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Preparation and X-ray Structures of $K[Ln(O\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_4]$ (Ln = La, Nd, Er). Extended Chain Structures of Lanthanide Tetrakis(aryloxide) Anions Bridged by Potassium−η-Arene Interactions

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Reaction of several lanthanide trichlorides $LnCl_3$ (Ln = La, Nd, Er, Lu) with 3 or 4 equiv of potassium 2,6-diisopropylphenoxide in THF solution leads to the formation of potassium salts of formula $K[Ln(O\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_4]$ [Ln = Nd (**5**), Er (**6**), Lu (**7**), La (**8**)]. These salts exhibit unusual solid-state structures involving multihapto potassium−π-arene interactions. Not all lanthanide trichlorides produce the potassium salt directly from this reaction, and the nature of the product appears to be related to the solubility of the $LnCl_3$ starting material in THF solution. Compounds **5** and **6** exist in the solid state as pseudo-one-dimensional infinite-chain structures featuring multihapto K−C interactions with phenyl rings from two adjacent $[Ln(OAr)_4]^-$ units. Compound **8** forms a pseudo-two-dimensional sheet structure, with multihapto K−C interactions linking three neighboring $[Ln(OAr)_4]^-$ units. Ln−O distances within the tetrahedral $[Ln(OAr)_4]^-$ units average 2.211(12) (**5**), 2.084(14) (**6**) and 2.253(6) Å (**8**). Potassium−carbon distances of the arene rings are in the ranges 3.097(8)−3.772(11) Å (**5**), 3.018(8)−3.484(10) Å (**6**) and 3.089(3)−3.519(4) Å (**8**). Crystal data for **5** (at −171 °C): monoclinic space group $P2_1/n$, $a = 12.990(4)$ Å, $b = 18.977(6)$ Å, $c = 18.594(5)$ Å, $\beta = 93.94(1)°$, $V = 4572.66$ Å^3, $d_{calc} = 1.296$ g cm^{-3}, $Z = 4$, $R = 0.0538$, $R_w = 0.0530$. Crystal data for **6** (at −161 °C): monoclinic space group $P2_1/n$, $a = 10.567(3)$ Å, $b = 20.856(6)$ Å, $c = 20.938(6)$ Å, $\beta = 102.72(1)°$, $V = 4500.93$ Å^3, $d_{calc} = 1.351$ g cm^{-3}, $Z = 4$, $R = 0.0362$, $R_w = 0.0368$. Crystal data for **8** (at −171 °C): orthorhombic space group $Pcab$, $a = 19.153(2)$ Å, $b = 20.898(3)$ Å, $c = 22.673(3)$ Å, $V = 9074.66$ Å^3, $d_{calc} = 1.299$ g cm^{-3}, $Z = 8$, $R = 0.0272$, $R_w = 0.0281$.

Introduction

Investigations into the chemistry of yttrium and the lanthanide elements containing alkoxide and aryloxide ligands of varying steric bulk have produced complexes exhibiting a variety of structural types ranging from monomeric $Ln(OAr)_3$ to polymeric $Ln_6(OR)_{17}Cl$, and even clustered lanthanide salt complexes such as $Na_3La_2(O\text{-}4\text{-}MeC_6H_4)_9(THF)_5$.[2-43] The formation of these "ate" or "double alkoxide" salts can be a pervasive problem in the chemistry of actinide and lanthanide metals, and for this reason many workers have employed the alcoholysis of amido or alkyl complexes such as $Ln[N(SiMe_3)_2]_3$ and $Ln[CH(SiMe_3)_2]_3$ for the preparation of salt-free lanthanide alkoxide

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and aryloxide complexes.[11,13,14,35–37,39] Alternatively, it has been demonstrated on a number of occasions that metathesis between lanthanide or actinide *iodides* and *potassium* alkoxide or alkyl salts provides a convenient methodology for mitigating the formation of double salt complexes (eqs 1–5).[44] The relatively

$$\mathrm{Th} + 2\mathrm{I}_2 \xrightarrow{\mathrm{THF}} \mathrm{ThI}_4(\mathrm{THF})_4 \qquad (1)$$

$$\mathrm{U} + {}^{3}/_{2}\mathrm{I}_2 \xrightarrow{\mathrm{THF}} \mathrm{UI}_3(\mathrm{THF})_4 \qquad (2)$$

$$\mathrm{ThI}_4(\mathrm{THF})_4 + 4\mathrm{KOAr} \xrightarrow{\mathrm{THF}} \mathrm{Th(OAr)}_4 + 4\mathrm{KI} \qquad (3)$$

$$\mathrm{UI}_3(\mathrm{THF})_4 + 3\mathrm{KOAr} \xrightarrow{\mathrm{THF}} \mathrm{U(OAr)}_3(\mathrm{THF})_2 + 3\mathrm{KI} \qquad (4)$$

$$\mathrm{LaI}_3(\mathrm{THF})_x + \mathrm{KC}_5\mathrm{Me}_5 \xrightarrow{\mathrm{THF}} (\eta\text{-}\mathrm{C}_5\mathrm{Me}_5)\mathrm{LaI}_2(\mathrm{THF})_3 + \mathrm{KI} \qquad (5)$$

clean iodide metathesis reactions (eq 3–5) presumably work well because the formation of THF-insoluble KI helps to drive the reaction to completion. The greater insolubility of KCl relative to KI suggested that the corresponding metathesis between lanthanide trichlorides and potassium alkoxide salts might provide a direct route to salt-free alkoxide and aryloxide complexes, thereby avoiding the intermediate preparation of $\mathrm{Ln[N(SiMe_3)_2]_3}$.

While this KCl metathesis strategy led to the formation of a salt complex during attempted preparation of a homoleptic lanthanide alkyl species (eq 6),[45] it has worked well for the preparation of certain lanthanide metal aryloxide complexes. We have found that the room-temperature reaction of anhydrous $\mathrm{LnCl_3}$ (Ln = Pr, Sm, Gd, Yb) with three equivalents of potassium 2,6-diisopropylphenoxide in THF, followed by crystallization from toluene, results in the isolation of monomeric bis-THF adducts $\mathrm{Ln(OAr)_3(THF)_2}$ (Ln = Sm (**1**), Pr (**2**), Gd (**3**), Yb (**4**)) in good yield according to eq 7.[46] However, we have also found that the reaction shown in eq 7 is not general for all of the lanthanide trichlorides, and the attempted preparation of $\mathrm{Nd(OAr)_3(THF)_2}$ from metathesis of $\mathrm{NdCl_3}$ with potassium 2,6-diisopropylphenoxide produced the potassium salt $\mathrm{K[Nd(O\text{-}2,6\text{-}\mathit{i}\text{-}Pr_2C_6H_3)_4]}$. Unexpectedly, this salt was found to possess a novel quasi-one-dimensional infinite-chain structure linked by multihapto potassium–π-arene bridges. We wished to investigate the generality of this structural unit across the lanthanide series and thus undertook the present study of the preparation of these tetrakis(aryloxide) anions using lanthanide trichlorides and potassium aryloxide. A portion of this work has been previously communicated.[38]

$$\mathrm{LuCl}_3 + 3\mathrm{KCH(SiMe_3)_2} \xrightarrow{\mathrm{ether}} \mathrm{Lu[CH(SiMe_3)_2]_3(\mu\text{-}Cl)K(ether)} \qquad (6)$$

$$\mathrm{LnCl}_3 + 3\mathrm{KOAr} \xrightarrow{\mathrm{THF}} \mathrm{Ln(OAr)_3(THF)_2} + 3\mathrm{KCl} \qquad (7)$$

$$\mathrm{Ln} = \mathrm{Sm}\ (\mathbf{1});\ \mathrm{Pr}\ (\mathbf{2});\ \mathrm{Gd}\ (\mathbf{3});\ \mathrm{Yb}\ (\mathbf{4});\ \mathrm{Ar} = 2,6\text{-}\mathit{i}\text{-}\mathrm{Pr_2C_6H_3}$$

