A Study of the Spin−State Transition and Phase Transformation in [Fe(bpp)$_2$][CF$_3$SO$_3$]$_2$·H$_2$O and [Fe(bpp)$_2$][BF$_4$]$_2$ Using Mn^{2+} Electron Spin Resonance

Raymond C. W. Sung and Bruce R. McGarvey*

School of Physical Sciences, Chemistry and Biochemistry, University of Windsor, Windsor, Ontario, Canada N9B 3P4

X-band ESR powder studies have been done on the spin transition in Mn^{2+}-doped [Fe(bpp)$_2$][CF$_3$SO$_3$]$_2$·H$_2$O and [Fe(bpp)$_2$][BF$_4$]$_2$ (bpp = 2,6-bis(pyrazol-3-yl) pyridine). The change in *D* value of Mn^{2+} during the thermally induced high-spin (HS) ↔ low-spin (LS) transition shows that the spin transition is accompanied by a phase transformation involving a domain mechanism. Irradiation experiments at 77 K have shown that a LS → HS spin change occurs without a change in the crystalline phase. The rate of the change from the HS phase to the LS phase in the vicinity of 100 K has been measured and is found to be the same as that measured for the corresponding spin change obtained from Mössbauer spectroscopy and magnetic susceptibility studies.

Introduction

The spin-state transition in [Fe(bpp)$_2$][CF$_3$SO$_3$]$_2$·H$_2$O and [Fe-(bpp)$_2$][BF$_4$]$_2$ (bpp = 2,6-bis(pyrazol-3-yl)pyridine) was first studied by Buchen et al.[1] and Goodwin and Sugiyarto,[2] respectively, using magnetic susceptibility measurement and Mössbauer spectroscopy. The second complex was later reinvestigated by Buchen et al.[3] using the same techniques. The transition temperatures for [Fe(bpp)$_2$][CF$_3$SO$_3$]$_2$·H$_2$O were reported to be 147 and 285 K in the cooling and heating directions, respectively. The warming curve shows a two stage process with one-third of the Fe^{2+} going from low-spin (LS) to high-spin (HS) between 150 and 190 K and the rest going to HS between 250 and 300 K. The transition temperatures for [Fe(bpp)$_2$][BF$_4$]$_2$ as reported by Goodwin and Sugiyarto[2] were 175 and 183 K in the respective cooling and heating directions, whereas Buchen et al.[3] reported 170 and 180 K. A metastable HS state in both systems can be formed by rapidly cooling the sample at liquid nitrogen temperature. This freezing-in of the HS state at low temperature has also been observed in other Fe^{2+} spin crossover systems.[4,5]

Both LIESST (light-induced excited spin-state trapping)[6−11] and reverse LIESST effects have been found in [Fe(bpp)$_2$]-[CF$_3$SO$_3$]$_2$·H$_2$O by Buchen et al.,[1] and in [Fe(bpp)$_2$][BF$_4$]$_2$ by Goodwin and Sugiyarto[2] and by Buchen et al.[3] These complexes undergo the spin-state transition with a color change, the HS state of both complexes being yellow; and the LS state of the first complex is orange-brown and that the second complex is red-brown. There is no direct proof of a phase change occurring in both of the complexes during the spin-state transition; it is only inferred from the thermal hysteresis behavior in both cases. In the Buchen et al.[1] studies of [Fe(bpp)$_2$][CF$_3$SO$_3$]$_2$·H$_2$O, a complete LS → HS transition has been observed during LIESST, but the reverse change is partial with only ca. 10% LS state formed in reverse LIESST. LIESST effect in [Fe(bpp)$_2$][BF$_4$]$_2$ has been observed at a temperature ≤80 K, the LS → HS transition is complete but the reverse change is also partial with only ca. 5% conversion of HS state in the reverse LIESST. These workers[1,3] also showed that both effects can be experimentally observed at temperatures above 77 K.

The kinetics of the HS → LS transition in [Fe(bpp)$_2$]-[CF$_3$SO$_3$]$_2$·H$_2$O and [Fe(bpp)$_2$][BF$_4$]$_2$ was also measured by these workers.[1−3] In the first system, both the LIESST effect and rapidly cooling method were used to generate the HS state at low temperatures. The subsequent HS → LS transition for the LIESST generated HS state was followed by Mössbauer spectroscopy over the temperature range 77.5−85 K, and for that produced by the rapidly cooling method was followed by magnetic susceptibility measurements over the temperature range 104−118 K. They found the rate of the HS → LS transition for LIESST generated HS states to be much faster than that found for HS states generated by rapid cooling. They postulated that a phase change was necessary before the HS → LS transformation could take place and therefore the rate of conversion measured for thermally generated HS states was a measure of the rate of the phase transformation. Goodwin and Sugiyarto,[2] using the rapidly cooling method to generate the HS state, reported first-order kinetics for the spin-state transition of [Fe(bpp)$_2$][BF$_4$]$_2$. In the Buchen et al.[3] study of the same compound a sigmoidal behavior rather than a first-order kinetics was found. The overall time to complete the conversion to the LS state was similar.

* To whom correspondence should be addressed. Tel.: (519) 253-3000, ext. 3530. Fax: (519) 973-7098. E-mail: beprm@uwindsor.ca.

(1) Buchen, T.; Gütlich, P.; Sugiyarto, K. H.; Goodwin, H. A. *Chem. Eur. J.* **1996**, *2, No. 9*, 1134.
(2) Goodwin, H. A.; Sugiyarto, K. H. *Chem. Phys. Lett.* **1987**, *139*, 470.
(3) Buchen, T.; Gütlich, P.; Goodwin, H. A. *Inorg. Chem.* **1994**, *33*, 4573.
(4) Ritter, G.; König, E.; Irler, W.; Goodwin, H. A. *Inorg. Chem.* **1978**, *17*, 224.
(5) König, E.; Ritter, G.; Dengler, J.; Nelson, S. M. *Inorg. Chem.* **1987**, *26*, 3582.
(6) Decurtins, S.; Gütlich, P.; Köhler, C. P.; Spiering, H.; Hauser, A. *Chem. Phys. Lett.* **1984**, *105*, 1.
(7) Decurtins, S.; Gütlich, P.; Hasselbach, K. M.; Hauser, A.; Spiering, H. *Inorg. Chem.* **1985**, *24*, 2174.
(8) Hauser, A.; *Chem. Phys. Lett.* **1986**, *124*, 543.
(9) Hauser, A.; Gütlich, P.; Spiering, H. *Inorg. Chem.* **1986**, *25*, 4245.
(10) Hauser, A.; *J. Chem. Phys.* **1991**, *94*, 2741.
(11) Hauser, A.; *Coord. Chem. Rev.* **1991**, *111*, 275.

