On the Anomalous Magnetic Properties of Tris(diselenocarbamato)iron(III) Compounds

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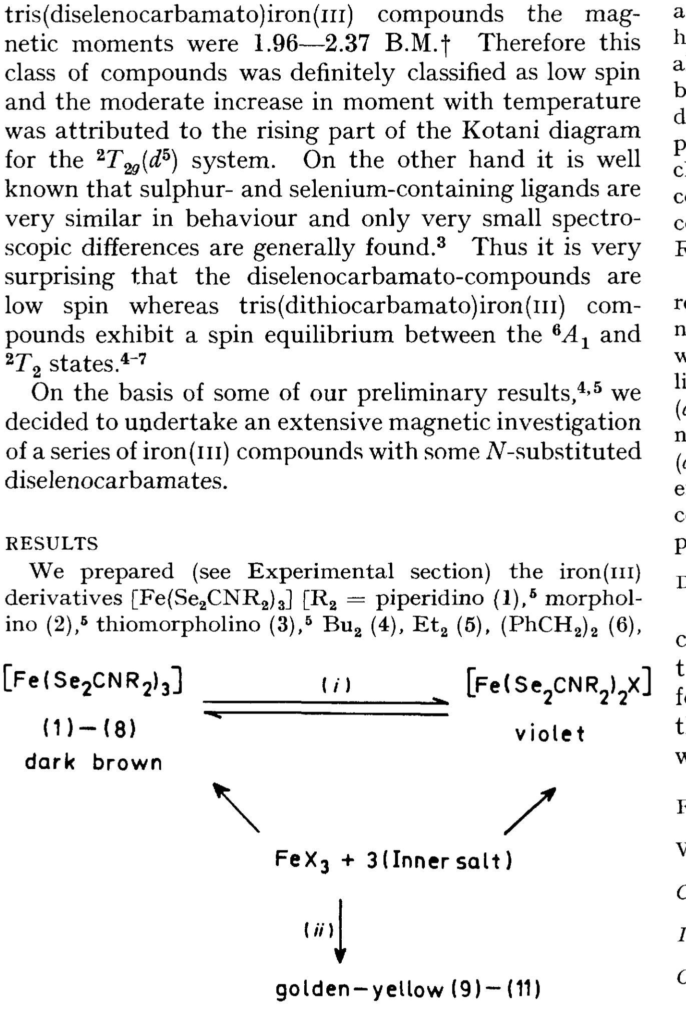
An extended magnetic investigation of a series of pseudo-octahedral [Fe(Se$_2$CNR$_2$)$_3$] compounds [R$_2$ = piperidino, morpholino, thiomorpholino, Bu$_2$, Et$_2$, (PhCH$_2$)$_2$, (C$_6$H$_{13}$)$_2$, and MePh] has been made at 90—400 K. Diamagnetic compounds not containing iron, Se(Se$_2$CNEt$_2$)$_2$, Se[Se$_2$CN(CH$_2$Ph)$_2$]$_2$, and (Se$_2$CNMePh)$_2$, have also been isolated and their presence could explain the previously reported low-spin classification of [Fe(Se$_2$CNR$_2$)$_3$] compounds. The reported measurements demonstrate that the magnetic behaviour of these compounds is anomalous, the μ values generally ranging between the limiting values typical for $^6A_1$ and $^2T_2$ states. Treatment of the experimental values by means of van Vleck's equation has enabled the evaluation of the crossover parameters, and a full comparison with the dithiocarbamate derivatives is made. The influence of the substituents on the nitrogen of the ligand on the position of the spin equilibrium is discussed.

IN the previously reported[1,2] magnetic behaviour of tris(diselenocarbamato)iron(III) compounds the magnetic moments were 1.96—2.37 B.M.† Therefore this class of compounds was definitely classified as low spin and the moderate increase in moment with temperature was attributed to the rising part of the Kotani diagram for the $^2T_{2g}(d^5)$ system. On the other hand it is well known that sulphur- and selenium-containing ligands are very similar in behaviour and only very small spectroscopic differences are generally found.[3] Thus it is very surprising that the diselenocarbamato-compounds are low spin whereas tris(dithiocarbamato)iron(III) compounds exhibit a spin equilibrium between the $^6A_1$ and $^2T_2$ states.[4-7]

On the basis of some of our preliminary results,[4,5] we decided to undertake an extensive magnetic investigation of a series of iron(III) compounds with some *N*-substituted diselenocarbamates.

