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Potassium Aluminum Alkoxides: Characterization of Polymeric $[(Pr^iOH)_2K(\mu\text{-}OPr^i)_2Al(\mu\text{-}OPr^i)_2]_n$

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Heterometallic alkoxides containing aluminum have been reported for a wide variety of metals.[1] Although many of these have been formulated as complexes of $[Al(OR)_4]^-$, details of the ligand properties of this ion are not well established and even chemical connectivities within the complexes are often uncertain. In structurally characterized examples, an $[Al(OR)_4]^-$ group bridges two metals through single alkoxide bridges in $Mo_2(O_2CCH_3)_2[Al(OPr^i)_4]_2$,[2] chelates a single metal in $\{Pr[Al(\mu\text{-}OPr^i)_2Al(OPr^i)_2]_2(Pr^iOH)(\mu\text{-}Cl)\}_2$,[3] $[(HOPr^i)_2Mg][(\mu\text{-}OPr^i)_2Al(OPr^i)_2]_2$,[4] and $[(thf)_2Mg][(\mu\text{-}OPh)_2Al(OPh)_2]_2$,[5] and bridges two metals by a double OR bridge to one and a single bridge to the second in $Mg_2Al_3(OPr^i)_{13}$.[6] We are studying the heterometallic alkoxide chemistry of aluminum and the heavier (and most ionic) alkali metals and have characterized a low-melting polymer, $[(Pr^iOH)_2K(\mu\text{-}OPr^i)_2Al(\mu\text{-}OPr^i)_2]_n$, in which the $[Al(OPr^i)_4]^-$ groups show a new coordination mode.

In 1929, titrations were reported which demonstrate that $KOPr^i$ reacts with 1 equiv of $Al(OPr^i)_3$.[7] Analysis of the products of such reactions, which were obtained as solid samples upon precipitation from chlorobenzene or a isopropyl alcohol/ether mixture, indicated $K[Al(OPr^i)_4]$.[7] Over the ensuing years $K[Al(OPr^i)_4]$ has been used as a starting material for preparations of $[Al(OPr^i)_4]^-$ complexes of various metals[1,8] but has not been further characterized.

Results and Discussion

$K[Al(OPr^i)_4]$, as described in the literature,[7] may be prepared by the reaction between $KOPr^i$ and $Al(OPr^i)_3$ carried out in isopropyl alcohol, provided the solvent is completely removed. When obtained in this way, $K[Al(OPr^i)_4]$ is a white solid whose melting point is 380 °C and which is insoluble in noncoordinating solvents. However, if the volume of the reaction mixture is reduced to a syrupy consistency, colorless crystals grow from the solution after cooling to 0 °C. These crystals are soluble in aromatic solvents and, most surprisingly, melt at 31 °C. The most intense peak in the mass spectrum of this material is $[K_2Al_2(OPr^i)_7(HOPr^i)]^+$, and major fragments occur which contain as many as three potassium and two aluminum atoms. Consistent with these data, an X-ray structure (Tables I–III) shows a polymer of composition $[(Pr^iOH)_2K(\mu\text{-}OPr^i)_2Al(\mu\text{-}OPr^i)_2]_n$, in which chains of alternating K and Al atoms are joined by double OPr^i bridges. (Figure 1: The polymer is generated along the 2_1 axis in the *c* direction.) The distorted octahedral coordination sphere about K is completed by two $HOPr^i$ molecules. Isopropyl groups sheath the metal–oxygen backbone and produce a nonpolar exterior (Figure 2), which probably explains the compound's low melting point and solubility in nonpolar solvents.

Table I. Crystallographic Data for $[(Pr^iOH)_2KAl(OPr^i)_4]_n$

formula	$C_{18}H_{44}AlKO_6$	fw	422.6
a, Å	11.935(4)	cryst system	orthorhombic
b, Å	16.513(6)	space group	$P2_12_12_1$ (No. 19)
c, Å	13.681(4)	*T*, K	210
V, Å³	2696(2)	d_{calc}, g/cm³	1.041
Z	4	μ, cm⁻¹	2.53
$R(F_o)^a$	0.0836	$R_w(F_o)^b$	0.0895

[a] $R(F_o) = \sum|F_o| - |F_c|/\sum|F_o|$. [b] $R_w(F_o) = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ with $w = 1/(\sigma^2|F_o| + 0.005405|F_o|^2)$.

