Communication

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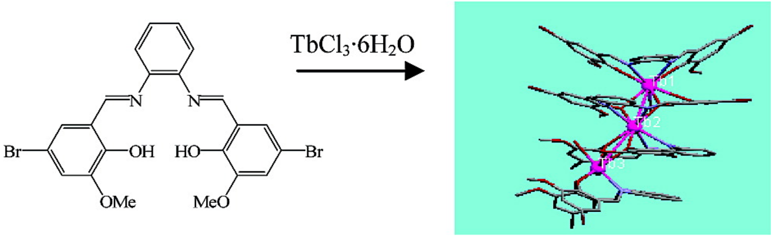

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Anion Dependent Self-Assembly of “Tetra-Decker” and “Triple-Decker” Luminescent Tb(III) Salen Complexes

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Polynuclear lanthanide complexes with distinct magnetic and luminescent properties are currently of interest for use in applications involving the fabrication of novel materials and as probes in biological systems.[1] For example, Eu^{3+} and Tb^{3+} are attractive luminescent centers due to their long-lived $^5D_0$ and $^5D_4$ excited states and their large Stokes’ shifts. However, the photophysical properties of these ions depend markedly on their environments. For efficient emissions, chromophoric ligands are often employed to transfer absorbed energy efficiently to the lanthanide ion. They should also be capable of protecting the Ln(III) center from solvent molecules which can quench emissions. A variety of multidentate cyclic and acyclic ligands designed to encapsulate lanthanides are known.[2] Recently, the use of phthalocyanines and porphyrins by Ishikawa and co-workers enabled the synthesis of several so-called “double-decker” or “triple-decker” lanthanide complexes, described as “stacked π-conjugate molecules”.[3] Since a multi-decker framework could be effective in keeping solvent and water molecules away from Ln(III) centers, it seemed reasonable to assume that enhanced luminescent properties could be achieved with these types of architectures. As part of our ongoing interest in luminescent lanthanide complexes,[4] we describe here the synthesis, structures, and photophysical properties of two multi-decker trinuclear Tb(III) complexes (**1** and **2**) which are formed with the Schiff base ligand *N*,*N*′-bis(5-bromo-3-methoxysalicylidene)phenylene-1,2-diamine (H_2L). Although numerous lanthanide derivatives of salen-type ligands have been described, many are poorly characterized with speculative structures proposed on the basis of elemental compositions and spectroscopic data.[5] Few structures of polynuclear lanthanide derivatives of salen-type ligands are known.[6] This paper describes definitive structural details of the interactions between Tb(III) and salen-type Schiff base ligands. These interactions occur between both N_2O_2 and O_2O_2 ligand donor sets and the metals. Furthermore, intramolecular $\pi-\pi$ interactions between aryl groups lead to unusual multi-decker stacked configurations.

Reaction of H_2L with $TbCl_3{\cdot}6H_2O$ (4:3) in an acetonitrile/methanol mixture resulted in the formation of the trimetallic tetra-decker complex $[Tb_3L_4(H_2O)_2]Cl$ (**1**) in 40% yield.[7] A view of the cationic moiety of **1** and skeletal view of the N and O donor framework are shown in Figure 1. The two outer Tb^{3+} ions, Tb(1) and Tb(3), have similar nine-coordinate environments comprising the N_2O_2 donor set of the outer L group, the O_2O_2 set of one inner L group and one H_2O molecule. The central Tb(2) ion has an eight-coordinate pseudo-square-based antiprismatic geometry formed by the two N_2O_2 donor sets of the internal L ligands. The phenolic oxygen atoms of the interior L group are bridging, while those of the outer L are monodentate. The Tb−Tb separations are similar at 3.884 and 3.872 Å for Tb(1)−Tb(2) and Tb(2)−Tb(3), respectively. The valence requirements for **1** are satisfied by the presence of a single uncoordinated Cl^- anion.

