such as W_1---W_4 would not require any thermal activation energy.

Conclusion

Decatungstate appears to be a promising candidate for photochromic applications due to the high values of the extinction coefficients. Moreover, the simultaneous uptake of two electrons in certain media should be useful for photocatalytic applications (water splitting for instance).

Acknowledgment. We thank F. Babonneau for computer simulations and helpful discussions on optical spectra.

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Dynamic Intersystem Crossing in Solid Bis(phenanthroline)bis(cyanotrihydroborato)iron(II)[1]

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Variable-temperature Mössbauer, magnetic susceptibility, and infrared studies of $Fe(phen)_2(NCBH_3)_2$ reveal the occurrence of a reversible, gradual singlet/quintet intersystem crossing above room temperature. Mössbauer spectra of the complex in the transition region are interpreted as showing the occurrence of a novel (for Fe(II)), fast singlet/quintet interconversion.

Introduction

The solid complexes $Fe(phen)_2X_2$ constitute a class of compounds in which the *cis*-$Fe(phen)_2X_2$ structure provides the opportunity, through the choice of X^-, for selection of the electronic ground-state configuration of Fe(II). With X = Cl^-, Br^-, and I^- the ground state is a quintet state,[3] while for X = CN^-, $CNBH_3^-$, and $CNBPh_3^-$ the ground state is a singlet to temperatures well above ambient.[4] With X^- = NCS^- and $NCSe^-$ the ground electronic state changes, rather sharply, from singlet to quintet at temperatures of 174 and 232 K, respectively.[5] For these last two complexes there is believed to be considerable cooperativity in the transitions,[6] due to the importance of intermolecular interactions in the solid state. Emphasizing in another way the importance to intersystem crossing of intermolecular interactions in solution and solids is the fact that the complex with X^- = $NCBPh_3^-$ remains low spin to 400 K as a solid but exhibits rapid intersystem crossing at 273 K in CH_2Cl_2 solution.[7]

The phenomenon referred to here as "intersystem crossing" has been referred to in the literature as "spin crossover" and "spin equilibrium". Since the molecular event in question is clearly that of change in the spin multiplicity of the molecular wave function and since such a change is widely designated by experimentalists and theorists in all areas of science as intersystem crossing, we prefer the generally accepted semantics, particularly since this removes an unnecessary element of mystique from the phenomenon.

The purpose of this paper is to report our studies on certain variable-temperature properties of the compound $Fe(phen)_2(NCBH_3)_2$. Our earlier studies of this compound at room temperature led to the conclusion that this compound exists as a spin triplet at room temperature.[8] New experimentation on this compound at temperatures other than ambient shows that $Fe(phen)_2(NCBH_3)_2$ does not have a spin triplet ground state but that it exhibits a singlet/quintet intersystem crossing equilibrium that becomes pronounced only above room temperature. Variable-temperature Mössbauer studies of ^{57}Fe-enriched samples of $Fe(phen)_2(NCBH_3)_2$ further reveal new effects at the molecular level that are not found in the intersystem crossing of other Fe(II) intersystem-crossing compounds.

Experimental Section

Preparation of $KNCBH_3$. The compound was prepared according to a previously developed synthesis.[9]

Preparation of $Fe(phen)_2Br_2$. The compound was synthesized by a new method introduced by J. P. Zapata, which may also be used in making the Cl^- and NCS^- complexes.[4] $Fe(phen)_3Br_2$ (6 mmol), prepared by literature methods,[10] was refluxed (438 K) in 150 mL of dry dimethylacetamide (DMA). The color of the solution changed from red ($Fe(phen)_3Br_2$) to dark blue ($Fe(phen)_2Br_2$) (dark blue for Cl^- and purple for NCS^-). After removal of the heating mantle, 100 mL of benzene was added quickly to the refluxing solution through the reflux condenser. (*Caution*: large amounts of boiling benzene are produced.) The solid was filtered, washed with diethyl ether, and dried in vacuo over P_2O_5 at 373 K. Occasionally, unreacted $Fe(phen)_3Br_2$ would appear in the product; in such cases, the process was simply repeated with the crude product as the starting material.

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(8) Purcell, K. F.; Yeh, S. M.; Eck, J. *Inorg. Chem.* **1977**, *16*, 1708. König has cast an element of doubt on all claims of triplet ground state $Fe(phen)_2X_2$ complexes with his findings that certain of his complexes, previously interpreted as possessing triplet ground states, are actually composed of $Fe(phen)_3^{2+}$ cations and $Fe(dianion)_3^{3-}$ anions in which the cation has a singlet electronic state and the anion exhibits a sextet state. His syntheses are performed in water, where air oxidation may occur. Rigorous exclusion of air leads to, for example, $Fe(phen)_2(ox)\cdot 5H_2O$, which exhibits intersystem crossing. $Fe(phen)_2(NCBH_3)_2$ is not a $Fe(phen)_3^{2+}$ salt; the cause of our earlier assignment of a spin triplet stems from the unusual effects reported here and their failure to appear in the IR and Mössbauer spectra at room temperature. See: König, E.; Ritter, G.; Goodwin, H. A. *Inorg. Chem.* **1981**, *20*, 3677; König, E.; et al. *Inorg. Chim. Acta* **1979**, *35*, 239.

