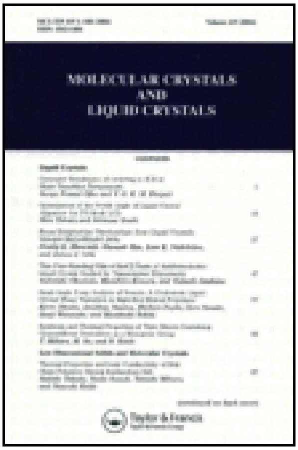

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Spin-Transition in [Fe(II)(2,6-Bis-(Benzimidazol-2′-yl)pyridine)2] $(ClO_4)_2$: Hysteresis Effect Dependent on the Matrix

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Spin-Transition in $[Fe(II)(2,6\text{-Bis-(Benzimidazol-2'-yl)pyridine})_2]$ $(ClO_4)_2$: Hysteresis Effect Dependent on the Matrix

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Far-Infrared spectroscopical investigation of the spin-crossover in $[Fe(II)(2,6\text{-bis-(benzimidazol-2'-yl)-pyridine})_2]$ $(ClO_4)_2$ exhibits a hysteresis in both CsI and polyethylene matrices within temperature cycles between 100K and 520K. The hysteresis broadening is dependent on the matrix and bigger in CsI. This can be explained due to polarity and hydrogen bonding. Two low spin vibrations, LS1 at 437 cm^{-1} and LS2 at 424cm^{-1}, are observed. On heating from 100K to 520K: during LS1 decreases, the LS2 raises temporarily, until both LS1 and LS2 disappear; for the HS only one raising species was observed. This gives raise to assume two different sub-lattices.

Keywords: spin crossover; sub-lattice; polymer; Far IR spectroscopy

INTRODUCTION

A temperature induced spin-state equilibrium between low-spin (LS) and high-spin (HS) states of transition metal complexes with an electronic

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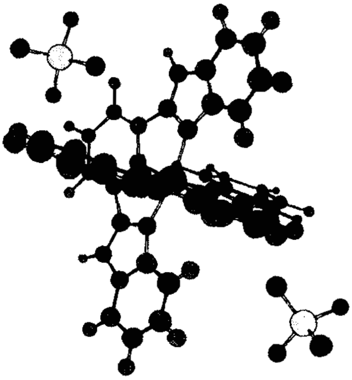
configuration d^4 - d^7 has been observed in many cases.[1-5] Various circumstances affect the spin crossover, e.g. in the solid state these are (i) the nature of the counter ions;[2-6] (ii) various degrees of hydrates/solvates in the crystal;[3-5,7] (iii) intermolecular long range exchange interactions between the magnetic centres[3,8] (iv) stereoisomerism;[3,9-10] (v) the method of preparation which affects acidic centres (such as the imidazole hydrogen sites); (vi) specific intermolecular interactions (e.g. ππ stacking). In solution the situation is complicated by (i) solvolysis;[11-12] (ii) ligand and anion-exchange reactions;[11,13-15] (iii) complex protonation/deprotonation;[11,16] (iv) hydrogen bonding;[15-17] (v) complex dissociation at higher temperature;[11] (vi) increased mobility of magnetic centres (the solute-solute interaction).



SCHEME 1 $[Fe(bzimpy)_2](ClO_4)_2$ (bzimpy = 2,6-bis-(benzimidazol-2′-yl)-pyridine) See Color Plate IV at the back of this issue.

Among these complexes are the $[Fe(4\text{-}X\text{-}bzimpy)_2]^{2+}$, with 4-X-bzimpy = 4-X-2,6-bis-(benzimidazol-2′-yl)-pyridine (X= H, Cl, OH), which exhibit a pronounced spin-crossover behavior in both solution and solid state.[11,13-15] Xray investigations clarified that the iron(II) is coordinated by two tridentate ligands in distorted octahedral symmetry.[11,13]

In the present investigation we found an hysteresis for the compound [Fe(bzimpy)$_2$](ClO$_4$)$_2$, with the ligand bzimpy = 2,6-bis-(benzimidazol-2′-yl)-pyridine (see SCHEME 1), in CsI and polyethylene matrices by means of Far-IR spectroscopy.

