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Spin crossover in mononuclear and binuclear iron(III) complexes with pentadentate Schiff-base ligands

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Abstract

A series of mononuclear hexacoordinate iron(III) complexes, $[Fe(^5L)(py)]BPh_4$, and binuclear hexacoordinate iron(III) complexes, $[(^5L)Fe(\mu^2\text{-bpy})Fe(^5L)](BPh_4)_2$, has been prepared and their magnetic properties were investigated; the pentadentate ligands were derivatives of ^5L = saldptn = N,N′-bis(2-hydroxybenzyliden)-1,7-diamino-4-azaheptane. Temperature variation of the effective magnetic moment for them shows that a spin transition from the low-spin to the high-spin state occurs. The magnetic data were fitted to an Ising-like model appropriate for the mono- and binuclear systems. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

The family of the spin crossover systems involving iron complexes is very numerous [1–4]. The most frequently observed is the case of the $S = 0$ to $S = 2$ transition for Fe(II) complexes. However, the spin transitions involving Fe(III) centres are well documented ($S = 1/2$ to $S = 5/2$ transition) by a few examples among which the tris(dithiocarbamato) iron(III) compounds (the 'Cambi compounds') are well known [5]. These complexes are abbreviated hereafter as $[Fe^{III}(^2L^{-I})_3]$, $^nL^q$ denotes an *n*-dentate ligand bearing a charge *q*. The Schiff-base Fe(III) complexes spanning that class are exemplified by $[Fe(X\text{-saleten})_2]Y$ systems and abbreviated as $[Fe^{III}(^3L^{-I})_2]^+$ (the tridentate monoanion saleten is a condensation product of (substituted) salicylaldehyde with N-ethylethylenediamine) [6].

An interesting behaviour is observed for [Fe(X-salen)(NO)] complexes which belong to the class of $[Fe^{III}(^4L^{-II})(A^{-I})]$ systems: the spin transition operates between the low-spin and the intermediate-spin states ($S = 1/2$ to $S = 3/2$ transition) [7]. An analogous property possesses the system $[Fe(TMC)(NO)](BPh_4)_2$ which spans the class of $[Fe^{III}(^4L^0)(A^{-I})](Y^{-I})_2$ systems (TMC = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane) [8]. Finally, an $S = 3/2$ to $S = 5/2$ spin transition has been reported for the system $[Fe^{III}(^2L^{-I})_3] \cdot$ sol (the

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bidentate monoanion is $^{2}L^{-I}$ = 4-morpholine-carbodithionate-S,S′) [9].

Our interest is focused to the possible spin transitions involving pentadentate Schiff-base complexes of the type $[Fe^{III}(^{5}L^{-II})py]Y^{-I}$ and their binuclear bridged analogues of the type $[\mu^{2}\text{-bpy}\{Fe^{III}\text{-}(^{5}L^{-II})\}_2](Y^{-I})_2$. Some of these compounds have been prepared and investigated previously [10–12]. Our main interest is focused to a theoretical analysis in order to obtain microscopic and/or macroscopic (thermodynamic) parameters describing the spin crossover. Such a set for Fe(III) systems has not been derived from the experimental data so far.

2. Experimental

2.1. Ligands H_2L-X

The pentadentate ligand H_2L = saldptn = N,N′-bis(2-hydroxybenzyliden)-1,7-diamino-4-azaheptane has been prepared by a Schiff-base condensation between 1,7-diamino-4-azaheptane and the corresponding salicyaldehyde at a ratio of 1:2. By mixing the salicylaldehyde (0.2 mol) and 1,7-diamino-4-azaheptane (0.1 mol) in methanol (100 cm^3) a yellow oily material, saldptn, results.

The ligand H_2L has been modified by substituting either the position 3 or 5 in the phenyl ring of the salicylaldehyde, yielding H_2L-X:

(i) for X = 3-MeO: N,N′-bis(2-hydroxy-3-methoxybenzyliden)-1,7-diamino-4-azaheptane,
(ii) for X = 5-MeO: N,N′-bis(2-hydroxy-5-methoxybenzyliden)-1,7-diamino-4-azaheptane,
(iii) for X = 5-Cl: N,N′-bis(2-hydroxy-5-chlorobenzyliden)-1,7-diamino-4-azaheptane.

2.2. Precursors $[Fe(^{5}L-X)Cl]$

A solution of anhydrous iron(III) chloride in methanol (50 cm^3) was added to a solution of H_2L-X (10 mmol) in methanol (50 cm^3). The mixture was stirred at 50°C for 10 min and then triethylamine (20 mmol) was added. The resulting solution was stirred at 50°C for 1 h until black crystals precipitated. These were collected, washed with methanol and diethyl ether, and dried in vacuum.

