Inorganica Chimica Acta, *177* (1990) 185–189

Magnetic properties of spin-crossover systems in iron(III) thioseleno- and diselenocarbamates. Effect of dilution in the corresponding cobalt(III) or indium(III) complex matrices on EPR spectra

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(Received June 6, 1990)

Abstract

The temperature-dependent magnetic moments between 8 and 310 K have been measured for a series of iron(III) tris-thioselenocarbamates, $Fe(SSeCNR_2)_3$, where NR_2 is $N(CH_2C_6H_5)_2$, $N(CH_2)_4$, $N(CH_2)_5$, $N(CH_2)_4O$ or $N(C_6H_{11})_2$. Whereas the dibenzyl, piperidyl and morpholyl derivatives clearly show spin-crossover behavior at room temperature reaching the low-spin state near liquid nitrogen temperature, the dicyclohexyl derivative is in the pure low-spin state at all temperatures measured. The pyrrolidyl complex, mainly high spin at higher temperatures, exhibits substantial spin-crossover behavior even at 8 K. The EPR powder spectra of the iron(III) tris-thioselenocarbamates, diluted (1:99%) with the corresponding cobalt(III) or indium(III) tris-thioselenocarbamate have been recorded between 120 K and room temperature. These spectra can be used as fingerprints to study qualitatively the influences of temperature and matrix effects on the electronic configuration of spin-crossover systems. In most cases they exhibit a relatively narrow signal at $g \approx 2$ and two broad signals with $g \approx 4$ and $g \approx 2$ which have been attributed to the $S = 1/2$ and $S = 5/2$ state, respectively. Spectra for the corresponding tris-diselenocarbamates are also included and correlated.

Introduction

Recently we reported [1] the temperature-dependent powder EPR of tris(diethylthioselenocarbamato)- and tris(diethyldiselenocarbamato)-iron(III) ($Fe(Et_2tsc)_3$ and $Fe(Et_2dsc)_3$) diluted in the analogous cobalt(III) or indium(III) complex matrices. The temperature-dependent magnetic moments of the undiluted iron(III) complexes indicated a spin-crossover electronic configuration and the EPR of the diluted complexes were interpreted in terms of separate signals for the $S = 5/2$ (broad lines at $g \approx 4$ and $g \approx 2$) and $S = 1/2$ (a narrow line at $g \approx 2$) electronic configurations. The overall features of the EPR spectra were similar to the spectra of the undiluted tris(morpholinecarboselenothioato)-iron(III) in the same temperature range [2]. We have extended this study to include several different organic substituents across the range of weak and strong field thioseleno- and diselenocarbamates of iron(III) and report their temperature-dependent EPR spectra when diluted in the corresponding cobalt(III) or indium(III) matrices.

Experimental

The iron(III) complexes have been prepared following procedures reported earlier and gave satisfactory elemental analyses [1–4]. The cobalt(III) and indium(III) complexes were prepared by methods similar to those reported previously [1, 3] and gave satisfactory elemental analyses. The ^1H, ^{13}C, ^{59}Co and ^{77}Se NMR spectra of each of the Co and In complexes have been measured and are in accord with the molecular formula [5].

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0020-1693/90/$3.50

Magnetic susceptibilities (4–320 K) were measured on a SQUID magnetometer. Temperature control was better than ±4 K. The calibration and method of operation are described elsewhere [6, 7].

For EPR spectra, samples were sealed in 4 mm (o.d.) quartz tubes under approximately 0.5 atm of nitrogen. Data were obtained by using an IBM 200-D-SRC spectrometer with an ER 044 MRDH X-band microwave bridge. The temperature was controlled with an IBM ER 411 VT temperature controller, which has a precision of 1 K.

Results and discussion

The temperature-dependent magnetic moments for each of the $Fe(R_2tsc)_3$ derivatives (where R = organic substituent) are reported in Table 1. The parent secondary amines were chosen from those of the corresponding tris(diorganodithiocarbamato)-iron(III) ($Fe(R_2dtc)_3$) to span the range from weak-field to strong-field ligands for these complexes [8, 9].

As shown in Table 1, the dibenzyl, piperidyl and morpholyl derivatives are spin-crossover complexes at room temperature, but reach their low-spin electronic configuration near liquid N_2 temperatures. The magnetic moment of the dicyclohexyl derivative at all temperatures is consistent with the behavior expected of a pure low-spin ($^2T_2$) state with the usual degree of distortion from octahedral geometry. The pyrrolidyl derivative continues to exhibit substantial spin-crossover behavior at 8 K. The solid magnetic moments reported in Table 1 parallel closely the solution magnetic moments reported earlier [3], exhibiting the same order (pyr > morph > Bz_2 > $cHex_2$), but generally lower values. Similar values are expected for the corresponding diselenocarbamates [3].