EXPERIMENTAL

The ligand bzimpy as well as the complex [Fe(bzimpy)$_2$](ClO$_4$)$_2$ (**1**) were prepared as described in previous papers.[11,14,17]

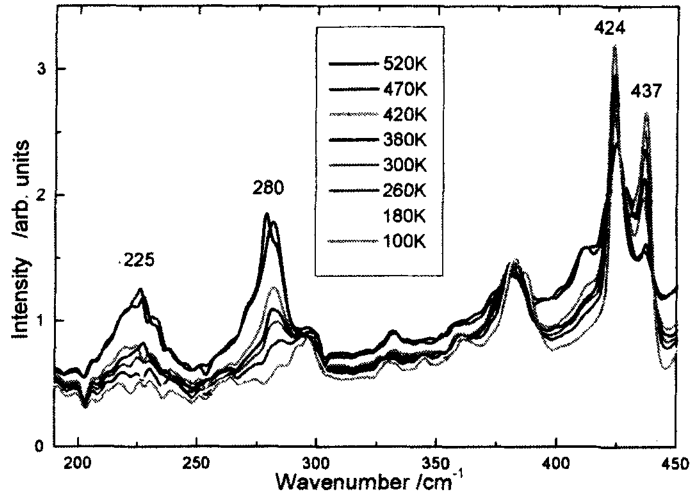


FIGURE 1 Far IR spectra [cm^{-1}] of **1** in CsI matrix at various temperatures [K] (at peak 280 cm^{-1} from top: 520, 470, 420, 380, 300, 260, 180, 100).

See Color Plate V at the back of this issue.

The measurements were performed in polyethylene and CsI matrices, where CsI was used dry and wet (water moisture from air). Due to the known explosiveness of perchlorate compounds the compound **1** was not grinded, just mixed with the matrix powder and pressed to a pellet. TGA and DSC measurements on **1** indicated that the thermal decomposition of **1** starts above 620K. The solid state Far FT-IR spectra of **1** were run on a Perkin Elmer FT-IR 2000 spectrophotometer between 710-50cm^{-1} over a temperature range of 100 to 520K. A resolution of 0.5cm^{-1} using a mirror velocity of 2.0mm s^{-1} was selected. In order to obtain a good resolution 1000 scans per spectrum were necessary. Temperature was controlled by thermocouple (Grasby/Specac) and adjusted via heating coils and liquid nitrogen and kept constant within ±5K.

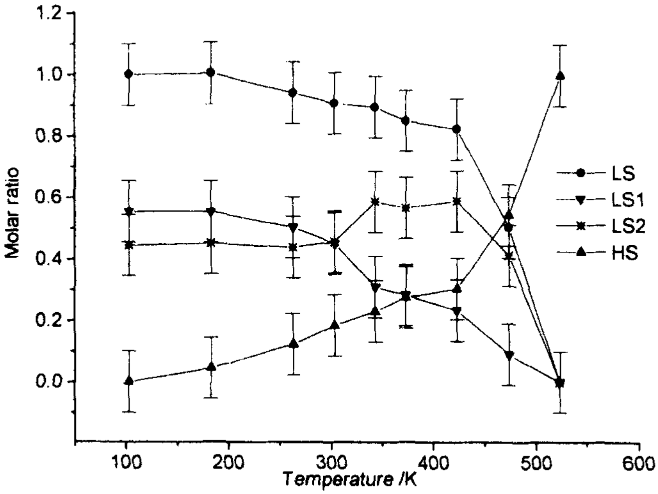


FIGURE 2 Bands from the Far IR spectra [cm^{-1}] of **1** in CsI matrix at various temperatures [K], where HS is the high spin at 270-310 cm^{-1}, LS is the low spin at 415-445 cm^{-1}, LS1 is the low spin at 445-430 cm^{-1}, LS2 is the low spin at 430-415 cm^{-1}. (The intensity was reduced to the amount of HS: x_{HS}.)

Assignment of the spectra

Evaluation of the spectra, given in FIGURE 1, revealed that several vibrations are changed during the spin-transition. The band at 437cm^{-1} (LS1) is attributed to the Fe-N stretching vibration of the LS-species (ν_{LS}).[11] The intensity rises on cooling due to the increasing population of the LS-state. Surprisingly the band at 423cm^{-1} (LS2) appeared to be sensitive for the spin-transition as well. In FIGURE 2 this dependence was plotted against the HS value. There appears to be a connection between LS1 and LS2. While LS1 decreases, LS2 grows, till both disappear. It seems that HS + LS1 + LS2 is constant.

