252 *Inorg. Chem.* **1990**, *29*, 252-256

Contribution from the School of Chemistry, The Queen's University of Belfast, Belfast BT9 5AG, N. Ireland,
Laboratory for Chemical and Biological Dynamics, University of Leuven, B3030 Leuven, Belgium,
and Department of Chemistry, University of Odense, Odense DK5230, Denmark

Kinetics of Spin-State Interconversion in Iron(II) Complexes in Solution as a Function of Pressure: Activation Volumes for the $^1A_1 \rightleftharpoons {}^5T_2$ Spin Change

John J. McGarvey,*[,1a] Ian Lawthers,[1a] Karel Heremans,[1b] and Hans Toftlund*[,1c]

Received May 5, 1989

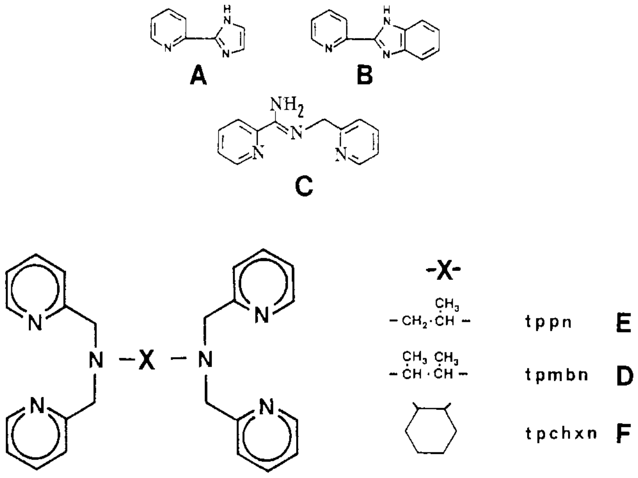
Relaxation times for the $^1A_1 \rightleftharpoons {}^5T_2$ spin-state interconversion in solution for a series of Fe(II) complexes have been investigated as a function of pressure (1–1200 bar) and temperature by means of the pulsed-laser photoperturbation technique. To assess the role of radial and twisting motions in the spin-crossover process, complexes with hexadentate ligands containing aliphatic amines and substituted pyridines as ligating groups and exhibiting varying degrees of conformational freedom have been studied alongside complexes with lower dentate ligands presenting fewer structural constraints. Reaction volumes, ΔV°, for the $^1A_1 \rightleftharpoons {}^5T_2$ spin equilibrium and the activation volumes, $\Delta V_{15}^{\ddagger}$ and $\Delta V_{51}^{\ddagger}$, for the respective spin-crossover processes are reported for the different systems in several solvents, together with the corresponding activation enthalpies and entropies, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$. Both ΔV° and $\Delta V_{15}^{\ddagger}$ are solvent-dependent, but for the $^5T \rightarrow {}^1A$ spin conversion, $\Delta V_{51}^{\ddagger}$ is negative (-6 cm^3 mol^{-1}) and virtually independent of solvent and of ligand type. An exception to this pattern is observed for the complex Fe(tpchxn)$(ClO_4)_2$, in which the structure of the ligand tpchxn (=tetrakis(2-pyridylmethyl)-*trans*-1,2-cyclohexanediamine) impedes motion along a rhomboid-twist coordinate. In DMF solution the relaxation time for spin crossover in this complex becomes significantly longer with increasing pressure and the activation volume $\Delta V_{51}^{\ddagger}$ is positive (+5.7 ± 2 cm^3 mol^{-1}). The findings are discussed in terms of a mechanism for spin crossover involving a combined angular and radial coordinate, with a larger contribution from a radial pathway arising in the case of the tpchxn complex, where the twist pathway is impeded. The data are also viewed in relation to the results of angular overlap calculations of a combined twist and expansion coordinate for the spin change, and a possible contribution from a solvent-assisted mechanism is considered.

Introduction

The dynamics of spin-state interconversion in transition-metal complexes, especially of Fe(II) and Fe(III), in both solution and the solid state is a topic of continuing interest, a recent development being the study of the crossover in complexes doped into polymer matrices.[2] From a kinetic standpoint, the light-induced spin-state-conversion method, first described and used by us to measure both Fe(II) and Fe(III) spin-relaxation rates in solution[3,4] and subsequently used by Decurtins et al. for studies in the solid phase,[5] has proved the most widely applicable way of investigating spin-crossover kinetics, making studies possible over a sufficient range of temperatures and pressures for the determination of reliable values of enthalpies, entropies, and volumes of activation for the spin relaxation. In the case of the last parameter, only limited data have so far been reported.[6] The exact nature of the reaction coordinate for the spin change is still a matter for discussion. A possible strategy[6a,7] for progress here is to investigate the kinetics of spin crossover in complexes constrained to follow a particular reaction coordinate, by reason of specifically designed structural or steric features in the ligands involved. This is the approach adopted in the present investigation, in which spin relaxation times have been measured as a function of both pressure and temperature for a series of complexes with bi-, tri-, and hexadentate ligands with the structures shown in Chart I.

