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Photochemical and Thermal Behaviour of Isocyanide Complexes. IV*. Photochemistry of $Fe(CNCH_3)_6(BF_4)_2$ in Acetonitrile

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Abstract

The irradiation of acetonitrile solutions of $Fe(CNCH_3)_6^{2+}$ in bands of the ligand field provoked consecutive reactions of photosubstitution $CNCH_3$–$NCCH_3$. Two partial steps of the process were evidenced: at the beginning a monosolvated intermediate $Fe(CNCH_3)_5(NCCH_3)^{2+}$ (I) was formed; subsequently this latter in turn underwent photosolvation to $Fe(CNCH_3)_4(NCCH_3)_2^{2+}$ (II). Both the solvated intermediates were isolated and characterized. The quantum yields of the two consecutive processes were calculated; it was found that both the quantum yields decreased as the irradiation wavelength increased. A general mechanism of photosolvation for isocyanides of Fe^{II} was proposed.

Introduction

From numerous studies on the photosensitivity of Fe^{II} complexes in aqueous medium [1–5], it was shown that on irradiation a progressive photoaquation, leading to Fe^{2+} or Fe^{3+} ions, occurred through indistinguishable primary photoreaction and secondary thermal and photochemical processes. Recently we have undertaken an investigation in acetonitrile on some isocyanide complexes of Fe^{II} with mixed ligands: $Fe(bpy)_2(CNCH_3)_2^{2+}$, $Fe(bpy)(CNCH_3)_4^{2+}$ and $Fe(bpy)(CNCH_3)_2(C_4H_{10}N_4)^{2+}$ [6–8]. The results showed that a photosolvation occurred also in this solvent, but it was possible to evidence the partial steps of the whole process, with formation of stable solvated intermediates. The previously studied compounds exhibit intraligand and charge transfer bands, the ligand field bands probably hidden by the more intense ones. In this paper we consider the compound $Fe(CNCH_3)_6^{2+}$, which exhibits only bands of the ligand field, in order to obtain information regarding the weight of the excited band nature on the photochemical process.

Experimental

The compound $Fe(CNCH_3)_6(BF_4)_2$ was prepared by treating $K_4Fe(CN)_6$ with $(CH_3)_2SO_4$ under reflux at 60 °C for some hours. Following extraction by water, the product was precipitated by saturated solution of $NaBF_4$ and recrystallized from methanol. All chemical reagents were reagent grade.

The elemental analysis was carried out with a Carlo Erba elemental analyzer Mod. 1106. The PMR spectra were obtained in CD_2Cl_2 at 80 MHz on a Bruker WP-80 spectrometer. All UV and visible spectra were obtained from a Perkin Elmer 330 spectrophotometer equipped with a 3600 data station.

The monochromatic radiations of 350 and 254 nm were obtained using a Rayonet photochemical reactor equipped with sixteen 24 W lamps. The intensity of the incident light was 5×10^{-6} einstein min^{-1} for both radiations. Before the irradiation, all samples were de-aerated by prolonged bubbling of nitrogen.

Results and Discussion

The compound $Fe(CNCH_3)_6(BF_4)_2$ exhibits in acetonitrile the absorption spectrum characteristic of an octahedral low spin compound d^6 with two bands in the UV range, attributable to ligand field transitions (λ_{max} 318 nm, ϵ 350; λ_{max} 267 nm, ϵ 360).

The compound was thermally inert, but irradiation at all wavelengths of its aborption spectrum caused release of isocyanide ligands and substitution by solvent molecules $NCCH_3$. By following the spectral changes (Fig. 1) of irradiated solutions at various times, at first we observed a shift of the absorption towards the visible with isosbestic points at 331, 297 and 276.5 nm and the appearance of a new maximum at about 365 nm. On continuing the irradiation, the optical density at 365 nm decreased and a new maximum at about 410 nm was evidenced; the isosbestic points shifted to new wavelengths (381, 328 and 307.5 nm).

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*For Parts I–III see refs. 6–8.

