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Ligand-Centered Near-Infrared Luminescence from Lanthanide Complexes with Chelating Nitronyl Nitroxide Free Radicals

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Several lanthanide complexes with free radical ligands have been prepared and characterized recently.[1−4] These compounds show a wide variation of magnetic properties, illustrated by gadolinium(III) complexes, for which both ferromagnetic[1,4] and antiferromagnetic[2,3] interactions between the unpaired electrons on the ligand and on the lanthanide center are observed. The nature of this ground-state magnetic coupling has been investigated in detail by comparing complexes with free radical and related diamagnetic ligands.[4]

The excited electronic states and the luminescence properties of these new lanthanide complexes have not been explored. Electronic emission and absorption spectroscopy is used to gain insight on the ground and lowest-energy excited states of a series of new complexes of the nitronyl nitroxide radical shown in Chart 1 (denoted as NITBzImH here) with trivalent lanthanum, europium, and gadolinium ions. We describe the preparation, crystal structure, and solid-state luminescence spectroscopy of the lanthanide-radical complexes, and we compare the results to the spectra of the free ligand. The magnetic properties of all materials have been measured and will be reported and analyzed in a comprehensive study.

Complexes of formula [Ln(III)(NITBzImH)$_2$(NO$_3$)$_3$] (Ln = La, Gd, Eu) were synthesized as air-stable single crystals by slowly evaporating a solution mixture of NITBzImH, prepared as described in ref 5, with stoichiometric amounts of [Ln(III)(NO$_3$)$_3$-(H$_2$O)$_n$] in ethanol.[6] These compounds are isostructural and crystallize in the noncentrosymmetric group *Pna*2$_1$.[7] A view of the molecular structure is shown for the gadolinium complex in Figure 1. The lanthanide ion is coordinated by two nitronyl nitroxide ligands through one oxygen atom of the NO groups and one nitrogen atom of the benzimidazole moiety. The two radicals are not symmetry-related. Three nitrate anions in η^2 mode complete the coordination sphere to a coordination number of 10. Similar molecular structures have been previously reported for lanthanide complexes with a closely related nitronyl nitroxide radical substituted with a triazole group.[1,4]

Chart 1. NITBzImH Ligand

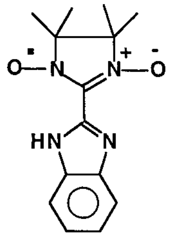

Figure 2 summarizes the luminescence properties of the free NITBzImH ligand and the three lanthanide complexes. All luminescence measurements were made with crystalline samples on instruments described in detail before.[8,9] The onset of the lowest-energy absorption band for all four solids is included in Figure 2 for comparison.

The luminescence spectra of the solid ligand are given at 5 and 50 K at the bottom of Figure 2. The ligand shows a well-defined luminescence onset at 14 700 cm^{-1}. The spectrum is less resolved than the absorption spectrum and less resolved than the luminescence spectra of the lanthanide complexes. The luminescence onset coincides with the lowest-energy absorption, indicating that the observed luminescence does not arise from deep traps. The 5 K absorption spectrum shows vibronic maxima separated by 230 ± 20 cm^{-1}. The first peak is most intense, its structure most likely corresponds to a short vibronic progression in a low-frequency mode.

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(6) All three complexes were unambiguously authenticated on the basis of elemental analysis, crystal structure, and powder X-ray diffraction. Anal. Found/Calcd for **1** (C$_{28}$H$_{34}$N$_{11}$O$_{13}$La): C, 38.36/38.60; H, 4.16/3.93 N, 17.29/17.68; La, 16.04/15.94. Anal. Found/Calcd for **2** (C$_{28}$H$_{34}$N$_{11}$O$_{13}$-Gd): C, 37.32/37.79; H, 3.93/3.85; N, 16.98/17.31; Gd, 17.17/17.67. Anal. Found/Calcd for **3** (C$_{28}$H$_{34}$N$_{11}$O$_{13}$Eu): C, 37.76/38.00; H, 4.16/3.90; N, 16.93/17.40; Eu, 16.72/17.20.

