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Spin Crossover

Mixed Spin-State [HS-LS] Pairs in a Dinuclear Spin-Transition Complex: Confirmation by Variable-Temperature ^{57}Fe Mössbauer Spectroscopy**

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Dedicated to Professor Dieter Fenske on the occasion of his 65th birthday

The dinuclear complex $[Fe^{II}_2(pmat)_2](BF_4)_4{\cdot}DMF$ (**1**), where pmat is 4-amino-3,5-bis{[(2-pyridylmethyl)amino]methyl}-4*H*-1,2,4-triazole, exhibiting thermal spin transition (ST) was reported in 2005.[1,2] At about 225 K the complex undergoes a half-ST from the high-spin (HS) state $^5T_2$ to a spin state containing 50 % HS and 50 % low-spin (LS) $^1A_1$ species (Figures 1 and 2). Single-crystal structural analysis at 123 K identified that the dinuclear complex contains one iron(II) ion in the LS state and one in the HS state; the latter has M−N bond lengths some 10 % longer and a wider spread of *cis*-N-Fe−N bond angles than the LS state. Comparison with the structure determined at 298 K showed that on warming above the spin-crossover (SCO) temperature the unit-cell volume halved and a center of inversion was introduced between the iron(II) centers.[1] The sharp decrease of the magnetic susceptibility below 30 K is due to zero-field splitting.

^{57}Fe Mössbauer spectroscopy can be used to determine the oxidation and spin states of iron atoms in complexes and is also sensitive to structural changes in the coordination sphere.[3] It has become a key tool to investigate SCO complexes of iron(II) and iron(III).[4] In the case of dinuclear SCO complexes the question of the mechanism of ST arises: whether the transition occurs directly from [HS-HS] pairs to [LS-LS] pairs or via intermediate [HS-LS] pairs. Until now, standard Mössbauer spectra have not been able to distinguish between the two possibilities, as the spectrum of HS iron(II) in a [HS-HS] pair usually does not differ from that of HS iron(II) in a [HS-LS] pair. Rather, the usual method of distinguishing between these is Mössbauer spectroscopy in an

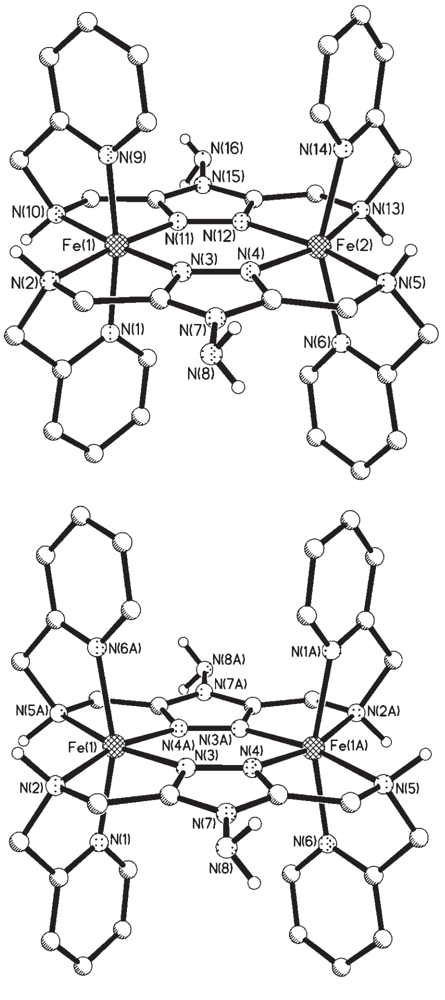

Figure 1. Structure determinations of **1**. Only [HS-LS] pairs exist at 123 K (top), whereas at 298 K (bottom) **1** is a centrosymmetric [HS-HS] dimer.[1]

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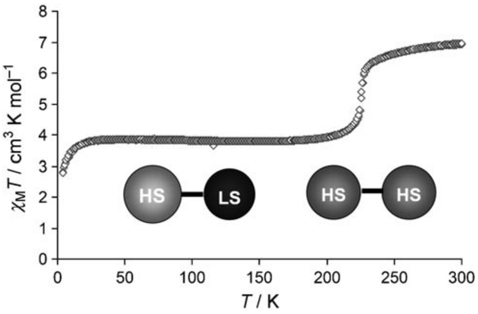

Figure 2. Magnetic properties of **1** versus *T*: only half of the iron(II) ions undergo thermal SCO from HS to LS.

applied magnetic field.[5,6] In dramatic contrast, in our study on **1** we now show, for the first time, that the spin states of the iron centers in a dinuclear complex can sometimes be identified by standard temperature-dependent Mössbauer spectroscopy without applying a magnetic field.

^{57}Fe Mössbauer spectra of dinuclear SCO complex **1** were recorded as a function of temperature between 298 and 4.2 K (see Figure 3 and the Supporting Information). At 298 K there is only one quadrupole doublet with isomer shift $\delta = 0.96\ \mathrm{mm\,s^{-1}}$ (relative to α-iron) and quadrupole splitting $\Delta E_Q = 2.34\ \mathrm{mm\,s^{-1}}$. These values are characteristic of iron(II) in the HS state and show the presence of only [HS-HS] pairs. The slight asymmetry of the intensity is due to texture (anisotropic mean-square vibrational amplitudes), as demonstrated by carrying out all further measurements with the sample mounted at the magic angle of 54° with respect to the γ-radiation source.