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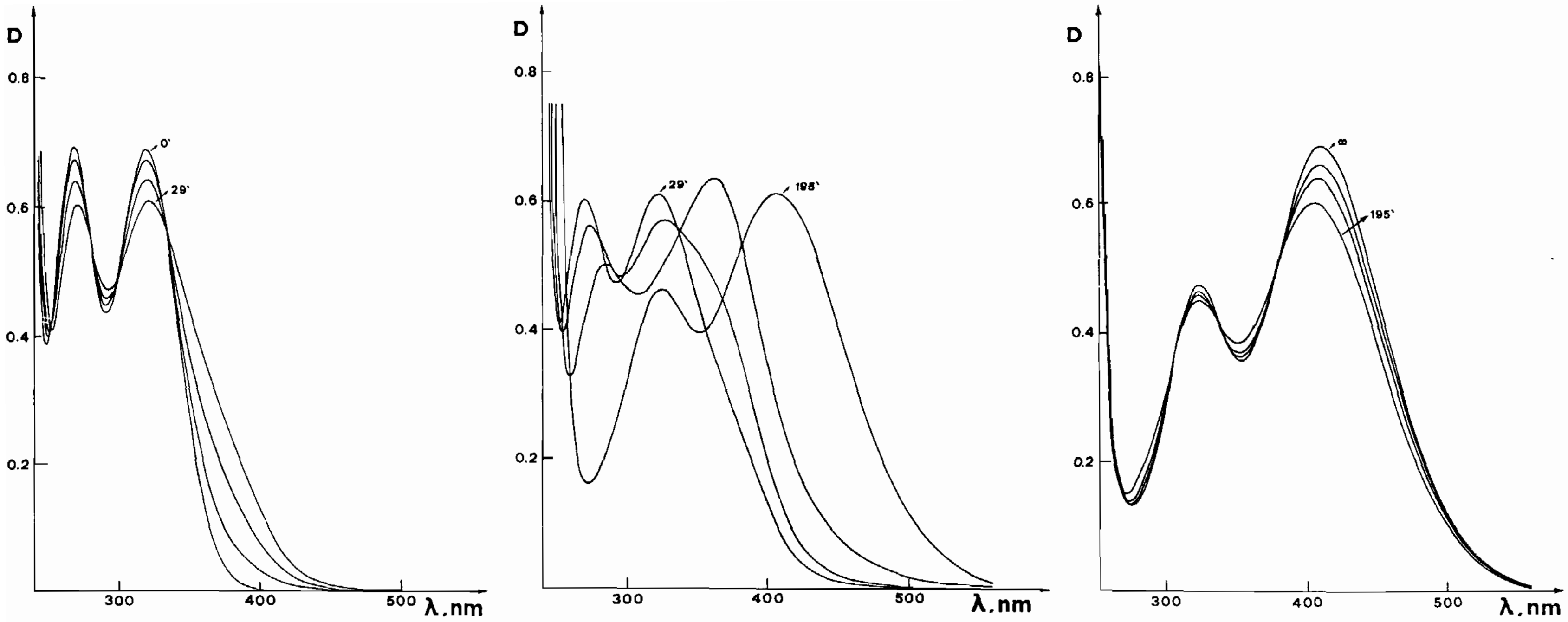


(a) (b) (c)

Fig. 1. Spectral changes of $Fe(CNCH_3)_6{}^{2+}$ solution in acetonitrile at 350 nm; the numbers refer to the irradiation times.

TABLE I. PMR Data in CD_2Cl_2.

	δ_{CNCH_3}, ppm	δ_{NCCH_3}, ppm
$Fe(CNCH_3)_6{}^{2+}$	3.49	
I	3.64; 3.47	2.34
II	3.63	2.46

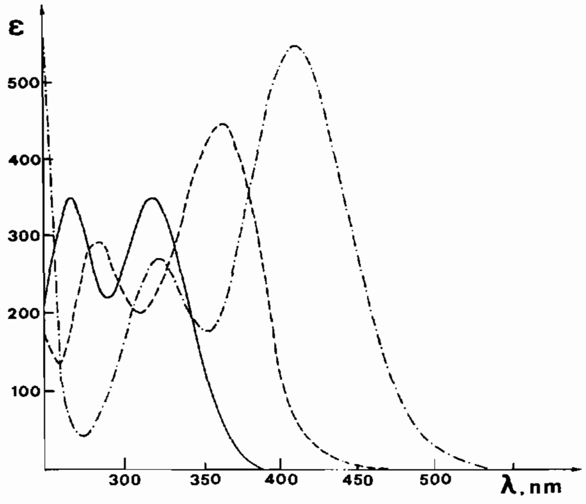
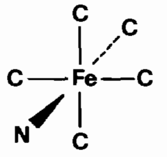


Fig. 2. UV spectra of the isolated photochemical intermediates I (– – – –) and II (–.–.–) (for comparison the spectrum of the initial compound (———) is reported).

