Spin-Crossover Complexes in Solution, II Solvent Effects on the High Spin-Low Spin-Equilibrium of [Fe(*bzimpy*)$_2$](ClO$_4$)$_2$**

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Summary. The influence of the solvent on the spin-equilibrium of [Fe(*bzimpy*)$_2$](ClO$_4$)$_2$ (*bzimpy* = 2,6-bis(benzimidazol-2'-yl)pyridine) has been investigated in several nonaqueous solvents by means of UV-Vis spectroscopy and magnetic susceptibility measurements. In methanol, a bis-tris ligation equilibrium is found. Both, the FeL_2^{2+} and FeL_3^{2+} species show spin-crossover behaviour in solution. Photometric and magnetic properties of the complex in various solvents are related. The spin-equilibrium of [Fe(*bzimpy*)$_2$](ClO$_4$)$_2$ shows the strongest sensitivity towards changes of the solvent that has ever been observed for spin-crossover compounds. Increase in solvent donor number (DN) from DN = 14.1 (Acetonitril) to DN = 19.1 (Methanol) causes a shift from μ_{exp} = 4.21 (78% High-Spin (HS)) to μ_{exp} = 3.0 (56% HS). In solvents with DN ⩾ 30 deprotonation of the complex occurs yielding a low-spin species. The solvent effects are discussed in terms of the donor–acceptor concept.

Keywords. 2,6-Bis(benzimidazol-2'-yl)pyridine; Solvent effects; Spin-crossover; Thermochromism.

Spin-Crossover-Komplexe in Lösung, 2. Mitt.: Lösungsmitteleinflüsse auf das High Spin-Low Spin-Gleichgewicht von [Fe(*bzimpy*)$_2$](ClO$_4$)$_2$

Zusammenfassung. Der Einfluß des Lösungsmittels auf das Spin-Gleichgewicht von [Fe(*bzimpy*)$_2$]·(ClO$_4$)$_2$ (*bzimpy* = 2,6-bis(benzimidazol-2'-yl)pyridin) wurde in mehreren nichtwäßrigen Lösungsmitteln durch UV-Vis-Spektroskopie und magnetische Suszeptibilitätsmessungen untersucht. In Methanol wird ein bis-tris-Komplexbildungs-gleichgewicht gefunden, wobei sowohl FeL_2^{2+} als auch FeL_3^{2+} Spin-crossover-Verhalten in Lösung zeigen. Die photometrischen und magnetischen Eigenschaften des Komplexes in verschiedenen Lösungsmitteln sind miteinander korreliert. Das Spin-Gleichgewicht von [Fe(*bzimpy*)$_2$](ClO$_4$)$_2$ zeigt von allen bisher untersuchten Spin-crossover-Verbindungen die stärkste Beeinflußbarkeit durch das Lösungsmittel. Eine Zunahme der Lösungsmittel-Donorzahl (DN) von DN = 14.1 (Acetonitril) auf 19.1 (Methanol) bewirkt eine Verschiebung von μ_{exp} = 4.21 (78% High-Spin (HS)) auf μ_{exp} = 3.0 (56% HS). In Lösungsmitteln mit DN ⩾ 30 erfolgt Deprotonierung zu einer Low-Spin Species. Der Lösungsmitteleinfluß wird unter Anwendung des Donor–Akzeptor-Konzeptes diskutiert.

** Dedicated to Professor Harry J. Eméleus with heartiest congratulations to his 90th birthday on 22th June 1993.

Introduction

Transition metal complexes which show thermally induced crossover equilibria between high spin (HS) and low spin (LS) electronic states are known for more than sixty years [1]. Since both spin-isomers differ only little in energy, their equilibria are affected by a variety of parameters within their environment. Static and dynamic aspects of such equilibria in the solid state have been reviewed [2–6] but little attention has been paid to systems in liquid solutions [5, 7–10]. With the extended donor–acceptor concept established by Gutmann [11], a useful tool is available for the qualitative and quantitative description of solute-solvent interactions. In the present paper we apply this concept to observations made with nonaqueous solutions of $[Fe(bzimpy)_2](ClO_4)_2$ ($bzimpy$ = 2,6-bis(benzimidazol-2'-yl)pyridine (I)). This compound has been shown to exhibit spin-crossover behaviour in the solid state [12, 13] and it provides the first example of an investigation on solvent effects towards a substitutional labile spin-crossover compound.