2.3. Mononuclear complexes $[Fe(^{5}L-X)py]BPh_4$

These were prepared by mixing the precursor $[Fe(^{5}L\text{-}X)Cl]$ with the pyridine in the presence of the sodium tetraphenylborate. Elemental analysis – calc. for X = H, (**1**), $BC_{49}H_{48}N_4O_2Fe$ (found): C, 74.3 (74.1); H, 6.25 (6.11); N, 7.08 (6.95); calc. for X = 3-MeO, (**2**), $BC_{51}H_{52}N_4O_2Fe$ (found): C, 71.9 (71.8); H, 6.15 (6.23); N, 6.58 (6.49); calc. for X = 5-Cl, (**3**), $BC_{49}H_{46}N_4O_2FeCl_2$ (found): C, 68.4 (68.0); H, 5.39 (5.41); N, 6.51 (6.62).

2.4. Binuclear complexes $[(^{5}L-X)Fe(bpy)Fe(^{5}L-X)](BPh_4)_2$

The binuclear iron(III) complexes bridged by bpy (bpy = 4,4′-bipyridine) were obtained by adding a methanolic solution of bpy (1 mmol) to $[Fe(^{5}L\text{-}X)Cl]$ (2 mmol) in 50 cm^3 of methanol. The mixture was stirred at 60°C for 10 min and then filtered. A slight excess of sodium tetraphenylborate (2.5 mmol) in 10 cm^3 was added to the filtrate. The resulting crystals were washed with methanol and diethylether, and

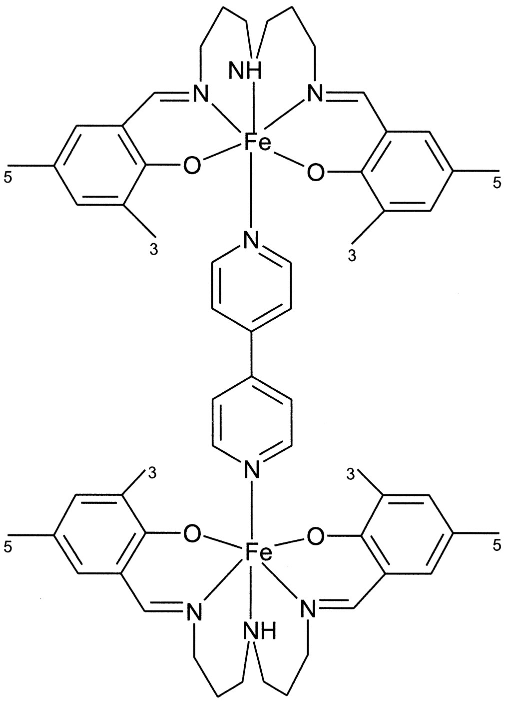

Fig. 1. A molecular structure of $[\mu^{2}\text{-bpy}(Fe^{III}L)_2]^{2+}$ complex.

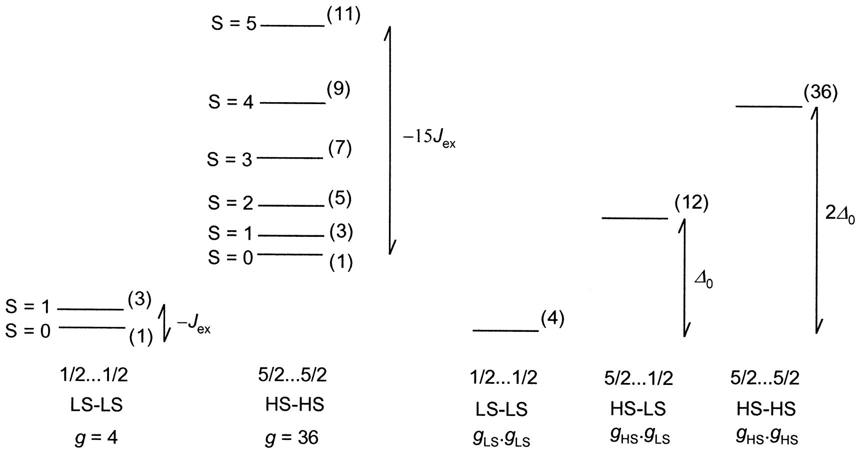

Fig. 2. A relationship between the energy levels of the Heisenberg exchange (left) and the Ising-like model of the spin crossover (right) for a binuclear Fe(III) complex. Degeneracies of the respective energy levels are given in parenthesis.

