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Bulky Bisphenol Ligand-Supported Aluminum−Sodium Inverse Crown Ether Complex

Jincai Wu,*[†] Xiaobo Pan,[†] Ning Tang,[†] and Chu-Chieh Lin[‡]

[†]*Key Laboratory of Nonferrous Metal Chemistry and Resources Utilization of Gansu Province,*
State Key Laboratory of Applied Organic Chemistry, College of Chemistry and Chemical Engineering,
Lanzhou University, Lanzhou 730000, People's Republic of China, and [‡]*Department of Chemistry,*
National Chung Hsing University, Taichung 402, Taiwan, Republic of China

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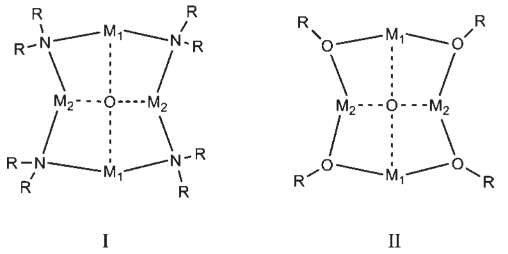
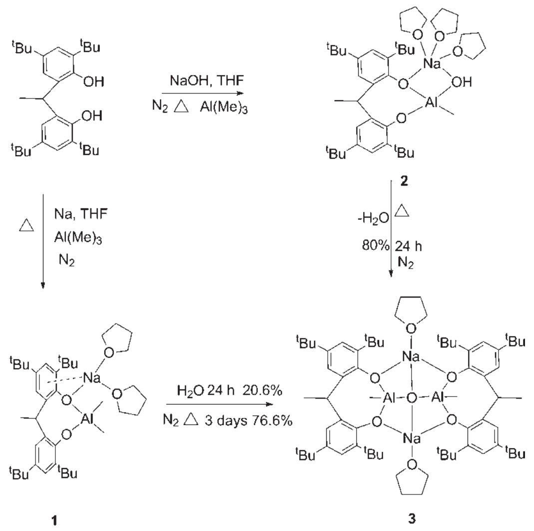
A mixed aluminum−sodium phenolate ring compound with an oxo core has been synthesized and crystallographically characterized as a new inverse crown ether complex, together with some of its precursors. The experimental results showed that the Al−Na inverse crown ether can be obtained from two different approaches: (1) hydrolysis of [(EDBP)Al$(CH_3)_2$Na$(THF)_2$] (**1**), followed by condensation with [(EDBP)Al$(CH_3)(\mu_2$-OH)Na$(THF)_3$] (**2**); (2) fast redox reaction by oxidation of a methyl group on complex **1** and reduction of molecular oxygen to oxide.

Mulvey et al. have previously reported many heterobimetallic complexes with the general structure of **I** in Chart 1 and have described them as "inverse crown ethers". Usually, M_1 is an alkali metal, whereas M_2 can be Mg^{II}, Zn^{II}, or Mn^{II}, and the anionic ligands are usually amides. In effect, they are mixed-metal, mixed-ligand oxoamido, or peroxoamido compounds, rather than organic ethers, but are loosely labeled as inverse crown ethers because of their topological similarity (but with interchanged Lewis acidic/Lewis basic positions) to conventional crown ether complexes. Alternatively, these complexes can be called mixed-metal amide crowns, and these inverse crown ethers have exhibited special regioselectivity for the metalation of toluene as a synergic base and can catalyze some synergic nucleophilic additions.[1−8]

Chart 1



Scheme 1. Synthesis of a Bulky Phenol-Supported Aluminum−Sodium Inverse Crown Ether Complex



We have recently synthesized some mixed-metal phenolates as catalysts for the ring-opening polymerization of cyclic esters,[9] and one new unexpected aluminum−sodium mixed complex **3** (Scheme 1) was found that can be viewed as an analogue of the inverse crown ether well-established structure **II** (Chart 1), in which oxygen atoms replace the nitrogen

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*To whom correspondence should be addressed. E-mail: wujc@lzu.edu.cn. Tel:86 0931 8912580. Fax:86 0931 8912582.

