

## Spin-state Relaxation Dynamics in Iron(II) Complexes: Solvent Effects on the Activation and Reaction Volumes for the $^1A \rightleftharpoons ^5T$ Interconversion

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Activation and reaction volumes are reported for the interconversion of the  $^1A$  and  $^5T$  isomers of Fe<sup>II</sup> complexes in several solvents; the reaction volume  $\Delta V^\circ$  and the activation volume  $\Delta V_{15}^\ddagger$  are solvent-dependent but  $\Delta V_{51}^\ddagger$  for the  $^5T \rightarrow ^1A$  crossover is markedly negative and virtually solvent-independent and a transition state geometry intermediate between the  $^1A$  and  $^5T$  isomers is implied.

The dynamics of the photophysically significant process of high-spin  $\rightarrow$  low-spin crossover in transition metal complexes, particularly of Fe<sup>II</sup> and Fe<sup>III</sup>, have been the subject of several investigations by chemical relaxation techniques.<sup>1,2</sup> As we have recently reported,<sup>3,4</sup> laser-induced photochemical perturbation of these spin equilibria permits investigation of the dynamics in a wide range of solvents. Although spin relaxation times,  $\tau$ , have been measured over limited ranges of temperature and solvent type,<sup>1,2</sup> the reaction co-ordinate for the spin change has not been fully elucidated. An important probe of this is the activation volume.

We now report<sup>†</sup> activation volumes for the dynamics of spin change in two structurally related Fe<sup>II</sup> complexes, in three solvents. The complexes are Fe(Hpyim)<sub>3</sub><sup>2+</sup> and Fe(Hpybim)<sub>3</sub><sup>2+</sup>

with ligand structures (1) and (2), respectively [Hpyim = 2-(2-pyridyl)imidazole; Hpybim = 2-(2-pyridyl)benzimidazole].

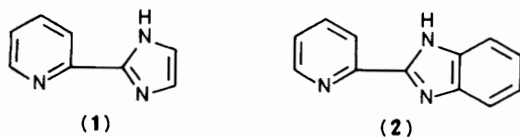
Relaxation of the  $^1A \xrightleftharpoons[k_{51}]{k_{15}} ^5T$  spin equilibrium following photochemical perturbation<sup>3</sup> at 530 nm by a Q-switched Nd<sup>3+</sup>/glass laser (pulse duration 15 ns) was monitored spectrophotometrically in the  $\lambda$  region 360–500 nm. The measurements were made over the pressure range 0.1–125 MPa in a steel vessel fitted with sapphire windows and thermostatted at –14 °C. The relaxation times,  $\tau$ , spanned the range 120–160 ns at  $P = 0.1$  MPa, depending on complex and solvent and decreased with increasing pressure.<sup>3b</sup> The pressure-dependent equilibrium constants  $K = k_{15}/k_{51}$  and hence the partial molar volume differences (reaction volumes),  $\Delta V^\circ$ , between the  $^1A$  and  $^5T$  isomers were determined from absorbance measurements in the range 0.1–150 MPa. The activation volumes  $\Delta V_{15}^\ddagger$  and  $\Delta V_{51}^\ddagger$ , computed from the slopes of  $\ln(1/\tau)$  vs.  $P$  plots combined with  $K$  and  $\Delta V^\circ$  values, are summarized in Table 1 which also shows the corresponding

<sup>†</sup> While the present paper was in preparation we received a pre-publication manuscript (ref. 5) which reports  $\Delta V^\ddagger$  data for Fe(Hpyim)<sub>3</sub><sup>2+</sup> in Me<sub>2</sub>CO. The results agree qualitatively with those presented here.

**Table 1.** Activation volumes, reaction volumes,<sup>a</sup> and activation entropies for <sup>1</sup>A ⇌ <sup>5</sup>T spin-state interconversion in Fe<sup>II</sup> complexes in several solvents.

Complex <sup>b</sup>	Solvent [D.N. <sup>c</sup> ]	$\Delta V^0/\text{cm}^3 \text{mol}^{-1}$	$\Delta V_{15}^\ddagger/\text{cm}^3 \text{mol}^{-1}$	$\Delta V_{51}^\ddagger/\text{cm}^3 \text{mol}^{-1}$	$\Delta S_{15}^\ddagger/\text{J K}^{-1} \text{mol}^{-1}$	$\Delta S_{51}^\ddagger/\text{J K}^{-1} \text{mol}^{-1}$
Fe(Hpyim) <sub>3</sub> <sup>3+</sup>	MeCN [14]	14.3 ± 0.5	8.9 ± 0.4	-5.4 ± 0.3	44 ± 5	-58 ± 5
..	Me <sub>2</sub> CO [17]	10.3 ± 0.4	4.9 ± 0.3	-5.4 ± 0.3	-9 ± 5	-58 ± 5
..	MeOH-20% MeCN [22 <sup>d</sup> ]	5.3 ± 0.2	0.0 ± 0.2	-5.3 ± 0.3	-23 ± 5	-75 ± 5
Fe(Hpybim) <sub>3</sub> <sup>3+</sup>	MeCN	12.4 ± 0.5	5.9 ± 0.4	-6.4 ± 0.4	21 ± 5	-61 ± 5
..	Me <sub>2</sub> CO	9.6 ± 0.4	4.7 ± 0.4	-4.9 ± 0.4	14 ± 5	-64 ± 5
..	MeOH-20% MeCN	4.3 ± 0.4	0.2 ± 0.3	-4.1 ± 0.4	1 ± 7	-91 ± 7

