# Low-temperature Magnetochemical and Spectroscopic Studies of Variable-spin Tris(monothiocarbamato)iron(III) and Tris(diselenocarbamato)iron(III) Complexes †

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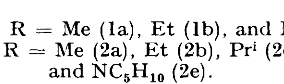
Two tris(dialkylmonothiocarbamato)iron(III) complexes, $[Fe(OSCNR_2)_3]$, with $FeS_3O_3$ cores and R = Me and Et, have been investigated in the solid state by low-temperature (4.2—80 K) magnetic susceptibility and $^{57}Fe$ Mössbauer spectroscopy measurements and in solid solution by e.s.r. spectroscopy. The magnetic and Mössbauer studies confirm our earlier report that the complexes $[Fe(OSCNMe_2)_3]$ and $[Fe(OSCNEt_2)_3]$ are new $^2T(S = \frac{1}{2}$, low-spin) $\rightleftharpoons$ $^6A(S = \frac{5}{2}$, high-spin) spin-equilibrium species, although $[Fe(OSCNMe_2)_3]$ can also be obtained in a crystalline modification that remains totally high-spin down to *ca.* 10 K. The complex $[Fe(OSCNMe_2)_3]$, with the $^2T$ and $^6A$ states nearly equally populated, gives a Mössbauer spectrum at 4.2 K that appears as an ' average ' of the two spin states, suggesting that the rates of $^2T \rightleftharpoons {}^6A$ spin interconversion are $\gtrsim 10^7\ s^{-1}$. The e.s.r. spectra at 12 K of the two compounds in solvent glasses display only one signal at *g ca.* 4.3 which probably arises from rhombically distorted high-spin iron(III). Finally, solid-solution state e.s.r. spectra for four known $^2T \rightleftharpoons {}^6A$ tris(disubstituted diselenocarbamato)iron(III) complexes, $[Fe(Se_2CNR_2)_3]$, with $FeSe_6$ cores are also reported; the spectra are complex with *g* values of approximately 2.0, 3.0, and 4.3. The four $FeSe_6$ centres are essentially Mössbauer silent, probably due to a selenium edge absorption at 12.6 keV or to effective $\gamma$-ray scattering by the selenium donor atoms.

ALTHOUGH Cambi [1] first introduced the concept of a $^2T$(low-spin, $S = \frac{1}{2}$) $\rightleftharpoons$ $^6A$(high-spin, $S = \frac{5}{2}$) spin-equilibrium process in iron(III) complexes nearly fifty years ago, much of the subsequent research reported in the literature involving the phenomenon still centres around the initially reported set of compounds in that study, the tris(dithiocarbamato)iron(III) species $[Fe(S_2CNR_2)_3]$, (1). A wide variety of experimental techniques such as variable-temperature magnetochemistry [2] and i.r.,[3] Mössbauer,[4] and e.s.r. spectroscopy [2] and *X*-ray crystallography [5] have been employed to more fully understand both the solid- and solution-state electronic processes that operate in this variable-spin system. In addition, such investigations have also included other $^2T \rightleftharpoons {}^6A$ iron(III) chelates (usually with non-$FeS_6$ cores) such as the salicylideneiminate complexes ($FeN_4O_2$ cores),[6-9] the tris(dithio-β-diketonato)iron(III) complexes ($FeS_6$ cores),[10] the tris(monothio-β-diketonato)iron(III) compounds ($FeS_3O_3$ cores); [11,12] and structural relatives of $[Fe(S_2CNR_2)_3]$, the tris(monothiocarbamato)iron(III) complexes $[Fe(OSCNR_2)_3]$, (2) ($FeS_3O_3$ cores),[13-15,‡] and the tris(diselenocarbamato)iron(III) species $[Fe(Se_2CNR_2)_3]$, (3) ($FeSe_6$ cores).[16]



X = Y = S; R = Me (1a), Et (1b), and $NC_4H_8$ (1c).
X = O, Y = S; R = Me (2a), Et (2b), $Pr^i$ (2c), $NC_4H_8$ (2d), and $NC_5H_{10}$ (2e).
X = Y = Se; R = $NC_5H_{10}$ (3a), $CH_2Ph$ (3c), and thiomorpholinyl (3d); R,R = Me, Ph (3b).

