

Short Communication

Ram Gopal, Nikita Sharma, Meena Nagar, Archana Chaudhary, Shaikh M. Mobin and Rakesh Bohra*

Synthesis and characterization of the coordination polymer $[(\text{THF})\text{K}(\mu\text{-OPr}^i)_2\text{Al}(\mu\text{-OPr}^i)_2]_n$

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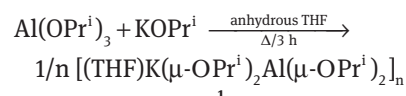
Abstract: Reaction of $[\text{Al}(\text{OPr}^i)_3]$ with $\text{K}(\text{OPr}^i)$, in 1:1 molar ratio in refluxing anhydrous tetrahydrofuran yields a polymeric complex $[(\text{THF})\text{K}(\mu\text{-OPr}^i)_2\text{Al}(\mu\text{-OPr}^i)_2]_n$. The complex is characterized by spectroscopic studies and single crystal X-ray diffraction analysis.

Keywords: aminopyramidiene; catalytic activity; $[\text{K}\{\text{Al}(\text{OPr}^i)_4\}]$; $[(\text{THF})\text{K}(\mu\text{-OPr}^i)_2\text{Al}(\mu\text{-OPr}^i)_2]_n$; X-ray structure.

There appears to be a growing interest in the chemistry of heterometal alkoxides as synthons for the preparation of ultra homogeneous ceramic materials by sol-gel technique (Caulton and Hubert-Pfalzgraf, 1990; Bradley et al., 2001; Turova et al., 2002; Sakka et al., 2005; Kessler et al., 2006; Seisenbaeva et al., 2008; Dhayal et al., 2012; Potdevin et al., 2016; Schubert, 2016). The potassium alkoxido aluminate $[\text{K}\{\text{Al}(\text{OPr}^i)_4\}]$ in benzene, propen-2-ol solution is an excellent and extensively used synthetic material (Caulton and Hubert-Pfalzgraf, 1990; Bradley et al., 2001; Turova et al., 2002), which may catalyze a variety of unusual reactions, particularly in coordinating solvents. Sometime ago Meese-Marktscheffel and colleagues reported the crystal and molecular structure of a polymeric potassium aluminum alkoxide $[(\text{Pr}^i\text{OH})_2\text{K}(\mu\text{-OPr}^i)_2\text{Al}(\mu\text{-OPr}^i)_2]_n$ in which chains of alternating K and Al atoms are joined together by double OPrⁱ bridges

(Meese-Marktscheffel et al., 1993). More recently, highly pure $\alpha\text{-Al}_2\text{O}_3$ nano-rods have been synthesized by sol-gel method from a new class of precursor of salicylaldehyde modified aluminum (III) isopropoxide (Sanwaria et al., 2014).

Here we report the corresponding polymeric complex $[(\text{THF})\text{K}(\mu\text{-OPr}^i)_2\text{Al}(\mu\text{-OPr}^i)_2]_n$ (**1**) in which the $[\text{Al}(\text{OPr}^i)_4]^-$ anion and the potassium cation show an interesting coordination mode with tetrahydrofuran (THF) (Figure 1). The reaction of $[\text{Al}(\text{OPr}^i)_3]$ (3.1785 g in ~30 mL of anhydrous THF) with KOPr^i (1.5267 g) in 1:1 molar ratio in anhydrous THF yields (**1**)



This reaction was found to be quite simple and quantitative, yielding (4.66 g, 94%) compound **1** as a white hygroscopic solid material. It is insoluble in non-coordinating solvents but can be recrystallized from THF to give a transparent crystal of $[(\text{THF})\text{K}(\mu\text{-OPr}^i)_2\text{Al}(\mu\text{-OPr}^i)_2]_n$. The characteristic peaks observed in a mass spectrum of this compound are summarized in the Experimental section. The most intense peak is $[\text{KAl}(\text{OPr}^i)_2\text{CH}_3\text{CHO}^+]$, and major fragments occur which contain as many as two potassium and two aluminum atoms.

