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High-Spin ⇌ Low-Spin Transition in Hexacoordinate Complexes of Iron(II) with Monodentate 1-Alkyltetrazole Ligands: A Variable-Temperature Mössbauer, Magnetic Susceptibility, and Far-Infrared Study†

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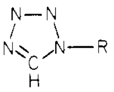
Iron(II) complexes of the type $[Fe(Rtz)_6](BF_4)_2$ with 1-alkyltetrazole as monofunctional ligands, where R = CH_3 (mtz), C_2H_5 (etz), *n*-C_3H_7 (ptz), and *i*-C_3H_7 (iptz), have been synthesized earlier and found in preliminary studies to undergo a temperature-dependent high-spin ($^5T_2$) ⇌ low-spin ($^1A_1$) transition. We report here on a more detailed characterization of the spin transition behavior using Mössbauer, magnetic susceptibility, and far-infrared spectroscopy at variable temperatures. The spin transition in the ptz complex induces a first-order phase transition with structural reordering in the vicinity of the iron center. The same phenomenon occurs in a zinc-diluted mixed crystal. A temperature-dependent spin transition also occurs in the mtz, etz, and iptz complexes but appears to be more gradual and incomplete; from the present studies there is no indication of a structural phase transition.

Introduction

A good number of iron(II) complexes exhibiting a temperature-induced high-spin (HS) ⇌ low-spin (LS) transition, in the approximation of O_h symmetry denoted as $^5T_{2g}(O_h) \rightleftharpoons {}^1A_1(O_h)$, have become known in the past.[1,2] Most of these contain bidentate, and in fewer cases polydentate, ligands with nitrogen donor atoms. The first example of a spin-crossover complex of iron(II) of the type $[FeL_6]X_2$ with six monofunctional ligands appeared in the literature in 1977.[3]

Stable iron(II) complexes of the $[FeL_6]X_2$ type with 1-alkyltetrazole as monofunctional nitrogen donor ligands were recently prepared by Franke and Groeneveld[4] and found to undergo a HS ⇌ LS transition in the solid state. The spin transition in these complexes was detected by magnetic susceptibility measurements (down to ca. 80 K), and preliminary results have been published earlier.[5,6] Here we report more detailed investigations of the spin transition phenomenon in the solid complexes $[FeL_6](BF_4)_2$, where L is 1-alkyltetrazole



and R = CH_3 (mtz), C_2H_5 (etz), *n*-C_3H_7 (ptz), and *i*-C_3H_7 (iptz). Magnetic susceptibility measurements and Mössbauer and far-infrared spectroscopy at variable temperatures were employed to follow the spin transition down to ca. 4 K.

Experimental Section

(a) Sample Preparation. The complexes were prepared as described in a previous publication.[5] The mixed-crystal system $[Fe_{0.79}Zn_{0.21}(ptz)_6](BF_4)_2$ was prepared by a corecrystallization of the pure iron and zinc complexes in the desired fractions. All samples were kindly supplied by P. L. Franke, Leiden, The Netherlands. The preparation of the ligands and the metal complexes turned out to be difficult, and the crystallization of the complexes was extremely tedious. Relatively pure samples could only be obtained in the case of the ptz complexes.

(b) Magnetic Susceptibility. The magnetic susceptibilities were measured at 10 kOe with a Foner type magnetometer equipped with a helium-flow cryostat. The temperature of the sample was measured with a calibrated thermocouple. The temperature stability was better than 0.04 K. The magnetometer was calibrated with $Hg[Co(NCS)_4]$. Effective magnetic moments were calculated from $\mu_{eff} = 2.828(\chi_m T)^{1/2}$, where χ_m is the corrected molar susceptibility. The diamagnetic corrections were calculated from Pascal's constants (mtz, 340×10^{-6}; etz, 414×10^{-6}; ptz, iptz, 503×10^{-6} cm^3 mol^{-1}). With the assumption of a simple Curie law behavior for the HS state and a temperature-independent susceptibility for the LS state (400×10^{-6} cm^3 mol^{-1}) the HS fraction γ may be calculated from the measured susceptibilities.