The electronic structures of the $^2T \rightleftharpoons {}^6A$ spin-equilibrium process in several $[Fe(OSCNR_2)_3]$ and $[Fe(Se_2CNR_2)_3]$ complexes have been previously investigated by variable-temperature magnetochemistry and Mössbauer spectroscopy,[13,14,16] but only down to liquid nitrogen temperatures. In this work, we wish to communicate extended lower temperature magnetic and Mössbauer data for two of the $[Fe(OSCNR_2)_3]$ complexes,[13] as well as the first report of the low-temperature e.s.r. spectral properties for both of the variable-spin $[Fe(OSCNR_2)_3]$ and $[Fe(Se_2CNR_2)_3]$ species. Since these compounds are close structural relatives of the much studied $[Fe(S_2CNR_2)_3]$ complexes, the magnetic and spectroscopic information in this work was sought as an opportunity to compare the $^2T \rightleftharpoons {}^6A$ electronic behaviour of these structurally similar (tris-bidentate ligands; four-membered chelate rings) yet donor-atom diverse ($FeS_6$, $FeS_3O_3$, or $FeSe_6$ cores), variable-spin species.§

## EXPERIMENTAL

The $[Fe(OSCNR_2)_3]$ compounds were prepared by previously reported methods [13] and checked for purity by C, H, and N, analyses performed by Chemalytics, Tempe, Arizona; the analyses were as satisfactory as those reported

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† Abstracted in part from the Ph.D dissertation of K. R. Kunze, William Marsh Rice University, 1978.

‡ An electrochemical study in solution of the $[Fe(OSCNR_2)_3]$ complexes has appeared: D. L. Perry and S. R. Cooper, *J. Inorg. Nucl. Chem.*, 1980, **42**, 1356.

§ While the monothiocarbamate anion is quite similar to its dithiocarbamate analogue, it exhibits a quite different chemistry for a number of reaction systems. It stabilises uranyl alkoxides by forming mixed uranyl thiocarbamate alkoxides (D. L. Perry, D. H. Templeton, and A. Zalkin, *Inorg. Chem.*, 1978, **17**, 3699; 1979, **18**, 879). These thiocarbamate alkoxides in turn serve as precursors to the uranyl thiocarbamate disulphides (D. L. Perry, A. Zalkin, and D. H. Templeton, 176th National Meeting of the American Chemical Society, Paper INOR 126, Miami, 1978; the first documented actinide chelate-disulphides).

earlier.* The $[Fe(Se_2CNR_2)_3]$ compounds used were the same samples as those reported in ref. 16.

Magnetic susceptibility measurements, using the Faraday technique, were made with a Cahn model 6600-2 research magnetic susceptometer using $Hg[Co(NCS)_4]$ as calibrant. The cryogenic system consisted of an Air Products Faraday Interface model DMX-19 Vacuum Shroud, an LT-3-110B Heli-tran system, and a model APD-TL digital temperature readout system monitoring an iron-doped gold *vs.* chromel thermocouple (20—300 K) or carbon resistor (7—20 K).

E.s.r. spectra were obtained using a Varian model E-6 paramagnetic resonance spectrometer with an Air Products liquid helium accessory. The spectra were taken on samples that had been dissolved in either a 2 : 1 : 1 solution of $Et_2O$–toluene–EtOH or chloroform (as indicated) and immediately frozen as glassy matrices in liquid nitrogen in order to avoid solution decomposition; the samples were then introduced into the spectrometer cavity and spectra recorded at 12 K.

Mössbauer spectra at 4.5 K were obtained as previously described[17] using an Austin Science Associates Mössbauer spectrometer operating in the constant-acceleration mode. The spectrometer was calibrated using laser interferometry (employing an Austin Science Associates laser system), and isomer shifts were referenced to sodium nitroprusside. The 4.5 K spectra were collected using polycrystalline samples with both the absorber and source at 4.5 K; the higher temperature data reported previously [13] were obtained with only the absorber cooled and were not corrected for second-order Doppler shifts.

