

Excited State Behavior of Uranyl Complexes with Salophen and Oxine as Chromophoric Ligands

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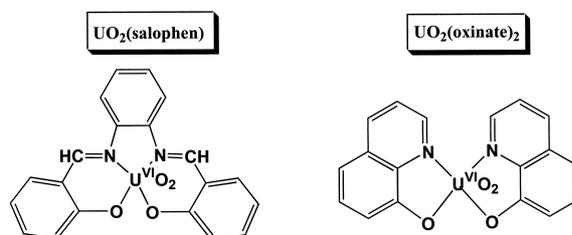
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Uranyl Complexes, Salen Complexes, Oxinate Complexes

The electronic spectra and the photochemistry of the uranyl complexes $\text{UO}_2(\text{salophen})$ and $\text{UO}_2(\text{oxinate})_2$ with $\text{H}_2\text{salophen} = \text{N,N}'\text{-bis(salicylidene)-}o\text{-phenylenediamine}$ and oxine = 8-hydroxyquinoline were studied. The excited state behavior of both complexes is determined by a low-energy $\text{salophen}^{2-} / \text{oxinate}^-$ to U(VI) ligand-to-metal charge transfer (LMCT) state which is not luminescent but can be reactive. In the case of $\text{UO}_2(\text{oxinate})_2$ the photolysis leads to the formation of free oxine with $\phi = 3.6 \times 10^{-3}$ at $\lambda_{\text{irr}} = 366 \text{ nm}$ in CHCl_3 . It is suggested that various redox processes with the participation of the solvent are involved in product formation. $\text{UO}_2(\text{salophen})$ is not light sensitive since the primary electron transfer is followed by recombination which is facilitated by the rigid $\text{UO}_2(\text{salophen})$ structure.

1. Introduction

The electronic spectra and photochemistry of the uranyl ion UO_2^{2+} have been extensively studied [1 - 8]. The linear $\text{O}=\text{U}=\text{O}^{2+}$ ion contains U(VI) as an oxidizing metal center with a $5f^0$ electron configuration. The uranyl ion is characterized by a low-energy oxide to uranium(VI) ligand-to-metal charge transfer (LMCT) state ($\sim 21000 \text{ cm}^{-1}$) which is emissive under ambient conditions. A variety of simple anions including halides and carboxylates can be coordinated as additional ligands in the plane perpendicular to the $\text{O}=\text{U}=\text{O}$ axis. The presence of such ligands is frequently associated with luminescence quenching and the occurrence of new LMCT states which may be reactive. When such simple anions are replaced by chromophoric ligands which have their absorption spectra extended to the visible region new excited states of the intraligand (IL) type are introduced. Since IL states can also be luminescent or reactive a variety of deactivation channels are available for electronically excited uranyl complexes with such chromophoric ligands. We explored this possibility and selected the complexes $\text{UO}_2(\text{salophen})$ [9, 10] and $\text{UO}_2(\text{oxinate})_2$ [11] with $\text{H}_2\text{salophen} = \text{N,N}'\text{-bis(salicylidene)-}o\text{-phenylenediamine}$ and oxine = 8-hydroxyquinoline or 8-quinolinol for the present study. The anionic ligands salophen^{2-} and oxinate^- pos-



sess low-energy excited states which are emissive in the coordinated state. These tetradentate and bidentate ligands form rather stable uranyl chelates. Since both complexes, $\text{UO}_2(\text{salophen})$ and $\text{UO}_2(\text{oxinate})_2$ are neutral their spectroscopic and photochemical properties can also be examined in less polar and non-coordinating solvents.