A preliminary account of one section of this work, on the bidentate ligand complexes, has been published.[6a]

Chart I



Experimental Section

The excitation source used for perturbation of the spin equilibria was a Q-switched Nd/glass laser[8] (frequency-doubled, at 530 nm with a pulse duration variable between 10 and 25 ns). A Q-switched Nd/YAG laser[9] fitted with harmonic generating crystals and a Raman λ-shifting cell was also used in some cases. In addition to the second harmonic output at 532 nm (pulse duration ca. 8 ns), this combination provided additional excitation wavelengths, for instance 416 nm, the first Stokes line generated by stimulated Raman scattering in H_2 of the third harmonic of the laser output at 354.7 nm.

The spin-state relaxations were monitored[3,9] spectrophotometrically by observing the recovery of the metal-to-ligand charge-transfer (MLCT) absorption of the $^1A_1$ species following depletion by the laser pulse. Relaxation times as a function of temperature in the range 300–240 K were measured in a 1-cm-path quartz fluorometer sample cell located in a copper block thermostated to ±0.5 K. Argon-flushed or air-saturated solutions yielded the same relaxation times within experimental error. Solutions of Fe(tpchxn)$(ClO_4)_2$ in DMF were generally prepared in vacuo by using standard freeze–pump–thaw techniques, since solutions in air tended to decompose slowly.

For the measurements as a function of pressure a stainless steel vessel was used, with four orthogonal ports fitted with 10 mm thick sapphire windows and O-ring seals (Kalrez, Du Pont Ltd.). The cell was thermostated (±1 K), and measurements were carried out in the presure range 0.1–120 MPa, generated by means of a Nova-Swiss pump (Type

---

(1) (a) The Queen's University of Belfast. (b) University of Leuven. (c) University of Odense.

(2) (a) Xie, C.-L.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1987**, *109*, 6981–6988. (b) Hauser, A.; Adler, J.; Gütlich, P. *Chem. Phys. Lett.* **1988**, *152*, 468–472.

(3) McGarvey, J. J.; Lawthers, I. *J. Chem. Soc., Chem. Commun.* **1982**, 906–907.

(4) Lawthers, I.; McGarvey, J. J. *J. Am. Chem. Soc.* **1984**, *106*, 4280–4282.

(5) Decurtins, S.; Gütlich, P.; Kohler, H.; Spiering, H.; Hauser, A. *Chem. Phys. Lett.* **1984**, *105*, 1–4.

(6) (a) McGarvey, J. J.; Lawthers, I.; Heremans, K.; Toftlund, H. *J. Chem. Soc., Chem. Commun.* **1984**, 1575–1576. (b) DiBenedetto, J.; Arkle, V.; Goodwin, H. A.; Ford, P. C. *Inorg. Chem.* **1985**, *24*, 455–456.

(7) Toftlund, H. *Spin-Ligevaegt i Jern(II) Komplekser*; Trykt Hos Mammen: Odense, Denmark, 1987.

(8) Lockwood, G.; McGarvey, J. J.; Devonshire, R. *Chem. Phys. Lett.* **1982**, *86*, 127–130.

(9) Bell, S. E. J.; McGarvey, J. J. *Chem. Phys. Lett.* **1986**, *124*, 336–340.

0020-1669/90/1329-0252$02.50/0

Table I. Reaction Volumes, Activation Volumes, Thermodynamic and Activation Parameters for $^1A \rightleftharpoons {}^5T$ Spin Crossover in Iron(II) Complexes in Solution

