Observation of Biphasic Kinetics in Light-induced Spin-state Crossover in an Iron(II) Complex in Solution

Ala H. R. Al-Obaidi,[a] **John J. McGarvey,***[a] **K. Paul Taylor,**[a] **Steven E. J. Bell,**[a] **Kenneth B. Jensen**[b] **and Hans Toftlund***[b]

[a] *School of Chemistry, Queen's University of Belfast, Belfast, N. Ireland BT9 5AG*
[b] *Department of Chemistry, University of Odense, Odense DK5230, Denmark*

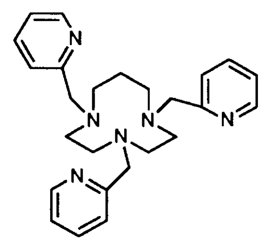
Relaxation of the ${}^1A_1 \rightleftharpoons {}^5T_2$ spin equilibrium in acetonitrile of the complex of Fe^{II} with the multidentate pyridyl macrocyclic ligand *N,N′,N″*-tris(2-pyridylmethyl)-1,4,7-triazacyclodecane (tp[10]aneN_3) after perturbation by a pulsed laser provides the first example of biphasic kinetics for spin crossover in solution with a fast ($\tau < 30$ ns) temperature-independent process coupled to a slower, temperature-dependent step; barrierless spin change is so far unique among spin equilibrium systems.

During studies of spin-state relaxation in Fe^{II} complexes in solution by pulsed laser photoperturbation we have observed a novel instance of biphasic relaxation kinetics following perturbation of the singlet (${}^1A_1$) $\rightleftharpoons$ quintet (${}^5T_2$) spin equilibrium.

Light-induced spin-state conversion, first reported[1] in solution some years ago and subsequently[2] in the solid state, is well established as a technique for studying the dynamics of the spin crossover process in Fe^{II} or Fe^{III} complexes.[3,4] There has been a renewal of interest in the phenomenon because of the potential offered by spin crossover systems for the development of advanced optical materials owing to the large differences in optical properties such as absorption cross sections or refractive indices of the high and low spin forms. The control of spin-state lifetimes by means of the ligand structure is a useful strategy in the design of spin crossover systems with potential application as molecular switches. In the present work we have been exploring the possibilities offered by ligand structures designed to couple the spin crossover to conformational changes in the molecule.

The ligands used are all hexadentate, derived from triazamacrocycles with pendant pyridyl arms and the novel biphasic kinetics were observed in the relaxation of the singlet-quintet spin equilibrium in the Fe^{II} complex with the ligand tp[10]aneN_3 which has the structure shown in **1**.

In solution the $[Fe(tp[10]aneN_3)]^{2+}$ ion showed a low-spin to high-spin transformation around room temperature. However, in the solid state the perchlorate salt has a rather constant μ_{eff} of 0.3–0.5 μ_B. The equilibrium constants in MeCN–H_2O mixtures were determined in the temperature range 278–350 K from an analysis of the electronic spectra. The ln *K vs.* 1/*T* plot yielded the thermodynamic parameters $\Delta H^o = 16.8$ kJ mol^{-1} and $\Delta S^o = 53.5$ J K^{-1} mol^{-1}.



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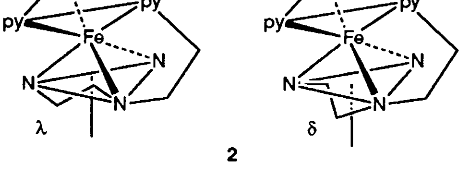

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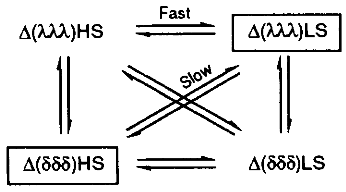

