PHOTOLUMINESCENCE OF RUTHENIUM COMPLEXES WITH MOLECULES EXHIBITING TWISTED INTERNAL CHARGE TRANSFER STATES

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(Received April 24, 1986)

Summary

The occurrence of dual fluorescence in ruthenium complexes containing dimethylaminobenzonitrile (DMABN) has been studied at liquid nitrogen and room temperatures. It was concluded that in the $[Ru^{II}(NH_3)_5DMABN]^{2+}$, $[Ru^{III}(NH_3)_5DMABN]^{3+}$ and $[Ru^{II}(bipy)_2Cl(DMABN)]^+$ complexes (bipy $\equiv$ bipyridyl) a typical twisted internal charge transfer (TICT) fluorescence of DMABN appears upon excitation on a $\pi-\pi^*$ ligand absorption band. The ratio of the two luminescence band intensities is modified with respect to the free ligand.

The excitation of $[Ru(NH_3)_5DMABN]^{n+}$ on a metal-to-ligand charge transfer (MLCT) band gives rise to fluorescence with maxima at 378 nm (77 K) and 393 nm (room temperature) for $[Ru(NH_3)_5DMABN]^{2+}$ and at 435 nm (room temperature) and 450 nm (77 K) for $[Ru(NH_3)_5DMABN]^{3+}$ complexes, which is the first example for an $Ru(NH_3)_5L$ system. The four emission bands at 555, 595, 635 and 690 nm which occur in the $[Ru(bipy)_2Cl(DMABN)]^+$ spectrum are members of a vibrational progression with $\Delta\nu \approx 1175$ cm^{-1} and they could be assigned to the excited states with electron localization on either the bipyridyl or the dimethylaminobenzonitrile ligand, *i.e.* $[Ru^{III}(bipy^-)(bipy)Cl(DMABN)]^+$ or $[Ru^{III}(bipy)_2Cl-(DMABN^-)]^+$ respectively.

1. Introduction

Dual luminescence in donor–acceptor molecules such as dimethylaminobenzonitrile (DMABN) is a well-documented process [1]. There is now

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an increasing amount of evidence that it is caused by a twisted intramolecular charge transfer (TICT) excited state [2] in which the donor group $-N(CH_3)_2$ has been rotated by 90° with respect to the remainder of the molecule. Thus, contrary to the usual charge transfer systems, these particular excited states obey the minimum overlap rule [2, 3]. Since this perpendicular geometry breaks down the conjugation between the two parts of the molecule, TICT states could have the potential for controlling an intramolecular electron transfer process. This concept agrees with Carter's idea of conformational switching at the molecular level [4].

The introduction of the TICT effect in the structure of a mixed valence compound is our long-term objective. In a preliminary step, we have undertaken the study of coordination complexes containing DMABN as a ligand, in order to investigate the mutual influences of this ligand and of a redox centre. The present paper describes the luminescence properties of the three complexes $[(NH_3)_5Ru^{II}(DMABN)]^{2+}$, $[(NH_3)_5Ru^{III}(DMABN)]^{3+}$ and $[(bipy)_2Ru^{II}Cl(DMABN)]^+$, in which coordination to the metal occurs through the nitrile nitrogen atom (bipy $\equiv$ bipyridyl).

2. Experimental details

2.1. Preparation of complexes

For all preparations, the DMABN was purified by several recrystallizations from an MeOH–H_2O mixture.

2.1.1. $[(NH_3)_5Ru^{II}(DMABN)](PF_6)_2$

This complex was prepared by a procedure analogous to that of Curtis et al. [5]. $[Ru(NH_3)_5Cl]Cl_2$ [6] was converted into $[Ru(NH_3)_5(H_2O)](PF_6)_2$ by reduction with zinc amalgam [7]. The reaction with DMABN in acetone readily yielded the pentammine ruthenium(II) complex which was precipitated by diethyl ether. The purity was checked by thin-layer chromatography (acetonitrile or acetone on Al_2O_3) and voltammetry. Two reversible oxidation waves are observed at +0.42 and +1.3 V vs. the standard calomel electrode (SCE) in acetonitrile containing 0.1 M $NBu_4^+BF_4^-$ as supporting electrolyte. Since free DMABN gives an irreversible wave near 1.0 V under the same conditions, cyclic voltammetry can be used to check the absence of free DMABN.