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The spectroscopic and magnetic properties of $Fe(phen)_2Br_2$ prepared in this way agree with those of the complex prepared by previously reported methods.[10]

Preparation of $Fe(phen)_2(NCBH_3)_2$. The synthesis is patterned after that used previously.[8] About 6 mmol of $Fe(phen)_2Br_2$ was placed in 150 mL of dry THF and added to a flask containing 20 mmol of $KNCBH_3$. The mixture was stirred under reflux for 2 days, while protected from moisture by a drying tube containing Drierite. The dark maroon microcrystalline solid was filtered, successively washed with THF, H_2O, and anhydrous diethyl ether, and finally dried in vacuo over P_2O_5 at 373 K. This compound was used to make variable-temperature IR measurements. Elemental analyses were carried out by Industrial Testing Laboratories. Anal. ($C_{26}H_{22}N_6B_2Fe$) Fe, H, N, B; C: calcd, 62.96; found, 62.12.

Preparation of $^{57}Fe(phen)_2(NCBH_3)_2$. This synthesis differs from that of the unenriched complex by the synthesis of the $Fe(phen)_2Br_2$ precursor from ^{57}Fe (99%; New England Nuclear) and by the rigorous exclusion of air. A 78.5-mg (1.5-mmol) amount of ^{57}Fe was covered with 15 mL of anhydrous degassed methanol; after the addition of 0.5 mL of concentrated HBr, the slurry was stirred and occasionally heated in a boiling water bath. Upon dissolution of all the iron, the $FeBr_2$ was isolated by evaporation of the methanol under argon purge and dried in vacuo.[11] To the dried $FeBr_2$ was added a solution of 0.542 g (3.0 mmol) of dry phenanthroline in 30–40 mL of pyridine and the reaction flask evacuated. The solution turned red, and after 1 h in a boiling water bath a deep purple precipitate formed. The $Fe(phen)_2Br_2$ was collected on a filter frit, washed with 30 mL of THF, and added to a solution of 0.5 g (6.3 mmol) of $KNCBH_3$ in 50 mL of dry THF. After the solution was refluxed for 24 h, the red-purple microcrystalline solid was collected on a frit, washed with 100 mL of water followed by 50 mL of THF, and dried in vacuo. The entire preceding procedure was done in Schlenk glassware. The total yield was 0.474 g or 69% yield.

This product gave room-temperature IR, variable-temperature magnetic susceptibility, and room-temperature Mössbauer data consistent with those of natural-abundance samples, but with a small amount (6% by chemical analysis) of unreacted $Fe(phen)_2Br_2$ present; it was decided to keep the reactant in the sample as a benchmark for the effect of high temperature on Mössbauer parameters of band intensity and width. Anal. Fe, C, N, B, H.

Infrared Spectra. IR measurements were obtained with KBr pellets and a Perkin-Elmer Model 180 infrared spectrophotometer. Low-temperature spectra were obtained with use of an unsilvered, evacuable, glass, double-walled Dewar with a copper cold finger, attached to the Dewar inner wall, for sample mounting. The outer wall of the Dewar/cold-finger assembly was mated though a ground-glass connection to the side of a section of large-bore cane. The ends of the cane were closed with NaCl disks. Thus, the Dewar and sample compartment were simultaneously evacuable. The temperature of the sample was assumed to be the same as that of the coolant contained in the Dewar.

High-temperature spectra were obtained by heating a stainless steel KBr pellet die containing the pressed sample; the die was mounted in a stainless steel pipe wrapped with heating tape; the temperature was monitored with a chromel/alumel thermocouple to an accuracy of ±2 K.

Magnetic Susceptibility. Magnetic susceptibilities from 163 to 473 K were obtained with a Cahn Instruments Model 7600 Faraday system equipped with a flow cryostat and a heating element. The temperatures were measured to an accuracy of ±2 K by means of a copper/constantan thermocouple referenced at 273 K. Magnetic moments were calculated by assuming the Curie law and a diamagnetic correction for $Fe(phen)_2(NCBH_3)_2$ of 336×10^{-6} cgsu. The calibrant was $HgCo(NCS)_4$. All samples were powdered and held either in a quartz pan (high temperatures) or in a plastic capsule (room temperature or below).

Table I. Magnetic Susceptibility Data for the ^{57}Fe-Enriched Complex[a]

temp/K	$10^{-3}\chi$/ cgsu	μ_{eff}	temp/K	$10^{-3}\chi$/ cgsu	μ_{eff}
163	0.887	1.07	330	3.232	2.92
185	0.877	1.14	341	3.603	3.11
196	0.913	1.19	343	4.122	3.36
243	0.870	1.30	347	4.313	3.46
248	0.860	1.31	348	4.484	3.53
256	1.135	1.52	349	4.415	3.51
273	1.207	1.62	355	4.646	3.64
279	1.335	1.72	359	5.465	3.95
290	1.558	1.90	362	5.299	3.92
293	1.685	1.99	364	5.571	4.03
296	1.695	2.00	368	5.591	4.06
297	1.785	2.05	370	5.548	4.05
301	2.068	2.23	387	7.150	4.71
306	2.172	2.31	396	7.160	4.77
308	2.191	2.32	407	7.366	4.90
317	2.500	2.52	426	7.962	5.21
328	2.923	2.77	449	7.600	5.22

[a] Corrected for the 6% $Fe(phen)_3Br_2$ benchmark.

