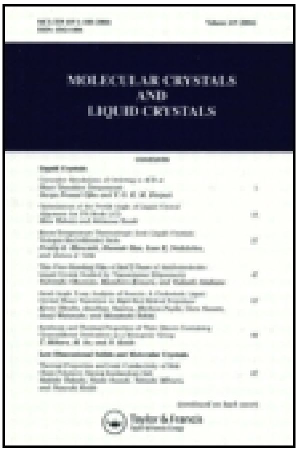

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Spin Transitions in Octahedral Iron(II) Compounds with Heterocyclic Ligands

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Spin Transitions in Octahedral Iron(II) Compounds with Heterocyclic Ligands

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Spin transitions (ST) in transition-metal complexes are a well-known phenomenon in coordination chemistry. Most studied are the systems with a d^6 electron configuration, where the transition goes between essentially diamagnetic and paramagnetic states. In many cases the transition temperature is different when heating or when cooling the sample, and the resulting hysteresis can be applied for storage. So, the colour change would allow possible applications such as in storage devices. Our approach has been the development of systems with Fe(II) and heterocyclic ligands, such as the triazoles and tetrazoles. An overview of recent results is given below, with a focus upon structures and changes in the physical properties. Most structures have the general formula $FeL_6(anion)_2$, with L is a monodentate, or half of a didentate ligand. A special case deals with the compound $Fe(btr)_2(NCS)_2(H_2O)$, the first compound with a trans geometry for the NCS ligands that shows a spin transition. The role of the water molecule in the lattice is crucial, as no ST is observed when water is absent or removed in vacuo.

Keywords: iron; coordination; spin transition; Mössbauer; magnetism;

INTRODUCTION

Most studies on Spin transitions (ST) in transition-metal complexes are dealing with systems having a d^6 electron configuration, where the transition goes between essentially diamagnetic and paramagnetic states with 4 unpaired electrons. The transition can be followed by several methods, such as by IR spectroscopy, colour change, magnetic susceptibility, Mössbauer spectra, specific heat, and even by muon spectroscopy[1].

In many cases the transition temperature is different when heating or when cooling the sample, and the resulting hysteresis can be applied for storage. So, the colour change would allow possible applications such as in storage devices.

A potential challenge of great importance is to design and synthesize systems that have a transition near room temperature and at the same time sufficient hysteresis width. Other interesting developments deal with optical induction of spin transitions, such as in the Liesst effect[1a].

Our approach has been the development of systems with Fe(II) and heterocyclic ligands, such as the triazoles and tetrazoles. In this paper a brief overview of recent results, many of which not yet published, will be given, with a focus upon structures and changes in the physical properties. Most structures have the general formula $FeL_6(anion)_2$, with L is a monodentate, or half of a didentate ligand[2-4].

A special case deals with the compound $Fe(btr)_2(NCS)_2(H_2O)$, the first compound with a trans geometry for the NCS ligands that shows a spin transition[5]. The role of the water molecule in the lattice is crucial (as no ST is observed when water is absent). Detailed studies on deuterated derivatives of the ligand and the water have revealed interesting and quantitative details on the ST process[6].

EXPERIMENTAL SECTION

The compounds described below have been synthesized as reported in our recent papers[2-5], generally starting from the hydrated metal salts and the ligand in the proper ratio. C,H,N determinations were performed on a Perkin Elmer 2400 Series II analyzer. UV-Vis-NIR spectra were obtained on a Perkin-Elmer Lambda-900 spectrophotometer using the diffuse reflectance technique, with MgO as a reference. Low-temperature UV-Vis was measured using a copper sample holder, cooled with liquid nitrogen to approximately 100 K. Magnetic susceptibilities were measured on a Quantum design MPMS-5S squid magnetometer from 5 and 300 K, and fields between 0.1 and 0.5 T. Mössbauer spectra were obtained on a constant-acceleration spectrometer with a source of ^{57}Co in a rhodium matrix. Calibration was performed with a metallic iron foil at room temperature. For LIESST effect experiments, a Y-shaped optical fiber was used as the SQUID sample holder, together with a Xe arc lamp and a blue-green filter (300-600 nm). Several measurements were performed at CNRS in Versailles.

