# Synthesis, Structure, and Reactivity of Polymetallic Sodium and Lanthanum 4-Methylphenoxide Complexes

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$LaCl_3$ reacts with 4.5 equiv of sodium 4-methylphenoxide, **1**, in THF to form $La_2Na_3(\mu_4\text{-}OR)_3(\mu\text{-}OR)_6(THF)_5$, **2**, in 80% yield (R = $C_6H_4Me$-4). Compound **2** crystallizes from toluene in the orthorhombic space group *Pcca* with $a = 18.159(6)$ Å, $b = 18.474(17)$ Å, $c = 25.145(18)$ Å, $V = 8435(9)$ Å$^3$, and $D_{calcd} = 1.32$ g cm$^{-3}$ for $Z = 8$. The five metal atoms in this complex define a trigonal bipyramid with lanthanum in the axial positions and sodium in the equatorial positions. Bridging aryloxide ligands are located at each of the nine edges of the trigonal bipyramid, and each metal is ligated by a terminal THF. When **2** is crystallized from THF/benzene/dioxane, a dioxane-solvated complex is formed in 88% yield: $\{[La_2Na_3(\mu_4\text{-}OR)_3(\mu\text{-}OR)_6](\mu\text{-dioxane})_2(\text{dioxane})_3](\text{dioxane})\}_n$, **3**. Compound **3** crystallizes in the monoclinic space group $P2_1/c$ with $a = 18.854(3)$ Å, $b = 16.624(2)$ Å, $c = 29.561(5)$ Å, $\beta = 108.36(1)°$, $V = 8793(2)$ Å$^3$, and $D_{calcd} = 1.39$ g cm$^{-3}$ for $Z = 4$. Least-squares refinement on the basis of 8127 observed reflections led to a final $R_F = 4.9\%$. The connectivity of the metals and aryloxide ligands in **2** is retained in **3**. However, dioxane molecules replace the THF in **2** and link the trigonal bipyramids together through Na–($\mu$-dioxane)–La bridges. Crystallization of **2** from dimethoxyethane (DME) generates the salt $[Na(DME)_3][La_2Na_2(\mu_3\text{-}OR)_3(\mu\text{-}OR)_4(OR)_2(THF)_2(DME)_2](DME)$, **4**, in 90% yield. Compound **4** crystallizes in the monoclinic space group $P2_1$ with $a = 13.604(3)$ Å, $b = 15.463(4)$ Å, $c = 48.572(12)$ Å, $\beta = 92.29(2)°$, $V = 10209(4)$ Å$^3$, and $D_{calcd} = 1.38$ g cm$^{-3}$ for $Z = 2$. The structure of **4** appears to derive from **2** by removal of one sodium atom which becomes solvated with DME and exists in the crystal as the $Na(DME)_3^+$ countercation. Compounds **3** and **4** are quantitatively converted back into **2** in THF. Complex **2** reacts with $Me_4NCl$ to generate $[Me_4N][La_2Na_2(\mu_4\text{-}OR)(\mu_3\text{-}OR)_2(\mu\text{-}OR)_4(OR)_2(THF)_5](THF)$, **5**, in quantitative yield. Complex **5** crystallizes from THF in the triclinic space group $P\bar{1}$ with $a = 14.726(3)$ Å, $b = 16.274(3)$ Å, $c = 20.121(3)$ Å, $\alpha = 99.98(1)°$, $\beta = 90.98(1)°$, $\gamma = 94.77(1)°$, $V = 4730(1)$ Å$^3$, and $D_{calcd} = 1.31$ g cm$^{-3}$ for $Z = 2$. Least-squares refinement on the basis of 15 205 observed reflections led to a final $R_F = 3.6\%$. The structure of **5** is similar to that of **4** with the noncoordinating $NMe_4^+$ cation in place of the solvated sodium countercation. When a THF solution of **2** is infused with hexanes, crystals of **1** form in the orthorhombic space group *Pccn* with $a = 21.941(6)$ Å, $b = 10.744(6)$ Å, $c = 5.626(2)$ Å, $V = 1326.4(9)$ Å$^3$, and $D_{calcd} = 1.30$ g cm$^{-3}$ for $Z = 8$. Least-squares refinement on the basis of 761 observed reflections led to a final $R_F = 7.9\%$. The crystal structure of **1** can be described as $[Na(\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^1{:}\eta^6\text{-}OR)]_n$. It can be viewed as a stacked array of interpenetrating $Na_4$ and $O_4$ tetrahedra offset such that a $Na_4O_4$ cube is not present. Each 4-methylphenoxide ligand bridges three sodium atoms within a $Na_4$ tetrahedron with its oxygen donor atom and interacts with a sodium atom of an adjacent $Na_4$ tetrahedron via an $\eta^6$-arene–Na interaction. When **5** was crystallized from DME, crystals of $[Na(DME)]_4(\mu_3\text{-}OR)_4$, **6**, were recovered. Complex **6** crystallizes in the tetragonal space group $P\bar{4}2_1c$ with $a = 14.362(1)$ Å, $c = 12.254(1)$ Å, $V = 2527.7(4)$ Å$^3$, and $D_{calcd} = 1.16$ g cm$^{-3}$ for $Z = 2$. Least-squares refinement on the basis of 934 observed reflections led to a final $R_F = 5.4\%$. The structure of **6** consists of interpenetrating $Na_4$ and $O_4$ tetrahedra arranged to generate a cube.

## Introduction

The alkoxide chemistry of yttrium and the lanthanide metals is currently being actively developed.[1-16] Recent studies have shown that alkoxide complexes of these elements only rarely have the simple $Ln(OR)_3$ formula (Ln = lanthanide or yttrium) commonly cited in the early literature.[17-19] Only with the very bulky 2,6-di-*tert*-butylphenoxide ligands have monometallic complexes of formula $Ln(OR)_3$ been crystallographically identified.[13-16] With less bulky alkoxide ligands, a wide range of polymetallic species have been identified by X-ray crystallography, and these species often contain solvent molecules, ligands other than alkoxides, and metal atoms other than yttrium and lanthanides.[1-9,20-26] The formation of such complexes provides

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new opportunities in the alkoxide chemistry of these metals, since (a) polymetallic compounds allow more steric control over reactivity,[26] (b) dissociation of ligated solvent molecules can provide sites of potential reactivity, and (c) incorporation of other metals can lead to heterobimetallic reactivity.[27]

We have been interested in lanthanide complexes of aryloxide ligands less bulky than the 2,6-di-*tert*-butyl phenoxide since these species should have more room around the metal center for reactions to occur and could form polymetallic structures. Investigation of the 2,6-dimethylphenoxide ligand[25] showed that both monometallic trisolvated species, $Ln(OR)_3(THF)_3$, and bimetallic monosolvated species, $[Ln(OR)_3(THF)]_2$, were obtainable and interconvertible ($R = C_6H_3Me_2$-2,6). We were interested in determining if higher nuclearity polymetallic species could be definitively *characterized* using an even less bulky aryloxide ligand. Certainly, a reaction should occur between less bulky aryloxide precursors and lanthanide metal starting materials, but it was uncertain if such complexes could be isolated and defined to an extent that their chemistry could be reliably pursued. To answer these questions, we investigated the chemistry of the 4-methylphenoxide ligand. This system was chosen because it has the least bulk in the positions close to the metal, but it retains one methyl group which would aid in NMR analysis.

## Experimental Section

The synthesis and manipulations of the compounds were conducted with the exclusion of air and water using Schlenk, vacuum line, and glovebox techniques. 4-Methylphenol was dried, degassed, and vacuum distilled from 3-Å molecular sieves. Anhydrous $LaCl_3$ was prepared as previously described.[29] $Me_4NCl$ (Aldrich) was recrystallized from 2-propanol and dried under vacuum ($5 \times 10^{-5}$ Torr) for several hours. $CD_2Cl_2$ was dried over 3-Å molecular sieves. All other solvents were distilled from sodium benzophenone ketyl. NMR data were recorded on a General Electric QE 300 MHz spectrometer. IR data were recorded on a Beckman AccuLab 2 spectrometer. Elemental analysis was performed by Analytische Laboratorien, Engelskirchen, Germany.

**$NaOC_6H_4Me$-4, 1.** In the glovebox, sodium (1.230 g, 54 mmol) was added to a solution of 4-methylphenol (5.266 g, 49 mmol) in THF (75 mL). After the reaction was stirred for 2 days, the remaining sodium was removed by centrifugation. THF was removed from the supernatant by rotary evaporation. The product was washed twice with hexane (2 × 50 mL) and dried at $5 \times 10^{-5}$ Torr to give a white powder (6.172 g, 97%). $^1H$ NMR (THF-$d_8$): $\delta$ 6.69 (d, 8.3 Hz), 6.30 (d, 8.4 Hz), 3.59 (s, THF), 2.10 (s), 1.74 (s, THF). $^1H$ NMR ($C_5D_5N$): $\delta$ 7.02 (d, $J$ = 8.1 Hz), 6.92 (d, $J$ = 8.3 Hz), 2.29 (s). IR (Nujol): 1860 (br), 1605 (s), 1500 (s), 1320 (w), 1300 (s), 1175 (w), 840 (s), 760 (m br), 725 (m br) cm$^{-1}$. Crystals of **1** were obtained from a THF solution of **2** (200 mg in 2 mL of THF) infused with hexanes.

**X-ray Data Collection, Structure Determination, and Refinement for $[Na(OR)]_n$, 1.** A colorless crystal of approximate dimensions 0.23 × 0.27 × 0.33 mm was mounted in a capillary under an inert nitrogen atmosphere and transferred to the Siemens P3 diffractometer (R3m/V system). Subsequent setup operations (determination of accurate unit cell dimensions and orientation matrix) and collection of room temperature (296 K) intensity data were carried out using standard techniques similar to those of Churchill.[30] Details appear in Table I.

All 1059 data were corrected for Lorentz and polarization effects and placed on an approximately absolute scale. A careful examination of the data set revealed the systematic extinctions $0kl$ for $l = 2n + 1$, $h0l$ for $l = 2n + 1$, and $hk0$ for $h + k = 2n + 1$. The centrosymmetric orthorhombic space group *Pccn* ($D_{2h}^{10}$; No. 56) is thus uniquely defined.

**Table I.** Crystallographic Data for Na(OR), **1**, $\{[La_2Na_3(\mu_4\text{-}OR)_3(\mu\text{-}OR)_6(\mu\text{-dioxane})_2(\text{dioxane})_3](\text{dioxane})\}_n$, **3**, $[NMe_4][La_2Na_2(\mu_4\text{-}OR)(\mu_3\text{-}OR)_2(\mu\text{-}OR)_4(OR)_2(THF)_5](THF)$, **5**, and $Na_4(OR)_4(DME)_4$, **6** (OR = $(OC_6H_4Me$-4))

| | 1 | 3 | 5 | 6 |
|---|---|---|---|---|
| formula | $C_7H_7ONa$ | $C_{87}H_{111}$-$O_{21}Na_3L_2$ | $C_{95}H_{131}N$-$O_{16}Na_2La_2$ | $C_{44}H_{68}$-$O_{12}Na_4$ |
| fw | 130.1 | 1839.5 | 1866.8 | 880.9 |
| temp (K) | 296 | 173 | 173 | 183 |
| space group | *Pccn* | $P2_1/c$ | $P\bar{1}$ | $P\bar{4}2_1c$ |
| $a$ (Å) | 21.941(6) | 18.854(3) | 14.726(3) | 14.362(1) |
| $b$ (Å) | 10.744(6) | 16.624(2) | 16.274(3) | |
| $c$ (Å) | 5.626(2) | 29.561(5) | 20.121(3) | 12.254(1) |
| $\alpha$ (deg) | | | 99.98(1) | |
| $\beta$ (deg) | | 108.36(1) | 90.98(1) | |
| $\gamma$ (deg) | | | 94.77(1) | |
| $V$ (Å$^3$) | 1326(1) | 8793(2) | 4730(1) | 2527.7(4) |
| $Z$ | 8 | 4 | 2 | 2 |
| $\rho_{calc}$ (g/cm$^3$) | 1.303 | 1.389 | 1.311 | 1.157 |
| $\lambda$(Mo K$\alpha$) | 0.710 73 | 0.710 73 | 0.710 73 | 0.710 73 |
| $\mu$ (mm$^{-1}$) | 0.134 | 1.041 | 0.962 | 0.105 |
| $R_F$ (%) | 7.9 | 4.9 | 3.6 | 5.4 |
| $R_{wF}$ (%) | 8.3 | 5.8 | 5.0 | 5.8 |

All crystallographic calculations were carried out using either our locally modified version of the UCLA Crystallographic Computing Package[31a] or the SHELXTL PLUS program set.[31b] The analytical scattering factors for neutral atoms were used throughout the analysis;[32a] both the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion[32b] were included. The quantity minimized during least-squares analysis was $\sum w(|F_o| - |F_c|)^2$, where $w^{-1} = \sigma^2(|F_o|) + 0.0015(|F_o|)^2$.

