The anomalous EPR spectra of the iron(III) dichalcogenocarbamates

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Abstract

Recently, a new limiting resonance structure was proposed to more completely explain the bonding in the spin-crossover tris(diorganodichalcogenocarbamato)iron(III) complexes, $Fe(XYCNRR')_3$ (where XY = SS, SSe or SeSe; R and R' are organic substituents). This new limiting resonance structure involved a low-spin Fe(II) and an unpaired electron on the N of the radical ligand. This proposal was the result of the observation of structure in the narrow X-band EPR line at $g \approx 2$ and a computer fit of this structured line which supported an assignment of electron density to an $I = 1$ nucleus. The X-band EPR spectra (120 K) of 20 of these complexes have been re-examined, as pure powders and diluted in the corresponding Co(III) or In(III) complex matrix; 14 of these exhibit this structure in the region $g \approx 2$ which can be fit to an electron on an $I = 1$ nucleus. An alternative explanation of the structured line resulting from an impurity of $Fe(XYNCRR')_2NO$ is possible, but, if this is correct, the source of the NO is not ligand decomposition, since the X-band EPR spectrum (120 K) of $Fe(S_2CNEt_2)_3$ prepared using ^{15}N ($I = 1/2$) is identical to the natural abundance complex. The EPR signal is believed to be of a common impurity in each of the $Fe(XYCNRR')_3$ complexes.

Key words: EPR spectroscopy; Iron complexes; Chalcogeno complexes; Carbamate complexes

Introduction

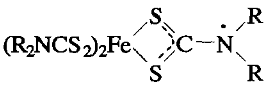
Iron(III) dithiocarbamate complexes, $Fe(dtc)_3$, were studied in 1931 by Cambi and co-workers [1, 2]. The magnetic moments of these complexes were intermediate between the magnetic moments for the two possible electronic configurations for a $3d^5$ iron(III) ($t_{2g}{}^3e_g{}^2$ and $t_{2g}{}^5$) and Cambi's proposal that these complexes were in a spin equilibrium between the high- and low-spin electronic configurations, an equilibrium which depends on the nature of the organic substituents, has been accepted for more than 60 years.

During this time there have been many studies of these and analogous spin-crossover systems [3–6]. Until recently, no one had questioned Cambi's basic postulation of a spin equilibrium between two different electronic configurations of Fe(III).

In 1990, Kirmse *et al.* observed [7], in addition to the iron $S = 5/2$ and $S = 1/2$ spin crossover signals, a three-line EPR spectrum in the region of $g = 2$ for both $Fe/In(S_2CN(C_2H_5)_2)_3$ and $Fe/In(SSeCN(C_2H_5)_2)_3$ single crystals (Fe:In ratio 1:99) between room temperature and 1.5 K. The location and line-splitting (≈ 15 G) of the spectrum is similar to that observed for nitroxide spin probes where the hyperfine and g tensors are completely averaged [8]. The three lines come from hyperfine interaction with the nitrogen nucleus ($I = 1$).

In 1991, Gelerinter *et al.* examined the powder EPR spectra for four different iron(III) dichalcogenocarbamates and reported [9] EPR evidence for a new limiting resonance structure **A**, involving an Fe(II) bonded to a radical ligand, with significant electron density of the unpaired electron on the ligand nitrogen.

A second possibility must also be considered, one related to the proposal of Hall and Hendrickson [10]


A

Proposed additional high-field limiting resonance structure for iron(III) dithiocarbamates [9].

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that the narrow line at $g=2$ results from an impurity. Earlier results showed conclusively that the peak is not due to a copper impurity [11], but the possibility of a nitrogen containing impurity, namely NO, must be considered.

This paper reports additional studies to determine evidence supporting the importance of limiting resonance structure A and examines new evidence that strongly supports the assignment of the narrow peak at $g=2$ being the result of an NO impurity from an undetermined source.

Experimental

The tris diorganodithio-, thioseleno- and diselenocarbamates of iron(III), cobalt(III) and indium(III) have been reported previously [12, 13].

