Comparison of the bond lengths for the lanthanide complexes of tripodal heptadentate ligands

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Abstract

The preparation and characterization of Ln(III) complexes (Ln = Sm, Yb) of tripodal heptadentate ligand trensal, tris[2-(salicylideneamino) ethyl]amine (H_3L^1) have been studied. The molecular structures of [LnL^1] were determined by X-ray structural analysis; these are heptadentate complexes in which the metal ions are coordinated by the three oxygen atoms and the four nitrogen atoms. [LnL^1] is a novel example because the coordination number is seven in the wide range of the series of [LnL^1] (Ln = Y, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu). This has made it possible to compare the bond lengths for the lanthanide and yttrium complexes under the same coordination number.
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1. Introduction

There is a general recognition that the coordination number of lanthanide complexes decreases with increase in the atomic number. This coordination number change may be a major cause of the irregularities observed for the properties of the lanthanide complexes [1]. There are numerous examples in which the solvent molecules contained in the formula are coordinated and thereby change the coordination number [2]. In addition it is quite often found that some of the anions present are coordinated. Both of these factors severely complicate the coordination number of lanthanide complexes. The common coordination number for the lanthanides is greater than that for the main-transition metals. The existence of complexes of the lanthanides with larger coordination numbers is a natural consequence of their large size, together with the predominantly ionic bonding which they exhibit [3]. In the absence of adverse steric factors, the coordination number of the lanthanides is usually eight [4] or larger. However, there are now a substantial number of complexes known to have a coordination number of seven. Nearly all of them have the basic formulation

[Ln(bidentate)$_3$(unidentate)]$^{3+}$ [5]. On the contrary, structurally characterized examples of a heptadentate ligand coordinating one metal ion are scarce [6,7].

We have reported lanthanide complexes of tripodal heptadentate (N_4O_3) ligand trensal, tris[2-(salicylideneamino) ethyl]amine (H_3L^1) [8] and its 5-substituted derivative (H_3L^2) [9,10] (Fig. 1). The X-ray crystallographic analysis revealed that these are examples of heptadentate complexes in which all the N_4O_3 donor atoms coordinate to the central metal ions. [LnL^1] is a novel example because the coordination number is seven and it does not change in the series of [LnL^1] [11–13]. In this paper, we report on the relationship between the metal ion radii and the bond lengths for the complexes in the wide range of the series of [LnL^1] (Ln = Y, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu), [LnL^2] (Ln = Sm, Gd), and a dinuclear yttrium cryptate ([Y_2L^3]) [14].

2. Experimental

2.1. Preparation of [SmL^1]·0.5CH$_3$CN and [YbL^1]

Tris(2-aminoethyl)amine (8 mmol) was added to a solution of 4 mmol of Ln(CF$_3$SO$_3$)$_3$ (Ln = Sm, Yb) in acetonitrile (100 cm^3) and stirred for 10 min at 70–80 °C. Then
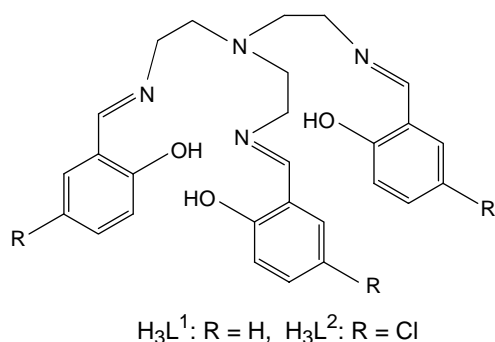

H₃L¹: R = H, H₃L²: R = Cl

Fig. 1. Structures of tripodal heptadentate ligands.

salicylaldehyde (12 mmol) was added to this solution and stirred for 2 min at 70–80 °C. The product was precipitated on cooling for 6 h. This product was clarified by filtration and washed with cold acetonitrile and dried. After the mother liquors were cooled for 3 days, single crystals suitable for single-crystal X-ray diffraction were obtained.

[SmL¹]·0.5CH₃CN; yield 1.80 g (72%). ESI–MS: m/z (%): 608 (100) [SmL¹ + H⁺]. Anal. calcd. for $C_{28}H_{28.5}N_{4.5}O_3Sm$: C, 53.68%; H, 4.59%; N, 10.06%; found: C, 53.83%; H, 4.46%; N, 9.88%. IR: ν (cm⁻¹) (KBr): 3047, 2894, 2850, 1626, 1597, 1542, 1471, 1447, 1402, 1339, 1323, 1217, 1193, 1146, 1029, 917, 895, 793, 760, 748, 597.

