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PHOTOCHEMICAL AND THERMAL BEHAVIOUR OF ISOCYANIDE COMPLEXES

II *. PHOTOLYSIS OF $Fe(bpy)_2(CNCH_3)_2(BF_4)_2$ IN ACETONITRILE

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Summary

The photolysis of $Fe(bpy)_2(CNCH_3)_2{}^{2+}$ in acetonitrile proceeds through heterolytic fission of the Fe–C bond, release of the $CNCH_3$ ligand, solvation, and subsequent thermal and photochemical reactions of the solvated intermediates. Addition of the free ligands (methylisocyanide and bipyridine) and of hydrazine, after or during the irradiation, has provided information about the photolysis mechanism and the nature of the intermediates. The process is independent of the excited CTTL or IL bands, but the quantum yields increase as the irradiation wavelength is decreased. This finding is consistent with the formation of a photodissociative state, $[Fe(bpy)_2(CNCH_3)^{2+}, CNCH_3]$ in the primary photochemical act, and with the two fragments, trapped in the solvent cage, either diffusing apart or undergoing recombination, depending on the excess energy necessary for the bond fission.

Introduction

Isocyanide complexes are particularly interesting from a photochemical standpoint as in these compounds it is possible to excite selectively intra-ligand, charge transfer and ligand field states. However, relatively few [1] of the numerous photochemical investigations on coordination compounds have involved isocyanide complexes.

Some of us have previously studied the photolysis in aqueous solution at various pH values of isocyanide complexes of iron(II) with mixed ligands, and related the results with those obtained in thermal processes [2–5]. Now, it is our aim to investigate the photochemical and thermal behaviour of isocyanide complexes in

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* For Part I see ref. 6.

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aprotic solvents under various conditions. In the first publication of this series [6] we reported a kinetic study of the $Fe(bpy)_2(CNCH_3)_2^{2+}$ hydrazine reaction in acetonitrile. In this paper we report the results of an investigation of the photochemical behaviour of $Fe(bpy)_2(CNCH_3)_2(BF_4)_2$ in acetonitrile.

Experimental

Materials. The preparation and characterization of *cis*-$Fe(bpy)_2(CNCH_3)_2$-$(BF_4)_2$ has been reported [6]. All chemicals were of reagent grade.

Apparatus and procedures. Normal equipment was used for the irradiation. The radiation at 254 nm was obtained using a low-pressure Hg vapour lamp (Hanau NN 15/44). Radiations of 333, 365, 405 and 436 nm from a Hg vapour lamp (Hanau Q 400) were separated by means of interference filters (Schott Gen.). Radiation of 350 nm was obtained using a Rayonet photochemical reactor equipped with sixteen 24-W lamps. The intensity of the incident light, measured by a ferric oxalate actinometer, was of the order of 10^{-6}–10^{-5} einstein min^{-1}.

The spectrophotometric measurements were obtained using a Perkin-Elmer 330 spectrophotometer. The samples were irradiated in spectrophotometric cells, and were deaerated by prolonged bubbling of nitrogen. The kinetics of the photolysis were followed in a suitable absorption region. The effect of the initial concentration was investigated in the range 10^{-3}–10^{-4} *M*. In the experiments carried out in the presence of ligands, the conditions were: $[Fe(bpy)_2(CNCH_3)_2^{2+}]$ $(1.5–2.2) \times 10^{-4}$ *M*, $[N_2H_4]$ 0.4×10^{-3}–0.75×10^{-2} *M*, [bpy] ca. 10^{-2} *M*, $[CNCH_3]$ 0.1 *M* to a large excess ($\simeq 2$ *M*).

Results

The $Fe(bpy)_2(CNCH_3)_2^{2+}$ ion in acetonitrile shows a CTTL band at 420 nm (ϵ 4600) and two IL bands at 290 nm (ϵ 40,000) and 245 nm (ϵ 22,600). No LF bands were evident, probably because they were hidden by the more intense ones. The compound was thermally inert in the dark and at room temperature even in the presence of free ligands, but was sensitive to irradiation at all wavelengths within the whole absorption spectrum. A photolysis occurred, involving release of methyl isocyanide, formation of solvated intermediates and, finally, of $Fe(bpy)_3^{2+}$. Because the overall process was the result of simultaneous photochemical and thermal reactions, we tried to minimize the contributions of the thermal processes by working at relatively high light intensity. As all of the intermediates were photochemically reactive, whose fate was dependent on competitive light absorption, the kinetics of the overall photolysis appeared to depend on the wavelength of the exciting radiation.

