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Journal of Photochemistry and Photobiology A: Chemistry 151 (2002) 45–47
Journal of Photochemistry and Photobiology A:Chemistry
www.elsevier.com/locate/jphotochem

Optical metal-to-ligand charge transfer in tris(pyrazine-2-carboxylato)cerium(III) Absorption and emission

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Received 12 April 2002; accepted 18 April 2002

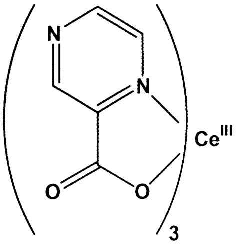
Abstract

The complex $Ce^{III}(pyz\text{-}COO)_3$, with pyz-COO = pyrazine-2-carboxylate, is characterized by a long-wavelength absorption at $\lambda_{max} = 388$ nm which is assigned to a ($Ce^{III} \rightarrow pyz\text{-}COO^-$) metal-to-ligand charge transfer (MLCT) transition. The blue-green luminescence of the complex at $\lambda_{max} = 470$ nm is assumed to originate from this MLCT state.

Keywords: Electronic spectra; Charge transfer; Luminescence; Cerium complexes

1. Introduction

Metal-to-ligand charge transfer (MLCT) excited states play a very important role in the photophysics and photochemistry of metal complexes [1,2]. MLCT states occur at low energies if a ligand with empty low-energy orbitals is coordinated to an electron-rich metal center. The overwhelming number of observations have been made on $d \rightarrow \pi^*$ MLCT states of polypyridyl (or 1,2-diimine) complexes with electron-donating transition metals such as Ru(II) [3,4], Re(I) [4–7] and Cu(I) [4,8,9]. However, the occurrence of MLCT states is not restricted to transition metals. MLCT bands have also been observed in the electronic spectra of complexes that contain reducing main group metals, including Sn(II), Sb(III) and Bi(III) [10]. In contrast to these transition and main group metal compounds, MLCT states of f-group metal complexes have apparently not yet been identified. The reason for this lack is not quite clear, but may be related to the fact that complexes of lanthanides (Ln) or actinides are only of limited stability. This applies, in particular, to complexes with neutral ligands such as 2,2′-bipyridine (bipy) or 9,10-phenanthroline. While such lanthanide complexes are known [11,12], the affinity of Ln^{3+} for these ligands seems to be rather small. The electronic spectra provide evidence for this notion. Generally, the longest-wavelength band of the bipy ligand undergoes a distinct red shift upon complex formation [13,14]. However, in the case of Ce(III) bipy complexes, such a shift has not been observed [15], indicating a rather weak electronic interaction between cerium and bipy. On the other hand, anionic ligands form relatively stable complexes with Ln^{3+}, owing to the electrostatic attraction between metal cations and ligand anions. Accordingly, a complex consisting of a reducing f-group metal cation and an electron-accepting anionic ligand should be a promising candidate for the observation of an optical MLCT transition. We explored this possibility and selected the compound $Ce^{III}(pyz\text{-}COO)_3$ with $pyz\text{-}COO^-$ = pyrazine-2-carboxylate for the present study.



This choice was based on the following considerations. Ce(III) is a one-electron donor of moderate reducing strength. The electronic spectra of Ce(III) complexes have been studied in some detail. They are characterized by a long-wavelength, metal-centered $f \rightarrow d$ absorption [16,17]. Pyrazine has been shown to be a rather strong acceptor for MLCT transitions [18]. As an electron-withdrawing substituent, the carboxylate group of $pyz\text{-}COO^-$ should even

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PII: S1010-6030(02)00171-5

enhance the acceptor strength of pyrazine. Finally, the anion pyz-COO$^-$ is a well-known bidentate ligand [19,20]. Accordingly, the target complex Ce^{III}(pyz-COO)$_3$ was expected to be accessible by a simple synthetic procedure.

2. Experimental

2.1. Materials

All solvents used for spectroscopic measurements were of spectrograde quality. The pyz-COOH and $CeCl_3 \cdot 7H_2O$ were commercially available (Aldrich) and used without further purification.