complex^{a,b}	solvent	ΔV°,^{d} cm^3 mol^{-1}	ΔV_{15}^{*}, cm^3 mol^{-1}	ΔV_{51}^{*}, cm^3 mol^{-1}	ΔH°, kJ mol^{-1}	ΔS°, J mol^{-1} K^{-1}	ΔH_{15}^{*}, kJ mol^{-1}	ΔH_{51}^{*}, kJ mol^{-1}	ΔS_{15}^{*}, J mol^{-1} K^{-1}	ΔS_{51}^{*}, J mol^{-1} K^{-1}
$Fe(pyimH)_3^{2+}$ (A)	MeOH–20% MeCN	5.3 ± 0.2	0.0 ± 0.2	-5.3 ± 0.3	$15.5^c \pm 0.8$	$52.7^c \pm 1.7$	26.7 ± 1.2	11.2 ± 0.6	-23 ± 5	-75 ± 5
	MeCN	14.3 ± 0.5	8.9 ± 0.4	-5.4 ± 0.3	32.3 ± 3.0	102 ± 6	46.6 ± 3.0	14.3 ± 1.0	41 ± 5	-61 ± 5
	Me_2CO	10.3 ± 0.4	4.9 ± 0.3	-5.4 ± 0.3	$15.9^c \pm 0.4$	$49^c \pm 1$	32.0 ± 3.0	16.1 ± 2.0	-7 ± 5	-56 ± 5
$Fe(pyBimH)_3^{2+}$ (B)	MeOH–20% MeCN	4.3 ± 0.4	0.2 ± 0.3	-4.1 ± 0.3	$21.3^c \pm 1.7$	$92^c \pm 7$	29.1 ± 2.0	7.8 ± 0.5	-6 ± 7	-98 ± 7
	MeCN	12.4 ± 0.5	5.9 ± 0.4	-6.4 ± 0.3	21.5 ± 2.0	82 ± 4	36.6 ± 3.2	15.1 ± 1.0	21 ± 5	-61 ± 5
	Me_2CO	9.6 ± 0.4	4.7 ± 0.4	-4.9 ± 0.4	$19.7^c \pm 0.4$	$78^c \pm 2$	33.3 ± 0.7	13.6 ± 0.3	10 ± 5	-68 ± 5
$Fe(ppa)_2^{2+}$ (C)	Me_2CO	8.7 ± 0.5	2.6 ± 0.5	-6.1 ± 0.5	20.3 ± 2.0	52 ± 5	33.7 ± 4.0	13.4 ± 4.0	-18 ± 5	-70 ± 5
	H_2O	–	–	-6.5						
$Fe(tpmbn)^{2+}$ (D)	DMF		10.5^e	-5.6^e	30 ± 1.6	75 ± 4	39.1 ± 2.0	9.1 ± 0.4	10 ± 5	-65 ± 5
$Fe(tppn)^{2+}$ (E)	DMF	16.1 ± 2.0	7 ± 3	-9 ± 3	25.4 ± 1.2	71 ± 5	30.6 ± 1.5	5.3 ± 2.0	-18 ± 6	-89 ± 6
	MeCN	10.7 ± 1.0	5.1 ± 0.7	-5.6 ± 0.7	29.8 ± 1.2	88 ± 5	38.2 ± 1.6	8.4 ± 0.4	17 ± 7	-71 ± 7
$Fe(tpchxn)^{2+}$ (F)	DMF	15.5 ± 2.0	21 ± 3	$+5.7 \pm 2.0$	21.1 ± 1.0	62 ± 3	55.6 ± 2.0	34.4 ± 1.2	64 ± 5	2 ± 5
	MeCN	11.5 ± 1.0	5.4 [illegible] 1.2	-6.1 ± 1.2	24.2 ± 1.2	75 ± 4	26 ± 1.2	1.8 ± 0.4	-27 ± 6	-102 ± 6

^{a} Ligand structures are shown in Chart I. ^{b} Counterions: for A and B, BPh_4^-; for C–F, ClO_4^-. Magnetic susceptibility measurements on E and F were made on PF_6^- salts. ^{c} Data from: Reeder, K. A.; Dose, E. V.; Wilson, L. J. *Inorg. Chem.* **1978**, *17*, 1071. ^{d} From absorbance measurements at 25 °C and the following solution concentrations (λ_{mon}, nm): A and B, 2×10^{-4} mol dm^{-3} (482); C, 3×10^{-4} mol dm^{-3} (500); E and F, ca. 1.8×10^{-4} mol dm^{-3} (420). ^{e} Preliminary data, calculated by using the ΔV° for complex E in DMF.

550.01). In several instances the measurements were carried out with the HP cell held at a low temperature (typically in the range −14 to −19 °C), which resulted in good signal:noise ratios for the relaxation traces. The photomultiplier signals due to the transients in both variable-temperature and -pressure experiments were captured on a Tektronix 7912AD digitizer and analyzed by means of a program based on the Guggenheim method for first-order kinetics.

Sample absorbances were measured before and after pressure runs to check for signs of sample decomposition. Some was observed in early experiments carried out in DMF. This was largely eliminated by further drying and purification of the solvent and by flushing the solution with argon prior to pressurization.

The pressure-dependent equilibrium constants $K_{eq} = k_{15}/k_{51}$ and thus the reaction volumes, ΔV° (partial molar volume differences between $^1A_1$ and $^5T_2$ isomers), were determined from absorbance measurements in the range 0.1–150 MPa with the sample held at a temperature of 298 K. Thermodynamic parameters, ΔH° and ΔS°, for the hexadentate ligand complexes were determined from magnetic susceptibility measurements in the temperature range 293–363 K by the Faraday method employing an electromagnet (Bruker-Physik), an electrical microbalance (Sartorius Type 411) and a temperature-control unit (BVT-1000). Airtight aluminum sample tubes were filled under argon. Calibrations were performed against the actual solvent used in each case.

The complexes $[Fe(tpchxn)](ClO_4)_2$, $[Fe(tpmbn)](ClO_4)_2$, and $[Fe(tppn)](ClO_4)_2$ were prepared as described by Toftlund.[10] The complexes $Fe(ppa)_2(ClO_4)_2$, $Fe(pyimH)_3(BPh_4)_2$, and $Fe(pyBimH)_3(BPh_4)_2$ have been described previously.[3] All solvents used were of spectroscopic grade (Aldrich Gold Label).

