into a consistent pattern. The nmr shifts of the paramagnetic compounds on the other hand do not show pronounced regularities even in such a series of closely related compounds, and it is apparent that several of the possible mechanisms for producing these shifts are combining to give a complex pattern.

Experimental Section

A. **Susceptibility Measurements.** Susceptibility measurements have been made in solution using an nmr method.[22] Measurements were made in $CHCl_3$ or CH_2Cl_2 depending on the solubility. The effective moments have been calculated using room-temperature data and assuming the Curie law is obeyed. The assumption is reasonable for all cases except the octahedrally coordinated Co complexes where a pronounced temperature dependence of effective moment is anticipated. The accuracy of the measurements varies because of the differing solubilities and susceptibilities involved. The variation of susceptibility with temperature could not be measured with sufficient accuracy to permit a meaningful verification of the Curie law behavior because of the limited temperature range which could be investigated.

B. **Optical Measurements.** Optical absorption studies were made in the region 17,000 to 2000 A using a Cary 14 recording spectrophotometer. Measurements at short wavelengths were made in hexane solution, and the remaining measurements were made in chloroform or dichloromethane. Infrared spectra were obtained using a Perkin-Elmer Model 21 spectrophotometer.

C. **Nmr Spectra.** The nmr spectra were recorded using a Varian HR-60 spectrometer for proton resonance studies of the paramagnetic species and an A-60 for the diamagnetic species. A 14.2-Mcps radiofrequency unit and probe were used for the boron studies. Measurements were made in deuteriochloroform except as noted. The proton shifts are measured *vs.* tetramethylsilane as an internal standard. The boron shifts are measured *vs.* trimethyl borate as an external standard.

D. **Synthesis of Compounds.** The synthesis of transition metal complexes with unsubstituted poly(1-pyrazolyl)borates[23] and poly(1-pyrazolyl)borates containing substituents on carbon or boron[24] will be published elsewhere.

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[22] D. F. Evans, *J. Chem. Soc.*, 2003 (1959).

[23] S. Trofimenko, *J. Am. Chem. Soc.*, **89**, 3165 (1967).

[24] Part IV: S. Trofimenko, submitted for publication.

Spin Equilibria in Octahedral Iron(II) Poly(1-pyrazolyl)borates

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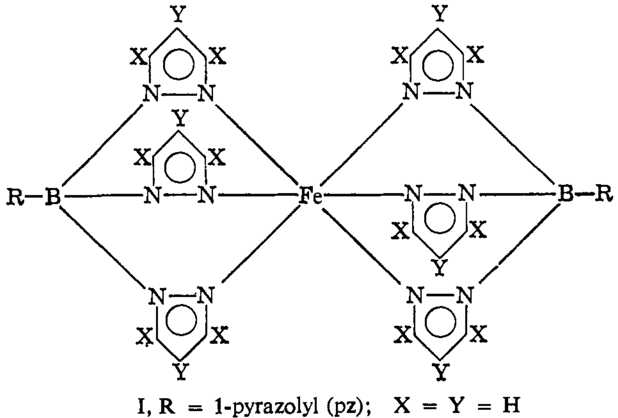
Abstract: The Fe^{2+} complexes based on the hydrotris(1-pyrazolyl)borate ligand provide an example of a "spin equilibrium" between high- and low-spin forms. Fully high-spin, fully low-spin, and complexes of intermediate spin can be produced by appropriate substitution. Optical spectra, susceptibility data, and magnetic resonance experiments leading to the characterization of these equilibria are presented.

The possibility of the occurrence of a thermally accessible electronic state of different multiplicity from the ground state has long been recognized for d^4, d^5, d^6, and d^7 ions in octahedral environments.[1] The experimental realization of an equilibrium of this type is determined by the availability of a complex for which the low-spin and high-spin ground states are separated by only a few hundred reciprocal centimeters. Since the energies involved in changes in chemical binding are in general much larger than this, the requirement is very restrictive and accounts for the fact that there are few, if any, well-documented cases of equilibria of this type.

For the d^5 and d^6 configurations, the susceptibility may be taken as the population weighted-average of the susceptibilities of the two terms of different multiplicity. For d^4 and d^7 the situation is more complicated as the spin–orbit coupling connects the two states involved. The presence of low-symmetry components in the crystal field is another factor which must also be considered.

The most favorable case for an unambiguous experimental observation of this type of equilibrium is the d^6 configuration where the low-spin system is diamagnetic and the change in the number of unpaired electrons is four.

The ferrous compounds of structures I–V present such an unambiguous example of a system in which both high- and low-spin ground states are thermally ac-



I, R = 1-pyrazolyl (pz); X = Y = H
II, R = C_6H_5; X = Y = H
III, R = H; X = Y = H
IV, R = H; X = CH_3; Y = H
V, R = H; X = Y = CH_3

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[1] L. E. Orgel, 10th Conseil Institute Chemie Solvay, Brussels, 1956.

