

Photoreactivity and Photoluminescence of Aluminum Maltolate

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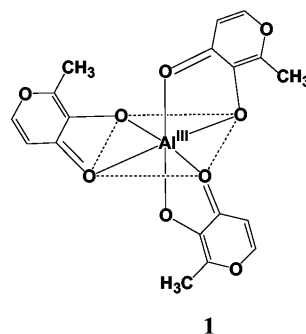
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Aluminium maltolate shows a longest-wavelength absorption at $\lambda_{\max} = 314$ nm which is of the intraligand (IL) type. IL excitation leads to a photodecomposition of the ligand ($\phi = 0.04$ at $\lambda_{\text{irr}} = 313$ nm, in ethanol). While a fluorescence is not observed, Al maltolate displays a phosphorescence in low-temperature glasses ($\lambda_{\max} = 510$ nm at 77 K, in ethanol).

Key words: Electronic Spectra, Luminescence, Aluminum, Maltol

Introduction

In biological systems coordination compounds play an important role as metallo enzymes. Moreover, they may be used for therapeutic and diagnostic purposes in medical applications. Finally, the toxicity of metal compounds is also a significant aspect of bioinorganic chemistry [1]. In this context aluminum has been originally regarded as a benign element, but in the last 30 years indications have accumulated, which point to a connection between aluminum and neurological dysfunctions including Alzheimer's disease [1]. However, the role of aluminum in such biochemical processes is not clear. An especially interesting compound is aluminum maltolate (**1**), which seems to be a very strong neurotoxin [2,3]. While this substance can be easily prepared from aluminum salts and maltol [3] it may also occur in natural products such as tea [4]. Recently, the influence of this compound on cell growth has been examined [5]. In this connection its light sensitivity should be of considerable interest. The luminescence behavior of Al maltolate (**1**) has not yet been examined. If this complex would be emissive, luminescence spectroscopy may provide a simple and sensitive probe for an analytical access. These questions stimulated our present study.



Experimental Section

Materials

Solvents used for spectroscopic measurements were of spectrograde quality. Maltol (3-hydroxy-2-methyl-4-pyrone) and aluminum maltolate were commercially available from Aldrich and used without further purification.

Instrumentation

Absorption spectra were measured with a Varian Cary 50 or a Kontron Uvikon 860 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.

Results

Al(mal)₃ is soluble in various solvents including water without decomposition [3]. Since in a previous study the photochemistry of free maltol (malH) has been examined in ethanol [6] we selected the same solvent for the present investigation in order to facilitate a comparison. The electronic spectrum of Al(mal)₃ in ethanol (Fig. 1.) shows absorptions at $\lambda_{\max} = 314$ ($\epsilon = 10800 \text{ M}^{-1} \text{ cm}^{-1}$), 247 (sh, 3900) and 222 nm (27 500). At r.t. in solution Al(mal)₃ does not exhibit any emission but is rather light sensitive. The photolysis is accompanied by spectral changes (Fig. 2.), which indicate the loss of the original chromophore. In addition, a new weak absorption appears at $\lambda_{\max} = 340$ nm. The same observations are made in the absence of oxygen. The photodecomposition of Al(mal)₃ can be monitored by measuring the decrease of the absorption at 314 nm. The complex disappears with $\phi = 0.04$ at $\lambda_{\text{irr}} = 313$ nm. In an ethanol glass at 77 K, Al(mal)₃

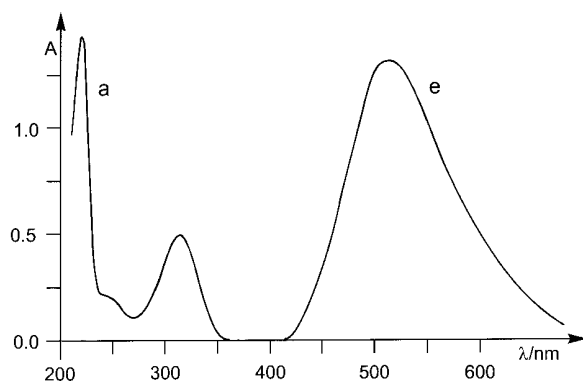


Fig. 1. Electronic absorption (a) and emission (e) spectra of 4.93×10^{-5} M aluminum maltolate in EtOH. Absorption: at room temperature, 1-cm cell. Emission: at 77 K, $\lambda_{\text{exc}} = 320$ nm, intensity in arbitrary units.