A typical EPR powder spectrum showing a substantial fraction of $S = 5/2$ Fe(III) is shown in Fig. 1(A). The narrow line at $g_{eff} \approx 2.0$ has been interpreted as the absorption for $S = 1/2$ Fe(III) and the broad lines at $g_{eff} \approx 2$ and ≈ 4.3 have been interpreted as resulting from the $S = 5/2$ electronic configuration. Figures 1(B) and (C) represent EPR spectra with decreasing relative amounts of high-spin ($S = 5/2$) Fe(III). A typical low-spin ($\mu_{eff} < 2.3\mu_B$) EPR spectrum is shown in Fig. 1(D). Except for variations in g_{eff} and other minor variations as noted in Table 2, this spectrum corresponds to $Fe(Pyr\text{-}dsc)_3$, $Fe(Mor\text{-}dsc)_3$ and $Fe(cHex_2tsc)_3$ diluted (1%) in either the corresponding Co(III) or In(III) complex over the entire temperature range studied (120–297 K), $Fe(Bz_2tsc)_3$, $Fe(Bz_2dsc)_3$, $Fe(Pip\text{-}tsc)_3$, $Fe(Pip\text{-}dsc)_3$ and $Fe(Mor\text{-}tsc)_3$ diluted in the corresponding Co(III) complex over the entire temperature range studied, and $Fe(Mor\text{-}tsc)_3$ (297 K) and $Fe(Pip\text{-}dsc)_3$ (120 K) diluted in the corresponding In(III) complex. Little or no absorption for $S = 5/2$ Fe(III) (broad absorptions at $g_{eff} \approx 4.3$ and ≈ 2.0) are detected. The EPR of both Fe(III) dibenzyl complexes are anomalous in In(III), each exhibiting a broad peak immediately before $g = 2$ and a broad peak at $g = 2$ without a well-defined narrow line. No explanations are offered for these anomalous spectra and the effect of the indium(III) matrix on the EPR and magnetic moments of these and similar complexes is the subject of further research.

TABLE 1. Temperature-dependent magnetic moments of $Fe(SSeCNR_2)_3$

T (K)[a]	$NR_2 =$				
	$N(CH_2C_6H_5)_2$	$N(CH_2)_4$	$N(CH_2)_5$	$N(CH_2)_4O$	$N(C_6H_{11})_2$
310	3.00		3.45	3.72	2.28
290	2.81		3.25	3.65	2.22
250	2.55		2.88	3.47	2.10
210	2.37		2.57	3.25	2.08
170	2.27		2.39	2.99	2.08
135	2.22		2.29	2.73	2.08
120	2.20	5.20	2.27	2.60	2.07
90	2.16	5.21	2.23	2.34	2.06
68	2.13	5.11	2.19	2.20	2.05
48	2.10	5.13	2.14	2.08	2.01
32	2.06	5.06	2.09	2.00	1.99
21	2.04	4.91	2.01	1.89	1.92
15	2.01	4.77	1.95	1.84	1.94
8	2.02	4.04	1.84	1.78	1.90

[a] Temperatures have been interpolated to temperatures other than those of measurement for convenience of tabulation.