Table I. Transition Temperatures $T_c{\uparrow}$ (Heating) and $T_c{\downarrow}$ (Cooling) and Hysteresis Width $\Delta T_c = T_c{\uparrow} - T_c{\downarrow}$ for $[Fe(ptz)_6](BF_4)_2$ and $[Fe_{0.79}Zn_{0.21}(ptz)_6](BF_4)_2$[a]

	$T_c{\uparrow}$, K	$T_c{\downarrow}$, K	ΔT_c, K
$[Fe(ptz)_6](BF_4)_2$	134.2 (5)	128.0 (5)	6.2 (5)
$[Fe_{0.79}Zn_{0.21}(ptz)_6](BF_4)_2$	133.4 (5)	125.6 (5)	7.8 (5)

[a] Estimated errors are in parentheses.

(c) Mössbauer Spectroscopy. Mössbauer spectra were recorded in transmission geometry with use of a 25-mCi $^{57}Co/Rh$ source (The Radiochemical Centre, Amersham, England) kept at room temperature and a conventional spectrometer operating in the constant-acceleration mode. The samples (ca. 0.15 mg of $^{57}Fe/cm^2$) were sealed in poly(methyl methacrylate) containers and mounted in a bath cryostat with helium exchange gas. The temperature was measured with a calibrated Si diode. The spectra were fitted to Lorentzians with use of the MOSFUN program.[7]

(d) Far-Infrared Spectroscopy. Far-infrared spectra in the range 100–600 cm^{-1} were recorded with a Bruker Fourier-transform far-infrared spectrometer Model IFS 113, between 60 and 296 K. The temperature of a polyethylene pellet of $[Fe(ptz)_6](BF_4)_2$ was maintained within ±0.5 K by means of a continuous-flow helium cryostat, Model S-500 (Thor Cryogenics Ltd., Oxford, England), equipped with polypropylene windows.

Results and Discussion

(a) The $[Fe(ptz)_6](BF_4)_2$ Complex. Among the complexes under study, $[Fe(ptz)_6](BF_4)_2$ is the only one that exhibits a complete and rather abrupt spin transition. In addition it shows a wide hysteresis with a peculiar form (see Figure 1). Both the heating and the cooling curve possess an abrupt step at high temperatures, which is followed by a gradual curvature at low temperatures.

In the steep parts of the curves no intermediate equilibrium data could be obtained, but a steady decrease (cooling) or increase (heating) was observed on time. The kinetics of this process was followed quantitatively as described below.

In order to study the influence of metal dilution on the HS ⇌ LS transition and, particularly, on the hysteresis, the iron complex was diluted with 21% of the zinc complex, which was shown to be isomorphous with the iron complex.[8] The

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† Dedicated to Professor R. Hoppe on the occasion of his 60th birthday.

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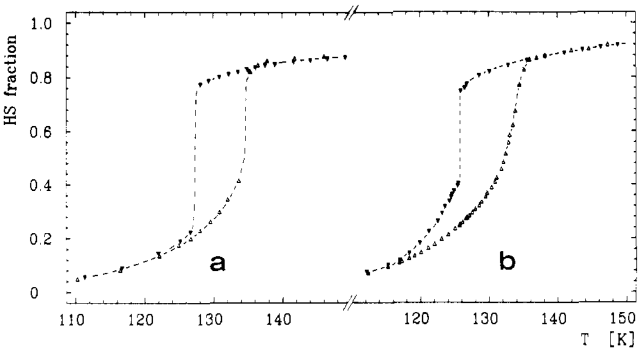

Figure 1. HS fraction as a function of temperature for (a) Fe$(ptz)_6(BF_4)_2$ and (b) $Fe_{0.79}Zn_{0.21}(ptz)_6(BF_4)_2$ (▼, falling temperature; △, rising temperature).

