Pentanuclear tetra-decker luminescent lanthanide Schiff base complexes†

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Received 28th January 2008, Accepted 1st February 2008

First published as an Advance Article on the web 20th February 2008

DOI: 10.1039/b801513a

Luminescent pentanuclear tetra-decker Ln(III) complexes $[\text{Eu}_5\text{L}_4(\text{OH})_2(\text{NO}_3)_4(\text{H}_2\text{O})_2]\cdot\text{NO}_3\cdot 3\text{H}_2\text{O}$ **1**, $[\text{Nd}_5\text{L}_4(\text{OH})_2(\text{NO}_3)_5\text{MeOH}]\cdot 3\text{MeOH}\cdot 2\text{H}_2\text{O}$ **2** and $[\text{Eu}_5\text{L}_4(\text{CF}_3\text{SO}_3)_4(\text{MeO})_2(\text{H}_2\text{O})_4]\cdot\text{CF}_3\text{SO}_3\cdot\text{H}_2\text{O}$ **3** are formed from $\text{Ln}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ ($\text{Ln} = \text{Eu}$ (**1**), Nd (**2**)) and $\text{Eu}(\text{CF}_3\text{SO}_3)_3$, respectively ($\text{H}_2\text{L} = N,N'$ -bis(5-bromo-3-methoxysalicylidene)phenylene-1,2-diamine).

Self-assembled polynuclear lanthanide(III) complexes have recently attracted much attention because of their potential use in materials science and as probes in biology.¹ For the lanthanide ions the f-f transitions are parity forbidden which results in very low absorption coefficients. In order to overcome this, suitable chromophors have been used to act as antennas or sensitizers which can transfer energy to the lanthanide ion indirectly.² The photophysical properties of Ln(III) ions therefore depend on their ligand environments which can be designed to protect the metal center from solvent molecules which can quench emissions. However, lanthanide coordination chemistry is challenging. It is characterized by high coordination numbers and flexible coordination geometries and structures often depend on a variety of factors such as ionic radius, the nature of counter anions and the metal-to-ligand ratio.³

Our recent studies have focused on the use of a variety of “salen” style Schiff base ligands to stabilize Ln(III) centers and to provide the antenna for lanthanide luminescence.⁴ An interesting emerging feature exhibited by these complexes is the self-assembly of stacked “multi-decker” structures in which Ln(III) ions are sandwiched between alternating layers of the Schiff base ligand. For example the reaction of bis(5-bromo-3-methoxysalicylidene)phenylene-1,2-diamine (H_2L) with $\text{TbCl}_3\cdot 6\text{H}_2\text{O}$ produces both “tetra-decker” ($[\text{Tb}_5\text{L}_4]^+$) and “triple-decker” ($[\text{Tb}_3\text{L}_3]^{3+}$) architectures depending on the nature of the anions present during their formation.^{4f} These studies raised a number of interesting questions. For example, is it possible to construct larger multidecker multimetallic lanthanide–Schiff base assemblies by careful adjustment of stoichiometry, anion selection and reaction conditions? As part of our continuing studies focused on the assembly of these multi-decker systems we describe here the syntheses, structures and photophysical properties of three new pentametallic tetra-decker complexes of

Eu(III) and Nd(III) formed from reactions of $\text{Ln}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ ($\text{Ln} = \text{Eu}, \text{Nd}$) and $\text{Eu}(\text{CF}_3\text{SO}_3)_3$ (Scheme 1). The compounds are the first examples of $[\text{Ln}_5\text{L}_4]^{7+}$ stacked multidecker lanthanide–Schiff base complexes.

Scheme 1 Self-assembly of pentanuclear tetra-decker lanthanide complexes.