Table II. Atomic Coordinates ($\times 10^4$), Equivalent Isotropic Displacement Coefficients ($pm^2 \times 10^{-1}$), and Site Occupancies for $[(Pr^iOH)_2KAl(OPr^i)_4]_n$

	x	*y*	*z*	$U(eq)^a$	occ
K	3163(2)	−523(1)	2187(1)	55(1)	1
Al	2100(2)	−77(2)	4608(2)	51(1)	1
O(1)	1324(5)	−596(4)	3728(4)	57(2)	1
C(11)	194(8)	−495(7)	3505(7)	77(4)	1
C(12)	69(13)	−465(9)	2383(11)	120(4)	1
C(13)	−524(13)	−1078(10)	3989(11)	118(5)	1
O(2)	2192(5)	−565(4)	5731(3)	62(2)	1
C(21)	2267(14)	−1377(8)	5888(7)	98(5)	1
C(22)	3180(22)	−1515(15)	6731(22)	107(10)	0.57(4)
C(23)	1456(27)	−1951(22)	5994(24)	137(14)	0.57(4)
C(22a)	3174(48)	−1828(39)	6096(48)	184(22)	0.43(4)
C(23a)	1271(31)	−1503(19)	6720(27)	111(15)	0.43(4)
O(3)	1460(6)	852(3)	4953(4)	62(2)	1
C(31)	1692(11)	1620(6)	4554(8)	86(4)	1
C(32)	2307(37)	2156(14)	5408(18)	107(9)	0.65(7)
C(33)	697(21)	1983(17)	4120(22)	89(8)	0.65(7)
C(32a)	1732(37)	2234(15)	5366(19)	53(14)	0.35(7)
C(33a)	566(37)	1766(33)	3806(42)	91(15)	0.35(7)
O(4)	2326(7)	−1927(4)	2939(6)	102(3)	1
C(41)	2470(14)	−2665(7)	3361(10)	112(6)	1
C(42)	1565(29)	−3213(21)	2891(28)	142(14)	0.53(4)
C(43)	3494(30)	−3125(21)	3089(26)	145(15)	0.53(4)
C(42a)	1523(26)	−3054(20)	3786(25)	111(14)	0.47(4)
C(43a)	2781(58)	−3359(40)	2418(53)	227(27)	0.47(4)
O(5)	5130(6)	−753(6)	1302(5)	107(4)	1
C(51)	6224(9)	−1061(9)	1159(10)	102(5)	1
C(52)	6914(22)	−624(19)	478(26)	90(10)	0.50(6)
C(53)	6833(32)	−1241(26)	2113(30)	130(15)	0.50(6)
C(52a)	6944(33)	−382(29)	888(38)	132(14)	0.50(6)
C(53a)	6490(32)	−1646(26)	1751(28)	122(16)	0.50(6)
O(6)	3359(5)	43(4)	4026(4)	72(2)	1
C(61)	4441(11)	165(10)	4521(9)	114(6)	1
C(62)	4933(25)	867(18)	3899(24)	133(12)	0.61(4)
C(63)	5159(28)	−659(23)	4492(27)	148(12)	0.61(4)
C(62a)	4686(25)	1105(19)	4596(27)	85(13)	0.39(4)
C(63a)	5335(28)	−341(21)	3960(28)	91(13)	0.39(4)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

There are only a few structures with which to compare $[(Pr^iOH)_2K(\mu\text{-}OPr^i)_2Al(\mu\text{-}OPr^i)_2]_n$. The coordination sphere of K is similar to those of Mg in $[(HOPr^i)_2Mg][(\mu\text{-}OPr^i)_2Al(OPr^i)_2]_2$[4] and $[Mg(thf)_2][(\mu\text{-}OPh)_2Al(OPh)_2]_2$,[5] but there are no other examples of an $Al(OR)_4^-$ group coordinating two metals through two double OR bridges. There are also no other examples in which all four alkoxides of an $Al(OR)_4^-$ group are coordinated by second metals. In the structurally characterized potassium alkoxides,[9–14] a variety of metal coordination numbers and geometries are observed as well as a wide range of K–O(alkoxide)

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Table III. Selected Bond Lengths (Å) and Angles (deg) for $[(Pr^{i}OH)_2KAl(OPr^{i})_4]_n$