transition in the diluted complex is shifted to lower temperatures, which is in accordance with earlier observations in other spin-crossover systems[9] and which may be understood on the basis of a recently published model.[10] It is, however, surprising that the width as well as the form of the hysteresis is nearly unchanged in the pure and the mixed crystal (see Figure 1 and Table I). The differences in the form of the hysteresis may even be smaller than it appears from the figure, because the data points of the cooling curve after the steep decrease do not represent true equilibrium values as could be seen from the quantitative study of the time dependence (see below). The model[10] predicts a reduction of the hysteresis width and finally a complete disappearance of the hysteresis at high dilution. The fact that, in the present case of a 21% diluted system, the hysteresis width did not change lends support to the assumption that a structural phase transition is induced by the HS $\rightleftharpoons$ LS transition. This is further supported by the time dependence and by the observation of a change in the quadrupole splitting of the HS doublet (see below). This hypothesis also gives a plausible explanation for the observed form of the hysteresis loop, which may be thought of as being composed of a gradual HS $\rightleftharpoons$ LS transition (without hysteresis) and a structural phase transition starting at some critical HS fraction. A study of more diluted samples can not yet be performed because of the above-mentioned preparation difficulties.

The time dependence of the HS $\rightleftharpoons$ LS conversion already mentioned above was followed in the undiluted complex for the cooling as well as for the heating process. The conversion LS → HS was found to proceed much faster than the reverse conversion HS → LS. The same is true for the diluted system, where the HS → LS conversion was found to be extremely retarded, whereas the time required for the LS → HS conversion was on the order of the time needed by the apparatus to reach thermal equilibrium and thus was too fast to be studied quantitatively.

Figure 2a gives a plot of the observed HS fractions as a function of time. At least the cooling curve of the undiluted system does not represent a simple first-order law as was claimed for the HS → LS conversion in $[Fe(phen)_2(NCS)_2]$[11], but an S-shaped form is typical for phase transitions proceeding by the nucleation and growth mechanism.[12] The kinetics thereof is commonly described by the Avrami equation[12]

$$x = 1 - \exp(-kt^n)$$

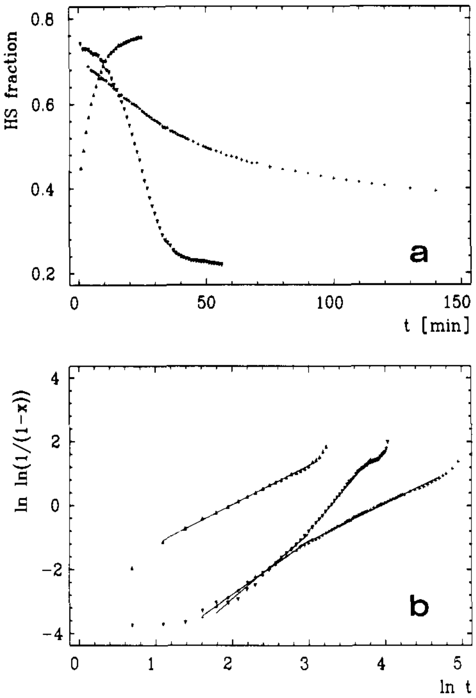

Figure 2. (a) HS fraction as a function of time and (b) Avrami plot for (▽) $[Fe(ptz)_6(BF_4)_2]$ cooling (T = 126.7 K), (△) $[Fe(ptz)_5(BF_4)_2]$ heating (T = 135.5 K), and (+) $[Fe_{0.79}Zn_{0.21}(ptz)_6](BF_4)_2$ cooling (T = 125.9 K).

Table II. Exponents n and Rate Constants k from the Avrami Plots

	n	k, min^{-n}
$[Fe(ptz)_6](BF_4)_2$ (cooling)	2.0–2.8	0.032–0.038
$[Fe(ptz)_6](BF_4)_2$ (heating)	1.2	0.14
$[Fe_{0.79}Zn_{0.21}(ptz)_6](BF_4)_2$ (cooling)	1.6–1.2	0.026–0.019

where x represents the fraction of the final phase formed during the time t. The exponent n can adopt values between 1 and 4 for structural phase transitions, where n = 4 describes a time-independent nucleation rate.