The structure was solved by direct methods (SHELXTL PLUS) and refined by full-matrix least-squares techniques. The aromatic hydrogen atoms were located from a difference-Fourier map and included with isotropic temperature parameters. The three methyl hydrogen atoms were included using a riding model with $d$(C–H) = 0.96 Å and $U$(iso) = 0.08 Å$^2$. Refinement of positional and thermal parameters led to convergence with $R_F$ = 7.9%, $R_{wF}$ = 8.3%, and GOF = 1.31 for 99 variables refined against all 761 data with $|F_o| > 0$. A final difference-Fourier map was devoid of significant features, $\rho$(max) = 0.36 e Å$^{-3}$.

**$La_2Na_3(\mu_4\text{-}OR)_3(\mu\text{-}OR)_6(THF)_5$, 2.** In the glovebox, **1** (4.78 g, 36.7 mmol), $LaCl_3$ (2.00 g, 8.2 mmol), and THF (125 mL) were added to a Schlenk flask fitted with a reflux condenser. The flask was attached to a Schlenk line and heated at reflux for 4 h. THF was removed in vacuo, and the solids were slurried in toluene (25 mL) in the glovebox. The slurry was centrifuged, and the solution was decanted and saved. The solids were slurried in THF (10 mL), dried by rotary evaporation, and then extracted once again with toluene (25 mL). The toluene solutions were combined, and the toluene was removed by rotary evaporation. The resulting solid was washed with hexanes and dissolved in THF. THF was removed by rotary evaporation, and the product was dried under high vacuum ($5 \times 10^{-5}$ Torr) to give **2** as a white powder (5.50 g, 80%). Crystals were grown from toluene. The best crystal chosen for an X-ray diffraction study did not provide a high-quality data set, but the connectivity of the atoms in the molecule was established.[33a] $^1H$ NMR (THF-$d_8$): $\delta$ 6.73 (br, 2H, $\Delta\nu_{1/2}$ = 16 Hz), 6.50 (br sh, 2H), 3.60 (THF), 2.13 (s, 3H), 1.74 (THF). $^1H$ NMR ($CD_2Cl_2$, −70 °C): $\delta$ 7.57 (d, 2H, $J$ = 8.0 Hz), 7.10 (d, 2H, $J$ = 8.0 Hz), 6.75 (d, 4H, $J$ = 7.8 Hz), 6.33 (d, 4H, $J$ = 7.7 Hz), 3.48 (br, THF), 2.79 (br, THF), 2.24 (s, 3H), 2.10 (s, 6H), 1.34 (br, THF), 1.19 (br, THF). $^{13}C$ NMR ($CD_2Cl_2$, −70 °C): $\delta$ 162.8, 160.5, 129.9, 129.0, 126.3, 123.4, 118.9, 118.2, 68.5, 66.9, 24.8, 24.5, 20.1, 19.9. IR (Nujol): 1860 br, 1605 s, 1500 s, 1290 w, 1270 m,

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(33) (a) **2** crystallizes from toluene in the orthorhombic space group *Pcca* with unit cell dimensions $a$ = 18.159(6) Å, $b$ = 18.474(17) Å, $c$ = 25.145(18) Å, and $V$ = 8435(9) Å$^3$ for $Z$ = 8 and $D_{calcd}$ = 1.32 g cm$^{-3}$. (b) **4** crystallizes in the monoclinic space group of $P2_1$ with unit cell dimensions $a$ = 13.604(3) Å, $b$ = 15.463(4) Å, $c$ = 48.572(12) Å, $\beta$ = 92.29(2)°, and $V$ = 10209(4) Å$^3$ for $Z$ = 2 and $D_{calcd}$ = 1.385 g cm$^{-3}$. See the supplementary material for details.

1240 w, 1170 s, 1035 br, 860 w, 830 s, 760 s cm$^{-1}$. Anal. Calcd for $La_2Na_3C_{83}H_{103}O_{14}$: La, 16.62; Na, 4.13; C, 59.64; H, 6.21. Found: La, 16.30; Na, 3.95; C, 59.42; H, 6.27; Cl, <0.10.

**$\{[La_2Na_3(\mu_4\text{-}OR)_3(\mu\text{-}OR)_6(\mu\text{-dioxane})_2(\text{dioxane})_3](\text{dioxane})\}_m$, 3.** In the glovebox, complex **2** (200 mg, 0.12 mmol) was dissolved in a THF/benzene/dioxane solution (4 mL, 2:1:1). Slow evaporation over a 2-week period gave crystals of **3** (171 mg, 88%). IR (Nujol): 1860 br, 1600 s, 1500 s, 1280 s, 1240 w, 1170 s, 1110 br, 1070 w, 875 w, 850 w, 825 s, 760 s cm$^{-1}$. Anal. Calcd for $La_2Na_3C_{83}H_{103}O_{14}$: La, 15.10; Na, 3.75; C, 56.80; H, 6.08. Found: La, 15.15; Na, 3.62; C, 56.58; H, 5.93.

**X-ray Data Collection, Structure Determination, and Refinement for $\{[La_2Na_3(\mu_4\text{-}OR)_3(\mu\text{-}OR)_6(\mu\text{-dioxane})_2(\text{dioxane})_3](\text{dioxane})\}_m$, 3.** A colorless crystal of approximate dimensions 0.30 × 0.33 × 0.60 mm was immersed in Paratone D oil, mounted on a glass fiber, and transferred to the Siemens P3 automated four-circle diffractometer which is equipped with a modified LT-2 low-temperature system. The determination of Laue symmetry, crystal class, unit cell parameters, and the crystal's orientation matrix were carried out by standard methods similar to those of Churchill.[30] Intensity data were collected at 173 K using an Ω scan technique with Mo K$\alpha$ radiation under the conditions described in Table I. All 12 370 data were corrected for absorption and for Lorentz and polarization effects and were placed on an approximately absolute scale. The diffraction symmetry was $2/m$ with systematic absences $k$ for $k = 2n+1$ and $l$ for $l = 2n+1$. The centrosymmetric monoclinic space group $P2_1/c$ ($C_{2h}^5$; No. 14) is therefore uniquely defined.

All crystallographic calculations were carried out as described for **1**. The quantity minimized during least-squares analysis was $\sum w(|F_o|-|F_c|)^2$, where $w^{-1} = \sigma^2(|F_o|) + 0.0004(|F_o|)^2$. The structure was solved by direct methods (SHELXTL PLUS) and refined by full-matrix least-squares techniques. Hydrogen atoms were included using a riding model with $d$(C–H) = 0.96 Å and $U$(iso) = 0.08 Å$^2$. Refinement of positional and thermal parameters led to convergence with $R_F = 4.9\%$; $R_{wF} = 5.8\%$, and GOF = 1.97 for 988 variables refined against those 9727 data with $|F_o| > 3.0\sigma(|F_o|)$. A final difference-Fourier synthesis showed no significant features, $\rho(\max) = 0.89$ e Å$^{-3}$.

**$[Na(DME)_3][La_2Na_2(\mu_3\text{-}OR)_3(\mu\text{-}OR)_4(OR)_2(THF)_2(DME)_2]$-(DME), 4.** In the glovebox, **2** (250 mg, 0.15 mmol) was dissolved in DME (2 mL) and the clear solution was cooled to –40 °C. After 1 week, crystals of **4** were recovered (328 mg, 96%). The best crystal chosen for an X-ray diffraction study was of insufficient quality to provide a high-quality data set, but the connectivity of the atoms in the molecule was established.[33b] $^1$H NMR ($CD_2Cl_2$, –70 °C): $\delta$ 7.58 (br, $\Delta\nu_{1/2} = 40$ Hz), 6.98 (br sh), 6.79 (br, $\Delta\nu_{1/2} = 36$ Hz), 6.46 (br, $\Delta\nu_{1/2} = 30$ Hz), 3.48 (br, THF), 3.22 (br, $\Delta\nu_{1/2} = 10$ Hz, DME), 2.97 (br, $\Delta\nu_{1/2} = 8$ Hz, DME), 2.17 (br), 1.39 (br, THF). IR (Nujol): 1860 br, 1600 s, 1495 s, 1275 s, 1240 w, 1160 s, 1110 br, 1080 w, 1025 w, 845 w, 820 s, 750 s cm$^{-1}$. Anal. Calcd for $La_2Na_3C_{91}H_{129}O_{21}$: La, 14.62. Found: La, 14.5.

**$[Me_4N][La_2Na_2(\mu_4\text{-}OR)(\mu_3\text{-}OR)_2(\mu\text{-}OR)_4(OR)_2(THF)_5](THF)$, 5.** Me$_4$NCl (36 mg, 0.33 mmol) was added to a solution of **2** (500 mg, 0.30 mmol) in THF (20 mL). The reaction mixture was stirred for 24 h and centrifuged. The solids were discarded and the solution rotary evaporated to dryness. After drying at 5 × 10$^{-5}$ Torr, **5** was recovered as a white crystalline powder (524 mg, 98%). X-ray-quality crystals were grown by slow evaporation of a THF solution. $^1$H NMR ($CD_2Cl_2$, –70 °C): $\delta$ 7.40 (br, $\Delta\nu_{1/2} = 14$ Hz), 7.01 (d, $J = 7.8$ Hz), 6.83 (br, $\Delta\nu_{1/2} = 20$ Hz), 6.59 (d, $J = 7.2$ Hz), 6.55 (br, sh), 6.49 (br, sh), 6.23 (br, sh), 6.17 (d, $J = 8.0$ Hz), 3.46, 2.17 (sh), 2.15 (br), 2.09, 2.06, 1.71, 1.64 cm$^{-1}$. $^{13}$C NMR ($CD_2Cl_2$, –70 °C): $\delta$ 160.7, 129.3, 123.9, 119.1, 67.5, 54.2, 25.1, 20.0, 19.9. IR (Nujol): 1860 br, 1605 s, 1500 s, 1290 w, 1270 s, 1260 w, 1240 w, 1170 s, 1035 br, 860 w, 830 s, 760 s cm$^{-1}$. Anal. Calcd for $La_2Na_2C_{83}H_{103}O_{14}N$: La, 15.48; Na, 2.56; C, 60.90; H, 6.91; N, 0.78. Found: La, 15.85; Na, 2.51; C, 60.41; H, 6.59; N, 0.85.

**X-ray Data Collection, Structure Determination, and Refinement for $[Me_4N][La_2Na_2(\mu_4\text{-}OR)(\mu_3\text{-}OR)_2(\mu\text{-}OR)_4(OR)_2(THF)_5](THF)$, 5.** A colorless crystal of approximate dimensions 0.20 × 0.32 × 0.38 mm was handled as described above for **3**. Low-temperature (173 K) intensity data were collected via a $\theta$–$2\theta$ scan technique with Mo K$\alpha$ radiation under the conditions given in Table I. All 15 205 data were corrected for Lorentz and polarization effects and placed on an approximately absolute scale. An absorption correction was not applied ($\mu = 0.962$ mm$^{-1}$). Any reflection with $I$(net) < 0 was assigned the value $|F_o| = 0$. Due to an interruption in nitrogen flow from the low-temperature system, the crystal decayed prior to the end of data collection. The final 753 data (indices 14,8,–10 to 17,3,–3 in the $2\theta$ range 45.0–50.0°) could not be measured and were not included in the refinement. There were no systematic extinctions nor any diffraction symmetry other than the Friedel condition. The two possible triclinic space groups are the noncentrosymmetric $P1$ ($C_1^1$; No. 1) or the centrosymmetric $P\bar{1}$ ($C_i^1$; No. 2). With $Z = 2$ and no expectation of a resolved chiral molecule, the latter centrosymmetric space group is far more probable[34] and was later shown to be the correct choice.