RESULTS AND DISCUSSION

A typical phenomenon connected with a spin transition is the colour change from pale yellow or colorless to purple or pink. However, often the colour change is not a sufficient criterion, as it would also be seen in a partial transition. The diffuse reflectance spectrum shown below in Figure 1 may illustrate this.

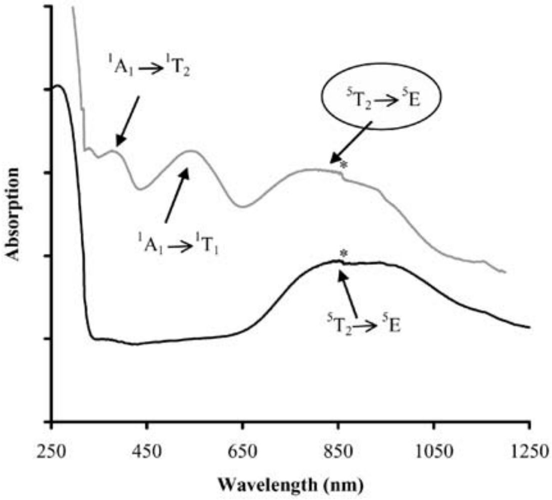


FIGURE 1 Diffuse reflectance spectra of $[Fe(mtz)_6](CF_3SO_3)_2$ at liquid nitrogen and room temperature, showing the partial change (encircled) to low spin at low T. (mtz = 1-methyltetrazole; * refers to a mirror switch in the used equipment).

At room temperature the $^5T_2 \rightarrow {}^5E$ transition is visible at 11,740 cm^{-1}. At low temperatures this signal becomes less intensive and shifts to 12,470 cm^{-1}. Two new transitions become visible, namely the $^1A_1 \rightarrow {}^1T_1$ transition at 18,510 cm^{-1} and the $^1A_1 \rightarrow {}^1T_2$ transition at 26,450 cm^{-1}, thus proving the presence of a partial high-spin ($^5T_2$) to low-spin ($^1A_1$) transition.

Most of the compounds studied so far, and exhibiting a spin transition, have the triazole or tetrazole as the azole ligands, with a substituent at the N position. Our studies have been focusing in particular at variations in the alkyl groups, and at variations in the used counter ions. In a number of cases, and in fact unexpected, also extra molecules in the lattice do influence the spin-transition behaviour, as already shown by our first example with the formula $Fe(btr)_2(NCS)_2(H_2O)$, in which the water molecule places a crucial role. In our recent studies with selective deuteration of ligands and water, we have found that the ST behaviour remains the same, but both temperatures go down with increasing deuteration as seen in Figure 2.

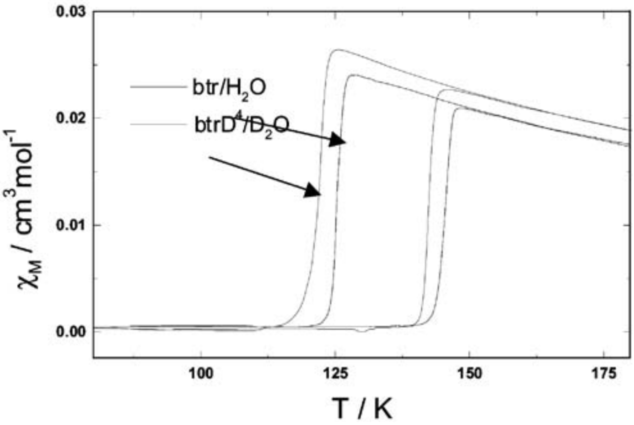
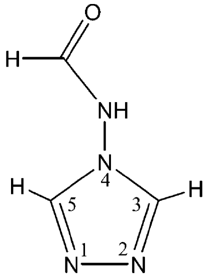


FIGURE 2 Change in spin-transition temperatures upon complete ligand and water deuteration in $Fe(btr)_2(NCS)_2(H_2O)$.