Scheme 1

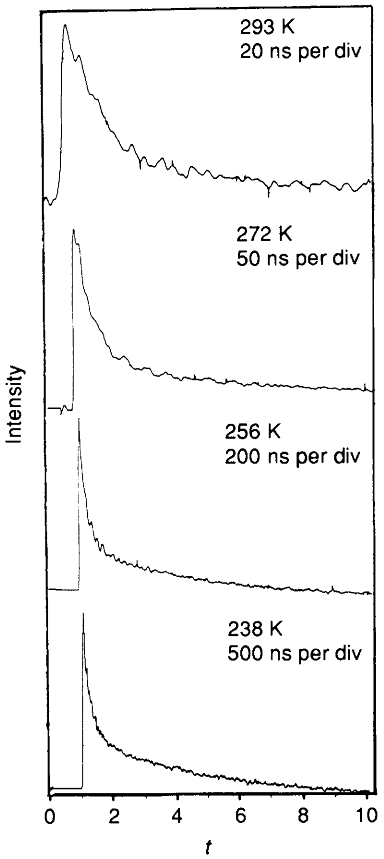

Fig. 1 Ground state depletion and relaxation to original absorbance level following pulsed laser irradiation at 396 nm of [Fe(tp-[10]aneN$_3$)]$^{2+}$ in MeCN (10^{-3} mol dm^{-3}) at different sample temperatures. Monitoring wavelenth 420 nm; laser pulse energy 7 mJ. Timescales for the relaxation traces vary as indicated.

For the photoperturbation and relaxation kinetics, solutions of the Fe^{II} complex of **1** in MeCN (*ca.* 10^{-3} mol dm^{-3}) were irradiated with a laser pulse[3] at 532 nm. (Quanta Ray DCR2 Nd/YAG laser, pulse duration 8 ns, typical pulse energy 7 mJ.) Following the fast, instrument-response-time-limited depletion of the ground-state absorbance a return to the original level occurred with a temporal profile independent of monitoring wavelength in the range 350–510 nm. The effect was studied over a wide temperature range (298–238) K. Representative relaxation traces recorded at several temperatures are shown in Fig. 1, from which the biphasic nature of the relaxation is evident. The traces correspond to depletion of the low spin $^1A_1$ isomer following pulsed laser irradiation into the metal-ligand charge-transfer (MLCT) band of the latter with subsequent relaxation from the ^{1}MLCT state so produced to the high spin isomer. Multichannel detection of the spectral changes in the sample following pulsed irradiation supports this interpretation. In Fig. 2, trace (*A*) shows the ground state absorption prior to pulsed irradiation and (*B*) shows the ground state depletion recorded at a delay of 100 ns after the perturbing laser pulse. The difference spectrum (*A* − *B*) clearly resembles that obtained by subtraction of the ground electronic state UV–VIS absorption spectrum (trace *C*) of the complex recorded at low temperature, 232 K, where the low-spin isomer is increasingly favoured, from that in (*D*) recorded at 295 K where the equilibrium population of the high spin isomer is significantly increased. The difference spectrum (*D* − *C*) is largely that of the high spin isomer.

