Inorganica Chimica Acta, *145* (1988) 13–15

EPR of Iron(III) Tris-thioselenocarbamates and -diselenocarbamates

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(Received November 20, 1987)

The spin-crossover behavior of the tris(diorganodichalcogenocarbamato)iron(III) complexes has been the subject of considerable research [1]. The EPR spectra of these complexes have been controversial as the result of contradictory interpretations. In 1970 Rickards *et al.* [2] published the first EPR powder spectrum (4.2 K) of iron(III) tris-dimethyldithiocarbamate, diluted in the corresponding cobalt complex. These authors were unable to observe signals at temperatures >100 K. The 4.2 K spectrum consisted of three lines (*g* values 2.015, 2.076 and 2.111) attributed to low-spin d^5 iron. Gelerinter and his coworkers [3, 4] successfully measured EPR spectra of undiluted iron tris-dithiocarbamates from 127 K to room temperature. The lines were attributed to the $S = 5/2$ and $S = 1/2$ state as well. Hall and Hendrickson [5] proposed that the relatively narrow lines at $g \sim 2$ were not from the iron(III) dithiocarbamate, but, instead, originated from copper impurities. Perry *et al.* [6], found similar lines in the spectra of frozen chloroform solutions (at 12 K) of iron(III) tris-diselenocarbamates but expressed doubt that such intense lines could be the result of impurities. In neither of these latter two studies were room temperature spectra of undiluted samples reported.

In connection with our research on iron thioselenocarbamates [7], we now report the first EPR spectra of some iron(III) tris-thioselenocarbamates, $Fe(R_2tsc)_3$, as well as the corresponding iron(III) tris-diselenocarbamates, $Fe(R_2dsc)_3$, taken mainly from undiluted powders at room temperature.

Experimental

$Fe(R_2tsc)_3$ and $Fe(R_2dsc)_3$ were prepared by published methods [7] from the corresponding ligand salts $(R_2NH_2^+)(R_2tsc^-)$ and $(R_2NH_2^+)(R_2dsc^-)$ (where R_2 = diethyl (Et_2), dibenzyl (Bz_2), dicyclohexyl ($CHex_2$) and R_2N = pyrrolidyl (Pyr), piperidyl (Pip) and morpholyl (Mor)). All of the EPR spectra were taken at X-band using an IBM ER200D spectrometer. Temperatures were held constant to better than 1 K.

Results and Discussion

Figure 1 shows three typical spectra of $Fe(Pyr\text{-}tsc)_3$, $Fe(Mor\text{-}tsc)_3$ and $Fe(CHex_2tsc)_3$ (exhibiting solution magnetic moments of 5.61, 3.84 and 2.84 [7]), respectively, at room temperature. In Fig. 2 the change in the spectra of $Fe(Mor\text{-}dsc)_3$ between 297 and 120 K is shown. Most other spectra have similar shapes with broad, poorly-resolved lines in the low field region ($g \sim 4$) and around $g \sim 2$. For all compounds, typical, relatively narrow signals are seen in the $g \sim 2$ region.

The suspicion that the narrow line at $g \sim 2$ was the result of a copper impurity was addressed as follows: a sample of tris(diethyldithiocarbamato)-cobalt(III), a diamagnetic d^6 species, was prepared from methanolic solutions of $Co(NO_3)_2 \cdot 6H_2O$ (which contained only 5×10^{-4}% Cu and 7×10^{-4}% Fe) and sodium diethyldithiocarbamate (both Fisher Scientific Co.). The solid exhibited little if any measurable EPR absorptions. Building in less than

