

Spin Crossover Studies on Bis{hydro-tris(1,2,4-triazolyl)borato}iron(II)

Christoph Janiak^{*a}, Tobias G. Scharmann^b, Thomas Bräuniger^b, Jana Holubová^c, Milan Nádvořník^c

^a Freiburg, Institut für Anorganische und Analytische Chemie, Universität Freiburg

^b Berlin, Institut für Anorganische und Analytische Chemie, Technische Universität Berlin

^c Pardubice, Faculty of Technical Chemistry, University of Pardubice, nám Legií 565, 53210 Pardubice, Czech Republic

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Dedicated to Professor Georg Brauer on the Occasion of his 90th Birthday

Abstract. The spin-crossover behavior of bis{hydro-tris(1,2,4-triazolyl)borato}iron(II) is investigated in bulk and as a magnetically diluted sample in the solid state and in solution as a function of temperature by magnetic susceptibility measurements and differential scanning calorimetry. In aqueous solution the low-spin to high-spin transition is shown in turn to decrease the longitudinal relaxation time T_1 of water pro-

tons with increasing temperature. The solid-state magnetically diluted samples were prepared by cocrystallization with the isostructural zinc complex.

Keywords: Spin Crossover; Magnetic Measurements; Iron(II) Compound; Nuclear Magnetic Resonance, T_1 -measurements; Poly(pyrazolyl)borate ligand, modified

Spincrossover-Untersuchungen an Bis{hydro-tris(1,2,4-triazolyl)borato}eisen(II)

Inhaltsverzeichnis. Das Spincrossover-Verhalten von Bis{hydro-tris(1,2,4-triazolyl)borato}eisen(II) wurde in Reinstanz und in magnetischer Verdünnung im Festkörper und in Lösung als Funktion der Temperatur mit Hilfe von magnetischen Suszeptibilitätsmessungen und der dynamischen Differenzkalorimetrie (DSC) untersucht. Es wurde au-

ßerdem gezeigt, daß in wäßriger Lösung durch den low-spin – high-spin Übergang im Gegenzug die longitudinale Relaxationszeit T_1 der Wasserprotonen mit zunehmender Temperatur verringert wird. Die magnetisch verdünnten Festkörperproben wurden durch Cokristallisation mit dem isostrukturellen Zinkkomplex erhalten.

Introduction

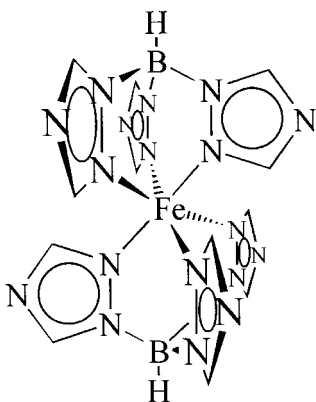
Thermally induced spin-state transitions are a fascinating area in the coordination chemistry of 3d-transition metals with a d^4 to d^7 electron configuration. Temperature induced spin crossover is documented for many Fe(II) systems. Hexacoordinated complexes of iron(II) with nitrogen donor ligands are often very good candidates for the spin transition between the diamagnetic $^1A_{1g}$ low-spin state

($S = 0$) and the paramagnetic $^5T_{2g}$ high-spin state ($S = 2$) with four unpaired electrons [1–3]. As such, the iron complexes of tris(pyrazolyl)borato ligands also exhibit such a spin equilibrium [4–12] and the transition temperature was found to vary strongly with substitution on the pyrazolyl rings or the boron atom [11, 13]. The interplay of the steric effects of substituents with the different sizes of the low- and high-spin Fe(II) ions was demonstrated to be the decisive factor in controlling the relative stability of the spin states [8, 12]. A partial study on the spin transition in the complex bis{hydrotris(1,2,4-triazolyl)borato}iron(II), $\{HB(C_2H_2N_3)_3\}_2Fe^{II}$ (**1**) has appeared [4, 5]. Here, we want to report now the results of the magnetic measurements for **1**, both in the solid state and in solution, thereby also including the behavior of magnetically diluted samples.