Experimental Part

Materials.– $FeCl_2 \cdot 4H_2O$ (Riedel, p.a.) was used as received. 2,6-Bis(benzimidazol-2'-yl)pyridine was prepared by the method of Addison and Burke [14] and recrystallized three times from pure *MeOH*. The purity of the ligand was satisfying according to ^{1}H-NMR measurements (δ in C_2D_5OD: 7.93–7.90 (pyridine ring), 7.68–7.61 (pyridine ring), 7.30–7.17 (benzene ring), 6.90–6.80 (benzene ring)). $[Fe(bzimpy)_2](ClO_4)_2$ was prepared according to literature [12] (Found: C 51.94, H 2.96, N 15.93, Cl 8.13%; calc. for $C_{38}H_{26}Cl_2FeN_{10}O_8$: C 52.02, H 2.99, N 15.96, Cl 8.08%).

Solvents. – For all distillations performed, the first 10% of the distillate was discarded. Starting materials were reagent grade unless otherwise noted. The water content of all solvents except acetone was analysed by Karl Fischer titration and was found to be below $100 \, mgl^{-1}$ throughout all measurements. Commercial grade acetone (Ac) was distilled twice off $CaSO_4$ and once off B_2O_3. Acetonitril (An) was refluxed once off NaOH and twice of P_2O_5. Spectroquality grade cyclohexane was used as purchased from Merck. Dimethylsulfoxide ($DMSO$) was dynamically dried with molecular sieve 4Å and subsequently distilled under reduced pressure. Hexamethylphosphoric acid triamide ($HMPA$) was fractionally distilled under reduced pressure. Commercial grade methanol ($MeOH$) was refluxed for 24 h over CaO and fractionally distilled. Nitrobenzene (NB) was refluxed for two hours over P_2O_5 under reduced pressure and was subsequently fractionally distilled. Nitromethane (NM) Fluka, p.a.) was used as received. Propanediolcarbonate (PDC) was refluxed for 24 h under reduced pressure and subsequently fractionally distilled.

Solutions.– Investigations on the bis/tris-equilibrium of the system $FeCl_2 \cdot 4H_2O/bzimpy/MeOH$ were performed at a Fe^{2+}-concentration range of $1 \cdot 10^{-4}M$–$1.4 \cdot 10^{-3}M$ with ligand to metal (L/M) ratios between 0 and 45. In contrast to prior experiments [14], air-saturated $MeOH$ was used as a solvent since a slow oxygen diffusion process towards air-free $MeOH$ was found to cause major disturbances with the NMR experiments than partial oxidation of Fe^{2+}. The actual Fe^{2+}-content was determined from photometric measurements. The magnetic moments were corrected for the Fe^{3+}-contribution.

UV-Vis and NMR measurements in further solvents were carried out in a concentration range of 1.6–$4.6 \cdot 10^{-4}M$ $[Fe(bzimpy)_2](ClO_4)_2$ using air saturated solvents. Oxidation effects were found to be neglegible for the L/M ratios applied ($\geqslant 2$) and within the period of measurements (3–5 h).

Physical Methods.– UV-Vis absorption spectra (190–1100 nm) were obtained on a Hitachi U-2000 spectrophotometer. A Hitachi electronic thermostatted cell holder in the range of 0–100 °C provided temperature control (± 0.5 °C) and temperatures were recorded using a CC thermocouple. A

homogeneous temperature and concentration distribution within the cells was ensured by a magnetic stirrer. Due to the pronounced thermochromism of the system under study, temperature-constancy could be easily followed on an absorbance vs. time plot; a constant value was reached after 6 minutes.

Solution state magnetic suszeptibilities were obtained by the NMR technique of Evans [15, 16]. Cyclohexane in concentrations of 0.1–0.2% v/v was used as the reference compound. Magnetic moments were calculated using Eqs. (1) and (2), where

$$\chi_M = (3\Delta\Delta v \cdot 10^{-3}/4\pi M)$$ (1)

$$\mu_{exp} = 2.84 \cdot \sqrt{\chi_M \cdot T}$$ (2)

$\Delta\Delta v$ is the paramagnetic shift of the reference compound that has been corrected for the diamagnetic contribution of the ligand and M is the molarity of the paramagnetic ion. The diamagnetic correction for bzimpy has been determined experimentally in a concentration range from 0–$7.8 \cdot 10^{-3} M$ in $MeOH$ at 298 K (Eq. 3).

