

Cooperative Binding of Na⁺ and Cl[−] in Na{M[OC₆H₂(CH₂NMe₂)₂-2,6-Me-4]₃Cl}: Synthesis (M = Lu, Y) and X-ray Structure (M = Lu) of New Heterometallic Complexes of Lutetium and Yttrium Containing Bis(*o*-amino)phenolate Ligands

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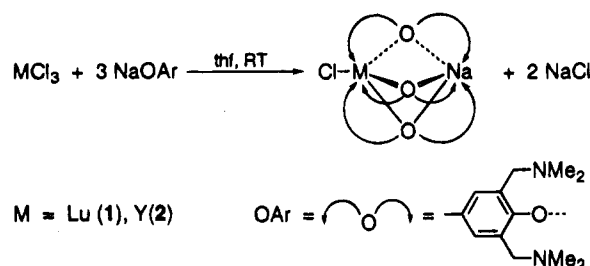
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We recently observed that phenols containing potentially chelating amino substituents are very useful ligands for the stabilization of tungsten(VI) phenylimido complexes.¹ Moreover, their lithium and sodium salts show unique coordination geometries.^{2,3}

We have now applied a terdentate bis(*o*-amino)-substituted phenolate ligand to early transition and lanthanide metals. Reaction of MCl₃ (7.5 mmol; M = Lu, Y) with 3 equiv of NaOC₆H₂(CH₂NMe₂)₂-2,6-Me-4 at room temperature in THF (THF = tetrahydrofuran) (150 mL) affords, after workup, a yellow crystalline solid which analyzes for M[OC₆H₂(CH₂NMe₂)₂-2,6-Me-4]₃·NaCl (M = Lu (1), M = Y (2)),⁵ in 80% yield (see Scheme 1). Both 1 and 2 are very soluble in both polar and nonpolar organic solvents.

Initial ¹H and ¹³C NMR characterization of these compounds indicated the presence of asymmetric phenolate bonding and temperature-dependent resonances. For example, in the case of 1, the ¹H NMR spectrum⁶ shows *four* resonances for the benzylic protons and two broad signals for the NMe₂ protons

Scheme 1. Synthesis and Schematic Representation of 1 and 2



(1.74 and 2.45 ppm). Together with the ¹³C NMR spectrum,⁶ which shows two separate resonances of both the benzylic carbons (65.81 and 63.01 ppm) and the NMe₂ carbons (47.03 and 46.19 ppm), these data indicate different binding modes for the two amino substituents.

At −40 °C in a toluene-*d*₈ solution of 2, the NMe₂ groups afford two separate ¹H NMR signals at 1.43 and 1.63 ppm and a further signal with double intensity at 2.53 ppm. This asymmetry is also reflected in the signals of the benzylic protons at this temperature where four doublets, integrating for three protons each, are visible. There are furthermore two aromatic signals. When the temperature is raised, line broadening and coalescence of the various resonances occur. At room temperature, the resonances of the benzylic protons are so broad that they are observed with difficulty and there are only two broad NMe₂ signals present. At higher temperature (343 K), the latter signals also coalesce. These observations indicate that both 1 and 2 have similar structures with asymmetric bonding of the bis(*o*-amino) phenolate ligand.

To gain insight into the asymmetric bonding of the ligands of 1 and 2 and the fluxional processes occurring in 2, as is apparent from its NMR spectra, the structure in the solid state of 1 was determined. The structure determination^{7,8} reveals the lutetium ion to be surrounded by three phenolate ligands, bonded through oxygen, and one chlorine atom. One of the two amino substituents of each phenolate moiety coordinates to the lutetium, resulting in a seven-coordinate metal center. Together with the three oxygen atoms the remaining three pendent *ortho*-amino substituents form a perfect six-coordinate pocket for the sodium ion (see Figure 1 and Scheme 1 for a schematic representation). The chlorine, lutetium, and sodium atoms lie on a pseudo-3-fold rotation axis (∠Cl–Lu···Na: 177.82(5)°) around which the three phenolate ligands are arranged.