Reaction of H_2L with $\text{Ln}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ (4:5) in refluxing MeOH in the presence of Et_3N gave the pentanuclear complexes $[\text{Eu}_5\text{L}_4(\text{OH})_2(\text{NO}_3)_4(\text{H}_2\text{O})_2]\cdot\text{NO}_3\cdot 3\text{H}_2\text{O}$ **1** and $[\text{Nd}_5\text{L}_4(\text{OH})_2(\text{NO}_3)_5\text{MeOH}]\cdot 3\text{MeOH}\cdot 2\text{H}_2\text{O}$ **2**.^{†§} A view of the cationic moiety of **1** is shown in Fig. 1. The two outer Eu^{3+} ions, Eu(1) and Eu(5), have similar nine-coordinate environments and each is bound to the O_2O_2 cavities of the outer Schiff base ligand and surrounded by nine oxygen atoms from one L group, one bidentate NO_3^- anion, one bridged NO_3^- anion, one OH^- anion and one H_2O molecule. The two inner Eu^{3+} ions, Eu(2) and Eu(4), also have similar nine-coordinate environments comprising the N_2O_2 donor set of one outer L group, the O_2O_2 set of one inner L group and one bridged NO_3^- anion. The central Eu (3)

Fig. 1 Crystal structure of **1** showing general ligand configurations. Coordinated NO_3^- and OH^- anions, H_2O molecules and H atoms have been omitted for clarity.

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† CCDC reference numbers 670094–670096. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b801513a

Electronic supplementary information (ESI) available: ¹H NMR spectrum of **2**. See DOI: 10.1039/b801513a

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 Eu–Eu separations are similar at 3.704 Å and 3.700 Å for Eu(1)–Eu(2) and Eu(4)–Eu(5), respectively, and 3.925 Å and 3.912 Å for Eu(2)–Eu(3) and Eu(4)–Eu(3), respectively. In **2**, the three inner Nd^{3+} ions (Nd(2), Nd(3) and Nd(4)) have coordination environments similar to the inner Eu^{3+} ions in **1**, while two outer Nd^{3+} ions (Nd(1) and Nd(5)) have slightly different sets of coordinating ligands (Fig. 2). For Nd(1) one methanol molecule replaces the coordinated H_2O molecule in **1**, and for Nd(5) an additional bidentate NO_3^- anion, results in a coordination number of ten. The differences between **1** and **2** could be due to the larger ionic radius of Nd^{3+} vs. Eu^{3+} . The Nd–Nd separations are similar at 3.937 Å and 3.940 Å for Nd(2)–Nd(3) and Nd(3)–Nd(4), respectively, while they are 3.660 Å and 3.744 Å for Nd(1)–Nd(2) and Nd(4)–Nd(5), respectively.

Fig. 2 A view of the molecular structure of **2**. Hydrogen atoms are omitted for clarity and thermal ellipsoids drawn at the 25% probability level. Intramolecular π – π stacking interactions: X1A...X1B: 3.705 Å, X1C...X1D: 3.619 Å, X1E...X1F: 3.731 Å.

Reaction of H_2L with $\text{Eu}(\text{CF}_3\text{SO}_3)_3$ gave the pentanuclear complex $[\text{Eu}_5\text{L}_4(\text{CF}_3\text{SO}_3)_4(\text{MeO})_2(\text{H}_2\text{O})_4]\cdot\text{CF}_3\text{SO}_3\cdot\text{H}_2\text{O}$ **3** which has a similar pentanuclear tetra-decker structure to **1** and **2**. A view of the cationic moiety of **3** is shown in Fig. 3. The framework contains a C_2 axis running through the central Eu(3) ion which has the same eight-coordinate environment as that in **1**. For each of the equal inner eight-coordinate Eu^{3+} ions (Eu(2) and Eu(2)*), one bridged MeO^- anion replaces the bridging NO_3^- anion in **1**. For each of the equal outer nine-coordinate Eu^{3+} ions (Eu(1) and Eu(1)*), two monodentate CF_3SO_3^- anions and one H_2O molecule replace the NO_3^- and OH^- anions in **1**. The distances of Eu(1)–Eu(2) and Eu(2)–Eu(3) are 3.636 Å and 4.037 Å, respectively. In all three complexes, the phenolic oxygen atoms of the Schiff base ligands L are bridging and the methoxy oxygen atoms and nitrogen atoms of L group are monodentate. In **1**–**3** the inner two L ligands are virtually planar while the outer two L ligands display a curved bowl-like configuration. A similar ligand arrangement was observed in the Tb multidecker complexes $[\text{Tb}_3\text{L}_4]^+$ and $[\text{Tb}_3\text{L}_3]^{3+}$.^{4f} The dihedral angles between these rings range from 121.9 to 149.5°. Intramolecular π – π stacking interactions between phenylene units are found in **1**–**3**. The distances between adjacent aryl units range from 3.511 Å to 3.802 Å (Fig. 2).

