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Synthesis, characterization and structural diversity of lanthanide chlorides supported by the β -diketiminate ligand $[\{(2,6-Me_2C_6H_3)NC(Me)\}_2CH]^-$

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Abstract

Reactions of the β -diketiminate lithium salt L^2 Li $[L^2 = \{(2,6-Me_2C_6H_3)NC(Me)\}_2CH]$ with anhydrous LnCl₃ (Ln = Yb, Sm, Nd) in 1:1 molar ratio in THF afforded the new β -diketiminate lanthanide complexes L^2 LnCl(THF)(μ -Cl)₂Li(THF)₂ (Ln = Yb (1), Sm (2), Nd (3)). Recrystallization of complexes 1–3 from toluene gave the neutral complexes L^2 LnCl₂(THF)₂ (Ln = Yb (4), Sm (5), Nd (6)). Recrystallization of complexes 4 and 5 in hot toluene for two times gave the dinuclear complexes L^2 ClLn(μ -Cl)₃LnL²(THF) (Ln = Yb (7), Sm (8)). Treatment of the mother liquor of complexes was well characterized, while complexes 3, 7 and 9 have been characterized by X-ray diffraction structure determination.

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Keywords: Lanthanide complexes; β-Diketiminate ligand; Synthesis; Crystal structure

1. Introduction

β-Diketiminates are important spectator ligands by virtue of their strong binding to metals, their tunable and extensive steric demands and their diversity of bonding modes [1]. The utilization of β-diketiminates in organolanthanides or organolanthanoids is of substantial current interest, and a variety of lanthanide complexes have been reported [2–22], and some of which have been shown interested reactivity [8,11,13,17]. Although there are big ionic radii for lanthanide elements, the β-diketiminate lanthanide dichlorides can be conveniently synthesized, due to the steric bulkiness of the β-diketiminate ligands, which serve as important precursors for further transformation. However, little is known about the structural details of these key species [3,9,16].

Recently, we became interested in studying the synthesis and reactivity of organolanthanide complexes supported by the β -diketiminate ligands [15–19], and found that the room-temperature reaction of anhydrous YbCl₃ with one equiv. of lithium β -diketiminate in THF, followed by crystallization from toluene, results in the isolation of monomeric bis-THF adducts LYbCl₂- $(THF)_2$ [L = {PhNC(Me)}_2CH (L¹), {(2,6-Me₂C₆H₃)- $NC(Me)_{2}CH (L^{2}), \{(2,6-Pr_{2}^{i}C_{6}H_{3})NC(Me)\}_{2}CH (L^{3}),$ $(4-ClC_6H_4)NC(Me)CHC(Me)N(C_6H_3Pr_2^{i}-2,6)$ (L^4)]. However, recrystallization of $L^{3}YbCl_{2}(THF)_{2}$ from hot toluene solution for two times gave the unexpected dinuclear β-diketiminate ytterbium dichlorides with a rare triple chlorine bridge in the molecule [15]. Generally, the central metals in dimeric lanthanide halides are connected by one or two halogen bridge(s). Only a few examples of crystallographically characterized multiple halogen bridges between two lanthanide atoms are those found in lanthanide clusters [23]. In order to elucidate the structural diversity of β-diketiminate lanthanide dichlorides, we used the β -diketiminate ligand L^2 as

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an ancillary ligand and synthesized a series of the β -diketiminate lanthanide dichlorides, and found that crystallization conditions have significant effect on the structure of the lanthanide dichlorides obtained. Here, we report the synthesis and characterization of these complexes and the crystal structures of the dinuclear complexes L²NdCl(THF)(μ -Cl)₂Li(THF)₂ (3), L²ClYb (μ -Cl)₃YbL²(THF) (7), and the trinuclear complex L²SmCl(μ -Cl)₃SmL²(μ -Cl)Li(L²H)(THF) (9).

2. Results and discussion

2.1. Synthesis

One equiv. of L^2Li was added to a slurry of $LnCl_3$ (Ln = Yb, Sm, Nd) in THF-hexane mixed solvent at room temperature, the color of the solution gradually changed to red (for Yb), yellow (for Sm) or blue (for Nd), respectively. After work up, the microcrystals of 1-**3** were obtained from concentrated THF solution in high yield. The compositions of complexes 1-3 were established as $L^2LnCl(THF)(\mu-Cl)_2Li(THF)_2$ (Ln = Yb (1), Sm (2), Nd (3)) by elemental analyses (C, H, N and Ln) and crystal structure determination for complex **3** (Scheme 1). The IR spectra of complexes 1-3 exhibited strong absorptions near 1555 cm⁻¹, which were consistent with partial C=N double-bond character [24].

