ELSEVIER

Available online at www.sciencedirect.com

ScienceDirect

Polyhedron 27 (2008) 709–716

POLYHEDRON

www.elsevier.com/locate/poly

Synthesis, reactivity and structural characterization of sodium and ytterbium complexes stabilized by a tridentate [*N*,*N*,*O*] Schiff base ligand

Bang-Yu Li [a], Ying-Ming Yao [a,*], Yao-Rong Wang [b], Yong Zhang [a], Qi Shen [a,*]

[a] *Key Laboratory of Organic Synthesis of Jiangsu Province, Department of Chemistry and Chemical Engineering, Dushu Lake Campus, Suzhou University, Suzhou 215123, PR China*

[b] *College of Material Engineering, Suzhou University, Suzhou 215123, PR China*

Received 16 October 2007; accepted 30 October 2007
Available online 4 December 2007

Abstract

A tridentate [*N*,*N*,*O*] Schiff base $[3,5\text{-Bu}^t_2\text{-2-(OH)-C}_6\text{H}_2\text{CH{=}N-8-C}_9\text{H}_6\text{N(LH)}]$ was prepared, and the corresponding sodium and ytterbium complexes were synthesized and characterized. Reaction of LH with NaH in THF at room temperature afforded the sodium salt of the Schiff base as a dimer $[\{\text{LNa(THF)}\}_2]$ (**1**). Complex **1** reacted with anhydrous YbCl_3 in THF, after workup, to give the monomeric ytterbium Schiff base dichloride complex, $[\text{LYbCl}_2\text{(DME)}]$ (**2**). Complex **2** is a good precursor for the synthesis of the corresponding ytterbium derivatives. Reaction of complex **2** with 1 equiv. of $\text{NaCH}_3\text{C}_5\text{H}_4$ in THF gave the expected product $[\text{LYb(CH}_3\text{C}_5\text{H}_4\text{)Cl(THF)}]$ (**3**) in a good isolated yield. Similar reaction of complex **2** with 2 equiv. of ArONa ($\text{ArO{=}OC}_6\text{H}_3\text{-Bu}^t_2\text{-2,6}$) in THF afforded the desired solvent-free ytterbium aryloxide $[\text{LYb(OAr)}_2]$ (**4**). Complex **4** can also be prepared by the protolytic exchange reaction of LH with $\text{(ArO)}_3\text{Yb}$ in a 1:1 molar ratio. All of these complexes were well characterized including X-ray structure determination.

Keywords: Alkali metal; Lanthanide; Schiff base; Synthesis; Crystal structure

1. Introduction

Over the past decade, significant efforts to explore ligands other than traditional ancillary ligand cyclopentadienyl set in organolanthanide chemistry have led to the fruitful design of new non-lanthanocene complexes [1–4]. Of these alternatives, Schiff base ligands, that have hard donor-atom frameworks, are attractive due to their stability and the ease by which modified variations can be obtained. Moreover, these lanthanide complexes are known to serve as precatalysts in homogeneous catalysis, such as asymmetric ring opening reaction of epoxide, ring opening polymerization of lactide and related cyclic esters [5–7], as the materials for the potential applications in biology, medicine as well as high-technology fields [8–12]. Generally, the tridentate Schiff base ligands with a flexible donor atom, in comparison with the bidentate ligands, can provide the protective shields for catalytically active metal centers leading to a “more stable” active species via the coordination of the additional donor atom. As a result, the activity of the complex with a tridentate Schiff base ligand is much higher than that of the complex with a bidentate ligand [13,14]. However, anhydrous preparation and reactivity of lanthanide complexes with a tridentate Schiff base ligand still remains poorly explored. Recently, monomeric lanthanocene aryloxide complexes with a tridentate Schiff base ligand *N*-1-(*ortho*-methoxyphenyl) salicylideneamine was synthesized and structurally characterized [15].

---

[*] Corresponding authors. Tel.: +86 512 65880306; fax: +86 512 65880305 (Q. Shen).
E-mail addresses: yaoym@suda.edu.cn (Y.-M. Yao), qshen@suda.edu.cn (Q. Shen).

0277-5387/$ - see front matter © 2007 Published by Elsevier Ltd.
doi:10.1016/j.poly.2007.10.025

Herein, we report the synthesis and molecular structure of a series of sodium and ytterbium complexes supported by a tridentate Schiff base ligand including the complexes of formulae [{LNa(THF)}$_2$], [LYbCl$_2$(DME)], [LYb(CH$_3$C$_5$H$_4$)Cl(THF)] and [LYb(OAr)$_2$], where L = [3,5-Bc$^t_2$-2-(O)C$_6$H$_2$CH=N-8-C$_9$H$_6$N]; ArO=OC$_6$H$_3$Bu$^t_2$-2,6. To our best knowledge, [LYbCl$_2$(DME)] is the first structurally characterized lanthanide dichloride complex stabilized by Schiff base ligand.