Results and Discussion

Synthesis. The reaction of anhydrous Nd, Er, or Lu trichloride with *3* equiv of potassium 2,6-diisopropylphenoxide in THF solution at room temperature for 24–72 h, followed by crystallization from toluene, produces the potassium salts $\mathrm{K[Ln(O\text{-}2,6\text{-}\mathit{i}\text{-}Pr_2C_6H_3)_4]}$ [Ln = Nd (**5**), Er (**6**), Lu (**7**)] in moderate yields. Alternatively, refluxing a suspension of lanthanum trichloride in THF with *4* equiv of potassium 2,6-diisopropylphenoxide, followed by removal of solvent and crystallization of the white residue from toluene, yields colorless crystals of the lanthanum salt $\mathrm{K[La(O\text{-}2,6\text{-}\mathit{i}\text{-}Pr_2C_6H_3)_4]}$ (**8**) as shown in eq 8. ^{1}H NMR spectroscopy confirmed the absence of THF ligands in complexes **5**–**8**, and microanalytical data are consistent with the proposed stoichiometry of $\mathrm{K[Ln(OAr)_4]}$. We believe that the synthesis of the Nd, Er, and Lu tetrakis(aryloxide) anions also proceeds according to the stoichiometry of eq 8. Since these lanthanide trichlorides are all relatively insoluble in THF solution, there is always an excess of KOAr in solution when performing these metathesis reactions. Subsequent work has in fact shown that the related $\mathrm{K[Sm(OAr)_4]}$ (Ar = $2,6\text{-}\mathit{i}\text{-}\mathrm{Pr_2C_6H_3}$) salt can be prepared in a more rational fashion by reaction of 1 equiv of KOAr with $\mathrm{Sm(OAr)_3(THF)_2}$ in THF solution as indicated in eq 9. This samarium analog shows a rich reaction chemistry, and this will be the subject of a separate report.

$$\mathrm{LnCl}_3 + 4\mathrm{KOAr} \xrightarrow{\mathrm{THF}} \mathrm{KLn(OAr)_4} + 3\mathrm{KCl} \qquad (8)$$

$$\mathrm{Ln} = \mathrm{Nd}\ (\mathbf{5}),\ \mathrm{Er}\ (\mathbf{6});\ \mathrm{Lu}\ (\mathbf{7}),\ \mathrm{La}\ (\mathbf{8});\ \mathrm{Ar} = 2,6\text{-i-}\mathrm{Pr_2C_6H_3}$$

$$\mathrm{Sm(OAr)_3(THF)_2} + \mathrm{KOAr} \xrightarrow{\mathrm{THF}} \mathrm{KSm(OAr)_4} \qquad (9)$$

Solid State and Molecular Structures. Three lanthanide aryloxide salts of general formula $\mathrm{K[Ln(OAr)]_4}$ [Ln = Nd (**5**), Er (**6**), La (**8**), Ar = $2,6\text{-}\mathit{i}\text{-}\mathrm{Pr_2C_6H_3}$] have been examined by single-crystal X-ray diffraction techniques during the course of this work. Data collection parameters are given in Table 1, and selected fractional atomic coordinates are given in Tables 2-4.

$\mathbf{K[Nd(O\text{-}2,6\text{-}\mathit{i}\text{-}Pr_2C_6H_3)_4]}$ (5). Single crystals of **5** were grown from concentrated toluene solutions at −40 °C. In the

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Table 1. Summary of Crystallographic Data[a]

	5	**6**	**8**
empirical formula	$C_{48}H_{68}KNdO_4$	$C_{48}H_{68}ErKO_4$	$C_{48}H_{68}KLaO_4$
color; habit	pale blue	pink	colorless
cryst dimen., mm	0.15 × 0.12 × 0.20	0.15 × 0.20 × 0.25	0.45 × 0.52 × 0.51
space group	$P2_1/n$	$P2_1/n$	*Pcab*
cell dimens			
a, Å	12.990(4)	10.567(3)	19.153(2)
b, Å	18.977(6)	20.856(6)	20.898(3)
c, Å	18.594(5)	20.938(6)	22.673(3)
β, deg	93.94(1)	102.72(1)	90.00
vol, Å^3	4572.66	4500.93	9074.66
Z (molecules/cell)	4	4	8
fw	892.40	915.42	887.08
D_{calc}, g cm^{-3}	1.296	1.351	1.299
abs coeff, cm^{-1}	12.675	20.199	10.743
λ(Mo Kα), Å	0.710 69	0.710 69	0.710 69
temp, °C	−171	−161	−171
2*θ* range, deg	6.0−45.0	6.0−45.0	6.0−45.0
no. of measd reflcns	6098	10004	7653
no. of unique intens	5738	5875	5912
observed reflections	3612 [$F > 2.33\sigma(F)$]	3137 [$F > 2.33\sigma(F)$]	3987 [$F > 2.33\sigma(F)$]
R^b	0.0538	0.0362	0.0272
$R_w{}^c$	0.0530	0.0368	0.0281
goodness-of-fit	1.041	0.723	0.817
largest diff peak, e Å^{-3}	0.56	0.80	0.40

[a] **5** = K[Nd(O-2,6-*i*-$Pr_2C_6H_3)_4$], **6** = K[Er(O-2,6-*i*-$Pr_2C_6H_3)_4$], **8** = K[La(O-2,6-*i*-$Pr_2C_6H_3)_4$]. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

Table 2. Selected Fractional Coordinates and Isotropic Thermal Parameters[a] for K[Nd(O-2,6-*i*-$Pr_2C_6H_3)_4$] (**5**)

	10^4x	10^4y	10^4z	10 B_{iso}, Å^2
Nd(1)	6361.0(4)	2023.1(3)	7789.3(3)	13
O(2)	7434(5)	2599(4)	7135(4)	16
C(3)	8282(7)	2923(6)	6924(6)	16
C(4)	9168(8)	2917(6)	7405(5)	15
C(5)	10052(8)	2361(6)	7186(6)	19
C(6)	10055(7)	3593(5)	6535(6)	14
C(7)	9169(8)	3579(6)	6064(6)	17
C(8)	8292(8)	3239(6)	6254(6)	17
C(9)	9161(8)	2523(5)	8118(6)	17
C(12)	7324(8)	3188(6)	5736(6)	19
O(15)	5061(5)	1564(4)	7104(4)	19
C(16)	4877(8)	925(6)	6872(6)	19
C(17)	4128(8)	500(6)	7200(6)	17
C(18)	3941(8)	−186(6)	6961(6)	18
C(19)	4474(9)	−462(6)	6415(6)	24
C(20)	5184(8)	−56(6)	6075(6)	19
C(21)	5373(8)	634(6)	6291(6)	17
C(22)	3559(9)	822(6)	7804(7)	26
C(25)	6061(8)	1116(6)	5877(6)	18
O(28)	5843(5)	2635(4)	8690(4)	17
C(29)	5264(8)	3159(5)	8953(6)	14
C(30)	4965(8)	4045(6)	9832(6)	21
C(32)	4106(9)	4266(6)	9439(7)	27
C(33)	3790(9)	3919(6)	8804(7)	29
C(34)	4354(8)	3370(6)	8557(6)	17
C(35)	6522(8)	3247(6)	10058(6)	19
C(38)	4039(8)	2992(7)	7849(7)	26
O(41)	7039(5)	985(4)	8145(4)	15
C(42)	7987(7)	775(5)	8408(5)	13
C(43)	8708(8)	499(6)	7955(6)	17
C(44)	9684(8)	308(6)	8250(6)	21
C(45)	9953(8)	387(6)	8967(6)	19
C(46)	9259(8)	655(6)	9423(6)	21
C(47)	8269(8)	863(6)	9168(6)	16
C(48)	8435(7)	423(5)	7151(5)	10
C(51)	7474(9)	1142(7)	9663(6)	27
K(54)	6254(2)	−301(1)	7702(1)	19

[a] Isotropic values for those atoms refined anisotropically are calculated by using the formula given by: Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 609.