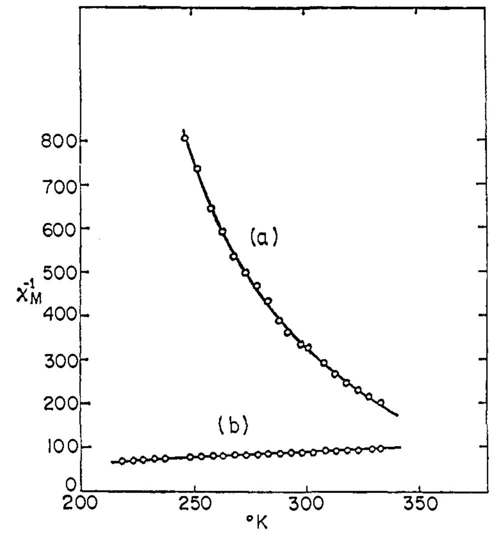

Figure 1. Plot of reciprocal molar susceptibility against temperature: (a) compound III in CH_2Cl_2, (b) compound V in $CHCl_3$.

cessible, without change of molecular geometry. (A possible difference could arise due to a Jahn–Teller distortion in the high-spin state. As indicated in the Discussion the large trigonal component in the crystal field leaves an orbital singlet lowest in the high-spin state, and Jahn–Teller effects will probably be small. There will, of course, be a difference in Fe–N bond lengths in the two states.)

Minor changes in molecular structure give rise to fully diamagnetic low-spin compounds, fully paramagnetic high-spin compounds (μ_{eff} at room temperature ~ 5.2 BM), and compounds for which the moment is intermediate and strongly temperature dependent. The diamagnetic or partially diamagnetic complexes are deeply colored magenta compounds, while the fully paramagnetic compounds are pale green, almost colorless.

Other possible examples of anomalous magnetic behavior close to the crossover point have been reported by Stoufer, *et al.*, for $Co^{2+}(d^7)$,[2] Ewald, *et al.*, for $Fe^{3+}(d^5)$,[3] and Melson, and Busch[4] for $Ni^{2+}(d^8)$. More recently a convincing example for $Fe^{2+}(d^6)$ has been reported by Konig and Madya.[5]

Magnetic Susceptibilities

The room-temperature moments for some of these complexes measured in solution by an nmr method, together with their molecular weights, are listed in Table I. (The molecular weights were measured in chloroform using the vapor-pressure osmometer technique.) It is clear from these molecular weights that we are dealing with monomeric species. The rigid tridentate character of the ligand eliminates the possibility of a conformational equilibrium of the type which has been reported for four-coordinate Ni(II) chelates such as nickel(II) N,N′-dimethylaminotroponeiminate.[6]

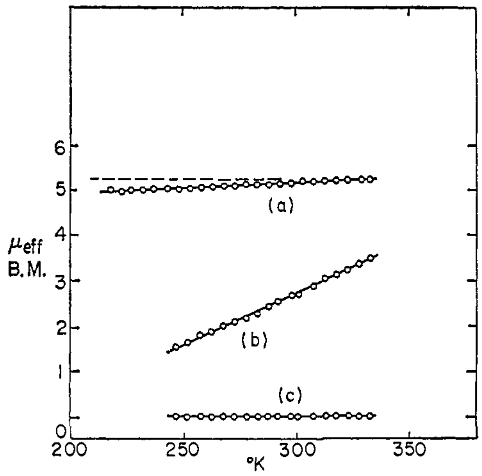

Figure 2. Plot of effective magnetic moment against temperature: (a) compound V in $CHCl_3$, (b) compound III in CH_2Cl_2, (c) compound I in $CHCl_3$.

Table I. Room-Temperature Moments and Molecular Weights of Octahedral Iron(II) Poly(1-pyrazolyl)borates

Compound	Moment, BM	Molecular weight	
		Calcd	Measured
I	~0	614	614
II	~0	634	630
III	2.71[a]	481	479
IV	5.03	650	647
V	5.22	734	716

[a] Measured in CH_2Cl_2 because of solubility. All others measured in $CHCl_3$.

The data of Table I show that the first two and last two complexes have moments corresponding essentially to fully low-spin and fully high-spin systems, respectively, and that the remaining complex bis[hydrotris(1-pyrazolyl)borate]iron(II) has an intermediate moment. If this arises from a spin equilibrium it should be strongly temperature dependent. This latter prediction is substantiated by the data shown in Figures 1 and 2. Figure 1 shows plots of the reciprocal molar susceptibility against temperature for the complexes III and V. The diamagnetic compounds cannot, of course, be included in this plot. Compound IV shows essentially the same behavior as V. Figure 2 shows a plot of the effective moments against temperature for complexes I, III, and V, complex I being diamagnetic at all temperatures studied. It appears there is some reduction in the effective moment of complex V with decreasing temperature, possibly indicating some favoring of the diamagnetic form. The moment is close to 5.2 BM at room temperature and about 5.0 BM at the lower temperatures. However, an alternative explanation could be that the ^5E_g component of the split $^5T_{2g}$

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(2) (a) R. C. Stoufer, D. H. Busch, and W. B. Hadley, *J. Am. Chem. Soc.*, **83**, 3732 (1961); (b) R. C. Stoufer, D. W. Smith, E. A. Clevenger, and T. E. Norris, *Inorg. Chem.*, **5**, 1167 (1966); (c) J. G. Schmidt, W. S. Brey, and R. C. Stoufer, *ibid.*, **6**, 268 (1967).

