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Crystal Structure and Luminescence of Lanthanide Monodentate Complexes $[Ln(C_4N_4H_6O)_2(H_2O)_6]Cl_3$ and $[Ln(C_4N_4H_6O)_2(H_2O)_3(NO_3)_3]$ (Ln = Tb or Eu)

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New eight- and nine-coordinate luminescent europium(III) and terbium(III) complexes **1**–**4** with carbonyl group coordination have been prepared using the monodentate ligand (**L**) 2,4-diamino-6-hydroxy pyrimidine and characterized by X-ray and spectroscopic methods.

The burgeoning interest in the study of lanthanides (Ln^{3+}), due to their unique characteristic properties, varied topologies, and potential use in a vast range of applications, has provided an expanding frontier in materials science.[1,2] This study reports an unusual monodentate coordination mode of Ln^{3+} via a carbonyl group and explores the structural and spectroscopic ramifications.

Direct reaction of the lanthanide chloride or nitrate salts gave complexes **1**−**4** (with molecular structures shown in Figure 1) in yields above 76%.[3] Upon evaporation, complexes **1** and **4** crystallized as single crystals that were isolated and examined by X-ray diffraction. Under the stated reaction conditions, the ligand undergoes tautomerization in the aromatic ring to form a carbonyl functional group that coordinates with the lanthanide ions. The crystal structure shows that the H atom has migrated from O in the ligand to N in the complex. Hence, the complex also shows the typical behavior associated with Ln^{3+} with the preference for Ln−O over Ln−N bonding. The two complexes, **1** and **2**, formed from the lanthanide chloride precursor contain metal centers that are coordinated not with chloride ions, but instead with six water molecules and two ligands that are arranged in a trans orientation to minimize steric hindrance. On the other hand, for the nitrate salts **3** and **4**, two of the original three nitrates are still attached to the Ln^{3+} center, hence reducing the number of coordinated water molecules.

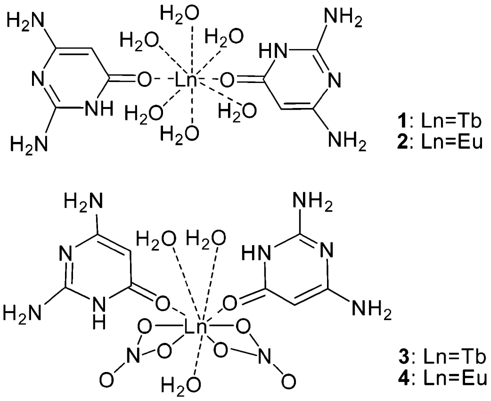

Figure 1. Molecular structures of the cations in complexes **1**−**4**.

For **1** and **2** in Figure 1, each Ln^{3+} ion (Tb in **1** and Eu in **2**) is coordinated by two pyrimidine groups separately with six water molecules in a distorted bicapped trigonal prism to give a coordination number of eight. The two capping ligands are also distorted. Although extensive intermolecular hydrogen bonding gives rise to a polymeric-like chain linked by the coordinating water molecules, there is no intramolecular hydrogen bonding within the complexes. For **3** and **4**, each Ln^{3+} ion (Tb in **3** and Eu in **4**) is coordinated by two pyrimidine groups separately and is doubly coordinated by two nitrate ions with three water molecules to give a coordination number of nine. Hence, the europium ion of complex **4** differs from the terbium ion of complex **1**, which exhibits eight coordination. This difference, arising from the use of a nitrate instead of a chloride salt, is because the metal center is coordinated with three water molecules and two ligands, yet has two nitrate groups still attached. In all cases, the ligand (pK_a 5.4) is not deprotonated because it exists in the acid/base forms in a 5:1 ratio at the solution pH (6.1) employed. The single-crystal X-ray diffraction structures of the cations in **1** and **4** are illustrated in Figure 2a and b.[4] In both **1** and **4,** the shortest M−O bonds are those toward the pyrimidines, followed by the longer $M-OH_2$, and yet longer $M-ONO_2$ bonds.

