Table IX. ^{57}Fe Mössbauer Parameters for $[Fe(C_5H_5)_2][(TCNQ)F_4]$ and $[Fe(C_5Me_5)_2]_2[(TCNQ)F_4]_3$

compd	temp (T), K	isomer shift (δ), mm/s	line width (Γ), mm/s
$[Fe(C_5Me_5)_2][(TCNQ)F_4]$	300	0.411	0.374
	4.23	0.528	0.395
	1.60	0.530	0.512
$[Fe(C_5Me_5)_2]_2[(TCNQ)F_4]_3$	300	0.439	0.360
	4.23	0.544	0.878
	1.60	0.539	0.734

sorptions at 2225 cm^{-1} ($(TCNQ)F_4{}^0$) and at 2179 and 2195 cm^{-1} ($[(TCNQ)F_4]^{\bullet -}$).

Solid-State Structure. The solid possesses a complex structure that is comprised of segregated chains of $S = {}^1/_2$ cations and anions. The anions reside as $[(TCNQ)F_4)]_2{}^{2-}$ dimers perpendicular to $(TCNQ)F_4{}^0$ and are best seen in Figures 8 and 9. This motif has not been reported for any simple or complex salts of TCNQ.

The $[(TCNQ)F_4]_2{}^{2-}$ dimers lie perpendicular to $(TCNQ)F_4{}^0$. Neutral $(TCNQ)F_4$, unlike TCNQ, possesses a similar motif[29] but exhibits short intermolecular C···N distances of 2.97 and 3.18 Å. As noted in Figure 8, there is a similar intermolecular N···C of 3.14 Å between the dimer and $(TCNQ)F_4{}^0$.

Electron Spin Resonance. At 100, 273, and 343 K, the 1:1 and 2:3 salts do not exhibit ESR spectra. $[(TCNQ)F_4]_2{}^{2-}$ dimers with similar interplanar separations were reported to exhibit triplet behavior.[27,28] However, such behavior was not observed. This presumably arises from fast relaxation, which is characteristic of $S = {}^1/_2$ $[Fe(C_5H_5)_2]^{\bullet +}$.[35] The ferrocenium cation couples with the $[TCNQ]_2{}^{2-}$ triplets and broadens the signal.

^{57}Fe Mössbauer Spectroscopy. The ^{57}Fe Mössbauer spectra were collected at 1.6, 4.2, and 300 K. Singlets characteristic of Fe^{III} ferrocenium were observed (Figure 10, Table IX). At low temperature there was no evidence for zero-field Zeeman-split Mössbauer spectra. This contrasts strongly with what we have reported for the $[DDQ]^{\bullet -}$,[8] $[TCNE]^{\bullet -}$,[9] $[TCNQ]^{\bullet -}$,[36] $[C_4(CN)_6]^{\bullet -}$,[11] and $[C_6(CN)_6]^{\bullet -}$ [12] salts, respectively. Decamethylferrocenium salts of these $S = {}^1/_2$ anions exhibit resolved magnetic hyperfine splitting. Our present observations are consistent with a $S_{total} = 0$ ground state of $[(TCNQ)F_4]_2{}^{2-}$ dimers and $S = 0$ for $(TCNQ)F_4{}^0$.

It was our observation that zero-field Zeeman-split ^{57}Fe Mössbauer spectra are a necessary, but not sufficient, condition to anticipate cooperative magnetic properties.[6b,37] Since the 1:1 and the 2:3 salts do not possess the structural motif we have identified to support meta/ferromagnetism, i.e., $\cdots D^+ \cdot A^- \cdot D^+ \cdot A^- \cdots$ (D = donor; A = acceptor), and these salts do not exhibit Zeeman-split ^{57}Fe Mössbauer spectra, we elected to not pursue the study of the magnetic properties.

Acknowledgment. We thank C. Vazquez (Du Pont) for synthetic assistance and M. Extine (Molecular Structure Corp.) for helpful discussions regarding the refinement of the structures.

Supplementary Material Available: Tables of the thermal parameters, general temperature factors, and weighted least-squares planes for both the 1:1 and 2:3 salts (13 pages); listings of structure factors for both compounds (29 pages). Ordering information is given on any current masthead page.

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Spin Equilibrium in Iron(II) Poly(1-pyrazolyl)borate Complexes: Low-Temperature and High-Pressure Mössbauer Spectral Studies

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Received July 22, 1986

A high-pressure and low-temperature applied field Mössbauer effect study has revealed that $Fe[HB(pz)_3]_2$, which contains low-spin iron(II) from room temperature down to 4.2 K, may be converted in part to high-spin iron(II) at pressures above ca. 40 kbar. In contrast, $Fe[HB(3,4,5\text{-}(CH_3)_3pz)_3]_2$, which our studies reveal remains high-spin down to 1.7 K, may be converted to the low-spin state at high pressure. Because of the weaker crystal field potential of the substituted ligand in this compound, a pressure of ca. 55 kbar is required to make the high-spin $^5T_{2g}$ state and low-spin $^1A_{1g}$ state equivalent in energy at room temperature. In $Fe[HB(3,5\text{-}(CH_3)_2pz)_3]_2$ the intermediate crystal field potential yields a spin crossover at low temperature (ca. 195 K), and in this case only 4 kbar is required to make the two spin states equivalent in energy at room temperature. All three compounds show a linear dependence of the isomer shift and quadrupole interaction upon the applied pressure, and the spin-state transitions are completely reversible.