dried in vacuum. Elemental analysis – calc. for X = H, (**4**), $B_2C_{98}H_{94}N_8O_4Fe_2$ (found): C, 74.4 (74.5); H, 5.99 (5.99); N, 7.08 (7.08); calc. for X = 5-Cl, (**5**), $B_2C_{98}H_{90}N_8O_4Fe_2Cl_4$ (found): C, 68.5 (68.3); H, 5.28 (5.32); N, 6.52 (6.54); calc. for X = 3-MeO, (**6**), $B_2C_{102}H_{102}N_8O_8Fe_2$ (found): C, 72.0 (71.6); H, 6.04 (6.09); N, 6.59 (6.66); calc. for X = 5-MeO, (**7**), $B_2C_{102}H_{102}N_8O_8Fe_2$ (found): C, 72.0 (72.3); H, 6.04 (6.25); N, 6.59 (6.49).

The distance d(N–N) in 4,4′-bipyridine is 715 pm and the estimate of the Fe–Fe separation is d(Fe–Fe) = d(N–N) + 2 × 200 pm = 1115 pm (Fig. 1). The X-ray structure analysis will be published elsewhere [13].

2.5. Magnetic measurements

The magnetic susceptibility for powder samples has been recorded using the Faraday balances in the temperature range from 4.2 K until 280 K.

3. Theoretical models

The fitting procedure for the binuclear complexes, outlined elsewhere [14], is based on the Ising-like spin Hamiltonian of the form

$$\hat{H} = -J_{\mathrm{AB}}(\hat{\sigma}_{\mathrm{A}} \cdot \hat{\sigma}_{\mathrm{B}}) + \frac{\Delta_0}{2}(\hat{\sigma}_{\mathrm{A}} + \hat{\sigma}_{\mathrm{B}}) - J(\langle \sigma_{\mathrm{A}} \rangle \hat{\sigma}_{\mathrm{A}} + \langle \sigma_{\mathrm{B}} \rangle \hat{\sigma}_{\mathrm{B}}) - J'(\langle \sigma_{\mathrm{A}} \rangle \hat{\sigma}_{\mathrm{B}} + \langle \sigma_{\mathrm{B}} \rangle \hat{\sigma}_{\mathrm{A}}). \quad (1)$$

Here the symbol $\hat{\sigma}_{\mathrm{A}}$ denotes a fictitious spin with eigenvalues ± 1 for the high-spin and low-spin states, respectively; its thermal average entering the mean-field approximation, which is a continuous variable, is $\langle \sigma_{\mathrm{A}} \rangle$. The intracomplex A–B coupling parameter J_{AB} adopts negative (positive) values for an 'antiferromagnetic' ('ferromagnetic') coupling of the fictitious spins. The intermolecular interaction parameters are J for A...A and B...B pairs, and J' for A...B and B...A, respectively (these are eventually neglected). The formation energy of the high-spin state is $\Delta_0 = E_{\mathrm{HS}} - _{\mathrm{LS}}$ (Fig. 2).

With the help of the substitutions $m = \langle \sigma_A \rangle + \langle \sigma_B \rangle$, $n = \langle \sigma_A \rangle - \langle \sigma_B \rangle$, $J_+ = J + J'$, and $J_- = J - J'$ the energy levels result:

$$E_1 = E_{\mathrm{LL}} = -\Delta_0 + mJ_+ - J_{\mathrm{AB}}; \quad (2a)$$

$$E_2 = E_{\mathrm{LH}} = nJ_- + J_{\mathrm{AB}}; \quad (2b)$$

$$E_3 = E_{\mathrm{HL}} = -nJ_- + J_{\mathrm{AB}}; \quad (2c)$$

$$E_4 = E_{\mathrm{HH}} = +\Delta_0 - mJ_+ - J_{\mathrm{AB}}. \quad (2d)$$

The partition function of the system is constructed as follows:

$$Z = \sum_{i=1}^{4} g_i \exp(-E_i/kT) = g_{\mathrm{LS}}^2 [\exp(-E_1/kT) + r_{\mathrm{eff}} \exp(-E_2/kT) + r_{\mathrm{eff}} \exp(-E_3/kT) + r_{\mathrm{eff}}^2 \exp(-E_4/kT)] \quad (3)$$

where the effective degeneracy ratio, r_{eff}, occurs

$$r_{\mathrm{eff}} = g_{\mathrm{HS}}/g_{\mathrm{LS}}\,. \tag{4}$$

The latter quantity, in fact, includes a degeneracy of the electronic states as well as that of the vibrational states; consequently $r_{\mathrm{eff}} > 3$ holds true for Fe(III).