$$\Delta v[\text{ppm}] = -0.913503 \cdot (bzimpy)_T [\text{mol}\,1^{-1}] - 4.7 \cdot 10^{-5}$$ (3)
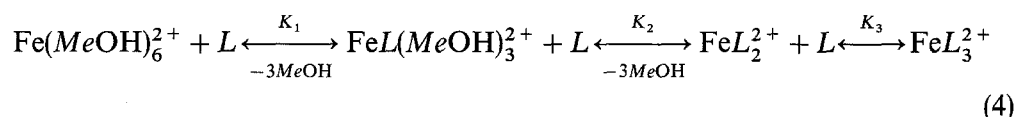
The value $\chi_M(\text{exp.}) = -218.1 \cdot 10^{-6}$ cgs mol^{-1} for *bzimpy* is significantly less than the value calculated from Pascal constants ($-184.4 \cdot 10^{-6}$ cgs mol^{-1}) [17]. Other aromatic systems like phenantrene or indol show deviations of a similar magnitude between calculated and experimental values [18].

Proton NMR spectra were measured on a Bruker AC 250 FT spektrometer operating at 250 MHz. All NMR spectra were recorded at a constant temperature of 298 ± 0.2 K, using a variable temperature accessory. High precision NMR sample tubes of type 528-PP were obtained from Wilmad Glass Co., New Jersey. A sealed Wilmad coaxial insert (WGS-5BL) containing 5% v/v TMS in acetone-d_6 was used as an external standard and instrument lock.

Results and Discussion

Complex Formation Equilibrium in Methanol

As pointed out [14], *bzimpy* is capable of forming three ligated species with Fe^{2+} in $MeOH$. The equilibria given in (4) are based on results obtained by the molar ratio method: a clearly distinct three step deprotonation behaviour of the complex solution

$$\text{Fe}(MeOH)_6^{2+} + L \underset{-3MeOH}{\overset{K_1}{\longleftrightarrow}} \text{Fe}L(MeOH)_3^{2+} + L \underset{-3MeOH}{\overset{K_2}{\longleftrightarrow}} \text{Fe}L_2^{2+} + L \overset{K_3}{\longleftrightarrow} \text{Fe}L_3^{2+}$$

(4)

and a good agreement between calculated and experimental values was obtained using a curve fitting procedure with Eq. (4). Two of the species, FeL_2^{2+} and FeL_3^{2+}, are supposed to show spin-crossover behaviour according to their photometric properties [14]. Formation constants (Table 1) have been obtained by fitting UV-Vis and magnetic data to the scheme given in Eq. (4).

Concerning the coordinating abilities, *bzimpy* has been argued to act most likely as tridendate in FeL_2^{2+} and as bidendate in FeL_3^{2+} [14]. For the double ligated species, the experimental results of photometric titrations in $MeOH$–CHCl$_3$ mixtures favour tridendate ligand molecules [14], the spectral and magnetic properties of FeL_2^{2+} (Table 1) are indicative for a weaker ligand field in comparison to FeL_3^{2+}. The latter results are consistent with a [Fe($MeOH$)$_2L_2$]$^{2+}$-structure and bidendate ligand molecules.

Table 1. Formation constants, photometric and magnetic parameters of $[\text{Fe}(bzimpy)_n]^{2+}$-complexes in MeOH at 25 °C

n	$\log K_n$[a]	ε_{557nm} $[\text{l}\,\text{mol}^{-1}\,\text{cm}^{-1}]$	μ_{exp} $[\mu_B]$
1	5.46 ± 0.1	270 ± 20	5.37 ± 0.1
2	4.65 ± 0.1	5580 ± 300	4.0 ± 0.1
3	3.49 ± 0.1	6400 ± 50	3.0 ± 0.1

[a] At higher Fe^{2+}-concentrations ($\sim 10^{-3}M$) small deviations of K_2 and K_3 to lower values have been observed. Ion-pairing, which has been reported for other Fe(II) spin-crossover systems [19, 20] is a possible explanation for this effect

Table 2. Electronic spectral and magnetic data for $[\text{Fe}(bzimpy)_2](\text{ClO}_4)_2$ in nonaqueous solvents

