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Comparison of the rates and mechanisms of formation and solvolysis of $[Fe(bipy)_3]^{2+}$ (bipy = 2,2′-bipyridine) and $[FeL]^{2+}$ [L = 1,4,7-tris(2,2′-bipyridyl-5-ylmethyl)-1,4,7-triazacyclononane] and their stabilities in dimethylformamide solution[†]

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Multiwavelength stopped-flow spectrophotometry has been used to compare the rates and mechanisms of formation of $[Fe(bipy)_3]^{2+}$ (bipy = 2,2′-bipyridine) and $[FeL]^{2+}$ [L = 1,4,7-tris(2,2′-bipyridyl-5-ylmethyl)-1,4,7-triazacyclononane, containing three co-ordinating bipy groups], in dimethylformamide (dmf) solution. Molecular modelling of L, and kinetic studies of its reaction with $[Fe(dmf)_6]^{2+}$, are consistent with the presence of two N-configurational isomers (*RRR* and *RRS*); at 25 °C, the *RRR* isomer reacts with $[Fe(dmf)_6]^{2+}$ to give $[FeL]^{2+}$ with a formation rate constant, $10^{-5}k_f = 2.34 \pm 0.09$ dm^3 mol^{-1} s^{-1}, and the *RRS* isomer reacts to give an intermediate bis(bipy) complex with $10^{-5}k_f = 1.04 \pm 0.01$ dm^3 mol^{-1} s^{-1}. This bis(bipy) intermediate rearranges to the tris(bipy) chelate with a first-order rate constant of 0.71 ± 0.02 s^{-1}, but is also involved in the formation of a small amount of an $[Fe_2L_2]^{4+}$ dimer. The kinetically determined dimer formation constant is $(1.2 \pm 0.1) \times 10^5$ dm^3 mol^{-1}. For the reaction of $[Fe(dmf)_6]^{2+}$ with bipy at 25 °C, rapid formation of $[Fe(dmf)_4(bipy)]^{2+}$ ($10^{-5}k_f = 1.4 \pm 0.1$ dm^3 mol^{-1} s^{-1}) is followed by the much slower formation of $[Fe(dmf)_2(bipy)_2]^{2+}$ ($k_f = 181 \pm 7$ dm^3 mol^{-1} s^{-1}) and $[Fe(bipy)_3]^{2+}$ ($k_f = 24.3 \pm 0.9$ dm^3 mol^{-1} s^{-1}). The complex $[FeL]^{2+}$ is significantly more stable than $[Fe(bipy)_3]^{2+}$, as shown by the ready solvolysis of $[Fe(bipy)_3]^{2+}$ at low dilution in dmf, whilst $[FeL]^{2+}$ is stable to solvolysis under the same conditions. At 25 °C first-order rate constants for the dissociation of bipy from $[Fe(bipy)_3]^{2+}$ and $[Fe(dmf)_2(bipy)_2]^{2+}$ are $(7.0 \pm 0.3) \times 10^{-3}$ s^{-1} and $(1.4 \pm 0.1) \times 10^{-3}$ s^{-1} respectively, showing that both are inert, low-spin, t_{2g}^6 systems. This contrasts with the behaviour in water, since $[Fe(OH_2)_2(bipy)_2]^{2+}$ is known to be high spin and labile. The kinetically determined stepwise formation constants in dmf confirm this conclusion; values vary in the order $10^{-3}K_1/\mathrm{dm^3\,mol^{-1}} = 9.6 \pm 0.7 < 10^{-5}K_2/\mathrm{dm^3\,mol^{-1}} = 1.3 \pm 0.7 > 10^{-3}K_3/\mathrm{dm^3\,mol^{-1}} = 3.5 \pm 0.2$ (in water $K_1 > K_2 \ll K_3$). Overall formation constants for $[Fe(bipy)_3]^{2+}$ in dmf ($\log_{10} \beta_3 = 12.6$) and in dimethyl sulfoxide ($\log_{10} \beta_3 = 10.7$) are significantly smaller than the value in water ($\log_{10} \beta_3 = 17.4$). Rates of solvolysis of $[M(bipy)_3]^{2+}$ (M = Fe or Ni) were also investigated in dimethyl sulfoxide solution.

Previously it was shown how the ligand 1,4,7-tris(2,2′-bipyridyl-5-ylmethyl)-1,4,7-triazacyclononane (L) forms very stable 1 : 1 mononuclear complexes with di- and tri-valent metal ions by co-ordination of all three pendant 2,2′-bipyridyl (bipy) groups.[1] The complex formed with Fe^{II} is diamagnetic (t_{2g}^6), and is directly analogous to the well known, red $[Fe(bipy)_3]^{2+}$ ion.[2] The visible spectra of $[FeL]^{2+}$ and $[Fe(bipy)_3]^{2+}$ are almost identical (Fig. 1), confirming the ability of L to co-ordinate through the three bipy arms, and with minimum distortion of the metal ion's octahedral geometry. In protic media the three non-co-ordinating azamacrocyclic N atoms of L were found to have a high affinity for a single proton, and this led to the isolation of a range of monoprotonated complexes of the type $[M(HL)]^{n+}$ [M = Fe^{II}, Ru^{II}, Co^{II}, Ni^{II}, Cu^{II} or Zn^{II}, $n = 3$; M = Co^{III}, $n = 4$].[1,3] The structures of these closely related species have been examined by molecular mechanics and dynamics calculations, and two of them established by X-ray crystallography [M = Ru^{II} or Cu^{II}].[1,3] The most stable isomer of the ligand L is that with an *RRR* set of azamacrocyclic N atoms, and it was shown that this isomer undergoes minimum reorganisation in forming the tris(bipy) chelates. Therefore, L can be regarded as 'pre-organised' for tris(bipy) chelation.[1]

