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Photooxidation of Bis(ethylxanthato)nickel(II) containing Aromatic Nitrogen Heterocyclic Ligands in Chloroform

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Abstract. The photochemistry of the complexes [Ni(*Etxn*)$_2$(*N-N*)] [*Etxn* = ethylxanthate, *N-N* = 2,2′-bipyridine(*bpy*), 4,4′-dimethyl-2,2′-bipyridine (4,4′-*Me-bpy*), 1,10-phenanthroline (*phen*) or 2,2′-bipyrimidine (*bpym*)] has been investigated. These complexes were not light sensitive in most solvents such as acetonitrile. Upon irradiation of chloroform solutions of these complexes, a photoredox reaction occurred giving the parent Ni(*Etxan*)$_2$. It is suggested that the reactive excited state is of the charge-transfer-to-solvent (CTTS) type. The energy of this state depends on the redox potentials of the solvent. When $CHCl_3$ as solvent was replaced by the stronger oxidant CCl_4, the photoactive wavelength region was shifted to the red. It was blue shifted when the weaker oxidant CH_2Cl_2 was used. From quantum yield measurements it is concluded that the photostability of the studied complexes decreases in the following order: *bpym* > *phen* > *bpy* > 4,4′-*Me-bpy*.

Keywords. Photooxidation; Bis(ethylxanthato)nickel(II) mixed ligand complexes; Charge transfer to solvent (CTTS).

Photooxidation von Bis(ethylxanthato)nickel(II) mit aromatischen Stickstoffheterocyclen enthaltenden Liganden in Chloroform

Zusammenfassung. Es wurde die Photochemie der Komplexe [Ni(*Etxn*)$_2$(*N-N*) [*Etxn* = Ethylxanthat, *N-N* = 2,2′-Bipyridin (*bpy*), 4,4′-Dimethyl-2,2′-bipyridin (4,4′-*Me-bpy*), 1,10-Phenanthrolin (*phen*) oder 2,2′-bipyrimidin (*bpym*)] untersucht. Diese Komplexe waren in den meisten Lösungsmitteln wie etwa Acetonitril nicht lichtsensitiv. Bei Bestrahlung von Chloroformlösungen der Komplexe trat jedoch eine Photoreaktion auf, die zum Stammkomplex Ni(*Etxn*)$_2$ führte. Es wird vorgeschlagen, für den reaktiven angeregten Zustand einen Charge-Transfer-zu-Lösungsmittel (CTTS)-Typ anzunehmen. Die Energie dieses Zustands hängt vom Redoxpotential des Lösungsmittels ab. Bei Ersatz von $CHCl_3$ als Lösungsmittel durch das stärkere Oxidans CCl_4 wurde die photoaktive Wellenlänge nach Rot verschoben. Eine Blauverschiebung ergab sich hingegen, wenn das schwächere Oxidans CH_2Cl_2 verwendet wurde. Aus Messungen der Quantenausbeuten ergab sich die folgende Ordnung nach abnehmender Photostabilität der untersuchten Komplexe: *bpym* > *phen* > *bpy* > 4,4′-*Me-bpy*.

Introduction

Photoredox reactions of transition metal complexes play an important role in inorganic photochemistry [1, 2]. The majority of photooxidations of a great variety of transition-metal complexes has been observed in halocarbon solvents, where solvent molecules act as electron acceptors [3 – 7]. To the best of our knowledge no reports are known on the photochemistry of xanthate mixed ligand complexes. Therefore, and as extension of our studies on the photochemistry of mixed ligand complexes [8, 9] we report herein the photooxidation of bis(ethylxanthato)nickel(II) containing aromatic nitrogen heterocyclic donors in chloroform.

Experimental

All chemicals used in this work were of analytical grade. Bis(ethylxanthato)nickel(II) [10], bis(ethylxanthato)(2,2′-bipyridine)nickel(II) [11] and bis(ethylxanthato)(1,10-phenanthroline)nickel(II) [11] were prepared according to reported literature procedures.

