4b, we obtain $h\nu = (1 + \rho)\Delta G = \alpha\Delta G$, where $\alpha = (1 + \rho)$. Then, recalling $\Delta G = nF\Delta E_{1/2}$(excitn)

$$h\nu \text{ (in eV)} = \alpha\Delta E_{1/2}(\text{excitn}) \qquad (5)$$

This is the physical justification for omitting an explicit constant in eqs 1 and 2.

Note that in situations outside the present context when E_0 becomes very small, as in intervalence charge transfer, ρ rises rapidly and $h\nu \gg E_0$.[26] Thus it is an abuse of the model to extrapolate the relationship to an intercept despite the excellent linearity in the present domain.

Finally, we take the opportunity to show that Lever's expression for relating $h\nu$ to measured electrode potentials (eq 4 of ref 23), though apparently more complex in form, corresponds to our starting point (eq 4b).

$$E_{\text{op}} = h\nu = [\chi_i + nF\Delta E(\text{redox}) + \Delta\Delta G_s + Q] + \chi_o + \Delta(\text{sol}) \qquad (6)$$

In ref 23, χ_i and χ_o are used expressly for the *free energy* of reorganization, ΔE(redox) refers to the disproportionation reaction, and $\Delta\Delta G_s$ and Δ(sol) are solvation terms. Standardizing symbols and regrouping gives

$$h\nu = [nF\Delta E_{1/2}(\text{dispro}) + Q + \sum\Delta G_{\text{solv}}(\text{ML}_g^{*} + \text{ML}_g^{0} - \text{ML}_g^{+} - \text{ML}_g^{-})] + \lambda_i + \lambda_o \qquad (7)$$

However Q is the "gas-phase resonance energy", so that $[Q + \sum\Delta G_{\text{solv}}]$ equals $nF\Delta E_{1/2}$(compro). Thus, eq 7 is equivalent to

$$h\nu = nF[\Delta E_{1/2}(\text{dispro}) + \Delta E_{1/2}(\text{compro})] + \lambda_i + \lambda_o \qquad (8)$$

The sum of the disproportionation and comproportionation/promotion reactions in solution is the excitation reaction, (c–a), above, so eq 6 is fully equivalent to eq 4b.

Supplementary Material Available: Tables of analytical data and data for Figures 5 and 6 (2 pages). Ordering information is given on any current masthead page.

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Evidence for Intermediate ($S = 1$) Spin State Stabilization in $\text{Fe}^{\text{II}}(4,4'\text{-dpb})_2(\text{NCS})_2$ and $\text{Fe}^{\text{II}}(4,4'\text{-dpb})_2(\text{NCSe})_2$ (dpb = Diphenyl-2,2′-bipyridyl) from Susceptibility, Infrared, and ^{57}Fe Mossbauer Data

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Magnetic susceptibility, ^{57}Fe Mossbauer spectroscopy, and variable-temperature FTIR spectroscopy have been used to characterize the spin states of $\text{Fe}^{\text{II}}(4,4'\text{-dpb})_2\text{X}_2$ (dpb = diphenyl-2,2′-bipyridyl; X = NCS^-, NCSe^-) in the temperature range $6 \le T \le 460$ K. Both complexes show a continuous variation of the field-dependent effective magnetic moment over this range. Below ~325 K, both the infrared and Mossbauer spectroscopic signatures are insufficient to permit characterization of the spin state(s) of the metal atom in these complexes, but at higher temperatures, the FTIR data can be accounted for by the increasing population of a high ($S = 2$) spin state, while the Mossbauer spectra can be accounted for by a rapid (on the Mossbauer time scale) relaxation between two spin states. The existence of an intermediate ($S = 1$) spin state for Fe(II) is a consequence of a major distortion from octahedral symmetry of the metal-based orbitals, permitting a (near) degeneracy of the d_{z^2} and d_{xy} levels around this atom.

Introduction

It is well understood that a triplet state ($S = 1$) cannot be the ground state for an iron(II) ion in an ideal octahedral environment due to the degeneracy of the t_{2g} energy levels. However, if the effective ligand field is less than cubic, the possibility of a triplet ground state becomes theoretically possible.[1] $[\text{Fe}^{\text{II}}([15]\text{ane-N}_4)(\text{NO}_2)](\text{PF}_6)$, where $[15]\text{ane-N}_4$ = 1,4,8,12-tetraazacyclopentadecane, is the single six-coordinated iron(II) complex that has been reported to have a triplet ground state throughout the temperature region studied (96–352 K).[2] This complex is expected to be severely distorted from octahedral symmetry if the nitro group is bonded to the iron atom through both of the oxygen atoms, as suggested by the infrared data reported by these authors. Other claims of such $S = 1$ six-coordinate iron(II) complexes have been reported in the past, but have been retracted, on the basis of further experiments that indicated ground states other than a triplet state.[3] A few four-coordinate Fe^{2+} porphyrins have been reported to be in a triplet ground state on the basis of several experimental techniques,[4a] and a crystal structure has been reported. However, these complexes have a square-planar geometry, and therefore, their triplet state results from, and is different from, the triplet state that would exist in a six-coordinate complex. An intermediate spin state for a five-coordinate Fe(II) reported by Bacci et al.[4b] shows a smooth variation of the magnetic moment between 86 K ($\mu_{\text{eff}} = 0.98\ \mu_B$) and 376 K ($\mu_{\text{eff}} = 2.26\ \mu_B$).