^{15}N labelled $Fe(S_2CN(C_2H_5)_2)_3$

0.50 g of $(C_2H_5)_2{}^{15}NH \cdot HCl$ (Isotec, Inc., Miamisburg, OH) was dissolved in 7.5 ml of absolute ethanol. To this was added 0.73 g of freshly prepared 50% (by weight) NaOH(aq). The cloudy solution was cooled in an ice bath and 0.28 ml of CS_2 was added slowly with stirring. To this mixture was added 0.25 g of $FeCl_3$ dissolved in a minimum amount of absolute ethanol. The mixture was stirred in an ice bath for 10 min, filtered cold and rinsed with two cold 5 ml portions of absolute ethanol. After drying in air, the black solid was dissolved in a minimum amount of $CHCl_3$, filtered, reduced to ~5 ml volume under vacuum, cooled in an ice bath and 5 ml of absolute ethanol added. The resulting black solid was filtered and rinsed with two cold 5 ml portions of absolute ethanol and dried, yielding 0.49 g of product. An elemental analysis (C, 33.57; H, 5.65; N, 8.14) and Mössbauer spectrum indicated a substantial impurity of $Fe(S_2CN(C_2H_5)_2)_2Cl$.

The product was slurried in 20 ml of cold benzene and filtered through a coarse sintered glass filter. The filtrate was evaporated to dryness, yielding a black solid. The Mössbauer spectrum revealed little or no impurity of $Fe(S_2CN(C_2H_5)_2)_2Cl$. *Anal.* Calc. for $C_{15}H_{30}Fe^{15}N_3S_6$: C, 35.77; H, 6.00; N, 8.94. Found: C, 35.14; H, 6.41; N, 8.37%.

A similar unenriched sample was prepared for comparison by mixing 0.25 g of $Fe(S_2CN(C_2H_5)_2)_2Cl$ and 0.25 g of $Fe(S_2CN(C_2H_5)_2)_3$ and eluting from a cold benzene slurry as described above, yielding a black solid. Again, the Mössbauer spectrum of the product revealed little or no impurity of $Fe(S_2CN(C_2H_5)_2)_2Cl$. *Anal.* Calc. for $C_{15}H_{30}FeN_3S_6$: C, 35.98; H, 6.04; N, 8.40. Found: C, 35.91; H, 6.18; N, 8.20%.

$Fe(Se_2CN(C_2H_5)_2NO$

This compound was prepared by a method similar to that reported by Ileperuma and Feltham [14] for the corresponding dithiocarbamate. The reaction was carried out in an Ar atmosphere in 1/8 the mole amounts described in the corresponding dithiocarbamate preparation, but in 30–50 ml of degassed distilled water. On addition of an aqueous solution of freshly prepared diselenocarbamate ligand, a brown solid was formed. After filtration, rinsing with distilled water and methanol and drying over $CaCl_2$, the solid was found to be soluble in chloroform and somewhat less soluble in acetone and benzene. The brown solid was recrystallized from chloroform–methanol, yielding a black solid. *Anal.* Calc. for $C_{10}H_{20}FeN_3OSe_4$: C, 21.07; H, 3.54; N, 7.37. Found: C, 21.38; H, 3.39; N, 7.13%.

EPR spectra

The materials used were sealed in quartz tubes under 0.5 atm of nitrogen and the corresponding paramagnetic spectrum (EPR) was observed using an IBM 200D-SRC X-band spectrometer interfaced to an IBM CS 9000 computer. The magnetic field was measured by the spectrometer's Hall probe which was previously calibrated near $g=2$ using an NMR gaussmeter. The frequency was measured using a Hewlett Packard 5351A microwave frequency counter. These data were combined to calculate g_{iso}, the value at the center of the spectrum near $g=2$. The temperature was controlled using an IBM ER 4111 VT temperature controller that had a precision of 1 K. The sample temperature was monitored using a thermocouple placed near the sample.

