Inorg. Chem. **2007**, *46*, 6794–6803

Inorganic Chemistry
Article

Solution NMR Studies of Iron(II) Spin-Crossover Complexes

Birgit Weber*,[†] and F. Ann Walker[‡]

Department of Chemistry and Biochemistry, Ludwig Maximilian University Munich,
Butenandtstrasse 5−13 (Haus D), D-81377 München, Germany, and Department of Chemistry,
The University of Arizona, Tucson, Arizona 85721-0041

Received December 8, 2006

The ^{1}H NMR spectra of a series of mono- and dinuclear pyridine complexes [FeL1(R^1/R^2)(py)$_2$] and [Fe$_2$L2(R^1/R^2)(py)$_4$] have been investigated in a mixed toluene-*d*$_8$/pyridine-*d*$_5$ solution. The equatorial tetradentade Schiff base like ligands L1(R^1/R^2) and L2(R^1/R^2) with a $N_2O_2{}^{2-}$ coordination sphere for each metal center have been obtained by condensation of a substituted malonodialdehyde (R^1/R^2 are Me/COOEt, Me/COMe, or OEt/COOEt) with *o*-phenylenediamine (L1(R^1/R^2)) or 1,2,4,5-tetraaminobenzene (L2(R^1/R^2)). The ^{1}H NMR resonances were assigned by comparison of differently substituted complexes in combination with a line-width comparison. The ^{1}H NMR shifts from 188 to 358 K show a strong influence of the spin state of the iron center. The behavior of the pure high-spin iron(II) complexes is close to ideal Curie behavior. Analysis of the resonance shifts of the spin-transition complexes can be used for determining the high-spin mole fraction of the complex in solution at different temperatures. Magnetic susceptibility measurements in solution using the Evans method were made for all six complexes. Significant differences between the spin-transition behavior of the complexes in solution of those in the solid state were found. However, the plots of μ_{eff} as a function of temperature obtained using the Evans method and those obtained by interpretation of the NMR shifts were virtually identical. The isotropic shifts of protons in the complexes proved to be suitable tools for following a spin transition in solution. Comparison of the μ_{eff} plots of the mono- and dinuclear complexes in solution reveals slight differences between the steepness of the curves that may be attributable to cooperative interactions between the metal centers in the case of the dinuclear complexes.

Introduction

Thermally induced spin transitions (spin crossover, SCO) without a change in the coordination number at the central atom are quoted to be one of the most spectacular examples of molecular bistability.[1,2] The mechanism of temperature-dependent spin transitions in mononuclear complexes, especially the high spin (HS; $S = 2$) $\rightleftharpoons$ low spin (LS; $S = 0$) transition in octahedral iron(II) complexes, is now well understood and investigated.[3−8] The change of the spin state is accompanied by a change in the molecular size that is transmitted cooperatively through the crystal via intermolecular interactions.[3−7] A high cooperativity between the molecules leads to sharp spin transitions, sometimes even with hysteresis (memory effect).[2,9] The mechanism of cooperativity in spin-transition compounds is well understood in terms of the model of internal pressure introduced by Spiering et al.[10,11] However, the question of how to design such strongly cooperative complexes has still not been answered satisfactorily. A key factor is the effectiveness of the intermolecular contacts. The use of rigid linkers, which

---

[*] To whom correspondence should be addressed. E-mail: bwmch@cup.uni-muenchen.de.
[†] Ludwig Maximilian University Munich.
[‡] The University of Arizona.

(1) Gütlich, P.; Hauser, A.; Spiering, H. *Angew. Chem., Int. Ed. Engl.* **1994**, *106*, 2109−2141.
(2) Kahn, O.; Martinez, J. C. *Science* **1998**, *279*, 44−48.
(3) Gütlich, P.; Goodwin, H. A. *Spin Crossover in Transition Metal Compounds*; Springer-Verlag: Heidelberg, Germany, 2004; Vols. I−III.
(4) König, E. *Struct. Bonding* **1991**, *76*, 51−152.
(5) Bousseksou, A.; Molnár, G.; Matouzenko, G. *Eur. J. Inorg. Chem.* **2004**, 4353−4369.
(6) Gütlich, P.; Ksenofontov, V.; Gaspar, A. B. *Coord. Chem. Rev.* **2005**, *249*, 1811−1829.
(7) Boillot, M.-L.; Sour, A.; Delhaès, P.; Mingotaud, C.; Soyer, H. *Coord. Chem. Rev.* **1999**, *190−192*, 47−59.
(8) Real, J. A.; Gaspar, A. B.; Muñoz, M. C. *Dalton Trans.* **2005**, 2062−2079.
(9) Real, J. A.; Gaspar, A. B.; Niel, V.; Muñoz, M. C. *Coord. Chem. Rev.* **2003**, *236*, 121−141.
(10) Spiering, H.; Kohlhaas, T.; Romstedt, H.; Hauser, A.; Bruns-Yilmaz, C.; Kusz, J.; Gütlich, P. *Coord. Chem. Rev.* **1999**, *190−192*, 629−647.
(11) Hauser, A.; Jeftic, J.; Romstedt, H.; Hinek, R.; Spiering, H. *Coord. Chem. Rev.* **1999**, *190−192*, 471−491.

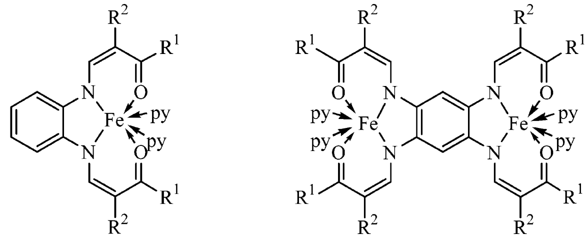
10.1021/ic062349e CCC: $37.00

allow communication between the SCO centers by the formation of 1D chains, 2D layers, or 3D networks, is one strategy for the designed synthesis of such compounds.[9,12]

The simplest spin-coupled polymer systems are dinuclear SCO with suitable bridging ligands. The investigation of such compounds provides fundamental information about the intramolecular magnetic interactions. At present, several families of dinuclear complexes have been investigated. One is the family of bpym (2,2′-bipyrimidine)-bridged complexes investigated by Real et al.[13−17] Partial, one-step, and two-step SCOs with spin-paired LS−LS, HS−LS, and HS−HS states have been achieved. Another family is bpypz (3,5-bis(pyridine-2-yl)pyrazolate)-bridged dinuclear iron complexes, where the first abrupt SCO without a two-step process was observed, and the X-ray structures for both the HS and LS forms were characterized.[18,19] We were able to introduce a new type of dinuclear iron(II) complex where, instead of bridging ligands, a dinucleating chelate ligand is used to link the two iron centers together.[20]

However, because the magnetic susceptibility of the complexes is measured in the solid state, the question arises as to whether the observed properties are due to intermolecular or intramolecular interactions. Indeed, the features of the spin transition are often influenced by sample preparation (e.g., grinding).[21,22] To switch off packing effects, investigations in diluted systems are necessary. The Evans method[23−26] is one possible means of measuring the susceptibility of paramagnetic compounds in solution, and it therefore allows one to obtain an answer to the question of whether the observed magnetic properties in dinuclear complexes are due to the dinucleating bridging unit or to packing effects. Recently, an example of dinuclear complexes that shows a stepwise or incomplete spin transition in the solid state but a gradual one-step transition in solution has been reported.[27] One disadvantage of the Evans method is a relatively high error of 5−10%,[28] depending on the concentration of the paramagnetic solute. Additionally, only the bulk susceptibility of the solution is measured, and diamagnetic or paramagnetic impurities can lead to incorrect conclusions. This is especially true in the case of air-sensitive iron(II) complexes. Therefore, we looked for an alternative technique for investigating iron(II) spin transitions in solution. The application of solution NMR spectroscopy to paramagnetic molecules and biomolecules has been reported for more than 35 years.[29−33] It was shown to be a useful and sensitive method for detecting changes in the electronic ground state (including spin transitions) in transition-metal complexes, and there are a number of textbooks and extensive reviews dealing with this topic.[29−33] We will show that it is possible to use this method for investigating iron(II) spin transitions in solution by interpreting the chemical shifts of the ^{1}H NMR spectra of these complexes.