However, at all wavelengths the same process occurred in two consecutive steps. At the beginning of the irradiation the release of $CNCH_3$ was evident, and the solution spectrum shifted towards the visible, with isosbestic points at 368 and 439 nm. The isosbestic points can be considered constant until a certain percentage transformation had occurred, which could be estimated from the ratio $\Delta d/d_0$ at 420 nm, and which varied with the exciting wavelength. As the irradiation was continued, a second step of the photochemical process occurred (Fig. 1), where the isosbestic points were absent and $Fe(bpy)_3^{2+}$ formation was observed. The reaction proceeded until a pseudo-photostationary state was reached.

Interesting thermal after-effects were observed when the irradiation was interrupted at the first or second step of the reaction. After interruption at the first step some absorption at 520 nm, due to $Fe(bpy)_3^{2+}$, appeared within a certain time: this indicated that the photochemical intermediate, probably a solvated compound, was thermally unstable and underwent a slow reaction to give $Fe(bpy)_3^{2+}$. After interruption of the irradiation at the second step, we noted a further increase in the $Fe(bpy)_3^{2+}$ concentration and a shift towards the UV region of the absorption maximum of the irradiated solution; this last effect indicated a thermal back reaction of intermediates with the released $CNCH_3$. The amount of these thermal after-effects depended on the initial concentration of the compound, the intensity and wavelength of the exciting light, and on the effective time of the experiment: all these were factors conditioning the relative concentrations of the species present at the time when the irradiation was interrupted.

In order to determine the nature of the intermediates and their reactivity, we have investigated the effect of the free ligands after and during the irradiation. When

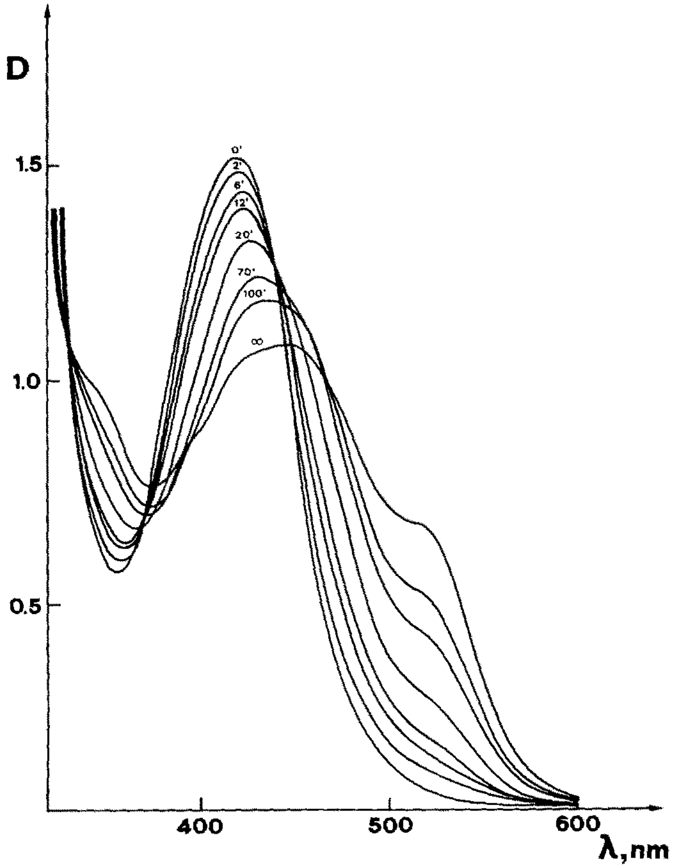


Fig. 1. Changes in the spectrum of the $Fe(bpy)_2(CNCH_3)_2^{2+}$ solution in acetonitrile after various irradiation times (min), $M = 3.3 \times 10^{-4}$, $\lambda(\text{exc}) > 330$ nm.

bipyridine was added to the solution at the first or second step of the photolysis, the kinetics of $Fe(bpy)_3{}^{2+}$ formation were of first order and independent of ligand concentration ($k = 0.9 \times 10^{-2}$ sec^{-1} at 25°C); the final spectrum was that of a mixture of $Fe(bpy)_3{}^{2+}$ and $Fe(bpy)_2(CNCH_3)_2{}^{2+}$ having a total concentration equal to that of the starting compound (Fig. 2). Therefore all the photochemical intermediates reacted with bipyridine to give $Fe(bpy)_3{}^{2+}$, giving a way to evaluate the total photolyzed compound at any moment, and thus the quantum yield. Also at the photostationary state the percentage of the photolyzed $Fe(bpy)_2(CNCH_3)_2{}^{2+}$ varied (between 80 and 100%) with the wavelength of the exciting radiation and the initial concentration.

