Summary

We may summarize as follows. The emission rules cited in the Introduction correctly predict that the emission lifetimes for aqueous $Cr(NH_3)_5(CN)^{2+}$ and *trans*-$Cr(NH_3)_4(CN)_2^+$ are relatively long. Both complexes show emission quenching by OH^-, and for the former, quenching by $Cr(CN)_6^{3-}$ was also studied (both in aqueous and in DMF solution). There are detailed temperature dependence data.

There were complexities in the case of the dicyano complex, stemming from interaction with the aquocyano thermal aquation product, probably excitation energy transfer. Biphasic emission decay was observed to progress in importance with the degree of thermal aquation.

In the case of $Cr(NH_3)_5(CN)^{2+}$, the quantum yield for aquation of ammonia (the observed mode of photoreaction) also shows both OH^- and $Cr(CN)_6^{3-}$ quenching, but with 27% of unquenchable yield. The photolysis produces both *trans*- and *cis*-$Cr(NH_3)_4(H_2O)(CN)^{2+}$, and the product isomer ratio is essentially the same for the quenchable and the unquenchable fractions of reaction. Again, there are temperature dependnece studies.

It seems likely that, following excitation, some prompt intersystem crossing occurs, so that both the thexi states D_1^0 and Q_1^0 are formed promptly. Neither the quenching behavior nor the temperature dependencies are diagnostic as to whether the quenchable portion of the photoreaction is due to direct reaction from D_1^0 or to reaction from Q_1^0 formed by back intersystem crossing. The invariance of the isomer ratio suggests the latter situation, however.

Acknowledgment. This investigation was supported in part by a grant from the U.S. National Science Foundation, and by the U.S. Office of Naval Research. In addition, E.Z. and P.R. wish to thank the National Research Council of Italy (CNR).

Registry No. $Cr(NH_3)_5(CN)^{2+}$, 42213-67-2; *trans*-$Cr(NH_3)_4(CN)_2^+$, 76299-50-8; $Cr(CN)_6^{3-}$, 14875-14-0; *cis*-$Cr(NH_3)_4(H_2O)(CN)^{2+}$, 74482-64-7; *trans*-$Cr(NH_3)_4(H_2O)(CN)^{2+}$, 74523-68-5; OH^-, 14280-30-9.

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Nature of the Residual Paramagnetic Fraction in Discontinuous and Continuous High-Spin ($^5T_2$) $\rightleftharpoons$ Low-Spin ($^1A_1$) Transitions of Iron(II) Complexes

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Detailed investigations of the ^{57}Fe Mössbauer-effect parameters and X-ray powder diffraction have been performed for the iron(II) complexes $[Fe(phy)_2](ClO_4)_2$ and $[Fe(bts)_2(NCS)_2]$ as a function of temperature (phy = 1,10-phenanthroline-2-carbaldehyde phenylhydrazone; bts = 2,2′-bi(5-methyl-2-thiazoline)). The high-spin ($^5T_2$) $\rightleftharpoons$ low-spin ($^1A_1$) transition in $[Fe(phy)_2](ClO_4)_2$ is of the discontinuous type ($T_c \simeq 247-252$ K); that in $[Fe(bts)_2(NCS)_2]$ is of the continuous type ($T_c \simeq 219.5$ K). For both compounds, the quadrupole splitting $\Delta E_Q(^5T_2)$ shows a pronounced discontinuity in the region of T_c. The discontinuity arises since the ΔE_Q values for the residual paramagnetic molecules are different from those of the bulk paramagnetic phase above T_c. It is proposed that, for the discontinuous spin transitions, the small crystallites that cannot participate in the crystallographic phase change are responsible for the residual paramagnetism at low temperatures. For the majority of the continuous transitions, the residual paramagnetic fraction is formed by those molecules that are trapped at defect sites within the lattice of the bulk low-spin isomer. The conclusions are supported by the results of grinding experiments as well as by the results for various additional crossover compounds.