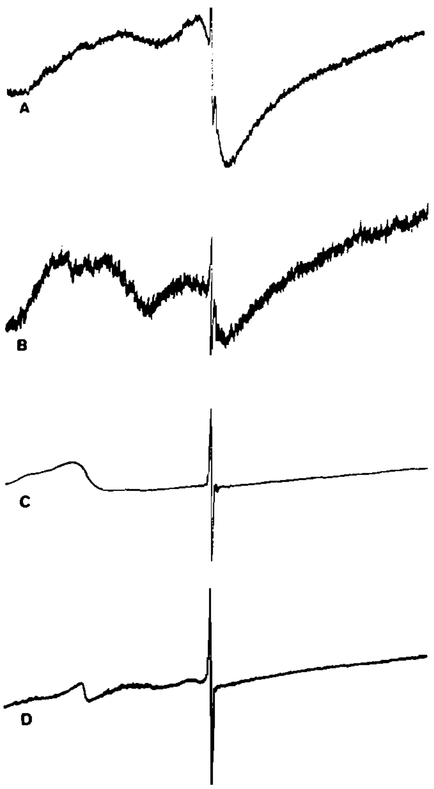

Fig. 1. Powder EPR spectra (X-band) of (A) 1% Fe(SSeCN(CH$_2$)$_4$)$_3$ in a solid matrix of Co(SSeCN(CH$_2$)$_4$)$_3$ at 297 K; (B) 1% Fe(SSeCN(CH$_2$)$_5$)$_3$ in a solid matrix of In(SSeCN(CH$_2$)$_5$)$_3$ at 297 K; (C) 1% Fe(SSeCN(CH$_2$)$_4$O)$_3$ in a solid matrix of In(SSeCN(CH$_2$)$_4$O)$_3$ at 120 K; (D) Fe(SSeCN(CH$_2$)$_5$)$_3$ in a solid matrix of Co(SSeCN(CH$_2$)$_5$)$_3$ at 120 K.

As noted earlier [1], the EPR spectra of these Fe(III) complexes were carried out in dilute Co(III) or In(III) matrices to minimize interactions between unpaired electrons of neighboring Fe(III) centers. Speculation that the increased size of the In(III) may provide a larger void to the Fe(III) than the Co(III) crystalline matrix [1] is in accord with the results of this study. As noted in Table 2, whenever a low-spin EPR spectrum is observed for a sample diluted in an In(III) matrix, a low-spin spectrum is also observed for the corresponding Co(III) dilution. The converse is not true, for example, the EPR spectra of Fe(Pip-tsc)$_3$ in In(Pip-tsc)$_3$ exhibits substantial peaks for $S=5/2$ at both 297 and 120 K, and little or no intensity for $S=5/2$ at either temperature in Co(Pip-tsc)$_3$.

As before [1], there are no substantial changes in the g values for these complexes as indicated in Table 2 and, except for the anomalous dibenzyl derivatives, the g values of the narrow $S=1/2$ signal appear to depend on the chalcogens in the coordination sphere: FeS$_6$ (2.038 ± 0.005 [10]) < FeS$_3$Se$_3$ (2.047 ± 0.005) < FeSe$_6$ (2.053 ± 0.003). This order of g values is observed in both diluted and undiluted samples and is generally independent of temperature. In most cases, the g values in the indium matrices are greater than in the corresponding cobalt(III) matrix.

We assign the narrow line discussed above to $S=1/2$ based on the variation of its intensity with temperature observed in these and many other compounds [1, 2, 11–13]. This assignment is a point of contention in the literature [2, 14], so we believe that it should be examined in more detail here. Several years ago, Flick and Gelerinter [11] observed a narrow line near $g=2$ when studying the compound tris(dicyclohexyldithiocarbamato)iron(III) and assigned it to the $S=1/2$ spin state based on the temperature-dependent EPR intensity and magnetic moment data. The EPR studies were performed in the temperature range of 120 K to room temperature. Hall and Hendrickson [14] later reported that they were unable to observe this line, but, at a low temperature of 12 K, they reported observing a powder pattern of an anisotropic g shifted line with an overall width in the order of 2000 gauss. Hall and Hendrickson assign this line to the $S=1/2$ and suggest that the line reported by Flick and Gelerinter may be due to copper impurities. Since then, we have observed the narrow line near $g=2$ for many iron(III) tris-dichalcogenocarbamates [1, 2, 11–13], and, more recently, have performed experiments to clearly demonstrate that the observed line is not due to copper [2]. The order of the g values (Fe(R$_2$dtc)$_3$ < Fe(R$_2$tsc)$_3$ < Fe(R$_2$dsc)$_3$) is the reverse of that reported for the Cu(II) dichalcogenocarbamates [15]. This is an important observation since it provides further confirmation that the narrow line at $g \approx 2$ cannot be the result of a Cu(II) impurity.

Another reasonable explanation for these apparently conflicting observations should be taken into account: consider the energy diagram for d orbitals in a site of octahedral symmetry with a trigonal distortion. The low-lying triply degenerate set of orbitals (t$_{2g}$: d$_{xy}$, d$_{yz}$, d$_{xz}$) in octahedral symmetry splits by the trigonal distortion into a single orbital (a$_1'$: d$_{xy}$) and a doubly degenerate pair (e$'$: d$_{xz}$, d$_{yz}$) at slightly higher energy [16]*. The low-temperature ground state for Fe(III) (d^5) consists of two electrons filling the d$_{xy}$ and the other three electrons partially filling the e$'$. The unpaired electron in e$'$ is in an orbital that carries orbital angular momentum, so a

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*Numerous crystal structures of Fe(R$_2$dtc)$_3$ derivatives [17] have indicated that the distortion is not purely trigonal, so that the degeneracy of the e$'$ pair may be lifted. So long as this pair remains close in energy, the proposed alternative explanation is valid.