2. Results and discussion

2.1. Synthesis and characterization of [{LNa(THF)}$_2$] (**1**)

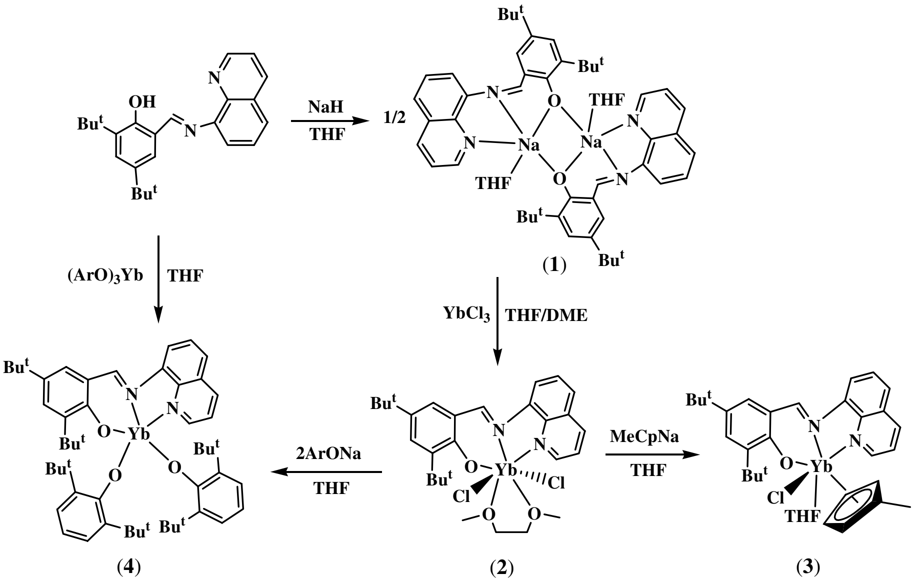
Alkali metal salts of Schiff base are known to be the starting reagents for the anhydrous preparation of lanthanide Schiff base complexes. It may be very informative to know the structure of these starting reagents. However, few structurally characterized Schiff base sodium complexes were reported in the literatures [16,17]. Thus, the sodium salt of the tridentate Schiff base HL, which was synthesized by the condensation reaction of 8-aminoquinoline with 3,5-di-*tert*-butyl-2-hydroxylbenzaldehyde [13], was synthesized and characterized. Reaction of NaH with HL in THF, after workup, afforded [{LNa(THF)}$_2$] (**1**) as yellow crystals as shown in Scheme 1. Complex **1** gave satisfactory elemental analysis results, and its IR spectrum shows the characteristic absorption bands of aromatic rings in the region 1400–1600 cm^{-1} (skeletal vibrations), and of the C=N stretching vibration at 1613 cm^{-1} and of the phenolic C–O bond at 1242 cm^{-1}. The definitive molecular structure was determined by single-crystal X-ray diffraction.

The molecular structure of complex **1** is shown in Fig. 1, and its selected bond lengths and angles are listed in Table 1. Complex **1** has a dimeric structure, and two molecules are connected together by two bridged oxygen atoms. The molecules have approximate C_2 symmetry. Each sodium atom is five-coordinated with one oxygen atom, two nitrogen atoms from one Schiff base ligand, one oxygen atom from another ligand and one oxygen atom from a THF molecule. The coordination geometry at sodium atom can be described as a distorted trigonal bipyramid, in which O(2), O(3) and N(1) can be considered to occupy the equatorial positions, and O(1) and N(2) to occupy the apical positions.

The average Na–O(Ar) bond lengths of 2.279(4) Å falls in the range of Na–O(Ar) bond lengths in [Na$_4$(salphen)$_2$(DME)$_2$] (salphen = *N*,*N*′-*o*-phenylenebis(salicylideneimine), 2.252(9)–2.291(9) Å) [16] and [Na(18-crown-6)(THF)$_2$]$_2$[Na$_2$(OC$_6$H$_4$-2-C=NCH$_2$CH$_2$OH)]$_4$ (2.221(3)–2.235(4) Å) [17]. The Na–N(imine) bond lengths of 2.407(3) (Na(1)–N(1)) and 2.388(3) Å (Na(2)–N(3)) are comparable with those found in [Na$_4$(salphen)$_2$(DME)$_2$] (2.38(1) and 2.37(1) Å) [16], but are smaller than those in [Na(18-crown-6)(THF)$_2$]$_2$[Na$_2$(OC$_6$H$_4$-2-C=NCH$_2$CH$_2$OH)]$_4$ (2.492(4) and 2.570(4) Å) [17]. The bond lengths of Na–N(quinoline) are 2.550(3) (Na(1)–N(2)) and 2.403(3) Å (Na(2)–N(4)), respectively, which are larger than the Na–N(imine) bond lengths.

2.2. Synthesis and characterization of ytterbium complexes

Although lanthanide dichloride complex supported by a Schiff base ligand might be an important precursor for the synthesis of the corresponding lanthanide derivatives via metathesis reactions, no example of such lanthanide dichloride was reported up to date. Thus, we intend to synthesize the ytterbium dichloride complex with the bulky tridentate Schiff base group L as an ancillary ligand. Reaction of



Scheme 1.

