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# Controlled synthesis of lanthanide–lithium inverse crown ether complexes

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## ABSTRACT

An ytterbium–lithium inverse crown ether complex stabilized by amine-bridged bis(phenolate) ligands $(LYbBr)_2(\mu_4\text{-O})(\mu_3\text{-Li})$ (**1**) [$L = Me_2NCH_2CH_2N\{CH_2\text{-}(2\text{-O-}C_6H_2\text{-}Bu^t{}_2\text{-}3,5)\}_2$] was isolated as a byproduct from the reaction of LYbCl(THF) with $CH_3Li$ in THF in a very low isolated yield. Further study revealed that the inverse crown ether complexes can be synthesized in a controlled manner by the reaction of bis(phenolate) lanthanide chloride with an *in situ* mixture of *n*-BuLi with water in THF. A second inverse crown ether complex $(L'YbCl)_2(\mu_4\text{-O})(\mu_3\text{-Li})$ (**2**) [$L' = Me_2NCH_2CH_2N\{CH_2\text{-}(2\text{-O-}C_6H_2\text{-}Bu^t\text{-}3\text{-Me-}5)\}_2$] was prepared in high isolated yield and well characterized.

In recent years, the synthesis and characterization of inverse crown ether complexes (II, Chart 1) have received considerable attention because of their interesting structural feature and wide applications in homogeneous catalysis [1–6]. In most cases, inverse crown ether complexes are heterobimetallic complexes ($M1 \neq M2$) or special ate complexes. Generally, M1 is an alkali metal, such as Li, Na or K, and M2 is a main group or transition metal, focused on Zn, Mg and Mn etc. Up to date, reports of inverse crown ether complexes based on rare-earth metals are rare. To the best of our knowledge, three structurally characterized inverse crown ether complexes containing rare-earth metals were synthesized. Aspinall et al. reported, for the first time, the yttrium-lithium inverse crown ether cluster, which was isolated from the reaction of anhydrous $YCl_3$ with lithium triaminoamide [7]. Subsequently, Gambarotta et al. [8] and Martins et al. [9] reported the syntheses and characterization of samarium-lithium and yttrium-lithium inverse crown ether complexes, respectively. However, all of these complexes are unexpected products, and their formation mechanism is unclear to date. In all of these cases, the oxygen source of the oxo anionic core was proposed to come from the THF solvent, e.g. the *in situ* C–O cleavage of THF. But this hypothesis cannot explain the fact that THF is commonly used as solvent in the preparation of lanthanide amido or alkyl complexes by the reaction of (organo)lanthanide halide with lithium amides or lithium alkyls. So it was believed that the oxygen is from other source presented in the reactions instead of THF. Herein we reported a controlled synthesis of ytterbium–lithium inverse crown ether complexes stabilized by amino-amino bis(phenolate) ligands.

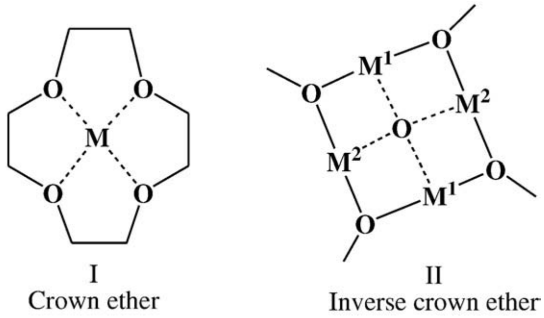

**Chart 1.** Structures of crown ether complex and inverse crown ether complex.

We previously reported that the reaction of amino-amino bridged bis(phenolate) ytterbium chloride LYbCl(THF) [$L = Me_2NCH_2CH_2N\{CH_2\text{-}(2\text{-O-}C_6H_2\text{-}Bu^t{}_2\text{-}3,5)\}_2$] with 1 equiv. of $LiCH_3$ in THF gave an ytterbium methyl complex in 50% isolated yield [10]. A further study revealed that, except the desired product, an unexpected byproduct can be isolated from this reaction in a low yield (<5%), which was characterized to be an ytterbium–lithium inverse crown ether complex $(LYbBr)_2(\mu_4\text{-O})(\mu_3\text{-Li})$ (**1**) by X-ray structure determination (Scheme 1) [11,12]. It was believed that the bromide in complex **1** came from the LiBr in the $LiCH_3$ solution through chloride-bromide exchange reaction.

