Photochemistry of barium(II) and lead(II) 2,4-dinitrostilbene-4'-monoaza-18-crown-6 complexes

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Abstract

The chromoionophore *trans*-2,4-dinitrostilbene-4'-monoaza-18-crown-6 (DMC) in CH_3OH is characterized by a long-wavelength absorption ($\lambda_{max} = 476$ nm) which is attributed to a charge transfer (CT) transition from the amine function to the nitro substituents. On protonation or complexation with Ba^{2+} or Pb^{2+} the amine is blocked and the CT transition is replaced by a $\pi\pi^*$ transition of the stilbene moiety at higher energies. The photochemistry of all species is in accord with these assignments. While the photolysis of DMC leads to the formation of an isatogen, $DMCH^+$, $[Ba(DMC)]^{2+}$ and $[Pb(DMC)]^{2+}$ undergo trans–cis photoisomerization of the stilbene moiety.

1. Introduction

Electronic transitions of coordination compounds are classified according to the predominant localization of the molecular orbitals on the metal or the ligands [1, 2]. The electronic transitions are of the metal-centred (MC), metal-to-ligand charge transfer (MLCT), ligand-to-metal charge transfer (LMCT), metal-to-metal charge transfer (MMCT), ligand-to-ligand charge transfer (LLCT) and intraligand (IL) types. Although the spectroscopy and photochemistry of MC, MLCT, LMCT, MMCT and LLCT states have received considerable attention [2–8], much less is known about IL states which do not show a common pattern of reactivity. Frequently, IL states occur at rather high energies. Generally, IL excitation is followed by a facile deactivation to lower states of different origin. If IL photoactivity is observed it is often similar to that of the free ligand, but modified by coordination. However, it is also possible that the coordination will change the photochemistry completely.

Stilbene derivatives which can coordinate to metals via certain substituents, such as carboxylic groups or nitrogen atoms, are of particular interest with regard to their photoreactivity [5, 9–11]. This is illustrated by the photochemical behaviour of complexes of the type $[M(NH_3)_5(trans$-4-stilbene-carboxylate)]^{2+}$, with $M \equiv Co$, Rh and Ir, which undergo redox reactions (Co) as well as trans–cis isomerization of the stilbene chromophore [9, 10]. Generally, the study of photoreactive ligands has been limited to transition metal complexes, whereas main group metal compounds [2, 8, 12, 13] have been largely ignored. Unfortunately, the choice of suitable complexes of the main group metals is hampered by their kinetic and, partially, thermodynamic instability. However, the latter drawback can be circumvented by the use of crown ethers [14] which are linked covalently to a suitable organic chromophore. If the metal can interact directly with the chromophore, the substituted crown ethers are called chromoionophores since the coordination by a metal ion affects the absorption spectrum [15, 16]. The thermodynamic stability of such main group metal complexes and their kinetic lability may be used for rapid, but reversible, complex formation with applications in analytical chemistry. Since a metal can alternate, modify or completely change the photoreactivity of a ligand, the reversible coordination to chromoionophores could lead to new applications in the general area of optoelectronics [17].

A photophysical study of a chromoionophore and its metal complexes has been reported recently

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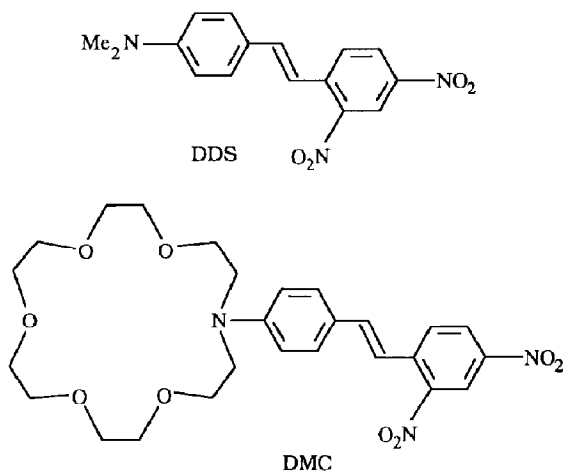[†]Author to whom correspondence should be addressed.