	Lengths		
K–O(1)	3.046(6)	K–O(4)	2.725(8)
K–O(5)	2.668(8)	K–O(6)	2.695(6)
K–O(2a)	2.717(6)	K–O(3a)	3.136(6)
Al–O(1)	1.745(6)	Al–O(2)	1.738(6)
Al–O(3)	1.776(6)	Al–O(6)	1.713(6)
	Angles		
O(1)–K–O(2a)	114.9(2)	O(1)–K–O(3a)	140.4(2)
O(1)–K–O(4)	56.0(2)	O(1)–K–O(5)	160.5(2)
O(1)–K–O(6)	55.2(2)	O(2a)–K–O(3a)	54.7(2)
O(4)–K–O(2a)	141.5(2)	O(4)–K–O(3a)	105.9(2)
O(4)–K–O(5)	111.9(3)	O(4)–K–O(6)	88.5(2)
O(5)–K–O(2a)	84.2(2)	O(5)–K–O(3a)	53.6(2)
O(5)–K–O(6)	113.4(2)	O(6)–K–O(2a)	118.0(2)
O(6)–K–O(3a)	163.2(2)	O(1)–Al–O(2)	114.5(3)
O(1)–Al–O(3)	112.3(3)	O(1)–Al–O(6)	101.6(3)
O(2)–Al–O(3)	101.2(3)	O(2)–Al–O(6)	114.1(3)
O(3)–Al–O(6)	113.7(3)	K–O(1)–Al	94.4(2)
Al–O(2)–K(0)	109.3(3)	Al–O(3)–K(0)	92.7(2)
K–O(6)–Al	108.6(3)		

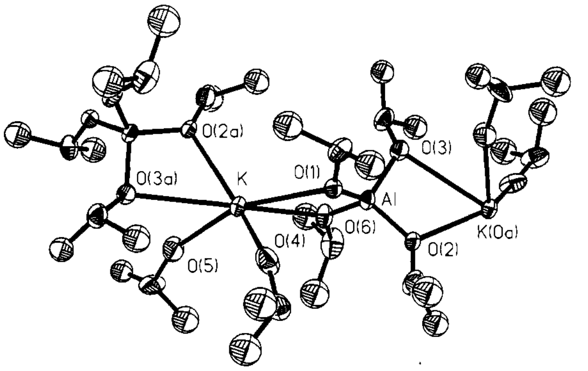

Figure 1. A portion of the $[(Pr^{i}OH)_2KAl(OPr^{i})_4]_n$ polymer with 25% thermal ellipsoids.

distances from 2.56 to 3.19 Å, with most falling between 2.7 and 2.9 Å, distance which are similar to those in $[(Pr^{i}OH)_2K(\mu\text{-}OPr^{i})_2Al(\mu\text{-}OPr^{i})_2]_n$.

In solution, the HOPr^i molecules which coordinate potassium exchange rapidly with free HOPr^i, as observed even in NMR spectra taken at −85 °C, and they can be slowly removed from a warm sample of pure material by pumping under high vacuum. As coordinated HOPr^i is lost from $[(Pr^{i}OH)_2K(\mu\text{-}OPr^{i})_2Al(\mu\text{-}OPr^{i})_2]_n$, the melting point increases and the solubility of the material in nonpolar solvents decreases. We imagine this reflects a rearrangement of the polymer in order to maintain a high coordination number at potassium, perhaps by cross-linking. However, these changes may be reversed and the alcohol-free $K[Al(OPr^{i})_4]$ will dissolve in, for example, toluene after the addition of a small amount of HOPr^i.

Sodium alkoxides also form 1:1 complexes with the corresponding aluminum alkoxides.[7] In contrast to the potassium analogs, these sodium compounds are much less soluble in alcoholic or aromatic solvents.[7] In preparations of $[(Pr^{i}OH)_2K(\mu\text{-}OPr^{i})_2Al(\mu\text{-}OPr^{i})_2]_n$ carried out in HOPr^i, homogeneous solutions were obtained a few hours after the reactants were mixed. In contrast, the addition of 1 equiv of $Al(OPr^{i})_3$ to a solution of NaOPr^i in HOPr^i never resulted in homogeneous solution. Rather, a thick suspension of a fine white powder was produced. Although NMR spectra, which do not show HOPr^i, could be obtained on dilute solutions in $DOCD_3$, this material is not markedly soluble in isopropyl alcohol or less polar solvents. The mass spectrum indicates polymeric $\{Na[Al(OPr^{i})_4]\}_n$. We are continuing the characterization of this compound.