(7) Crystal data: BRUKER SMART CCD diffractometer equipped with a normal focus molybdenum-target X-ray tube. The data were processed through the SAINT reduction and SADABS absorption software packages, and the structures were solved with the SHELXTL software.[16] **1**. C$_{28}$H$_{34}$N$_{11}$O$_{13}$La, MW = 871.57, dark-blue parallelipipedal, orthorhombic, space group *Pna*2$_1$ (No. 33), a = 19.500(1) Å, b = 13.0582(8) Å, c = 14.5741(9) Å, Z = 4, V = 3711.1(4) Å^3, 22 715 reflections measured, 8875 independent reflections ($R_{\rm int}$ = 0.0609), $R(F)$ = 0.0331 ($I > 2\sigma(I)$), wR(F^2) = 0.1146 (all data). **2**. C$_{28}$H$_{34}$N$_{11}$O$_{13}$Gd, MW = 889.91, dark-blue parallelipipedal, orthorhombic, space group *Pna*2$_1$ (No. 33), a = 19.183(1) Å, b = 13.1600(7) Å, c = 14.4107(7) Å, Z = 4, V = 3638.0(3) Å^3, 22 941 reflections measured, 7728 independent reflections ($R_{\rm int}$ = 0.0370), $R(F)$ = 0.0206 ($I > 2\sigma(I)$), wR(F^2) = 0.0625 (all data). **3**. C$_{28}$H$_{34}$N$_{11}$O$_{13}$Eu, MW = 884.62, dark-blue parallelipipedal, orthorhombic, space group *Pna*2$_1$ (No. 33), a = 19.210(1) Å, b = 13.1447(7) Å, c = 14.4200(7) Å, Z = 4, V = 3641.4(3) Å^3, 13 092 reflections measured, 4769 independent reflections ($R_{\rm int}$ = 0.0519), $R(F)$ = 0.0347 ($I > 2\sigma(I)$), wR(F^2) = 0.1048 (all data).

(8) Luminescence was excited with a 150 W Xe lamp filtered through a copper sulfate solution and a Schott BG 18 filter, leading to an excitation wavelength range from 300 to 400 nm. All samples were cooled in a helium-gas-flow cryostat. The emitted light was dispersed by a 0.75 m monochromator and detected by a cooled Hamamatsu R928 photomultiplier and a photon-counting system. All spectra reported here are not corrected for system response. Absorption spectra were measured with a Cary 5E spectrometer.

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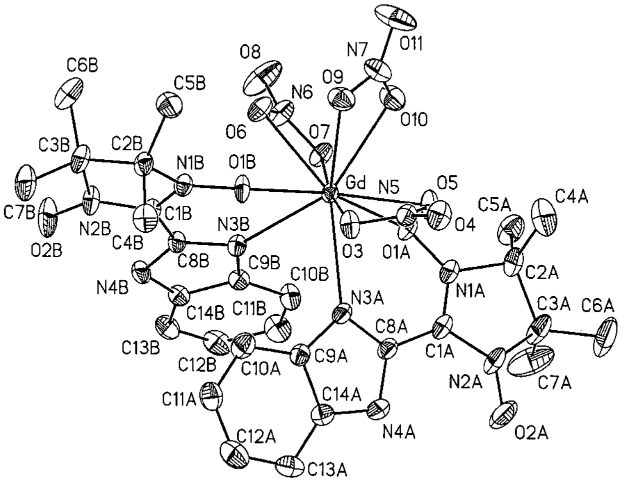

Figure 1. Representation of $Gd(NITBzImH)_2(NO_3)_3$ with thermal ellipsoids at the 30% probability level.

