undergoes the typical base-on/base-off transition between neutral solution and pH 0.3, and the spectrum of the base-off complex is virtually identical to that of β-CH$_3$CH$_2$Cbi above 300 nm (i.e., where the axial nucleotide is transparent). The newly obtained α-CH$_3$CH$_2$Cbl fails to show a base-on/base-off transition in the visible region upon acidification[39] (i.e., only UV spectral changes associated with protonation of the axial nucleotide[6] occur), and its spectrum is identical to that of α-CH$_3$CH$_2$Cbi[21] above 300 nm. The new compound was also characterized by FAB MS,[40] unambiguously demonstrating the isomeric relationship between the CH$_3$CH$_2$Cbl diastereomers. As was the case for the CH$_3$Cbl's, anaerobic photolysis of the newly obtained α-CH$_3$CH$_2$Cbl at pH 1.2 produced the same stationary-state mixture of diastereomers as photolysis of β-CH$_3$CH$_2$Cbl under these conditions (Table I). Similarly, at neutral pH, photolysis had no effect on β-CH$_3$CH$_2$Cbl (other than slow dealkylation), while α-CH$_3$CH$_2$Cbl was converted completely to the β diastereomer under this condition.

It is not clear if the photoinduced isomerization by recombination of R$^\bullet$ and Co^{II} observed here occurs within the solvent cage or via recombination of separated, free radicals, although available evidence favors the latter.[34,35,42] Alelyunas et al.[35] have obtained evidence from trapping experiments that free radicals are involved in the photoinduced isomerization of α-(2-oxo-1,3-dioxolan-4-yl)cobalamin to the β-diastereomer in neutral solution.[42] If it is correct that α/β isomerization in organocobalt corrinoids requires escape from the solvent cage prior to radical recombination, then the product distribution in the photolytic steady state represents kinetic control of the reaction of R$^\bullet$ with Co^{II}. This would suggest that the 2–3-fold preference of R$^\bullet$ for the β face of cob(II)inamide (Table I) reflects the greater steric congestion at the α face, due to the downward projecting b, d, and e propionamides and the secondary amide f side chain, than at the β face, which has only three upwardly projecting acetamide side chains. This line of reasoning is supported by the results of the photoinduced isomerization of the base-off RCbl's, where the preference for the β face is increased relative to the RCbi's (Table I), possibly due to the presence of the pendent, bulky dimethylbenzimidazole nucleotide in the former complexes. The mechanism of this synthetically useful photoisomerization is currently under further investigation.

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(39) β-CH$_3$CH$_2$Cbl, base-on: λ (log ϵ) 511 (3.96), 345 (4.11), 314 (4.17), 266 nm (4.28). β-CH$_3$CH$_2$Cbl, base-off (pH 0.3): λ (log ϵ) 442 (3.91), 382 (3.95), 304 (4.44), 262 (4.49). α-CH$_3$CH$_2$Cbl (neutral solution): λ (log ϵ) 476 (4.01), 377 (3.96), 306 (4.38), 264 (4.33). α-CH$_3$CH$_2$Cbl (pH 0.3): λ (log ϵ) 476 (4.01), 378 (3.94), 306 (4.40), 265 (4.39).
(40) FAB MS was performed as described previously:[23] β-CH$_3$CH$_2$Cbl, *m/e* 1359.2 (calc, 1359.4); α-CH$_3$CH$_2$Cbl, *m/e* 1359.4 (calc, 1359.4).[41]
(41) As discussed elsewhere,[1,23] the parent ion for the zwitterionic RCbl's in positive ion FAB MS contains a proton from the matrix (*m*-nitrobenzyl alcohol). For the α-RCbl's, the axial water ligand is lost, so that the parent ion has the same mass for β-RCbl's (MH$^+$) and for α-RCbl's (MH$^+$ – H$_2$O).
(42) Similarly, the reversible, thermal cobalt-to-carbon migration of a benzyl radical in C$_6$H$_5$CH$_2$–Co^{III}[C$_2$(DO)(DOH)pn]I (benzyliodo(2,10-diethyl-3,9-dimethyl-1,4,8,11-tetraazaundeca-1,3,8,10-tetraene-1,11-diol)cobalt(III) is also known to involve escape from the solvent cage followed by recombination.[17]

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Preparation and X-ray Crystal Structure of K[Nd(O-2,6-*i*-Pr$_2$C$_6$H$_3$)$_4$]: A One-Dimensional Chain of Lanthanide Aryloxide Anions Joined by Bis(η^6-arene)–Potassium Interactions