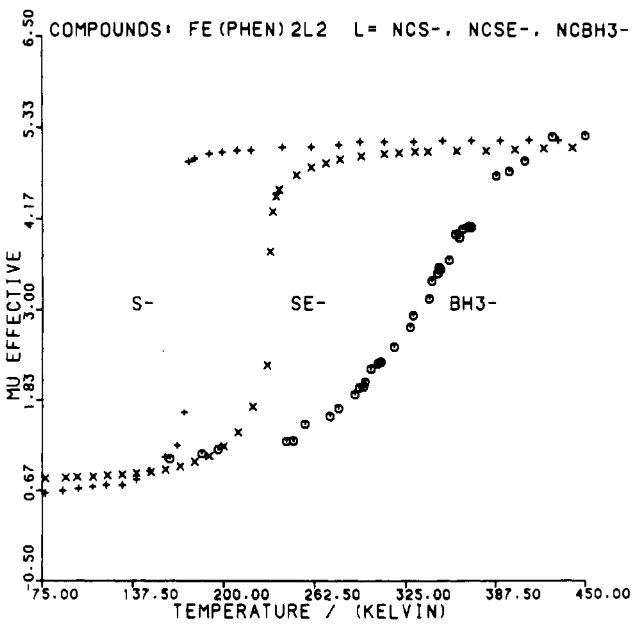

Figure 1. Temperature dependence of μ_{eff} for X = NCS^-, $NCSe^-$, $NCBH_3^-$.

Mössbauer Absorption Spectra. Mössbauer absorption spectra were obtained with a locally constructed speaker drive system operating in the constant-acceleration mode.[12] The output pulses from a Harshaw NaI(Tl) scintillation counter were collected in a multichannel analyzer (Nuclear Data N-100) operating in the multiscaling mode. Both positive and negative source acceleration data were collected and subsequently overlaid to obtain the final spectrum. A $^{57}Co/Pd$ source was used for all spectra, and the velocity scale was calibrated with an iron-57 enriched foil absorber. The instrumental resolution for these experiments was 0.0184 mm Hz for series I and 0.0262 mm Hz for series II (see Results). The iron-foil line widths ((source + absorber)/2) were 0.13 mm Hz. The data were least-squares fitted to Lorentzian line shapes by local fitting programs.

The absorbers were polycrystalline samples, packed in aluminum-foil pouches clamped between copper rings attached to one end of a copper post, which protruded through a thin stainless steel bottom of an evacuable copper canister. The canister windows consisted of beryllium sheets with O-ring seals. The lid for the can provided for a vacuum connection and a thermocouple (chromel/alumel) and temperature controller leads. Sample temperature variations was achieved by use of an Athena Model 61 constant-temperature controller connected to heating tape that had been wrapped around the external part of the copper post. The sample temperature was monitored to an accuracy of ±1 K by means of the thermocouple imbedded in a drilled cavity in one of the copper sample mounting rings.

Results

The corrected molar magnetic susceptibilities and the effective magnetic moments of $Fe(phen)_2(NCBH_3)_2$ from 163 to 473 K are listed in Table I, and a plot of μ_{eff} vs. T is shown

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Table II. Mössbauer Lorentzian Parameters of Enriched $^{57}Fe(phen)_2(NCBH_3)_2$

temp/K	δ[a]/(mm Hz)	Δ/(mm Hz)	Γ[b]/(mm Hz)	% of total[c]	var[d]
77[e]	0.43 (0.001)	0.28 (0.001)	0.19 (0.001)	100 (0.5)	2.8
297[f]	0.37 (0.007)	0.34 (0.007)	0.27 (0.006)	<100 (2)	5.7
298[f]	0.36 (0.005)	0.35 (0.005)	0.27 (0.004)	<100 (1)	4.6
323[g]	0.36 (0.005)	0.30 (0.005)	0.25 (0.004)	<82 (5)	1.9
	0.94 (0.4)	1.30 (0.4)	0.90 (0.4)	18 (5)	
339[h]	0.37 (0.06)	0.22 (0.06)	0.25 (0.006)	42 (10)	1.6
	0.40 (0.1)	0.36 (0.1)	0.31 (0.04)	38 (10)	
	0.80 (0.2)	1.30 (0.2)	0.44 (0.06)	19 (6)	
343[h]	0.34 (0.03)	0.22 (0.03)	0.19 (0.1)	32 (2)	2.0
	0.41 (0.1)	0.47 (0.1)	0.32 (0.02)	51 (20)	
	0.82 (0.5)	1.30 (0.5)	0.38 (0.05)	16 (7)	
348[i]	0.25 (0.01)	0.00 (0.0)	0.17 (0.02)	12 (2)	1.5
	0.47 (0.2)	0.45 (0.2)	0.33 (0.001)	71 (9)	
	0.85 (0.7)	1.28 (0.7)	0.34 (0.04)	17 (2)	
352[i]	0.24 (0.007)	0.00 (0.0)	0.14 (0.01)	10 (7)	1.0
	0.49 (0.04)	0.56 (0.04)	0.35 (0.01)	74 (30)	
	0.86 (0.2)	1.26 (0.2)	0.30 (0.04)	16 (6)	
357[i]	0.17 (0.007)	0.00 (0.0)	0.14 (0.002)	12 (6)	1.2
	0.58 (0.2)	0.86 (0.2)	0.33 (0.02)	65 (20)	
	0.81 (0.6)	1.33 (0.6)	0.31 (0.04)	23 (6)	
362[i]	0.13 (0.1)	0.00 (0.0)	0.12 (0.3)	11 (30)	1.2
	0.69 (0.02)	1.10 (0.02)	0.33 (0.02)	56 (20)	
	0.79 (0.2)	1.33 (0.2)	0.26 (0.02)	33 (10)	
369[i]	0.12 (0.007)	0.00 (0.0)	0.13 (0.006)	11 (10)	1.4
	0.68 (0.1)	1.12 (0.1)	0.34 (0.04)	35 (20)	
	0.76 (0.06)	1.31 (0.06)	0.27 (0.002)	54 (20)	