(3) A. H. Ewald, R. L. Martin, I. G. Ross, and A. H. White, *Proc. Roy Soc.* (London), **A280**, 235 (1964).

(4) G. A. Melson and D. H. Busch, *J. Am. Chem. Soc.*, **86**, 4830 (1964).

(5) E. Konig and K. Madya, *Chem. Commun.*, **3**, 61 (1966).

(6) D. R. Eaton, W. D. Phillips, and D. J. Caldwell, *J. Am. Chem. Soc.* **85**, 397 (1963).

ground state lies lowest and that the temperature dependence of the effective moment is due to varying populations of the sublevels in the E state. The behavior of complex III, though, is only interpretable in terms of a spin equilibrium. The variation of the effective moment with temperature is as nearly intermediate between the high-spin and low-spin cases as one could expect to realize. Several other complexes have also been studied. The compound with R = X = H, Y = *i*-Pr showed intermediate behavior analogous to complex III, and the compound with R = *n*-Bu, X = Y = H proved to be diamagnetic.

Optical Spectra

The positions of absorption maxima and the extinction coefficients for these Fe(II) complexes are given in Table II. Results for compound II have been omitted as the spectrum is closely similar to those of complexes I and III. The relatively small extinction coefficient of the absorption at ~19,000 cm^{-1} in complex III indicates that it is probably a d–d transition, and since this band is also found in the fully diamagnetic molecule I it must be a singlet–singlet transition. We assign the absorption to the expected $^1T_{1g}(^1I) \leftarrow {}^1A_{1g}$ transition. It might be noted that complex III is almost completely diamagnetic at room temperature in the solid state. Mössbauer and magnetic susceptibility studies have shown that the same general type of behavior with temperature is observed in the solid as is found in solution. However, the equilibrium has shifted in favor of the diamagnetic form.[7]

Table II. Electron Spectra of Octahedral Iron(II) Poly(1-pyrazolyl)borates

Compound	λ, mμ,	ν, cm^{-1}	ε	Assignment
I in $CHCl_3$	529	18,900	90	$^1T_{1g}(^1I) \leftarrow {}^1A_{1g}$
	342	29,200	13,700	Metal-to-ligand charge transfer
	318	31,400	8,600	
	286	35,000	4,000	
	207[a]	48,300	20,000	Ligand
III in CH_2Cl_2	535	18,700	57	$^1T_{1g}(^1I) \leftarrow {}^1A_{1g}$
	337	29,700	12,100	Metal-to-ligand charge transfer
	322	31,100	8,200	
	288	34,700	5,400	
	206[a]	48,500	25,000	Ligand
IV in $CHCl_3$	800	12,500	3.2	$^5E_g \leftarrow {}^5T_{2g}$
	220[a]	45,400	34,000	
V in C_6H_6	800	12,500	3.2	$^5E_g \leftarrow {}^5T_{2g}$
	225[a]	44,400	39,000	

[a] Measured in cyclohexane.

The absorption spectra and appearance of complexes IV and V are similar to those of hydrated ferrous salts. Only one d–d transition of any intensity is observed, and as indicated in Table II this is assigned to the $^5E_g \leftarrow {}^5T_{2g}$ transition. In the hydrated ferrous salts this transition usually shows a pronounced doubling which has been ascribed to either Jahn–Teller distortions or to low-symmetry components in the crystal field.[8] In the present case the band is quite symmetrical and shows no evidence of splitting. The transition should occur at a frequency Δ, showing that $\Delta \approx 12{,}500\ \text{cm}^{-1}$ for the high-spin systems. Δ is the octahedral splitting parameter.