solid state, **5** displays a quasi-one-dimensional infinite chain of pseudo-tetrahedral [Nd(OAr)$_4$]$^-$ anions bridged by potassium−*η*-arene interactions between adjacent [Nd(OAr)$_4$]$^-$ units. A ball-and-stick drawing giving the atom-numbering scheme used in the tables is shown in Figure 1. Selected bond lengths and angles are listed in Table 5. The neodymium metal center of the [Nd(OAr)$_4$]$^-$ anion in **5** is coordinated to four oxygen atoms of aryloxide ligands in a pseudo-tetrahedral fashion. The Nd−O distances average 2.211(12) Å, which is somewhat longer than the 2.122(9) Å average distance observed for the related aryloxide complex Nd_2(O-2,6-*i*-$Pr_2C_6H_3)_6$.[46] This distance can also be compared to the average terminal Nd−O distances of 2.153(4), 2.146(4), 2.145(6), 2.05(2), 2.174(2) 2.148(16), 2.138-(8), and 2.162(5) Å seen in the aliphatic alkoxide complexes Nd_2(OCH-*i*-$Pr_2)_6(THF)_2$,[40] Nd_2(OCH-*i*-$Pr_2)_6(py)_2$,[40] Nd_2(OCH-*i*-$Pr_2)_6$(*μ*-dme),[40] Nd_6(O-*i*-Pr)$_{17}$Cl,[15] Nd(OC-*t*-$Bu_2CH_2PMe_2)_3$,[7] Nd_5O(O-*i*-Pr)$_{13}$(HO-*i*-Pr)$_2$,[22] Nd_4(OCH_2-*t*-Bu)$_{12}$,[41] and Nd(OC-*t*-$Bu_3)_3(CH_3CN)_2$,[39] respectively. One of the six O−Nd−O angles deviates significantly from an ideal tetrahedral value [O(15)−Nd(1)−O(41) = 95.29(26)°], while the remainder average 112.0(6)°. The Nd−O−C(*ipso*) angles range from 132.0(7) to 162.1(7)°, with the smallest Nd−O−C angle occurring in the aryloxide ligand with the shortest potassium-oxygen contact.

The closest contact between the potassium cation and the [Nd(OAr)$_4$]$^-$ anion in the solid state structure of **5** is with an oxygen atom [K(54)−O(41)] of one of the aryloxide ligands and displays a K−O distance of 2.760(8) Å (Figure 1). This distance is comparable to the average K−O distances [2.76(3) Å average] seen in the [K(DME)$_4$]$^+$ cation of [K(DME)$_4$]-[Y(OSiPh$_3$)$_4$(DME)][35] and the K−O contacts with the siloxide ligand in KBa$_2$(OSiPh$_3$)$_5$(DME)$_2$[47] [2.77(4) Å average], but is shorter than the K−O distances to the DME ligand in K_8-(OSiPh$_3$)$_8$(DME)$_3$ [2.921(13) Å average].[48a] The remainder of the coordination sphere of the potassium cation is comprised of K−C interactions with three phenyl rings from two adjacent [Nd(OAr)$_4$]$^-$ units. This structural feature is seen in Figure 1,

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(47) Coan, P. S.; Streib, W. E.; Caulton, K. G. *Inorg. Chem.* **1991**, *30*, 5019.

(48) (a) McGeary, M. J.; Folting, K.; Streib, W. E.; Huffman, J. C.; Caulton, K. G. *Polyhedron* **1991**, *10*, 2699. (b) Fuentes, G. R.; Coan, P. S.; Streib, W. E.; Caulton, K. G. *Polyhedron* **1991**, *10*, 2371.

Table 3. Selected Fractional Coordinates and Isotropic Thermal Parameters[a] for K[Er(O-2,6-*i*-$Pr_2C_6H_3)_4$] (**6**)

	10^4x	10^4y	10^4z	$10B_{iso}$, Å^2
Er(1)	1282.4(4)	2468.4(2)	7914.2(2)	14
O(2)	−684(6)	2587(3)	7432(3)	29
C(3)	−1406(10)	2620(5)	6815(4)	29
C(4)	−2184(12)	2102(5)	6541(6)	45
C(5)	−2822(13)	2143(5)	5897(5)	42
C(6)	−2750(12)	2679(5)	5519(5)	38
C(7)	−2074(12)	3205(5)	5808(5)	29
C(8)	−1399(10)	3194(4)	6463(5)	21
C(9)	−745(9)	3784(4)	6793(5)	18
C(12)	−2377(15)	1554(5)	6992(7)	55
O(15)	2343(6)	3284(3)	8312(3)	19
C(16)	2876(9)	3625(4)	8838(5)	20
C(17)	4256(10)	3680(4)	9010(6)	31
C(18)	4806(9)	4026(5)	9573(6)	29
C(19)	4040(11)	4308(5)	9954(5)	32
C(20)	2717(10)	4269(5)	9764(5)	24
C(21)	2112(10)	3943(4)	9212(5)	22
C(22)	648(9)	3890(5)	8959(5)	18
C(25)	5060(11)	3390(5)	8562(7)	39
O(28)	1464(6)	1763(3)	8612(3)	19
C(29)	1810(10)	1198(5)	8932(5)	21
C(30)	823(11)	784(5)	9030(5)	27
C(31)	1199(13)	200(5)	9335(5)	41
C(32)	2471(15)	44(5)	9548(6)	49
C(33)	3425(12)	460(6)	9454(5)	39
C(34)	3126(10)	1056(5)	9134(5)	26
C(35)	4164(11)	1531(6)	9043(6)	33
C(38)	−584(11)	976(5)	8793(5)	32
O(41)	2151(10)	2142(3)	7185(4)	60
C(42)	2589(10)	1858(5)	6705(5)	25
C(43)	3159(10)	2261(6)	6288(5)	31
C(44)	3496(11)	1953(9)	5765(6)	63
C(45)	3247(13)	1337(11)	5633(7)	94
C(46)	2805(11)	946(7)	6070(7)	53
C(47)	2470(10)	1201(5)	6613(5)	28
C(48)	1989(16)	786(5)	7117(6)	53
C(51)	3420(11)	2955(6)	6472(6)	41
K(54)	−22(3)	2027(1)	5670(1)	53

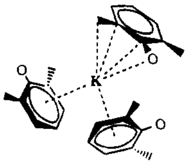
[a] Isotropic values for those atoms refined anisotropically are calculated by using the formula given by: Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 609.

Table 4. Selected Fractional Coordinates and Isotropic Thermal Parameters[a] for K[La(O-2,6-*i*-$Pr_2C_6H_3)_4$] (**8**)

	10^4x	10^4y	10^4z	$10B_{iso}$, Å^2
La(1)	2481.4(1)	74.0(1)	4324.6(1)	11
O(2)	2368(1)	−236(1)	5264(1)	16
C(3)	2485(3)	−505(2)	5791(2)	15
C(4)	1977(2)	−466(2)	6241(2)	14
C(5)	2109(3)	−758(2)	6778(2)	19
C(6)	2728(2)	−1078(2)	6881(2)	20
C(7)	3232(2)	−1101(2)	6447(2)	20
C(8)	3133(2)	−817(2)	5896(2)	16
C(9)	1318(2)	−76(2)	6119(2)	19
C(12)	3689(2)	−804(2)	5424(2)	20
O(15)	1543(1)	520(1)	3872(1)	17
C(16)	1236(2)	1030(2)	3623(2)	14
C(17)	887(2)	1484(2)	3978(2)	14
C(18)	615(2)	2025(2)	3702(2)	17
C(19)	661(2)	2114(2)	3100(2)	17
C(20)	961(2)	1648(2)	2753(2)	15
C(21)	1246(2)	1095(2)	2999(2)	14
C(22)	786(2)	1344(2)	4631(2)	17
C(25)	1492(2)	539(2)	2615(2)	17
O(28)	3170(2)	949(1)	4288(1)	18
C(29)	3350(2)	1542(2)	4135(2)	14
C(30)	3746(2)	1648(2)	3618(2)	14
C(31)	3926(2)	2268(2)	3465(2)	16
C(32)	3720(2)	2783(2)	3805(2)	21
C(33)	3333(2)	2681(2)	4310(2)	20
C(34)	3142(2)	2069(2)	4483(2)	15
C(35)	3942(2)	1064(2)	3252(2)	16
C(38)	2735(2)	1942(2)	5045(2)	21
O(41)	2847(1)	−775(1)	3797(1)	16
C(42)	2836(2)	−1358(2)	3562(2)	17
C(43)	3467(2)	−1688(2)	3459(2)	20
C(44)	3441(3)	−2293(2)	3211(2)	29
C(45)	2814(3)	−2579(2)	3078(2)	31
C(46)	2194(3)	−2264(2)	3184(2)	26
C(47)	2186(2)	−1649(2)	3430(2)	18
C(48)	4146(2)	−1362(2)	3639(2)	23
C(51)	1520(3)	−1284(2)	3562(2)	22
K(54)	2261(1)	2390.5(5)	3328.1(5)	20

