Synthesis and Electronic Spectra of (N-1-Naphthyl-ethylenediamine)-dichloroplatinum(II). Fluorescence of the Appended Naphthyl Substituent

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Z. Naturforsch. **57b,** 709–711 (2002);
received April 4, 2002

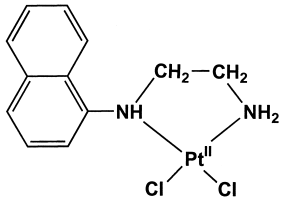
Electronic Spectra, Luminescence, Platinum Complexes

$Pt(naph\text{-}en)Cl_2$ with naph-en = N-(1-naphthyl)-ethylenediamine was synthesized and spectroscopically characterized. The complex shows a fluorescence at λ_{max} = 405 nm, which originates from the appended naphthyl substituent present as an electronically isolated chromophore.

1. Introduction

The excited state properties of organic chromophores which are covalently attached to metal complexes have attracted much recent interest [1–4]. Frequently, the metal complex quenches the luminescence of the organic chromophore by electronic energy transfer or excited state electron transfer. Such metal-sensitive fluorescent probes can be used for a variety of signaling processes, including metal ion sensing. However, this fluorescence quenching is a rather general process and does not discriminate between different types of quenchers. Accordingly, more specific interactions between organic chromophores and metal complexes are desired. To that end, the fluorescence of the organic chromophore should not be quenched but shifted by coordination. Unfortunately, this is difficult to realize because it requires a rather strong electronic interaction, which may even facilitate quenching. However, under favorable conditions such a quenching could be prevented. We explored this possibility and selected the complex $Pt^{II}(naph\text{-}en)Cl_2$ (Scheme 1) with naph-en = N-(1-naphthyl)-ethylenediamine for the present study.

This choice was guided by several considerations. The free naph-en ligand is fluorescent in analogy to the parent naphthylamine itself [5]. Upon coordination the electronic structure and the electronic spectra of naph-en are expected to change. Accordingly, complex formation should be associated with a diagnostic shift of the fluorescence. However, at the same time the electronic interaction between the naphthyl fluorophore and the complex moiety could lead to fluorescence quenching by energy or electron transfer. In this case, no useful signal would be generated. Fortunately, in the coordinated state the naphthyl group is electronically separated from the complex fragment by the ammonium bridge naphthylNRHPt. This assumption is based on the analogy to insulating $-CR_2-$ and $-BR_2-$ [6] bridges, which are well known to restrict or exclude the electronic communication between covalently attached chromophores. It follows that the complex $Pt(naph\text{-}en)Cl_2$ is a promising candidate to display a diagnostic fluorescence of the appended naphthyl substituent.



Scheme 1

The selection of $PtCl_2$ as complex fragment for the naph-en ligand is a further intriguing feature of the present study. Complexes of the type $Pt(en)Cl_2$ are derivatives of *cis*-$Pt(NH_3)_2Cl_2$ ("*cis*-platin"), which is the parent compound of a family of important antitumor drugs [7–10]. A fluorescence detection of such compounds could be applied to optical sensing. Finally, the current investigation should be facilitated by a previous report on the electronic spectra of various *cis*-$Pt(NH_2R)_2Cl_2$ complexes [11].

2. Experimental Section

2.1. Materials

All solvents used for spectroscopic measurements were of spectrograde quality. K_2PtCl_4 and N-(1-naphthyl)-ethylenediamine dihydrochloride (naph-en·2HCl) were commercially available from Aldrich and used without further purification.

$Pt^{II}(naph\text{-}en)Cl_2$ was obtained by the following procedure: To a warm (40 °C) solution of K_2PtCl_4 (2.9 g, 7 mmol) in 25 ml of H_2O was added a solu-

tion of naph-en·2HCl (1.82 g, 7 mmol) in 30 ml of water (30 °C) in portions under stirring. The combined solutions were allowed to stand at 0 °C for 20 min. Large reddish cystals of analytically pure [naph-enH_2][$PtCl_4$] slowly precipitated. This salt was collected by filtration, washed with a small amount of H_2O and ether, and dried under reduced pressure, yielding 2.8 g of product (75%).

A suspension of [naph-enH_2][$PtCl_4$] (1.31 g, 2.5 mmol) in 50 ml of water was heated giving a red solution. This solution was refluxed. The colour of the reaction mixture slowly turned yellow and a yellow powder started to deposit after ~ 15 min. After standing for 1 h at r.t. the precipitated yellow solid was collected by filtration, washed with water and then with EtOH/ether (1:10), and dried under vacuum, yielding 0.53 g of product (47%), which was purified by repeated recrystallization from CH_2Cl_2.

Analysis for $C_{12}H_{14}Cl_2N_2Pt$ (452.24): calcd. C 31.87, H 3.12, Cl 15.68, N, 6.19; found: C 31.92, H 3.13, Cl 15.62, N, 6.17.

2.2. Instrumentation

Absorption spectra were measured with a Hewlett Packard 8452A diode array spectrophotometer. Emission and excitation spectra were recorded 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 electronic spectrum of naph-en in EtOH (Fig. 1) displays absorptions at λ_{max} = 334 (ε = 6700 M^1 cm^1) and 250 (15600) nm. The spectrum of the salt naph-en·2HCl in EtOH shows bands at 326 (6800), 312 (sh, 6000) and 246 (17300) nm. The complex Pt^{II}(naph-en)Cl_2 in CH_2Cl_2 (Fig. 2) absorbs at λ_{max} = 386 (sh, 250), 330 (sh, 2300), 297 (sh, 11000), 287 (13500) and 276 (sh, 11500) nm.