Introduction

In a number of investigations[2-4] of various iron(II) complexes it has been observed that the high-spin ($^5T_2$) $\rightleftharpoons$ low-spin ($^1A_1$) transition is not completed at the two extreme temperatures and that there exists a certain fraction of molecules that do not participate in the transition. These molecules have been termed, in particular at the low-temperature extreme of the measurements, the residual paramagnetic fraction, their magnitude being strongly dependent on the method of preparation and the physical status of the sample. Although it is possible to establish reliably the existence of this type of molecule, e.g. from magnetic susceptibility studies, thus far only speculations concerning its origin and characterization have been published. The application of ^{57}Fe Mössbauer spectroscopy should assist in the determination of the nature of these molecules, since it is a microscopic technique. In particular, it may be of interest to compare the temperature dependence of the Mössbauer parameters for the residual fraction with that for the bulk paramagnetic phase above the transition temperature. Whereas for the high-spin ($^5T_2$) state of iron(II) the value of the quadrupole splitting is rather sensitive to lattice distortions,[5] for the low-spin ($^1A_1$) state this is not the case. Consequently, it may be expected that at least for the high-spin ($^5T_2$) state it should be possible to distinguish the residual paramagnetic fraction from the main part of the high-spin phase of the substance.

Indeed, a clear discontinuity in the values of the quadrupole splitting $\Delta E_Q(^5T_2)$ has been reported in the spin-transition region for *precipitated* samples of $[Fe(phen)_2(NCS)_2]$ by Ganguli et al.[6] (phen = 1,10-phenanthroline). The observed discontinuity has been attributed to a crystallographic phase change that is believed to be associated with the high-spin ($^5T_2$) $\rightleftharpoons$ low-spin ($^1A_1$) transition in the compound. However, subsequent studies[7] of the Mn^{2+} ion EPR on samples of $[Fe(phen)_2(NCS)_2]$ doped with 1 mol % Mn^{2+} did not reveal any indication for the proposed crystallographic phase change.

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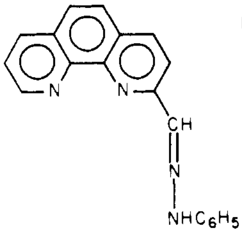
Only recently has it been possible to discover a hysteresis[8,9] of $\Delta T_c \simeq 0.15$ K, which does give definite support for a phase change in the *extracted* sample of $[Fe(phen)_2(NCS)_2]$. However, the very narrow hysteresis suggests that the structural change must be rather small and, moreover, the transition may show partial higher order character. In any case, the suggested explanation for the discontinuity in the temperature dependence of $\Delta E_Q(^5T_2)$ should be considered with extreme caution. We shall demonstrate below that, in the compound $[Fe(bts)_2(NCS)_2]$, a clear discontinuity exists for the quantity $\Delta E_Q(^5T_2)$ close to the transition temperature $T_c \simeq 219.5$ K (bts = 2,2′-bi(5-methyl-2-thiazoline)). However, this compound does *not* undergo a crystallographic phase change, since the high-spin ($^5T_2$) $\rightleftharpoons$ low-spin ($^1A_1$) transition is of the continuous type, the two spin isomers of the molecule being involved in a solid solution within the same lattice.[10]

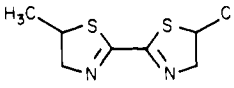
It should be noted that, for many spin-transition compounds, there is a contribution from the low-spin ($^1A_1$) state at the upper limit of the experimental temperature range. Sometimes, it is obvious from a plot of the effective magnetic moment vs. temperature that the low-spin contribution would continue to decrease if the experimental temperature range could be extended higher. Since, moreover, the value of $\Delta E_Q(^1A_1)$ is not very sensitive to lattice distortions, the existence of a residual diamagnetic fraction is not easily established.

