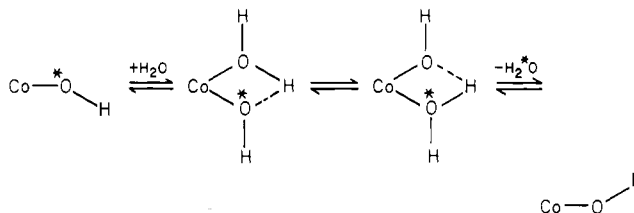


the possibility of direct OH<sup>-</sup> exchange.<sup>33</sup>

On the other hand the catalytic efficiency of the enzyme would require that, if the active species is in the hydroxo form, the oxygen atom is also in fast exchange with the bulk solution.<sup>34</sup> As a matter of fact, fast <sup>17</sup>O exchange has been detected through <sup>17</sup>O NMR on the copper derivative over the entire pH range of existence of the enzyme.<sup>35</sup> From the aforementioned observation<sup>28,31,32</sup> that intramolecular protonation can be a very fast process if the basic groups between which the proton is transferred are close enough in space and have close pK<sub>a</sub> values, a pathway is going to be proposed for the fast exchange of the OH moiety as part of a water molecule.<sup>36</sup>

The proposed pathway stems from the availability of a fifth coordination position on the metal ion in the active site of carbonic anhydrase.<sup>23</sup> The exchange is allowed by the transient binding of a water molecule as a fifth ligand; a proton can be then transferred to the hydroxide group,<sup>31,32</sup> which can exchange as a water molecule leaving a coordinated hydroxide.



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**Registry No.** I, 82110-97-2; I, azide adduct, 81899-99-2; II, 56627-65-7; II, azide adduct, 82080-84-0.

Contribution from the Institut für Anorganische und Analytische Chemie, Johannes Gutenberg-Universität, D-6500 Mainz, Federal Republic of Germany

## Effect of Metal Dilution on the Spin-Crossover Behavior in [Fe<sub>x</sub>M<sub>1-x</sub>(phen)<sub>2</sub>(NCS)<sub>2</sub>] (M = Mn, Co, Ni, Zn)

P. GANGULI, P. GÜTLICH,\* and E. W. MÜLLER

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The effect of metal dilution on the spin-crossover behavior of [Fe(phen)<sub>2</sub>(NCS)<sub>2</sub>] has been studied in the mixed-crystal series [Fe<sub>x</sub>M<sub>1-x</sub>(phen)<sub>2</sub>(NCS)<sub>2</sub>] (M = Mn<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup>) by using the <sup>57</sup>Fe Mössbauer-effect technique. It has been found that, in the host lattice with ionic radius  $r(M^{2+}) > r(Fe^{2+})$ , the amount of rest paramagnetism in the region well below the transition temperature  $T_c$  increases with metal dilution, whereas in the host lattice with  $r(M^{2+}) < r(Fe^{2+})$ , the residual diamagnetism in the region well above  $T_c$  decreases with metal dilution. These observations are interpreted qualitatively in terms of "negative" and "positive" local pressure, respectively, changing the Fe-N bond length and thus influencing the ligand field potential accordingly.

### Introduction

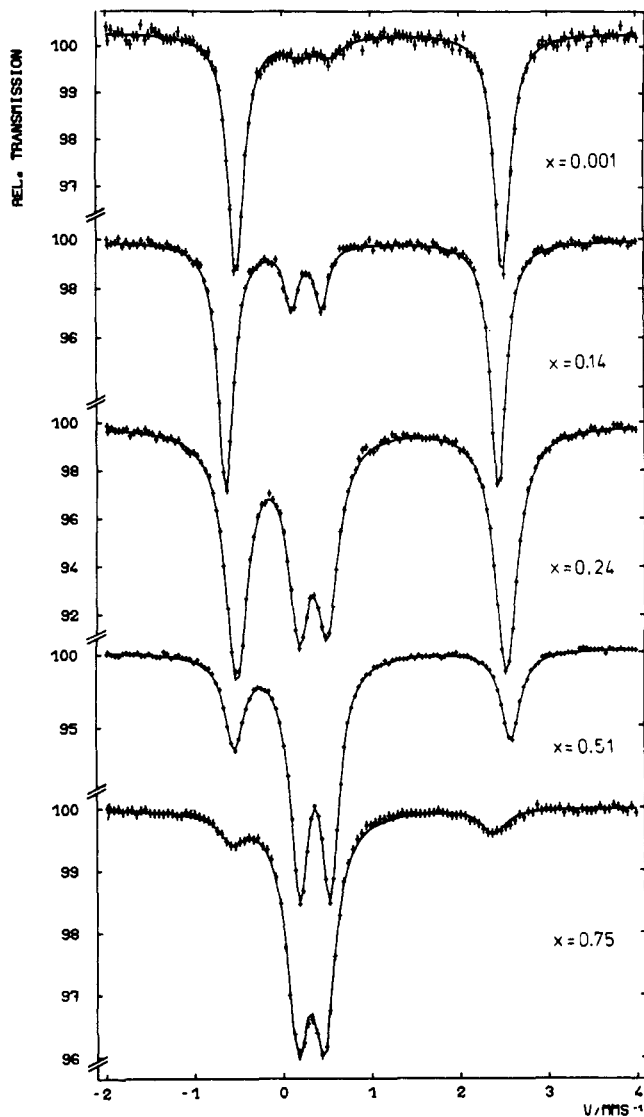
In the last few years, studies in the field of spin crossover in transition-metal complexes have established that the spin-transition characteristics depend very markedly on the ligand, nature of the noncoordinating anion, minor intraligand substitutions, solvent molecules trapped in the lattice, metal dilution, temperature, pressure, etc.<sup>1-6</sup> All these influences on the <sup>5</sup>T<sub>2</sub>(O<sub>h</sub>) ⇌ <sup>1</sup>A<sub>1</sub>(O<sub>h</sub>) spin-transition behavior of iron(II) systems have been discussed in a recent review article.<sup>7</sup>