Fig. 1. Structures of DMC and DDS.

[18]. In the present work, we deal with the photochemical properties. We selected the ligand *trans*-2,4-dinitrostilbene-4'-monoaza-18-crown-6 (DMC) (Fig. 1) which offers several interesting features [15, 19]. The free ligand is characterized by an intense long-wavelength absorption which is attributed to a charge transfer (CT) transition from the amine donor to the nitro acceptor groups. On incorporation of a metal into the crown ether, the amine donor is blocked. The CT absorption is then lost or shifted to shorter wavelength [15, 19]. A concomitant change in the photochemical behaviour is expected to occur. As metal centres, we selected Ba^{2+} [15, 19] and Pb^{2+}. Although the coordination by Ba^{2+} is largely ionic, Pb^{2+} should form bonds with considerable covalent character [20, 21]. For comparison, the protonated ionochromophore and the crown-free chromophore *trans*-2,4-dinitro-4'-dimethylaminostilbene (DDS) were also included in this study.

2. Experimental section

2.1. Materials
The compounds DDS [22] and DMC [19] were prepared according to published procedures. Ba(SCN)$_2$ and Pb(NO$_3$)$_2$ were purchased from Aldrich and Merck and used as received. Methanol was of spectrograde.

2.2. Spectroscopy
The absorption spectra were recorded on a Uvikon 860 double-beam spectrophotometer. The method for the determination of quantum yields was the same as used in previous work [23]. For $\phi_{t \to c}$ measurements, a 1 kW high-pressure Xe/Hg lamp and a monochromator (Schoeffel; bandwidth,

12 nm) were used. The progress of the photolysis was monitored by UV–visible spectral measurements. The emission spectra were recorded on a Hitachi 850 spectrofluorometer which was equipped with a Hamamatsu 928 photomultiplier.

3. Results

3.1. Electronic spectra
The absorption spectra of DMC and its Ba^{2+} complex have been reported previously [15, 19]. The long-wavelength absorption of DMC in CH$_3$OH (Table 1) was blue shifted on complexation with Ba^{2+} or Pb^{2+} (Figs. 2 and 3) and on protonation with HCl (Fig. 4). The complexes were of moderate stability with $K = 3.1 \times 10^2$ l mol^{-1} for the barium complex and 3.2×10^3 l mol^{-1} for the lead complex. The absorption spectrum of the crown-free chromophore DDS in methanol ($\lambda_{max} = 471$ nm, $\epsilon = 24\ 500$ l mol^{-1} cm^{-1}) resembled closely that of DMC. Protonation of the free chromophore in HCl/CH$_3$OH shifted the low-energy band to $\lambda_{max} = 338$ nm ($\epsilon = 21\ 000$ l mol^{-1} cm^{-1}).

The crown ether DMC, its protonated form and the complex cations [Ba(DMC)]$^{2+}$ and [Pb(DMC)]$^{2+}$ in methanol were not luminescent under ambient conditions. The free chromophore DDS and the protonated form DDSH$^+$ showed no emission under the same conditions.

3.2. Photochemistry
The photochemistry of DDS in benzene has been studied previously [24]. On irradiation ($\lambda_{irr} = 366$ nm) in benzene or methanol, it was converted to 2-(p-dimethylaminophenyl)-4,6-dinitroisatogen, which can be identified by its absorption bands at $\lambda_{max} = 680$ nm ($\epsilon = 22\ 000$ l mol^{-1} cm^{-1}) and 465 nm ($\epsilon = 6000$ l mol^{-1} cm^{-1}). In addition, some other photoproducts were isolated. The crown ether DMC showed similar behaviour. The spectral variations accompanying photolysis (Fig. 5) indicated the formation of the isatogen with absorptions at $\lambda_{max} = 419$ and 621 nm. Owing to secondary processes, the isosbestic points at 293, 328 and 400 nm were lost at the later stages of photolysis.