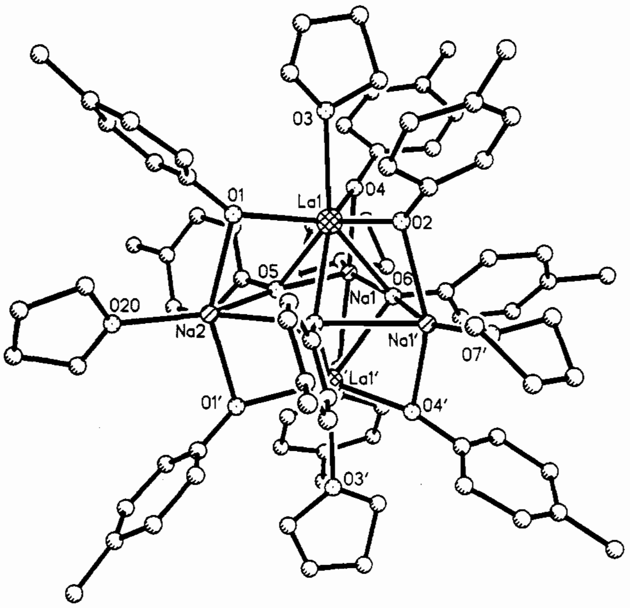

Figure 1. Molecular structure of $La_2Na_3(\mu_4\text{-}OR)_3(\mu\text{-}OR)_6(THF)_5$, **2** (R = $C_6H_4Me$-4).

All crystallographic calculations were carried out as described above for **1**. The quantity minimized during least-squares analysis was $\sum w(|F_o| - |F_c|)^2$, where $w^{-1} = \sigma^2(|F_o|) + 0.0005(|F_o|)^2$. The structure was solved by direct methods (SHELXTL PLUS) and refined by blocked full-matrix least-squares techniques. Hydrogen atoms were included using a riding model with $d$(C–H) = 0.96 Å and $U$(iso) = 0.08 Å$^2$. There is one $NMe_4^+$ cation and two THF solvent molecules present in the asymmetric unit. Refinement of the model led to convergence with $R_F = 3.6\%$, $R_{wF} = 5.0\%$, and GOF = 1.67 for 1020 variables refined against those 11 228 data with $|F_o| > 6\sigma(|F_o|)$. A final difference-Fourier map yielded $\rho(\max) = 0.87$ e Å$^{-3}$. The large $\Delta/\sigma$ observed in the final least-squares cycle is associated with the THF molecule (O(16) to C(95)), which was included with fixed distances and angles.

**X-ray Data Collection, Structure Determination, and Refinement for $Na_4(OR)_4(DME)_4$, 6.** A solution of **5** (100 mg, 0.05 mmol) in DME (2 mL) deposited crystals upon cooling to –40 °C. The crystals were washed with hexanes and dried in vacuo. A colorless crystal of approximate dimensions 0.27 × 0.30 × 0.40 mm was immersed in Paratone-D oil, mounted on a glass fiber, and transferred to the Syntex P2$_1$ diffractometer (Siemens R3m/V system) which is equipped with a modified LT-1 low-temperature system. Determination of Laue symmetry, crystal class, unit cell parameters, and the crystal's orientation matrix were carried out by standard techniques similar to those of Churchill.[30] Low-temperature (183 K) intensity data were collected via a $\theta$–$2\theta$ scan technique with Mo K$\alpha$ radiation under the conditions given in Table I.

All 1931 data were corrected for Lorentz and polarization effects, merged to yield a unique data set ($R_{int} = 1.3\%$), and placed on an approximately absolute scale. Any reflection with $I$(net) < 0 was assigned the value $|F_o| = 0$. Systematic absences revealed the space group to be the noncentrosymmetric tetragonal $P\bar{4}2_1c$ ($D_{2d}^4$; No. 114).

All crystallographic calculations were carried out as described for **1**. The quantity minimized during least-squares analysis was $\sum w(|F_o|-|F_c|)^2$, where $w^{-1} = \sigma^2(|F_o|) + 0.0010(|F_o|)^2$. The structure was solved by direct methods (SHELXTL PLUS) and refined by full-matrix least-squares techniques. The molecule is tetrameric and is located about a $\bar{4}$ element at (1,1,1). Hydrogen atoms were included using a riding model with $d$(C–H) = 0.96 Å and $U$(iso) = 0.08 Å$^2$. Refinement of the model led to convergence with $R_F = 5.4$, $R_{wF} = 5.8\%$, and GOF = 1.18 for 137 variables refined against all 934 unique data with $|F_o| > 0$. A final difference-Fourier map was "clean", $\rho(\max) = 0.22$ e Å$^{-3}$. The absolute

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[34] Nowacki, W.; Matsumoto, T.; Edenharter, A. *Acta Crystallogr.* **1967**, *22*, 935–940.

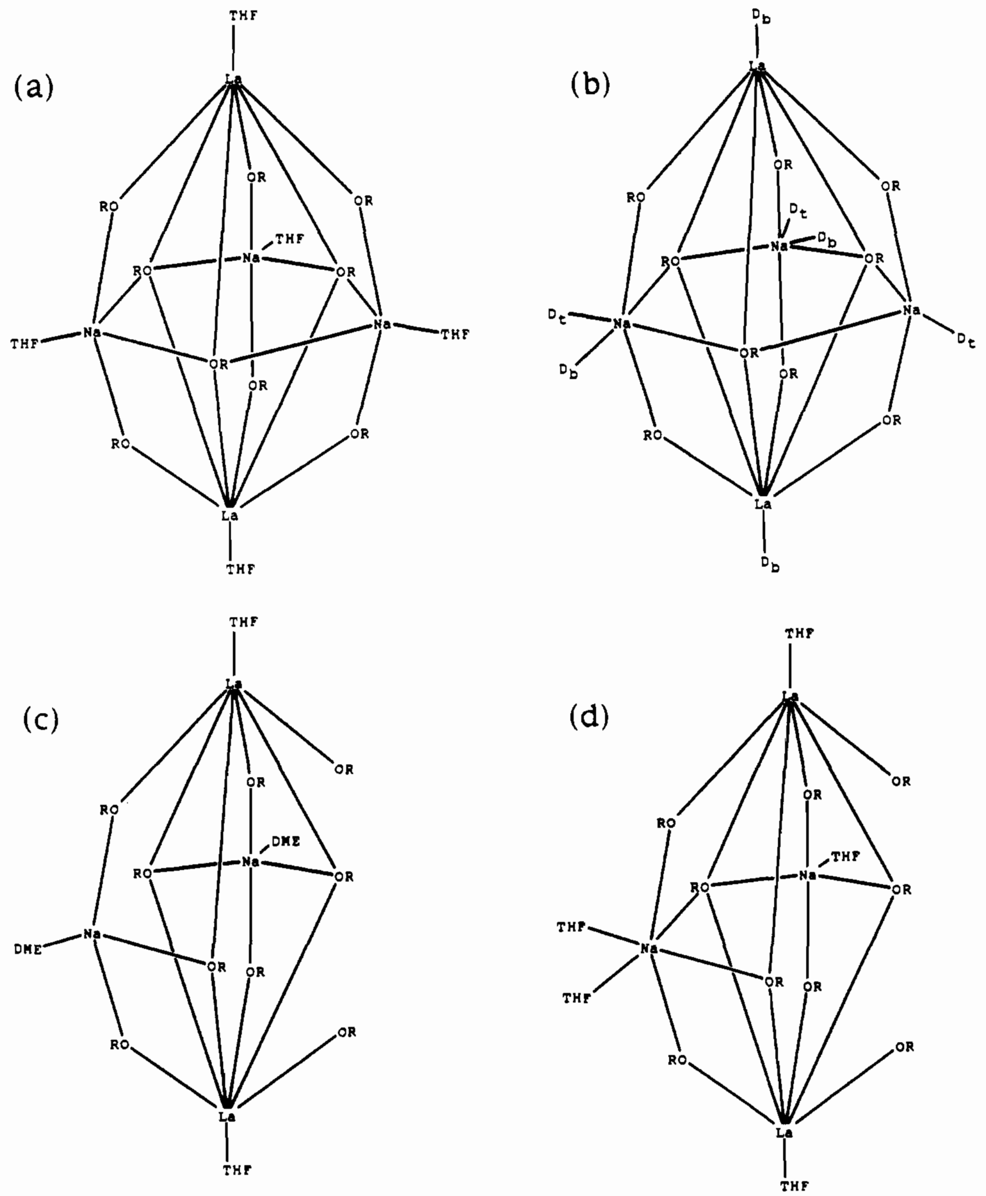

**Figure 2.** Schematic diagram of (a) $La_2Na_3(\mu_4\text{-}OR)_3(\mu\text{-}OR)_6(THF)_5$, **2**, (b) $\{[La_2Na_3(\mu_4\text{-}OR)_3(\mu\text{-}OR)_6(\mu\text{-dioxane})_2(\text{dioxane})_3](\text{dioxane})\}_n$, **3** ($D_t$ = terminal dioxane, $D_b$ = bridging dioxane), (c) the anion in $[Na(DME)_3][La_2Na_2(\mu_3\text{-}OR)_3(\mu\text{-}OR)_4(OR)_2(THF)_2(DME)_2](DME)$, **4**, and (d) the anion in $[NMe_4][La_2Na_2(\mu_4\text{-}OR)(\mu_3\text{-}OR)_2(\mu\text{-}OR)_4(OR)_2(THF)_5](THF)$, **5**.

structure could not be determined from the diffraction experiment either by refinement of the Rogers' $\eta$ parameter[35] or by inversion $(-x, -y, -z)$ of the model.

## Results

**Synthesis of the Pentametallic $La_2Na_3$ Skeleton in $La_2Na_3(OR)_9(THF)_5$, 2 (R = $C_6H_4Me$-4).** Three equivalents of sodium 4-methylphenoxide, **1**, react with a slurry of lanthanum trichloride in THF at room temperature to form a toluene-soluble product, **2**, which could be isolated by removal of THF and extraction with toluene. The $^1H$ NMR spectrum of **2** in $C_6D_6$ contained resonances consistent with the 4-methylphenoxide ligand, but it was not structurally informative. X-ray crystallographic analysis of crystals obtained by diffusing hexane into a THF solution of **2** showed that these crystals were not a lanthanum 4-methylphenoxide complex, as anticipated, but a form of $NaOC_6H_4Me$-4, whose structure is described in a later section. Since $NaOC_6H_4Me$-4 is not soluble in toluene, the crystals must have formed by decomposition of toluene-soluble **2**, which must contain sodium.

Subsequently, reactions of $LaCl_3$ with 4, 5, and 6 equiv of $NaOC_6H_4Me$-4 were examined to determine if a higher yield of the sodium-containing **2** could be obtained. Higher yields of **2** were obtained in the 4- and 5-equiv reactions, and this was understandable once the structure of **2** was determined. Recrystallization of **2** from concentrated, almost syrupy solutions in toluene gave crystals identified by an X-ray diffraction study as $La_2Na_3(OR)_9(THF)_5$, **2**, Figure 1. Once this structure was known, a 2:9 $LaCl_3$:NaOR ratio was used in subsequent reactions. With this ratio, **2** can be obtained in 80% yield in 4 h in THF at reflux, eq 1.

$$2LaCl_3 + \underset{\mathbf{1}}{9NaOC_6H_4Me\text{-}4} \xrightarrow{THF} \underset{\mathbf{2}}{La_2Na_3(OC_6H_4Me\text{-}4)_9(THF)_5} + 6NaCl \quad (1)$$

The structure of **2**, Figure 1 (see also Figures 2 and 3), consists of a trigonal bipyramid of metal atoms with the lanthanum atoms in the apical positions and the sodium atoms in the equatorial sites. Each of the five metals has a terminal THF ligand attached to it. Six of the nine $OC_6H_4Me$-4 ligands occupy doubly bridging positions, and three $OC_6H_4Me$-4 ligands are quadruply bridging. Crystallographically characterized quadruply bridging alkoxide

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[35] Rogers, D. *Acta Crystallogr.* **1981**, *A37*, 734–741.