RESULTS

We prepared (see Experimental section) the iron(III) derivatives [Fe(Se$_2$CNR$_2$)$_3$] [R$_2$ = piperidino (1),[5] morpholino (2),[5] thiomorpholino (3),[5] Bu$_2$ (4), Et$_2$ (5), (PhCH$_2$)$_2$ (6), (C$_6$H$_{13}$)$_2$ (7), and MePh (8)] according to the Scheme starting from FeX$_3$ (X = Cl, Br, ClO$_4$, or CCl$_3$CO$_2$) and the inner salt of the diselenocarbamates. Using a strong excess of the inner salt the equilibrium between the five- and six-co-ordinate forms is completely shifted to the left-hand side. The golden-yellow products (9)—(11) were always present and, in some cases, have been characterized by C, H, and N analysis and i.r. and mass spectra. They do not contain iron and are, obviously, diamagnetic; their presence may be responsible for the previous 'low-spin' classification of the iron(III) diselenocarbamates.‡ These compounds are oxidation products of the ligands; similar compounds have already been prepared and identified by Rosembaum *et al.*[8]



SCHEME (i) X$^-$, – [Se$_2$CNR$_2$]$^-$; (ii) fractional crystallization under nitrogen

The dark brown compounds [Fe(Se$_2$CNR$_2$)$_3$] (1)—(8) were repeatedly purified by fractional crystallization under nitrogen.§ The absence of the ligand oxidation products was tested by: (*a*) microscopic examination of well crystallized samples; (*b*) C, H, N, and Fe analysis (see Table 1); (*c*) repeating the fractional crystallization until the magnetic moments were consistent to within ±0.1 B.M.; and (*d*) using samples of the same compound derived from different preparations and having coherent μ values [for example, compound (5): preparation (*a*) 292 K, μ = 3.76 B.M.; preparation (*b*) 288 K, μ = 3.78 B.M.].

DISCUSSION

The cause of magnetic anomalies in iron(III) dithiochelates was attributed by Cambi and his co-workers[9-11] to 'an equilibrium between two magnetically isomeric forms' and this hypothesis was strongly supported by the more recent conclusions of White and his co-workers.[6,7,12,13] Merrithew and Rasmussen,[14] on the

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† Throughout this paper: 1 B.M. ≈ 9.27 × 10^{-24} A m^2.

‡ Among other things, our previously reported [5] magnetic data for compounds (1)—(3) were complicated due to the presence of this impurity.

§ It is impossible to use the t.l.c. method because of their ready decomposition.

[1] E. Cervone, F. Diomedi Camassei, M. L. Luciani, and C. Furlani, *J. Inorg. Nuclear Chem.*, 1969, **31**, 1101.

[2] 'Organic Selenium Compounds,' eds. D. L. Klayman and W. H. H. Günther, Wiley, New York, 1973, p. 1029.

[3] K. A. Jensen, V. Krishnan, and C. K. Jørgensen, *Acta Chem. Scand.*, 1970, **24**, 743.

[4] D. De Filippo, P. Deplano, F. Devillanova, and E. F. Trogu, *Inorg. Chim. Acta*, 1976, **17**, 199.

[5] D. De Filippo, P. Deplano, A. Diaz, and E. F. Trogu, *Inorg. Chim. Acta*, 1976, **17**, 139.

[6] A. H. White, R. Roper, E. Kokot, H. Waterman, and R. L. Martin, *Austral. J. Chem.*, 1964, **17**, 294.

[7] A. H. Ewald, R. L. Martin, I. G. Ross, and A. H. White, *Proc. Roy. Soc.*, 1964, **A280**, 235.

[8] A. von Rosembaum, H. Kirchberg, and E. Leibnitz, *J. prakt. Chem.*, 1963, **4**, 19.

[9] L. Cambi and L. Szego, *Ber.*, 1931, **64**, 2591.

[10] L. Cambi, L. Szego, and A. Cagnasso, *Atti Accad. Naz. Lincei, Rend. Classe Sci. fis. mat. natur.*, 1932, **15**, 266, 329.

[11] L. Cambi and L. Malatesta, *Ber.*, 1937, **70**, 2067.

[12] A. H. Ewald, R. L. Martin, E. Sinn, and A. H. White, *Inorg. Chem.*, 1969, **8**, 1837.

[13] P. C. Healy and A. H. White, *J.C.S. Dalton*, 1972, 1163.

[14] P. B. Merrithew and P. G. Rasmussen, *Inorg. Chem.*, 1972, **11**, 325.

basis of the Mössbauer spectra of several tris(dithiocarbamate)iron(III) compounds, doubted whether a thermal equilibrium truly exists and suggested that 'the magnetic susceptibility and Mössbauer spectral data of these complexes could be better explained in terms of spin-mixed states'.[15,16] This hypothesis was shown to be incorrect by Mössbauer results on tris(monothio-β-diketonato)iron(III) compounds whose spectra show simultaneous signals for both low- and high-spin states.[17] Since the detection of both spin isomers is possible, a slow exchange rate and a favourable quadrupole-splitting difference between the two spin states seem necessary.