Previous ESR studies[12−16] of Fe^{2+} spin crossover systems were done by following the spectral changes of Mn^{2+} ion doped into the sample. In all cases studied so far,[12−16] the amount of dopant used is less than 5 mol % to prevent any appreciable dipolar broadening of the Mn^{2+} spectral lines. The presence of the impurity Mn^{2+} ion in an Fe^{2+} spin crossover system at the concentration used here has also been shown[12] to have no effect on the spin-state transition. Mn^{2+}-ESR has also revealed other information concerning the nature and dynamics of spin crossover in different Fe^{2+} systems, for instance, the existence of domain,[13,14] the absence[12,15] and presence[14,16] of a phase change during a spin transition.

In this paper, we report the study of the Mn^{2+}-doped [Fe-(bpp)$_2$][CF$_3$SO$_3$]$_2$·H$_2$O and [Fe(bpp)$_2$][BF$_4$]$_2$ over a range of temperatures that span the spin transition. In addition to studying the changes in the ESR spectra of Mn^{2+} with temperature, we were able to follow the changes in the ESR spectra with time for a sample in which the metastable HS state was produced by rapid cooling. These kinetics experiments were done over the same temperature interval in the Mn^{2+}-doped [Fe(bpp)$_2$]-[CF$_3$SO$_3$]$_2$·H$_2$O studied by Buchen et al.[1] using magnetic susceptibility. We also report interesting studies on samples irradiated by light at liquid nitrogen temperatures.

Experimental Section

Preparation of Compounds. 1. 2,6-Bis(pyrazol-3-yl)pyridine (bpp). The ligand 2,6-bis(pyrazol-3-yl) pyridine (bpp) was synthesized by the method of Lin and Lang.[17] The ligand bpp was obtained as a white solid, mp 258−260 °C. Elemental analysis was performed by Guelph Chemical Laboratories Ltd. (Guelph, ON). Anal. Calcd for bpp: C, 62.55; H, 4.30; N, 33.16. Found: C, 62.33; H, 4.28; N, 32.93. The ^{1}H NMR characterization of bpp dissolved in DMSO-d_6 was done at room temperature using the Bruker AVANCE DPX 300 MHz NMR spectrometer, δ values 6.7−8.2 ppm (ArH), 13.04 ppm (NH) and 13.50 ppm (NH).

2. Mn^{2+}-Doped [Fe(bpp)$_2$][CF$_3$SO$_3$]$_2$·H$_2$O. The Mn^{2+}-doped [Fe-(bpp)$_2$][CF$_3$SO$_3$]$_2$·3H$_2$O was made by reacting the ligand bpp (2.2 mmol) in 20 mL hot water with aqueous solutions of FeCl$_2$·4H$_2$O (1 mmol) and MnCl$_2$·4H$_2$O (0.1 mmol) under N$_2$ atmosphere; this was followed by the addition of NaCF$_3$SO$_3$ (2.2 mmol) to the cooled filtrate and the trihydrate was obtained as red-brown crystals after the contents were left to stand overnight. The monohydrate was obtained, as yellow powder, by heating the trihydrate at 65 °C for 24 h in an oven. Elemental analysis was performed by Guelph Chemical Laboratories Ltd., Guelph, ON. Anal. Calcd for [Fe(bpp)$_2$][CF$_3$SO$_3$]$_2$·3H$_2$O: C, 34.71; H, 2.91; N, 16.87; Fe, 6.72. Found: C, 34.98; H, 2.86; N, 17.05; Fe, 6.80. Anal. Calcd for [Fe(bpp)$_2$][CF$_3$SO$_3$]$_2$·H$_2$O: C, 36.29; H, 2.54; N, 17.63; S, 8.07; F, 14.35; Fe, 7.03. Found: C, 36.14; H, 2.48; N, 17.90; S, 7.94; F, 14.20; Fe, 7.20.

3. Mn^{2+}-Doped [Fe(bpp)$_2$][BF$_4$]$_2$. The [Fe(bpp)$_2$][BF$_4$]$_2$·2H$_2$O complex was made according to the procedure given elsewhere.[18] The Mn^{2+}-doped [Fe(bpp)$_2$][BF$_4$]$_2$·2H$_2$O complex was made by recrystallizing a mixture of the pure Fe^{2+} complex and Mn(BF$_4$)$_2$ (ca. 3 mol % with respect to the Fe^{2+} complex) in ethanol solution, it was obtained as a red-brown flaky solid. The anhydrous form was obtained, as a yellow powder, by heating the hydrated form at 110 °C for 1 h in an oven. Anal. Calcd for [Fe(bpp)$_2$][BF$_4$]$_2$·2H$_2$O: C, 38.41; H, 3.22; N, 20.36; Fe, 8.12. Found: C, 38.87; H, 3.16; N, 20.73; Fe, 8.01; Mn, 0.05. Anal.

(12) Rao, P. S.; Reuveni, A.; McGarvey, B. R.; Ganguli, P.; Gütlich, P. *Inorg. Chem.* **1981**, *20*, 204.
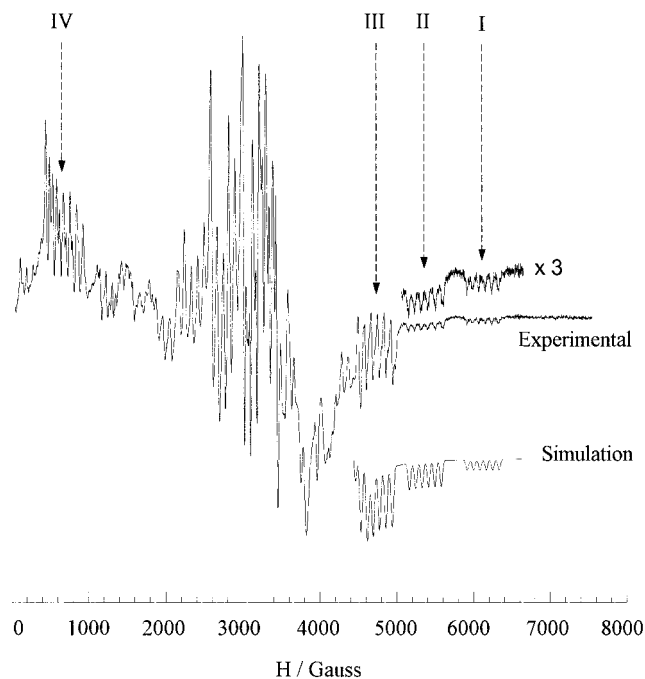(13) Doan, P. E.; McGarvey, B. R. *Inorg. Chem.* **1990**, *29*, 874.
(14) Ozarowski, A.; Shunzhong, Y.; McGarvey, B. R.; Mislankar, A.; Drake, J. E. *Inorg. Chem.* **1991**, *30*, 3167.
(15) Ozarowski, A.; McGarvey, B. R. *Inorg. Chem.* **1989**, *28*, 2262.
(16) Ozarowski, A.; McGarvey, B. R.; Sarkar, A. B.; Drake, J. E. *Inorg. Chem.* **1988**, *27*, 628.
(17) Lin, Y.-L.; Lang, S. A., Jr. *J. Heterocylic Chem.* **1977**, *14*, 345.
(18) Sugiyarto, K. H.; Goodwin, H. A. *Aust. J. Chem.* **1988**, *41*, 1645.

