Charge Transfer Interaction in (Riboflavin)tricarbonylrhenium(I) Chloride

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[Re(riboflavin)(CO)₃Cl] shows intraligand ($\lambda_{\text{max}} = 476$ and 518 nm) and Re(I) to $\pi^*$ (riboflavin) metal-to-ligand charge transfer, MLCT, ($\lambda_{\text{max}} = 556$ nm, in CH₃CN) absorptions in close proximity. The MLCT band undergoes a moderate solvent-dependent shift (negative solvatochromism) indicating a partial charge separation in the excited state. The complex is not photoluminescent.

1. Introduction

Riboflavin (vitamin B₂) is one of the most important organic redox coenzymes [1 - 4]. It participates in biological electron transfer with redox-active metalloenzymes. Accordingly, the nature of flavin transition metal complexes is of considerable interest [5 - 16]. If electron transfer between metal and riboflavin takes place in the coordinated state (inner sphere electron transfer) this process can be related to optical charge transfer transitions. Since riboflavin is an oxidant, its complexes with reducing metals should display metal-to-ligand charge transfer (MLCT) absorptions in their electronic spectra. Indeed, such MLCT transitions have been assigned to long-wavelength absorptions of various riboflavin complexes with donor metals [11, 12, 15, 16] including [Re(I)(riboflavin)(CO)₃Cl] [16]. Unfortunately, the original preparation of this compound yielded only a mixture of the product with the starting material [16]. Moreover, only very little is known on the electronic spectra of this complex. In order to gain more insight in the CT interaction we decided to prepare and examine [Re(I)(riboflavin)(CO)₃Cl] in a pure state.

Complexes of the type [ReL₂(CO)₅Cl], with L₂ = bidentate acceptor ligand such as 1,2-diimines (e.g. 2,2'-bipyridyl), display a negative solvatochromism [17,18] which can be used to evaluate the extent of CT interaction. In addition, these complexes frequently show a photoluminescence which helps to reveal the nature of the lowest excited state [17-19]. In summary, the optical spectra of [Re(I)(riboflavin)(CO)₃Cl] should be quite informative and contribute to a better understanding of the electron donor / acceptor interactions in riboflavin transition metal complexes.

2. Experimental

2.1. Materials

Riboflavin and [Re(CO)₅Cl] were commercially available from Aldrich. All solvents were spectrograde.

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.

2.3. Synthesis of [Re(riboflavin)(CO)₃Cl]

A suspension of [Re(CO)₅Cl] (376 mg, 1 mmol) and riboflavin (376 mg, 1 mmol) in argon-saturated acetic acid (25 ml) was stirred under reflux for 10 min. The orange reaction mixture turned dark red. It was cooled to room temperature and filtered. To the filtrate was added a mixture of ether (60 ml) and n-pentane (140 ml) with...
stirring. The dark violet precipitate was isolated by filtration, washed with a small amount of ether, and dried under reduced pressure. The crude product was recrystallized twice from acetone/ether.

Analysis for C_{20}H_{30}N_{10}O_{2}Re  
Calcd C 35.22 H 2.96 N 8.21 %  
Found C 35.19 H 3.11 N 8.13 %.

3. Results and Discussion

The riboflavin complex is obtained as an air-stable dark-violet solid which is soluble in various organic solvents and even in water owing to the carbohydrate substituent.

The absorption spectrum of riboflavin in various solvents such as EtOH shows bands at $\lambda_{\text{max}} = 473$ nm ($\varepsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ sh, 10 100), 444 (13 000), 360 (10 800), 270 (33 000), and 224 (29 700). The complex [Re(riboflavin)(CO)$_3$Cl] in CH$_3$CN shows absorptions (Fig. 1) at $\lambda_{\text{max}} = 556$ nm (sh, 6 400), 518 (8 200), 476 (sh, 7 000), 406 (7 800), 388 (sh, 6 800), 276 (25 200), 226 (29 000). The longest-wavelength band (at 556 nm in Fig. 1) undergoes a red shift with decreasing solvent polarity. This negative solvatochromism [17, 18] can be evaluated by several solvent polarity parameters. We apply here (Fig. 2) Lees' $E^*$ scale which has been developed for MLCT transitions [20].

While riboflavin emits a green fluorescence ($\lambda_{\text{max}} = 565$ nm, in water) [Re(riboflavin)(CO)$_3$Cl] does not show any luminescence up to 900 nm at r.t. in solution, in low-temperature glasses, or in the solid state.
Finally, it should be emphasized that an increased delocalization between electron donor and acceptor as it occurs in the rhenium-riboflavin moiety facilitates electron transfer. Ligand-bridged binuclear complexes are well known examples of this notion [24].

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