TABLE 1

Analytical data (%)

Compound	Calc. Fe	Calc. C	Calc. H	Calc. N	Found Fe	Found C	Found H	Found N
$[Fe(Se_2CNC_5H_{10})_3]$ (1)		26.4	3.7			26.7	3.6	
$[Fe(Se_2CNC_4H_8O)_3]$ (2)	6.8	21.9	2.9		6.9	21.9	2.8	
$[Fe(Se_2CNC_4H_8S)_3]$ (3)	6.4	20.7	2.8		6.2	20.8	3.0	
$[Fe(Se_2CNBu_2)_3]$ (4)		34.1	5.7			34.4	5.8	
$[Fe(Se_2CNEt_2)_3]$ (5)	7.1	23.0	3.9	5.4	7.2	22.8	3.6	5.2
$[Fe\{Se_2CN(CH_2Ph)_2\}_3]$ (6)	4.8	46.8	3.7		5.0	47.3	3.9	
$[Fe\{Se_2CN(C_6H_{13})_2\}_3]$ (7)		41.9	7.0			40.8	7.1	
$[Fe(Se_2CNMePh)_3]$ (8)	6.3	32.6	2.7		6.1	32.1	2.8	
$Se(Se_2CNEt_2)_2$ (9)		21.3	3.6	5.0		21.0	3.5	4.7
$Se[Se_2CN(CH_2Ph)_2]$ (10)		44.4	3.5			44.1	3.8	
$(Se_2CNMePh)_2$ (11)		34.8	2.9	5.1		34.5	2.7	4.9

All the iron(III) compounds are dark brown prismatic crystals, soluble in CH_2Cl_2, $CHCl_3$, acetone, and benzene, and non-electrolytes. Compounds (9)—(11) are golden-yellow crystals, stable in the solid state.

In other cases, as in tris(dithiocarbamate) derivatives, only averaged signals are detectable in the Mössbauer spectra. Hall and Hendrickson,[18] in an e.s.r. study, demonstrated that the spin-flipping rate between the $^6A_1$ and $^2T_2$ levels in $[Fe(S_2CNR_2)_3]$ compounds is of the order of 10^{10} s^{-1}, *i.e.* faster than the ^{57}Fe Mössbauer time scale (*ca.* 10^7 s^{-1}).

TABLE 2

Mössbauer data for some tris(dithiocarbamato)- and tris(diselenocarbamato)-iron(III) compounds

Compound		T/K 110	210	295
$[Fe(S_2CNC_5H_{10})_3]$	ΔE_Q ± 0.03 mm s^{-1}	0.71	0.49	0.14
	Isomer shift ± 0.03 mm s^{-1}	0.59	0.58	0.56
	$I_{\frac{3}{2}} : I_{\frac{1}{2}}$	0.96	1.02	1
(1)	ΔE_Q ± 0.03 mm s^{-1}	0.76	0.57	0.43
	Isomer shift ± 0.03 mm s^{-1}	0.70	0.64	0.60
	$I_{\frac{3}{2}} : I_{\frac{1}{2}}$	0.98	0.98	0.98
(4)	ΔE_Q ± 0.03 mm s^{-1}	0.87	0.65	0.57
	Isomer shift ± 0.03 mm s^{-1}	0.68	0.60	0.46
	$I_{\frac{3}{2}} : I_{\frac{1}{2}}$	1.02	1.13	1.20

For the $[Fe(Se_2CNR_2)_3]$ compounds, our Mössbauer spectra were recorded at 110, 210, and 295 K using iron enriched by up to 90% ^{57}Fe. This was done to limit the effect of X-ray scattering on the Se atoms, giving better accuracy. The results (Table 2) are compared with those previously obtained for tris(piperidinodithiocarbamato)iron(III).[19,20] Both dithio- and diselenocarbamato-compounds show quadrupole splittings (ΔE_Q) which increased on cooling the samples. {The five-co-ordinate derivatives, $[Fe(S_2CNR_2)_2X]$ and $[Fe(Se_2CNR_2)_2X]$, on the contrary, have temperature-independent ΔE_Q values.} The ratios $I_{\frac{3}{2}} : I_{\frac{1}{2}}$ of the quadrupole-peak intensity are very close to 1 : 1 except for compound (4). In this case, when the temperature was increased from 110 to 295 K this ratio increased from 1.02 to 1.20 : 1, perhaps as a consequence of distortion of the octahedral structure allowing for the Goldanski effect. The strong resemblance between the Mössbauer spectra of these two types of compound supports the hypothesis that the anomalous magnetic behaviour of diselenocarbamate derivatives can be attributed to a spin-state equilibrium.