Results

The temperature dependence of the effective magnetic moment, μ_{eff}, of acetonitrile and dimethylformamide solutions of the complexes $[Fe(tpmbn)](ClO_4)_2$, $[Fe(tppn)](ClO_4)_2$, and $[Fe(tpchxn)](ClO_4)_2$ (D, E, and F in Table I) in the temperature range 293–363 K show that these systems exhibit a spin equilibrium in solution similar to that previously shown[10] to exist in the solid state.

All measurements were made at three different field strengths and in no case was any field dependence observed. The data were recorded with both descending and ascending temperatures and there was no evidence of thermal hysteresis or of sample decomposition. Over the temperature interval 293–363 K the magnetic moments of D, E, and F changed by about 2 units. Two other complexes, $[Fe(blbpen)](ClO_4)_2$ (**1**) and $[Fe(tptn)](ClO_4)_2$ (**2**) exhibited typical high-spin (5.25 μ_B) and low-spin (0.75 μ_B) values, respectively, over this same interval (blbpen = bis((6-methyl-2-pyridyl)methylbis(2-pyridylmethyl)ethylenediamine; tptn = tetrakis(2-pyridylmethyl)triethylenediamine).

The thermodynamic parameters for the LS ⇌ HS equilibrium were evaluated by using the equation[10]

$$K_{eq} = \frac{\chi_m - \chi_{ls}}{\chi_{hs} - \chi_m}$$

where χ_m is the experimental molar susceptibility at a given temperature and χ_{hs} and χ_{ls} are the molar susceptibilities of pure high- and low-spin components, taken to be those measured for complexes **1** and **2** above, respectively.

Plots of ln K_{eq} vs $1/T$ were linear, and the parameters ΔH° and ΔS° for the LS ⇌ HS equilibrium were obtained by a least-squares fit to the data. The results are listed in Table I. In comparison with the values obtained for the solids, the enthalpies are slightly smaller whereas the entropies are higher with the result that the high-spin populations at a given temperature are higher in solution.[11] The spin-crossover reaction volumes, ΔV°, derived from absorbance measurements as a function of pressure and corrected for solvent compressibility, are shown in Table I.

In accord with the thermodynamic evidence for the spin equilibria in solution, pulsed-laser irradiation in the low-spin MLCT absorption region of the complexes resulted in rapid depletion and recovery of the ground-state absorbance of the singlet isomer. In the case of complexes with the bidentate and tridentate ligands (A–C, Table I), in which application of the laser photoperturbation method[12] to the study of spin-interconversion kinetics in Fe(II) complexes had first been reported,[3] relaxation of the perturbed spin equilibrium was monitored in the wavelength range 450–490 nm, within the MLCT absorption band of the LS isomer. The relaxation times were independent of monitoring wavelengths and of solution concentrations in the range $(1–5) \times 10^{-4}$ mol dm^{-3}, within the experimental errors. (The possibility cannot be excluded however of some concentration dependence in the relaxation times becoming apparent over concentration ranges wider than it has so far been possible to study here. Concentration-dependent relaxation times have been reported[13] recently for other spin-crossover systems and attributed to ion-pairing effects.)

The relaxation times did vary with temperature. The spin-relaxation rate constants k_{15} and k_{51} as a function of temperature were calculated by using the measured τ values, where $\tau^{-1} = k_{15} + k_{51}$, in combination with the thermodynamic parameters ΔH° and ΔS° for the spin equilibria in Table I. The corresponding activation parameters in Table I were derived from plots of ln

---

(10) (a) Toftlund, H.; Yde-Andersen, S. *Acta Chem. Scand.* **1981**, *A35*, 575–585. (b) Toftlund, H. Unpublished results.

(11) Toftlund, H. To be submitted for publication in *Coord. Chem. Rev.*

(12) Ivin, K. J.; Jamison, R. S.; McGarvey, J. J. *J. Am. Chem. Soc.* **1972**, *94*, 1763–1764.

(13) Conti, A. J.; Xie, C.-L.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1989**, *111*, 1171–1180.

(k/T) vs. $1/T$ according to the Eyring equation

$$k = (\kappa k_B T/h)[\exp(\Delta S^{*}/R)][\exp(-\Delta H^{*}/RT)]$$

with the transmission coefficient κ set equal to unity. For the hexadentate ligand complexes, D, E, and F, excitation at 530 nm, the low-energy edge of the low-spin MLCT absorption,[10,14] also resulted in prompt depletion of the ground-state absorbance, monitored in the range 440–480 nm, followed by relaxation to the equilibrium absorbance level. The signal:noise ratio for these transients was lower than in the case of the bidentate systems, but the relaxation times were again independent of λ_{mon} (mon = monitoring) and also of complex concentration, over the limited range (see earlier comment) of $(1.5–4.5) \times 10^{-4}$ mol dm^{-3}. As for the bidentate systems, the relaxation times varied with temperature; the corresponding activation parameters computed as above are shown in Table I. Although the third harmonic output at 354.7 nm of the Nd/YAG laser coincides with a more intense region of the MLCT absorption, irradiation at this wavelength resulted in some photodecomposition of samples of complex F, and experiments at this wavelength were discontinued. Some subsequent studies on complexes E and F using 416-nm excitation confirmed the original findings of the 530-nm-based experiments.