Introduction

The preparation of the poly(1-pyrazolyl)borate ions[1] led to the immediate investigation of their chelating ability with divalent transition-metal ions.[2,3] Perhaps most interesting were the iron(II) complexes formed with the hydrotris(1-pyrazolyl)borate ligand and its dimethyl and trimethyl derivatives.[4-6] These ligands formed complexes of stoichiometry $Fe[B(pz)_4]_2$, $Fe[HB(pz)_3]_2$, $Fe[HB(3,5\text{-}(CH_3)_2pz)_3]_2$, and $Fe[HB(3,4,5\text{-}(CH_3)_3pz)_3]_2$ (pz is 1-pyrazolyl), in which the crystal field potential of the different ligands spanned the range needed to produce iron(II) in its high- and low-spin states. Hence in the solid state $Fe[HB(pz)_3]_2$ is low spin, $Fe[HB(3,4,5\text{-}(CH_3)_3pz)_3]_2$ is high spin, and $Fe[HB(3,5\text{-}(CH_3)_2pz)_3]_2$ is high spin at room temperature and low spin at 78 K and below.[6] This set of complexes thus provides a range

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Table I. Mössbauer Spectral Parameters Obtained at Various Temperatures and Applied Fields[a]

			high-spin iron(II)					low-spin iron(II)				
compd	T, K	H_{app}, T	δ, mm/s	ΔE_Q, mm/s	η	Γ, mm/s	% A	δ, mm/s	ΔE_Q, mm/s	η	Γ, mm/s	% A
$Fe[B(pz)_4]_2$	295	0					0	0.40	0.32	...	0.30	100
	78	0					0	0.46	0.34	...	0,33	100
	4.2	0					0	0.48	0.32	...	0.34	100
	4.2	6					0	0.47	0.35	0.1	0.29	100
$Fe[HB(pz)_3]_2$	295	0					0	0.41	0.20	...	0.29	100
	78	0					0	0.47	0.22	...	0.27	100
	4.2	0					0	0.48	0.22	...	0.27	100
	4.2	6					0	0.48	0.24	0.15	0.26	100
$Fe[HB(3,5\text{-}(CH_3)_2pz)_3]_2$	400	0	0.96	3.59	...	0.29	100					0
	350	0	1.00	3.64	...	0.31	100					0
	300	0	1.03	3.67	...	0.33	100					0
	195	0	1.06	3.68	...	0.31	53	0.52	0.11	...	0.35	47
	78	0					0	0.55	0.11	...	0.26	100
	4.2	0					0	0.56	0.12	...	0.27	100
	4.2	6					0	0.55	0.12	...	0.27	100
$Fe[HB(3,5\text{-}(CH_3)_2pz)_3]_2$[b]	292	0	1.03	3.65	...	0.30	100					0
	78	0	1.14	3.67	...	0.32	50	0.55	0.10	...	0.28	50
	4.2	0	1.15	3.66	...	0.30	42	0.56	0.11	...	0.30	58
$Fe[HB(3,4,5\text{-}(CH_3)_3pz)_3]_2$	293	0	1.04	3.70	...	0.26	100					0
	195	0	1.09	3.72	...	0.27	100					0
	78	0	1.13	3.72	...	0.26	100					0
	4.2	0	1.20	3.70	...	0.25	100					0
	4.2	3	1.17	−3.80	0.2	0.30	100					0
	4.2	6	1.17	−3.70	0.1	0.35	100					0
	1.7	0	1.20	−3.71	...	0.29	100					0

[a] Isomer shift relative to room-temperature natural α-iron foil. [b] Recrystallized from toluene and not vacuum dried.

of electronic spin states and comprises a convenient basis for the study of the influence of high pressure upon the electronic spin state of divalent iron.

The purpose of this paper is to present Mössbauer effect spectral results obtained at high-pressure and at low temperature in an applied magnetic field. These results further illustrate the variety of spin states that may be produced at iron(II) in these complexes. Specifically, we will show that high pressure may be used to produce a spin-state crossover from low spin to high spin in $Fe[HB(pz)_3]_2$ and from high spin to low spin in both $Fe[HB(3,5\text{-}(CH_3)_2pz)_3]_2$ and $Fe[HB(3,4,5\text{-}(CH_3)_3pz)_3]_2$.

Experimental Section

These complexes, which are the same samples used in earlier studies,[7] were prepared by the standard literature methods[2] by using ca. 90% enriched iron-57 obtained from Oak Ridge National Laboratory. In the case of $Fe[HB(3,5\text{-}(CH_3)_2pz)_3]_2$ measurements were made on samples that were recrystallized from toluene and vacuum-dried at 100 °C for 1 h. The sample of $Fe[HB(pz)_3]_2$ was sublimed before the measurements.