Calcd for [Fe(bpp)$_2$][BF$_4$]$_2$: C, 40.53; H, 2.78; N, 21.49; Fe, 8.57. Found: C, 40.14; H, 2.71; N, 21.20; Fe, 8.50; Mn, 0.05.

ESR Spectra. All ESR spectra were recorded on an X-band Bruker ESP 300E spectrometer equipped with a NMR magnetometer, a microwave counter, a variable-temperature (VT) accessory and an electromagnet capable of providing a magnetic field range from 50 G to 15 kG. Typical measurement conditions were microwave power 20 mW, microwave frequency 9.5 GHz, modulation frequency 100 kHz, modulation amplitude 4.062 G and 4 k of data points covering a magnetic field range from 50 G to 7500 G. The powder samples used in the experimental measurements were sealed under vacuum in quartz tubes. The temperature was calibrated by using a copper−constantan thermocouple thermometer, model 8528-12, obtained from the Cole-Parmer Instrument Company. The temperature reported should be correct to ± 1 K.

1. Temperature-Dependence Studies. Variable-temperature spectra were obtained by slowly cooling the sample from room temperature to the lowest attainable temperature, then heating to room temperature again. Rapid-cooled spectra at 77 K were obtained by plunging the sample directly in liquid nitrogen.

2. Rate of HS → LS Phase Transformation. The powder spectra for [Fe(bpp)$_2$][CF$_3$SO$_3$]$_2$·H$_2$O and for [Fe(bpp)$_2$][BF$_4$]$_2$ were obtained at 104, 108, 113, and 118, and at 100, 103, and 105 K, respectively. The HS phase at 77 K was generated by rapidly cooling the sample in liquid nitrogen.

3. Irradiation Experiments. The irradiation experiments were performed at 77 K using a Lexel 95 Ar-laser operating at 100 mW power and a Spectra Physics 2000 Kr-laser operating at 50 mW power. The wavelength of the radiation was 514.5 nm for Ar-laser and 670.0 nm for Kr-laser. All irradiations were done outside the microwave cavity.

Spectral Analysis and Simulations. The spectral features of $S = {}^5/_2$ systems can be fitted to the following spin Hamiltonian.

$$\hat{\mathcal{H}} = g\beta_e\hat{S}\cdot\mathbf{H} + D\left(\hat{S}_z^2 - \frac{35}{12}\right) + E(\hat{S}_x^2 - \hat{S}_y^2) + A\hat{S}\cdot\hat{I} + \frac{1}{6}a\left(\hat{S}_x^4 + \hat{S}_y^4 + \hat{S}_z^4 - \frac{707}{16}\right) + \frac{1}{180}F\left(35\hat{S}_z^4 - \frac{475}{2}\hat{S}_z^2 + \frac{2835}{16}\right) \quad (1)$$

Some of our powder spectra are sharp enough with sufficient detail that with a proper simulation program we might be able to determine most of the parameters in eq 1, but not having such a program available we have chosen to estimate D and E from the spectra because that is all we require to determine the existence of any phase changes in the lattice. Therefore we have assumed g and A to be isotropic with $g \sim 2.00$ and have assumed a and F to be zero.

To get reasonable estimates of D and E we have used two approaches. One is to simulate only the higher field region of the spectrum where second order perturbation solutions to the spin Hamiltonian are reasonably accurate. For this we used the SimFonia program of Bruker Spectrospin, Inc. A visual confirmation of the fit for fields above 4400 G was used in this case. An example is shown in Figure 1 for Mn^{2+} in [Fe(bpp)$_2$][CF$_3$SO$_3$]$_2$·H$_2$O. Values of $D = 685$ G and $E = 87$ G were used in the simulation. A second method was to identify four characteristic turning points in the spectrum and use exact solutions of eq 1 for these points to determine g, D, and E assuming A, a, and F to be zero. The four points are identified in Figure 1 by Roman numerals. I is the point associated with $M_s = -{}^5/_2 \rightarrow M_s = -{}^3/_2$ transition when the magnetic field is along the z principal axis. II is the $M_s = {}^3/_2 \rightarrow M_s = {}^5/_2$ transition when the magnetic field is along the x principal axis, while IV is the same transition when the magnetic field is along the z axis. III is the $M_s = -{}^3/_2 \rightarrow M_s = -{}^1/_2$ transition along the z principal axis. We have written a small computer program that calculates a best fit for these four experimental points. In Figure 1 the calculated values of I, II, III, and IV differ from the experimental values by 4 G or less for $g = 2.003$, $D = 687$ G, and $E = 93$ G which are satisfactorily close to the values obtained from the simulation. In general we found the two methods gave the same D values within 1−2 G while the E values using the turning points were 6−11 G higher than those obtained by simulation using the SimFonia program.

Figure 1. Powder ESR spectrum of Mn^{2+} in $[Fe(bpp)_2][CF_3SO_3]_2\cdot H_2O$ at 290.5 K. The turning points I, III, and IV are associated with $M_s = -^5/_2 \rightarrow M_s = -^3/_2$, $M_s = -^3/_2 \rightarrow M_s = -^1/_2$ and $M_s = ^3/_2 \rightarrow M_s = ^5/_2$ transitions, respectively, when the magnetic field is along the z principal axis of the zero field. Turning point II is associated with the $M_s = ^3/_2 \rightarrow M_s = ^5/_2$ transition when the magnetic field is along either the x or y principal axis of the zero field. The computer-simulated spectrum above 4400 G is shown below.