A closer examination of the bond lengths and bond angles around the sodium ion shows that it is bonded more strongly to one of the phenolate ligands than to the other two. The Na–O2 bond length of 2.391(4) Å is substantially shorter than the other Na–O bond lengths (2.550(4) and 2.571(4) Å, but is comparable

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(5) Anal. Calcd for C₃₉H₆₃N₆O₃LuNaCl·1.5C₇H₈: C, 57.41; H, 7.30; N, 8.12. Found: C, 56.97; H, 6.79; N, 8.18. Anal. Calcd for C₃₉H₆₃N₆O₃YNaCl: C, 57.74; H, 7.83; N, 10.36. Found: C, 57.79; H, 7.96; N, 10.30.

(6) ¹H NMR data for 1 (C₆D₆, 200 MHz, 298 K): δ 6.81 (s, 6 H, Ar), 4.42 (br, 3 H, CH(H)N), 3.79 (br, 3 H, CH(H)N), 3.29 (br, 3 H, CH(H)N), 2.84 (br, 3 H, CH(H)N), 2.45 (s, 18 H, NMe₂), 2.26 (s, 9 H, *p*-CH₃), 1.74 (s, 18 H, NMe₂). ¹³C NMR data for 1 (C₆D₆, 50 MHz, 298 K): δ 161.72 (CO), 137.83, 129.32, 125.68 (toluene), 132.64, 131.62, 125.80, 122.50 (Ar), 65.81 (CH₂N), 63.01 (CH₂N), 47.03 (NMe₂), 46.19 (NMe₂), 21.46 (toluene, CH₃), 20.65 (*p*-Me). ¹H NMR data for 2 (C₆D₆, 200 MHz, 298 K): δ 6.79 (s, 6 H, Ar), 2.48 (s, 18 H, NMe₂), 2.25 (s, 9 H, *p*-CH₃), 1.70 (s, 18 H, NMe₂). ¹H NMR data for 2 (C₆D₆, 200 MHz, 263 K): δ 6.77 (s, 3 H, Ar), 6.75 (s, 3 H, Ar), 5.19 (d, 3 H, ²J_{H₂H₃} = 12 Hz, CH_AH_BN), 4.21 (d, 3 H, ²J_{H₂H₃} = 10 Hz, CH_CH_DN), 2.65 (d, 3 H, ²J_{H₂H₃} = 12 Hz, CH_AH_BN), 2.51 (s, 18 H, NMe₂), 2.27 (s, 9 H, *p*-Me), 2.16 (d, 3 H, ²J_{H₂H₃} = 10 Hz, CH_CH_DN), 1.55 (s, 18 H, NMe₂). ¹H NMR data for 2 (C₆D₆, 200 MHz, 228 K): δ 6.77 (s, 3 H, Ar), 6.76 (s, 3 H, Ar), 5.23 (d, 3 H, ²J_{H₂H₃} = 12 Hz, CH_AH_BN), 4.25 (d, 3 H, ²J_{H₂H₃} = 11 Hz, CH_CH_DN), 2.63 (d, 3 H, ²J_{H₂H₃} = 12 Hz, CH_AH_BN), 2.53 (s, 18 H, NMe₂); 2.32 (s, 9 H, *p*-Me), 2.16 (d, 3 H, ²J_{H₂H₃} = 11 Hz, CH_CH_DN), 1.63 (s, 9 H, NMeMe), 1.43 (s, 9 H, NMeMe). ¹³C NMR data for 2 (C₆D₆, 50 MHz, 298 K): δ 161.79 (CO), 132.61, 131.72, 125.70, 125.40, 122.26 (Ar), 66.23 (CH₂N), 63.24 (CH₂N), 46.21 (NMe₂), 20.62 (*p*-Me). ¹³C NMR data for 2 (C₆D₆, 50 MHz, 228 K): δ 162.12 (CO), 133.01, 131.88, 125.63, 125.54, 122.11 (Ar), 66.86 (CH₂N), 63.22 (CH₂N), 48.37 (NMe₂), 45.05 (NMe₂), 44.82 (NMe₂), 20.99 (*p*-Me).

(7) Crystals suitable for an X-ray analysis of 1 were grown by allowing a hot, concentrated solution of 1 in toluene to cool to room temperature.