When a large excess of free isocyanide was added to the irradiated solution within the first step, a back reaction of the intermediate to the starting compound occurred; when it was added during the following step, where $Fe(bpy)_2(CNCH_3)_2{}^{2+}$, solvated intermediates and $Fe(bpy)_3{}^{2+}$ were present, the spectrum of the solution matched that of a mixture containing only $Fe(bpy)_2(CNCH_3)_2{}^{2+}$ and $Fe(bpy)(CNCH_3)_4{}^{2+}$, whose total concentration was equal to that of the starting compound (Fig. 3). However, the relative concentrations of the two compounds were dependent on the experimental parameters (concentration, irradiation intensity and wavelength), which control the kinetics of the thermal and photochemical processes. It was noteworthy

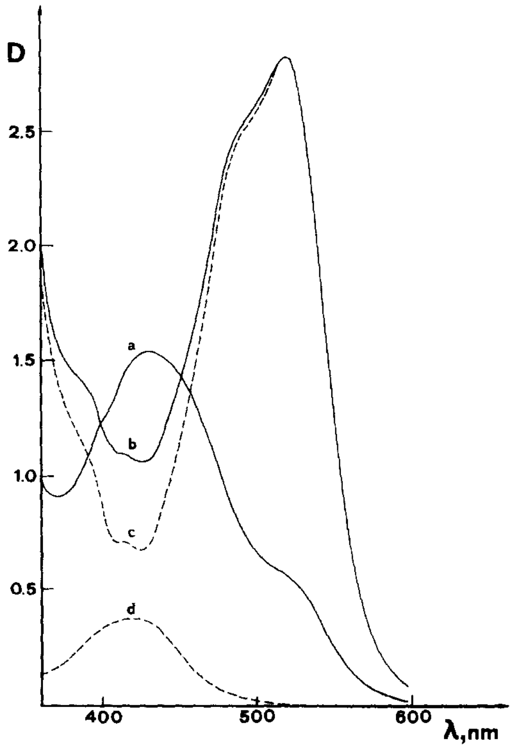


Fig. 2. Effect of addition of bipyridine to the photolyzed solution of $Fe(bpy)_2(CNCH_3)_2{}^{2+}$ (4.2×10^{-4} M). Solution irradiated for 345 min at 350 nm (a) before, and (b) after addition of bipyridine. Composition of the final mixture (b) is (d) $Fe(bpy)_2(CNCH_3)_2{}^{2+}$ (0.8×10^{-4} M) and (c) $Fe(bpy)_3{}^{2+}$ (3.4×10^{-4} M).

that the $Fe(bpy)_2(CNCH_3)_2^{2+}$ found was partly from the non-reacted compound and partly that formed from the reaction of the $Fe(bpy)_3^{2+}$ with isocyanide. In fact we have verified that under our experimental conditions, the bipyridine of $Fe(bpy)_3^{2+}$ was displaced by isocyanide, with the formation of $Fe(bpy)_2(CNCH_3)_2^{2+}$.

When the solutions were irradiated in the presence of free bipyridine, a net conversion $Fe(bpy)_2(CNCH_3)_2^{2+} \rightarrow Fe(bpy)_3^{2+}$ was observed (Fig. 4), with two isosbestic points at 384 nm and at 438 nm until the conversion was complete, and no intermediates were detected.

When the solutions were irradiated in the presence of isocyanide, the photoreaction rate, estimated from the $\Delta d/d_0$ ratio at 420 nm, decreased as amount of isocyanide was increased, and with a large excess of the ligand no photochemical process was detectable. Precise evaluation of the isosbestic points was difficult because of the small variation in the spectra. No $Fe(bpy)_3^{2+}$ formation was observed; after the irradiation had been interrupted a back reaction occurred.