* Korrespondenzadresse:

Priv.-Doz. Dr. C. Janiak
Institut für Anorganische und Analytische Chemie
Universität Freiburg
Albertstr. 21
D-79104 Freiburg

Magnetic dilution was achieved by cocrystallization of **1** with the isostructural diamagnetic zinc complex [14] from a solution containing both Fe^{2+} and Zn^{2+} ions.



1

Experimental

Preparation of the compounds: The pure compound **1** was prepared as described previously [4]. The mixed iron/zinc compounds were obtained by dissolving a mixture of combined 1.0 mmol of FeSO_4 and ZnCl_2 (different ratios, see Table 1) in 10 ml of deionized water and overlaying this solution with a solution of 2.0 mmol (510 mg) of $\text{K}[\text{HB}(\text{C}_2\text{H}_2\text{N}_3)_3]$. In the course of days to weeks magenta crystals were growing, which were eventually collected and dried. The yield was in the range of 20 to 50%. The samples were analyzed for their metal content by atom absorption spectroscopy (Perkin-Elmer 2380). Table 1 lists the analyses for the different experiments together with the starting Fe/Zn ratios. The theoretical metal content for **1** is 11.45%, for the analogous zinc complex 13.15%. From the results in Table 1 it is evident that the preset ratio requires verification by the metal analysis. The built-in iron content is usually higher than the starting metal ratio.

Table 1 Analytical results of the magnetically diluted Fe/Zn complexes.

Experiment/ Sample No.	Fe/Zn starting ratio	metal content by AAS [mass %]		Fe/Zn ratio based on metal analyses
		Fe	Zn	
1	20/80	2.7	10.1	24/76
2	40/60	5.5	6.5	48/52
3	60/40	4.8	7.5	42/58
4	80/20	10.5	1.5	92/8
5	60/40	9.1	2.7	79/21
6	70/30	9.8	1.9	86/14
7	80/20	10.6	0.9	93/7
8	90/10	10.5	1.1	92/8

Table 2 Magnetic susceptibility data for **1** in solution determined by the Evans-method^{a)}

Temperature, T [°C/K]	$\Delta\delta$ [ppm]	$\chi_{\text{mass}}^{\text{b)}}$ [$10^{-3} \text{ cm}^3/\text{g}$]	$\chi_{\text{mol}}^{\text{c)}}$ [$10^{-3} \text{ cm}^3/\text{mol}$]	$\mu^{\text{d)}}$ [μ_B]
21.0/294.2	0.046	3.311	1.849	2.095
26.5/299.7	0.055	3.945	2.203	2.308
36.5/309.7	0.074	5.283	2.951	2.715
46.5/319.7	0.088	6.269	3.501	3.005
52.0/325.2	0.096	6.833	3.816	3.163
57.5/330.7	0.105	7.466	4.170	3.335
62.5/335.7	0.116	8.241	4.603	3.530
67.5/340.7	0.124	8.804	4.917	3.676
77.5/350.7	0.140	9.931	5.547	3.961

a) concentration of **1** in H_2O : $c = 3.4 \cdot 10^{-4} \text{ g/ml}$, respectively $7.0 \cdot 10^{-7} \text{ mol/cm}^3$, $M(\text{complex}) = 487.8 \text{ g/mol}$.

b) $\chi_{\text{mass}} = 3/(4\pi) \cdot \Delta\delta \cdot 10^{-6} \cdot 1/c + \chi_{\text{solv}}$; $\chi_{\text{solv}} = 0.72 \cdot 10^{-6} \text{ cm}^3/\text{g}$.

c) $\chi_{\text{mol}} = M(\text{metal}) \cdot \chi_{\text{mass}}$; $M(\text{metal}) = 55.85 \text{ g/mol}$.

d) $\mu/\mu_B = 2.84 \cdot (T \cdot \chi_{\text{mol}})^{1/2}$.