Reports in the literature of the preparation of alkoxide,[1,2] and to a lesser extent aryloxide,[2,3] complexes of the lanthanide elements are numerous, and these complexes have received considerable attention in recent years as potential precursors to high-temperature superconductors, nonlinear optics, and optical fibers.[4] However, the amount of X-ray structural data available for these complexes is somewhat limited, and in the case of lanthanide aryloxide complexes, only the homoleptic species Ce(O-2,6-*t*-Bu$_2$C$_6$H$_3$)$_3$[3a] and Yb(O-2,6-Ph$_2$C$_6$H$_3$)$_3$[3c] and the Lewis base adducts Na$_3$[La$_2$(O-4-MeC$_6$H$_4$)$_6$(THF)$_5$],[3b] Yb(O-2,6-Ph$_2$C$_6$H$_3$)$_3$-(THF)$_2$·THF,[3c] and Yb(O-2,6-*t*-Bu$_2$-4-MeC$_6$H$_2$)$_2$(THF)$_n$ (n = 2, 3)[3d] have been crystallographically characterized. Lappert and co-workers have also prepared a series of homoleptic M(OAr)$_3$ (Ar = 2,6-*t*-Bu$_2$-4-MeC$_6$H$_2$) derivatives of many of the lanthanide elements,[3e] yttrium, and scandium, the last of which has been structurally characterized.[3g]

One of the most general synthetic routes to metal alkoxides is the simple metathesis of a metal halide and an alkali-metal alkoxide. While this strategy has great utility in transition-metal chemistry, retention of the alkali metal and formation of "ate" or "double alkoxide" complexes can be a pervasive problem in the chemistry of actinide and lanthanide metals.[2] For alkoxide or aryloxide complexes, the most common type of alkali-metal interaction in "ate" complexes is between the electronegative oxygen atom and the alkali-metal cation, with donor solvent molecules often completing the coordination sphere.[2] This ubiquitous interaction type is illustrated qualitatively in I and has been observed in both early-transition-metal[5,6] and lanthanide[3f] aryloxide complexes. Notably rare are examples of "ate" complexes in which

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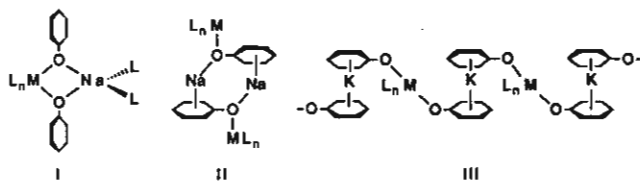
the alkali-metal cation is not primarily coordinated to oxygen atoms of alkoxide ligands. Occasionally η^6-arene coordination to the alkali metal is observed in aryloxide structures, as exemplified by Na[Ti(O-2,6-Me$_2$C$_6$H$_3$)$_4$py$_2$] in which the Na coordination environment is as depicted in II.[7] We report herein the synthesis and X-ray structural characterization of the potassium salt of a neodymium tetrakis(aryloxide) anion, K[Nd(O-2,6-i-Pr$_2$C$_6$H$_3$)$_4$], in which the potassium cation displays an unprecedented bis(η^6-arene) interaction with the arene rings of aryloxide ligands of adjacent anions and thus makes up a quasi-one-dimensional infinite chain structure as shown in III. This is a rare example of an infinite chain structure based upon a bis(η^6-arene)–alkali-metal interaction.

The room-temperature reaction of anhydrous neodymium trichloride with 3 equiv of potassium 2,6-diisopropylphenoxide in THF solution, followed by crystallization from toluene, allows the isolation of the salt K[Nd(O-2,6-i-Pr$_2$C$_6$H$_3$)$_4$] (**1**) in good yield.[8] Satisfactory microanalytical data have been obtained for **1**. Compound **1** is sparingly soluble in hexane but highly soluble in toluene and THF. Solution ^{1}H NMR spectra (C$_6$D$_6$) show one type of aryloxide ligand environment at room temperature and no resonances assignable to THF.[9] It is noteworthy that while the reaction to prepare **1** is conducted in THF solution, the experimental workup procedures yield **1** as a base-free complex. The lack of THF in the formula of **1** precluded a structural assignment of the type depicted in I and prompted a structural study by X-ray diffraction. Single crystals were grown from toluene solution at −40 °C, and the structure was determined from X-ray diffraction data collected at −171 °C.[10] In the solid state, **1** displays a quasi-one-dimensional infinite chain of [Nd(OAr)$_4^-$] anions bridged by potassium cations through the agency of bis(η^6-arene) interactions between adjacent [Nd(OAr)$_4^-$] units (Figure 1).