The synthesis of new complexes that are related to known iron(II) spin-crossover complexes [complexes known to undergo a thermally driven spin-state transition between the high-spin state (HS, $S = 2$) and the low-spin state (LS, $S = 0$)] has been one objective of the present investigation. Such studies have been motivated by an effort to understand the effects that small changes in the microstructure of a complex have on the details of the spin-crossover transitions. Two new complexes have been synthesized: $\text{Fe}(4,4'\text{-dpb})_2(\text{NCS})_2$ and $\text{Fe}(4,4'\text{-dpb})_2(\text{NCSe})_2$, where 4,4′-dpb is a 4,4′-diphenyl-2,2′-bipyridine. These complexes are related to the well-studied spin-crossover complex $\text{Fe}(\text{bpy})_2(\text{NCS})_2$, where bpy = 2,2′-bipyridine. The magnetic and spectroscopic properties of the diphenyl complexes are quite different from those of $\text{Fe}(\text{bpy})_2(\text{NCS})_2$. This paper reports and discusses the magnetic, infrared, and ^{57}Fe Mossbauer data for the newly synthesized

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complexes and presents a model that can be used to account for their unusual properties.

Experimental Section

Synthesis. $Fe(4,4'\text{-}dpb)_2(NCS)_2$ and $Fe(4,4'\text{-}dpb)_2(NCSe)_2$ were synthesized by using modification of the general literature method, which consists of first preparing the corresponding "tris" $[Fe(4,4'\text{-}dpb)_3][NCS]_2$ and $[Fe(4,4'\text{-}dpb)_3][NCSe]_2$ complexes[5] and then refluxing these in an appropriate solvent to obtain the desired "bis" product. All manipulations were performed under an argon atmosphere. Specific modifications employed in the present instances are as follows: In order to make the tris compound, 3 equiv of 4,4'-dpb was dissolved in warm ethanol, and the solution was added to 1 equiv of $(NH_4)_2Fe(SO_4)_2{\cdot}6H_2O$ dissolved in warm H_2O to which 2 equiv of KNCS or KNCSe, dissolved in H_2O, was then added. The red solution was maintained at 70–90 °C for 2–3 h and then allowed to cool slowly overnight. The resulting black precipitate was filtered out, washed with a small amount of argon-purged H_2O, and dried under vacuum. $Fe(4,4'\text{-}dpb)_2(NCS)_2$ and $Fe(4,4'\text{-}dpb)_2(NCSe)_2$ were obtained by refluxing the appropriate tris compound in dry toluene for 2 days and were characterized by VTFTIR and ^{57}Fe Mossbauer spectroscopy, SQUID magnetic susceptibility, and elemental analysis. Anal. Found (calcd) for $C_{46}H_{32}FeN_6S_2$: C, 70.1 (69.1); H, 4.1 (4.1); N, 10.6 (10.2). Found (calcd) for $C_{45}H_{32}FeN_5Se_2$: C, 62.1 (62.6); H, 3.5 (3.7); N, 8.9 (9.5). The color of these two compounds is dark green, in contrast to the usual red to maroon color of the closely related complexes $[Fe(L)_2(X)_2]$, where L is a bipyridyl or 1,10-phenanthroline type ligand and X = NCS^- or $NCSe^-$.

An ^{57}Fe-enriched sample of $Fe(4,4'\text{-}dpb)_2(NCS)_2$ was synthesized as follows: An enriched sample of Fe_2O_3 was reduced to the metal at 750 °C over 6 h in forming gas (15% H_2; 85% N_2) and then transferred to Schlenk glassware. From this point on, all synthetic manipulations were carried out under an argon atmosphere. An excess of HBr (in H_2O) was then added, and the solution was allowed to react at room temperature until all of the metal had dissolved. At this point, the solution was filtered and the solvent removed under vacuum. The resulting solid $FeBr_2$ was dissolved in a small amount of H_2O and 3 equiv of 4,4'-dpb, partially dissolved in warm ethanol, was added to the $FeBr_2$ solution. An excess of NaSCN, dissolved in H_2O, was added. The resulting solution was maintained at ~70 °C for 1 h and then allowed to cool slowly with stirring overnight. The resulting tris complex was filtered out, vacuum-dried, and then refluxed in dry toluene for 2 days. The dark green solid was filtered from the hot toluene solvent and washed with more hot toluene. The sample was characterized by variable-temperature FTIR and ^{57}Fe Mossbauer spectroscopy.

Physical Measurements. Variable-temperature magnetic data were collected by using a SQUID magnetic susceptometer (Quantum Design, Inc.) with the (~12–22-mg) samples held in a Lilly No. 5 clear gelatin capsule. Effective magnetic moments were calculated from $\mu_{eff} = 2.828[\chi_m(T - \Theta)]^{1/2}$, where χ_m is the corrected molar susceptibility and the Weiss constant is assumed to be zero. Diamagnetic corrections were made for the sample holder and for the diamagnetic contribution of the complex being measured. The diamagnetic contributions were determined by using values of -35×10^{-6} cgsu mol^{-1} for the NCS complex and -40×10^{-6} cgsu mol^{-1} for the NCSe complex as determined previously.[6] The remaining contributions were calculated by using Pascal constants. The corrections for the two complexes were -469.56×10^{-6} cgsu mol^{-1} for $Fe(4,4'\text{-}dpb)_2(NCS)_2$ and -479.56×10^{-6} cgsu mol^{-1} for $Fe(4,4'\text{-}dpb)_2(NCSe)_2$.