By recrystallization of complexes 1-3 from hot toluene, after work up, the microcrystals of complexes 4-6were obtained in good yield (Scheme 2). Lithium analysis shows that no lithium exists in these complexes. The results by elemental analysis and IR spectrum demonstrate that complex 4 is the known complex $L^2YbCl_2(THF)_2$ that we have previously synthesized by direct method [17]. Elemental analysis data of complexes



Ln = Yb (4), Sm (5), Nd (6)



5 and **6** are also consistent with the proposed stoichiometry of $L^2LnCl_2(THF)_2$ (Ln = Sm (5), Nd (6)), and their infrared spectra showed absorptions characteristic of the β -diketiminate ligand. Blue crystals of **6** were obtained in concentrated toluene solution and analyzed by X-ray diffraction. Although an adequate data set was obtained, structure solution has not yet been possible.¹

After further recrystallization of complex 4 from hot toluene for two times, the color of the solution changed from red to violet. The dark violet crystals of 7 were obtained from concentrated toluene solution, which was characterized to be part of coordinated THF lost (Scheme 3). Structural analysis of complex 7 reveals that it has a dinuclear structure with a triple chlorine bridge, $L^{2}YbCl(\mu-Cl)_{3}YbL^{2}(THF)$ (see below). Similar recrystallization of complex 5 from toluene produced the orange red microcrystals (8). Elemental analysis and IR spectrum reveal that complex 8 is the analogue of complex 7. The effort to obtain crystals suitable for X-ray structure studies was unsuccessful. Treatment of the mother liquor of complex 2 as described above gave the orange red crystals suitable for structure analysis in extremely small yield. However, elemental analysis and X-ray structure study demonstrate that this complex is not the complex 8, but a new complex $L^2SmCl(\mu$ - $Cl)_3SmL^2ClLi(L^2H)(THF)$ (9). It is quite unexpected that a lithium chloride incorporated with a neutral β diketimine molecule is coordinated to one samarium atom via a single chlorine bridge. The formation of complex 9 may be attributed to the presence of excess of β -diketimine molecule in the reaction system, which coordinates to the lithium atom and increases the solubility of lithium chloride in toluene. The sparing solubility of complex 6 in toluene prevents its further recrystallization.

Complexes 1–6 are slightly sensitive to air and moisture, and the crystals can be exposed in air for a few hours without apparent decomposition; however, complexes 7–9 are very sensitive to air and moisture.

2.2. Crystal structure determination

ORTEP diagram depicting the molecular structure of complex 3 is shown in Fig. 1, the selected bond lengths and bond angles are given in Table 1. As shown in Fig. 1, complex 3 is a dinuclear neodymium–lithium complex with two chlorine bridges; this is different from the β -diketiminate lanthanide dihalides reported in the literature, in which all of them have neutral structure in solid state. The LNd moiety is bonded through two chlorine bridges to a lithium cation, which in turn is bonded to two oxygen atoms of two THF molecules.

¹ The crystal data for complex 6: monoclinic, space group P21/n, a = 20.718(9), b = 14.008(6), c = 20.728(9) Å, $\beta = 93.799(4)^{\circ}$, V = 6002(4) Å³.



Scheme 3.



Fig. 1. Molecular structure of complex **3**. Thermal ellipsoids are drawn at the 50% probability level.

The Nd ion displays a distorted octahedral geometry defined by the two nitrogen atoms of the chelating bidentate β -diketiminate ligand, three chlorine atoms, and one oxygen atom from THF molecule (Cl(1), Cl(3), O(1) and N(2) form a plane, N(1) and Cl(2) serve as two vertexes), while Li ion adopts a distorted tetrahedral geometry formed by two chlorine ligands and two oxygen atoms of THF molecules.

The β -diketiminate ligand is symmetrically coordinated to the neodymium atom, which is similar to those found in L⁴SmCl₂(THF)₂ [16] and L¹GdBr₂(THF)₂ [3], but different from those in L¹SmCl₂(THF)₂ [16] and L³ScCl₂(THF) [7], in which two nitrogen atoms are