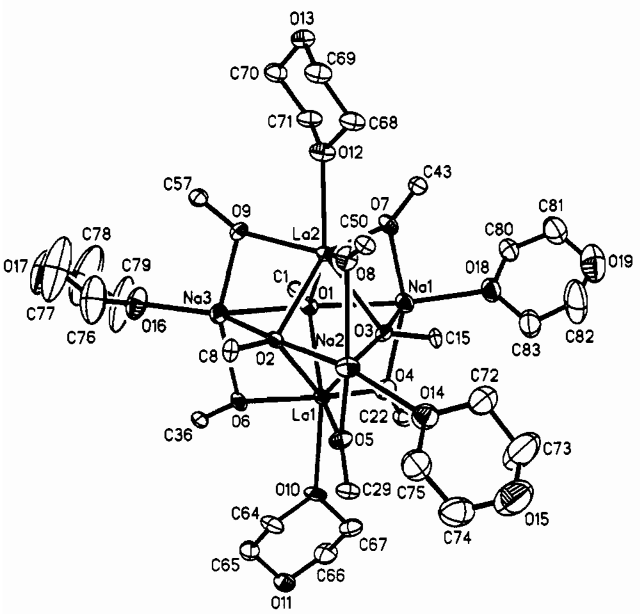

**Figure 3.** ORTEP diagram of $\{[\mathrm{La_2Na_3(\mu_4\text{-}OR)_3(\mu\text{-}OR)_6(\mu\text{-}dioxane)_2(dioxane)_3}](\mathrm{dioxane})\}_n$, 3. For clarity, only the oxygen and ipso carbon atoms of the 4-methylphenoxide ligands are shown. Also not shown are the coordination of O(11′) from a bridging dioxane in another molecule to Na(1), the coordination of O(13′) from a bridging dioxane in another molecule to Na(2), and the dioxane in the lattice. Thermal ellipsoids are drawn at the 40% probability level.

ligands are rare.[2] The structure of LiOMe is one other example in which a $\mu_4$-OR bridge is known.[36]

With this ligand arrangement, each sodium is five-coordinate and each lanthanum is seven-coordinate. This is the first example of such a high coordination number for a lanthanide aryloxide. In general, coordination numbers of 6 or less are the most common for lanthanide and yttrium alkoxide and aryloxide complexes, and coordination numbers as low as 3 have been crystallographically observed in di-*tert*-butyl aryloxide compounds.[13,15] $[\mathrm{Y(OC_2H_4OMe)_3}]_{10}$ is a rare example of an alkoxide complex which contains seven-coordinate yttrium.[6]

Although the molecular structure of 2 was defined by the crystallographic data, the poor quality of the crystal did not allow a detailed discussion of bond distances and angles. Subsequent crystallographic studies of the dioxane derivative (see below) provided better data on the $\mathrm{La_2Na_3(OR)_9}$ structural unit.

The $^1$H NMR spectrum of 2 in $\mathrm{C_4D_8O}$, $\mathrm{C_6D_6}$, and $\mathrm{CD_2Cl_2}$, showed just one type of 4-methylphenoxide resonance at room temperature, which indicated a nonrigid structure. Upon lowering of the temperature in THF, both the ortho and meta aryl proton resonances split into two signals with the 2:1 ratio of areas expected for the solid-state structure. Even at −80 °C, however, the two smaller of these signals, attributable to the $\mu_4$-OR ligands, remained broad (width at half-height = 23 and 60 Hz) and the methyl signal did not split into two. At −70 °C in $\mathrm{CD_2Cl_2}$, a spectrum consistent with the solid-state structure was also observed, including two sets of THF resonances. Equilibration of the ligand resonances at room temperature could occur via intramolecular rearrangement or by reversible dissociation of some of the components of the polymetallic compound. Dissociation of a $\mathrm{NaOC_6H_4Me\text{-}4}$ unit in toluene or methylene chloride is unlikely, since this would cause a precipitate to form. However, the ease with which THF can be substituted and sodium can be removed from the $\mathrm{La_2Na_3}$ unit (see below) suggests that dissociative pathways involving components of 2 are possible.

**Formation of a Network of $\mathrm{La_2Na_3}$ Units in $\{[\mathrm{La_2Na_3(OR)_9(dioxane)_5}](\mathrm{dioxane})\}_n$, 3.** When 2 is recrystallized from a mixture of benzene, THF, and dioxane, crystals of a dioxane-substituted complex, 3, form as shown in eq 2. This compound could not be characterized by NMR spectroscopy, since it is insoluble in arenes and $\mathrm{CD_2Cl_2}$ and since it reverts to 2 in THF. Necessarily, the complex was characterized by X-ray crystallographic methods.

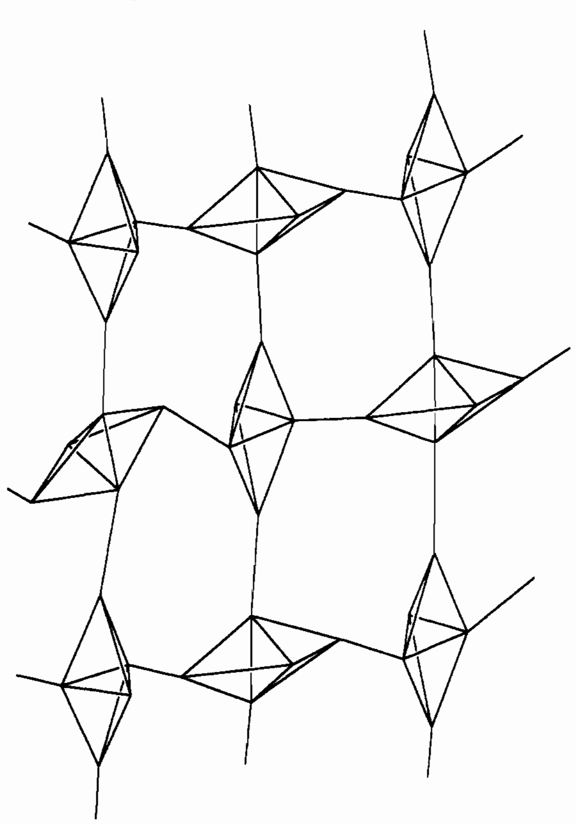

**Figure 4.** Schematic diagram of the extended structure of $\{[\mathrm{La_2Na_3(\mu_4\text{-}OR)_3(\mu\text{-}OR)_6(\mu\text{-}dioxane)_2(dioxane)_3}](\mathrm{dioxane})\}_n$, 3. The vertices of the trigonal bipyramids represent the lanthanum and sodium atoms and the lines connecting the trigonal bipyramids represent bridging dioxane molecules.

**Table II.** Selected La–O Bond Distances (Å) in $\{[\mathrm{La_2Na_2(\mu_4\text{-}OR)_3(\mu\text{-}OR)_6(dioxane)_5}](\mathrm{dioxane})\}_n$, 3, and $[\mathrm{Me_4N}][\mathrm{La_2Na_2(\mu_4\text{-}OR)(\mu_3\text{-}OR)_2(\mu\text{-}OR)_4(OR)_2(THF)_5}]$, 5 ($\mathrm{OR = OC_6H_4Me\text{-}4}$)

| | 3 | | 5 | |
|---|---|---|---|---|
| La–($\mu_4$-O) | La(1)–O(1) | 2.575(4) | La(1)–O(3) | 2.549(3) |
| | La(1)–O(2) | 2.545(5) | La(2)–O(3) | 2.568(3) |
| | La(1)–O(3) | 2.527(4) | | |
| | La(2)–O(1) | 2.548(4) | | |
| | La(2)–O(2) | 2.562(4) | | |
| | La(2)–O(3) | 2.535(5) | | |
| La–($\mu_3$-O) | | | La(1)–O(1) | 2.543(3) |
| | | | La(1)–O(2) | 2.558(3) |
| | | | La(2)–O(1) | 2.555(3) |
| | | | La(2)–O(2) | 2.545(3) |
| La–($\mu$-O) | La(1)–O(4) | 2.332(5) | La(1)–O(5) | 2.378(3) |
| | La(1)–O(5) | 2.349(4) | La(1)–O(6) | 2.385(3) |
| | La(1)–O(6) | 2.344(4) | La(2)–O(7) | 2.363(3) |
| | La(2)–O(7) | 2.345(4) | La(2)–O(8) | 2.374(3) |
| | La(2)–O(8) | 2.326(4) | | |
| | La(2)–O(9) | 2.349(4) | | |
| La–O | | | La(1)–O(4) | 2.296(3) |
| | | | La(2)–O(9) | 2.284(3) |
| La–O(solvent)[a] | La(1)–O(10) | 2.675(4) | La(1)–O(10) | 2.623(3) |
| | La(2)–O(12) | 2.619(5) | La(2)–O(11) | 2.613(3) |

[a] Solvent = dioxane for 3 and THF for 5.

$$\underset{\mathbf{2}}{n\mathrm{La_2Na_3(OC_6H_4Me\text{-}4)_9(THF)_5}} \xrightarrow[\text{benzene}]{\text{THF/dioxane}} \underset{\mathbf{3}}{\{[\mathrm{La_2Na_3(OC_6H_4Me\text{-}4)_9(dioxane)_5}](\mathrm{dioxane})\}_n} \quad (2)$$

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(36) Wheatley, P. J. *J. Chem. Soc.* **1960**, 4270–4274.

**Table III.** Selected Na–O Bond Distances (Å) in $[Na(OR)]_n$, **1**, $\{[La_2Na_3(\mu_4\text{-}OR)_3(\mu\text{-}OR)_6(dioxane)_5](dioxane)\}_n$, **3**, $[Me_4N][La_2Na_2(\mu_4\text{-}OR)(\mu_3\text{-}OR)_2(\mu\text{-}OR)_4(OR)_2(THF)_5]$, **5**, and $[Na(OR)(DME)]_4$, **6** ($OR = OC_6H_4Me\text{-}4$)

| | 1 | | 3 | | 5 | | 6 | |
|---|---|---|---|---|---|---|---|---|
| Na–($\mu_4$-O) | | | Na(1)–O(1) | 2.651(5) | Na(1)–O(3) | 2.750(4) | | |
| | | | Na(1)–O(3) | 2.815(5) | Na(2)–O(3) | 2.595(4) | | |
| | | | Na(2)–O(2) | 2.709(4) | | | | |
| | | | Na(2)–O(3) | 2.842(5) | | | | |
| | | | Na(3)–O(1) | 2.469(5) | | | | |
| | | | Na(3)–O(2) | 2.514(4) | | | | |
| Na–($\mu_3$-O) | Na(1)–O(1) | 2.344(4) | | | Na(1)–O(1) | 2.536(4) | Na(1)–O(1) | 2.281(4) |
| | Na(1)–O(1a) | 2.346(4) | | | Na(2)–O(2) | 2.627(3) | Na(1)–O(1a) | 2.332(4) |
| | Na(1)–O(1b) | 2.231(4) | | | | | Na(1)–O(1b) | 2.328(4) |
| Na–($\mu$-O) | | | Na(1)–O(4) | 2.385(5) | Na(1)–O(6) | 2.298(4) | | |
| | | | Na(1)–O(7) | 2.503(5) | Na(1)–O(8) | 2.298(4) | | |
| | | | Na(2)–O(5) | 2.400(5) | Na(2)–O(5) | 2.373(4) | | |
| | | | Na(2)–O(8) | 2.539(5) | Na(2)–O(7) | 2.389(4) | | |
| | | | Na(3)–O(6) | 2.449(5) | | | | |
| | | | Na(3)–O(9) | 2.371(5) | | | | |
| Na–O(solvent)[a] | | | Na(1)–O(18) | 2.390(5) | Na(1)–O(13) | 2.323(4) | Na(1)–O(2) | 2.494(4) |
| | | | Na(1)–O(11′) | 2.577(5) | Na(2)–O(12) | 2.437(4) | Na(1)–O(3) | 2.350(4) |
| | | | Na(2)–O(4) | 2.524(5) | Na(2)–O(4) | 2.325(5) | | |
| | | | Na(2)–O(13′) | 2.549(5) | | | | |
| | | | Na(3)–O(16) | 2.228(5) | | | | |

[a] Solvent = dioxane for **3**, THF for **5**, and DME for **6**.

