The Nature of the Spin-State Variation of $[Fe^{II}(BPMEN)(CH_3CN)_2](ClO_4)_2$ in Solution

Konstantin P. Bryliakov,*[a] Eduard A. Duban,[a] and Evgenii P. Talsi[a]

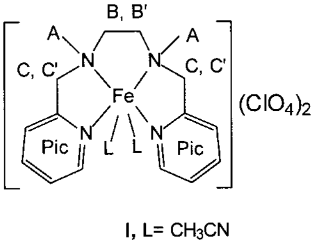
Keywords: Magnetic properties / Iron(II) complexes / Spin crossover / Liquid state / Solvent effects

Thermally-induced spin variation behavior of $[Fe^{II}(BPMEN)(CH_3CN)_2](ClO_4)_2$ in CD_3CN solution [low spin (LS)–high spin (HS)] was investigated. Variable temperature solution magnetic susceptibility measurements gave $\Delta H°_{LS-HS} = 39.7 \pm 2.0$ kJ·mol^{-1} and $\Delta S°_{LS-HS} = 135 \pm 9$ J·mol^{-1} K^{-1} values. These values are too high for a pure spin transition and reflect a significant contribution of chemical processes to the spin transition, namely, the detected dissociation of one bound acetonitrile molecule. Thus, LS–HS conversion should be regarded as a chemical equilibrium overlapped with a thermal spin crossover. The thermodynamic parameters for the overall process estimated from the variation of the NMR shifts with temperature ($\Delta H° = 40 \pm 3$ kJ·mol^{-1}, $\Delta S° = 137 \pm 10$ J·mol^{-1} K^{-1}) are in perfect agreement with those obtained by magnetic susceptibility measurements.

Introduction

In recent years, Que and co-workers reported a series of non-heme Fe^{II}(BPMEN)- and Fe^{II}(TPA)-type catalysts for stereospecific oxidation of hydrocarbons with H_2O_2 [TPA is tris(2-pyridylmethyl)amine ligand and BPMEN is *N,N′*-dimethyl-*N,N′*-bis(2-pyridylmethyl)-1,2-diaminoethane ligand].[1–4] These species can be functional models for non-heme iron oxygenases, such as Rieske dioxygenases capable of olefin *cis*-dihydroxylation.[3] The catalysts reported were either diamagnetic or paramagnetic complexes, depending on the substituent at the 6-position of the pyridine rings. Interestingly, the parent $[Fe^{II}(BPMEN)(CH_3CN)_2](ClO_4)_2$ complex displayed solution spin-transition behavior in the temperature range −40 to +30 °C. However, the authors only mentioned this phenomenon and did not report a detailed spectroscopic/magnetic susceptibility investigation. Recently, a theoretical study appeared where the structure and spin states of Fe-BPMEN complexes were evaluated by DFT.[5] Apparently, knowledge on the nature of this low-to-high spin transition could be of help in understanding the reactivity of these systems.

The temperature-induced LS−HS transitions in Fe^{II} complexes[6−8] have been extensively studied over the last few years, mostly in the solid state; however, variable-temperature studies in solution have also appeared.[8−10] Solid-state spin equilibria in some diisothiocyanato iron(II) complexes with BPMEN type ligands were studied by Toftlund et al.[11] In this paper, we present a detailed magnetic susceptibility and ^{1}H NMR study of $[Fe^{II}(BPMEN)(CH_3CN)_2](ClO_4)_2$ in solution (**I**, Scheme 1) spin variation in [D$_3$]acetonitrile and the thermodynamic parameters of this reaction. The results of magnetic susceptibility measurements on solutions are compared with those obtained by a paramagnetic ^{1}H NMR study.