On the basis of some metal dilution of [Fe(2-pic)<sub>3</sub>]Cl<sub>2</sub>·EtOH in the corresponding isomorphous [Zn(2-pic)<sub>3</sub>]Cl<sub>2</sub>·EtOH lattice, Renovitch and Baker<sup>8</sup> ruled out any antiferromagnetic interactions in [Fe<sub>0.15</sub>Zn<sub>0.85</sub>(2-pic)<sub>3</sub>]Cl<sub>2</sub>·EtOH. Recent detailed Mössbauer spectroscopic studies on [Fe<sub>x</sub>Zn<sub>1-x</sub>(2-pic)<sub>3</sub>]Cl<sub>2</sub>·

EtOH ( $x = 1-0.0009$ )<sup>9,10</sup> have shown that the transition temperature  $T_c$ , defined as the temperature at which equal amounts of the high-spin (HS) state and the low-spin (LS) state coexist, decreases on dilution. However, the thermally induced HS ⇌ LS crossover is still observable even at the lowest possible iron concentrations. These results have been interpreted on the basis of a "domain model",<sup>9-12</sup> which suggests that the spin transition takes place through a coupling between the electronic state and the vibrational modes and that the conversion of the electronic state occurs simultaneously in a group of molecules that form a so-called "cooperative domain". Heat capacity measurements on [Fe(phen)<sub>2</sub>(NCS)<sub>2</sub>] were earlier interpreted by Sorai and Seki<sup>9</sup> on the basis of this "domain model". They had proposed that the abrupt transition in [Fe(phen)<sub>2</sub>(NCS)<sub>2</sub>] was due to a "strong coupling" in domains consisting of about 100 molecules. The present investigation on [Fe<sub>x</sub>M<sub>1-x</sub>(phen)<sub>2</sub>(NCS)<sub>2</sub>] ( $x = 0.001-1$  and M = Mn, Co, Ni, Zn) was undertaken to study how metal dilution of the "strongly coupled" system [Fe(phen)<sub>2</sub>(NCS)<sub>2</sub>]

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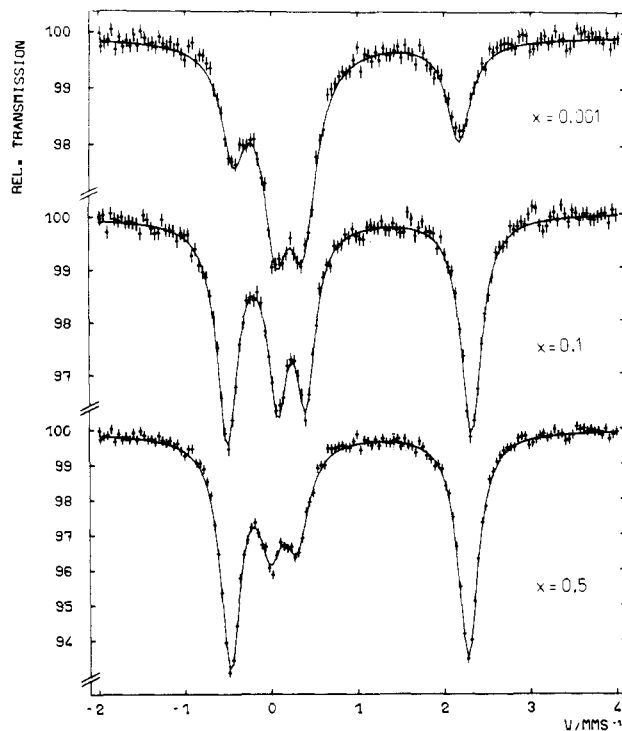
**Figure 1.** Mössbauer spectra of  $[\text{Fe}_x\text{Mn}_{1-x}(\text{phen})_2(\text{NCS})_2]$  at 5 K and various iron concentrations. The spectra demonstrate that the intensity of the iron(II) HS doublet (outer two lines) increases with decreasing iron concentration.

would affect its  ${}^5T_2(O_h) \rightleftharpoons {}^1A_1(O_h)$  crossover characteristics and, in this process, to learn more about the nature of the interactions responsible for the spin crossover.