Scheme 1. General Formulas of the Mono- and Dinuclear Complexes of Schiff Base Like Ligands Investigated in This Work and the Abbreviations Used



[FeL1(R^1/R^2)(py)$_2$]   **[Fe$_2$L2(R^1/R^2)(py)$_4$]**

R^1 = Me; R^2 = COOEt
R^1 = Me; R^2 = COMe
R^1 = OEt; R^2 = COOEt

Scheme 1 displays the structures of the complexes investigated in this work and the abbreviations used. The mononuclear complexes were first investigated by Jäger et al.[34,35] The corresponding dinuclear complexes were obtained by using 1,2,4,5-tetraaminobenzene instead of *o*-phenylenediamine. The solid-state magnetic properties of the mono- and dinuclear complexes with pyridine as axial ligands were reported previously.[20,34] For mononuclear [FeL1(Me/COO-

---

(12) Niel, V.; Thompson, A. L.; Muñoz, M. C.; Galet, A.; Goeta, A. E.; Real, J. A. *Angew. Chem., Int. Ed.* **2003**, *42*, 3760−3763.

(13) Real, A.; Zarembowitch, J.; Kahn, O.; Solans, X. *Inorg. Chem.* **1987**, *26*, 2939−2943.

(14) Real, J. A.; Castro, I.; Bousseksou, A.; Verdaguer, M.; Burriel, R.; Castro, M.; Linares, J.; Varret, F. *Inorg. Chem.* **1991**, *36*, 455−464.

(15) Real, J. A.; Bolvin, H.; Bousseksou, A.; Dworkin, A.; Kahn, O.; Varret, F.; Zarembowitch, J. *J. Am. Chem. Soc.* **1992**, *114*, 4650−4658.

(16) Ksenofontov, V.; Spiering, H.; Reiman, S.; Garcia, Y.; Gaspar, A. B.; Moliner, N.; Real, J. A.; Gütlich, P. *Chem. Phys. Lett.* **2001**, *348*, 381−386.

(17) Gaspar, A. B.; Ksenofontov, V.; Real, J. A.; Gütlich, P. *Chem. Phys. Lett.* **2003**, *373*, 385−391.

(18) Leita, B. A.; Moubaraki. B.; Murray, K. S.; Smith, J. P.; Cashion, J. D. *Chem. Commun.* **2004**, 156−157.

(19) Nakano, K.; Suemura, N.; Kawata, S.; Fuyuhiro, A.; Yagi, T.; Nasu, S.; Morimoto, S.; Kaizaki, S. *Dalton Trans.* **2004**, 982−988.

(20) Weber, B.; Kaps, E. *Heteroatom Chem.* **2005**, *16*, 391−397.

(21) Haddad, M. S.; Lynch, M. W.; Federer, W. D.; Hendrickson, D. N. *Inorg. Chem.* **1981**, *20*, 123−131.

(22) Haddad, M. S.; Federer, W. D.; Lynch, M. W.; Hendrickson, D. N. *Inorg. Chem.* **1981**, *20*, 131−139.

(23) Evans, D. F. J. *J. Chem. Soc.* **1959**, 2003−2005.

(24) Live, D. H.; Chan, S. I. *Anal. Chem.* **1970**, *42*, 791−792.

(25) Ostfeld, D.; Cohen, I. A. *J. Chem. Educ.* **1972**, *49*, 829.

(26) Schubert, E. M. *J. Chem. Educ.* **1992**, *69*, 62.

(27) Ortega-Villar, N.; Thompson, A. L.; Munoz, M. C.; Ugalde-Saldivar, V. M.; Goeta, A. E.; Moreno-Esparza, R.; Real, J. A. *Chem.−Eur. J.* **2005**, *11*, 5721−5734.

(28) Yatsunyk, L. A.; Walker, F. A. *Inorg. Chem.* **2004**, *43*, 757−777.

(29) *NMR of Paramagnetic Molecules*; La Mar, G. N., Horrocks, W. D., Holm, R. H., Eds.; Academic Press: New York, 1973.

(30) La Mar, G. N.; Walker, F. A. NMR Studies of Paramagnetic Metalloporphyrins. In *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1979; Vol. IV, pp 61−157.

(31) Bertini, I.; Luchinat, C.; Parigi, G. *Solution NMR of Paramagnetic Molecules*; Springer-Verlag: Heidelberg, Germany, 2001.

(32) Köhler, F. H. Probing Spin Densities by Use of NMR Spectroscopy. In *Magnetism: Molecules to Materials. Models and Experiments*; Miller, J. S., Drillon, M., Eds.; Wiley-VCH: Weinheim, Germany, 2001; Vol. IV, pp 379−430.

(33) Walker, F. A. Proton NMR and EPR Spectroscopy of Paramagnetic Metalloporphyrins. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: London, U.K., 2000; Vol. 5, pp 81−183.

(34) Jäger, E.-G. In *Chemistry at the Beginning of the Third Millenium*; Fabbrizzi, L., Poggi, A., Eds.; Springer-Verlag: Heidelberg, Germany, 2000; pp 103−138.

(35) Leibeling, G. Offenkettige Eisen(II/III)-, Cobalt(II)- und Kupfer(II)-Chelatkomplexe - Bioanorganische Modelle und Verbindungsklassen für neue magnetische Materialien auf molekularer Basis, Ph.D. Thesis, Universiy of Jena, Jena, Germany, 2003.

Et)(py)$_2$] and [FeL1(Me/COMe)(py)$_2$], a complete spin transition was observed. In the case of the dinuclear complexes, [Fe$_2$L2(OEt/COOEt)(py)$_4$] is the only complex that remains in the HS state over the entire temperature range investigated. Incomplete spin transitions are observed for the other two complexes. Results from X-ray structure analysis indicate that this is more probably due to crystal packing effects rather than intramolecular interactions.[20] Investigations in solution will show whether this is indeed the case.

Experimental Section

Materials and Sample Preparation. The synthesis of the mono-[35,36] and dinuclear[20,37] iron(II) complexes with two pyridine molecules as axial ligands was described previously. Deuterated chemicals, pyridine-d_5 (D, 99.5%) and toluene-d_8 (D, 99.6%), were purchased from Euriso-top. The solvents were degassed with argon and stored over molecular sieves. The NMR samples were prepared under argon using Schlenk techniques and locally made sealing equipment. Saturated solutions of the iron(II) complexes were prepared in pyridine-d_5 or toluene-d_8/pyridine-d_5 mixtures (50/50, v/v) and stored in sealed or airtight 5 mm NMR tubes. NMR samples for susceptibility measurements using the Evans method were prepared by dissolving a weighed amount of the iron(II) complex with pyridine as the axial ligand in a measured amount of a deuterated pyridine/toluene solvent mixture. The concentration of the paramagnetic solute was in the range of 5−10 mg mL^{-1}. The temperature-dependent density changes of the solvent were corrected using equations and data from the International Critical Tables.[38,39] The equations for the expansion/contraction of pyridine are only available over the temperature range −45 to +18 °C. Because the density changes are fairly similar to those for toluene over the same temperature range, the toluene data were used for the 50/50 (v/v) toluene-d_8/pyridine-d_5 mixtures. The complex solution was transferred into a 5 mm NMR tube containing a 1 mm capillary with the deuterated diamagnetic pyridine/toluene mixture as a reference. The residual ^{1}H NMR resonance of the toluene methyl group was used for determining the susceptibility in solution.

NMR Spectroscopy. The NMR spectra of the pyridine solution samples were recorded on a Varian Unity-300 spectrometer operating at 299.955 MHz equipped with a Varian variable-temperature unit over the temperature range −45 to +80 °C, referenced to the resonance from residual solvent protons (7.2 and 7.5 ppm relative to tetramethylsilane, TMS). The temperature was calibrated using the standard Wilmad methanol and ethylene glycol samples. The NMR spectra of the pyridine/toluene solution samples were recorded on a JEOL EX 400e spectrometer operating at 400.182 MHz equipped with a variable-temperature unit over the temperature range −85 to +85 °C.