The reason for the dramatic color change from pale green to deep magenta on going from fully high-spin to fully low-spin compounds is now clear. The first d–d transition occurs at a much shorter wavelength for the spin-paired compound. This is to be anticipated on the basis of a simple crystal-field calculation, as is shown in the Discussion. The singlet–singlet transition is 20–30 times more intense than the quintet–quintet. This is probably due to intensity borrowing from nearby charge-transfer absorption in the former case. For the high-spin systems, the d–d transition is well separated from the charge-transfer absorption. The charge-transfer absorption is at considerably shorter wavelengths in the high-spin systems. These high-spin chelates all have methyl substituents, and the shift may be ascribed to the hyperconjugative effect of these groups. Hyperconjugation raises the energy of the highest filled ligand π orbital. Thus the ionization potentials of alkyl-substituted ethylenes are lower than that of ethylene. Calculations indicate that the lowest antibonding π orbital is also raised in energy by alkyl substitution, but by a smaller amount so that the energy gap is decreased. This is supported by the red shift in the long wave absorption in ethylene on alkyl substitution. Thus the lowest unfilled ligand orbital is expected to occur at higher energies in the high-spin complexes than in the low-spin complexes. The energies of the d orbitals are unlikely to be grossly different in the high-spin and low-spin complexes. The large blue shift observed on passing from low spin to high spin is therefore consistent with the assignment of these bands to metal-to-ligand charge-transfer transitions.

Nuclear Magnetic Resonance Spectra

Nmr assignments for the octahedral ferrous complexes are complicated by the high-spin–low-spin equilibrium. The resonances for the 4-H proton in the parent complex and the 3,5-dimethyl complex, which are in essentially the same positions for the Co^{2+} derivatives,[9] are very different for the Fe^{2+} case since a large proportion of the parent complex is in the diamagnetic state. Assignments have been made mainly on the basis of line intensities and widths, although the effect of substitution can be utilized by comparing complexes IV and V. Chemical shifts at 30° and assignments for the octahedral Fe(II) complexes are given in Table III.

It is clear that the nmr data are in qualitative agreement with the conclusions from the susceptibility data. Thus the resonances in compounds I and II are in the positions anticipated for diamagnetic complexes, the positions of the resonances for the 3-, 4-, and 5-H on the pyrazolyl groups being close to those for the corresponding zinc complexes.[9] Complex III shows intermediate shifts which are compatible with the assumed spin equilibrium, and much larger shifts are observed for the fully paramagnetic complexes IV and V. More direct evidence for the spin equilibrium in complex

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(7) J. P. Jesson and J. F. Weiher, *J. Chem. Phys.*, **46**, 1955 (1967).

(8) F. A. Cotton and M. D. Meyers, *J. Am. Chem. Soc.*, **82**, 5023 (1960).

(9) J. P. Jesson, S. Trofimenko, and D. R. Eaton, *ibid.*, **89**, 3148 (1967).

Table III. 60-Mcps Nmr Data for Octahedral Fe(II) Complexes[a]

Compound	Shift, mμ	Assignment
I	−486	3-, 4-, 5-H
	−433	
	−397	
II	−474	3-, 4-, 5-H
	−425	
	−379	
	−491	*p*-H
	−457	*o*- and *m*-H
	−430	
III	−815	3-, 4-, 5-H
	−815	
	−480	
	∼+240	H on boron
IV	−2870	4-H
	−2350	3-CH_3
	−770	5-CH_3
	+2570	H on boron
V	−2330	3-CH_3
	−820	5-CH_3
	−570	4-CH_3
	+2625	H on boron

[a] Shifts measured from TMS as internal standard.

III is provided by the temperature dependence of the shifts. The temperature dependence of the shifts for complexes IV and V (see Figure 3b and c) show the normal Curie-type behavior expected in paramagnetic systems. Complex III, however (Figure 3a), shows the opposite type of behavior, the shifts converging toward the diamagnetic positions as the temperature is lowered.

Discussion

An approximate estimate of the magnitude of the octahedral splitting parameter Δ required to induce spin pairing may be obtained by equating the first-order expressions for the energies of the electronic states involved, using the strong-field scheme. The Δ found in this way is equal to the mean-pairing energy π.

Griffiths[10] has found expressions for the mean pairing energies in these configurations and obtained the following approximate conditions for the occurrence of the low-spin form (in cm^{-1}).

$$\begin{aligned} d^5\ \Delta &> 7.5B + 5C \approx 24{,}000 \\ d^6\ \Delta &> 2.5B + 4C \approx 16{,}400\,(12{,}500) \qquad (1) \\ d^7\ \Delta &> 7B + 4C \approx 20{,}000\,(10{,}000) \end{aligned}$$

The values after the expressions have been calculated assuming $B = 800$ and $C = 4.5B = 3600\ \text{cm}^{-1}$. The numbers in parentheses are the Δ values estimated from the spectra of the octahedral high-spin iron(II) and cobalt(II) poly(1-pyrazolyl)borates.[9] It can be seen that spin pairing is more easily achieved for the d^6 than for the d^5 or d^7 configurations.

