

# Excited state behavior of tetrakis(2,2,6,6-tetramethyl-3,5-heptane-dionato)cerium(IV) Emission and photoredox reaction from ligand-to-metal charge transfer states

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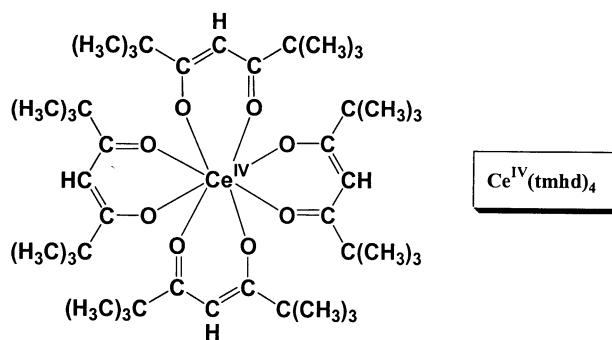
## Abstract

The complex  $\text{Ce}^{\text{IV}}(\text{tmhd})_4$  with  $\text{tmhd}^- = 2,2,6,6\text{-tetramethyl-3,5-heptane-dionato}$  anion is luminescent and photoreactive. It is suggested that the emission originates from a higher-energy ligand-to-metal charge transfer (LMCT) state and terminates at the lowest-energy LMCT state. This luminescence is thus equivalent to the well-known metal-centered fluorescence of  $\text{Ce}(\text{III})$  compounds. In addition, LMCT excitation of  $\text{Ce}^{\text{IV}}(\text{tmhd})_4$  induces a reduction of  $\text{Ce}(\text{IV})$  to  $\text{Ce}(\text{III})$ . © 2001 Elsevier Science B.V. All rights reserved.

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

## 1. Introduction

Coordination compounds of oxidizing metals with an empty valence shell ( $s^0$ ,  $d^0$  or  $f^0$  electronic configuration) are characterized by low-energy ligand-to-metal charge transfer (LMCT) states [1] which may be reactive [2] and/or emissive [3]. Uranyl complexes are the best known examples of this behavior [4–11]. The  $\text{UO}_2^{2+}$  ion shows an intense emission which originates from an  $\text{O}^{2-}$  to  $\text{U}(\text{VI})$  LMCT state. When additional ligands which are strong electron donors are coordinated to  $\text{UO}_2^{2+}$ , new low-energy LMCT states are introduced. These LMCT states are not emissive but reactive. Such reactive LMCT states of  $f^0$  complexes are not restricted to actinides.  $\text{Ce}(\text{IV})$  as an  $f^0$  lanthanide metal is also well known to participate in photoredox reactions which are induced by LMCT excitation [12–14]. On the contrary, luminescent  $\text{Ce}(\text{IV})$  compounds are apparently unknown. In the present work, we describe the excited state behavior of the  $\beta$ -diketonato complex  $\text{Ce}^{\text{IV}}(\text{tmhd})_4$  with  $\text{tmhd}^- = 2,2,6,6\text{-tetramethyl-3,5-heptane-dionato}$  anion. This is a unique example of a  $\text{Ce}(\text{IV})$  complex which is not only photoreactive but also luminescent.



## 2. Experimental

### 2.1. Materials

All solvents used were of spectrograde quality.  $\text{Ce}^{\text{IV}}(\text{tmhd})_4$  and  $\text{Ce}(\text{acac})_3 \cdot n\text{H}_2\text{O}$  were commercially available (Strem) and used without further purification.

### 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 a Hanovia Xe/Hg 977 B-1 (1 kW) lamp. Additional cutoff

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filters (Schott) were applied to avoid short-wavelength and second-order photolysis. Monochromatic light was obtained using a Schoeffel GM/1 high-intensity monochromator (bandwidth 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. Absolute emission quantum yields were determined by comparison of the integrated emission intensity with that of Rhodamine B under identical conditions such as exciting wavelength, optical density, and apparatus parameters.

### 2.3. Photolyses

The photolyses were carried out in solutions of  $\text{CH}_3\text{CN}$  and  $\text{CHCl}_3$  in 1 cm spectrophotometer cells at room temperature. Progress of the photolyses was monitored by UV–Vis spectrophotometry. For quantum yield determinations, the complex concentrations were such as to have essentially complete light absorption. The total amount of photolysis was limited to less than 5% to avoid light absorption by the photoproduct. Absorbed light intensities were determined by a Polytec pyroelectric radiometer which was calibrated by Ferrioxalate actinometry and equipped with a RkP-345 detector.