The IR nitrile stretching frequency is found at 2230 cm^{-1} instead of at 2240 cm^{-1} in the free ligand, showing that coordination occurs through the nitrile nitrogen atom.

2.1.2. $[(NH_3)_5Ru^{III}(DMABN)]^{3+}$

This oxidized form was obtained from the above-mentioned compound by oxidation using bromine in acetonitrile. Spontaneous precipitation occurs and the product can be isolated by filtration.

2.1.3. [(bipy)$_2$Ru^{II}Cl(DMABN)](PF$_6$)

This compound was obtained from the labile intermediate [Ru(bipy)$_2$-ClS]$^+$ (S ≡ methanol or acetone) following the method of Adeyemi *et al.* [8]. The complex [Ru(bipy)$_2$(NO)Cl](PF$_6$)$_2$ (614 mg, 0.8 mmol) was dissolved in acetone (65 ml), and sodium azide (52 mg, 0.8 mmol) in 44 ml of methanol was gradually added. An equimolar solution of DMABN was then added and the mixture was refluxed and stirred under an argon atmosphere for 24 h. The orange–red solution was filtered while hot and its volume was reduced to about 20 ml. The red compound was precipitated by addition of anhydrous diethyl ether, collected by filtration and dried under vacuum. Analysis of [Ru(bipy)$_2$Cl(DMABN)](PF$_6$)·2H$_2$O gave the following results. Calculated: C, 45.4; H, 3.9; N, 10.9; Cl, 4.6. Found: C, 44.4; H, 3.36; N, 10.8; Cl, 4.6. A cyclic voltammogram in acetonitrile containing 0.1 M NBu$_4$$^+BF_4$$^-$ as supporting electrolyte shows a single reversible wave with redox potential +0.83 V.

2.2. Physical measurements

Absorption spectra were recorded using a Beckman 5240 UV–visible–near-IR spectrophotometer.

The corrected emission spectra were obtained on a modified Aminco SPF 500 spectrofluorometer interfaced to a Kontron Psi 80 microcomputer for storage, correction and analysis of spectra. The source used for excitation was a 450 W Osram xenon lamp equipped with an SLM monochromator.

For correction of emission spectra we used an Osram tungsten lamp (64380, 200 W, 6.6 A) which we had calibrated at the Institut National de Metrologie (CNAM).

For room temperature measurements quartz cells (1 cm × 1 cm) were used. For low temperature (77 K) emission spectra, the solutions were placed in quartz tubes of diameter 5 mm and mounted in a quartz Dewar filled with liquid nitrogen.

The phosphorescence spectra were recorded using the phosphoroscope accessory of the Aminco SPF 500 spectrofluorometer. We observed no change in the phosphorescence emission spectra when the chopper motor speed was varied from 500 to 10 000 rev min^{-1}.

All the spectra were measured in 90vol.%EtOH–10vol.%MeOH solution.

Electrochemical measurements were performed with a Tacussel system consisting of a PRT 30-0.1 potentiostat equipped with a GSATP generator and an *x–y* recorder. All measurements were made at a platinum electrode with respect to a saturated calomel electrode.

The solvents used for luminescence measurements were from Merck (fluorescence grade for MeOH and pro Analysi for EtOH).

3. Results and discussion

Since our goal was to look at the differences in the DMABN behaviour caused by complexation we first recorded the spectra of the free ligand under the same conditions, *i.e.* at room temperature and 77 K.

