If the average observed Cu–N bond distance is plotted against the dihedral angle between ligands, an interesting trend emerges for the $Cu(dmp)_2^+$ and $Cu(bcp)_2^+$ systems (Figure 2). The Cu–N distance increases with the degree of flattening. This is reasonable because interligand repulsions between opposing methyl groups are expected to increase as the dihedral angle decreases. Consistent with this interpretation, the $Cu(phen)_2^+$ system subtends a wide range of dihedral angles with little change in the average Cu–N bond distance.[16] The trend in the data reported in Figure 2 also strongly supports the contention that lattice forces, rather than intramolecular bonding interactions, are responsible for the flattening distortion.[30]

The fact that the dihedral angles subtended by the phenyl groups are much less than 90° is in accord with a previous analysis of the charge-transfer absorption intensity.[4] Although the interplanar angles are smaller in the complex than in the free ligand, it is not clear whether this occurs as a result of an intramolecular π-bonding interaction or a lattice effect. In any event, neither the intramolecular nor the intermolecular forces that exist in the solid state suffice to overcome the severe hydrogen atom/hydrogen atom contacts required for the phenyl substitutents to be coplanar with the phenanthroline core. It remains to be seen whether intercalation into DNA depends upon an in-plane orientation of the phenyl groups.

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Supplementary Material Available: Tables listing positional parameters and their estimated standard deviations, bond angles and bond distances, general temperature factor expressions, and least-squares planes along with their dihedral angles (12 pages); a table of calculated and observed structure factors (26 pages). Ordering information is given on any current masthead page.

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Powder EPR of Tris(diethylthioselenocarbamato)- and Tris(diethyldiselenocarbamato)iron(III) Diluted in the Analogous Cobalt(III) and Indium(III) Complex Matrices

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The tris(diorganodichalcogenocarbamato)iron(III) complexes are a well-characterized $^6A_1 \rightleftharpoons {}^2T_2$ spin-crossover system and the relative population of high-spin and low-spin electronic configurations depends on the coordinating chalcogen (O, S, or Se), temperature, pressure, physical state (solution or solid, solvated or without solvents of crystallization), and the nature of the organic substituents.[2]

While Mössbauer spectroscopy sees only the averaged spectra of the two electronic configurations,[3] the EPR[4,5] and infrared spectroscopic[4,6] time scales are sufficiently short to see separate signals from both high-spin ($^6A_1$) and low-spin ($^2T_2$) states. The potential problem of intermolecular spin-coupling between adjacent Fe(III) ($3d^5$) atoms in the EPR has been addressed by diluting the sample in a host matrix of the corresponding Co(III) ($3d^6$) complex or a frozen glass.[4,7,8]