Results and Discussion

1. Temperature-Dependence Studies. Due to the large number of VT spectra obtained for both $[Fe(bpp)_2][CF_3SO_3]_2\cdot H_2O$ and $[Fe(bpp)_2][BF_4]_2$, we limit their presentations by selecting those obtained within the temperature range that covers the spin-state transitions in the systems. They are shown in Figures 2 and 4.

In the case of $[Fe(bpp)_2][CF_3SO_3]_2\cdot H_2O$, numerical values of D and E for Mn^{2+} in the system have been calculated for some of the VT spectra obtained above the HS → LS transition and those obtained at 77 K using both the SimFonia program and the method of the turning points. The results are given in Table 1. The large difference in the D values between the room temperature spectrum ($S = 2$) and that at 77 K ($S = 0$) indicates that the HS and LS states are in two distinct types of lattice. The small increase in the D value as temperature decreases is due to an overall contraction of the crystal lattice with decreasing temperature 290.5−150 K. This is also shown in the VT spectra by the gradual shifting of the high-field features at turning points I and II toward higher fields with decreasing temperatures. These features become unrecognizable and disappear completely at temperatures below 134.5 K (see Figure 2); this is due to the disappearance of the HS domains accompanying the spin crossover in the temperature interval of 134.5−132.5 K. The HS → LS phase transformation is easily spotted in the more prominent spectral features in the regions of 600, 4000, and 4800 G. These features can be used as a measure of the formation of the LS phase of the complex. The reverse change from LS → HS occurs over the increasing temperature range 127.5−298.0 K; it is also accompanied by a reverse phase transformation in the lattice. As shown in Figure 2, the ESR spectrum of Mn^{2+} undergoes a change with the appearance of features in the region of 600 and 6000 G at 174.8 K typical of
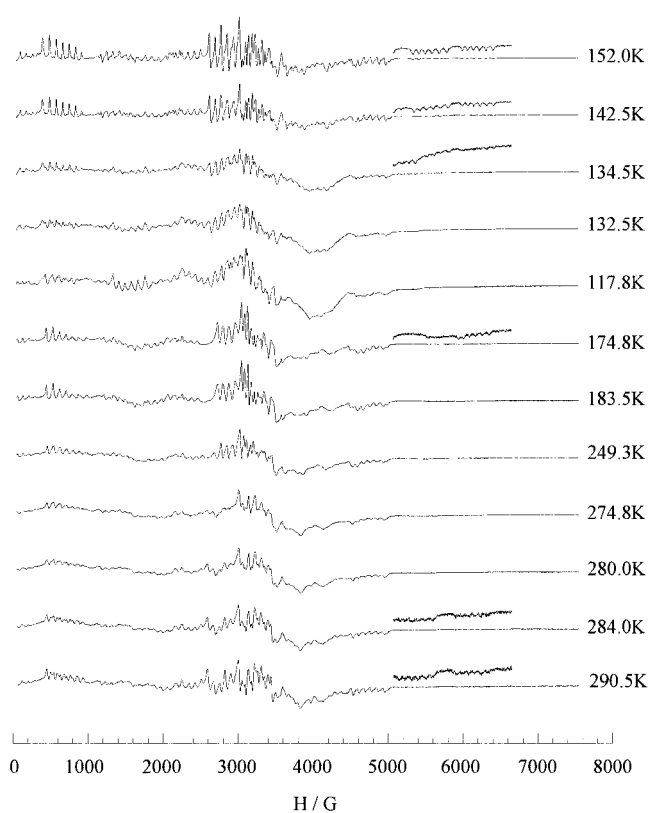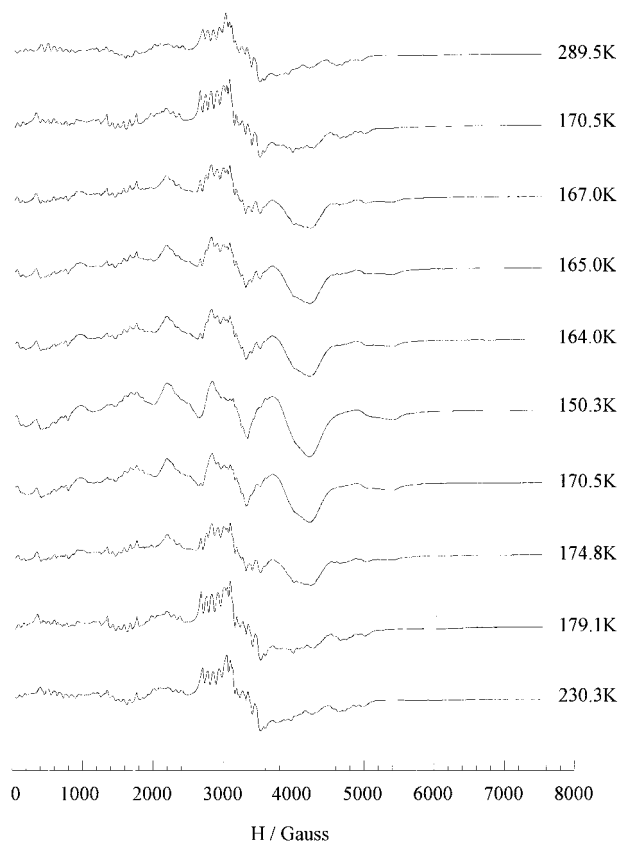