There is no theoretical model that can explain the existence of the residual paramagnetic fraction. In general, the influence of lattice defects in the close vicinity of the particular molecules has been invoked or the location of these molecules on the surface of the crystallites has been assumed. In a recent investigation, Haddad et al.[11] have shown that the residual paramagnetic fraction for the iron(III) complex $[Fe(3\text{-}OCH_3SalEen)_2]PF_6$ is significantly increased on sample grinding as well as upon metal dilution, i.e. on studying the crystalline doped system $[Fe_xM_{1-x}(3\text{-}OCH_3\text{-}SalEen)_2]PF_6$, where M = Cr^{3+}, Co^{3+} ($3\text{-}OCH_3SalEen$ is the monoanion of the condensation product from 3-methoxysalicylaldehyde and *N,N′*-ethylenediamine). Closely similar results have been obtained by Ganguli et al.[9] for the mixed-crystal series $[Fe_xM_{1-x}(phen)_2(NCS)_2]$, where M = Mn^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}. These studies have shown that the magnitude of the residual paramagnetic fraction is dependent on the nature of the metal ion dopant and on its relative concentration. As far as the effect of sample grinding is concerned, similar results have also been observed for the iron(II) complex $[Fe(4,7\text{-}(CH_3)_2phen)_2(NCS)_2]\cdot\alpha\text{-pic}$[12] ($\alpha$-pic = α-picoline). For all these systems it was found that the sharpness of the transition is seriously affected by the doping and/or grinding of the sample. It should be noted that in $[Fe(3\text{-}OCH_3SalEen)_2]PF_6$ and $[Fe(4,7\text{-}(CH_3)_2phen)_2(NCS)_2]\cdot\alpha\text{-pic}$, the spin transition is of the discontinuous type and, judging from the observed hysteresis effects, it is also associated with a crystallographic phase change. On the other hand, for the pure and the metal-diluted $[Fe(phen)_2(NCS)_2]$ complex, the association of a first-order phase change with the spin transition is still not unequivocally established.[6-9]

In order to obtain more definite evidence concerning the nature of the residual paramagnetic fraction, we have performed detailed and accurate investigations of the temperature dependence of various Mössbauer parameters for a number of iron(II) crossover complexes. In the following, we report in particular the results obtained for the compounds $[Fe(phy)_2](ClO_4)_2$ and $[Fe(bts)_2(NCS)_2]$ (phy = 1,10-phenanthroline-2-carbaldehyde phenylhydrazone and bts = 2,2′-bi(5-methyl-2-thiazoline)). For $[Fe(phy)_2](ClO_4)_2$, a



phy



bts

discontinuous type high-spin ($^5T_2$) $\rightleftharpoons$ low-spin ($^1A_1$) transition associated with a crystallographic phase change has been established,[13] whereas, as has been mentioned above, for $[Fe(bts)_2(NCS)_2]$ a continuous high-spin ($^5T_2$) $\rightleftharpoons$ low-spin ($^1A_1$) transition is observed.[10]

Experimental Section

Materials. Samples of the complex bis(1,10-phenanthroline-2-carbaldehyde phenylhydrazone)iron(II) diperchlorate, $[Fe(phy)_2](ClO_4)_2$, enriched to more than 90% in iron-57 have been prepared as previously reported.[13] The preparation of bis(isothiocyanato)-bis(2,2′-bi(5-methyl-2-thiazoline))iron(II), $[Fe(bts)_2(NCS)_2]$, has been described elsewhere.[10] All samples gave satisfactory analyses, their physical data being in agreement with those previously reported.[10,13]

Methods. ^{57}Fe Mössbauer spectra have been measured as described in our earlier publications.[10,12,13] The experimental uncertainty for the values of the quadrupole splitting $\Delta E_Q(^5T_2)$ displayed in Figures 1 and 3 is ±0.01 mm s^{-1} except at temperatures where only the residual high-spin fraction is observed. For $[Fe(phy)_2](ClO_4)_2$, the limiting temperature is approximately 230 K, whereas for $[Fe(bts)_2(NCS)_2]$ it may be estimated to about 190 K. Below this temperature, the contribution by the (residual) high-spin $^5T_2$ fraction is rather low and the experimental uncertainty thus increases, assuming, in the case of $[Fe(bts)_2(NCS)_2]$, values up to ±0.08 mm s^{-1} (cf. associated values of $n_{^5T_2}$). From the background-corrected Mössbauer absorption areas A_i, the effective thickness corresponding to both the spin components, $t_{^5T_2}$ and $t_{^1A_1}$, has been obtained with use of the relation[10]

$$A_i = 0.5\pi\Gamma f_S \frac{t_i}{1 + 0.25t_i} \tag{1}$$

The effective thickness for the two components is also given by

$$t_{^5T_2} = dn_{^5T_2}f_{^5T_2} \qquad t_{^1A_1} = d(1 - n_{^5T_2})f_{^1A_1} \tag{2}$$