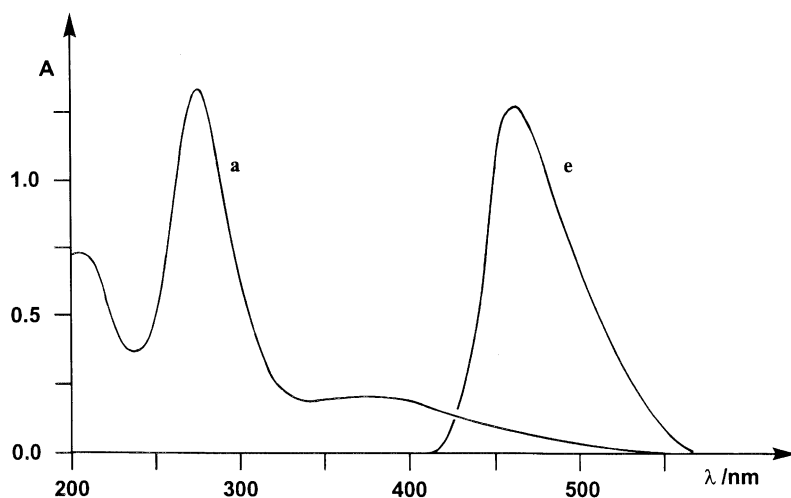


Fig. 1. Electronic absorption (a) and emission (e) spectrum of  $3.34 \times 10^{-5}$  M  $\text{Ce}^{\text{IV}}(\text{tmhd})_4$  in  $\text{CH}_3\text{CN}$  at r.t., 1 cm cell. Emission:  $\lambda_{\text{exc}} = 370$  nm, intensity in arbitrary units.

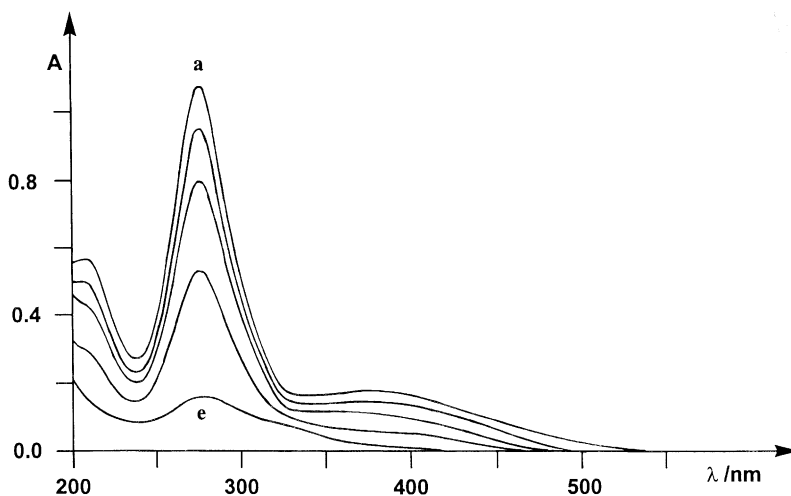


Fig. 2. Spectral changes during the photolysis of  $2.68 \times 10^{-5}$  M  $\text{Ce}^{\text{IV}}(\text{tmhd})_4$  in  $\text{CH}_3\text{CN}$  at r.t. after 0 min (a); 5, 10, 20 and 40 min (e) irradiation times with  $\lambda_{\text{irr}} = 366$  nm (1 kW Hanovia Xe/Hg 977 B-1 lamp), 1 cm cell.