Figure 2. Selected powder ESR spectra of Mn^{2+} in $[Fe(bpp)_2]$-$[CF_3SO_3]_2\cdot H_2O$ at different temperatures as indicated. Sample temperature was slowly lowered from room temperature to the lowest temperature of 117.8 K, then raised to room temperature again.
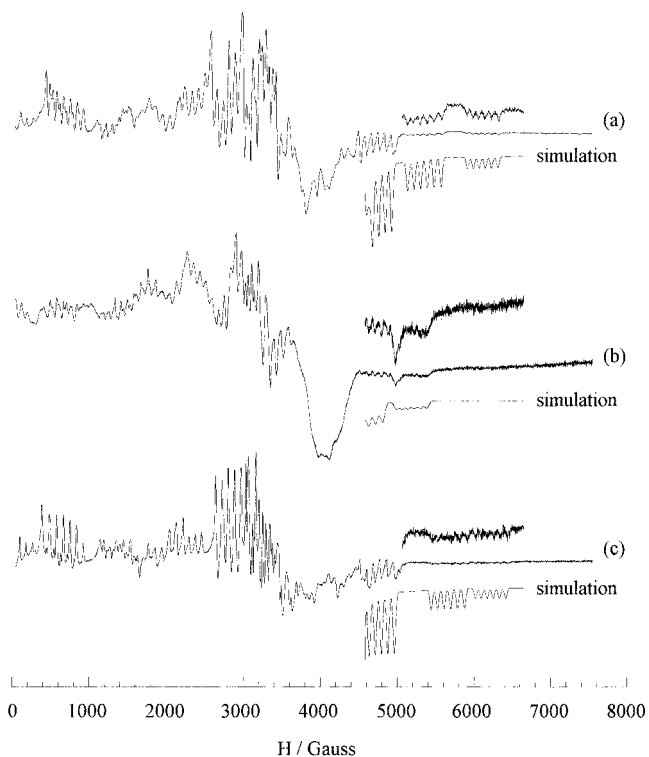
Figure 3. Powder ESR spectra of Mn^{2+} in $[Fe(bpp)_2][CF_3SO_3]_2\cdot H_2O$ at (a) room temperature for $S = 2$, (b) 77 K for $S = 0$ after slow cooling, and (c) 77 K for $S = 2$ after rapid cooling. The computer-simulated spectra above 4400 G are obtained using parameters from Table 1.

the HS phase. From 180 K until about 275 K the spectrum changes little. There is a second change in the spectrum in the

Figure 4. Selected powder ESR spectra of Mn^{2+} in $[Fe(bpp)_2][BF_4]_2$ at different temperatures as indicated. Sample temperature was slowly lowered from room temperature to the lowest temperature of 150.3 K, then raised to room temperature again.

Table 1. Zero-Field Splitting Parameters of Mn^{2+} in $[Fe(bpp)_2][CF_3SO_3]_2 \cdot H_2O$ at Different Temperatures above the HS $\rightarrow$ LS Transition[a]

temperature/K	g	A/G	D/G	E/G
290.5	2.0000	83 ± 1	685 (687)	87 (93)
239.5	2.0000	83 ± 1	687 (688)	90 (102)
196.3	2.0000	83 ± 1	692 (694)	100 (110)
179.1	2.0000	83 ± 1	695 (698)	104 (114)
156.7	2.0000	83 ± 1	698 (701)	109 (120)
152.0	2.0000	83 ± 1	700 (704)	112 (122)
142.5	2.0000	83 ± 1	701 (704)	113 (125)
77 ($S = 2$)	2.0000	83 ± 1	706 (710)	128 (136)
77 ($S = 0$)	2.0000	83 ± 1	453	44
RT ($S = 2$)	2.0000	83 ± 1	684 (686)	85 (93)

[a] The values given in parentheses were obtained by using the method of the turning points.

Table 2. Observed HS $\leftrightarrow$ LS Transition Temperatures ($\pm T$ gives Temperature Interval of Observed Change)

compound	by ESR[a]		by other methods	
	$T_\downarrow$	$T_\uparrow$	$T_\downarrow$	$T_\uparrow$
$[Fe(bpp)_2][CF_3SO_3]_2 \cdot H_2O$	134 ± 1	177 ± 3 (stage 1)	147 ± 3[b]	170 ± 20[b] (stage 1)
		280 ± 5 (stage 2)		285 ± 25[b] (stage 2)
$[Fe(bpp)_2][BF_4]_2$	165 ± 2	173 ± 2	170 ± 5[b]	180 ± 5[b]
			173 ± 5[c]	183 ± 5[c]

[a] This work. [b] Buchen et al. (refs 1 and 3). [c] Goodwin and Sugiyarto (ref 2).

region 275−285 K resulting in the HS phase spectrum observed originally. Table 2 summarizes the observed HS $\leftrightarrow$ LS transition temperatures. The quantitative estimation of the fractional

amount of each of the two crystal forms during the LS $\rightarrow$ HS transition is not possible due to the complicated nature of the Mn^{2+} spectra. This two stage LS $\rightarrow$ HS conversion was originally detected in the magnetic susceptibility measurements of the complex by Buchen et al.,[1] and the reported transition temperatures are also given in Table 2. There is a difference of 13 K in the HS $\rightarrow$ LS transition temperature as determined by ESR and that found by Buchen et al., but the reverse transition temperatures are in good agreement except that the LS $\rightarrow$ HS changes in the spectrum are seen over a much smaller temperature interval of 6 and 10 K for the first and second stage transition, respectively, in the ESR measurements relative to the 40 and 50 K for the corresponding stages reported by Buchen et al.[1] These discrepancies may simply be due to differences in the final process of drying the samples. The presence of varying amounts of water molecules within the crystal lattice may have a profound effect on the spin crossover phenomenon. This has been shown by König et al. in their studies of the significance of lattice water on the spin-state transition in $[Fe(phen)_2][C_2O_4] \cdot 5H_2O$.[19]

The powder spectra of Mn^{2+} given in Figure 3 show the results of the slow and rapid cooling of the $S = 2$ system at 77 K. The $S = 0$ system, as shown in Figure 3(b), can only be obtained by a slow cooling process, and it is stable over time. Visual observation has revealed a color change from yellow to orange-brown indicating that the HS $\rightarrow$ LS transition has also occurred. Rapid cooling of the $S = 2$ system in liquid nitrogen has produced no new features in the observed spectrum as shown in Figure 3c, and the yellow color of the HS state of the complex also remains unchanged. The spectral features are similar to those observed for the $S = 2$ system at room temperature as shown in Figure 3a. As shown in Table 1, the small difference in the D values of Mn^{2+} for the $S = 2$ system at room temperature and 77 K suggests that the rapidly cooled complex has a structure similar to that at room temperature. The crystal structure of the rapidly cooled complex is also stable over time. At higher temperatures above 77 K, the normal HS $\rightarrow$ LS transition occurs.

