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One-pot synthesis and structural characterization of a Tb(III) coordination polymer based on a tripodal Schiff base ligand adopting an *exo*-bridging coordination mode

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ABSTRACT

A novel Tb(III) coordination polymer and discrete complexes have been synthesized by one-pot reaction utilising flexible tripodal Schiff base ligands, tris[2-(salicylideneamino)ethyl]amine (H_3L) derivatives. Condensation of 5-methylsalicylaldehyde (5-MeSal) with tris(2-aminoethyl)amine (tren) in the presence of $Tb(CF_3SO_3)_3$ in a 3:2:1 (=5-MeSal:tren:Tb(III)) molar ratio gives Tb^1L, and the deprotonated ligand encapsulates the Tb(III) in its N_4O_3 cavity in *endo*-coordination. Here, the excess tren acts as a base to dissociate the proton of the ligand. Decreasing the amount of tren to a 3:1:1 ratio gives $[Tb(H_3{}^1L)_2](CF_3SO_3)_3\cdot H_2O$. In this compound, the Tb(III) centre is coordinated by two $H_3{}^1L$ ligands adopting the *exo*-capping mode to provide three O atoms outside the cavity of $H_3{}^1L$. Replacing $Tb(CF_3SO_3)_3$ with $Tb(NO_3)_3$ in the above reaction induced a substantial structural change to coordination polymer $[Tb(H_3{}^1L)(NO_3)_3\cdot DMF\cdot 1/6H_2O]_n$. In this polymer, the ligand adopts an unprecedented *exo*-bridging coordination mode, which is the first bridging mode observed for this tripodal Schiff base ligands. Three aromatic rings of the *exo*-bridging ligand are close to each other by CH···π interactions and each O atom coordinates to three different Tb(III) ions to construct a three-dimensional polymeric connection. The 3D framework has the nano-pore structure with inner walls that consisted of alternately appearing hydrophilic and hydrophobic regions. The present study shows that the tripodal Schiff base ligand can be a novel class of flexible building block to construct the Ln(III) coordination polymer.

1. Introduction

Construction of lanthanide (Ln(III)) coordination polymers has been of growing subject due to their interesting structural topology as well as potential applications such as catalysis [1], gas adsorption [2], ion exchange [3], magnetism [4] and luminescence [5]. Ln(III) ions have variable coordination number and flexible coordination geometry, thus, Ln(III) coordination polymers are more difficult to be designed than transition metal based coordination polymers. In particular, it is a challenging task to construct Ln(III) coordination polymer using a flexible ligand, since the coordination mode of the ligand can be easily changed by reaction conditions as well as Ln(III) coordination geometry. Several Ln(III) coordination polymers with unique topologies have so far been produced by using flexible ligands [6].

In the present work, as a candidate of the novel class of a flexible building block to construct polymer, we focus on a tripodal Schiff base ligand, tris[2-(salicylideneamino)ethyl]amine (H_3L, Fig. 1), which can be prepared by a facile condensation reaction of tris(2-aminoethyl)amine (tren) with three equivalents of salicylaldehyde (Sal) [7]. For the last few decades, there have been many investigations on the Ln(III) coordination chemistry with H_3L and its substituted derivatives as well as amine phenol ligands prepared by the reduction of the CH=N moiety [8–10]. Depending on the reaction conditions, these ligands formed four types of discrete complexes, I–IV, as classified by Orvig [8d]. Among them, type I, II, and IV complexes shown in Scheme 1a–c were formed using Schiff base ligands [8a,8b,9,10]. As shown in Scheme 1, the classification depends on the coordination mode of the ligand, *endo*-coordination and *exo*-capping, as well as the ligand-to-metal stoichiometry. In the *endo*-coordination, the ligand encapsulates a Ln(III) ion by full participation of all the ligating atoms, N_4O_3, in the coordination. By contrast, a ligand in the *exo*-capping mode provides three phenol O atoms to the coordination at the periphery and three N atoms to the protonation.