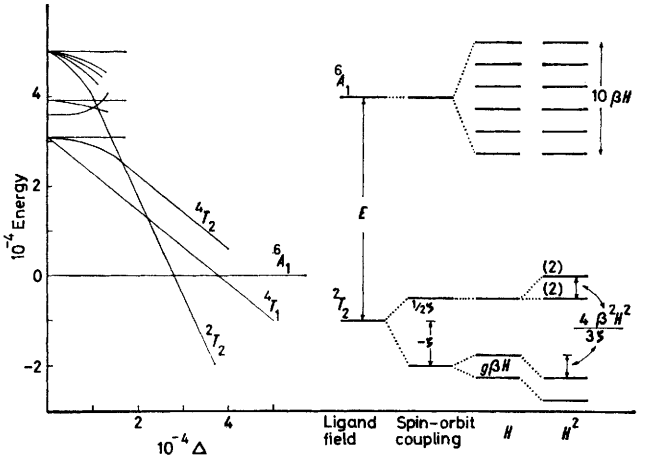

FIGURE 1 Term diagram for a d^5 configuration (left) and energy levels (arbitrary scale) in the crossover region (right)

The experimental magnetic data can be rationalized by van Vleck's equation adapted to the present case (as a weighted mean of μ^2 values for the population of the three sublevels of the two states), in agreement with

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[15] G. Harris, *Theor. Chim. Acta*, 1966, **5**, 379.

[16] G. Harris, *Theor. Chim. Acta*, 1968, **10**, 119.

[17] M. Cox, J. Darken, B. W. Fitzsimmons, A. W. Smith, L. F. Larkworthy, and K. A. Rogers, *J.C.S. Dalton*, 1972, 1192.

[18] G. R. Hall and D. N. Hendrickson, *Inorg. Chem.*, 1976, **15**, 3607.

[19] L. M. Epstein and D. K. Straub, *Inorg. Chem.*, 1968, **8**, 784.

[20] F. Aramu, V. Maxia, D. De Filippo, and E. F. Trogu, *Abs., Internat. Conf. Applications Mössbauer Effects*, Corfu, 1976, C3, 10, p. 67.

the energy levels for a d^5 configuration in the cross-over region (see Figure 1).* Thus van Vleck's equation is as in (1) where the splitting factor g is *ca.* 2 and $x = \zeta/\boldsymbol{k}T$, where ζ is the one-electron spin–orbit coupling constant.

$$\mu^2 = \frac{0.75g^2 + 8x^{-1}[1 - \exp(-3x/2)] + 105C\exp[-(E + \zeta)/\boldsymbol{k}T]}{1 + 2\exp(-3x/2) + 3C\exp[-(E + \zeta)/\boldsymbol{k}T]} \qquad (1)$$

For the free Fe^{3+} ion $\zeta = 460\ cm^{-1}$,[22] but it is to be expected that in a compound this value will differ. In fact for dithiocarbamate derivatives White *et al.*[6] adopted a value of $370\ cm^{-1}$, while in the previously reported studies of diselenocarbamates values ranging between 350 and $390\ cm^{-1}$ were used.[1] The correction factor C is taken as the quotient of the molecular-vibrational partition functions in the $^6A_1$ and $^2T_2$ states, *i.e.* $C = Q_a/Q_t$. Assuming that the only contributions to Q_a/Q_t are from the six Fe–Se stretching and the nine Se–Fe–Se bending modes, C can be defined as in equation (2). Therefore C is generally dependent

$$C = \frac{Q_a}{Q_t} = \left[\frac{1 - \exp(-\nu_{ts}/\boldsymbol{k}T)}{1 - \exp[-\nu_{as}/\boldsymbol{k}T)}\right]^6 \left[\frac{1 - \exp(-\nu_{tb}/\boldsymbol{k}T)}{1 - \exp(-\nu_{ab}/\boldsymbol{k}T)}\right]^9 \qquad (2)$$

on T and its value determines the gradients at higher temperature (Figure 3).