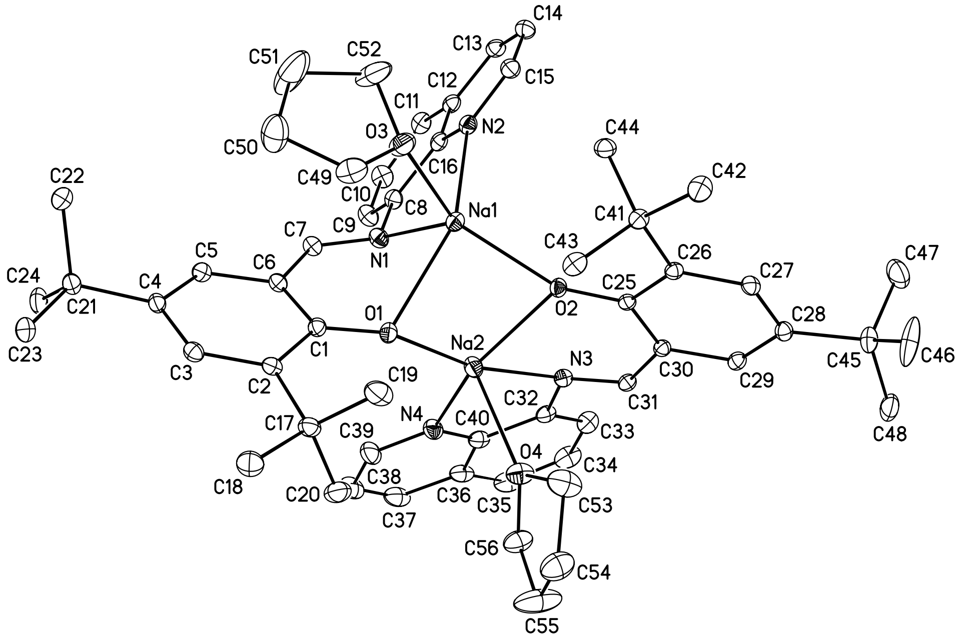


Fig. 1. ORTEP diagram of complex **1** showing atom-numbering scheme. Thermal ellipsoids are drawn at the 20% probability level. Hydrogen atoms are omitted for clarity.

Table 1
Selected bond distances (Å) and angles (°) for complexes **1**–**4**

	1	2	3	4
Bond distances				
M(1)–O(1)	2.365(2)	2.115(2)	2.116(3)	2.104(2)
M(1)–O(2)	2.274(2)	2.526(2)	2.450(3)	2.089(2)
M(1)–O(3)	2.341(3)	2.417(2)		2.082(2)
M(1)–N(1)	2.407(3)	2.386(3)	2.400(3)	2.359(3)
M(1)–N(2)	2.550(3)	2.470(3)	2.436(4)	2.410(3)
Yb(1)–Cl(1)		2.5934(8)	2.594(1)	
Yb(1)–Cl(2)		2.5654(9)		
Yb(1)–C(8)				3.197(3)
Yb(1)–C(25)			2.675(5)	
Yb(1)–C(26)			2.644(5)	
Yb(1)–C(27)			2.636(5)	
Yb(1)–C(28)			2.640(5)	
Yb(1)–C(29)			2.645(4)	
Bond angles				
O(1)–M(1)–O(2)	89.83(8)	151.59(8)	78.8(1)	96.25(9)
N(1)–M(1)–N(2)	67.01(8)	66.40(9)	67.5(1)	68.50(9)
N(1)–M(1)–O(2)	108.36(9)	130.53(8)	73.7(1)	132.39(9)
O(1)–M(1)–N(2)	140.10(9)	135.70(9)	142.4(1)	135.22(9)
N(1)–M(1)–O(1)	73.11(8)	75.96(9)	77.2(1)	76.73(8)
O(2)–M(1)–N(2)	101.46(8)	72.18(8)	79.2(1)	87.45(9)

anhydrous $YbCl_3$ with complex **1** in THF, after workup, gave the first Schiff base lanthanide dichloride complex $[LYbCl_2(DME)]$ (**2**) in high isolated yield from toluene/DME mixed solvent as shown in Scheme 1. Complex **2** was characterized by elemental analysis and IR spectrum, and its definitive molecular structure was provided by single-crystal X-ray diffraction. Complex **2** is soluble in THF and DME, and slightly soluble in toluene.

The molecular structure of complex **2** is shown in Fig. 2, and the selected bond lengths and angles are provided in Table 1. Complex **2** has a solvated monomeric structure, and the central metal ytterbium atom is seven-coordinated by one oxygen atom and two nitrogen atoms from one Schiff base ligand, and two chlorine atoms and two oxygen atoms from one DME molecule. The coordination geometry around ytterbium atom can be described as a distorted pentagonal bipyramid, in which O(1), N(1), N(2) (from Schiff base ligand), O(2) and O(3) (from DME) can be considered to occupy the equatorial positions with the sum of the bond angles of 366° and Cl(1) and Cl(2) to occupy the axis positions. The bond angle of Cl(1)–Yb–Cl(2) is slightly distorted away from the ideal value of 180° to 162.29(3)°. The Yb–O(Ar) bond distance is 2.115(2) Å, which is very close to those observed in related ytterbium Schiff base complexes $[\{2\text{-}OC_6H_4CH{=}(2,6\text{-}{}^iPr_2C_6H_3)\}_2YbCl(THF)]$ (2.110(7) and 2.10(1) Å) [6], $[\{(\eta^5\text{-}C_5H_5)Yb(\mu\text{-}OC_{20}H_{20}N_2\text{-}O)\}_2(\mu\text{-}THF)(THF)]$ (2.15(2) Å) [18]. The Yb–N(imine) bond distance is 2.386(3) Å, which is slightly smaller than those found in the ytterbium Schiff base complexes mentioned above. The Yb–N(quinoline) bond distance of 2.470(3) Å is apparently larger than the Yb–N(imine) bond distance, indicating the bond strength being somewhat weaker than that of the Yb–N(imine) bond.