The magnetic susceptibility measurements of the solid mixed iron/zinc complexes (magnetically diluted samples) were carried out with a Faraday magnetic balance. The magnetic susceptibility measurements in solution were carried out according to the Evans method [15]. The concentration of **1** was $3.39 \cdot 10^{-4} \text{ g/ml}$ in H_2O . A 5 mm sample tube with an inner pure H_2O capillary as external reference was employed. The single-scan measurement was done without spinning, sweep and lock. The peak difference ($\Delta\delta$) between the H_2O proton signal of the solution and the capillary was measured. From there the molar susceptibility was calculated with solvent correction. This data is given in Table 2.

All T_1 NMR measurements were performed with degassed and sealed 5 mm samples on a Bruker ARX400 spectrometer using a ^1H inverse detection probe. D_2O was obtained from Merck Sharp & Dohme and the minimum isotopic purity was 99.7%. The T_1 values were determined by the standard inversion recovery method [16] combined with a two parameter non-linear fit of the line intensities. The standard deviations of the fitting parameters were of the order of 1 to 3 percent.

The differential-scanning calorimetry measurements were carried out on a Mettler-DSC.

Solid-state magnetic measurements

Figure 1 shows the result of the temperature-variable magnetic measurement of pure **1**. In agreement with an earlier differential-scanning calorimetry (DSC) measurement and a temperature-variable ^{57}Fe -Mössbauer study a rather steep phase change [1] is observed in the solid state, with a transition temperature $T_{1/2}$ (50% low- and high-spin state) of about 60 °C. The experimental magnetic moment reached above 360 K compares well with spin only value ($\mu_{\text{eff}}/\mu_B = 2[S(S+1)]^{1/2}$) of 4.90 μ_B for a ^5D free ion (Fe^{2+}). The

calculated effective magnetic moment with spin-orbit coupling ($\mu_{\text{eff}}/\mu_{\text{B}} = [L(L+1) + 4S(S+1)]^{1/2}$) would be $5.48 \mu_{\text{B}}$ for a ^5D free-ion ground term.

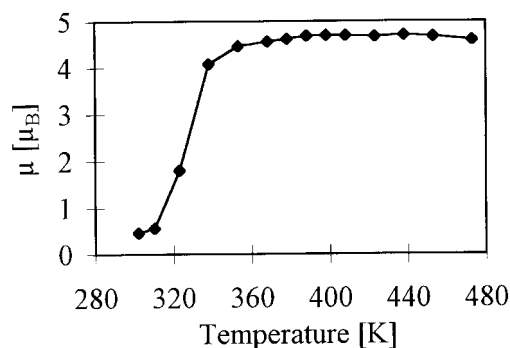


Fig. 1 Temperature variation of the magnetic moment of pure **1** (solid sample)

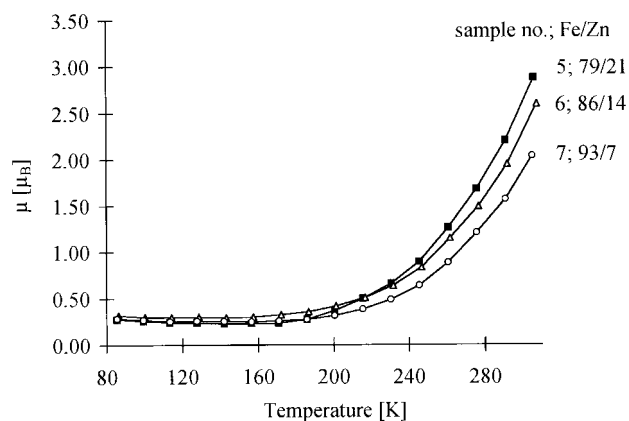
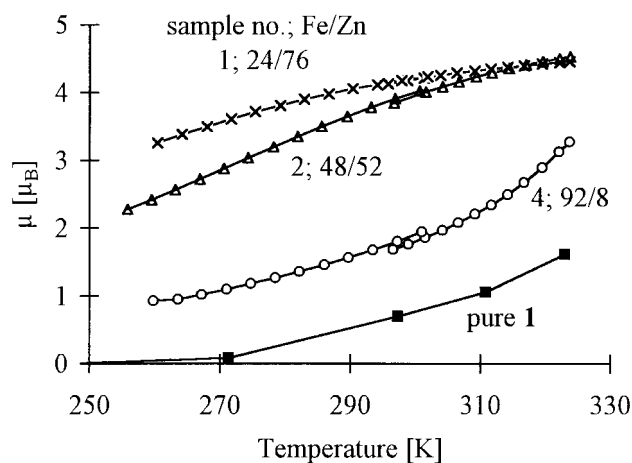