[YbL¹]; yield 2.08 g (83%). ESI–MS: m/z (%): 630 (100) [YbL¹ + H⁺]. Anal. calcd. for $C_{27}H_{27}N_4O_3Yb$: C, 51.59%; H, 4.33%; N, 8.91%; found: C, 51.35%; H, 4.27%; N, 9.01%. IR: ν (cm⁻¹) (KBr): 3047, 2899, 2852, 1631, 1598, 1539, 1471, 1451, 1397, 1343, 1324, 1212, 1188, 1149, 1029, 916, 898, 793, 760, 748, 594.

2.2. Crystal structure determination

Crystal data for complex [SmL¹]·0.5CH₃CN; $C_{27}H_{27}SmN_4O_3 \cdot 0.5CH_3CN$, $M = 626.41$, pale yellow block of 0.20 mm × 0.15 mm × 0.20 mm in size, trigonal, space group P-3, $a = 13.809(2)$, $c = 7.962(1)$ Å, $V = 1314.8(2)$ Å³, $Z = 2$, Dc = 1.530 g/cm³, $F(0\,0\,0) = 606.00$, μ(Mo Kα) = 22.72 cm⁻¹.

Crystal data for complex [YbL¹]; $C_{27}H_{27}YbN_4O_3$, $M = 620.47$, pale yellow block of 0.15 mm × 0.10 mm × 0.20 mm in size, trigonal, space group P-3$c1$, $a = 12.952(1)$, $c = 16.594(3)$ Å, $V = 2410.6(4)$ Å³, $Z = 4$, Dc = 1.732 g/cm³, $F(0\,0\,0) = 1244.00$, μ(Mo Kα) = 39.17 cm⁻¹.

All measurements were made on a Rigaku AFC7S diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.71069$ Å). The structures were solved by direct methods [15] and expanded using Fourier techniques [16] and were refined by full-matrix least-squares procedures to $R = 0.031$ and $R_w = 0.036$ for 1568 observed reflections with $I > 3\sigma(I)$ ([SmL¹]·0.5CH₃CN) and $R = 0.026$ and $R_w = 0.031$ for 1013 observed reflections with $I > 3\sigma(I)$ ([YbL¹]). The non hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined.

Ln(CF₃SO₃)₃
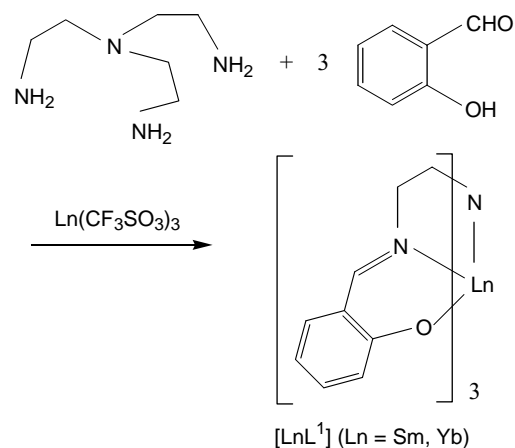
[LnL¹] (Ln = Sm, Yb)

Scheme 1. Synthetic route of [LnL¹] (Ln = Sm, Yb).

Full crystallographic details have been deposited at the Cambridge Crystallographic Data Center (CCDC). CCDC reference numbers are 159,805 and 159,806.

3. Results and discussion

Tris(2-aminoethyl)amine (tren) condenses with salicy-laldehyde or its substituted analogs in a 1:3 molar ratio to form Schiff-bases which are potentially tribasic hep-tadentate ligands. The samarium and ytterbium complexes with the ligand H₃L¹ were prepared by the reaction of tren and salicylaldehyde in the presence of samarium(III) or ytterbium(III) salt in acetonitrile (Scheme 1).