On the other hand the HS grows without any indication for a second band. Accordingly, the Fe-N stretching vibration of the HS-species (ν_{HS}) occurs at 281cm^{-1}.[11] The bands at ~297cm^{-1}, ~386cm^{-1}, and ~382cm^{-1} have been assigned to consist of unresolved vibrations and refer to both LS- and HS-contributions.[11]

DISCUSSION

Thermodynamic parameters for the spin transition were estimated (see TABLE 1). The equilibrium constant is (1) $K_{sc}=x_{HS}/x_{LS}$, where the molar ratio is (2) $x_{HS}+x_{LS}=1$. Then we assume that the peak area A is given by (3) $A=x_{HS}*A_{HS}+x_{LS}*A_{LS}$. Out of (2) and (3) we derive (4) $x_{HS}=(A-A_{LS})/(A_{HS}-A_{LS})$. Then (1) and (4) yield (5) $K_{sc}=(A-A_{LS})/(A_{HS}-A)$. At the equilibrium (6) $\Delta G=\Delta H-T*\Delta S$ leads to (7) $T_c=\Delta H/\Delta S$. Due to the fact that there are many ways of distributing xN HS-molecules and (1-x)N LS-molecules within an assembly of N molecules we have to account for the mixing entropy (8) $S_{mix}=-R[x\ln x+(1-x)\ln(1-x)]$. Now (6), (7), and (8) lead to (9) $x_{HS}=1/(1+\exp[(\Delta H/R)*(1/T-1/T_c)])$. Our data exhibit hysteresis. Usually hysteresis is explained through intermolecular interaction between the molecules. In the past this was described by the regular solution model[18] and the domain model.[19] The domain model assumes that the LS and HS molecules form domains of like spin, hence, they are not randomly distributed. This yields (10) $x_{HS}=1/(1+\exp[(n*\Delta H/R)*(1/T-1/T_c)])$, where n denotes the number of molecules per domain. In the regular solution model[18] the intermolecular interaction parameter (γ) can be estimated as (11) $\gamma>2RT_c$, e.g. in our case bigger then 5.7 kJmole^{-1}. Therefore we estimate n in CsI for heating:cooling as at least 6:3 whereas in the dry CsI it reduces to 4:3, and in PE 4:4.

From FIGURE 2 we learned that there are two interrelated LS present: LS1 and LS2. Therefore our analysis needs to be more elaborated, so that the quality of the evaluated data in TABLE 1 are on the level of an estimation.

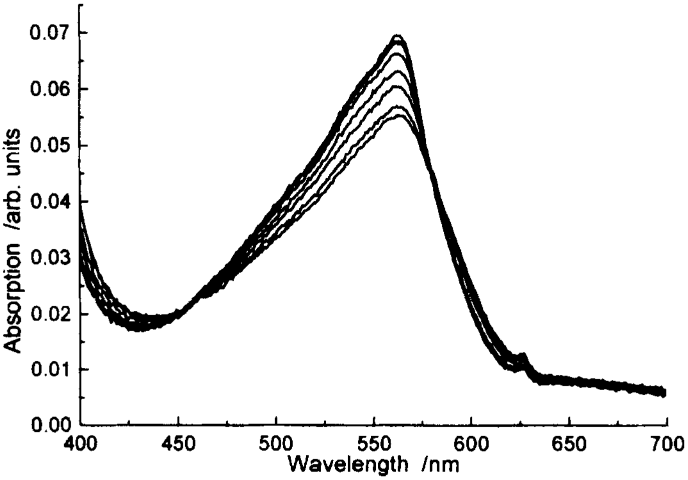


FIGURE 3 UV/VIS spectra of **1** in PVA (Temperatures [K] at 556nm from bottom: 300, 265, 225, 195, 150, 100, 50, 15)

