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Permalink
https://escholarship.org/uc/item/8n92r26c

Journal
Journal of the American Chemical Society, 137(8)

ISSN
0002-7863

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Publication Date
2015-03-01

DOI
10.1021/ja5116524

Peer reviewed
New Insights into Structure and Luminescence of Eu\textsuperscript{III} and Sm\textsuperscript{III} Complexes of the 3,4,3-LI(1,2-HOPO) Ligand

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Supporting Information

ABSTRACT: We report the preparation and new insight into photophysical properties of luminescent hydroxypyridonate complexes [M\textsuperscript{III}L\textsubscript{4}]	extsuperscript{−} (M = Eu or Sm) of the versatile 3,4,3-LI(1,2-HOPO) ligand (L). We report the crystal structure of this ligand with Eu\textsuperscript{III} as well as insights into the coordination behavior and geometry in solution by using magnetic circular dichroism. In addition TD-DFT calculations were used to examine the excited states of the two different chromophores present in the 3,4,3-LI(1,2-HOPO) ligand. We find that the Eu\textsuperscript{III} and Sm\textsuperscript{III} complexes of this ligand undergo a transformation after in situ preparation to yield complexes with higher quantum yield (QY) over time. It is proposed that the lower QY in the in situ complexes is not only due to water quenching but could also be due to a lower degree of f-orbital overlap (in a kinetic isomer) as indicated by magnetic circular dichroism measurements.

Ligand-sensitized luminescent lanthanide(III) complexes have unique photophysical properties, which make them exciting candidates for a wide range of applications, including fluorescence-based bioassays; as has been extensively reviewed.\textsuperscript{1−5} We have shown that the 6-amide derivatives of 1-hydroxy-pyridin-2-one (1,2-HOPO) in tetradentate ligands form Eu\textsuperscript{III} complexes with high thermodynamic stability (p\textsubscript{Eu\textsuperscript{III}}\textsubscript{7.4} ≈ 18.6) and excellent photophysical properties (quantum yields up to 21.5%).\textsuperscript{6} This chromophore has also been previously shown to efficiently sensitize Sm\textsuperscript{III}. Studies of the aryl bridged tetradentate 1,2-HOPO ligands have shown that the geometries of the ligand backbones significantly affect the quantum yields of the corresponding europium complexes.\textsuperscript{7}

We have also recently confirmed the sensitization and emission efficiencies of these 1,2-HOPO complexes by time-resolved X-ray absorption near edge structure measurements at the Eu L\textsubscript{3} edge.\textsuperscript{8} Octadentate ligands, such as the branched H(2,2′)-1,2-HOPO ligand and the linear spermine linked 3,4,3-LI(1,2-HOPO) ligand (L\textsubscript{H4}), Scheme 1, form significantly more stable europium complexes (p\textsubscript{Eu\textsuperscript{III}}\textsubscript{7.4} > 21.2) than tetradentate 1,2-HOPO ligands.\textsuperscript{9,10} The 3,4,3-LI(1,2-HOPO) ligand (L\textsubscript{H4}) has been reported as an efficient actinide sequestration agent in vivo,\textsuperscript{11} however, the detailed coordination behavior toward Ln(III) and An(III) ions of this ligand are to date unknown.\textsuperscript{10−16} This ligand has also been discussed as a chelator for \textsuperscript{99}Zr radiotherapeutics.\textsuperscript{17} Abergel et al. recently demonstrated the capability of L to act as an effective chelator for Cm\textsuperscript{III} while also sensitizing Cm\textsuperscript{III} photoluminescence, with a long lifetime (383 μs) and a remarkable quantum yield in water (45%).\textsuperscript{18} Previously, the Eu\textsuperscript{III} and Sm\textsuperscript{III} complexes have been prepared in situ and QYs of 7.0 and 0.2% have been reported.\textsuperscript{9}

We propose that upon mixing L with Eu\textsuperscript{III} (and Sm\textsuperscript{III}) two isomers form, A and B. A is a kinetic product that slowly converts fully to the brighter thermodynamic isomer, B. The isolated complexes [ML\textsubscript{4}(C\textsubscript{5}H\textsubscript{6}N)]\textsubscript{2} were prepared by refluxing a 1:1 mixture of LH\textsubscript{4} and the corresponding M\textsuperscript{III} salt in methanol using pyridine as base, yielding the complexes as white solids. Experimental details and mass spectral data can be found in the Supporting Information (Figures S1−S3). X-ray-quality crystals of [EuL\textsubscript{4}](DMF) were obtained by slow diffusion of a mixture of THF and cyclohexane into a DMF solution containing the complex and KCl. As shown in Figure 1, a ML complex is formed, in which the Eu\textsuperscript{III} ion is coordinated to eight oxygen atoms from the four 1,2-HOPO units. In addition, a K+ ion and a highly ordered DMF molecule are present in the crystal lattice, which show intermolecular interactions with the [EuL\textsubscript{4}]− units to form a one-dimensional chain (Figures S4 and S5). The Eu−O distances in [EuL\textsubscript{4}]− range from 2.36 to 2.44 Å and are similar to previously reported tetradentate 1,2-HOPO complexes.\textsuperscript{6}