Low-temperature FTIR spectroscopy (6 K to room temperature) was carried out on an IBM 32 spectrometer as previously described.[7] Changes in the CN stretching modes of the NCS or NCSe ligand were used to follow the thermal conversion between spin states. All VTFTIR measurements were carried out as described previously[8,10] on neat samples dispersed in Kel-F mulls, to minimize effects due to crushing and pelletizing.[8,9]

High-temperature FTIR spectroscopy (room temperature to 460 K) was carried out on a Mattson Cygnus 100 spectrometer using KBr optics. The cell used in these studies employed a resistance wire heated brass sample holder fitted with a chromel–alumel thermocouple controlled feedback circuit to maintain temperature stability (±1 K in the range 295 < T < 461 K). All IR spectra were normalized to room temperature KBr blank data, but not otherwise corrected.

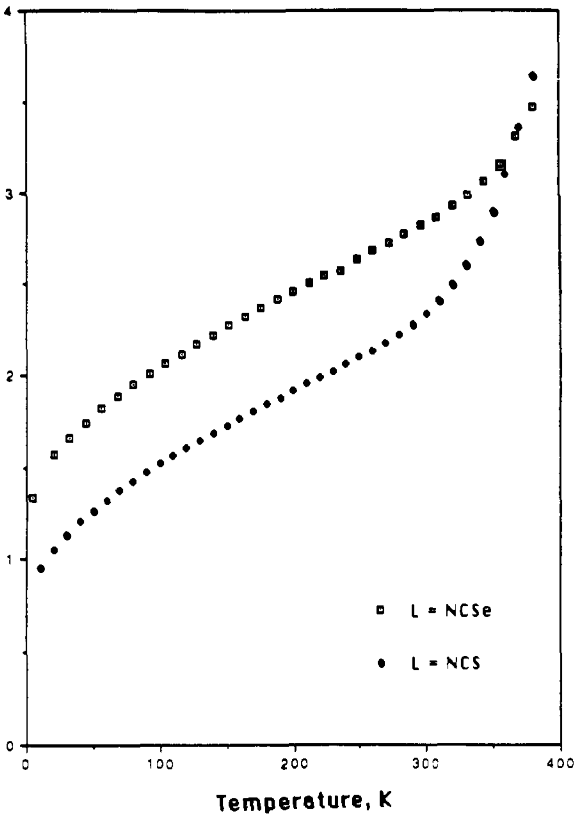

Figure 1. Effective magnetic moment of $Fe^{II}(4,4'\text{-}dpb)_2L_2$ (dpb = diphenyl-2,2'-bipyridine; L = NCS, NCSe) as a function of temperature.

For ^{57}Mossbauer spectroscopy, γ-ray resonance spectra were obtained at 90 and 295 K for $Fe(4,4'\text{-}dpb)_2(NCS)_2$ and $Fe(4,4'\text{-}dpb)_2(NCSe)_2$ and at various temperatures between 90 and 425 K for the ^{57}Fe-enriched sample of $Fe(4,4'\text{-}dpb)_2(NCS)_2$ by using a standard, constant-acceleration spectrometer calibrated with 0.5-mil metallic iron at room temperature. The neat microcrystalline powder sample was layered in a plastic sample holder and examined in transmission geometry. To reduce random statistical noise, $>10^6$ counts/channel were scaled at all temperatures, by using a 100-mCi $^{57}Co(Rh)$ source at room temperature in conjunction with a Harwell fast proportional counter. All isomer shifts are reported with respect to the centroid of the four inner lines of a room-temperature Fe(0) transmission spectrum.

Results and Discussion

Magnetic Susceptibility. The temperature dependence of μ_{eff}, as measured in a field strength of 1000 G, is shown for both $Fe(4,4'\text{-}dpb)_2(NCS)_2$ and $Fe(4,4'\text{-}dpb)_2(NCSe)_2$ in Figure 1. As can be seen, the effective moments of both complexes are sensitively temperature dependent in the ranges $10 \leq T \leq 380$ K for the NCS complex and $5 \leq T \leq 380$ K for the NCSe complex. The effective moment of the thiocyanate complex gradually increases from a value of 0.95 μ_B at 10 K to 2.34 μ_B at 300 K and then increases more rapidly to 3.64 μ_B at 380 K. Attempts to obtain meaningful data at higher temperatures were unsuccessful. Since the change in susceptibility is large, and a plot of χ^{-1} versus temperature (T < 300 K) is not linear (Figure 2), ferro- or antiferromagnetic coupling cannot be used to explain the temperature dependence of the effective moment. The most likely explanation for the magnetic data is that of a spin-state transition. If the spin-state transition is of the normal type, that is, a transition between the HS (S = 2) and LS (S = 0) forms of the complex, both forms should be present at room temperature. The presently discussed transition would be an unusual HS–LS transition in that the transition appears to occur in two steps, although such two-step HS–LS transitions have previously been reported.[11] It should

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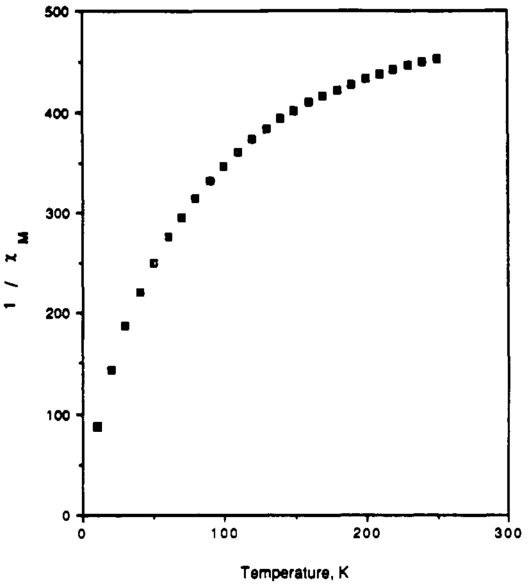

Figure 2. Reciprocal of the molar susceptibility of $Fe^{II}(4,4'\text{-dpb})_2(NCS)_2$ as a function of temperature.