Scheme 1. Complex **I**

Results and Discussion

At room temperature, complex **I** exhibits a magnetic moment of 4.1 μ_B in acetonitrile solutions, which is indicative of a spin-crossover system. Temperature-dependent magnetic susceptibility measurements were carried out to explore the equilibria that occur in acetonitrile solutions of complex **I** (see a in Figure 1, trace 1). Fitting the observed magnetic moment dependencies μ_{eff} versus T to Equation (5) (see Exp. Sect.) gave the limiting magnetic moment values $\mu_{LS} = 1.30 \pm 0.1\ \mu_B$ and $\mu_{HS} = 5.45 \pm 0.1\ \mu_B$, which are higher than the spin-only values 0 and 4.90 μ_B, thus suggesting significant orbital contributions to the observed

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[a] G. K. Boreskov Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences,
630090 Novosibirsk, Russian Federation
Fax: (internat.) + 7-3832-308766
E-mail: bryliako@catalysis.nsk.su

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magnetic moments (see ref.[8,11]). Spin transition is accomplished within the temperatures accessible for acetonitrile: the $\mu_{eff}(T)$ values practically level off in the higher and lower limits of the temperature range considered. The μ_{LS} value is in good agreement with the solid-state magnetic moment 1.40 μ_B ($T = 294$ K).

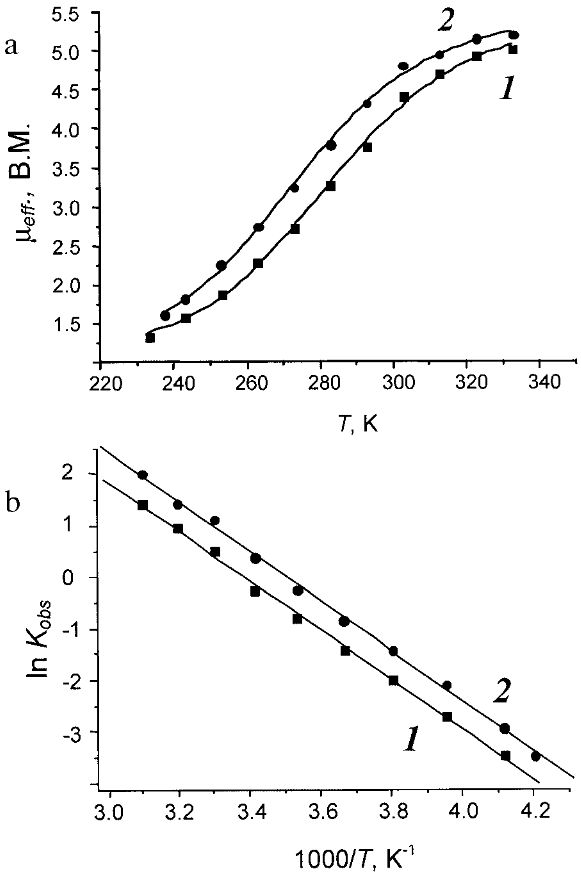

Figure 1. Fits of $\mu_{eff}(T)$ to Equation (5) for complex **I** (a) and linear fits of ln K_{obs} versus $1000/T$ (b) in [D$_3$]acetonitrile - trace 1 (■) and in [D$_3$]acetonitrile/[D$_6$]acetone - trace 2 (•) (in Table 1, see entries 1 and 7, respectively)

The equilibrium parameters $\Delta S°$ and $\Delta H°$ (see b in Figure 1, trace 1) measured in [D$_3$]acetonitrile gave $\Delta S° = 135 \pm 9$ J mol^{-1} K^{-1} (in which the contribution of R ln 5 arises from spin degeneracy of the HS state) and $\Delta H° = 39.7 \pm 2.0$ kJ mol^{-1}. Both values are substantially higher than those reported in the literature for solution spin-crossover systems.[7,10,12] This lead us to suggest that spin change in this system could overlap with other (chemical) processes. The fact that in other solvents (e.g. [D$_6$]acetone, see Supporting Information) a conventional Curie dependence of ^{1}H paramagnetic shifts is observed is in favor of dissociation of bound acetonitrile molecules at elevated temperatures, see Equation (1).