### 3. Results

The electronic spectrum of  $\text{Ce}^{\text{IV}}(\text{tmhd})_4$  [15] in  $\text{CH}_3\text{CN}$  (Fig. 1) shows absorptions at  $\lambda_{\text{max}} = 372$  ( $\epsilon = 7100 \text{ dm}^3 \text{ M}^{-1} \text{ cm}^{-1}$ ), 276 ( $40,300 \text{ dm}^3 \text{ M}^{-1} \text{ cm}^{-1}$ ) and 210 nm ( $22,600 \text{ dm}^3 \text{ M}^{-1} \text{ cm}^{-1}$ ). This spectrum is hardly solvent dependent. The complex is luminescent. The emission spectrum (Fig. 1) displays a band at  $\lambda_{\text{max}} = 462$  nm with  $\phi = 4.1 \times 10^{-4}$  at  $\lambda_{\text{exc}} = 380$  nm. If the excitation is restricted to shorter-wavelength irradiation ( $\lambda_{\text{exc}} < 400$  nm), the excitation spectrum roughly matches the absorption spectrum. Since  $\text{Ce}^{\text{IV}}(\text{tmhd})_4$  is light sensitive, reliable luminescence lifetimes cannot be obtained. The photolysis of  $\text{Ce}^{\text{IV}}(\text{tmhd})_4$  in  $\text{CH}_3\text{CN}$  is accompanied by spectral changes (Fig. 2) which indicate the formation of a  $\text{Ce}^{\text{III}}$  tmhd complex. The photolyzed solution shows weak bands at 370 (sh) and 400 nm (sh) which coincide with the longest-wavelength absorptions of  $[\text{Ce}^{\text{III}}(\text{tmhd})_4]^-$  at  $\lambda_{\text{max}} = 400$  nm ( $\epsilon = 214 \text{ dm}^3 \text{ M}^{-1} \text{ cm}^{-1}$ ) and 369 nm ( $224 \text{ dm}^3 \text{ M}^{-1} \text{ cm}^{-1}$ ) [15]. The progress of the photolysis is monitored by measuring the decrease of the optical density at  $\lambda_{\text{max}} = 276$  nm.  $\text{Ce}^{\text{IV}}(\text{tmhd})_4$  disappears with  $\phi = 2.1 \times 10^{-3}$  at  $\lambda_{\text{irr}} = 366$  nm. Since  $\text{Ce}^{\text{III}}$  compounds are generally luminescent (see below) the formation of  $\text{Ce}^{\text{III}}$  tmhd complexes as photoproducts can also be detected by emission spectroscopy. The photolyzed solution shows a luminescence at  $\lambda_{\text{max}} = 452$  nm. This emission is very close to that of  $[\text{Ce}^{\text{III}}(\text{tmhd})_4]^-$  ( $\lambda_{\text{max}} = 453$  nm) which is generated by the reduction of  $\text{Ce}^{\text{IV}}(\text{tmhd})_4$  with dithionite. For comparison, the electronic spectra of  $\text{Ce}^{\text{III}}(\text{acac})_3$  with  $\text{acac}^- = \text{acetylacetonate}$  were also measured. The absorption spectrum shows more intense bands at  $\lambda_{\text{max}} = 314$  (sh) and 280 nm and weaker bands at  $\lambda_{\text{max}} = 374$  (sh) and 408 nm (sh). The emission at  $\lambda_{\text{max}} = 443$  nm appears in the same spectral region as that of  $[\text{Ce}^{\text{III}}(\text{tmhd})_4]^-$ .

### 4. Discussion

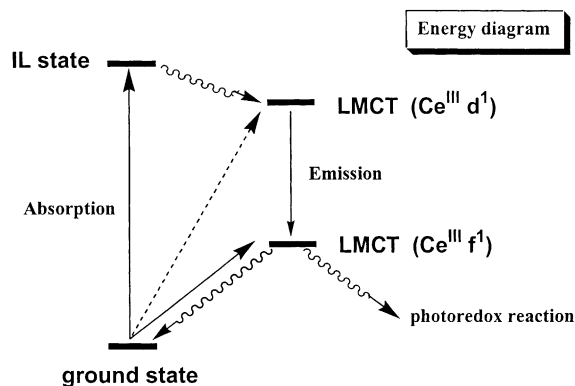
Generally,  $\text{Ce}(\text{IV})$  compounds are characterized by intense colors which are caused by long-wavelength LMCT absorptions [12–14]. In agreement with a previous report [15], the broad band of  $[\text{Ce}^{\text{IV}}(\text{tmhd})_4]$  at  $\lambda_{\text{max}} = 372$  nm (Fig. 1) is assigned to a  $\text{tmhd}^-$  to  $\text{Ce}(\text{IV})$  LMCT transition. The shorter-wavelength absorption at  $\lambda_{\text{max}} = 276$  nm is attributed to a  $\text{tmhd}^-$  intraligand (IL) transition.

Solutions of  $\text{Ce}(\text{IV})$  complexes are frequently light sensitive [12–14]. LMCT excitation induces redox reactions which lead to the reduction of  $\text{Ce}(\text{IV})$  to  $\text{Ce}(\text{III})$  and the oxidation of ligands or the solvent. In agreement with these observations, it is concluded that the photolysis of  $\text{Ce}^{\text{IV}}(\text{tmhd})_4$  proceeds according to the equation



Photoredox reactions of  $\beta$ -diketonato complexes with other metals are well known [16]. Generally, LMCT excitation leads to ligand oxidation. Depending on the particular complex and the solvent various oxidation products are formed.