Results

Susceptibility Measurements in Solution Using the Evans Method. The magnetic susceptibility of the mono- and dinuclear iron(II) complexes was measured in a pyridine-d_5/toluene-d_8 mixture (50/50, v/v) with the toluene CD$_2$H residual methyl proton signal as a reference. One advantage of the use of a pyridine/toluene mixture instead of pure pyridine (maximum ratio of the axial ligand to iron complex to ensure the formation of octahedral complexes) as the solvent for the complexes is the wider temperature range available (pyridine, mp −42 °C, bp 115 °C; toluene, mp −93 °C, bp 110 °C), especially for the lower temperatures. The change in the solvent density with temperature was calculated using the equation and data from the International Critical Tables.[38,39]

Magnetic susceptibility measurements of powder samples indicate that mononuclear [FeL1(OEt/COOEt)(py)$_2$)] and the corresponding dinuclear [Fe$_2$L2(OEt/COOEt)(py)$_4$] are HS over the entire temperature range investigated (185−350 K). This corresponds well with the outcome of susceptibility measurements in solution using the Evans method. The room-temperature effective magnetic moment, μ_{eff}, of 5.5 μ_{B} for [FeL1(OEt/COOEt)(py)$_2$] is within the range expected for a mononuclear iron(II) HS complex. For [Fe$_2$L2(OEt/COOEt)(py)$_4$], it is at 6.7 μ_{B}, lower than expected for a dinuclear iron(II) HS complex according to $\mu_S = 2\sqrt{S_1(S_1+1)+S_2(S_2+1)} = 6.92\ \mu_{\mathrm{B}}$. This can be attributed to difficulties in obtaining an accurately weighted amount of the air-sensitive iron(II) compound. Additionally, the NMR spectra indicate the existence of a small amount of diamagnetic impurities. Nevertheless, the value is still within the error range reported for the Evans method.[28] The μ_{eff} of both compounds is constant within the temperature range investigated (185−350 K), indicating that the complexes remain in the HS state throughout this range. Therefore, plots of the temperature dependence of μ_{eff} for these two compounds are not included in Figure 1.

Figure 1 shows the plots of μ_{eff} as a function of temperature for the two mononuclear and two dinuclear SCO complexes [FeL1(Me/COOEt)(py)$_2$] (A), [FeL1(Me/COMe)(py)$_2$] (B), [Fe$_2$L2(Me/COOEt)(py)$_4$] (C), and [Fe$_2$L2(Me/COMe)(py)$_4$] (D). For comparison purposes, the results from solid-state susceptibility measurements are given as well (solid triangles in Figure 1). At room temperature, all four complexes are in the HS state, with μ_{eff} around 5 μ_{B} for mononuclear and 7 μ_{B} for dinuclear complexes ([FeL1(Me/COOEt)(py)$_2$], μ_{eff} = 4.45 μ_{B}; [FeL1(Me/COMe)(py)$_2$], μ_{eff} = 5.10 μ_{B}; [Fe$_2$L2-(Me/COOEt)(py)$_4$], μ_{eff} = 7.31 μ_{B}; [Fe$_2$L2(Me/COMe)(py)$_4$], μ_{eff} = 7.33 μ_{B}). Deviations from the theoretically expected values are due to difficulties in obtaining an accurately weighed amount of the air-sensitive iron(II) compound. As the temperature is lowered, the magnetic moment decreases in all of the cases. Significant differences can be found between the behavior in solution and that in the solid state for all but mononuclear [FeL1(Me/COOEt)(py)$_2$].

[FeL1(Me/COOEt)(py)$_2$] is the only one with a gradual spin transition in the solid state,[35] and the transition curve obtained in solution is very similar (Figure 1A). In comparison, a powder sample of [FeL1(Me/COMe)(py)$_2$] shows an abrupt spin transition, whereas the transition curve in solution is gradual, as shown in Figure 1B, as expected for

---

(36) Jäger, E.-G.; Häussler, E.; Rudolph, M.; Schneider, A. *Z. Anorg. Allg. Chem.* **1985**, *525*, 67−85.

(37) Hasty, E. F.; Colburn, T. J.; Hendrickson, D. N. *Inorg. Chem.* **1973**, *12*, 2414−2421.

(38) Washburn, E. W. *International Critical Tables of Numerical Data, Physics, Chemistry and Technology*; 1926−1930; 2003 (1st Electronic Edition); Vol. III, pp 27−29. Online version available at: http://www.knovel.com/knovel2/Toc.jsp?BookID=735&VerticalID=0

(39) For toluene, from −95 to +18 °C, $d_t = (0.88448 - 0.9159) \times 10^{-3}t + 0.368 \times 10^{-6}t^2$; from 0 to +99 °C, $d_t = (0.88412 - 0.92249) \times 10^{-3}t + 0.0152 \times 10^{-6}t^2 - 4.223 \times 10^{-9}t^3$.

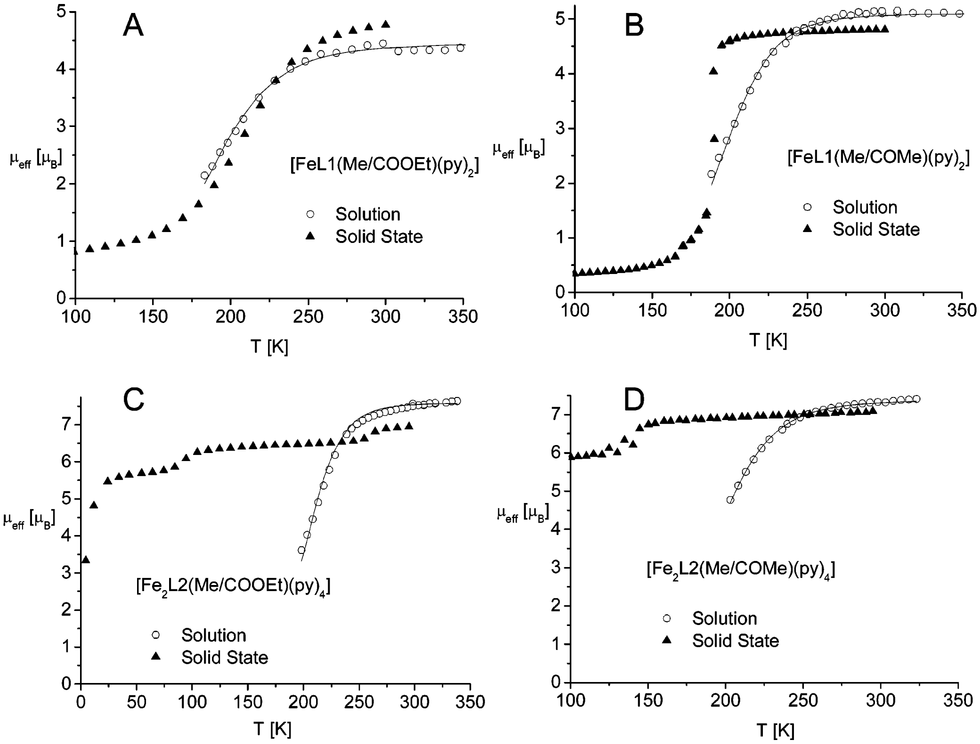


Figure 1. Magnetic properties of two mononuclear and two dinuclear SCO complexes [FeL1(Me/COOEt)(py)$_2$] (A), [FeL1(Me/COMe)(py)$_2$] (B), [Fe$_2$L2(Me/COOEt)(py)$_4$] (C), and [Fe$_2$L2(Me/COMe)(py)$_4$] (D) determined in solution (open circles) and in the solid state (solid triangles). The solid lines represent the curves obtained with the regular solution model (eq 1) and the fitting parameters given in Table 1. Plot of the effective magnetic moment per mole of compound versus temperature.

a mononuclear complex. The critical temperatures $T_{1/2}$ with $\gamma_{HS} = 0.5$ are very similar for the three gradual transition curves (220/208 K for [FeL1(Me/COOEt)(py)$_2$] powder/solution and 210 K for the pyridine/toluene solution of [FeL1(Me/COMe)(py)$_2$]). A significantly lower critical temperature is found only for the abrupt spin transition of the powder sample of [FeL1(Me/COMe)(py)$_2$] (177 K). The different substituents of the two complexes therefore do not influence the thermodynamic parameters of the spin transition but only the packing of the molecules in the crystal.