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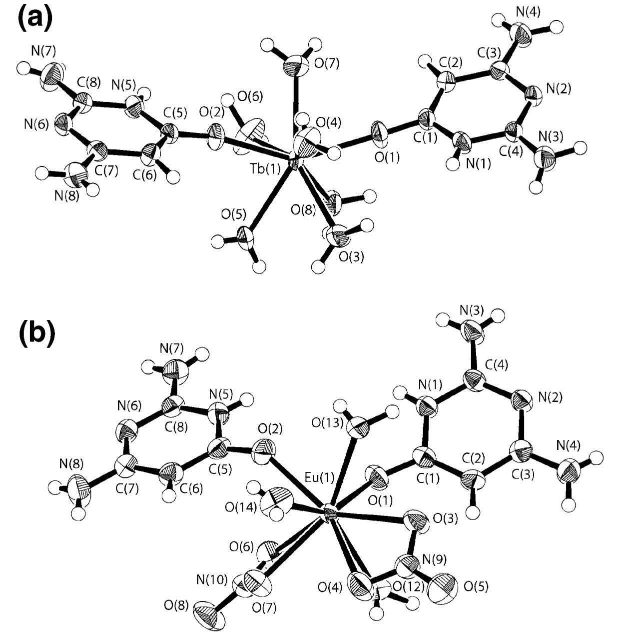

Figure 2. ORTEP drawing of cation coordination in (a) **1** and (b) **4**.

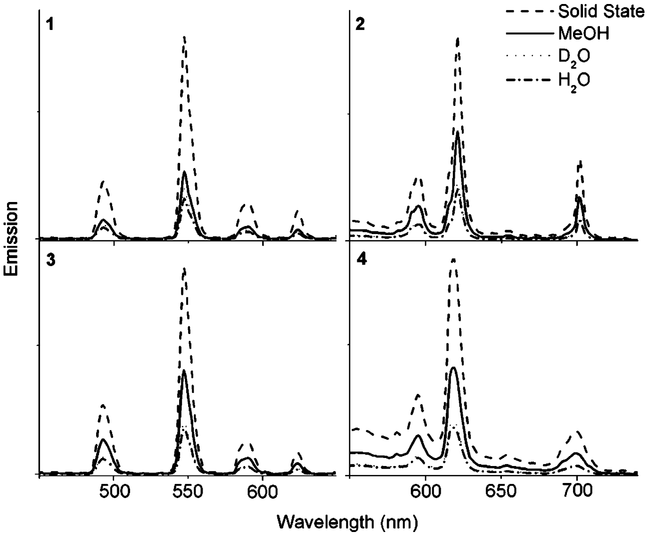

Figure 3. 325-nm excited emission spectra of **1**−**4** in the solid state and in various solvents (10^{-5} M) at room temperature.

Characterization of the complexes was carried out by FT-IR spectroscopy, thermogravimetric analysis (TGA), and UV absorption spectroscopy. The IR vibrational spectra are complex, and at least four features are resolved in each of the regions near 1650 and 3100−3500 cm^{-1}, corresponding to X−H (X = N, O) bending and stretching modes, with the ν(C═O) mode contributing most of the intensity at the former energy. Most IR bands shift by several wavenmbers in complexes **1**−**4** compared to ligand **L**, and a clear distinguishing feature between the pairs **3**, **4** and **1**, **2** is the strong ν_d(NO) nitrate mode in the former complexes at 1384 cm^{-1}. TGA of the powders of complexes **1**−**4** under a N_2 atmosphere showed two mass-loss steps. Approximately 17.8% (**1** and **2**) and 9% (**3** and **4**) of the mass is lost in the first step, which is already underway at room temperature and terminates abruptly at approximately 118 °C. This agrees with the calculated mass losses for the water molecules as follows: **1**, 16.8%; **2**, 17.0%; **3**, 8.4%; and **4**, 8.2%. A second, less abrupt step, which is the major decomposition, sets in above 380 °C. UV−visible absorption spectra of complexes **1**−**4** were recorded in the range 200−1100 nm in MeOH, D_2O, and H_2O at 298 K. Ligand **L** exhibits an intense band near 260 nm due to the pyrimidine ring, which is slightly red-shifted in the complexes: for the terbium complexes **1** and **3** in various solvents, it appears at 267 and 271 nm, respectively.[5,6] The positions of the absorption bands are almost independent of the solvent employed so that the coordination of the terbium or europium ions with the pyrimidine ring is not affected by the change of solvent.