## RESULTS AND DISCUSSION

*Magnetic Susceptibility Data.*—As noted in our previous report which detailed variable-temperature magnetochemical data in the 77—300 K range for several $[Fe(OSCNR_2)_3]$ complexes [R = Me (2a), Et (2b), $Pr^i$ (2c), pyrrolidinyl (2d), or piperidyl (2e)],[13] room-temperature magnetic moments for all the derivatives are >5.7 B.M.† and consistent with a high-spin $S = \frac{5}{2}$ ground state. Furthermore, the report established that only (2a) and (2b) exhibited non-Curie behaviour typical of a $^2T(S = \frac{1}{2}) \rightleftharpoons {}^6A(S = \frac{5}{2})$ spin-equilibrium process. For this reason, these two derivatives have been singled out here for extended temperature studies. Table 1 gives the new 7—80 K magnetic data for (2a), and (2b) (preparations I and II). Unlike our earlier report where (2b) was obtained as a dihydrate, $[Fe(OSCNEt_2)_3]\cdot 2H_2O$, the present compound analysed pure as being anhydrous,* although the two different preparations exhibit similar magnetic properties with the present anhydrous preparation [$\mu_{eff.}$ (76 K) = 3.72, $\mu_{eff.}$ (294 K) = 5.48 B.M.] and the earlier dihydrate [$\mu_{eff.}$ (78 K) = 3.61, $\mu_{eff.}$ (299 K) = 5.73 B.M.] possessing similar magnetic moments for a given temperature. As seen from Table 1, the new low magnetic moments for (2b) are further supportive of an $(S = \frac{1}{2}) \rightleftharpoons (S = \frac{5}{2})$ spin equilibrium for this derivative, in which the $S = \frac{1}{2}$ state becomes increasingly populated with decreasing temperature. However, one problem exists. At the very lowest temperatures, the magnetic moment actually drops below the spin-only value (1.73 B.M.) for a fully populated $S = \frac{1}{2}$ state, *i.e.*, $\mu_{eff.}$ (8.6 K) = 1.22 B.M. While unusual, this behaviour is not without precedent, and, in fact, it has also been observed for some $[Fe(S_2CNR_2)_3]$ and $[Ru(S_2CNR_2)_3]$ complexes [2,18] where it has been attributed to weak *inter*molecular antiferromagnetic exchange interactions. This being the case, it does not seem unreasonable to also postulate a weak *inter*molecular exchange interaction for (2b) in view of the structural similarities between the $S_2CNR_2$ and $OSCNR_2$ ligands and their tris complexes.

TABLE 1

Low-temperature (7—80 K) magnetic data for the $[Fe(OSCNR_2)_3]$ complexes

| Compound | $T$/K | $\mu_{eff.}$/B.M. |
|---|---|---|
| (2b) $[Fe(OSCNEt_2)_3]$ | 294.0 | 5.48 |
| | 75.7 | 3.72 |
| | 52.1 | 3.21 |
| | 41.5 | 2.78 |
| | 30.4 | 2.20 |
| | 20.8 | 1.71 |
| | 12.5 | 1.38 |
| | 8.6 | 1.22 |
| (2a) $[Fe(OSCNMe_2)_3]$ (preparation I) | 295.0 | 5.81 |
| | 71.0 | 5.52 |
| | 60.2 | 5.49 |
| | 49.1 | 5.46 |
| | 32.3 | 5.10 |
| | 18.5 | 4.69 |
| | 10.8 | 4.60 |
| | 7.3 | 4.51 |
| | 6.9 | 4.46 |
| (preparation II) | 293.0 | 5.98 |
| | 80.0 | 5.77 |
| | 61.9 | 5.75 |
| | 43.3 | 5.72 |
| | 25.9 | 5.70 |
| | 12.5 | 5.72 |
| | 8.9 | 5.75 |

In contrast to (2b), magnetic data for $[Fe(OSCNMe_2)_3]$, (2a), are markedly dependent on the particular preparation. For example, low-temperature magnetic data for two separate preparations of (2a) (I and II) are given in Table 1. While both compounds were prepared under the same conditions and have essentially indistinguishable i.r. spectra and elemental analyses for anhydrous $[Fe(OSCNMe_2)_3]$, their low-temperature magnetic behaviour differ greatly. Preparation I exhibits a room-temperature magnetic moment of 5.81 B.M. which is in good agreement with our previous report,[13] but at 6.9 K the magnetic moment drops to 4.46 B.M. or a value much lower than the $\mu_{eff.}$ (8.9 K) = 5.75 B.M. high-spin value exhibited by preparation II at a similar temperature. Thus, while the compound of I demonstrates variable-temperature magnetic data consistent with a $(S = \frac{1}{2}) \rightleftharpoons (S = \frac{5}{2})$ spin-equilibrium process, II behaves as only a normal high-spin $S = \frac{5}{2}$ species, at even the lowest temperatures investigated. This result appears to

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* Analysis for $[Fe(OSCNEt_2)_3]$, found (calc.): C, 39.5 (39.75); H, 6.40 (6.60); N, 9.40 (9.25). Analysis for $[Fe(OSCNMe_2)_3]$, preparations I, II (calc.): C, 29.1, 29.45 (29.35); H, 4.90, 4.80 (4.95); N, 11.5, 11.65 (11.4).

† Throughout this paper: 1 B.M. ≈ $0.927 \times 10^{-23}$ A m$^2$; 1 eV ≈ $1.6022 \times 10^{-19}$ J.