Naph-en is strongly fluorescent under ambient conditions (Fig. 1) with λ_{max} = 423 nm. The excitation spectrum of naph-en matches the absorption spectrum. The salt naph-en·2HCl is also fluorescent with λ_{max} = 405 nm. The complex Pt^{II}(naph-en)Cl_2 in CH_2Cl_2 shows a luminescence (Fig. 2) at λ_{max} = 405 nm. The excitation spectrum of Pt^{II}(naph-en)Cl_2 matches the absorption spectrum only at λ_{exc} < 340 nm. Light absorption by the longer-wavelength band at λ_{max} = 386 nm does not induce any luminescence.

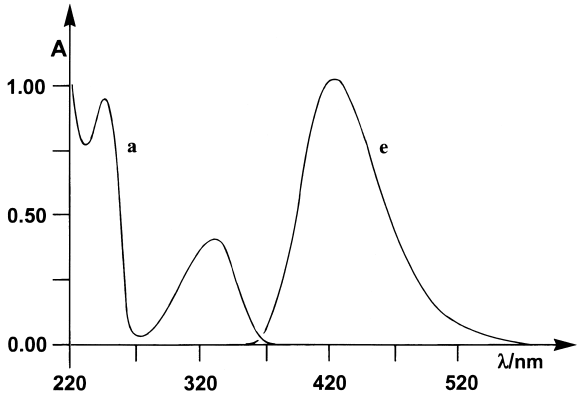


Fig. 1. Electronic absorption (a) and emission (e) spectrum of 6.09×10^{-5} M naph-en in EtOH at room temperature, 1-cm cell. Emission: λ_{exc} = 340 nm, intensity in arbitrary units.

4. Discussion

The electronic spectra of naphthylamine are determined by the interaction of the nitrogen lone pair and the π-electron system of the naphthyl substituent [5]. Upon protonation of the amine the longest-wavelength absorption and the fluorescence are shifted to shorter wavelength. The same observation and conclusion apply to naph-en: The longest-wavelength absorption (λ_{max} = 334 nm, Fig. 1) and the fluorescence (λ_{max} = 423 nm, Fig. 1) undergo a blue shift to λ_{max} = 326 and 405 nm, respectively, upon protonation.

The coordination of $PtCl_2$ to naph-en and the protonation are expected to have similar effects on the absorption spectrum of naph-en. Indeed, the complexation of naph-en causes a blue shift of the 334 nm band (Fig. 1) to 330 nm (Fig. 2). Moreover, Pt(naph-en)Cl_2 shows an additional low-energy absorption at λ_{max} = 386 nm which is assigned to a ligand-field (LF) transition in analogy to various other *cis*-Pt(amine)$_2Cl_2$ complexes [11] including Pt(en)Cl_2 [12] which also display LF bands around 380 nm.

The salt naph-en·2HCl and the complex Pt^{II}(naph-en)Cl_2 show a luminescence at the same wavelength (λ_{max} = 405 nm). In both cases it is certainly the fluorescence of the naphthyl chromophore. However, the appearance of the naphthyl fluorescence from Pt(naph-en)Cl_2 is remarkable since it does not originate from the lowest-energy excited state of the complex, which is of the LF type and emits around 600 nm, but only at low temperatures [11]. As shown by the excitation spectrum the naphthyl substituent is a separate

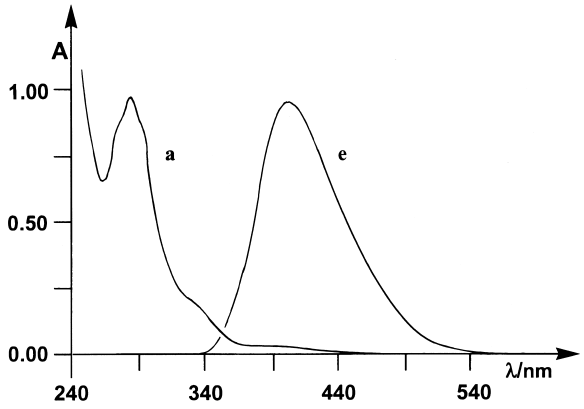


Fig. 2. Electronic absorption (a) and emission (e) spectrum of 7.22×10^{-5} M Pt^{II}(naph-en)Cl_2 in CH_2Cl_2 at room temperature, 1-cm cell. Emission: $\lambda_{exc} = 330$ nm, intensity in arbitrary units.

chromophore and does not strongly interact with the complex moiety because the ammonium bridge which connects the naphthyl group and the platinum atom is electronically saturated. An analogous situation applies to the complexes *cis*-Pt(naphthylamine)$_2Cl_2$ [13] and Pt(2,2′-diamino-1,1′-binaphthyl)Cl_2 [14]. Unfortunately, the naphthyl fluorescence of the coordinated ligands has not been detected in these cases. It seems to be obscured by the fluorescence of the free ligand, which is present as an impurity [14].

In summary, the naph-en ligand offers two favorable properties for the fluorescence detection of a metal complex. The coordination leads to a blue shift of the fluorescence and is associated with an electronic insulation of the naphthyl fluorophore, which prevents fluorescence quenching by the complex moiety. The complex Pt(naph-en)Cl_2, which belongs to a family of important antitumor drugs, can thus be traced by fluorescence analysis. In this context it should also be mentioned that luminescence spectroscopy has been widely applied for the study of interactions between metal complexes and DNA [15–17]. Pt(naph-en)Cl_2 may bind to DNA by intercalation, owing to the presence of the planar naphthyl substituent.

Acknowledgment

Support of this research by the Fonds der Chemischen Industrie is gratefully acknowledged.

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Satz und Druck: AZ Druck und Datentechnik GmbH, Kempten