The Mössbauer spectra were obtained on a Harwell constant-acceleration spectrometer, which utilized a room-temperature rhodium-matrix cobalt-57 source and was calibrated at room-temperature with natural α-iron foil. The liquid helium spectra were obtained in cryostats in which the sample was placed directly in the liquid helium. The sample temperature was determined from the vapor pressure above the liquid helium. The magnetically perturbed spectra were obtained with a British Oxygen Corp. superconducting magnet and cryostat, which produced a transverse magnetic field that was calibrated by measuring the change in the iron-foil internal hyperfine field produced by the magnet. The high-pressure spectra were obtained in a gold-gasketed opposed-diamond-anvil cell in a configuration described in an earlier paper, which also discussed the method of pressure calibration.[8] The point source[8] used in these experiments typically exhibited a linewidth of 0.31 mm/s. Approximately 12–24 h were required to obtain each high-pressure spectrum. Spectra above room temperature were obtained with a Ricor high-vacuum furnace. The zero-field Mössbauer spectra were fit to symmetric quadrupole doublets with Lorentzian line shapes by using standard least-squares computer minimization techniques. The resulting spectral parameters are accurate to at least ±0.02 mm/s. The applied field spectra were evaluated by using the method of Lang and Dale.[9]

Results and Discussion

The Mössbauer spectral parameters for each of the compounds studied herein are reported as a function of temperature in Table I. These results are in good agreement with the results presented in the earlier studies[4,6] and extend the results to a wider range of temperatures as well as to applied magnetic fields. The Mössbauer spectral results obtained at room temperature at various applied pressures in an opposed-diamond-anvil cell are presented to Table II. The results were all obtained by using a gold gasket to produce a hydrostatic pressure throughout the sample. Our earlier results[8] were obtained in an ungasketed cell, which may account for the small differences observed. In all cases the hyperfine parameters show a virtually linear variation with pressure with the least-squares fits given in Table III.

The Mössbauer spectral parameters for $Fe[B(pz)_4]_2$ are typical of low-spin iron(II) in an octahedral coordination environment. This electronic configuration corresponds to a $^1A_{1g}$ ground state in pure octahedral symmetry, and, hence, there is little or no valence contribution to the electric field gradient tensor. The small quadrupole interaction no doubt arises from a small ligand or lattice contribution to the EFG tensor. The small asymmetry parameter provides further support for this conclusion. Because the quadrupole interaction in this compound is small, it is hard to determine the asymmetry parameter with great accuracy and we estimate that the 0.1 value is only valid to ca. ±0.1. The resulting fit to the magnetically perturbed spectrum indicates that the internal field is exactly equal to the applied field as is shown in Figure 1. No high-pressure results were obtained for this compound.

Mössbauer spectral parameters for $Fe[HB(pz)_3]_2$ are surprisingly similar to those of $Fe[B(pz)_4]_2$ and are typical of low-spin iron(II) complexes. The asymmetry parameter is close to zero, as would be expected for a compound whose X-ray structure shows[10] very little variation in the iron to nitrogen bond distances. As expected for a diamagnetic material, the observed internal field is equal to the applied field. The simplicity of the resulting spectra is illustrated in Figure 2. In no case do we see any indication of a high-spin component in this compound at ambient pressure and room or lower temperatures. However, a high-temperature

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Table II. Mössbauer Spectral Parameters Obtained at High-Pressure[a]

		high-spin iron(II)				low-spin iron(II)				
compd	P, kbar	δ, mm/s	ΔE_Q, mm/s	Γ, mm/s	% A	δ, mm/s	ΔE_Q, mm/s	Γ, mm/s	% A	abs area, %ϵ mm/s
$Fe[HB(pz)_3]_2$	0				0	0.41	0.19	0.31	100	6.4
	45	0.88	3.36	0.70	15.3	0.33	0.32	0.45	84.7	11.0
	78	0.86	3.23	0.65	21.8	0.33	0.30	0.41	78.2	16.9
	0				0	0.40	0.19	0.30	100	
$Fe[HB(3,5\text{-}(CH_3)_2pz)_3]_2$	0	1.03	3.65	0.46	100				0	3.2
	2	1.02	3.65	0.46	70.4	0.43	0.48	0.82	24.6	4.7
	4	1.01	3.64	0.49	50.7	0.45	0.01	0.66	49.3	5.8
	6	1.02	3.64	0.38	41.5	0.44	0.13	0.41	58.5	6.8
	8	1.01	3.63	0.37	33.6	0.43	0.16	0.38	66.4	7.5
	15	1.00	3.64	0.32	21.2	0.42	0.20	0.35	78.8	8.6
	32	1.01	3.63	0.37	16.6	0.41	0.25	0.37	83.4	10.2
	40	0.99	3.63	0.38	16.2	0.39	0.32	0.41	83.8	
	70	0.97	3.61	0.41	14.5	0.35	0.43	0.49	85.5	
	0	1.02	3.66	0.36	100				0	
$Fe[HB(3,4,5\text{-}(CH_3)_3pz)_3]_2$	0	1.05	3.71	0.40	100				0	11.1
	24	1.03	3.66	0.42	72.1	0.45	0.32	0.55	27.9	11.2
	46	1.01	3.61	0.48	51.8	0.42	0.43	0.51	48.2	11.4
	68	0.98	3.58	0.54	46.7	0.38	0.52	0.55	53.3	12.9
	86	0.96	3.52	0.62	41.2	0.36	0.61	0.59	58.8	13.7
	43	0.99	3.58	0.54	54.0	0.41	0.46	0.54	46.0	
	0	1.06	3.72	0.36	100				0	

[a] All data obtained at room temperature; isomer shift relative to room-temperature natural α-iron foil.