Fig. 3 Crystal structure of **3** showing general ligand configurations. H atoms have been omitted for clarity. Symmetry operator: $(-x, y, \frac{1}{2} - z)$ is used to generate Eu* atoms.

The ^1H NMR spectrum of **2** in CD_3CN contains multiple broad peaks ranging from –21 to +46 ppm (Fig. S1, ESI†). The photophysical properties of **1**–**3** have been studied in CH_3CN . UV-Vis spectra show that absorption bands of the free ligand H_2L are red-shifted on metal ion coordination in **1**–**3** (Fig. 4). The excitation and emission spectra of **1** and emission spectrum of **2** are shown in Fig. 5 and Fig. 6, respectively. Upon excitation of the ligand centered (L) absorption band, **1** and **3** show visible emission bands typical of the Eu^{3+} ion ($^5\text{D}_0 \rightarrow ^7\text{F}_j$ transitions, $j = 1, 2, 3$ and 4), and **2** shows NIR luminescence of Nd^{3+} ion ($^4\text{F}_{3/2} \rightarrow ^4\text{I}_{j/2}$ transitions, $j = 9, 11, 13$). The ligand centered $^1\pi$ – π^* emission was not detected in either **1** or **3**. The fluorescence quantum yields (Φ_{em}) of **1** and **3** in CH_3CN are 0.084 and 0.077, respectively,⁵ while the NIR luminescence quantum yield of **2** could not be measured due to instrumental limitations. The absence of typical Eu^{3+} ion excitation bands in the excitation spectra and the ligand-centered luminescence in the emission spectra of **1** and **3** indicates that the ligand-to-metal energy transfer takes place efficiently.⁶

Fig. 4 UV-Vis spectra of free H_2L and complexes **1** and **3** in CH_3CN .

Fig. 5 The excitation and emission spectra of **1** in CH_3CN (1×10^{-6} M) at room temperature.

Fig. 6 NIR luminescence of **2** in CH_3CN (1×10^{-6} M) at room temperature.

Acknowledgements

We thank the Robert A. Welch Foundation (Grant F-816), the Texas Higher Education Coordinating Board (ARP 003658-0010-2006), The Petroleum Research Fund, administered by the American Chemical Society (47014-AC5) and the Hong Kong Research Grants Council (HKBU 202407) for support.

Notes and references

‡ *Experimental procedure*: The Schiff base ligand H_2L was prepared according to well-established procedures.⁷ For **1** triethylamine (4 mL of 0.1 M MeCN solution) was added to a solution of H_2L (0.106 g, 0.20 mmol) and $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.107 g, 0.25 mmol) in 30 mL of MeOH. The resulting solution was stirred and refluxed for 30 min. The color of the solution changed from red to yellow during reflux. The mixture was then cooled to room temperature and filtered. Diethyl ether was allowed to diffuse slowly into this solution at room temperature and yellow single crystals were obtained in one week. Yield 0.085 g (50%). Mp > 330 °C (decomp.). ESI-MS (CH_3CN) m/z : 1013 [$\text{M} - 3\text{NO}_3^- - 7\text{H}_2\text{O}$]³⁺. IR