the individual quantities having been defined elsewhere.[10,13] From the effective thickness values, the high-spin fraction $n_{^5T_2}$ has been estimated on the basis of the high-temperature approximation of the Debye–Waller factor. In this procedure (viz. method II[10]), it is assumed that the recoil-free fractions $f_{^5T_2}$ and $f_{^1A_1}$ are continuous functions throughout the spin transition region:

$$f_{^5T_2} = e^{-HT} \qquad f_{^1A_1} = e^{-LT} \tag{3}$$

Here, H and L are characteristic constants for the two types of lattices. It may then be shown that at any temperature T_k

$$H_k = -\frac{1}{T_k}[\ln\,(t_{^5T_2}{}^k + t_{^1A_1}{}^k e^{-(\bar{H}-\bar{L})T_k}) - \ln d] \tag{4}$$

$$L_k = -\frac{1}{T_k}[\ln\,(t_{^1A_1}{}^k + t_{^5T_2}{}^k e^{-(\bar{H}-\bar{L})T_k}) - \ln d]$$

In eq 4, $\bar{H} = 1/n\sum H_k$ is the average for n measurements and similarly $\bar{L} = 1/n\sum L_k$. Equation 4 may be solved by iteration on the condition that $\sum(\bar{H} - H_k)^2$ or $\sum(\bar{L} - L_k)^2$ is minimum. The resulting values

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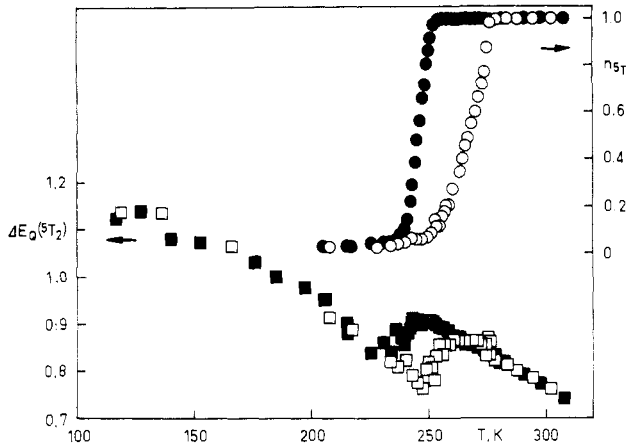

Figure 1. High-spin fraction $n_{^5T_2}$ (circles) and quadrupole splitting of the high-spin $^5T_2$ phase $\Delta E_Q(^5T_2)$ (squares) for $[Fe(phy)_2](ClO_4)_2$ as a function of temperature. Open signs refer to measurements for increasing temperatures; solid signs correspond to decreasing temperatures.

of $\bar{H}$ and $\bar{L}$ in conjunction with $d = N\beta\delta\sigma_0$ determine the unknown quantities $f_{^5T_2}$, $f_{^1A_1}$ and $n_{^5T_2}$ as a function of temperature.

Measurements of X-ray powder diffraction have been performed at variable temperatures in the step-scanning mode of a Siemens counter diffractometer. The angular steps for the 2θ values have been 0.02 or 0.005°. More details have been given elsewhere.[13,14]

Results

$[Fe(phy)_2](ClO_4)_2$. For a particular iron-57-enriched sample of this compound, a total of about 100 Mössbauer spectra were recorded for both increasing and decreasing temperature sequences. Apart from the transition temperature region, the least-squares fitting of the spectra resulted in almost the same values of the quadrupole splitting ΔE_Q and the isomer shift δ^{IS} for the majority spin phase as has been reported earlier.[13] The detailed values of $\Delta E_Q(^5T_2)$ and of the high-spin fraction $n_{^5T_2}$ resulting from the application of the iterative procedure are plotted, as a function of temperature, in Figure 1. According to the data for the particular sample used, there is about 3% of the residual paramagnetic fraction at low temperatures whereas at high temperatures, the transition is complete. The values of the transition temperatures and the width of the hysteresis loop are slightly different from the values reported previously.[13] It has been shown earlier that these properties are closely related to the sample history.[13] From the figure, a discontinuity in $\Delta E_Q(^5T_2)$ is clearly evident and, therefore, the temperature dependence of $\Delta E_Q(^5T_2)$ for the residual paramagnetic fraction, i.e. below the transition temperature T_c, is significantly different from that for the majority high-spin phase above T_c. It should be noted that the use of an enriched sample allowed the determination of the Mössbauer parameters for the very small residual paramagnetic fraction ($n_{^5T_2} \simeq 0.03$) with reasonable accuracy. The hysteresis that is associated with the spin transition clearly shows up in the temperature function of $\Delta E_Q(^5T_2)$ values (cf. Figure 1). Finally, neither a discontinuity in the values of $\delta^{IS}(^5T_2)$ nor any anomaly within the spin-transition region in the values of ΔE_Q and δ^{IS} for the low-spin $^1A_1$ phase has been observed.