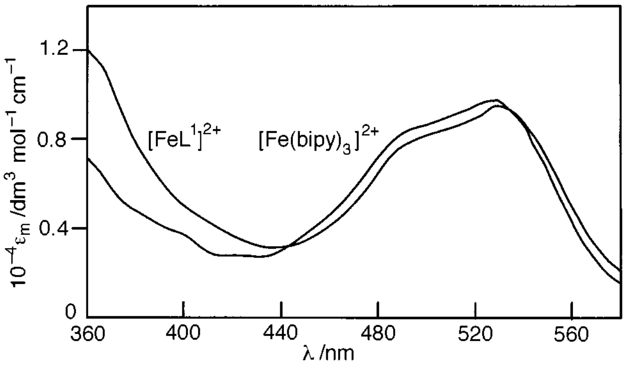
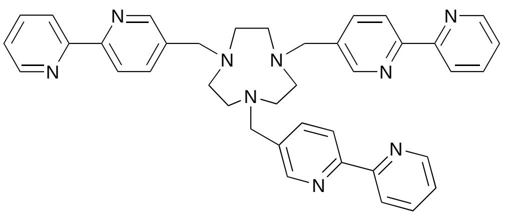


Fig. 1 Comparison of the visible spectra of $[FeL]^{2+}$ and $[Fe(bipy)_3]^{2+}$



L

In this study multiwavelength stopped-flow spectrophotometry has been used to compare the kinetics and mechanisms of the reactions of L, and of 2,2′-bipyridine (bipy), with $[Fe(dmf)_6]^{2+}$ in dmf (dimethylformamide). Studies were carried out in an aprotic solvent to avoid complications from ligand protonation which occur when basic amines such as L are studied in aqueous media. Previous studies of the reaction of L with $[Ru(dmso)_4Cl_2]$ (dmso = dimethyl sulfoxide) showed that for this more inert metal both the monoprotonated monomer $[Ru(HL)]^{3+}$ and the monoprotonated dimer $[Ru_2HL_2]^{5+}$ can be isolated.[1] In the dimer two of the three bipy arms of L are co-ordinated to one ruthenium, and the third bipy arm to the

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[†] Dedicated to Professor R. G. Wilkins on the occasion of his 70th birthday.

second ruthenium. The mechanism by which both the monomer and dimer form has not been established, and in this study we have examined the possibility that the dimer might be produced as an intermediate on the way to forming the monomer.

Based on the chelate effect, it is to be expected that β_1 for the formation of $[FeL]^{2+}$ will be significantly larger than β_3 for the formation of $[Fe(bipy)_3]^{2+}$, and a kinetic investigation of their relative rates of solvolysis was undertaken in dmf to confirm this expectation, and to establish the relative labilities of the mono-, bis- and tris-(bipy) complexes of Fe^{2+} in dmf. For comparison, the kinetics of the solvolysis of $[M(bipy)_3]^{2+}$ (M = Ni or Fe) was also investigated in dimethyl sulfoxide; the nickel(II) complex was studied since, unlike $[Fe(bipy)_3]^{2+}$, complications from spin-state changes do not occur during the solvolysis of $[Ni(bipy)_3]^{2+}$. In aqueous solution it is well known that whereas $[Fe(bipy)_3]^{2+}$ is low spin (t_{2g}^6) and inert, $[Fe(OH_2)_2(bipy)_2]^{2+}$ and $[Fe(OH_2)_4(bipy)]^{2+}$ are high spin ($t_{2g}^4e_g^{*2}$) and labile.[2] In contrast to the behaviour in water, the rates of solvolysis in dmf indicate that this spin-state change occurs after the loss of two rather than one of the bipy ligands.

