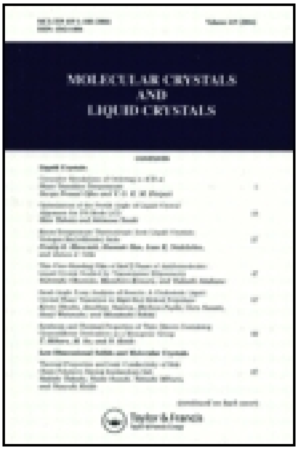

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Cooperativeness of the Spin Crossover Systems

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Cooperativeness of the Spin Crossover Systems

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Spin crossover systems exhibiting the transition temperature below and above the room temperature are investigated. The magnetic susceptibility data are fitted to the two-level Ising-like model from which the thermodynamic parameters and the cooperativity parameter are obtained.

Keywords: spin crossover; cooperativeness; iron(II) complexes

INTRODUCTION

The monodentate and bidentate ligands accommodate the six vertices of the (nearly) octahedral chromophore quite firmly. Therefore the low–spin (LS) to the high–spin (HS) transition, which is accompanied by the metal–ligand bond stretching, is associated with a moderate energy gap $\Delta E = E_{\mathrm{HS}} - E_{\mathrm{LS}}$. The tridentate ligands, like the tris(pyridine), tris(imidazole) and bis(benzimidazole) pyridine, on the contrary, represent much more rigid units which under the spin crossover (SC) increase the energy gap considerably. The (electronic) energy gap predetermines the enthalpy of the spin transition, ΔH, which influences the temperature of the transition $T_c = \Delta H / \Delta S$ (valid for mononuclear, one-step spin crossover systems). Thus the substitution of the bidentate for

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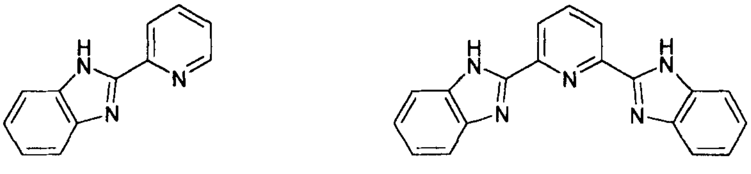
tridentate heterocyclic ligands can systematically raise the temperature of the spin transition towards or even above the room temperature. For this reason the iron(II) complexes of the bidentate benzimidazole-pyridine and the tridentate bis(benzimidazole)pyridine ligands have been prepared, investigated experimentally and theoretically and the results finally compared – see Fig. 1.



L²   **L³**

FIGURE 1 Bidentate and tridentate ligands under the investigation.

EXPERIMENTAL

Experimental details about the preparation of the ligands and complexes can be found elsewhere[1-3]. The abbreviation of the complexes under study are:

1 = $[Fe(L^2)_3](ClO_4)_2.H_2O$, **2** = $[Fe(L^2)_3](BPh_4)_2$,
3 = $[Fe(L^3)_2](ClO_4)_2.0.25H_2O$, **4** = $[Fe(L^3)_2](BPh_4)_2.4H_2O$.

The temperature variation of the magnetic susceptibility has been measured either using an AC susceptometer (LakeShore, 7221) or the Faraday-type balance equipped with low- and high-temperature facilities, respectively.

THEORETICAL MODEL

Following closely the approach outlined elsewhere[4,5], the two-level Ising–like model has been implemented in the theoretical analysis of experimental data. The model is based on the following postulates: a) Ising–like Hamiltonian; b) molecular field approximation; c) existence of two sublattices A and B. For the most complex case (two-step SC) we have the electronic Hamiltonian in the form

$$\hat{H}_A = \Delta_A \hat{\sigma}_A - J_A \langle \sigma_A \rangle \hat{\sigma}_A - J_{AB} \langle \sigma_B \rangle \hat{\sigma}_A$$

$$\hat{H}_B = \Delta_B \hat{\sigma}_B - J_B \langle \sigma_B \rangle \hat{\sigma}_B - J_{AB} \langle \sigma_A \rangle \hat{\sigma}_B$$