(CH_3CN , cm^{-1}): 3379, 3370, 2843, 2395, 2014, 1654, 1279, 1221, 1172, 1098, 1029, 763, 665, 637. For **2** the procedure was the same as that for **1** using $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$. Yellow single crystals of **2** were formed in one week. Yield 0.100 g (59%). Mp > 335 °C (decomp.). ESI-MS (CH_3CN) m/z : 1180 [$\text{M} - 3\text{NO}_3^- - 4\text{MeOH} - 2\text{H}_2\text{O}$]³⁺. ¹H NMR (400 MHz, CD_3CN): δ (ppm) –20.407 (3H), –5.319 (2H), –4.218 (10H), –2.890 (2H), –1.495 (2H), –1.107 (2H), –0.625 (2H), 0.479 (2H), 1.188 (9H), 1.257 (9H), 3.118 (6H), 3.496 (6H), 4.497 (2H), 11.344 (4H), 14.499 (6H), 29.279 (4H), 38.275 (9H), 45.654 (2H). IR (CH_3CN , cm^{-1}): 3352, 2879, 2382, 1658, 1251, 1220, 1176, 1099, 1028, 765, 665. For **3** the procedure was the same as that for **1** using $\text{Eu}(\text{CF}_3\text{SO}_3)_3$. Yellow single crystals of **3** were formed in two weeks. Yield 0.119 g (63%). Mp > 350 °C (decomp.). ESI-MS (CH_3CN) m/z : 1081 [$\text{M} - 3\text{CF}_3\text{SO}_3^- - 4\text{H}_2\text{O}$]³⁺. IR (CH_3CN , cm^{-1}): 3342, 2945, 2831, 2361, 1658, 1511, 1470, 1409, 1311, 1237, 1196, 1106, 1025, 816, 739, 665. § *Crystal data* for **1**: $\text{C}_{88}\text{H}_{66}\text{Br}_8\text{N}_{13}\text{O}_{38}\text{Eu}_5$, triclinic, space group $P\bar{1}$, $a = 17.300(3)$, $b = 18.267(4)$, $c = 20.124(4)$ Å, $\alpha = 75.52(3)^\circ$, $\beta = 87.75(4)^\circ$, $\gamma = 74.48(3)^\circ$, $V = 5930(2)$ Å³, $Z = 2$, $D_c = 1.855$ g cm^{–3}, $\mu(\text{Mo-K}\alpha) = 5.381$ mm^{–1}, $F(000) = 3168$, $T = 153$ K. $R_1 = 0.0775$, $wR_2 = 0.2127$ for 20848 independent reflections with a goodness-of-fit of 1.060. For **2**: $\text{C}_{92}\text{H}_{82}\text{Br}_8\text{N}_{13}\text{O}_{38}\text{Nd}_5$, triclinic, space group $P\bar{1}$, $a = 16.878(3)$, $b = 19.282(4)$, $c = 22.601(5)$ Å, $\alpha = 96.53(3)^\circ$, $\beta = 102.92(4)^\circ$, $\gamma = 104.75(3)^\circ$, $V = 6818(2)$ Å³, $Z = 2$, $D_c = 1.634$ g cm^{–3}, $\mu(\text{Mo-K}\alpha) = 4.287$ mm^{–1}, $F(000) = 3234$, $T = 153$ K. $R_1 = 0.0709$, $wR_2 = 0.2027$ for 23946 independent reflections with a goodness-of-fit of 1.067. For **3**: $\text{C}_{95}\text{H}_{70}\text{Br}_8\text{F}_{15}\text{N}_8\text{O}_{38}\text{S}_5\text{Eu}_5$, monoclinic, space group $C2/c$, $a = 24.973(5)$, $b = 23.003(6)$, $c = 23.628(5)$ Å, $\beta = 105.21(3)^\circ$, $V = 13098(5)$ Å³, $Z = 4$, $D_c = 1.915$ g cm^{–3}, $\mu(\text{Mo-K}\alpha) = 4.977$ mm^{–1}, $F(000) = 7240$, $T = 153$ K. $R_1 = 0.0488$, $wR_2 = 0.1354$ for 11510 independent reflections with a goodness-of-fit of 1.045. All data were collected on a Nonius Kappa CCD diffractometer and structures solved using the program SHELXL-97.⁸ CCDC reference numbers 670094–670096. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b801513a.

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