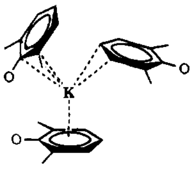
[a] Isotropic values for those atoms refined anisotropically are calculated by using the formula given by: Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 609.

and illustrated schematically in **I**. The cation is involved in η^6-arene interactions with the phenyl ring containing C(16)−C(21) [K−C 3.257(20) Å average] and also the phenyl ring from an adjacent $[Nd(OAr)_4]^-$ unit containing C(3A)−C(8A), although in this case three of the carbon atoms [C(5A), C(6A) and C(7A)] have much shorter K−C distances [3.17(3) Å average] than the remaining three within the same arene ring [C(3A), C(4A) and C(8A); K−C 3.43(2) Å average (Figure 1)]. The potassium cation makes further weak interactions with C(42), C(43) (ring carbons), and C(48) (methyl group) at K−C distances of 3.256(9), 3.538(10) and 3.375(10) Å, respectively. The closest Nd−K contact within the infinite chain structure of **5** is 4.426 Å. These multihapto interactions generate a quasi-one-dimensional infinite chain of alternating $[Nd(OAr)_4]^-$ anions and K^+ cations that are bridged by the potassium-η-arene interactions, and the resulting linear chain structure is shown in Figure 2a.



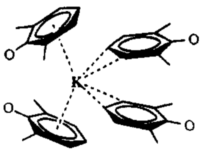
Nd - η^6,η^6,η^4

I



Er - η^6,η^3,η^2

II



La - $\eta^6,\eta^6,\eta^2,\eta^2$

III

K[Er(O-2,6-*i*-$Pr_2C_6H_3)_4$] (6). Single crystals of **6** were obtained by slow evaporation of a toluene solution in the drybox atmosphere at 20 °C. A ball-and-stick drawing giving the atom-numbering scheme used in the tables is shown in Figure 3. Selected bond lengths and angles are listed in Table 6. Like the neodymium congener, the erbium complex forms a quasi one-dimensional infinite chain structure of alternating cations and anions. The central ErO_4 core of the $[Er(OAr)_4]^-$ anion is essentially tetrahedral. The average Er−O distance of 2.084(14) Å in **6** is very similar to the 2.078(4) Å (average) distance seen in the bis-THF adduct Er(O-2,6-*i*-$Pr_2C_6H_3)_3(THF)_2$,[46] while being substantially shorter than the Er−O distances seen for the interstitial oxo ligand in (η-C_5H_4-*c*-$C_5H_9)_3Er_4(\mu_2$-$Cl)_6(\mu_3$-Cl)(μ_4-O)$(THF)_3$ (Er−O = 2.128−2.317 Å).[43b] The O−Er−O angles vary from 103.6(3)° to 118.42(24)°, and the Er−O−C(*ipso*) angles range from 138.7(6) to 171.4(8)°, with the smallest angle being present in the aryloxide ligand which makes the closest potassium−π-arene K−C contact.

The potassium cation is in an environment consisting almost exclusively of multihapto K−C contacts to arene rings of the aryloxide ligands as shown in Figure 3 and illustrated schematically in **II**. The only interaction made with an aryloxide oxygen atom is a very long contact of 3.364(9) Å to O(41) (compare this with the K−O distance of 2.760(8) Å seen in **5**). There is a K−η^6-arene interaction between the potassium cation and the phenyl ring containing C(3)−C(8), although the range of K−C distances is relatively large (3.124(8) to 3.373(9) Å) and

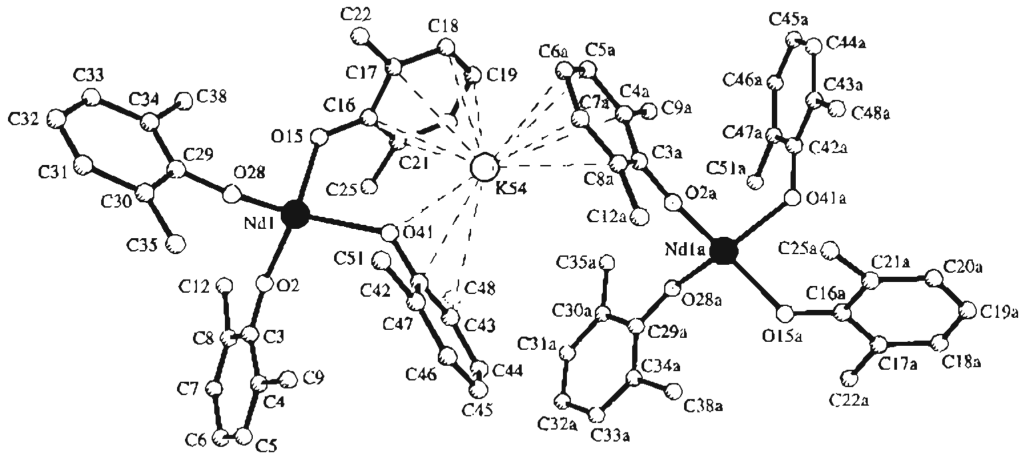


Figure 1. Ball and stick drawing of the solid-state structure of $K[Nd(O\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_4]$ (**5**) giving the atom number scheme used in the tables and emphasizing the multihapto interaction between the potassium cation and the arene rings of the aryloxide ligands. Methyl carbon atoms have been omitted for clarity.

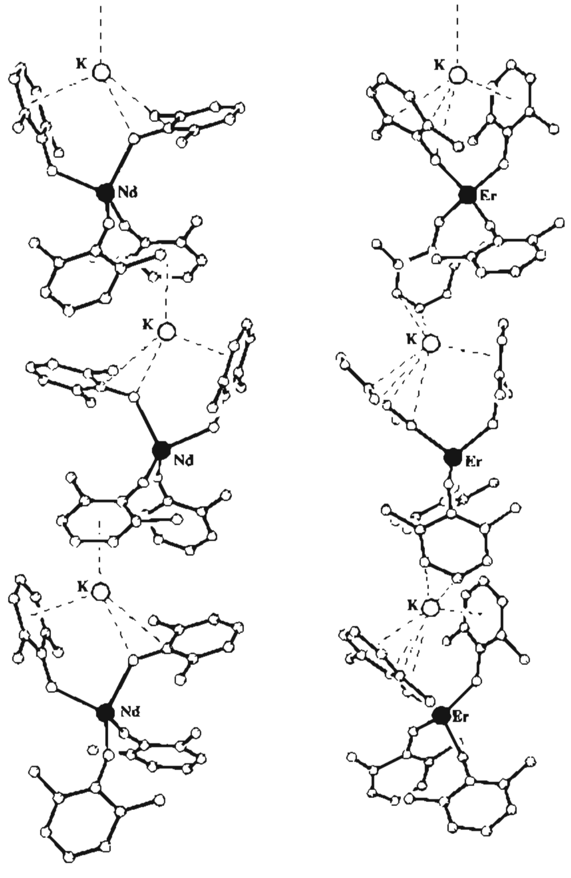
Table 5. Selected Bond Distances (Å) and Angles (deg) for $K[Nd(O\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_4]$ (**5**)