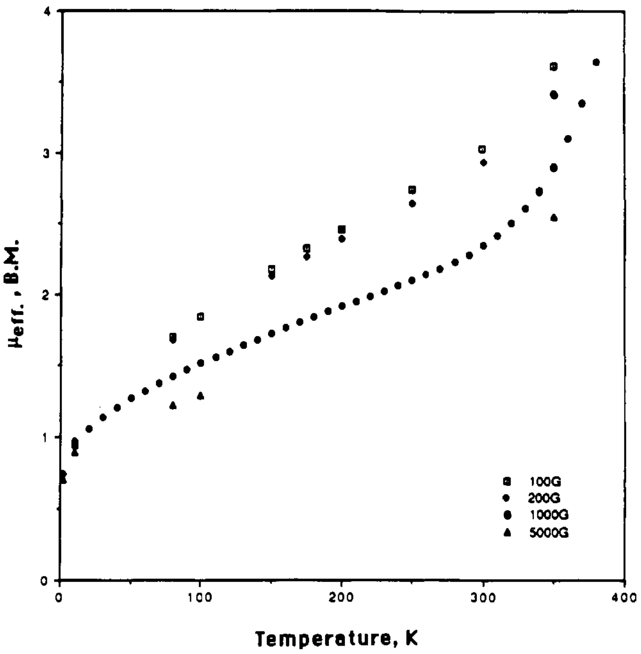

Figure 3. Effective magnetic moment of $Fe^{II}(4,4'\text{-dpb})_2(NCS)_2$ as a function of temperature at various field strengths.

be noted, however, that the two-step spin conversion in $[Fe(2\text{-pic})_3]Cl_2$ (2-pic = 2-picolylamine) reported by Guetlich et al.[11a] evidences distinct transitions at 120.7 and 114.0 K, with sharp maxima noted in the $d\chi/dT$ plot at these temperatures. Both the Mossbauer and susceptibility data are qualitatively different from the results noted in the present study. Similarly, the susceptibility data on the $Fe^{II}N_4O_2$ complex[11b] show two distinct crossover transitions separated by 30 K, which are interpreted by the authors as involving only HS and LS states, and a single structural phase over the range $90 < T < 300$ K. In contrast, the two-step transition observed by Koenig et al.[11c] involves a change from a seven-coordinate HS state to a six-coordinate LS state of the Fe(II) atom. In the case of the 4,4'-dpb complexes of the present study, both the infrared and ^{57}Fe Mossbauer data imply that such interpretations cannot account for the observed data (vide infra). Thus, it is appropriate to consider another possibility, namely that of an LS to intermediate-spin transition at $T < 300$ K and a transition of intermediate spin to HS at temperatures above 300 K. This type of transition has not previously been reported, but is possible on the basis of theoretical considerations.[1a]

A field-dependent study of the thiocyanate complex was carried out, and the results indicate that the effective moment is also field dependent, as shown in Figure 3. The effective moment of a pure spin state is expected to be field independent. Guetlich and co-workers have previously reported that the HS → LS transition temperature of $Fe(phen)_2(NCS)_2$ shifts by -0.11 ± 0.04 K when the applied field is changed from 1 to 5.5 T.[12] The rather large field dependence of the effective moment of $Fe(4,4'\text{-dpb})_2(NCS)_2$ suggests that the ground state at a given temperature (within the range studied) is not a pure spin state. The present data indicate the presence of some type of interaction or coupling that allows the ground and/or low-lying states to be substantially spin-mixed to some extent. In the theoretical calculations that have been reported,[1,13] spin-mixed states become possible when spin–orbit coupling is considered.

Variable-Temperature FTIR Spectroscopy. In previous variable-temperature infrared studies of Fe^{2+} spin-crossover complexes that contain coordinated NCS or NCSe ligands, the CN stretching mode of the NCS or NCSe ligand has been noted to be very sensitive to the spin state; that is, the stretch corresponding to the LS form is observed at a frequency that is 20–40 cm^{-1} higher than that arising from the HS form. Monitoring the relative absorbance of the CN stretching modes corresponding to the two states as a function of temperature (or irradiation as is the case for light-induced excited spin-state trapping experiments, LIESST) has been found to be a convenient method for monitoring such transitions.[8,10,14] In the context of the present discussion, such a study was carried out on $Fe(4,4'\text{-dpb})_2(NCS)_2$ and $Fe(4,4'\text{-dpb})_2(NCSe)_2$.