Results and Discussion

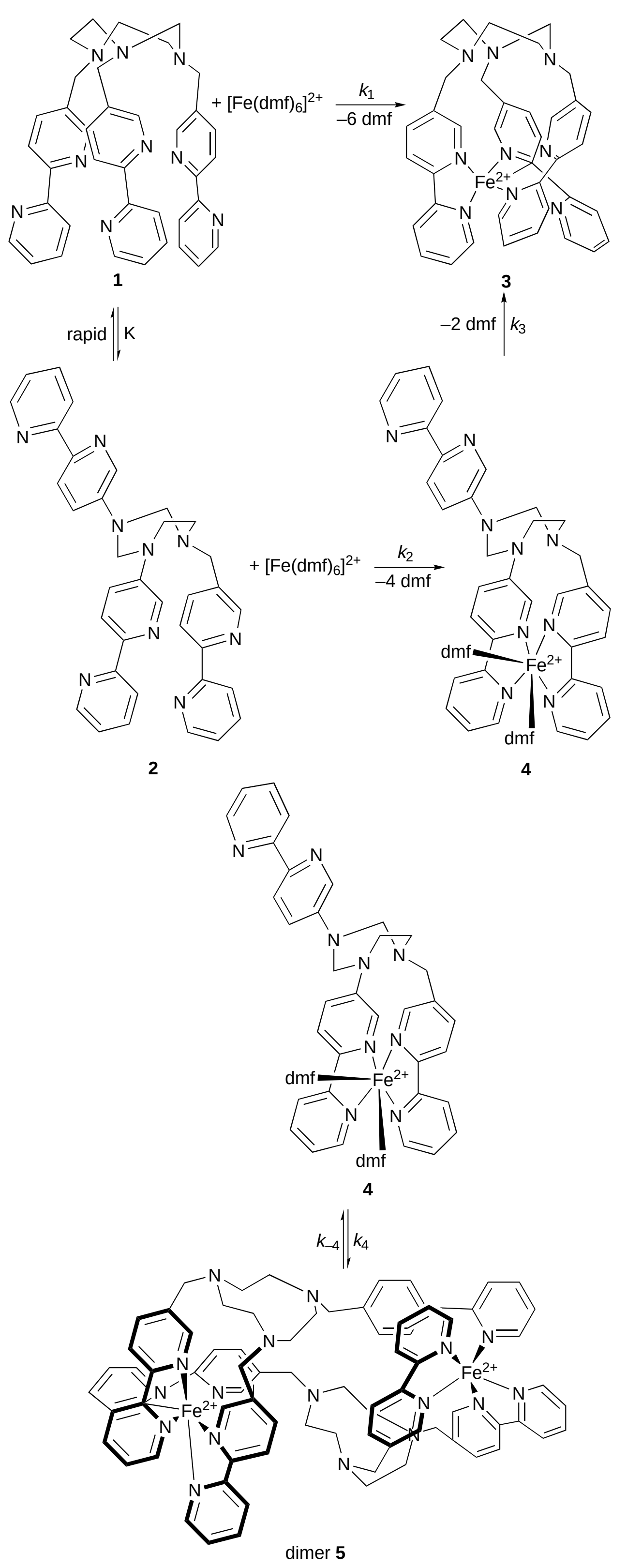
Molecular modelling

We have shown previously how molecular mechanics and dynamics calculations may be used to establish the relative stabilities of the five N-configurational isomers of the macrocycle 1,4,8,11-tetraazacyclotetradecane (cyclam).[4] Application of the same molecular modelling methods revealed the relative energies of the two possible energy-minimised N-configurational isomers of L (*RRR* and *RRS*), and showed that the lowest-energy structure has the *RRR* set of conformations at N (*i.e.* that with all three bipy arms on the same side of the macrocyclic plane). The molecule with an *RRS* arrangement was found to be 11 kJ mol^{-1} higher in energy, and calculations based on this energy difference alone suggest the relative amounts of the two conformers to be $[RRR]/[RRS] \approx 84$. The geometries of the two energy-minimised structures are shown in Scheme 1 (**1** and **2**). Proton NMR studies show that the two structures are in rapid equilibrium at room temperature, and attempts to freeze out the NMR spectrum at low temperatures were unsuccessful. However, kinetic studies indicate that both species are involved in the rapid reaction of L with $[Fe(dmf)_6]^{2+}$.

Formation of $[FeL]^{2+}$ in dmf

Kinetic studies were carried out at 25 °C by stopped-flow spectrophotometry in the 350–650 nm wavelength range, using equimolar concentrations of both ligand and metal ion [in the range $(1.5–4.0) \times 10^{-4}$ mol dm^{-3}]. The multiwavelength kinetic data indicated at least three kinetic processes: a fast initial stage (accompanied by a *ca.* 60% absorbance change and over in less than 0.2 s) is followed by a second fairly rapid stage (characterised by a 28% change in absorbance and complete in *ca.* 1.5 s), and finally a slow third stage (which accounts for the final 12% change in absorbance and takes longer than 500 s). A postulated mechanism to account for the observed rate processes is presented in Scheme 1. In this scheme, **1** and **2** are the two possible N-configurational isomers of L (*RRR* and *RRS* respectively) which are in rapid equilibrium, the final product is **3**, and **5** is directly analogous to the dimer found previously for Ru^{II}.[1] Intermediate **4** has two of the bipy arms of L co-ordinated and the third arm unco-ordinated. To allow co-ordination of the unco-ordinated bipy arm of **4**, inversion at N must occur before the formation of monomeric **3** is possible. Intermediate **4** can also dimerise to give **5** without such inversion occurring. Complex **5** is in slow equilibrium with **4**, which accounts for the slow final stage in the formation of the final product **3**.

A global analysis of the multiwavelength kinetic data in terms of the proposed mechanism in Scheme 1 gave good fits, and at 25 °C $10^{-5}k_1 = 2.34 \pm 0.09$ dm^3 mol^{-1} s^{-1}, $10^{-5}k_2 = 1.04 \pm 0.01$ dm^3 mol^{-1} s^{-1}, $k_3 = 0.71 \pm 0.02$ s^{-1}, $10^{-3}k_4 = 1.78 \pm 0.14$ dm^3 mol^{-1} s^{-1} and $10^2k_{-4} = 1.49 \pm 0.03$ s^{-1}. The calculated spectra of complexes **3**–**5** are very similar in appearance to that of $[FeL]^{2+}$ shown in Fig. 1, but with different molar absorption coefficients (**4** < **3** < **5**). This is an indication that all three species have a t_{2g}^6 electronic configuration, since the high-spin complexes absorb at a different wavelength. The calculated concentration *versus* time profiles show that **4** reaches its



Scheme 1

maximum concentration soon after mixing (*ca.* 0.2 s), and that 90% of the total amount of **3** forms in less than 5 s. Complex **5** forms in very small amounts and slowly rearranges to the more stable monomeric form, **3**.

The stability constant for the dimeric species **5** is obtained kinetically [$K_4 = k_4/k_{-4} = (1.2 \pm 0.1) \times 10^5$ dm^3 mol^{-1}]. Stability constants for the other species involved, namely the monomeric tris-chelate **3** and the bis-chelate **4**, cannot be determined at the present time. Unlike $[Fe(bipy)_3]^{2+}$, the intensely red coloured monomer **3** is indefinitely stable in the dark in dmf solution, and attempts to study the rate of dissociation by reaction with Hg^{II} were unsuccessful, again confirming that it is a very stable complex. Although a quantitative comparison with the stability of $[Fe(bipy)_3]^{2+}$ has not been possible, the ready solvolysis of the latter in dmf shows that **3** is substantially more stable than $[Fe(bipy)_3]^{2+}$, as expected based on the chelate effect.