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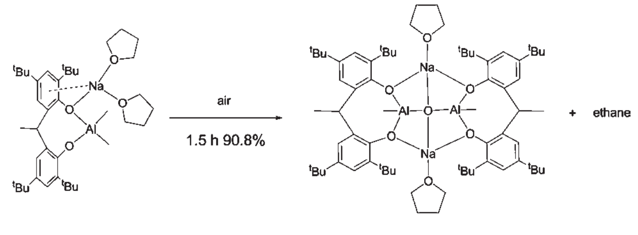
Scheme 2. Oxidation of Complex **1** by O_2



1

3

atoms in structure **I**. To date, most inverse crown ether complexes have been based on pairing an alkali metal with M^{2+} metal ions such as Mg^{2+}, Zn^{2+}, or Mn^{2+}.[10-12] We now report an extension of this class of compounds to include Al^{3+}. The aluminum complex also showed that inverse crown ether complexes can be made using bulky dianionic ligands in addition to the well-established ligands for monoanions. As reported herein, we found that the aluminum−sodium inverse crown ether complex **3** can be readily synthesized (Schemes 1 and 2).[13]

Complex **3** is a colorless solid that is soluble in toluene and tetrahydrofuran (THF). Crystals of **3** suitable for X-ray structural analysis were obtained from a saturated solution in toluene at room temperature. The molecular structure of complex **3** revealed a discrete eight-membered $Na_2Al_2O_4$ ring made up of alternating oxygen and metal atoms (Figure 1). Oxide ions occupy the core of the ring to render the molecule neutral overall. Usually, oxo inverse crowns have square-planar oxygen environments;[14] the nonplanar oxygen environment in complex **3** is possibly due to the two tetrahedral aluminum centers, as observed in the sodium inverse crown ether complex.[15]

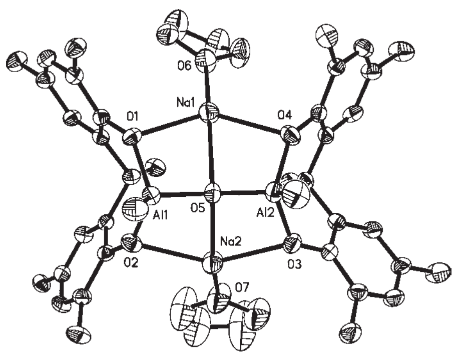


Figure 1. Molecular structure of **3** as 25% ellipsoids (the methyl carbon atoms of the *tert*-butyl groups and all of the hydrogen atoms are omitted for clarity). Selected bond lengths (Å): Al1−O1 1.766(5), Al1−O2 1.768(5), Al1−O5 1.732(5), Al1−C31 1.938(8), Al2−O3 1.785(6), Al2−O4 1.770(6), Al2−O5 1.723(5), Al2−C70 1.960(8), Na1−O1 2.373(5), Na1−O4 2.418(6), Na1−O5 2.397(6), Na1−O6 2.279(6), Na2−O2 2.453(6), Na2−O3 2.417(6), Na2−O5 2.342(6), Na2−O7 2.277(7).

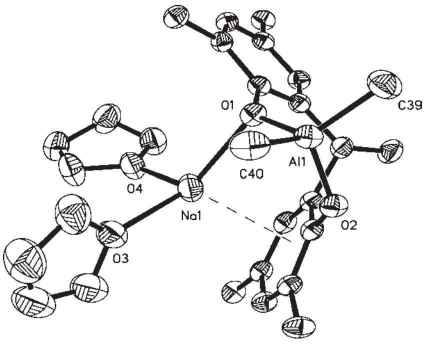


Figure 2. Molecular structure of **1** as 30% ellipsoids (the methyl carbon atoms of the *tert*-butyl groups and all of the hydrogen atoms are omitted for clarity). Selected bond lengths (Å): Al1−O1 1.8007(19), Al1−O2 1.792(2), Al1−C39 1.963(3), Al1−C40 1.966(3), Na1−O1 2.413(2), Na1−O3 2.319(3), Na1−O4 2.294(3), Na1−C1, 2.887(3), Na1−C5, 3.029(3), Na1−C6 2.834(3), Na1−C13 2.963(3).