The molecular structure of [SmL¹] is shown in Fig. 2 together with atom-labeling schemes. The individual metal ions and the apical nitrogen atoms (N2), lie on a 3-fold axis in each crystal; the molecules possess a C_3 molecular symmetry. The metal ions are coordinated by three oxygen atoms (O1, O1′, O1″) and four nitrogen atoms (N1, N1′,
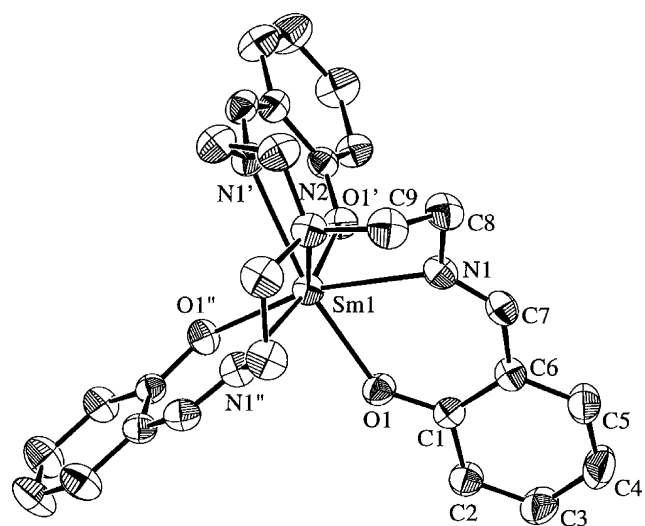

Fig. 2. Molecular structure of [SmL¹] in [SmL¹]·0.5CH₃CN. The hydrogen atoms and solvent molecules are omitted for clarity.
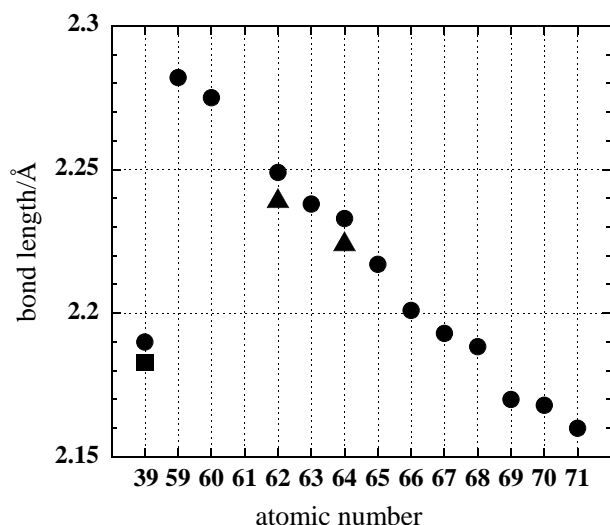
Fig. 3. The bond lengths of Ln–O1 vs. atomic number. Closed circles are the bond lengths of $[LnL^1]$. Closed triangles are the bond lengths of $[LnL^2]$. Closed square is the bond length of $[Y_2L^3]$.

Fig. 4. The bond lengths of Ln–N1 vs. atomic number. Closed circles are the bond lengths of $[LnL^1]$. Closed triangles are the bond lengths of $[LnL^2]$. Closed square is the bond length of $[Y_2L^3]$.

N1″, N2). The unit cell contains two metal complexes and one acetonitrile molecule.

In contrast with complexes with higher coordination numbers, structurally characterized examples of a heptadentate ligand coordinating one metal ion are rare in the lanthanides. Yb(trac) [6] is the first example of a structurally characterized lanthanide complex of a heptadentate ligand. It is reported that the geometry around the Yb atoms is that of a monocapped octahedron, since the trigonal prismatic coordination of the Schiff-base arms would leave the apical N atom far removed from Yb. In the present complexes the coordination geometry around the Sm or Yb atom is a monocapped distorted octahedron in a manner similar to that of the Yb(trac). The apical nitrogen atom caps the triangular face formed by the other three coordinating N atoms. The Sm and Yb atoms are displaced toward the three nitrogen triangular face from the center of the octahedron.