Formation of $[Fe(bipy)_3]^{2+}$ in dmf

The reaction between $[Fe(dmf)_6]^{2+}$ and bipy in dmf was studied by stopped-flow spectrophotometry between 320 and 580 nm. Pseudo-first-order conditions were used, with Fe^{II} in large excess over bipy, and in the concentration ranges $[Fe(dmf)_6{}^{2+}] = (1.6–4.9) \times 10^{-3}$ and $[bipy] = 1.52 \times 10^{-4}$ mol dm^{-3}. Under these conditions a family of stopped-flow multiwavelength kinetic traces indicated at least two kinetic processes: a very fast initial stage, accompanied by a *ca.* 12% increase in absorbance and over in less than 0.03 s, and a slow subsequent process characterised by 88% change in absorbance and still incomplete after 1000 s, during which time an intense red colour has developed. Even though a large excess of Fe^{2+} was used, formation of bis and some tris complexes is not prevented due to a change from a paramagnetic, high-spin to diamagnetic, low-spin iron(II) species as the reaction proceeds.

The initial rapid increase in absorbance was attributed to the fast formation of the high-spin mono-chelate $[Fe(dmf)_4(bipy)]^{2+}$ as the main increase in absorbance has λ_{max} 490 nm, where only the mono species is expected to absorb. In the next 1000 s the slow formation of largely bis and some tris species could be monitored. A postulated mechanism to support the observed data is presented in Scheme 2 (solv = dmf). Global analysis of the multiwavelength data based on the mechanism in Scheme 2 (neglecting k_{-3}, which was found to be negligibly small from studies of the solvolysis reactions) gave $10^{-5}k_1 = 1.4 \pm 0.1$ dm^3 mol^{-1} s^{-1}, $k_{-1} = 14.5 \pm 0.1$ s^{-1}, $k_2 = 181 \pm 7$ dm^3 mol^{-1} s^{-1}, $10^3k_{-2} = 1.33 \pm 0.08$ s^{-1} and $k_3 = 24.3 \pm 0.9$ dm^3 mol^{-1} s^{-1}. The large value of k_1 is as expected for a reaction of the high-spin $[Fe(dmf)_6]^{2+}$ ion, for which the solvent exchange rate is 9.7×10^5 s^{-1} at 25 °C.[5] The much smaller value of k_2 was unexpected, but can be attributed to a change from high to low spin upon addition of the second bipy group. Since $[Fe(terpy)]^{2+}$ (terpy = 2,2′:6′,2″-terpyridine) is low spin,[2] it seems likely that in dmf rapid co-ordination of the first pyridine ring of the second bipy molecule may cause a change from high to low spin, thereby making chelate ring closure and the overall rate of formation of the bis(bipy) complex much slower than the formation of the mono-chelate. The small value of k_{-2} was confirmed by studies of the back (solvolysis) reactions, and the computed relative rates, $k_{-2} \ll k_{-1}$, support the conclusion that in dmf both $[Fe(dmf)_2(bipy)_2]^{2+}$ and $[Fe(bipy)_3]^{2+}$ are low-spin systems. The kinetic analysis also provides a spectrum for $[Fe(dmf)_2(bipy)_2]^{2+}$ which has a maximum at approximately the same wavelength as that of $[Fe(bipy)_3]^{2+}$ but with a reduced molar absorption coefficient. This is further evidence that both the bis and tris complexes are low-spin systems, since the high-spin complexes do not have the characteristic red colour. The observed behaviour is directly analogous to that found for the reaction between L and $[Fe(dmf)_6]^{2+}$, where species **3** and **4** (Scheme 1) have approximately the same λ_{max}, but different molar absorption coefficients. Furthermore, the electronic spectra of either $[Fe(bipy)_3]^{2+}$ and **3**, or $[Fe(bipy)_2(dmf)_2]^{2+}$ and **4**, are calculated to be very similar. In aqueous solution there is no literature information regarding the absorption spectrum of $[Fe(OH_2)_2(bipy)_2]^{2+}$, which is understandable since in water it is only ever present in extremely low concentrations. This is due to the change from high to low spin which occurs between the bis and tris species in aqueous media, and which favours formation of the tris complex (*i.e.* $K_3 \gg K_2$).

$$[Fe(solv)_6]^{2+} + bipy \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Fe(solv)_4(bipy)]^{2+} + 2\ solv \qquad (rapid)$$

$$[Fe(solv)_4(bipy)]^{2+} + bipy \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [Fe(solv)_2(bipy)_2]^{2+} + 2\ solv \qquad (slow)$$

$$[Fe(solv)_2(bipy)_2]^{2+} + bipy \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} [Fe(bipy)_3]^{2+} + 2\ solv \qquad (slow)$$