Low-resolution 325-nm excited emission spectra of **L** and **1**−**4** were recorded in the region 350−800 nm at room temperature. **L** exhibits a broad feature (fwhm ≈ 40 nm) peaking at 378 nm, with a tail to longer wavelength. **1** and **3** exhibit characteristic $^5D_4 \rightarrow {}^7F_J$ (J = 6−0), and **2** and **4** exhibit $^5D_0 \rightarrow {}^7F_J$ (J = 0−6) f−f electron luminescence in solution and in the solid state (Figure 3).

At room temperature, the ligand emission (with lifetimes of 18 ns for **2** and 13 ns for **4**) is partially quenched and

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(3) **1 and 2.** 2,4-Diamino-6-hydroxy pyrimidine (**L**) (0.5 g, 3.96 mmol) was added to MeOH (25 mL) to give a cream solution. Upon addition of hydrated terbium chloride (**1**, 0.74 g, 1.98 mmol) or hydrated europium chloride (**2**, 0.74 g, 1.98 mmol), the solution changed to a clear yellow solution that was stirred for 24 h. The reaction in a 2:1 ratio afforded complexes **1** and **2** in high yields (**1**, 1.12 g, 90.4%; **2**, 1.03 g, 81.6%). Single, medium yellow crystals of the terbium complex suitable for X-ray study and microanalysis were obtained by slow evaporation from methanol. **1**: Anal. Found: C, 15.38; H, 3.85; N, 17.89. Calcd for $[Tb(C_4N_4H_6O)_2(H_2O)_6]Cl_3$: C, 15.35; H, 3.84; N, 17.91. IR (KBr, cm^{-1}): 3446, 3331, 1642, 1485, 1465, 1351, 1309, 1257, 994, 800, 755, 688. ESI-MS *m*/*z*: 625.5 [M], 519 [M − 3Cl], 411 [M − 3Cl − 6H$_2$O]. **2**: Anal. Found: C, 15.57; H, 3.88; N, 18.12. Calcd for $[Eu(C_4N_4H_6O)_2(H_2O)_6]Cl_3$: C, 15.53; H, 3.91; N, 18.11; IR (KBr, cm^{-1}): 3447, 3330, 1640, 1484, 1464, 1350, 1309, 1256, 994, 801, 687. ESI-MS *m*/*z*: 618.5 [M], 512 [M − 3Cl], 404 [M − 3Cl − 6H$_2$O). **3 and 4. L** (0.5 g, 3.96 mmol) was added to MeOH (25 mL) to give a cream solution. Upon addition of the hydrated terbium nitrate (**3**, 0.90 g, 1.98 mmol) or hydrated europium nitrate (**4**, 0.88 g, 1.98 mmol), the solution changed to a clear solution. The resulting solution was stirred for 24 h. The reaction in a 2:1 ratio afforded complexes **3** and **4** in high yields (**3**, 0.98 g, 76.0%; **4**, 1.16 g, 91.0%). Single, medium yellow crystals of the europium complex suitable for X-ray study and microanalysis were obtained by slow evaporation from methanol. **3**: Anal. Found: C, 14.76; H, 2.75; N, 23.65. Calcd for $[Tb(C_4N_4H_6O)_2(H_2O)_3(NO_3)_3]$: C, 14.75; H, 2.79; N, 23.66. IR (KBr, cm^{-1}): 3442, 3353, 1642, 1384. ESI-MS *m*/*z*: 651 [M], 597 [M − 3H$_2$O], 535 [M − 3H$_2$O − NO$_3$], 473 [M − 3H$_2$O − 2NO$_3$], 411 [M − 3H$_2$O − 3NO$_3$]. **4**: Anal. Found: C, 14.91; H, 2.83; N, 23.92. Calcd for $[Eu(C_4N_4H_6O)_2(H_2O)_3(NO_3)_3]$: C, 14.91; H, 2.82; N, 23.91. IR (KBr, cm^{-1}): 3442, 3353, 1642, 1479, 1465, 1384, 1256. ESI-MS *m*/*z*: 644 [M], 590 [M − 3H$_2$O], 528 [M − 3H$_2$O − NO$_3$], 467 [M − 3H$_2$O − 2NO$_3$], 404 [M − 3H$_2$O − 3NO$_3$]. **L**: IR (KBr, cm^{-1}): 3431, 3353, 3240, 3168, 1653, 1497, 1467, 1376, 1303, 1249, 983, 783.