[a] Relative to center of iron-foil reference. [b] Observed half-width at half-maximum. [c] Fraction of total area of $Fe(phen)_2(NCBH_3)_2$ absorption. [d] Variance ratios = $[\Sigma_i(I_i^{\mathrm{calcd}} - I_i^{\mathrm{obsd}})^2/I_i^{\mathrm{obsd}}]/(N_{\mathrm{ch}} - N_{\mathrm{v}})$, where N_{ch} is the number of spectral points, N_{v} is the number of variables, and I_i = spectral intensity for point i. [e] Natural-abundance complex. [f] Spectrum was fitted by two Lorentzian lines of equal area. [g] Spectrum was fitted with two quadrupole doublets (equal area components). [h] Spectrum was fitted with three quadrupole doublets (equal area components). [i] Spectrum was fitted with two quadrupole doublets (equal area components) and one Lorentzian line.

in Figure 1, along with those for the NCS^- and $NCSe^-$ analogues for comparison.[5] The values shown have been corrected for the 6% $Fe(phen)_2Br_2$ benchmark.[13] The magnetic measurements were taken in a random temperature sequence; were hysteresis effects operative, the data would then show scatter in the transition region. Preparation of natural-abundance ^{57}Fe samples by the method used for the enriched compound, but excluding $Fe(phen)_2Br_2$, gave the same results, within experimental error.

The effect of temperature on the intensities of the BH_3 and the CN stretching bands (2500–2100 cm^{-1}) for unenriched $Fe(phen)_2(NCBH_3)_2$ are shown in Figure 2. The room-temperature spectrum of the ^{57}Fe-enriched sample is indistinguishable from that in Figure 2.

A composite of the calculated variable-temperature Mössbauer spectra of enriched $^{57}Fe(phen)_2(NCBH_3)_2$ (scaled to a common base line and normalized to constant spectral area) is shown in Figure 3 in two forms: spectral traces and a contour map; the individual observed and calculated spectra are given in Figure 4. Figure 4 consists of two series of spectra recorded from two samples from the same synthesis. Series I is limited because heating of that sample to 373 K for 4 days resulted in about 5% decomposition of $Fe(phen)_2(NCBH_3)_2$ to $Fe(phen)_2(CN)_2$, which necessitated replacement of the sample. The decomposition was detected and monitored by the procedure of recording a room-temperature spectrum following each high-temperature run. The spectra of series II are free of $Fe(phen)_2(CN)_2$ bands. The decomposition was not encountered in the infrared or magnetic susceptibility measurements because of the much shorter times required for data collection (4 days for the Mössbauer spectra). The higher temperature data were taken in random order of temperature. The center shifts, quadrupole splittings, and line widths from least-squares fitting of Lorentzian bands to the data are listed in Table II.

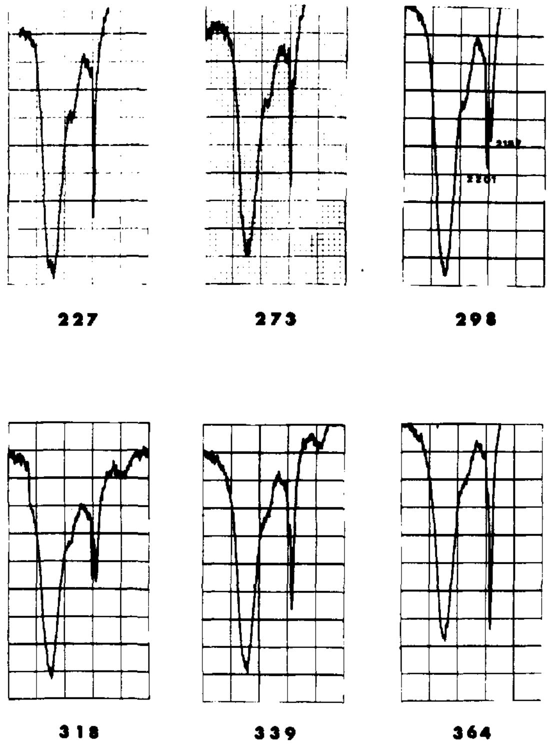

Figure 2. Temperature dependence of BH_3 and CN stretching bands of $Fe(phen)_2(NCBH_3)_2$. The spectral range shown is 2000–2500 cm^{-1}, with 100-cm^{-1} intervals indicated by vertical lines.