### Experimental Section

**Chemical Preparations.** Calculated molar quantities (depending on the dilution degree  $x$ ) of  $\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{MCl}_2$  ( $M = \text{Mn}, \text{Co}, \text{Ni}, \text{Zn}$ ) were dissolved in dry and freshly distilled methanol. Stoichiometric amounts of  $\text{KSCN}$  in methanol was added to the above solution. The mixture was stirred well and  $\text{KCl}$  precipitated. This was filtered off. Calculated amounts of 1,10-phenanthroline monohydrate in methanol were added dropwise to the well-stirred filtrate containing  $\text{Fe}^{2+}$ ,  $\text{M}^{2+}$ , and  $\text{SCN}^-$  ions. The precipitated  $[\text{Fe}_x\text{Mn}_{1-x}(\text{phen})_2(\text{NCS})_2]$  was filtered, washed with methanol, and dried under vacuum with  $\text{P}_2\text{O}_5$ . All the preparations were carried out in a drybox in nitrogen atmosphere. The mixed crystals with very small quantities of Fe(II) (i.e., small  $x$ ) were prepared with 81% enriched  ${}^{57}\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$ .

Elemental analysis of C, H, N was performed, and the results agreed well with the calculated data. The content of Fe(II) and M(II) was estimated by standard potentiometric procedures.<sup>13</sup> Far-infrared spectra<sup>14</sup> were recorded in these samples. The dilution degree  $x$



**Figure 2.**  ${}^{57}\text{Fe}$  Mössbauer spectra of  $[\text{Fe}_x\text{Co}_{1-x}(\text{phen})_2(\text{NCS})_2]$  at 260 K and various iron concentrations. The spectra demonstrate that the intensity of the iron(II) LS doublet (inner two lines) increases with decreasing iron concentration.

estimated from the relative areas under the far-IR peaks agreed fairly well with those determined by the photometric procedures.

X-ray photographs of the polycrystalline samples of  $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ ,  $[\text{M}(\text{phen})_2(\text{NCS})_2]$  ( $M = \text{Mn}, \text{Co}, \text{Ni}, \text{Zn}$ ), and  $[\text{Fe}_x\text{M}_{1-x}(\text{phen})_2(\text{NCS})_2]$  were taken to establish the isomorphous nature of the systems.

**Mössbauer Spectra.** The Mössbauer spectra were recorded in transmission geometry; details of the measurements have already been described in an earlier communication.<sup>15</sup> The  ${}^{57}\text{Co}/\text{Rh}$  source (The Radiochemical Centre, Amersham, England) was kept at room temperature. The isomer shifts reported here refer to metallic iron. The measured Mössbauer spectra were fitted to lorentzians by using a least-squares iteration computer program.<sup>16</sup>

**Differential Thermal Analysis (DTA).** The DTA measurements on  $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$  and  $[\text{Fe}_x\text{Mn}_{1-x}(\text{phen})_2(\text{NCS})_2]$  were recorded by Dr. M. Sorai and Professor H. G. von Schnering, in Osaka, Japan, and Stuttgart, Germany, respectively.

### Results and Discussion

The X-ray photographs of  $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ ,  $[\text{Mn}(\text{phen})_2(\text{NCS})_2]$ ,  $[\text{Ni}(\text{phen})_2(\text{NCS})_2]$ , and  $[\text{Co}(\text{phen})_2(\text{NCS})_2]$  showed that all these compounds are isomorphous with each other but not with  $[\text{Zn}(\text{phen})_2(\text{NCS})_2]$ . For this reason, our study in the Zn lattice has been restricted to very small Fe(II) concentrations ( $x = 0.001$  and  $x = 0.01$ ), where good solid solutions could be prepared.

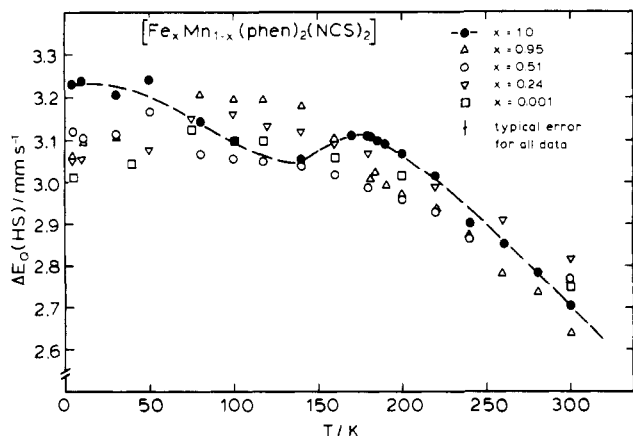
A few representative Mössbauer spectra of  $[\text{Fe}_x\text{Mn}_{1-x}(\text{phen})_2(\text{NCS})_2]$  at  $T = 5$  K and of  $[\text{Fe}_x\text{Co}_{1-x}(\text{phen})_2(\text{NCS})_2]$  at  $T = 260$  K and different concentrations of Fe(II) are shown in Figures 1 and 2, respectively. From these spectra as well as from all the other measured spectra not shown here, it is clear that in all these mixed crystals of  $[\text{Fe}_x\text{M}_{1-x}(\text{phen})_2(\text{NCS})_2]$  ( $M = \text{Mn}, \text{Co}, \text{Ni}, \text{Zn}$ ) there is a coexistence of only the HS and the LS species. The outer two resonance lines refer to the quadrupole doublet of the Fe(II) HS species; the inner two lines are the quadrupole doublet of the Fe(II) LS species.