Nd(1)−O(2)	2.202(7)	K(54)−C(16)	3.267(9)
Nd(1)−O(15)	2.222(7)	K(54)−C(17)	3.240(9)
Nd(1)−O(28)	2.181(7)	K(54)−C(18)	3.227(9)
Nd(1)−O(41)	2.239(7)	K(54)−C(19)	3.224(9)
K(54)−O(41)	2.760(8)	K(54)−C(20)	3.277(10)
K(54)−C(3A)	3.473(10)	K(54)−C(21)	3.313(10)
K(54)−C(4A)	3.418(10)	K(54)−C(24)	3.772(10)
K(54)−C(5A)	3.217(9)	K(54)−C(42)	3.256(9)
K(54)−C(6A)	3.097(8)	K(54)−C(43)	3.538(10)
K(54)−C(7A)	3.196(8)	K(54)−C(48)	3.375(10)
K(54)−C(8A)	3.401(10)	K(54)−C(50)	3.519(10)
O(2)−Nd(1)−O(15)	111.30(30)	O(28)−Nd(1)−O(41)	112.15(3)
O(2)−Nd(1)−O(28)	113.57(30)	Nd(1)−O(2)−C(3)	162.1(7)
O(2)−Nd(1)−O(41)	110.41(30)	Nd(1)−O(15)−C(16)	132.0(7)
O(15)−Nd(1)−O(28)	112.74(30)	Nd(1)−O(28)−C(29)	150.9(6)
O(15)−Nd(1)−O(41)	95.29(30)	Nd(1)−O(41)−C(42)	134.1(6)

indicates a somewhat asymmetric interaction. The potassium cation also interacts in η^3-fashion to C(42), C(43), and C(47) (K−C 3.018(8), 3.288(9), and 3.296(9) Å, respectively), and makes a significant η^2-interaction with C(18A) and C(19A) from an adjacent $[Er(OAr)_4]^-$ unit (K−C 3.156(8) and 3.184(8) Å, respectively). The closest Er−K contact within the chain structure is 4.608 Å. These multihapto interactions generate a similar quasi one-dimensional infinite chain structure to that seen in the Nd analog, and the linear chain structure is shown in Figure 2b.

$K[La(O\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_4]$ (8). Single crystals of **8** were grown from concentrated toluene solution at −40 °C. A ball-and-stick drawing giving the atom-numbering scheme used in the tables is shown in Figure 4. Selected bond lengths and angles are listed in Table 7. Unlike the Nd and Er analogs, the interaction between cations and anions generates a pseudo-two-dimensional sheet structure as shown in Figure 5. The lanthanum metal center in **8** displays the same pseudo-tetrahedral coordination environment as **5** and **6**. The average La−O distance of 2.253(6) Å may be compared with the average terminal La−O distances of 2.163(7), 2.226(7), 2.244(10), 2.180(3), and 2.294(19) Å in $[La(OCH_2\text{-}t\text{-}Bu)_3]_4$,[41] $La(OSiPh_3)_3(THF)_3$,[35] $\{La[CH(SiMe_3)_2][1,1'\text{-}(2\text{-}O\text{-}C_6H_2\text{-}t\text{-}Bu_2\text{-}3,5)_2](THF)_3\}$,[36] $[La(OCPh_3)_2(\mu\text{-}OCPh_3)]_2$,[37] and $La_3(O\text{-}t\text{-}Bu)_9(HO\text{-}t\text{-}Bu)_2$,[31] respectively. The O−La−O angles vary between 96.52(10) and 118.23(10)°, while the La−O−C(*ipso*) angles span the range 149.75(26) to 162.8(3)°.

The potassium environment in the solid state structure of the lanthanum salt **8** consists exclusively of multihapto K−C contacts; no K−O contacts of less than 4.0 Å are present within the structure, and this is seen in Figure 5 and illustrated schematically in **III**. The principal potassium−carbon contacts of the cation are a relatively symmetric η^6-arene interaction with C(29)−C(34) [K−C 3.199(35) Å average], and an asymmetric η^5-interaction with the phenyl ring containing C(19) and C(20) [short K−C distances of 3.186(9) Å average], and C(16), C(18), and C(21) [long K−C contacts of 3.429(30) Å average]. The pseudo-two dimensional sheet structure of **8** arises from the fact that, besides the interactions noted above, the potassium cation makes modest η^2-K−C interactions with C(6A) and C(7A) [3.283(17) Å average] with the phenyl ring of a second



(A) $KNd(OAr)_4$ (B) $KEr(OAr)_4$

Figure 2. A ball and stick drawing comparing the quasi-one-dimensional chain structures for $K[Nd(OAr)_4]$ (a) and $K[Er(OAr)_4]$ (b). Methyl carbon atoms have been omitted for clarity.

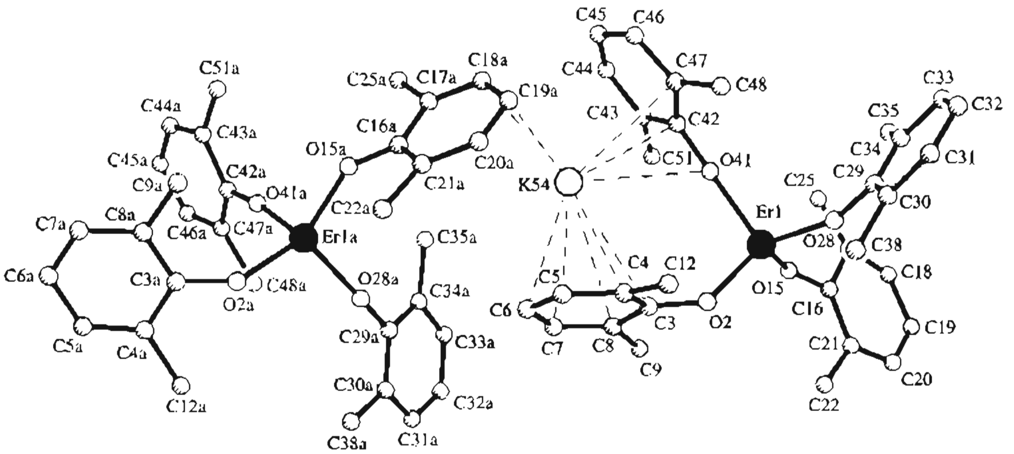


Figure 3. Ball and stick drawing of the solid-state structure of $K[Er(O\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_4]$ (**6**) giving the atom number scheme used in the tables and emphasizing the multihapto interaction between the potassium cation and the arene rings of the aryloxide ligands. Methyl carbon atoms have been omitted for clarity.

Table 6. Selected Bond Distances (Å) and Angles (deg) for $K[Er(O\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_4]$ (**6**)

Er(1)−O(2)	2.115(6)	K(54)−O(41)	3.364(9)
Er(1)−O(15)	2.104(6)	K(54)−C(42)	3.018(8)
Er(1)−O(28)	2.053(6)	K(54)−C(43)	3.288(9)
Er(1)−O(41)	2.063(7)	K(54)−C(47)	3.296(9)
K(54)−C(3)	3.373(9)	K(54)−C(18A)	3.156(8)
K(54)−C(4)	3.298(9)	K(54)−C(19A)	3.184(8)
K(54)−C(5)	3.139(8)	K(54)−C(36A)	3.299(9)
K(54)−C(6)	3.124(8)		
K(54)−C(7)	3.349(9)		
K(54)−C(8)	3.484(10)		
O(2)−Er(1)−O(15)	118.42(20)	O(28)−Er(1)−O(41)	107.64(30)
O(2)−Er(1)−O(28)	110.58(30)	Er(1)−O(2)−C(3)	138.7(6)
O(2)−Er(1)−O(41)	103.6(3)	Er(1)−O(15)−C(16)	148.6(6)
O(15)−Er(1)−O(28)	109.83(30)	Er(1)−O(28)−C(29)	160.2(6)
O(15)−Er(1)−O(41)	106.0(3)	Er(1)−O(41)−C(42)	171.4(8)

$[La(OAr)_4]^-$ group, as well as with C(45B) and C(46B) [3.433(24) Å average] from a *third* $[La(OAr)_4]^-$ unit (Figure 5). The shortest K−La distance within this structure is 5.359 Å, considerably more distant than observed in either **5** or **6** above.