Table 1. Thermodynamic Parameters of the Spin Transition of the Mono- and Dinuclear Complexes Obtained from the Susceptibility Measurements in Solution Using the Regular Solution Model (eq 1)

system	ΔH_{HL} (kJ mol^{-1})	ΔS_{HL} (J mol^{-1} K^{-1})	$T_{1/2}$ (K)
[FeL1(Me/COOEt)(py)$_2$]	18.2	88	207
[FeL1(Me/COMe)(py)$_2$]	25.5	121	211
[Fe$_2$L2(Me/COOEt)(py)$_4$]	28.3	130	218
[Fe$_2$L2(Me/COMe)(py)$_4$]	22.4	107	209

Powder measurements for the dinuclear complexes show only incomplete, stepwise spin transitions with a remaining HS mole fraction around $\gamma_{HS} = 0.7$ ([Fe$_2$L2(Me/COOEt)(py)$_4$], $\mu_{eff} = 5.69\ \mu_B$; $\chi T = 4.40$ cm^3 K mol^{-1}, $\gamma_{HS} = 0.67$ at 55 K; [Fe$_2$L2(Me/COMe)(py)$_4$], $\mu_{eff} = 5.90\ \mu_B$, $\chi T = 4.35$ cm^3 K mol^{-1}, $\gamma_{HS} = 0.70$ at 105 K). The only indication that the steps are indeed due to a spin transition is an X-ray structure analysis of [Fe$_2$L2(Me/COMe)(py)$_4$] below the step in the transition curve. Here, half of the molecules are in the HS state, and the other half are in the LS state ($\gamma_{HS} = 0.5$).[20] The differences in the remaining HS mole fraction for the two different methods are due to differences in the composition of the powder and the crystals. Seven additional pyridine molecules per complex molecule are found in the crystal according to X-ray structure analysis. The magnetic measurements were performed on pulverized samples. According to elemental analysis, all of the additional pyridine molecules are lost in those samples.[20] The spin transition in solution is gradual for both complexes with $T_{1/2} = 215$ K for [Fe$_2$L2(Me/COOEt)(py)$_4$] and $T_{1/2} = 210$ K for [Fe$_2$L2(Me/COMe)(py)$_4$]. Again no significant difference between the transition temperatures of the two complexes can be found, and $T_{1/2}$ is in the same region as that found for the mononuclear complexes. The transition curves show no indication for preference of a stepwise spin transition because of the formation of a preferred mixed-HS/LS species. A similar behavior was reported for two dinuclear dicyanamide-bridged iron(II) complexes.[27]

The spin-transition data in solution, obtained from the Evans method, were simulated using the regular solution model:

$$R \ln((1 - \gamma_{HS})/\gamma_{HS}) = \Delta H_{HL} - T\Delta S_{HL} \qquad (1)$$

where ΔH_{HL} and ΔS_{HL} are the thermodynamic enthalpy and entropy values associated with the spin transition. The calculated curves are given in Figure 1 as solid lines. The results are summarized in Table 1.

Comparison of the thermodynamic parameters shows that there are nearly no differences between the mono- and dinuclear complexes with the substituents Me/COMe; no indications of an increased cooperativity in the dinuclear complex are found. This is different for the pair with the substituents Me/COOEt. Here, the enthalpy and entropy changes for the dinuclear complex are significantly higher. Assuming a domainlike behavior, the domain size *n* can be introduced in eq 1, leading to

$$R \ln((1 - \gamma_{\mathrm{HS}})/\gamma_{\mathrm{HS}}) = n\Delta H_{\mathrm{HL}} - Tn\Delta S_{\mathrm{HL}} \qquad (2)$$

If the changes in the thermodynamic parameters are caused by changes in the domain size, *n* would be in the region of 1.5, which could correspond with the number of linked iron centers. However, it is also possible that the phenylene bridge in the dinuclear complexes influences the thermodynamic parameters of the SCO complex and the changes occur independent of any cooperative effect.

Signal Assignment of the ^{1}H NMR Spectra. Figure 2 shows the NMR spectra of the three mononuclear iron(II) complexes and dinuclear [Fe_2L2(Me/COOEt)$(py)_4$] in a pyridine/toluene mixture (50/50, v/v) at 25 °C. The signal assignment for each of the complexes is given at the right. Because of the different substituents, the assignment can be accomplished by spectral comparison and by taking the different line widths into consideration. The broad signal around −25 ppm (a) with a relative intensity of three can be found in three (A−C) of the four spectra in Figure 2 and was assigned to the CH_3 group of the substituent R^2. In the spectrum of [FeL1(Me/COMe)$(py)_2$] of Figure 2C, one other signal with a relative intensity of 3 appears at 13 ppm. A similar signal does not appear in the other three spectra. The line width is about one quarter of the line width of signal a, and the resonance was therefore assigned to CH_3 group b, which is farther away from the paramagnetic center. The substituent R^1 for the complexes in the spectra of parts A, B, and D of Figure 2 is the same, and the resonances c and d that appear in those three spectra with relative intensities of two and three were assigned to the ethyl group of R^1. In the spectrum of Figure 2D, a second pair of resonances with relative intensities of 2 and 3, e and f, respectively, was found; these were assigned to the ethyl group of the substituent R^2. The ethyl group of R^2 is closer to the paramagnetic center, and the line widths of the resonances are about 5 times greater than those of R^1. Comparison of the spectra of the mononuclear complexes with those of the dinuclear complexes reveals one resonance that appears in the region between 8 and 11 ppm with a relative intensity of 1 that can only be found in the spectra of the mononuclear complexes. This resonance was therefore assigned to the protons g of the phenylene bridge. The remaining protons are present in all of the complexes and cannot be assigned by comparison of the spectra. In spectrum D of [FeL1(OEt/COOEt)$(py)_2$] in Figure 2, one signal with a relative intensity of 1 can be found in the region around −1 ppm. This could correspond to one of the two remaining protons. Indications for a similar signal in the spectra of the other complexes are also found. Considering the NMR spectra of Fe(Salen) complexes, in particular of [Fe^{III}(Salen)OAc-d_3], where the Schiff base HC−N proton was thought to be located near 159 ppm,[40] suggests that the last missing signal could be in the 120−160 ppm region of the spectrum for the iron(II) compounds of the present study but is likely very broad and difficult to detect. Using pyridine-d_5 as the solvent for [FeL1-(OEt/COOEt)$(py)_2$] (highest solubility of the compounds investigated), we were able to detect one additional signal with a relative intensity of 1 in the 450−470 ppm region of