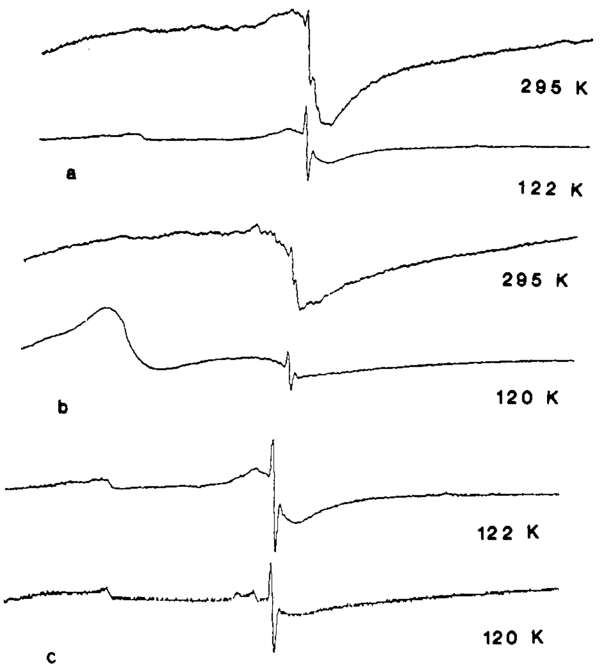

Figure 1. Powder EPR (X-band) spectra of (a) 1% $Fe(SSeCN(C_2H_5)_2)_3$ in a solid matrix of $Co(SSeCN(C_2H_5)_2)_3$ as a function of temperature, (b) 1% $Fe(SSeCN(C_2H_5)_2)_3$ in a solid matrix of $In(SSeCN(C_2H_5)_2)_3$ as a function of temperature, and (c) 1% $Fe(SSeCN(C_2H_5)_2)_3$ in a solid matrix of $Co(SSeCN(C_2H_5)_2)_3$ (upper spectrum) and 1% $Fe(Se_2CN(C_2H_5)_2)_3$ in $Co(Se_2CN(C_2H_5)_2)_3$ (lower spectrum) at the temperature indicated. Sweep width is from 510 to 6310 G. Amplitudes have been normalized so that the narrow line at $g = 2$ has approximately the same amplitude in all spectra.

We report the first EPR spectra of magnetically dilute tris(thioselenocarbamato)- and tris(diselenocarbamato)iron(III) complexes.

Experimental Section

Each of the following complexes have been prepared by methods similar to those reported in the literature and gave satisfactory elemental analyses: $Fe(SSeCN(C_2H_5)_2)_3$;[9,10] $Co(SSeCN(C_2H_5)_2)_3$ and $In(SSeCN(C_2H_5)_2)_3$;[9] $Fe(Se_2CN(C_2H_5)_2)_3$;[11,12] $Co(Se_2CN(C_2H_5)_2)_3$;[13-15] $In(Se_2CN(C_2H_5)_2)_3$.[16]

Magnetic Data. Magnetic susceptibilities (4–320 K) were measured on a SQUID magnetometer. The calibration and method of operation are described elsewhere.[17]

EPR Spectra. The samples were sealed in 4-mm-o.d. quartz tubes under approximately 0.5 atm of nitrogen. Data were obtained by using an IBM 200D-SRC spectrometer with an ER 044 MRDH X-band microwave bridge. The temperature was controlled with an IBM ER 4111

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Table I. Comparison of Temperature-Dependent Magnetic Moments (Solid State) for Fe(XYCNEt$_2$)$_3$, Where X, Y = O, S, or Se

	magnetic moment, μ_B			
T,[a] K	Fe-(OSCNEt$_2$)$_3$[b]	Fe-(S$_2$CNEt$_2$)$_3$[c]	Fe-(SeSCNEt$_2$)$_3$	Fe-(Se$_2$CNEt$_2$)$_3$[d]
310		4.40	4.54	3.93
298	5.71	4.29		
288		4.17	4.37	3.87
228	5.42		3.80	3.66
188		2.86	3.29	3.48
169	4.94	2.67	3.04	3.41
148	4.72	2.52	2.80	3.33
134	4.54	2.40	2.67	3.23
90	3.86	2.22	2.42	3.09
80	3.65		2.39	3.04
40	2.78[e]		2.29	2.62
10	1.22[e]		2.11	1.73
7				1.60

[a] Temperature ±2 K for convenience in setting up the table. [b] Reference 19. [c] Reference 20 (values estimated from graph). [d] Earlier studies[11,12] reported magnetic moments ranging from 2.37 (292 K) to 1.98 μ_B (98 K) and 4.39 (364 K) to 2.28 μ_B (102 K), respectively. [e] Reference 8. At 294 K, 5.48 μ_B; magnetic moment values below 30 K were attributed to weak antiferromagnetic interactions.

VT temperature controller, which has a precision of 1 K.

Results

Parts a and b of Figure 1 show the EPR spectra of tris(diethylthioselenocarbamato)iron(III), Fe(Et$_2$tsc)$_3$, as a 1% powder in a matrix of tris(diethylthioselenocarbamato)cobalt(III) or -indium(III), at 295 and 120–122 K. The magnetic moment of the undiluted iron(III) complex as a function of temperature, along with the temperature-dependent magnetic moments of other tris(diethyldichalcogenocarbamato)iron(III) complexes, is shown in Table I. The magnetically dilute samples are expected to be in a spin-crossover configuration as well. (The magnetic moment of Fe(Et$_2$tsc)$_3$ in chloroform solution has been reported as 3.95 μ_B at room temperature.[10]) The overall features of the spectra correspond to those reported earlier[18] for the undiluted Fe(R$_2$tsc)$_3$ complexes (where R is an organic substituent, e.g., C$_2$H$_5$), namely broad, poorly resolved lines in the low-field region (approximately $g = 4$) and two signals around $g = 2$: a broad, poorly resolved line and a relatively narrow line. Figure 1 indicates that, with deceasing temperature, the spectral changes in both cobalt(III) or indium(III) matrices parallel the changes reported for the undiluted tris(morpholinecarboselenothioato)iron(III) in the same temperature range,[18] a narrowing of the $g = 4$ line and a decrease in the intensity of the broad $g = 2$ line (both assigned to the $^6A_1$ state) relative to the narrow $g = 2$ line (assigned to the $^2T_2$ state). Figure 1 also indicates that dilution in Co(III) and In(III) are not equivalent; the same features are seen in each spectra, but there is a substantial difference in the broadening and relative intensities of the broad absorptions between these two different matrices. In this and all subsequent compared spectra, the spectra have been normalized so that the narrow lines at $g = 2$ are of comparable amplitude.