Spectroscopic Studies. NMR Spectroscopy. Ambient temperature ^1H NMR spectra of **5**, **7**, and **8** in benzene-d_6 or THF-d_8 reveal only one type of aryloxide ligand environment in solution. Spectra of the erbium complex **6** were too broadened by the paramagnetic metal center to be of any diagnostic value. Since the solid state structures of the chain molecules indicate distinct asymmetry between the aryloxide ligands, it may be speculated that a fluxional process is operating in solution which renders the ligands equivalent on the NMR timescale.

Infrared Spectroscopy. The infrared spectra of compounds **5**−**8** (Nujol mull, KBr plates) show strong absorptions characteristic of alkoxide ligation.[49] In a recent study, we found that the dimeric π-arene bridged lanthanide aryloxide complexes $Ln_2(O\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_6$ (Ln = Nd, Sm, Er) exhibited two ν(C═C) stretching frequencies both in the solid state and in solution.[46] One band was assigned to terminal aryloxide ligands (*ca.* 1588 cm^{-1}), while a second lower-energy band (*ca.* 1572 cm^{-1}) was attributed to the bridging aryloxide ligands which make π-arene interactions with the other lanthanide metal center within the dimeric unit. In all of the potassium-chain complexes studied in this work, however, only *one* ν(C═C) stretching band is observed in the solid state Nujol mull spectra [1582 (**5**), 1581 (**6**), 1581 (**8**), and 1582 cm^{-1} (**7**)]. These data indicate that the multihapto K−C interactions in $K[Ln(OAr)_4]$ complexes are considerably weaker than the multihapto Ln−C interactions seen in $Ln_2(OAr)_6$. In the latter complexes, the Ln−C distances averaged 2.99−3.04 Å, whereas in the $K[Ln(OAr)_4]$ complexes the K−C distances range from 3.02−3.50 Å. Allowing for the much smaller ionic radius of potassium compared to the lanthanide elements, the relatively weak nature of the potassium−arene interactions is readily apparent.

Concluding Remarks

We have described the preparation and characterization of a series of lanthanide tetrakis(aryloxide) anions which exist in the solid state as infinite chain or sheet structures bridged through the agency of potassium cation−arene interactions. The preparation of aryloxide complexes with alkali metal cation−arene interactions has been reported previously,[42,48,50] but only in the case of $[Na(O\text{-}4\text{-}MeC_6H_4)]_n$[42] is an infinite-chain structure observed. Although the trichlorides of La, Nd, Er, and Lu react with potassium 2,6-diisopropylphenoxide in THF to yield $K[Ln(OAr)_4]$ complexes, additional work has shown that the trichlorides of Pr, Sm, Gd, and Yb yield the bis-THF adducts $Ln(O\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_3(THF)_2$ from directly analogous reactions.[46] At the present time, the reason behind this difference in reactivity is not fully understood. However, we speculate that the widely differing solubilities and reactivities of commercially-obtained samples of the lanthanide trichlorides may play a significant role. These results seem to reiterate that lanthanide alkoxide and aryloxide chemistry is not straightforward.

Alkali-metal cation interactions with arene moieties are well documented,[51] and have been observed most recently in the structures of $Ph_3CK(THF)(PMDTA)$[51d] [PMDTA = $(Me_2NCH_2CH_2)_2NMe$], $Ph_2C(2\text{-}C_5H_4N)K(THF)(PMDTA)$,[51e] $Na_2(Ph_2CCPh_2)(OEt_2)_2$,[52] $PhCH_2K{\cdot}PMDTA{\cdot}0.5PhCH_3$,[53] and $PhCH_2Rb{\cdot}PMDTA$.[53] The latter three structures, together with that of

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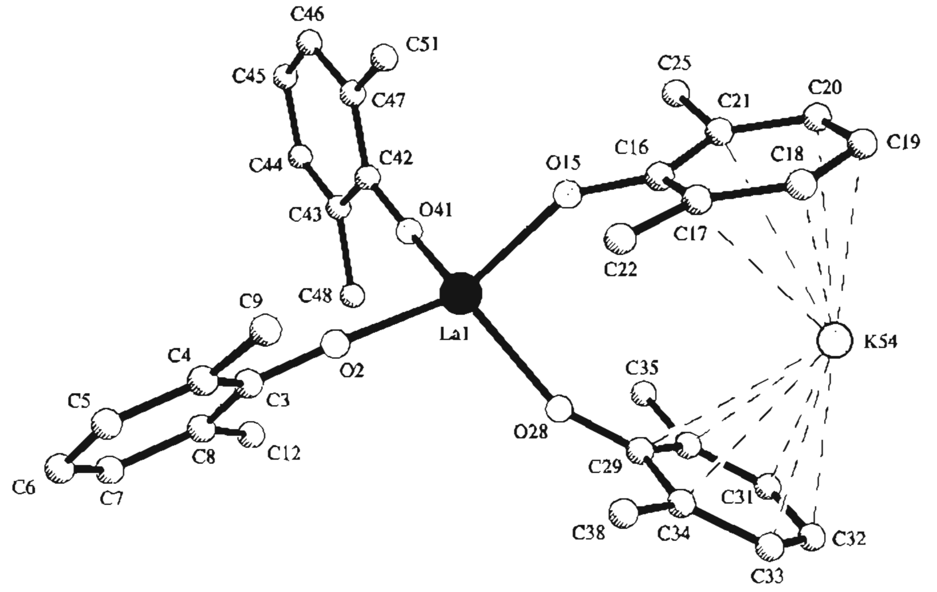

Figure 4. Ball and stick drawing of the solid-state structure of K[La(O-2,6-*i*-Pr$_2$C$_6$H$_3$)$_4$] (**8**) giving the atom number scheme used in the tables and emphasizing the multihapto interaction between the potassium cation and the arene rings of the aryloxide ligands. Methyl carbon atoms have been omitted for clarity.

Table 7. Selected Bond Distances (Å) and Angles (deg) for K[La(O-2,6-*i*-Pr$_2$C$_6$H$_3$)$_4$] (**8**)

La(1)−O(2)	2.2363(30)	K(54)−C(21)	3.416(4)
La(1)−O(15)	2.2693(30)	K(54)−C(29)	3.293(3)
La(1)−O(28)	2.2564(30)	K(54)−C(30)	3.306(3)
La(1)−O(41)	2.2510(30)	K(54)−C(31)	3.214(3)
K(54)−C(6A)	3.235(3)	K(54)−C(32)	3.107(3)
K(54)−C(7A)	3.330(4)	K(54)−C(33)	3.089(3)
K(54)−C(16)	3.519(4)	K(54)−C(34)	3.187(3)
K(54)−C(18)	3.353(4)	K(54)−C(45B)	3.360(4)
K(54)−C(19)	3.161(3)	K(54)−C(46B)	3.506(4)
K(54)−C(20)	3.211(3)		
O(2)−La(1)−O(15)	118.23(10)	O(28)−La(1)−O(41)	115.95(10)
O(2)−La(1)−O(28)	109.02(10)	La(1)−O(2)−C(3)	162.8(3)
O(2)−La(1)−O(41)	107.9(10)	La(1)−O(15)−C(16)	149.75(30)
O(15)−La(1)−O(28)	96.52(10)	La(1)−O(28)−C(29)	156.08(30)
O(15)−La(1)−O(41)	109.26(10)	La(1)−O(41)−C(42)	158.46(30)

KBPh$_4$,[54] show other rare examples of an alkali-metal bis η^6-arene bridge between adjacent molecules of a linear chain.

