Anion dependant self-assembly and the first X-ray structure of a neutral homoleptic lanthanide salen complex $Tb_4(salen)_6$†

Xiaoping Yang,[a] Richard A Jones*[a] and Wai-Kwok Wong*[b]

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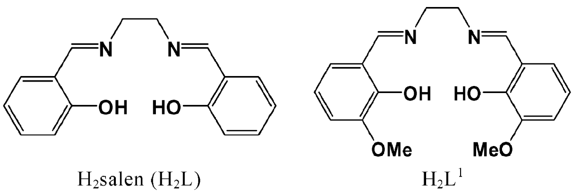
Reaction of H_2salen (H_2L) with $Tb(OAc)_3{\cdot}4H_2O$ (3 : 2) in MeOH–MeCN under reflux gave homoleptic Tb_4L_6 (1) in 40% yield; in contrast, similar reactions of $Tb(NO_3)_3{\cdot}6H_2O$ and $LnCl_3{\cdot}6H_2O$ (Ln = Tb, Nd and Yb) gave $[TbL(NO_3)(MeOH)]_2(\mu\text{-}H_2L)$ (2) and $[LnL(Cl)(MeOH)]_2(\mu\text{-}H_2L)$ (Ln = Tb (3), Nd (4) and Yb (5); H_2L = *N*,*N*′-ethylenebis(salicylideneimine)).

The unusual magnetic and photophysical properties of the lanthanide(III) ions have resulted in a great deal of interest in their compounds for use as probes in biological systems and in new materials.[1] However, synthesis is often problematic due to the high coordination numbers and flexible coordination geometries adopted by the Ln(III) ions. Structures are often influenced by a variety of factors such as ionic radius and the nature of the counter ions. A wide variety of multidentate ligands have been employed in order to address these issues.[2] One of the best known multidentate ligands is the Schiff-base "H_2salen" (*N*,*N*′-ethylenebis(salicylideneimine, H_2L, Scheme 1).[1,3] Numerous variations on the original salen structure have been explored, including systems designed to incorporate both f- and d-block transition metals.[3] For example, pioneering studies by Costes and co-workers focussed on the magnetic properties of systems based on substituted Schiff-base ligands such as H_2L^1.[4] In many cases, especially in the absence of definitive X-ray data, lanthanide Schiff-base complexes have been assigned very speculative structures proposed on the basis of elemental composition and spectroscopic data.[4,5]

Recent studies in our laboratories 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.[6] Many of the compounds that we have isolated and characterized have polynuclear frameworks. An interesting feature is the self-assembly of stacked "multi-decker" structures in which Ln(III) ions are sandwiched between alternating layers of the Schiff-base ligands.[6e] The structures invariably contain coordinated solvent molecules in addition to ancillary anions such as OAc^-, Cl^- or NO_3^-. We were therefore interested in the structure(s) of the homoleptic lanthanide Schiff base complexes of formula $Ln_2(salen)_3$, involving the original salen ligand H_2L, first reported by Dutt and Nag in 1968.[7] However, to the best of our knowledge, there has been no single-crystal X-ray diffraction study reported for these classic complexes. Indeed, the literature suggests that crystals suitable for single crystal X-ray studies could not be obtained.[4a] Definitive structural information would represent a fundamental contribution to the coordination chemistry of lanthanide complexes and aid in the design of luminescent compounds where coordination saturation and the absence of coordinated solvents such as H_2O or MeOH is desirable.[2] We have now prepared the model homoleptic complex Tb_4L_6 (**1**) from the reaction of $Tb(OAc)_3{\cdot}4H_2O$ and H_2L and successfully determined its X-ray crystal structure. The formation of **1** appears to be anion dependent since the use of $Ln(NO_3)_3{\cdot}6H_2O$ or $LnCl_3{\cdot}6H_2O$ under similar reaction conditions results in the retention of Cl^- or NO_3^- and the formation of dinuclear compounds in which a neutral H_2L group bridges two [LnLX(MeOH)] moieties (X = Cl, NO_3).



Scheme 1 Structures of salen ligands.