The CN stretching modes of the NCS complex at five temperatures between 6.5 and 305 K are shown in Figure 4. When the sample is cooled from 305 K, the two bands show only a normal thermal blue shift, and the relative absorbance of the two bands remains constant. If one of the two bands represented one spin state and the other band arose from another spin state, then the relative absorbance between the two bands should change, consistent with the magnetic susceptibility data. Since this is not observed, it can be inferred that the two IR modes at ~2100 cm^{-1} are the symmetric and asymmetric CN stretches, both of which are expected to be infrared active in a distorted cis octahedral ligand symmetry. The top spectrum in Figure 4, taken at 305 K, shows the two bands at 2107 and 2091 cm^{-1} (i.e., separated by 16 cm^{-1}). This separation between the symmetric and asymmetric stretches lies within the range reported earlier for related complexes, although the absolute positions are red-shifted by ~10 cm^{-1} relative to those of other LS complexes studied earlier at the same temperature. The IR data in the range $6 \leq T \leq 305$ K appear to suggest the presence of only a single spin state, in disagreement with the magnetic data. It should be noted that the promotion of two electrons from the t_{2g} to the e_g orbitals can change the CN stretching frequency by as much as 40–50 cm^{-1}.[8] Thus, the presence of the intermediate-spin state was expected to be readily noticeable in the IR spectra accumulated at 2-cm^{-1} resolution. This is not observed in the experimental data (see, for example, the data summarized in Figure 4). On the other hand, if only the HS and LS forms are present at 300 K, the μ_{eff} data suggest that the HS fraction should be about 50%, and this form should thus be readily noted in the IR spectra, with ν_{CN} at about 2074 cm^{-1}. Clearly, this is not the case. Similar low-temperature data are obtained for the NCSe complex, including the positions of the CN stretches, which are at 2108 and 2091 cm^{-1} at 305 K. Finally, it is worth noting that the IR spectra were carefully monitored for evidence of the formation of a trapped

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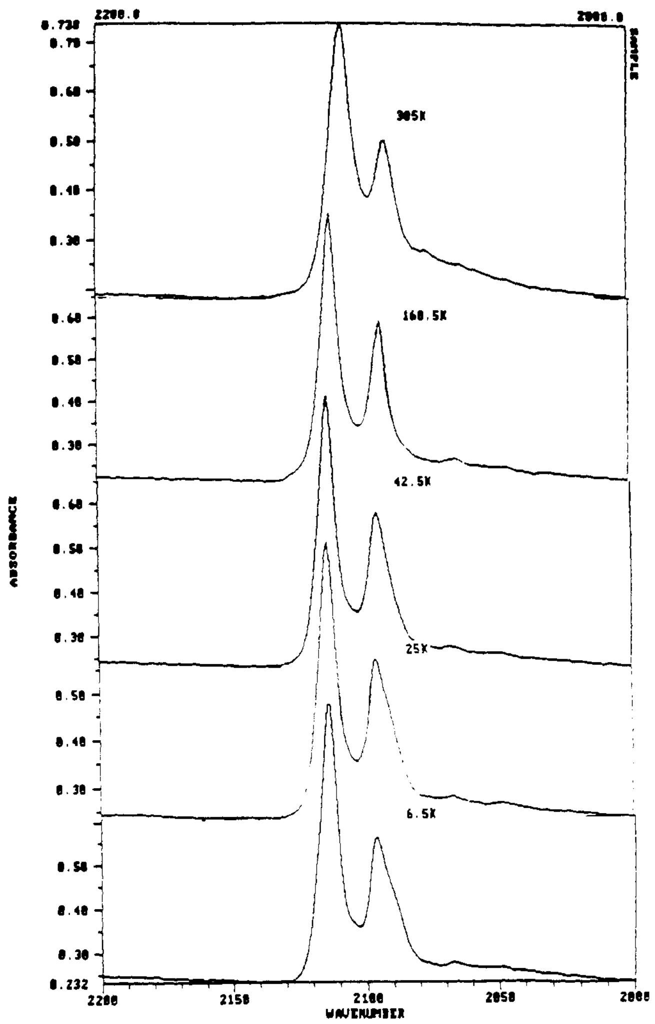

Figure 4. Infrared spectra of Fe^{II}(4,4'-dpb)$_2$(NCS)$_2$ in the CN stretching mode region in the temperature range $6.5 < T < 305$ K. The two absorbances arise from the symmetric and asymmetric stretching frequencies of the pseudohalide ligand and show the usual band sharpening at low temperatures. The intensity ratio of the two bands is essentially temperature independent in this range.

HS form (LIESST) in the NCS complex when it was irradiated with white light (under the same conditions as employed previously[8,10,14]) at 6 K for over 40 min. This experiment was carried out with the neat sample dispersed in Kel-F grease as well as with a sample pelletized in KBr. No evidence for the LIESST phenomenon was observed in any of these experiments.