Solvent	DN	λ_{max} [nm]	ε[a,b] $[\text{l}\,\text{mol}^{-1}\,\text{cm}^{-1}]$	μ_{exp}[a,c] $[\mu_B]$
MeOH	19.1	557	6770 ± 100	3.0 ± 0.1
Ac	17.0	555	5600 ± 200	3.86 ± 0.1
An	14.1	552	4700 ± 300	4.21 ± 0.1
NB	4.4	557	6800 ± 400	3.29 ± 0.2
NM	2.7	554	6800 ± 300	3.35 ± 0.2
PDC	15.1	554	5900 ± 200	4.80 ± 0.2

[a] With an excess of $bzimpy$ to suppress ligand dissoziation
[b] At 20 °C
[c] At 25 °C

Table 3. Thermodynamic parameters for the thermochromic behaviour of $[\text{Fe}(bzimpy)_2](\text{ClO}_4)_2$ in nonaqueous solvents

Solvent	ΔH[a] $[\text{kJ}\,\text{mol}^{-1}]$	ΔS[a] $[\text{J}\,\text{mol}^{-1}\,\text{K}^{-1}]$	$K\,(298\,\text{K})$[b]	$\mu_{calc.}$[c,d] $[\mu_B]$	μ_{exp}[d] $[\mu_B]$
MeOH	17.0	60.9	1.63	3.33	3.00
Ac	19.0	71.6	2.53	3.85	3.86
An	21.3	82.9	3.91	4.28	4.21
NM	18.1	67.3	2.21	3.70	3.35
PDC[e]	19.7 ± 2.3	68.3 ± 6	1.30	3.04	4.80

[a] Errors are estimated to be $\pm 10\%$
[b] Calculated (Eq. 5)
[c] Under the assumption of $\mu_{HS} = 5.37\,\mu_B$ and $\mu_{LS} = 0.0\,\mu_B$
[d] At 25 °C
[e] Resulting from a four parameter fit; $\varepsilon_{HS} = 1130 \pm 360\,\text{l}\,\text{mol}^{-1}\,\text{cm}^{-1}$, $\varepsilon_{LS} = 12000 \pm 1000\,\text{l}\,\text{mol}^{-1}\,\text{cm}^{-1}$

Regardless of the structure of the inner coordination sphere, magnetic moments and molar absorbance coefficients for FeL_2^{2+} as well as FeL_3^{2+} are typical for a mixture of two spin isomers in both cases. This is the first time that simultaneous spin-crossover behaviour of differently ligated species is observed in one solution.

Solvent Effects on [Fe(*bzimpy*)₂])(ClO₄)₂

The data on optical and magnetochemical properties of [Fe(*bzimpy*)₂](ClO₄)₂ in various solvents of low and medium DN are summarised in Table 2. To eliminate all dissoziation and ligation equilibria, a sufficient ligand excess has been applied to obtain the highest ligated species. Since characterization of these species was not successful in other solvents than *Me*OH, both possibilities found in *Me*OH (FeL_2^{2+} and FeL_3^{2+}) have to be taken into account.

As can be seen from Fig. 1, both, molar absorbance coefficients and magnetic moments can be used for evaluating the spin equilibrium constant. The intensity of the metal to ligand charge transfer (MLCT)-band in the visible region increases with the low spin (LS)-fraction of the complex solution (i.e. decreasing magnetic moments), the band position is simultaneously shifted towards higher wavelength. This observation is in accordance with the assumption of an equilibrium of two spin isomers with different electron spectra. The LS-form is absorbing at higher wavelength than the HS-form, having approximately the ten-fold absorbance coefficients in comparison to the latter.

