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Photosubstitution of dichloro(2,2′-diamino-1,1′-binaphthyl)-platinum(II)

Horst Kunkely, Arnd Vogler *

Institut für Anorganische Chemie, Universität Regensburg, D-93040 Regensburg, Germany

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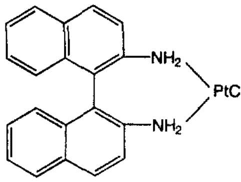
Abstract

The absorption spectrum of Pt(DABN)Cl_2 (DABN = 2,2′-diamino-1,1′-binaphthyl) shows a ligand field (LF) band at λ_{max} = 385 nm and intraligand (IL) bands of DABN at shorter wavelengths (λ_{max} = 364, 330, 316, 288, 266, 241, 224 and 212 nm). The photolysis of Pt(DABN)Cl_2 in CH_3CN leads to the release of the DABN ligand. The quantum yield of this photosubstitution is $\phi \sim 0.036$ and independent of the irradiating wavelength. It is suggested that this photoreaction is induced by LF or IL excitation.

Keywords: Diaminobinaphthyl; Platinum complexes; Substitution

1. Introduction

The complex *cis*-Pt(NH_3)$_2$$Cl_2$ ('*cis*-platin') and some of its derivatives have found wide applications as antitumour drugs [1–4]. New drug generations are developed in order to decrease the toxicity of *cis*-platin and to avoid resistance. One of the new concepts involves the photochemical activation of suitable metal complexes ('Photo *cis*-Platin Reagents') [5,6] which takes place site-specific in the tumour cells. A further step in this direction is the combination and probably synergism of the action of *cis*-platin [1–4] and photodynamic therapy (PDT) [7–9]. In this case, the photolysis of an appropriate platinum complex should generate a cytostatic Pt compound and a sensitizer for the production of singlet oxygen that attacks oxidatively tumour cells. The 'sitting-atop' porphyrin complex Pt^{II}(hematoporphyrin-H_2)Cl_2 shows some of the required properties [10]. The photolysis leads to the release of the porphyrin, which subsequently sensitizes the generation of singlet oxygen. A related approach was explored in the present study. The ammine ligands of *cis*-Pt(NH_3)$_2$$Cl_2$ were replaced by the bidentate ligand 2,2′-diamino-1,1′-binaphthyl (DABN). The resulting complex



has several interesting features with regard to potential applications. The planar naphthyl groups may bind to DNA by intercalation [11]. Since the DABN ligand is chiral, the binding could show enantiomeric selectivity. Moreover, the DABN ligand is characterized by coordinating N–H groups which are related to the biological activity [4]. While these properties warrant a separate investigation, we were interested in the photochemical behavior of this complex. In analogy to other Pt(II) complexes [12,13], a photosubstitution may take place. If the DABN ligand is released, it should show its own excited state properties including fluorescence, which can be used to monitor the photolysis. Since free DABN is an aromatic amine, its fluorescence depends on the medium [14]. Accordingly, the luminescence of the photolyzed complex might serve as a probe of its environment.

2. Experimental

2.1. Materials

K_2PtCl_4 and DABN were commercially available by Aldrich. All solvents were spectrograde.

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* Corresponding author.

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2.2. Synthesis of $Pt(DABN)Cl_2$

To a hot (~70°C) solution of 0.852 g (3×10^{-3} mol) DABN in 120 ml 0.2 M HCl were added portions of a solution of 1.24 g (3×10^{-3} mol) K_2PtCl_4 in 30 ml water. The combined solutions turned immediately turbid and brownish owing to the formation of $(DABN\text{-}H_2)PtCl_4$. The reaction mixture was stirred for 1 h at 60°C. During this time, $(DABN\text{-}H_2)PtCl_4$ was converted to the desired product, which precipitated as a yellow crystalline solid. The mixture was cooled to room temperature. The precipitate was collected by filtration, washed twice with 50 ml 0.1 M HCl, and then with water to remove the HCl. Finally, the yellow solid was washed with ether/methanol (9:1), ether, and dried under reduced pressure. Yield: 1.46 g (88%). Anal. Calc. for $C_{20}H_{16}N_2Cl_2Pt$: C, 43.65; H, 2.93; N,5.09; Cl, 12.88. Found: C, 43.58; H, 3.05; N, 5.03; Cl, 12.79%.