The absorption at 12,500 cm^{-1} in complexes IV and V has been assigned to the transition $^5\text{E}_g \rightarrow {}^5\text{T}_{2g}$ which on simple crystal-field theory has an energy Δ(hs) = 12,500 cm^{-1} (hs = high spin). However, as Ewald, *et al.*,[3] have pointed out, because of the expected in-

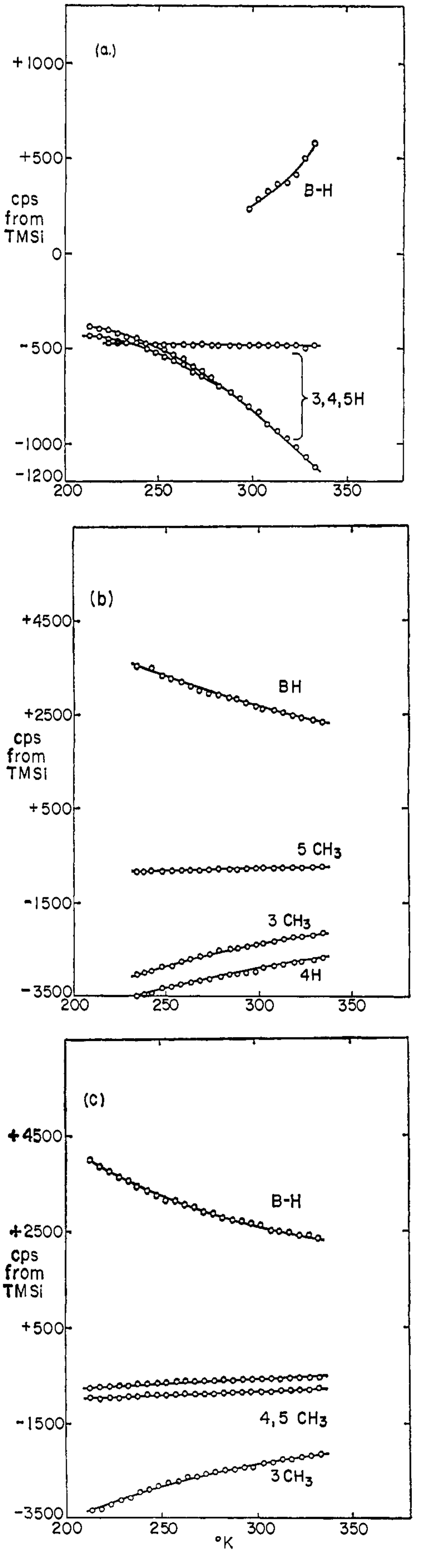

Figure 3. Proton resonance spectra of octahedral ferrous complexes as a function of temperature measured in CDCl_3 (shifts from TMS at 60 Mcps): (a) compound III, (b) compound IV, (c) compound V.

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(10) J. S. Griffiths, *J. Inorg. Nucl. Chem.*, 2, 1 (1956).

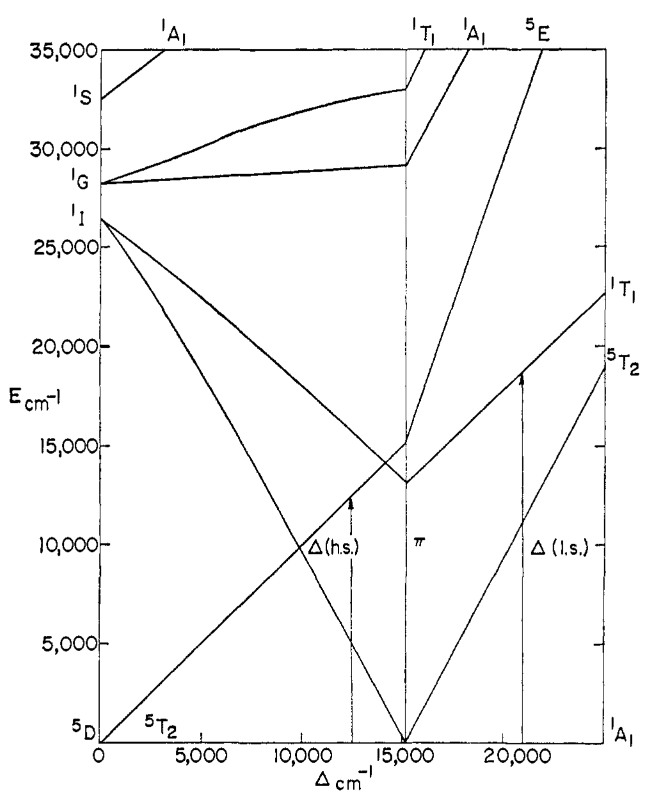

Figure 4. Tanabe diagram for d^6 configuration. Only the quintet states and the $^1T_{1g}$ and $^1A_{1g}$ states below 35,000 cm^{-1} have been included. The positions of the experimentally observed high-spin transition and first low-spin transition are indicated in the figure; B = 800 and C = 3600 cm^{-1}.

crease in bond lengths on transferring an electron from the t_{2g} orbitals (nonbonding) to the e_g orbitals (antibonding), the Δ values for the high- and low-spin states in their equilibrium geometries will be different, and one has the approximate condition

$$\Delta(\text{hs}) < \pi < \Delta(\text{ls}) \qquad (2)$$

the Δ values referring to the equilibrium situations (ls = low spin).