Interesting additional information, which could be useful for an understanding of the mechanism, was obtained by studying the photolysis in the presence of hydrazine. Previously [6], we had found that the $Fe(bpy)_2(CNCH_3)_2^{2+}$-hydrazine system reacted thermally under suitable conditions to give a dicarbene species, and no displacement of the $CNCH_3$ was observed. In the irradiation experiments 1.5×10^{-4} *M* solutions of the starting compound and $(0.4–0.75) \times 10^{-2}$ *M* hy-

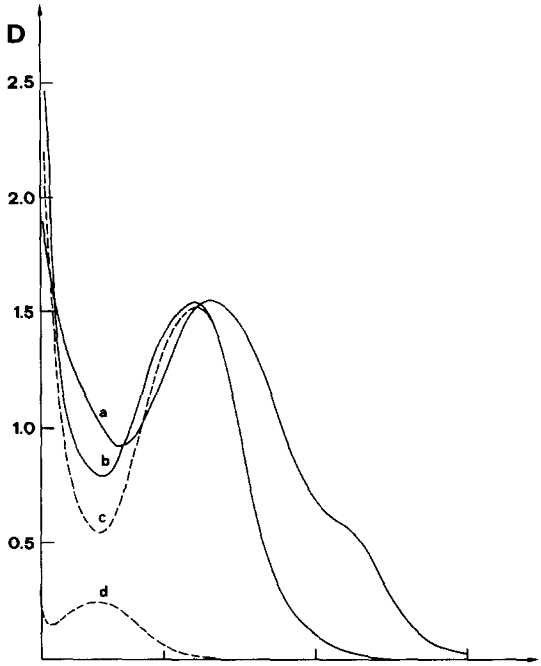


Fig. 3. Effect of the addition of $CNCH_3$ to the photolyzed solution of $Fe(bpy)_2(CNCH_3)_2^{2+}$ (4.2×10^{-4} *M*). Solution irradiated for 345 min at 350 nm (a) before, and (b) after addition of an excess of $CNCH_3$. Composition of the final mixture (b) is (c) $Fe(bpy)_2(CNCH_3)_2^{2+}$ (3.3×10^{-4} *M*) and (d) $Fe(bpy)(CNCH_3)_4^{2+}$ (0.9×10^{-4} *M*).

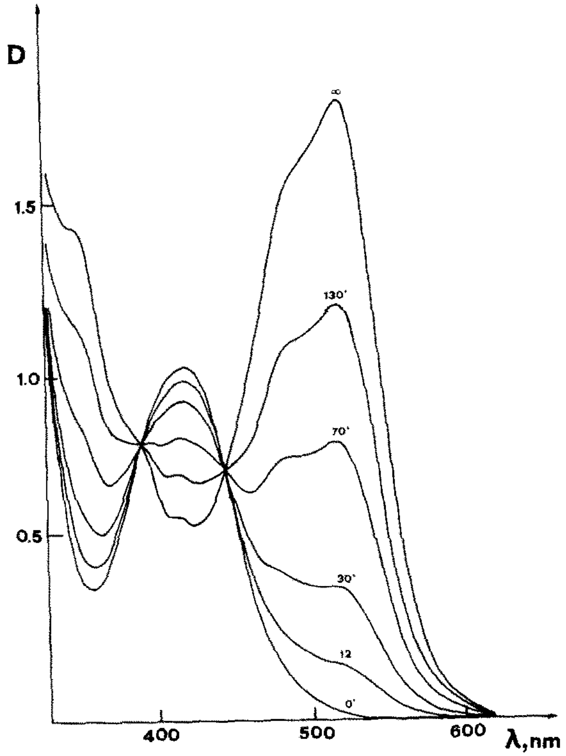


Fig. 4. Changes in the spectrum of the $Fe(bpy)_2(CNCH_3)_2^{2+}$ solution (2.2×10^{-4} *M*) when irradiated for various times (min) at 350 nm in the presence of bipyridine.

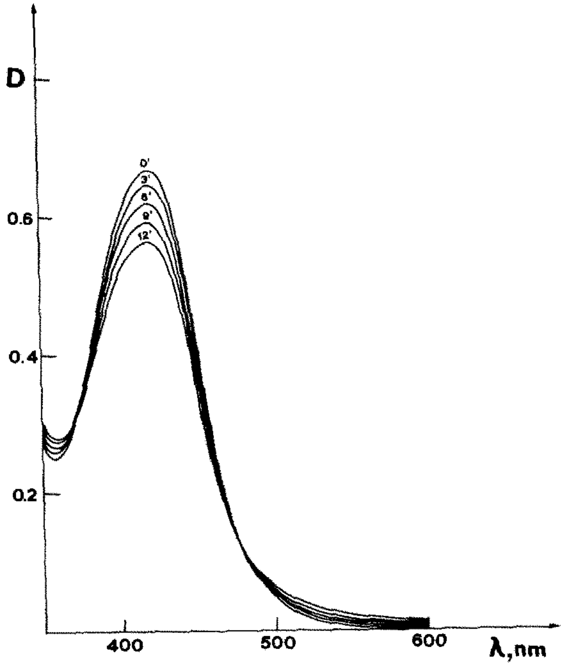


Fig. 5. Changes in the spectrum of the $Fe(bpy)_2(CNCH_3)_2^{2+}$ solution (1.5×10^{-4} *M*) when irradiated for various times (min) at 350 nm in the presence of hydrazine (0.75×10^{-2} *M*).