Table III. Linear Dependence of the Mössbauer Hyperfine Parameters on Pressure[a]

	high spin				low spin			
	δ		ΔE_Q		δ		ΔE_Q	
compd	slope	intercept	slope	intercept	slope	intercept	slope	intercept
$Fe[HB(pz)_3]_2$	-0.61×10^{-3}	0.907	-3.94×10^{-3}	3.537	-1.01×10^{-3}	0.394	1.48×10^{-3}	0.206
$Fe[HB(3,5\text{-}(CH_3)_2pz)_3]_2$	-0.73×10^{-3}	1.022	-0.48×10^{-3}	3.645	-1.37×10^{-3}	0.446	4.54×10^{-3}	0.119
$Fe[HB(3,4,5\text{-}(CH_3)_3pz)_3]_2$	-1.06×10^{-3}	1.054	-2.12×10^{-3}	3.711	-1.49×10^{-3}	0.486	4.61×10^{-3}	0.212

[a] All data obtained at room temperature. The slope is in units of (mm/s)/kbar and the intercept is in mm/s relative to natural α-iron foil.

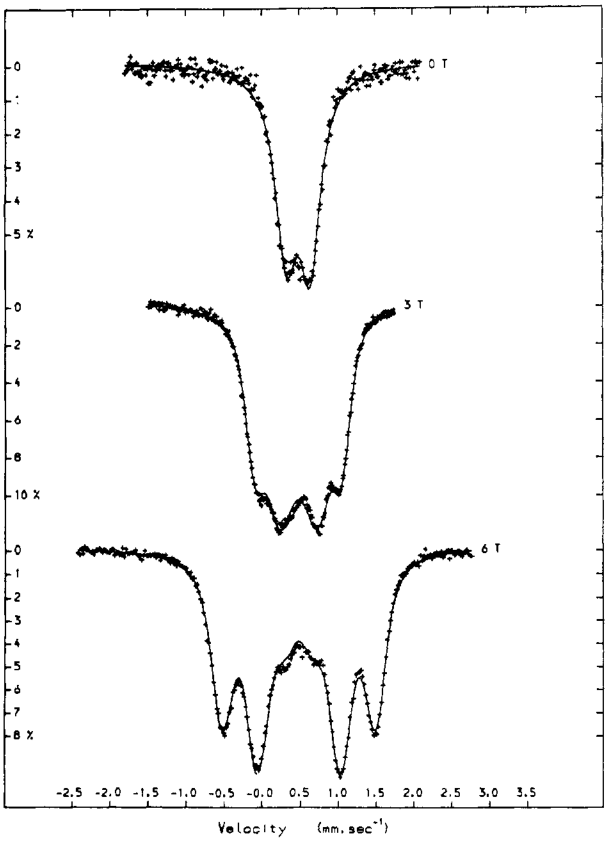

Figure 1. Mössbauer spectra of $Fe[B(pz)_4]_2$ obtained at 4.2 K in 0-, 3-, and 6-T applied field.

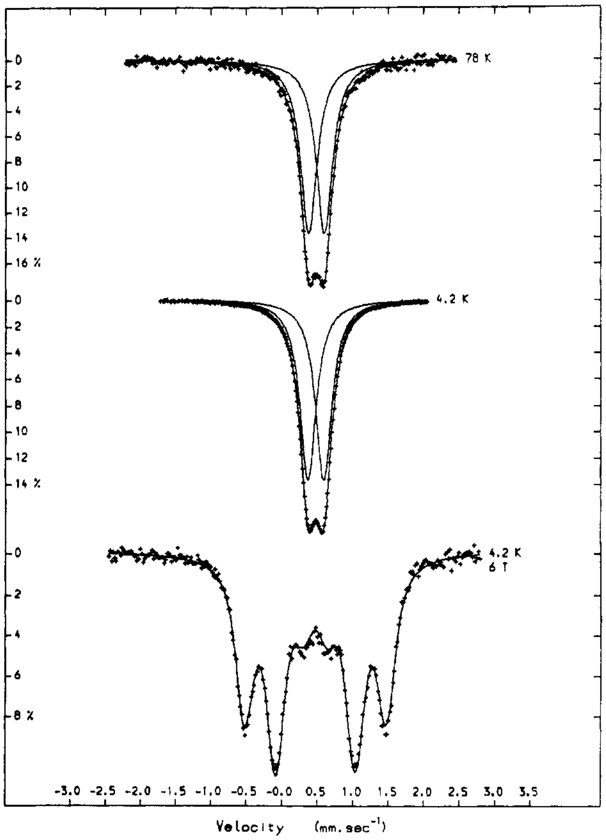

Figure 2. Mössbauer spectra of $Fe[HB(pz)_3]_2$ obtained at 78 and 4.2 K and at 4.2 K in a 6-T applied field.

study of this compound[11] indicates the formation of a high-spin component in $Fe[HB(pz)_3]_2$ at ca. 400 K and above. Perhaps the most surprising aspect of this compound is the appearance of an additional spectral component at high-pressure, as is illustrated