Theoretical spectra were calculated using the literature method of Siderer and Luz [15] using an IBM mainframe computer, and results were compared to the experimental data that had previously been read into the mainframe. While simulating, the value of g_{iso} was held to that measured as described above. For this application, the calculation of Siderer and Luz is superior to that of Moro and Freed [16], which we had previously used [9], since this former method assumes a powder sample. Thus the parameters reported here are more accurate than those we have previously reported [9]. It is also interesting to note that the powder results reported here (see Table 1) for $Fe/In(Et_2dtc)_3$ are in good agreement with the results obtained from the single crystal (2.0351, 2.0430, 2.0396; 11.6 G, 12.0 G, 14.8 G for the x, y, z values of the g and hyperfine tensors, respectively [7]).

Elemental analyses

Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN, or the analytical services of the University of Leipzig, Leipzig, Germany.

Results and discussion

Re-examination of earlier spectra

In our earlier paper [9], we examined the powder EPR spectra for four different iron(III) dichalcogenocarbamates and reported structure of the narrow peak in the region of $g=2$ and fit this data using the model of an unpaired electron on an $I=1$ nucleus (e.g. ^{14}N). We have now extended the fitting of all of our current EPR results to this model, making minor corrections to our results reported previously [9].

In Figs. 1 and 2, we show representative experimental spectra along with the corresponding theoretical spectra. In all cases the experimental spectra were taken at approximately 120 K with a 200 gauss sweep width centered at approximately 3330 gauss. The calculations illustrated assume a spin 1/2 electron interacting with a nucleus of spin 1, i.e. the nitrogen nucleus. The calculated spectral parameters for those compounds that we were able to simulate using this model appear in Table 1. The following conventions are adopted in labelling the *x*, *y* and *z* directions. If the hyperfine tensor is axial, then the symmetry axis is taken as the *z* axis. Otherwise the direction corresponding to the maximum component of the hyperfine tensor is chosen to be the *z* axis. One should note that we tried to simulate many of these spectra assuming no hyperfine interaction, but the agreement between the calculated and observed spectra was extremely poor. The *g* values increase as Se replaces S as previously reported [11, 12].

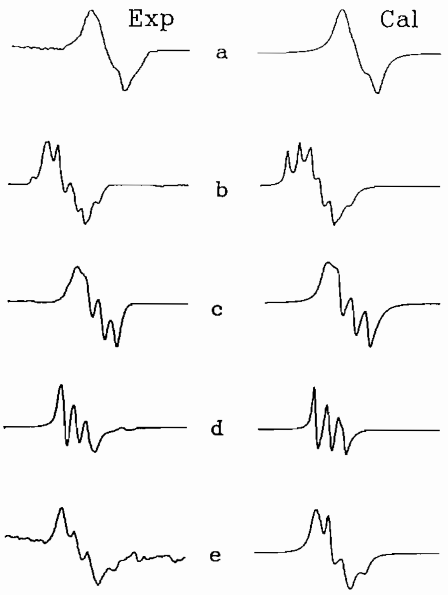

Fig. 1. Experimental and calculated [15] X-band EPR spectra (120 K) of $Fe(XYCN(C_2H_5)_2)_3$ powder samples diluted in the corresponding $M(XYCN(C_2H_5)_2)_3$ matrix. (a) M = Co, XY = SSe; (b) M = In, XY = SSe; (c) M = In, XY = SeSe; (d) M = In, XY = SS; (e) undiluted, XY = SS.