To evaluate the data we need to know whether the spin transition was complete within the interval from 100 to 520K in the Far-IR. Unfortunately our apparatus was at the experimental limit: allowing neither further cooling nor heating. Therefore another method was used: the UV/VIS spectroscopy. FIGURE 3 shows a temperature series of **1** in polyvinylalcohol at various temperatures down to 15K. Among others the charge transfer band at 557nm shows both: LS and HS. The increase in intensity on cooling indicates raising amount of LS, i.e. the LS has the higher extinction. Fortunately, the band is saturated at 100K. Hence, our Far-IR spectrum at 100K shows the LS spectra (x_{HS}=0). For the HS no similar method was found at 520K. The complete conversion to either LS or HS was confirmed with magnetic measurement of the pure compound **1** in solid state, where a gradual transition followed by a sharp one at 403K to the HS was observed.[20]

TABLE 1 Estimated Thermodynamic Parameters for the Spin Transition in [Fe(bzimpy)$_2$](ClO$_4$)$_2$ observed in CsI and PE-matrix from Eq. (10) (with n=1 as lower limit).

Matrix	water-wet matrix		dry matrix	
	ΔH /kJmole^{-1}	ΔS /JK^{-1}mole^{-1}	ΔH /kJmole^{-1}	ΔS /JK^{-1}mole^{-1}
CsI				
Heating	38.4±7.2	90±12	24.6±4.9	61±13
Cooling	18.9±2.8	55±10	17.4±3.1	50±10
PE				
Heating			21.8±3.3	61±10
Cooling			21.1±3.2	63±10

The x_{HS} for compound 1 in CsI and PE have been plotted in FIGURE 4. The broadening of the hysteresis is smallest in PE and follows the series: PE < CsI < wet CsI (moisture from air). Noticing that CsI is a much more polar matrix than PE, we referred the increased broadening in CsI to a coulomb interaction between the polar sides of the molecule and the matrix. A quantum-mechanical study[21] confirmed that the most

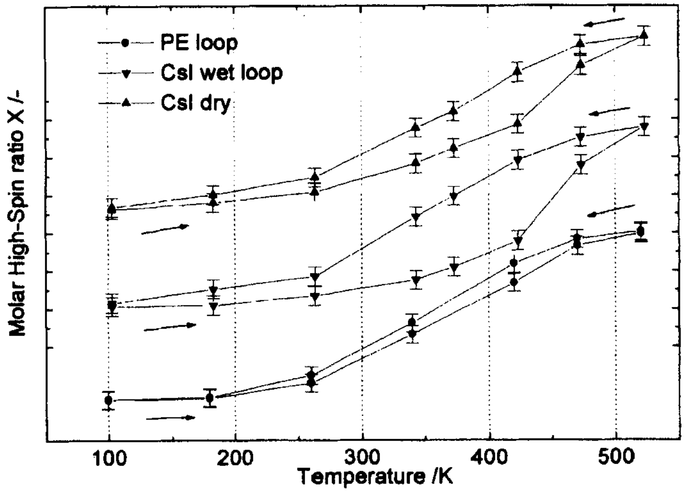


FIGURE 4 HS molar ratio (X) versus temperature (T) curves of the spin transition measured by means of Far-IR spectroscopy of $[Fe(bzimpy)_2](ClO_4)_2$ in CsI and PE matrix. X was evaluated around 430-445cm^{-1} within a temperature cycle range of 100K to 520K (arrow up...heating, arrow down...cooling).

exposed, acidic and polar sides are the imidazole hydrogens of the imidazolering (N-H). Hence, polar solvents are most stable there due to hydrogen bonding. Enhanced broadening in CsI was achieved after absorption of moisture from air. This tentatively confirms our assumption. Furthermore we observed a sensitivity of the acidic imidazole N-H group by means of Mid-IR measurements.[22] Additionally, drying of the complex in vacuum at 500K narrowed the hysteresis loop.

CONCLUSION

It has been shown that mirocrystals of the spin crossover compound **1**, incorporated into a matrix, are affected by the matrix: **1** in CsI behaves different than in PE. Two vibrations have been found to be sensitive for the low spin: LS1 and LS2. While LS1 decreases LS2 increased till both disappear at 520K. On the contrary the HS shows no second band. This indicates two different sublattices. The hysteresis for compound **1** in both CsI and polyethylene matrices within temperature cycles between 100K and 520K may be caused by the two sublattices. The hysteresis broadening is dependent on the matrix and bigger in CsI. This can be explained due to polarity and hydrogen bonding.

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