The spectra in Figure 4 are novel for an intersystem-crossing Fe(II) sample: normally one observes cleanly defined doublets for the singlet and quintet states. Clearly there are more than four lines in these spectra. The question arises whether these data should be treated as arising from a five-line or a six-line spectrum. The five-line pattern would consist of a high-velocity

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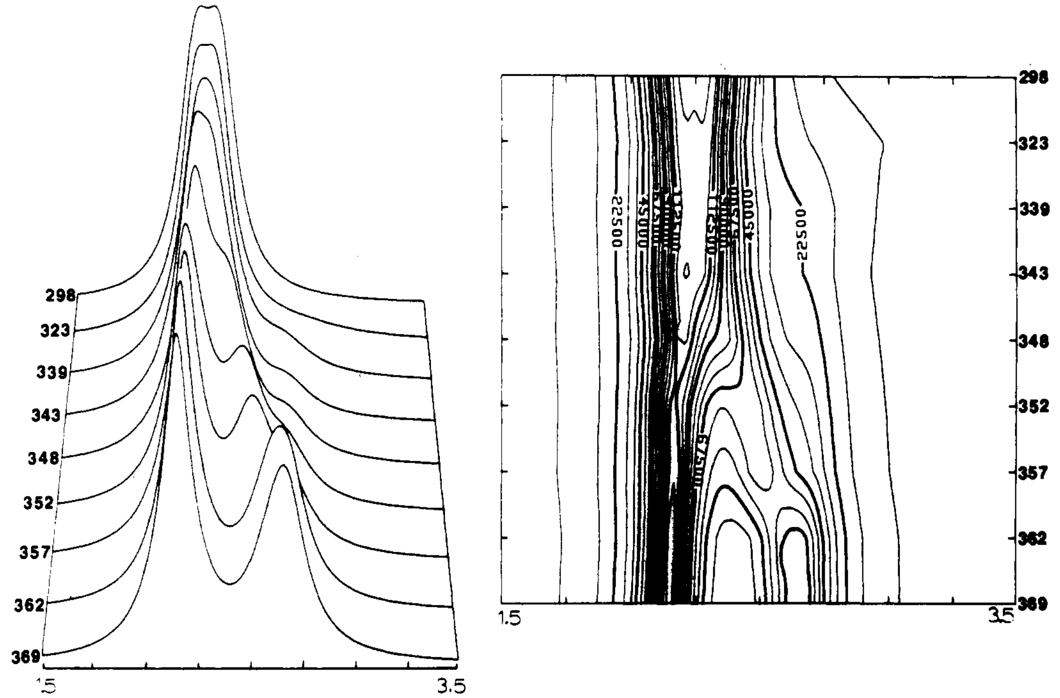

Figure 3. Composite calculated Mössbauer spectra of $Fe(phen)_2(NCBH_3)_2$; all spectral areas normalized to the room-temperature value. The ordinate values in both the contour map and the spectral traces give the sample temperature in K. The abscissa is velocity in mm Hz.

peak with a counterpart under the main envelope, a second doublet under the main envelope, and a fifth line rapidly shifting with temperature from under the main envelope to merge with the high-energy peak. A six-line pattern can be envisioned in which the shifting fifth band has a counterpart also under the main envelope region. We exhaustively searched for both five- and six-line resolutions. While the five-line fits are mathematically possible, they require the resonance doublet under the main envelope to collapse and then expand with increasing temperature. Furthermore, the fifth resonance line shift to 1.44 mm Hz as the temperature increases cannot be understood. These results forced us to accept the six-line deconvolution shown in Figure 4.

The spectra reported in Figure 3, but not in Figure 4, have had the $Fe(phen)_2Br_2$ benchmark peaks omitted for clarity of the $Fe(phen)_2(NCBH_3)_2$ spectrum. The Lorentzian parameters for the benchmark $Fe(phen)_2Br_2$ are fully consistent with literature values.[13]

Some of the spectral parameters in Table II have uncertainties that exceed the instrument resolution in spite of the highly statistically significant data base (noise level <0.5%) and the good instrument resolution. This is an unavoidable consequence of the overlap of four bands (some of which are low in area at certain temperatures) in the low-energy region. The uncertainties of the spectral parameters are root mean square values of the uncertainties of the two components of each doublet; the uncertainties are seen to be large when the components are weak in intensity and one or the other is overlapped by other peaks. For two of the quadrupole doublets it is generally the case that one component of the doublet is well-defined and the other is not.

The magnetic susceptibility, infrared, and Mössbauer data show no evidence of hysteresis.

Discussion

Magnetic and Infrared Data. The magnetic susceptibility data for $Fe(phen)_2(NCBH_3)_2$ reveal a gradual transition from the singlet state to the quintet state with increasing temperature. The lowest and highest measured magnetic moments of 1.07 and 5.24 μ_B are characteristic of singlet and quintet $Fe(phen)_2X_2$ complexes, respectively, and constitute primary evidence for a singlet/quintet intersystem crossing. The lowest value suggests that, at 163 K (the lowest temperature obtainable with our apparatus), some quintet-state population occurs; the slope of $\mu_{eff}(T)$ indicates that the lowest value of μ_{eff} has not been reached at this temperature.

Comparison of the shapes of the $\mu_{eff}(T)$ curves for the NCS^-, $NCSe^-$, and $NCBH_3^-$ analogues suggests the transition is less cooperative for the $NCBH_3^-$ complex. Although crystallite quality can alter the appearance of $\mu_{eff}(T)$,[14] a gradual transition due to lattice physical defects is also associated with an incomplete transition at high and low temperatures; the transitions in Figure 1 are essentially complete.