Scheme 2

Further evidence in support of the postulated mechanism came from comparisons of these iron(II) reactions with analogous reactions of nickel(II) where no spin-state changes are involved. Based on the Eigen–Wilkins mechanism, the second-order rate constant for the formation of a metal complex (k_f/dm^3 mol^{-1} s^{-1}) is the product of the overall first-order rate constant for solvent exchange at the metal ion (k_{ex}/s^{-1}) and the outer-sphere pre-association constant (K_o/dm^3 mol^{-1}): $k_f = k_{ex}K_o$. It is reasonable to assume that during the reactions of either solvated Fe^{2+} or Ni^{2+} with bipy in the same solvent the values of K_o will be very similar, and therefore the relationship $k_f^{Fe}/k_f^{Ni} = k_{ex}^{Fe}/k_{ex}^{Ni}$ will hold {k_{ex}^{Fe} and k_{ex}^{Ni} are the first-order solvent exchange rate constants for $[Fe(dmf)_6]^{2+}$ and $[Ni(dmf)_6]^{2+}$ (9.7×10^5 and 3.8×10^3 s^{-1} respectively), and k_f^{Fe} and k_f^{Ni} the second-order rate constants for formation of the complexes of Fe^{2+} and Ni^{2+} respectively}.[5,6] Therefore, the rate constant for the formation of $[Fe(dmf)_4(bipy)]^{2+}$ can be estimated based on the kinetic data available for reactions of $[Ni(dmf)_6]^{2+}$ with bipy in dmf (at 25 °C, $k_f = 540$ dm^3 mol^{-1} s^{-1})[6] and the ratio of the known solvent exchange rates.[5,6] For the formation of $[Fe(dmf)_4(bipy)]^{2+}$ in dmf the calculated rate constant is estimated to be $k_f = 9.5 \times 10^5 \times 540/3.8 \times 10^3 = 1.38 \times 10^5$ dm^3 mol^{-1} s^{-1}. This value compares very well with that determined experimentally ($10^{-5}k_f = 1.4 \pm 0.1$ dm^3 mol^{-1} s^{-1}), and gives further support to the proposed mechanism in Scheme 2. The calculated value for the outer-sphere pre-association constant in dmf ($K_o^{dmf} = 0.156$ dm^3 mol^{-1}) is, as expected, larger than the value of K_o in water ($K_o{}^{H_2O} = 0.036$ dm^3 mol^{-1}), and confirms that the aprotic medium of lower relative permittivity favours a stronger pre-association between the two reactants.

Dissociation of $[Fe(bipy)_3]^{2+}$ in dmf

In contrast to the behaviour in water, $[Fe(bipy)_3]^{2+}$ readily solvolyses in some non-aqueous solvents such as dimethylformamide and dimethyl sulfoxide, as previous kinetic studies at a fixed wavelength have shown.[7,8] For a more detailed picture of these reactions, multiwavelength studies of the solvolysis of $[Fe(bipy)_3]^{2+}$ were carried out in dmf in two wavelength ranges, 280–320 {when $[Fe(bipy)_3{}^{2+}]$ was adjusted in the range $(0.8–2.7) \times 10^{-5}$ mol dm^{-3}}, and 350–600 nm {$[Fe(bipy)_3{}^{2+}] = (0.1–2.0) \times 10^{-4}$ mol dm^{-3}}. In the visible region (Fig. 2) no isosbestic points are observed, although the decay of the spectrum with time shows that the reaction goes to completion under these conditions. When the reaction is monitored in the UV region an indication that the reaction involves a multistep process is apparent (Fig. 3). The absence of a clean isosbestic point around 288 nm was the first sign that the reaction does not proceed in a single step, which was the conclusion which had been reached from earlier studies in the visible region.[7,8] Previous studies had assumed that the main absorbing species

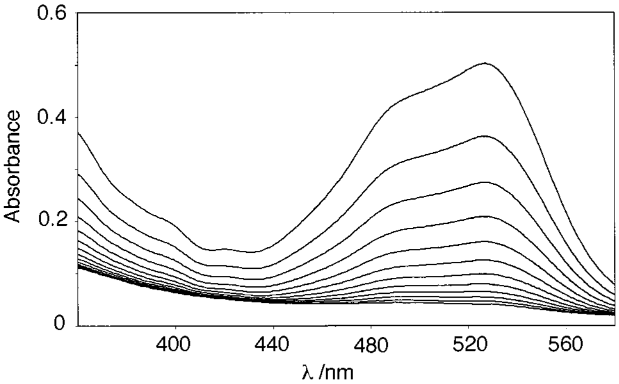


Fig. 2 Visible spectral changes for a solution of $[Fe(bipy)_3]^{2+}$ (4.2×10^{-5} mol dm^{-3}) in dimethylformamide at 25 °C. Initial spectrum (top) recorded 22 s after dissolution of the solid complex, and successive spectra taken at 230 s intervals

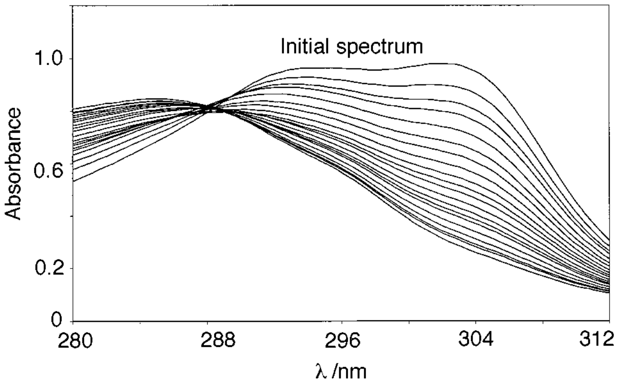


Fig. 3 The UV spectral changes for a solution of $[Fe(bipy)_3]^{2+}$ (1.3×10^{-5} mol dm^{-3}) in dimethylformamide at 25 °C. Initial spectrum (top) recorded 23 s after dissolution of the solid complex, and successive spectra taken at 25 s intervals