3.1. Free DMABN

The absorption spectrum of DMABN exhibits a sharp maximum at 290 nm at room temperature, which is only very weakly modified on cooling. Thus the excitation was performed at this wavelength for room temperature or liquid nitrogen temperature studies. At 298 K, the luminescence spectrum shows the F_a emission (498 nm) corresponding to the TICT state, and the F_b emission (343 nm) due to the planar excited state (Fig. 1). This spectrum agrees with previous work [9].

Very few low temperature spectra (in rigid glasses) have been reported. On cooling to 77 K, the F_b emission is found at the same energy but the F_a band is replaced by two bands at higher energies (415 and 430 nm, see Fig. 1). These two bands have long lifetimes so that they should correspond to phosphorescence. This assignment can also be found in other papers, probably on the basis of lifetimes [10]. More recently, Cazeau-Dubroca *et al.* have shown by polarization measurements that low temperature emission near 450 nm is indeed phosphorescence and not delayed F_a fluorescence [11].

For all complexes of DMABN with ruthenium(II) or ruthenium(III) a decrease in the luminescence intensity is observed. This is likely to be a consequence of the internal heavy-atom effect which favours intersystem crossing.
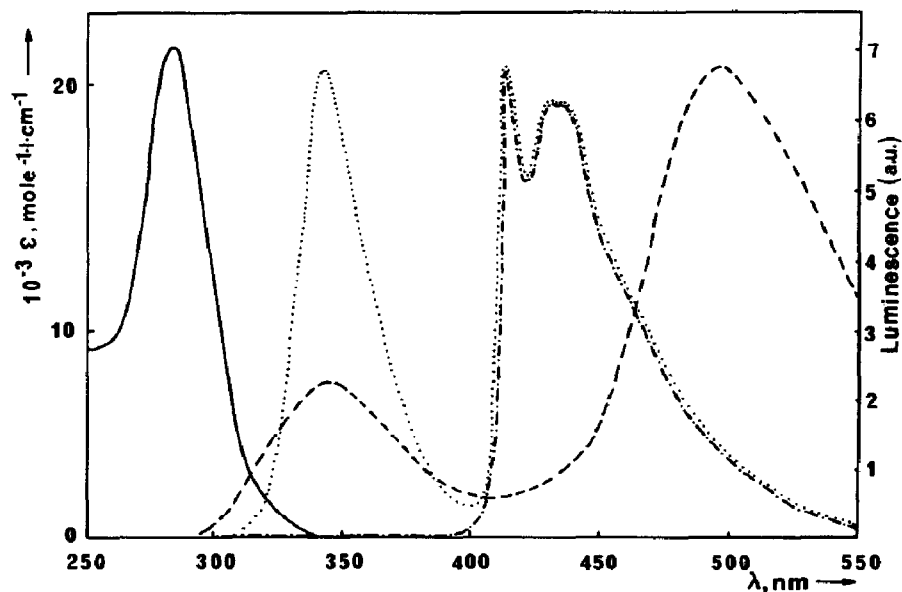

Fig. 1. Absorption (———) and corrected luminescence spectra of DMABN in 10vol.%-MeOH–90vol.%EtOH (λ_{exc} = 290 nm): — — —, room temperature fluorescence; . . . , 77 K luminescence; — · —, 77 K phosphorescence.