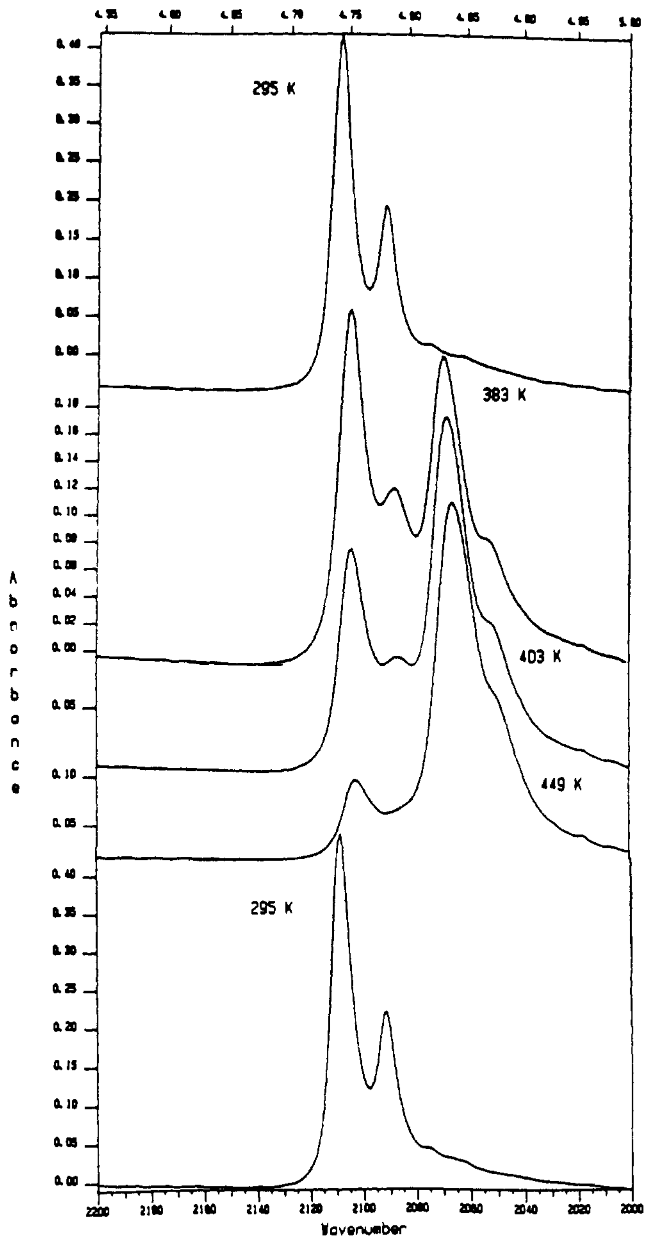

Figure 5. Same as Figure 4 for the temperature range $295 < T < 449$ K. The bottom spectrum is that of the sample heated to 449 K and then cooled slowly to room temperature, showing the reversibility of the spin-change transition.

Figure 5 shows the CN stretching region of the IR spectra of the thiocyanate complex at temperatures between 295 and 460 K. As the sample is warmed, a band begins to appear at ~2074 cm^{-1} (at ~325 K) and becomes more intense as the temperature is increased. In addition, a shoulder at ~2050 cm^{-1} becomes noticeable, while the absorbance of the two original bands (at ~2107 and 2090 cm^{-1}) decreases. These spectral changes are completely reversible, as evidenced by the data summarized in the bottom trace of Figure 5, which is of the sample warmed to 449 K and then recooled to room temperature. These results are similar to those observed previously for a system undergoing a spin-state transition and suggest that in the high-temperature regime a typical HS state is being populated. At 460 K (the high-temperature limit in this study), the more intense CN stretching mode is at 2071 cm^{-1} with a shoulder at ~2050 cm^{-1}. These values are within the range observed for similar complexes that are known to be in the HS form. On the basis of this evidence and the effective moments calculated at these higher temperatures, it is believed that at temperatures greater than 300 K a gradual spin-state transition to the HS form occurs. The nature of the spin state at $T < 300$ K cannot be elucidated solely from IR data, but the present evidence suggests that the (presumed) $S = 1$ state and the $S = 0$ state have infrared (CN stretching mode) signatures that cannot be resolved from each other.

The high-temperature FTIR data obtained for the NCSe complex are very similar to those of the NCS complex, the major difference being that the transition to the HS state appears to begin at a higher temperature (~350 K). In the few cases where the NCSe homologue of an NCS spin-crossover complex has been investigated, the HS–LS transition of the NCSe complex invariably occurs at a slightly higher temperature than that in the NCS complex. The present data agree with previous observations that the NCSe ligand gives rise to a somewhat larger crystal field strength at the metal center than does the NCS ligand, resulting in a higher spin-crossover transition temperature. The CN stretching mode, at the highest temperature monitored (452 K), of the presently discussed NCSe complex is observed at 2071 cm^{-1} with a shoulder at ~2050 cm^{-1}.

^{57}Fe Mossbauer Spectroscopy. Mossbauer spectroscopic data in the range $90 \leq T \leq 295$ K were obtained for both complexes in attempts to further characterize the spin state of these complexes in this regime, and a typical 90 K spectrum is shown in the top

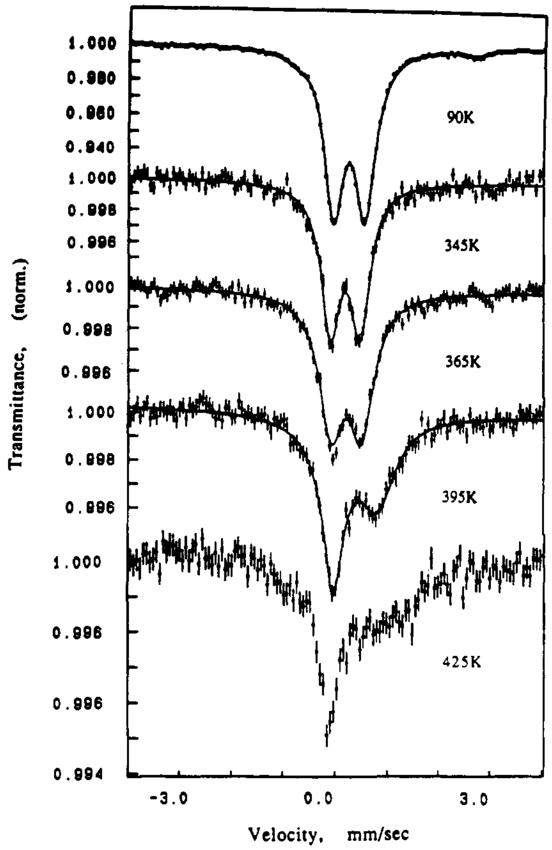

Figure 6. ^{57}Fe Mossbauer spectra of Fe^{II}(4,4′-dpb)$_2$(NCS)$_2$. The isomer shifts are indicated with respect to the centroid of a room-temperature absorption spectrum of metallic iron using the same source. The small absorbance at about 3 mm s^{-1} is due to an impurity component in the sample.

