First crystal structure of a Tb^{3+} complex derived from an aromatic hydroxamate ligand: sensitized luminescence properties

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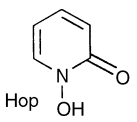
The neutral terbium complex $[Tb(op)_3]\cdot 3H_2O$ derived from the 1-hydroxy-2(1*H*)-pyridinone ligand displays a good luminescent quantum yield ($\Phi = 0.41$ in MeOD solution), due to an efficient energy transfer through the hydroxamate linkage. The coordination properties of the hydroxamate functionality were established by X-ray analysis.

New types of organo-chromophores capable of sensitizing lanthanide(III) emission are of great interest for designing lanthanide luminescent probes. The high potential of rare earth metal labels in analytical and clinical chemistry is now well established.[1] All luminescent lanthanide complexes of practical use contain two domains. A strongly binding domain ensures a high thermodynamic stability and the kinetic inertness of the complex in water solution, as well as shielding the ion from deactivating solvent molecules. The second domain contains an organic chromophore (sometimes referred to as an antenna)[2] that, to a great extent, determines the sensitivity of the probe. The function of the chromophore consists in absorbing light and transferring its excitation energy to the metal ion, thereby overcoming the intrinsic low absorption coefficients of the lanthanide ions. Although light-harvesters remote from the binding sites (*e.g.* phenyl or polyarene units) have been successfully employed to enhance, in some cases, the lanthanide emission,[3] light-harvesters with direct ligation to the metal ion[4] are preferentially used for practical biological purposes.[1]

On the other hand, it is noteworthy that the use of hydroxamate groups [CO–N(R)O^-] in luminescent lanthanide complexes has not been reported up to now, in spite of the high affinity of these binding units toward lanthanide ions.[5] So we have studied the behavior of a relatively simple compound, 1-hydroxy-2(1*H*)-pyridinone (Hop), to determine the



potential of efficient energy transfer to Tb^{3+} and Eu^{3+} from aromatic hydroxamate structures. In such a ligand system, the excited-state energy of the chromogenic moiety may be directly transferred to complexed lanthanide ions. Moreover, the hydroxamate functionality may provide a more rigid Ln(III) environment (Ln–O bonds are shorter than Ln–N ones), favoring radiative deexcitation processes. In addition, functionalization of the aromatic ring should enable the introduction of this chromophoric unit in a multidentate structure.

In methanol solution, the free ligand presents a $\pi \rightarrow \pi^*$ transition at 307 nm with a molar extinction coefficient of 4500 M^{-1} cm^{-1}. It also displays at room temperature a luminescence band at 395 nm assigned to a $^1\pi\pi^*$ state.[6] The ligand-centered luminescence is completely quenched in the $Ln(op)_3$ (Ln = Eu, Tb) complexes; instead, excitation in LC absorption bands results in the typical narrow emission bands of the Eu^{3+} and Tb^{3+} ions. Thus, the Tb complex exhibits a strong, structured luminescence in the visible region (highest energy band, 490 nm; highest intensity band, 548 nm), with a luminescence lifetime of 0.83 ms. The Eu complex shows a weaker, structured luminescence characteristic of the Eu^{3+} ion (highest energy band, 583 nm; highest intensity band, 616 nm), with a luminescence lifetime of 0.24 ms. The corrected excitation spectra are similar to the absorption bands of the complexes arising from the ligand groups (Fig. 1). These results support the view that an intramolecular energy transfer can take place from the oxypyridinone unit to bound Ln^{3+} in these complexes. In aqueous solutions, at room temperature we observed an important quenching of luminescence for the europium complex, while the terbium complex gives a reasonable luminescence lifetime of 0.69 ms. Therefore, in order to compare the properties of both complexes we limited our study in this preliminary communication to methanol solutions. An increase in the luminescence lifetimes was observed in methanol-d_1, revealing a quenching of the Ln^{3+} excited states by the O–H high-energy vibrational modes of the solvent. The solvation parameter calculated for the terbium complex ($q = 2.2$) indicates the presence of two coordinated hydroxylated molecules and is in agreement with the crystallographic results (*vide infra*). On the other hand, for the europium complex, only one methanol molecule ($q = 1.2$) should be present in the first coordination sphere of the metal ion.