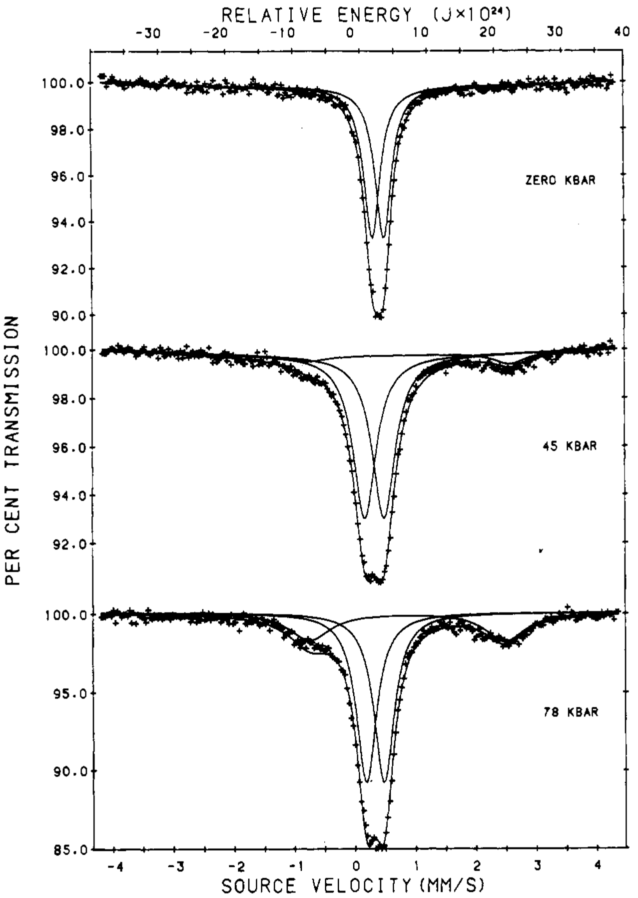

Figure 3. Mössbauer spectra of Fe[HB(pz)$_3$]$_2$ obtained at room temperature and ambient pressure and 45 and 78 kbar.

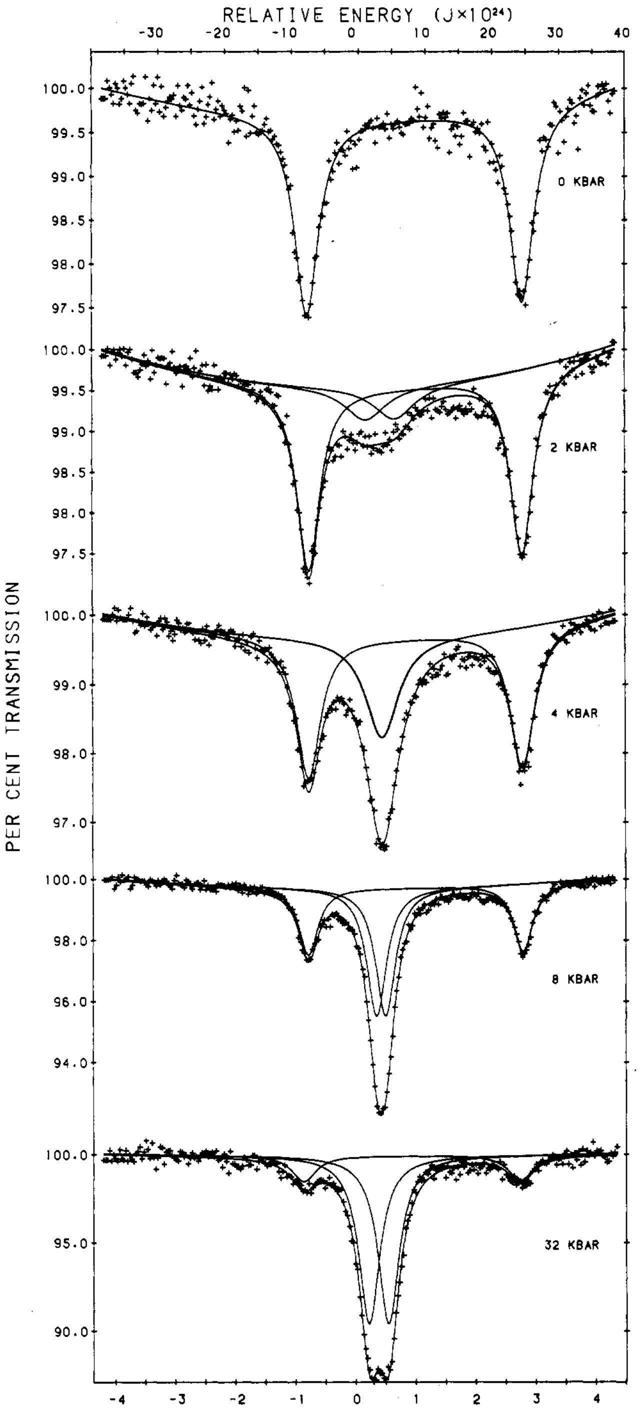

Figure 4. Mössbauer spectra of Fe[HB(3,5-(CH$_3$)$_2$pz)$_3$]$_2$ obtained at room temperature and ambient pressure and 2, 4, 8, and 32 kbar.

in Figure 3. It should be noted that the hyperfine parameters for this additional component are typical of high-spin iron(II) and, in fact, extrapolate to ambient pressure values that are typical of those observed[11] at high temperature. Because of its high isomer shift, it seems very unlikely that this component could correspond to an iron(III) species. The appearance of this added component is completely reversible.