2. Results

The electronic spectrum of $\text{UO}_2(\text{salophen})$ in CHCl_3 (Fig. 1) shows absorptions at $\lambda_{\text{max}} = 417$ ($\epsilon = 8600 \text{ dm}^3 \text{ M}^{-1} \text{ cm}^{-1}$), 380 (sh, 10800), 346 (15400) 302 (sh, 18000), and 286 nm (sh, 18600). The absorption spectrum of $\text{UO}_2(\text{oxinate})_2$ in CHCl_3 (Fig. 1) displays bands at $\lambda_{\text{max}} = 520$ (sh, 1400), 374 (9500), 332 (9630), 320 (sh, 9670), and 308 nm (sh, 9060). These spectra are rather similar to those obtained in coordinating and polar solvents such as acetonitrile and ethanol. Both complexes are not luminescent at ambient conditions. While solutions

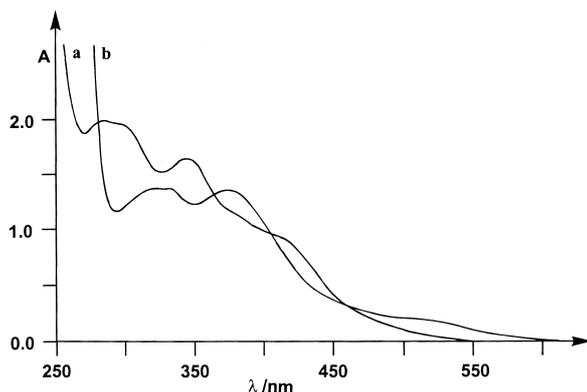


Fig. 1. Electronic absorption spectra of 1.08×10^{-4} M $\text{UO}_2(\text{salophen})$ (a) and 1.42×10^{-4} M $\text{UO}_2(\text{oxinate})_2$ (b) in CHCl_3 at room temperature, 1-cm cell.

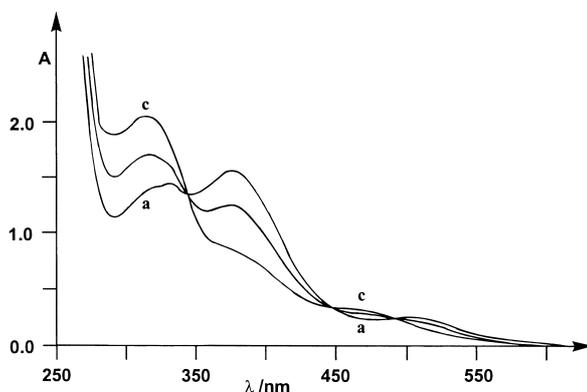


Fig. 2. Spectral changes during the photolysis of 1.54×10^{-4} M $\text{UO}_2(\text{oxinate})_2$ in EtOH at r. t. after 0 (a), 10 and 20 (c) min irradiation times with white light (Osram HBO 200 W/2 lamp), 1-cm cell.

of $\text{UO}_2(\text{salophen})$ are not light sensitive, $\text{UO}_2(\text{oxinate})_2$ undergoes a photolysis in various solvents including CHCl_3 and EtOH. The irradiation is accompanied by spectral changes (Fig. 2) which indicate the formation of free oxine ($\lambda_{\text{max}} = 316$ and 243 nm in EtOH). The presence of free oxine in the photolyzed solution is confirmed by its strong fluorescence at $\lambda_{\text{max}} = 414$ nm. The progress of the photolysis is monitored by measuring the decrease of the optical density at $\lambda = 376$ nm taking into account the residual absorption of the released oxine at this wavelength. $\text{UO}_2(\text{oxinate})_2$ in EtOH disappears with $\phi = 8.3 \times 10^{-4}$ at $\lambda_{\text{irr}} = 366$ nm. In CHCl_3 the quantum yield is distinctly larger with $\phi = 3.6 \times 10^{-3}$ at $\lambda_{\text{irr}} = 366$ nm. The photolysis takes place also upon irradiation of the longest-

wavelength band (Fig. 2) with $\phi \sim 2 \times 10^{-3}$ at $\lambda_{\text{irr}} = 546$ nm. However, owing to the limited solubility of $\text{UO}_2(\text{oxinate})_2$ a precise quantum yield could not be obtained.