TABLE 2

Mössbauer spectral parameters for the tris(dialkylmonothiocarbamato)iron(III) complexes

| Compound | $T$/K | $\delta$/mm s$^{-1}$ [a,b] | $\Gamma$ [c] | $\Delta E_Q$/mm s$^{-1}$ [b] |
|---|---|---|---|---|
| (2a) [Fe(OSCNMe$_2$)$_3$] | 297.0 | 0.62(0.01) | 0.30 | |
| (preparation I) | 105.0 | 0.72(0.03) | 0.19, 0.41 | 0.19(0.03) |
| | 4.5 | 0.67(0.01) | 0.46, 0.47 | 0.30(0.05) |
| (2b) [Fe(OSCNEt$_2$)$_3$] | 296.0 | 0.60(0.01) | 0.31 | |
| | 93.0 | 0.75(0.01) | 0.25, 0.26 | 0.35(0.01) |
| | 4.5 | 0.67(0.01) | 0.31, 0.31 | 0.39(0.03) |
| (2c) [Fe(OSCNPr$^i{}_2$)$_3$] | 297.0 | 0.59(0.02) | 0.35 | |
| | 123.0 | 0.81(0.02) | 0.58 | |
| (2d) [Fe{OSCN(NC$_4$H$_8$)$_2$}$_3$] | 297.0 | 0.63(0.01) | 0.35 | |
| | 123.0 | 0.82(0.03) | 0.66 | *d* |
| (2e) [Fe{OSCN(NC$_5$H$_{10}$)$_2$}$_3$] | 297.0 | 0.60(0.01) | 0.40 | |
| | 99.0 | 0.76(0.01) | 0.60 | *e* |

[a] Relative to sodium nitroprusside. Spectral parameters at 4.5 K are reported for the case where both the absorber and the source are at 4.5 K; spectra run at higher temperatures are with the source at room temperature and are taken from ref. 13. [b] Standard deviations in parentheses. [c] Half width at half height (h.w.h.h.) in mm s$^{-1}$ for the absorption peak(s). [d] If fit as a doublet: $\delta$ = 0.83(0.05) mm s$^{-1}$ with h.w.h.h. of 0.23 and 1.13 mm s$^{-1}$ and $\Delta E_Q$ = 0.08(0.08) mm s$^{-1}$. [e] If fit as a doublet: $\delta$ = 0.77(0.14) mm s$^{-1}$ with h.w.h.h. of 0.46 and 0.51 mm s$^{-1}$ and $\Delta E_Q$ = 0.42(0.08) mm s$^{-1}$.

reconcile our previous report[13] of a spin-equilibrium process for [Fe(OSCNMe$_2$)$_3$] and the observations of Nakajima *et al.*,[14] who found the compound to be only a normal high-spin species.

Since the [Fe(Se$_2$CNR$_2$)$_3$] complexes [R = piperidyl (3a), R, R = Me, Ph (3b), R = CH$_2$Ph (3c), thiomorpholinyl (3d)] are all nearly low-spin by *ca.* 100 K,[16] they have not been subjected to extended temperature studies.

*Mössbauer Data.*—Variable-temperature Mössbauer parameters for the [Fe(OSCNR$_2$)$_3$] complexes (2a—e) are given in Table 2. Previously reported room-temperature spectra (with the $S = \frac{5}{2}$ spin state predominating in all complexes) for the series all appear to be best fit as singlets with positive isomer shifts ranging from 0.59 mm s$^{-1}$ relative to sodium nitroprusside for (2c) to 0.63 mm s$^{-1}$ for (2d).[13] By comparison, $\delta$ = 0.66 mm s$^{-1}$ for the totally high-spin $S = \frac{5}{2}$ [Fe{S$_2$CN(NC$_4$H$_8$)$_2$}$_3$] complex.[19] Both [Fe{OSCN(NC$_4$H$_8$)$_2$}$_3$] (2d) and [Fe{S$_2$CN(NC$_4$H$_8$)$_2$}$_3$] appear to remain high-spin, even at temperatures down to 80 K, but with increasing isomer shifts until $\delta$ = 0.83 mm s$^{-1}$ (123 K) and 0.77 mm s$^{-1}$ (77 K) respectively. It is reasonable to expect an increase in the isomer shift with decreasing temperature for these spin-invariant iron centres because of the temperature dependence of the second-order Doppler shift term in the equation for the isomer shift.[20]