Figure 2b represents a plot of ln ln $(1/(1 - x))$ vs. ln t (Avrami plot), where the exponent n is represented by the slope and the rate constant k is deduced from the intercept ln k = ln ln $(1/(1 - x))$ at t = 1 of a straight line. If the very first and the very last points were neglected, the heating process in $[Fe(ptz)_6](BF_4)_2$ could be fitted with a single straight line, whereas the cooling curves of both the undiluted complex and the mixed-crystal system change their slopes near ln t = 2.8, and two straight lines were required to match each of these curves. Table II gives the resulting values of n and k. The conversion process HS → LS differs from the process LS → HS as is apparent from the different exponents n. In addition the dilution with Zn changes the exponent n and, most likely, the mechanism of the HS → LS conversion. If the nucleation rate (rate of formation of nuclei) is much faster than the propagation rate (rate of growth of nuclei) the exponent n is known to be lowered by 1.[12] Presumably the zinc complex molecules act as nuclei for the transformation HS → LS. The change of the rate of transformation, as compared to the rate for the undiluted complex, may result from a different extent of undercooling. But as this was observed in a number of experiments, we consider it to be significant. The reason may be a hindered phase propagation due to the defects in the lattice introduced by the zinc complex molecules.

The Mössbauer spectra of $[Fe(ptz)_6](BF_4)_2$ taken at 10 temperatures between room temperature and 97 K also reflect the HS $\rightleftharpoons$ LS transition; five typical spectra are shown in Figure 3. The evaluation of the Mössbauer parameters (given

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(9) M. Sorai, J. Ensling, and P. Gütlich, *Chem. Phys.*, **18**, 199 (1976).
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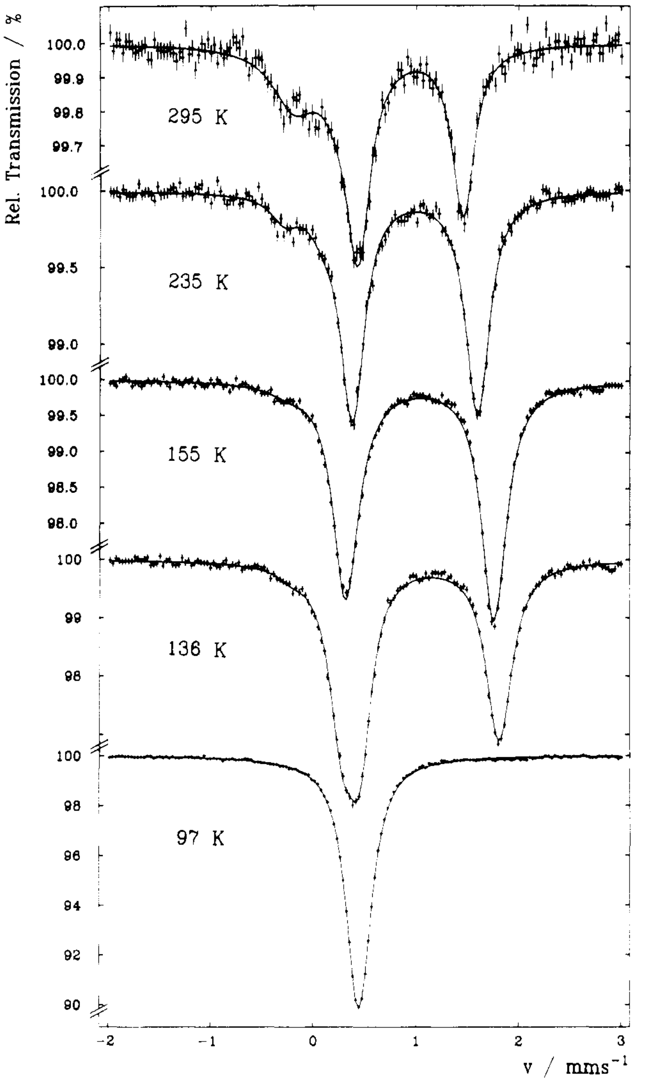

Figure 3. Mössbauer spectra of $[Fe(ptz)_6](BF_4)_2$ at various temperatures. The shoulder on the left in the high-temperature spectra is due to an impurity.