Initially, the appearance of the high-spin iron(II) in Fe[HB(pz)$_3$]$_2$ would not be expected because it seems unlikely that the application of high-pressure should decrease the crystal field potential and, hence, promote the population of the high-spin $^5T_{2g}$ state. Indeed, no such component was found, at least up to 50 kbar, in a recent study[12] of Fe(phen)$_2$X$_2$, where X is NCS, NCSe, and N$_3$ and phen is phenanthroline. However, Drickamer and his co-workers[13-15] have reported the formation of a high-spin component in normally low-spin compounds at pressures above about 50 kbar. They propose that this unusual behavior is the result of a pressure-induced thermal population of the high-spin state whose energy is lowered at high pressure because of extensive changes in the ligand to metal π-bonding. Although extensive changes in such bonding are not expected in Fe[HB(pz)$_3$]$_2$, the high-temperature studies[11] do indicate the presence of the high-spin, $^5T_{1g}$, ground state that is populated via a spin-crossover transition, which occurs upon heating to 400 K.

The study of the Mössbauer spectra of Fe[HB(3,5-(CH$_3$)$_2$pz)$_3$]$_2$ and its spin-state crossover is complicated by its preparative method. A sample of this compound that was recrystallized from toluene showed an incomplete spin-state change at 78 and 4.2 K (see Table I) whereas a sample that was recrystallized from toluene and vacuum dried at 100 °C for at least 1 h showed complete conversion to the low-spin state at 78 K. All subsequent studies used this vacuum-dried material. The approximately equal fractions of the high-spin and low-spin state in Fe[HB(3,5-(CH$_3$)$_2$pz)$_3$]$_2$ at 195 K are in excellent agreement with the results of Jesson et al.[6] as are the hyperfine parameters obtained for each state. The low-temperature applied magnetic field spectrum of Fe[HB(3,5-(CH$_3$)$_2$pz)$_3$]$_2$ indicates that the internal field is equivalent to the applied field and confirms the presence of a very small quadrupole interaction for the low-spin state; this is an interaction similar to that found in Fe[HB(pz)$_3$]$_2$ and indicates that the two compounds have a similar geometry in the low-spin state.

The application of pressure to Fe[HB(3,5-(CH$_3$)$_2$pz)$_3$]$_2$ results in the formation of the low-spin state even at pressures as low as

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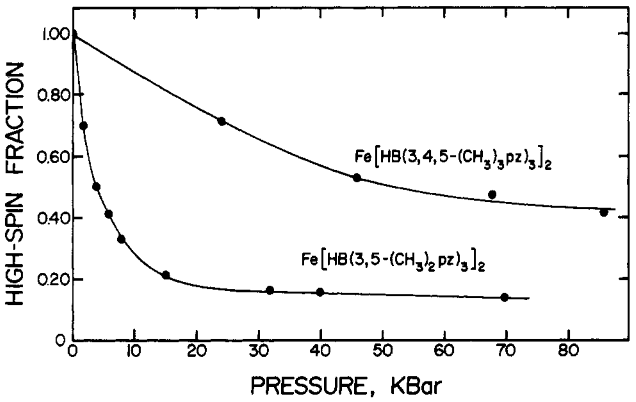

Figure 5. High-spin fraction as a function of pressure for $Fe[HB(3,5-(CH_3)_2pz)_3]_2$ and $Fe[HB(3,4,5-(CH_3)_3pz)_3]_2$.

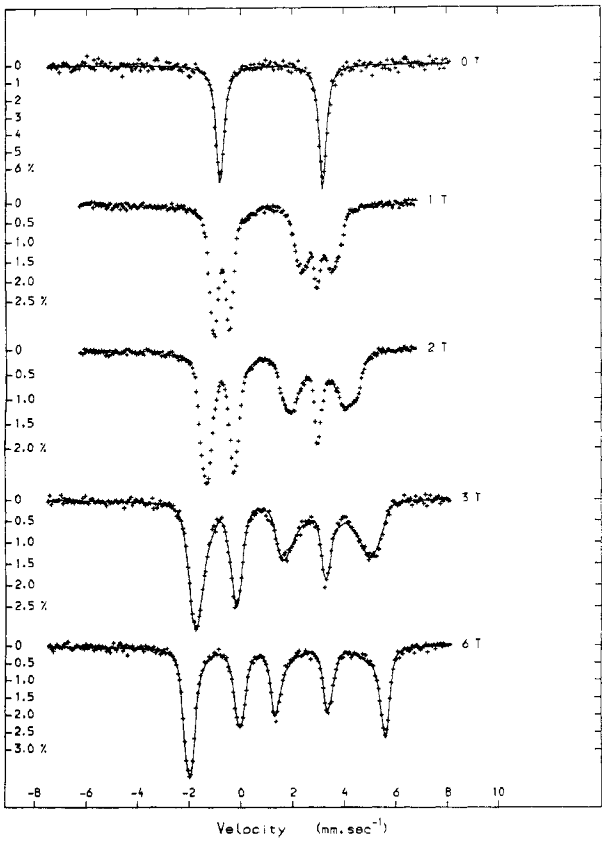

Figure 6. Mössbauer spectra of $Fe[HB(3,4,5-(CH_3)_3pz)_3]_2$ obtained at 4.2 K in applied fields of 0, 1, 2, 3, and 6 T.