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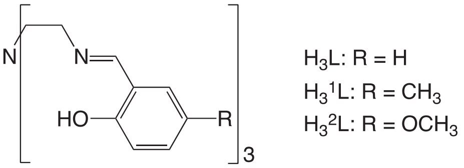


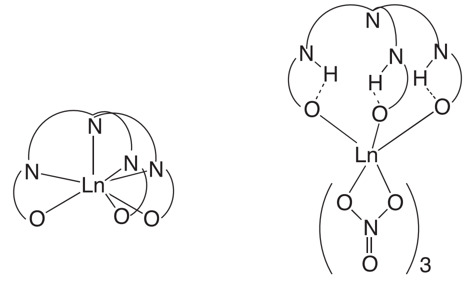
Fig. 1. Structure of tripodal Schiff base ligands prepared by condensation of tren with salicylaldehyde or its 5-substituted derivatives.

Encouraged by the interesting structural diversity of the Ln(III) Schiff base complexes, we began to explore novel coordination modes of this flexible ligand, especially, bridging mode to afford coordination polymer by simply changing the reaction conditions such as pH, ratio of starting material, anions, and substituent of the ligand. Previously, one of the authors showed that the one-pot template reaction of 3-methylsalicylaldehyde (3-MeSal) with tren in the presence of $Ln(CF_3SO_3)_3$ in a 3:2:1 molar ratio gave the type I complex [9e]. In the present paper, we extend this template approach to see how the position of a Me group affect the structure of the Ln(III) complex, resulting in formation of a Tb(III) coordination polymer constructed with the ligand adopting an *exo*-bridging coordination mode (Scheme 1d), which is the first bridging mode observed for this flexible tripodal Schiff base ligand. We report the one-pot synthesis of the Tb(III) coordination polymer and conventional types of Tb(III) complexes by using 5-methylsalicylaldehyde (5-MeSal) as a starting material. Each complex is obtained under completely distinguishable reaction conditions and is structurally characterised by X-ray crystallography.

2. Materials and methods

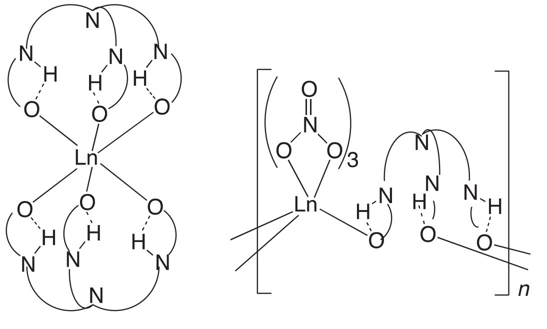
2.1. Materials

Terbium(III) trifluoromethanesulfonate ($Tb(CF_3SO_3)_3$) was purchased from Sigma Aldrich. Terbium(III) nitrate hexahydrate ($Tb(NO_3)_3{\cdot}6H_2O$) was purchased from Kanto Chemical Co., Inc. Tris(2-aminoethyl)amine (tren), 5-methylsalicylaldehyde (5-MeSal), and 5-methoxysalicylaldehyde (5-MeOSal) were purchased from Tokyo Chemical Industry Co., Ltd. All reagents were used without further purification.



(a) type I
(*endo*-coordination)

(b) type II
(*exo*-capping)



(c) type IV
(*exo*-capping)

(d) coordination polymer
(*exo*-bridging)

Scheme 1. Structural diversity of Ln(III) complexes with the tripodal Schiff base ligands.

2.2. Synthesis of metal complexes

2.2.1. Tb^1L (1) prepared from $Tb(CF_3SO_3)_3$

A solution of tren (0.146 g, 1 mmol) dissolved in methanol (2 mL) was added to a hot solution of $Tb(CF_3SO_3)_3$ (0.303 g, 0.5 mmol) dissolved in methanol (13 mL) and stirred for 10 min at 60 °C. Then, a solution of 5-MeSal (0.204 g, 1.5 mmol) dissolved in methanol (2 mL) was added and stirred for 5 min at 60 °C. The yellow product precipitated during cooling for 2 h. The product was filtered off and washed with cold methanol. The crude yellow product was dissolved in DMF and filtered. A small portion of methanol was added to the filtrate. After cooling the solution at −15 °C for a day, yellow coloured micro-crystals precipitated. This recrystallization process was repeated twice to obtain analytically pure **1**. Yield: 0.096 g (29.4%, based on 5-MeSal). *Anal.* Calc. for $C_{30}H_{33}N_4O_3Tb$: C, 54.87; H, 5.08; N, 8.53. Found: C, 54.90; H, 5.11; N, 8.50%. MS (FAB): found *m*/*z* 657.19, calc. *m*/*z* 657.19 ($Tb(H^1L)^+$). IR (cm^{-1}): 3042(m), 3010(m), 2921(s), 2854(s), 1622(s), 1537(s), 1469(s), 1390(s), 1336(m), 1320(s), 1217(m), 1159(m), 1135(m), 1036(m), 917(m), 826(m), 807(s). Single crystals of **1**·3/2DMF suitable for X-ray analysis were obtained by evaporation of DMF *in vacuo* over a period of two days.