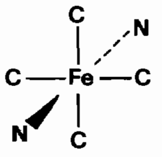
The course of the spectral changes was consistent with two consecutive steps of photochemical solvation. At the beginning, the light was absorbed mainly by the starting compound and only the formation of the first solvated intermediate **I** (λ_{max} 365 nm) was noted. When the concentration of **I** attained a value such as to compete with the starting compound in the light absorption, the formation of another intermediate **II** (λ_{max} 410 nm) became evident. The second group of isosbestic points appeared when the concentration of $Fe(CNCH_3)_6{}^{2+}$ was negligible. It was noteworthy that at an adequate concentration of **II** the irradiation caused no further increase of the maximum at 410 nm, but a widening of the band and a shift of the isosbestic points. On interrupting the irradiation, the absorbance at 410 nm increased until a constant value was reached and the original isosbestic points between **I** and **II** were reestablished. This latter process indicated that for light absorption the intermediate **II** released further isocyanide ligands, that in the dark back-displaced solvent molecules.

In order to clarify the nature of the solvated intermediates we attempted to isolate the intermediates **I** and **II**. To this purpose we prepared enriched solutions of **I** or **II** through irradiation at suitable wavelengths (respectively, at 254 nm for the enrichment of **I** and at 350 nm for that of **II**). These intermediates were precipitated from the solutions by the addition of a small amount of ether and were analyzed without further purification, to avoid the alterations occurring during this process. The elemental analysis showed that both intermediates had the same composition percentage as the starting compound, within experimental error. The PMR data, obtained in CD_2Cl_2, are reported in Table I. In the starting compound the peak at 3.49 ppm is due to the methyl protons of the six equivalent isocyanides. In compound **I** the peak at 2.34 ppm is attributable to the methyl protons of the coordinated acetonitrile, while the peak at 3.64 ppm is due to the four isocyanide molecules in plane that are in *cis* position to the acetonitrile; the peak at 3.47 ppm is due to the protons of the isocyanide in axial *trans* position to the acetonitrile. In compound **II** the peak at 2.46 ppm is due to the two acetonitrile molecules both in axial positions, while the peak at 3.63 ppm is due to the four isocyanides in plane. Therefore on the basis of these symmetry considerations and in agreement with the peak areas we concluded that the intermediates **I** and **II** are respectively the mono- and bisolvated compounds:



I

$Fe(CNCH_3)_5(NCCH_3)^{2+}$



II

$Fe(CNCH_3)_4(NCCH_3)_2^{2+}$

No useful indication was provided by the IR spectra, as in our experimental conditions the stretching band ν_{CN} at 2240 cm^{-1} of the solvated intermediates is not significantly altered in respect of the starting compound.

The UV spectra (Fig. 2) confirm that the isolated intermediates were the mono- and bisolvated compounds. In fact we found two bands, respectively at 365 nm (ϵ 450) and at 285 nm (ϵ 290) for **I**; at 410 nm (ϵ 550) and at 322.5 nm (ϵ 270) for **II**. It was noteworthy that the positions of the absorption bands were those expected respectively for the compounds $Fe(CNCH_3)_5(NCCH_3)^{2+}$ and $Fe(CNCH_3)_4(NCCH_3)_2{}^{2+}$ on the basis of the rule of the average environment [9]. According to this rule the wavenumbers of the d–d bands of the mixed compounds are given by the following relation:

$$\bar{\nu}_{\mathrm{Fe(CNCH_3)_n(NCCH_3)_{6-n}^{++}}} \simeq \frac{n}{6} \times \bar{\nu}_{\mathrm{Fe(CNCH_3)_6^{++}}} + \frac{6-n}{6} \times \bar{\nu}_{\mathrm{Fe(NCCH_3)_6^{++}}}$$