observed in the *visible* region is $[Fe(bipy)_3]^{2+}$ (in dmf, $\lambda_{max} = 525$ nm, $\varepsilon = 9.7 \times 10^3$ dm^3 mol^{-1} cm^{-1}), whereas our studies indicate that in dmf the low-spin $[Fe(dmf)_2(bipy)_2]^{2+}$ also absorbs in the same region, but with a lower molar absorption coefficient. A band analogous to that reported for $[Fe(OH_2)_4(bipy)]^{2+}$ in aqueous solutions [$\lambda_{max} = 435$ nm ($\varepsilon = 310$ dm^3 mol^{-1} cm^{-1})][9] was not detected, indicating that the concentration of the mono complex is negligible during the course of the reaction in dmf. This is as expected if this species is high spin and hence very labile. Analysis of the 280–320 nm multiwavelength data indicated at least three kinetic processes. The final, very slow stage was identified as a decomposition of the product $[Fe(dmf)_6]^{2+}$, probably due to slow ingress of oxygen and water to give $[Fe(dmf)_6]^{3+}$ and/or hydrolysis products {the same behaviour was observed for a solution of $[Fe(dmf)_6]^{2+}$ alone}. The first two kinetic steps are associated with the loss of bipy from the low-spin $[Fe(bipy)_3]^{2+}$ and $[Fe(bipy)_2(dmf)_2]^{2+}$, and a spin-state change occurs after the loss of two bipy ligands, making the final step rapid (reverse of Scheme 2; solv = dmf). Global analysis of the experimental data, using fixed spectra for bipy and $[Fe(dmf)_6]^{2+}$, gave the following constants: $10^3k_{-3} = 7.01 \pm 0.25$ s^{-1}, $k_3 = 26.6 \pm 1.3$ dm^3 mol^{-1} s^{-1}, $10^3k_{-2} = 1.39 \pm 0.10$ s^{-1}, $10^{-5}k_2K_1 = 3.01 \pm 0.42$ dm^6 mol^{-2} s^{-1} ($K_1 = k_1/k_{-1}$), and the UV spectra of the intermediates shown in Fig. 4. The value obtained for k_3 from the solvolysis experiments compares reasonably with the rather more precise value obtained from the complex formation studies ($k_3 = 24.3 \pm 0.9$ dm^3 mol^{-1} s^{-1}). The calculated spectra for the tris and bis complexes are again very similar in the UV region, which is as expected for complexes with the same spin state. The lower molar absorption coefficient for the bis compared with that for the tris species is reasonable for these charge-transfer bands, since there are two rather than three co-ordinated bipy groups present.

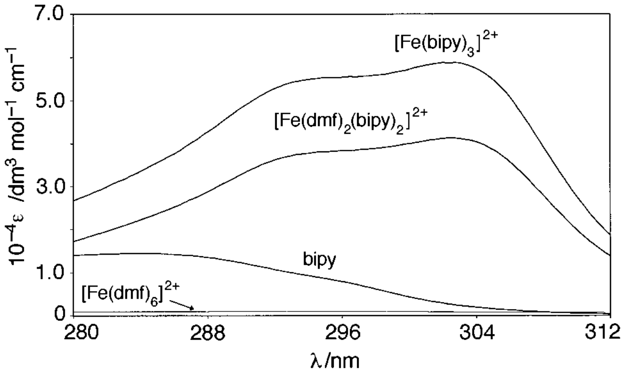


Fig. 4 The UV spectra of $[Fe(bipy)_3]^{2+}$, $[Fe(dmf)_2(bipy)_2]^{2+}$ and 2,2′-bipyridine in dimethylformamide solution, computed after global analysis of the spectral changes shown in Fig. 3

The rate constants obtained from studies of the rates of formation and dissociation of $[Fe(bipy)_3]^{2+}$ in dmf allow an estimate of the overall equilibrium formation constant, β_3, as well as the stepwise formation constants; $K_1 = k_1/k_{-1} = (9.60 \pm 0.67) \times 10^3$ dm^3 mol^{-1}, $K_2 = k_2/k_{-2} = (1.30 \pm 0.65) \times 10^5$ dm^3 mol^{-1}, $K_3 = k_3/k_{-3} = (3.47 \pm 0.18) \times 10^3$ dm^3 mol^{-1}, and therefore the kinetically determined value of $\log_{10}(\beta_3/\text{dm}^9\ \text{mol}^{-3})$ for $[Fe(bipy)_3]^{2+}$ in dmf is 12.6 ± 0.1.

In aqueous solution $[Fe(bipy)_3]^{2+}$ has an overall formation constant β_3 of $10^{17.4}$ dm^9 mol^{-3}, and the stepwise formation constants K_1 (1.6×10^4) $> K_2$ (5.0×10^3) $\ll K_3$ (3.5×10^9 dm^3 mol^{-1}).[10,11] The atypical trend $K_2 \ll K_3$ is good evidence that in water the only low-spin species is $[Fe(bipy)_3]^{2+}$, and the trend $K_1 > K_2$ is consistent with the mono and bis species having the same, high-spin state. In dmf the consecutive formation constants follow a different pattern, $K_1 < K_2 > K_3$, and the differences between the absolute values are less marked than for the aqueous system. This suggests a more active part is played by the aprotic solvent dmf. The trend $K_1 < K_2$ is consistent with a change from high to low spin occurring when the second bipy group becomes attached to the iron(II), and the trend $K_2 > K_3$ is the normal one which is consistent with both the bis and tris complexes having the same spin state in dmf. More direct evidence for the location of the spin-state change is difficult to obtain. Attempts to confirm the position by magnetic susceptibility measurements using an Evans susceptibility balance proved to be impossible at the relatively high concentrations required.

Dissociation of $[Fe(bipy)_3]^{2+}$ in dimethyl sulfoxide

An earlier study of this system at a single wavelength (522 nm) conflicted with our results in dmf, since only a single kinetic process was observed.[7] Therefore, we reinvestigated the reaction in the 268–330 nm wavelength range, using a lower concentration of complex than that used in the visible study, since it was from studies in this region of the spectrum that direct evidence for more than one step was found during the solvolysis in dmf. Surprisingly, in dmso the reaction was found to proceed with a single isosbestic point at 289 nm, and this was a first indication that it might involve a single step as reported from the visible studies. However, when the multiwavelength data were fitted by use of a single first-order equation, the difference between observed and calculated absorbances at each wavelength (the residuals) was non-random. Global analysis of the data was therefore carried out as described for the reaction in dmf (reverse of Scheme 2, solv = dmso), and this gave a much better fit to the multiwavelength data, and the expected random residuals plot. At 25 °C this analysis gave the following values in dmso: $10^3k_{-3} = 5.49 \pm 0.08$ s^{-1}, $k_3 = 26.1 \pm 2.2$ dm^3 mol^{-1} s^{-1}, $10^3k_{-2} = 1.32 \pm 0.01$ s^{-1}, and $10^{-4}k_2K_1 = 1.45 \pm 0.12$ dm^6 mol^{-2} s^{-1}. The overall formation constant in dmso, β_3, and the stepwise formation constant, K_3, are: $\log_{10}(\beta_3/\text{dm}^9\ \text{mol}^{-3}) =$