While the photoredox behavior of  $\text{Ce}^{\text{IV}}(\text{tmhd})_4$  is not unusual, the luminescence of this complex (Fig. 1) is quite surprising. First of all, in addition to the  $\text{UO}_2^{2+}$  ion [4–11],  $\text{Ce}^{\text{IV}}(\text{tmhd})_4$  seems to be only the second example of an emitting  $f^0$  complex. Even more intriguing, the luminescence does apparently not originate from the lowest-energy LMCT state since the emission and the longest-wavelength LMCT absorption appear at similar energies (Fig. 1). We suggest that this emission involves a radiative transition from a higher-energy LMCT state to the lowest-energy LMCT state.  $\text{Ce}(\text{IV})$  has available two different acceptor orbitals, the 5d orbitals at higher energy and the 4f orbitals at lower energies. Accordingly, the longest-wavelength band of  $\text{Ce}^{\text{IV}}(\text{tmhd})_4$  at  $\lambda_{\text{max}} = 372$  nm is attributed to the (ligand  $\rightarrow$  4f  $\text{Ce}^{\text{IV}}$ ) LMCT transition. The shorter-wavelength (ligand  $\rightarrow$  5d  $\text{Ce}^{\text{IV}}$ ) LMCT absorption has not been identified but may be obscured by the intense IL band at  $\lambda_{\text{max}} = 276$  nm. However, irrespective of the nature of the shorter wavelength bands higher-energy excitation can lead to the population of the (ligand  $\rightarrow$  5d  $\text{Ce}^{\text{IV}}$ ) LMCT state. Its radiative transition to the (ligand  $\rightarrow$  4f  $\text{Ce}^{\text{IV}}$ ) LMCT state is then nothing else but an emission from an fd excited state of  $\text{Ce}(\text{III})$ . Numerous  $\text{Ce}(\text{III})$  compounds are characterized by this metal-centered luminescence which appears in the near UV but also in the visible region depending on the particular compound [3,17–20]. Our suggestion is supported by the observation that  $[\text{Ce}^{\text{III}}(\text{tmhd})_4]^-$  as well as  $\text{Ce}^{\text{III}}(\text{acac})_3$  emit at similar energies as  $\text{Ce}^{\text{IV}}(\text{tmhd})_4$ . Usually, the emission of  $\text{Ce}(\text{III})$  compounds is relatively intense and short-lived (ns-range) since it is a spin-allowed process [3,17–20]. According to these considerations, the excited state behavior of  $\text{Ce}^{\text{IV}}(\text{tmhd})_4$  can now be summarized by the following qualitative energy diagram:



The population of the LMCT ( $\text{Ce}^{\text{III}} d^1$ ) state may be facilitated by its energetic proximity to the IL state and by the larger extension or the cerium 5d orbitals which certainly provide a better electronic coupling with the ligands than the

well-shielded 4f orbitals. Since the emission is a rather rapid process, it apparently competes successfully with radiationless deactivation including photoredox processes which are assumed to start from the lowest-energy LMCT state. This conclusion is supported by the observation that the photolysis of  $\text{Ce}^{\text{IV}}(\text{tmhd})_4$  is also initiated by long-wavelength irradiation.

At this point, an analogy between the emission of  $\text{Ce}^{\text{IV}}(\text{tmhd})_4$  and the chemiluminescence of  $[\text{Ru}^{\text{III}}(\text{bipy})_3]^{3+}$  should be emphasized. The luminescence of  $\text{Ce}^{\text{IV}}(\text{tmhd})_4$  can be viewed as an emission of Ce(III) from an MC fd excited state which is generated by electron transfer from a  $\text{tmhd}^-$  ligand to Ce(IV). This behavior corresponds to that of  $[\text{Ru}(\text{bipy})_3]^{3+}$ . Electron transfer from strong reductants yields  $[\text{Ru}(\text{bipy})_3]^{2+}$  not only in the ground state but also in the emissive MLCT excited state [21–23].

Finally, it should be mentioned that the emission of  $\text{Ce}^{\text{IV}}(\text{tmhd})_4$  could also originate from IL excited states since the IL phosphorescence of complexes with  $\beta$ -diketonato ligands appears in the same wavelength region as that of  $\text{Ce}^{\text{IV}}(\text{tmhd})_4$ . However, this IL phosphorescence appears exclusively at low temperatures (77 K) and is restricted to complexes with lowest-energy  $\beta$ -diketonato IL states [16,24,25]. Accordingly, such an IL assignment does not seem to apply to the luminescence of  $\text{Ce}^{\text{IV}}(\text{tmhd})_4$ .

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