Generally, organolanthanide or organolanthanoid chlorides are useful precursors for the synthesis of lanthanide derivatives. Thus, the chloride substitution reactions of complex **2** with other reagents were studied. The reaction of complex **2** with 1 equiv. of $NaCH_3C_5H_4$ in THF went smoothly and, after workup, afforded the desired lanthanide complex $[LYb(CH_3C_5H_4)Cl(THF)]$ (**3**) in good

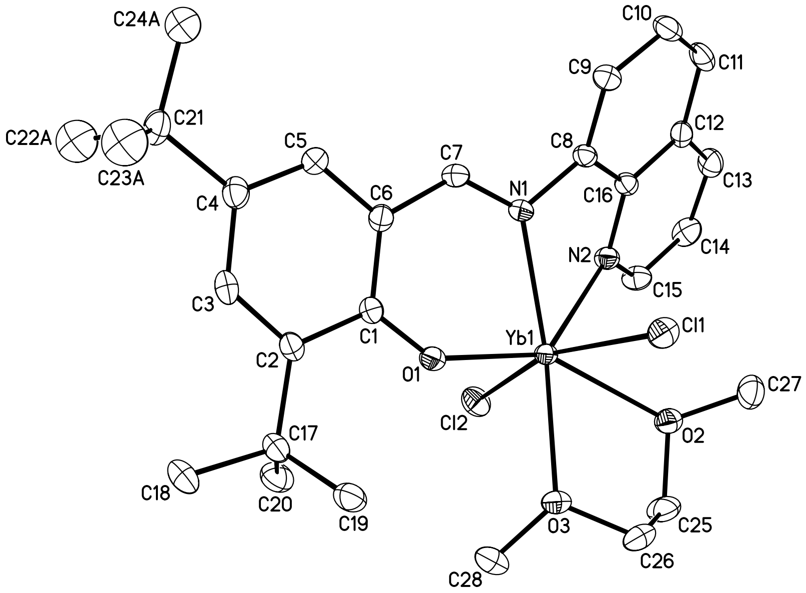


Fig. 2. ORTEP diagram of complex **2** showing atom-numbering scheme. Thermal ellipsoids are drawn at the 40% probability level. Hydrogen atoms are omitted for clarity.

isolated yield (Scheme 1). Similar reaction of complex **2** with 2 equiv. of ArONa in THF, after workup, gave the solvent-free ytterbium aryloxide [LYb(ArO)$_2$] (**4**) as orange-yellow crystals in high yield. Further study revealed that complex **4** can also be conveniently prepared by the direct protolytic exchange reaction of Schiff base LH with Yb(ArO)$_3$ in a 1:1 molar ratio in THF. The compositions of complexes **3** and **4** were confirmed with elemental analysis, and there are characteristic absorption bands of the aryloxo group in their IR spectra. The definitive molecular structures of complexes **3** and **4** were determined by single-crystal structure analysis. Complexes **3** and **4** are well soluble in THF and diethyl ether, and soluble in toluene.

Crystals of complex **3** suitable for an X-ray diffraction study were obtained from THF/Et$_2$O solution at low temperature. An ORTEP diagram of the molecular structure of complex **3** is shown in Fig. 3, and the selected bond lengths and angles are listed in Table 1. Complex **3** has a monomeric structure. The ytterbium atom is coordinated by two nitrogen atoms and one oxygen atom from the Schiff base ligand, one Cp ring, one chlorine atom and another oxygen atom from THF molecule to form a distorted octahedral geometry, when the Cp ring was considered to occupy one coordination site. Two nitrogen atoms, one oxygen atom of the Schiff base ligand and one chlorine atom can be considered to occupy the equatorial positions with the sum of the bond angles of 359.4°, and the centroid

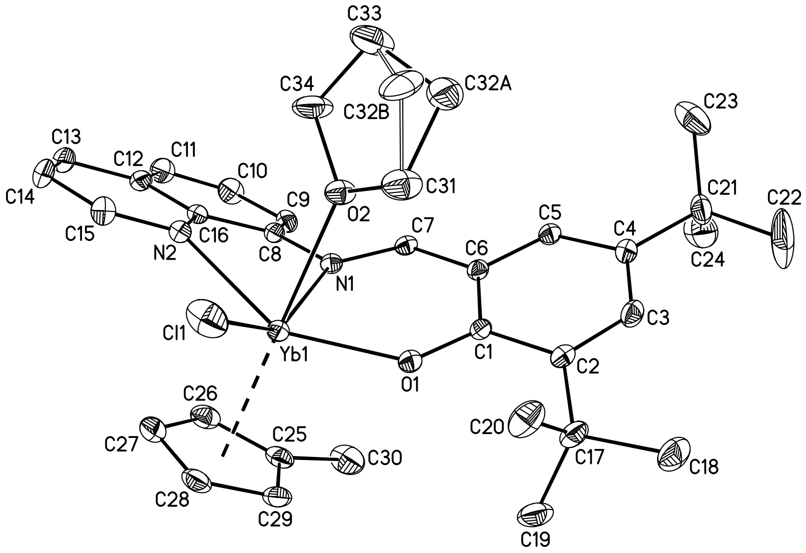


Fig. 3. ORTEP diagram of complex **3** showing atom-numbering scheme. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Disordered THF molecule is shown in two possible orientations.