The structure of **3** is shown in Figures 2–4. Figure 2 shows that the composition and connectivity of the $La_2Na_3(OR)_9$ skeleton in **3** is identical to that in **2**. The metal–oxygen substructure is shown more clearly in Figure 3. The difference between **2** and **3** lies in the ether solvation. In **3**, dioxane has replaced every terminal THF ligand in **2** and two of the dioxane molecules per formula unit are bridging. The network which results from this bridging is shown in Figure 4. Each lanthanum atom is dioxane-bridged to a sodium atom of an adjacent trigonal bipyramidal unit. This generates the (apical lanthanum)–(equatorial sodium) connections between trigonal bipyramids in Figure 4. The overall result of the bridging is a sheet of $La_2Na_3$ trigonal bipyramids in which all of the apical sites are connected to two-thirds of the equatorial sites via the bridging dioxane molecules. Dioxane commonly bridges metal atoms[37] and forms a polymeric material in $[trans\text{-}Sr(N(SiMe_3)_2)_2(\mu\text{-}1,4\text{-}dioxane)]_n$.[38]

Good structural data were obtainable on **3** and provided accurate bond distance and angle data (Tables II–IV). As in **2**, the lanthanum atoms are seven-coordinate. The average La–O($\mu_4$-OR) distance of 2.549(8) Å (range 2.527(1)–2.575(1) Å) is not directly comparable to other lanthanide or yttrium alkoxide complexes since these are the first $\mu_4$-OR ligands identified crystallographically for these metals. However, this average can be compared with the average of the six La–O($\mu$-OR) distances, 2.341(9) Å (range 2.326(4)–2.349(4) Å). As expected, the bond lengths are longer for ligands with a higher degree of bridging, and the difference between these $\mu_4$-OR and $\mu$-OR averages, 0.21 Å, is somewhat longer than the range of differences between $\mu$-OR′ and $\mu_3$-OR′ ligands, 0.02–0.16 Å, in previously characterized yttrium and lanthanide alkoxide complexes such as $[Y(OC_6H_3Me_2\text{-}2,6)_3(THF)]_2$,[25] $Y_3(OCMe_3)_8Cl(THF)_2$,[20] $Y_3(OCMe_3)_7Cl_2(THF)_2$,[21] $[Y_7Cl_5(OCMe_3)_{14}(THF)_2O]_2$,[21] $[Y_4Cl_2(OCMe_3)_{10}O]^{2-}$,[20] $Y_5(OCHMe_2)_{13}O$,[7] $[Y(OCH_2CH_2OCH_3)_3]_{10}$,[6] $[La(OCPh_3)_3]_2$,[23] $Nd_6(OCHMe_2)_{17}Cl$,[39] and $La_3(OCMe_3)_9(HOCMe_3)_2$.[3]

Comparison of the 2.341(9) Å La–O($\mu$-OR) average lanthanum aryloxide distance with the La–O($\mu$-OR′) lanthanum alkoxide average distance of 2.44(3) Å found in both $La_3(OCMe_3)_9(HOCMe_3)_2$[3] and $La_2(OCPh_3)_6$[23] shows that the 4-methylphenoxide ligand forms shorter bonds in **3**. In contrast, the 2,6-dimethylphenoxide ligand in $Y_2(OC_6H_3Me_2\text{-}2,6)_6(THF)_2$ had Y–O($\mu$-OR′) distances similar to those in comparable yttrium alkoxide complexes.[25] The shorter La–O($\mu$-OR) distance in **3** is consistent with the reduced steric demands of the 4-methylphenoxide ligand. The La–O(dioxane) average distance of 2.647(28) Å (range 2.619(5)–2.675(4) Å) is similar to the 2.604(15) Å La–O(R′OH) distance in $La_3(OCMe_3)_9(HOCMe_3)_2$.[3]

Complex **3** contains one five-coordinate sodium atom (Na(3)), like those in **2**, and two six-coordinate sodium atoms (Na(1) and Na(2)) which have additional coordination due to connections with bridging dioxane molecules attached to lanthanum. As expected, the Na–O average distances for the six-coordinate sodium atoms are longer than those for the five-coordinate atoms, Table II. However, the range of Na–O distances is much greater than the range found for the La–O distances. This is surprising considering the regularity of the overall structure. For example, the three sodium atoms and the three $\mu_4$-oxygen atoms are all coplanar to within 0.027 Å and the dihedral angles between each of the arene rings and the plane defined by the attached $\mu$-oxygen and the lanthanum and sodium atoms it connects fall in the narrow range 83–87°. Clearly the sodium atoms in this structure tolerate a wider range of bonding interactions. In this regard, it may not be so surprising that the sodium atoms can be easily removed from the overall structure as described below.

**Loss of One Metallic Component from the $La_2Na_3$ Skeleton in Dimethoxyethane (DME). Formation of $[La_2Na_2(OR)_9(THF)_2(DME)_2][Na(DME)_3]$, 4.** When **2** is recrystallized from DME, the result is not simply substitution of THF by DME; i.e., the reaction is not analogous to the dioxane reaction. The complex isolated, **4**, contains two lanthanum and three sodium atoms, but its structure is different. Since **4**, like **3**, is insoluble in arenes and reverts back to **2** in THF, it was necessarily characterized by X-ray crystallography. Unfortunately, the large size of the unit cell led to a data to parameter ratio too low to provide detailed metrical data. The overall structure was established, however.

The structure of **4**, Figure 5, is best viewed in comparison with **2** and **3**. The anionic fragment in **4**, $[La_2Na_2(OR)_9]^-$, is similar to the trigonal bipyramid in **2** less one sodium atom. The two lanthanum atoms retain their terminal THF ligands, as in **2**, but each of the remaining sodium atoms is ligated by a DME molecule. The cation in **4** is $Na(DME)_3{}^+$; i.e., formally, the sodium lost from the structure of **2** has been retained in the crystal as the counterion. Since all of the original skeletal atoms of **2** are present in **4**, and since the $La_2Na_2$ part of **4** retains the overall structure

---

(37) E.g.: Belforte, A.; Calderazzo, R.; Morvillo, A.; Pelizzi, G.; Vitali, D. *Inorg. Chem.* **1984**, *23*, 1504–1508.

(38) Cloke, F. G. N.; Hitchcock, P. B.; Lappert, M. F.; Lawless, G. A.; Royo, B. *J. Chem. Soc., Chem. Commun.* **1991**, 724–726.

(39) Andersen, R. A.; Templeton, D. H.; Zalkin, A. *Inorg. Chem.* **1978**, *17*, 1962–1965.

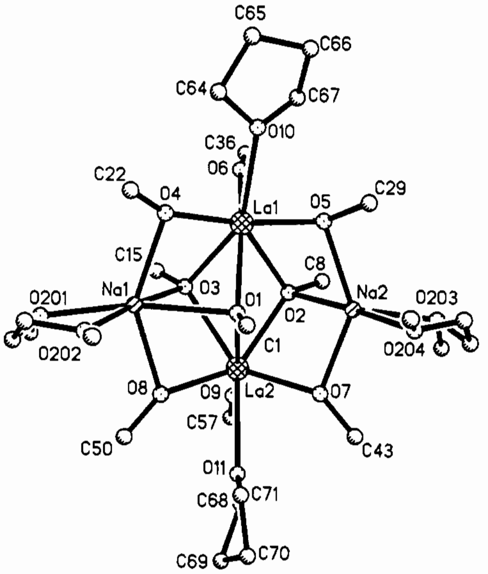

**Figure 5.** Molecular structure of the anion in $[Na(DME)_3][La_2Na_2(\mu_3\text{-}OR)_3(\mu\text{-}OR)_4(OR)_2(THF)_2(DME)_2](DME)$, **4**. For clarity, only the oxygen and ipso carbon atoms of the 4-methylphenoxide ligands are shown.

of **2**, it is easy to see why facile conversion of **4** back to **2** occurs in THF. The reaction which describes this system is shown in eq 3.

$$\underset{\mathbf{2}}{La_2Na_3(OC_6H_4Me\text{-}4)_9(THF)_5} \underset{\text{THF}}{\overset{\text{DME, }-40\text{ °C}}{\rightleftharpoons}} \underset{\mathbf{4}}{[La_2Na_2(OC_6H_4Me\text{-}4)_9(THF)_2(DME)_2][Na(DME)_3]} \qquad (3)$$

The absence of one sodium atom in **4** vs **2** causes some changes in the coordination numbers of the remaining metals and the degree of bridging of the ligands. Both lanthanum atoms are still seven-coordinate, but now each is attached to a terminal and two $\mu$-(OR) ligands, instead of three $\mu$-(OR) ligands. Simple removal of one sodium atom from **2** would have changed two of the three $\mu_4$-ligands to $\mu_3$-ligands. However, in **4**, Na(2) has moved away from O(1) such that there are no $\mu_4$-ligands in **4** (cf. complex **5** below). As in **3**, there are both five- and six-coordinate sodium atoms.

**Removal of One Metallic Component from the $La_2Na_3$ Skeleton Using Ionic Metathesis. Formation of $[Me_4N][La_2Na_2(OR)_9(THF)_5]$, 5.** After it was determined that a sodium atom could be reversibly removed from the $La_2Na_3$ skeleton in **2** to form a salt with a sodium counterion, irreversible removal of sodium with a precipitating cation was examined. $Me_4NCl$ can accomplish this in THF as shown in eq 4.

$$La_2Na_3(OC_6H_4Me\text{-}4)_9(THF)_5 + Me_4NCl \xrightarrow{\text{THF}} \underset{\mathbf{5}}{[Me_4N][La_2Na_2(OC_6H_4Me\text{-}4)_9(THF)_5]} + NaCl \qquad (4)$$

The structure of **5**, shown in Figure 6, is very similar to those of **2** and **3** except that a sodium atom has been removed. In fact, the structure of **5** more closely resembles **2** than **4** does because the Na(1)–O(3) connection is retained. Related to this, Na(1) in **5** is solvated with just one THF (instead of the two DME oxygen atoms in **4**) such that it is five coordinate as in **4**. The other sodium atom in **5** is ligated by two THF molecules (instead of one DME in **4**) to achieve six coordination as in **4**. The lanthanum atoms are both seven coordinate as in **2**–**4**. NMR data obtainable on **5** in $CD_2Cl_2$ show that the two sodium positions are equivalent in solution.