The molecular structure of complex **1** with selected bond lengths and angles is shown in Fig. 1. Complex **1** is an ytterbium–lithium heterobimetallic species, and has centrosymmetric structure. Two ytterbium atoms, two lithium atoms and four oxygen atoms consist of an eight-membered ring, and one oxygen atom lies in the middle of the ring in $\mu_4$ mode to form an inverse crown ether structure. The

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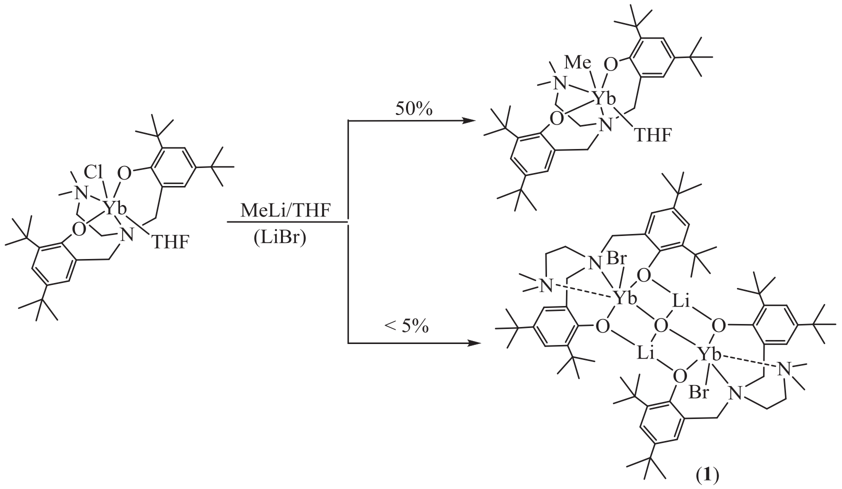


(**1**)

**Scheme 1.** Synthesis of amine bridged bis(phenolate) ytterbium methyl complex and inverse crown ether complex **1**.

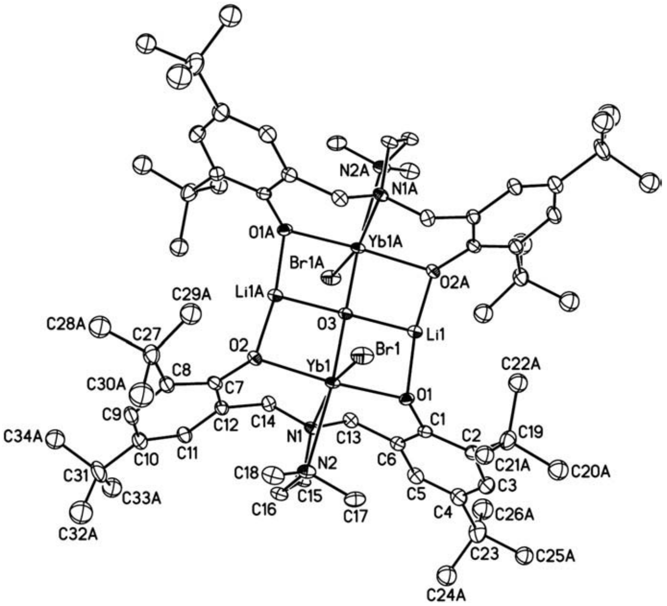
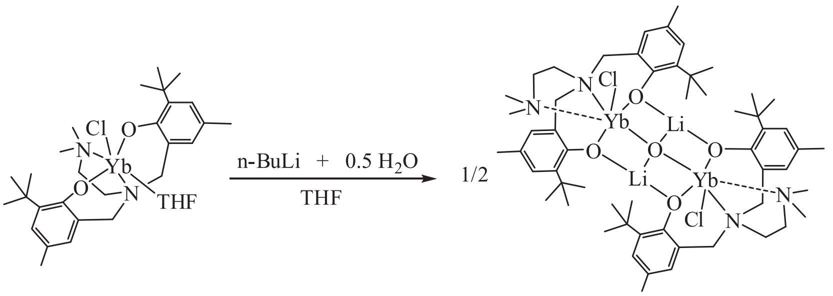