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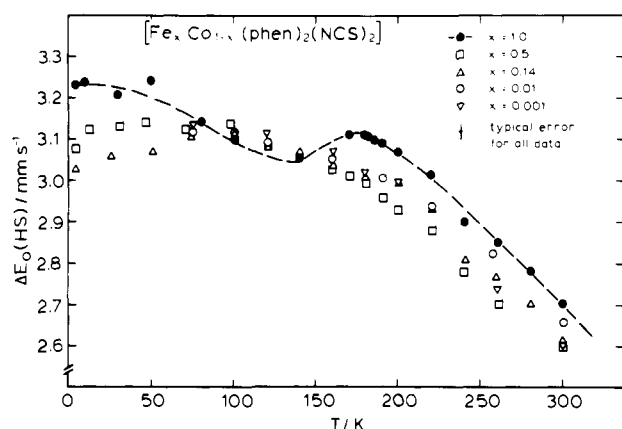
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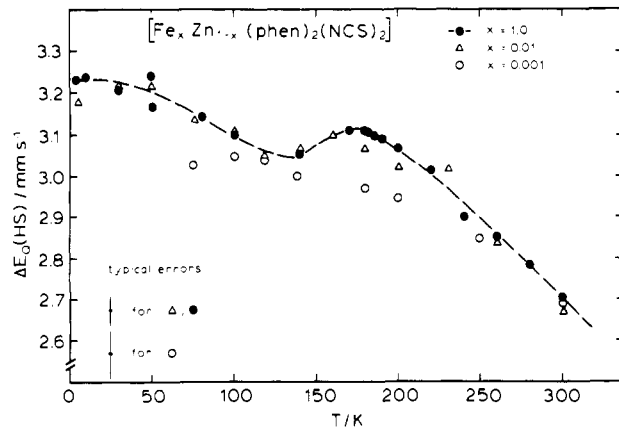
**Figure 3.** Quadrupole splitting of the HS state of Fe(II),  $\Delta E_Q(\text{HS})$ , in  $[\text{Fe}_x\text{Mn}_{1-x}(\text{phen})_2(\text{NCS})_2]$  as a function of temperature. The dashed line (full circles) refers to the pure iron compound, which shows a discontinuity near the transition temperature  $T_c \approx 175$  K.



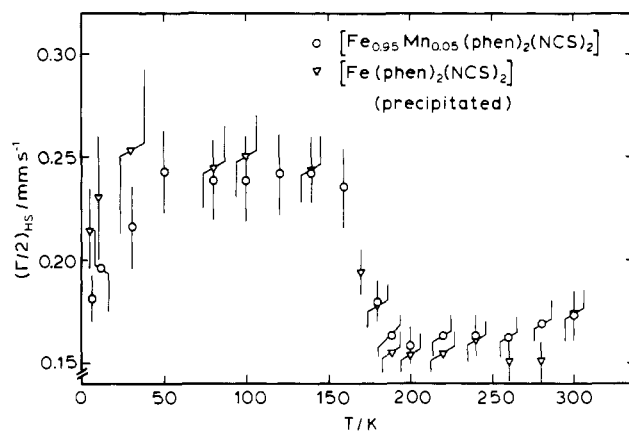
**Figure 4.** Quadrupole splitting of the HS state of Fe(II),  $\Delta E_Q(\text{HS})$ , in  $[\text{Fe}_x\text{Co}_{1-x}(\text{phen})_2(\text{NCS})_2]$  as a function of temperature.