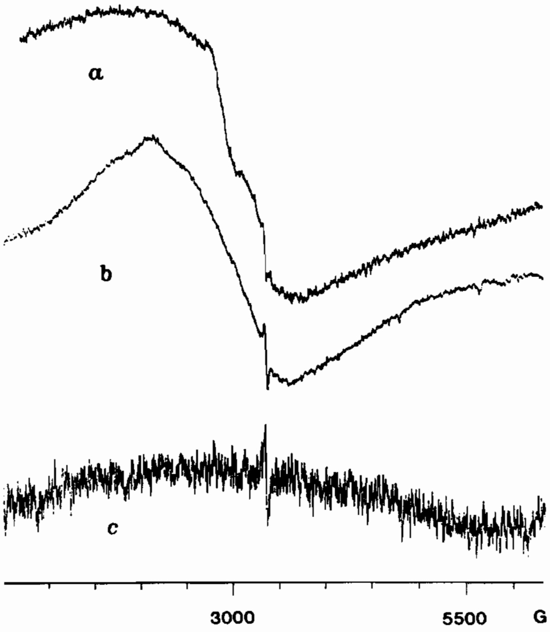

Fig. 1. EPR spectra of $Fe(Pyr\text{-}tsc)_3$ (a), $Fe(Mor\text{-}tsc)_3$ (b) and $Fe(CHex_2tsc)_3$ (c) taken from undiluted powders at room temperature (vertical scales arbitrary).

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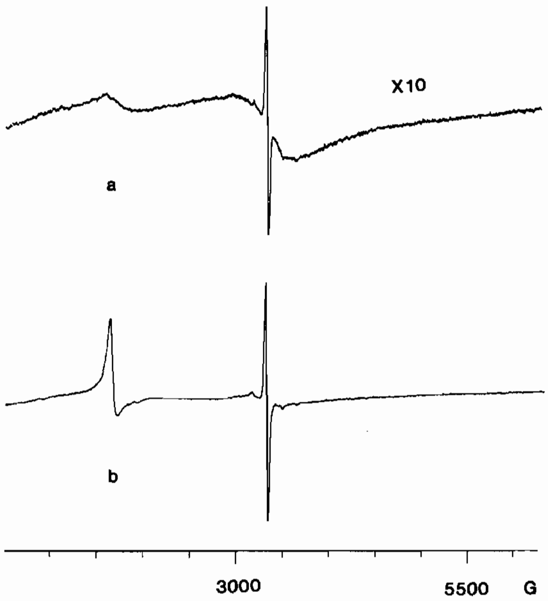

Fig. 2. EPR spectra of Fe(Mor-dsc)$_3$ taken from an undiluted powder at 297 K (a) and 120 K (b).

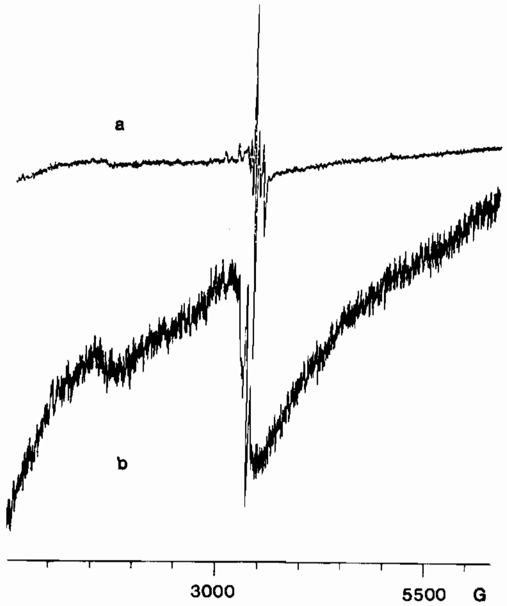

Fig. 3. EPR spectra of a Co(Et$_2$dtc)$_3$ powder containing less than 0.1% Cu(Et$_2$dtc)$_2$ (a) and of a Fe/Co(Et$_2$dtc)$_3$ powder (~1% Fe compound) (b) taken at room temperature (vertical scales arbitrary).