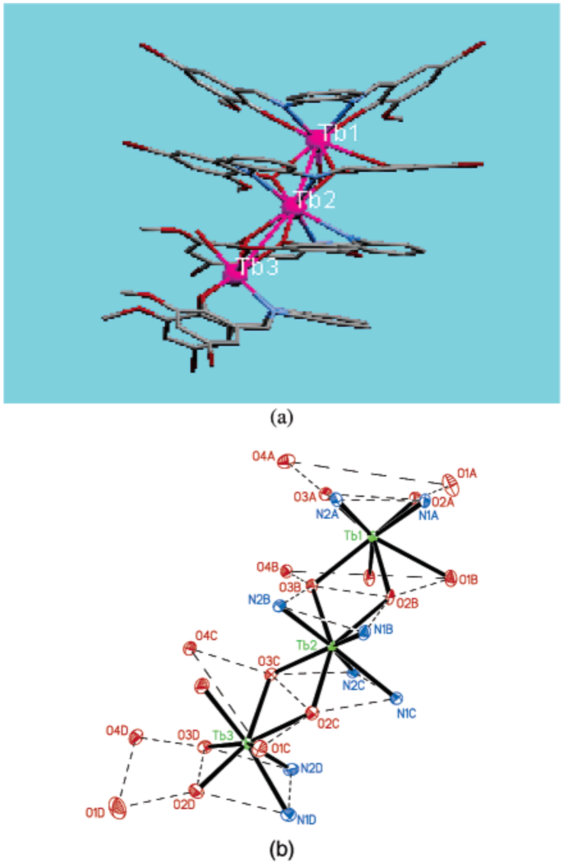

Figure 1. (a) Crystal structure of **1** showing general ligand configurations. (b) Skeletal view of **1** showing locations of the N and O donor atoms.

The self-assembly process of Tb^{3+}/L multi-decker systems appears to be anion dependent. Thus, if the reaction between $TbCl_3{\cdot}6H_2O$ and H_2L is conducted in the presence of $Zn(OAc)_2{\cdot}2H_2O$, the triple-decker complex $[Tb_3L_3(OAc)_2Cl]$ (**2**) is produced (Figure 2).[8,9] We assume that OAc^- groups are able to coordinate effectively to one Tb^{3+} ion and prevent coordination of the fourth L ligand. A discussion of the structural differences between **1** and **2** is provided in the Supporting Information. A key feature in both **1** and **2** is the presence of intramolecular $\pi-\pi$ stacking interactions between phenylene units. The distances range from 3.491 to 3.962 Å. These interactions may add to the stability of these multi-decker architectures. To coordinate effectively to two Tb^{3+} ions, the inner L ligands in both **1** and **2** are virtually planar. In contrast, the outer L ligands adopt angular configurations in which the two salicylaldehyde rings of the Schiff base are pinned back into a wing-like formation. The dihedral angles between these rings in **1** are 116.7 and 121.3°. In **2**, where the steric restraints are less severe, the dihedral angle for the analogous outer L is 146.5°.

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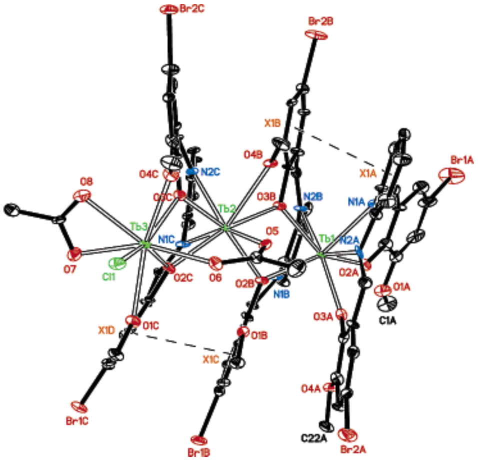

Figure 2. A view of the molecular structure of **2**. Hydrogen atoms are omitted for clarity. X1A···X1B 3.955 Å, X1C···X1D 3.593 Å.

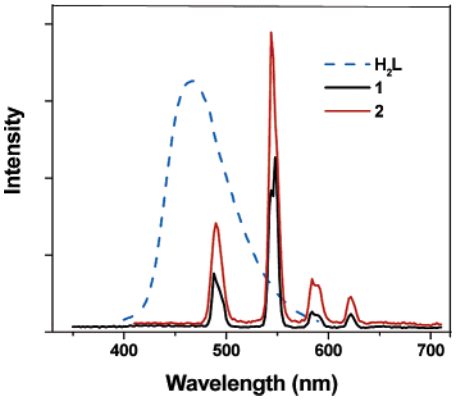

Figure 3. The emission spectra of free H_2L, **1**, and **2** in CH_3CN. Concentrations: 1.2×10^{-6} M (H_2L); 5.6×10^{-5} M (**1**); 5.2×10^{-5} M (**2**).