Table 1		
Selected bo	nd lengths (Å) and angles (°) in complex 3	
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Bond lengths			
Nd(1)-N(1)	2.445(5)	Nd(1)–N(2)	2.422(5)
Nd(1)–O(1)	2.497(4)	Nd(1)–Cl(1)	2.746(2)
Nd(1)-Cl(2)	2.783(2)	Nd(1)-Cl(3)	2.664(2)
Li(1)–Cl(1)	2.38(1)	Li(1)–Cl(2)	2.36(1)
Li(1)–O(2)	1.91(2)	Li(1)-O(3)	1.92(1)
N(1)-C(1)	1.324(7)	N(2)–C(3)	1.335(7)
C(1)–C(2)	1.382(9)	C(2)–C(3)	1.391(9)
Bond angles			
O(1) - Nd(1) - N(1)	91.1(2)	N(1)-Nd(1)-N(2)	76.9(2)
O(1)-Nd(1)-N(2)	167.2(2)	O(1)-Nd(1)-Cl(3)	89.0(1)
O(1)-Nd(1)-Cl(2)	85.0(1)	O(1)-Nd(1)-Cl(1)	81.5(1)
N(1)-Nd(1)-Cl(3)	93.7(1)	N(2)-Nd(1)-Cl(3)	96.1(1)
N(1)-Nd(1)-Cl(2)	175.1(1)	N(1)-Nd(1)-Cl(1)	96.2(1)
N(2)-Nd(1)-Cl(2)	106.7(1)	N(2)-Nd(1)-Cl(1)	95.3(1)
Cl(2)-Nd(1)-Cl(3)	89.33(5)	Cl(1)-Nd(1)-Cl(2)	80.22(5)
Cl(1)-Nd(1)-Cl(3)	166.38(5)	Cl(1)-Li(1)-Cl(2)	97.6(5)

asymmetrically coordinated to the central metal. The average Nd–N bond length of 2.433(7) Å is comparable with the corresponding bond lengths in $L^2YbCl_2(THF)_2$ [17], $L^{3}ScCl_{2}(THF)$ [7], and $L^{4}SmCl_{2}(THF)_{2}$ [16], but apparently longer than that in $L^{1}SmCl_{2}(THF)_{2}$ [16], when the difference in ionic radii is considered [25]. It is reasonable to ascribe these differences in bond parameters to the less steric congestion in the latter due to no substituent on the arene ring of the ligand. The bond lengths of Nd–Cl(1) and Nd–Cl(2) are apparently longer than that of Nd-Cl(3), due to the formation of bridge bonds. The Nd–C(1,2,3) distances are quite long, suggesting a negligible π contribution to the β -diketiminate-Nd bonding in this complex. The bond distances of C(1)-C(2), C(2)-C(3), N(1)-C(1) and N(2)-C(3) lie intermediate between the corresponding single- and double-bond distances (see Table 1), which suggest

significant delocalization within the π -system of β -diketiminate backbone.

The molecular structure of complex 7 is shown in Fig. 2, and the selected bond lengths and angles are listed in Table 2. Complex 7 has a dinuclear structure in the solid state. The interesting feature of this structure is that the two ytterbium centers are triply chlorine-bridged. Moreover, the coordination environment around the two ytterbium centers in complex 7 is in-equivalent, although the coordination geometry around



Fig. 2. Molecular structure of complex **7**. Thermal ellipsoids are drawn at the 20% probability level. Hydrogen atoms are omitted for the sake of clarity.

Table 2 Selected bond lengths (Å) and angles (°) in complex 7

Bond lengths			
Yb(1)–N(1)	2.278(4)	Yb(2)–N(3)	2.286(4)
Yb(1)–N(2)	2.284(4)	Yb(2)–N(4)	2.285(4)
Yb(1)–Cl(1)	2.496(1)	Yb(2)–O(1)	2.273(4)
Yb(1)-Cl(2)	2.701(1)	Yb(2)–Cl(2)	2.662(1)
Yb(1)-Cl(3)	2.720(1)	Yb(2)–Cl(3)	2.671(1)
Yb(1)-Cl(4)	2.745(1)	Yb(2)–Cl(4)	2.624(1)
N(1)–C(2)	1.328(7)	C(23)–N(3)	1.332(7)
C(2)–C(3)	1.417(8)	C(23)–C(24)	1.401(9)
C(3)–C(4)	1.392(8)	C(24)-C(25)	1.401(9)
C(4)–N(2)	1.325(7)	C(25)–N(4)	1.336(7)
Yb(1)–Yb(2)	3.648		
Bond angles			
N(1) - Yb(1) - N(2)	80.3(2)	N(3)-Yb(2)-N(4)	81.3(2)
N(1)-Yb(1)-Cl(1)	101.2(1)	N(3)-Yb(2)-O(1)	93.9(2)
Cl(1)-Yb(1)-Cl(3)	91.78(5)	O(1)-Yb(2)-Cl(2)	84.3(1)
Cl(3)-Yb(1)-Cl(4)	77.02(4)	Cl(2)-Yb(2)-Cl(4)	79.82(4)
N(1)-Yb(1)-Cl(4)	89.7(1)	N(3)-Yb(2)-Cl(4)	102.0(1)
N(2)-Yb(1)-Cl(2)	166.4(3)	N(4)-Yb(2)-Cl(3)	179.4(1)
Yb(1)–Cl(2)–Yb(1)	85.75(3)	Yb(1)–Cl(3)–Yb(2)	85.19(4)
Yb(1)-Cl(4)-Yb(2)	85.60(4)		