Fig. 2 Temperature variation of the magnetic moment in magnetically diluted samples of **1** (cocrystallized Fe/Zn-complexes). The magnetic moment is based on the iron content of the probe. The sample number (cf. Table 1) together with the iron/zinc ratio is indicated in the diagrams. For clarity, two separate diagrams are provided here, with four or three samples each. The slight discontinuity in the curves for sample 2 and 4 in the upper diagram is due to switching from automatic to manual susceptibility measurements.

In the magnetically diluted samples (Figure 2) one recognizes an increasingly gradual spin-crossover behavior with decreasing iron content. At the same time, the transition temperature is shifted to lower values. This effect demonstrates the importance of cooperative interactions in the spin equilibrium. The key event is the increase of the complex volume with the shift from the shorter metal-ligand bond lengths in the low-spin compound to the longer metal-ligand contacts in the high-spin component. The shift in $T_{1/2}$ to lower temperatures is indicative of a stabilization of the high-spin state. Because of their size difference with respect to iron, the zinc-complex molecules are equivalent in their effect to an external lower pressure. A higher pressure favors the smaller low-spin complex, a lower pressure the larger high-spin derivative [1].

With the spin transition becoming more and more gradual, also the DSC signal which can be used to monitor the phase transition broadens before it eventually vanishes (Figure 3).

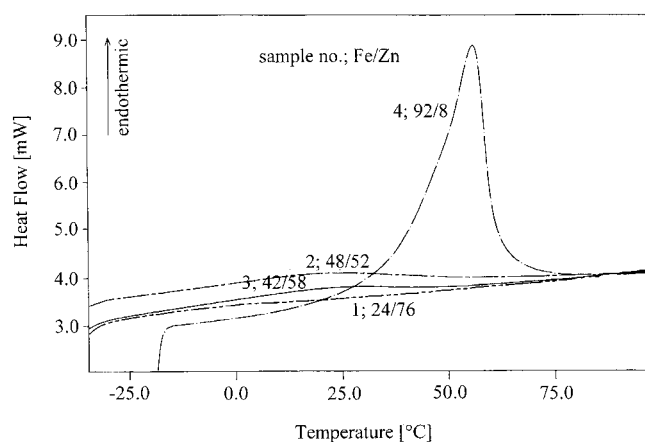


Fig. 3 DSC diagram for magnetically diluted samples of **1** (cocrystallized Fe/Zn-complexes). The sample number (cf. Table 1) together with the iron/zinc ratio is indicated in the diagram

Solution magnetic measurements

The spin-crossover phenomenon of **1** could also be verified in an aqueous solution of the compound. Figure 4 shows the temperature dependence of the magnetic moment in solution as measured according to the Evans method [15]. Again a gradual spin transition is evident, as expected [1]. The fact that the spin equilibrium even exists in very dilute solution (concentration = $3.4 \cdot 10^{-4}$ g/ml or $7.0 \cdot 10^{-7}$ mol/ml) indicates that the spin crossover in **1** is primarily an entropy-driven intramolecular phenomenon. An interaction with neighboring complex molecules is no prerequisite in **1**.