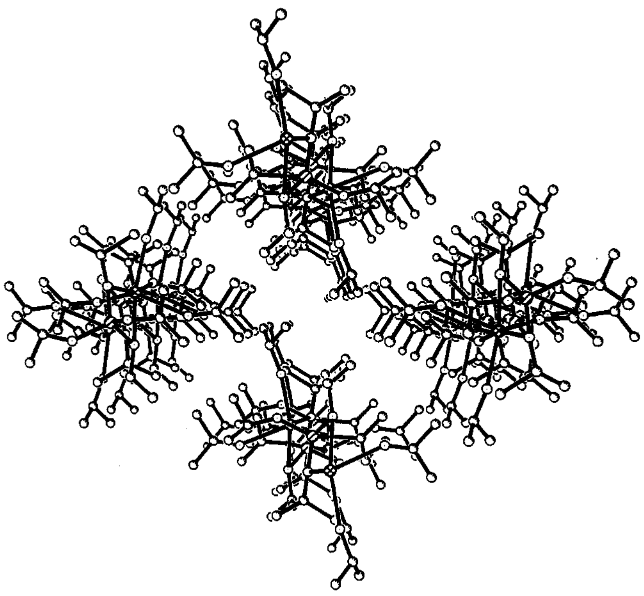

Figure 2. Packing diagram for $[(Pr^{i}OH)_2KAl(OPr^{i})_4]_n$ viewed down the crystallographic *c* axis.

Consistent with our ability to obtain mass spectra in the vapor phase, we have been able to obtain films of a potassium aluminum oxide phase by chemical vapor deposition using $[(Pr^{i}OH)_2K(\mu\text{-}OPr^{i})_2Al(\mu\text{-}OPr^{i})_2]_n$ as a precursor.[15]

Experimental Section

All operations were carried out under a dry dinitrogen atmosphere, and all solvents were carefully dried and distilled before use.

Reaction of $Al(O^{i}Pr)_3$ with KO^{i}Pr. A 1.82-g (46.5-mmol) sample of K was added to 250 mL of dry HOPr^i. After hydrogen evolution had ceased, 9.51 g (46.5 mmol) of $Al(OPr^{i})_3$ was added. After being refluxed for 12 h, the mixture was allowed to cool to room temperature and filtered to remove a *small* amount of insoluble material. The clear filtrate was evaporated under vacuum to about one-fourth of its original volume and cooled to 0 °C. From this viscous solution, $[(Pr^{i}OH)_2K(\mu\text{-}OPr^{i})_2Al(\mu\text{-}OPr^{i})_2]_n$ (15.63 g, 80%) crystallized as colorless needles within a few hours. ^{1}H NMR (500 MHz, [D$_8$]toluol, 25 °C): δ (ppm) = 4.72 (s$_{br}$; *H*OCH(CH$_3$)$_2$), 4.26 (sept$_{br}$, ^3J(H,H) = 6.0 Hz; OC*H*(CH$_3$)$_2$), 3.91 (sept, ^3J(H,H) = 6.0 Hz; HOC*H*(CH$_3$)$_2$, 1.72 (d, ^3J(H,H) = 6.0 Hz; OCH(C*H*$_3$)$_2$), 1.13 (d, ^3J(H,H) = 6.0 Hz; HOCH(C*H*$_3$)$_2$). ^{13}C NMR (125 MHz, [D$_8$]toluol, 25 °C): δ (ppm) = 63.63 (O*C*H(CH$_3$)$_2$), 62.95 (HO*C*H(CH$_3$)$_2$), 28.13 (OCH(*C*H$_3$)$_2$), 25.43 (HOCH(*C*H$_3$)$_2$). MS (EI, 260 °C), *m/e* (%): 605 (0.1), $[K_2Al_2(OPr^{i})_7(HOPr^{i})]^+$; 545 (3), $[K_2Al_2(OPr^{i})_7]^+$; 393 (10), $[K_3Al_2(OPr^{i})_2(HOPr^{i})(OCHMe)]^+$; 349 (25) $[K_3Al_2(OPr^{i})_2(OCHMe)(O)]^+$; 343 (16), $[K_2Al(OPr^{i})_2(HOPr^{i})_2]^+$; 342 (14), $[K_2Al(OPr^{i})_3(HOPr^{i})]^+$; 341 (100), $[K_2Al(OPr^{i})_4]^+$; 335 (14), $[KAl(OPr^{i})_3(HOPr^{i})(O)_2]^+$; 291 (11), $[KAl(OPr^{i})_3(O)_3]^+$; 287 (10), $[KAl(OPr^{i})_3(OCHMe)]^+$; 243 (27), $[KAl(OPr^{i})_3]^+$; 229 (9), $[KAl(OPr^{i})(HOPr^{i})(OCHMe)]^+$; 189 (7), $[Al(OPr^{i})_2(OCHMe)]^+$; 145 (6), $[Al(OPr^{i})_2]^+$; 131 (5), $[Al(HOPr^{i})(OCHMe)]^+$; 103 (6), $[Al(OPr^{i})(OH)]^+$; 87 (5), $[Al(HOPr^{i})]^+$.