At lower temperatures (4.5–120 K), the singlets observed at room temperature for the fully high-spin complexes (2a—e) tend to broaden or, in the case of the compounds (2a) and (2b) [the complex (2a) designated preparation I in Table 2 was used for both the Mössbauer and the e.s.r. studies below], to resolve into clearly defined quadrupole-split doublets as shown, for example, for [Fe(OSCNEt$_2$)$_3$] (2b) at 4.5 K in Figure 1. Only the low-temperature spectra of (2a) and (2b) can be legitimately analysed as doublets, while spectra for the remaining derivatives appear to also fit well as broadened singlets at temperatures down to *ca.* 100 K. Table 2 shows results of some of the various fitting alternatives for the low-temperature spectra. For the variable-spin compounds (2a) and (2b), the increase in quadrupole splitting appears to parallel an increase in the $^2T$ low-spin isomer population as the temperature is lowered, *i.e.*, $\Delta E_Q$ (2b) (at 297 K with *ca.* 0% $^2T$) < $\Delta E_Q$(2b) (at 93 K with *ca.* 64% $^2T$) < $\Delta E_Q$(2b) (at 4.5 K with *ca.* 100% $^2T$). This is as expected for an increasing contribution to the spectrum by the $^2T$ state and, in general, the variable-spin [Fe(S$_2$CNR$_2$)$_3$] complexes (1) also impart the same pattern to their Mössbauer spectra as the low-spin $^2T$ state is more extensively populated. While it is expected that the $^2T$ spin state (with its larger electric field gradient) would exhibit a greater quadrupole splitting than the $^6A$ state, it is somewhat surprising that the asymmetrical *cis*-FeS$_3$O$_3$ core of the [Fe(OSCNR$_2$)$_3$] complexes[15,*] does not produce larger $\Delta E_Q$ values than displayed by the [Fe(S$_2$CNR$_2$)$_3$] complexes with their more symmetrical FeS$_6$ centres.

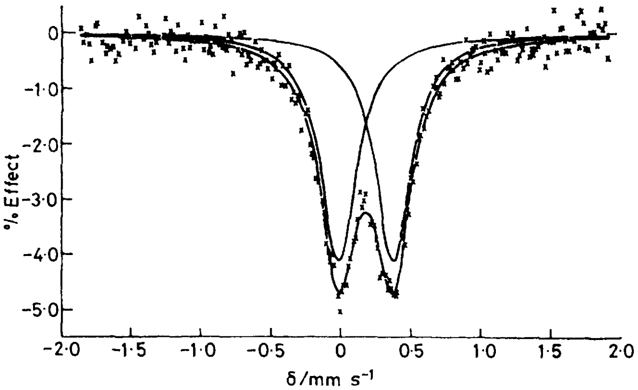

FIGURE 1 Mössbauer spectrum of [Fe(OSCNEt$_2$)$_3$] (2b) at 4.2 K

The new Mössbauer data at 4.2 K for (2a) and (2b) also serve to further confirm an important and rather intriguing similarity between the ($S = \frac{1}{2}$) $\rightleftharpoons$ ($S = \frac{5}{2}$) electronic equilibria that are operative in both the [Fe(OSCNR$_2$)$_3$] and [Fe(S$_2$CNR$_2$)$_3$] families of complexes. For example, at 4.2 K the compound (2a) (preparation I) is *ca.* 50% $^6A$ and *ca.* 50% $^2T$ in spin-state populations, and yet the Mössbauer spectrum does *not* display separate high-spin and low-spin signals, but rather a spectrum that appears to be an ' average ' of the two spin states.

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[*] The core of the [Fe(OSCNMe$_2$)$_3$] complex is in a *cis* or *fac* configuration (see ref. 15).

In this behaviour, the $[Fe(OSCNR_2)_3]$ complexes resemble the $[Fe(S_2CNR_2)_3]$ complexes and differ from all other variable-spin iron(II) and iron(III) species. In these other cases, such as for the tris(monothio-β-diketonato)iron(III) series with *cis*-$FeS_3O_3$ centres like those present in the $[Fe(OSCNR_2)_3]$ complexes,[12] a ' doublet of doublets ' Mössbauer spectrum is observed [11] where each separate spin state is detected as a closely or widely spaced doublet. The possible reasons for this rather unique Mössbauer spectral behaviour for the $[Fe(S_2CNR_2)_3]$ and $[Fe(OSCNR_2)_3]$ complexes have been extensively considered elsewhere,[2,4,13] with the most likely explanation being that the $(S = \frac{1}{2}) \rightleftharpoons (S = \frac{5}{2})$ spin-interconversion (intersystem crossing) rates are *faster* in these species than the Mössbauer transition time scale (*ca.* $7 \times 10^8\ s^{-1}$). While this is possibly true, it still remains unexplained why the $[Fe(S_2CNR_2)_3]$ and $[Fe(OSCNR_2)_3]$ complexes should stand alone as the only variable-spin systems to exhibit this behaviour.