Reaction of H_2salen (H_2L) with $Tb(OAc)_3{\cdot}4H_2O$ (3 : 2) in MeOH–MeCN under reflux produces Tb_4L_6 which may be isolated in 40% yield as the mixed solvate $Tb_4L_6{\cdot}6MeOH{\cdot}4H_2O$ (**1**).‡ A view of the crystal structure of **1** is shown in Fig. 1, and reveals a tetranuclear centrosymmetric core with two equivalent Tb_2L_3 moieties linked by two μ-O phenoxide atoms. None of the MeOH or H_2O molecules found in the structure are bound to a metal center. The unique outer Tb ion (Tb(1)) is 8-coordinate and bound by the inner N_2O_2 cavities of two salen groups. The inner Tb ion (Tb(2)) is bound by the N_2O_2 core of just one salen group in addition to phenoxide O atoms from three other ligands resulting in a 7-coordinate geometry. The two unique Tb–Tb distances are similar at 3.857 and 3.869 Å for Tb(1)–Tb(2) and Tb(2)–Tb(2A), respectively. It is interesting to note that each salen group is bound to a Tb(III) center through its N_2O_2 core with only one of its phenoxide O atoms adopting a bridging role. The molecular structure of **1** also features π–π stacking between aryl groups which may add to the overall stability of the compound.[8] The

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[a] *Department of Chemistry and Biochemistry, The University of Texas at Austin, 1 University Station A5300, Austin, Texas 78712-0165, USA. E-mail: rajones@mail.utexas.edu; Fax: +1 (512) 471-6822; Tel: +1 (512) 471-1706*
[b] *Chemistry Department, Hong Kong Baptist University, Kowloon Tong, Hong Kong, P. R. China. E-mail: wkwong@hkbu.edu.hk; Fax: +852 3411 7348; Tel: +852 3411 7075*

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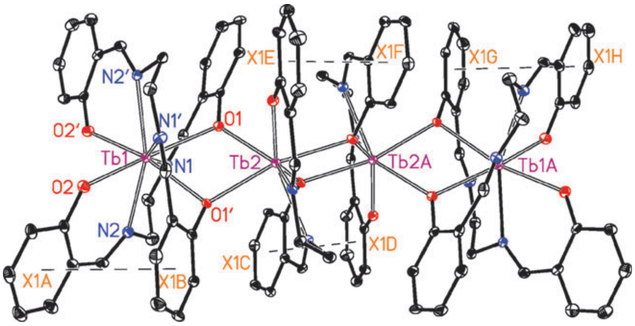

Fig. 1 A view of the molecular structure of **1**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 25% probability level. Intramolecular π–π stacking interactions: X1A···X1B and X1G···X1H: 3.805 Å, X1C···X1D and X1E···X1F: 3.994 Å. Atoms whose labels are appended by an A are related by 1 − *x*, 1 − *y*, 1 − *z*.

distances between adjacent aryl units range from 3.805 to 3.994 Å and fall within reasonable limits.[6e]

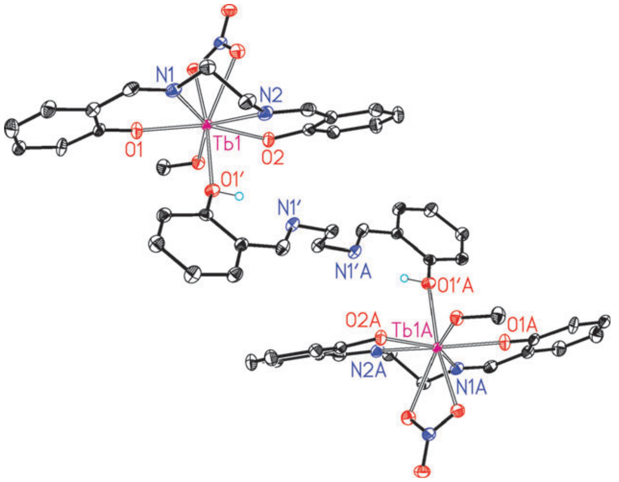

Fig. 2 A view of the molecular structure of **2**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 25% probability level. Atoms whose labels are appended by an A are related by 1 − *x*, 1 − *y*, −*z*.

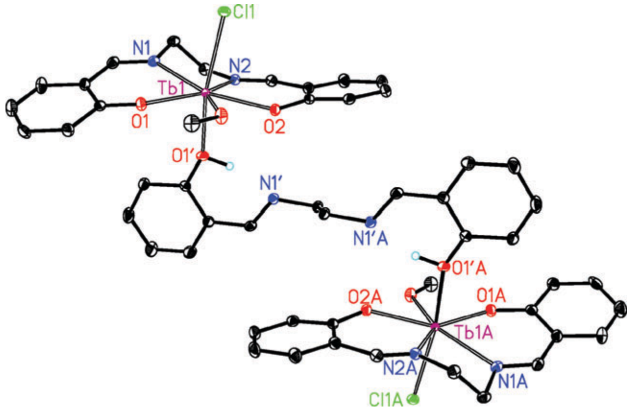

Fig. 3 A view of the molecular structure of **3**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 25% probability level. Atoms whose labels are appended by an A are related by −*x*, 2 − *y*, −*z*.