**Fig. 1.** Structure of complex **1** drawn with 20% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Yb(1)–O(1) 2.175(4), Yb(1)–O(2) 2.179(4), Yb(1)–O(3) 2.0918(2), Yb(1)–N(1) 2.453(5), Yb(1)–N(2) 2.515(5), Yb(1)–Br(1) 2.7170(7), Li(1)–O(1) 1.882(11), Li(1A)–O(2) 1.854(12), Li(1)–O(3) 1.975(11); O(1)–Yb(1)–O(2) 157.6(2), O(3)–Yb(1)–N(2) 168.8(1), Br(1)–Yb(1)–O(1) 95.7(1), O(1)–Yb(1)–N(1) 81.0(2), N(1)–Yb(1)–O(2) 83.7(2), O(2)–Yb(1)–Br(1) 103.5(1), O(1)–Li(1)–O(2A) 169.7(8), O(1)–Li(1)–O(3) 94.9(5), O(3)–Li(1)–O(2A) 94.9(5), Li(1)–O(3)–Li(1A) 180.0(2).

ytterbium center is six-coordinate and bound to three oxygen atoms and two nitrogen atoms and one bromide to form a slightly distorted octahedral coordination geometry, in which O(1), O(2), N(1) and Br(1) can be considered to occupy the equatorial positions with the sum of the bond angles of 363.9(1)°, and N(2) and O(3) to occupy the axial positions. The average Yb–O(Ar) bond distance of 2.177(4) Å is obviously longer than that in LYbCl(THF) (2.111(4) Å) [10] because of the formation of bridge bonding, but it compares well with the corresponding bond distance in $(LYCH_2SiMe_3)_2(\mu_4\text{-}O)(\mu_3\text{-}Li)$ (2.230(3) Å) [9] when the difference in ionic radii is considered. The lithium



(**2**)

**Scheme 2.** Synthesis of inverse crown ether complex **2**.

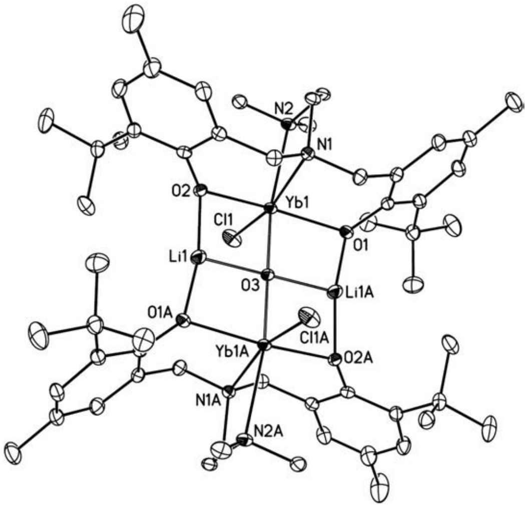


**Fig. 2.** Structure of complex **2** drawn with 20% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Yb(1)–O(1) 2.187 (2), Yb(1)–O(2) 2.179(2), Yb(1)–O(3) 2.1145(3), Yb(1)–N(1) 2.460(2), Yb(1)–N(2) 2.542(2), Yb(1)–Cl(1) 2.5464(8), Li(1A)–O(1) 1.853(6), Li(1)–O(2) 1.889(5), Li(1)–O (3) 1.948(5); O(1)–Yb(1)–O(2) 158.97(7), O(3)–Yb(1)–N(2) 164.88(5), Cl(1)–Yb(1)–O(1) 101.02(6), O(1)–Yb(1)–N(1) 84.32(7), N(1)–Yb(1)–O(2) 81.99(7), O(2)–Yb(1)–Cl(1) 96.36(5), O(1A)–Li(1)–O(2) 167.6(3), O(2)–Li(1)–O(3) 95.9(2), O(3)–Li(1)–O (1A) 96.2(2), Li(1)–O(3)–Li(1A) 180.0(1).

atom is coordinated by three oxygen atoms, and the bond distances of Li–O are in the range usually found between Li cations and neutral oxygen donor ligands.