A similar behavior was previously proposed to describe the spin-state variation of $[Fe(Me_3tacn)(MeCN)_3]$ in solution.[9] The observed equilibrium constant [$K_{obs}(T) = C_{HS}/C_{LS}$] values should be related to the thermodynamic equilibrium constant as shown in Equation (2).

$$K_{obs}(T) = K/[L]^n \qquad (2)$$

[L] is the concentration of acetonitrile in solution. Dilution of acetonitrile with a noncoordinating solvent would result in higher K_{obs} values, so that $K_{obs}([L_o])/K_{obs}([L_1]) = ([L_1]/[L_o])^n$. Also, taking the logarithm of Equation (2) and assuming that $\Delta H°$ is independent of acetonitrile concentration, one obtains Equation (3).

$$\Delta S°_{obs} = \Delta S° - nR \ln [L] \qquad (3)$$

$\Delta S°_{obs}$ and $\Delta S°$ correspond to K_{obs} and K (i.e. ΔS related at some standard conditions), respectively, and R is the gas constant. Thus, the 1.63-fold decrease in CD_3CN concentration would result in a $(1.63)^n$-fold increase in the K_{obs} value and an nR ln(1.63) = $4n$ J mol^{-1} K^{-1} increase in $\Delta S°_{obs}$. Unfortunately, the low precision of μ_{eff} measurements did not allow reliable detection of these small effects. In the temperature range considered, such experiments with combined $CD_3CN/CDCl_3$, CD_3CN/CCl_4, CD_3CN/[D$_6$]acetone solvents (Table 1, Figure 1) showed a 1.3-fold increase in the value of K_{obs} with a 1.63-fold decrease in CD_3CN concentration and a 1.7-fold increase in the value of K_{obs} with a 2.65-fold decrease in [CD_3CN] (these values are lower than those expected, indicating that $\Delta H°$ also changes with changing CD_3CN concentration). In the $\mu_{eff}(T) - T$ diagram, this resulted in a $T_{1/2}$ change from 284 to 275 K (see a in Figure 1). The question, what is n in Equation (3), could be answered as follows: if both acetonitrile molecules dissociated at high temperatures, we should observe similar high-temperature spectra in [D$_6$]acetone and in [D$_3$]acetonitrile/[D$_6$]acetone combined solvent. However, the spectra are substantially different (Supporting Information), indicating, apparently, the existence of $[Fe^{II}(BPMEN)]^{2+}$ in the first case and $[Fe^{II}(BPMEN)(CD_3CN)]^{2+}$ in the second case. We conclude that the experimentally observed picture is consistent with dissociation of one acetonitrile molecule, therefore leading to a weaker ligand field.

^{1}H NMR spectra of complex **I** in [D$_3$]acetonitrile gradually change from diamagnetic at −40 °C to paramagnetic at +60 °C (see a in Figure 2), indicating that the process in Equation (1) is fast on the NMR timescale. At high temperatures the spectrum is typical for high-spin Fe^{II} complexes,[9,13–14] and the peaks can be assigned unambiguously based on the relative intensities and linewidths of the peaks by assuming a dipolar line broadening mechanism.[15] The thermodynamic parameters estimated from NMR shifts according to Equation (9): $\Delta S° = 137 \pm 10$ J·mol^{-1} K^{-1} and $\Delta H° = 40 \pm 3$ kJ·mol^{-1} (see b in Figure 2), do not differ from those obtained by magnetic

$$\underset{LS}{[Fe^{II}(BPMEN)(CH_3CN)_2]^{2+}} \xrightleftharpoons{K} \underset{HS}{[Fe^{II}(BPMEN)(CH_3CN)_{2-n}]^{2+}} + n\,CH_3CN \qquad (1)$$

Table 1. Thermodynamic parameters for $[Fe^{II}(BPMEN)(CH_3CN)_2](ClO_4)_2$ (**I**) spin crossover in different solutions

Entry	Solvent	c^0(D_3CN/CCD_3CN)	$T_{1/2}$, K	K_{obs}/K[a]	$\Delta H°$ (±2.0), kJ mol^{-1}	$\Delta S°$ (±9.0), J mol^{-1} K^{-1}
1	CD_3CN	1	284	1.0	40.6	138
2	CD_3CN	1	284.5	0.96	38.7	131
3	CD_3CN/[D$_6$]acetone	1.63	279	1.2	38.5	132
4	$CD_3CN/CDCl_3$	1.63	280.5	1.3	36.0	124
5	CD_3CN/CCl_4	2.0	280	1.1	40.5	139
6	$CD_3CN/CDCl_3$	2.65	277	1.2	40.3	138
7	CD_3CN/[D$_6$]acetone	2.65	275	1.7	39.5	139

[a] Average values over the temperature range −40 to +60 °C.