Infrared spectra were obtained as KBr pellets on a Perkin-Elmer 599 B recording spectrophotometer. Electronic spectra of the compounds as well as the spectral changes during the photolysis were recorded using a Shimadzu UV-200 S spectrophotometer and matched 1 cm quartz cells. The monochromatic radiation of 365 nm or 300 nm was obtained using a Rayonate photochemical chamber reactor model RPR-100 equipped with eight 24 W lamps. For quantum yield determinations the complex concentrations ($\sim 10^{-2} M$) were such as to have essentially complete light absorption. Absorbed light intensities were determined by ferrioxalate actinometry [12]. The photoproduct $\mathrm{Ni}(Etxn)_2$ was identified by its absorption spectrum [13]. The absorption at the maximum of 478 nm was used to determine the concentration of the photoproduct after substracting the absorbance of the starting complex. Owing to the great difference between the absorbance at 478 nm of the starting complexes ($\varepsilon = 170 - 500$) and that of the product $\mathrm{Ni}(Etxn)_2$ ($\varepsilon = 2700$) [13] and to the limitation of the total amount of photolysis to less than 5%, the experimental error of the quantum yield determinations was found to be ±4%. All experiments were carried out at room temperature (25°C). It is to be noted that the results in the presence of air and in deareated solutions (nitrogen atmosphere) are the same, indicating that oxygen has no effect.

Preparation of Bis(ethylxanthato)(4,4′-dimethyl-2,2′-bipyridine)nickel(II) and Bis(ethylxanthato)(2,2′-bipyrimidine)nickel(II) (General Method)

A 50 ml solution of bis(ethylxanthato)nickel(II) (5 mmol) in ether was mixed with 10 ml acetone solution of 4,4′-dimethyl-2,2′-bipyridine or 2,2′-bipyrimidine (5 mmol). The solution mixture was stirred for about 5 h at room temperature whereupon a green precipitate occurred, which was filtered, washed with ether and air dried. Anal. Calcd. (found) for $\mathrm{Ni}(Etxn)_2(4,4'\text{-}Me\text{-}bpy)$: C 44.54 (44.70), H 4.56 (4.62), N 5.77 (5.81), S 26.42 (26.23). Anal. Calcd. (found) for $\mathrm{Ni}(Etxn)_2(bpym)$: C 36.61 (36.70), H 3.51 (3.55), N 12.20 (12.08), S 27.92 (27.42).

Results and Discussion

Spectra

The electronic and IR spectra of $\mathrm{Ni}(Etxn)_2(bpy)$ and $\mathrm{Ni}(Etxn)_2(phen)$ have been previously reported [11]. The electronic spectrum of $\mathrm{Ni}(Etxn)_2(4,4'\text{-}Me\text{-}bpy)$ in $CHCl_3$ solution exhibits a d-d band at 610 nm ($\varepsilon = 65$) assignable to the transition $^3A_{2g} \leftarrow {}^3T_{1g}(F)$ typical of pseudooctahedral environment around Ni(II). The compound shows further two bands at 465 nm ($\varepsilon = 170$) and 315 nm ($\varepsilon = 14400$) corresponding to CT and intraligand transitions, respectively. The spectrum of $\mathrm{Ni}(Etxn)_2(bpym)$ consists of a d-d band at 610 nm ($\varepsilon = 65$), two CT bands at 470 nm ($\varepsilon = 520$) and 410 nm ($\varepsilon = 1060$) and an intraligand band at 315 nm ($\varepsilon = 16000$). The IR spectra of the two new complexes, $\mathrm{Ni}(Etxn)_2(4,4'\text{-}Me\text{-}bpy)$ and

Ni(*Etxn*)$_2$(*bpym*) show the ν C-O and ν C=S of the xanthate moiety at 1 180 – 1 185 and 1 040 – 1 045 cm^{-1}, respectively. The position of these bands is similar to that of related mixed complexes [11] and indicates the bidentate coordination of xanthate.