X-ray powder diffraction peak profiles that have been recorded above and below T_c clearly show the progress of a crystallographic phase transition (cf. Figure 2). In the spin-transition region, individual peak profiles corresponding to the two spin phases, high-spin $^5T_2$ and low-spin $^1A_1$, may be clearly distinguished. It should be noted that, in the low-temperature region where the $^1A_1$ phase is predominant, e.g. at 243 K, X-ray diffraction shows the indication of a separate pattern characteristic of the residual paramagnetic fraction. The particular peaks have been marked, in Figure 2, by arrows.

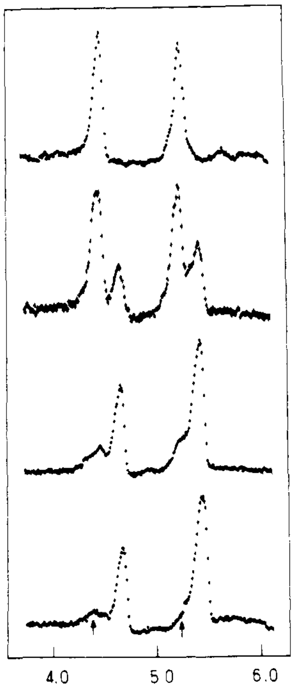

Figure 2. X-ray powder diffraction peak profiles for $[Fe(phy)_2](ClO_4)_2$ at the temperatures of 243, 250, 255, and 270 K. The measurements have been performed for increasing temperatures with angular steps of 0.02° for 2θ. Arrows mark the residual paramagnetic fraction.

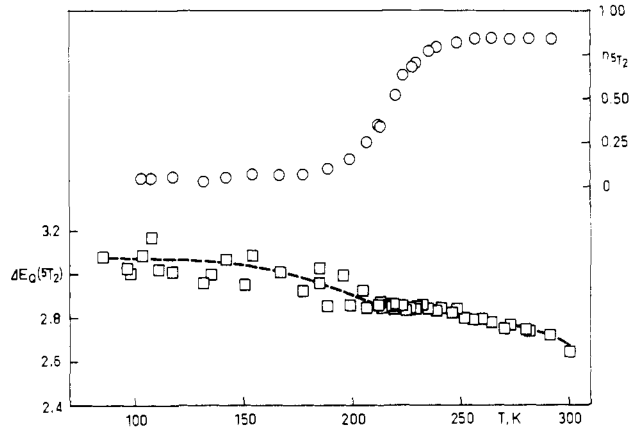

Figure 3. High-spin fraction $n_{^5T_2}$ (○) and quadrupole splitting of the high-spin isomer $\Delta E_Q(^5T_2)$ (□) for $[Fe(bts)_2(NCS)_2]$ as a function of temperature.

$[Fe(bts)_2(NCS)_2]$. For this compound, which is known to undergo a continuous type of high-spin ($^5T_2$) $\rightleftharpoons$ low-spin ($^1A_1$) transition,[10] about 50 Mössbauer spectra have been recorded over two separate temperature sequences. The values of $\Delta E_Q(^5T_2)$ and $n_{^5T_2}$ as derived from the analysis of the spectra are displayed in Figure 3, as a function of temperature. Again, a clear discontinuity in the values of $\Delta E_Q(^5T_2)$ may be recognized at about 210 K, i.e. where the transition begins or is complete as the temperature is raised or decreased, respectively. Similar to the result for $[Fe(phy)_2](ClO_4)_2$, it follows that the temperature function of $\Delta E_Q(^5T_2)$ for the residual paramagnetic fraction is different from that for the bulk of the high-spin constituent above T_c. The transition is incomplete at both temperature ends, $n_{^5T_2} = 0.04$ at the lowest temperature, whereas $n_{^5T_2} = 0.85$ at the highest temperature

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[14] Irler, W.; Ritter, G.; König, E.; Goodwin, H. A.; Nelson, S. M. *Solid State Commun.* **1979**, *29*, 39.