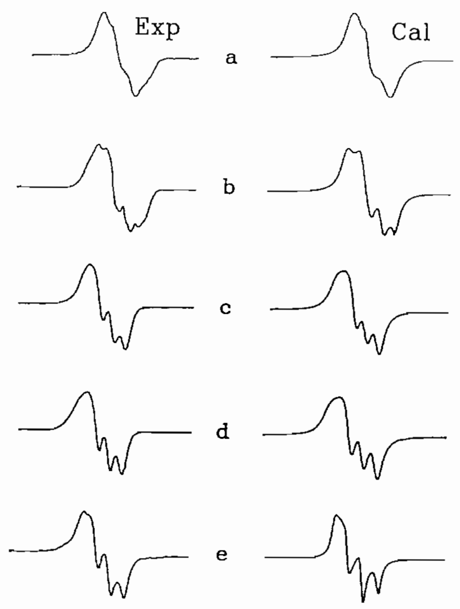

Fig. 2. Experimental and calculated [15] X-band EPR spectra (120 K) of $Fe(XYCN(CH_2)_4O)_3$ powder samples diluted in the corresponding $M(XYCN(CH_2)_4O)_3$ matrix. (a) M = Co, XY = SSe; (b) M = In, XY = SSe; (c) M = Co, XY = SeSe; (d) M = In, XY = SeSe; (e) undiluted, XY = SeSe.

There are nine cases for which we are not able to observe spectra near $g=2$ (pure powder: Bz_2dtc, Bz_2dsc, i-pr_2dtc, Me_2dtc, mordtc, piptsc and pyrdtc; indium complex matrix: Bz_2tsc and Bz_2dsc, where tsc = thioselenocarbamate and dsc = diselenocarbamate) and at least one instance (pure powder: $cHex_2dtc$) for which the spectra requires an assumption of no hyperfine interaction for good agreement between the calculated and observed results.

Possible impurities

The EPR spectra of several powdered complexes, freshly prepared by a variety of different methods, were determined at room temperature and 120 K to examine the possibility of the peak resulting from an impurity.

The possibility of a Cu impurity has been dealt with in an earlier publication [11].

The EPR spectra of pure, powdered $Co(Se_2CNEt_2)_3$ and $In(Se_2CNEt_2)_3$ showed no measurable signal in the region of $g=2$ at either 297 or 120 K.

In 1978, Sarte *et al.* reported [19] the room temperature EPR spectra of a variety of $Fe(S_2CNRR')_2NO$ complexes in $CHCl_3$ solution (R, R' = C_2H_5: g_{iso}, 2.040; A_{iso}, 12.8 G). In 1984, Yordanov *et al.* reported [17] the EPR of the diethyl derivative in a toluene matrix at 125 K (g_x, 2.045; g_y, 2.041; g_z, 2.025; A_x, 13.2 G; A_y, 12.9 G; A_z, 15.6 G). In 1984, Jezierski and Jezowska-Trzebiatowska reported [18] similar values in toluene

TABLE 1. Fitted [15] EPR parameters for structure at $g=2$ for powder samples of $Fe(XYCNR_2)_3$ (where XY = SS, SSe, SeSe)