two ytterbium centers is similar (six-coordinate distorted octahedral). The Yb(1) atom is coordinated by two nitrogen atoms of the β -diketiminate ligand, and one terminal chlorine atom and three bridged chlorine atoms; the Yb(2) center is coordinated by two nitrogen atoms, and three bridged chlorine atoms and one oxygen atom of THF molecule.

The backbone of the ligand (NC₃N) and ytterbium atom form a stable six-membered ring, which adopts a boat conformation with C(3) and Yb(1) lying 0.14 and 0.69 Å out of the N(1)C(2)C(4)N(2) plane; and C(24) and Yb(2) lying 0.10 and 0.62 Å out of the N(3)C(23)-C(25)N(4) plane, respectively. The dihedral angle between these planes is 106.56°, which indicates that the orientation of the two β -diketiminate ligands is approximately perpendicular. The orientation of the arene rings relative to the NC₂N plane is also approximately perpendicular (the average dihedral angles between the arene rings and the NC₂N planes range from 80.84° to 91.73°). This disposition can release the steric repulsion among the methyl substituents on the arene rings and the backbone of the β -diketiminate.

Two β-diketiminate ligands are symmetrically coordinated to Yb(1) and Yb(2), respectively, and the Yb-N bond distances range from 2.278(4) to 2.286(4) Å, which is comparable with those found in $L^{3}YbCl(\mu$ - $Cl_3YbL^3(THF)$ [15] and $L^2YbCl_2(THF)_2$ [17]. The Yb(1)-Cl(1) and Yb(2)-O(1) bond lengths are also comparable with those in $L^{3}YbCl(\mu-Cl)_{3}YbL^{3}(THF)$ [15], but apparently shorter than the corresponding bond lengths in $L^2YbCl_2(THF)_2$ [17], although the latter has monomeric structure. The three chlorine bridges in complex 7 are asymmetrical. The averaged Yb(1)-Cl(2,3,4) bond length of 2.722(1) Å is ca. 0.07 Å longer than that of Yb(2)-Cl(2,3,4), which is well comparable with that found in $L^{3}YbCl(\mu-Cl)_{3}YbL^{3}(THF)$ [15]. There is an expected pattern of delocalization within the π -system of the β -diketiminate ligand.

The molecular structure of complex 9 is shown in Fig. 3, and the selected bond lengths and angles are listed in Table 3. Complex 9 is a trinuclear species; there is also a triple chlorine bridge between two samarium atoms in complex 9. The apparent difference between complex 9 and 7 is that one lithium chloride incorporated with a neutral β -diketimine and a THF molecule in place of the THF is coordinated to Sm(2) in complex 9. The coordination geometry around the samarium atom also resembles that in complex 7 and the coordination environment around samarium atoms in complex 9 is still inequivalent. By comparison of the molecular structures of complexes 7 and 9 and the analogous complex $L^{3}YbCl(\mu-Cl)_{3}YbL^{3}(THF)$ [15], it seems that the formation of triple chlorine bridge in β -diketiminate lanthanide dichlorides is popular under the lack of coordinated solvent. This may be attributed to the structural property of the β -diketiminate ligands. Due to the



Fig. 3. Molecular structure of complex **9**. Thermal ellipsoids are drawn at the 20% probability level. Hydrogen atoms are omitted for the sake of clarity.