As the temperature is decreased to 240 K, two new doublets (blue and red, Figure 3) appear at the expense of the original HS doublet (pink). The signal shown in blue, with $\delta = 0.36\ \mathrm{mm\,s^{-1}}$, $\Delta E_Q = 0.26\ \mathrm{mm\,s^{-1}}$, and area fraction $A = 10.3\,\%$, arises from LS iron(II) in a [HS-LS] pair, formed as a result of thermal HS-to-LS transition at this site. The signal shown in red, a quadrupole doublet with $\delta = 0.96\ \mathrm{mm\,s^{-1}}$, $\Delta E_Q = 1.66\ \mathrm{mm\,s^{-1}}$, and area fraction $A = 10.3\,\%$, is unambiguously due to HS iron(II) in [HS-LS] pairs. The original HS iron(II) doublet, shown in pink, arising from the [HS-HS] pairs now has an area fraction of 79.6%, an isomer shift of $\delta = 0.92\ \mathrm{mm\,s^{-1}}$, and a slightly larger ΔE_Q of $2.65\ \mathrm{mm\,s^{-1}}$ (due to the increased population of low-lying d orbitals increasing the valence-electron contribution to the electric field gradient). With further lowering of the temperature the original HS doublet (pink) arising from [HS-HS] pairs continues to lose intensity in favor of the new doublets (red and blue) with equal area fractions arising from LS iron(II) and HS iron(II) in the [HS-LS] pairs. In the plateau region, at 180 K and below, half-ST is complete, the original HS doublet (pink) has vanished, and the remaining signals are those due to HS (red) and LS (blue) iron(II) in the [HS-LS] pairs, with intensity ratio 1:1.

Clearly, one of the two HS iron(II) lattice sites in the [HS-HS] pair undergoes thermal SCO to generate a [HS-LS] pair. The unique feature is the concomitant appearance of the new HS quadrupole doublet with a smaller ΔE_Q than the original HS doublet.[7] This is clearly due to local distortion at the HS lattice site induced by the newly formed LS state, communicated through the bridging ligand. The molecular distortion at the iron center presumably increases the original lattice contribution to the electric field gradient at the ^{57}Fe nucleus, which in turn, by virtue of the opposite sign to the valence-electron contribution, causes a reduction in ΔE_Q of the new HS quadrupole doublet. This is the first time that such an observation has been made for a dinuclear SCO complex. A similar phenomenon has, however, been observed in a

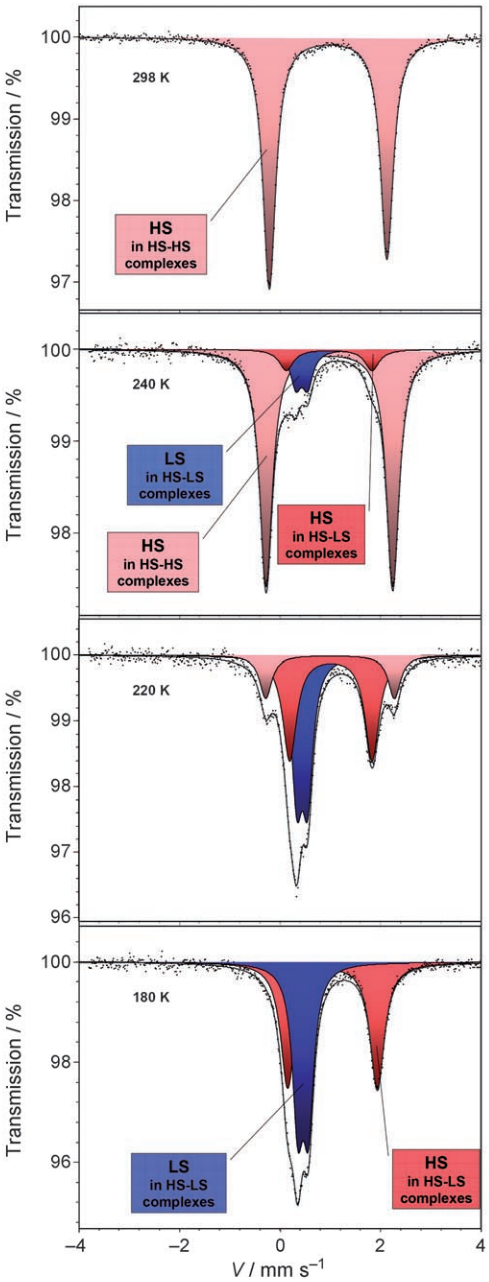

Figure 3. ^{57}Fe Mössbauer spectra of **1** at selected temperatures. SCO from $S = 2$ (HS) to $S = 0$ (LS) occurs at one iron(II) site of the dinuclear complex at about 225 K. The second iron(II) site remains in the HS state, but the spin-state transition of the neighboring atom to LS is communicated by local distortions through the two highly constrained bridging ligands giving rise to a new quadrupole doublet, for HS in [HS-LS], in the Mössbauer spectrum. The intensity ratio of the resonance signals of HS in [HS-LS] to that of LS in [HS-LS] is close to 1:1 at all temperatures.