The VT spectra of $[Fe(bpp)_2][BF_4]_2$, as shown in Figure 4, show a gradual change of the spectral features for the Mn^{2+} resonance during the spin-state transitions. The major features in the regions 3200 and 4200 G indicate that the spin-state transition occurs at 167.0−164.0 K for the decreasing temperature and 170.5−174.8 K for the increasing temperature. As shown in Table 2, the differences in the transition temperatures found by ESR and those reported by Buchen et al.[3] and Goodwin et al.[2] are small. The width of the hysteresis loop ΔT is 8 K in our ESR results and 10 K in the other studies.[2,3] Again the small discrepancies in ΔT and the transition temperatures could be attributed to the slight differences in the drying process. The D value of Mn^{2+} in the $S = 2$ system at room temperature and 77 K are 635 and 665 G, respectively, and that in $S = 0$ at 77 K is 855 G. These values are obtained by using the SimFonia program. The much larger D value for Mn^{2+} in the $S = 0$ system at 77 K suggests that there is also a phase change with the HS $\rightarrow$ LS conversion. Visual observation shows a color change from yellow to red-brown during the slow cooling of the complex at 77 K. Figure 5c shows the result of the rapidly cooled complex at liquid nitrogen temperature. The spectral features and D values are very similar to those observed at room temperature, indicating that a change of the phase of the lattice has not occurred. The yellow color of the complex also remains

(19) König, E.; Schnakig, R.; Ritter, G.; Irler, W.; Kanellakopulos, B.; Powietzka, B. *Inorg. Chim. Acta* **1979**, *35*, 239.
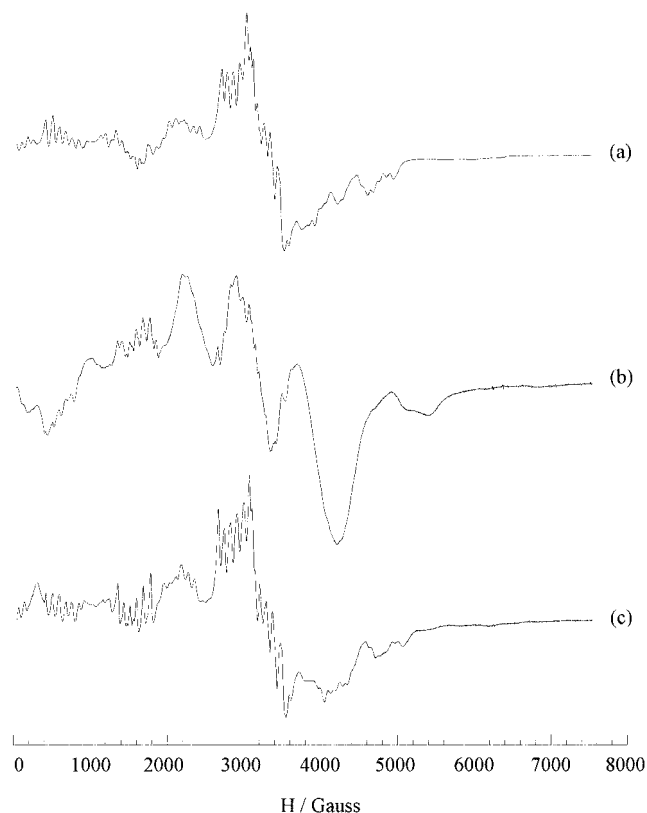
Figure 5. Powder ESR spectra of Mn^{2+} in $[Fe(bpp)_2][BF_4]_2$ at (a) room temperature for $S = 2$, (b) 77 K for $S = 0$ after slow cooling, and (c) 77 K for $S = 2$ after rapid cooling.

unchanged during the rapid cooling process, indicating, also, that the HS state has been trapped at low temperature for the complex. The phase and spin state of the rapidly cooled complex is stable over time as long as the temperature remains at 77 K, but at higher temperatures the usual HS $\rightarrow$ LS phase transformation begins to set in. The change of the more prominent spectral features at about 600, 1600, and 4200 G as observed in the VT-measurements of the complex may be used to provide a qualitative measure of the formation of the LS phase of the complex.

2. Rate of HS $\rightarrow$ LS Phase Transformation. The kinetics experiments for $[Fe(bpp)_2][CF_3SO_3]_2\cdot H_2O$ were done at the same temperatures of 104, 108, 113, and 118 K as reported by Buchen et al.[1] during their kinetics studies of the HS $\rightarrow$ LS transition. In the case of $[Fe(bpp)_2][BF_4]_2$, they were done at 100, 103, and 105 K. In each case at a fixed temperature, the spectra show a continuous phase transformation of the system during the HS $\rightarrow$ LS transition. The gradual disappearance of the HS phase was quantitatively determined by following the changes of the Mn^{2+} spectral feature in the region of 600 G. The Mn^{2+} spectrum obtained after a long time was subtracted from each of those obtained at different times to determine the intensity $[I(t) - I(t \sim \infty)]$. The results are given in Figures 6 and 7 for $[Fe(bpp)_2][CF_3SO_3]_2\cdot H_2O$ and $[Fe(bpp)_2][BF_4]_2$, respectively. It can be clearly seen in Figure 6 that the HS phase of $[Fe(bpp)_2][CF_3SO_3]_2\cdot H_2O$ reaches a minimum in about 160 min at 104 K, 80 min at 108 K, 35 min at 113 K, and 20 min at 118 K, which are comparable to the time scales in the Buchen et al. results during their kinetic studies of the HS $\rightarrow$ LS transition over the same temperature range.[1] The important result of the present study is that the HS $\rightarrow$ LS phase transformation follows a curve very similar to that for the HS $\rightarrow$ LS transition in the system. The results for $[Fe(bpp)_2][BF_4]_2$, as given in
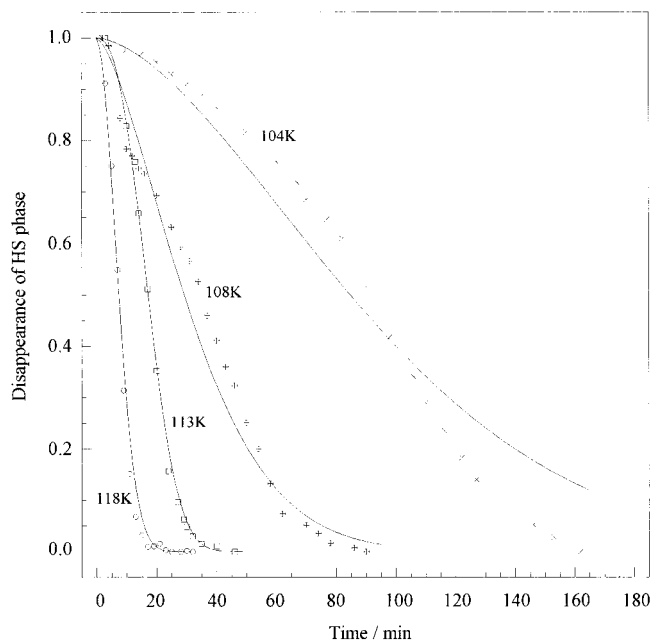