Figure 1c compares the low-temperature (122 K) EPR spectrum of Fe(Et$_2$tsc)$_3$ in a matrix of Co(Et$_2$tsc)$_3$ to the corresponding diselenocarbamates (1% Fe(Et$_2$dsc)$_3$ in Co(Et$_2$dsc)$_3$) at 120 K. The same features are observed in each spectrum, except for a decrease in the relative intensity of the broad lines in the diselenocarbamate.

Table II gives the g values for the most prominent features of each spectrum. The g value of the broad line in the $g = 2$ range is difficult to measure because of its width and the narrow line superimposed within it. The measurement of relative intensities of these lines is complicated for the same reasons.

Table II. *g* Values of the Low-Field and Narrow High-Field Signals for Tris(diethylthioselenocarbamato)- and Tris(diethyldiselenocarbamato)iron(III)

	g values			
	Co(III) matrix		In(III) matrix	
compd	low-field line	narrow high-field line	low-field line	narrow high-field line
Fe(Et$_2$tsc)$_3$				
295 K		2.047	4.25	2.044
122 K	4.26	2.045	4.15	2.045
Fe(Et$_2$dsc)$_3$				
295 K		2.053		2.05[a]
120 K		2.051		2.053

[a] Line superimposed on broad line making precise determination of *g* value difficult.

Discussion

The interpretation applied to the undiluted complexes[18] fits these spectra as well: the relatively narrow signal at $g = 2$ is the result of the $^2T_2$ state, the broader lines at $g = 4$ and $g = 2$ are the result of the higher spin configuration, almost certainly a $^6A_1$ state. In Figure 1, decreasing temperature results in a decreased magnetic moment, caused by a relatively higher population of the $^2T_2$ state. The spectrum of the magnetically dilute sample exhibits the same peaks as the undiluted samples. There is no evidence that any of these signals involve intermolecular coupling of adjacent Fe(III) atoms.

Comparison of spectra of Fe(Et$_2$tsc)$_3$ and Fe(Et$_2$dsc)$_3$, diluted in the appropriate Co(III) matrix, parallels that of the spectra of the undiluted morpholyl derivatives at room temperature. The greater relative intensity of the $^2T_2$ narrow line for Fe(Et$_2$dsc)$_3$ is surprising, since the solid-state, low-temperature (approximately 120 K) magnetic moment for *undiluted* Fe(Et$_2$dsc)$_3$ (3.20 μ_B) is higher than that for *undiluted* Fe(Et$_2$tsc)$_3$ (2.60 μ_B), but this may due to the effect of the dilution matrix upon the ligand field.

The selection of an "inert" matrix to minimize intermolecular electronic interactions between neighboring Fe(III) centers is difficult. The analogous Co(III) complex has been used before, and in this study, both Co(III) and indium(III) have been used. Ideally, the inert crystalline matrix should be identical with the iron complex with the sole exception of being diamagnetic.