The potassium−carbon distances observed in the structures of **5**, **6**, and **8** appear to be among the shortest yet reported for potassium−arene interactions. In the other structurally characterized examples of η^6-coordination of an arene to a potassium cation (Table 8), the K−C distances have ranged from 3.21(1) to 3.72(1) Å, with average values being in the range 3.275−3.59 Å. By comparison, **5** contains a potassium−η^6-arene interaction of 3.257(20) Å (average), and **8** features an even shorter interaction of 3.20(4) Å (average). The shortest individual K−C distances seen in the three structures above are 3.097(8) Å (**5**), 3.018(8) Å (**6**) and 3.089(3) Å (**8**). These distances are comparable to the K-η^1-phenyl interaction seen in {K$_4$(μ_3-OSiPh$_3$)$_3$[μ_3-OSiPh$_2$(η^1-Ph)](η^2-DME)}$_2$(μ_2-DME) [3.078(4) Å],[48a] and are only slightly longer than the K−C distances seen in the alkali metal−cyclopentadienyl structures K[C$_5$H$_4$(SiMe$_3$)] [shortest K−C 2.988(10) Å][51g] and K[C$_5$(CH$_2$-Ph)$_5$](THF)$_3$ [shortest K−C 2.968(5) Å].[51f] It is now recognized that larger, more polarizable alkali metal cations (K, Rb, Cs) usually prefer multihapto interactions involving aromatic ring carbons. Detailed computational studies have shown that potential energy surfaces of ion pairs involving delocalized carbanions are usually very flat, especially with increasing ring to metal distance, as observed in the softer, more polarizable cations such as K$^+$.[53]

Experimental Section

General Procedures and Techniques. All manipulations were carried out under an inert atmosphere of oxygen-free UHP grade argon using standard Schlenk techniques, or under oxygen-free helium in a Vacuum Atmospheres glovebox. Anhydrous lanthanide trichlorides were purchased from Aldrich (La, Nd) or Strem (Er, Lu) and used as received. 2,6-Diisopropylphenol was purchased from Aldrich and degassed before use. Potassium hydride was purchased as a 60% dispersion in mineral oil (Aldrich), washed with hexane, and dried *in vacuo*. Potassium 2,6-diisopropylphenoxide was prepared by the reaction of potassium hydride with 2,6-diisopropylphenol in THF. Solvents were degassed and distilled from Na−K alloy under nitrogen. Benzene-d_6 and THF-d_8 were degassed, dried over Na−K alloy and then trap-to-trap distilled before use. Solvents were taken into the glovebox and a small amount tested with a solution of sodium benzophenone in THF. Solvents that failed to maintain a purple coloration from this test were not used.

NMR spectra were recorded at 22 °C on Brüker AF 250, or at 17 °C on Varian Unity 300 spectrometers in benzene-d_6 or THF-d_8. All ^{1}H NMR chemical shifts are reported in ppm relative to the ^{1}H impurity in benzene-d_6 or THF-d_8 set at δ 7.15 or 1.73, respectively. NMR spectra of paramagnetic lanthanide species are highly temperature dependent; thus it is important to note that the temperatures quoted represent average room temperatures and are approximate values. Infrared spectra were recorded on a Digilab FTS-40 spectrometer. Solid-state spectra were taken as Nujol mulls between KBr plates. Elemental analyses were performed on a Perkin-Elmer 2400 CHN analyzer. Elemental analysis samples were prepared and sealed in tin capsules in the glovebox prior to combustion.

K[Nd(O-2,6-*i*-Pr$_2$C$_6$H$_3$)$_4$] (5). To a THF solution of potassium 2,6-diisopropylphenoxide, prepared from 0.79 g (19.7 mmol) of potassium

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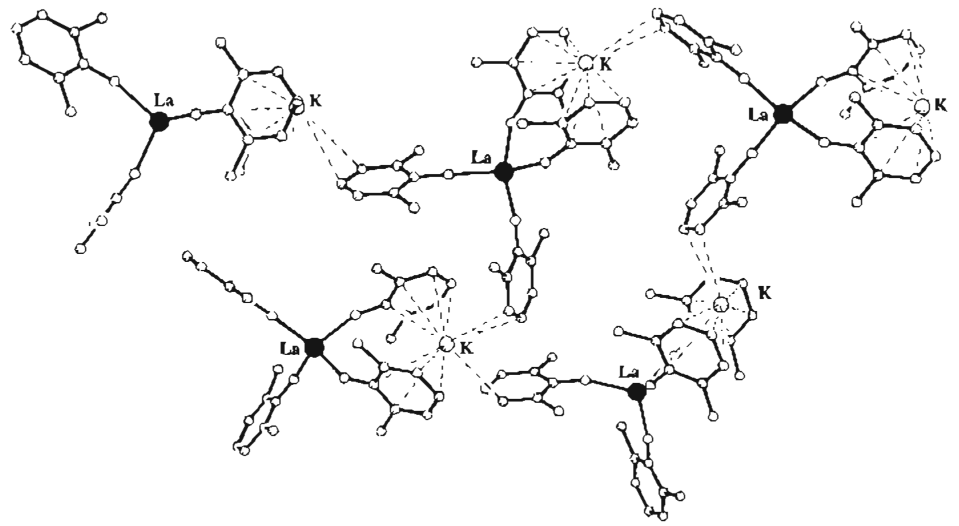

Figure 5. Ball and stick drawing showing the two-dimensional layered structure for $K[La(OAr)_4]$. Methyl carbon atoms have been omitted for clarity.

Table 8. Summary of Crystallographically Characterized K−C Interactions

	K−C (av), Å	ref
$Lu[CH(SiMe_3)_2]_3(\mu\text{-}Cl)K(C_7H_8)_2$	3.36	45
$K(AlMe_3NO_3)(C_6H_6)$	3.36	55
$K(Al_7O_6Me_{16})(C_6H_6)$	3.33	56
$[K(dibenzo\text{-}18\text{-}crown\text{-}6)](Al_2Me_6Cl)(C_6H_6)_2$	3.39	57
$[K(dibenzo\text{-}18\text{-}crown\text{-}6)](GaMe_3NCS)(C_6H_6)_2$	3.59	57
$[(C_6H_6)KOSiMe_2Ph]_4$	3.275	48b
$KBPh_4$	3.29	54

hydride and 3.52 g (19.7 mmol) of 2,6-diisopropylphenol, was added 1.65 g (6.58 mmol) of anhydrous neodymium trichloride. The resulting pale blue suspension was stirred at room temperature for 24 h and then filtered through a Celite pad to give a pale blue solution. All solvent was removed *in vacuo* to leave a sticky oil, which was triturated with 75 mL of hexane to produce a pale blue solid. The hexane was decanted and the solid dried *in vacuo*. Yield: 3.45 g (78%, based on potassium aryloxide). Recrystallization from toluene at −40 °C produced pale blue/purple crystals. ^1H NMR (300 MHz, C_6D_6): δ 18.18 (br s, 2H, $CHMe_2$), 14.72 (s, 2H, meta H), 11.82 (s, 1H, para H), 3.88 (br s, 12H, $CHMe_2$). IR (cm^{-1}): 1582 (m), 1425 (s), 1361 (m), 1327 (s), 1267 (s), 1206 (m), 1142 (w), 1110 (m), 1056 (w), 1041 (m), 934 (w), 886 (m), 852 (s), 799 (w), 758 (s), 748 (s), 688 (m), 670 (w), 550 (m). Anal. Calcd for $C_{48}H_{68}KNdO_4$: C, 64.60; H, 7.68. Found: C, 64.81; H, 8.39.

$K[Er(O\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_4]$ (6). In the drybox, 3.00 g (10.96 mmol) of anhydrous $ErCl_3$ was added to a Schlenk reaction vessel containing a stirred solution of 7.12 g (32.91 mmol) of $KO\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3$ in 125 mL of THF, and vigorous stirring was continued for 72 h at room temperature. The resulting pink suspension was filtered through Celite to give a clear pink filtrate, and the volatiles were removed in vacuo to yield a pink solid. The solid was extracted with 125 mL of hot toluene for 1 h with stirring, and the extract filtered again through Celite. The volume of the filtrate was then reduced to 20 mL *in vacuo*, by which time a mass of microcrystalline pink solid had been deposited. Then 50 mL of hexane was added to the filtrate to complete the precipitation and the pink solid collected on a frit and pumped to dryness. Yield: 3.54 g (47%, based on potassium aryloxide). The solid can be recrystallized from toluene. ^1H NMR (250 MHz, THF-d_8)—very broad resonances seen at δ 3.90 and 1.70. IR (cm^{-1}): 1581 (m), 1428 (s), 1361 (m), 1338 (s), 1276 (s), 1212 (m), 1155 (w), 1138 (w), 1110 (m), 1096 (sh, w), 1061 (w), 1044 (s), 956 (w), 937 (w), 886 (s), 863 (s), 793 (m), 760 (s), 748 (s), 688 (m), 615 (w), 591 (w), 572 (m), 549 (m), 543 (sh, m), 422 (m). Anal. Calcd for $C_{48}H_{68}ErKO_4$: C, 62.98; H, 7.49. Found: C, 62.03; H, 7.22.