For the relaxation measurements as a function of pressure, similar solution concentrations ($\sim 10^{-4}$ mol dm^{-3}) and the same monitoring wavelengths were used as for the variable-temperature studies. For complexes A to E the relaxation times showed a moderate decrease with increasing pressure over the 120-MPa range investigated. Plots of ln ($1/\tau$) vs P in Figure 1A,B for two cases illustrate the general type of behavior. An exception to the pattern is shown by the corresponding plot in Figure 1C for complex F in DMF solution, where the relaxation time increased with increasing pressure. Activation volumes, ΔV_{15}^{*} and ΔV_{51}^{*}, were computed from such plots, in combination with the reaction volumes, ΔV°, by means of the equation[15]

$$RT(\mathrm{d}\ \ln \tau^{-1}/\mathrm{d}P) = -\Delta V_{51}^{*} - K_{eq}\Delta V^{\circ}/(1 + K_{eq})$$

where $K_{eq} = k_{15}/k_{51}$, the spin equilibrium constant at atmospheric pressure, 0.1 MPa. As mentioned above, the reaction volumes, ΔV°, were derived from absorbance data recorded at 25 °C whereas in several instances the variable-pressure kinetic measurements were made at lower temperatures. Use of the above equations to calculate activation volumes therefore assumes that the reaction volumes, ΔV°, are temperature-independent. This assumption was checked in the case of complex A in acetone (Table I), where relaxation measurements at room temperature in combination with the ΔV° value at 25 °C gave the same activation volumes within experimental error as those derived from the low-temperature relaxation studies.

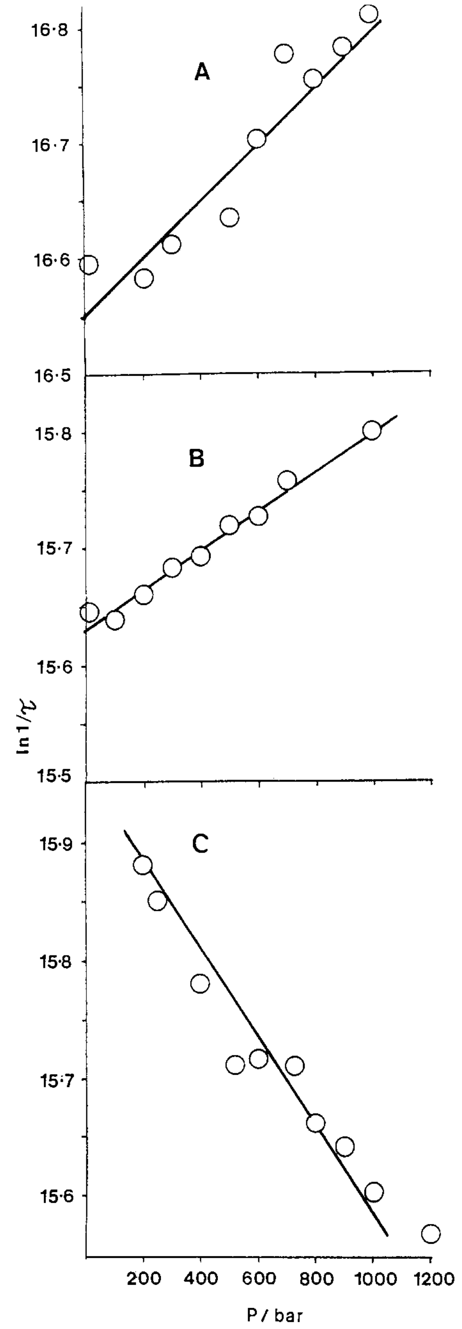


Figure 1. Influence of pressure on the relaxation time, τ, $(=k_{15} + k_{51})^{-1}$ for $^1A \rightleftharpoons {}^5T$ spin crossover in Fe(II) complexes in solution. Plots of ln ($1/\tau$) vs P in the range 1–1200 bar (1 bar = 0.1 MPa): (A) Fe(tppn)$(ClO_4)_2$ in MeCN (sample temperature 253 K); (B) Fe(py-imH)$_3(BPh_4)_2$ in Me$_2$CO (sample temperature 259 K); (C) Fe(tpchxn)$(ClO_4)_2$ in DMF (sample temperature 294 K).

Discussion

The activation enthalpies derived from the Eyring equation of absolute-rate theory are in the range reported[3,6,16] for other singlet $\rightleftharpoons$ quintet spin interconversions of Fe(II) complexes in solution and, more recently,[17] in the solid state. With the exception of the results for complex F measured in DMF, the activation entropies (calculated by using the above equation with $\kappa = 1$) also span a range similar to that observed for other Fe(II) spin-state transitions. Some earlier assessments[18] of activation enthalpies for spin-crossover kinetics in Fe(II) complexes, based upon relaxation studies over a limited temperature range, assumed an enthalpy barrier close to zero for the quintet → singlet spin change and a low value of 10^{-3} for the transmission coefficient in the Eyring equation, which would have been indicative of a nonadiabatic reaction. Our more extensive data on activation enthalpies from measurements over a wide temperature range show that both ΔH_{15}^{*} and ΔH_{51}^{*} are considerable and frequently of the same order as ΔH°.