From the above results we conclude that the overall photochemical process was the following:

$$\mathrm{Fe(CNCH_3)_6^{++}} \xrightarrow[\mathrm{NCCH_3}]{h\nu} \mathrm{Fe(CNCH_3)_5(NCCH_3)^{++}} + \mathrm{CNCH_3} \qquad (1)$$

$$\mathrm{Fe(CNCH_3)_5(NCCH_3)^{++}} \xrightarrow[\mathrm{NCCH_3}]{h\nu} \mathrm{Fe(CNCH_3)_4(NCCH_3)_2^{++}} + \mathrm{CNCH_3} \qquad (2)$$

$$\mathrm{Fe(CNCH_3)_4(NCCH_3)_2} \underset{h\nu,\ \mathrm{NCCH_3}}{\overset{\Delta}{\rightleftarrows}} \mathrm{Fe(CNCH_3)_{4-x}(NCCH_3)_{2+x}} + x\mathrm{CNCH_3} \qquad (3)$$

The quantum yields of the first (Φ_1) and the second step (Φ_2) of the process were calculated from spectral data which allowed us to obtain experimental values of the concentrations of the initial compound and of the intermediates I and II *vs.* time (Fig. 3). Spectral data were collected after the absorbance at 410 nm was constant; this ensured that the re-entry of $\mathrm{CNCH_3}$ in eqn. 3 was completed. From Fig. 3 we noted that at all times the concentration sum of the components of the irradiated solution was equal to the initial one; this observation supports the validity of the proposed mechanism. Upon constant stirring the kinetic rate equations describing the variation in concentrations can be written as follows:

$$-\frac{d[\mathrm{Fe(CNCH_3)_6^{++}}]}{dt} = \frac{\Phi_1 L}{V} \frac{\epsilon_0[\mathrm{Fe(CNCH_3)_6^{++}}]\,(1-10^{-\Sigma\epsilon c})}{\Sigma\epsilon c}$$

$$\frac{d[\mathrm{I}]}{dt} = \frac{\mathrm{L}}{\mathrm{V}} \frac{(\Phi_1\epsilon_0[\mathrm{Fe(CNCH_3)_6^{++}}] - \Phi_2\epsilon_1[\mathrm{I}])(1-10^{-\Sigma\epsilon c})}{\Sigma\epsilon c}$$

$$\frac{d[\mathrm{II}]}{dt} = \frac{\mathrm{L}}{\mathrm{V}} \frac{\Phi_2\epsilon_2[\mathrm{I}](1-10^{-\Sigma\epsilon c})}{\Sigma\epsilon c}$$

where L is the light intensity, ϵ is the extinction coefficient of the species considered, $\Sigma\epsilon c$ is the absorption of all the species present and V is the cell volume.