Figure 6. Kinetics of the HS $\rightarrow$ LS phase transformation in $[Fe(bpp)_2]$-$[CF_3SO_3]_2\cdot H_2O$ at temperatures as indicated. The HS phase was obtained by rapidly cooling the sample in liquid nitrogen. Solid lines are fitted curves using $y = 1 - \exp(kt)^n$. At 104 K, $k = 0.0095$ and $n = 1.68$; 108 K, $k = 0.027$ and $n = 1.54$; 113 K, $k = 0.0504$ and $n = 2.52$; 118 K, $k = 0.1118$ and $n = 1.94$.
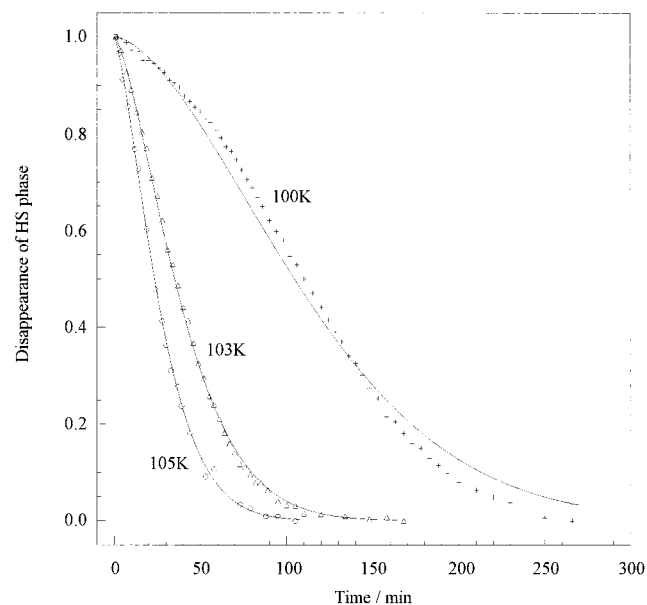
Figure 7. Kinetics of the HS $\rightarrow$ LS phase transformation in $[Fe(bpp)_2]$-$[BF_4]_2$ at temperatures as indicated. The HS phase was obtained by rapidly cooling the sample in liquid nitrogen. Solid lines are fitted curves using $y = 1 - \exp(ht)^n$. At 100 K, $k = 0.0077$ and $n = 1.68$; 103 K, $k = 0.0222$ and $n = 1.46$; 105 K, $k = 0.0329$ and $n = 1.41$.

Figure 7, show that the HS phase reaches a minimum in about 260 min at 100 K, 110 minutes at 103 K, and 100 minutes at 105 K. The kinetics results reported by Buchen et al. show that the time required for the HS state to decay to a minimum during the HS $\rightarrow$ LS transition is about 167 min at 100 K, indicating that the overall rate of the HS $\rightarrow$ LS phase transformation in $[Fe(bpp)_2][BF_4]_2$ is slower than the spin-state transition in the system.[3] However, the time required for the initial 20% HS $\rightarrow$ LS conversion is about 67 min which is comparable to the 65 min observed in the ESR result for the same amount of HS $\rightarrow$
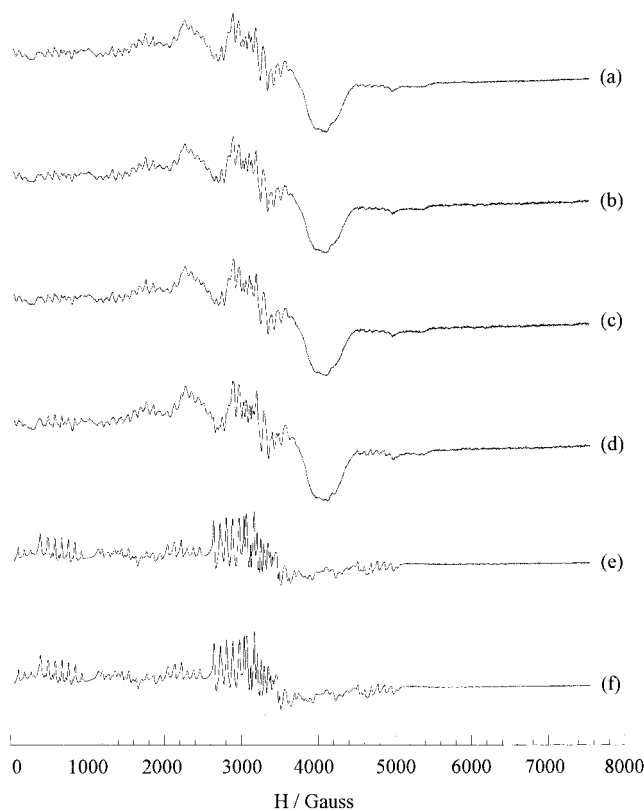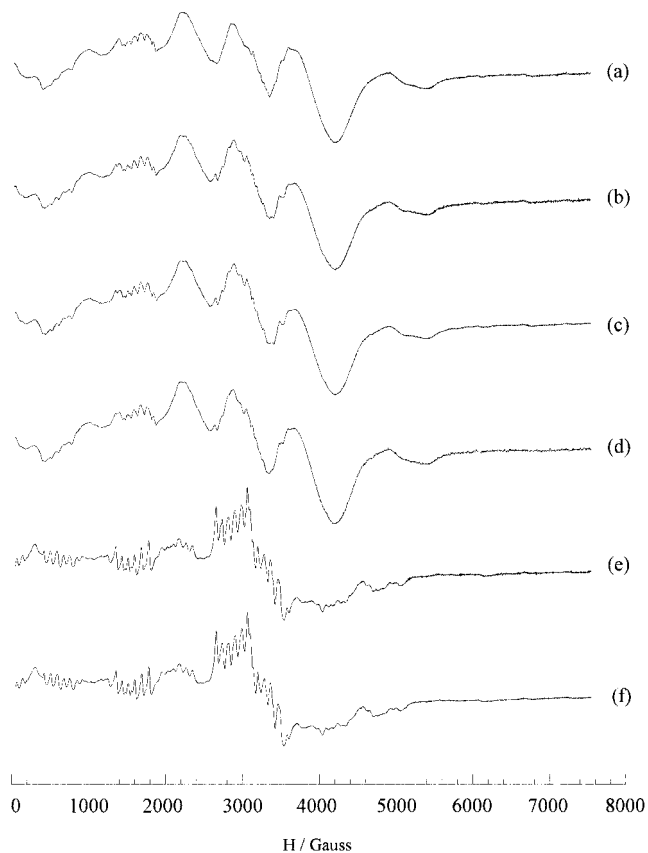
Figure 8. Powder ESR spectra of Mn^{2+} in $[Fe(bpp)_2][CF_3SO_3]_2 \cdot H_2O$ at 77 K after various treatments. (a) Spectrum of a sample slowly cooled to 77 K, spin state $S = 0$. (b) Spectrum of $S = 0$ sample, (a), after irradiation by Ar-laser for 20 min. (c) Spectrum of sample shown in (b) after an additional irradiation by Kr-laser for 20 min. (d) Spectrum of $S = 0$ sample, (a), after irradiation by Kr-laser for 90 min. (e) Spectrum of a sample rapidly cooled to 77 K, spin state $S = 2$. (f) Spectrum of $S = 2$ sample, (e), after irradiation by Kr-laser for 20 min.