The oxygen source of the oxo anionic core in complex **3** attracted our interest, and different synthesis approaches were tried to determine this source. As a precursor of complex **3**, complex **1** was obtained by the reaction of 2,2-ethylidenebis(4,6-di-*tert*-butylphenol) ($EDBPH_2$), sodium metal, and $AlMe_3$.[16] Crystals of complex **1** were obtained from a saturated solution in hexane/THF. In complex **1**, the Na^+ ion is stabilized by p−π interactions[17] between Na^+ and the

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[13] **Method A:** To a rapidly stirred solution of complex **1** (1.32 g, 2.0 mmol) in toluene (25 mL) was added water (18 μL) at 100 °C. Stirring was continued for 72 h, the solvent was removed under vacuum until about 5 mL of toluene remained, and about 15 mL of hexane was added to the solution. The solution was then filtered through Celite, and the filtrate was allowed to stand for 2 weeks at room temperature. Later, colorless crystals were obtained. **Method B:** Complex **2** (1.47 g, 2.0 mmol) was dissolved in 25 mL of toluene. After stirring for 24 h at 100 °C, the solvent was removed under vacuum. As a result, the white solid was dissolved in 25 mL of hexane. The hexane solution was then filtered, and the filtrate was allowed to stand for several days at room temperature. Then colorless crystals were obtained. **Method C:** Complex **1** (1.32 g, 2.0 mmol) was dissolved in toluene and heated at 100 °C in an air atmosphere for 1.5 h. The solvent was then removed under vacuum to afford a white solid. Then the white solid was dissolved in 5 mL of THF, and about 10 mL of hexane was added to the THF solution. The hexane solution was then filtered, and the filtrate was allowed to stand for several days at room temperature. Then a white solid was obtained. Anal. Calcd for $C_{70}H_{110}Al_2Na_2O_7$: C, 72.26; H, 9.53. Found: C, 72.83; H, 10.36. ^1H NMR ($CDCl_3$, ppm): δ 7.28 (d, 4H, Ph, J = 3.0 Hz), 7.03 (d, 4H, Ph, J = 3.0 Hz), 4.99 (q, 2H, C*H*(CH_3), J = 7.8 Hz), 2.76 (t, 8H, O−C*H*$_2$), 1.48 (m, 14H, C*H*$_2$ and CH(C*H*$_3$)), 1.35 (s, 36H, C(C*H*$_3$)$_3$), 1.23 (s, 36H, C(C*H*$_3$)$_3$), −0.673 (s, 6H, C*H*$_3$). ^{13}C NMR ($CDCl_3$, ppm): δ 152.39, 140.11, 137.19, 134.93, 121.31, 120.77 (Ph); 67.53 (O−CH_2); 35.18, 34.24, 31.67, 30.25 (*t*-Bu); 25.06 (CH_2); 22.19 (CH(CH_3)).

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[16] A solution of 2,2-ethylidenebis(4,6-di-*tert*-butylphenol) (0.876 g, 2.0 mmol) and sodium (0.050 g, 2.2 mmol) was stirred in THF (20 mL) at 50 °C under a N_2 atmosphere for 4.0 h. $Al(Me)_3$ (2.2 mL, 2.2 mmol, 1.0 M in hexane) was then slowly added to the solution. After stirring for 12 h, the solvent was removed under vacuum to afford a white solid. The white solid was dissolved in 5 mL of THF, and about 15 mL of hexane was added to the THF solution. The THF/hexane solution was then filtered through Celite, and the filtrate was allowed to stand for several days at room temperature. Then colorless crystals were obtained. Yield: 1.20 g (91%). Anal. Calcd for $C_{70}H_{110}Al_2Na_2O_7$: C, 72.26; H, 9.53. Found: C, 72.83; H, 10.36. ^1H NMR ($CDCl_3$, ppm): δ 7.28 (d, 4H, Ph, J = 3.0 Hz), 7.03 (d, 4H, Ph, J = 3.0 Hz), 4.99 (q, 2H, C*H*(CH_3), J = 7.8 Hz), 2.76 (t, 8H, O−C*H*$_2$), 1.48 (t, 14H, C*H*$_2$ and CH(C*H*$_3$)), 1.35 (s, 36H, C(C*H*$_3$)$_3$), 1.23 (s, 36H, C(C*H*$_3$)$_3$), −0.673 (s, 6H, C*H*$_3$). ^{13}C NMR ($CDCl_3$, ppm): δ 152.39, 140.11, 137.19, 134.93, 121.31, 120.77 (Ph); 67.53 (O−CH_2); 35.18, 34.24, 31.67, 30.25 (*t*-Bu); 25.06 (CH_2); 22.19 (CH(CH_3)).