**Table IV.** Selected Bond Angles (deg) in $\{[La_2Na_3(\mu_4\text{-}OR)_3(\mu\text{-}OR)_6(dioxane)_5](dioxane)\}_n$, **3** ($OR = OC_6H_4Me\text{-}4$)

| | | | |
|---|---|---|---|
| O(1)–La(1)–O(2) | 68.1(1) | O(1)–La(1)–O(3) | 67.7(1) |
| O(2)–La(1)–O(3) | 67.8(1) | O(1)–La(1)–O(4) | 78.3(2) |
| O(2)–La(1)–O(4) | 138.4(1) | O(3)–La(1)–O(4) | 77.4(1) |
| O(1)–La(1)–O(5) | 137.3(1) | O(2)–La(1)–O(5) | 76.1(1) |
| O(3)–La(1)–O(5) | 77.8(1) | O(4)–La(1)–O(5) | 118.7(2) |
| O(1)–La(1)–O(6) | 79.2(1) | O(2)–La(1)–O(6) | 80.4(1) |
| O(3)–La(1)–O(6) | 140.5(1) | O(4)–La(1)–O(6) | 117.3(1) |
| O(5)–La(1)–O(6) | 117.5(1) | O(1)–La(1)–O(10) | 143.1(1) |
| O(2)–La(1)–O(10) | 135.0(1) | O(3)–La(1)–O(10) | 141.2(1) |
| O(4)–La(1)–O(10) | 86.6(2) | O(5)–La(1)–O(10) | 79.5(1) |
| O(6)–La(1)–O(10) | 78.2(1) | O(1)–La(2)–O(2) | 68.2(1) |
| O(1)–La(2)–O(3) | 68.0(1) | O(2)–La(2)–O(3) | 67.4(1) |
| O(1)–La(2)–O(7) | 77.6(1) | O(2)–La(2)–O(7) | 139.0(2) |
| O(3)–La(2)–O(7) | 79.3(2) | O(1)–La(2)–O(8) | 143.5(1) |
| O(2)–La(2)–O(8) | 81.9(1) | O(3)–La(2)–O(8) | 81.7(1) |
| O(7)–La(2)–O(8) | 117.3(1) | O(1)–La(2)–O(9) | 77.6(1) |
| O(2)–La(2)–O(9) | 78.6(1) | O(3)–La(2)–O(9) | 138.3(1) |
| O(7)–La(2)–O(9) | 116.2(1) | O(8)–La(2)–O(9) | 117.4(2) |
| O(1)–La(2)–O(12) | 133.9(1) | O(2)–La(2)–O(12) | 141.4(1) |
| O(3)–La(2)–O(12) | 143.7(1) | O(7)–La(2)–O(12) | 79.2(2) |
| O(8)–La(2)–O(12) | 82.6(1) | O(9)–La(2)–O(12) | 77.7(1) |
| O(1)–Na(1)–O(3) | 62.6(1) | O(1)–Na(1)–O(4) | 75.9(2) |
| O(3)–Na(1)–O(4) | 71.1(1) | O(1)–Na(1)–O(7) | 73.1(1) |
| O(3)–Na(1)–O(7) | 71.5(1) | O(4)–Na(1)–O(7) | 139.3(2) |
| O(1)–Na(1)–O(18) | 168.9(2) | O(3)–Na(1)–O(18) | 110.4(2) |
| O(4)–Na(1)–O(18) | 110.8(2) | O(7)–Na(1)–O(18) | 96.8(2) |
| O(1)–Na(1)–O(11′) | 110.8(1) | O(3)–Na(1)–O(11′) | 163.5(2) |
| O(4)–Na(1)–O(11′) | 92.9(2) | O(7)–Na(1)–O(11′) | 122.5(2) |
| O(18)–Na(1)–O(11′) | 78.2(2) | O(2)–Na(2)–O(3) | 61.2(1) |
| O(2)–Na(2)–O(5) | 72.2(1) | O(3)–Na(2)–O(5) | 71.0(1) |
| O(2)–Na(2)–O(8) | 73.7(1) | O(3)–Na(2)–O(8) | 70.9(1) |
| O(5)–Na(2)–O(8) | 137.6(2) | O(2)–Na(2)–O(14) | 165.0(2) |
| O(3)–Na(2)–O(14) | 112.6(2) | O(5)–Na(2)–O(14) | 93.0(2) |
| O(8)–Na(2)–O(14) | 118.5(2) | O(2)–Na(2)–O(13′) | 108.6(2) |
| O(3)–Na(2)–O(13′) | 165.4(2) | O(5)–Na(2)–O(13′) | 117.6(2) |
| O(8)–Na(2)–O(13′) | 96.6(2) | O(14)–Na(2)–O(13′) | 79.8(2) |
| O(1)–Na(3)–O(2) | 70.2(1) | O(1)–Na(3)–O(6) | 79.3(2) |
| O(2)–Na(3)–O(6) | 79.0(1) | O(1)–Na(3)–O(9) | 78.8(2) |
| O(2)–Na(3)–O(9) | 79.1(1) | O(6)–Na(3)–O(9) | 153.2(2) |
| O(1)–Na(3)–O(16) | 149.8(2) | O(2)–Na(3)–O(16) | 139.9(2) |
| O(6)–Na(3)–O(16) | 105.6(2) | O(9)–Na(3)–O(16) | 101.1(2) |
| La(1)–O(1)–La(2) | 99.0(1) | La(1)–O(1)–Na(1) | 89.5(1) |
| La(2)–O(1)–Na(1) | 91.7(1) | La(1)–O(1)–Na(3) | 86.9(1) |
| La(2)–O(1)–Na(3) | 87.5(1) | Na(1)–O(1)–Na(3) | 176.1(2) |
| La(1)–O(1)–C(1) | 133.2(4) | La(2)–O(1)–C(1) | 127.7(4) |
| Na(1)–O(1)–C(1) | 92.3(3) | Na(3)–O(1)–C(1) | 91.2(3) |
| La(1)–O(2)–La(2) | 99.5(1) | La(1)–O(2)–Na(2) | 91.0(1) |
| La(2)–O(2)–Na(2) | 90.7(1) | La(1)–O(2)–Na(3) | 86.6(1) |
| La(2)–O(2)–Na(3) | 86.3(1) | Na(2)–O(2)–Na(3) | 175.8(2) |
| La(1)–O(2)–C(8) | 129.2(4) | La(2)–O(2)–C(8) | 130.9(4) |
| Na(2)–O(2)–C(8) | 94.0(3) | Na(3)–O(2)–C(8) | 90.2(3) |
| La(1)–O(3)–La(2) | 100.6(1) | La(1)–O(3)–Na(1) | 86.9(1) |
| La(2)–O(3)–Na(1) | 88.2(1) | La(1)–O(3)–Na(2) | 88.4(1) |
| La(2)–O(3)–Na(2) | 88.3(1) | Na(1)–O(3)–Na(2) | 173.5(2) |
| La(1)–O(3)–C(15) | 130.8(4) | La(2)–O(3)–C(15) | 128.6(4) |
| Na(1)–O(3)–C(15) | 94.1(3) | Na(2)–O(3)–C(15) | 92.3(3) |
| La(1)–O(4)–Na(1) | 102.5(2) | La(1)–O(4)–C(22) | 135.6(4) |
| Na(1)–O(4)–C(22) | 120.7(4) | La(1)–O(5)–Na(2) | 104.3(2) |
| La(1)–O(5)–C(29) | 137.6(4) | Na(2)–O(5)–C(29) | 118.1(3) |
| La(1)–O(6)–Na(3) | 92.7(1) | La(1)–O(6)–C(36) | 158.7(4) |
| Na(3)–O(6)–C(36) | 108.3(4) | La(2)–O(7)–Na(1) | 100.6(2) |
| La(2)–O(7)–C(43) | 144.6(4) | Na(1)–O(7)–C(43) | 114.6(4) |
| La(2)–O(8)–Na(2) | 98.0(2) | La(2)–O(8)–C(50) | 162.2(4) |
| Na(2)–O(8)–C(50) | 99.2(4) | La(2)–O(9)–Na(3) | 94.7(2) |
| La(2)–O(9)–C(57) | 150.3(3) | Na(3)–O(9)–C(57) | 114.7(3) |

Complex **5** shows the remarkable flexibility of the 4-methylphenoxide ligand: four different ligating modes, terminal, $\mu$, $\mu_3$, and $\mu_4$, are present. Good crystallographic data were obtainable on **5**, and bond distances and angles are given in Tables II–V. The data compare well with those obtained on complex **3**, i.e., the La–($\mu$-O), La–($\mu_4$-O), and La–O(solvent) distances are all in the same range as previously observed. The Na–O distances are also similar in the two structures although the range of distances in **5** is less extreme than it was in **3**.

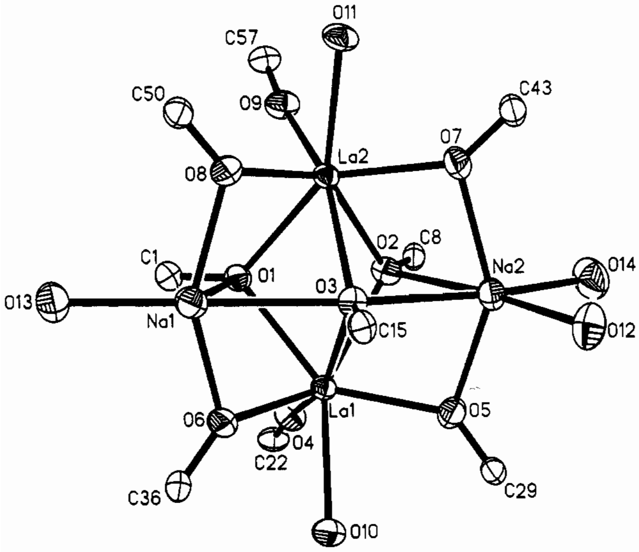

**Figure 6.** ORTEP diagram of the anion in $[NMe_4][La_2Na_2(\mu_4\text{-}OR)(\mu_3\text{-}OR)_2(\mu\text{-}OR)_4(OR)_2(THF)_5](THF)$, **5**. For clarity, only the oxygen and ipso carbon atoms of the 4-methylphenoxide ligands and only the oxygen atoms of the THF ligands are shown. Thermal ellipsoids are drawn at the 50% probability level.

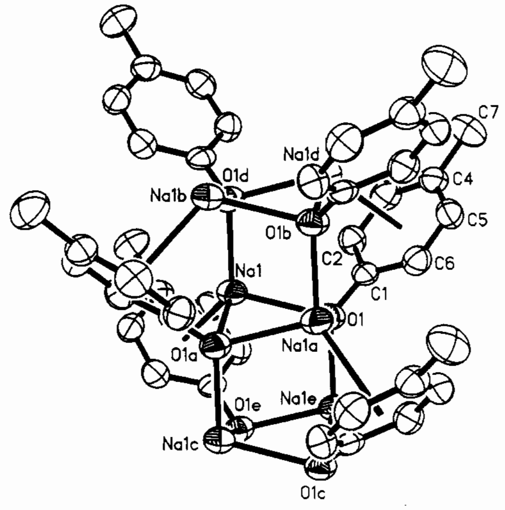

**Figure 7.** Portion of the extended array of the structure of $(NaOC_6H_4\text{-}Me\text{-}4)_n$, **1**. Six $NaOC_6H_4Me\text{-}4$ units are shown here. Thermal ellipsoids are drawn at the 50% probability level.