Ce^{III}(pyz-COO)$_3 \cdot 1.5\ H_2O$ was obtained by the following procedure: To a suspension of pyz-COOH (3.72 g, 30 mmol) in 50 ml methanol (95%) was added dropwise under stirring 2.7 ml aqueous ammonia (25%). The reaction mixture became neutral and a clear colorless solution was obtained. A colorless solution of $CeCl_3 \cdot 7H_2O$ (3.72 g, 10 mmol) in 35 ml methanol was added, yielding a bright yellow solution. After stirring for ~30 min, a yellow powder slowly precipitated. It was collected by filtration, washed four times with 50 ml methanol (90%), then with warm methanol and ether, and dried under reduced pressure, yielding the analytically pure product, 4.0 g (78%).

Anal. calcd. for $C_{15}H_9N_6O_6Ce \cdot 1.5H_2O$ (536.41): C, 33.59%; H, 2.20%; N, 15.66%. Found: C, 33.55%; H, 2.28%; N, 15.59%.

2.2. Instrumentation

Absorption spectra were measured with a Hewlett-Packard 8452A diode array or an Uvikon 860 absorption spectrometer. The light source used was an Osram HBO 200 W/2 or an Osram XBO 450 W/4 lamp. Additional cut-off filters (Schott) were applied to avoid short-wavelength and second-order photolysis. Monochromatic light was

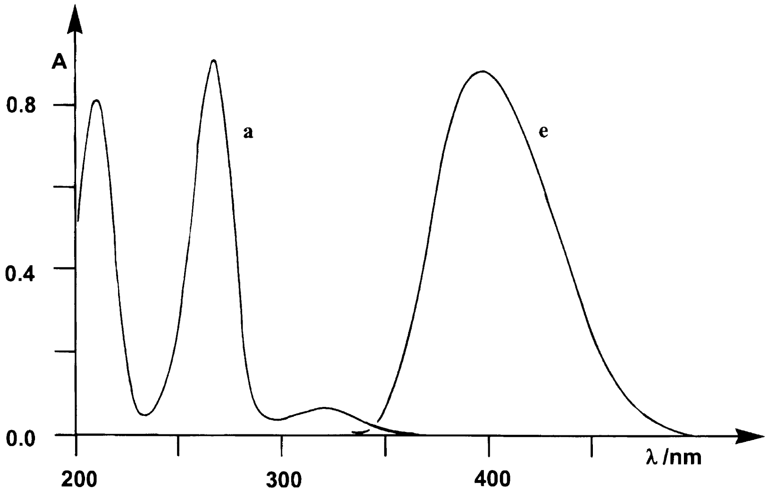

Fig. 1. Electronic absorption (a) and emission (e) spectrum of 1.30×10^{-4} M pyz-COOH in CH_3CN at room temperature, 1 cm cell. Emission: $\lambda_{exc} = 320$ nm, intensity in arbitrary units.

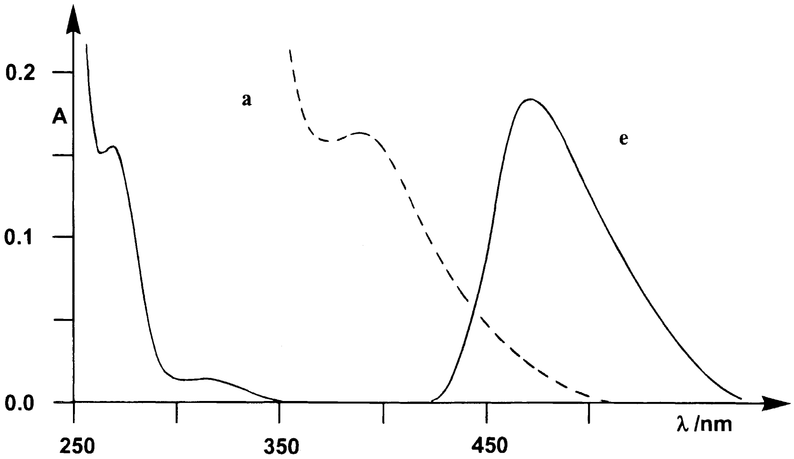

Fig. 2. Electronic absorption (a) and emission (e) spectrum of 1.31×10^{-3} M Ce^{III}(pyz-COO)$_3 \cdot 1.5H_2O$ in CH_3CN/DMF = 100/1 at room temperature. Absorption: 1 cm cell (- - -) and 0.01 cm cell (—). Emission: $\lambda_{exc} = 360$ nm, intensity in arbitrary units.