Table 3 Selected bond lengths (Å) and angles (°) in complex ${\bf 9}$

Bond lengths			
Sm(1)-N(1)	2.38(1)	Sm(2)–N(3)	2.380(9)
Sm(1)–N(2)	2.38(1)	Sm(2)–N(4)	2.357(9)
Sm(1)-Cl(1)	2.799(3)	Sm(2)–Cl(1)	2.805(3)
Sm(1)–Cl(2)	2.794(3)	Sm(2)–Cl(2)	2.789(3)
Sm(1)–Cl(3)	2.803(3)	Sm(2)–Cl(3)	2.816(3)
Sm(1)–Cl(4)	2.670(3)	Sm(2)–Cl(5)	2.622(3)
Li(1)-N(5)	2.01(3)	Li(1)-N(6)	2.08(3)
N(5)-C(44)	1.28(2)	N(6)-C(46)	1.26(2)
Li(1)-Cl(4)	2.45(2)	Li(1)-O(1)	1.89(2)
N(1)–C(2)	1.36(2)	N(3)–C(23)	1.33(2)
C(2)–C(3)	1.38(2)	C(23)-C(24)	1.43(2)
C(3)–C(4)	1.39(2)	C(24)–C(25)	1.38(2)
N(2)–C(4)	1.34(2)	N(4)-C(25)	1.36(2)
N(5)-C(44)	1.28(2)	C(45)-C(46)	1.50(2)
C(44)-C(45)	1.50(2)	N(6)-C(46)	1.26(2)
Bond angles			
N(1)-Sm(1)-N(2)	76.4(3)	N(3)-Sm(2)-N(4)	79.1(4)
Cl(1)-Sm(1)-Cl(4)	91.4(1)	N(4)-Sm(2)-Cl(2)	93.4(3)
Cl(2)-Sm(1)-Cl(1)	76.72(9)	Cl(2)-Sm(2)-Cl(1)	76.71(9)
N(2)-Sm(1)-Cl(2)	89.0(3)	Cl(1)-Sm(2)-Cl(5)	93.7(1)
N(2)-Sm(1)-Cl(4)	103.0(3)	N(4)-Sm(2)-Cl(5)	96.5(3)
N(1)-Sm(1)-Cl(3)	165.8(3)	N(3)-Sm(2)-Cl(3)	170.1(3)
N(5)-Li(1)-N(6)	95.7(11)	Sm(1)-Cl(1)-Sm(2)	88.12(9)
Sm(2)–Cl(2)–Sm(1)	88.54(9)	Sm(1)–Cl(3)–Sm(2)	87.86(8)
Cl(2)-Sm(2)-Cl(5)	167.9(1)	Cl(4)–Sm(1)–Cl(2) 164.	
Sm(1)Cl(4)Li(1)	136.2(5)		

bulkiness of these ligands, one β -diketiminate ligand can stabilize the lanthanide dichloride, but one edge of the coordination sphere of the complex formed is much more open, and the triple chlorine bridge is formed to meet the coordination saturation when Lewis base is lacking.

The six-membered chelating rings formed by metal atoms and the backbone of the ligands also adopt boat conformation, with Sm(1) and C(3), Sm(2) and C(24), Li(1) and C(45) out of the planes N(1)C(2)C(4)N(2)(plane 1), N(3)C(23)C(25)N(4) (plane 2) and N(5)C(44)-C(46)N(6) (plane 3), respectively. The dihedral angles between plane 1 and plane 2, plane 2 and plane 3 are 103.06° and 96.53°, respectively; while the dihedral angle between plane 1 and plane 3 is 6.86°, which indicates that the orientation of plane 1 and plane 2, as well as plane 2 and plane 3 is approximately perpendicular, while the orientation of plane 1 and plane 3 is nearly parallel. This disposition can effectively release the steric congestion among the two β-diketiminate ligands and the neutral β -diketimine. It is worthy to note that the six atoms Cl(5), Sm(2), Cl(2), Sm(1), Cl(4) and Li(1) are nearly coplanar (plane 4) (the mean deviation from the least-squares plane is 0.007 Å). The dihedral angles between plane 4 and plane 1–3 vary from 88.66° to 91.15°, which reveals that the orientations of plane 4 and plane 1–3 are also nearly perpendicular.