drazine solutions were used; from earlier kinetic data, it could be expected that at these concentrations the system would remain unchanged for some hours. On irradiating these solutions, the isocyanide ligand was released and the spectrum underwent a regular change, with two isosbestic points at 370 and 478 nm which were constant until a certain percentage conversion was achieved, which was extimated from the $\Delta d/d_0$ ratio at 420 nm, and which depended on the hydrazine concentration (see Fig. 5). When the irradiation was stopped, no after-effect was observed and no reaction was detectable on addition of free bipyridine. Therefore the photochemical intermediate was quite stable. However, it was not possible to accumulate and separate it because, on continuing the irradiation, this intermediate underwent photochemical decomposition, when its absorption competed with that of the initial compound. We consider that during the initial period of irradiation a $CNCH_3$-N_2H_4 exchange occurred, giving $Fe(bpy)_2(CNCH_3)(N_2H_4)^{2+}$, which then decomposed photochemically.

With regard to this, it is worth noting that no reaction was observed when the same concentration of hydrazine was added after the first period of irradiation, that is to say after the formation of the solvated intermediate; therefore, hydrazine did not displace the solvent in a thermal reaction.

Calculation of the quantum yield

The initial values of the quantum yield, ϕ, were determined at different wavelengths for the first step, by adding bipyridine to solutions which had been irradiated for very short times. The $Fe(bpy)_3{}^{2+}$ formed was equal to the $Fe(bpy)_2(CNCH_3)_2{}^{2+}$ photolyzed. It is noteworthy that the same values for the quantum yield were obtained (after making suitable corrections for absorption of the light by the bipyridine) for solutions irradiated in the presence of bipyridine, therefore the bipyridine functioned by reacting fast with the primary photochemical intermediate and had no effect on the rate of the photochemical reaction. At the wavelengths used, the values of the quantum yield were (error within 10%):

λ(nm)	436	405	365	350	333	254
$\phi\,(\times 10^2)$	0.18	0.26	0.35	0.38	0.51	1.0

Discussion

The overall results are consistent with the following reaction scheme, which takes into account all the experimental observations:

$$Fe(bpy)_2(CNCH_3)_2{}^{2+} \underset{\Delta}{\overset{h\nu}{\rightleftarrows}} Fe(bpy)_2(CNCH_3)(S)^{2+} + CNCH_3 \tag{1}$$

$$Fe(bpy)_2(CNCH_3)(S)^{2+} \underset{\Delta}{\overset{h\nu,\Delta}{\rightleftarrows}} Fe(bpy)_2(S)_2{}^{2+} + CNCH_3 \tag{2}$$

$$Fe(bpy)_2(S)_2{}^{2+} \underset{\Delta}{\overset{h\nu,\Delta}{\rightleftarrows}} Fe(bpy)(S)_4{}^{2+} + bpy \tag{3}$$

$$Fe(bpy)_2(S)_2{}^{2+} + bpy \underset{\Delta}{\overset{\Delta}{\rightleftarrows}} Fe(bpy)_3{}^{2+} + 2S \tag{4}$$

The first step of the photolysis is the release of the methylisocyanide ligand, followed by capture of a solvent molecule; in the absence of free ligands a mono-solvated intermediate is formed, which undergoes solvation to a bi-solvated intermediate. The two isosbestic points, associated with the first photoreaction step, point to the formation of a fairly stable solvated intermediate which accumulates until the fraction of light it absorbs can be considered as negligible. There is no direct experimental evidence to show whether this intermediate is the mono-solvated one (slow k_2) or the bi-solvated one (fast k_2 and slow k_3); and attempts to calculate the spectrum have not been successful. However, on the basis of the effect of the free ligands on the photolysis pathway, we think that very probably the fairly stable intermediate is the mono-substituted one (slow k_2); on continuing the irradiation no isosbestic point can be observed because the intermediates breakdown in the thermal and photochemical steps, eqs. 2–4, whose kinetics depend on the various experimental factors; this leads to a different composition of the irradiated mixture at the end of photoreaction. In the proposed scheme the rate of disappearance of the starting compound is