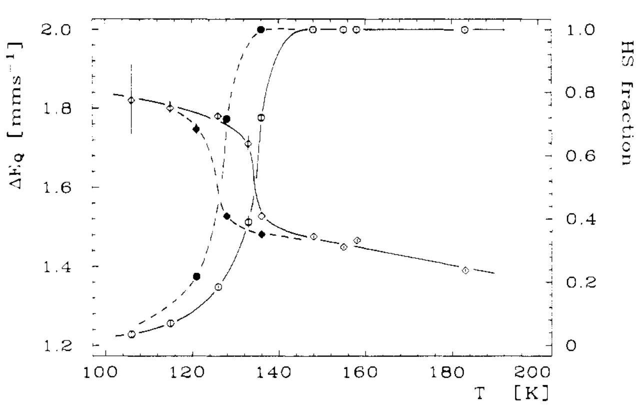

Figure 4. Quadrupole splitting ΔE_Q (◇) and area fraction (○) of the HS state of $[Fe(ptz)_6](BF_4)_2$ as a function of temperature. Solid symbols (◆, ●) represent the corresponding parameters of $[Fe_{0.79}Zn_{0.21}(ptz)_6](BF_4)_2$.

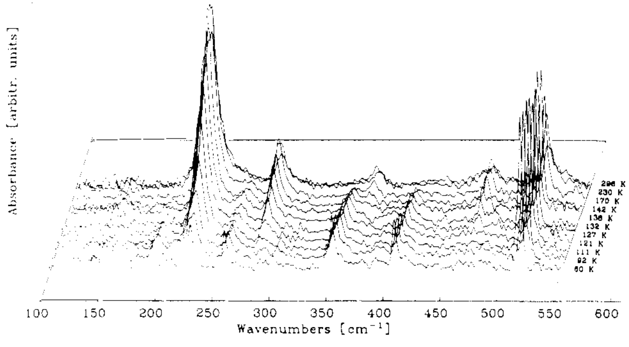

Figure 5. Far-infrared absorbance spectra of $[Fe(ptz)_6](BF_4)_2$ between 100 and 550 cm^{-1} at various temperatures between 60 and 296 K.

as supplementary material), however, was difficult because of a small impurity (possibly iron(III)) and an asymmetry in the intensity of the HS quadrupole doublet due to the texture in the absorber. The texture resulted from the form of the crystals (thin plates). The usual procedure of grinding the crystals to remove the texture could not be applied here, because, as is known from other cases,[13-15] this probably would have modified the spin transition characteristics. Mixing the crystals with polyethylene was not satisfactory.

The LS state shows a single line in the spectrum. In the class of iron(II) spin-crossover complexes this has so far only been observed for the similar isoxazole complex.[3] This apparently implies the presence of a highly symmetric coordination sphere, which is also supported by the remarkably simple far-infrared spectra (see below).

The HS state is represented by a quadrupole doublet with the parameter values given as supplementary material. A pronounced change in the quadrupole splitting was found to accompany the HS $\rightleftharpoons$ LS transition (Figure 4). A similar change appears in the zinc-diluted complex but is shifted to lower temperatures. Outside the transition region the pure and the zinc-diluted complexes show the same values of the quadrupole splitting and the isomer shift in the two spin states. The change in the quadrupole splitting reflects a significant change of the microsymmetry around the iron ion and is further evidence for a structural phase transition.

The temperature dependence of the IR absorbance spectra of $[Fe(ptz)_6](BF_4)_2$ in the range 100–550 cm^{-1} (Figure 5) shows that, with decreasing temperature, new bands at 202, 265, 309, 360, 398, and 413 cm^{-1} gradually appear while those at 290, 373, and 476 cm^{-1} disappear. The very intense band at 227 cm^{-1} (296 K) shifts to 235 cm^{-1} and does not vanish completely at 60 K. The band at 524 cm^{-1}, the $\tilde{\nu}_4(F_2)$ mode of the BF_4^- anion, sharpens considerably with decreasing temperature.