Crystal structures of the thioselenocarbamates of iron, cobalt, and indium have not yet been determined, but they are expected to be similar to those of the corresponding dithiocarbamates. A comparison of the room-temperature crystal structures of tris(diethyldithiocarbamato)iron(III),[21] -cobalt(III),[22,23] and -indium(III)[24] reveals that the iron(III) ($3d^5$) structure is more like the cobalt(III) ($3d^6$) structure than the indium(III) ($4d^{10}$) structure: M–S, 2.35_7, 2.25_8, and 2.59_1 Å; C–S, 1.70_8, 1.70_4, and 1.72_5 Å; S–C–S, 112.7, 111.6, and 118.3°; C(Et)–N–C(Et): 119.6, 120.2, and 116.4°. The three complexes do exhibit three different space groups ($P2_1/c$, $C2/c$, and $A2/a$, respectively) but the Fe(III) complex changes to $C2/c$ at low temperature. The three complexes differ substantially, however, in two parameters that are quite important to spin-crossover behavior: S$_2$C–NC$_2$, 1.33_7, 1.31_4, and 1.32_8 Å; θ (half the angle between the two C_3 faces of the distorted octahedron), 18.8, 21.9, and 17.2°.

It seems reasonable that an important difference is the increased size of the In(III), resulting in longer M–S bond distances and significant differences in the M(S$_2$C–)$_3$ core. Indium(III) may provide a larger void to Fe(III) than the Co(III) crystalline matrix. Pressure studies on Fe(S$_2$CN(C$_2$H$_5$)$_2$)$_3$ have shown a decreasing magnetic moment with increasing pressure,[20] so that the presumably larger void in In(III) could shift the spin-crossover Fe(III) to *higher* spin. Hamilton and Sinn have found[25] that the magnetic

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moments of ferric dithiocarbamates are *lowered* by doping them into the cobalt(III) analogues that were isostructural between the two metals. The effect of doping the $Fe(dtc)_3$ into the low-spin $Co(dtc)_3$ crystal is analogous to an applied external pressure of hundreds of atmospheres.[25] We observed a greater relative intensity of the peaks assigned to the $^6A_1$ state in the In(III) matrix compared to the Co(III) matrix (cf., low-temperature spectra in Figure 1c). The previous dithiocarbamate results[20,25] support our present work.

The EPR spectra of $Fe(SSeCN(C_2H_5)_2)_3$ indicate changes in the strength of the ligand field, and indeed, there is no evidence of significant intermolecular interaction between neighboring Fe(III) atoms in the undiluted system.

The comparison of the solid magnetic moments in Table I reveals that, for these diethyl complexes in the solid state, the expected ligand-field strength increases with increasing size of chalcogen: $^-OSCNR_2 < {}^-S_2CNR_2 < {}^-SSeCNR_2 < {}^-Se_2CNR_2$ is not uniformly observed; $^-S_2CNEt_2 > {}^-SSeCNEt_2$ at room temperature; $^-S_2CNEt_2 > {}^-SSeCNEt_2 > {}^-Se_2CNEt_2$ at 90 K. Also noteworthy is the anomalously low magnetic moment for $Fe(Et_2dsc)_3$ at temperatures below 20 K. Similar low-temperature results have been reported for $Fe(OSCNEt_2)_3$[8] and were ascribed to weak antiferromagnetic interactions. An alternative explanation involves the presence of diamagnetic impurities. Magnetic susceptibility studies are now in progress on other thioseleno- and diselenocarbamates of iron(III) derivatives to examine this trend.

The comparison of g values in Table II reveals no significant changes in g values for Fe(III) in going from a Co(III) to In(III) matrix, but does support earlier reports[18] of g values for the narrow line in the $g = 2$ region increasing: $^-SSeCNR_2 < {}^-Se_2CNR_2$.

These results, combined with an earlier study[18] on undiluted complexes, indicate clearly that the thioselenocarbamates and diselenocarbamates of Fe(III), like the dithiocarbamates of Fe(III),[4–6] are in spin-state equilibrium, involving two distinct electronic states.

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Solid-State Emission of Dicyanoplatinum(II) and -palladium(II) Complexes of Substituted 2,2′-Bipyridines and 1,10-Phenanthroline and X-ray Crystal Structures of Isomorphous $M(bpy)(CN)_2$ (bpy = 2,2′-Bipyridine; M = Pt, Pd)