2 kbar as is illustrated in Figure 4. At 4 kbar approximately 50% of the compound has been converted to the low-spin state. The pressure dependence of the high-spin fraction is illustrated in Figure 5, which shows that the change is gradual and never reaches 100%. In this figure, the high-spin fraction has been obtained from the area of the high-spin component in the Mössbauer spectrum by assuming equal recoil-free fractions for the two spin states. This approximation, although reasonable, probably slightly underestimates the high-spin fraction. It has already been noted[10] that $Fe[HB(3,5-(CH_3)_2pz)_3]_2$ has one of the longest iron–nitrogen bond lengths for the high-spin iron(II) ion as compared to bond lengths for the low-spin state. Apparently, the application of pressure slowly decreases this bond distance with increasing pressure, lowers the relative energy of the low-spin state, and increases the population of the low-spin state. It appears that this process "saturates" at about 30 kbar with the two states both populated at highest pressures. Assuming a Boltzmann distribution between the two states separated in energy by Δ, it is possible to calculate the approximate value of Δ as a function of pressure.

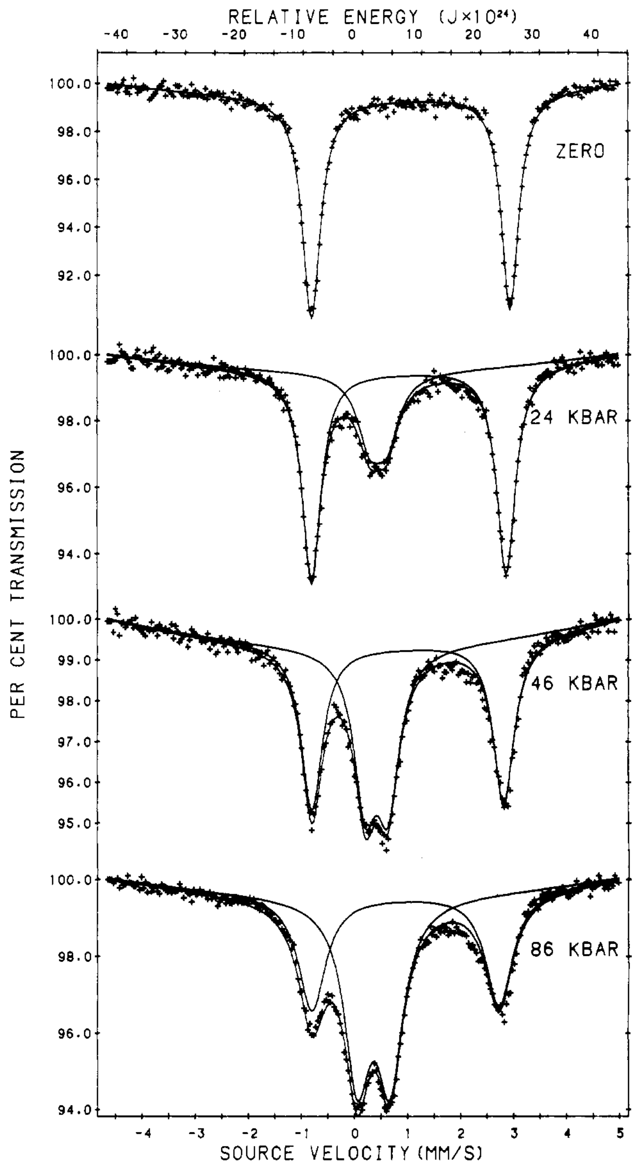

Figure 7. Mössbauer spectra of $Fe[HB(3,4,5-(CH_3)_3pz)_3]_2$ obtained at room temperature and various applied pressures.

Because we estimate that the Mössbauer spectrum at ambient pressure would clearly indicate the presence of 5% of the low-spin state, we can calculate that, at ambient pressure, the low-spin state is at least 600 cm^{-1} higher in energy than the high-spin ground state. At 2 kbar the splitting is ca. 175 cm^{-1}, whereas at 4 kbar the two states are of approximately equivalent energy. At 6, 8, 15, 40, and 70 kbar the high-spin state is now higher in energy than the low-spin ground state by approximately 85, 140, 270, 340, and 360 cm^{-1}. Hence, as might be expected for a compound with a long iron–nitrogen bond,[10] there is a gradual shift in the relative energy of the two spin states with increasing pressure. This behavior should be contrasted with the sudden change in spin state with pressure that is observed[12] in the $Fe(phen)_2X_2$ complexes. In this case there is a dramatic drop in the high-spin fraction over a very small pressure range of ca. 2 kbar. This sharp change is typical of the cooperative spin crossover[16] found in many compounds such as $Fe(phen)_2(NCS)_2$ and noted[6] in the temperature dependence of the spin states in $Fe[HB(3,5-(CH_3)_2pz)_3]_2$.

The isomer shift of both spin states in $Fe[HB(3,5-(CH_3)_2pz)_3]_2$ shows a decrease with increasing pressure as expected as the pressure increases the s-electron density at the iron-57 nucleus. The rate change is faster for the low-spin state as seen in Table

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III. The quadrupole splitting for the high-spin state is almost independent of pressure and has a small negative slope (Table III). In contrast, the quadrupole splitting in the low-spin state, which is dominated by the lattice contribution to the ECG tensor, increases by a factor of at least 3 between 3 and 70 kbar. The applied pressure apparently has a significant influence upon the symmetry of the "packing" of the ligands about the iron(II) ion. In the high-spin state a difference in sign for the pressure dependence of the valence and lattice contribution to the EFG tensor may account for the small change in the quadrupole splitting with pressure.