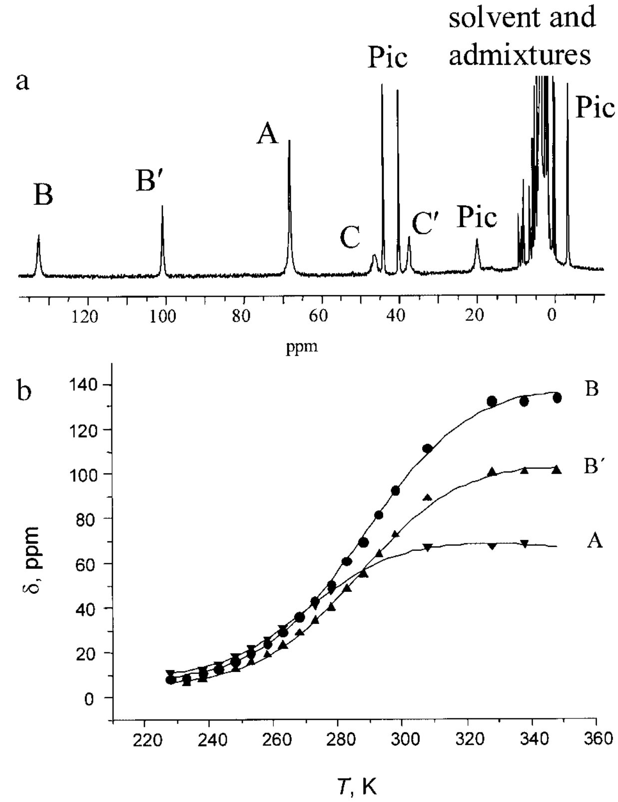

Figure 2. ^1H NMR spectrum (0.01 M solution in [D$_3$]acetonitrile, 60 °C) of complex **I** (a); plot of variation of chemical shifts with temperature for ^1H resonances of **I** (b); symbols A, B, B′ and Pic mark the same protons as in Scheme 1; "solvent and admixtures" stands for residual protons of [D$_3$]acetonitrile and unidentified proton-containing admixtures

measurements. In weaker coordinating solvents (e.g. [D$_6$]-acetone), **I** displays a paramagnetic spectrum from 130 to −10 ppm, which is indicative of loss of both coordinated CH_3CN molecules.

The phenomenon of ligand dissociation induced spin transition has a nice interpretation in terms of crystal field theory. If one looks at the Tanabe−Sugano diagram for the d^6 configuration (Figure 3), one can see that a conventional spin equilibrium $^1A_1(LS) \rightleftarrows {}^5T_2(HS)$ should be represented by the vertical arrow, which indicates gradual population of the higher lying $^5T_2$ HS state with increasing temperature. On the contrary, the spin conversion caused by ligand dissociation could be associated with the *horizontal* arrow, which represents the dislocation from the high-field region to the low-field one. In our case, an intermediate process seems to take place: an attempt to split the spin interconversion and ligand dissociation processes was made (see Supporting Information), and this revealed comparable contributions of both processes to the observed equilibrium.