R_2	XY	Matrix[a]	g_{xx}	g_{yy}	g_{zz}	g_{iso}	A_{xx} (G)	A_{yy} (G)	A_{zz} (G)
Bz_2	S, Se	none	2.0355	2.0442	2.0478	2.0425	12.2	12.5	10.0
Bz_2	S, Se	Co	2.0552	2.0310	2.0397	2.0431	3.7	9.0	7.0
Bz_2	Se, Se	Co	2.0575	2.0415	2.0440	2.0499	13.0	10.5	13.5
$cHex_2$	S, Se	Co	2.0465	2.0330	2.0455	2.0417	7.0	13.5	17.0
Et_2	S, S	none	2.0397	2.0395	2.0258	2.0351	7.3	15.5	14.2
Et_2	S, S	In	2.0350	2.0425	2.0400	2.0401	12.0	14.9	11.7
Et_2	S, Se	Co	2.0485	2.0415	2.0485	2.0462	5.0	13.0	16.5
Et_2	S, Se	In	2.0497	2.0372	2.0635	2.0475	12.0	11.0	11.5
Et_2	Se, Se	In	2.0660	2.0420	2.0495	2.0525	3.5	10.5	14.5
$i\text{-}pr_2$	S, Se	Co	2.0490	2.0348	2.0490	2.0443	14.0	14.5	8.3
$i\text{-}pr_2$	S, Se	In	2.0415	2.0485	2.0360	2.0420	11.0	12.5	14.5
$i\text{-}pr_2$	Se, Se	Co	2.0635	2.0448	2.0480	2.0521	4.3	7.5	13.5
$i\text{-}pr_2$	Se, Se	In	2.0615	2.0450	2.0495	2.0520	10.5	11.5	14.0
mor	S, Se	Co	2.0485	2.0390	2.0475	2.0450	5.0	12.3	17.5
mor	S, Se	In	2.0510	2.0360	2.0485	2.0452	2.5	12.0	17.5
mor	Se, Se	none	2.0645	2.0489	2.0490	2.0541	3.0	5.5	15.5
mor	Se, Se	Co	2.0410	2.0390	2.0570	2.0523	11.5	11.5	5.0
mor	Se, Se	In	2.0420	2.0440	2.0620	2.0493	12.5	13.5	5.5
pip	S, Se	Co	2.0500	2.0405	2.0490	2.0465	6.0	11.5	17.5
pip	S, Se	In	2.0510	2.0405	2.0460	2.0458	6.0	8.0	14.5
pip	Se, Se	Co	2.0485	2.0424	2.0555	2.0485	11.5	12.0	12.5
pip	Se, Se	In	2.0450	2.0450	2.0620	2.0507	12.0	13.5	8.0
pyr	S, Se	Co	2.0470	2.0405	2.0470	2.0448	5.0	11.2	17.5
pyr	S, Se	In	2.0435	2.0340	2.0535	2.0441	13.0	14.5	9.6
pyr	Se, Se	In	2.0370	2.0165	2.0125	2.0275	12.7	13.0	13.0

[a] Pure powders or as 1% solid solutions in the corresponding Co(III) or In(III) complex matrix.

at 130 K. These values are quite close to the values reported in Table 1.

This observation led to the following series of experiments. The EPR powder spectrum of $Fe(Se_2CN(CH_2CH_3)_2)_2NO$ was determined at 120 K. The spectrum shows a broad signal in the region of $g=2$, but dipolar broadening smears out the signal considerably. The nitrosyl complex was diluted in a solid matrix of $In(Se_2CN(CH_2CH_3)_2)_3$ (1:100). The EPR spectra of this powder at 300 and 120 K are shown in Figs. 3(a) and 4(a), respectively. In these same Figures are the EPR spectra of $Fe(Se_2CN(CH_2CH_3)_2)_3$ diluted in a solid matrix of $In(Se_2CN(CH_2CH_3)_2)_3$ (2.5:100) (Figs. 3(b) and 4(b)). For comparison, these Figures also show identical samples as Figs. 3(b) and 4(b), but with NO(g) bubbled through the solution before crystallization (Figs. 3(c) and 4(c)). It is significant to note that the amplification of Figs. 3(b) and 4(b) is 16 times that of Figs. 3(c) and 4(c). The EPR for $Fe(Se_2CN(CH_2CH_3)_2)_3$ dissolved in $In(Se_2CN(CH_2CH_3)_2)_3$ is the same (Fig. 4(b) and (d)) whether the starting material is $Fe(NO_3)_3 \cdot 9H_2O$ or $Fe(NH_4)(SO_4)_2 \cdot 12H_2O$. These results are consistent with the structured narrow line at $g=2$ being the result of an impurity of $Fe(Se_2CN(CH_2CH_3)_2)_2NO$ from an unknown source. The presence of this signal in the complex prepared from $Fe(NH_4)(SO_4)_2 \cdot 12H_2O$ rules out NO_3^- as the source. While the results presented here are for diselenocarbamates, the situation appears generalized to the dithio- and thioselenocarbamates (Table 1).

Decomposition of the dithiocarbamate ligand has been reported previously, but as organodithiocarbamates to thiocyanates [20]. The tris(di-*sec*-butyldithiocarbamato)iron(III) complex also appears to decompose to the thiocyanato derivative [21], but there are no reports of the decomposition of the ligand to form NO.