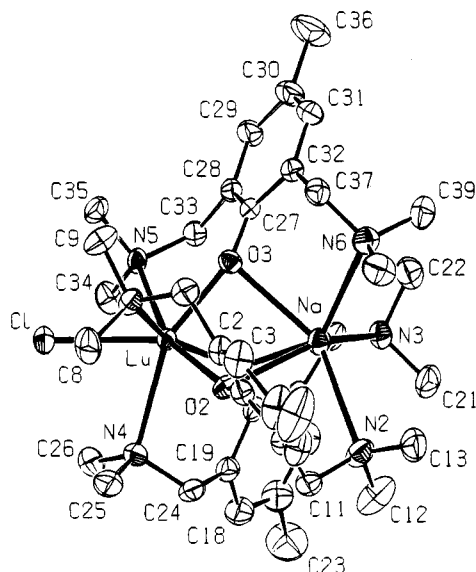


Figure 1. Structure and numbering scheme of **1** with 30% probability of thermal ellipsoids. Selected bond lengths (Å) and angles (deg): Lu—C1 = 2.6561(15), Lu—O1 = 2.143(3), Lu—O2 = 2.174(3), Lu—O3 = 2.150(3), Lu—N1 = 2.649(4), Lu—N4 = 2.656(4), Lu—N5 = 2.605(4), C1—O1 = 1.333(7), C14—O2 = 1.330(6), C27—O3 = 1.323(6), Na—O1 = 2.550(4), Na—O2 = 2.391(4), Na—O3 = 2.571(4), Na—N2 = 2.759(6), Na—N3 = 2.738(4), Na—N6 = 2.743(5), Lu—Na = 3.292(2); Lu—O1—C1 = 145.5(4), Lu—O2—C14 = 143.0(3), Lu—O3—C27 = 143.9(3), Na—O1—C1 = 105.9(3), Na—O2—C14 = 116.6(3), Na—O3—C27 = 107.7(3), Na—Lu—C1 = 177.82(5).

to the Na—O bond lengths in $[\text{NaOC}_6\text{H}_2(\text{CH}_2\text{NMe}_2)_2\text{-2,6-Me-4}]_4$.² In addition, the Na—O2—C14 bond angle of 116.6(3)° differs substantially from the corresponding bond angles found for the two other ligands (105.9(3) and 107.7(3) Å). As a result of the coordination of the two amino substituents of each phenolate ligand to two different metal ions, i.e. Lu^{3+} and Na^+ , the aromatic plane is tilted from a position perpendicular to the $\text{Lu}^{3+}\cdots\text{Na}^+$ axis, leading to a “propeller-like” molecule with screw-type chirality. Both possible enantiomers are present in the crystal lattice.

A remarkable feature concerns the crystal packing of the complex.⁹ In this packing the lutetium—chloride vector of one residue points to the sodium ion captured in the pocket of the

next complex, thus forming a continuous $\{(\text{Na}\cdots\text{Lu}-\text{Cl})\cdots(\text{Na}\cdots\text{Lu}-\text{Cl})\}_n$ string through the crystal. The intermolecular distance between the chloride of one unit and the sodium of the next is 4.765(3) Å (nearly double the sum of the covalent radii: 2.53 Å), while the intramolecular distance is much larger at 5.947(3) Å.

The Lu—O—C bond angles, which are in the range 143.0(3)–145.5(4)° for **1**, are small compared to those usually found in lanthanide phenolates, where they range from 160 to 180°. This is caused by the intramolecular coordination of the amino substituent to the lutetium, which pulls the ligand over, making the angle smaller. The effect of intramolecular coordination on this angle has previously been observed in the crystal structure of $\text{Yb}(\text{O-2,6-Ph}_2\text{C}_6\text{H}_3)_3$, in which the Yb— π -arene interaction of the ytterbium ion with a phenyl substituent of one of the ligands leads to an even smaller Yb—O—C angle of 135.0°. The Lu—N distances (2.605(4)–2.656(4) Å) are slightly larger than those reported for $\text{Lu}[\text{o-C}_6\text{H}_4\text{CH}_2\text{NMe}_2]_3$,¹² which lie in the range 2.47–2.59 Å.