The Nd atom of the anion in **1** is coordinated to four oxygen atoms of the aryloxide ligands in a pseudotetrahedral fashion. The
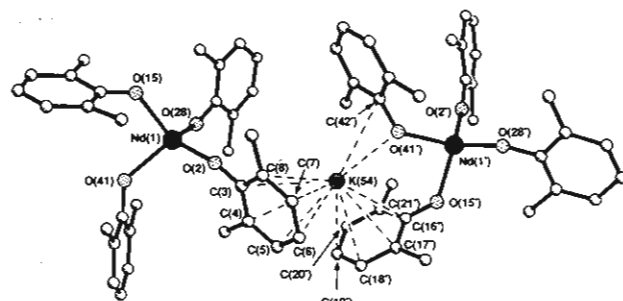
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(8) To a THF solution of potassium 2,6-diisopropylphenoxide [prepared from 0.79 g (19.7 mmol) of potassium hydride and 3.52 g (19.7 mmol) of 2,6-diisopropylphenol] was added 1.65 g (6.58 mmol) of anhydrous neodymium trichloride. The resulting pale 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 phenoxide). Recrystallization from toluene at −40 °C produced pale blue/purple crystals of **1**.

(9) ^{1}H NMR (300 MHz, 22 °C, benzene-d_6) for K[Nd(O-2,6-i-Pr$_2$C$_6$H$_3$)$_4$] (**1**): δ 18.18 (br s, 2 H, CHMe$_2$), 14.72 (s, 2 H, m-H), 11.82 (s, 1 H, p-H), 3.88 (br s, 12 H, CHMe_2).

(10) Crystal data for **1** (at −171 °C): C$_{48}$H$_{68}$KNdO$_4$, $M = 892.40$, monoclinic, space group $P2_1/n$ (an alternate setting of $P2_1/c$), $a = 12.990$ (4) Å, $b = 18.977$ (6) Å, $c = 18.594$ (5) Å, $\beta = 93.94$ (1)°, $V = 4572.66$ Å^3, $Z = 4$, $D_c = 1.296$ g cm^{-3}, and μ(Mo Kα) = 12.675 cm^{-1}. A crystal measuring 0.15 × 0.12 × 0.20 mm was affixed to the end of a glass fiber using silicone grease and transferred to a Picker four-circle goniostat equipped with a Furnas monochromator (HOG crystal) and Picker X-ray generator where it was cooled to −171 °C. Data were collected using standard moving crystal/moving detector techniques with stationary background counts. When 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 background, 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 map phased on the non-hydrogen atoms, and all were placed in fixed idealized positions for the final cycles of least squares. Final discrepancy indices were $R = 0.0538$, $R_w = 0.0530$ for those 3612 reflections with $F > 2.33\sigma(F)$. A final difference Fourier was featureless, the largest peak being 0.56 e/Å^3.

Figure 1. View of the molecular structure of **1**, emphasizing the bis-(η^6-arene) bridging interaction between the potassium cation and aryloxide groups of adjacent molecules. Methyl carbon atoms of the isopropyl substituents have been omitted for clarity. Important bond lengths (Å) and angles (deg): Nd(1)–O(2), 2.202 (7); Nd(1)–O(15), 2.222 (7); Nd(1)–O(28), 2.181 (7); Nd(1)–O(41), 2.239 (7); K(54)–O(41′), 2.760 (9); K(54)–C(8), 3.401 (10); K(54)–C(7), 3.196 (11); K(54)–C(6), 3.097 (10); K(54)–C(5), 3.217 (10); K(54)–C(4), 3.418 (11); K(54)–C(3), 3.473 (11); K(54)–C(21′), 3.313 (11); K(54)–C(20′), 3.277 (10); K-(54)–C(19′), 3.224 (12); K(54)–C(18′), 3.227 (10); K(54)–C(17′), 3.240 (9); K(54)–C(16′), 3.267 (10); K(54)–C(42′), 3.256 (11); K(54)–C(48′), 3.375 (10); O(2)–Nd(1)–O(15), 111.30 (26); O(2)–Nd(1)–O(28), 113.57 (26); O(2)–Nd(1)–O(41), 110.41 (25); O(15)–Nd(1)–O(28), 112.74 (26); O(15)–Nd(1)–O(41), 95.29 (26); O(28)–Nd(1)–O(41), 112.15 (26); Nd(1)–O(2)–C(3), 162.1 (7); Nd(1)–O(28)–C(29), 150.9 (6); Nd(1)–O(15)–C(16), 132.0 (7); Nd(1)–O(41)–C(42), 134.1 (6).
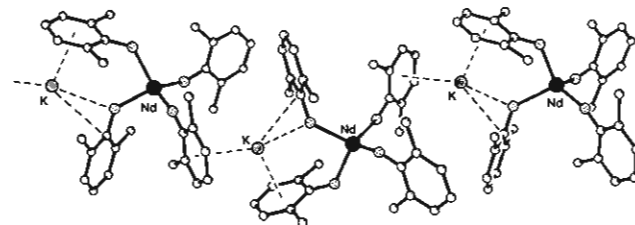