3.2. [(NH₃)₅Ru^{II}DMABN]²⁺

3.2. [(NH$_3$)$_5$Ru^{II}DMABN]$^{2+}$

The room temperature absorption spectrum of [(NH$_3$)$_5$Ru^{II}DMABN]$^{2+}$ exhibits an intraligand charge transfer transition at 290 nm. An additional band is also observed at 342 nm with a shoulder on the low energy side (see Fig. 2(a)). This feature is assigned to metal-to-ligand charge transfer (MLCT) [12]; it is interesting to notice that in [(NH$_3$)$_5$Ru^{II}(benzonitrile)]$^{2+}$ this MLCT band appears at a lower energy (λ_{max} = 376 nm). This shows the
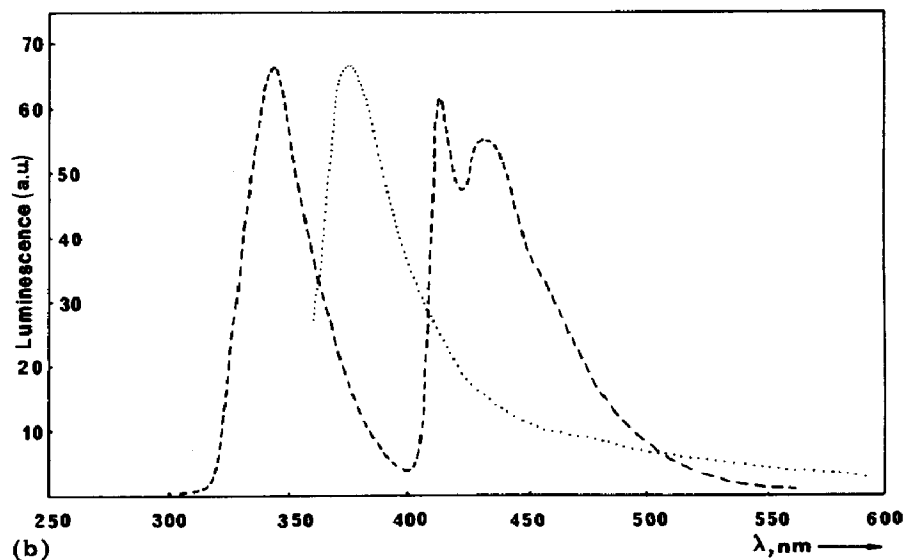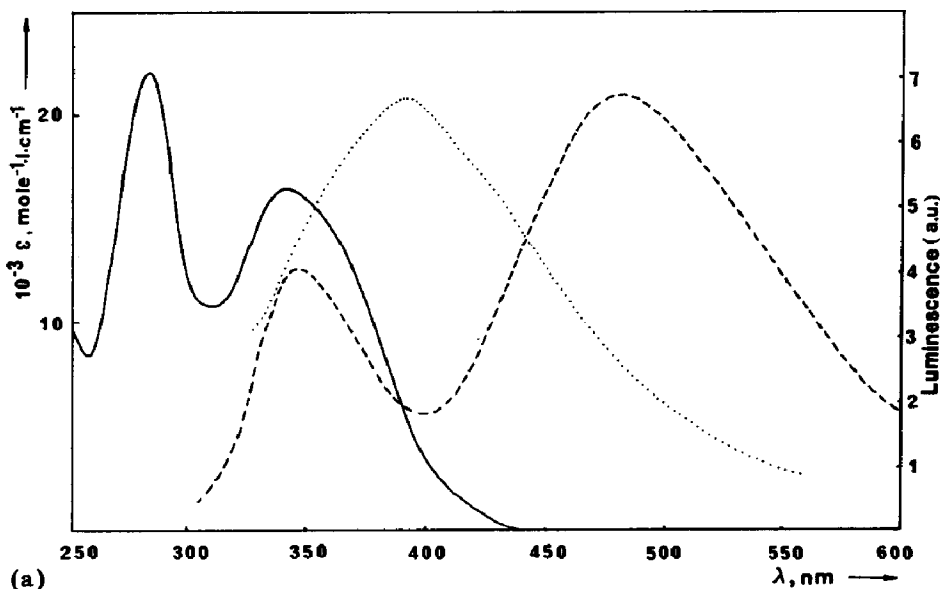

Fig. 2. Absorption (———) and corrected luminescence spectra of [Ru(NH$_3$)$_5$DMABN]$^{2+}$ in 10vol.%MeOH–90vol.%EtOH at (a) room temperature and (b) liquid nitrogen temperature; — — —, λ_{exc} = 290 nm; . . . , λ_{exc} = 342 nm.

influence of the dimethylamino donor group on the energy levels: it makes the DMABN ligand a less good acceptor than benzonitrile so that the MLCT band is blue shifted on the introduction of this group. The position of the band is roughly the same as for $[(NH_3)_5Ru^{II}(NC-C_6H_4-OCH_3)]^{2+}$ [12].