**Table V.** Selected Bond Angles (deg) in $[Me_4N][La_2Na_2(\mu_4\text{-}OR)(\mu_3\text{-}OR)_2(\mu\text{-}OR)_4(OR)_2(THF)_5]$, **5** ($OR = OC_6H_4Me\text{-}4$)

| | | | |
|---|---|---|---|
| O(1)–La(1)–O(2) | 67.7(1) | O(1)–La(1)–O(3) | 69.2(1) |
| O(2)–La(1)–O(3) | 67.7(1) | O(1)–La(1)–O(4) | 92.4(1) |
| O(2)–La(1)–O(4) | 95.8(1) | O(3)–La(1)–O(4) | 158.6(1) |
| O(1)–La(1)–O(5) | 138.1(1) | O(2)–La(1)–O(5) | 75.1(1) |
| O(3)–La(1)–O(5) | 79.5(1) | O(4)–La(1)–O(5) | 110.4(1) |
| O(1)–La(1)–O(6) | 74.4(1) | O(2)–La(1)–O(6) | 135.3(1) |
| O(3)–La(1)–O(6) | 77.5(1) | O(4)–La(1)–O(6) | 108.8(1) |
| O(5)–La(1)–O(6) | 125.7(1) | O(1)–La(1)–O(10) | 143.9(1) |
| O(2)–La(1)–O(10) | 147.6(1) | O(3)–La(1)–O(10) | 92.4(1) |
| O(4)–La(1)–O(10) | 79.4(1) | O(5)–La(1)–O(10) | 76.6(1) |
| O(6)–La(1)–O(10) | 75.2(1) | O(1)–La(2)–O(2) | 67.8(1) |
| O(1)–La(2)–O(3) | 68.7(1) | O(2)–La(2)–O(3) | 67.6(1) |
| O(3)–La(2)–O(7) | 78.4(1) | O(1)–La(2)–O(8) | 77.0(1) |
| O(2)–La(2)–O(8) | 137.5(1) | O(3)–La(2)–O(8) | 78.1(1) |
| O(7)–La(2)–O(8) | 121.8(1) | O(1)–La(2)–O(9) | 90.3(1) |
| O(2)–La(2)–O(9) | 99.6(1) | O(3)–La(2)–O(9) | 158.2(1) |
| O(7)–La(2)–O(9) | 116.7(1) | O(8)–La(2)–O(9) | 103.7(1) |
| O(1)–La(2)–O(11) | 146.2(1) | O(2)–La(2)–O(11) | 145.0(1) |
| O(3)–La(2)–O(11) | 122.9(1) | O(7)–La(2)–O(11) | 74.6(1) |
| O(8)–La(2)–O(11) | 75.3(1) | O(9)–La(2)–O(11) | 77.8(1) |
| O(1)–Na(1)–O(3) | 66.2(1) | O(1)–Na(1)–O(6) | 76.0(1) |
| O(3)–Na(1)–O(6) | 74.9(1) | O(1)–Na(1)–O(8) | 78.8(1) |
| O(3)–Na(1)–O(8) | 75.7(1) | O(6)–Na(1)–O(8) | 147.0(1) |
| O(1)–Na(1)–O(13) | 119.6(1) | O(3)–Na(1)–O(13) | 174.1(1) |
| O(6)–Na(1)–O(13) | 107.2(1) | O(8)–Na(1)–O(13) | 103.5(1) |
| O(2)–Na(2)–O(3) | 66.0(1) | O(2)–Na(2)–O(5) | 73.9(1) |
| O(3)–Na(2)–O(5) | 78.6(1) | O(2)–Na(2)–O(7) | 73.8(1) |
| O(3)–Na(2)–O(7) | 77.4(1) | O(5)–Na(2)–O(7) | 145.4(1) |
| O(2)–Na(2)–O(12) | 173.2(1) | O(3)–Na(2)–O(12) | 107.5(1) |
| O(5)–Na(2)–O(12) | 103.1(1) | O(7)–Na(2)–O(12) | 107.7(1) |
| O(2)–Na(2)–O(14) | 99.8(1) | O(3)–Na(2)–O(14) | 165.8(1) |
| O(5)–Na(2)–O(14) | 99.1(1) | O(7)–Na(2)–O(14) | 98.1(1) |
| O(12)–Na(2)–O(14) | 86.7(1) | La(1)–O(1)–Na(1) | 90.6(1) |
| La(1)–O(1)–La(2) | 99.6(1) | La(1)–O(1)–C(1) | 127.9(3) |
| La(2)–O(1)–Na(1) | 88.8(1) | Na(1)–O(1)–C(1) | 91.5(2) |
| La(2)–O(1)–C(1) | 132.5(3) | La(1)–O(2)–Na(2) | 87.8(1) |
| La(1)–O(2)–La(2) | 99.5(1) | La(1)–O(2)–C(8) | 129.6(3) |
| La(2)–O(2)–Na(2) | 88.6(1) | Na(2)–O(2)–C(8) | 112.1(2) |
| La(2)–O(2)–C(8) | 125.5(3) | La(1)–O(3)–Na(1) | 85.8(1) |
| La(1)–O(3)–La(2) | 99.1(1) | La(1)–O(3)–Na(2) | 88.7(1) |
| La(2)–O(3)–Na(1) | 84.1(1) | Na(1)–O(3)–Na(2) | 170.2(1) |
| La(2)–O(3)–Na(2) | 88.8(1) | La(2)–O(3)–C(15) | 134.8(3) |
| La(1)–O(3)–C(15) | 124.3(3) | Na(2)–O(3)–C(15) | 102.7(2) |
| Na(1)–O(3)–C(15) | 87.1(2) | La(1)–O(5)–Na(2) | 98.4(1) |
| La(1)–O(4)–C(22) | 171.9(3) | Na(2)–O(5)–C(29) | 127.6(3) |
| La(1)–O(5)–C(29) | 134.0(3) | La(1)–O(6)–C(36) | 137.2(3) |
| La(1)–O(6)–Na(1) | 100.8(1) | La(2)–O(7)–Na(2) | 99.0(1) |
| Na(1)–O(6)–C(36) | 121.6(3) | Na(2)–O(7)–C(43) | 118.6(3) |
| La(2)–O(7)–C(43) | 142.4(3) | La(2)–O(8)–C(50) | 135.5(3) |
| La(2)–O(8)–Na(1) | 99.4(1) | La(2)–O(9)–C(57) | 172.1(3) |
| Na(1)–O(8)–C(50) | 122.6(3) | C(84)–N(1)–C(86) | 112.5(6) |
| C(84)–N(1)–C(85) | 113.2(5) | C(84)–N(1)–C(87) | 102.5(6) |
| C(85)–N(1)–C(86) | 115.2(6) | C(86)–N(1)–C(87) | 105.2(8) |
| C(85)–N(1)–C(87) | 106.9(8) | | |

**X-ray Crystal Structures of the Sodium 4-Methylphenoxide Complexes $[Na(OR)]_n$, 1, and $Na_4(OR)_4(DME)_4$, 6.** In the course of this study, crystallographic data were obtained on two polymetallic 4-methylphenoxide complexes which contained sodium as the only metal. In both cases, the crystals were obtained from recrystallizations of mixed-metal lanthanum sodium complexes. The crystals formed in this way were not readily obtainable under the same crystallization conditions from pure $NaOC_6H_4$-Me-4. The most unusual case is the isolation of crystals of unsolvated $(NaOC_6H_4Me\text{-}4)_n$, **1**, which were obtained from a recrystallization of **2** from THF/hexane. Another example of this type, namely, the crystallization of an unsolvated, polymeric alkali metal containing species from a THF solution of a mixed-metal precursor, has recently been reported for $(LiC_5H_4SiMe_3)_n$.[40] Hence, the slow dissociation or decomposition of a mixed-metal precursor may be a generally useful method for the formation of unusual polymeric alkali metal structures.

**$[(NaOC_6H_4Me\text{-}4)]_n$.** As shown in Figures 7 and 8, $[NaOC_6H_4\text{-}Me\text{-}4]_n$ crystallizes as a polymer which forms an extended chain along the *c*-axis. Pairs of sodium atoms lie in planes perpendicular to the *c*-axis such that the vectors between the pairs of atoms form 90° angles from one layer to another. For four sodium atoms, this generates a distorted tetrahedron; for six, a distorted edge fused bitetrahedron. The chain is held together not only by the 4-methylphenoxide oxygen atoms, which are triply bridging, but also by arene groups which are oriented toward the metals. Each sodium atom interacts with three $\mu_3$-oxygen atoms and one $\eta^6$-arene ring from another $NaOC_6H_4Me\text{-}4$ unit. The Na–O bond distances (Table III), 2.231(4)–2.346(4) Å, are not unusual (see below), and the Na–C(arene) average distance of 2.94(11) Å is similar to the average Na–C($\eta^6$-arene) distance of 2.89(11) Å in $Na_2(Ph_2CCPh_2)$[41] and $Na(Ph_2CCHCPh_2)$.[42] Finally, the ligand arrangement in **1** is such that only two faces of the distorted tetrahedron formed by any four sodium atoms are capped by

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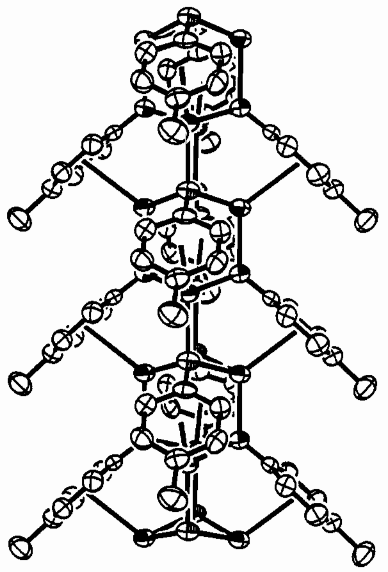

**Figure 8.** Extended structure of $(NaOC_6H_4Me\text{-}4)_n$, **1**. Fourteen $NaOC_6H_4Me$-4 units are shown here. Thermal ellipsoids are drawn at the 50% probability level.

**Table VI.** Selected Bond Angles (deg) in $[Na(OC_6H_4Me\text{-}4)]_n$, **1**, and $[Na(OC_6H_4Me\text{-}4)(DME)]_4$, **6**[a]

| **1** | | **6** | |
|---|---|---|---|
| O(1)–Na(1)–O(1a) | 86.3(1) | O(1)–Na(1)–O(1a) | 89.4(1) |
| O(1)–Na(1)–O(1b) | 103.9(1) | O(1)–Na(1)–O(1b) | 91.9(1) |
| O(1)–Na(1)–Cnt | 113.4 | O(1)–Na(1)–O(2) | 90.2(1) |
| O(1a)–Na(1)–O(1b) | 104.7(1) | O(1)–Na(1)–O(3) | 143.1(1) |
| O(1a)–Na(1)–Cnt | 112.9 | O(1a)–Na(1)–O(1b) | 89.2(1) |
| O(1b)–Na(1)–Cnt | 127.6 | O(1a)–Na(1)–O(2) | 103.4(1) |
| | | O(1a)–Na(1)–O(3) | 120.9(1) |
| | | O(1b)–Na(1)–O(2) | 167.2(1) |
| | | O(1b)–Na(1)–O(3) | 104.1(1) |
| | | O(2)–Na(1)–O(3) | 67.5(1) |

[a] Cnt is the centroid of the C(1d)–C(6d) ring.

$\mu_3$-oxygen atoms. Any four of the ligand oxygen atoms also define a distorted tetrahedron, but the two interpenetrating $Na_4$ and $O_4$ units are not evenly positioned to generate a cube. The $Na_2O_2$ units form a butterfly geometry rather than a square plane. The result is a surprisingly open structure. Bond angles are given in Table VI.

Attempts to obtain crystals of **1** for X-ray analysis by recrystallization of THF solutions of **1** did not give suitable material. The transparent crystals obtained in this way immediately turn into a powder upon removal from the mother liquor, which suggests that a solvated form of $NaOC_6H_4Me$-4 different from that just described is being formed.

**$Na_4(OC_6H_4Me\text{-}4)_4(DME)_4$, 6.** When **5** was recrystallized from DME, crystals of a tetrameric DME adduct of sodium 4-methylphenoxide complex, **6**, were obtained. The structure, shown in Figure 9, provides an interesting contrast to the polymeric unsolvated **1** and also provides useful comparative data on Na–(O) bonds (Tables III and VI).

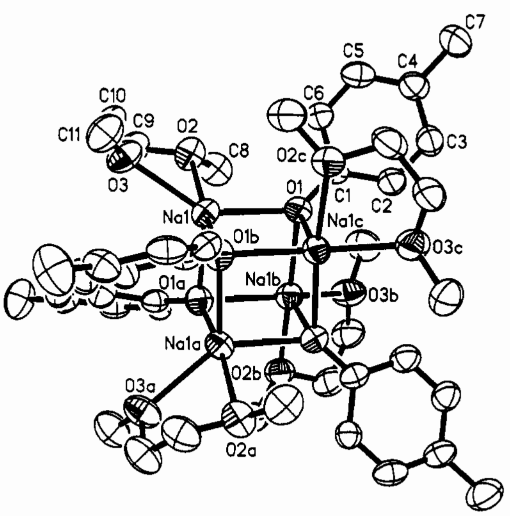

**Figure 9.** Molecular structure of $Na_4(OR)_4(DME)_4$, **6**. Thermal ellipsoids are drawn at the 50% probability level.