The quadrupole splitting of the HS species,  $\Delta E_Q(\text{HS})$ , as a function of temperature for the mixed crystals  $[\text{Fe}_x\text{M}_{1-x}(\text{phen})_2(\text{NCS})_2]$  ( $M = \text{Mn}, \text{Co}, \text{Zn}$ ) at different concentrations is plotted in Figures 3–5. The dashed line (full circles) refers to the pure iron compound, whose quadrupole splitting  $\Delta E_Q(\text{HS})$  shows a discontinuity near the transition temperature  $T_c \approx 175$  K, most likely due to a structural change accompanying the spin crossover.<sup>15,17</sup> The temperature dependence of the quadrupole splitting  $\Delta E_Q(\text{HS})$  in all the systems, except in the Zn host, are very similar, indicating that the electronic environments around the Fe(II) are not very different in all the mixed crystals. It is, however, interesting to note that the anomaly in the temperature dependence of  $\Delta E_Q(\text{HS})$ , which was found in the nondiluted precipitated  $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$  and which was taken as an indication of a structural change accompanying the spin crossover,<sup>17</sup> no longer appears in any of the mixed crystals except in the case of  $[\text{Fe}_{0.01}\text{Zn}_{0.99}(\text{phen})_2(\text{NCS})_2]$ . The measurements in the case of  $[\text{Fe}_{0.001}\text{Zn}_{0.999}(\text{phen})_2(\text{NCS})_2]$  were not very satisfactory, and hence the fitted parameters are not considered as accurate.

The isomer shifts of the HS state of Fe(II) in all the systems under study range from ca.  $0.94 \text{ mm s}^{-1}$  at room temperature to ca.  $1.10 \text{ mm s}^{-1}$  near 4 K (relative to metallic iron). The temperature dependence of the isomer shift of the HS state is also very similar in all the mixed crystals and can be rationalized as due to the second-order Doppler shift. The temperature dependence of the isomer shift for the LS doublet



**Figure 5.** Quadrupole splitting of the HS state of Fe(II),  $\Delta E_Q(\text{HS})$ , in  $[\text{Fe}_x\text{Zn}_{1-x}(\text{phen})_2(\text{NCS})_2]$  as a function of temperature.

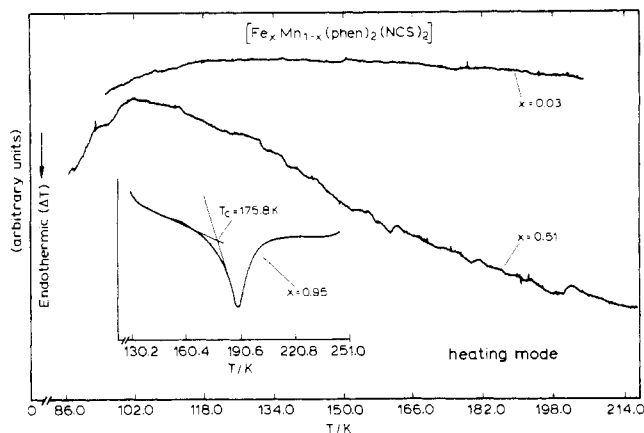


**Figure 6.** Line width  $\Gamma/2(\text{HS})$  of the HS state of Fe(II) in pure  $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$  and in the mixed crystal  $[\text{Fe}_{0.95}\text{Mn}_{0.05}(\text{phen})_2(\text{NCS})_2]$  as a function of temperature. An abrupt change of  $\Gamma/2(\text{HS})$  near the transition temperature  $T_c \approx 175$  K is seen in both systems.

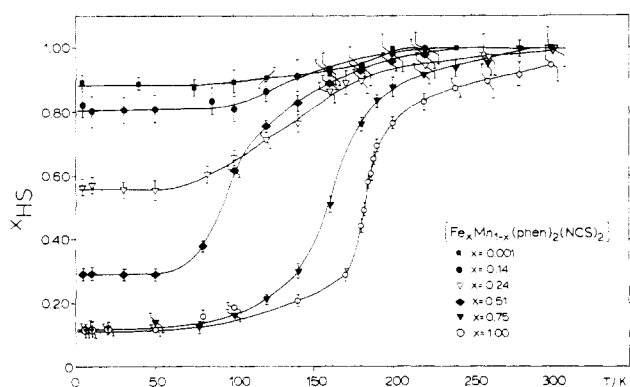
is less pronounced. The quadrupole splitting of the LS doublet is  $0.30 \text{ mm s}^{-1}$  on the average and remains fairly constant in all the systems over the whole temperature range of the present investigation.

It has previously been shown<sup>15,17</sup> that in the precipitated  $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$  the line width,  $\Gamma/2(\text{HS})$ , of the HS doublet as a function of temperature also shows an irregularity between 140 and 200 K as does the quadrupole splitting  $\Delta E_Q(\text{HS})$ . Such an anomaly is not seen in any of the mixed crystals except  $[\text{Fe}_{0.95}\text{Mn}_{0.05}(\text{phen})_2(\text{NCS})_2]$  (see Figure 6). The line width of the HS doublet is between 20 and 60% broader than the natural line width of  $2\Gamma_{\text{nat}} = 0.19 \text{ mm s}^{-1}$ . These may arise from inhomogeneities of the hyperfine interactions and from finite absorber thickness. In the case of  $[\text{Fe}_{0.95}\text{Mn}_{0.05}(\text{phen})_2(\text{NCS})_2]$  the variation of the line width is very similar to that in the pure compound. An abrupt change of  $\Gamma/2(\text{HS})$  occurs near the transition temperature  $T_c \approx 175$  K in both systems. A differential thermal analysis on the  $[\text{Fe}_x\text{Mn}_{1-x}(\text{phen})_2(\text{NCS})_2]$  mixed crystals was carried out, and the results are shown in Figure 7. The phase transition that is so prominent in the pure compound  $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ <sup>17</sup> becomes broadened in the sample with  $x = 0.95$  and is no more detectable in the samples with  $x \leq 0.5$  in the temperature range 86–300 K. The above-mentioned anomaly in the quadrupole splitting  $\Delta E_Q(\text{HS})$  and in the line width  $\Gamma/2(\text{HS})$  may be indicative of a first-order phase change. High-resolution magnetic susceptibility measurements that are presently undertaken to clarify the nature of the phase transition in  $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$  support this. A sample of polycrystalline material of  $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ , prepared by