<sup>a</sup> Measured at 298 K. <sup>b</sup> Solutions of the BPh<sub>4</sub><sup>-</sup> salts were prepared in dry solvents; concentration range 10<sup>-3</sup>–10<sup>-4</sup> mol dm<sup>-3</sup>. <sup>c</sup> Solvent donor number, from ref. 7. <sup>d</sup> Value for pure MeOH.



activation entropies,  $\Delta S^\ddagger$ , derived from variable temperature  $\tau$  and  $K$  measurements.

For both complexes the parameters  $\Delta V^0$  and  $\Delta V_{15}^\ddagger$  show a marked solvent dependence, but the activation volume,  $\Delta V_{51}^\ddagger$  for the quintet → singlet transition is independent of solvent in the case of Fe(Hpyim)<sub>3</sub><sup>3+</sup> and exhibits a small trend only for Fe(Hpybim)<sub>3</sub><sup>3+</sup>. Although the  $\Delta V_{51}^\ddagger$  values are appreciably negative, indicating significant contraction of the transition state relative to the <sup>5</sup>T isomer, both intrinsic factors (metal–ligand bond length changes) and changes in solvation may contribute to observed volume changes in an activation step, *i.e.*  $\Delta V_{\text{obs}}^\ddagger = \Delta V_{\text{intr}}^\ddagger + \Delta V_{\text{solv}}^\ddagger$ , and the relative importance of these contributions cannot readily be assessed from measurements in one solvent alone. However our observation of virtually constant  $\Delta V_{51}^\ddagger$  in three different solvents suggests that the  $\Delta V_{\text{solv}}^\ddagger$  term must tend to zero, *i.e.* that the transition state and <sup>5</sup>T species are solvated to a similar extent. We therefore conclude that the major contribution to  $\Delta V_{51}^\ddagger$  must be *intrinsic*, arising from Fe–N ligand bond contraction in the <sup>5</sup>T → <sup>1</sup>A activation step.

The longer Fe–N bonds and larger partial molar volumes of <sup>5</sup>T( $t_{2g}^4 e_g^2$ ) isomers compared to <sup>1</sup>A( $t_{2g}^6$ ) can be rationalized<sup>6</sup> in terms of the transfer of two electrons from the antibonding  $e_g$  orbitals to the  $t_{2g}$  set. The intrinsic  $\Delta V_{51}^\ddagger$  of  $-5 \text{ cm}^3 \text{ mol}^{-1}$  observed in the present work is indicative of a transition state geometry intermediate between the <sup>1</sup>A and <sup>5</sup>T spin isomers. The solvent dependent  $\Delta V_{15}^\ddagger$  for the reverse spin change supports this interpretation, reflecting the opposing contributions of intrinsic volume expansion and solvent contraction. Both  $\Delta V^0$  and  $\Delta V_{15}^\ddagger$  are correlated with the nucleophilic properties of the solvent, becoming less positive with increasing solvent donor number (Table 1).<sup>7</sup> This suggests that the charge distribution in the complex significantly influences the extent of solvation, with the <sup>1</sup>A isomer being less strongly solvated than the transition state and the <sup>5</sup>T species. We attribute this to a lowering of the effective charges on the ligands due to  $\pi$  back donation from the metal  $t_{2g}$  orbitals, an effect which will be most pronounced for the <sup>1</sup>A isomer.<sup>8</sup> The trend in  $\Delta V_{51}^\ddagger$  with solvent observed for Fe(Hpybim)<sub>3</sub><sup>3+</sup> is not surprising in view<sup>9</sup> of the greater steric demands and consequent Fe–N bond lengthening effects of the 2-(2-pyridyl)benzimidazole ligand.

Table 1 shows that the activation entropies  $\Delta S_{51}^\ddagger$  for the <sup>5</sup>T → <sup>1</sup>A transition are also markedly negative, a feature reported<sup>2b</sup> for other Fe<sup>II</sup> spin-state transitions. In the latter work, the  $\Delta S_{51}^\ddagger$  values have been used<sup>2b</sup> to estimate non-adiabatic factors for the spin-crossover. The underlying assumption<sup>1,2b</sup> of these calculations, that the transition state resembles the <sup>5</sup>T isomer, may require some scrutiny in the light of the  $\Delta V_{51}^\ddagger$  data from the present work. While these negative  $\Delta V_{51}^\ddagger$  values do imply significant radial contraction in the <sup>5</sup>T → <sup>1</sup>A activation step, they do not exclude the possibility<sup>10,11</sup> that a pseudorotational motion is also involved. A twist process would be expected<sup>12</sup> to make a negligible contribution to the observed volume changes. In pursuit of this matter, variable pressure studies are in progress on complexes with conformationally restricted ligands.

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