Two β -diketiminate ligands are also symmetrically coordinated to Sm(1) and Sm(2), respectively, and the averaged Sm-N bond length of 2.374(5) Å compares well with the 2.392(3) Å found in $L^4SmCl_2(THF)_2$ [16], but it is slightly longer than that in $L^{1}SmCl_{2}(THF)_{2}$ (2.33(1) Å) [16]. In contrast to that in complex 7, the three chlorine bridges in complex 9 are symmetrically coordinated to the two samarium atoms. The Sm-Cl(1,2,3) bond lengths range from 2.789(3) to 2.816(3) A, giving the average bond length of 2.801(3) A, which is comparable with the corresponding values in complex 7, and $L^{3}YbCl(\mu-Cl)_{3}YbL^{3}(THF)$ [15], when the difference in ionic radii is considered. Interestingly, the terminal Sm(1)–Cl(4) bond length is only 0.05 Å shorter than the bridged Sm(2)-Cl(5) bond length; and this bond length is also apparently longer than those in complex 7, and $L^{3}YbCl(\mu-Cl)_{3}YbL^{3}(THF)$ [15], even the difference in ionic radii is considered. But this value is still comparable with that in $L^4SmCl_2(THF)_2$ [16]. The Sm(1)–C(14) distance of 3.19(2) A is comparable with that of 3.180(9) Å for bridging η^2 -C₅H₅ bonding in $(C_5Me_5)_2Sm(\mu-C_5H_5)Sm(C_5Me_5)_2$ [26], which indicates that the complex may be considered to involve π coordination of the β -diketiminate ligand to the samarium(1) atom. However, the Sm(2)-C distances are beyond 3.30 A, which indicates that there is only pure σ bonding between the β -diketiminate ligand and the samarium(2) atom. The bond lengths of N(5)-C(44)and N(6)–C(46) are 1.28(2) and 1.26(2) Å, respectively, which is consistent with the C=N double bond length; furthermore, the C(44)–C(45) and C(45)–C(46) bond lengths compare well with the C–C single bond length. Thus the neutral β -diketimine adopts the diimine tautomer, which is different from that of the free β -diketimine [27,28].

3. Experimental

Reactions were performed under pure argon atmosphere with exclusion of air and moisture by Schlenk techniques. Solvents were dried and freed of oxygen by refluxing over sodium or sodium benzophenone ketyl and distilled under argon prior to use. Anhydrous LnCl₃ [29] and L²Li [28] were prepared according to the literature methods. Melting points were determined in sealed argon-filled capillaries and are uncorrected. Metal analyses were carried out using complexometric titration. Carbon, hydrogen and nitrogen analyses were performed by direct combustion on a Carlo Erba-1110 instrument; quoted data are the average of at least two independent determinations. The IR spectra were recorded on a Nicolet-550 FTIR spectrometer as KBr.

3.1. Synthesis of L^2 YbCl(THF)(μ -Cl)₂Li(THF)₂ (1)

A solution of L^2Li (25 ml, 5.56 mmol) in THF/hexane was slowly added to a suspension of YbCl₃ (1.55 g, 5.56 mmol) in 40 ml THF at room temperature (r.t.). The color of the solution gradually changed to red. The reaction mixture was stirred overnight at r.t., then the solution was concentrated to 25 ml and cooled at -5 °C. Complex 1 was obtained as a red microcrystal (3.50 g, 78%). M.p. 169–171 °C (dec.). IR (KBr, cm⁻¹): 3137(s), 2966(s), 2847(s), 2658(w), 1624(m), 1597(m), 1555(s), 1474(s), 1300(s), 1200(m), 1096(w), 1042(w), 768(m), 667(w). *Anal.* Calc. for C₃₃H₄₉Cl₃N₂O₃LiYb: C, 49.05; H, 6.11; N, 3.47; Yb, 21.41; Found: C, 48.97; H, 5.98; N, 3.41; Yb, 21.12%.

3.2. Synthesis of L^2 SmCl(THF)(μ -Cl)₂Li(THF)₂ (2)

The synthesis of complex **2** was carried out as described for **1**, but anhydrous SmCl₃ (1.59 g, 6.0 mmol) was used in place of YbCl₃. The yellow microcrystals of **2** were obtained from concentrated THF solution at r.t. (3.56 g, 73%). M.p. 165–167 °C (dec.). IR (KBr, cm⁻¹): 3144(s), 2963(s), 2843(s), 2658(w), 1628(s), 1555(s), 1447(s), 1377(m), 1323(s), 1200(m), 1096(w), 1042(m), 764(m). *Anal.* Calc. for C₃₃H₄₉Cl₃N₂O₃LiSm: C, 50.47; H, 6.29; N, 3.57; Sm, 19.14; Found: C, 50.27; H, 6.61; N, 3.87; Sm, 19.03%.

3.3. Synthesis of $L^2NdCl(THF)(\mu-Cl)_2Li(THF)_2$ (3)

The synthesis of complex **3** was carried out as described for **1**, but anhydrous NdCl₃ (1.33 g, 5.32 mmol) was used in place of YbCl₃. The blue crystals were obtained from concentrated THF solution at r.t. (3.08 g, 71%). M.p. 241–242 °C (dec.). IR (KBr, cm⁻¹): 3171(m), 2963(m), 2843(m), 2658(w), 1624(m), 1555(s), 1474(m), 1296(m), 1381(w), 1188(w), 1034(w), 768(w). *Anal.* Calc. for $C_{33}H_{49}Cl_3N_2O_3LiNd$: C, 50.86; H, 6.34; N, 3.59;

Nd, 18.51; Found: C, 50.84; H, 5.82; N, 3.63; Nd, 18.36%.