Franke[5] has tenatively assigned the bands in the far-infrared spectra of $[Fe(ptz)_6](BF_4)_2$ in the HS state (296 K spectrum) and in the LS state (90 K spectrum). His assignment of the high-spin $\tilde{\nu}$(Fe–N) band at 227 cm^{-1} is consistent with our findings on the basis of the partial isomorphous substitution of Fe(II) by Zn(II) on the one hand and on the temperature dependence of the area under this band on the other hand. The far-infrared spectra (100–600 cm^{-1}) of the isomorphous Fe and Zn complexes are completely identical except for the position of the very strong band at 189 cm^{-1} for $[Zn(ptz)_6](BF_4)_2$ and 227 cm^{-1} for $[Fe(ptz)_6](BF_4)_2$. This shift fits well to the Irving–Williams series of $\tilde{\nu}$(M–L) of divalent transition-metal complexes. Both bands are observed in the spectrum of the mixed crystals $[Fe_{0.79}Zn_{0.21}(ptz)_6](BF_4)_2$ with the relative peak area fractions of 20 ± 2% for the band at 189 cm^{-1} and 80 ± 2% for the band at 227 cm^{-1}. This result supports the assignment for the high-spin $\tilde{\nu}$(Fe–N) band. Furthermore, as seen in Figure 6, the area vs. temperature

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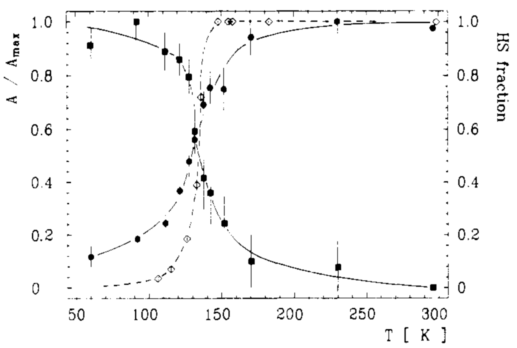

Figure 6. Temperature dependence of the normalized area of two characteristic IR bands (heating curve) at 227 (○) and 413 (■) cm^{-1} and of the HS content derived from Mössbauer measurements (◇).

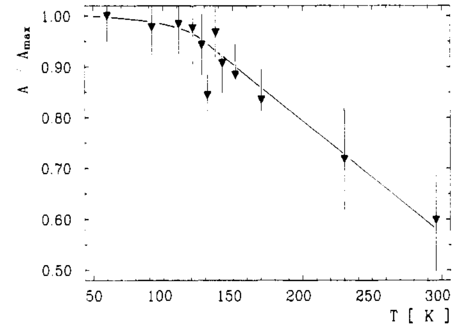

Figure 7. Temperature dependence of the normalized area of the $\tilde{\nu}_4(F_2)$ vibrational band of the BF_4^- anion at 524 cm^{-1}.

curve of the band at 227 cm^{-1} follows quite well the HS content obtained from the Mössbauer measurements when the temperature was varied. However, the vibrational peak area curve is smoother and appears to be shifted to slightly lower temperatures. This is probably due to the method of preparation of the polyethylene pellet of the compounds. The rather coarse crystals of $[Fe(ptz)_6](BF_4)_2$ had to be ground in order to obtain a uniform distribution of the crystals in the polyethylene matrix. It has been observed recently[13-15] that mechanical treatment such as grinding leads to a residual HS fraction at low temperatures and more gradual transition curves. Thus the assignment of the band at 227 cm^{-1} to the high-spin $\tilde{\nu}$(Fe–N) band appears to be unequivocal.

The remaining three weak bands at 290, 373, and 476 cm^{-1} also reduce their intensity upon cooling, but their temperature dependence is smooth and does not show this S-shaped transition curve. It is therefore likely that these bands originate from ligand vibrations which do not feel directly the spin transition at the metal center.

The assignment of the low-spin $\tilde{\nu}$(Fe–N) bands turned out to be more difficult. Two of the new bands—at 360 and 413 cm^{-1}—in the 60 K spectrum exhibit a temperature dependence of the peak area which reflects the spin transition. Figure 6 shows the area vs. temperature curve of the band at 413 cm^{-1}. The difference of the position of this band with respect to that of the high-spin $\tilde{\nu}$(Fe–N) band is within the range found for other spin-crossover complexes of iron(II).[16-18] Consequently, the band at 413 cm^{-1} most probably stems from the low-spin $\tilde{\nu}$(Fe–N) vibration.

In addition to the critical behavior of the high-spin and the low-spin $\tilde{\nu}$(Fe–N) bands, the $\tilde{\nu}_4(F_2)$ mode of the BF_4^- anion at 524 cm^{-1} displays a discontinuous change in its intensity in the spin-transition region (see Figure 7). We believe that this behavior is related to a structure change at the spin-transition temperature.