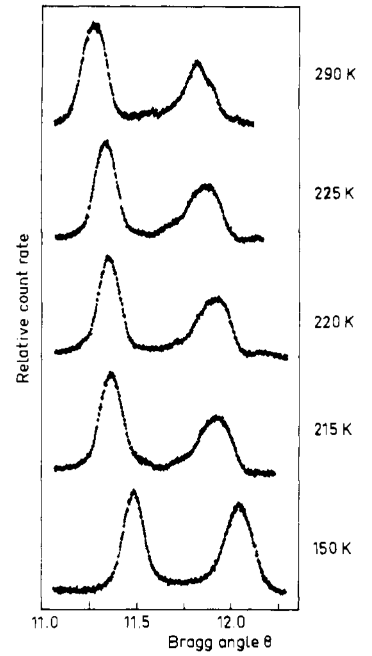

Figure 4. X-ray powder diffraction peak profiles for $[Fe(bts)_2(NCS)_2]$ at the temperatures of 150, 215, 220, 225, and 290 K. The measurements have been performed with angular steps of 0.005° for 2*θ*.

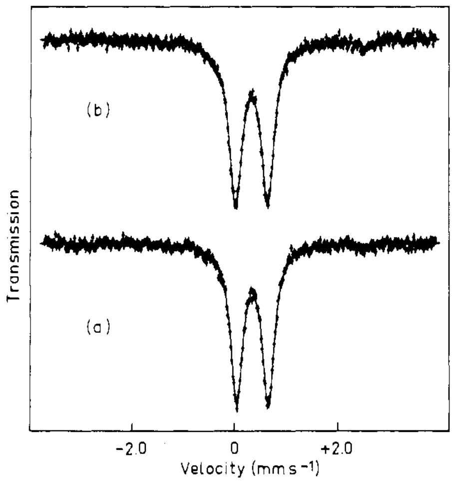

Figure 5. ^{57}Fe Mössbauer-effect spectra for $[Fe(bts)_2(NCS)_2]$ at 78 K for a virgin sample (a) and for the ground substance (b).

studied. No anomalies have been detected in the temperature dependence of the quantities $\delta^{IS}(^5T_2)$, $\Delta E_Q(^1A_1)$, and $\delta^{IS}(^1A_1)$.

X-ray powder diffraction peak profiles of $[Fe(bts)_2(NCS)_2]$, which have been studied between 90 and 300 K, showed only a continous shift of their positions throughout the spin-transition region. This result may be clearly visualized, for a selected region of the diffraction angle, from Figure 4. It is evident that no new peaks are observed, in contrast to the results reported above for $[Fe(phy)_2](ClO)_4)_2$.

Grinding Experiments. ^{57}Fe Mössbauer spectra of $[Fe(bts)_2(NCS)_2]$ have been recorded at 78 and 300 K before and after grinding of the sample with sintered MgO powder, the results for 78 K being displayed in Figure 5. No change in the values of the residual paramagnetic (or diamagnetic) fraction is detected as a result of the grinding process. Contrary to this finding, grinding of a crystalline sample of $[Fe(4,7\text{-}(CH_3)_2phen)_2(NCS)_2]$·α-pic under similar conditions produced significant changes in the observed Mössbauer spectra (cf. Figure 6). Thus, for the ground sample, both the residual paramagnetic and diamagnetic fractions showed a significant increase at the extreme temperatures of the measurement.[12] At the same time, the sharpness of the spin transition was considerably diminished. The residual paramagnetic fraction for the ground samples did not change down to 4.2 K.