Molar conductivity studies in CH_3CN confirmed a 1:1 electrolyte for **1**, while **2** was neutral, in accordance with the solid-state structures. ^1H NMR spectra of **1** and **2** in CD_3CN contain multiple broad peaks ranging from −60 to +60 ppm (Figure S6, Supporting Information) and remain unchanged over a month-long period. However, in CD_3OD, ^1H NMR spectra develop additional peaks over this time frame, suggesting that a slow decomposition process takes place in this solvent. Both **1** and **2** exhibit green luminescence in the solid state. In solutions of CH_3CN, CH_3OH, and CD_3OD, the free ligand H_2L exhibits strong absorption bands at 235, 280, and 335 nm. These maxima are all red-shifted on metal ion coordination. Excitation of the ligand-centered absorption bands of both **1** and **2** produces the typical emission bands of the Tb(III) ion ($^5D_4 \rightarrow {}^7F_n$ transitions, $n = 6, 5, 4$, and 3; Figure 3), while the ligand-centered $^1\pi-\pi^*$ emission was not detected. The fluorescence quantum yields (Φ_{em}) of **1** and **2** in CH_3CN are 0.153 and 0.181, respectively.[10] The quantum yield of **1** is slightly lower than that of **2**, probably due to the coordination of two water molecules which can quench lanthanide luminescence. With the same absorbance value of 255 nm for both **1** and **2**, the emission intensities in CH_3CN and CD_3OD are much higher than those in CH_3OH. This suggests a strong interaction between the complexes and CH_3OH, which eventually leads to some decomposition (as evidenced by the NMR data). The absence of typical Tb^{3+} ion excitation bands in the excitation spectra and the ligand-centered luminescence in the emission spectra of the **1** and **2** indicates that the ligand-to-metal energy transfer takes place efficiently.[11]

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Supporting Information Available: Details of the synthesis and characterization of H_2L, **1** and **2**, a discussion of the structural differences between **1** and **2**, views of the crystal structures of **1** and **2**, view of the structure of the monolanthanide complex $[LnZnL(NO_3)_3]$, ^1H NMR spectra of **1** in CD_3CN, UV−vis spectra of free H_2L and **1** in CH_3CN, excitation and emission spectrum of **1** in CH_3OH. Crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) Crystal data: (**1**) $[Tb_3L_4(H_2O)_2]\cdot Cl\cdot 9CH_3OH\cdot 4H_2O$, $C_{97}H_{112}Br_8ClN_8O_{31}Tb_3$, $M = 3037.42$, monoclinic, space group $P2(1)/c$, $a = 22.764(5)$ Å, $b = 19.015(4)$ Å, $c = 29.285(6)$ Å, $\beta = 104.78(3)°$, $V = 12257$ (4) Å^3, $Z = 4$, $D_c = 1.621$ g cm^{-3}, μ(Mo Kα) = 4.412 mm^{-1}, $F(000) = 5776$, $T = 153$ K, $R_1 = 0.0845$, $wR_2 = 0.1694$ for 27 837 independent reflections with a goodness of fit of 0.976. The crystal of **1** was sealed in a glass capillary along with the solution.

(8) Crystal data: (**2**) $[Tb_3L_3(OAc)_2Cl]\cdot 2C_2H_5OH\cdot H_2O\cdot (C_2H_5)_2O$, $C_{78}H_{78}Br_6ClN_6O_{20}Tb_3$, $M = 2411.14$, monoclinic, space group $P2(1)/n$, $a = 20.211(4)$ Å, $b = 22.089(4)$ Å, $c = 20.519(4)$ Å, $\beta = 114.69(3)°$, $V = 8323$ (3) Å^3, $Z = 4$, $D_c = 1.919$ g cm^{-3}, μ(Mo Kα) = 5.507 mm^{-1}, $F(000) = 4656$, $T = 153$ K, $R_1 = 0.0814$, $wR_2 = 0.1519$ for 17 651 independent reflections with a goodness of fit of 1.015. The crystal of **2** was sealed in a glass capillary along with the solution.

(9) Reaction of $Ln(NO_3)_3\cdot 6H_2O$, $Zn(OAc)_2\cdot 2H_2O$, and H_2L produced the heterobimetallic complexes, $[ZnLnL(NO_3)_3]$ (Ln = Eu, Nd): Yang, X.-P.; Jones, R. A. Unpublished data.

(10) Fluorescence quantum yields were determined by using quinine sulfate ($\Phi_{em} = 0.546$ in 0.5 M H_2SO_4) as standard for the Tb^{3+} complex: Meech, S. R.; Philips, D. J. *J. Photochem.* **1983**, *23*, 193−217. Values of relative emission intensities (298 K) at 546 nm for **1** and **2**: CH_3CN (12.5, 14.8), CH_3OH (1.0, 1.3), CD_3OD (9.8, 3.1). Concentrations were adjusted to give the same absorbance value at 255 nm for all samples.

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