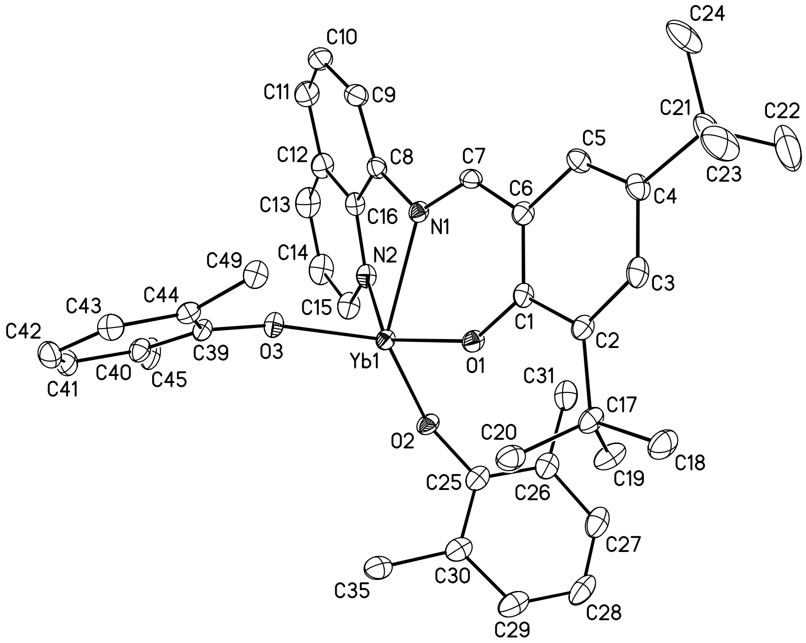


Fig. 4. ORTEP diagram of complex **4** showing atom-numbering scheme. Thermal ellipsoids are drawn at the 30% probability level. Methyl groups of the *tert*-butyl groups of aryloxides and hydrogen atoms are omitted for clarity.

of the Cp ring and the oxygen atom of the THF molecule occupy the apical positions.

The Ln–C(Cp) bond distances range from 2.636(5) to 2.675(5) Å, giving the average 2.648(5) Å, which is slightly smaller than that in lanthanide cyclopentadienyl Schiff base complexes $[\{(\eta^5\text{-}C_5H_5)Ln(\mu\text{-}OC_{20}H_{20}N_2O)\}_2(\mu\text{-THF})(THF)]$ (Ln = Yb, 2.70(3) Å [18]; Ln = Sm, 2.778 Å [19]), and $[(\eta^5\text{-}C_5H_5)_2Sm(OC_{14}H_{13}ON)]$ (2.723 Å) [15], when the difference in ionic radius is considered. The Yb–O(Ar) bond distance of 2.116(3) Å is well comparable with those values in $[\{2\text{-}OC_6H_4CH{=}NC_6H_3\text{-}{}^iPr_2\text{-}2,6\}_2YbCl(THF)]$ (2.107(7) Å) [6], and other lanthanide Schiff base complexes mentioned above. The Yb–N(imine) bond distance of 2.400(3) Å is comparable with the Yb–N(quinoline) bond distance (2.436(4) Å), which is different from that in complex **2**. The Yb–Cl bond distance of 2.594(1) Å is apparently larger than the corresponding value in $[\{2\text{-}OC_6H_4CH{=}N(2,6\text{-}{}^iPr_2C_6H_3)\}_2YbCl(THF)]$ (2.497(2) Å) [6], whereas this bond distance is comparable with that in complex **2**.

Crystals of complex **4** suitable for X-ray diffraction were obtained by recrystallization from toluene. The molecular structure diagram with atom-numbering scheme is presented in Fig. 4, and its selected bond lengths and angles are listed in Table 1. The ytterbium atom is coordinated by one oxygen atom, two nitrogen atoms from the Schiff base ligand and two oxygen atoms from two aryloxo groups to form a five-coordinated highly distorted trigonal bipyramidal geometry. O(2), O(3) and N(1) can be considered to occupy the equatorial positions with the sum of the angles of 355.47°, and O(1) and N(2) to occupy the apical positions. Usually, lanthanide Schiff base complexes have high coordination numbers (>6) via oligomerisation or solvent stabilization, these is few structurally characterized five-coordinated mononuclear lanthanide complexes bearing Schiff base ligands in the literatures [20–23].