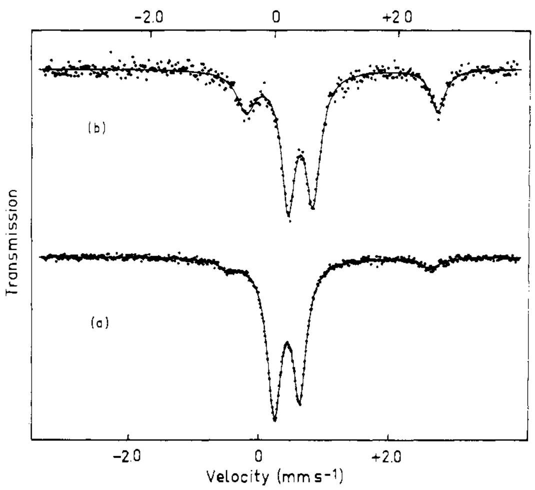

Figure 6. ^{57}Fe Mössbauer-effect spectra for $[Fe(4,7\text{-}(CH_3)_2phen)_2(NCS)_2]$·α-pic at 90 K for a virgin sample (a) and for the ground sample from the same preparation (b). The velocity scales for the two spectra, which are different, have been marked on the top and bottom of the diagram.

Discussion

From the results described in the previous section, it is evident that for both the compounds, $[Fe(phy)_2](ClO_4)_2$ and $[Fe(bts)_2(NCS)_2]$, there is a discontinuity in the values of $\Delta E_Q(^5T_2)$ for the residual paramagnetic fraction, despite the basic difference in the nature of the spin transition for these two complexes. Similar results are apparent for various other complexes of iron(II),[6,15-17] although the necessary detailed investigations have not been performed at this time. In the following, we provide a consistent interpretation of the above and of numerous other results on spin-transition compounds for which a residual paramagnetic fraction has been observed.

Discontinuous High-Spin $\rightleftharpoons$ Low-Spin Transitions. For discontinuous type high-spin $(^5T_2) \rightleftharpoons$ low-spin $(^1A_1)$ transitions, the existence and magnitude of the residual paramagnetic fraction have been revealed by X-ray powder diffraction studies. Results are available for $[Fe(phy)_2](ClO_4)_2$ as well as for $[Fe(4,7\text{-}(CH_3)_2phen)_2(NCS)_2]$[18] and its α-picoline solvate.[12] The important fact is that a separate powder pattern is observed for the residual paramagnetic fraction in all these systems. This result implies that the corresponding molecules are not localized on the surface of the crystallites as has been previously suggested, nor can these molecules be those within the bulk matrix of the low-spin phase that are associated with defects in their immediate vicinity. Moreover, it has been found that the amount of the residual paramagnetic fraction is increased by grinding of the sample.[11,12] These observations suggest that the corresponding molecules form crystallites having a size that is sufficiently large, *i.e.* ~1000 Å, to give their own X-ray diffraction pattern. On the other hand, the size of these crystallites must be too small to undergo a crystallographic phase transition, and they also do not participate in the associated spin transition. The reason for this behavior seems to be the enhanced surface energy of the small

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(17) König, E.; Schnakig, R.; Ritter, G.; Irler, W.; Kanellakopulos, B.; Powietzka, W. *Inorg. Chim. Acta* **1979**, *35*, 239.
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crystallites. Evidently, the discontinuous type of spin transition takes place by a cooperative mechanism that encompasses the whole of the crystallite, whereas, if the crystallite is below a certain critical size, the phase transition is inhibited. If this interpretation is correct, the high-spin ($^5T_2$) $\rightleftharpoons$ low-spin ($^1A_1$) transition in the compound being considered must be triggered by the crystallographic phase transition. It should be mentioned that, on the basis of the thermodynamic investigation of the spin transition in [Fe(phen)$_2$X$_2$], X = NCS, NCSe, Sorai and Seki[19] arrived at a similar cooperative mechanism. These authors estimated that domains of the solid incorporating less than 70 molecules may not participate in the spin transition. This estimate compares favorably with the estimated domain size for the residual paramagnetic phase as based on the results of the present study. Obviously, the temperature dependence of $\Delta E_Q(^5T_2)$ will be different for the small crystallites, as observed above, because of the enhanced surface effects. A similar explanation will apply for the residual diamagnetic fraction which is also associated with small crystallites and which may be encountered at the high-temperature limit of the measurements.