2.3. Photolyses

The light source was an Osram HBO 100 W/2 or a Hanovia Xe/Hg 977 B-1 (1 kW) lamp. Monochromatic light was obtained using a Schoeffel GM 250/1 high-intensity monochromator (band width 20 nm). The photolyses were carried out in solutions of CH_3CN in 1 cm spectrophotometer cells at room temperature. Solutions were air-saturated since deaeration did not affect the results. Progress of the photolyses was monitored by UV–visible spectrophotometry. The photoproducts were identified by their absorption spectra. For quantum yield determinations, the complex concentrations were such as to have essentially complete light absorption. The total amount of photolysis was limited to less than 5% to avoid light absorption by the photoproduct. Absorbed light intensities were determined by a Polytec pyroelectric radiometer, which was calibrated by actinometry and equipped with a RkP-345 detector.

2.4. Instrumentation

Absorption spectra were measured with a Hewlett Packard 8452A diode array or an Uvikon 860 absorption spectrometer. Emission and excitation spectra were obtained on a Hitachi 850 spectrofluorometer equipped with a Hamamatsu 928 photomultiplier for measurements up to 900 nm. The luminescence spectra were corrected for monochromator and photomultiplier efficiency variations.

3. Results

The desired complex was prepared according to the reaction scheme:

$$(DABN{-}H_2)Cl_2+K_2[PtCl_4]\rightarrow(DABN{-}H_2)[PtCl_4]+2KCl$$

$$(DABN{-}H_2)[PtCl_4]\rightarrow Pt(DABN)Cl_2+2HCl$$

The electronic spectrum of $Pt(DABN)Cl_2$ in CH_3CN (Fig. 1) shows absorptions at $\lambda_{max}=385$ (sh, $\varepsilon=190$ dm^3 M^{-1} cm^{-1}), 364 (sh, 490), 328 (3500), 316 (4200), 288 (9000), 266 (sh, 13 000), 241 (49 000), 224 (60 500) and 212 (sh, 48 000) nm. The complex is not emissive although a weak luminescence is observed which is, however, attributed to traces of free DABN. Free DABN in CH_3CN absorbs at $\lambda_{max}=360$ (sh, 4000), 347 (4800), 294 (7300), 284 (9500), 274 (sh, 8100), 242 (58 800) and 216 (27 700) nm and displays an intense fluorescence at $\lambda_{max}=402$ nm (Fig. 2) which is independent of the exciting wavelength.

Solutions of $Pt(DABN)Cl_2$ are light-sensitive. The photolysis is accompanied by spectral changes (Fig. 3), which are consistent with the release of DABN. The reaction is rather clean as indicated by the presence of sharp isosbestic points at $\lambda=321$, 291, 270, 251, 232 and 202 nm. Moreover, the formation of free DABN is associated with the appearance of its intense fluorescence at $\lambda_{max}=402$ nm (Fig. 3). The progress of the photolysis was monitored by measuring the change of optical density at $\lambda=347$ nm. The photosubstitution is rather efficient and nearly independent of the irradi-

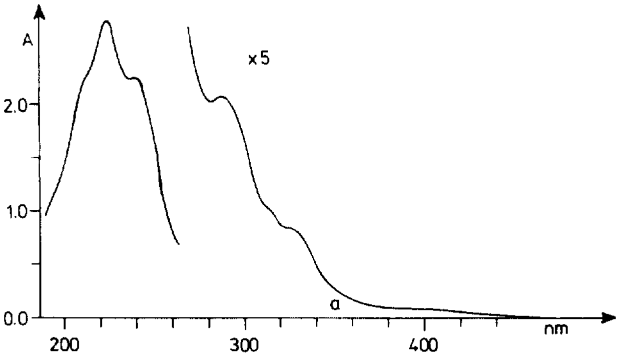

Fig. 1. Electronic absorption spectrum of 4.54×10^{-5} M $Pt(DABN)Cl_2$ at room temperature in CH_3CN, 1-cm cell.

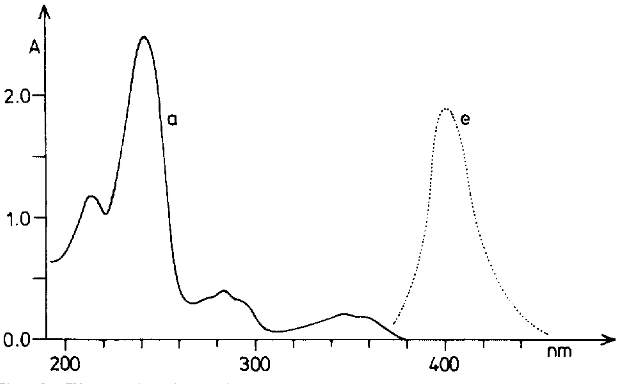

Fig. 2. Electronic absorption (———) and emission (...) spectra of 4.23×10^{-5} M DABN at room temperature in CH_3CN, 1-cm cell. Emission: $\lambda_{exc}=350$ nm, intensity in arbitrary units.