[17] Pan, X.; Liu, A.; Yang, X.; Wu, J.; Tang, N. *Inorg. Chem. Commun.* **2010**, *13*, 376.

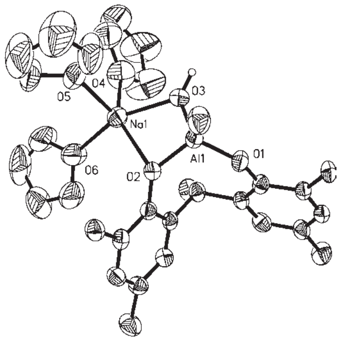

Figure 3. Molecular structure of **2** as 30% ellipsoids (the methyl carbon atoms of the *tert*-butyl groups and the hydrogen atoms, except for *OH*, are omitted for clarity). Selected bond lengths (Å): Al1−O1 1.714(4), Al1−O2 1.750(4), Al1−O3 1.742(5), Al1−C30 1.932(7), Na1−O2 2.516(4), Na1−O3 2.279(5), Na1−O4 2.354(7), Na1−O5 2.318(6), Na1−O6 2.312(6).

benzene ring at a distance of 2.710(5) Å along with coordination of three oxygen atoms from two THF and EDBP ligands (Figure 2). Inverse crown ether complex **3** was initially obtained during recrystallization of complex **1** for 2 weeks, which gave a yield of about 50%. We instinctually thought that the oxygen atom of the oxo core came from water. To test this hypothesis, complex **2** was also synthesized by the reaction of $EDBPH_2$, NaOH, and $AlMe_3$ in a ratio of 1:1:1 at 50 °C in THF, which proceeded in a yield of 88%.[18] The crystal of complex **2** was obtained from a saturated solution in hexane/THF and was only weakly diffracting, which led to a high *R* factor. Nevertheless, the structure was refined with acceptable standard uncertainties in the bond lengths and angles. In complex **2**, the hydroxyl group bridges aluminum and sodium, and one methyl group is present on aluminum (Figure 3). Heating complex **2** in toluene gave complex **3** in 80% yield after 24 h. Therefore, the condensation of two molecules of complex **2** to furnish complex **3** with one methyl group on aluminum indicates that the oxo core came from the hydroxyl group in complex **2**. During the heating process, the ^1H NMR chemical signal of the methyl group on aluminum in complex **2** decreased, together with an increase at −0.673 ppm, which was attributed to the methyl group on complex **3**. One single crystal obtained from this process was analyzed and showed the same structure as that of complex **3**. We also prepared complex **3** in 20.6% yield by heating complex **1** for 24 h with the addition of 0.5 equiv of water under a N_2 atmosphere. Additionally, the yield increased to 76.6% after 3 days. Therefore, complex **3** can be obtained by hydrolysis of complex **1**, followed by condensation of complex **2**, and the oxygen atom of the oxo anion core can come from water.