TABLE 3

The most important i.r. absorptions (cm^{-1}) of the iron(III) compounds

Compound	Approximate descriptions					
	$\nu(CN) + \delta(CH_2)$		$\nu(CNC) + \nu(CSe_2)$		$\nu(CSe_2)$	$\nu(MSe)$
(1)	1 480vs	1 427s	855m	822ms	475w	267m, 237m
(2)	1 480vs	1 422s	865s	840 (sh)	485m	273m, 249m
(3)	1 470vs	1 430s	855ms			267s, 233s
(4)	1 490vs	1 423s	871m	830w	422w	260 (sh), 235m
(5)	1 490vs	1 425s	850m	828ms	450w	253m, 236m
(6)	1 475vs	1 426s	873ms	822w	482m	282m, 248m
(7)	1 490vs	1 420s	870m		481w	280 (sh), 248ms
(8)	1 486vs	1 460s	880w	840w		259m, 227m

In our i.r. spectra (Table 3), as in those of $[Fe(S_2CNR_2)_3]$, the absorptions attributable to ν(Fe–Se) are always doublets, whereas in the spectra of $[Fe(Se_2CNR_2)_2X]$ only one absorption is present. This indicates that at least the molecular-vibration frequencies do change on excitation, those due to the $^6A_1$ state being lower than for $^2T_2$. Consequently we attribute the two bands at *ca.* 260 and $230\ cm^{-1}$ to the stretching modes ν_{ts} and ν_{as} of the $^2T_2$ and $^6A_1$ states respectively. These values are in very good agreement with that ($353\ cm^{-1}$) [23] generally adopted for ν(Fe–Se), if the same force constant is used for both Fe–S and Fe–Se linkages. The bending frequencies, ν_{tb} and ν_{ab}, are also probably doublets but these absorptions occur much lower than $200\ cm^{-1}$, the limit of our instrument.

In the first approach the C factor was evaluated by extrapolating to $T = \infty$. Defining a constant K as the ratio between the populations in $^6A_1$, and in the lower, doubly degenerate, component of the $^2T_2$ state [equation (3)], equation (4) is obtained.

$$K = \frac{6C\exp[-(E + \zeta)/\boldsymbol{k}T]}{2} \qquad (3)$$

$$\ln(K/3) = \ln C - [(E + \zeta)/\boldsymbol{k}T] \qquad (4)$$

On the other hand K can be evaluated from the experimental values by use of equation (5) where $A = 0.75\,g^2 + 8x^{-1}[1 - \exp(-3x/2)]$ and $B = 1 + 2\exp(-3x/2)$.

$$K = \frac{\mu^2 B - A}{35 - \mu^2} \qquad (5)$$

Using the above procedure for our experimental data, straight lines were generally obtained (Figure 2) for compounds (4), (5), and (7), at least for the values at higher temperatures. From the gradients of these plots a first evaluation of the $(E + \zeta)$ value can be made. Using these results as starting data, a more complete fitting was made (Figure 3).

Assuming C = constant in equation (1), best values for g, E, ζ, and C were obtained for $\Sigma(\chi_{calc.} - \chi_{expt.})^2$ = minimum and are reported in Table 4. Then, from equation (6), ν_{tb}/ν_{ab} can be evaluated using the best values of C and the experimental values of ν_{ts} and ν_{as}

$$\lim_{T \to \infty}(Q_a/Q_t) = \left(\frac{\nu_{ts}}{\nu_{as}}\right)^6 \left(\frac{\nu_{tb}}{\nu_{ab}}\right)^9 \qquad (6)$$

(see Table 3), thus obtaining values ranging between 1.01 and 1.08.

In the second approach the previously obtained g, E, and ζ values were used as starting data together with ν_{tb}/ν_{ab}, whereas for C equation (2) was used. The explored range for ν_{ab} was 70—$130\ cm^{-1}$, and the best values obtained are reported in italics in Table 4. How-

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* The $[M(S_2CNR_2)_3]$ compounds of various transition metals are in trigonally compressed octahedral environments, but Figgis[21] showed that the μ values are not sensitive to this trigonal distortion above 90 K.

[21] B. N. Figgis, *Trans. Faraday Soc.*, 1961, **57**, 198.

[22] A. Earnshaw, 'Introduction to Magnetochemistry,' Academic Press, London, 1968, p. 59.

[23] K. A. Jensen and V. Krishnan, *Acta Chem. Scand.*, 1970, **24**, 1088.

ever, the curves obtained in the second approach (Figure 3) (which are in very good agreement with the experimental values) practically do not change together with g and ζ while E slightly decreases and the ν_{tb}/ν_{ab} increases.