2.2.2. Tb^1L (1) prepared from $Tb(NO_3)_3$

A yellow coloured product was obtained using a procedure similar to the above mentioned procedure for **1** except $Tb(NO_3)_3{\cdot}6H_2O$ was used instead of $Tb(CF_3SO_3)_3$. Yield: 0.080 g (24.3%, based on 5-MeSal). Found: C, 54.90; H, 5.11; N, 8.50. Calc. for $C_{30}H_{33}N_4O_3Tb$: C, 54.85; H, 5.16; N, 8.51. MS (FAB): found *m*/*z* 657.19, calc. *m*/*z* 657.19 ($Tb(H^1L)^+$). IR (cm^{-1}): 3044(m), 3009(m), 2917(s), 2854(s), 1618(s), 1536(s), 1469(s), 1389(s), 1319(s), 1217(m), 1158(m), 1135(m), 1036(m), 916(m), 825(m), 806(s).

2.2.3. $[Tb(H_3{}^1L)_2](CF_3SO_3)_3{\cdot}H_2O$ (**2**)

A solution of tren (0.073 g, 0.5 mmol) dissolved in methanol (2 mL) was added to a hot solution of $Tb(CF_3SO_3)_3$ (0.303 g, 0.5 mmol) dissolved in methanol (13 mL) and stirred for 10 min at 60 °C. Then, a solution of 5-MeSal (0.204 g, 1.5 mmol) dissolved in methanol (2 mL) was added and stirred for 5 min at 60 °C. The volume of the solution was reduced to *ca.* 5 mL under a vacuum. Then, a small portion of diethyl ether was added to the solution. After cooling the solution at −15 °C for a day, yellow coloured single crystals precipitated. Yield: 0.210 g (51.6%, based on 5-MeSal). *Anal.* Calc. for $C_{63}H_{74}N_8O_{16}F_9S_3Tb$: C, 46.55; H, 4.59; N, 6.89; F, 10.52; S, 5.92. Found: C, 46.83; H, 4.64; N, 6.81; F, 10.35; S, 5.89%. MS (FAB): found *m*/*z* 1457.39, calc. *m*/*z* 1457.39 ($Tb(H_3{}^1L)_2(CF_3SO_3)_2^+$). IR ($cm^{-1}$): 3513(br, w), 3173(br, w), 3050(m), 2928(m), 2867(m), 1641(s), 1541(s), 1485(s), 1405(m), 1350(m), 1332(m), 1253(s), 1212(s), 1149(s), 1026(s), 947(w), 909(w), 867(m), 832(m), 796(s), 754(m), 735(m).

2.2.4. $[Tb(H_3{}^1L)(NO_3)_3{\cdot}DMF{\cdot}1/6H_2O]_n$ (**3**)

A solution of tren (0.073 g, 0.5 mmol) dissolved in methanol (2 mL) was added to a hot solution of $Tb(NO_3)_3{\cdot}6H_2O$ (0.227 g, 0.5 mmol) dissolved in methanol (13 mL) and stirred for 10 min at 60 °C. Then, a solution of 5-MeSal (0.204 g, 1.5 mmol) dissolved in methanol (2 mL) was added and stirred for 2 min at 60 °C. After cooling the solution at room temperature for 2 h, yellow coloured product was obtained. Recrystallization from DMF afforded single crystals of **3**. Yield: 0.162 g (35.1%, based on 5-MeSal). *Anal.* Calc.