A study of the pressure dependence of the spin state in Fe[HB(3,4,5-$(CH_3)_3$pz$)_3$$]_2$ provides a nice contrast to the above work. For this compound, the low-temperature results (see Table I) indicate that it is always completely high spin, at least down to 1.7 K. In this case, the thermal contraction upon cooling is not significant enough to increase the crystal field and promote the population of the low-spin state. The spectra obtained for Fe[HB(3,4,5-$(CH_3)_3$pz$)_3$$]_2$ at 4.2 K in an applied field are shown in Figure 6. In this case, because of the large quadrupole interaction, the applied field results clearly indicate a negative quadrupole interaction and a small asymmetry parameter. As expected for a paramagnetic material, the internal field is equal to the applied field. The quadrupole interaction is virtually independent of temperature, and the isomer shift shows values typical of high-spin iron(II) with a temperature dependence that is typical of the second-order Doppler shift.

The Mössbauer effect spectra of Fe[HB(3,4,5-$(CH_3)_3$pz$)_3$$]_2$, obtained at various pressures and illustrated in Figure 7, indicate that, as expected, a much higher pressure is required to observe the low-spin state in this compound. In fact, as illustrated in Figure 5, approximately 12 times higher applied pressures are required to produce the same fraction of the low-spin state in Fe[HB(3,4,5-$(CH_3)_3$pz$)_3$$]_2$ as is found in Fe[HB(3,5-$(CH_3)_2$pz$)_3$$]_2$. Once again the conversion to the low-spin state is gradual, and the results indicate that at 24 kbar the low-spin state is 200 cm^{-1} above the high-spin ground state. The two spin states are equivalent in energy at ca. 55 kbar and the low-spin state is 75 cm^{-1} below the high-spin state at 86 kbar. These results are an indication that the application of high pressure is sufficient to produce a spin-state change in iron(II) even when no such change is indicated at low temperature. The pressure dependence of the hyperfine parameters are reasonable for Fe[HB(3,4,5-$(CH_3)_3$pz$)_3$$]_2$ in that the isomer shift decreases with increasing temperature, whereas the quadrupole interaction decreases for the high-spin state and increases for the low-spin state with increasing pressure. This latter difference again may indicate a different pressure dependence for the valence and lattice contribution to the EPG tensor in the high-spin state.

Acknowledgment. The authors thank Drs. I. Hall, T. E. Cranshaw, G. Longworth, and F. Grandjean for many helpful discussions during the course of this work. G.J.L. thanks the Science and Engineeering Research Council of the U.K. for a Faculty Science Fellowship, the donors of the Petroleum Research Fund, administered by the American Chemical Society, for their support of this work, and the NSF for support through Grant INT-8202403. B.B.H. acknowledges the support of the Robert A. Welch Foundation through Grant No. B-483 and the Abilene Christian University Research Council.

Registry No. Fe[HB(pz$)_3$$]_2$, 16949-45-4; Fe[HB(3,4,5-$(CH_3)_3$pz$)_3$$]_2$, 16949-44-3; Fe[HB(3,5-$(CH_3)_2pz)_3$$]_2$, 17567-19-0.

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Oxidation of a Dinuclear Platinum(II) Complex with Hydrogen Peroxide

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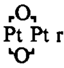
Received June 27, 1986

The oxidation of a dinuclear Pt(II) complex with hydrogen peroxide is described. The dinuclear complex ion [*cis*-Pt^{II}-$(^{15}NH_2CH_2CH_3)_2$(μ-OH$)]_2^{2+}$ undergoes oxidation in aqueous H_2O_2 to produce dinuclear Pt(IV) ions of the type [*cis*-Pt^{IV}-$(^{15}NH_2CH_2CH_3)_2(OH)_2$($\mu$-OH$)]_2^{2+}$. Following the reaction by using ^{195}Pt NMR spectroscopy and isolation of the major product revealed that oxidation primarily yields a D_{2h}-symmetry dinuclear compound having a four-membered  $\mathrm{Pt}\overset{\mathrm{O}}{\underset{\mathrm{O}}{\;}}\mathrm{Pt}$ ring. However, the fact that the reaction also yields lower symmetry dinuclear Pt(IV) compounds possessing this ring indicates that the oxidation, at least in part, proceeds through an "open-ring" intermediate that allows isomerization to occur. The ^{195}Pt NMR chemical shifts and $^1J(^{195}Pt-^{15}N)$ values, the latter measured by using both ^{195}Pt and ^{15}N NMR spectroscopies, were used to examine the effects of the four-membered ring and the various ligands on the electronic properties of the platinum ion.

Introduction

Recent interest in platinum coordination chemistry has been greatly stimulated by the finding that the simple square-planar complex *cis*-$Pt(NH_3)_2Cl_2$, cisplatin, is a potent anticancer agent.[1] Studies on the mechanism of action of the compound have suggested that its cytotoxic effects are related to its ability to bind to cellular DNA.[2] In addition to complexes of Pt(II), many Pt(IV) compounds have been found to be effective as anticancer agents.[3-5] Since Pt(IV) complexes are generally slow to undergo substitution reactions,[6] it has been suggested that their ability to kill tumor cells requires reduction to active Pt(II) compounds.[7] Supporting this hypothesis is the observation that divalent platinum complexes have been found in the urine and plasma of cancer patients receiving the Pt(IV) antitumor agent iproplatin, *cis,-cis,trans*-$Pt^{IV}(NH_2CH(CH_3)_2)_2Cl_2(OH)_2$. Moreover, chemical reduction of iproplatin using Fe(III) salts or ascorbate has been shown to produce a Pt(II) complex that is known to be active as

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