The Yb–O(Schiff base), Yb–N(imine) and Yb–N(quinoline) bond distances in complex **4** are 2.104(2), 2.359(3) and 2.410(3) Å, respectively, which are in accordance with the corresponding values in complexes **2** and **3**. The bond distances of Yb–O(Ar) of 2.082(2) and 2.089(2) Å, respectively, compare well with the corresponding value in $[(ArO)_2YbCl(THF)_2]$ (2.080(1) Å) [24], but are slightly larger than that in $[\{(DIPPh)_2nacnac\}Yb(ArO)Cl(THF)]$ [2.024(2) Å, $(DIPPh)_2$nacnac=*N*,*N*-diisopropylphenyl-2,4-pentanediimine anion] [25]. In addition, remote π interaction of C(8) with Yb(1) was observed in complex **4**. The bond distance of Yb(1)–C(8) is 3.197(3) Å, which is comparable to those of 3.207(9) and 3.179(10) Å for imidazolidine-bridged bis(phenolate) ytterbium dichloride [26], and 2.814(4) to 3.148(6) Å for chelating η^6-,η^1-Ph–Yb bonding in $[\{Yb(Odpp)_3\}_2]$ (Odpp=2,6-diphenylphenolate) [27].

3. Conclusion

A bulky tridentate Schiff base was prepared, and this compound can be used as an ancillary ligand for a series of sodium and ytterbium complexes. The Schiff base reacted with NaH to give the corresponding sodium salt as a dimeric complex, which reacted with anhydrous $YbCl_3$ to produce the first structurally characterized soluble ytterbium dichloride bearing Schiff base ligand. It was found that this ytterbium dichloride can be used as a useful precursor for the synthesis of the corresponding ytterbium derivatives by direct salt metathesis reactions. All of these complexes were well characterized, and their molecular structures were determined by X-ray diffraction.

4. Experimental

4.1. Materials and methods

All of the manipulations described below were performed under an argon atmosphere, using the standard Schlenk techniques. Solvents were dried and freed of oxygen by refluxing over sodium or sodium benzophenone ketyl and distilled under argon prior to use. Schiff base ligand HL [3,5-Bu^t_2-2-(OH)$C_6H_2CH{=}N$-8-C_9H_6N] [13], anhydrous $YbCl_3$ [28] and $Yb(OAr)_3$ [29] were prepared according to the literature methods. $NaCH_3C_5H_4$ was prepared by the reaction of $CH_3C_5H_5$ with sodium in THF. The other reagents were purchased from Acros and used as received without further purification. 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. IR spectra were recorded on a Nicolet-550 FTIR spectrometer as KBr pellets. ^{1}H NMR spectrum was obtained on an INOVA-400 MHz apparatus. The uncorrected melting points of crystalline samples in sealed capillaries (under argon) are reported as ranges.

4.2. Synthesis of [{NaL(THF)}$_2$] (*1*)

A solution of HL (1.80 g, 5.0 mmol) in THF (20 mL) was added dropwise to a NaH suspension (1.5 equiv.) in THF at room temperature. The mixture was stirred for 14 h, and then was filtered. The resulting dark red solution was concentrated. Yellow crystals were obtained from the mixture of THF and toluene (6:1) at room temperature in a few days (3.87 g, 85%), m.p.: 279–281 °C (dec). *Anal.* Calc. for $C_{56}H_{70}N_4Na_2O_4$: C, 73.97; H, 7.76; N, 6.16. Found: C, 73.58; H, 7.95; N, 5.76%. IR (KBr pellet, cm^{-1}): 2956(vs), 2909(m), 2871(m), 1613(vs), 1458(vs), 1389(m), 1366(m), 1242(s), 1157(s), 1088(w), 1057(w), 1026(w), 980(w), 880(m), 826(m), 795(m), 640(w), 502(m). ^{1}H NMR (400 MHz, C_6H_6): 8.50–8.48 (m, 1H, C_9H_6N), 8.43 (s, 1H, CH=N), 7.43–7.40 (m, 1H, C_9H_6N), 7.30–7.25 (m, 3H, C_9H_6N), 6.98 (d, 2H, J = 2.6 Hz, C_6H_2), 6.65–6.60 (m, 1H, C_9H_6N), 4.06 (m, 4H, THF), 2.09 (m, 4H, THF), 1.79 (s, 9H, $C(CH_3)_3$), 1.33 (s, 9H, $C(CH_3)_3$).

4.3. Synthesis of [LYbCl$_2$(DME)] (*2*)

A THF solution (10 mL) of complex **1** (0.91 g, 1.0 mmol) was added to a suspension of anhydrous $YbCl_3$ (0.56 mg, 2.0 mmol) in THF (20 mL) at room temperature. After the solution was stirred overnight, the precipitate was separated from the reaction mixture by centrifugation. The solution was concentrated, and then DME (0.5 mL) was added. Yellow crystals were obtained at room temperature in a few days (1.10 g, 80%), m.p.: 266–268 °C (dec). *Anal.* Calc. for $C_{28}H_{37}Cl_2N_2O_3Yb$: C, 48.49; H, 5.38; N, 4.04; Yb, 24.95. Found: C, 48.87; H, 5.67; N, 3.98; Yb, 24.87%. IR (KBr, cm^{-1}): 2956(m), 2928(m), 1613(s), 1535(m), 1498(m), 1427(m),1319(m), 1234(vs), 1158(vs), 833(m),787(m), 633(m), 556(m), 509(s). The crystals suitable for an X-ray crystal structure determination were obtained by recrystallization from THF–DME solution at room temperature.