A direct comparison of the crossover behavior in dilute solution and in a magnetically diluted solid-state sample as given in Figure 5 is interesting. Despite the higher dilution in the solution probe, the

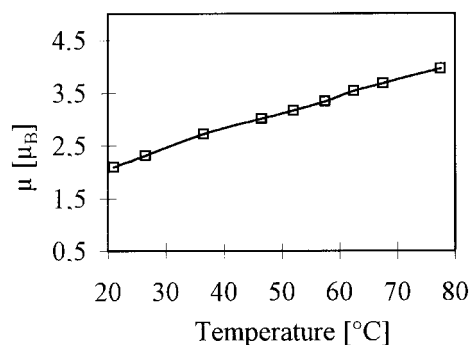


Fig. 4 Temperature variation of the magnetic moment of **1** in aqueous solution

transition temperature clearly still lies at a higher value. This may be traced to a matrix effect, such that in solution the water cage around the complex molecule creates a positive pressure and thereby stabilizes the low-spin form, in contrast to the zinc complex matrix which exerts a negative pressure (see above). Secondly, the water matrix may also slightly modify the energy separation between the low- and high-spin state through (exodentate) $N \cdots H-O$ bonding which in turn influences slightly the ligand-field strength of the nitrogen donor atoms. The existence of such $N \cdots H-O$ hydrogen bridge bonding has been proven by the single-crystal X-ray structures of **1** and related molecules which showed the incorporation of six water molecules of crystallization, two of which were hydrogen bonded to the complex fragment [14, 17].

The effect of spin-crossover on the water matrix of a solution of **1**

Conversely, we wanted to test how the spin transition of **1** effects the surrounding matrix. The magnetic properties of **1**, i. e. low-spin to high-spin crossover phenomenon and the concomitant transition from a diamagnetic to a paramagnetic species, suggested that it

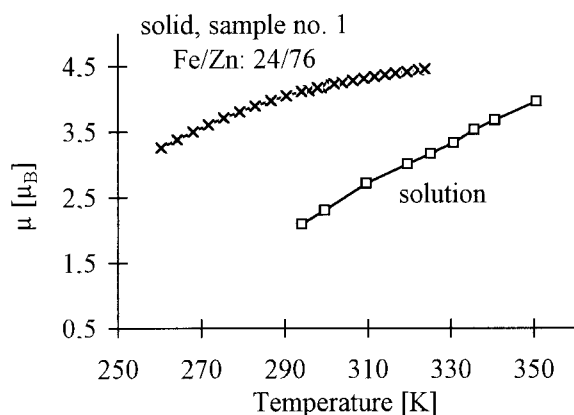


Fig. 5 Comparison of the temperature variation of **1** in a magnetically diluted solid-state sample and in aqueous solution

should influence the longitudinal relaxation time T_1 of protons. To test for such an effect of dissolved **1** we measured the relaxation time T_1 and their temperature dependence for protons in D_2O for different concentrations of **1**.

The time T_1 determines the rate of reestablishing the thermal equilibrium of nuclear magnetic moments after applying a radiofrequency pulse to a sample placed in a magnetic field, as done in nuclear magnetic resonance (NMR) spectroscopy or magnetic resonance imaging (MRI). As the relaxation process is mediated by fluctuating local magnetic fields [18, 19], paramagnetic species have generally a significant effect on the relaxation time of the surrounding solvent. The large magnetic moment of the unpaired electron(s) in such species leads to a decrease in T_1 [20]. Moreover, a solution of 1,2,4-triazole in an equivalent concentration was prepared to model the ligand without the central atom.