Both, the magnetic moment and the absorbance of the dissolved complex are found to depend highly on the solvent. The behaviour of [Fe(*bzimpy*)₂](ClO₄)₂ deviates in PDC. According to Fig. 1, a lower magnetic moment than the experimental one is expected. This may be explained by a structure of the inner
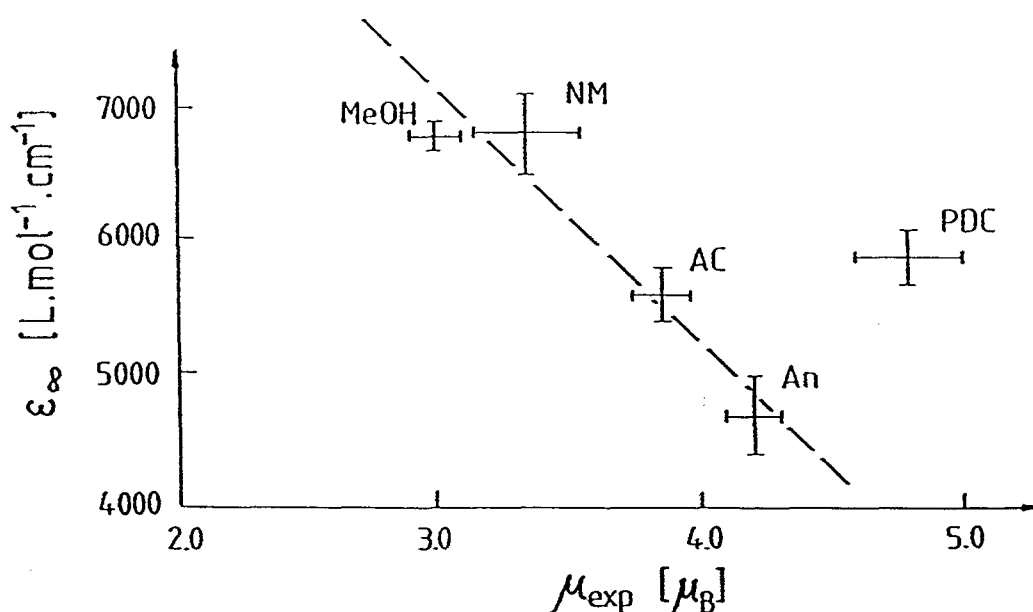

Fig. 1. Relation between molar absorbance coefficients and magnetic moments of [Fe(*bzimpy*)₂](ClO₄)₂ with ligand excess in various solvents
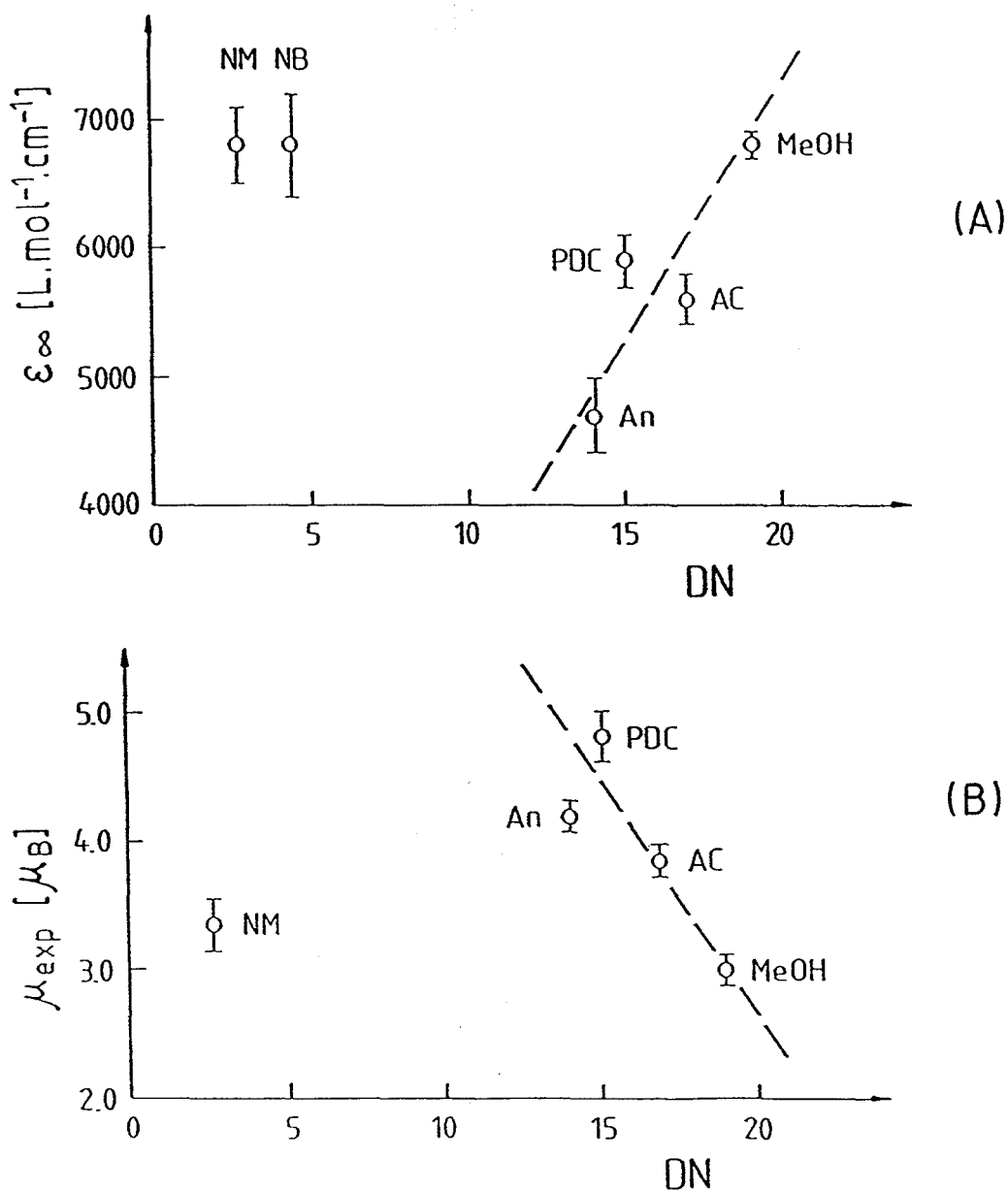
Fig. 2. Dependence of molar absorbance coefficients (A) and magnetic moments (B) of $[Fe(bzimpy)_2]$·$(ClO_4)_2$ – solutions on the solvent donor number