Photolyses

Upon irradiation with light of wavelength of 365 nm or 300 nm all complexes investigated in the present study are not light sensitive in most solvents, e. g. acetonitrile. On the other hand, these complexes undergo a photochemical reaction in chloroform, as indicated by the increase of the absorption at 478 nm during the photolyses. Owing to the close similarity in spectral changes exhibited by all studied complexes, the behaviour of one representative complex, namely, Ni(*Etxn*)$_2$(4,4'-*Me-bpy*) is depicted in Fig. 1. The photoproduct in all cases was identified to be Ni(*Etxn*)$_2$, which displays an absorption band of 478 nm (ε = 2 700) [13]. The increase of the absorption at this wavelength was used to determine the concentration of Ni(*Etxn*)$_2$ formed upon irradiation as mentioned above. The quantum yields of the photoreaction are given in Table 1.

By analogy with other photooxidations in halocarbon solvents, where solvent molecules act as electron acceptors, the following mechanism could be suggested

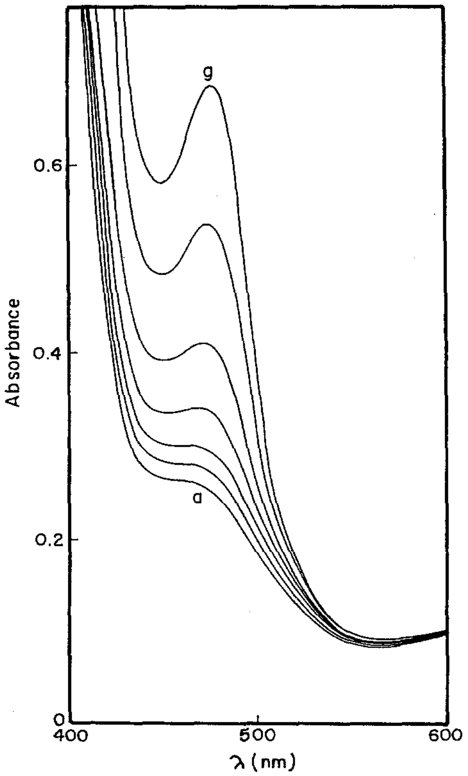

Fig. 1. Spectral changes during the photolysis of $1.5 \cdot 10^{-3} M$ [Ni(*Etxn*)$_2$(4,4'-*Me-bpy*)] in $CHCl_3$ at (**a**) 0 and (**g**) 64 min irradiation time, λ_{irr} = 365 m, 1 cm cell

Table 1. Photooxidation quantum yields of $[Ni(Etxn)_2(N\text{-}N)]$ in $CHCl_3$

N-N	∅	
	$\lambda_{irr} = 365$ m	$\lambda_{irr} = 300$ m
bpym	0.014	0.25
phen	0.14	0.33
bpy	0.23	0.39
4,4'-*Me-bpy*	0.28	0.43

to account for our results:

$$[Ni(Etxn)_2(N\text{-}N)] + CHCl_3 \rightarrow^{h\nu} [Ni(Etxn)_2(N\text{-}N)]^+ + Cl^- + .CHCl_2 \qquad (1)$$

$$[Ni(Etxn)_2(N\text{-}N)]^+ \rightarrow^{\text{dissociation}} [Ni(Etxn)_2] + \text{N-N}^+ \qquad (2)$$

$$N\text{-}N^+ + Cl^- + .CHCl_2 \rightarrow N\text{-}N + CHCl_3 \qquad (3)$$

(*N-N* refers to *bpy*, 4,4'-*Me-bpy*, *phen* or *bpym*)

In the charge-transfer-to-solvent (CTTS) excited state, the starting complex transfers an electron to $CHCl_3$ in a primary photochemical step, Reaction (1). The resulting cation complex is apparently not stable but decomposes to the stable product $Ni(Etxn)_2$ in a secondary reaction, Reaction (2). The formed Cl^-, $.CHCl_2$ and $(N\text{-}N)^+$ may react to regenerate the neutral (*N-N*) ligand and $CHCl_3$, Reaction (3).