Unfortunately, it was impossible to observe a Mössbauer spectrum for any of the $[Fe(Se_2CNR_2)_3]$ complexes, even at 4.5 K with collection times of >12 h; this is probably due to a selenium edge absorption at 12.6 keV, which is near the 14.4 keV Mössbauer transition energy, or to effective γ-ray scattering by the six selenium donor atoms. This effect was also noted earlier [21] where $^{57}Fe$ enrichment of 90% was needed to observe a reasonable spectrum for the compound with R = piperidyl, (3a).

*Electron Spin Resonance Data.—The* $[Fe(S_2CNR_2)_3]$ *and* $[Fe(OSCNR_2)_3]$ *complexes.* E.s.r. studies of the R = Me and Et derivatives (2a) and (2b) were initiated to determine whether the spin equilibria were also operable in the solid-solution state, as has been observed for the $[Fe(S_2CNR_2)_3]$ systems [2] and to determine the characteristic high- and low-spin spectra. E.s.r. spectra for *pseudo*-octahedral iron(III) complexes experiencing various tetragonal ($D$) and rhombic ($E$) distortion parameters are well established,[22-30] excepting that expected for a high-spin complex experiencing a trigonal distortion. The complexes $[Fe(S_2CNR_2)_3]$ and $[Fe(OSCNR_2)_3]$ possess this trigonal symmetry, belonging to the $D_3$ and $C_3$ point groups respectively.[27,28] E.s.r. experiments on the dithiocarbamates at 12 K and 85 K have indicated the presence of two temperature-dependent spin states,[2] with the high-spin $^6A$ signals appearing in the vicinities of $g$ = 6.2 and 4.3—4.8, and with the low-spin $^2T$ signals being at $g$ = 3.3 and 1.8. However, earlier work on $[Fe(S_2CNMe_2)_3]$ doped into a diamagnetic host, $[Co(S_2CNMe_2)_3]$, produced a very different spectrum, with the principal $g$ values near 2 ($g_x = 2.706$, $g_y = 2.111$, and $g_z = 2.015$).[31] Signals with similar $g$ values were also found in the later work of Hall and Hendrickson,[2] who attributed them to a copper impurity. In fact, a perusal of reported e.s.r. data for $[Fe(S_2CNR_2)_3]$ complexes illustrates that the spectral properties of the system are still very poorly understood to the extent that they cannot even be unambiguously assigned to particular species, much less to a particular transition.

Experimental $g$ values obtained for the present $[Fe(OSCNR_2)_3]$ complexes at 12 K in frozen glass matrices are listed in Table 3, along with values for the analogous $[Fe(S_2CNR_2)_3]$ species. Representative spectra for (2a) and (2b) are given in Figure 2. The striking feature of all the $[Fe(OSCNR_2)_3]$ spectra is that they have signals at only $g$ *ca.* 4.3, the characteristic iron(III) high-spin value for a system exhibiting maximum rhombicity $E/D = \frac{1}{3}$.[26,32] If these spectra are representative of the intact tris complexes, it can only be concluded that the spin-equilibrium process for (2a) and (2b) is not transferred to the solid-solution state, but rather is induced by solid-state lattice effects. This result has been previously

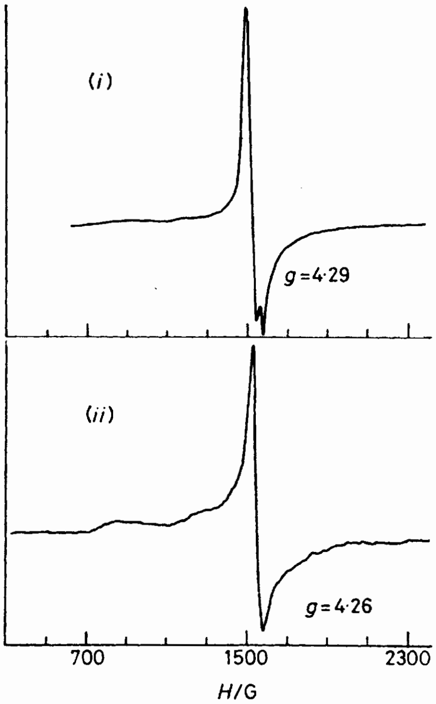

FIGURE 2 $X$-Band e.s.r. spectrum of ($i$) $[Fe(OSCNMe_2)_3]$ (2a) (preparation I) and ($ii$) $[Fe(OSCNEt_2)_3]$ (2b) at 12 K in a 2 : 1 : 1 $Et_2O$–toluene–EtOH glass

