Luminescence Detection and Photodimerization of 1,3-Dimethyluracil Coordinated to Copper(I)

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1,3-Dimethyluracil (DMU) forms a complex with copper(I) iodide which shows a green luminescence at $\lambda_{\text{max}} = 505$ nm. With PF$_6^-$ counter ions a photoactive Cu(I)DMU complex is generated which shows a long-wavelength absorption at $\lambda_{\text{max}} = 335$ nm. Light absorption by this band leads to a dimerization of DMU to its cyclobutane dimer.

1. Introduction

Transition metals play an important role in DNA chemistry. Metal complexes are utilized as chemotherapeutic agents, spectroscopic probes and artificial nucleases. In particular, photoactivated processes have attracted much attention [1 - 4]. In this context it is of considerable interest to investigate the photoreactivity of DNA bases as ligands in transition metal complexes.

It is well known that thymine or uracil undergo photodimerizations by a 2+2 cycloaddition:

\[
\begin{align*}
\text{H} & \quad \text{N} \\
\text{O} & \quad \text{O} \\
\text{R} & \quad \text{R} \\
\text{H} & \quad \text{N} \\
\text{O} & \quad \text{O} \\ 
& \quad \text{H} \\
\end{align*}
\]

The resulting DNA damage which is associated with the cyclobutane formation causes mutations and skin cancer [5, 6]. In model systems it has been shown that the cycloaddition of dimethylthymine [7] and dimethyluracil [8] can be also photosensitized by suitable ketones. We suspected that this photodimerization could be induced by transition metals, too. Our assumption is based on related observations on the photochemistry of complexes with cyclic olefins as ligands [9, 10]. An olefin dimerization to cyclobutanes takes place upon irradiation of various organometallics such as Cr$^0$(norbornadiene)(CO)$_4$ [11], Fe$^0$(cyclooctatetraene)(CO)$_3$ [12, 13] and, in particular, [Cu$^+$(olefin)$_6$]$^+$ with olefin = norbornene, cyclopentene, cyclohexene, and cycloheptene [9, 10, 14 - 17]. The photoactive absorption of the Cu(I) olefin complexes occurs at lower energies than that of the free olefins. If such a metal-assisted olefin photodimerization would also apply to DNA bases their light sensitivity might be extended to longer wavelength. Under ambient conditions this effect would enhance the DNA damage. Although the relevance of such metal complexes in biological environments is currently unknown this type of photoreaction should be quite interesting in its own right. We explored this possibility and selected the system Cu(I)/1,3-dimethyluracil for an initial study.

2. Experimental

2.1. Materials

1,3-Dimethyluracil and [Cu(acetonitrile)$_4$]PF$_6$ were commercially available (Aldrich) and used as received. All solvents were spectrograde, carefully dried and saturated with argon.

2.2. 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 spectrofluorimeter equipped with a Hamamatsu 928 photomultiplier for measurements up to 900 nm. The luminescence spectra were corrected for monochromator and photomultiplier efficiency variations. Absolute emission quantum yields were determined.
Fig 1. Luminescence spectrum of a toluene solution containing Cul and 1,3-dimethyluracil at r.t., 1-cm cell, $\lambda_{\text{exc}} = 313 \text{ nm}$; intensity in arbitrary units.

by comparison of the integrated emission intensity with that of Rhodamine B under identical conditions such as exciting wavelength, optical density, and apparatus parameters. The light source used 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 23 nm). The photolyses were carried out in solutions of CH$_3$CN in spectrophotometer cells at room temperature. Progress of the photolyses was monitored by UV-visible spectrophotometry.

3. Results

Cul reacts with 1,3-dimethyluracil (DMU) in toluene to form a soluble complex which shows a rather intense green luminescence (Fig. 1) at $\lambda_{\text{max}} = 505 \text{ nm}$ with $\phi = 0.01$ at $\lambda_{\text{exc}} = 313 \text{ nm}$. This luminescence is also observed when filter paper is first impregnated by Cul and then treated with a solution of DMU in toluene.