The photolysis ($\lambda_{irr} = 366$ nm) of protonated DDS in HCl/CH$_3$OH led to trans–cis isomerization at the olefinic double bond. In analogy with 4'-hydroxy-1-methyl-stilbazolium betaine [25], the isomerization of DDS could be completely reversed by deprotonation with a base (KOH or alkylamines) and heating of the solution to 60 °C for several hours. An analysis of the spectral changes

TABLE 1. Absorption maxima and photochemical data of 2,4-dinitrostilbene-4'-monoaza-18-crown-6 (DMC) and 2,4-dinitro-4'-dimethylaminostilbene (DDS) in CH_3OH

Compound	λ_{max} [a] (ϵ)	K_s	λ_{irr}	$\phi_{t \to c}$ [b]	$(\%\ cis)_{eq}$ [c]	$(\lambda_{max})_{cis}$ (ϵ)
DDS	471 (24500)					
DDSH⁺	338 (21000)		366	0.138	79	332 (10700)[d]
			306		69	
DMC	476 (52000)					
DMCH⁺	340 (42000)		366	0.078	95	
			405		100	333 (17000)
[Ba(DMC)]²⁺	364 (44000)	3.1×10^2	366	0.6×10^{-3}	94	
			405		100	337 (31000)
[Pb(DMC)]²⁺	361 (41000)	3.2×10^3	366	1.5×10^{-3}	100	
			405		100	335 (17000)

[a]Trans isomer.
[b]Quantum yield of trans–cis isomerization.
[c]Percentage of cis isomer in the photostationary state.
[d]Cis isomer (calculated).
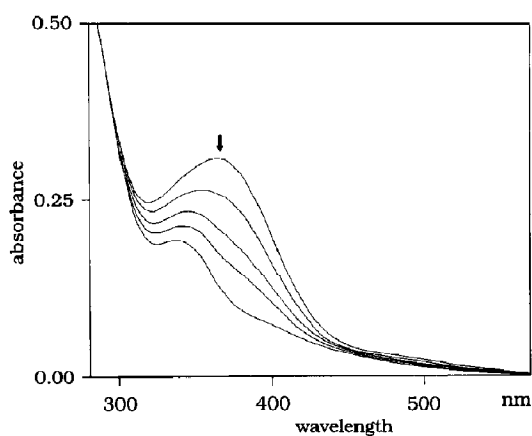
Fig. 2. Spectral changes during the photolysis of 6.92×10^{-6} M of the crown ether $[Ba(DMC)]^{2+}$ in CH_3OH for times of 0, 1, 3, 6 and 12 min ($\lambda_{irr} = 366$ nm; 1 cm cell).
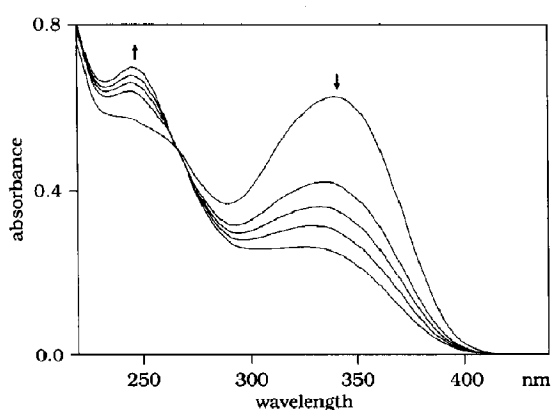
Fig. 4. Spectral changes during the photolysis of 1.36×10^{-5} M of the crown ether DMCH⁺ in CH_3OH for times of 0, 10, 15, 20 and 40 s ($\lambda_{irr} = 366$ nm; 1 cm cell).
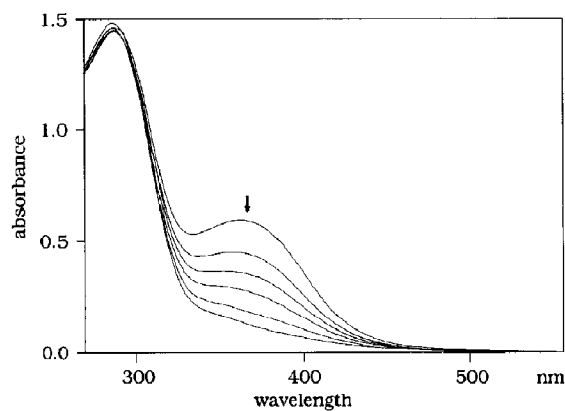
Fig. 3. Spectral changes during the photolysis of 1.50×10^{-5} M of the crown ether $[Pb(DMC)]^{2+}$ in CH_3OH for times of 0, 1, 2, 3, 5 and 8 min ($\lambda_{irr} = 366$ nm; 1 cm cell).
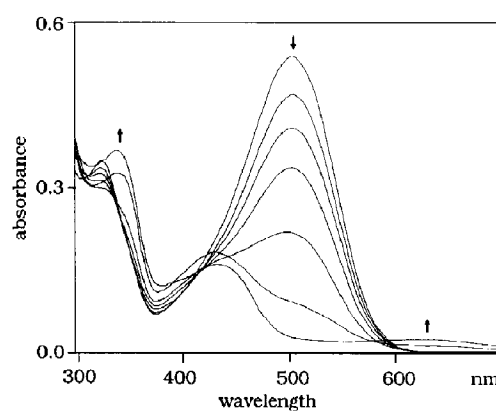
Fig. 5. Spectral changes during the photolysis of DMC in benzene for times of 0, 1, 2, 4, 8, 16 and 32 min ($\lambda_{irr} = 366$ nm; 1 cm cell).