The nuclear magnetic resonance (NMR) (¹H and ¹³C{¹H}) spectra of $[(\text{THF})\text{K}(\mu\text{-OPr}^i)_2\text{Al}(\mu\text{-OPr}^i)_2]_n$ were recorded in DMSO-d₆. It is difficult to assign bridging and terminal ligand. Since the polymer will break apart upon dissolution, the spectra could very well be interpreted in terms of free and coordinated OPrⁱ groups only. There may even be an equilibrium between both sets of signals. The characteristic NMR signals of complex (**1**) are summarized in the Experimental section. The important signals of the NMR spectral studies are observed at the expected positions, supporting the crystal structure. The other chemical shift values appeared in the range of 4.10 and 1.91 ppm in proton and 66.97 and 28.38 ppm in ¹³C for O-CH₂ and -CH₂, respectively, indicating coordination of THF with potassium.

*Corresponding author: Rakesh Bohra, Department of Chemistry, University of Rajasthan, Jaipur 302004, Rajasthan, India, e-mail: rkbohrachem@gmail.com

Ram Gopal and Meena Nagar: Department of Chemistry, University of Rajasthan, Jaipur 302004, Rajasthan, India

Nikita Sharma: Department of Chemistry, Government Girls College, Chomu, Jaipur, Rajasthan, India

Archana Chaudhary and Shaikh M. Mobin: Discipline of Chemistry, School of Basic Sciences, Indian Institute of Technology Indore, Khandwa Road, Indore 452017, India

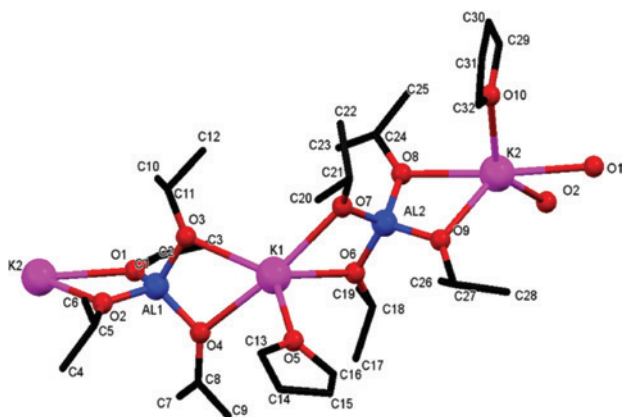
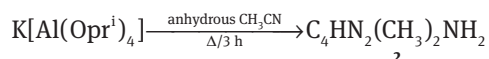


Figure 1: ORTEP plot of a cutout of the polymeric chain of [(THF)K(μ -OPr) $_2$ Al(μ -OPr) $_2$] $_n$.

Selected interatomic distances (Å): K(2)-O(1) 2.722(3), K(2)-O(9) 2.660(2), K(2)-O(8) 2.720(3), K(2)-O(10) 2.721(4), K(1)-O(5) 2.667(4), K(1)-O(3) 2.669(3), Al(2)-O(7) 1.748(3), Al(2)-O(9) 1.747(2), Al(2)-O(8) 1.742(3), Al(1)-O(2) 1.742(3), Al(1)-O(4) 1.745(3). Selected interatomic angles (°): O(10)-K(2)-O(1)#2 91.81(13), O(9)-K(2)-O(8) 59.33(7), O(9)-K(2)-O(10) 99.93(14), O(8)-K(2)-O(10) 92.97(13), O(2)#2-K(2)-O(8) 111.50(8), O(9)-K(2)-O(1)#2 130.47(10), O(9)-K(2)-O(2)#2 118.86(9), O(9)-Al(2)-O(7) 114.84(13), O(6)-Al(2)-O(9) 113.38(13), O(8)-Al(2)-O(7) 114.52(13), Al(2)-O(8)-K(2) 99.52(11), Al(2)-O(7)-K(1) 99.38(10), Al(2)-O(6)-K(1) 101.06(11), Al(2)-O(9)-K(2) 101.62(11).