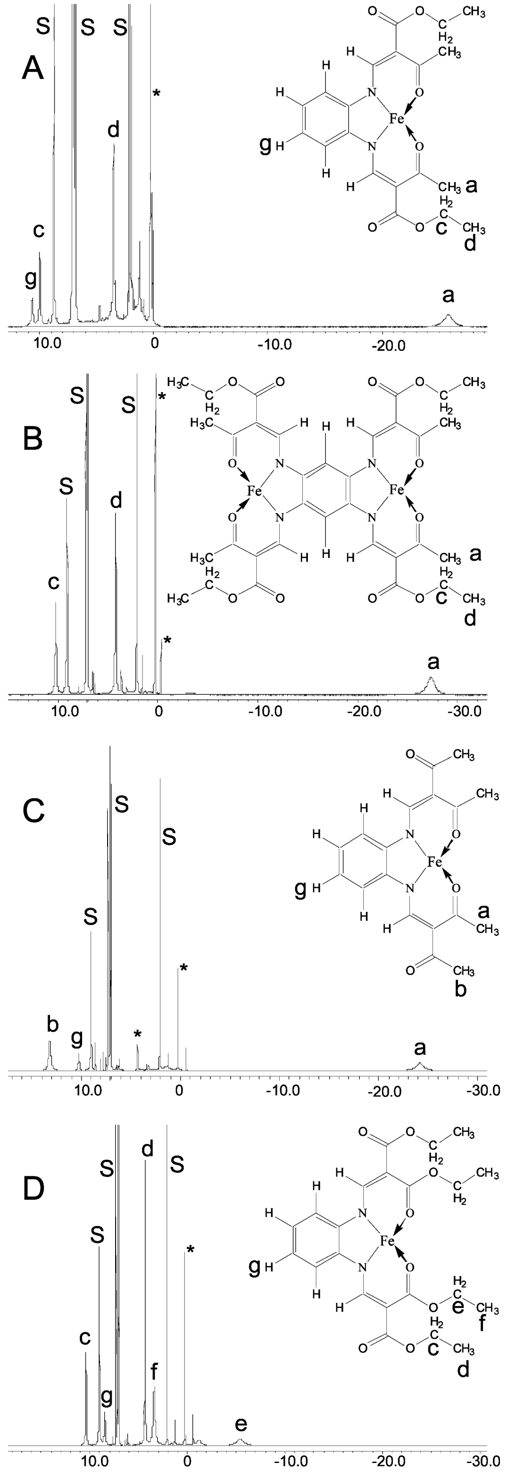


Figure 2. ^{1}H NMR spectra of three mononuclear complexes [FeL1(Me/COOEt)$(py)_2$] (A), [FeL1(Me/COMe)$(py)_2$] (C), and [FeL1(OEt/COOEt)-$(py)_2$] (D) and dinuclear [Fe_2L2(Me/COOEt)$(py)_4$] (B) in a pyridine-d_5/toluene-d_8 mixture at 25 °C. The signal assignment is given to the right of each spectrum. S denotes the solvent pyridine/toluene residual proton resonances, and asterisk denotes an impurity.

---

(40) La Mar, G. N.; Eaton, G. R.; Holm, R. H.; Walker, F. A. *J. Am. Chem. Soc.* **1973**, *95*, 63−75.

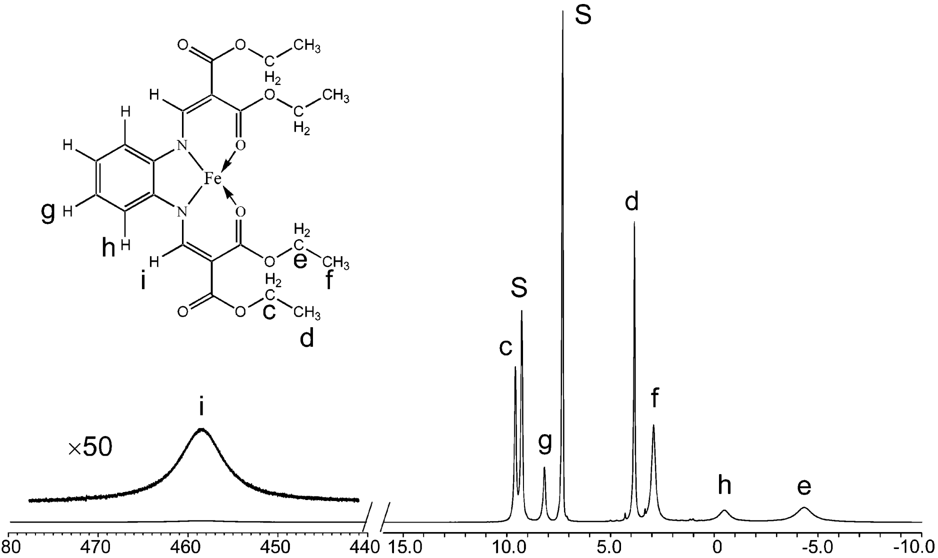


Figure 3. ^{1}H NMR spectrum of [FeL1(OEt/COOEt)(py)$_2$] in a pyridine at 55 °C. The signal assignment is given at the left. S denotes the solvent pyridine.

the spectrum. The corresponding spectrum at 55 °C is given in Figure 3 with the signal assignment to the left.

The assignment of the three signals with relative intensities of 1 each can be accomplished by considering the line width and taking the distance between the iron center and the proton into account by measuring the distance $R_{\mathrm{Fe-H}}$ from the X-ray crystal structure. The values for [FeL1(OEt/COOEt)(py)$_2$] are 3.9 Å for proton i, 4.7 Å for proton h, and 6.2 Å for proton g.[41] If there is no through-bond spin delocalization, the line half-width at half-height ($\mathrm{LW}_{1/2}$) should be proportional to $(R_{\mathrm{Fe-H}})^{-6}$ plus an added term because of the contact shift; the $(R_{\mathrm{Fe-H}})^{-6}$ term usually dominates:

$$\mathrm{LW}_{1/2} = T_2^{-1} = (7/15)\gamma_{\mathrm{H}}^{2}\langle g\rangle^{2}\mu_{\mathrm{B}}^{2}S(S+1)T_{1e}(R_{\mathrm{Fe-H}})^{-6} + (1/3)S(S+1)(A_{\mathrm{h}}/\hbar)^{2}T_{1e} \quad (3)$$

where γ_{H} is the magnetogyric ratio of the proton, $\langle g\rangle$ is the average g value of the iron complex, μ_{B} is the Bohr magneton, $R_{\mathrm{Fe-H}}$ is the distance from the iron center to the proton of interest, T_{1e} is the electron spin relaxation time for the metal ion of interest, and A_{h} is the hyperfine coupling constant for the proton of interest.[42] However, if there is through-bond spin delocalization (a contact shift), the line is likely to be considerably broader than expected by the inverse distance to the sixth power. La Mar and co-workers have shown that when there is significant spin density at the carbon to which the proton is attached, there is an added term that depends upon the spin density at that carbon, ρ_{C}, and the C−H bond length, in the form $(\rho_{\mathrm{C}})^2(R_{\mathrm{C-H}})^{-6}$, that can be very large because of the small value of $R_{\mathrm{C-H}}$;[42] the relationship was derived for delocalization through π bonds, and thus involved the McConnell equation ($A_{\mathrm{h}} = Q\rho_{\mathrm{C}}$, where ρ_{C} is the electron density in the carbon π orbital to which the proton is attached and Q is a constant). However, in the present case it is very likely that delocalization through σ bonds (via the $d_{x^2-y^2}$ unpaired electron) dominates the spin density at the Schiff's base carbon because two of the protons common to all mononuclear complexes have significantly smaller line widths than does the resonance at 460 ppm shown in Figure 3. This proton has a line width of 2280 Hz and is thus by far the broadest of the three resonances; it was therefore assigned to the Schiff base proton i. This resonance has a much larger chemical shift than the Schiff base resonance of Fe(Salen),[40] indicating that the Salen ligand system is not a good model for the Schiff base ligands created for the present study. The large positive isotropic shift of this proton indicates a large contact shift, and the positive value indicates that σ spin delocalization of the $d_{x^2-y^2}$ unpaired electron strongly dominates the expected π delocalization of the d_{xz} and/or d_{yz} electron(s).[29−33] Beyond that statement, we have not attempted to separate the σ and π contributions (as well as the through-space pseudocontact contribution) to the chemical shift of proton i.

In comparison, the other two resonances with a relative intensity of 1 have opposite-sign isotropic shifts, suggesting a small π spin density in the aromatic ring derived from *o*-phenylenediamine[43] and a vanishingly small σ spin density (which is expected to fall off very sharply with the number of chemical bonds).[29−33] The resonance near −1 ppm, with a line width of 240 Hz in Figure 3, is broader than the resonance at 8 ppm, with a line width of 40 Hz, that was already assigned to proton g. It therefore belongs to proton h. Knowing where to search, one can find the resonances for all six of the complexes; h and i are present for all, and g is present only for the mononuclear complexes. Proton i has a chemical shift of 450−600 ppm and proton h has a chemical shift of −5 to +5 ppm over the temperature range of 298.15−338.15 K. The chemical shifts of all of the protons of all of the complexes at 318.15 K are summarized in Supporting Information Table S1. Because the signals of protons h and i are very broad and difficult to detect, they

---

(41) Unpublished results.