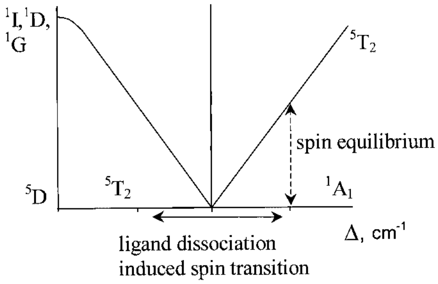

Figure 3. Schematic representation of the Tanabe−Sugano diagram (fragment) for d^6 configuration; the abscissa and ordinate are the crystal field parameter Δ and energy, respectively

In a series of works on bis(benzimidazole)pyridine iron(II) and other iron(II) complexes, it was shown that solvent effects can overlap with the true spin crossover,[16−22] so that substitution or dissociation of coordinated ligands lead to the change in spin state. As Toftlund mentioned, phenomena like these should not be considered as true spin-crossover interconversions.[23] LS/HS transition systems like the one presented (where the spin transition is due to the substantial contribution of the ligand dissociation, and thus weakening the ligand field splitting) seem to be fairly rare in the literature. In this paper we have reported the first measurements of thermodynamic parameters defining the LS/HS transition in $[Fe^{II}(BPMEN)(CH_3CN)_2](ClO_4)_2$ in solution, and demonstrated the high utility of the combined solution magnetic susceptibility/^1H NMR spectroscopic measurements for the detailed physico-chemical investigations of one of the few systems of this type documented so far.

Experimental Section

Materials: BPMEN[11] and **I**[1] were prepared as described. For solution magnetic susceptibility measurements, **I** was recrystallized from CH_3CN/Et_2O at +4 °C.[1] Deuterated solvents ([D$_3$]acetonitrile, [D]chloroform) were dried with molecular sieves prior to use.

Physical Measurements: ^{1}H NMR spectra were recorded in standard 5-mm cylindrical glass tubes on a Bruker DPX-250 NMR spectrometer at 250.13 MHz and referenced to TMS (samples volume 0.50 cm^3 at 298 K). Operating conditions for ^{1}H NMR measurements: high temperature, spectral width 50 kHz, spectrum accumulation frequency 5 Hz; low temperature, spectral width 5 kHz, spectrum accumulation frequency 0.5 Hz; 90° pulse at 8.2 μs.

Solid state magnetic susceptibility was measured by the Faraday method, with $(NH_4)_2Fe(SO_4)_2·6H_2O$ as calibrant. Solution magnetic susceptibility measurements were measured as a function of temperature (−50 to +70 °C) in deuterated solvents CD_3CN, CD_3CN/[D$_6$]acetone, CD_3CN/CCl_4 and $CD_3CN/CDCl_3$ by the Evans method,[24] with TMS as an internal reference. To prepare the "1.63-fold diluted" CD_3CN solutions, $CDCl_3$ was added to CD_3CN (0.61 mL) to make the volume 1.00 mL. To prepare the "2.65-fold diluted" CD_3CN solutions, [D$_6$]acetone was added to CD_3CN (0.375 mL) to make the volume 1.00 mL. To prepare the "2-fold diluted" CCl_4 solutions, CCl_4 was added to CD_3CN (0.500 mL) to make the volume 1.00 mL. Temperature uncertainty was ±1 °C. Special stem coaxial insert tubes (203 mm × 4 mm o.d.) with a capillary reference volume of 60 μL (50 mm × 2 mm o.d.) were purchased from Wilmad Glass Co. Mass magnetic susceptibilities χ_g (cm^3 g^{-1}), were calculated from Equation (4).

$$\chi_g = -3\Delta f/4\pi f m + [\chi_o + \chi_o(d_o - d_s)/m] \tag{4}$$

Δf is the frequency shift in Hz of the reference compound, f is the spectrometer frequency in Hz, m is the mass in g of the complex in 1 cm^3 of the solution, χ_o is the mass susceptibility of the solvent in cm^3 g^{-1}, and d_o and d_s are the densities of the solvent and solution, respectively. The term in square brackets disappears, because at the concentrations used (10−15 mM), the solution density was approximated as $d_s = d_o + m$. We note that the original Evans technique[24] was developed for the cylindrical sample axis perpendicular to the magnetic field, whereas for the sample axis parallel to the magnetic field, a factor of 3/4π rather than 3/2π[1,25] should be applied in Equation (4).[10,26] To take into account the solution volume changes with temperature, a correction was introduced in the m values so that $m = m_o h_o/h$, where m_o is the mass in g of the complex in 1 cm^3 of the solution at 298 K, and h_o and h are sample heights at 298 K and at the given temperature, respectively.