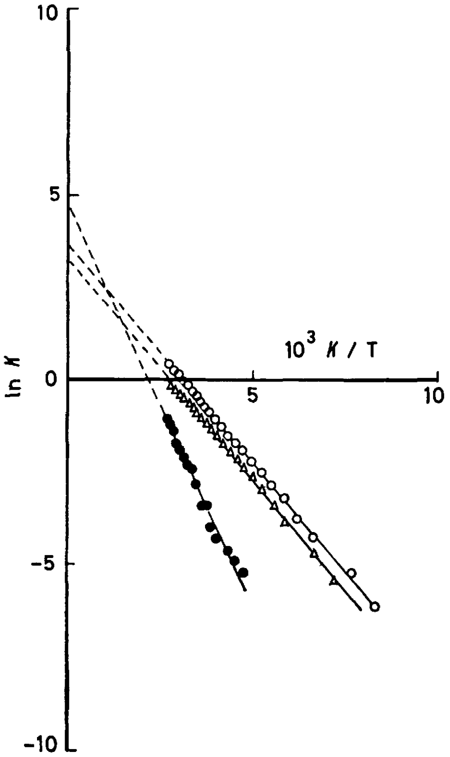


FIGURE 2 Examples of the first approach evaluating ($E + \zeta$) and ln$C$ using equations (4)—(6) and compounds (4) (○), (5) (△), and (6) (●)

TABLE 4

Crossover parameters for the [$Fe(Se_2CNR_2)_3$] compounds (ζ, E, ν_{tb}, and ν_{ab} in cm^{-1}). Italicized values were obtained from values of C as defined in equation (2)

Compound	g	ζ	E	ln$C$	ν_{tb}	ν_{ab}
(1)	2.8	150	890	2.5		
	2.8	*150*	*840*		*117*	*90*
(2)	1.5	150	110	1.2		
	1.5	*150*	*60*		*130*	*118*
(3)	2.0	180	1 060	3.4		
	2.0	*180*	*812*		*110*	*85*
(4)	2.2	305	520	2.6		
	2.2	*320*	*340*		*104*	*85*
(5)	2.2	370	430	2.0		
	2.2	*370*	*350*		*110*	*90*
(6)	2.8	90	600	1.0		
	2.8	*150*	*710*		*98*	*85*
(7)	2.2	230	1 220	3.6		
	2.2	*230*	*1 000*		*140*	*100*
(8)	2.2	100	270	0.7		
	2.2	*100*	*270*		*100*	*95*

It is important to point out that, taking as constants g, ζ, and ν_{tb}/ν_{ab}, appreciable variations of ν_{ab} can be balanced by slight variations in E. Consequently the ν_{tb} and ν_{ab} values must be regarded as indicative parameters, while g, E, ζ, and ν_{tb}/ν_{ab} seem more reliable.

Conclusions.—By comparison of the [$Fe(S_2CNR_2)_3$] and [$Fe(Se_2CNR_2)_3$] series it can be seen that the magnetic properties are similar, although the spin equilibrium is slightly shifted towards the low-spin state in the diselenocarbamates [except for compound (8)] (see Figure 4). In the previous paper[1] in which a low-spin state was attributed to the diselenocarbamato-compounds, the different behaviour with respect to the dithiocarbamates was rationalized on the basis of a slightly smaller Δ and much smaller β values for the selenium compounds. In other words, this explanation is based on the assumption that π-back donation occurs to a larger extent with selenium- than with sulphur-containing ligands. However, on the basis of spectroscopic evidence, Jensen *et al.*[3] do not believe that π-back donation must be invoked to explain the very small spectrochemical difference.

In fact, the spectrochemical positions of [S_2CNR_2]$^-$ and [Se_2CNR_2]$^-$ are almost equivalent, with the latter a little lower than the former with regard to Δ parameters. On this basis, in [$Fe(Se_2CNR_2)_3$] the spin equilibrium should be slightly shifted towards the high-spin state, in contrast to our results. Consequently we partially agree with the π-back-donation hypothesis, while the strong similarity between the two types of ligand is again confirmed by the existence of the same electronic equilibrium in both iron series.