(42) Unger, S. W.; Jue, T.; La Mar, G. N. *J. Magn. Reson.* **1984**, *61*, 448−456.

(43) Walker, F. A. *Inorg. Chem.* **2003**, *42*, 4526−4544.

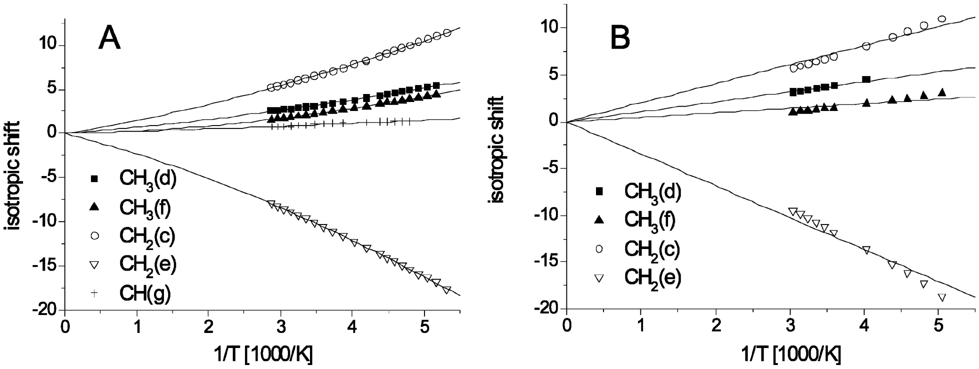


Figure 4. Isotropic shift of [FeL1(OEt/COOEt)(py)$_2$] (A) and [Fe$_2$L2(OEt/COOEt)(py)$_4$] (B) plotted versus 1/T (dots). The temperature dependence of [FeL1(OEt/COOEt)(py)$_2$] (A) was simulated using the TDF program,[44] taking an extended Curie law into account (solid line). The fitting parameters are given in Table 2. The temperature dependence of the isotropic shift of the dinuclear complex could not be analyzed using the extended Curie law but is close to ideal Curie behavior. The best fit is indicated with the solid lines, and the parameters are summarized in Table 2.

Table 2. Summary of Results Obtained from the TDFw Fits of the Temperature Dependence of the Assigned Protons for the Complexes in This Study

system	E_1 (GS)	E_2 (ES)	$\Delta E_{1,2}$ [cm^{-1}]	MSD	spin densities, comments
FeL1(OEt/COOEt)	2	2	110	0.043	1: 0.0029 (d), 0.0034 (f), 0.0057 (c), 0.0088 (e), 0.0009 (g) 2: −0.0007 (d), −0.0029 (f), −0.0013 (c), 0.0018 (e), −0.00003 (g)
	2			0.421	1: 0.0016 (d), 0.0012 (f), 0.0034 (c), −0.0052 (e), −0.0006 (g), one-level fit
FeL1(Me/COOEt)[a]	2	2	573	0.029	1: −0.0134 (a), 0.0011 (d), 0.0027 (c), −0.0023 (g) 2: −0.0302 (a), 0.0039 (d), 0.0071 (c), 0.0009 (g)
	2			0.198	1: −0.0146 (a), 0.0013 (d), 0.0030 (c), −0.0022 (g), one-level fit
FeL1(Me/COMe)[a]	2	2	1040	0.032	1: −0.0130 (a), 0.0054 (b), −0.0017 (g) 2: −0.0786 (a), 0.0039 (b), 0.0097 (g)
FeL1(Me/COMe)[b]	2	2	577	0.039	1: −0.0124 (a), 0.0055 (b), −0.0018 (g) 2: −0.0300 (a), 0.0044 (b), 0.0011 (g)
	2			0.248	1: −0.0136 (a), 0.0054 (b), −0.0016 (g), one-level fit
Fe$_2$L2(OEt/COOEt)	2	2			fitting parameters are not reasonable
	2			0.486	1: 0.0018 (d), 0.0008 (f), 0.0034 (c), −0.0058 (e), one-level fit
Fe$_2$L2(Me/COOEt)[c]	2	2	753	0.025	1: −0.0147 (a), 0.0014 (d), 0.0030 (c) 2: −0.0275 (a), 0.0002 (d), 0.0069 (c)
	2			0.215	1: −0.0150 (a), 0.0013 (d), 0.0031 (c), one-level fit
Fe$_2$L2(Me/COMe)[a]	2	2			fitting parameters are not reasonable
	2			0.075	1: −0.0135 (a), 0.0058 (b), one-level fit

[a] Data points in the temperature range from 15 to 85 °C used. [b] Data points in the temperature range from 10 to 85 °C used. [c] Data points in the temperature range from 20 to 85 °C used.

were not considered for further investigations involving variable-temperature studies discussed below.

To ensure the formation of octahedral complexes in the 1/1 pyridine-d_5/toluene-d_8 mixture, the spectra were compared with those recorded in a pure pyridine-d_5 solution. The spectra are very similar, and the resonances assigned above were also found in the spectra with pure pyridine-d_5 as the solvent, with very similar chemical shifts at a given temperature. No indication of the existence of a second species (pentacoordinated complex) in the 1/1 pyridine/toluene mixture was found.

Temperature Dependence of the Isotropic Shifts. According to the susceptibility measurements, [FeL1(OEt/COOEt)(py)$_2$] and [Fe$_2$L2(OEt/COOEt)(py)$_4$] remain in the HS state over the entire temperature range investigated. The temperature dependence of the isotropic shifts (Curie plots) of [FeL1(OEt/COOEt)(py)$_2$] is given in Figure 4A and is discussed below.

At first glance, the mononuclear complex appears to show Curie behavior. However, closer inspection reveals some deviation from the ideal Curie law straight line (i.e., curvature of the plot as shown in Figure 4A or intercepts different from zero if the simple Curie behavior is forced by plotting straight lines). Several possible reasons may be given for this deviation: Thermally accessible excited states, hindered rotation of ethyl groups, or large dipolar shifts due to large magnetic anisotropy (zero-field splitting) of the iron center are three obvious possibilities. If the dipolar shift were large, then it should show a D/T^2 dependence, where D is the zero-field-splitting constant. A D/T^2 dependence in addition to a C/T dependence is not what is observed here. Furthermore, for most $S = 2$ iron(II) as well as $S = {}^5/_2$ iron(III) macrocycle complexes, the zero-field-splitting constant has been shown to be quite small.[40] Hindered ethyl group rotation could contribute to the curvature, but ethoxy groups should not exhibit hindered rotation because of the additional single bond that removes the ethyl group from the congestion of the macrocycle. Instead, the most likely reason for curvature of the Curie plots is a thermally accessible excited state. The experimental data in Figure 4 (dots) were fit by taking an extended Curie law into account with different Curie constants (or spin densities) for the ground and excited states:

$$\delta_n^{\text{con}} = (F/T)(W_1 C_{n1}^2 + W_2 C_{n2}^2 e^{-\Delta E/kT})/(W_1 + W_2 e^{-\Delta E/kT}) \quad (4)$$