It should be noted that for one of the samples of [^{57}Fe(phy)$_2$](ClO$_4$)$_2$, which showed a significant paramagnetic fraction associated with a quasi-continuous behavior of the spin transition and pronounced hysteresis effects, it was possible to obtain a sharp and complete spin transition after recrystallization of the sample.[13] Obviously, the small crystallites responsible for the initial behavior have been lost in the recrystallization process. A distribution of crystallite sizes, as will be found in such samples, results in a distribution of the transition temperatures T_c, and this fact is responsible for the observation that for the ground samples the appearance of the overall transition is not sharp.[9,11,12]

Continuous High-Spin $\rightleftharpoons$ Low-Spin Transitions. For the continuous type high-spin ($^5T_2$) $\rightleftharpoons$ low-spin ($^1A_1$) transitions, no crystallographic phase change is associated with the spin transition.[10,20] However, there is a change in the volume of the unit cell which arises as a consequence of the variation of Fe–N bond distances and the changes in geometry which are associated with the spin transition.[21-23] It has been proposed that the two spin isomers of the molecule are present as a solid solution within the same lattice. In view of the results from X-ray powder diffraction studies on a number of complexes that show a continuous type spin transition,[10,20,24] the situation here is quite unlike that for the discontinuous transitions. Since no separate diffraction pattern is found, the small crystallites are not responsible for the residual paramagnetic fraction. This conclusion is obvious from the data for [Fe(bts)$_2$(NCS)$_2$] represented in Figure 4. For the two complexes [Fe(4-CH$_3$paptH)$_2$X$_2$]·2H$_2$O, where X = ClO$_4$, BF$_4$,[20] the residual paramagnetic fraction is about 0.20 and, even for this high contribution, a separate X-ray diffraction pattern for these molecules has not been obtained. Rather, the diffraction pattern remains unchanged over the temperature region 100–300 K, where the spin transition is taking place, only a slight shift in the peak positions being apparent. No line broadening has been observed. It is evident that a crystallographic phase change is not involved. For [Fe(bts)$_2$(NCS)$_2$], it has been demonstrated above on the basis of Mössbauer-effect studies that even the small crystallites that are produced by grinding of the sample are participating in the spin transition; indeed, no separate diffraction pattern for these is found. On the basis of these facts it is suggested that, for the continuous type of spin transitions, the residual paramagnetic molecules are trapped within the lattice of the low-spin $^1A_1$ isomer at some kind of defects. Due to the difference in size, these molecules are under compression, and this results in a change of the value of quadrupole splitting, $\Delta E_Q(^5T_2)$, for the residual paramagnetic fraction, in agreement with the observations.

Another finding associated with the residual paramagnetic fraction is the excessive line width in the Mössbauer spectra.[6,10,12] In view of the above discussion there will be a distribution of quadrupole splittings due to the nonhomogeneous environment of these molecules. Obviously, this will lead to an increase of line width. It should be noted that the residual paramagnetic molecules will retain their identity even at temperatures high above T_c. However, it will not be possible to detect the consequent changes in the $\Delta E_q(^5T_2)$ values, because of the small concentration of these molecules as compared to the majority of the high-spin isomer.

The results collected on the isomorphous mixed-crystal series of compounds[9] [Fe$_x$M$_{1-x}$(phen)$_2$(NCS)$_2$], which exhibit significant residual paramagnetic and diamagnetic fractions, are consistent with the present interpretation. For the mixed systems, it is reasonable to assume that a crystallographic phase change is not involved. This is particularly so since, for some of the mixed crystals, the concentration of the two spin isomers is comparable, whereas the structure has been reported[9] to be isomorphous with those pure systems that are completely in the high-spin state. The conclusion is further supported by the results of a DTA study[9] as well as by EPR measurements[7] on Mn^{2+}-doped [Fe(phen)$_2$(NCS)$_2$]. It may be assumed that, in these systems, the dopant ions will act as the defect centers.

The above explanation for the residual paramagnetic fraction is most likely not applicable to those systems where only a small fraction of the molecules is involved in a continuous high-spin ($^5T_2$) $\rightleftharpoons$ low-spin ($^1A_1$) transition, whereas the larger part of the molecules remains in the high-spin $^5T_2$ state as the temperature is lowered. Examples for this sort of behavior are provided, for example, by the CHCl$_3$ and C$_6$H$_6$ solvates of [Fe(papt)$_2$], where papt is the monoanion of 2-(2-pyridylamino)-4-(2-pyridyl)thiazole.[25] Additional examples of spin transition compounds with a highly incomplete transition are indicated by the magnetic data published in the literature.

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