It is customary to analyze[15] experimentally observed activation volumes in terms of intrinsic contributions, due to bond expansion or contraction, and contributions from the solvent, $\Delta V_{obs}^{*} = \Delta V_{int}^{*} + \Delta V_{solv}^{*}$. The activation volumes, ΔV_{51}^{*}, in Table I span a remarkably narrow range despite the range of complexes and ligand structures and the different solvents used, suggesting that the high-spin species, $^5T_2$, and the transition state for the spin change are solvated to a similar extent. The primary contribution to ΔV_{51}^{*} appears therefore to be intrinsic, arising from contraction of the Fe–N distance in the quintet to singlet activation step. The

---

(14) At 530 nm the MLCT band overlaps with the ligand field $^1T_1 \leftarrow {}^1A_1$ transition so that $^1T_1$ and ^{1}MLCT states may be populated at this excitation wavelength, the photophysical decay of both contributing to population of $^5T_2$ state and thus to perturbation of the LS $\rightleftharpoons$ HS spin equilibrium.

(15) Van Eldik, R., Ed. *Inorganic High Pressure Chemistry: Kinetics and Mechanism*; Elsevier: Amsterdam, 1986.

(16) Beattie, J. K. *Adv. Inorg. Chem.* **1988**, *32*, 1–53.

(17) Adler, P.; Spiering, H.; Gütlich, P. *Inorg. Chem.* **1987**, *26*, 3840–3845.

(18) Dose, E. V.; Hoselton, M. A.; Sutin, N.; Tweedle, M.; Wilson, L. *J. Am. Chem. Soc.* **1978**, *100*, 1141–1147.

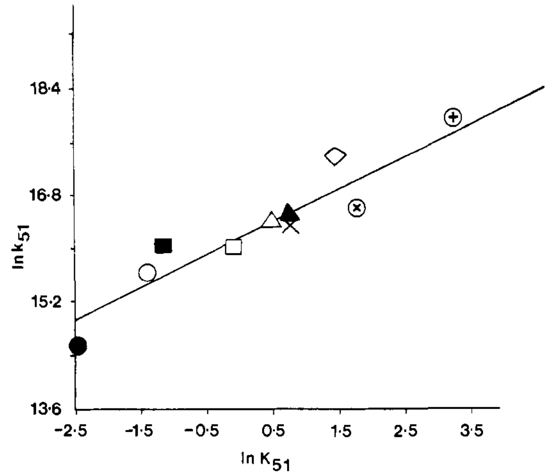


Figure 2. Free energy plot of ln k_{51} vs ln K_{51}: (●) B in MeOH–MeCN; (○) B in Me_2CO; (■) B in MeCN; (□) A in MeOH–MeCN; (△) A in Me_2CO; (▲) F in MeCN; (×) A in MeCN; (◇) E in MeCN; (⊗) E in DMF; (⊕) D in DMF. (See Table I and Chart I for details of complexes A–F and ligand structures.)

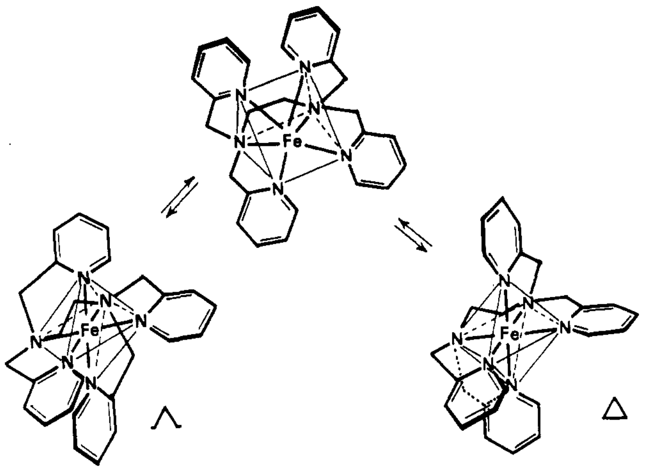


Figure 3. Illustration[7] of racemization in an Fe^{II} hexadentate ligand complex along a rhomboid-twist coordinate via a trigonal-prismatic intermediate.

magnitudes of the observed ΔV° values in Table I, which include solvational and intrinsic contributions, are relatively small and in most cases significantly less than typical intrinsic volume differences (ca. 25–30 $cm^3\ mol^{-1}$) between high- and low-spin states in Fe(II) complexes, as estimated for spin-crossover systems from suitable X-ray structural data.[19,20] This points toward a stronger solvation of the high-spin as compared to the low-spin form in the complexes under investigation here.