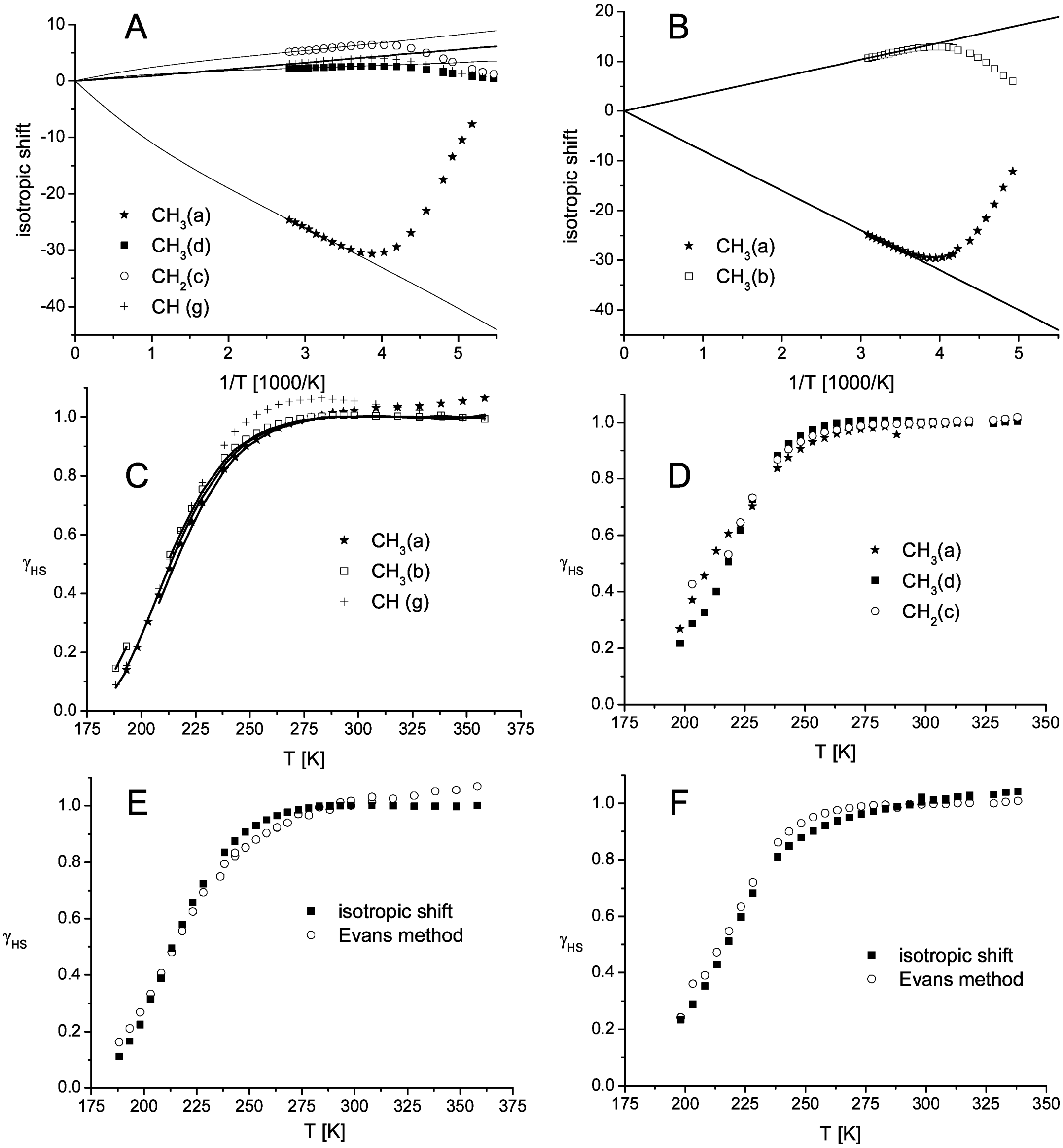


Figure 5. Isotropic shifts of [FeL1(Me/COOEt)(py)$_2$] (A) and [Fe$_2$L2(Me/COMe)(py)$_4$] (B) plotted versus 1/T. The solid lines represent the calculated shifts of the pure HS complex using the extended Curie law for the mononuclear complex (A) and the simple Curie law for the dinuclear complex (B). Panel C shows the HS mole fraction (γ_{HS}) of [FeL1(Me/COMe)(py)$_2$] obtained by interpretation of the isotropic shift assuming ideal Curie behavior (points) and using the expanded Curie law (eq 4) for the temperature dependence of the HS species. Panel D shows the HS mole fraction (γ_{HS}) of [Fe$_2$L2(Me/COOEt)(py)$_4$] obtained by interpretation of the isotropic shift assuming ideal Curie behavior. In panels E and F, the HS mole fractions of [FeL1(Me/COMe)(py)$_2$] (E) and [Fe$_2$L2(Me/COOEt)(py)$_4$] (F) obtained by interpretation of the isotropic shifts and using the Evans method are compared. Good agreement between the two methods is observed in both cases.

where W_1 and W_2 are the weighting factors for the ground and excited states, respectively ($S(S + 1)$ in each case), C_{n1} and C_{n2} are the orbital coefficients (spin densities) for the ground and excited states, respectively, F is the Curie constant, ΔE is the energy difference between the ground state and the first excited state, and k is the Boltzmann constant. Because the most likely excited state is that in which the formerly t_{2g} electrons are rearranged between the d_{xy} and d_{yz} orbitals, both the ground state and the first excited state were assumed to exhibit a total spin of $S = 2$. Other possible spin states were also tried and shown not to produce reliable fits. The fit obtained with the temperature-dependent fitting (TDF) program written by Shokhirev and Walker[44] (solid lines) simulates the temperature dependence of the isotropic shift very well. The best-fit parameters are given in Table 2. Considering the orbitals involved, if the electron configuration of the iron is $(d_{xy})^2(d_{xz},d_{yz})^2(d_{z^2})^1(d_{x^2-y^2})^1$, then the thermally accessible excited state would be $(d_{xy})^1(d_{xz},d_{yz})^3(d_{z^2})^1(d_{x^2-y^2})^1$, and thus of the same spin state. The ΔE obtained, 110 cm^{-1}, is typical of those observed for other similar systems having half-filled d_{xz} and/or d_{yz} orbitals, including LS iron(III) porphyrinates.[45−47]

The temperature dependence of the isotropic shift of dinuclear [Fe$_2$L2(OEt/COOEt)(py)$_4$] is very similar to that of the mononuclear complex. The deviation from ideal Curie

---

[44] Shokhirev, N. V.; Walker, F. A. Temperature-Dependent Fitting. http://www.shokhirev.com/nikolai/programs/prgsciedu.html.

[45] Yatsunyk, L. A.; Shokhirev, N. V.; Walker, F. A. *Inorg. Chem.* **2005**, *44*, 2848−2866.

[46] Watson, C. T.; Cai, S.; Shokhirev, N. V.; Walker, F. A. *Inorg. Chem.* **2005**, *44*, 7468−7484.

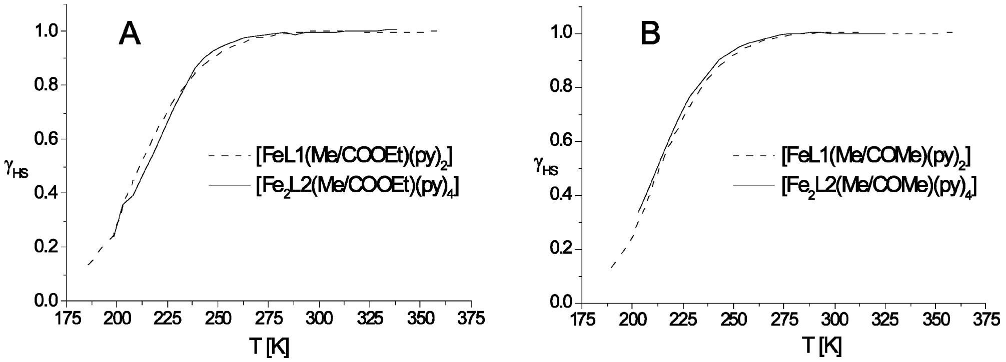


Figure 6. HS mole fraction (γ_{HS}) of the four SCO complexes obtained by interpretation of the isotropic shifts.

behavior is small; however, it cannot be successfully treated by an expanded version of the Curie law (eq 4) discussed above. The most likely reason for this is an exchange interaction between the two iron centers over the bridging ligand. Magnetic susceptibility measurements in the solid state indicate that this is indeed the case.[20] Weak antiferromagnetic interactions were observed, and the coupling constant was estimated to be $J = -1.08$ cm^{-1}.[20] In Figure 4B, the isotropic shifts are plotted versus 1/*T*, with a straight line representing the ideal Curie behavior.