Robinson, *et al.*,[11] have made an estimate of the critical Δ(hs) value for crossover to the low-spin form by comparison of a series of iron(II) and the corresponding nickel(II) complexes. They note that the ratio $\Delta_{Fe^{2+}}/\Delta_{Ni^{2+}} = 1.11 \pm 0.07$ for a series of five complexes. The weakest ligand which produced spin pairing in the iron(II) complexes gave an extrapolated Δ(hs) ≈ 13,400 cm^{-1}. The strongest ligand which did not give spin pairing has Δ(hs) = 11,600 cm^{-1}. It was therefore estimated that the critical value of Δ(hs) is 12,500 ± 800 cm^{-1}, in remarkably good agreement with the value found from the iron poly(1-pyrazolyl)borates. Some variation in the critical value of Δ(hs) is possible since the mean pairing energy π depends on the interelectronic repulsion parameters (B and C) which themselves vary with the degree of covalent bonding in the complexes.

The relevant electronic levels of d^6 as a function of crystal-field strength Δ, for octahedral coordination, are shown in Figure 4. The levels were calculated using the matrices of Tanabe and Sugano[12] with B = 800 and C = 3600 cm^{-1}. The choice of values for B and C is based on the following considerations. The free ion value of B for Fe^{2+} (~940 cm^{-1}) is somewhat lower than the values for Co^{2+} (~980 cm^{-1}) and Ni^{2+} (~1040 cm^{-1}).[13] It seems likely that the value in the complex will also be lower. Values of B of ~830 and ~850 were found for the corresponding Co(II) and Ni(II) complexes. A value of B = 800 cm^{-1} for the Fe(II) complexes is therefore reasonable. The assumption $C = 4.5B$ = 3600 cm^{-1} leads to a mean pairing energy of $\pi \approx$ 16,400 cm^{-1} from eq 1. The crossover point "π" in the full calculations is seen to be ~15,000 cm^{-1} rather than the value of 16,400 cm^{-1} given by the approximate formula. The difference is due to the interaction between the four $^1A_1$ states of the configuration, which has been neglected in the simple formulas.

The positions of the first high-spin and first low-spin transitions are marked on Figure 4, occurring at Δ(hs) = 12,500 cm^{-1} and Δ(ls) = 21,000 cm^{-1}. In view of the neglect of the low-symmetry component of the field, the uncertainty in the values of the interelectronic repulsion integrals, and the fact that they are assumed to have the same value for high- and low-spin compounds, there may be considerable error in the Δ(ls) value. In the iron(III) dithiocarbamates, Ewald, *et al.*,[3] found that their electronic spectral data gave a quite low value for Δ(hs) ≈ 12,800 cm^{-1}. This value is even lower than Δ for $Fe(H_2O)_6^{3+}$. A similar situation was noted in the Co(II) complexes of Stoufer, *et al.*[2] The results of Ewald, *et al.*,[3] were rationalized in terms of a very large nephelauxetic effect with B(complex)/B(free ion) = $\beta \approx 0.47$. Values of β and Δ could not be obtained directly from electronic spectral data and were estimated by comparison of optical data for other dithiocarbamates with the corresponding hexaaquo complexes.

In the present case Δ(hs) is already considerably larger than $\Delta[Fe(H_2O)_6^{2+}]$, ~10,400 cm^{-1}. The β value, on the basis of our assumption that the reduction in B is similar to that found in the Co(II) and Ni(II) cases,[9] is ~0.85.

It is anticipated that in the complex $Fe[HB(pz)_3]_2$ which has D_{3d} symmetry, there will be a large trigonal component in the crystal field. Such a trigonal component has been established for $Co[HB(pz)_3]_2$, and it has been shown that the splitting of the $^4T_{1g}$ ground state is approximately 2000 cm^{-1} with the orbital doublet lying lowest.[14] It is also anticipated that the orbital splitting of the $^5T_{2g}$ state in $Fe[HB(pz)_3]_2$ due to this trigonal component will have the opposite sign to that of the Co(II) complex, giving an orbital singlet as the lowest component.[15] This follows from simple one-electron theory since the high-spin d^7 system has a single hole in the t_{2g} shell, and the high-spin d^6 ground state is degenerate owing to a single electron in the t_{2g} shell. However, it has been suggested that the inclusion of Coulomb and exchange interactions can reverse the sign of the ground-state splitting for Co^{2+}.[16] In addition the assumption that the low-symmetry

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[11] M. A. Robinson, J. D. Curry, and D. H. Busch, *Inorg. Chem.*, **2**, 1178 (1963).

[12] Y. Tanabe and S. Sugano, *J. Phys. Soc. Japan*, **9**, 753 (1954).