For complexes A and B both $\Delta V_{15}^{\ddagger}$ and ΔV° decrease with increasing solvent donor number,[6a] suggesting that it is the local charge distribution in the complexes rather than their absolute size that exerts the primary influence on the extent of solvation. A common feature of all the complexes studied in the present work is that the ligands are heterocyclic amines in which the interaction with the central Fe(II) ion involves the ligand π-orbitals. Using ^{13}C NMR shift data as a measure of electron density, Toftlund and Yde-Andersen[10] have shown that for low-spin complexes most of the decrease in electron density that the pyridine nitrogens experience by complexation via σ-donation is compensated by back-π-donation through the π-system, whereas this is not the case for the corresponding high-spin complexes. Thus the charge distribution within the complex ion changes with the spin state in such a way that the positive field strength close to the surface of the ion is larger for high spin than for low spin and therefore the high-spin form is the more strongly solvated. The net effect will be that although the radius of the high-spin ion is larger, most of the increase in the intrinsic volume will be compensated by stronger solvation of the high-spin entity.

A free energy plot of ln k_{51} vs K_{51} for the data in Table I is shown in Figure 2. Despite the range of systems investigated, a reasonably good line with a slope of 0.5 can be drawn, suggesting that spin crossover in these complexes follows a common mechanism via a transition state located midway between the high- and low-spin states. This is consistent with the activation and reaction volume data in Table I, which indicate that the volume of the transition state lies approximately midway between the volumes of the quintet and singlet states.

The detailed mechanism for the spin change and whether it involves a twisting coordinate and/or motion along a radial coordinate remain to be determined. One aim of the present investigation has been to attempt to clarify this matter through the study of systems that for steric reasons are constrained to follow a specific reaction coordinate. Calculations based upon the angular overlap model (AOM) by Purcell,[21] later confirmed and extended by Toftlund,[11] suggest that an energetically favorable pathway for spin crossover is provided by a pseudorotational mechanism via an intermediate of triplet multiplicity and trigonal-prismatic geometry, as depicted in Figure 3 for an $Fe^{II}N_6$ system. Since the species is achiral only in the trigonal-prismatic geometry, this reaction coordinate may also be envisaged as a pathway for racemization in these types of complexes. It has been suggested[7,11,21] therefore that spin crossover and racemization may occur along a common reaction coordinate involving a rhomboid twist. In this context the structure of complex F is pertinent. The cyclohexane ring of the tpchxn ligand of complex F effectively prevents the central diamine chelate rings from altering conformation; a full-twist pathway is therefore impeded, and the complex cannot racemize. Examination of the kinetic data and activation parameters for spin crossover (Table I) shows that, of all the systems we have so far investigated, complex F in DMF is the only one for which the activation parameters deviate significantly from the general trend. An increase in pressure causes an increase in the spin-state relaxation time (Figure 1C). $\Delta V_{51}^{\ddagger}$ is positive in this one instance, and $\Delta V_{15}^{\ddagger}$ exhibits the largest positive value of all the systems listed in Table I, suggesting that the quintet → singlet and singlet → quintet spin-state changes both involve significant volume expansion. It is tempting to suppose that this might be linked to the fact that the energetically more favorable reaction path via a rhomboid twist is partly blocked in this case. In this regard it is relevant to compare the activation parameters for F with those for systems in which a twisting motion is unimpeded, as for instance structures D and E (Chart I). In structure D alternative equienergetic conformations of the *meso*-2,3-butanediamine chelate ring can be adopted while in E a twist motion is also not inhibited although in this case there is some preference for one conformation because the CH_3 group in the 1-methyl-1,2-propanediamine chelate ring adopts an equatorial position. The activation parameters for both these systems follow the general trend, unlike complex F in DMF. Although the activation volumes for D in Table I are preliminary, being calculated with an assumed value for ΔV° (taken to be equal to that for complex E) the spin-crossover relaxation time for complex D does decrease with increasing pressure, in line with the general pattern observed for the other cases. This all suggests that complexes D and E, in which the full-twist pathway can occur, may be taken to represent "normal" behavior, with spin crossover occurring along a combined angular and radial coordinate, whereas in F, where the full-twist pathway is blocked, there is a larger contribution from a radial pathway. The measurements for F in a different solvent, CH_3CN, are significant in this context. In contrast to the data recorded in DMF, the activation parameters, notably $\Delta V_{51}^{\ddagger}$, tend to follow the general pattern exhibited by the other systems in Table I. This points to some contribution from a solvent-assisted mechanism.[22]

---

(19) Katz, B. A.; Strouse, C. E. *Inorg. Chem.* **1980**, *19*, 658–665.

(20) Mikaki, M.; Konno, M.; Saito, Y. *Acta Crystallogr.* **1980**, *B36*, 275–287.

(21) Purcell, K. F. *J. Am. Chem. Soc.* **1979**, *101*, 5147–5151.