On excitation at 290 nm at room temperature, the DMABN spectrum is observed with a much lower intensity, roughly one sixth of the intensity of free DMABN. In this medium, there is no tendency for ligand labilization and, furthermore, we confirmed by voltammetry the absence of free DMABN in the solution. Thus the observed spectrum is characteristic of the complexed ligand. The ratio of emission intensities $I(F_a)/I(F_b)$ is 1.65 instead of 3.0 in the free ligand. Thus the F_a emission is relatively weakened upon complexation which seems to indicate that the coordination of a ruthenium atom on the nitrile end has unfavourable consequences on the formation of the TICT state. This might be due to an increase in the probability of intersystem crossing (heavy-atom effect) which causes both the quantum yield and the lifetime to decrease. The lifetime being smaller, this would decrease the probability of formation of the TICT state. Picosecond experiments are in progress to clarify this point.

At a low temperature (77 K), the characteristic spectrum of DMABN appears (Fig. 2(b)). On excitation at 342 nm, i.e. on the top of the MLCT band, the DMABN emission band is replaced by an emission occurring at 393 nm at room temperature or at 378 nm at 77 K. The room temperature emission band is broad and exhibits a shoulder near 440 nm (Fig. 2(a)), whereas the low temperature band is sharper with a shoulder near 470 nm. We checked that under these conditions there is no DMABN emission. Therefore, to our knowledge, this would be the first example of an intrinsic luminescence of a pentammine–ruthenium(II) species originating from a charge transfer state. It should be mentioned that this luminescence is especially weak and requires the 450 W lamp for easy observation.

3.3. $[(NH_3)_5Ru^{III}(DMABN)]^{3+}$

The absorption spectrum of $[(NH_3)_5Ru^{III}(DMABN)]^{3+}$ exhibits three bands with maxima at 700, 380 and 318 nm (Fig. 3(a)). The third band corresponds to the intraligand $\pi-\pi^*$ charge transfer transition which has been shifted from 290 nm as a result of the change in oxidation state. The 700 nm band has been recently shown to be a ligand-to-metal charge transfer transition [5]. This reversal of the charge transfer direction with respect to the ruthenium(II) complex can be explained by the π acceptor character of ruthenium(III) and the presence of the dimethylamino donor group. The 380 nm band has not yet been assigned but is usually encountered in ruthenium-(III) complexes with nitriles [12, 13].