The variable-temperature infrared data for $Fe(phen)_2(NCBH_3)_2$ are not as informative about the molecular level aspects of the transition as hoped; in fact, these data reveal an atypical situation in the CN stretching region which contributed to the earlier claim that $Fe(phen)_2(NCBH_3)_2$ exhibits a single electronic state at room temperature. Where known, all $Fe(phen)_2X_2$ complexes have a cis stereochemistry and those containing a cyano linkage usually display infrared activity of *both* the symmetric and the antisymmetric CN stretching modes. The splitting of 14 cm^{-1} for $Fe(phen)_2(NCBH_3)_2$ is of the same order as exhibited by the other singlet- and quintet-state cyano complexes and is considerably less than the 40 cm^{-1} separating the doublets of singlet and quintet $Fe(phen)_2(NCS)_2$.[15,16] Thus, our observation of the simple CN doublet for $Fe(phen)_2(NCBH_3)_2$ at room temperature was previously taken to imply coupled oscillators in a cis configuration for a single electronic state of Fe(II). Nevertheless, the variation in the relative CN band intensities with temperature (Figure 2) shows that only one band is observed for each electronic state and the CN oscillators for either electronic state do *not* exhibit the expected doublets. The low-frequency CN band is to be associated with the quintet-state molecules of $Fe(phen)_2(NCBH_3)_2$, as expected for the weaker Fe–N bonds.[8]

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(15) König, E.; Madeja, K. *Spectrochim. Acta, Part A* **1967**, *23A*, 45.

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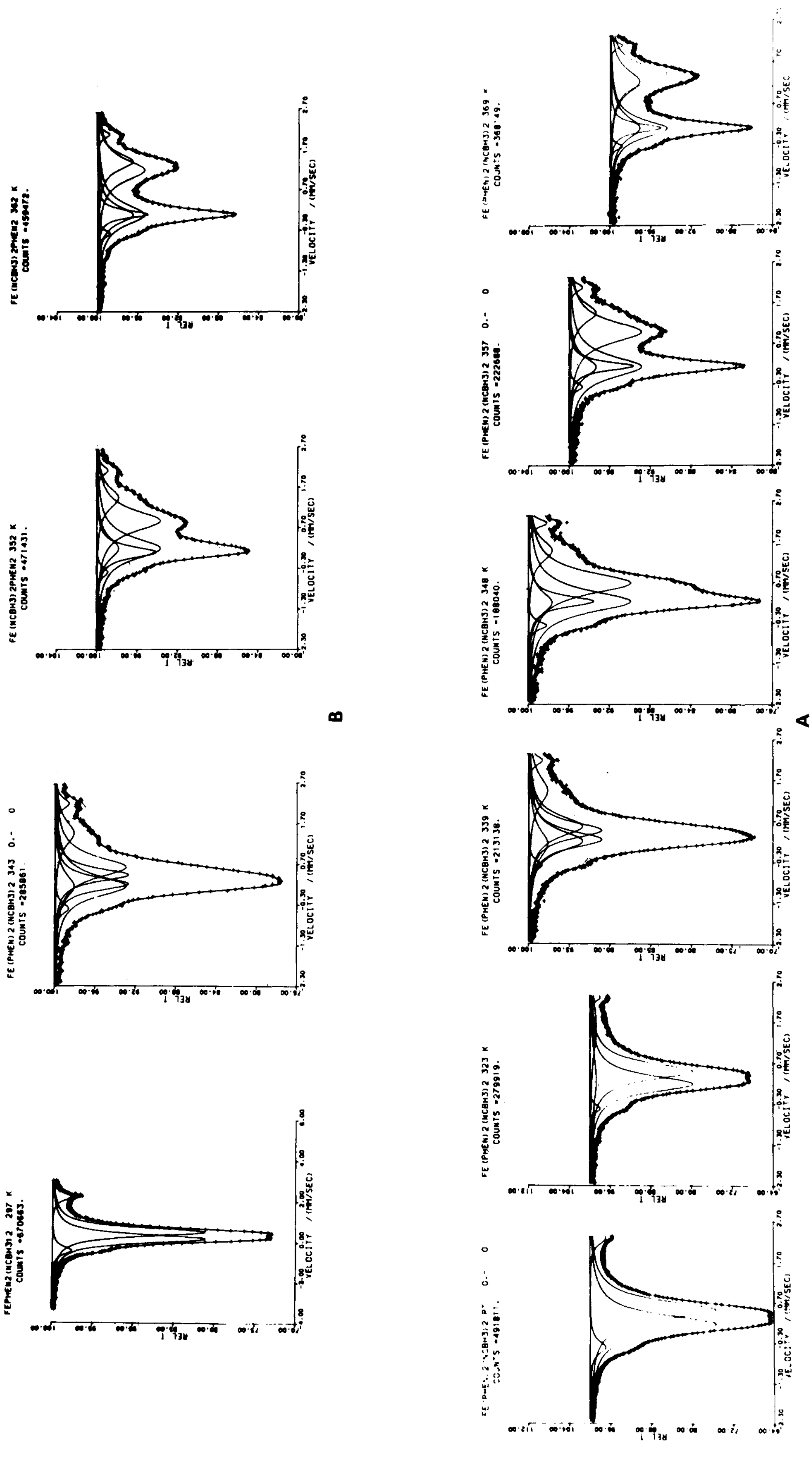

Figure 4. Observed and calculated Mössbauer spectra of the two Fe(phen)$_2$(NCBH$_3$)$_2$ samples at the temperatures noted on the individual spectra: (A) series I; (B) series II (see Results). Temperatures are listed on each plot following the compound name.