[13] J. S. Griffiths, "The Theory of Transition Metal Ions," Cambridge University Press, London, 1961.

[14] J. P. Jesson, *J. Chem. Phys.*, **45**, 1049 (1966).

[15] J. H. van Vleck, *Discussions Faraday Soc.*, **26**, 96 (1958).

[16] P. K. Baltzer, private communication.

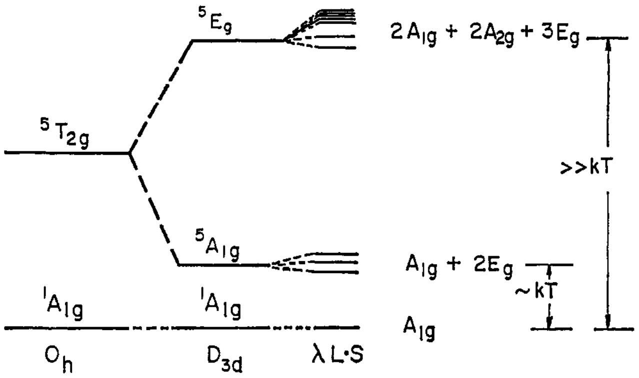

Figure 5. Level scheme for ground-state manifold of Fe[HB(pz)$_3$]$_2$.

component of the crystal field is of the same form for the Co^{2+} and Fe^{2+} cases may not be completely justified. Since the orbital degeneracy of the ground state affects the interpretation of the susceptibility data, the experimental evidence bearing on this point will be examined.

Paramagnetic resonance experiments for Fe^{2+} and Co^{2+} in the cadmium chloride lattice give the following results.[17]

Fe^{2+} $g_\parallel = 7.4$ $g_\perp = 0?$
Co^{2+} $g_\parallel = 3.06$ $g_\perp = 4.98$

Similar results have been obtained in this laboratory for the same ions in $MgTiO_3$.

Fe^{2+} $g_\parallel \approx 12$ $g_\perp = 0\ ?$
Co^{2+} $g_\parallel = 2.78$ $g_\perp = 5.02$

The measurements were made on powders at 4.2°K, and there is considerable uncertainty in the $g_\parallel$ value for Fe^{2+} due to the breadth of the absorption. In both cases the Co^{2+} results show unambiguously that the orbital singlet lies lowest in the split ground state.[18] The corresponding treatment for the $^5T_{2g}$ state of Fe^{2+} has been given by Griffiths.[13] $g_\parallel$ varies from about 4 to 10, depending on the magnitude and sign of the axial component in the crystal field. $g_\perp = 0$. Values of $g_\parallel$ between 7 and 10 correspond to the orbital doublet lying lowest, suggesting that this is the case for the $CdCl_2$ and $MgTiO_3$ systems. This interpretation could be invalidated in the even-electron Fe^{2+} system by the presence of rhombic components in the crystal fields. The crystal structures for the two cases demand accurately trigonal symmetry about the metal in the host material. The substitution of the Fe^{2+} impurity could introduce slight rhombic components into the fields. It is difficult to say whether the distortions would be sufficiently large to reverse the assignment. Thus the paramagnetic resonance data do seem to indicate that the ground-state splittings for Fe^{2+} and Co^{2+} in the same trigonal field are of the opposite sign, and for the present discussion we shall therefore assume that the splitting of the orbital triplet in the ferrous poly(1-pyrazolyl)borates is large and leaves an orbital singlet lowest.

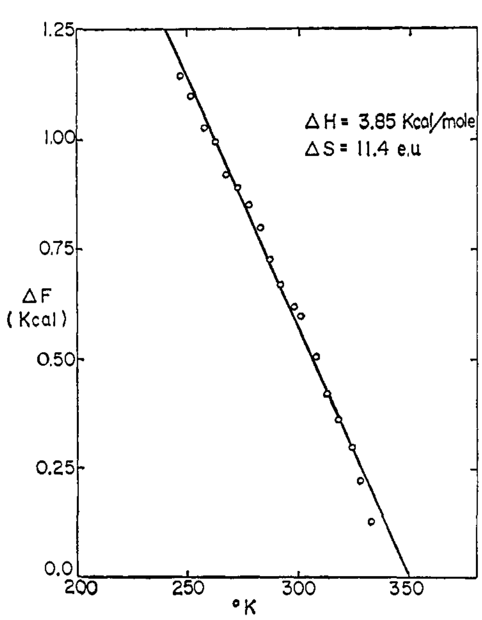

Figure 6. Plot of free energy against temperature for spin equilibrium in Fe[HB(pz)$_3$]$_2$.