The structure of **6** is like that of **1** in that it contains two interpenetrating tetrahedra of four sodium atoms and four oxygen atoms. In this case, however, the overall geometry is symmetrical such that a cube is formed by the eight atoms and an $S_4$ axis runs through the molecule. Each 4-methylphenoxide ligand is triply bridging and each sodium atom is attached to a bidentate DME molecule. The average Na–O($\mu_3$-OR) distance is 2.31(2) Å. In comparison, $NaOCMe_3$ crystallizes as a hexamer and a nonamer, i.e. as $[(NaOCMe_3)_9(NaOCMe_3)_6]$, with Na–O($\mu_3$-OR) distances of 2.191(18)–2.501(16) and 2.176(17)–2.335(16) Å, respectively.[43] Although the Na–O($\mu_3$-OR) distances in **6** are not abnormal, they are significantly shorter than any of the Na–O distances in **3** including Na–O($\mu$-OR) distances which should be shorter.

## Discussion

**Utility of the 4-Methylphenoxide Ligand.** As anticipated, the 4-methylphenoxide ligand reacts with $LaCl_3$ to form new lanthanum alkoxide complexes. Given the tendency of phenoxides to bridge[25,44–49] and the reduced steric bulk of this particular phenoxide, the observed formation of bridged polymetallic complexes is quite reasonable. In fact, the 4-methylphenoxide ligand is so good at bridging that it readily incorporates other metals, in this case, sodium, into the lanthanide-bridged complex. The results indicate that lanthanide phenoxide complexes can be characterized with small phenoxide ligands lacking substituents at the 2 and 6 positions and that this may be a particularly useful ligand in the assembly of heteropolymetallic systems.

**Predominance of the Trigonal Bipyramidal Geometry.** In this $NaOC_6H_4Me\text{-}4/LaCl_3$ system, there is a clear preference to form not just polymetallic complexes, but polymetallic complexes which have a trigonal bipyramidal pentametallic framework. The trigonal bipyramidal $M_5(OR)_9L_5$ entity found in **2** and **3** appears to be a preferred basic structural unit for this combination of metals and ligand.

Specific types of preferred polymetallic structural units have also been observed in the reactions of yttrium and lanthanide halides and amides with other types of alkoxides. For example, these metals and *tert*-butoxide ligands often form trimetallic $M_3(OR)_9L_2$ complexes of general structure $Ln_3(OR')_3(\mu\text{-}OR')_3(\mu_3\text{-}OR')(\mu_3\text{-}Z)ZL_2$ (Ln = Y, La; R' = $CMe_3$; Z = OR', halide; L = THF, R'OH).[3,9,20–22] Another common structural entity is the square pyramidal $M_5(anion)_{13}O$ structure, $M_5(\mu_3\text{-}OR'')_4(\mu\text{-}OR'')_4(anion)_5(\mu_5\text{-}O)$ (M = Y, Gd, Yb, In; R'' = $CHMe_2$, Me; anion = $OCHMe_2$, $C_5H_5$), which forms with isopropoxide ligands and with a combination of cyclopentadienyl and methoxide ligands which is apparently equivalent to isopropoxide ligands.[4,7,50–52]

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Complexes **2**–**5** may constitute a third general structural class of polymetallic lanthanide alkoxide complexes. The formation of a specific preferred polymetallic form for a given combination of metals and ligands may be general for alkoxide complexes of these metals.

The basic trigonal bipyramidal geometry generated by the 4-methylphenoxide ligand with lanthanum and sodium has some unusual features for the individual components. (a) The seven-coordinate $(L)La(\mu\text{-}OR)_3(\mu_4\text{-}OR)_3$ local coordination environment around each lanthanum atom is unusual in that with one exception[6] all previously characterized lanthanide and yttrium alkoxides have contained a maximum coordination number of no more than 6. (b) The quadruply-bridging nature of the three 4-methylphenoxide ligands in **2** and **3** is in itself unusual.[2] (c) The arrangement of ligands in complex **2** is unique in lanthanide and yttrium alkoxide chemistry in two respects. First, the complex has no terminal alkoxide ligands, i.e., its alkoxide ligands are used to a maximum extent to bridge the component metals into a stable polymetallic entity. Second, the complex has one substitutionally-labile neutral ligand on each metal and this is the only terminal ligand on each metal. In terms of uniform derivatization at each metal center while the polynuclear core is maintained, this is ideal. The conversion of **2** to **3** demonstrates how successfully this can be utilized, in this case, to generate a sheet structure of polymetallic complexes.

Although there are numerous pentametallic lanthanide and yttrium oxo alkoxide complexes in the literature,[4,7,50–52] as described above these generally have a square pyramidal geometry. We are aware of only one other lanthanide or yttrium alkoxide complex which approaches trigonal bipyramidal geometry, namely, the oxo alkoxide $Nd_5(OCHMe_2)_{13}(HOCHMe_2)_2O$.[24] This low-symmetry complex can be viewed as arising from double ROH solvation of one of the basal vertices of the square pyramidal $M_5(anion)_{13}O$ complexes described above. The disolvated vertex has two less bridging alkoxide connections which maintains six-coordination for each metal in the complex. Hence, this complex differs from **2**–**5** in the lanthanide coordination number and the composition of the metals as well as the low symmetry and presence of the oxide ligand.

Two crystallographically characterized trigonal bipyramidal complexes more closely related in structure to **2**–**5** are the 3,5-dimethylpyrazolyl (pz) complexes $Yb_3Na_2(pz)_9O(THF)_2$ and $Ho_3Na_2(pz)_9O(Hpz)_2$.[53] These compounds have a lanthanide: sodium ratio inverse to that in **2**–**5**, and the positions of the metals are correspondingly inverse: the three lanthanide metals are in the equatorial positions and the two alkali metals are in the apical locations. Although the pyrazolyl complexes differ from **2**–**5** in the ligand binding arrangement since the pyrazolyl ligands are bidentate and an oxo ligand is present, it is nonetheless interesting to see that this alternative 3:2 heterometallic complex adopts the trigonal bipyramidal geometry. This geometry may be preferred for 3:2 heteropentametallic systems because it has two types of vertices in a 3:2 ratio compared to the 4:1 situation in a square pyramid.

**Flexibility of the Trigonal Bipyramidal Structure.** The trigonal bipyramidal geometry found in **2** and **3** is remarkably resilient in that loss of one of the component metals yields tetrametallic complexes, **4** and **5**, which retain the overall geometry of the trigonal bipyramid. The facile conversion of **2** to **4**, eq 3, is reminiscent of polyhedral borane chemistry in which removal of a vertex from a closo complex can generate a nido complex which has the same structure as a closo parent compound.[54] The reverse of eq 3, i.e., the re-formation of **2** from **4**, also has parallels in borane chemistry in that vertices can be added to nido compounds to form the original closo geometry.[55] These systems differ in that, for boron hydride systems, electron count is important in determining the structure,[56] and for **2** and **4**, the analogous electron count component is unclear. The structural similarities between yttrium alkoxide complexes and boranes have been noted before[50] with $M_5(anion)_{13}O$ and $B_5H_9$, both of which are square pyramidal assemblies of five [(trivalent element)–(terminal ligand)] units with four doubly-bridging ligands along the sides of the square face.

Although complex **2** tends to retain the trigonal bipyramidal structure even when a vertex is lost, its NMR spectra indicate that it is nonrigid in solution at room temperature. Hence, the 4-methylphenoxide ligand appears to display dual behavior in its heteropolymetallic chemistry: this ligand can readily form a stable heteropolymetallic framework of preferred geometry, but it can also provide complexes which are flexible in solution in terms of ligand position.

**Sodium 4-Methylphenoxide Complexes.** The crystallographic studies on **1** and **6** showed that the lanthanide atoms are important in determining the structures of **2**–**5** since the sodium 4-methylphenoxide complexes have significantly different structures. The polymetallic nature of the sodium 4-methylphenoxide complexes is precedented in alkali metal alkoxide chemistry from structures on systems such as $(NaOCMe_3)_6$,[43] $(NaOCMe_3)_9$,[43] $(LiOCMe_2Ph)_6$,[57] and MOMe (M = Li,[36] K,[58] Cs[58]), $[Li(OSiPh_3)(DME)]_2$,[59] $[K_4(OSiPh_3)_4]_2(DME)_3$,[59] and $[KOSiMe_2Ph(C_6H_6)]_4$.[60]

$[Na(OC_6H_4Me\text{-}4)(DME)]_4$ is also like many tetrametallic compounds in that the four metals form a tetrahedron, the four ligands form an interpenetrating tetrahedron, and a cubic structure results.[59–62] The bond distances in **6** are normal compared to the distances observed in hexameric and nonameric $(NaOCMe_3)_n$.[43]

When sodium 4-methylphenoxide crystallizes in an unsolvated form, **1**, coordination of the arene rings to sodium atoms apparently compensates for the absence of electron density provided by solvate molecules, e.g. the DME in **6**. Since the sodium–arene interactions in **1** involve a $\mu_3$-$(NaOC_6H_4Me\text{-}4)$ ligand with a sodium atom other than the three that the $\mu_3$-oxygen atom connected, a polymeric structure results. This geometry and the interaction distances are such that four sodium atoms no longer form a tetrahedron as in **6**. Hence, **1** is comprised of linked pairs of sodium atoms instead of linked tetrahedra.

Recently, several complexes have been crystallographically characterized which contain arene rings in the coordination environment of alkali metals including $Na_2(Ph_2CCPh_2)$,[41] $Na_2(Ph_2CCHCPh_2)$,[42] $(toluene)_2K(\mu\text{-}Cl)Lu[CH(SiMe_3)_2]_3$,[63] $(C_6H_6)K[AlMe_3NO_3]$,[64] $(C_6H_6)K[Al_7O_6Me_{16}]$,[65] K(dibenzo-18-crown-

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6)X$(C_6H_6)_2$ (X = $Al_2Me_6Cl$, $GaMe_3NCS$),[66] $\{K_4(\mu_3\text{-}OSiPh_3)_3[\mu_3\text{-}OSiPh_2(\eta^1\text{-}Ph)](DME)_2\}_2(\mu\text{-}DME)$,[60] and $[(C_6H_6)K(OSiMe_2\text{-}Ph)]_4$.[60] From these structures and the structure of **1**, it is clear that, in the absence of other ligands or coordinating solvents, arene rings will provide the electron density needed to complete the coordination sphere of an alkali metal. A similar situation has previously been observed with lanthanide and actinide metals.[23,67–69]

**Flexibility of the 4-Methylphenoxide Ligand.** The 4-methylphenoxide structures reported here show that this ligand is not only versatile in its bridging mode, i.e., $\mu$, $\mu_3$, or $\mu_4$, but it is also flexible in organizing metals in a variety of forms, i.e., triangles, tetrahedra, or linear pairs, depending on the nature of the other available ligands present. It is surprising that this ligand has not been used more extensively in the past. Previous crystallographic studies of the 4-methylphenoxide ligand have not involved metals further to the left in the periodic table than tantalum.[70,71] Related to this structural flexibility, the 4-methylphenoxide ligand can accommodate a wide range of metal–oxygen bond distances as shown in Table III.

## Conclusion

The 4-methylphenoxide ligand has proven to be a viable group for the formation of characterizable lanthanide complexes and appears to be very useful in assembling heteropolymetallic complexes of lanthanum and sodium. It can bridge as many as four of these metals and can keep them assembled even in light of significantly disruptive reactions which remove one of the component metals. The ligand appears to be flexible in accommodating a range of bond lengths and geometries. The combination of this ligand with lanthanum and sodium shows a propensity to form a trigonal bipyramidal pentametallic framework which may prove to be another general structural type in lanthanide alkoxide chemistry.

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**Supplementary Material Available:** Text describing crystallographic procedures, figures showing completely numbered ORTEP plots, and tables of crystal data, bond distances and angles, thermal parameters, and hydrogen atom coordinates (67 pages). Ordering information is given on any current masthead page.

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