Table III. High- and Low-Temperature Infrared Band Correlations for Phenanthroline Ligands

$X = NCBH_3^-$	assignt	$X = NCS^-$
1590 (m → w, split)	C-C	1592 (m → vw)
1517 (s → w)	C-N str	1515 (vs → w)
1495 (vs → w, split)		1495 (s → w, br)
1425 (vs → s, split)		1427 (vs → vs, split)
1415 (s → s)		1416 (vs → vs, split)
868 (m → vw)	γ-CH	867 (m → not obsd)
641 (m → vvw)	α-CCC	636 (s → vvw)

[a] Descriptions in parentheses denote changes in band shape from low- to high-temperature spectra.

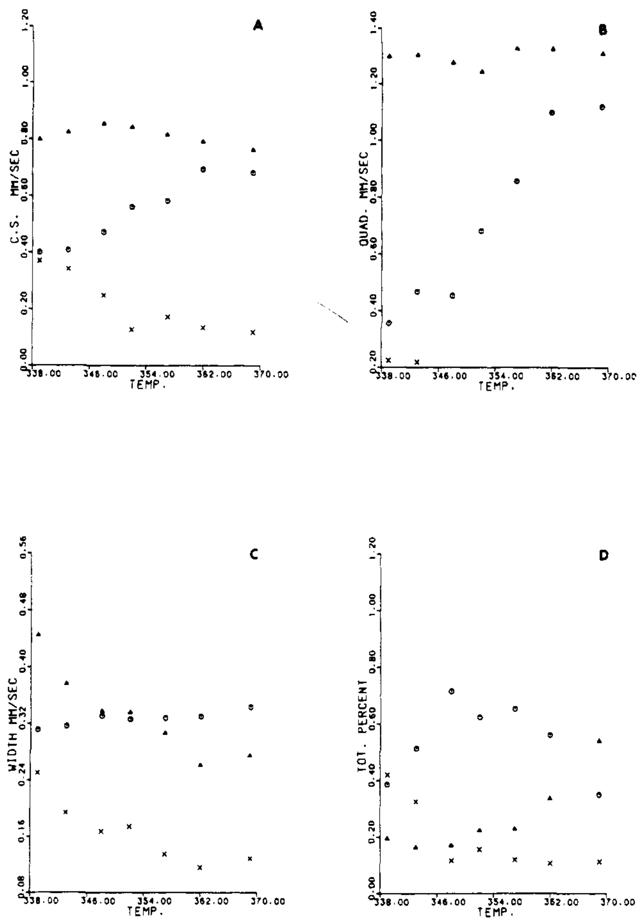

Figure 5. Temperature dependence of (A) center shifts, (B) quadrupole splitting, (C) line widths, and (D) relative intensities (percent of total band area). Error values are given in Table II. Δ represents the quintet sites, O represents the intermediate sites, and × represents the singlet sites.

The lack of CN splitting has been observed[4] also for the related low-spin complex $Fe(phen)_2(NCBPh_3)_2$ and has been reported in one other instance of which we are aware: *cis*-$Cr(en)_2(CN)_2$.[17] One or more of three effects might be in operation to account for these unusual results: Fermi resonance shifting of one component to the position of the other component, fortuitous intensity annihilation of one mode, and decoupling of the oscillators through annihilating kinetic and potential energies of coupling.

While the lack of CN coupling in this type of compound is atypical, the remainder of the infrared spectra for these samples are normal. The lack of appreciable change in the BH_3 stretching bands, the lack of C=N absorptions, and the analogous behavior of the BPh_3 complex mitigate against intramolecular rearrangements, such as H atom shifts, on heating. The infrared bands of the phenanthroline ligands (Table III) follow the general pattern found for $Fe(phen)_2(NCS)_2$ on passing from the singlet to the quintet state.[15]

Mössbauer Spectra. On the basis of the infrared and magnetic susceptibility data, the Mössbauer spectra for $Fe(phen)_2(NCBH_3)_2$ are expected to consist of a low-energy, slightly split quadrupole doublet (singlet state), which loses intensity, and flanking quadrupole doublet lines (quintet state), which gain intensity, with increasing temperature. At low temperature the Mössbauer spectrum of $Fe(phen)_2(NCBH_3)_2$ is that of a quadrupole doublet centered at 0.43 mm Hz with a very small quadrupole splitting of 0.28 mm Hz and at high temperature is that of a quadrupole doublet centered at 0.76 mm Hz with a splitting of 1.31 mm Hz. These values are well within the expected values for the respective electronic states.[18]

The novelty, which is not at all forecast by the appearance of the infrared and magnetic data, of the intersystem crossing in $Fe(phen)_2(NCBH_3)_2$ lies in the occurrence of additional resonance bands at temperatures well into the transition region. Figure 4 shows our interpretation that these novel features are due to a quadrupole doublet (rather than a single resonance) for which the center shift and quadrupole splitting gradually progress, with increasing temperature, from those of the singlet-state doublet to those of the quintet-state doublet. Figure 5 shows the calculated spectral parameters as a function of temperature.

The temperature dependence of the center shift of the quintet sites (Figure 5A) is weak, as is normal, and parallels that of the bromide benchmark (not shown). That of the singlet sites is also negative (which is normal) but is about 100 times stronger than is normal in the temperature range where the intermediate sites are growing; this implies larger than normal Fe vibrational velocities (second-order center shift) for the singlet sites at temperatures in the transition range.