Discussion

Metal complexes with oxinate [12 - 14] and salen-type [15] ligands such as salophen are characterized by long-wavelength IL absorptions in their electronic spectra. Moreover, owing to the presence of phenolate groups these ligands can act as electron donors. Since uranyl complexes contain U(VI) with an empty valence shell the metal center is only capable to function as acceptor site for LMCT transitions. Accordingly, the salophen and oxinate ligands as well as the oxide ligands of $\text{UO}_2(\text{salophen})$ and $\text{UO}_2(\text{oxinate})_2$ provide the donor function for such LMCT transitions. The uranyl ion itself displays a complicated system of weak oxide to U(VI) LMCT bands ($\epsilon < 10$) between 330 and 500 nm [1 - 5, 8]. On the basis of these considerations the electronic spectra of $\text{UO}_2(\text{salophen})$ and $\text{UO}_2(\text{oxinate})_2$ can be interpreted. Fortunately, in distinction to most other uranyl complexes the absorption spectra of $\text{UO}_2(\text{salophen})$ and $\text{UO}_2(\text{oxinate})_2$ (Fig. 1) show well discernible features. By comparison with other salophen and oxinate complexes the IL absorptions of $\text{UO}_2(\text{salophen})$ and $\text{UO}_2(\text{oxinate})_2$ can be identified. All other bands must then be of the LMCT type.

$\text{Ni}(\text{salophen})$ displays a well resolved IL absorption at $\lambda_{\text{max}} = 381$ nm [16]. Accordingly, the shoulder at 380 nm in the spectrum of $\text{UO}_2(\text{salophen})$ is also assigned to this IL transition. Moreover, there are two closely spaced absorptions around 300 nm ($\lambda_{\text{max}} = 286$ and 302 nm) which appear also in the spectrum of $\text{Ni}(\text{salophen})$ [16]. It follows that these bands are also of the IL type. The remaining absorptions of $\text{UO}_2(\text{salophen})$ at $\lambda_{\text{max}} = 346$ and 417 nm (sh) are then assigned to $\text{salophen}^{2-} \rightarrow \text{U(VI)}$ LMCT transitions. The weak uranyl LMCT bands are hidden under the intense IL and $\text{salophen}^{2-} \rightarrow \text{U(VI)}$ LMCT absorptions.

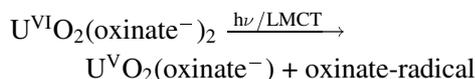
The absorption spectrum of $\text{UO}_2(\text{oxinate})_2$ (Fig. 1) between 300 and 450 nm is strikingly similar to that of $\text{Re}^{\text{VII}}\text{O}_3(\text{oxinate})$ [13] and some other oxinate complexes [12, 14] which show only oxinate IL transitions in this region. It follows that the bands of $\text{UO}_2(\text{oxinate})_2$ at 308, 320, 332, and 374

nm are also of the oxinate IL type. Consequently, the longest-wavelength band at $\lambda_{\max} = 520$ nm (sh) must be assigned to an oxinate to U(VI) LMCT transition.