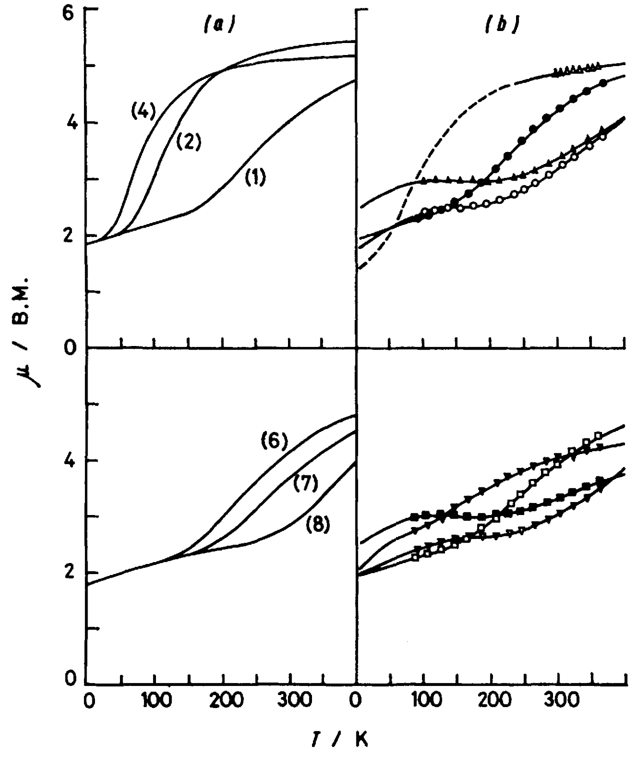


FIGURE 3 Comparison between the dithiocarbamate (*a*) and diselenocarbamate series (*b*). The curves in (*a*) were calculated by means of crossover parameters reported in ref. 7, those in (*b*) were derived from best fitting and are compared with the experimental data. Compounds: (1) (▲), (2) (△), (3) (○), (4) (●), (5) (□), (6) (■), 7 (▽), and (8) (▼)

The $\mu_{eff.}$ values in these two series of compounds are strongly affected by the nature of the substituents on the nitrogen of the ligands. For the dithiocarbamate series Eley *et al.*,[24] studying the dependence of solution magnetic moments on the pK_a of the parent amines, found an approximately linear relation, and this demonstrates the strong electronic influence of the nitrogen substituents on the electronic state of the compounds.

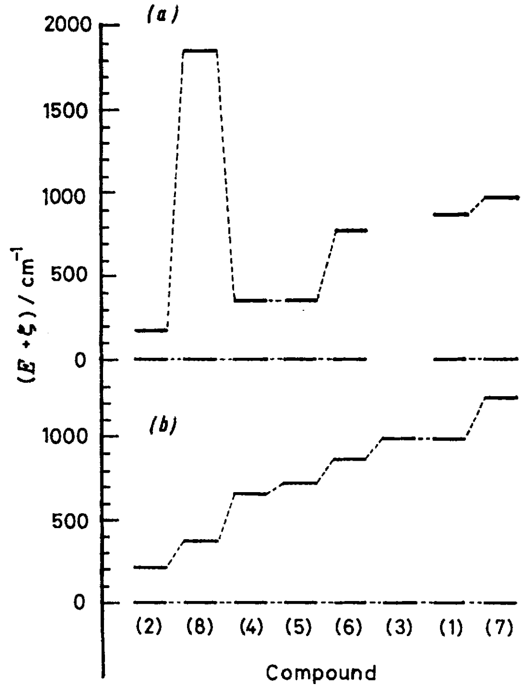
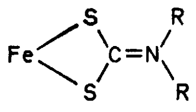
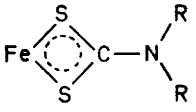


FIGURE 4 Influence of substituents on the crossover energies in the dithiocarbamate (*a*) (from ref. 7) and diselenocarbamate series (*b*)

White proposed that an increase in the C–N bond order, depending on almost sp^2 hybridization at N [structure (I)], corresponds to an increase in the RNR angle (resulting from steric interactions). If the N=C double-bond character induces an increase in electron density at sulphur, the ligand-field strength will increase resulting in a more pronounced low-spin effect. Unfortunately the structural results demonstrated that in the predominantly high-spin $[Fe\{S_2CN(CH_2)_4\}_3]$ the N–C bond (1.29 Å) is significantly shorter than in the predominantly low-spin $[Fe(S_2CNMePh)_3]$ (1.35 Å). On the other hand, Eley *et al.*,[24] attributing structure (II) to the iron compounds, in which the sulphur electron pair is delocalized over the metal chelate ring, explained the function of the R substituent in terms of an electron releasing effect. Moreover in structure (II) the Fe–S bonds are shorter than in (I), while the C–N bond is longer.



(I)



(II)

Our previous i.r. results[4,5] showed that in both the dithio- and diseleno-carbamate series, on passing from the free ligands to the compounds: (*i*) absorptions with predominant ν(CN) character move towards higher energies; (*ii*) the bond-order trend in the diselenocarbamates is Fe (square pyramidal) > square planar > tetrahedral > Fe (octahedral) > free ligand. Furthermore, comparing N–C bond cleavage in carbamate and dithio- and diseleno-carbamate, we have demonstrated[25–27] that the different kinetic behaviour can be rationalized by admitting that the NC bond order in E_2CNR_2 strongly increases as follows: $E = Se > S \gg O$. The same result was also previously postulated from spectroscopic evidence.[28,29] Therefore we believe that in the free diselenocarbamate ligands the NC linkage is almost double bond in character, while its order increases again in the pseudo-octahedral iron(III) compounds.