Table 1 Rate constants at 25 °C for the formation (k_f) and solvolysis (k_d) of $[M(solv)_{6-2n}(bipy)_n]^{2+}$ (n = 1–3, M = Fe^{II} or Ni^{II}), and stepwise formation constants (K_i, i = 1–3) in different solvents (solv)

Constant	Solvent (solv)	$[Fe(solv)_6]^{2+}$	$[Ni(solv)_6]^{2+}$
$k_f^{[M(bipy)]}/dm^3\ mol^{-1}\ s^{-1}$	dmf[a,b]	1.4×10^5	540
	Water[c,d]	1.6×10^5	1.6×10^3
$k_d^{[M(bipy)]}/s^{-1}$	dmf[a]	14.5	
	Water[d]		5×10^{-5}
$k_f^{[M(bipy)_2]}/dm^3\ mol^{-1}\ s^{-1}$	dmf[a]	1.8×10^2	
	Water[b]	1.3×10^5	
$k_d^{[M(bipy)_2]}/s^{-1}$	dmf[a]	1.4×10^{-3}	
	dmso[a]	1.3×10^{-3}	3.7×10^{-3}
$k_f^{[M(bipy)_3]}/dm^3\ mol^{-1}\ s^{-1}$	dmf[a]	24	
	dmso[a,b]	26	17.5
	Water[d]		4.7×10^3
$k_d^{[M(bipy)_3]}/s^{-1}$	dmf[a]	7.0×10^{-3}	
	dmso[a]	5.5×10^{-3}	1.3×10^{-2}
	Water[d]		3.2×10^{-3}
log K_1	dmf[a]	3.98	
	Water[e]	4.20	7.1
log K_2	dmf[a]	5.11	
	Water[e]	3.70	6.8
log K_3	dmf[a]	3.54	
	dmso[a]	3.68	3.23
	Water[e]	9.54	6.2

[a] This study. [b] Ref. 13. [c] Ref. 14. [d] Refs. 12 and 15. [e] Refs. 10 and 11.

10.72 ± 0.05 and $10^{-3}K_3 = 4.8 \pm 0.4$ $dm^3\ mol^{-1}$. The corresponding values in dmf are $\log_{10}(\beta_3/dm^9\ mol^{-3}) = 12.6 \pm 0.1$ and $10^{-3}K_3 = 3.5 \pm 0.2$ $dm^3\ mol^{-1}$.

Although the previous kinetic study in dmso at 522 nm gave evidence for only one rate process, due to the stabilising effect of the solvent it was suggested that there might be a spin-state change taking place at a later stage in the reaction than is observed in water. However, the conclusion one might reach from such a prediction that there should be more than one slow kinetic step in the solvolysis was not made.[7]

Solvolysis of $[Ni(bipy)_3]^{2+}$ in dmso

This system was investigated to give further credence to the observed kinetic behaviour found for the solvolysis of $[Fe(bipy)_3]^{2+}$ in dmf and dmso. The solvolysis of $[Ni(bipy)_3]^{2+}$ was investigated since this ion forms and dissociates without complications from changes in the metal ion spin state, and without atmospheric oxidation occurring. Kinetic studies of the formation of the mono- and tris-(bipy) complexes of Ni^{2+} in several solvents have been reported previously,[12,13] but less information is available regarding the dissociation in aprotic media. The reaction in dmso was studied between 268 and 330 nm, and it was found that, even after very long reaction times, due to the greater stability of the nickel(II) complexes the final spectrum was largely that of the mono species. Global analysis of the multiwavelength data gave rate constants for the dissociation to the tris and bis complexes as shown in Table 1. Of particular significance is the normal trend observed for $[Ni(bipy)_3]^{2+}$, k_{-3} [$(1.30 \pm 0.04) \times 10^{-2}$ s^{-1}] > k_{-2} [$(3.68 \pm 0.03) \times 10^{-3}$ s^{-1}], and the rate ratios for the solvolysis of the tris- and bis-(bipy) complexes of Ni^{2+} and Fe^{2+} (k_{-3}/k_{-2}) which were found to be very similar (3.5 and 4.1 respectively). This is good confirmation that the same mechanism applies, and that in dmf or dmso loss of the first bipy from $[Fe(bipy)_3]^{2+}$ does not result in a change from a low- to a high-spin species as found in water. If $[Fe(solv)_2(bipy)_2]^{2+}$ ions (solv = dmf or dmso) were high-spin species they would be very labile, and the ratio of k_{-3} to k_{-2} would be very different to that found for the corresponding nickel(II) complexes.

In Table 1, a comparison is made of all of the known kinetic and thermodynamic data obtained for the formation and dissociation of mono-, bis- and tris-(bipy) complexes of Fe^{2+} and Ni^{2+} in dmf, dmso and water. Thus, for Ni^{2+} reacting with bipy the normal statistical trend of $K_1 > K_2 > K_3$ is observed, whereas for Fe^{2+} the trend is $K_1 < K_2 > K_3$. For the Fe^{2+} system the variation $K_2 > K_3$ is again the normal statistical one observed when changes in spin state are not involved, whereas the reverse trend ($K_1 < K_2$) is indicative of a change in spin state on addition of the second bipy group. Also, the values of K_3 for the reactions of bipy with $[Fe(solv)_2(bipy)_2]^{2+}$ (solv = dmso or dmf) are significantly less than when solv is water, indicating a change from high to low spin on adding the third bipy group in aqueous solution, but not in dmf and dmso. It would appear, therefore, that non-aqueous solvents like dmf and dmso have a larger ligand-field stabilising effect than that of water in these bis(bipy)iron(II) complexes.