The isolation and characterization of complex **1** encouraged us to further explore its formation mechanism. The structure of complex **1** can be considered as two LYbBr moieties connected by one $Li_2O$ molecule. So we tried to synthesize the inverse crown ether complex by the reaction of L′YbCl(THF) [$L' = Me_2NCH_2CH_2N\{CH_2\text{-}(2\text{-}O\text{-}C_6H_2\text{-}Bu^t\text{-}3\text{-}Me\text{-}5)\}_2$] [13] with $Li_2O$ in THF. But the attempts were unsuccessful because $Li_2O$ is insoluble in THF. We noticed that all of the rare-earth metal containing inverse crown ether complexes were isolated from the reactions of lanthanide chlorides with lithium amide or lithium alkyls, whereas these lithium reagents are extremely sensitive to moisture. Therefore, it was postulated that the $Li_2O$ might be from the *in situ* hydrolysis reaction of the lithium reagent by moisture. To prove this hypothesis, a reaction was designed. Firstly, n-BuLi was mixed with 0.5 equiv of water in THF to give a transparent solution. To this solution was added a THF solution of L′YbCl(THF). After workup, the desired inverse crown ether complex $(L'YbCl)_2(\mu_4\text{-}O)(\mu_3\text{-}Li)$ was isolated from a concentrated toluene solution in high yield as colorless crystals (Scheme 2) [14].

Complex **2** was well characterized including X-ray structure determination [15]. The molecular diagram is depicted in Fig. 2, with selected bond lengths and angles. Complex **2** also has a square-like $Yb_2Li_2$ structure linked by four oxygen atoms from two amino-amino bridged bis (phenolate) ligands, and one $\mu_4$-O lies in the core of the ring to form an inverse crown ether structure. Each of the ytterbium atoms is coordinated by three oxygen atoms, two nitrogen atoms and one chloride to form a distorted octahedral geometry. The Yb–O, Yb–N, and Li–O bond distances accord with the corresponding bond distances in complex **1**.

In summary, we have synthesized and structurally characterized two ytterbium–lithium inverse crown ether complexes. An efficient and straightforward approach was developed for the controlled synthesis of this kind of complexes.

## Acknowledgements

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## Appendix A. Supplementary material

CCDC 787033 and 787034 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data to this article can be found online at doi:10.1016/j.inoche.2010.09.013.

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[11] Preparation of complex **1**: During the synthesis of complex LYbMe(THF) [10], a small amount of colorless crystals (complex **1**) were isolated from a concentrated toluene solution at −10 °C. IR (KBr pellet, $cm^{-1}$): 2953 (s), 2900 (s), 2872 (s), 1625 (m), 1527 (m), 1540 (m), 1458 (s), 1416 (m), 1360 (m), 1226 (s), 1195 (s), 1048 (m), 981 (m), 928 (m), 795 (m), 722 (m), 639 (s), 553 (m), 502 (s).