(17) P. Ganguli, P. Gülich, E. W. Müller, and W. Irlner, *J. Chem. Soc., Dalton Trans.*, 441 (1981).



**Figure 7.** Differential thermal analysis curves for  $[\text{Fe}_x\text{Mn}_{1-x}(\text{phen})_2(\text{NCS})_2]$ . The system with  $x = 0.95$  (inserted figure) still shows a similar phase transition signal as is known for the pure iron compound.<sup>17</sup> Such a signal is absent in the curves for  $x \lesssim 0.5$ .



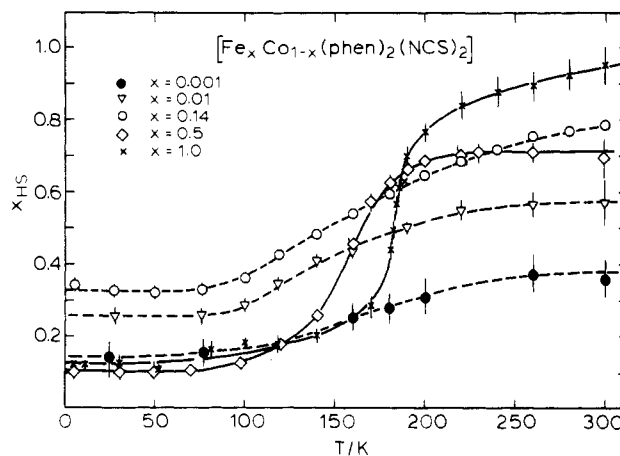
**Figure 8.** Area fraction  $x_{\text{HS}}$  of the iron(II) high-spin doublet from the Mössbauer spectra of  $[\text{Fe}_x\text{Mn}_{1-x}(\text{phen})_2(\text{NCS})_2]$  with variable iron concentration  $x$  as a function of temperature.

an extraction method as described in ref 17, showed a small hysteresis of  $\Delta T_c = 0.20 \pm 0.05$  K in the  $\mu_{\text{eff}}(T)$  function,<sup>18</sup> which has never been seen before.

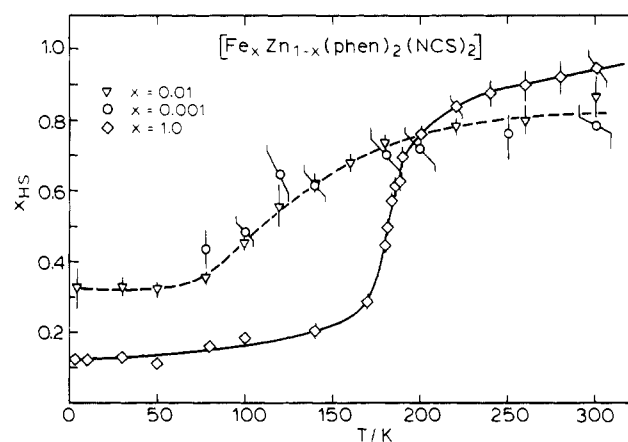
The temperature dependence of the HS fraction determined from the relative areas under the HS and LS doublets shows some interesting and systematic trends.

In the case of  $[\text{Fe}_x\text{Mn}_{1-x}(\text{phen})_2(\text{NCS})_2]$  the transition temperature  $T_c$  shifts to lower temperatures upon dilution and the residual paramagnetism (RP) increases systematically with decreasing  $x$  (Figure 8). The rather sharp transition in the undiluted  $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$  becomes broad on dilution, and from such a trend it appears that in the limit of infinite dilution the spin crossover would be totally lost and all the isolated  $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$  embedded in the manganese host should stabilize in the  $^5T_2$  ground state. It may be significant to note here that metal-dilution experiments on  $[\text{Fe}_x\text{Zn}_{1-x}(\text{pic})_3]\text{Cl}_2 \cdot \text{EtOH}$ <sup>10,11</sup> showed that even though  $T_c$  is lowered on dilution, the HS  $\rightleftharpoons$  LS crossover is still observable even at the lowest possible iron concentrations under study. The common result in both series of experiments is that some cooperative interactions would be necessary to cause the spin crossover in these systems.