The thermal average of the individual (formal) spin values are calculated as follows:

$$\begin{aligned}\langle \sigma_{\mathrm{A}} \rangle &= \sum_{i=1}^{4} \sigma_{\mathrm{A},i}\, g_i \exp(-E_i/kT) \\ &= g_{\mathrm{LS}}^2\big[-\exp(-E_1/kT) - r_{\mathrm{eff}}\exp(-E_2/kT) \\ &\quad + r_{\mathrm{eff}}\exp(-E_3/kT) \\ &\quad + r_{\mathrm{eff}}^2\exp(-E_4/kT)\big]/Z \end{aligned} \tag{5a}$$

and

$$\begin{aligned}\langle \sigma_{\mathrm{B}} \rangle &= g_{\mathrm{LS}}^2\big[-\exp(-E_1/kT) + r_{\mathrm{eff}}\exp(-E_2/kT) \\ &\quad - r_{\mathrm{eff}}\exp(-E_3/kT) \\ &\quad + r_{\mathrm{eff}}^2\exp(-E_4/kT)\big]/Z\,. \end{aligned} \tag{5b}$$

Such a pair of the coupled equations can be solved by an iterative procedure [14]. The starting values in the heating direction are $\langle \sigma_A \rangle^{(0)} = \langle \sigma_B \rangle^{(0)} = -1$. For the given temperature point and the trial set of free parameters (J_{AB}, J, J', Δ_0, and r_{eff}) the first estimate $\langle \sigma_{\mathrm{A}} \rangle^{(1)}$ is evaluated according to Eq. (5a); then $\langle \sigma_{\mathrm{B}} \rangle^{(1)}$ is calculated with the help of Eq. (5b) by using $\langle \sigma_{\mathrm{B}} \rangle^{(0)}$ and $\langle \sigma_{\mathrm{A}} \rangle^{(1)}$ on the right side. Having the first estimates $\langle \sigma_{\mathrm{A}} \rangle^{(1)}$ and $\langle \sigma_{\mathrm{B}} \rangle^{(1)}$ determined, the procedure is repeated until a selfconsistency is reached. Typically 20–50 iterations yield a convergence under the threshold of 10^{-4}. When $J = J'$ are assumed, the values of $\langle \sigma_A \rangle$ and $\langle \sigma_B \rangle$ are necessarily equal.

The formal spin value are interrelated to the high-spin mole fraction as follows:

$$x_{\mathrm{HS}} = \left(2 + \langle \sigma_{\mathrm{A}} \rangle + \langle \sigma_{\mathrm{B}} \rangle\right)/4\,. \tag{6}$$

In the case of the mononuclear complexes the Ising-like spin Hamiltonian simplifies to [15]

$$\hat{H} = \frac{\Delta_0}{2}\hat{\sigma}_{\mathrm{A}} - J\langle \sigma_{\mathrm{A}} \rangle \hat{\sigma}_{\mathrm{A}} \tag{7}$$

and consequently only a single implicit equation results

$$\langle \sigma_{\mathrm{A}} \rangle = \frac{-1 + r_{\mathrm{eff}}\exp\left[-\left(\Delta_0 - 2J\langle \sigma_{\mathrm{A}} \rangle\right)/kT\right]}{1 + r_{\mathrm{eff}}\exp\left[-\left(\Delta_0 - 2J\langle \sigma_{\mathrm{A}} \rangle\right)/kT\right]}\,. \tag{8}$$

Finally,

$$x_{\mathrm{HS}} = \left(1 + \langle \sigma_{\mathrm{A}} \rangle\right)/2 \tag{9}$$

holds true for the high-spin mole fraction.

The microscopic parameters interrelate to the enthalpy and entropy of the spin transition as follows

$$\Delta H = N_{\mathrm{A}}\Delta_0 \tag{10}$$

$$\Delta S = R \ln r_{\mathrm{eff}} \tag{11}$$

and the equilibrium temperature becomes expressed as

$$T_{\mathrm{c}} = \Delta H/\Delta S\,. \tag{12}$$

Thus, the greater the ΔH, the greater the T_{c} (at the constant ΔS). For a vanishing cooperativity parameter J the Arrhenius plot

$$\ln K = \ln\left(\frac{x_{\mathrm{HS}}}{1 - x_{\mathrm{HS}}}\right) = f(1/T) \tag{13}$$

is a straight line that determines ΔH and ΔS. For $J > 0$, however, a non-linear dependence is obtained. The greater J, the greater the steepness of the spin transition expressed, for instance, by x_{HS} versus T function.