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Square-planar metal d^8 complexes are known to exhibit metal–metal bonding interactions in the solid state.[2] Such interactions between molecules stacked within a chain lead to anisotropic and characteristic spectral properties. In the course of designing new catalysts for photochemical substrate reduction and oxidation, we become interested in square-planar platinum(II) complexes having planar and nonbulky π-acid ligands such as 2,2′-bipyridine, cyanide, and alkyl isocyanides. Platinum(II) complexes of this type are likely to have long-lived excited $(d_{\sigma}{}^{*}p_{\sigma})$ triplets, which are emissive as suggested by the studies of Gray and co-workers.[3] We report here solid-state emission properties of a class of $Pt(L\text{-}L)(CN)_2$ compounds (L-L represents a chelating aromatic diamine) that are stacked and columnar as illustrated by the X-ray structure of $Pt(bpy)(CN)_2$ (bpy = 2,2′-bipyridine).[4] The X-ray structure of $Pd(bpy)(CN)_2$ and its spectroscopic properties are also included for comparison.

Experimental Section

Reagents and Chemicals. K_2PtCl_4 and $Pd(CN)_2$ were purchased from Strem. The ligands 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen), and 4,4′-dimethyl-2,2′-bipyridine (4,4′-Me_2bpy) were obtained from Aldrich. $Pt(CN)_2\cdot xH_2O$ was prepared by literature methods.[5,6]

Instruments. Steady-state emission spectra (corrected) were recorded with Corning filters on a Hitachi 650-60 fluorescence spectrophotometer. Solid-state emission lifetimes were measured with a Quanta-Ray Q-switched DCR-3 pulsed Nd:YAG laser (excitation 355 nm).

$Pt(bpy)(CN)_2$. The complex was prepared by the following two methods.

Method A. A mixture of $Pt(CN)_2\cdot xH_2O$ (0.5 mmol) and 2,2′-bipyridine (3 mmol) in pyridine (15 mL) was stirred and refluxed for 20 h. An orange-red suspension was obtained. Upon cooling of the solution to room temperature and addition of diethyl ether, an orange-red solid precipitated out, which was filtered out and washed with diethyl ether. The yield was 52%.

Method B. $Pt(CN)_2\cdot xH_2O$ (1 mmol) was dissolved in aqueous ammonia (20%, 20 mL), which was then added dropwise to a refluxing dimethylformamide solution of 2,2′-bipyridine (9 mmol in 20 mL). After addition, the solution was refluxed for 5 h, during which the color changed from yellowish green to orange and then red. After refluxing, the solution mixture was cooled to 0 °C. An orange-red solid was deposited, which was filtered out and washed with ice-cooled dimethylformamide and diethyl ether. The yield was 63%. The crude product was then recrystallized in hot dimethylformamide (0.3 g in 200 mL) to give red needle-shaped crystals.

Both methods gave the same product as judged by their identical UV–vis spectra in dimethylformamide.

Anal. Calcd for $Pt(bpy)(CN)_2$: C, 35.7; H, 2.0; N, 13.9. Found: C, 35.5; H, 2.3; N, 14.1. IR (Nujol mull): ν(CN), 2130, 2120 cm^{-1}.

$Pt(4,4'\text{-}Me_2bpy)(CN)_2\cdot 2H_2O$. $Pt(CN)_2\cdot xH_2O$ (2.4 mmol) was dissolved in aqueous ammonia (25%, 50 mL), which was added dropwise to a refluxing dimethylformamide solution of 4,4′-Me_2bpy (24 mmol in 70 mL). The solution was heated at 100 °C for 7 h. Upon cooling of the solution, a yellow solid together with the white free ligand was deposited. The free ligand was separated from the product by washing with dichloromethane. The crude product was yellowish green in color and was purified by recrystallization in hot acetonitrile. The yield was 60%.

Anal. Calcd for $Pt(4,4'\text{-}Me_2bpy)(CN)_2\cdot 2H_2O$: C, 36.0; H, 3.5; N, 12.0. Found: C, 35.7; H, 3.1; N, 12.0. IR: ν(OH), 3400 cm^{-1} ν(CN), 2130, 2120 cm^{-1}.

$Pt(phen)(CN)_2$. It is similarly prepared as its bpy analogue. The crude product was recrystallized in hot dimethylformamide to give violet needle-shaped crystals. The yield was 31%.

Anal. Calcd for $Pt(phen)(CN)_2$: C, 39.3; H, 1.9; N, 13.1. Found: C, 39.1; H, 1.9; N, 13.2. IR: ν(CN), 2120, 2105 cm^{-1}.

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