Here $\hat{\sigma}_A$ and $\hat{\sigma}_B$ are the formal spin operators with discrete eigenvalues equal to -1 for the low-spin state and $+1$ for the high-spin state, respectively. The continuous variables $\langle \sigma_A \rangle = 2x_A - 1$ and $\langle \sigma_B \rangle = 2x_B - 1$ account for the Boltzmann average within the mean-field approximation and they are interrelated to the mole fraction of the high-spin species, x_{HS}, as follows

$$x_{\mathrm{HS}} = \frac{1}{2}\left(x_A + x_B\right) = \frac{1}{4}\left(2 + \langle \sigma_A \rangle + \langle \sigma_B \rangle\right)$$

The site formation energy is denoted as Δ_A and Δ_B, respectively. The interaction constants describe either the intra-sublattice coupling, J_A and J_B, or the inter-sublattice coupling J_{AB}. With the sign convention in the Hamiltonian term, $J_A \approx J_B > 0$ describe the ferromagnetic coupling whereas $J_{AB} < 0$ accounts for the antiferromagnetic coupling.

The electronic partition function of N distinguishable particles is introduced through

$$Z^{\mathrm{el}} = (z_A^{\mathrm{el}})^{N/2} (z_B^{\mathrm{el}})^{N/2}$$

with the terms

$$z_A^{\mathrm{el}} = g_{\mathrm{HS}} \exp[-\varepsilon_A / kT] + g_{\mathrm{LS}} \exp[+\varepsilon_A / kT]$$

$$z_B^{\mathrm{el}} = g_{\mathrm{HS}} \exp[-\varepsilon_B / kT] + g_{\mathrm{LS}} \exp[+\varepsilon_B / kT]$$

where we used the substitutions for the ‘energy levels’

$$\varepsilon_A = \Delta_A - J_A \langle \sigma_A \rangle - J_{AB} \langle \sigma_B \rangle$$

$$\varepsilon_B = \Delta_B - J_B\langle\sigma_B\rangle - J_{AB}\langle\sigma_A\rangle$$

Then the standard methods of the statistical thermodynamics lead to the expressions for the thermodynamic functions (F, G, H, S, C_p).

The involvement of the molecular vibrations can be done via the vibration partition function

$$z^{\mathrm{vib}}_{A,\mathrm{LS}} = \left[\prod_{i=1}^{3n-6}\frac{1}{1-\exp(h\nu_{A,\mathrm{LS},i}/kT)}\right]\exp\left[-\sum_{i=1}^{3n-6}(h\nu_{A,\mathrm{LS},i}/2kT)\right]\approx$$

$$\approx\left[\frac{1}{1-\exp(h\bar{\nu}_{A,\mathrm{LS}}/kT)}\right]^{3n-6}\exp\left[-\frac{3n-6}{2}\frac{h\bar{\nu}_{A,\mathrm{LS}}}{kT}\right]$$

where we introduced an averaged vibration energy over the number of active modes, $h\bar{\nu}_{A,\mathrm{LS}}$. Analogous expressions hold true for the low–spin site B and the high–spin sites. Then the electron–vibration partition functions become

$$Z_{A,\mathrm{LS}} = (z^{\mathrm{vib}}_{A,\mathrm{LS}})^{N/2}(z^{\mathrm{el}}_{A,\mathrm{LS}})^{N/2} =$$

$$=\left\{\left[\frac{1}{1-\exp(h\bar{\nu}_{A,\mathrm{LS}}/kT)}\right]^{3n-6}\exp\left[-\frac{3n-6}{2}\frac{h\bar{\nu}_{A,\mathrm{LS}}}{kT}\right]\left[g_{\mathrm{LS}}\exp(+\varepsilon_A/kT)\right]\right\}^{N/2}$$

$$Z_{A,\mathrm{HS}} = (z^{\mathrm{vib}}_{A,\mathrm{HS}})^{N/2}(z^{\mathrm{el}}_{A,\mathrm{HS}})^{N/2} =$$

$$=\left\{\left[\frac{1}{1-\exp(h\bar{\nu}_{A,\mathrm{HS}}/kT)}\right]^{3n-6}\exp\left[-\frac{3n-6}{2}\frac{h\bar{\nu}_{A,\mathrm{HS}}}{kT}\right]\left[g_{\mathrm{HS}}\exp(-\varepsilon_A/kT)\right]\right\}^{N/2}$$