4.4. Synthesis of [($CH_3C_5H_4$)YbLCl(THF) · THF] (*3* · THF)

A Schlenk flask was charged with complex **2** (0.69 g, 1.0 mmol) and THF (20 mL). A THF solution of $NaCH_3C_5H_4$ (1.0 mL, 1.0 mmol) was added by syringe. The reaction mixture was stirred overnight at room temperature. After removed the volatiles in vacuum, the yellow residue was extracted with Et_2O, and NaCl was removed by centrifugation. Orange-yellow crystals were obtained at room temperature, (0.47 g, 60%), m.p.: 158–160 °C (dec). *Anal.* Calc. for $C_{38}H_{50}ClN_2O_3Yb$ (**3** · THF): C, 57.68; H, 6.37; N, 3.54; Yb, 21.87. Found: C, 57.45; H, 6.63; N, 3.57; Yb, 21.51%. IR (KBr, cm^{-1}): 2956(s), 2905(m), 1608 (s), 1534(m), 1503(m), 1463(m), 1425(m), 1330(m), 1223(vs), 1159(vs), 1086(m), 835(m), 792(m), 506(s).

4.5. Synthesis of [LYb(OAr)$_2$] (*4*)

4.5.1. Method A

A Schlenk flask was charged with complex **2** (0.69 g, 1.0 mmol) and THF (20 mL). A THF solution of NaOAr (2.0 mL, 2.00 mmol) was added by syringe. The reaction mixture was stirred overnight at room temperature. After removed the volatiles in vacuum, the yellow residue was extracted with toluene, and the precipitate was removed by centrifugation. Complex **4** was obtained as yellow crystals at room temperature (0.56 g. 60%), m.p.: 189–191 °C (dec). *Anal.* Calc. for $C_{52}H_{69}N_2O_3Yb$: C, 66.22; H, 7.37; N, 2.97; Yb, 18.35. Found: C, 66.38; H, 7.53; N, 2.91; Yb, 18.27%. IR (KBr, cm^{-1}): 2956(vs), 2909(s), 2871(s), 1613(s), 1528(s), 1505(s), 1466(s), 1428(vs), 1235(s), 1196(s), 1165(s), 1088(m), 1065(m), 833(m), 795(m), 748(m), 656(w), 594(w), 509(w).

4.5.2. Method B

$Yb(OAr)_3$ (0.81 g, 1.0 mmol) in toluene was added dropwise to a THF solution of HL (0.36 g, 1.0 mmol) (30 mL). The reaction mixture was stirred at room temperature for 12 h, and then concentrated in vacuum. Orange-yellow crystals obtained after 4 days at room temperature, (0.66 g. 70%).

4.6. X-ray structures determination

Suitable single crystals of complexes **1**–**4** were sealed in a thin-walled glass capillary for determining the single-crystal structure. Intensity data were collected with a Rigaku Mercury CCD area detector in ω scan mode using Mo

Table 2
Details of the crystallographic data and refinements for complexes **1–4**

Compound	**1** · THF	**2**	**3** · THF	**4**
Formula	$C_{60}H_{78}N_4Na_2O_5$	$C_{28}H_{37}Cl_2N_2O_3Yb$	$C_{38}H_{50}ClN_2O_3Yb$	$C_{52}H_{69}N_2O_3Yb$
F_w	981.24	693.54	791.29	943.13
T (K)	153(2)	193(2)	193(2)	193(2)
Crystal system	monoclinic	monoclinic	monoclinic	triclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a (Å)	12.824(1)	13.680(1)	13.509(2)	10.5557(6)
b (Å)	24.651(2)	21.014(1)	15.101(1)	14.1107(9)
c (Å)	18.352(2)	10.5822(9)	18.660(2)	16.980(1)
α (°)				84.492(4)
β (°)	107.192(2)	105.830(3)	109.404(3)	84.294(4)
γ (°)				76.306(3)
V (Å^3)	5542.0(10)	2926.8(4)	3590.5(7)	2438.2(3)
Z	4	4	4	2
D_{calc} (g/cm^{-3})	1.176	1.574	1.464	1.285
μ (mm^{-1})	0.087	3.408	2.716	1.959
$F(000)$	2112	1388	1612	978
Crystal size (mm)	0.45 × 0.37 × 0.20	0.55 × 0.30 × 0.28	0.25 × 0.20 × 0.12	0.78 × 0.42 × 0.20
2θ Range (°)	50.7	50.7	50.7	50.7
Reflections collected	54227	28349	35016	23349
Independent reflections	10128	5351	6566	8818
Reflections with $I \geqslant 2.0\sigma(I)$	7968	5105	5815	8272
Parameters refined	653	340	414	542
Goodness-of-fit	1.129	1.066	1.149	1.108
R	0.0778	0.0233	0.0369	0.0316
wR	0.1677	0.0569	0.0765	0.0757

Kα radiation ($\lambda = 0.71070$ Å). The diffracted intensities were corrected for Lorentz polarization effects and empirical absorption corrections. Details of the intensity data collection and crystal data are given in Table 2.