This crystal structure is consistent with the low-temperature NMR data and indicates asymmetric bonding of the phenolate ligands both in the solid state and in solution.

Complexes **1** and **2** are “ate” complexes with a most unusual structure that we see as a result of cooperative anion—cation bonding. In detail, the structure can be thought of as starting from a lutetium tris phenolate $\text{Lu}(\text{OAr})_3$, which is six-coordinate on account of the rigidity of the ligand systems. Coordination of chloride anion completes the coordination sphere and preorganizes the pendent amino substituents to form an organized O_3N_3 pocket, which, on account of the negative charge, is able to positively bind the sodium cation.

The complexes described here are examples of $\text{Ln}(\text{OAr})_3$ complexes which, through anion coordination, have preorganized molecular arrangements suitable for selective coordination of Lewis acidic species (cations or metal complexes). These new complexes have prompted us to currently develop methods for the preparation of salt-free lanthanide trisphenolates, which can be used to test the postulated anion—cation cooperativity. Such $\text{Ln}(\text{OAr})_3$ complexes may also be useful for the selective complexation and activation of Lewis bases, since the site on the metal center, which in **1** and **2** is occupied by a chloride anion, can in principle be tuned by binding different types of cations in the N_3O_3 cavity at the other side of the molecule. At the moment, we are extending this principle of cooperative binding by varying both the anions and cations in these and related species.

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Supplementary Material Available: Figures of (a) the crystal lattice of **1**, showing the $\{(\text{Na}\cdots\text{Lu}-\text{Cl})\cdots(\text{Na}\cdots\text{Lu}-\text{Cl})\}_n$ alignment, and (b) a view along the pseudo-3-fold axis of **1**, showing the screw-type chirality, and tables of crystallographic data, thermal and hydrogen atom parameters, bond distances and angles, and non-hydrogen atom parameters (12 pages). Ordering information is given on any current masthead page.

- (8) Crystal data for **1**: $\text{C}_{39}\text{H}_{63}\text{N}_6\text{O}_3\text{LuNaCl}\cdot\frac{1}{2}\text{C}_7\text{H}_8$, $M_r = 1035.58$, yellow block shaped crystal (0.50 × 0.50 × 0.25 mm), triclinic, space group $P\bar{1}$, with $a = 10.706(1)$ Å, $b = 14.099(2)$ Å, $c = 18.882(3)$ Å, $\alpha = 93.48(1)^\circ$, $\beta = 99.49(1)^\circ$, $\gamma = 108.72(11)^\circ$, $V = 2642.7(6)$ Å³, $Z = 2$, $d_{\text{calc}} = 1.301$ g cm^{−3}, $F(000) = 1074$, and $\mu(\text{Mo K}\alpha) = 20.7$ cm^{−1}; 12042 independent reflections ($1.10 < \theta < 27.5^\circ$; $\omega/2\theta$ scan; $T = 300$ K) were measured on an Enraf-Nonius CAD-4T rotating anode diffractometer using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). Data were corrected for Lorentz—polarization effects and for a linear decay (17%) of the intensity control reflections. The structure was solved by Patterson (DIRDIF) and difference Fourier techniques. The unit cell contains a cavity of 745 Å³, located around an inversion site, containing three toluene solvate molecules. These toluene molecules could not be located from difference Fourier maps unambiguously and were taken into account in the structure factor and refinement calculations by Fourier transformation of the diffuse electron density in the cavity (bypass procedure: Van der Sluis, P.; Spek, A. L. *Acta Crystallogr., Sect. A* **1990**, *46*, 194). Hydrogen atoms were introduced at calculated positions and refined riding on their carrier atoms (C—H = 0.98 Å). All non-H atoms were refined with anisotropic thermal parameters, convergence was reached at $R = 0.0411$, $R_w = 0.0454$, $w = 1/[\sigma^2(F) + 0.000735F^2]$ for 8527 reflections with $I > 2.5\sigma(I)$ and 461 parameters. A final difference Fourier map shows no residual density outside −0.98 and +1.33 e/Å³ (near Lu). Geometrical details of the structure are provided as supplementary material.
- (9) The crystal packing also contains 1.5 equiv of the crystallization solvent, toluene, the disorder of which could not be modeled.

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