A schematic energy level diagram based on this assumption is shown in Figure 5. The spin equilibrium involves the $^5A_{1g}$ and $^1A_{1g}$ states. Diagrams such as Figure 5 must be viewed with caution when temperature studies are involved since the level scheme may be a fairly sensitive function of temperature. If $^5A_{1g} \leftrightarrow {}^1A_{1g}$ separation varies approximately linearly with temperature, the effect will appear as an entropy term when the free energy of the equilibrium is considered. Such an effect can also be produced by differences in the vibrational partition functions for the high-spin and low-spin states.[3] In a previous paper it was suggested[6] that an appreciable entropy term in the apparent free energy for an equilibrium of this type would argue for a geometrical difference between the species involved. The arguments given above, however, suggest that this is not the only possible origin of the term.

Splitting of the $^5A_{1g}$ state due to spin–orbit effects and the low-symmetry component of the field will be of the order of tens of wavenumbers, and for our purposes the state will behave as a simple spin quintet with $g \sim 2$. g will be slightly larger than 2 owing to spin–orbit mixing from excited states, and a value of 2.13 is obtained from the moment of the fully paramagnetic complex.

The susceptibility of the system as a function of temperature is then given by

$$\chi_M = \frac{Ng^2\beta^2S(S+1)}{3kT}[e^{\Delta G/RT} + 1]^{-1} \tag{3}$$

ΔG being the molar free-energy change in the process. The expression may be written in terms of the effective moments as

$$\Delta G = RT \ln \left[\frac{\mu_\infty^{2}}{\mu^2} - 1\right] \tag{4}$$

where μ_∞ is the moment for the fully paramagnetic form, and this is taken as 5.22 BM from the moment of V.

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In Figure 6 the free-energy change for the spin equilibrium in $Fe[HB(pz)_3]_2$ is plotted against temperature, giving $\Delta H = 3.85$ kcal/mole and $\Delta S = 11.4$ eu. If our assumptions about the energy level scheme are correct, the entropy term of 11.4 eu will contain a contribution $R \ln 5 = 3.2$ eu due to the spin degeneracy of the quintet state but no contribution from orbital degeneracy. The remaining 8.2 eu must be accounted for in terms of a temperature dependence of the effective crystal field, variable solvation effects, and differences in the vibrational partition functions between the two states.

There are two possible mechanisms for the paramagnetic shifts observed in the nuclear resonance spectra. Spin delocalization to the ligand can result in a Fermi contact interaction, the shifts being given by an expression of the form

$$\Delta \nu_i = -a_i \frac{2\pi g \beta \nu S(S + 1)}{3kT\gamma} \tag{5}$$

where a_i is in cycles per second. The expression is based on the assumption of a Curie law magnetic behavior of the ground state, a situation which is seldom if ever realized in paramagnetic compounds showing well-resolved nmr spectra.

The second mechanism involves the dipolar coupling of the electron and nuclear magnetic moments and gives a net shift for the nuclear resonances in solution only if the electron moment is anisotropic. With the limiting assumption of a Curie law situation, an expression of the form

$$\Delta \nu = -\frac{1}{15}\nu\left(\frac{3\cos^2\theta - 1}{r_3}\right)\frac{\beta^2 S(S + 1)}{3kT}[g_{\parallel} - g_{\perp}][3g_{\parallel} + 4g_{\perp}] \tag{6}$$

is derived. The additional assumption has been made, in averaging over the tumbling motion, that the spin–lattice relaxation time is short relative to the correlation time for tumbling. This situation is likely to apply to cases where well-resolved nmr spectra are observed since we have the criterion $T_1^{-1} \gg a_i$, required for sharp spectra, T_1 being the electron spin–lattice relaxation time and a_i the electron–nuclear hyperfine coupling constant.

If either or both types of interaction are present, the shifts are inversely proportional to temperature for the paramagnetic species. The diamagnetic–paramagnetic equilibrium can be allowed for by the factor $[e^{\Delta G/RT} + 1]^{-1}$ as in the susceptibility equations. Quite large anisotropies can be induced in the $^5T_2$ ground state by low-symmetry components in the field,[13] and it would be unwarranted to assume that the observed shifts are due only to the scalar interaction. In addition to the departures from the simple $1/T$ behavior due to the spin equilibrium, departures can also be produced by non-Curie law behavior. Differences in g-tensor components and hyperfine coupling constants for the split levels of the ground state would require a more complicated Boltzmann averaging, giving a relatively complex temperature dependence.

In view of the limitations imposed on the formulas and the difficulty in establishing the proton shifts for the fully paramagnetic system, the data do not seem to merit analysis in terms of an enthalpy and entropy change for the equilibrium.

Experimental Section

The epr measurements were made using a Varian 100-kcps X-band spectrometer equipped with a 12-in. magnet having a fixed 1.75-in. gap. Field measurements were made using a Harvey Wells FC-502 gaussmeter and CMC 709C frequency counter. Frequency measurements were made with a Hewlett-Packard X5332A frequency meter. A quartz helium finger was used to maintain the samples at 4.2°K.

Other experimental techniques used have been described in a previous paper.[9]