TABLE 3

Experimental $g$ values for the $[Fe(S_2CNR_2)_3]$ and $[Fe(OSCNR_2)_3]$ complexes ($X$-band spectra at 12 K)

| | Compound | Solvent glass [a] | $g$ Value | Reference |
|---|---|---|---|---|
| (2a) | $[Fe(OSCNMe_2)_3]$ (preparation I) | $b$ | 4.29 | This work |
| (2b) | $[Fe(OSCNEt_2)_3]$ | $b$ | 4.22 | This work |
| (2d) | $[Fe\{OSCN(NC_4H_8)_2\}_3]$ | $b$ | 4.27 | This work |
| (2e) | $[Fe\{OSCN(NC_5H_{10})_2\}_3]$ | $b$ | 4.27 | This work |
| (1a) | $[Fe(S_2CNMe_2)_3]$ | $c$ | 4.56<br>3.30<br>1.85 | 4 |
| (1b) | $[Fe(S_2CNEt_2)_3]$ | $c$ | 4.36<br>3.27<br>1.83 | 4 |
| (1c) | $[Fe\{S_2CN(NC_4H_8)_2\}_3]$ | $c$ | 7.70<br>6.23<br>4.28<br>2.00 | 4 |

[a] Concentrations of the $[Fe(OSCNR_2)_3]$ samples were: 3.4 for (2a), 2.5 (2b), 5.4 (2d), and 2.25 mol $dm^{-3}$ (2e). [b] 2 : 1 : 1 $Et_2O$–toluene–EtOH. [c] Chloroform.

observed for spin-equilibrium complexes where the property is present in the solid state but lacking in solution.[33] Furthermore, the $C_3$ axial symmetry of the *cis*-[Fe(OSCNR$_2$)$_3$] complexes would have to have been reduced by the lattice of the frozen solution since a *g* value of 4.3 is not at all expected for an axially symmetric iron(III) compound. Alternatively, it can be argued that the *g* values of 4.3 originate from decomposition products of the complexes, a supposition not wholly unreasonable in the light of their solution sensitivity.[13] However, if this were the case, it would seem that the spectra would be more complex due to a variety of decomposition products, along with signals from undecomposed material.

*The* [Fe(Se$_2$CNR$_2$)$_3$] *complexes*. Samples of [Fe{Se$_2$CN(NC$_5$H$_{10}$)$_2$}$_3$] (3a), [Fe(Se$_2$CNMePh)$_3$] (3b), [Fe{Se$_2$CN(CH$_2$Ph)$_2$}$_3$] (3c), and [Fe(btmdsc)$_3$] (3d) [btmdsc = bis(thiomorpholinyl)diselenocarbamate] were dissolved in chloroform to give 1.5, 0.8, 1.0, and 1.7 mmol dm$^{-3}$ solutions respectively, quickly introduced into e.s.r. tubes, and immediately frozen in liquid nitrogen. All e.s.r. spectra were run at 12 K, with resulting *g* values listed in Table 4. The actual spectra are shown in Figure 3. The spectra tended to be broad and ill resolved, except for a series of three resonances centred around $g = 2$.

TABLE 4

Experimental *g* values for the tris(diselenocarbamato)iron(III) complexes (3) in CHCl$_3$ glasses (*X*-band spectra at 12 K)

| Complex | | | |
|---|---|---|---|
| (3a) | (3b) | (3c) | (3d) |
| 4.37 | 4.25 | 4.28 | 4.20 |
| 3.88 | | 4.17 | 3.77 |
| | | 3.92 | |
| 2.78 | 2.84 | 2.84 | 2.79 |
| 2.16 | 2.14 | 2.12 | 2.12 |
| 2.04 | 2.08 | 2.04 | 2.04 |
| 1.98 | 1.98 | 1.99 | 1.98 |
| 1.78 | 1.71 | | 1.73 |