Table 1 Key Tb–O (phenolic) and Tb–N bond lengths (Å) for **1–3**

	1 (Tb_4L_6)	**2** (Tb–NO_3)	**3** (Tb–Cl)
Tb–O terminal	2.246	2.177	2.214
Tb–O bridging	2.360	—	—
Tb–OH dative	—	2.201	2.207
Tb–N	2.524	2.469	2.475

The use of $Tb(OAc)_3·4H_2O$ for the preparation of **1** is critical to the formation of the homoleptic complex. Reactions of H_2L with $Tb(NO_3)_3·6H_2O$ and $LnCl_3·6H_2O$ (Ln = Tb, Nd and Yb) under similar conditions gave good yields of $[TbL(NO_3)(MeOH)]_2(\mu\text{-}H_2L)$ (**2**) and $[LnL(Cl)(MeOH)]_2(\mu\text{-}H_2L)$ (Ln = Tb (**3**), Nd (**4**) and Yb (**5**). Views of the Tb complexes **2** and **3** are shown in Fig. 2 and 3, respectively. Compounds **3–5** are isomorphous and their structures are similar to that of **2**. The common feature in both structures is the retention of one Cl^- or NO_3^- per Ln^{3+} ion which is bound to the central N_2O_2 core of a salen ligand. Two Ln^{3+} centers are also bridged by a single neutral molecule of H_2salen, each bound to one of the two phenolic OH groups of the non-deprotonated H_2L molecule. The imine N atoms of these groups do not participate in bonding. Thus, as for **1**, the overall metal to ligand stoichiometry is 2 : 3. For **2**, the coordination environment of the Tb^{3+} ions is completed by the binding of one bidentate NO_3^- and one MeOH group resulting in an 8-coordinate geometry. The overall structures of **3–5** are similar to that of **2** with the replacement of NO_3^- by Cl^-. Thus the Ln^{3+} ions in **3–5** are all seven coordinate. Table 1 shows the average values for key Tb–O and Tb–N bond lengths in **1–3**. Interestingly the Tb–OH (dative) distances in **2** and **3** are slightly shorter than the terminal phenolic Tb–O lengths in **1**. This is possibly due to the H_2L ligand acting as a monodentate ligand in **2** and **3**, and so is less sterically demanding in this configuration.

The photophysical properties of the Tb(III) complexes **1–3** were studied in MeOH. The free ligand (H_2L) exhibits absorption bands at 216, 255 and 316 nm which are shifted upon coordination (Fig. 4). The emission and excitation spectra of both H_2L and **1** are shown in Fig. 5. Excitation of the absorption band at 366 nm in the free ligand H_2L produces a broad emission band at λ_{max} = 455 nm. Excitation of the ligand centered absorption bands (at 237, 266, and 246 nm for

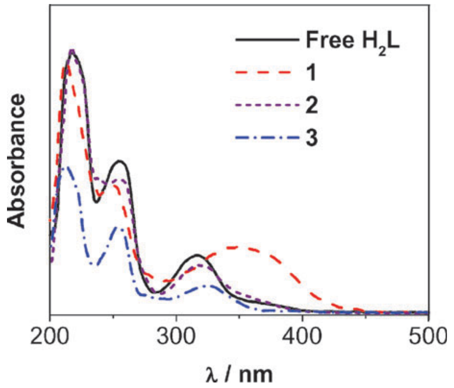

Fig. 4 Absorption spectra of free H_2L and the Tb(III) complexes **1–3**.

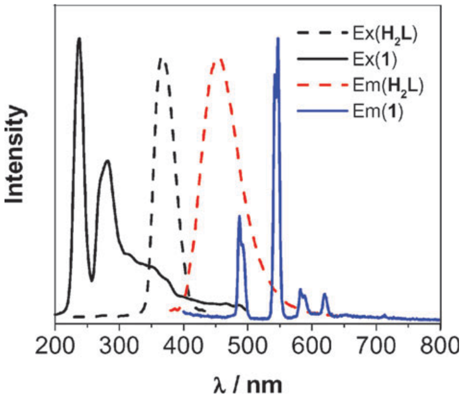

Fig. 5 Excitation and emission spectra of free H_2L (—) and **1** (—).