The effects of pressure on some HS  $\rightleftharpoons$  LS systems have previously been investigated,<sup>2</sup> and it has been shown that, on application of moderate pressures, these systems can be made to exhibit the HS  $\rightleftharpoons$  LS transition at ambient temperatures. Mössbauer experiments<sup>19</sup> on  $\text{FeS}_2$  show that it remains in the



**Figure 9.** Area fraction  $x_{\text{HS}}$  of the iron(II) high-spin doublet from the Mössbauer spectra of  $[\text{Fe}_x\text{Co}_{1-x}(\text{phen})_2(\text{NCS})_2]$  with variable iron concentration  $x$  as a function of temperature.



**Figure 10.** Area fraction  $x_{\text{HS}}$  of the iron(II) high-spin doublet from the Mössbauer spectra of  $[\text{Fe}_x\text{Zn}_{1-x}(\text{phen})_2(\text{NCS})_2]$  with variable iron concentration  $x$  as a function of temperature.

low-spin state at all pressures. However, on dilution of  $\text{FeS}_2$  in  $\text{MnS}_2$ , the Fe(II) ions could be stabilized predominantly in the HS state at atmospheric pressure. The amount of the high-spin state was also found to increase with successive dilution. These samples, when subjected to moderate pressures, were made to exhibit a HS  $\rightleftharpoons$  LS crossover. Similar results were obtained in samples containing 2%  $^{57}\text{Fe}$  in  $\text{MnSe}_2$  and  $\text{MnTe}_2$ . These results have been interpreted as being due to larger lattice parameters in the  $\text{MnS}_2$  lattice, and the correspondingly smaller crystal field potential at the iron site leading to the stabilization of the HS state in the highly diluted  $\text{FeS}_2$  in  $\text{MnS}_2$ .

It is possible that the systematic increase in the residual paramagnetism, i.e., the increase of the  $x_{\text{HS}}$  fraction at low temperatures in  $[\text{Fe}_x\text{Mn}_{1-x}(\text{phen})_2(\text{NCS})_2]$ , could likewise occur due to the larger lattice constants of  $[\text{Mn}(\text{phen})_2(\text{NCS})_2]$  caused by the fact that the ionic radius of  $\text{Mn}^{2+}$  (0.80 Å) is larger than that of  $\text{Fe}^{2+}$  (0.74 Å). This can be considered as applying "negative" lattice pressure on the Fe(II) site leading to an increase in the Fe–N bond length in the diluted  $[\text{Fe}_x\text{Mn}_{1-x}(\text{phen})_2(\text{NCS})_2]$ .

In order to support the validity of the above argument on the effect of internal "negative" lattice pressure, we studied the Mössbauer spectra of  $[\text{Fe}_x\text{Co}_{1-x}(\text{phen})_2(\text{NCS})_2]$ ,  $[\text{Fe}_x\text{Ni}_{1-x}(\text{phen})_2(\text{NCS})_2]$ , and  $[\text{Fe}_x\text{Zn}_{1-x}(\text{phen})_2(\text{NCS})_2]$  down to very low concentrations. The results of the Fe/Co and Fe/Zn systems are shown in Figures 9 and 10, where again the area fraction  $x_{\text{HS}}$  of the HS doublet in the Mössbauer spectra of these mixed-crystal systems is plotted as a function

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of temperature. In the cobalt, nickel, and zinc lattices the spin crossover does not go to completion, leaving a residual paramagnetism at temperatures well below  $T_c$  and a very high "residual diamagnetism" (RD) at temperatures well above  $T_c$ . The transition in the mixed crystals is no longer sharp as in the pure  $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ , again indicating that the cooperative forces may be considerably weakened on dilution. In the case of  $[\text{Fe}_x\text{Co}_{1-x}(\text{phen})_2(\text{NCS})_2]$  as in  $[\text{Fe}_x\text{Mn}_{1-x}(\text{phen})_2(\text{NCS})_2]$  the HS  $\rightleftharpoons$  LS crossover appears to be quenched at infinite dilution. However, in the cobalt lattice the residual paramagnetism at low temperatures decreases and the residual diamagnetism at high temperatures increases with metal dilution. This would imply that the isolated  $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$  molecules buried in the cobalt lattice would tend to stabilize in the ( $^1A_1$ ) low-spin ground state, a result exactly opposite to what was obtained in the case of the Mn-diluted mixed crystals. A similar systematic partial stabilization of the low-spin  $^2T_2(O_h)$  ground state in the case of tris(1-pyrrolidinedecarboxylato)iron(III) (FeP) diluted in the corresponding Co(III) lattice has also been reported.<sup>20</sup> Here, too, it was assumed that the structure of the FeP molecule is modified slightly, presumably with shortening of the Fe-S bonds, to approach that of the CoP host lattice which has shorter metal-sulfur bonds.