Applying this hypothesis to White's theory of the *N*-substituent effect, only the methylphenyl derivative does not fit this scheme. In fact, $[Fe(S_2CNMePh)_3]$ is predominantly low spin, while $[Fe(Se_2CNMePh)_3]$ is predominantly high spin; this behaviour fits in with the presence of the aromatic π system. The delocalization of the lone pair of nitrogen over the benzene ring could induce a decrease in NC bond order. Nevertheless it is not so clear why the dithiocarbamate derivative is predominantly low spin.

Unfortunately, *X*-ray results for the $[Fe(Se_2CNR_2)_3]$ series are not available for a comparison of the N–C and Fe–Se bond length with the corresponding values for the dithiocarbamate series. We believe that the N-substituent effect has simultaneously a steric and inductive character, and all the reported theories should contribute to the explanation of this problem.

EXPERIMENTAL

Preparation of Compounds.—The preparation of the ligands has been described earlier.[4] All the iron(III) compounds (1)—(8) were obtained by double-exchange reactions at room temperature in ethanolic solution between an excess of the diselenocarbamate inner salt and iron(III) chloride. The crude $[Fe(Se_2CNR_2)_3]$ products were recrystallized from dichloromethane–ethanol as dark brown prismatic crystals. Analytical data are in Table 1. From the mother liquid, golden-yellow diamagnetic crystals of compounds (9)—(11) were isolated {Found: C, 21.5; H, 3.5; N, 4.7. $Se(Se_2CNEt_2)_2$ (9) requires C, 21.3; H, 3.6; N, 5.0. Found:

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TABLE 5

Experimental values of the magnetic moments (B.M.)

	Compound							
$T \pm 2$K *	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
102	2.99		2.44	2.36	2.28	2.98	2.42	2.74
110	3.00		2.47	2.38	2.31	2.98	2.46	2.83
119	2.99		2.47	2.40	2.34	3.01	2.46	2.92
129	2.99		2.48	2.45	2.35	2.96	2.53	3.00
139	2.98		2.46	2.47	2.41	2.96	2.63	3.08
148	2.99		2.47	2.55	2.46	2.97	2.56	3.15
158	2.98		2.50	2.62	2.48	2.98	2.56	3.22
168	2.98		2.50	2.73	2.58	2.97	2.61	3.28
178	2.99		2.51	2.82	2.66	2.96	2.62	3.35
188	2.99		2.52	2.94	2.77	2.95	2.64	3.39
197	2.97		2.57	3.03	2.87	2.94	2.65	3.47
207	2.99		2.58	3.17	2.94	2.94	2.69	3.53
217	2.99		2.65	3.28	3.06	3.04	2.70	3.58
230	3.04		2.80	3.39	3.17	2.97	2.72	3.63
240	3.06		2.82	3.52	3.29	3.06	2.71	3.70
250	3.09		2.81	3.66	3.40	3.10	2.75	3.73
260	3.11		2.88	3.79	3.50	3.08	2.77	3.79
270	3.22		3.00	3.87	3.61	3.12	2.82	3.81
278	3.21		3.02	3.98	3.69	3.18	2.83	3.87
288	3.28		3.10	4.10	3.78	3.26	2.91	3.91
297	3.37	4.88	3.16	4.17	3.86	3.24	3.00	3.97
306	3.41	4.89	3.27	4.30	3.99	3.29	3.03	4.00
316	3.46	4.91	3.38	4.35	4.07	3.32	3.10	4.06
326	3.53	4.92	3.47	4.45	4.13	3.40	3.15	4.11
335	3.57	4.92	3.54	4.51	4.17	3.41	3.21	4.17
345	3.64	4.95	3.56	4.57	4.25	3.51	3.36	4.20
355	3.69	4.96	3.66	4.65	4.32	3.54	3.48	4.24
364	3.75	4.98	3.77	4.68	4.39	3.60	3.53	4.43

* In order to shorten the Table.

C, 44.1; H, 3.9. $Se[Se_2CN(CH_2Ph)_2]_2$ (10) requires C, 44.4; H, 3.5. Found: C, 34.5; H, 2.7; N, 4.8%; *M* (mass spectra) 556. $(Se_2CNMePh)_2$ (11) requires C, 34.8; H, 2.9; N, 5.1%; *M* 556}.

Spectrophotometric Measurements.—Electronic spectra were recorded with a Pye–Unicam SP 700C spectrophotometer in CH_2Cl_2 solution in the range 5 000—40 000 cm^{-1}. Infrared spectra were obtained in the range 200—4 000 cm^{-1} with a Perkin-Elmer 325 instrument as KBr discs or as Nujol mulls between CsI plates.

Magnetic Measurements.—These measurements (Table 5) were made by the Gouy method with a Newport instrument in a nitrogen atmosphere at 90—400 K (±0.25 K). All the measurements were carried out at three *H* values and in tubes free from ferromagnetic impurities. The results were corrected by use of Pascal's constants.

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