1–3, respectively) in all three complexes result in typical visible emission bands for the Tb^{3+} ion ($^5D_4 \rightarrow {}^7F_n$ transitions, n = 6,5,4 and 3), while the ligand centered $^1\pi$–π^* emissions were not detected. The fluorescence quantum yields (Φ_{em}) for **1–3** are 0.230, 0.127 and 0.096, respectively.[9] The quantum yield of **1** is noticeably higher than those of **2** and **3**. This difference in luminescence may be due to the different Tb^{3+} environments in these complexes. In **1**, the Tb^{3+} ions are completely encapsulated by the Schiff base ligands and are protected from solvent molecules. In **2** and **3**, one MeOH is directly coordinated to the Tb^{3+} ion. The Tb^{3+} ions are also considerably more exposed to potential interactions with solvent molecules. The absence of typical Tb^{3+} ion excitation bands in the excitation spectra and the ligand-centered luminescence in the emission spectra of **1–3** indicates that the ligand-to-metal energy transfer takes place efficiently.[10]

In summary, we have determined the solid state structure of the model homoleptic lanthanide complex $Tb_4(salen)_6$ (**1**), a member of a key class of compounds for which a variety of speculative structures have appeared in the literature for many years. Formation of **1** is highly dependant on the choice of Ln(III) starting material.

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Notes and references

‡ *Experimental procedures*: the Schiff-base ligand H_2L was prepared according to well-established procedures.[11] For **1**, a solution of $Tb(OAc)_3 \cdot 4H_2O$ (0.067 g, 0.20 mmol) in MeOH (10 ml) was added to a solution of H_2L (0.081 g, 0.30 mmol) in MeCN (10 ml). The mixture was stirred and heated under reflux for 2 h. The color of the solution changed from pale yellow to brown during this time. The mixture was then cooled to room temperature and filtered. Diethyl ether was allowed to diffuse slowly into this solution at room temperature and dark yellow single crystals were obtained in three weeks. Yield 0.050 g (40%). mp > 355 °C (dec). ESI-MS (CH_3OH) m/z: 426 $[TbL]^+$. IR (CH_3OH, cm^{-1}): 3387(m), 2913(m), 1629(s), 1552(s), 1446(m), 1413(m), 1339(w), 1278(w), 1021(m), 751(w), 665(s). ^1H NMR (400 MHz, CD_3OD): δ (ppm) −123.735 (2H), −114.862 (6H), −92.780 (2H), −71.238 (2H), −49.436 (2H), −44.953 (2H), −27.371 (2H), −0.643 (2H), 16.874 (8H), 19.734 (2H), 27.611 (4H), 36.701 (4H), 55.777 (2H), 63.562 (2H). For **2**, same procedure as for **1** using $Tb(NO_3)_3 \cdot 6H_2O$. The color of solution changed from pale yellow to dark yellow during reflux. Yellow single crystals of **2** formed in two weeks. Yield 0.098 g (75%). mp > 330 °C (dec). ESI-MS (CH_3OH) m/z: 426 $[TbL]^+$. IR (CH_3OH, cm^{-1}): 3395(m), 3227(m), 1723(w), 1634(s), 1601(s), 1540(s), 1491(m), 1458(s), 1315(w), 1237(w), 1094(m), 1036(w), 818(w), 751(w), 665(s). For **3**, same procedure as for **1** using $TbCl_3 \cdot 6H_2O$. Yellow single crystals of **3** formed in two weeks. Yield 0.098 g (80%). mp > 320 °C (dec). ESI-MS (CH_3OH) m/z: 426 $[TbL]^+$. IR (CH_3OH, cm^{-1}): 3381(m), 3135(m), 1729(w), 1625(s), 1555(m), 1490(m), 1415(m), 1366(w), 1225(w), 1169(m), 1029(m), 930(w), 666(s). For **4**, same procedure as for **3** using $NdCl_3 \cdot 6H_2O$. The color of solution changed from pale yellow to dark yellow during reflux. Yellow single crystals of **4** formed in two weeks. Yield 0.101 g (82%). mp > 320 °C (dec). ESI-MS (CH_3OH) m/z: 410 $[NdL]^+$. IR (CH_3OH, cm^{-1}): 3372(m), 3125(m), 1731(w), 1630(s), 1557(m), 1492(m), 1409(m), 1368(w), 1228(w), 1172(m), 1037(w), 931(w), 665(s). For **5**, same procedure as for **3** using $YbCl_3 \cdot 6H_2O$. Yellow single crystals of **5** formed in two weeks. Yield 0.109 g (85%). mp > 326 °C (dec). ESI-MS (CH_3OH) m/z: 440 $[YbL]^+$. IR (CH_3OH, cm^{-1}): 3389(m), 3129(m), 1738(w), 1627(s), 1560(s), 1488(m), 1412(m), 1363(w), 1220(w), 1170(m), 1030(w), 935(w), 665(s).

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