Similarities do exist between the [Fe(Se$_2$CNR$_2$)$_3$] spectra and those of the $^2T \rightleftharpoons {}^6A$ [Fe(S$_2$CNR$_2$)$_3$] system,[2] notably in the high-spin region. Hall and Hendrickson have predicted *g* values of *ca.* 3.0, 4.0, and 6.1 for the $^6A$ spin state of the [Fe(S$_2$CNR$_2$)$_3$] complexes, and, indeed, the *X*-band spectrum of high-spin (1c) exhibits a strong signal at $g = 4.28$, a weaker signal at $g = 6.23$, and one in the vicinity of $g = 3.0$.[2] The *X*-band spectra at 12 K of the [Fe(Se$_2$CNR$_2$)$_3$] complexes all show resonances near $g = 2.8$ and 4.25 with very little indication of a $g = 6$ signal, although this resonance might possibly be very weak. Alternatively, these *g* values may represent those of a high-spin iron(III) complex with near rhombic symmetry and with the multiplicity near *g ca.* 4.25 due to divergence from the extreme rhombic $g = 4.3$ case.[27] Very weak signals near $g = 1.7$ are also seen for the diselenocarbamates, which would seem to indicate the presence of a small low-spin fraction; a corresponding low-spin signal near $g = 3.25$, seen by Hall and Hendrickson for the dithiocarbamates [2] is not apparent, possibly due to a combination of its expected low intensity and the complexity of this region.

As previously mentioned, the region near $g = 2$ is occupied by three signals in each spectrum and is similar to those observed for (1a) doped into [Co(S$_2$CNMe$_2$)$_3$].[31] The more recent work of Hall and Hendrickson reports resonances in this region but attributes them to copper impurities.[2] It seems improbable that signals of such great intensity could be due to impurities, but this possibility cannot be totally discounted {also no such $g = 2$ signals are present in the above e.s.r. spectra of [Fe(OSCNR$_2$)$_3$]}. However, a particularly interesting observation is that these *g* values are also similar to those obtained for some [Mn(S$_2$CNR$_2$)$_3$] and [Cu(S$_2$CNR$_2$)$_3$] complexes.[32,34] If it is assumed that such *g* values are true representatives of all of the above systems collectively, then electron delocalisation onto the ligand sulphur or

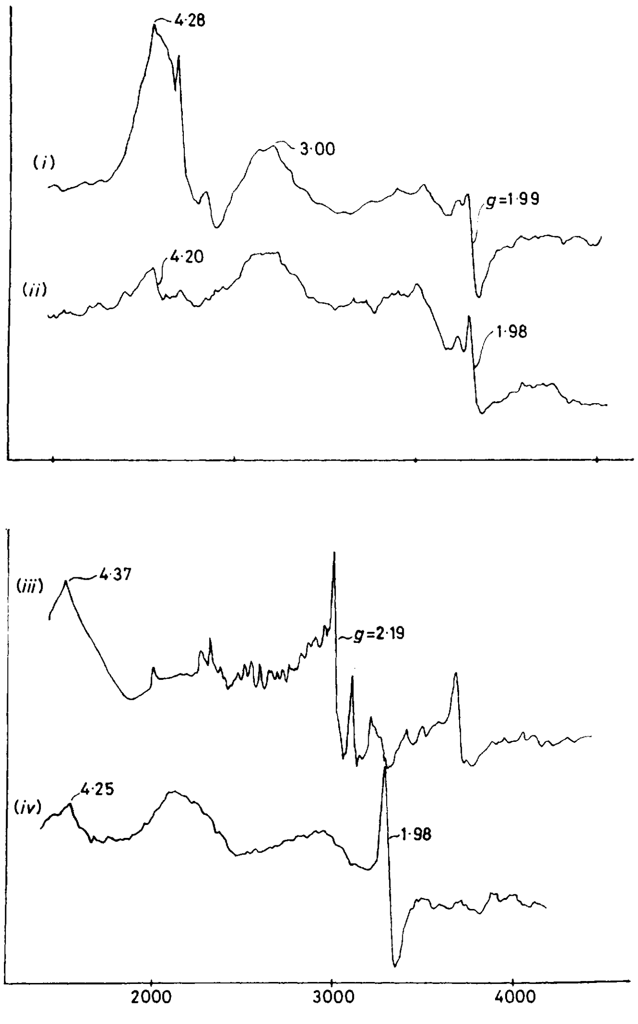

FIGURE 3 *X*-Band e.s.r. spectrum of (*i*) [Fe{Se$_2$CN(CH$_2$Ph)$_2$}$_3$] (3c), (*ii*) [Fe(btmdsc)$_3$] (3d), (*iii*) [Fe{Se$_2$CN(NC$_5$H$_{10}$)$_2$}$_3$] (3a), and (*iv*) [Fe(Se$_2$CNMePh)$_3$] at 12 K in a chloroform glass

selenium donor atoms of the $S_2CNR_2$ and $Se_2CNR_2$ ligands would account for the spectral similarities, and, indeed, this possibility gains some credence by the resemblance of the spectra to those of simple sulphur and selenium radicals.[35]

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