In methanol, the quantum yields of luminescence emission with an excitation into the lowest energy ligand-centered

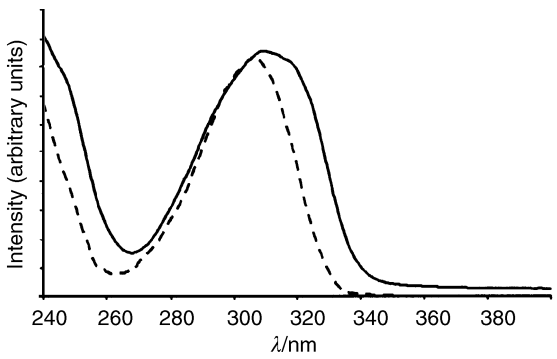


Fig. 1 Metal luminescence excitation spectra of the europium (——, $\lambda_{em} = 616$ nm) and terbium (– –, $\lambda_{em} = 548$ nm) complexes in methanol.

absorption band (310 nm) are 0.3 and 20% for the europium and terbium complexes. Upon solvent deuteration, they are increased to 0.8 and 41%, respectively. In light of the low luminescence lifetime ($\tau = 0.28$ ms) and quantum yield of the europium complex in CH_3OD, it appears that the non-radiative deactivation of the luminescent Eu^{3+} excited state by hydroxylated solvent molecules should be a minor phenomenon. As found in other Eu^{3+} complexes,[2] the main quenching pathway for this complex should be due to an efficient nonradiative deactivation by low-lying ligand-to-metal charge-transfer (LMCT) excited states. This quantum yield for the terbium complex is good and indicates a high energy of the $^3\pi\pi^*$ ligand-centered excited states in Hop, inducing a reduced back-transfer $Tb(^5D_4) \rightarrow {}^3\pi\pi^*$. The quantum yield is comparable and even higher than those reported for bipyridine branched macrocycles.[7] Further photochemical experiments are currently underway to better understand the role played by the various factors that determine the luminescent efficiency in these systems.

On the other hand, we would like to point out that these Eu^{3+} and Tb^{3+} complexes are photochemically stable. Unlike the free ligand Hop,[8] no homolytic N–O bond cleavage was observed upon prolonged irradiation at 310 nm of a methanol solution of these complexes.

Single crystals of the terbium complex suitable for X-ray structure analysis were obtained by slow evaporation from an aqueous solution (pH = 7) containing $TbCl_3$ and 3 equiv. of Hop. The crystal structure (Fig. 2) reveals that this Tb(III) complex has a structure with no crystallographically imposed symmetry. The terbium(III) ion is surrounded by eight oxygen atoms from three bidentate oxypyridinone ligands and two water molecules. A third water molecule, which is not bonded to the metal [the Tb–O distance is 4.518(3) Å] but hydrogen-bonded to a oxypyridinone moiety, is also found in the second coordination sphere of Tb(III). The corresponding effective ionic radius of Tb(III), estimated according to Shannon's definition[9] with $r_O = 1.32$ Å, amounts to 1.05 Å and corresponds well to the radius quoted for an eightfold coordination (1.04 Å).[10] The Tb–O_N and Tb–O_C bond lengths (2.37 ± 0.04 Å) are comparable with those observed in other complexes of terbium with ligands containing amide or *N*-oxide pyridine ligating groups. Finally, the small difference between the Tb–O_N and Tb–O_C bonds ($\leqslant$0.09 Å) is consistent with extensive charge delocalization on this aromatic ligand.

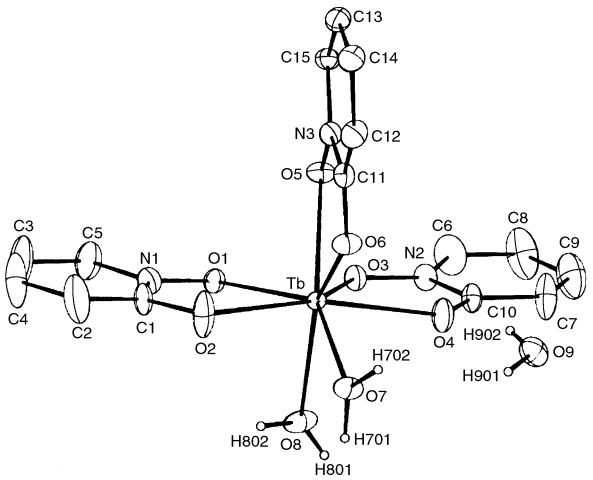


Fig. 2 An ORTEP drawing showing the coordination environment of the Tb(III) center in $[Tb(op)_3]$ (50% probability ellipsoids). Selected bond lengths (Å) and angles (°): Tb–O(1) 2.411(2), Tb–(O2) 2.315(2), Tb–O(3) 2.368(2), Tb–O(4) 2.376(2), Tb–O(5) 2.366(2), Tb–O(6) 2.370(2), Tb–O(7) 2.350(3), Tb–O(8) 2.434(3), Tb–O(9) 4.518(3); O(1)–Tb–O(2) 65.50(8), O(3)–Tb–O(4) 65.55(8), O(5)–Tb–O(6) 65.87(8), O(7)–Tb–O(8) 72.20(11).