In the cases of the spin-transition complexes, the temperature dependence of the NMR parameters differs significantly. The isotropic shift plotted versus 1/*T* is given in parts A and B of Figure 5 for [FeL1(Me/COOEt)(py)$_2$] and [Fe$_2$-L2(Me/COMe)(py)$_4$], respectively, as typical representatives. The solid lines represent the calculated shifts of the pure HS complex using the extended Curie law for the mononuclear complex (A) and the simple Curie law for the dinuclear complex (B). Above room temperature ($1/T = 3.4$ 1000/K), the behavior is similar to that of the pure HS complexes. At lower temperatures, the isotropic shifts move rapidly toward zero. This behavior can be easily explained by considering the diamagnetic nature of the LS iron(II) center. The spin-flip frequency between the HS and LS states is clearly much faster than the time scale of the NMR experiment. At the beginning of the spin transition, the averaged signal of the isotropic shift of the diamagnetic (zero) and paramagnetic species is measured. Additionally, with decreasing temperature, a strong broadening of the lines is observed that is due to the increasing percentage of the paramagnetic form and chemical exchange between the two. At first glance, the line broadening appears to be more pronounced for the SCO complexes than for the pure HS complexes. However, upon comparison of the line-width changes for the proton g of the three mononuclear complexes, the values are very similar. The broadening of the lines therefore cannot be attributed solely to the chemical exchange between HS and LS forms within individual molecules of the complexes. Assuming Curie behavior for the HS species, the isotropic shift multiplied by the temperature is constant as long as the spin state does not change. A normalized plot of $\delta_{iso}T$ versus *T* should therefore reflect the HS mole fraction (γ_{HS}) of the complex as a function of temperature.

Figure 5C illustrates the corresponding plot for mononuclear [FeL1(Me/COMe)(py)$_2$] and Figure 5D for dinuclear [Fe$_2$L2(Me/COOEt)(py)$_4$] as typical examples. In the case of the mononuclear complexes, the HS mole fraction obtained for the different protons of the complex show significant differences. Thus, the above assumption of ideal Curie behavior for the HS complex is not sufficient for describing the isotropic shift. This problem can be solved if the paramagnetic shifts above room temperature are analyzed using eq 4. This enables us to calculate the isotropic shift of the pure HS complex at lower temperatures, and a more accurate plot of γ_{HS} that is reflected in a better agreement of the single curves (solid lines) is obtained. The fitting parameters and the temperature region used for characterizing the pure HS complex are given in Table 2. For the dinuclear complexes, the extended Curie law given in eq 4 is not suitable for analyzing the curvature of the temperature dependence of the isotropic shift; the fitting parameters obtained are not reasonable, as mentioned above. However, the differences between the HS mole fraction of the different protons are not as pronounced as those of the mononuclear complexes, and the treatment with the simple Curie law appears to be sufficient.

In parts E and F of Figure 5, the average of the spin-transition curves obtained by interpretation of the NMR resonances is compared with the transition curve obtained by the Evans method for mononuclear [FeL1(Me/COMe)-(py)$_2$] (E) and dinuclear [Fe$_2$L2(Me/COOEt)(py)$_4$] (F). Good agreement is observed in both cases.

In Figure 6, the transition curves obtained by interpretation of the NMR isotropic shifts for the mono- and dinuclear complexes are compared. The question is whether the transition curve of the dinuclear complexes is steeper than the curve obtained for the mononuclear complexes. For the substituents Me/COMe (B), no difference in the steepness is observed. The dependence is different for the substituents Me/COOEt (A). Here, curve progression for the dinuclear complex (continuous line) is slightly steeper than that for the mononuclear complex (dashed line). This could be attributed to cooperative interactions between the two iron centers in the dinuclear complex, as was already discussed

---

(47) Cai, S.; Shokhireva, T. Kh.; Lichtenberger, D. L.; Walker, F. A. *Inorg. Chem.* **2006**, *45*, 3519−3531.

for the susceptibility measurements in solution. However, the difference is very small and is very close to the error range of the method. Nevertheless, we are optimistic that, for larger systems (three or more coupled metal centers), differences in the transition curves can be observed if cooperative interactions exist.

Discussion

In this work, we have introduced a method for analyzing the spin transitions of iron(II) complexes in solution. Iron(II) is the most important metal center for SCO complexes and is widely used (about 90% of all complexes). Most of the investigations on spin-transition complexes are focused on solid-state properties. However, whereas packing effects are sometimes useful and lead to the desired properties (abrupt transition, if possible with wide hysteresis), there are several other cases where experiments in solution give more detailed answers to open questions. In solution, packing effects are switched off and a better comparison/study of the effect of different substituents or, as in our case, the influence of the bridging ligand on the “communication” between the linked iron centers is possible. Such investigations are important for the understanding of cooperative interactions in the solid state and therefore for designed syntheses of new spin-transition compounds.

The Evans method is one possibility for investigating spin transitions in solution, but several disadvantages must be taken into account. The exact concentration of the paramagnetic solute must be determined to high accuracy, and for air-sensitive complexes and considering the small quantities used, very careful work is required. The method determines the bulk susceptibility of the solution, and impurities are difficult to detect and can lead to erroneous results. The inner capillary should be fixed properly, and a suitable inert reference substance must be used. Taking all these points into consideration, for the interpretation of NMR shifts, the samples are much easier to prepare and the information obtained is at least of the same and usually of much higher quality. The main disadvantage of this method is the necessity of assigning at least some of the resonances in the NMR spectrum in order to correct the observed shift with the diamagnetic shift. However, successful signal assignment makes it clear whether or not the investigated species is still intact in solution. This is particularly important for dinuclear complexes with bridging ligands, where dissociation into monomers might occur. Last but not least, both methods can be applied in parallel in the same series of experiments and thereby combine the advantages of both.

In our opinion, a further development of this method for SCO complexes is worthwhile and necessary. A key point is the understanding of the NMR parameters of the HS species. There are several possible reasons for a deviation from ideal Curie behavior for the mononuclear complexes. Our investigations showed that thermally accessible excited states are the most likely. For the dinuclear complexes, this is more complicated and more than one effect might contribute to the curvature of the isotropic shift versus $1/T$ (Curie) plot. Exactly calculated paramagnetic shifts lead to more accurate transition curves and therefore an easier detection of the influence of modifications of the characteristics of the spin transition. In this context, the influence of various solvents and sample concentrations should also be investigated, and the error of the method should be evaluated. All of these will be the topics of a subsequent paper.

With regard to the results for the complexes of this study, within the limits of experimental error, it appears that the dinuclear complexes behave as two independent iron(II) SCO centers that are not in communication with each other, in that the isotropic shifts and the temperature dependence of both the magnetic moment and the isotropic shifts are very similar to those of the analogous monomer. So far, the general idea is that rigid linkers should enable communication between the spin-transition centers and thereby lead to cooperative interactions during the spin transition. Several questions now arise: How many metal centers have to be linked together before an influence on the spin-transition curve is observed? Which ligands are rigid linkers? Can we have too-rigid ligands? Are electronic interactions between the metal centers important? Detailed investigations in solution can give answers to these questions and thereby help the design of highly cooperative SCO compounds. The interpretation of the isotropic shift of the ^{1}H NMR spectra is a well-suited approach.

Acknowledgment. We gratefully acknowledge financial support from the Deutsche Forschungsgemeinschaft (SPP 1137) and the Fonds der Chemischen Industrie. The authors thank E. Kaps and A. F. Glas for the preparation of some of the NMR samples. This Article is dedicated to the late Professor Ernst-Gottfried Jäger, who inspired the work on these complexes.

Supporting Information Available: Chemical shifts of free ligands and their complexes in pyridine-d_5. This material is available free of charge via the Internet at http://pubs.acs.org.

IC062349E