The bond lengths of Ln–O1, Ln–N1, and Ln–N2 for $[SmL^1]$ and $[YbL^1]$ are compared with those of other lanthanide and yttrium complexes. Figs. 3 and 4 show the bond lengths of Ln–O1 and Ln–N1 of $[LnL^1]$, $[LnL^2]$, and $[Y_2L^3]$, respectively. Ionic radii of lanthanide ions decrease smoothly from Pr^{3+} to Lu^{3+} due to the lanthanide contraction, and the ionic radius of Y^{3+} is between those of Dy^{3+} and Ho^{3+}. The bond lengths of Ln–O1 decrease with decrease in the ionic radii of the central metal ions. The variation of bond lengths is consistent with the smooth decrease in the ionic radii from Pr^{3+} to Lu^{3+} except that the value for Gd^{3+} slightly deviates. The bond lengths of Ln–N1 also decrease with decrease in the ionic radii of the central metal ions. In this case, it is observed that the value for Gd^{3+} clearly deviates from the smooth decrease of bond lengths. Fig. 5 shows the bond lengths of Ln–N2 for lanthanide and yttrium complexes. The results indicate that the bond lengths of Ln–N2
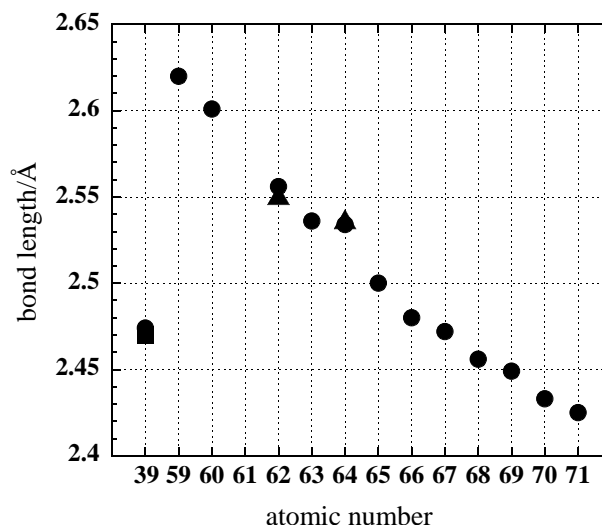
decrease with decrease in the ionic radii of the central metal ions for Pr^{3+} and Tb^{3+}. However, a change or actual reversal in these trends was found between Tb^{3+} and Lu^{3+}. One explanation for these changes may be that the N2 gradually separates from the central metal ion in case the size of the metal ion is small. Although the ligand trensal and its substituted ligands are potentially heptadentate, most of the main-transition metal complexes so far studied involve an N_3O_3 donor set of the ligands, with the apical nitrogen atom remaining uncoordinated [17]. This is because the cavity offered by the N_4O_3 ligand is too large for all seven donor atoms to coordinate to these metal ions [18]. We are interested in the coordination geometry of scandium complexes of trensal and its substituted ligands. The metal-ligand
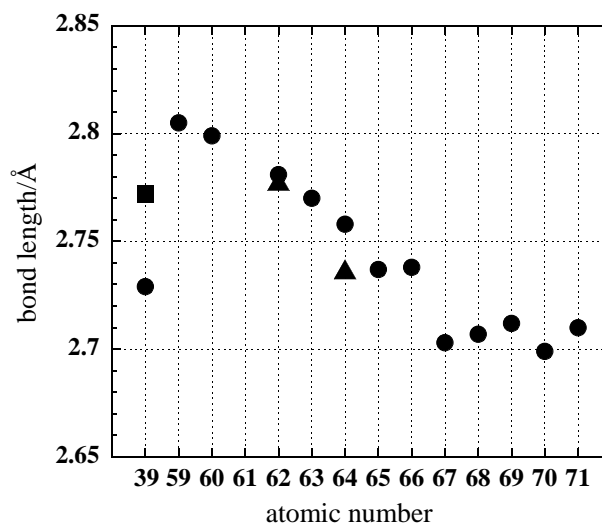

Fig. 5. The bond lengths of Ln–N2 vs. atomic number. Closed circles are the bond lengths of $[LnL^1]$. Closed triangles are the bond lengths of $[LnL^2]$. Closed square is the bond length of $[Y_2L^3]$.

bond lengths of Ln–N2 of the present complexes lie in between those of Yb(trac) (2.43(1) Å) and a $Ni^{II}N7$ complex of tris[1-(2-pyridyl)-2-azabuten-4-yl]amine (3.25 Å) [19], in which the coordination of the apical nitrogen atoms to the metal ions was confirmed.

4. Conclusion

Samarium and ytterbium complexes of tripodal heptadentate ligand trensal, have been prepared. The X-ray crystallographic analysis revealed that [LnL[1]] is a heptadentate complex in which all the N_4O_3 donor atoms coordinate to the central metal ions. [LnL[1]] is a novel example because the coordination number of the lanthanide and yttrium complexes does not change in the wide range of the series of [LnL[1]] (Ln = Y, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu). The bond lengths of Ln–O1 and Ln–N1 were found to be decreased with increase in the atomic number. On the other hand, the bond length of Ln–N2 was not smoothly decreased with increase in the atomic number.

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