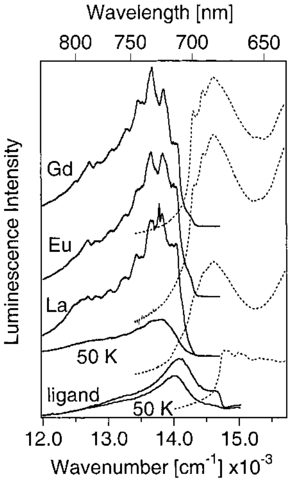

Figure 2. Top to bottom: luminescence (solid lines) and absorption spectra (dotted lines) of $Gd(NITBzImH)_2(NO_3)_3$, $Eu(NITBzImH)_2(NO_3)_3$, $La(NITBzImH)_2(NO_3)_3$, and NITBzImH (ligand). All spectra were measured at 5 K unless indicated otherwise in the figure.

The La complex shows a structured low-temperature luminescence spectrum with an onset at 14 300 cm^{-1}, lower in energy by 400 cm^{-1} than for the free ligand. The absorption band shows a corresponding shift to lower energy. Resolved structure with an average interval of 200 ± 20 cm^{-1} is observed in luminescence at 5 K, compared to the shoulders separated by 170 ± 20 cm^{-1} in absorption. This energy difference is smaller than for the free ligand, and the intensity distribution is distinctly different: the main intensity of the ligand spectrum is at the first peak of the progression, in contrast to all lanthanide complexes, where the main intensity occurs after the second member of the progression in absorption and at approximately the third member of the progression in the resolved luminescence spectra. Figure 2 shows that the luminescence spectra of the lanthanide complexes have a larger overall width than the band of the uncoordinated ligand, indicating that distortions along low-frequency normal coordinates that are absent for the ligand occur for the lanthanide complexes. A likely reason for all these observations is that the change of the π-electron density within the ligand caused by the electronic transition influences metal−ligand bonding and leads to progressions in low-frequency metal−ligand modes, which are not observed in the spectrum of the free ligand. The electronic structure of a model nitronyl nitroxide related to the ligand in Chart 1 has been explored by detailed density functional calculations[10] and qualitatively illustrates these changes of π-electron density involving both the nitronyl nitroxide and imidazole groups of the ligand. The lowest-energy electronic transition of the free ligand has been classified as $n \rightarrow \pi^*$.[11] The spectra of the lanthanide complexes in Figure 2 occur in a very similar energy range as for the uncoordinated ligand, and we conclude that this qualitative overall assignment still applies. The resolved spectra of the lanthanide complexes in Figure 2 reveal the influence of metal−ligand bonding.

The luminescence spectra of the europium and gadolinium complexes are similar to those of the lanthanum compound. Their onsets show an additional weak shoulder at 14 400 cm^{-1}, and the positions of their vibronic maxima vary slightly. A well-resolved low-energy progression with an interval of 190 ± 10 cm^{-1} is observed in the absorption spectra of both the europium and gadolinium complexes. These progressions are again longer than for the uncoordinated ligand. The luminescence of the three metal complexes becomes weaker with temperature, as illustrated by the comparison of the 5 and 50 K spectra for the La complex in Figure 2, but it can still be measured at room temperature.

To our knowledge, Figure 2 depicts the first luminescence spectra of a nitronyl nitroxide ligand and its lanthanide complexes. The spectra show more resolution than observed in the absorption spectra of transition metal complexes with nitronyl nitroxide ligands.[12,13] Detailed absorption, magnetic circular dichroism (MCD), and Raman spectra have been reported for octahedral (β-diketonato)nickel(II) complexes with one nitronyl nitroxide ligand.[14] A luminescence maximum at 12 000 cm^{-1} is mentioned for $Cr(acac)_2(NIT2\text{-}pyridine)$,[15] significantly lower in energy than the onset of the ligand absorption and the luminescence spectra shown in Figure 2.

The luminescence spectra of lanthanide complexes with nitronyl nitroxide ligands correspond to ligand-centered transitions. Their resolved vibronic structure is affected by the lanthanide coordination. We will further explore the potential of the title compounds as materials with combined optical and magnetic properties.

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