Crystallographic parameters and selected bond lengths can be found in Tables S1 and S2. There are two types of 1,2-HOPO units present within the ligand and Ln(III) complexes. Two of the 1,2-HOPO units are connected to the backbone by secondary amide groups (N\textsubscript{5}) and K+ ions (N\textsubscript{6}) in the crystal structure of this ligand with Eu(III) as well as insights into the coordination behavior and geometry in solution by using magnetic circular dichroism. In addition TD-DFT calculations were used to examine the excited states of the two different chromophores present in the 3,4,3-LI(1,2-HOPO) ligand. We find that the Eu(III) and Sm(III) complexes of this ligand undergo a transformation after in situ preparation to yield complexes with higher quantum yield (QY) over time. It is proposed that the lower QY in the in situ complexes is not only due to water quenching but could also be due to a lower degree of f-orbital overlap (in a kinetic isomer) as indicated by magnetic circular dichroism measurements.

Received: December 11, 2014
Published: January 21, 2015
and N8), which show intramolecular hydrogen bonding interactions (N—H···O ≈ 1.85 Å) with the adjacent O

The tertiary amide groups, however, display large torsion angles (ca. 62.1 and 64.0°) relative to the respective 1,2-HOPO planes, which partially breaks the aforementioned π-conjugation. Such dramatic differences highlight the importance of intramolecular N—H···O hydrogen bonding interactions for preorganization of the ligand. Gas-phase DFT ground state minimization (B3LYP/6-31G(d,p)) of [EuL]− closely matches the crystal structure. Only one of the four 1,2-HOPO units deviates significantly from its supersoned partner, which is likely due to crystal packing effects in the solid state, including interactions with the K+ ion and solvent (Figure S6). The shape measurements19 of the calculated and crystal structure yield slightly different results. While the crystal structure shows a slight preference for a C2v symmetry the calculated structure yields a dodecahedral (D2h) geometry for the coordinating oxygen atoms around the EuIII ion (Table S3).

For the isolated EuIII and SmIII complexes, quantum yields of 15.6% and 0.41% were measured in aqueous solution (λex = 325 nm). In addition, a new protocol reported here for the in situ preparation (the samples were prepared by combining L and MIII20 in TRIS buffer and measuring photophysical data no later than 10 minutes after mixing) yields similar yet slightly lower QYSs for [EuL]− and [SmL]− (14.0% and 0.39%, respectively). Notably the initially measured (T=0) luminescence QYSs of the in situ EuIII and SmIII complexes increased over time (2–4 h, Figure 2) to reach the values of the isolated complexes (Figures S9–S11). We do not attribute this effect to slow crystallization, since no luminescence from free ligand was observed. We conclude that the lower QY for the in situ generated complex is due to slow rearrangement of some fraction (a kinetic isomer) of the initially formed complex.

First-order luminescence decay measurements indicated that the quantum yield for EuIII and SmIII complexes increased over time (2 × 10−5–5 × 10−6 M) the luminescence lifetimes measured remained unchanged. The lifetimes were best fit to a mono exponential decay, consistent with but not conclusive of one species in solution. Intriguingly the measured lifetimes (τobs) in H2O and D2O for [EuL]− were longer than for [EuL]− in situ (Table 1). A slightly increased q value for the in situ complex could indicate that a portion of the formed complex (isomer A) leaves the EuIII sites open for coordination of a water molecule. A similar observation was found for [SmL]− where lifetimes in H2O and D2O for the isolated complex were longer (19.4 ± 0.1 and 180.9 ± 0.6 µs) than for the in situ complex (18.4 ± 0.1 and 155.0 ± 0.3 µs), respectively. The conversion of kinetic isomer A to the longer lived B is also provided by an experiment which showed that τobs of in situ generated complex converged toward the τobs of the isolated complex (Figure S12).

A close examination of the photophysical parameters was conducted for the EuIII complex, the parameters in Table 1 can be obtained from the ratio of the magnetic dipole transition (D0→F1) intensity to the total emission intensity, from which the radiative lifetime (τrad) can be estimated.21,22 Analysis showed that the metal and sensitization efficiencies ηrad and ηsens are similar within error for both methods of preparation (Table 1). The most significant difference is seen for knonrad, which is higher (792 s−1) for the in situ complex, thus the lower QY is attributed to increased rates of nonradiative quenching. The q value is higher (0.14) for the in situ complex but over time (∼2 h) reaches the value of the isolated complex (0.04), suggesting that some portion of the initially formed [EuL]− rearranges, and in the process displaces the quenching water molecule.