In a search towards compounds having the spin transition as close as possible to room temperature we have recently synthesized new compounds with the ligand **fatrz**, which is 4-formylamino-1,2,4-triazole, and which is a bridging ligand (i.e. threefold) between the Fe(II) ions, thereby yielding the general formula $[Fe(fatrz)_3](A)_2(H_2O)_x$, which x = 0-3 and a variation of non-coordinating anions. Again the amount of water has an effect on the spin-transition behaviour, and even determines whether or not hysteresis occurs[6] in this class of chain compounds.



It is clear that hydrogen bonding of the formyl amino group must play an important role in the behaviour of the Fe(II) compounds, as its interaction with the counter ions will be influenced significantly by such interactions. The general chain structure is given below in Figure 3.

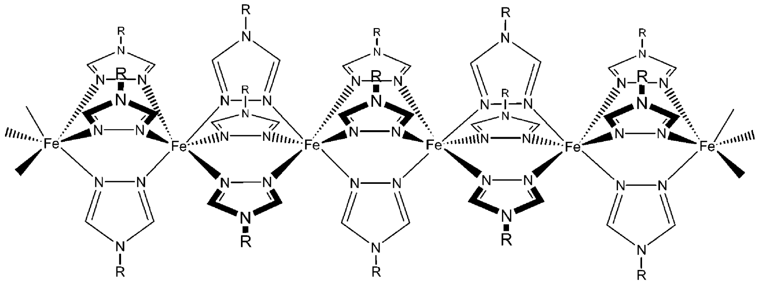


FIGURE 3 Schematic representation of the chain structure in $[Fe(fatrz)_3](A)_2(H_2O)_x$, where anions and water are left out, R = aminoformyl.

In some compounds the spin transition is not complete and occurs only for 50% or for 33% for example. In such cases different lattice sites differ slightly, but significantly, and this results in partial transitions, which are easily detected by magnetic susceptibility, Mössbauer spectroscopy and even by the LIESST effect (LIESST = light-induced excited spin-state trapping). So, for a group of compounds with all having the general formula $[Fe(teec)_6](anion)_2$ in which the anion is large and non coordinating, such as in the case of perchlorate and tetrafluoroborate, and where teec stands for 1-chloroethyltetrazole, the transition occurs in two steps, with and without hysteresis, as easily seen from their magnetic susceptibility as a function of temperature. In fact three different cases were observed, i.e.

(1) A simple two-step process, without hysteresis (seen for the tetrafluoroborate salt);
(2) A two-step process, with hysteresis only in the low-T step range (for the rapidly precipitated perchlorate salt) and without hysteresis. and this is shown in Figure 4 in detail;
(3) A one-step process, where the transition only occurs for 50%, i.e. for one half of the Fe(II) sites (for the crystalline perchlorate product).

The 3-D structure of such a series of compounds has been determined by powder diffraction using synchrotron radiation[7].

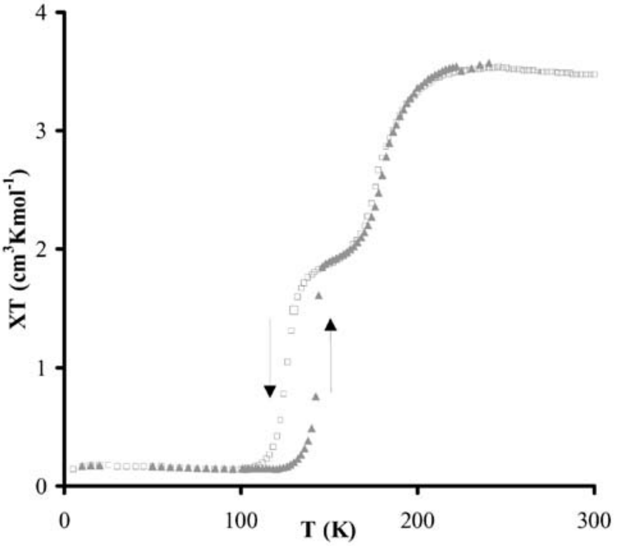


FIGURE 4 Magnetic susceptibility (as χT) as a function of T for the compound $[Fe(teec)_6](ClO_4)_2$. The high-T value corresponds with 100% high-spin Fe(II). Hysteresis is observed only the low-T spin transition.