To determine if the source of the supposed NO impurity was from the ligand, a sample of $Fe(S_2C^{15}N(CH_2CH_3)_2)_3$ was prepared from $FeCl_3$ in a preparative method which avoided any use of a nitrogen containing reagent. This preparative method necessitated the separation of an $Fe(S_2C^{15}N(CH_2CH_3)_2)_2Cl$ impurity. The EPR of the ^{15}N complex is shown in Fig. 5 compared to the natural abundance sample

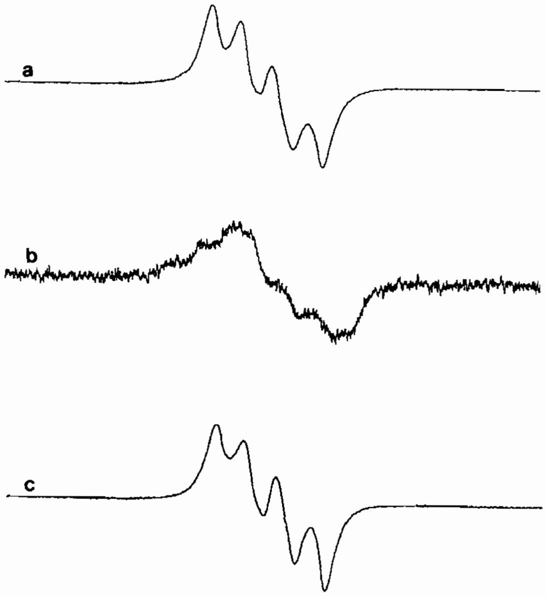

Fig. 3. X-band EPR spectra (300 K) in the region $g \approx 2$ (sweep width = 200 G). (a) 1% $Fe(Se_2CNEt_2)_2NO$ in a solid matrix of $In(Se_2CNEt_2)_3$; (b) 2.5% $Fe(Se_2CNEt_2)_3$ prepared from $Fe(NH_4)(SO_4)_2 \cdot 12H_2O$ in a solid matrix of $In(Se_2CNEt_2)_3$; (c) as (b), but with NO(g) bubbled through the solution before crystallization Relative amplification: (a), (b), (c): 1, 16, 1.

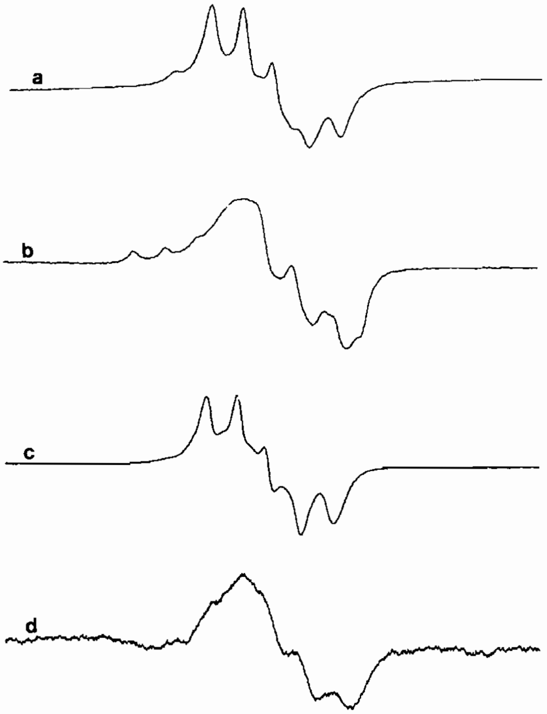

Fig. 4 (a), (b) and (c) as Fig. 3, but at 120 K; (d) as (b) but prepared from $Fe(NO_3)_3 \cdot 9H_2O$. Relative amplification: (a), (b), (c), (d): 1, 16, 1, 63.

prepared in a similar manner. If the source of the structured narrow line at $g = 2$ was an electron on a ligand nitrogen or a nitrogen derived from the ligand, the signal should be markedly different for ^{15}N ($I = 1/2$) compared to ^{14}N ($I = 1$). But the signals are quite similar. This was a most unexpected result.