Figure 2. View emphasizing the quasi-one-dimensional linear chain structure of alternating [Nd(OAr)$_4^-$] anions and potassium cations in **1**. Methyl carbon atoms of the isopropyl substituents have been omitted for clarity.

Nd–O distances average 2.211 Å and can be compared to the average terminal Nd–O distances of 2.05 (2), 2.174 (2), and 2.148 (16) Å seen in the structures of Nd$_6$(O-i-Pr)$_{17}$Cl,[1k] $\overline{\text{Nd}(\text{OC-}t\text{-}}$ $\overline{\text{Bu}_2\text{CH}_2\text{PMe}_2)_3}$,[2c] and Nd$_5$O(O-$i$-Pr)$_{13}$(HO-$i$-Pr)$_2$,[1r] respectively. Of the six O–Nd–O angles, the average value is 109.24°, and only one angle [O(15)–Nd(1)–O(41) = 95.29 (26)°] deviates significantly from the ideal tetrahedral value. The Nd–O–C(ipso) angles are pairwise different, with Nd–O–C angles averaging 156.5 (7) [O(2), O(28)] and 133.1 (7)° [O(15), O(41)], respectively.

The coordination environment of the potassium cation is, however, very unusual. The principal interaction made by the potassium cation is to the oxygen atom of one of the aryloxide ligands [K(54)–O(41) = 2.760 (9) Å], but the remainder of its coordination sphere is made up of close K–C contacts with the arene rings of three separate aryloxide ligands. The K–C contacts with one arene ring [C(3)–C(8)] range from 3.097 (10) to 3.473 (11) Å (3.30 Å, average), while those to the arene ring from an aryloxide ligand on an adjacent molecule [C(16)–C(21)] range from 3.224 (12) to 3.313 (11) Å (3.26 Å, average), thus forming a potassium bis(η^6-arene) bridge between neighboring molecules (Figure 2) of a quasi-one-dimensional infinite chain. Another infinite chain structure based upon potassium bis(η^6-arene) interactions is that of KBPh$_4$, in which the K$^+$ ion is bound to four arene rings, the centroids of which make up the corners of a tetrahedron with an average K–C distance of 3.29 Å.[11]

Alkali-metal cation interactions with arene moieties are well documented[12] and have been observed recently in the structures

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of [K$_4$(OSiPh$_3$)$_4$(DME)]$_2$(DME),[13] HC(CPh$_2$)$_2$Na(OEt$_2$),[14] and Na$_2$(Ph$_2$CCPh$_2$)·2OEt$_2$,[15] the last showing another rare example of an alkali-metal bis(η^6-arene) bridge between adjacent molecules of a linear chain. However, to the best of our knowledge, KBPh$_4$ is the only other example of the formation of an infinite chain structure through potassium–η^6-arene interactions. Work is currently in progress to characterize the potassium salts of other lanthanide aryloxide anions to provide more information on the generality of this phenomenon. To this end, we have found at least one other example in the solid-state structure of K[Er(O-2,6-*i*-Pr$_2$C$_6$H$_3$)$_4$].[16]

Acknowledgment. We thank Dr. A. P. Sattelberger and Dr. J. L. Atwood for helpful discussions, the Office of Energy Research, Division of Chemical Sciences, U.S. Department of Energy, under Contract No. W-7405-eng-36.

Supplementary Material Available: Tables of data collection parameters, fractional coordinates and isotropic thermal parameters, bond distances, bond angles, and anisotropic thermal parameters (8 pages); a table of observed and calculated structure factors for K[Nd(O-2,6-*i*-Pr$_2$C$_6$H$_3$)$_4$] (10 pages). Ordering information is given on any current masthead page.