$K[Lu(O\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_4]$ (7). To a vigorously stirred solution of 6.10 g (28.19 mmol) of $KO\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3$ in 125 mL of THF was added 2.645 g (9.40 mmol) of anhydrous $LuCl_3$. The resulting white suspension was stirred at room temperature for 24 h before being filtered through Celite to give a clear, colorless filtrate. All solvent was removed *in vacuo* to leave a white solid. This solid was dissolved in 150 mL of hot toluene and filtered again through Celite before being placed in the freezer at −40 °C. Over several days a mass of colorless crystals were deposited. These were filtered off and allowed to dry under a helium atmosphere. Yield: 2.662 g (41% based on potassium aryloxide). ^1H NMR (250 MHz, THF-d_8): δ 6.73 (d, J = 7 Hz, 2 H, meta OAr), 6.31 (t, J = 7 Hz, 1 H, para OAr), 3.66 (septet, J = 7 Hz, 2 H, $CHMe_2$), 0.98 (d, J = 7 Hz, 12 H, $CHMe_2$). IR (cm^{-1}): 1582 (m), 1429 (s), 1361 (m), 1336 (s), 1274 (s), 1213 (m), 1111 (m), 1044 (m), 957 (w), 935 (w), 887 (m), 865 (m), 854 (m), 797 (w), 761 (s), 748 (s), 689 (m), 574 (m), 555 (w), 544 (w). Anal. Calcd for $C_{48}H_{68}KLuO_4$: C, 62.45; H, 7.42. Found: C, 62.10; H, 6.25.

$K[La(O\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_4]$ (8). To a THF solution of $KO\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3$, prepared from 0.453 g (11.3 mmol) of KH and 2.015 g (11.3 mmol) of $HO\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3$, was added 0.687 g (2.80 mmol) of anhydrous $LaCl_3$. The resulting pale yellow suspension was refluxed for 18 h and then filtered through a Celite pad to give a pale yellow solution. All solvent was removed under reduced pressure to leave a sticky oil, which was triturated with 75 mL of hexane to produce a pale off-white solid. The hexane was decanted and the solid dried in vacuo. The solid was then extracted into toluene, filtered and the solvent removed in vacuo to leave a pale off-white solid. Yield: 0.851 g (34%). Recrystallization from toluene at −40 °C produced colorless crystals. ^1H NMR (300 MHz, C_6D_6): δ 6.98 (d, J = 7 Hz, 2 H, meta OAr), 6.61 (br t, 1 H, para OAr), 3.66 (br septet, 2 H, $CHMe_2$), 1.21 (d, J = 7 Hz, 12 H, $CHMe_2$). $^{13}C\{^1H\}$ NMR (75 MHz, C_7D_8): δ 160.46 (C, ipso), 135.95 (C, ortho), 123.28 (C, meta), 116.91 (C, para), 28.21 ($CHMe_2$), 23.52 ($CHMe_2$). IR (cm^{-1}): 1581 (m), 1425 (s), 1377 (m), 1350(w), 1332 (s), 1270 (s), 1206 (m), 1180 (sh, w), 1155 (w), 1140 (w), 1111 (m), 1095 (w), 1051 (w), 1043 (m), 955 (w), 933(w), 885 (m), 854 (s), 804(w) 796 (w), 760 (s), 749 (s), 724 (sh, w), 684 (m), 658 (w), 568 (m), 544 (m). Anal. Calcd for $C_{48}H_{68}KLaO_4$: C, 64.99; H, 7.73. Found: C, 64.23; H, 7.89.

Crystallographic Studies. The diffractometer utilized for data collection was designed and constructed locally at the IUMSC.[58] A Picker four-circle goniostat equipped with a Furnas Monochromator (HOG crystal) and Picker X-ray generator is interfaced to a Z80 microprocessor which is controlled by an RS232 serial port on an IBM PC microcomputer. Motors are Slo-Syn stepping motors, and a special top/bottom-left right slit assembly is used to align the crystal. Data were collected using standard moving crystal/moving detector techniques with stationary background counts at each extreme of the scan. All computations are performed on IBM compatible microcomputer systems. The ball-and-stick drawings used in the figures were generated

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from the diffraction data using the SHELXTL PLUS suite of computer programs (Siemens Analytical X-ray Instruments, Inc., 1990).

K[Nd(O-2,6-*i*-$Pr_2C_6H_3)_4$] (5). A suitable crystal was affixed to the end of a glass fiber using silicone grease and transferred to the goniostat where it was cooled to −171 °C. Standard inert atmosphere handling techniques were used. A systematic search of a limited hemisphere of reciprocal space revealed a set of diffraction maxima and symmetry consistent with the monoclinic space group $P2_1/n$ (an alternate setting of $P2_1/c$).

When the data collection was nearly complete, the crystal fractured and approximately 75% was lost. An attempt to use a scale factor to include the lost 134 data was unsuccessful, and since the number lost was less than 5%, it was decided to continue. After correction for backgrounds, Lorentz, and polarization terms, redundant data were averaged to yield a set of unique intensities. The structure was solved by a combination of direct methods (MULTAN78) and Fourier techniques. Most hydrogen atoms were visible in a difference Fourier phased on the non-hydrogen atoms and all were placed in fixed idealized positions for the final cycles of least squares. A final difference Fourier was featureless, the largest peak being 0.56 e/Å^3.

K[Er(O-2,6-*i*-$Pr_2C_6H_3)_4$] (6). The sample consisted of clumps of crystals, and a suitable fragment was cleaved from a larger crystal. The crystal was affixed to the end of a glass fiber using silicone grease and transferred to the goniostat where it was cooled to −161 °C. Standard inert atmosphere handling techniques were used. A systematic search of a limited hemisphere of reciprocal space revealed a set of diffraction maxima and symmetry consistent with the monoclinic space group $P2_1/n$ (an alternate setting of $P2_1/c$). After correction for Lorentz and polarization terms, equivalent data were averaged. Examination of ψ scans for several reflections indicated that no absorption correction was needed.

The structure was readily solved by a combination of direct methods (MULTAN78) and Fourier techniques. Some hydrogen atom positions were visible in a difference Fourier, and all were calculated and placed in fixed idealized positions for the final cycles of least squares. A final difference Fourier was featureless, the largest peaks being 0.80 e/Å^3, and several were located in the vicinity of C(36) and C(37).

K[La(O-2,6-*i*-$Pr_2C_6H_3)_4$] (8). A suitable crystal was affixed to the end of a glass fiber using silicone grease and transferred to the goniostat where it was cooled to −171 °C. Standard inert atmosphere handling techniques were used. A systematic search of a limited hemisphere of reciprocal space revealed a set of diffraction maxima with orthorhombic symmetry and extinctions corresponding to the unique space group *Pcab*.

After correction for Lorentz and polarization terms, equivalent data were averaged. The structure was readily solved by a combination of direct methods (MULTAN78) and standard Fourier techniques. A difference map phased on the non-hydrogen atoms clearly located the position of most hydrogen atoms. All hydrogens were then introduced into fixed, idealized positions and no attempt was made to vary their positions during the final cycles of refinement. A final difference Fourier was essentially featureless, with the exception of several peaks of approximate density 0.40 e/Å^3 in the vicinity of the metal.

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Supplementary Material Available: Tables of fractional coordinates and isotropic thermal parameters, bond distances, bond angles, and anisotropic thermal parameters for **5**, **6**, and **8** (22 pages). Ordering information is given on any current masthead page.