The high-spin mole fraction can be derived from the experimental susceptibility data in the following way. The expression for the molar magnetic susceptibility is

$$\chi_{\mathrm{mol}} = x_{\mathrm{HS}}\,\chi_{\mathrm{HS}} + (1 - x_{\mathrm{HS}})\,\chi_{\mathrm{LS}} \tag{14}$$

and then

$$x_{\mathrm{HS}} = \frac{\chi T - \chi_{\mathrm{LS}} T}{\chi_{\mathrm{HS}} T - \chi_{\mathrm{LS}} T}\,. \tag{15}$$

Such a formula is usually applied when constant low-temperature limit and high-temperature limit are experimentally available. Subsequently, the fitting of the function $x_{\mathrm{HS}} = f(\Delta_0, J_{\mathrm{AB}}, J, J', r_{\mathrm{eff}})$ is done. However, our low-temperature data show a non-con-

Table 1
Characteristic functions for the magnetic susceptibility of binuclear systems [a]

S_A, S_B	$F_{S_A,S_B}(a)$
$1/2, 1/2$	$\dfrac{\exp(a)}{1+3\exp(a)}$
$3/2, 3/2$	$\dfrac{\exp(a)+5\exp(3a)+14\exp(6a)}{1+3\exp(a)+5\exp(3a)+7\exp(6a)}$
$5/2, 5/2$	$\dfrac{\exp(a)+5\exp(3a)+14\exp(6a)+30\exp(10a)+55\exp(15a)}{1+3\exp(a)+5\exp(3a)+7\exp(6a)+9\exp(10a)+11\exp(15a)}$

[a] The argument $a = J_{ex}/kT$ accounts for the true magnetic exchange interaction.

stant value of $x_{LS}T$ owing to an antiferromagnetic exchange inside the binuclear complex. Therefore the individual-spin magnetic susceptibility for a binuclear system was expressed via the formula [16]

$$\chi_S = \frac{N_A \mu_0 \mu_B^2}{k} \frac{2 g_S^2}{T} F_{S_A,S_B}(a) \tag{16}$$

where the characteristic functions $F_{S_A,S_B}(a)$ are given in Table 1 for the argument $a = J_{ex}/kT$ (the fundamental physical constants adopt their usual meaning).

The characteristic functions for the magnetic susceptibility of a mononuclear species in low-spin and the high-spin states account for the Curie–Weiss law

$$\chi_S = \frac{N_A \mu_0 \mu_B^2}{k} \frac{g_S^2 S(S+1)}{3(T-\Theta)} \tag{17}$$

These assumptions allow a direct fitting of the function $\chi_{mol} = f(\Delta_0, J, r_{eff}; g_{LS}, \Theta_{LS}, g_{HS})$ for the mononuclear species and $\chi_{mol} = f(\Delta_0, J_{AB}, J, J', r_{eff}; g_{LS}, J_{ex}, g_{HS})$ for the binuclear species, respectively. In order to avoid an overparametrization of the model, some additional simplifications will be done as explained in discussion. An important note follows: while the parameters g_{LS}, J_{ex}, g_{HS} describe the magnetic interactions inside the binuclear complex, the set of parameters $\Delta_0, J_{AB}, J, J', r_{eff}$ is characteristic for the Ising-like spin crossover model and its nature is non-magnetic (most probably elastic).

4. Results and discussion

The possible spin states for the mononuclear Fe(III) species are $S = 1/2$ (low-spin), $3/2$ (intermediate-spin), and $5/2$ (high-spin) with the spin-only (s.o.) effective magnetic moment being $\mu_{eff}/\mu_B =$ 1.7, 3.9, and 5.9, respectively. The measured temperature variation of the effective magnetic moment per complex, $\mu_{eff}/\mu_B = 798(\chi'_{mol}T)^{1/2}$, is displayed in Fig. 3.

For two mononuclear complexes (X = H and X = 3-MeO) the low-temperature data (below 100 K) show almost constant value of the effective magnetic moment; this, however, exceeds the spin-only value for $S = 1/2$ so that a magnetogyric factor $g > 2$ is needed. For Fe(III) in a strong ligand field of octahedral symmetry the ground state is ^{2}T, i.e., magnetic active. The six magnetic levels might be thermally accessible also on a symmetry lowering and when dealing only with the lowest Kramers doublet, the presence of the remaining levels will reflect itself in the increasing value of g_{eff}. Therefore, $g_{eff,(S=1/2)} > 2$ should be considered as a free parameter. On the contrary, for $S = 5/2$ the ground state is $^6A_1$ and thus $g_{eff,(S=5/2)} \approx 2$ can be safely assumed. A small decrease of the effective magnetic moment below 10 K can be attributed to the intermolecular interactions and covered by the Weiss constant Θ (paramagnetic Curie temperature).