associated with photolysis at two different irradiation wavelengths showed that the trans isomer underwent isomerization which reached a photostationary state with 79% of the cis isomer at $\lambda_{irr} = 366$ nm and 69% at $\lambda_{irr} = 306$ nm.

Similar results were obtained for the protonated crown ether DMC in HCl/CH$_3$OH. The photolysis was accompanied by spectral changes with a clean isosbestic point at 262 nm (Fig. 4), indicating the absence of secondary processes. Deprotonation by tributylamine and heating of the solution to 60 °C for 8 h led to the complete recovery of the absorption spectrum of the trans isomer. In the photostationary state, 95% of the protonated DMC was converted to the cis isomer at $\lambda_{irr} = 366$ nm and 100% at $\lambda_{irr} = 405$ nm. The quantum yield of trans to cis isomerization was $\phi_{t \rightarrow c} = 0.078$ at $\lambda_{irr} = 366$ nm.

The Ba^{2+} and Pb^{2+} complexes of DMC in methanol also underwent trans–cis photoisomerization of the stilbene moiety. The concomitant spectral changes (Figs. 2 and 3) were reproduced by the spectra resulting from complexation of mixtures containing constant overall concentrations of the crown ether, but different trans to cis ratios. These mixtures were obtained by irradiation of DMCH$^+$ at various irradiation times, followed by subsequent deprotonation with tributylamine and complexation with Ba^{2+} and Pb^{2+}. At $\lambda_{irr} = 366$ nm, [Ba(DMC)]$^{2+}$ was converted to 94% cis-[Ba(DMC)]$^{2+}$ in the photostationary state with $\phi_{t \rightarrow c} = 0.6 \times 10^{-3}$. [Pb(DMC)]$^{2+}$ yielded, at $\lambda_{irr} = 366$ nm, 100% of the cis isomer with $\phi_{t \rightarrow c} = 1.5 \times 10^{-3}$ and 100% at $\lambda_{irr} = 405$ nm.

4. Discussion

4.1. Electronic spectra

Substituted stilbenes of the type 4-donor-4'-acceptor-stilbene, with donor substituents such as NR$_2$ and acceptor groups such as NO$_2$ or CN, show a long-wavelength absorption in the visible region which is attributed to an intramolecular CT transition from the donor to the acceptor [26–28]. If the donor function at the amine is blocked, this band is shifted to shorter wavelength according to the extent to which the lone pair at the amine is stabilized. This is achieved by the interaction with protons or metals. Finally, the new band at higher energies is assigned to the $\pi\pi^*$ transition of the stilbene chromophore. The compound DDS is a member of this family of donor–acceptor-substituted stilbenes. It displays a CT band at 471 nm. On protonation of the amine substituent, the $\pi\pi^*$ stilbene absorption appears