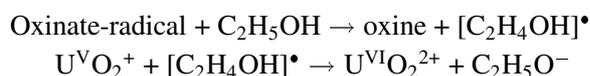
Both complexes, $\text{UO}_2(\text{salophen})$ and $\text{UO}_2(\text{oxinate})_2$ are not luminescent under ambient conditions. At low temperatures (77 K) rather weak emissions are observed but they are attributed to impurities. In principle, emissions from the uranyl ion [1 - 8] and the salophen^{2-} or oxinate^- ligands are conceivable. However, the emissive state of the uranyl ion is not easily populated from other excited states [17, 18]. Accordingly, the absence of the uranyl emission upon IL or CT excitation is not surprising. On the other hand, various complexes with salen-type [15] and oxinate [12 - 14] ligands are well known to show an IL fluorescence and / or phosphorescence following IL excitation. An IL phosphorescence may appear even under ambient conditions if the metal exerts a heavy atom effect. The fluorescence of the coordinated salophen^{2-} ligand appears at $\lambda_{\max} = 499$ nm [19]. Although the IL phosphorescence of salophen complexes has not yet been observed it should appear around 600 nm. In the case of $[\text{Au}(\text{salen})]^+$ it occurs at $\lambda_{\max} = 570$ nm [15]. The IL emissions of oxinate complexes appear at approximately 510 (fluorescence) and 780 nm (phosphorescence) [12 - 14]. The absence of any luminescence of $\text{UO}_2(\text{salophen})$ and $\text{UO}_2(\text{oxinate})_2$ can then be only explained by the presence of lower-energy $\text{salophen}^{2-}/\text{oxinate}^-$ to U(VI) LMCT states which are rapidly populated from the IL states. These LMCT states are apparently not emissive. In this context it should be noted that the uranyl emission of simple uranyl salts is also quenched by electron transfer from suitable electron donors [1 - 7]. Although this excited state electron transfer takes place frequently as an intermolecular process it corresponds to a LMCT excitation. In both cases light absorption is followed by the reduction of the uranyl ion and oxidation of an electron donor.

$\text{UO}_2(\text{oxinate})_2$ undergoes a photolysis in various solvents including CHCl_3 and ethanol. Since the IL states of coordinated oxinate are not photoreactive [12 - 14] the photolysis must originate from the oxinate to U(VI) LMCT states. This assumption is supported by the observation that the light sensitivity of $\text{UO}_2(\text{oxinate})_2$ extends to its longest-wavelength absorption which is of the LMCT type. Moreover, the photochemistry of uranyl complexes

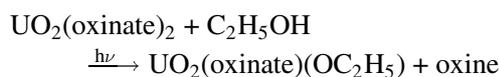
with simple ligands such as halide or oxalate is also determined by reactive LMCT states [1 - 7]. Generally, LMCT excitation of such complexes leads to the reduction of UO_2^{2+} to UO_2^+ and oxidation of the halide or oxalate in the primary photochemical step. This takes certainly place also in the case of the oxinate complex:



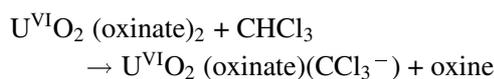
However, secondary reactions apparently prevent the generation of redox products as indicated by the formation of free oxine as final photolysis product. It is suggested that in analogy to a variety of other organic radicals which are generated by LMCT excitation of metal complexes [20, 21] the released oxinate radical abstracts a hydrogen atom from the solvent. The resulting solvent radical then reoxidizes U(V), *e. g.*:



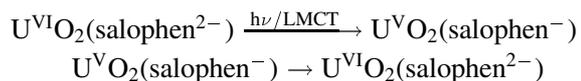
It may be argued that the photolysis simply occurs as a ligand substitution which could proceed without the intermediate formation of redox products:



However, this reaction would be difficult to explain on the basis of a reactive LMCT state. Moreover, the photolysis does not only take place in protic solvents but also in CHCl_3 which cannot coordinate but is a well-known donor for hydrogen abstraction. The overall stoichiometry may be expressed by the following equation:



Surprisingly, $\text{UO}_2(\text{salophen})$ is not light sensitive although its electronic structure and excited state behavior should be rather similar to those of $\text{U}^{\text{VI}}\text{O}_2(\text{oxinate})_2$. Why is then the LMCT state of $\text{UO}_2(\text{salophen})$ not reactive? Two influences may determine this light stability. First of all, in distinction to the bidentate oxinate the salophen ligand is tetradentate and attached to the uranyl ion as a clamp which is not easily released. Accordingly, back electron transfer is certainly favored in this case:



Moreover, the salophen ligand is characterized by a very large π -electron system which is extended over the whole tetradentate ligand. Generally, the reactivity of radicals decreases with an increasing

delocalization. Again, back electron transfer should be facilitated.

Acknowledgment

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