Further studies of the system Cu(I)/DMU were carried out with [Cu(AN)$_4$]PF$_6$ (AN = acetonitrile) as starting complex in order to avoid any interference by iodide. The electronic spectrum of [Cu$^1$(AN)$_4$]$^+$ in acetonitrile shows absorptions at $\lambda_{\text{max}} = 232$ (sh, $\varepsilon = 6400 \text{ dm}^3 \text{ M}^{-1} \text{ cm}^{-1}$) and 210 (15700) nm. 1,3-Dimethyluracil (DMU) displays two bands at $\lambda_{\text{max}} = 265$ (sh; 8400) and 207 (7750) nm. DMU and [Cu$^1$(AN)$_4$]$^+$ do not absorb at $\lambda > 300 \text{ nm}$. When a large excess of DMU is added to a solution of [Cu$^1$(AN)$_4$]$^+$ a new absorption appears at $\lambda_{\text{max}} = 335 \text{ nm}$ with an apparent extinction coefficient of $\varepsilon = 400$ (Fig. 2). At shorter wavelength the absorption spectrum is dominated by that of free DMU. This solution does not show a visible luminescence. Upon irradiation of the mixture with $\lambda = 333 \text{ nm}$ the absorption of DMU at $\lambda_{\text{max}} = 265 \text{ nm}$ decreases (Fig. 2) indicating its disappearance. Owing to the low optical density at the irradiating wavelength ($A \sim 0.007$) the photoreaction is rather slow as shown by the large time intervals of irradiation. It was assumed that the photochemical loss of DMU is associated with its dimerization to the cyclobutane derivative which absorbs only at very short wavelength ($\lambda_{\text{max}} = 224 \text{ nm}$, shoulder) [18]. Unfortunately, the disappearance of the DMU absorption at $\lambda_{\text{max}} = 265 \text{ nm}$ is a rather unspecific feature and may be caused by any type of photodecomposition. However, the DMU dimer is well known to undergo a photomonomerization to DMU upon short-wavelength irradiation ($\lambda < 270 \text{ nm}$) [18]. Indeed, irradiation of the photolyzed solution with $\lambda = 254 \text{ nm}$ leads to the recovery of the DMU absorption at $\lambda_{\text{max}} = 265 \text{ nm}$. This observation provides sufficient evidence for the initial photodimerization of DMU sensitized by Cu(I).

4. Discussion

Cu(I) halides are well known to form luminescent complexes with a variety of aliphatic and aromatic nitrogen bases [19 - 21]. Complex formation between Cul and DMU is confirmed by the detection of a green fluorescence which appears under ambient conditions. Since the luminescence colour
of copper(I) halide amine complexes depends on the amine it can be utilized for its identification. The filter paper test described above has been suggested to serve as a general method for the identification of nitrogen bases by luminescence spectroscopy [19, 22, 23]. According to our observation it seems to be also a useful probe for DNA bases.

The long-wavelength absorption of the Cu(I) DMU complex at $\lambda_{\text{max}} = 335 \text{ nm}$ which is formed by the reaction of DMU with $[\text{Cu(AN)}_4]^+$ in the absence of iodide is attributed to a CT transition in analogy to various copper(I) complexes with cyclic olefins [24 - 26]. Since Cu(I) as well as olefins may act as donor and acceptor, respectively, the optical CT transition may be of the LMCT (ligand-to-metal charge transfer) or MLCT (metal-to-ligand charge transfer) type [9, 10, 24 - 26]. Accordingly, CT excitation leads to the generation of a ligand radical or anion. The intermediate formation of such radicals may facilitate an intramolecular or intermolecular dimerization of cyclic olefins [10]. However, DMU could coordinate as an amine or via the olefinic double bond. Nevertheless, the photodimerization of olefins and DMU coordinated to Cu(I) suggests that a common excited state is operative in both cases.

In summary, Cu(I) forms luminescent or photoactive complexes with 1,3-dimethyl-uracil. The photodimerization of the free uracil which requires light with $\lambda_{\text{irr}} < 270 \text{ nm}$ is extended to wavelength above 330 nm by coordination to Cu(I).

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