$$-\frac{d\left[\mathrm{Fe(bpy)_2(CNCH_3)_2^{2+}}\right]}{dt} = \phi I \frac{\epsilon'\left[\mathrm{Fe(bpy)_2(CNCH_3)_2^{2+}}\right](1-10^{-\Sigma\epsilon c})}{V\Sigma\epsilon c} - k_{-1}\left[\mathrm{Fe(bpy)_2(CNCH_3)(S)^{2+}}\right]\left[\mathrm{CNCH_3}\right] \quad (5)$$

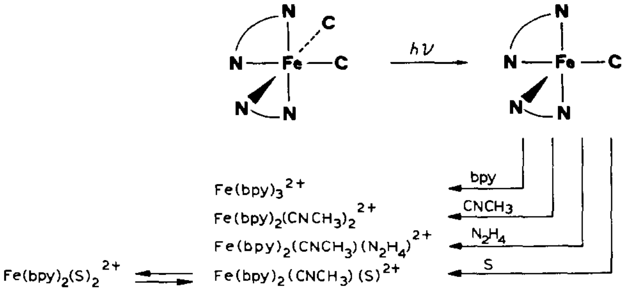
where I is the light intensity, ϕ is the quantum yield, V is the solution volume in l, ϵ' is the extinction coefficient of $\mathrm{Fe(bpy)_2(CNCH_3)_2^{2+}}$ at the irradiation wavelength and $\Sigma\epsilon c$ indicates the absorption at the same wavelength of all the species present. In the initial period, the concentrations of the mono-solvated intermediate and $\mathrm{CNCH_3}$ are small and therefore the second term of the right hand side of eq. 5 is negligible. The variation obeys the classical photochemical law and the quantum yield can be calculated correctly. On continuing the irradiation, the intermediate and $\mathrm{CNCH_3}$ concentrations increase and the thermal back-reactions cannot be neglected. The photolysis process attains a pseudo-equilibrium state which depends on the initial concentration, the irradiation wavelength and the light intensity. However, with a small initial concentration and high intensity, the initial compound is completely decomposed.

In the proposed scheme, the first photochemical act is the one where, following excitation, heterolytic fission of the Fe–C occurs with the formation of a photodissociative state $[\mathrm{Fe(bpy)_2(CNCH_3)^{2+}}, \mathrm{CNCH_3}]$. In agreement with the finding that the quantum yields increased with the irradiation energy, the two fragments, trapped in the solvent cage, either diffuse apart or undergo recombination, depending on the excess energy necessary for bond cleavage. The solvent substitutes for the released isocyanide, but in the presence of $\mathrm{CNCH_3}$, or $\mathrm{N_2H_4}$, or bipyridine, these ligands compete with the solvent in attacking the free position of the pentacoordinated intermediate. This hypothesis is clearly supported by the results of the experiments carried out with the free ligands.

In the case of bipyridine, a rapid formation of $\mathrm{Fe(bpy)_3^{2+}}$ was found to occur on irradiating in the presence of free bipyridine; this ligand attacked the free position and quickly expelled the second $\mathrm{CNCH_3}$. When the bipyridine replaced the solvent in the solvated intermediate, the substitution rate was measurable. With hydrazine, it was found that a mixed-ligand compound could be obtained only by irradiating in the presence of hydrazine, and not by a thermal displacement of the solvent molecule.

Additionally, we consider the pentacoordinated intermediate to be a tetragonal pyramid, since a trigonal bipyramid would lead to the formation of isomers, which would be found on irradiating in the presence of $CNCH_3$; this is not found in our case.

In conclusion, the primary photochemical reaction in the presence and in the absence of free ligand can be summarised in the following way:



(N—N = bpy ; C = $CNCH_3$)

Finally, it is noteworthy that in the $Fe(bpy)_2(CNCH_3)_2^{2+}$ photolysis, the nature of the excited bands, CTTL or IL, does not play a specific role. On the contrary, the observed reaction (heterolytic bond fission and replacement of the released ligand) was that expected for the excitation of ligand field bands. This behaviour points to a conversion of excited IL and CT states to lower states of the LF or to higher vibrationally-excited levels of the ground state.

Acknowledgement

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