[12] Crystal data determined at 193(2) K for complex $\mathbf{1 \cdot 2C_7H_8}$: $C_{82}H_{124}Br_2Li_2N_4O_5Yb_2$, $M = 1765.63$, monoclinic, space group $P2_1/n$, $a = 11.7904(8)$, $b = 21.6051(17)$, $c = 26.9307(13)$ Å, $\beta = 91.358(2)°$, $V = 4311.6(6)$ Å$^3$, $Z = 2$, $D_c = 1.360$ g/cm$^3$, $R_1 = 0.0529$, $wR_2 = 0.1297$. Data were collected on a Rigaku Mercury CCD area detector in $\omega$ scan mode using graphite-monochromated Mo-K$\alpha$ radiation ($\lambda = 0.71070$ Å). Of 47452 data collected, 9860 were unique reflections ($R_{int} = 0.0394$), and 8819 were observed reflections ($I > 2.0\ \sigma(I)$). The corrections for Lp factors and empirical absorption were applied to the intensity data. The structure was solved by direct methods with SHELX-97 program and expanded with difference Fourier technique. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located at the calculated positions. The anisotropic thermal parameters for the non-hydrogen atoms were refined by full-matrix least-squares techniques on $F^2$. Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center CCDC No. 787033.

[13] Preparation of L′YbCl(THF): A solution of $LH_2$ (2.82 g, 6.40 mmol) in THF (20 mL) was added dropwise to a NaH suspension (14.02 mmol) in THF at room temperature. After 14 h, the mixture was filtered. The resulting pale yellow solution was added to a suspension of $YbCl_3$ (1.79 g, 6.40 mmol) in THF (20 mL). After the solution was stirred overnight at room temperature, the precipitation was separated from the reaction mixture by centrifugation. The solvent was removed under vacuum, and the residue was extracted with toluene. Pale yellow crystals were obtained from a toluene solution at room temperature in a few days (3.45 g, 75%). Mp: 183 185 °C (dec). Anal. Calcd. for $C_{32}H_{50}ClN_2O_3Yb$: C, 53.44; H, 7.01; N, 3.89; Cl, 4.93; Yb, 24.06. Found: C, 53.61; H, 7.06; N, 3.47; Cl, 4.81; Yb, 24.43. IR (KBr pellet, cm $^{1}$): 2956 (s), 2917 (s), 2871 (s), 1752 (m), 1605 (m), 1562 (m), 1451 (s), 1382 (m), 1027 (m), 864 (m), 826 (m), 524 (s).

[14] Preparation of complex **2**: To a stirred THF solution containing water (1.08 mmol) was added n-BuLi in hexane (1.48 ml, 2.16 mmol). The mixture was stirred at room temperature for 6 hours, and then was added to a THF solution of L′YbCl (THF) (1.55 g, 2.16 mmol) (50 mL). The solution was stirred overnight, and then the solvent was evaporated to dryness under vacuum. The residual solid was extracted with toluene. Colorless crystals were obtained at −10 °C in a few days (1.05 g, 73%). Mp: 218 220 °C (dec). Anal. Calcd for $C_{56}H_{84}Cl_2Li_2N_4O_5Yb_2$: C, 50.80; H, 6.39; N, 4.23; Cl, 5.35; Yb, 26.14. Found: C, 50.42; H, 6.12; N, 4.55; Cl, 5.03; Yb, 26.57. IR (KBr pellet, $cm^{-1}$): 2964 (s), 2913 (s), 2849 (s), 1779 (m), 1592 (m), 1548 (m), 1463 (s), 1403 (m), 1391 (m), 1347 (m), 1245 (m), 1149 (m), 1028 (m), 865 (m), 815 (m), 770 (m), 718 (m), 535 (s).

[15] Crystal data determined at 193(2) K for complex **2**: $C_{56}H_{84}Cl_2Li_2N_4O_5Yb_2$, $M = 1324.13$, monoclinic, space group $P2_1/c$, $a = 14.222(3)$, $b = 9.5773(15)$, $c = 22.257(4)$ Å, $\beta = 102.013(4)°$, $V = 2965.1(9)$ Å$^3$, $Z = 4$, $D_c = 1.483$ g/cm$^3$, $R_1 = 0.0259$, $wR_2 = 0.0595$. Of 31157 data collected, 6779 were unique reflections ($R_{int} = 0.0294$), and 6422 were observed reflections ($I > 2.0\ \sigma(I)$). The structure was solved as that described for complex **1**. The CCDC No. is 787034.