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Received January 24, 1992

Hexavanadium Polyoxo Alkoxide Anion Clusters: Structures of the Mixed-Valence Species (Me$_3$NH)[V$^{IV}_5$V^{V}O$_7$(OH)$_3${CH$_3$C(CH$_2$O)$_3$}$_3$] and of the Reduced Complex Na$_2$[V$^{IV}_6$O$_7${CH$_3$CH$_2$C(CH$_2$O)$_3$}$_4$]

While the coordination chemistry of polyoxomolybdates has received considerable attention,[1] the chemistry of covalent polyoxovanadium derivatives remains largely unexplored. By employment of the tetraalkylammonium salts of polyvanadates,[2] a number of polyvanadate coordination complexes have been prepared in aprotic, polar solvents.[3-5] Among these is an example of the hexavanadate core, stabilized by organic ligand subunits, [V$_6$O$_{13}${RC(CH$_2$O)$_3$}$_2$]$^{2-}$,[4] whose structural core is similar to that of [(C$_5$Me$_5$)Rh]$_4$(V$_6$O$_{19}$).[6] The latter species provides an example of the emerging class of oxoalkoxometalate aggregates.[4,7]

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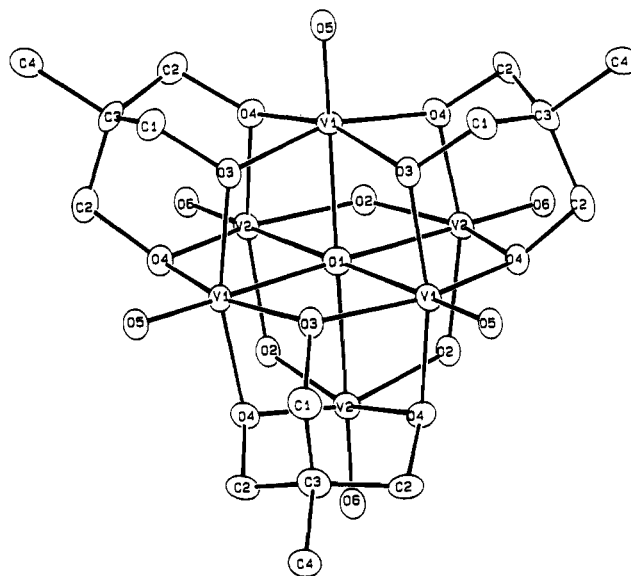
Figure 1. ORTEP view of the structure of [V$_6$O$_7$(OH)$_3${CH$_3$C(CH$_2$O)$_3$}$_3$]$^-$ (**1a**). Selected bond lengths (Å): V1–O1, 2.236 (7); V1–O3, 2.001 (4); V1–O4, 2.010 (4); V1–O5, 1.608 (7); V2–O1, 2.382 (8); V2–O2, 1.974 (4); V2–O4, 1.976 (4); V2–O6, 1.600 (7).

Furthermore, the [V$_6$O$_{13}${RC(CH$_2$O)$_3$}$_2$]$^{2-}$ clusters were found to undergo well-behaved reduction processes to give a series of mixed-valence and fully reduced clusters, [V$^V_{6-n}$V$^{IV}_n$O$_{13-n}$(OH)$_n${RC(CH$_2$O)$_3$}$_2$]$^{2-}$ (n = 2, 4, 6),[8] novel examples of the growing class of V(IV)-containing polyoxoanions.[9-16] In an effort to extend the chemistry of oxoalkoxovanadium clusters, we have exploited hydrothermal synthesis[17] in the preparation of a series of hexavanadium clusters with variable alkoxide stoichiometries and numbers of reduced metal sites, as represented by (Me$_3$NH)[V$^{IV}_5$VO$_7$(OH)$_3${CH$_3$C(CH$_2$O)$_3$}$_3$] (1) and Na$_2$[V$^{IV}_6$O$_7${CH$_3$CH$_2$C(CH$_2$O)$_3$}$_4$]. The results demonstrate that the hydrothermal technique, which has been shown to give numerous unusual polyoxomolybdates and polyoxovanadates of phosphorus,[18,19] may also be applied to the synthesis of complexes of polyoxometalates with common organic ligands.

The reaction of NH$_4$VO$_3$, V$_2$O$_3$, CH$_3$C(CH$_2$OH)$_3$, (Me$_3$NH)Cl, and water in the mole ratio 3:6:10:5:200 at 200 °C for 3 days gave sky blue crystals of (Me$_3$NH)[V$_6$O$_7$(OH)$_3$-

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