(4) Crystal data for **1**: $[Tb(C_4N_4H_6O)_2(H_2O)_6]Cl_3$, $M = 625.61$, triclinic, $P\bar{1}$ (No. 2), $a = 9.084(5)$ Å, $b = 10.772(8)$ Å, $c = 12.959\ (8)$ Å, $V = 3775(1)$ Å^3, $T = 298$ K, $Z = 2$, μ(Mo Kα) = 55.224 cm^{-1}, 26 158 reflections measured, 5130 unique ($R_{int} = 0.048$), 4829 observed reflections [$I > 2\sigma(I)$] were used in all calculations. F to $R = 0.032$, $R_w = 0.038$. CCDC 242 135. Crystal data for **4**: $[Eu(C_4N_4H_6O)_2(H_2O)_3(NO_3)_3]$, $M = 644.26$, triclinic, $P\bar{1}$ (No. 2), $a = 6.814(2)$ Å, $b = 10.659(3)$ Å, $c = 16.074\ (5)$ Å, $V = 1105.6$ Å^3, $T = 298$ K, $Z = 2$, μ(Mo Kα) = 55.224 cm^{-1}, 26 158 reflections measured, 5130 unique ($R_{int} = 0.048$), 4829 observed reflections [$I > 2\sigma(I)$] were used in all calculations. F to $R = 0.019$, $R_w = 0.024$. CCDC 251900.

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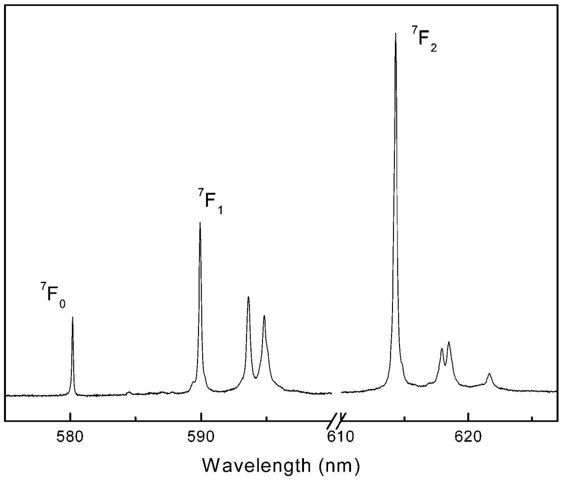

Figure 4. Selected transitions in the 355-nm excited $^5D_0$ 10 K emission spectrum of **4**. Terminal states are marked. The ordinate is emission.