trace of Figure 6. The spectra of both complexes are again very similar, consisting of the expected doublet signature of Fe(II) in a noncubic ligand field. A small absorption is noted in the 90 K spectrum of the ^{57}Fe-enriched sample ($>10^6$ counts/channel) at a Doppler velocity of about 2.9 mm s^{-1}; this can be ascribed to one component of a minority impurity, which has a very small temperature dependence of the recoil-free fraction and is not further considered in the discussion. Throughout the above temperature regime, the hyperfine parameters do not change significantly for either complex, and are summarized in Table I. The spectra could be fit by a single doublet, with no relaxation effects observable within experimental error. The values of the Mossbauer parameters are typical for iron(II) LS complexes. The Mossbauer parameters obtained by Watkins et al.[2] for a six-coordinate iron(II) complex having a triplet ground state are $\Delta E_q \leq 0.40$ mm s^{-1} and $\delta_{IS} = 0.33$ mm s^{-1} at 298 K. The Mossbauer parameters obtained for both 4,4′-dpb complexes are very similar to these values, and thus the low-temperature Mossbauer spectra of the presently studied complexes can be attributed to either spin state, and are not adequate for distinguishing between the two.

A sample of Fe(4,4′-dpb)$_2$(NCS)$_2$ enriched in ^{57}Fe was used for high-temperature Mossbauer experiments to compensate for the reduction in the recoil-free fraction of the probe atom. The experiments were undertaken to further characterize the spin state at temperatures above ambient. Both the IR and magnetic data suggest that the spin state which is increasingly populated above $T \sim 325$ K is an $S = 2$ (HS) state. Figure 6 shows sample spectra obtained in the high-temperature regime. As can be seen, at $T > \sim 365$ K the spectra resemble typical relaxation spectra involving two spin states. In a recent study, Adler et al.[15] have reported simulating the thermodynamics and kinetics of the spin-state-conversion process in a system in which the fluctuation of the electric hyperfine interaction between the two states covers the range $10^5 < \tau < 10^9$ s^{-1} and for the two cases where V_{zz}(HS) = V_{zz}(LS) and V_{zz}(HS) = V_{zz}(LS). These authors show that the relaxation spectra depend only on the magnitude of the quadrupole splitting and the relative sign of V_{zz} for the two spin states. Qualitatively, the data reported in the present study strongly resemble the simulated spectra of Adler et al. at 425 K, in agreement with the presence of relaxation effects in the Mossbauer spectra. Such relaxation effects prevent the estimation of a unique value for the hyperfine parameters of the HS state. The usual value of the quadrupole splitting of HS iron(II) complexes that contain two N-donor, symmetrical, bidentate ligands is ~2.6 mm/s. This value coupled with an isomer shift of ~0.96 ± 0.05 mm s^{-1}, which is typical for this state, leads to expected line positions at ~0.34 and ~2.30 mm s^{-1}, but these are not observed due to the (presumed) relaxation process occurring on a time scale $\leq 10^8$ s^{-1}.

Table I. Summary of Susceptibility and Spectroscopic Data[a]

	T/K	Fe(dpb)$_2$(NCS)$_2$	Fe(dpb)$_2$(NCSe)$_2$
		Infrared Data	
ν_{CN}, cm^{-1}	6.5	2113.9, 2095.8	2112.3, 2098.0
	85.5	2112.7, 2093.9	2111.9, 2096.4
	305	2107.1, 2090.8	2108.5, 2090.6
		^{57}Fe Mossbauer Data	
δ_{IS},[b] mm/s	90	0.35	0.39
	295	0.28	0.33
	345	0.22	
	365	0.23	
Δ_{QS}, mm/s	90	0.58	0.53
	295	0.58	0.53
	345	0.56	
	365	0.58	
		Magnetic Data	
μ_{eff} (1000 kOe), μ_B	5.0		1.34
	10.0	0.95	
	20.0		1.57
	90.0	1.47	
	92.0		2.01
	296.0		2.82
	300.5	2.34	
	344.7		3.06
	350.5	2.90	
	380.5	3.64	3.47

[a] The estimated errors are ±0.2 cm^{-1} for the IR data, ±0.01 mm/s for the Mossbauer data, ±0.01 μ_B for the susceptibility data, and ±0.5 K for the temperatures cited. [b] With respect to the centroid of a 295 K spectrum of 0.5-mil Fe(0).

Conclusions

The magnetic susceptibility data below 300 K give a clear indication of the existence of (at least) two spin states for the subject Fe(II) complexes, while the IR and ^{57}Fe Mossbauer data show only a single spectroscopic signature. On the other hand, the existence of a distinct spin-state transition (to the HS state) at temperatures above 325 K is clearly indicated by the IR data, and suggested by the Mossbauer results, and can account for the susceptibility data in the high-temperature limit. Thus, these data can be understood on the basis of the existence of three spin states in the temperature range $6 < T < 460$ K. The postulated spin complexity then requires that the infrared and Mossbauer signatures of the LS ($S = 0$) and intermediate-spin (IS, $S = 1$) states are sufficiently similar that they cannot be resolved under the conditions employed in the present study. Moreover, the Mossbauer data at $T > 325$ K can be understood on the basis of rapid (on the Mossbauer time scale) relaxation between the HS form and the states that dominate at lower temperatures.