Table III. Transition Temperature, T_c, and Residual HS Fraction at Low Temperatures, γ_{LT}, for $[Fe(mtz)_6](BF_4)_2$, $[Fe(etz)_6](BF_4)_2$, and $[Fe(iptz)_6](BF_4)_2$[a]

	T_c, K	γ_{LT}
$[Fe(mtz)_6](BF_4)_2$	107.5 (8)	0.13 (1)
$[Fe(etz)_6](BF_4)_2$	106 (2)	0.48 (8)
$[Fe(iptz)_6](BF_4)_2$	72 (5)	0.7 (2)

[a] Estimated errors are in parentheses.

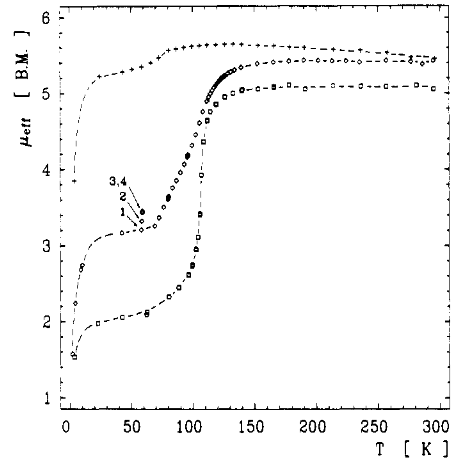

Figure 8. Effective magnetic moment as a function of temperature for (□) $[Fe(mtz)_6](BF_4)_2$, (◇) $[Fe(etz)_6](BF_4)_2$, and (+) $[Fe(iptz)_6](BF_4)_2$. The points 1–4 were measured in different cooling cycles.

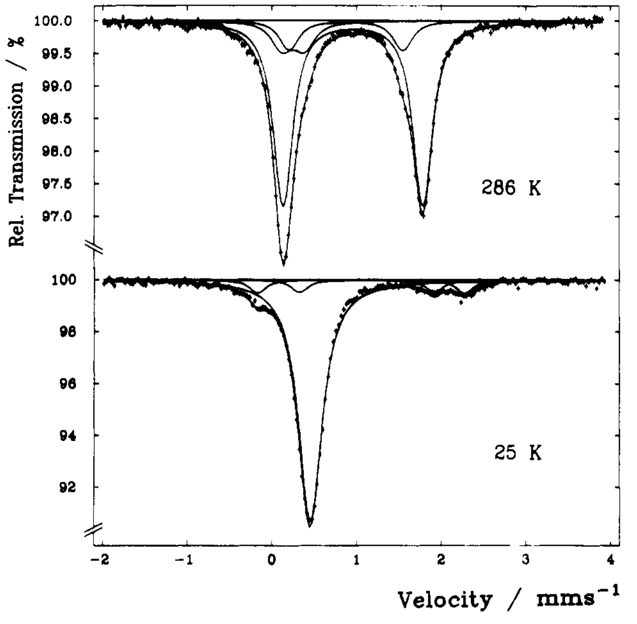

Figure 9. Mössbauer spectra of $[Fe(mtz)_6](BF_4)_2$ at 286 and 25 K.

(b) Other Complexes with 1-Alkyltetrazoles. The complexes with other 1-alkyltetrazoles (R = CH_3, C_2H_5, and i-C_3H_7) were also studied by Mössbauer spectroscopy and susceptibility measurements. All of them show incomplete transitions (see Figure 8 and Table III) which are more gradual than in the case of $[Fe(ptz)_6](BF_4)_2$ and did not reveal any hysteresis. In the case of $[Fe(etz)_6](BF_4)_2$, part of the HS phase could be "frozen" by cooling it down rapidly: cooling down slowly led to point 1 in Figure 8; the points 2, 3, and 4 were reached by cooling more and more rapidly. Similar effects were observed by Ritter et al.[19] in another spin-crossover system of iron(II).