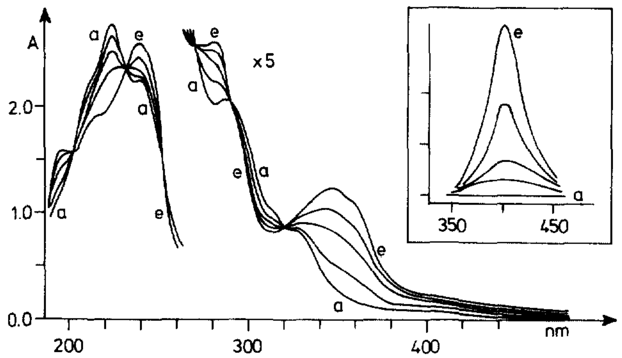

Fig. 3. Spectral changes during the photolysis ($\lambda_{irr}=313$ nm) of 4.54×10^{-5} M $Pt(DABN)Cl_2$ in CH_3CN at room temperature. Absorption and (inset) emission ($\lambda_{exc}=350$ nm, intensity in arbitrary units) after 0 (a), 0.3, 1.5, 3 and 7 (e) min irradiation time.

ating wavelength. The quantum yields are $\phi=0.036$ at $\lambda_{irr}=405$ and $\phi=0.035$ at $\lambda_{irr}=313$ nm.

4. Discussion

The electronic spectrum of $Pt(DABN)Cl_2$ (Fig. 1) consists essentially of the intraligand (IL) absorptions of the coordinated DABN. These bands are slightly shifted compared to the free ligand (Fig. 2). For example, the longest-wavelength absorptions of DABN at $\lambda_{max}=347$ and 360 nm (sh) appear at $\lambda_{max}=316$ (sh) and 327 nm (sh) in the complex. A similar shift has been observed for such IL bands of $Pt(1\text{-naphthylamine})_2Cl_2$ [15]. The weak longest-wavelength absorption of $Pt(DABN)Cl_2$ at $\lambda_{max}=385$ nm (sh) is assigned to a ligand field (LF) transition in analogy to related platinum complexes such as $Pt(en)Cl_2$ ($\lambda_{max}=360$ nm) [16] and $Pt(1\text{-naphthylamine})_2Cl_2$ ($\lambda_{max}=380$ nm) [15].

The irradiation of $Pt(DABN)Cl_2$ leads to a substitution according to the equation:

$$Pt(DABN)Cl_2+2CH_3CN\xrightarrow{h\nu}Pt(CH_3CN)_2Cl_2+DABN$$

Since the efficiency of this photosubstitution hardly depends on the wavelength of irradiation, it is assumed that the lowest-energy excited state, which is of the LF type, induces the photolysis. However, similar complexes such as *cis*-$Pt(NH_3)_2Cl_2$ [17] and $Pt(en)Cl_2$ [K. Oldenburg, A. Vogler, unpublished results] undergo a photosubstitution of chloride instead of amine. The different behavior of $Pt(DABN)Cl_2$ might be explained by the coordinating properties of DABN. This bidentate ligand forms a 7-membered ring which could be exposed to steric strain. In the LF excited state, this stress may be relieved by expulsion of the DABN ligand. A related interpretation has been applied to the photosubstitution of $Pt(\text{hematoporphyrin-}H_2)Cl_2$ [10]. As an alternative, the photoactivity of $Pt(DABN)Cl_2$ can be attributed to a reactive IL or intraligand charge transfer (ILCT) state, respectively. It is well known that the excitation of aromatic amines is associated with a shift of electron density from the nitrogen lone pair to the π^* orbitals of the aromatic moiety [14]. If this process takes place in the complex, it can be viewed as an IL or ILCT excitation that leads to the loss of the coordinating ability of the DABN ligand. Accordingly, the photosubstitution of $Pt(DABN)Cl_2$ is also compatible with a reactive IL or ILCT excited state. An analogous mechanism involving reactive IL [15] or ILCT states [18,19] seems to apply to the photosubstitution of $Pt(1\text{-naphthylamine})_2Cl_2$ [15].

Acknowledgements

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