red-shifted upon complexation. The 298 K emission lifetimes of the lanthanide ion emissions ($^5D_4$ for Tb^{3+} and $^5D_0$ for Eu^{3+}) in the solid complexes are (in ms): **1**, 0.6; **2**, 0.6; **3**, 2.7; and **4**, 1.8. The quantum efficiencies are 0.24 for **1**, 0.22 for **2**, 0.36 for **3**, and 0.33 for **4**, and they decrease by more than an order of magnitude for the complexes in 10^{-5} M aqueous solution. However, because the ESI-MS spectra show parent ion peaks corresponding to the complexes and the emission spectra (Figure 3) are essentially unchanged from the solid state to aqueous solution, it is reasonable to assume that the complexes remain intact in aqueous solutions even at such low concentrations. The complexes are excited more efficiently by 325-nm radiation than by 270-nm radiation, although the ligand singlet-state absorption corresponds to the latter.

Low-temperature emission spectra were also recorded in an effort to investigate the $2J + 1$ crystal-field levels of each $^{2S+1}L_J$-multiplet term and to obtain an independent assessment of the Ln^{3+} ion environment. Although there are two Ln^{3+} ions in the Bravais cell of each **1**−**4**, these ions are symmetry-related by an inversion center, and each has C_1 site symmetry. It is then expected that pure electronic transitions are electric-dipole-allowed at this site symmetry, but that the $|\Delta J| = 1$ transitions of Eu^{3+} also have appreciable magnetic dipole intensity.[7] We focus here on the emission spectra of **4**, which were the most clearly resolved at 10 K, but similar conclusions concerning the site symmetry of Ln^{3+} apply to the other complexes as well.

Figure 4 shows part of the 355-nm excited 10 K emission spectrum of **4** corresponding to the $^5D_0 \rightarrow {}^7F_J$ ($J = 0, 1, 2$) transitions. Only one sharp, medium-intensity band (17 237 cm^{-1}) is observed for the $^5D_0 \rightarrow {}^7F_0$ zero-phonon line, thus confirming not only the noncentrosymmetry of Eu^{3+} but also the presence of only one type of Eu^{3+} site in the unit cell. It is interesting that, under 355-nm excitation, luminescence is also observed from the three closely spaced $^5D_1$ crystal-field levels as well as from $^5D_0$, although the energy gap between these two terms is only 1740 cm^{-1} and can be spanned by one phonon of the ligand. All of the emission bands in the spectrum of **4** between 500 and 850 nm have been assigned to pure electronic transitions of Eu^{3+} [with the derived ^5D_J ($J = 0,1$) and ^7F_J ($J = 0-6$) energies listed in the Supporting Information], with the exceptions of some very weak features that correspond to electronic transitions of Tb^{3+} impurity. The crystal-field splittings of $^7F_1$ and $^7F_2$ are greater in **2** than in **4**.

In conclusion, four lanthanide complexes have been synthesized and characterized by X-ray and spectroscopic methods that have two pyrimidine ligands and three or six coordinated water molecules. The coordination in **1** and **2** is reminiscent of that in the $[Tb(H_2O)_6(QzS)]^+$ cation,[8] which also contains six water molecules. However, the one QzS (quinizarine-2-sulfonate) ligand is bidentate, whereas there are two trans ligands in the present case. The Ln−O distances are standard[9,10] and average about 0.08 Å longer in the nine- compared to the eight-coordinate complexes. Complexes **1**−**4** are water-soluble, and all exhibit luminescence in the solid state and in aqueous and methanolic solutions.

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Supporting Information Available: Descriptions of measurements; IR, UV−vis, MS, excitation, and emission spectra; and H-bonding is available free of charge via the Internet at http://pubs.acs.org. Crystallographic information is available as records CCDC 251900 and CCDC 242135 from The Cambridge Crystallographic Data Centre (CCDC). These data can be obtained free of charge from the CCDC via the Web link www.ccdc.cam.ac.uk/data_request/cif.

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