Upon comparison of the excitation and absorption spectra of [EuL]− and with the aid of TD-DFT calculations we also found that the chromophore absorbing at longer wavelength (NH-1,2-HOPO) is better at sensitizing EuIII than the one at shorter wavelength (N-1,2-HOPO, Figures S7, S8, and S13, Table S4). Consistent with the differences between the excitation and absorption spectrum, we observed that the quantum yield increases upon red-shifting the excitation wavelength.

An examination of the D0→F1 transition of isolated and in situ [EuL]− in TRIS buffer suggests, due to the splitting into three symmetrical peaks, a low symmetry in solution (Figure S14).23 To further analyze potential geometric differences that

![Figure 1. X-ray structure of [EuL]− (50% probability) without hydrogen atoms, except for the amide hydrogens (NH). Left, side on view; right, top view through C2 axis.](https://example.com/fig1)

![Figure 2. Increase of luminescence intensity of in situ generated [EuL]− (a) and [SmL]− (b) measured in TRIS (pH 7.4).](https://example.com/fig2)

Table 1. Photophysical Parameters for [EuL]− (λex = 325 nm)

| Parameter | Unit | Value |
|-----------|------|-------|
| krad | s−1 | 586 ± 60 |
| τrad | µs | 1705 ± 177 |
| ηrad | | 0.147 ± 0.004 |
| knonrad | s−1 | 2.7 × 10−6 |
| q | | 0.65 |
| τobs | µs | 792 ± 62 |

DOI: 10.1021/ja5116524
J. Am. Chem. Soc. 2015, 137, 2816–2819
might arise from the different preparation methods, we studied the magnetic circular dichroism spectra. A buffer/glycerol solvent system was unsuitable due to the poor solubility of [ML]− at high concentration, thus a 2:1 mixture of DMF and MeOH was used. The luminescence spectra of [EuL]− and [SmL]− were also recorded under these conditions and the absence of splitting of the 5D0→7F2 transition points to a higher symmetry than in buffer (Figure S15). Indeed, for both [EuL]_{isolated} and [EuL]_{in situ} a negative A-term around 465 nm, arising from the 5D2→7F0 transition, typical for D2g symmetry, was found (Figure 3, Figure S16). Remarkably, this is in accordance with the findings from shape analysis for the DFT calculated structure. In addition we also observed the 5L6→7F0 transition. While both methods of preparation yield similar MCD spectra, the relative intensities (based on the normalized 5L6→7F0 transition) are different (for the in situ prepared complex the 5D2→7F0 MCD transition is ~16% less intense). For octahedral EuIII complexes the intensity ratio between the 5L6→7F0 and 5L6→7F2 transitions has been used to describe the degree of f-orbital overlap. If this concept is transferred to the MCD of [EuL]− it could suggest a higher degree of orbital overlap for [EuL]_{isolated}.

Combining the results from magnetic circular dichroism and the luminescence quantum yield and lifetime measurements it appears that for maximal quantum yields and optimal water shielding, complex preparation plays a crucial role. In order for L3− to fully coordinate the metal ion with all four HOPO units the complexes should be isolated prior to luminescence measurements. We propose that the lower QY in the in situ complex is not only due to water quenching but could also be due to a lower degree of f-orbital overlap (in the kinetic isomer) as indicated by magnetic circular dichroism measurements. We are currently investigating if this technique, combined with luminescence measurements, could be potentially used to probe a Dexter mechanism of energy transfer.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures, crystal structure parameters, DFT calculation details, and mass spectral and photophysical data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare the following competing financial interest(s): This technology is licensed to Lumisphere, Inc., in which K.N.R. has a financial interest.

■ ACKNOWLEDGMENTS

We thank Benjamin Allred, Manuel Sturzbecher-Hoehne, and Jide Xu for helpful discussions. The ligand 3,4,3-LI(1,2-HOPO) that was used for growing X-ray-quality crystals of K[EuL] was a kind donation from Dr. Rebecca Abergel at LBNL and prepared by Ash Stevens, Inc. (Detroit, MI, Lot ML-11-276). This research is supported by U.S. Department of Energy at LBNL under Contract No. DE-AC02-05CH11231 and NIH grant HL069832. L.J.D. is grateful for a scholarship of the Alexander von Humboldt Foundation. E.S. acknowledges support from the NSF (CHE-1560046), and B.E.R.S. acknowledges support from the Munger, Pollock, Reynolds, Robinson, Smith & Yocedieck Stanford Graduate Fellowship. The Small Molecule X-ray Crystallography Facility is supported by NIH Shared Instrumentation Grant S10-RR027172, and the Molecular Graphics and Computation Facility wishes to acknowledge the NSF CHE-0233882 and CHE-0846505 grants.

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Figure 3. Observed MCD transitions for [EuL]_{isolated} and [EuL]_{in situ} measured in DMF:MeOH (2:1) at 7 T and 250 K.
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