Conclusion

Unlike the behaviour in aqueous solution where Fe^{2+} undergoes a change from high to low spin on adding a third bipy ligand, in dmf and dmso this change occurs upon formation of the bis complex. The complex $[FeL]^{2+}$, which contains a tris(bipy) core, is substantially more stable than the analogous $[Fe(bipy)_3]^{2+}$ ion, as expected on the basis of the chelate effect.

Experimental

Materials and methods

All reagents were the best commercially available (analytical grade). 1,4,7-Tris(2,2′-bipyridyl-5-ylmethyl)-1,4,7-triazacyclononane (L) was prepared by the published method.[1] 2,2′-Bipyridine (Aldrich) was recrystallised from ethanol. Dimethylformamide (HPLC grade dmf) and dimethyl sulfoxide (Aldrich) were checked for impurities by gas chromatography, and dried by storing over activated 4 Å molecular sieves in a dry-box. The only impurity detected was a trace of ethylmethylformamide in the dmf, which was ignored in the kinetic studies. Anhydrous trifluoromethanesulfonic acid (Avocado) was distilled under reduced pressure in an all-glass apparatus, and stored under dry dinitrogen. Hydrated iron(II) trifluoromethanesulfonate was obtained following a literature procedure.[5] The anhydrous salt was obtained by heating the hydrate at *ca.* 50 °C and 0.1 mbar (10 Pa) for 48 h (Found: C, 6.77, Fe, 15.8; S, 18.1. Calc. for $C_2F_6FeO_6S_2$: C, 6.73; Fe, 15.7; S, 18.2%). Throughout the synthesis and work-up, the iron(II) salt was protected from light and oxygen. It was stored in the dark, in a dry nitrogen atmosphere. A stock solution of $[Fe(dmf)_6][CF_3SO_3]_2$ was conveniently prepared by direct addition of a weighed amount of the anhydrous salt to the dry solvent in a dry atmosphere. After 24 h over activated 4 Å molecular sieves, the solution was analysed for iron(II) content by redox titration in an aqueous acidic medium under argon using a standard aqueous argon-scrubbed $K_2Cr_2O_7$ solution and $Na(O_3SC_6H_4NHC_6H_5)$ as internal indicator.[16] The complexes $[Fe(bipy)_3][PF_6]_2$, $[Fe(bipy)_3][ClO_4]_2$ and $[Ni(bipy)_3][ClO_4]_2$ were obtained following a slightly modified published method.[17] To a fresh aqueous solution of either $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ (Fluka) or $Ni(BF_4)_2 \cdot 6H_2O$ (BDH) was added a solution containing 3.1 mol equivalents of 2,2′-bipyridine dissolved in the minimum volume of acetone. The perchlorate or hexafluorophosphate salts were precipitated by adding saturated aqueous $NaClO_4$ or NH_4PF_6 solutions respectively, filtered off, washed several times with ice-cold distilled water, and dried over anhydrous silica gel in a vacuum desiccator. The products were recrystallised from acetone and isolated as anhydrous salts.

Kinetic measurements

Rates of formation in dmf were investigated at 25 °C by multiwavelength stopped-flow spectrophotometry, using an Applied Photophysics kinetic workstation in the wavelength range 350–

650 nm. Data were recorded at 5 nm intervals, taking 4000 data points per run. Second-order conditions were used to study the formation of $[FeL]^{2+}$, and pseudo-first-order conditions (using an excess of metal) for $[Fe(bipy)_3]^{2+}$. Experiments were carried out under anaerobic conditions. Solutions of $[Fe(dmf)_6]^{2+}$, L and bipy in dmf were prepared in an oxygen-free atmosphere (nitrogen dry-box) and used shortly thereafter. Precautions were taken to eliminate water and oxygen from the stopped-flow flow line before experiments commenced,‡ and the stock solutions were protected with an argon atmosphere by holding them in special glass reservoirs attached to the stopped-flow inlet valves. The kinetics of dissociation of $[Fe(bipy)_3][PF_6]_2$, $[Fe(bipy)_3][ClO_4]_2$ and $[Ni(bipy)_3][ClO_4]_2$ in dmf and/or dimethyl sulfoxide was investigated at 25 °C by conventional absorption spectrophotometry in the 280–650 nm range, using a Philips-Unicam PU 8700 spectrophotometer coupled to a personal computer for data collection. The argon-saturated solvent (3.0 cm^3) was allowed to come to thermal equilibrium in a Suba-seal stoppered 1 cm pathlength quartz cell in the thermostatted (±0.1 °C) cell holder of the spectrophotometer. The required amount of solid complex was accurately weighed, thermally equilibrated and carefully dissolved in the solvent. Scan spectra were recorded at fixed time intervals in the visible or UV regions. Temperature changes caused by the mixing procedure were found to be no more than ±0.1 °C. Temperatures were recorded with a digital platinum-resistance thermometer.

The multiwavelength experimental data from both formation and dissociation experiments were analysed with an Acorn A5000 personal computer, using the stopped-flow GLINT global analysis software.[18] This software uses the technique of single-value decomposition described in the literature.[19] Whenever possible, spectra of individual species were recorded with the Philips-Unicam PU 8700 spectrophotometer, edited as ASCII files and used as fixed spectra in the global analysis.

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‡ The PTFE flow line was flushed with argon-scrubbed dmf. More recently Applied Photophysics have replaced the PTFE tubing with oxygen-impermeable and more rigid Peek (polyether ketone) tubing.