0.1% bis(diethyldithiocarbamato)copper(II) gave the EPR spectrum shown in Fig. 3a. The g value of the most intense line is 2.013 ± 0.001 and the linewidth 23 G. A Fe/Co(Et$_2$dtc)$_3$ powder containing about 1% iron compound, investigated under similar conditions, exhibits, however, the expected iron signal with $g = 2.044 \pm 0.005$ and a linewidth of 32 G (see Fig. 3b), quite different from copper impurities.

TABLE I. g Values of the $S = 1/2$ Signal Measured on Undiluted Tris(thioselenocarbamato)iron(III) and Tris(diselenocarbamato)iron(III) or Diluted Powders[a] at Room Temperature

R_2N	Thioselenocarbamates Fe(SSeCNR$_2$)$_3$ g (±0.001)	Diselenocarbamates Fe(Se$_2$CNR$_2$)$_3$ g (±0.001)
Et$_2$N	2.047[a]	2.053[a]
Bz$_2$N	2.047	2.055
CHex$_2$N	2.047	[b]
Piperidyl	2.046[a]	2.053
Pyrrolidyl	2.048	2.053
Morpholyl	2.049	2.052

[a]Diluted powders, Fe/Co, 1%. [b]No pure compound available.

Preliminary results, obtained with iron trisdiselenocarbamates, show a g value dependence upon the sulfur/selenium ratio in the coordination sphere, especially for this narrow line in thioselenocarbamate and diselenocarbamate systems. On the other hand, we were unable to see any difference (within experimental precision) between dithiocarbamates and thioselenocarbamates. Whereas the g value for planar copper bis-dichalcogenocarbamate ligand complexes decreases with increasing selenium content in the CuS$_n$Se$_{4-n}$ core [8], the g values of the iron compounds increase with increasing selenium content (Table I). This correlation was also observed for diamagnetic diluted systems Fe/Co(R$_2$tsc)$_3$, Fe/In(R$_2$tsc)$_3$, Fe/Co(R$_2$dsc)$_3$ and Fe/In(R$_2$dsc)$_3$ (investigations are now in progress). Sometimes satellites are observed on the narrow $g \sim 2$ line; these, however, cannot be attributed unequivocally to ^{77}Se interactions.

It appears that the relatively narrow signal found in most spectra at $g \sim 2$ is the result of molecules in the ^2T_g state. On the other hand, the broader lines at $g > 4$ (which narrows with decreasing temperature) and at $g \sim 2$ (that, in some cases gets a fine structure with decreasing temperature) may come from molecules in the $^6A_1$ state, although the concept of an intermediate $S = 3/2$ state ($^4T_1$) cannot be excluded completely.

The temperature dependence of the EPR spectra is in accord with the assignments above. The morpholylthioselenocarbamate complex of iron(III) is a spin-crossover equilibrium system in solution [7] and in the solid state [9] at room temperature. The intensity of the narrow line ($S = ½$) increases with decreasing temperature at a greater rate than the Curie law predicts ($1/T$) indicating an increasing $S = ½$ population with decreasing temperature. The intensity of the broad line ($S = 5/2$?) decreases in intensity with decreasing temperature (about X1.6 less from 296 to 110 K) indicating a decreasing population with decreasing temperature. The mainly low-spin (in solution [7]) Fe(CHex$_2$tsc)$_3$ exhibits no broad line and the narrow line shows no unusual temperature dependence with decreasing temperature. The mainly high-spin (in solution [7]) Fe(Pyr-tsc)$_3$ exhibits a very broad EPR absorption and the intensity decreases with decreasing temperature, but at a slower rate than the corresponding morpholyl derivative.

The EPR spectra of these undiluted powders of the tris(thioselenocarbamato)iron(III) compounds are similar to those of undiluted tris(dithiocarbamato)iron(III) complex powders [3, 4], as well as those of Fe(Pyr-dtc)$_3$ in frozen chloroform solution (at 12 K), of Fe/Co(Me$_2$dtc)$_3$ powder (1%, at 85 K) [5] and of some tris(diselenocarbamato)iron(III) compounds in chloroform glass (at 12 K) [6].

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