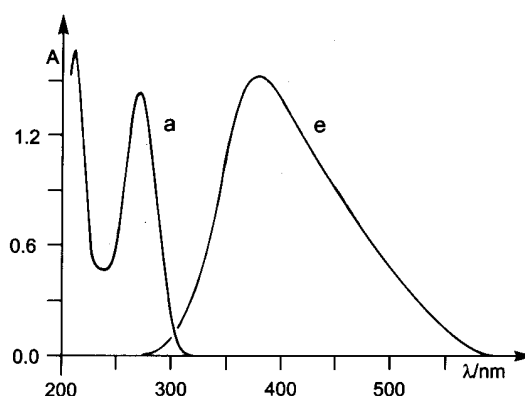


Fig. 3. Electronic absorption (a) and emission (e) spectra of 1.85×10^{-4} M maltol in EtOH. Absorption: at room temperature, 1-cm cell. Emission: at 77 K, $\lambda_{\text{exc}} = 270$ nm, intensity in arbitrary units.

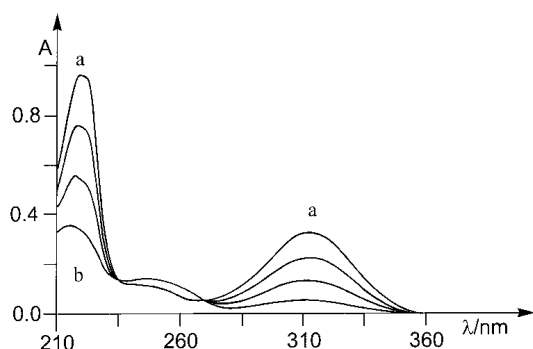


Fig. 2. Spectral changes during the photolysis of 3.08×10^{-5} M aluminum maltolate in EtOH at room temperature after 0 min (a), 0.5, 1 and 2 min (b) irradiation times with $\lambda_{\text{irr}} = 313$ nm (Osram HBO 200 W/2 lamp; Schott interference filter UV-PIL 313), 1-cm cell.

shows an intense green emission at 510 nm (Fig. 2) which decays with $\tau \sim 0.5$ s. The excitation spectrum matches the absorption spectrum.

The absorption spectrum of maltol in ethanol (Fig. 3) displays absorptions at $\lambda_{\text{max}} = 271$ (7600), 222 (sh, 6050) and 213 nm (7900). Maltol does not show any luminescence at r.t., but is also light sensitive in agreement with previous observations [6]. While in general the concomitant spectral variations (Fig. 4) are similar to those which occur during the photolysis of $\text{Al}(\text{mal})_3$ in ethanol, a direct comparison cannot be made owing to the different spectra of both species. However, the irradiation of maltol leads also to the appearance of a new weak absorption at $\lambda_{\text{max}} = 340$ nm as in the case of $\text{Al}(\text{mal})_3$. The photolysis of maltol was monitored by measuring the absorption at 271 nm. Maltol disappears with $\phi = 0.18$ at $\lambda_{\text{irr}} = 280$ nm. In

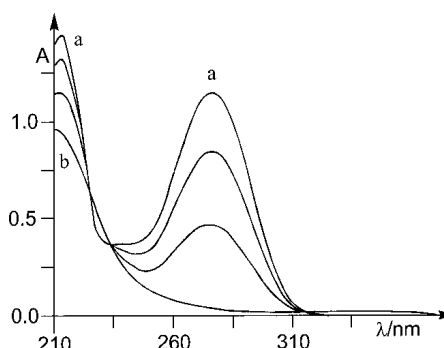
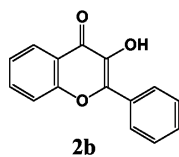
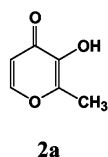