The remaining mononuclear complex for X = 5-Cl shows features of an intermediate-spin ground state $^4A_2$ (C_{4v} group of symmetry). A valuable discussion of such a case can be found elsewhere [3]. Again $g_{eff,(S=3/2)} > 2$ can be expected. A possible zero-field splitting can be simply accounted for considering the Weiss constant Θ.

The results of the fitting procedure are listed in Table 2 and displayed in Fig. 4. In all cases $g_{HS} =$ 2.0023 has been fixed.

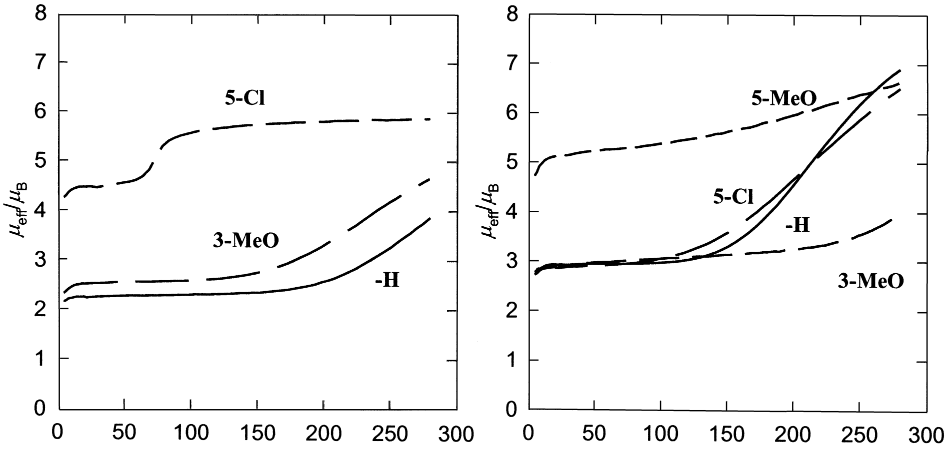

Fig. 3. Measured temperature dependence of the effective magnetic moment (per unit formula) for a series of mononuclear (left) and binuclear (right) complexes with substituted ligand L–X.

In accordance with expectations, g_{LS} overcomes the free-electron value for **1** through **3**. A small value of the Weiss constant (Θ_{LS}: -1 K) describes a drop of the effective magnetic moment at the lowest temperatures. The value of the effective degeneracy ratio, r_{eff}, highly overreaches the its minimum value given by the electronic degeneracy only, i.e. 3.0 for Fe(III). This indicates an important contribution of the vibrational partition function. The values of r_{eff} and Δ_0, both are very sensitive for the consideration of the cooperativity parameter J (compare fitted parameters, for instance, for **1a** and **1b**). However, a reliable determination of J requires experimental data along the whole transition curve, which is not the present case, except **3**.

For the complex **3** the model of the spin-crossover has been improved by considering the molecular vibrations as described elsewhere [17,18]; the param-

Table 2
Calculated magnetic parameters for mononuclear complexes

Parameters	Complex, substituent						
	X = H		X = 3-MeO		X = 5-Cl		
Model [a]	**1a**	**1b**	**2a**	**2b**	**3a**	**3b**	**3c**
Fitted							
g_{LS} [b]	2.63	2.63	2.98	2.98	2.35	2.35	2.35
Θ_{LS}/K [b]	-0.56	-0.56	-1.12	-1.12	-0.67	-0.67	-0.67
r_{eff}	112	7.1	79	4.4	110	28	$(h\bar{\nu}_{LS})/k = 797$ $(h\bar{\nu}_{HS})/k = 514$
$(\Delta_0/k)/K$	1540	627	1204	406	386	265	2246
$(J/k)/K$	–	197	–	168	–	42	64
$R/\%$ [c]	0.76	0.71	0.79	0.72	0.81	0.67	0.65
Derived							
$\Delta S/J\ K^{-1}\ mol^{-1}$	39.3	16.3	36.3	12.3	39.1	27.7	
$\Delta H/kJ\ mol^{-1}$	12.8	5.2	10.0	3.4	3.2	2.2	
T_c/K	326	319	276	275	82	80	78

[a] Model **a**, no cooperativity; model **b**, cooperativity parameter; model **c**, cooperativity + molecular vibrations. Error estimates: 1.0 for Δ_0, r_{eff}, and J; 0.01 for Θ_{LS} and g_{LS}.

[b] Fixed parameters using the low-temperature data.

[c] Discrepancy factor of the regression.