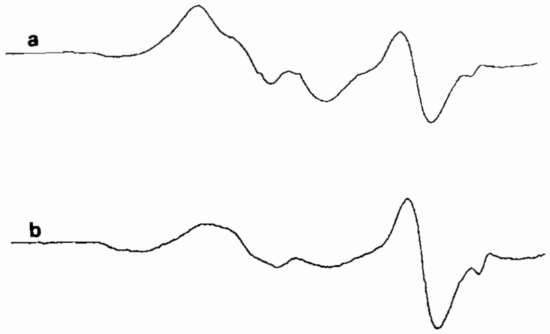

Fig. 5. X-band EPR spectra (120 K) in the region $g \approx 2$ (sweep width = 150 G): (a) $Fe(S_2CNEt_2)_3$; (b) $Fe(S_2C^{15}NEt_2)_3$.

Models

Many related materials have been studied and the spectra from a large portion of these materials have been successfully matched to spectra calculated using the assumption of electron density on a nitrogen nucleus. In addition we find good agreement between single crystal data and the data reported here.

Two models are presented here: Model I supporting the earlier postulation of an unpaired electron on the nitrogen atom of a dichalcogenocarbamate ligand, which implies a new limiting resonance structure in the explanation of the bonding of the complex and Model II which involves the presence of a small amount of NO impurity from an as yet unidentified source.

Model I: an unpaired electron on the N atom of the ligand

The proposal of a free radical ligand in Fe dithiocarbamates is not unprecedented. In 1975, Gregson and Doddrell reported [22] the ^1H and ^{13}C NMR spectra of nine diamagnetic Co(III) and paramagnetic Fe(III) dithiocarbamate complexes in $CDCl_3$. The spin-crossover Fe(III) complexes exhibited much larger chemical shifts than the corresponding Co(III) complexes. They suggested that "for the high-spin complexes where the isotropic shift of C_α is large and negative, unpaired spin delocalization affecting the ^{13}C isotropic shifts occurs mainly by the ligand sigma-framework (direct delocalization of the e_g electrons)". This essentially proposes delocalization of unpaired electron density through the ligand which could result in unpaired electron density on the amine nitrogen. Note, however, that the postulation involves the delocalization of e_g electrons from the *high-spin* electronic configuration.

In 1975, Golding and Lehtonen compared [23] the ^1H NMR of a series of iron(III) dithiocarbamates and their redox behavior. These authors agree that the limiting resonance structure with the sp^3 N is the strong field resonance structure [13] and report a correlation between the hyperfine interaction constant for iron(III) and the half-wave potentials $E_{1/2}$ for the reversible one-electron reduction step for these complexes. They argue that this is expected, since, as the extent of 3d electron delocalization increases, the positive charge on the nitrogen will decrease, making the complex more difficult to reduce. In their discussion, they state, "(t)hus an *unpaired electron in a nitrogen p orbital* (our emphasis) can bring about electron spin density at an adjacent aliphatic group due to delocalization of the unpaired electron by overlap of the hydrogen 1s and the p orbital of the nitrogen". Again, without elaborating further, they have hinted at the importance of our proposed limiting resonance structure **A**.

Model II: an impurity of Fe(S$_2$CNR$_2$)$_2$NO

The sequence of experiments described above presents a very strong case for the signal resulting from an NO complex impurity. Table 2 presents a comparison of the $g = \sim 2$ line observed for the Fe(Et$_2$dtc)$_3$ complexes and the corresponding NO complexes. The results are strikingly similar. Our earlier interpretations of this signal increasing in intensity while the intensity of the broader signals assigned to the high-spin electronic configuration are proportionally less intense are consistent with these results. As the $S = 5/2 \leftrightarrow S = 1/2$ equilibrium moves towards the low-spin case, the intensity of the 5/2 line dies away. The population corresponding to the $g \approx 2$ line may remain constant, but its intensity must still follow the Curie law and grow inversely with the temperature.