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The Mössbauer spectra of the three complexes revealed two different quadrupole doublets typical of HS iron(II) instead of only one as seen in case of the ptz complex (see Figure 9). The evaluation of the spectra was even more difficult than for the ptz complex, and for the etz and the iptz complexes satisfactory fits could not be obtained. Not only may texture and an iron(III) impurity similar to that found in the ptz complex be responsible for that but also other unknown impurities may be present.

Unfortunately it was not yet possible to prepare sufficiently pure samples of this class of complexes, but the essential results and statements reported above are not affected by the impurities of the present samples.

Conclusions

The HS $\rightleftharpoons$ LS transition in $[Fe(ptz)_6](BF_4)_2$ induces a first-order phase transition with structural reordering in the vicinity of the iron center. The same phenomenon occurs in a zinc-diluted mixed crystal.

Temperature-dependent spin transition also occurs in the corresponding complexes with other 1-alkyltetrazoles (mtz, etz, iptz) but appears to be more gradual and incomplete, and from the present studies, there is not evidence for a structural phase transition. Unfortunately, it was not possible to prepare sufficiently pure samples of the last three complexes suited for more extensive studies.

Acknowledgment. We wish to thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support. Dr. P. L. Franke (Rijksuniversiteit Leiden, Leiden, The Netherlands) kindly supplied the samples.

Registry No. $[Fe(mtz)_6](BF_4)_2$, 82285-66-3; $[Fe(etz)_6](BF_4)_2$, 82285-68-5; $[Fe(ptz)_6](BF_4)_2$, 82285-70-9; $[Fe(iptz)_6](BF_4)_2$, 82285-72-1.

Supplementary Material Available: Tables of Mössbauer parameters for the mtz, etz, ptz, and iptz complexes (2 pages). Ordering information is given on any current masthead page.

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Laser Raman Spectroscopic Studies of Metal α-Diimine Complexes. 1. Imine Stretching Frequencies and Bonding Implications

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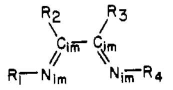
Raman spectroscopy was used to accurately and unambiguously determine the imine stretching frequencies for some solid-state transition-metal α-diimine complexes, including those of low-spin Fe(II), and to provide the basis for a critical reevaluation of vibrational assignments for some low-spin Fe(II) complexes. The greatly enhanced sensitivity of the Raman technique compared to infrared spectroscopy led to evidence for the presence of measurable amounts of a low-spin Fe(II) complex at room temperature in a system known to undergo a spin-state transition at lower temperatures. These findings, in turn, allowed an evaluation of the role of the metal's spin state and atomic number in determining the position of the imine stretching frequency of the complex.

Introduction

The α-diimines are neutral, bidentate ligands that are represented by the general structure



where the R_i may be H, alkyl, or aromatic groups and where the imine linkages may be part of a larger aromatic group as in 2,2′-bipyridine (bpy) or 1,10-phenanthroline (phen). Investigations[2-6] of α-diimine complexes have revealed that the Fe(II) complexes are often unique among first-row transition metals, with this unique nature being attributed to the ability of Fe(II) to donate electron density from its d orbitals into the π* orbitals on the ligand.[4] One probe for investigating the nature of the metal–ligand interactions has been the dependence of the $M-N_{im}$, $N_{im}-C_{im}$, and $C_{im}-C_{im}$ vibrations on the identity of the metal. Nakamoto performed normal-coordinate analysis for $[Fe(GMI)_3]^{2+}$, $R_1 = R_4 = CH_3$, $R_2 = R_3 = H$, based on the infrared spectrum of the complex and an idealized geometry in which the N atoms were placed at the vertices of an octahedron, and concluded that the $Fe-N_{im}$ stretching force constant was larger than normal while the $N_{im}-C_{im}$ and $C_{im}-C_{im}$ stretching force constants were smaller than those expected for double bonds. Furthermore, he found strong coupling between the in-plane modes of the Fe(GMI) units.[3] In general, however, determining the position of the high-energy stretch (~1500–1700 cm^{-1}) associated with the five-membered metal α-diimine unit is difficult for many low-spin Fe(II) complexes because of the low infrared intensity of the band.[2,7] Since the imine stretch is a major contributor to this band,[3,8] the inability to definitively observe it has been

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