The Mössbauer spectra of  $[\text{Fe}_x\text{Ni}_{1-x}(\text{phen})_2(\text{NCS})_2]$  for  $x < 0.1$  were not very satisfactory due to very high electronic absorption of the 14-keV  $\gamma$  rays by the Ni atoms, but the low-spin state appears to be more readily stabilized in the Ni host lattice than in the Fe/Co mixed crystals. In  $[\text{Fe}_x\text{Zn}_{1-x}(\text{phen})_2(\text{NCS})_2]$  the HS  $\rightleftharpoons$  LS crossover characteristics are almost independent of concentration in the range  $x = 0.001-0.01$ , although the transition is much more gradual with a high residual paramagnetism and diamagnetism as in the Co and Ni mixed crystals. The rest paramagnetism in the Fe/Zn mixed crystals with  $x = 0.01$  and  $x = 0.001$  is much

higher than in the corresponding Fe/Co or Fe/Ni mixed crystals.

The observations seem to qualitatively show that the amount of rest paramagnetism in the low temperature region and the rest diamagnetism in the high-temperature region, respectively, exhibited by the  $[\text{Fe}_x\text{M}_{1-x}(\text{phen})_2(\text{NCS})_2]$  mixed crystals depend on the relative ionic radii of the host  $M^{2+}$  and  $\text{Fe}^{2+}$  ions. The ionic radii are known to decrease in the following order:  $\text{Mn}^{2+}$  (0.80 Å) >  $\text{Fe}^{2+}$  (0.74 Å)  $\sim$   $\text{Zn}^{2+}$  >  $\text{Co}^{2+}$  (0.72 Å) >  $\text{Ni}^{2+}$  (0.69 Å).<sup>21</sup>

From our Mössbauer experiments it appears that the host lattices with  $r(M^{2+}) > r(\text{Fe}^{2+})$  favor the stabilization of the HS state as in the case of  $[\text{Fe}_x\text{Mn}_{1-x}(\text{phen})_2(\text{NCS})_2]$  and the host lattices with  $r(M^{2+}) < r(\text{Fe}^{2+})$  favor the stabilization of the LS state as in  $[\text{Fe}_x\text{Co}_{1-x}(\text{phen})_2(\text{NCS})_2]$  and  $[\text{Fe}_x\text{Ni}_{1-x}(\text{phen})_2(\text{NCS})_2]$ . The above suggestion of "negative" and "positive" lattice pressures could decrease or increase the Fe-N bond lengths ( $R$ ), respectively, leading to an increase or decrease, respectively, of the crystal field potential (which is known to vary as  $R^{-5}$ ) at the Fe(II) site. This could stabilize the low-spin or high-spin state accordingly. It must be noted that no realistic quantitative analysis based on the simple point-charge approximation can be done on such highly covalent systems, and therefore, our results have only been rationalized in qualitative terms. An X-ray investigation on the whole series of  $[\text{M}^{\text{II}}(\text{phen})_2(\text{NCS})_2]$  could, however, confirm the above suggestion.

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Contribution from the Departments of Chemistry, University of Houston, Houston, Texas 77004, and William Marsh Rice University, Houston, Texas 77001

## Effect of Spin State on the Redox and Electron-Transfer Properties of the Variable-Spin Family of $[\text{Fe}^{\text{II}}(\text{6-Mepy})_n(\text{py})_{3-n}\text{tren}](\text{PF}_6)_2$ Complexes in Solution

KARL M. KADISH,\*<sup>1</sup> CHIH-HO SU,<sup>1</sup> D. SCHAEFER,<sup>1</sup> CONNIE L. MERRILL,<sup>2</sup> and LON J. WILSON<sup>2</sup>

The effect of spin state on the electron-transfer properties of the variable-spin family of  $[\text{Fe}^{\text{II}}(\text{6-Mepy})_n(\text{py})_{3-n}\text{tren}](\text{PF}_6)_2$  complexes ( $n = 1-3$ ) has been investigated in acetone, benzonitrile, and butyronitrile. For all complexes an Fe(II)  $\rightleftharpoons$  Fe(III) oxidation wave is observed between +1.05 and +1.30 V vs. a saturated lithium chloride calomel electrode (SLCE). The potential of the reaction is dependent on the number of methyl groups attached to the pyridine rings with  $E_{1/2}$  shifting anodically as the number increases from 0 to 3 groups. Heterogeneous electron-transfer rate constants vary between  $3.1 \times 10^{-2}$  and  $1.9 \times 10^{-1}$  cm/s depending on the solvent and the complex. In a given solvent, the standard rate constants are virtually identical for oxidation of the low-spin and high-spin complexes. The  $k^\circ$  for the spin-equilibrium complex is smaller than for either the high-spin or the low-spin complex. A discussion of the effect of spin state on rates of electron-transfer is presented.

### Introduction

Numerous spin-equilibrium compounds containing Fe(II) and Fe(III) have been prepared and characterized with respect to their electronic and structural properties,<sup>3,4</sup> and much de-

tailed information has been gathered as to how changes in spin state relate to changes in the various physicochemical properties of these complexes. However, one relationship which has not been extensively investigated is how a change of spin state affects the standard redox potential and electron-transfer

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