Consequently the reaction Gibbs energy for $A_{\mathrm{LS}} \rightarrow A_{\mathrm{HS}}$ adopts the form of

$$\Delta_{\mathrm{r}}G_A = -RT\ln\left\{\begin{matrix}\left[\dfrac{1-\exp(h\bar{\nu}_{A,\mathrm{LS}}/kT)}{1-\exp(h\bar{\nu}_{A,\mathrm{HS}}/kT)}\right]^{3n-6}\dfrac{g_{\mathrm{HS}}}{g_{\mathrm{LS}}}\times\\ \times\exp\left[\dfrac{-2\varepsilon_A-(3n-6)(h\bar{\nu}_{A,\mathrm{HS}}-h\bar{\nu}_{A,\mathrm{LS}})/2}{kT}\right]\end{matrix}\right\}^{1/2} = -RT\ln f_A$$

The equilibrium constant becomes

$$K_A = \frac{x_A}{1-x_A} = \exp(-\Delta_r G_A / RT)$$

Making use the substitution

$$f_A = \left\{ \left[\frac{1-\exp(h\bar{\nu}_{A,\mathrm{LS}} / kT)}{1-\exp(h\bar{\nu}_{A,\mathrm{HS}} / kT)} \right]^{3n-6} r_{\mathrm{eff}} \right\}^{1/2} \times$$

$$\times \exp\{-[\Delta_A - J_A\langle\sigma_A\rangle - J_{AB}\langle\sigma_B\rangle + (3n-6)(h\bar{\nu}_{A,\mathrm{HS}} - h\bar{\nu}_{A,\mathrm{LS}})/4]/kT\}$$

and its *B*-site counterpart

$$f_B = \left\{ \left[\frac{1-\exp(h\bar{\nu}_{B,\mathrm{LS}} / kT)}{1-\exp(h\bar{\nu}_{B,\mathrm{HS}} / kT)} \right]^{3n-6} r_{\mathrm{eff}} \right\}^{1/2} \times$$

$$\times \exp\{-[\Delta_B - J_B\langle\sigma_B\rangle - J_{AB}\langle\sigma_A\rangle + (3n-6)(h\bar{\nu}_{B,\mathrm{HS}} - h\bar{\nu}_{B,\mathrm{LS}})/4]/kT\}$$

then two coupled equations should simultaneously be obeyed

$$\langle\sigma_A\rangle = \left[-1 + f_A(\langle\sigma_A\rangle,\langle\sigma_B\rangle)\right]\left[+1 + f_A(\langle\sigma_A\rangle,\langle\sigma_B\rangle)\right]^{-1}$$

$$\langle\sigma_B\rangle = \left[-1 + f_B(\langle\sigma_A\rangle,\langle\sigma_B\rangle)\right]\left[+1 + f_B(\langle\sigma_A\rangle,\langle\sigma_B\rangle)\right]^{-1}$$

These equations can be solved by an iterative procedure for the given set of the Hamiltonian parameters (Δ_A, Δ_B, J_A, J_B, J_{AB} and r_{eff}) and a fixed temperature point until selfconsistency.

The only difference with respect to the case of the pure electronic contribution is that instead of $r_{\mathrm{eff}} = g_{\mathrm{HS}} / g_{\mathrm{LS}}$ as a free parameter one deals with averaged vibration energies which can be fixed on the basis of vibration spectra. Then, in fact, the inclusion of the vibration partition function can result in a reduced number of free parameters.

In the presence of the paramagnetic impurity the one-step Ising–like spin crossover model is modified to the form

$$K = x_{\mathrm{HS}}\left[1 - x_{\mathrm{HS}} - x_{\mathrm{PI}}\right]^{-1} = r_{\mathrm{eff}} \exp\left\{-\left[\Delta_{\mathrm{eff}} - 2J(2x_{\mathrm{HS}} - 1)\right]/kT\right\}$$

and then the set of free parameters covers $r_{\rm eff}$, $\Delta_{\rm eff}$, and J. The last equation is solved numerically: for a trial set of $r_{\rm eff}$, $\Delta_{\rm eff}$ and J parameters and an initial value of $x_{\rm HS}$ (say $x_{\rm HS} = 0$) the following function

$$f(x_{\rm HS}) = r_{\rm eff}\exp\{-[\Delta_{\rm eff} - 2J(2x_{\rm HS} - 1)]/kT\}$$

is evaluated; this gives a subsequent estimate of $x_{\rm HS}$ as*

$$x_{\rm HS} = (1 - x_{\rm PI})f(1+f)^{-1}$$

and this is cycled until self-consistency is reached. The enthalpy and the entropy of the transitions are respectively