3.4. Synthesis of $L^2 YbCl_2(THF)_2$ (4)

Complex 1 (2.93 g, 3.63 mmol) was dissolved in 50 ml of toluene. The reaction mixture was stirred overnight at 50 °C oil bath. The precipitation was removed by centrifugation. Complex 4 was obtained as red microcrystals from concentrated toluene solution (1.86 g, 74%). M.p. 172–174 °C (dec). IR (KBr pellet, cm⁻¹): 3418(s), 3144(s), 2967(s), 2923(m), 2847(m), 1597(m), 1559(vs), 1539(vs), 1474(s), 1443(m), 1381(m), 1364(s), 1300(s), 1044(m), 1096(w), 922(w), 764(m). *Anal.* Calc. for C₂₉H₄₁Cl₂N₂O₂Yb: C, 50.00; H, 6.37; N, 4.02; Yb, 24.83. Found: C, 49.66; H, 5.91; N, 4.08; Yb, 24.37%.

3.5. Synthesis of $L^2 SmCl_2(THF)_2$ (5)

Complex **5** was prepared similar to that of complex **4**, but complex **2** (2.78 g, 3.54 mmol) was used in place of complex **1**. The orange yellow microcrystals of **5** were obtained (1.59 g, 67%). M.p. 235–237 °C (dec.) IR (KBr, cm⁻¹): 3136.5(m), 2962.9(s), 2847.1(m), 1624.2(s), 1597.2(m), 1554.7(s), 1469.9(m), 1442.9(m), 1381.1(m), 1296.3(s), 1199.8(w), 1091.8(w), 1041.6(m), 918.2(w), 763.9(m). *Anal.* Calc. for C₂₉H₄₁Cl₂N₂O₂Sm: C, 51.92; H, 6.16; N, 4.18; Sm, 22.41; Found: C, 52.02; H, 6.03; N, 4.23; Sm, 22.29%.

3.6. Synthesis of $L^2 NdCl_2(THF)_2$ (6)

Complex **6** was prepared similar to that of complex **4**, but complex **3** (2.90 g, 3.72 mmol) was used in place of complex **1**. The pale blue crystals were obtained from concentrated toluene solution (1.76 g, 71%). M.p. 175–177 °C (dec.) IR (KBr, cm⁻¹): 3137(s), 2967(s), 2847(s), 2658(w), 1597(s), 1555(s), 1443(s), 1381(m), 1300(s), 1200(m), 1096(s), 1042(m), 968(w), 763(m). *Anal.* Calc. for $C_{29}H_{41}Cl_2N_2O_2Nd$: C, 52.40; H, 6.22; N, 4.21; Nd, 21.70; Found: C, 51.98; H, 6.31; N, 3.95; Nd, 21.82%.

3.7. Synthesis of $L^2 ClYb(\mu-Cl)_3 YbL^2(THF)$ (7)

A Schlenk flask was charged with complex 4 (1.26 g, 1.82 mmol) and 50 ml of toluene. The red solution was warmed to about 70 °C for 10 min, then the supernatant was removed in vacuum at about 50 °C and the residue was extracted with toluene. The color of the solution gradually changed to violet red. The following manipulations were similar to those described above. The violet red crystals suitable for structural analysis were obtained from concentrated toluene solution at r.t. (0.58 g, 54%). M.p. 214–216 °C (dec.). IR (KBr, cm⁻¹): 2963(w), 2932(w), 2855(w), 1628(m), 1559(s), 1439(m), 1385(m), 1339(w), 1192(w), 1088(w), 1034(m), 968(w),

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768(w). Anal. Calc. for $C_{46}H_{58}Cl_4N_4OYb_2$: C, 47.19; H, 4.99; N, 4.79; Yb, 29.56; Found: C, 46.73; H, 5.31; N, 4.62; Yb, 29.15%.

3.8. Synthesis of $L^2 ClSm(\mu-Cl)_3 SmL^2(THF)$ (8)

Compound **8** was prepared similar to complex **7**, but complex **5** (1.02 g, 1.52 mmol) was used in place of complex **4** and the color of the solution was changed to orange. The orange red microcrystals were obtained from concentrated toluene solution at -5 °C (0.44 g, 51%). M.p. 236–238 °C (dec.). IR (KBr, cm⁻¹): 2974.5(m), 2939.7(s), 2878.0(w), 2739.1(s), 2677.4(s), 2492.2(s), 1604.9(m), 1512.3(w), 1473.7(m), 1396.6(m), 1365.7(w), 1169.0(m), 1037.8(m), 752.3(w). *Anal.* Calc. for C₄₆H₅₈Cl₄N₄OSm₂: C, 49.09; H, 5.19; N, 4.98; Sm, 26.72; Found: C, 48.70; H, 5.76; N, 4.98; Sm, 26.54%.