Figure 9. Powder ESR spectra of Mn^{2+} in $[Fe(bpp)_2][BF_4]_2$ at 77 K after various treatments. (a) Spectrum of a sample slowly cooled to 77 K, spin state $S = 0$. (b) Spectrum of $S = 0$ sample, (a), after irradiation by Ar-laser for 12 min. (c) Spectrum of sample shown in (b) after an additional irradiation by Kr-laser for 11 min. (d) Spectrum of $S = 0$ sample, (a), after irradiation by Kr-laser for 30 min. (e) Spectrum of a sample rapidly cooled to 77 K, spin state $S = 2$. (f) Spectrum of $S = 2$ sample, (e), after irradiation by Kr-laser for 20 min.

LS phase transformation. This suggests that both processes have a similar initial rate of change; the slowing down of the latter process is probably caused by a decrease in nucleation sites and a decrease in the growth rate as the reaction progresses.

We attempted to obtain useful information on the rate and mechanism of the transformation process in the present systems using the Avrami's equation,[20–22] $y = 1 - \exp(kt)^n$ which is commonly employed by physicists and metallurgists to fit the kinetics of phase change, by assuming $(1 - y)$ as the disappearance of HS phase, t is the time, and k and n are fitted constants at a fixed temperature. The results for $[Fe(bpp)_2]$-$[CF_3SO_3]_2 \cdot H_2O$ and $[Fe(bpp)_2][BF_4]_2$ as given in Figures 6 and 7, respectively, appear to be unsatisfactory and in both cases the goodness of the statistical fit deteriorates with decreasing temperatures. A more elaborate theoretical study of the transformation process appears necessary in order to better understand the mechanism of the process.

3. Irradiation Experiments. Both $[Fe(bpp)_2][CF_3SO_3]_2 \cdot H_2O$ and $[Fe(bpp)_2][BF_4]_2$ show almost identical behavior during their irradiation experiments using the same procedure, the results are given in Figures 8 and 9, respectively. Figures 8(a) and 9(a) show the result after the sample of the respective complex has been slowly cooled to 77 K. As shown in Figures 8b and 9b, the irradiation of the $S = 0$ system at 77 K using the Ar-laser

has produced no change in the Mn^{2+} spectrum in the LS phase of complex. However, visual observation detects a color change from orange-brown to yellow for $[Fe(bpp)_2][CF_3SO_3]_2 \cdot H_2O$, red-brown to yellow for $[Fe(bpp)_2][BF_4]_2$, indicating that the LS → HS transition has occurred. The subsequent irradiation of the same system using the Kr-laser has produced neither a color change nor phase change. As shown in Figures 8(c) and 9(c), all the spectral features of Mn^{2+} in the system remain practically the same as those observed for the corresponding $S = 0$ system. The unchanged yellow color, in both cases, indicates the reverse HS → LS transition has not occurred. Figures 8(d) and 9(d) show the results after irradiating the $S = 0$ system at 77 K using the Kr-laser only, the Mn^{2+} spectrum also remains identical to that in the LS phase, but this time the color of the complex changes from orange-brown to yellow for $[Fe(bpp)_2][CF_3SO_3]_2 \cdot H_2O$ and red-brown to yellow for $[Fe(bpp)_2][BF_4]_2$, which again is indicative of the LS → HS transition. It appears that the lattice for the HS state created by irradiation of the LS state is identical to that of the LS state. Additional evidence is also seen in the result given in Figures 8f and 9f after the $S = 2$ system at 77 K has been irradiated with the Kr-laser. The Mn^{2+} spectrum in the HS phase of the complex is practically identical to that given in Figures 8e and 9e, also no color change is observed. The important result of these experiments is that the LIESST effect observed at these temperatures does not involve the phase transformation observed in the thermal spin crossover. Further

(20) Avrami, M.; *J. Chem. Phys.* **1939**, *7*, 1103.
(21) Avrami, M.; *J. Chem. Phys.* **1940**, *8*, 212.
(22) Avrami, M.; *J. Chem. Phys.* **1941**, *9*, 177.

no reverse LIESST effect has been observed for HS state in either the LS or HS phase.

Conclusions

The use of Mn^{2+} ion as an ESR probe to study the spin crossover in powder samples of $[Fe(bpp)_2][CF_3SO_3]_2 \cdot H_2O$ and $[Fe(bpp)_2][BF_4]_2$ has provided new information on the nature of spin-state transition and phase transformation in these systems. We have shown that the magnitudes of D for Mn^{2+} ion are very different in the HS and LS phase for both systems. The large change in D during HS $\leftrightarrow$ LS crossover shows a crystal phase change accompanies thermal spin change for both systems. The appearance of both HS and LS spectra during spin change indicates a domain mechanism for phase change with spin change. Rate study of ESR, which measures the rate of crystal phase change, shows that the rate of spin change measured by Mössbauer spectroscopy and magnetic susceptibility is the same for HS $\rightarrow$ LS change when HS state was formed by rapid cooling. Therefore the rate for HS $\rightarrow$ LS change is rapid in the LS crystalline phase and very slow in the HS crystalline phase. Thus a phase change must occur before the HS $\rightarrow$ LS change takes place. This confirms the conclusions of Buchen et al. that the rates they measured were controlled by the rate of a phase change.[1,3] The fact that there is no change in the ESR spectrum upon irradiation shows that the LS $\rightarrow$ HS change caused by the LIESST effect at 77 K has no crystalline phase change. Thus we have a HS state trapped in a LS crystalline phase unlike the rapid cooling method which produces a HS state in a HS crystalline lattice. This explains why the rate of HS $\rightarrow$ LS change is different in the two situations.