Our initial postulation was to blame the use of Fe(NO$_3$)$_3$ in some of our preparations, but, comparing Fig. 4(b) (d), the complex prepared from Fe(NH$_4$)(SO$_4$)$_2$·12H$_2$O exhibits a signal of approximately 4 × the amplitude as that of the complex prepared from Fe(NO$_3$)$_3$. It is also shown, using the ^{15}N labelled complex, that even if the complex is prepared from a non-nitrogen containing starting material, the signal is still observed. Three possibilities have been considered: (i) contamination of products from sintered glass filters cleaned with aqua regia, (ii) contamination of products from NO in the laboratory atmosphere, (iii) ligand decomposition during the preparation of the complexes. The first two possibilities seem highly unlikely since the complexes were prepared by three different re-

TABLE 2 EPR parameters in $g = 2$ region for Fe(S$_2$CNEt$_2$)$_2$NO and Fe(S$_2$CNEt$_2$)$_3$

Compound	g_{iso}	g_{xx}	g_{yy}	g_{zz}	A_{iso} (G)	A_{xx} (G)	A_{yy} (G)	A_{zz} (G)	Reference
Fe(S$_2$CNEt$_2$)$_3$ powder, 298 K	2.035	2.040	2 040	2.026		7.3	15.5	14.2	this work
Fe(S$_2$CNEt$_2$)$_3$ in In(dtc)$_3$ powder, 298 K	2.040	2.043	2 040	2.035		12.0	14.9	11.7	this work
Fe(S$_2$CNEt$_2$)$_3$ single crystal, 4.2 K	2.039	2 043	2 040	2.035		13.9	11.2	10.9	this work
Fe(S$_2$CNEt$_2$)$_3$ in toluene		no spectrum, 4.2–350 K							24
Fe(S$_2$CNEt$_2$)$_3$ powder, ~85 K	~2.0[a]								10
Fe(S$_2$CNEt$_2$)$_3$ in Co(dtc)$_3$, 298 K	2.044								11
Fe(S$_2$CNEt$_2$)$_3$ in toluene or CHCl$_3$		no spectrum, 77–300 K							17
Fe(S$_2$CNEt$_2$)$_2$NO reaction of Fe(dtc)$_3$ and NO$_2$	2.040	2.045	2.041	2.025	12.9	13.2	12.9	15.6	17
Fe(S$_2$CNEt$_2$)$_2$NO toluene, 130 K		2.045	2.041	2.025					18
toluene, 300 K	2.037				13.8				18
Fe(S$_2$CNEt$_2$)$_2$NO CHCl$_3$, 300 K	2.040				12.8				19

[a] Suspected to be the result of a copper impurity; see also ref. 11.

searchers in two different laboratories, and the results of the parallel studies are identical. In the absence of other explanations, a decomposition of the ligand is favored.

Conclusions

The following points can be drawn.

(i) For most $Fe(dtc)_3$, $Fe(tsc)_3$ and $Fe(dsc)_3$ complexes, the narrow line at $g=2$ in the EPR spectrum exhibits considerable structure. This structure is only slightly dependent on whether the sample is a pure powder or a solid solution in the corresponding diamagnetic Co(III) or In(III) matrix;

(ii) For most of these compounds, the structured narrow line at $g=2$ may be simulated as a system involving some unpaired electron density residing on an $N(I=1)$ nucleus;

(iii) Although the simulation is consistent with a limiting resonance structure involving a low-spin Fe(II) and a free radical ligand, the EPR spectra are disturbingly similar to the EPR spectra of the corresponding nitrosyl complex;

(iv) The substitution of ^{15}N for ^{14}N in the ligand does not change the EPR spectrum.

This final result is incompatible with the low-spin Fe(II), nitrogen free-radical limiting resonance structure **A**. There must either be some other explanation for this fine structure or it is a nitrosyl impurity with the NO derived from some other source than the ligand. No evidence was found to support any modification in Cambi's proposal [1, 2] involving a spin equilibrium between high- and low-spin electronic configurations of Fe(III).

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