The structures were solved by direct methods and refined by full-matrix least-squares procedures based on $|F|^2$. All of the non-hydrogen atoms were refined anisotropically. All of the hydrogen atoms were held stationary and included in the structure factor calculation in the final stage of full-matrix least-squares refinement. The structures were solved and refined using SHELEXL-97 programs.

Acknowledgements

The financial support from the National Natural Science Foundation of China (Grants 20632040 and 20771078), the Natural Science Foundation of Jiangsu province (BK2007505), the Major Basic Research Project of the Natural Science Foundation of the Jiangsu Higher Education Institutions (07KJA15014), and Key Laboratory of Organic Synthesis of Jiangsu Province is gratefully acknowledged.

Appendix A. Supplementary material

CCDC 662844, 662845, 662846 and 662847 contain the supplementary crystallographic data for **1**, **2**, **3** and **4**. These data can be obtained free of charge via www.ccdc.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2007.10.025.

References

[1] K. Dehnicke, A. Greiner, Angew. Chem., Int. Ed. 42 (2003) 1340.
[2] W.E. Piers, J.J.H. Emslie, Coord. Chem. Rev. 131 (2002) 233.
[3] H.C. Aspinall, Chem. Rev. 102 (2002) 1807.
[4] P.W. Roesky, Chem. Soc. Rev. 29 (2000) 335.
[5] M.O. Tina, W.C. Geoffrey, J. Am. Chem. Soc. 121 (1999) 4072.
[6] L.B. Yu, Y.M. Yao, Q. Shen, J. Zhang, L.X. Wu, L. Ye, Chin. J. Chem. 1 (2003) 442.
[7] S.A. Schuetz, C.M. Silvernail, C.D. Incarvito, A.L. Rheingold, J.L. Clark, V.W. Day, J.A. Belot, Inorg. Chem. 43 (2004) 6203.
[8] V. Patroniak, A.R. Stefankiewicz, J.M. Lehn, M. Kubicki, M. Hoffmann, Eur. J. Inorg. Chem. (2006) 144.
[9] R.D. Archer, H.Y. Chen, L.C. Thompson, Inorg. Chem. 37 (1998) 2089.
[10] R.D. Jones, D.A. Summerville, F. Basalo, Chem. Rev. 79 (1979) 139.
[11] R. Rodriguez-Cortinas, F. Avecilla, C. Platas-Iglesias, D. Imbert, J.-C.G. Bunzli, A. Blas, T. Rodriguez-Blas, Inorg. Chem. 41 (2002) 5336.
[12] M. Gonza'lez-Lorenzo, C. Platas-Iglesias, F. Avecilla, C.F.G.C. Geraldes, D. Imbert, J.-C.G. Bunzli, A. Blas, T.R. Blas, Inorg. Chem. 42 (2003) 6946.
[13] P.A. Cameron, V.C. Gibson, C. Redshaw, J.A. Segal, A.J.P. White, D.J. Williams, J. Chem. Soc., Dalton Trans. (2002) 415.
[14] R.K. O'Reilly, V.C. Gibson, A.J.P. White, D.J. Williams, J. Am. Chem. Soc. 125 (2003) 8450.
[15] M. Yousaf, Q.C. Liu, J.L. Huang, Y.L. Qian, A.S.-C. Chan, Inorg. Chem. Commun. 3 (2000) 105.
[16] E. Solari, S. De Angelis, C. Floriani, A. Chiesi-Villa, C. Rizzoli, J. Chem. Soc., Dalton. Trans. (1991) 2471.
[17] R. Fisher, H. Gorls, D. Walther, Z. Anorg. Allg. Chem. 630 (2004) 1387.
[18] Q.C. Liu, M.X. Ding, J. Organomet. Chem. 553 (1998) 179.

[19] Q.C. Liu, M.X. Ding, Y.H. Lin, Y. Xing, Polyhedron 17 (1998) 555.

[20] Y.P. Cai, H.Z. Ma, B.S. Kang, C.Y. Su, W. Zhang, J. Sun, Y.L. Xiong, J. Organomet. Chem. 628 (2001) 99.

[21] P. Blech, C. Floriani, A. Chiesivilla, C. Guastini, J. Chem. Soc., Dalton Trans. (1990) 3557.

[22] S.A. Schuetz, V.W. Day, A.L. Rheingold, J.A. Belot, J. Chem. Soc., Dalton Trans. (2003) 4303.

[23] W.J. Evans, C.H. Fujimoto, J.W. Ziller, Polyhedron 21 (2002) 1683.

[24] Y.M. Yao, Q. Shen, Y. Zhang, M.Q. Xue, J. Sun, Polyhedron 20 (2001) 3201.

[25] Y. Zhang, Y.M. Yao, Y.J. Luo, Q. Shen, Y. Cui, K.B. Yu, Polyhedron 22 (2003) 1241.

[26] X.P. Xu, Y.M. Yao, Y. Zhang, Q. Shen, Inorg. Chem. 46 (2007) 3743.

[27] G.B. Deacon, S. Nickle, P.I. Mackinnon, E.R.T. Tiekink, Aust. J. Chem. 43 (1990) 1245.

[28] M.D. Taylor, C.P. Carter, J. Inorg. Nucl. Chem. 24 (1962) 387.

[29] P.B. Hitchcock, M.F. Lappert, R.G. Smith, Inorg. Chim. Acta 139 (1987) 183.