It is important to note that the relaxation time of H_2O in D_2O is a function of the D_2O/H_2O ratio and differs substantially from that of pure H_2O due to the smaller magnetic moment of the deuteron. The T_1 value for the 99.7% D_2O was about 34 s at room temperature, as has to be expected for this concentration range [21]. With rising temperature and increasing mobility of the water molecules, the relaxation time T_1 increases (Figure 6), as predicted by theory [18, 19]. Upon addition of 1*H*-1,2,4-triazole essentially the same behaviour is observed (Figure 6); T_1 increases from 28.6 s at 27 °C to 57 s at 77 °C. The triazole concentration was set such as to correspond to the concentration of the triazole moieties or six times to the concentrations of the iron complex in the subsequent experiments with **1**.

The presence of the iron complex **1** lowers the relaxation times dramatically, as shown in Figure 7. It should be stressed here that the relaxation time of the water protons in the D_2O solution of **1** decreases with rising temperature, quite in contrast to the general tendency of T_1 in non-paramagnetic solutions. This is

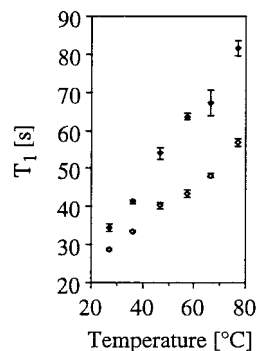


Fig. 6 Relaxation time T_1 of the H_2O -protons as a function of temperature in a 99.7% D_2O mixture (◆) and upon addition of 1*H*-1,2,4-triazole (conc. 16 mmol/l) (◇) (data points with error bars)

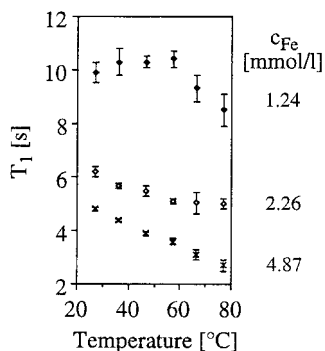


Fig. 7 Relaxation time T_1 of the H_2O -protons in 99.7% D_2O in the presence of **1** as a function and for three different concentrations of **1** (data points with error bars)

obviously caused by the largening portion of paramagnetic iron centers with higher temperature in line with the magnetic measurements or the Mößbauer studies [5]. Solvent relaxation must proceed by an outer-sphere relaxation mechanism here, as there is no likely opening in the iron coordination sphere provided by the two tris-chelate ligands. Hydrogen bonding interactions to the exodentate nitrogens of triazolyl rings which were shown to be present in the crystalline state [16, 17] can play a dominant role in the electron-nuclear dipolar interaction.

To examine the concentration dependence of the described effect, the relaxation time was measured for three different concentrations of **1** in D_2O (cf. Figure 7). For 77 °C, where the iron complex is predominantly paramagnetic, the results are plotted in Figure 8. Generally, the longitudinal relaxation rate, $1/T_1$, should be linearly dependent on the concentration of the paramagnetic species [19]. The three concentrations measured give a reasonably good linear correlation ($R = 0.998$) as can be seen in Figure 8. The slope of the line, commonly referred to as relaxivity, was determined to be 0.069.

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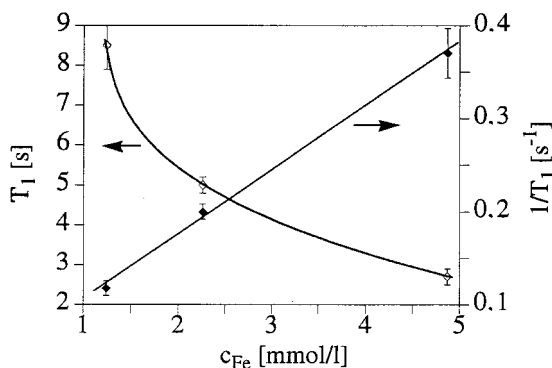


Fig. 8 Change of the relaxation time T_1 and relaxivity $1/T_1$ for the H_2O -protons with the concentration of **1** at 77 °C

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