obtained using a Schoeffel GM/1 high-intensity monochromator (band width 23 nm). In all cases, the light beam was focused on a thermostated photolysis cell by a quartz lens. 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 the free acid pyz-COOH in CH_3CN (Fig. 1) shows absorptions at $\lambda_{max} = 320$ ($\varepsilon = 480\,M^{-1}\,cm^{-1}$), 268 (6900) and 211 (6300) nm. The spectrum of the anion pyz-COO^- is practically the same as that of the acid. The free acid as well as the anion pyz-COO^- display a weak fluorescence (Fig. 1) at $\lambda_{max} = 395$ nm.

Since Ce^{III}(pyz-COO)$_3$ is almost insoluble in pure CH_3CN, it was dissolved in DMF which was then diluted with CH_3CN. The absorption spectrum of Ce^{III}(pyz-COO)$_3$ in CH_3CN/DMF = 100/1 (Fig. 2) exhibits bands at $\lambda_{max} =$ 388 nm (sh, 130), 318 (sh, 1500), and 271 (12200) nm. The 388 nm band causes the yellow color of the compound. Ce^{III}(pyz-COO)$_3$ shows a weak blue-green luminescence (Fig. 2) at $\lambda_{max} = 470$ nm. This luminescence is not affected by oxygen. The excitation spectrum matches roughly the absorption spectrum.

4. Discussion

Cerium(III) as an f^1 ion contains a single electron in its valence shell. The lowest-energy electronic transition of Ce^{3+} involves the promotion of this electron from the 4f to the 5d orbitals [16,17]. Generally, simple Ce(III) compounds are colorless since this metal-centered f → d transition gives rise to an absorption in the near UV region.

The free acid pyz-COOH or its deprotonated anion pyz-COO^- are also colorless, because their absorptions (Fig. 1) appear below 400 nm. Upon coordination, these intraligand (IL) bands remain in the UV region, as indicated by the observation that Zn^{II}(pyz-COO)$_2$ is a white compound which does not show any absorption in the visible region [20]. In distinction to this zinc complex, Ce^{III}(pyz-COO)$_3$ is a yellow substance. This color is caused by the longest-wavelength absorption of the complex at $\lambda_{max} = 388$ nm, which extends into the visible spectral region. We suggest that this band belongs to an MLCT transition from the Ce(III) 4f orbitals to the π^* orbitals of the pyz-COO^- ligand. This assignment is consistent with the reducing character of Ce(III) and electron-accepting nature of the pyz-COO^- ligand. In this context, it is of interest that an iron(II) complex of pyz-COO^- is a dark-violet material. It shows a characteristic absorption at $\lambda_{max} = 470$ nm, which has been tentatively assigned to an MLCT transition [20].

Simple Ce(III) complexes are frequently luminescent [16,17]. Generally, this emission appears in the near UV and undergoes only a slight red shift when compared with the longest-wavelength absorption. The emissive state is a metal-centered df excited state [16,17]. The luminescence is a spin-allowed doublet–doublet transition which takes place in the ns range. We suggest that in contrast to this UV emission, the weak blue-green luminescence of Ce^{III}(pyz-COO)$_3$ originates from the lowest-energy $Ce^{III} \rightarrow$ pyz-COO^- MLCT excited state which is also observed as the longest-wavelength absorption. Owing to the f^1 electron configuration, absorption and emission are both spin-allowed processes. The small Stokes shift of $\Delta E = 4497\,cm^{-1}$ reflects the fact that the f-electron that takes part in the MLCT transition is hardly involved in any bonding interaction.

In summary, the complex Ce^{III}(pyz-COO)$_3$ seems to be the first example of an f-group metal complex with an MLCT excited state. This MLCT state occurs at rather low energies and is observed in absorption and emission.

Acknowledgements

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

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