Phosphorescence of gadolinium(III) chelates under ambient conditions

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Abstract

The gadolinium(III) chelates Gd(dtpaH₂), Gd(hfac)₃, Gd(tta)₃ and Gd(qu)₃ with dtpa = 1,1,4,7,7-diethylenetriaminepentaacetate, hfac = hexafluoroacetylacetonate, tta = thenoyltrifluoroacetonate and qu = 8-quinolinolate (or oxinate) show a phosphorescence under ambient conditions. While the UV emission of Gd(dtpaH₂) at λmax = 312 nm comes from a metal-centered ff state, the bluish (λmax = 462 nm), green (λmax = 505 nm) and red (λmax = 650 nm) luminescence of Gd(hfac)₃, Gd(tta)₃ and Gd(qu)₃, respectively, originates from the lowest-energy intraligand triplets.

1. Introduction

Lanthanide compounds have attracted much attention in the field of luminescence spectroscopy. The excited state behavior of lanthanide ions Ln³⁺ have been investigated extensively [1–6]. The electronic spectra of Ln³⁺ with fn (n = 1–13) electron configuration are dominated by electronic transitions between f orbitals. Transitions between f orbitals of Ln³⁺ are strictly parity-forbidden. In addition, many ff transitions are also spin-forbidden although spin–orbit coupling facilitates a mixing with spin-allowed transitions. Nevertheless, ff bands have rather small absorption coefficients and the radiative lifetime of ff states are relatively large. Light absorption by Ln(III) complexes can be enhanced by suitable ligands which transfer the excitation energy to emissive Ln³⁺ ions.

However, the ff states of Gd³⁺ are located at exceptionally high energies owing to the extreme stability of its half-filled f-shell (f⁷). The lowest-energy ff transition appears as an emission line at 312 nm. Accordingly, Gd(III) complexes are frequently characterized by emissive intraligand (IL) states at lower energies. Owing to its heavy-atom effect and paramagnetism, Gd³⁺ induces a strong singlet/triplet mixing in the ligands [7]. It follows that the IL fluorescence is largely quenched while the IL phosphorescence is facilitated [8–11]. The IL luminescence of Gd(III) complexes is usually studied at low temperatures, mostly at 77 K. Quite recently, we reported that GdCp₃ with Cp = cyclopentadienyl shows an IL phosphorescence at r.t. [12]. It follows that IL triplets of gadolinium complexes may generally emit under ambient conditions. We explored this possibility and selected the chelates Gd(dtpaH₂), Gd(hfac)₃, Gd(tta)₃ and Gd(qu)₃ with dtpa = 1,1,4,7,7-diethylenetriaminepentaacetate, hfac = hexafluoroacetylacetate, tta = thenoyltrifluoroacetonate and qu = 8-quinolinolate (or oxinate) for the present study.
The ligands were chosen according to different emission colours (UV, blue, green and red) of the gadolinium complexes. Various applications are conceivable. For example, triplet emissions under ambient conditions could be utilized in organic light emitting diodes (OLED) and sensor technology.

2. Experimental

2.1. Materials

All solvents used for spectroscopic measurements were of spectrograde quality. For polymer films a polyester resin was used as a commercial product (Paraloid B72 from Roth, Germany). The compounds Gd(dtpaH₂)·2H₂O (Aldrich), Hhfac (ABCR), Htta (Aldrich), Hqu (Merck) were commercially available and used without further purification. The complex Gd(qu)₃ was prepared according to literature methods [13]. The synthesis of the diketonates Gd(hfac)₃ and Gd(tta)₃ was modified.

2.1.1. Synthesis of Gd(hfac)₃·3H₂O

To a solution of GdCl₃·2H₂O (300 mg, 1.14 mmol) and sodium acetate (1 g) in 5 ml water and Htta (760 mg, 3.42 mmol) in 8 ml ethanol were used. Yield: 520 mg. Anal. Calc. for C_{36}H_{15}O_{7}F_{18}Gd: C, 34.00; H, 1.78. Found: C, 34.03; H, 1.75%.

2.1.2. Synthesis of Gd(tta)₃·1.5H₂O

The same procedure as that for the synthesis of Gd(hfac)₃ was applied. Solutions of GdCl₃·2H₂O (300 mg, 1.14 mmol), sodium acetate (1 g) in 5 ml water and Htta (760 mg, 3.42 mmol) in 8 ml ethanol were used. Yield: 520 mg. Anal. Calc. for C_{36}H_{15}O_{7}F_{18}Gd: C, 34.00; H, 1.78. Found: C, 34.03; H, 1.75%.

2.2. Methods

Absorption spectra were measured with a Kontron Uvikon 932 double beam spectrophotometer. Emission and excitation spectra were recorded on a Hitachi 850 spectrofluorometer equipped with a Hamamatsu 928 photomultiplier. A band pass of 5 nm was employed. The luminescence spectra were corrected for monochromator and photomultiplier efficiency.