Interestingly, Mulvey et al. reported that, in Mg−alkali or Mn−alkali inverse crown ether systems, the oxygen atom of the oxo anion core comes from O_2, which oxidizes the alky group and inserts into the inverse crown ether. This was proposed based on the presence of substituted ethane $Me_3SiCH_2CH_2SiMe_3$.[12]

To determine whether the oxygen atom can also come from O_2, a toluene solution of complex **1** was deliberately exposed to air and refluxed for 1.5 h (Scheme 2). As a result, complex **3** was obtained in 90.8% yield. We should note that complex **3** can continue to react with air, as indicated by the disappearance of the methyl group on aluminum and the appearance of many sets of *tert*-butyl groups due to the formation of aggregated products. The very short reaction time required to form complex **3** compared to hydrolysis of complex **1** demonstrates that formation of the inverse crown ether complex **3** can also be achieved by oxidation of the methyl group on aluminum with O_2, as Mulvey et al. reported in the synthesis of $[Na_2Zn_2(HMDS)_4(O)]$.[11] Additionally, the second methyl group on aluminum can also be oxidized. To eliminate interference from water, pure dry O_2 was introduced into this system. The colorless solution quickly turned brown, and ^1H NMR analysis of the reaction mixture showed that complex **1** was oxidized into a mixture of complex **3** and some aggregates after 20 min, which indicated that the two methyl groups on aluminum can be easily oxidized. As expected, the methyl groups were oxidized to ethane, which was detected in the headspace of the sealed reaction mixture by mass spectroscopy (Figure S1 in the Supporting Information).

Therefore, inverse crown ether complex **3** can be obtained in two ways: (1) hydrolysis of complex **1**, followed by condensation of complex **2**; (2) fast redox reaction with oxidation of the methyl group on complex **1** and reduction of molecular oxygen to oxide. In other words, the oxygen atom of the oxo anionic core can come from water or O_2 depending on the synthetic approach.

In conclusion, the first bulky phenol ligand-supported inverse crown ether complex has been synthesized and crystallographically characterized. We proved that the oxygen source of the center oxo anion in Al−Na inverse crown ethers can come from water or O_2. Further applications of the bulky ligand-supported inverse crown ethers are in progress.

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Supporting Information Available: CIF files giving crystallographic data for **1**−**3** with CCDC reference numbers of 771480, 771478, and 771479, respectively, mass spectra, experimental procedures and syntheses, refinement data, and selected bond lengths and angles of **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[18] A solution of 2,2-ethylidenebis(4,6-di-*tert*-butylphenol) (0.876 g, 2.0 mmol) and sodium hydroxide (0.080 g, 2.0 mmol) was stirred in THF (20 mL) at 50 °C under a N_2 atmosphere for 12 h. $Al(Me)_3$ (2.2 mL, 2.2 mmol, 1.0 M in hexane) was then slowly added to the solution. After stirring for another 12 h, the solvent was removed under vacuum to afford a white solid. The white solid was dissolved in 5 mL of THF, and about 10 mL of hexane was added to the THF solution. The THF/hexane solution was then filtered through Celite, and the filtrate was allowed to stand for several hours at room temperature. Then colorless crystals were obtained. Yield: 1.29 g (88%). Anal. Calcd for $C_{43}H_{72}AlNaO_6$: C, 70.27; H, 9.87. Found: C, 70.95; H, 10.06. ^1H NMR ($CDCl_3$, ppm): δ 7.34 (s, 2H, Ph), 7.10 (s, 2H, Ph), 4.88 (q, 1H, C*H*(CH_3), J = 7.0 Hz), 3.66 (t, 12H, C*H*$_2$), 1.81 (t, 12H, O−C*H*$_2$), 1.56 (d, 3H, CH(C*H*$_3$), J = 7.0 Hz), 1.35 (s, 18H, C(C*H*$_3$)$_3$), 1.29 (s, 18H, C(C*H*$_3$)$_3$), −0.86 and −0.90 (d, 3H, C*H*$_3$). ^{13}C NMR ($CDCl_3$, ppm): δ 153.70, 139.75, 138.76, 134.10, 121.24, 120.79 (Ph); 67.94 (O−*C*H$_2$); 35.42, 34.27, 31.75, 31.68 (*t*-Bu); 30.08 (*C*H(CH_3)); 25.39 (*C*H$_2$); 21.72 (CH(*C*H$_3$)).