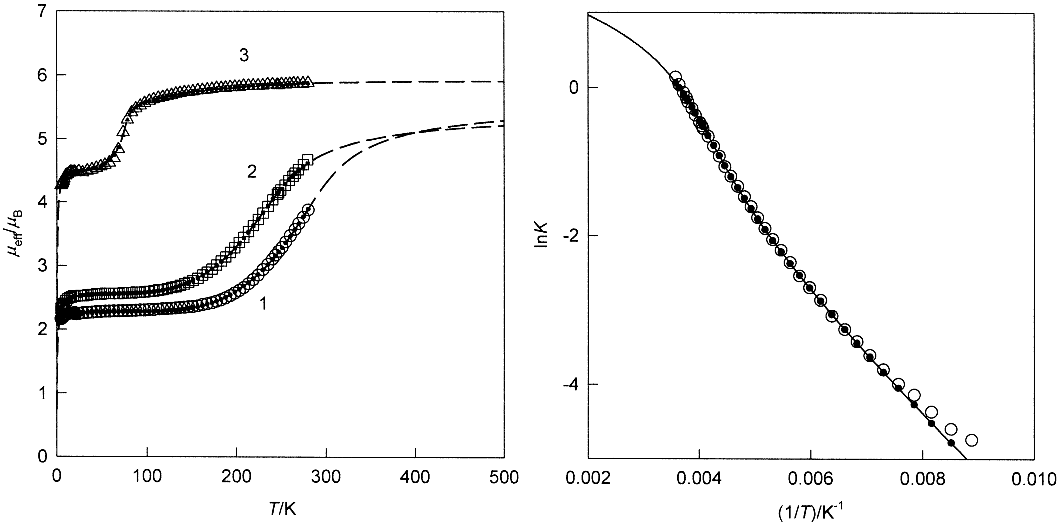

Fig. 4. Fit of the magnetic data for mononuclear complexes (left): X = H, **1**, X = 3-MeO, **2**, and X = 5-Cl, **3**; empty symbols – experimental data, full circles – calculated points, dashed line – theoretical curve; Arrhenius plot for **3** (right).

eter set **3c** consists of g_{LS}, Θ_{LS}, Δ_0, J, $h\bar{v}_{LS}$, and $h\bar{v}_{HS}$ (the last pair accounts for a mean vibrational energy for the low-spin and the high-spin state, respectively). In this case the quality of the fit is perfect as seen also from the Arrhenius plot $\ln K$ versus $1/T$ (Fig. 4). Evidently, deviation from the linearity, which represents cooperativeness as well as the effect of molecular vibrations [17,19], is well covered by the theoretical model. The reason why the vibrations can be relevantly introduced for compound 3 is the following (according to [17]): the low value of the equilibrium temperature, which implies a small energy difference between the LS and HS lowest vibronic levels. The site formation enthalpy then relaxes to $\Delta_0' = \Delta_0 + (15/2)(h\bar{v}_{HS} - h\bar{v}_{LS})$ so that the electronic level difference $\Delta_0/k = 2246$ K is reduced to $\Delta_0'/k = 124$ K.

The characteristic susceptibility function for $(S_A,S_B) = (1/2,1/2)$ pair in the high-temperature limit becomes $F_{1/2,1/2}$ $(a \to 0) = 1/4$ and then the Curie-like behaviour is predicted

$$\chi_{LS} = \frac{N_A\,\mu_0\,\mu_B^2}{k}\,\frac{g_{LS}^2}{2T} \tag{18}$$

yielding $\mu_{eff} = \sqrt{(3k/N_A\,\mu_0)\,\chi T} = g_{LS}\sqrt{3/2}\,\mu_B$. Such behaviour is observed for three binuclear complexes (**4**, **5**, and **6**) showing the effective magnetic moment $\mu_{eff}/\mu_B \sim 3$ in the temperature interval of 10–100 K (Fig. 2). A drop below 10 K indicates an antiferromagnetic interaction ($J_{ex} < 0$) leading to the $S = 0$ ground state.

On temperature increase above 100 K a spin transition to $(S_A,S_B) = (5/2,5/2)$ becomes evident; its saturation value

$$\chi_{HS} = \frac{N_A\,\mu_0\,\mu_B^2}{k}\,\frac{g_{HS}^2}{T}\,\frac{2\cdot 105}{36} \tag{19}$$

yielding $\mu_{eff}/\mu_B = g_{HS}\sqrt{3\cdot 2\cdot 105/36} \sim 8.38$, however, is not reached until 300 K.