coordination sphere which is different in this solvent. In Fig. 2 both parameters are plotted versus the solvent donor number. The weak donating nitro-compounds NM and NB deviate from the observed relationship.

An increase in DN causes a shift to the LS-side of the spin equilibrium. Thus, increasing donor number of the solvent has the same effect as decreasing temperature. Similar behaviour has been found for the coordination spin equilibria of Ni(II)-diamine-diketonate complexes [21]: At high DN's resp. low temperatures, a

paramagnetic form with octahedral structure and at high temperatures resp. low DN's a planar, diamagnetic form is favoured.

The spin-equilibrium of [Fe(*bzimpy*)₂](ClO₄)₂ shows the most pronounced sensitivity towards changes of the solvent that has ever been observed for spin-crossover compounds. An increase in the solvent donor number (DN) from $DN = 14.1$ (Acetonitrile) to $DN = 19.1$ (Methanol) causes a shift from $\mu_{exp} = 4.21$ (78% High-Spin (HS)) to $\mu_{exp} = 3.0$ (56% HS). For the substitutional stable [Fe(*Sal₂trien*)]PF₆, the solvent effects are much smaller (μ_{exp} in *An*: 5.01 μ_B (78.3% HS) and in *MeOH*: 4.81 μ_B (73.5% HS)) [8].

In analogy to [Fe(*Sal₂trien*)]PF₆, a coordinative bond between the imidazol proton of bzimpy and the donor solvent is obvious. A strengthening of this bond with increasing solvent donor number causes a lengthening of the amine N–H-bond [11] until deprotonation occurs at $DN \sim 30$. The deprotonating power of solvents with $DN \geqslant 30$ has been shown before by means of spectrophotometric titrations [4]. Susceptibility measurements revealed that a solution of [Fe(*bzimpy*)₂](ClO₄)₂ in *HMPA* contains only the LS-form

Since the thermochromic behaviour of the complex-solvent system reflects the temperature sensitivity of the spin equilibrium, temperature dependent absorbance measurements have been made to obtain information on the thermodynamics of the spin-crossover in solution. The experimental data were corrected with respect to temperature induced density changes and were fitted to Eqs. (5) and (6).

$$\Delta H - T\Delta S = -RT \ln K \tag{5}$$

$$K = x_{HS}/x_{LS} = (\varepsilon_{obs} - \varepsilon_{LS})/(\varepsilon_{HS} - \varepsilon_{obs}) \tag{6}$$

For *MeOH*, *Ac*, *An*, and *NM*, the linear dependence between ε and μ_{exp} (Fig. 1) was used to calculate ε_{HS} and ε_{LS}: The Equation $\varepsilon_{obs} = x_{HS} \cdot \varepsilon_{HS} + (1 - x_{HS}) \cdot \varepsilon_{LS}$ was solved for these four solvents using x_{HS} from suszeptibility measurements. Values of $\varepsilon_{HS} = 2030 \, l \, mol^{-1} cm^{-1}$ and $\varepsilon_{LS} = 14550 \, l \, mol^{-1} cm^{-1}$ have been obtained this way.

Spin equilibrium constants and the corresponding magnetic moments have been calculated from $\Delta H°$ and $\Delta S°$. The correlation between μ_{exp} and μ_{calc} is satisfying and confirms the agreement between spectrophotometric and magnetic results as stated above.

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