A next topic to be mentioned in this short overview deals with the LIESST effect for a well-known compound that has only a partial spin transition, i.e. $[Fe(mtz)_6](BF_4)_2$, which contains two different lattice sites, with a slightly different magnetic behaviour, resulting in a spin-transition for only 50%. The thermal trapping process has clearly shown this[3].

The thermal trapping can be reached by freezing in of the high-spin state, by rapid cooling over the range of temperatures where, normally speaking, the HS-LS transition would occur. When this is done for the present compound, indeed one site remains HS, the spin-transition of the other can be quantitatively trapped in HS by the thermal quenching process. Gradual heating from 10 K to higher T still allows the high-spin, but above 50 K the transition to the low-spin state starts to be seen. In Figure 5 the process is shown schematically. Full details, including relaxation studies between 50 and 70 K have allowed to determine an activation energy of 6.02 kJ/mol for this process.

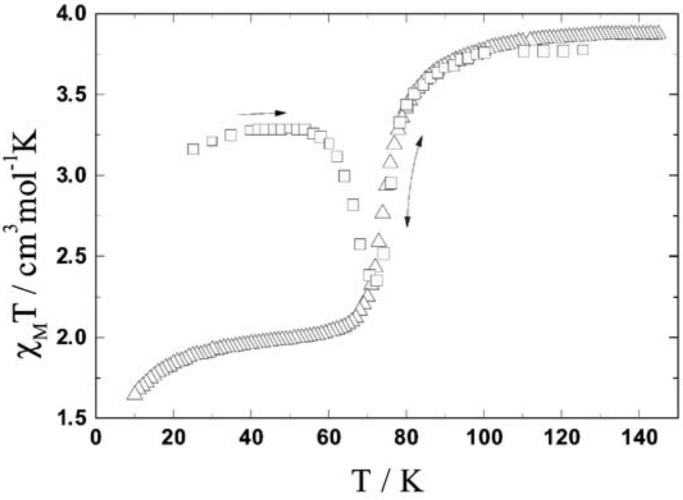


FIGURE 5 The temperature dependence of the χT values for the compound $[Fe(mtz)_6](BF_4)_2$ obtained after rapid field cooling from 120 K to 5 K (squares), and also after slow cooling without thermal trapping (triangles).

Finally, it should be mentioned that a major problem in coupled lattice compounds, such as the above-mentioned $Fe(btr)_2(NCS)_2(H_2O)$, and in our earlier published[8] polymeric species $Fe(abpt)_2(TCNQ)_2$, (abpt = 4-amino-3,5-bis(pyridin-2-yl)-1,2,4-triazole; TCNQ = tetracyanoquinodimethane), deals with the prediction of the shape of the ST curve. The first compound has a rather steep transition, with proper hysteresis; in the last compound, despite the strong coupling through the stacked and bridged ligands and anions (TCNQ pairs), only a single, sharp spin transition is seen.

FUTURE DEVELOPMENTS

In conclusion, it can be stated that the Fe(II) complexes of the azole ligands, and in particular those with triazoles and tetrazoles, have shown to be extremely useful for the development of understanding in the high-spin to low-spin spin transitions and in the nature of the ground and excited states.

So, the future developments in this research area are likely to move in the following directions:

1. Fine tuning of the transition temperature, by changes in ligands, counter ions and lattice molecules.
2. Control of the hysteresis as a function of the counter ion and the ligand details.
3. Studies on (new) spectroscopic techniques to study the ground state and the excited states, and to generate (controlled) spin transitions.
4. The use of chelating ligands and bridging ligands to generate 2D and 3D systems.

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