Reaction of $Al(O^{i}Pr)_3$ with NaO^{i}Pr. In a reaction analogous to that used for the preparation of $[(Pr^{i}OH)_2K(\mu\text{-}OPr^{i})_2Al(\mu\text{-}OPr^{i})_2]_n$, 22.20 g (108.7 mmol) of $Al(OPr^{i})_3$ was added to the solution obtained from 2.50 g (109 mmol) of Na and 800 mL of HOPr^i. Unlike the case of the KOPr^i reaction, a homogeneous solution never formed and a thick suspension of a fine, white, high-melting powder was obtained (29.92 g, 96% assuming $Na[Al(OR)_4]_2$). ^{1}H NMR (500 MHz, [D$_4$]methanol, 25 °C): δ (ppm) = 3.91 (sept, ^3J(H,H) = 6.5 Hz; CH), 1.14 (d, ^3J(H,H) = 6.5 Hz; CH$_3$). ^{13}C NMR (125 MHz, [D$_4$]methanol, 25 °C): δ = 64.74 (CH), 25.24 (CH$_3$). MS (EI, 360 °C), *m/e* (%): 513 (14), $[Na_2Al_2(OPr^{i})_7]^+$, 353

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(5), $[Na_2Al(OPr^i)_4(OCHCH_3)]^+$; 310 (13), $[Na_2Al(OPr^i)_3(HOPr^i)]^+$; 309 (100), $[Na_2Al(PrO^i)_4]^+$; 308 (8), $[Na_2Al(OPr^i)_3(OCHC_2H_5)]^+$; 227 (17), $[NaAl(OPr^i)_3]^+$; 213 (6), $[NaAl(OPr^i)(HOPr^i)(OCHCH_3)]^+$; 87 (4), $[Al(HOPr^i)]^+$.

X-ray Structural Analysis. Crystal data are summarized in Table I. An air-sensitive 0.15 × 0.15 × 0.30 mm colorless crystal of $[(Pr^iOH)_2K(\mu\text{-}OPr^i)_2Al(\mu\text{-}OPr^i)_2]_n$ was selected and mounted as described previously.[16] X-ray data were collected at 210 K using an Enraf-Nonius CAD-4 diffractometer and graphite-monochromatized Mo Kα radiation. Three standard reflections were monitored every 200 measurements, and the data were corrected for a 3.3% decay. Lorentz, polarization,[17] and empirical absorption (DIFABS[18]) corrections were applied. The 3838 total reflections were merged to 3214 independent data ($R_{int} = 0.0445$), and 2450 with $F > 4.0\sigma(F)$ were used in subsequent calculations. The structure solution and refinement were carried out in a straightforward fashion by direct methods (SHELX86[19]) and least-squares procedures (SHELXTL Plus[20]). Anisotropic refinement was applied to the methine carbon, oxygen, aluminum, and potassium atoms, while the methyl carbons were refined isotropically. Refinements were carried out on both enantiomers with indistinguishable results. The methyl groups in the isopropyl groups attached to oxygens 2–6 were found to be disordered over two sites. The occupancies of the two conformations were refined for each with the relative populations ranging from about 1:1 to 3:2. The most populated sites are shown in the figures. Final error indices are $R = 0.084$ and $R_w = 0.090$.

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Supplementary Material Available: Complete listings of anisotropic displacement parameters, bond distances and angles, and crystallographic details for $[(Pr^iOH)_2K(\mu\text{-}OPr^i)_2Al(\mu\text{-}OPr^i)_2]_n$ (5 pages). Ordering information is given on any current masthead page.

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