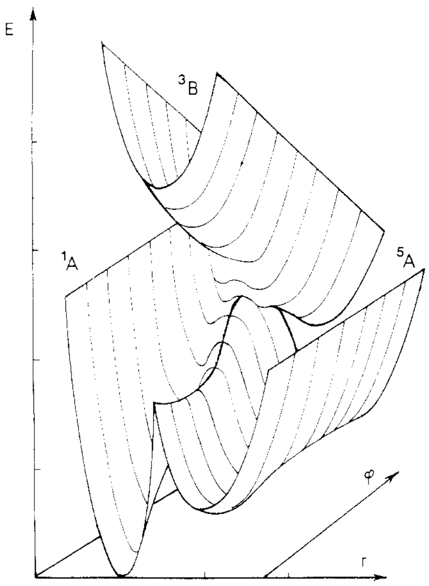


Figure 4. Potential energy surfaces for singlet → quintet crossover along a combined twist (φ) and expansion (r) coordinate calculated[11] by the AOM technique using ligand field parameters appropriate to [Fe(tpchxn)]$^{2+}$.

This could arise if the activated complex for the spin change were stabilized by increased solvation. From the AOM and ligand field parameters appropriate to Fe(tpchxn)$^{2+}$, the energy of a trigonal-prismatic triplet state relative to the singlet ground state can be calculated.[11] Figure 4 shows semiquantitatively the twist pathway (combined with a significant contribution from radial expansion) derived from this computation. The triplet state shown is only involved via second-order perturbation from the nearest state. Nevertheless, the computations suggest that the triplet state could assume the role of a transition state for a sufficiently large twist angle, φ. The vertical singlet–triplet energy gap, calculated for $\varphi = 0°$ is ca. 90 kJ mol^{-1}, which is considerably higher than the experimental activation enthalpy, $\Delta H_{15}^{\ddagger}$, for the singlet → quintet spin change in Fe(tpchxn)$^{2+}$. However, a significantly lower barrier may be possible if the activated complex can be stabilized by increased solvent coordination.

Regardless of the detailed mechanism for the spin crossover however, the activation volume data reported here add significantly to previous evidence,[6a] calling for revision of earlier views[16,18,23] that the transition state for the spin crossover resembles the ${}^5T$ isomer and that the process is nonadiabatic with a transmission coefficient κ of 10^{-2}–10^{-3}. The latter is determined mainly by the electronic interaction, V, between the high- and low-spin states, which in symmetrical systems must be relatively small. A value of $V \sim 170$ cm^{-1} has been used by Jortner and co-workers[24] to calculate rate constants for the spin change on the basis of a model of the spin crossover as a nonadibatic multiphonon radiationless transition between two spin states. More realistic estimates[11] of V must take account of the actual distortions generated in the complex by the ligand field. Such estimates yield in the case of Fe(tpchxn)$^{2+}$ $V \sim 270$ cm^{-1}, almost twice the value employed in the theoretical calculations. The latter lead to rate constants approximately 2 orders of magnitude greater than experimentally observed. This discrepancy will be significantly increased with a more realistic choice of electronic interaction parameter.

Although it is well-known[11,16] that no matrix element connects the quintet and singlet spin states directly, the transmission coefficient may approach unity if a triplet state is sufficiently close in energy so that a second-order perturbation mixes the quintet and singlet states significantly. Our findings, particularly the activation volume data, are consistent with a transmission coefficient of ~ 1.

We have also carried out some variable-pressure[25] studies of ${}^2T \rightleftharpoons {}^6A$ spin relaxation in Fe(III) complexes. The activation volumes show a similar (although as yet less extensively investigated) variation with solvent despite the relaxation times[4] being an order of magnitude faster than for the Fe(II) complexes reported here, suggesting that κ is also close to unity.

Acknowledgment. We thank the SERC for support and the Department of Education (N. Ireland) for a postgraduate award (to I.L.). The assistance of K. P. Taylor and F. Vanhecke with some of the experiments is gratefully acknowledged.

---

(22) The possibility has been suggested by a reviewer that the results observed for complex F in DMF might be indicative either of a change in mechanism or of a different photochemical process occurring in this solvent. Although it is difficult to exclude such possibilities rigorously, there are no indications in support of them from the relaxation measurements as a function of monitoring wavelength. In particular, the transient absorbance difference spectra recorded for complex F less than 50 ns after the laser pulse were the same in DMF and CH_3CN solutions, suggesting that the same perturbation and relaxation phenomena are occurring in both media. Furthermore, a virtually identical absorbance difference profile was recorded for complex D in CH_3CN solution. It should also be noted that these hexadentate ligand complexes display little tendency toward ligand dissociation in solution, being highly resistant for example to acid hydrolysis.[7]

(23) Beattie, J. K.; Binstead, R. A.; West, R. J. *J. Am. Chem. Soc.* **1978**, *100*, 3044–3050.

(24) Bukhs, E.; Navon, G.; Bixon, M.; Jortner, J. *J. Am. Chem. Soc.* **1980**, *102*, 2918–2923.

(25) McGarvey, J. J.; Lawthers, I. Manuscript in preparation.