On excitation at 318 nm, the DMABN emission is observed, but the ratio of F_a to F_b intensities is reversed so that F_b is now more intense than F_a, both at room temperature and at 77 K (Figs. 3(a) and 3(b)). Therefore the oxidation of ruthenium does not favour the formation of the TICT state.
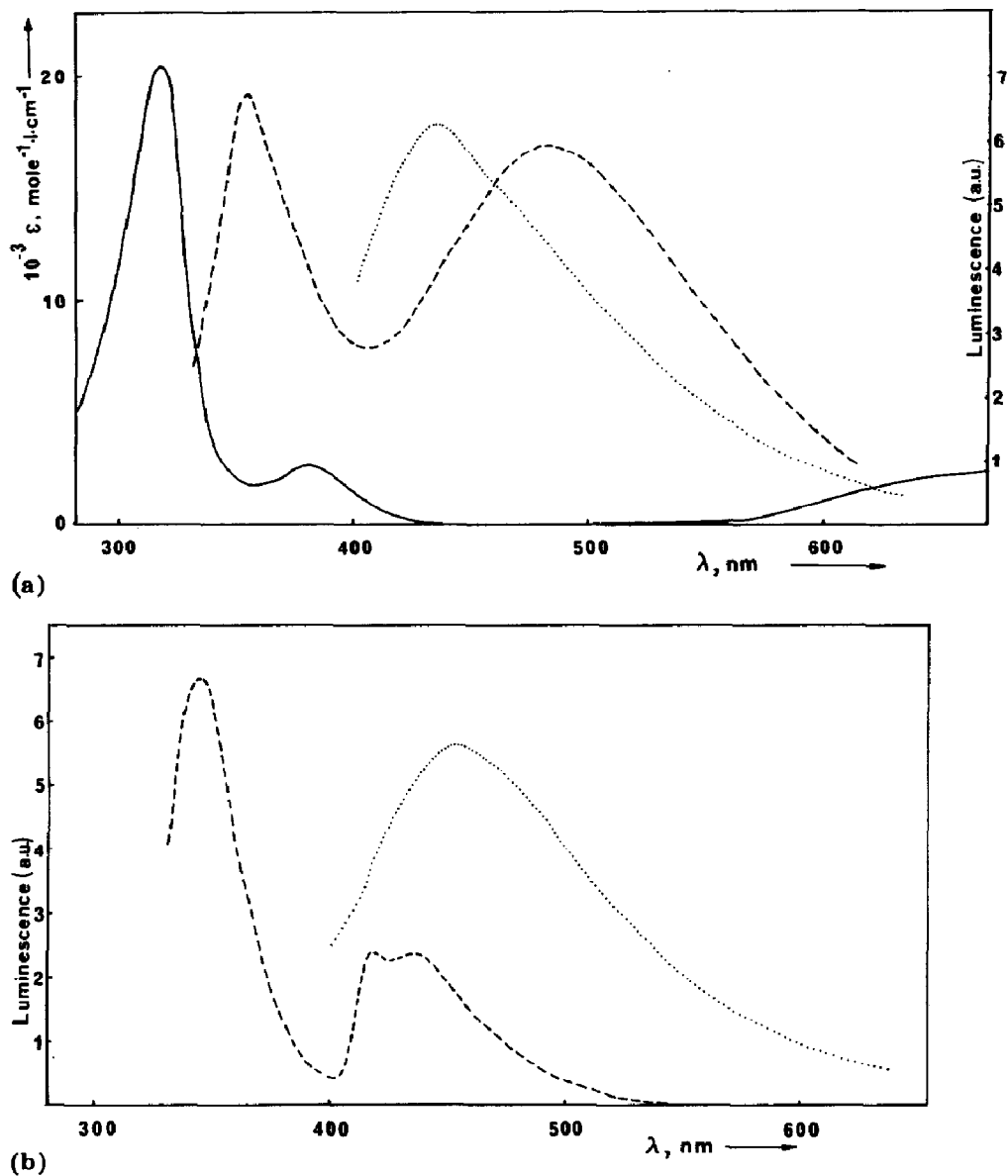
Fig. 3. Absorption (———) and corrected luminescence spectra of [Ru(NH₃)₅DMABN]³⁺ in 10vol.%MeOH–90vol.%EtOH at (a) room temperature and (b) liquid nitrogen temperature; — — —, λ_{exc} = 318 nm; . . . , λ_{exc} = 380 nm.

When the excitation is performed at 380 nm, an emission band is observed at 435 nm (room temperature) or 450 nm (77 K). This is again assigned to a specific luminescence of the complex, but curiously the influence of temperature is reversed with respect to the case of ruthenium(II). Finally the excitation was performed at 700 nm, but nothing was observed up to the sensitivity limit of the photomultiplier (about 850 nm).

3.4. [(bipy)₂RuᴵᴵCl(DMABN)]⁺

For this species, the absorption spectrum (Fig. 4) exhibits three main bands, at 470, 330 and 290 nm. The first two correspond to the usual metal-to-ligand charge transfer transitions for $Ru(bipy)_2ClX$ complexes with $X \equiv Cl$ [14], CH_3CN [14], pyridine [15], pyrazine [16], and 4,4'-bipyridine [17]. The intense 290 nm absorption corresponds to DMABN as well as to $\pi-\pi^*$ transition energies in bipyridyl complexes [14 - 17].