3.9. Synthesis of $L^2 SmCl(\mu-Cl)_3 SmL^2(\mu-Cl)Li(L^2H)$ (THF) (9)

The solvent of the mother liquor of complex 2 was evaporated to dryness under reduced pressure and the residue was extracted with toluene. After separation the precipitation was removed by centrifugation, the toluene solution was treated as described for 7, and the color of the solution was changed to orange red. Crystals suitable for X-ray structure studies were obtained at -5 °C (0.08 g). M.p. 215–217 °C (dec.). IR (KBr, cm⁻¹):

Table 4

Crystallographic data for complexes $\textbf{3}\cdot 0.5C_4H_8O,\,\textbf{7}\cdot 1.5C_7H_8$ and $\textbf{9}\cdot 2C_7H_8$

3021(s), 2959(s), 2920(s), 2855(s), 1845(s), 1624(s), 1539(s), 1377(s), 1281(s), 1181(s), 1092(m), 1030(m), 984(w), 968(s), 918(w), 810(m), 729(m), 694(m), 598(w), 467(w). *Anal.* Calc. for $C_{67}H_{84}Cl_5N_6OLiSm_2$: C, 54.58; H, 5.74; N, 5.70; Sm, 20.40; Found: C, 54.11; H, 5.90; N, 5.23; Sm, 20.01%.

3.10. X-ray structure determination

Suitable single crystals of complexes 3, 7 and 9 were each sealed in a thin-walled glass capillary and intensity data were collected on a MSC/AFC diffractometer (for 3), Rigaku Mercury CCD (for 7 and 9) equipped with graphite monochromatized Mo K α ($\lambda = 0.71073$ Å) radiation. Details of the intensity data collection and crystal data are given in Table 4. The crystal structures of these complexes were solved by direct methods and expanded by Fourier techniques. Atomic coordinates and thermal parameters were refined by full-matrix leastsquares analysis on F^2 . All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were all generated geometrically (C–H bond lengths fixed at 0.95 Å) with assigned appropriate isotropic thermal parameters.

4. Supplementary data

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic

	$3 \cdot 0.5 C_4 H_8 O$	$7 \cdot 1.5 C_7 H_8$	$9 \cdot 2C_7H_8$
Formula	C35H53Cl3N2O3.5LiNd	$C_{56,50}H_{70}Cl_4N_4OYb_2$	C ₈₁ H ₁₀₀ Cl ₅ N ₆ OLiSm ₂
Molecular weight	815.25	1309.09	1658.56
Temperature (K)	273(2)	193(2)	193(2)
Crystal system	monoclinic	triclinic	monoclinic
Crystal color and habit	pale blue, block	red, chunk	yellow, chip
Space group	C2/c	Р	P21/n
Unit cell dimensions			
a (Å)	34.570(1)	13.2325(1)	19.061(2)
b (Å)	14.0550(9)	14.6918(2)	26.744(2)
<i>c</i> (Å)	20.999(1)	16.0271(3)	18.506(2)
α (°)	90	100.57(1)	90
β (°)	126.960(5)	110.697(7)	110.022(4)
γ (°)	90	96.64(1)	90
$V(Å^3)$	8152.8(8)	2809.50(7)	8863(2)
Ζ	8	2	4
$D_{\text{calc}} (\text{g cm}^{-3})$	1.328	1.547	1.243
$\mu (\mathrm{mm}^{-1})$	1.503	3.539	1.504
F(000)	3352	1298	3392
Crystal size (mm)	0.22 imes 0.18 imes 0.18	0.40 imes 0.30 imes 0.15	0.30 imes 0.40 imes 0.21
$2\theta_{\rm max}$ (°)	55.0	55.0	50.1
Reflections collected	25 0 5 3	28 353	81 156
Independent reflections	9457	12676	15 508
Observed reflections	5914 ($I \ge 1.5\sigma(I)$)	$11410 \ (I \ge 2.0\sigma(I))$	14451 $(I \ge 2.0\sigma(I))$
Parameters refined	388	584	815
R	0.0463	0.0464	0.1265
wR_2	0.545	0.1024	0.2124

Data Center, CCDC No. 222574–222576 for complexes **3**, **7** and **9**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +/44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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