Fig. 4. Spectral changes during the photolysis of 1.47×10^{-4} M maltol in EtOH at room temperature after 0 sec (a), 20, 40 and 160 sec (b) irradiation times with white light (Osram HBO 200 W/2 lamp), 1-cm cell.

an ethanol glass at 77 K maltol exhibits a blue luminescence (Fig. 3) at $\lambda_{\text{max}} = 380$ nm.

Discussion

Maltol (**2a**) is a hydroxy- γ -pyrone. While its absorption spectrum has been reported before [7], further spectroscopic details have not been described and discussed. In contrast, much more is known about 3-hydroxyflavones (**2b**) such as flavonol, quercetin or morin. These compounds contain also the hydroxy- γ -pyrone chromophore. They are not light-sensitive but are fluorescent and undergo an intramolecular excited state proton transfer from the hydroxy substituent to the keto oxygen atom [8–10]. This is a very fast and reversible process. Flavonols are apparently not phosphorescent [11]. The lowest excited states are $\pi\pi^*$ in nature [9].



The excited state behavior of maltol is quite different from that of flavonols. Maltol is light sensitive, not fluorescent, but phosphorescent at low temperatures (Fig. 3; $\lambda_{\text{max}} = 380$ nm). In distinction to flavonols the π -electron system of maltol is rather restricted and its lowest excited state resembles more the $n\pi^*$ states of ketones such as benzophenone which are also not fluorescent, but photoreactive and phosphorescent at low temperatures [12]. However, the nature of the photoproducts of maltol [6] cannot be related to a simple mechanism of this photo-reaction.

Flavonols form a variety of luminescent coordination compounds in solution [13–15]. In particular, complexes with main group metal ions such as Al^{3+} , Ga^{3+} , In^{3+} , Ge^{4+} and Sn^{4+} display an intense fluorescence. In contrast, $\text{Al}(\text{mal})_3$ is not luminescent, but shows a relatively strong phosphorescence at 77 K (Fig. 1; $\lambda_{\text{max}} = 510$ nm) which decays with $\tau \sim 0.5$ s. As a light metal, aluminum does not exert any heavy-

atom effect as indicated by the long phosphorescence lifetime. Moreover, $\text{Al}(\text{mal})_3$ is light-sensitive and the photoproducts are similar to those which are obtained by the photolysis of maltol itself. The resemblance of the excited state behavior of maltol and $\text{Al}(\text{mal})_3$ suggests that the nature of the lowest excited states is also comparable in both cases. This is not so surprising since the bonding in $\text{Al}(\text{mal})_3$ is certainly rather ionic and Al^{3+} does not participate in any low-energy transitions. In this context, it is of interest that iron(III) complexes of kojic acid (kojH) are also light sensitive [16, 17]. Kojic acid differs from maltol only by the position of the methyl substituent in the γ -pyrone ring system. However, in contrast to $\text{Al}(\text{III})$, $\text{Fe}(\text{III})$ is redox active. The complex $\text{Fe}^{\text{III}}(\text{koj})_3$ is characterized by a low-energy ($\text{koj}^- \rightarrow \text{Fe}^{\text{III}}$) ligand-to-metal charge transfer (LMCT) excited state which is photoreactive. LMCT excitation leads to the reduction of $\text{Fe}(\text{III})$ and the oxidation of the koj^- ligand in the primary photochemical step.

In conclusion, aluminum maltolate is not fluorescent, but phosphorescent at 77 K. At r.t. in solution it undergoes a photodecomposition by UV light. The reactive excited state is of the intraligand type and shows features which are characteristic for $n\pi^*$ states of aromatic ketones.

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