at 338 nm. In the crown ether DMC, the DDS chromophore is essentially preserved. The CT band of DMC appears at $\lambda_{max} = 476$ nm and the protonated form absorbs at $\lambda_{max} = 340$ nm. Although the crown-free chromophore does not form stable complexes with metals such as Ba^{2+} or Pb^{2+}, the crown ether DMC undergoes complexation which is apparently facilitated by the suitable size of these cations. For example, it has been shown that Pb^{2+} resides exactly in the centre of the crown ether 18-crown-6 [29, 30]. In the case of the Ba^{2+} complex, the stabilization of the amine lone pair takes place by electrostatic interaction with the cation. Nevertheless, the considerable shift of the long-wavelength band from 476 to 364 nm implies a large degree of lone pair stabilization. The blue-shifted absorption can be assigned to a stilbene $\pi\pi^*$ transition with a small residual CT contribution. When Ba^{2+} is replaced by Pb^{2+} the position of the long-wavelength band at $\lambda_{max} = 361$ nm indicates an even smaller CT contribution. It is assumed that this effect is caused by covalent interaction of the amine lone pair with Pb^{2+} which provides low-energy s and p valence orbitals [20, 21].

The free chromophore DDS, the crown ether DMC, and its protonated and complexed forms are not emissive under ambient conditions, in contrast with many other trans-stilbenes which show fluorescence at room temperature in solution [31]. It is assumed that the absence of fluorescence is related to the presence of two nitro groups in the stilbene moiety. Nitro substituents are well known to induce radiationless deactivation of singlet excited states [32]. Moreover, in the case of the complexes, the Ba^{2+} and Pb^{2+} cations may quench IL fluorescence by facilitating intersystem crossing due to increased spin–orbit coupling (heavy atom effect). Since Pb^{2+} shows phosphorescence from its lowest sp excited state under ambient conditions (e.g. PbCl$_3^-$ in CH$_3$CN, $\lambda_{max} = 538$ nm) [20, 21], such an emission could also occur for [Pb(DMC)]$^{2+}$. However, contrary to this expectation such phosphorescence was not detected. Other excited state deactivation channels are apparently available to this complex as indicated by its photochemical behaviour.

4.2. Photochemistry

Stilbenes undergo a variety of excited state processes, including photochemical reactions [33–35]. The donor–acceptor-substituted derivative trans-4-nitro-4'-dimethylaminostilbene has been reported not to be light sensitive in polar solvents [26, 27]. The lowest energy excited state, which

is of the CT type, is apparently not photoactive in this case. In contrast, the related chromophore DDS is photochemically converted to an isatogen not only in benzene [24], but also in polar solvents such as methanol. According to Splitter and Calvin [24], this reaction requires a donor–acceptor interaction in the stilbene and, additionally, the presence of a nitro group in an ortho position of one of the phenyl rings. Therefore it is not surprising that isatogen formation also takes place on irradiation of DMC.

The photolysis of the protonated forms of DDS and DMC leads to different results. Trans–cis photoisomerization of the stilbene moiety occurs in agreement with the general behaviour of stilbenes [33, 34], including nitro derivatives [35], with $\pi\pi^*$ states as the lowest energy excited states. Since [Ba(DMC)]$^{2+}$ and [Pb(DMC)]$^{2+}$ also undergo trans–cis photoisomerization, it is concluded that their lowest excited states are of the $\pi\pi^*$ type. In this context, it is interesting that the Ca^{2+} complex of the related crown ether stilbene-4'-monoaza-15-crown-5 shows a different behaviour [18]. In this case, the lowest excited state is apparently CT in nature. Irradiation can lead to a reversible ejection of the Ca^{2+} ion. It has been suggested that this reaction is induced by the reduction of the electron density at the nitrogen in the CT state. The attenuation of the coordinating ability of the crown ether thus initiates the release of the metal ion. A similar reaction has been observed previously. The complex Pt(1-naphthyl-amine)$_2$Cl$_2$ undergoes photosubstitution of the amine, since this ligand also loses its coordinating properties due to IL (or ILCT) excitation [2, 36].

Acknowledgment

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