trinuclear SCO complex, in which the central iron(II) ion undergoes thermal ST, but the two peripheral iron(II) ions, each capped by three water molecules, remain in the HS state at all temperatures.[8] These centers, however, "feel" the thermal ST at the central iron(II) site through local distortions, which is reflected by the appearance of a new HS doublet with an area fraction comparable to that of the newly appearing LS state. In contrast, the observations made herein are due to the use of the carefully designed bis-terdentate, highly constrained bridging ligand pmat, two of which supply all of the donors to the two iron(II) centers.[1,2] Zein and Borshch, in a theoretical thermodynamic study of dinuclear complexes, predicted that the formation of [HS-LS] intermediates is favored by bridging ligands that facilitate M···M communication, giving rise to stepwise ST from [HS-HS] via [HS-LS] to [LS-LS].[9]

Figure 4 shows the isomer shifts and quadrupole splitting values of the three signals—HS in [HS-HS] pairs, HS in [HS-LS] pairs, and LS in [HS-LS] pairs—as a function of temperature. The δ values for both HS species—HS in [HS-HS] pairs and HS in [HS-LS] pairs–-are practically identical, and this implies no noticeable change in electron density at the HS ^{57}Fe nucleus due to the ST at the neighboring iron site. The slight increase of the δ values with decreasing temperature is due to the second-order Doppler effect (in this case with a value of $(\mathrm{d}\delta/\mathrm{d}T) \approx 5\times10^{-4}\,\mathrm{mm\,s^{-1}\,K^{-1}}$). The ΔE_Q of the LS doublet is temperature independent, which is typical for LS iron(II) species with no valence-electron contribution and only little (temperature-independent) lattice contribution to the field gradient. As explained above, the ΔE_Q values of the two HS species increase with decreasing temperature.

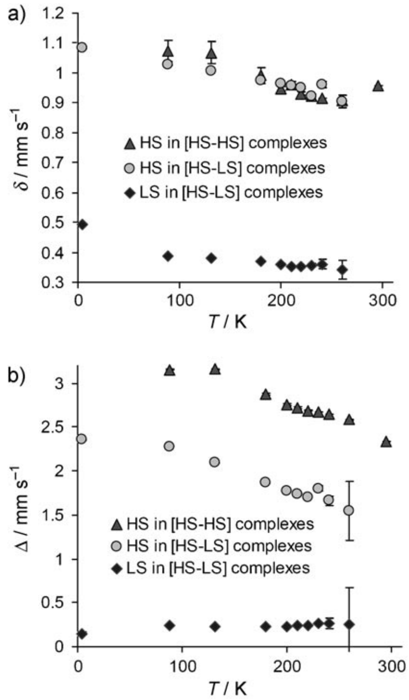

Figure 4. Isomer shift δ relative to α-iron (a) and quadrupole splitting ΔE_Q obtained from fitting the measured spectra (b) as a function of temperature for the three dinuclear species—HS in [HS-HS], HS in [HS-LS], and LS in [HS-LS]—involved in thermal ST in **1**.

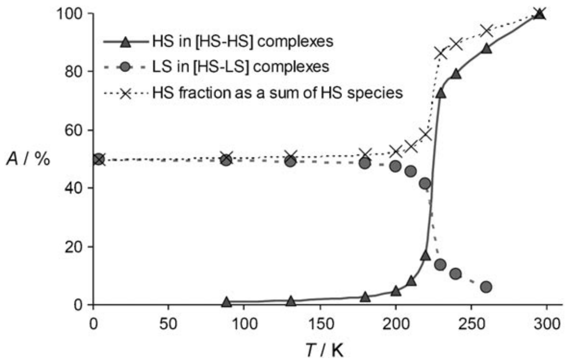

Figure 5. Area fractions A [%] as a function of temperature for the three Mössbauer resonance signals, HS in [HS-HS] and LS in [HS-LS], involved in thermal ST in **1**. The area fraction of HS in [HS-LS] is equal to the LS fraction.

The area fractions of the three signals are plotted as a function of temperature in Figure 5. The curve for HS iron(II) in [HS-HS] pairs shows a very sharp decrease near 225 K, consistent with the ST temperature determined from magnetic susceptibility measurements (Figure 2). In the same temperature range the area fractions of both HS iron(II) and LS iron(II) in [HS-LS] pairs increase sharply and reach a plateau at 50%.

The present Mössbauer study confirms the conclusion from single-crystal X-ray crystallography[1] that thermal ST in dinuclear complex **1** occurs from [HS-HS] pairs to [HS-LS] pairs rather than to a mixture of [HS-HS] and [LS-LS] pairs. In addition, it elegantly demonstrates the role of highly constrained bridging ligands in communicating the change in spin state at one iron(II) center to the neighboring iron(II) ion, because the newly created neighboring LS state causes distortions in the coordination sphere of the second iron(II) center.

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