3. Results

The electronic spectrum of Gd(dtpaH₂) (Fig. 1) shows a weak structured absorption at λ_{max} = 273 nm (ε = 2 l mol⁻¹ cm⁻¹) and a continuous absorption at shorter wavelength. The emission spectrum (Fig. 1) displays a narrow band at λ_{max} = 312 nm. The absorption spectra of Gd(hfac)₃ and Gd(tta)₃ (Figs. 2 and 3) contain bands at λ_{max} = 302 nm (ε = 30 000 l mol⁻¹ cm⁻¹) and λ_{max} = 268 (20 000), 337 (58 000) nm, respectively. Both complexes emit only very weakly in fluid solution (e.g., acetonitrile) but exhibit a strong luminescence in a rigid polymer matrix with λ_{max} = 462 nm for Gd(hfac)₃ and λ_{max} = 505 nm for Gd(tta)₃. The complex Gd(qu)₃ shows a long-wavelength absorption at λ_{max} = 369 nm and an emission at λ_{max} = 510 nm with a shoulder at ≈650 nm (Fig. 4). In the presence of air this shoulder disappears. Gd(qu)₃ undergoes a decomposition in solution as indicated by a concomitant change of the absorption spectrum. The excitation band

![Fig. 1. Electronic absorption (a) and emission (b) spectrum of Gd(dtpaH₂). Absorption: ε = 2.6 × 10⁻² mol⁻¹ cm⁻¹; d = 1 cm; water. Emission: water; room temperature; λ_{exc} = 275 nm.](image-url)
of Gd(qu)₃ (Fig. 4) at λₘₐₓ = 370 nm matches nicely to the absorption of the complex.

4. Discussion

The complex Gd(dtpaH₂) is widely used and commercially available as a MRI agent for medical diagnosis. The dtpaH₂ ligand does not provide IL excited states at low energies owing to the absence of a conjugated π-electron system. Accordingly, the IL absorption of Gd(dtpaH₂) (Fig. 1) appears only at rather short-wavelength (λ < 265 nm). The metal-centered ff absorptions occur at longer wavelength. In particular, the structured absorption at λₘₐₓ = 273 nm is rather characteristic [2]. It is thus not surprising that Gd(dtpaH₂) does not exhibit an IL luminescence, but the typical narrow UV emission at λₘₐₓ = 312 nm which belongs to the spin-forbidden ⁶P₇/₂ → ⁸S₇/₂ ff transition of the Gd³⁺ ion [6]. Since it is associated with a multiplicity change of two it is equivalent with a phosphorescence (or triplet emission) of diamagnetic compounds.

The other chelates used in this work have their IL states available at energies well below the ⁶P₇/₂ ff state. The longest-wavelength absorption of Gd(hfac)₃, Gd(tta)₃ and Gd(qu)₃ at λₘₐₓ = 302, 337 and 368 nm, respectively, are assigned to the lowest-energy spin-allowed IL transition of the hfac [8], tta [8] and qu [14] ligand. Spin forbidden IL absorptions are not observed since they are apparently too weak.

As previously shown, Gd(hfac)₃ [8], Gd(tta)₃ [8] and Gd(qu)₃ [15] show an IL phosphorescence at low temperatures. Gd(qu)₃ displays an additional fluorescence at shorter wavelength [15]. However, singlet/triplet mixing in Gd(III) chelates is so strong that the IL phosphorescence of these chelates does not only appear at low temperatures but also under ambient conditions in analogy to the phosphorescence of many other complexes of heavy metals [16].

The greenish blue phosphorescence of Gd(hfac)₃ at λₘₐₓ = 470 nm and the green phosphorescence of Gd(tta)₃ at λₘₐₓ = 510 nm in fluid acetonitrile solution are very weak. In contrast, these emissions are quite strong if the compounds are incorporated in a rigid matrix (Figs. 2 and 3). Generally, Gd(III) complexes have variable coordination numbers, mainly six and nine. Accordingly, the chelate structures are certainly rather flexible. This flexibility may provide a channel for radiationless deactivation which is restricted in a rigid matrix. Besides, flexibility of the diketonate ligand itself might play a role.

In analogy to various other oxinates of heavy metals [17], Gd(qu)₃ shows a fluorescence and a phosphorescence at r.t. (Fig. 4). The red phosphorescence which appears as a shoulder at ≈650 nm is quenched by oxygen. The appearance of a r.t. phosphorescence in
solution which can be quenched by O₂ is a typical feature of heavy metal oxinates including the Th(IV) complex [17].

In summary, several Gd(III) chelates are characterized by a r.t. phosphorescence which extends from the UV to the red spectral region depending on the ligands. While the UV luminescence of Gd(dtpaH₂) originates from a metal-centered ff state, the bluish, green and red emissions of Gd(hfac)₃, Gd(tta)₃ and Gd(qu)₃, respectively, are of the IL type. Since these triplet emissions occur under ambient conditions, various applications are conceivable.

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References