The temperature variations of the relative band areas, shown in Figure 5D, reveal that the conversion from a singlet site to a quintet site proceeds through an intermediate site in two distinct steps. Thus the absorption due to the intermediate sites rises to a maximum at 350 K as the absorption due to the singlet sites decreases markedly. The quintet resonance band area is essentially constant at a very low level below 350 K, above which temperature the quintet intensity grows as the intermediate band area decreases.

The line widths provide additional information for formulating a description of the intermediate (Figure 5C). That the Lorentzian line widths of the quintet and singlet (and benchmark $Fe(phen)_2Br_2$) resonance bands show comparable narrowing as the temperature increases excludes an important role for absorber "thickness" contributions to the line width.[19] The narrowing presumably derives from increasingly less efficient nuclear quadrupolar relaxation and/or (for the quintet and benchmark molecules) increasingly efficient electron spin "spin–lattice" relaxation. Alternately, line narrowing at higher temperature might be associated with lattice annealing so as to improve the environmental uniformity of singlet and quintet lattices; that the spectra were recorded at random temperatures argues against this interpretation of the line width behavior. Importantly, increasing "disorder" of the singlet and quintet sites with increasing temperature does not occur because this would lead to line broadening. Quite distinct from the singlet, quintet, and benchmark sites, the line width of the intermediate remains relatively invariant at a value normal for Mössbauer resonances.

The key preceding observations for formulation of a description of the intermediate sites are as follows.

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(1) The magnetic and infrared data show a smooth, gradual reduction in the number of singlet molecules and increase in the number of quintet molecules, as temperature increases.

(2) There exist distinct, well-ordered singlet and quintet sites which do not experience rapid ($\geq 10^7$ Hz) intersystem crossing.

(3) The spectral singlet sites initially have iron atom vibrational velocities that increase rapidly, and depopulate early, in the transition range, while the spectral quintet sites rapidly populate late in the transition range.

(4) Throughout the transition range there appears a single pair of spectral lines not assignable to singlet or quintet states alone.

(5) The relative intensities of these intermediate lines increase, then decrease, with increasing temperature through the transition range.

(6) The electric field gradient and center shift for the intermediate gradually evolve with temperature from the values of the singlet sites to those of the quintet sites and do so without collapse of the quadrupole doublet by rapid quadrupolar relaxation.

(7) The phenomena are reversible, and hysteresis, if present, is too small to have been detected.

Observation 1 requires that the intermediate resonances be characterized by a temperature-dependent distribution over singlet and quintet states. Crystallographic characterization of the sites responsible for the new resonances is not possible from the spectral and magnetic results, but the following interpretation can be given. In the early stages of the transition the solid permits individual molecules to experience rapid singlet/quintet intersystem crossing. The line width behavior can be interpreted to mean the dynamic molecules find themselves in a less homogeneous environment than the singlet and quintet lattices.[20] As the temperature further increases, the structural characteristics of the dynamic molecules become progressively weighted toward those of the quintet type and a well-ordered, nondynamic lattice of quintet molecules begins to grow. That quadrupole splitting is maintained by the intermediate sites is particularly interesting. Whatever the molecular level reaction coordinate for the intersystem crossing, and whatever the crystallographic properties of the lattice, both permit intersystem crossing without collapse of the electric field gradient tensor.

An interesting question arises as to whether the existence of the intermediate sites observed for Fe(phen)$_2$(NCBH$_3$)$_2$ is attributable in some way to the size of defect-free crystallites.[14] A direct test of such a hypothesis would entail synthesis of the complex to yield larger, and presumably more perfect, crystallites for study. Unfortunately, we have so far been unable to prepare such crystals. However, those materials that do exhibit lattice continuity effects on the $\mu(T)$ curves (especially X = NCS$^-$, NCSe$^-$) fail to show the intermediate sites observed for X = NCBH$_3^-$, so that lattice irregularities are not expected to produce the results seen here. In the same vein, highly defective crystallites produce incomplete intersystem crossing at high and low temperature, a characteristic also not observed for Fe(phen)$_2$(NCBH$_3$)$_2$. It may be that the intermediate sites are observed here because the transition temperature for X = NCBH$_3^-$ is so much higher than those of its analogues and/or because the intermolecular forces are weaker for the complex with X = NCBH$_3^-$.[21]

Finally, we mention that rapid intersystem crossing has been observed in fluid phases for six-coordinate Fe(II) and other transition-metal complexes.[22] Theoretical work on six-coordinate Fe(II) complexes has shown that the rate of intersystem crossing (for independent molecules) is primarily derived from the singlet/quintet energy gap and the crossing can be achieved by partial pseudorotation of the ligands.[23] This last point is of particular importance to solid materials where full racemization of the complex may be impossible.[24]

Conclusion

We observe that Fe(phen)$_2$(NCBH$_3$)$_2$ is not a spin triplet compound but undergoes an intersystem crossing from a singlet to a quintet state, in analogy with Fe(phen)$_2$(NCS)$_2$ and Fe(phen)$_2$(NCSe)$_2$. It differs from them through the appearance, in the transition region, of intermediate sites which experience dynamic intersystem crossing.

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(20) This interpretation, however, can only be tentative because there may also be quadrupole and electron spin relaxation rate differences between the intermediate and singlet, quintet sites.

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