Multiplying the χ_g values by the molecular weight, the molar susceptibility χ_M was obtained. The latter was corrected for the diamagnetic contributions of BPMEN ligands, counteranions and Fe^{II} core electrons using Pascal's constants to give the corrected molar susceptibility χ_M'.[25] The latter was used to calculate the effective magnetic moment $\mu_{eff} = 2.828(\chi_M' T)^{1/2}$ (μ_B), where T is temperature in K.[26] μ_{eff} was fit to Equation (5) in a manner similar to that applied in ref.[10]

$$\mu_{eff}(T) = \{\mu_{LS}^2 + \mu_{HS}^2\,[\exp(\Delta S°/R)\exp(-\Delta H°/RT)]\}^{1/2} \\ \{1 + \exp(\Delta S°/R)\exp(-\Delta H°/RT)\}^{-1/2} \tag{5}$$

μ_{LS} and μ_{HS} are the limiting magnetic moments of the low-spin and high-spin states, and $\exp(\Delta S°/R)\exp(-\Delta H°/RT)$ is the observed equilibrium constant K_{obs} = [HS-Fe^{II}]/[LS-Fe^{II}].

Calculation of Observed Equilibrium Constant Values K_{obs}: Equation (5) implies a four-parameter fit that gives significant uncertainties for $\Delta S°$ and $\Delta H°$. For more precise $\Delta S°$ and $\Delta H°$ measurements, the solution equilibrium treatment of Crawford and Swanson was applied.[27] Namely, after μ_{LS} and μ_{HS} were obtained from Equation (5) (and averaged over all experiments), the probabilities of Fe^{II} to be in LS and HS forms were calculated as according to Equation (6) and $K_{obs}(T) = P_{HS}(T)/P_{LS}(T)$. Then, $\Delta S°$ and $\Delta H°$ were obtained from linear logarithmic plots of ln K_{obs} versus $1/T$.

$$P_{LS}(T) = (\mu_{HS}^2 - \mu_{eff}(T)^2)/(\mu_{HS}^2 - \mu_{LS}^2) \\ P_{HS}(T) = 1 - P_{LS}(T) \tag{6}$$

Calculation of ΔH° and ΔS° from the Temperature Dependence of the Observed ^{1}H NMR Chemical Shifts: For LS and HS forms in fast equilibrium, a single paramagnetically broadened ^{1}H resonance was observed, see Equation (7).

$$\delta_{obs} = \delta_{LS}P_{LS} + \delta_{HS}P_{HS} \tag{7}$$

δ_{LS} is the chemical shift for the diamagnetic state,

$$P_{LS}(T) = 1/(1 + K_{obs}).$$

$$P_{HS}(T) = K_{obs}/(1 + K_{obs}) \tag{8}$$

δ_{HS} stands for the chemical shift of the HS (paramagnetic) state. According to ref.[28−29] $\delta_{HS} = \delta_{dia} + \delta_{hf}$, where δ_{hf} is the hyperfine (contact + pseudocontact) contribution and diamagnetic contribution δ_{dia} is the same as δ_{LS}. Assuming that δ_{hf} has the theoretically expected Curie temperature dependence (C/T), one could calculate δ_{obs} according to Equation (9).

$$\delta_{obs} = \{\delta_{LS} + (\delta_{LS} + C/T)[\exp(\Delta S°/R)\exp(-\Delta H°/RT)]\}/ \\ \{1 + \exp(\Delta S°/R)\exp(-\Delta H°/RT)\} \tag{9}$$

C is a constant and $\exp(\Delta S°/R)\exp(-\Delta H°/RT) = K_{obs}$. Thus, $\Delta S°$ and $\Delta H°$ were obtained from the plots of δ_{obs} versus T.

Supporting Information (see also the footnote on the first page of this article): ^{1}H NMR spectroscopic data, spectra, chemical shift plots for complex **I** in different solvents.

Acknowledgments

This work was supported by the Russian Foundation for basic research, grant 03-03-32009.

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Received May 24, 2004