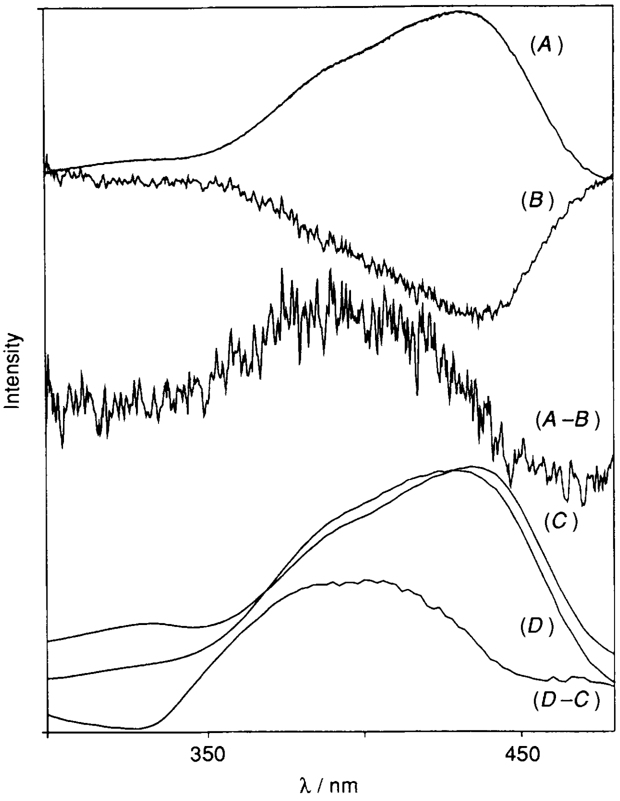

Fig. 2 Ground state and transient electronic absorption spectra of [Fe(tp[10]aneN$_3$)]$^{2+}$ in MeCN (10^{-3} mol dm^{-3}), recorded using a multichannel detector. (*A*): absorption spectrum recorded at −25 °C; (*B*): ground state depletion spectrum following pulsed laser irradiation at 532 nm of solution used in (*A*). Spectrum recorded 100 ns after laser pulse using a gated multichannel detector, gate pulse width 7 ns. Laser pulse energy 7 mJ; (*A* − *B*): Difference spectrum; (*C*) and (*D*): ground state absorption spectra recorded of same solution used in (*A*) and (*B*), recorded at −41 and 22 °C respectively; (*D* − *C*): difference spectrum.

The observed bleaching of the $^1A_1 \rightarrow {}^1$MLCT absorption and the build up of the quintet absorption indicates that at least one of the observed kinetic processes is associated with the $^5A_2 \rightsquigarrow {}^1A_1$ relaxation. For a related system [Fe(tpen)]$^{2+}$ [tpen = tetrakis(2-pyridylmethyl)-1,2-ethylenediamine], Hendrickson *et al.* have shown[5] that the quintet state population builds up in less than a few ps after the $^1A_1 \rightarrow {}^1$MLCT excitation. Hence an internal conversion *via* low-lying singlet and triplet ligand-field states seems very unlikely. Assuming that the present system behaves similarly we can exclude any path involving ligand field triplet states as a candidate for one of the observed kinetic processes. Another possible way of accounting for the observed biphasic kinetics would be to assign one of the reactions as ligand dissociation. However ligand dissociation in these systems is very difficult to achieve, even under acidic conditions. Furthermore, since the dissociation would give rise to spectral changes and would have to precede the spin change there should be a finite rise-time step prior to the relaxation. This is not observed experimentally. To account for the biphasic behaviour of the spin relaxation process as illustrated by Fig. 1 we propose that the spin change is strongly coupled to conformational changes in the molecule through radial (*i.e.* Fe–N distance) changes.

The structure of a complex such as Fe(tp[10]aneN$_3$)$^{2+}$ is restricted by the fusion of six chelate rings. For a given configuration, Δ or Λ there are two different conformations, δ or λ, of the aliphatic rings of the macrocyclic moiety, as illustrated in **2**. By comparison with published structures[6,7] of $[M(tptcn)]^{2+}$ [tptcn = *N,N′,N″*-tris(2-pyridylmethyl)-1,4,7-triazanonane, M = Fe;[6] M = Ni, Mn[7]] it can be concluded that in the most stable low spin structure the configuration and conformations are opposite whereas in the most stable high spin structure they are expected to be equal. The isomerisation rates (configuration as well as conformation), are slow compared to the spin change rates. If the radial changes accompanying the spin change are indeed coupled to conformational change in the molecule the situation could arise in which the spin change is slowed down compared to that in other typical spin crossover sytems. On the other hand a very stiff coordination sphere could inhibit ligand reorganization, resulting in a very fast spin change. These proposals are summarized in Scheme 1.

The biphasic behaviour of the present system as shown by the relaxation traces in Fig. 1 suggests that both mechanisms are operating. From the temperature dependence of the slower process, an Eyring plot of the data in combination with the thermodynamic parameters for the spin equilibrium give the activation parameters, $\Delta H^{\ddagger}_{15}$ = 36.9 kJ mol^{-1}; $\Delta H^{\ddagger}_{51}$ = 20.1 kJ mol^{-1}; $\Delta S^{\ddagger}_{15}$ = −40.9 J mol^{-1} K^{-1}; $\Delta S^{\ddagger}_{51}$ = −94.4 J mol^{-1} K^{-1}. These are in the range previously reported[8] for similar systems. In contrast, the faster decay process shows no variation with temperature over the range 234–295 K investigated. Such a barrierless process is unique among spin crossover systems. However the result is in accord with the common assumption that ligand reorganization represents the main contribution to the activation energy since it suggests that the molecular rearrangement between the two spin states is hindered by the stiffness of this particular ligand.

It is clear that the lifetimes of the spin states can to some extent be controlled by the ligand in systems of the present type which therefore fulfil at least one of the requirements for the construction of a molecular switch. The strategy of trapping the spin states by means of a stiff ligand system has only been partly successful in this instance due to the creation of a competing spin relaxation route.

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