The results of the fitting procedure are presented in Table 3 and are exemplified in Fig. 5. In all cases $g_{HS} = 2.0023$ has been fixed and the intermolecular interaction parameters, J and J', deleted from the consideration. Eventually, an approximation $J_+ = J + J' \approx 2\,J_{av}$ and $J_- = J - J' \approx 0$ has been applied.

It can be seen that the quality of the fit is very good for X = H and 5-Cl. The remaining binuclear complexes suffer for the lack of the high-temperature data that prevents a reliable determination of the spin crossover parameters.

In the last binuclear complex (**7**, X = 5-MeO) the spin crossover starts from the intermediate-spin case $(S_A,S_B) = (3/2,3/2)$. Analogously to the mononuclear case for **3**, X = 5-Cl, the site formation energy

Table 3
Calculated magnetic parameters for binuclear complexes

Parameter	Complex, substituent					
	X = H		X = 5-Cl		X = 3-MeO	X = 5-MeO
Model [a]	**4a**	**4b**	**5a**	**5b**	**6a**	**7a**
Fitted						
g_{LS} [b]	2.42	2.42	2.38	2.38	2.43	1.91
$(J_{ex}/k)/K$ [b]	−2.80	−2.80	−2.32	−2.32	−2.45	−0.73
$(J/k = J'/k)/k$	–	46	–	78	–	–
r_{eff}	167	26	26	2.8	[3.0][d]	[3.0][d]
$(\Delta_0/k)/K$	1301	823	894	287	931	493
$R/\%$ [c]	1.32	1.15	1.31	1.19	1.70	1.70
Derived						
$\Delta S/J\ K^{-1}\ mol^{-1}$	42.6	27.0	27.1	8.6	[9.1]	[9.1]
$\Delta H/kJ\ mol^{-1}$	10.8	6.8	7.4	2.4	7.7	4.1
T_c/K	254	253	275	276	[847]	[449]

[a] Model **a**, no cooperativity; model **b**, cooperativity parameter. Error estimates: 1.0 for Δ_0, r_{eff} and J; 0.01 for J_{ex} and g_{LS}.

[b] Fixed parameters using the low-temperature data.

[c] Discrepancy factor of the regression.

[d] Values in brackets were fixed.

Δ_0 (or the enthalpy of the transition ΔH) is only a half of the value for the $(S_A,S_B) = (1/2,1/2)$ to $(S_A,S_B) = (5/2,5/2)$ transition (when the same model is considered, e.g. data set **7a** vs. **6a**).

On conclusion, the Ising-like model is successful in fitting the magnetic data for binuclear Fe(III) complexes exhibiting the spin crossover. The spin transition is rather gradual and centred at quite high temperature. The cooperativity parameter is much lower than the enthalpy of the transition that reflects in the absence of the steepness and the eventual hysteresis. Therefore the binuclear character of the compounds under study does not result in any specific effect like a two-step process.

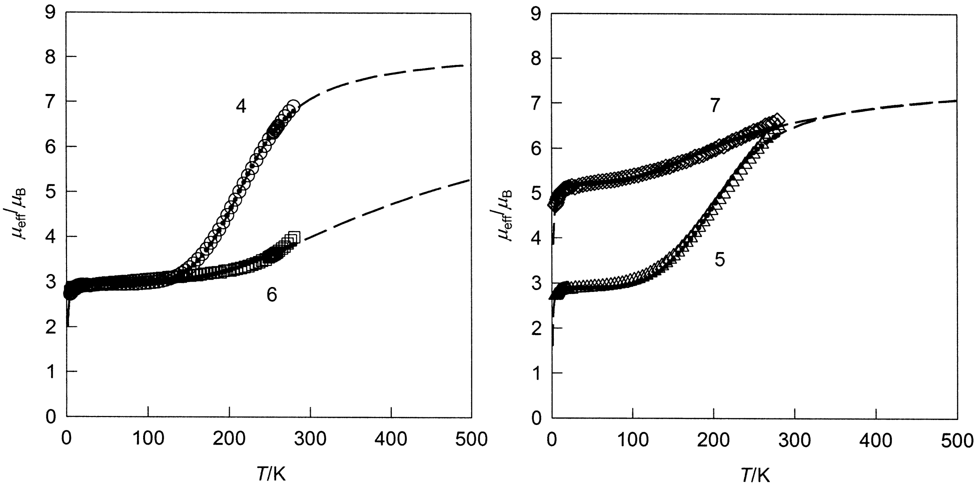

Fig. 5. A fit of the magnetic data for X = H, **4**, X = 3-MeO, **6**, X = 5-Cl, **5**, and X = 5-MeO, **7**; empty symbols – experimental data, full circles – calculated points, dashed line – theoretical curve.

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