For low energy excitations (460 or 330 nm) at 77 K, a complex luminescence spectrum is observed with emission bands at 555, 595, 635 and 690 nm, the relative heights depending on the excitation wavelength (Fig. 5). The luminescence in this energy range is typical of $[(bipy)_2Ru^{II}XY]$ species and it corresponds to an emission from a metal-to-ligand charge transfer state which is largely triplet in character. However, most bis(2,2'-bipyridine)-ruthenium(II) complexes exhibit only two emission bands at 77 K, usually separated by 1200 - 1300 cm⁻¹ [18]. In the present complex, careful examination of the spacings between the emission bands suggests that these bands are members of a vibrational progression with $\Delta\nu \approx 1175$ cm⁻¹. Thus the 595 nm band seems to be of different origin. It seems logical to assign the vibrational progression to an excited state with electron localization on the bipyridyl ligand, i.e. $[Ru^{III}(bipy^-)(bipy)Cl(DMABN)]^+$. The 595 nm band would then correspond to $[Ru^{III}(bipy)_2Cl(DMABN^-)]^+$. It is interesting to note that this 595 nm emission band is activated mainly when the excitation is performed at 330 and 290 nm. Therefore the 330 nm band could corre-
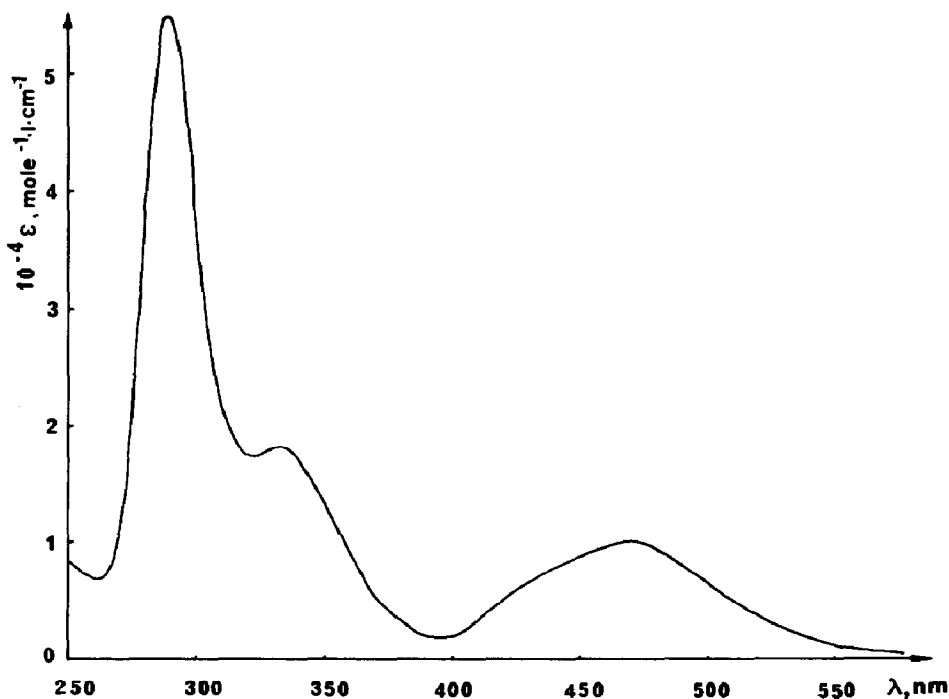