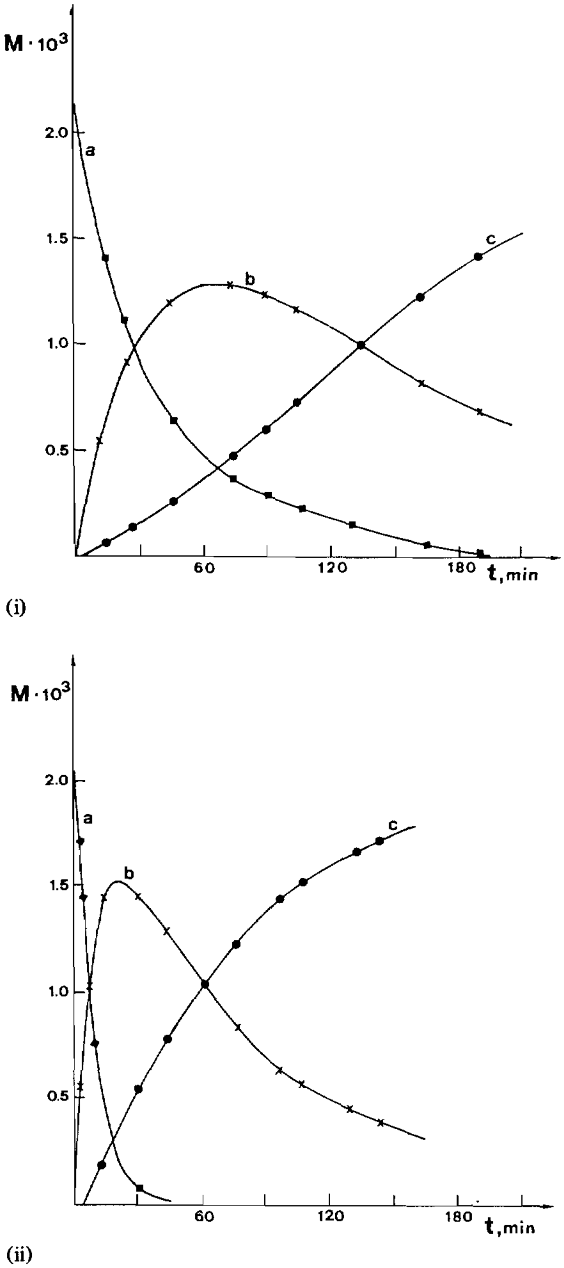


Fig. 3. Variation of the concentration of the initial compound (a) and of the intermediates I (b) and II (c) with time; (i) λ_{exc} 350 nm, (ii) λ_{exc} 254 nm.

The derivatives of the concentrations *vs.* time and subsequent calculations were obtained by a suitable computer program; the values of Φ_1 and Φ_2 found were (error within 10%):

λ	Φ_1	Φ_2
254	1.60×10^{-2}	0.25×10^{-2}
350	0.95×10^{-2}	0.15×10^{-2}

We noted that analogously to the findings in the dicarbene compound [8], the ratio of the partial quantum yields was constant at the two wavelengths and the first step of the photosolvation was more efficient than the second one The increasing quantum yields with exciting radiation pointed to a dissociative mechanism heterolytic fission of the Fe–C bond and the consequent diffusion apart or re-entry of the released ligand, dependent on the energy of the exciting irradiation A further finding supports this mechanism Upon irradiation of a solution in the presence of bipyridine, we noted the formation of $Fe(bpy)(CNCH_3)_4^{2+}$

$$Fe(CNCH_3)_6{}^{2+} \xrightarrow{h\nu,bpy} Fe(bpy)(CNCH_3)_4{}^{2+} + 2CNCH_3$$

Unfortunately a quantitative study of the process was not possible because of the relative extinction coefficients of $Fe(CNCH_3)_6^{2+}$ and $Fe(bpy)(CNCH_3)_4^{2+}$ (respectively 130 and 2750 at 350 nm) Besides, we controlled that the initial compound and the intermediate **I** underwent no thermal reaction after addition of bipyridine, that is to say, this ligand was not able to displace solvent molecules It is reasonable to suppose that the photochemical formation of $Fe(bpy)(CNCH_3)_4^{2+}$ occurred by reaction of bipyridine with an unsolvated pentacoordinate intermediate formed in the dissociative primary act the bipyridine competed with solvent in attacking with one end the free position and it rapidly expelled a second $CNCH_3$, thereby leading to the formation of a chelate

The overall results obtained in our investigation on the isocyanide complexes of Fe^{II} [2–8], tend to suggest that the primary photochemical act is the same for all the compounds studied, independently of the solvent used, while the whole process is typical for each case because the thermal and photochemical stability of the formed intermediates is influenced by the nature of the substituents and of the solvent For light absorption an heterolytic fission of the Fe–C bond occurs, with formation of a dissociative state [pentacoordinate intermediate, $CNCH_3$] The solvent substitutes the isocyanide but, in the presence of free ligands, they can compete with the solvent in attacking the sixth position. In agreement with the increase of the quantum yields with the energy of the incident light, the two fragments, trapped in the solvent cage, can either diffuse apart or undergo recombination, depending on the excess energy necessary for the bond fission

From the independence of the photochemical process of the excited band nature, we conclude that the ligand field states, populated by direct excitation as in $Fe(CNCH_3)_6^{2+}$, or by fast decay from higher charge transfer states as in the isocyanides at mixed ligands, are responsible for photosolvation The decrease of the quantum yields from the $Fe(CNCH_3)_6^{2+}$ to $Fe(bpy)_2(CNCH_3)_2^{2+}$ confirms this hypothesis, because this decrease is in accord with the increase of the stabilization of the ligand field caused by bipyridine or carbene groups

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