 and those reported in the literature follow the order (the complex is denoted by the parent amine): pyrrole, 2.19 B.M. [2] < 2,6-dimethylpiperidine, 2.40 B.M. < octamethyleneimine, 3.03 B.M. < 2-methylpiperidine, 3.75 B.M. [11] < piperidine, 4.01 B.M. [3,8] < 2,5-dimethyl-3-pyrroline, 4.47 B.M. < hexamethyleneimine, 4.64 B.M. < dodecahydrocarbazole, 5.13 B. M. = morpholine, 5.12 B.M. [4] < 2,5-dimethylpyrrolidine, 5.31 B.M. < thiazolidine, 5.95 B.M. = pyrrolidine, 5.88 B.M. [3, 5] = 3-pyrroline, 6.1 B.M. [7]. Azetidine also forms a high-spin iron(III) complex [12–14], as well as 2-methylazetidine [13].

There is a marked inverse dependence of moment on ring size, of purely steric origin, although the relationship is not simply monotonic. Despite their very great differences in basicity, both pyrrolidine (pK_a = 11.31 [15]) and thiazolidine (pK_a = 6.22 [16]) give iron(III) complexes which are perfectly high-spin above 30 K. Morpholine and piperidine might be expected then to give iron(III) complexes with very similar moments, contrary to what is found. However, the magnetism of [Fe(Morph dtc)$_3$] is especially sensitive to small perturbations from solvation by benzene, chloroform, etc. (for [Fe(Morph dtc)$_3$]·2C$_6$H$_6$, μ_{eff} = 2.92 B.M. [17] or 3.53 B.M. [18] at 300 K, while for [Fe(Morph dtc)$_3$]·CH$_2$Cl$_2$, μ_{eff} = 5.45 B.M. [18] or 5.92 B.M. [17, 19] at 300 K), and to desolvation procedures [17–20]*.

Sensitivity to solvation effects may also be reflected in the moment of [Fe(Hexa dtc)$_3$]·$\frac{1}{2}$C$_6$H$_6$, the only solvated complex of those shown in Table 1, since the moment appears somewhat high compared to the value expected on a simple ring size basis, *i.e.* ~3.7 B.M. at room temperature.

Methyl substitution on carbon atoms α to the nitrogen in these cyclic amines markedly decreases the moment. The effect is greater with piperidine than with pyrrolidine or 3-pyrroline, since there is greater steric interaction between the α-methyl group(s) and the –CS$_2$ group in a 6-membered ring

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*The chlorobenzene solvate reported in ref. 20 is actually the unsolvated complex.

than in a 5-membered one (in general), especially with the thiolate form of the dithiocarbamate. For 2,6-dimethylpiperidine *N*-carbodithioate, Fisher–Hirschfelder–Taylor models show that the thiolate form is sterically impossible with both methyl groups equatorial, and is only marginally possible with both methyl groups axial. However, there are no steric interactions in the thione form with both methyl groups equatorial, and the lone pair on the nitrogen axial. This ligand must exist entirely in the thione form, giving a low-spin iron(III) complex.

Detailed comparisons of 2,5-dimethylpyrrolidine and 2,5-dimethyl-3-pyrroline are not very useful because of the unknown orientation of the methyl groups (*cis* and/or *trans*) with differing steric effects. It is clear however, that the rather large difference of 1 B.M. in the magnetic moments of their complexes is not due to electronic effects arising from differences in pK_a values of the parent amines.

In summary, it thus appears that the magnetic moments of ferric tris(dithiocarbamates) derived from cyclic amines can be rationalized reasonably well simply on a steric basis, with the assumption that the thiolate form of the dithiocarbamate gives high-spin iron(III).

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