The CTTS excited state can be reached by direct absorption into a CTTS band or by internal conversion from the other excited states. Even when a CTTS band was not detected, an efficient production of solvated electrons was observed [14]. In the present study the presence of a CTTS band was not detected, since such a low intensity band may be obscured by the intense intramolecular absorption of the complexes [14]. Irrespective of the presence of CTTS bands, most of light causing photooxidation of $Ni(Etxn)_2(N\text{-}N)$ is certainly absorbed by bands of a different origin. Such conclusion was also adopted in the photooxidation of 1,2-dithiolene complexes of Ni(II), Pd(II) and Pt(II) in chloroform [15].

The energy of the CTTS state should depend on the redox potential of the solvent. The photoactive wavelength region shifted to the red, as expected, with increasing oxidizing power of the solvent. In addition to $CHCl_3$ ($E = -1.67$ V vs. SCE) [16], the complex $Ni(Etxn)_2$(4,4'-*Me-bpy*) was also photolysed in CH_2Cl_2 ($E = -2.33$ V) [16] and in CCl_4 ($E = -0.78$ V) [16]. The quantum yield ($\lambda_{irr} = 300$ nm) of photooxidation increased from $\phi = 0.38$ in CH_2Cl_2 to $\phi = 0.43$ in $CHCl_3$ and $\phi = 0.47$ in CCl_4. While 365 nm light leads to fairly efficient population of the reactive CTTS state in CCl_4, it is apparently not sufficient to reach this state in CH_2Cl_2 as solvent. Such a solvent dependence was also observed for the photooxidation of $[\eta^5\text{-}C_5H_5Fe(CO)]_4$ [3].

Table 1 shows that the quantum yield of photooxidation increases with decreasing wavelength of irradiation. This behaviour seems to be characteristic for the reactivity of CTTS excited states. It has been suggested that the electron ejection is rapid enough to occur from higher vibrational levels of the CTTS excited state [17]. Such a hot excited state mechanism may account for the observed wavelength dependence.

It is interesting to note that the quantum yield of photooxidation of the investigated complexes in chloroform is sensitive to the nature of *N-N*. The quantum yield (Table 1) increases in the order: *bpym* < *phen* < *bpy* < 4,4-*Me-bpy*. Consequently the photostability of the complexes towards conversion to $\mathrm{Ni}(Etxn)_2$ decreases in the order: *bpym* > *phen* > *bpy* > 4,4-*Me-bpy*. Since the key step of the detected photoconversion is the electron transfer from (*N-N*) to $CHCl_3$, Reaction (1), the last order indicates the ease of electron-removal from the (*N-N*) ligand on going from *bpym* to 4,4′-*Me-bpy*. This is consistent with the fact that the removal of an electron becomes more difficult when electron-withdrawing groups (as in *bpym*) are inserted in the ligand or when the amount of electron density delocalization over ligand orbitals (as in *phen*) increases. On the other hand, the presence of electron-donating groups (as in 4,4′-*Me-bpy*) in the ligand facilitates the electron transfer from the ligand.

It is concluded that although the photolysis of the studied complexes leads to no net redox products, however, certainly the primary photochemical step, Reaction (1), is a redox process. This can be supported by the following considerations: (i) the photoreaction occurs only in halocarbon solvents, which are known as electron acceptors [3 – 7]; (ii) the quantum yield of the photoreaction depends on the redox potential of the solvent; (iii) dependence of the process on the nature of the nitrogen donor ligands, which exhibit different tendencies towards the removal of electrons.

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