$$\Delta H = N_A\Delta_{\rm eff} = R(\Delta_{\rm eff}/k)$$

$$\Delta S = R\ln r_{\rm eff}$$

DATA FITTING

The molar magnetic susceptibility consists of the low–spin and the high–spin part which in the presence of a paramagnetic impurity should be written as

$$\chi_{\rm mol} = x_{\rm HS}(\chi_{\rm HS} + \alpha_{\rm HS}) + x_{\rm LS}\alpha_{\rm LS} + x_{\rm PI}(\chi_{\rm PI} + \alpha_{\rm PI})$$

with the mole fractions obeying the constraint $x_{\rm PI} + x_{\rm HS} + x_{\rm LS} = 1$. For the data fitting in the presence of the paramagnetic impurity the reader can consult a recent paper [3]. The final equation is

$$\chi_{\rm mol} = x_{\rm hs}\left[2C_0\frac{g_{\rm HS}^2}{T-\Theta_{\rm HS}} + \alpha_{\rm HS}\right] + (1 - x_{\rm PI} - x_{\rm HS})\alpha_{\rm LS} + x_{\rm PI}\left[\frac{35}{12}C_0\frac{g_{\rm PI}^2}{T-\Theta_{\rm PI}}\right]$$

The parameters $x_{\rm PI}$ and $\Theta_{\rm PI}$ can be determined from the low-temperature data.

On summary, the two-level spin crossover model involves the following set of parameters: (i) parameters of the paramagnetism (diamagnetism), i.e. $g_{\rm HS}$, $\Theta_{\rm HS}$, $\alpha_{\rm HS}$, $\alpha_{\rm LS}$ and eventually $x_{\rm PI}g_{\rm PI}^2$ and $\Theta_{\rm PI}$; (ii) parameters of the Ising-like model, i.e. Δ_A, Δ_B, J_A, J_B, J_{AB} and eventually $r_{\rm eff}$.

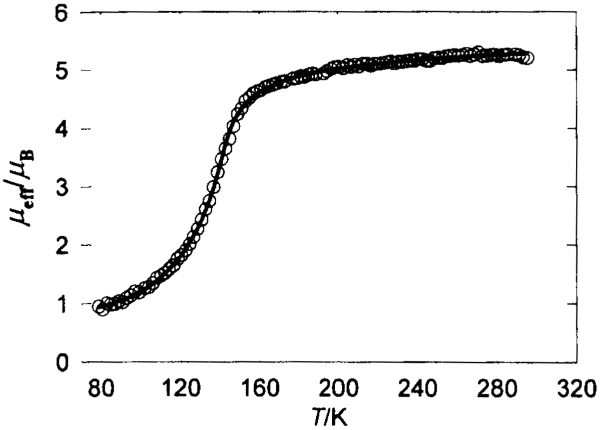


FIGURE 2 Temperature variation of the effective magnetic moment for **1**. Open circles – experimental data, full line – calculated data.

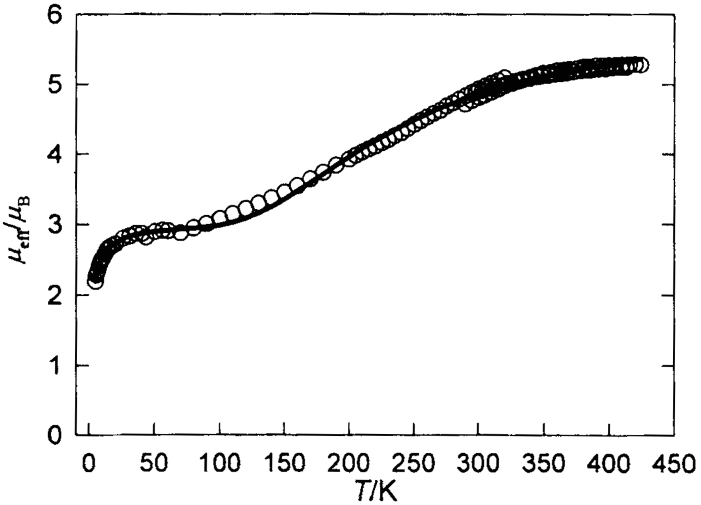


FIGURE 3 Temperature variation of the effective magnetic moment for **2**. Open circles – experimental data, full line – calculated data.