The stabilization of the $S = 1$ state of Fe(II) complexes can be rationalized on the basis of a major distortion from octahedral symmetry of the six nearest-neighbor ligand atoms around the metal atom. As a result of this distortion, the d_{z^2} orbital, which moves down relative to $d_{x^2-y^2}$, and the d_{xy} orbital, which moves

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2540 *Inorg. Chem.* **1991**, *30*, 2540–2547

up relative to d_{yz} and d_{xz}, become degenerate and are equally occupied in the intermediate-temperature regime. On further thermal excitation, where the splitting between the lowest occupied manifold and the unoccupied $d_{x^2-y^2}$ level becomes comparable to kT, the $S = 2$ state becomes the lowest energy configuration for the metal center. If this model is valid, it implies that the change in the electron density at the iron atom in going from a d_{yz^2}, d_{xz^2}, d_{xy^2} configuration is a d_{yz^2}, d_{xz^2}, d_{xy}, d_z configuration is sufficiently small that neither the infrared (i.e., the frequency of the CN stretching mode) nor the ^{57}Fe Mossbauer hyperfine parameters differ sufficiently for the two states to be resolvable by these spectroscopic techniques. Because of the apparent degeneracy between these two states ($S = 0$ and $S = 1$) and the large magnetic field dependence of μ_{eff}, it is suggested that, at $T < 300$ K, the ground state is a spin-mixed state that has a varying contribution from the LS and IS states as a function of temperature and magnetic field. In the high-temperature regime, promotion of an electron from the d_{xz}, d_{yz} level to the unoccupied $d_{x^2-y^2}$ level is reflected in a major shift of the IR-active CN stretching mode of the pseudohalide ligand, permitting spectroscopic distinction between the LS/IS states, on the one hand, and the HS state, on the other. Clearly, additional experimental data (e.g., a temperature-dependent spin resonance study in an appropriate diluent matrix,[16] magnetic circular dichroism, corresponding crystallographic data, etc.) will be required to test further the proposed interpretation of the presently available characterizations.

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(16) Exploratory experiments with neat solid samples were unsuccessful due to the short spin–lattice relaxation times under these conditions. An appropriate spin-inert solvent has not yet been found for such experiments. We are indebted to Prof. H. J. Schugar for fruitful discussion of these problems.

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Homo- and Heteropolychalcogenide Anions Ch^{2-}, HCh^-, Ch_2^{2-}, Ch_3^{2-}, and Ch_4^{2-} (Ch = Se and/or Te): Solution ^{1}H, ^{77}Se, ^{123}Te, and ^{125}Te NMR Study

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The homo- and heteropolychalcogenide anions, Ch_n^{2-} (n = 1, 2, 3, 4; Ch = Se and/or Te) and the hydrochalcogenide anions, HCh^-, have been prepared and characterized in solution by ^{1}H, ^{77}Se, ^{123}Te and ^{125}Te nuclear magnetic resonance spectroscopy. The polychalcogenide anions were prepared in ethylenediamine and/or liquid ammonia by the reaction of the alkali-metal monochalcogenide with the appropriate chalcogen in the presence or absence of 2,2,2-crypt or by the direct reaction of the alkali metal with the chalcogen in liquid ammonia. With the exception of the pyramidal shaped $TeSe_3^{2-}$ anion, the polychalcogenide anions have open-chain structures. In addition, the more electronegative selenium atoms are found to be in terminal positions in the heteropolychalcogenide anions $Te_nSe_{3-n}^{2-}$ and $Te_mSe_{4-m}^{2-}$ (n = 1, 2; m = 2, 3), which can be rationalized by using the topological charge stabilization rule. The chemical shifts and unusually large spin–spin coupling constants are reported for the polychalcogenide anions and their trends discussed.

Introduction

Numerous homopolychalcogenide anions of selenium and tellurium have been structurally characterized in the solid state, e.g., Se_2^{2-},[1] Se_3^{2-},[2] Se_4^{2-},[3-5] Se_5^{2-},[5-7] Se_6^{2-},[8,9] Te_2^{2-},[10] Te_3^{2-},[11,12] Te_4^{2-},[13,14] and Te_5^{2-}.[8] Many of the crystalline homopolychalcogenide anion salts were isolated from solutions of main-group or transition-metal chalcogenide anions, suggesting complex equilibria and the existence of mixtures of anions in solution.[5,8,13] Furthermore, our previous solution NMR studies of the mixed Se/Te main-group metal chalcogenide anions suggested that homo- and heteropolychalcogenide anions played an important role in main-group metal chalcogenide anion formation.[15,16] In general, the chemistry of heteropolychalcogenide anions has been less well studied,[17] and only the structures of the K_2TeSe_4,[18] Na_2TeSe_3,[19] and K_2TeSe_3[19] phases have been reported in the literature.

The present paper reports a systematic investigation of the selenium, tellurium, and selenium/tellurium polyanions in ethylenediamine (en) and/or liquid ammonia solvents using multinuclear magnetic resonance spectroscopy. Multi-NMR spectroscopy is particularly well suited for structurally characterizing and studying the chemistry of homo- and heteropolychalcogenide anions of selenium and tellurium in solution as both elements have naturally occurring NMR-active spin-$^1/_2$ isotopes, namely, ^{77}Se (7.58%), ^{125}Te (6.99%), and ^{123}Te (0.89%).[20]

Results and Discussion

Solution NMR Studies of Polychalcogenide Anions, Ch_n^{2-}. Preparation of Ch_n^{2-} Anion Solutions. The general approach to the syntheses of polychalcogenide anions involved the reaction of the potassium monochalcogenide with an appropriate amount of

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