TABLE 2. *g* Values of the low-field and narrow high-field signals for diluted tris(diorganothioselenocarbamato)- and tris(diorganodiselenocarbamato)iron(III)

Compound	*g* Values					
	Cobalt(III) matrix			Indium(III) matrix		
	Class[a]	Low-field line	Narrow high-field line	Class[a]	Low-field line	Narrow high-field line
$Fe(Et_2tsc)_3$[b]						
295 K	A		2.047	A	4.25	2.044
122 K	C	4.26	2.045	C	4.15	2.045
$Fe(Et_2dsc)_3$[b]						
295 K	B		2.053	B		2.05[c]
120 K	D		2.051	C[d]		2.053
$Fe(Pyr\text{-}tsc)_3$						
297 K	A		2.047	A[d]	4.13	2.050
120 K	C	4.24	2.046	C[e]	4.23	2.049
$Fe(Pyr\text{-}dsc)_3$						
297 K	D[f]		2.053	D		2.056
120 K	D[e]	4.3	2.053	D	42.7	2.055
$Fe(Mor\text{-}tsc)_3$						
297 K	D	4.25	2.046	D[g]		2.048
120 K	D		2.045	C	4.17	2.045
$Fe(Mor\text{-}dsc)_3$						
297 K	D[e]	4.12	2.054	D		2.056
120 K	D[e]	4.28	2.051	D	4.21[e]	2.054
$Fe(Pip\text{-}tsc)_3$						
297 K	D	4.24	2.042	B		2.049
120 K	D	4.29	2.044	C[d]	4.28	2.049
$Fe(Pip\text{-}dsc)_3$						
297 K	D		2.054	B	4.21	2.055
120 K	D	4.28	2.052	D	4.26	2.053
$Fe(Bz_2tsc)_3$						
297 K	D	4.21	2.046	*[h]		2.027[c]
120 K	D	4.27	2.044	*[i]	4.25	2.052
$Fe(Bz_2dsc)_3$						
297 K	D[j]		2.055[c]	*[h]	4.1	2.054
120 K	D[j]		2.054[c]	*[d]	4.29	2.052
$Fe(cHex_2tsc)_3$						
297 K	D[k]	4.22	2.043	D	4.2[g]	2.047
120 K	D[k]	4.22	2.043	D	4.5[g]	2.045

[a] Classification as to overall shape of spectrum as shown in Fig. 1, * does not correspond to the classification scheme.
[b] Ref. 1.
[c] Narrow line superimposed on broad peak.
[d] Three relatively narrow lines in the region $g \approx 2.0$.
[e] Small peak at $g \approx 2.4$.
[f] A number of peaks of low intensity between $g = 2$ and 4.
[g] Very broad absorption line.
[h] A peak at $g \approx 2.4$ and a broad absorption at $g \approx 2.0$.
[i] Absorption at $g \approx 2$ is broad.
[j] Some structure around narrow line.
[k] Additional weak absorption in the region $g \approx 2$.

substantial, possible anisotropic, *g* shift away from the free electron value is predicted. This is in agreement with Hall and Hendrickson's assignment for the $S = 1/2$ line. If the temperature is above the low-temperature limit, one expects the excited state consisting of a full e′ and the paramagnetic electron in the low-lying a_1' to be somewhat populated. This configuration would yield a narrow EPR line with a *g* value close to the free electron value. The width would be in the order of 10 gauss compared to the 2000 gauss line which one gets for the ground state line, so that even if the excited state line had an intensity of 10% of that of the ground state, one would crudely expect the height of the narrow line to be 1000 times that of the broad line. This is consistent with our assignment [1, 2, 11–13], and our observation that the narrow line is not the EPR spectrum of a copper impurity.

Acknowledgements

We acknowledge the assistance of D. Patterson in obtaining preliminary EPR spectra. W.D. wishes to express his appreciation to the Center for International and Comparative Programs, Kent State University for support. Support from NSF Grant CHE86-09272 is gratefully acknowledged.

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