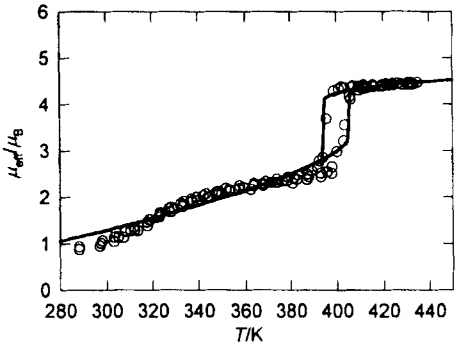


FIGURE 4 Temperature variation of the effective magnetic moment for **3**. Open circles – experimental data, full lines – calculated data.

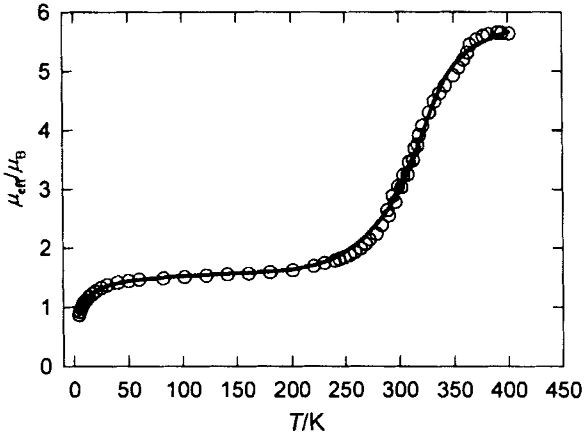


FIGURE 5 Temperature variation of the effective magnetic moment for **4**. Open circles – experimental data, full line – calculated data.

RESULTS AND DISCUSSION

The experimental data along with the calculated values are displayed in Figs. 2–5. The fitted magnetic parameters are collected in Table I.

According to the experimental data the complexes **1**, **2** and **4** are one–step spin crossover systems. The last one (containing $4H_2O$) turns to the anhydrous complex above 400 K which remains high–spin.

The complex **3** is a two–step spin crossover system. The first step is rather continuous: it starts at 200 K and culminates at 330 K. The second step is very sharp and accompanied by a hysteresis: $T_c^{\uparrow}$ = 405 K, $T_c^{\downarrow}$ = 397 K. The existence of the hysteresis is conditioned by a considerable ferromagnetic coupling for one of the sublattices ($J_A / k \approx 900$ K).

TABLE I Magnetic parameters from fitting procedure

Model 1 – without explicit inclusion of molecular vibrations

	ΔH /kJ mol^{-1}	ΔS /JK^{-1}mol^{-1}	T_c /K	(J_A / k) /K	(J_{AB} / k) /K
1	6.2	43.4	144	104	
2	6.5	22.8	285	[0]	
3	13.9	34.7	1st: 330 2nd:406, 397	833, 411	132
4	14.9	45.2	330	226	

Model 2 – with explicit inclusion of molecular vibrations

	(Δ_0 / k) /K	$(h\bar{\nu}_{ls} / k)$ /K	$(h\bar{\nu}_{hs} / k)$ /K	$(\bar{\nu}_{ls} / \bar{\nu}_{hs})$	(J_A / k) /K	(J_{AB} / k) /K
1	1018	301	225	1.34	105	
3	2356	[608, 630]^a	[329]^a	1.88	897, 236	3
4	1793	320	251	1.27	246	

^{a} Fixed on the basis of experimental data[6].

A passage from the bidentate to the tridentate ligands manifests itself in the increased singlet–quintet separation Δ_0 and consequently in a higher value of ΔH. For an approximately same ΔS value it leads to the shift of the transition temperature $T_c = \Delta H / \Delta S$ above the room value.

The cooperativity in the solid state is described by the inter-center coupling parameters J_A and in the case of the two-step spin crossover also by J_B and J_{AB}. Just this parameter is responsible for the deviation of the Arrhenius-like plot, $\ln K$ *vs.* T^{-1}, from the linear function. With the non-zero cooperativity the Arrhenius function is S-shaped. For moderate J_A the function is continuous but when $J_A / k > T_c$ holds true then the function exhibits an abrupt step and a hysteresis can occur. The unique property of the system 3 is that the second, abrupt step is accompanied by a considerable cooperativeness ($J_A / k \approx$ 900 K) despite the long Fe–Fe contacts (of about 10 Å) in the solid state [2].

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