Fig. 4. Electronic absorption spectrum of [(bipy)₂Ru(DMABN)Cl]⁺ complex in 10vol.%-MeOH–90vol.%EtOH solution.
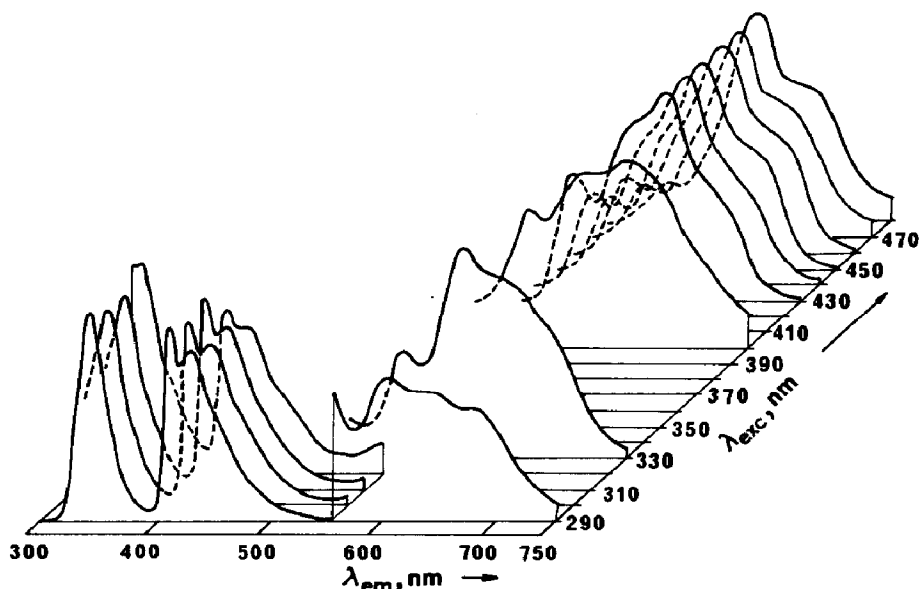
Fig. 5. Excitation wavelength dependence luminescence spectra (corrected) of [(bipy)$_2$-Ru(DMABN)Cl]$^+$ in 10vol.%MeOH–90vol.%EtOH rigid glasses. The right-hand side of the spectra has been magnified 10 times.
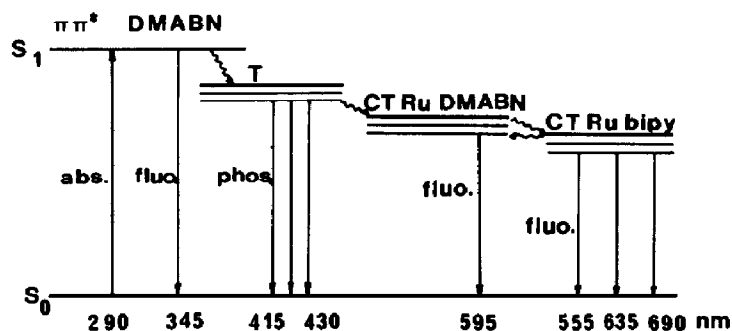

Fig. 6. Electronic states reached by excitation of [(bipy)$_2$Ru(DMABN)Cl]$^+$ complex at 290 nm at liquid nitrogen temperature.

spond to the position of a ruthenium-to-DMABN charge transfer absorption. The presence of different ligands in the coordination sphere of ruthenium is a favourable factor for the observation of dual luminescence [19].

When the excitation wavelength is progressively shifted towards 290 nm, *i.e.* towards the DMABN absorption, the emission gradually changes with the appearance of the DMABN emission spectrum (see Fig. 5). For λ_{exc} = 290 mn, six bands are observed in the emission spectrum, *i.e.* the three DMABN bands plus bands originating from the Ru(bipy)$_2$ClX entity. This is indicative of energy transfer between the two chromophores. The different excited states originating from the 290 nm excitation are depicted in Fig. 6.

4. Concluding remarks

The present work has shown that the TICT effect is still observed in ruthenium complexes of the DMABN ligand. This opens up interesting possibilities for controlling electron transfer at the molecular level and we are presently preparing bridging ligands which could give the TICT effect [20]. The occurrence of luminescence in an $(NH_3)_5RuL$ system has been observed for the first time. However, the influence of coordination by a metal atom is not fully understood. In most cases, the F_a luminescence is weakened with respect to the F_b, but this apparent hindering of the twisting motion could be explained by different processes. It is possible that either the formation of the TICT state is slower or that its lifetime is shortened as a result of more efficient intersystem crossing. We are presently performing picosecond experiments in order to understand these points more completely.

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