In conclusion, we report for the first time a crystal structure of a lanthanide complex[11] derived from the aromatic hydroxamate ligand and we demonstrate that such a heterocycle can serve as a useful antenna for energy-transfer luminescence. Future work will be directed towards increasing the absorption efficiency of this bidentate ligand and to controlling the number of coordinated water molecules; this could be realized by incorporating these moieties into a supramolecular structure containing other lanthanide binding sites.

Experimental

Preparation of complexes

The Eu^{3+} and Tb^{3+} complexes were prepared in MeOH using a 3 : 1 Hop : metal ratio in the presence of 3 equiv. of NaOH as a base.

Terbium complex: $[Tb(op)_3]\cdot 3H_2O$. IR (KBr disc, ν/cm^{-1}): 1625 ($\nu_{C=O}$), 1526 ($\nu_{C=C}$), 1031 (ν_{N-O}). MS (ES^+, 5.0×10^{-5} M in MeOH): m/z 512 ($[Tb(op)_3Na]^+$, 100%). UV (MeOH) λ/nm (ε/M^{-1} cm^{-1}): 310 (12 000). Luminescence (MeOH) λ/nm [rel. int. (%)]: 490 (28), 548 (100), 588 (16), 621 (9), 654 (3). Anal. calc. for $C_{15}H_{12}N_3O_6Tb\cdot 3H_2O$: C, 33.16; H, 3.34; N, 7.73. Found: C, 33.25; H, 3.17; N, 7.64%.

Europium complex: $[Eu(op)_3]\cdot 2H_2O$. IR (KBr disc, ν/cm^{-1}): 1621 ($\nu_{C=O}$), 1525 ($\nu_{C=C}$), 1033 (ν_{N-O}). MS (ES^+, 5.0×10^{-5} M in MeOH): m/z 506 ($[Eu(op)_3Na]^+$, 100%). UV (MeOH) λ/nm (ε/M^{-1} cm^{-1}): 307 (16 800). Luminescence (MeOH) λ/nm [(rel. int. (%)]: 583 (1), 595 (7), 616 (100), 653 (4), 704 (14). Anal. calc. for $C_{15}H_{12}N_3O_6Eu\cdot 2H_2O$: C, 34.76; H, 3.11; N, 8.11. Found: C, 34.71; H, 3.04; N, 7.97%.

Luminescence data

The luminescence data of the complexes were determined at room temperature in 5.0×10^{-5} M methanol solution using a Perkin–Elmer LS-50B spectrofluorimeter equipped with a Hamamatsu R928 photomultiplier tube. Phosphorescence lifetimes (τ) were measured with the instrument in time-resolved mode, and are the average of at least three independent measurements.

The 'conventional' Horrocks equation[12] was used to determine q, the number of bound methanol molecules in lanthanide complexes: $q = A(\tau^{-1}_{MeOH} - \tau^{-1}_{MeOD})$, where A is 2.1 and 8.4 for the europium and terbium complexes, respectively, and τ^{-1} is the reciprocal excited-state lifetime, measured separately in MeOH and MeOD.

The quantum yields of the complexes were obtained by the method described by Haas and Stein,[13] using as standards $[Ru(bipy)_3]Cl_2$ ($\Phi = 0.028$ in water) and quinine sulfate ($\Phi = 0.546$ in 0.5 M H_2SO_4) for the europium and terbium complexes, respectively.

X-Ray structure determination

Data were collected at low temperature ($T = 140$ K) on a Stoe Imaging Plate Diffraction System (IPDS), equipped with an Oxford Cryosystems Cryostream cooler device and using graphite-monochromated Mo-Kα radiation. All hydrogen atoms were located on difference Fourier maps and refined with an idealized model, except for the hydrogen atoms of water molecules, their coordinates were refined with isotropic parameters.

$[Tb(op)_3]\cdot 3H_2O$, $C_{15}H_{18}N_3O_9Tb$, $M = 543.25$, triclinic, space group $P\bar{1}$, $T = 140(2)$ K, $a = 6.3087(11)$, $b = 11.7069(19)$, $c = 13.559(2)$ Å, $\alpha = 103.736(19)$, $\beta = 100.89(2)$, $\gamma = 104.556(19)°$, $U = 908.0(3)$ Å^3, $Z = 2$, $\mu = 3.950$ mm^{-1}, reflections collected/unique = 7818/2882, R(int = 0.0424, $R_1 = 0.0225$, $wR_2 = 0.0518$ for $I > 2\sigma(I)$.

CCDC reference number 440/199. See http://www.rsc.org/suppdata/nj/b0/b004288i/ for crystallographic files in .cif format.

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