Single crystals of **1** suitable for X-ray diffraction analysis were obtained from its solution in THF. Surprisingly, the Cambridge structural database indicates that only a few structurally characterized potassium aluminum alkoxides have been reported (Allen et al., 1979). To our knowledge, no polymeric potassium aluminum alkoxide in which THF is attached to the potassium cation in penta-coordination mode has been structurally characterized. Compound **1** is believed to be the first example for such a structure. An attempt to prepare the corresponding acetonitrile derivative by the reaction of $K[Al(OPr^i)_4]$ (0.74g) with anhydrous CH_3CN (~10 mL) resulted in the formation of an unexpected aminopyramidiene (**2**) (0.81 g, 10%) after crystallization in acetonitrile (Figure 2), which is characterized only by single crystal X-ray analysis. It appears that the reaction is catalyzed by $K[Al(OPr^i)_4]$. The action of the alkoxide catalyst in the trimerization of acetonitrile could be the effect of a base/nucleophile. The structure of **2** has already been reported by Zhaoxiang and Wenfeng (2004).



The important signals of the spectroscopic studies [Electrospray ionization (ESI)] of the (**1**) are observed at the expected positions, supporting the crystal structure. The mass spectrometric studies (ESI) and X-ray crystallographic details suggest formation of a polymeric structure

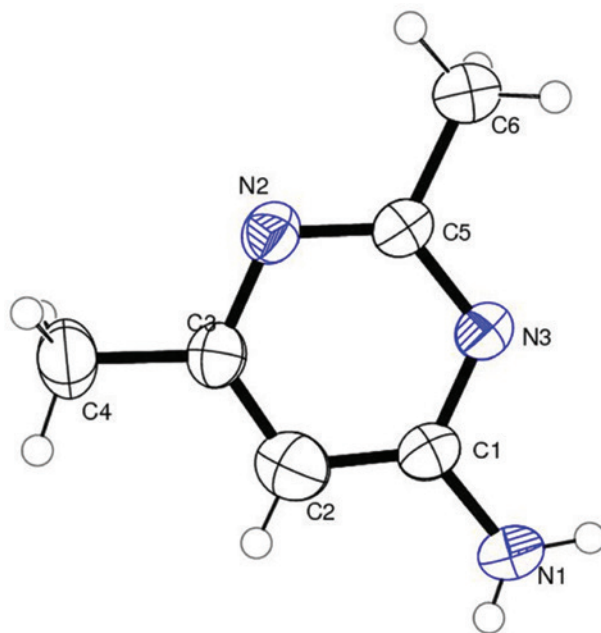


Figure 2: ORTEP plot of $[C_4HN_2(CH_3)_2NH_2]$.

Selected interatomic distances (Å): N(2)-C(3) 1.342(3), N(3)-C(1) 1.338(3), N(1)-C(1) 1.326(3), N(3)-C(5) 1.327(2), N(1)-H(2)N 0.85(3), N(1)-H(1)N 0.85(3), C(2)-C(1) 1.391(3), C(6)-H(6)A 0.9600, C(6)-H(6)B 0.9600, C(6)-H(6)C 0.9600. Selected interatomic angles (°): C(5)-N(3)-C(1) 116.94(17), N(2)-C(3)-C(4) 115.59(18), N(2)-C(3)-C(2) 121.65(17), N(2)-C(5)-N(3) 126.67(18).

(Figure 1) in which four [(THF)K(μ -OPr) $_2$ Al(μ -OPr) $_2$] units containing penta-coordinated potassium cations and tetra-coordinated aluminate anions are linked by double OPrⁱ bridges. The geometry around aluminum is distorted tetrahedral, and potassium is distorted square pyramidal. In compound **1**, each potassium atom is coordinated by four oxygen of OPrⁱ and one oxygen of THF molecule.

The K-O distance of 2.721 Å for the THF ligand in **1** is quite comparable with that reported in potassium THF coordinated complexes (Brooker et al., 1991; Janiak and Hemling, 1994; Ruhlandt-Senge and English, 1996). The observed K-O distances of potassium alkoxide range from 2.669(4) to 2.799(4) Å (average 2.700 Å). These values are in good agreement with the range found in other potassium alkoxide derivatives (2.7–2.9 Å) (Veith and Rosler, 1986; Vaartstra et al., 1990; Brooker et al., 1991; Coan et al., 1991; McGeary et al., 1991, 1992; Meese-Marktscheffel et al., 1993).

Most of the interatomic distances and angles of **1** are very similar to those reported earlier in the polymeric structure (Meese-Marktscheffel et al., 1993). The observed average Al-O bond distance in **1** is 1.743 Å, which may be comparable with that of an average Al-O distance in $[Al(OPr^i)_3]_n$ (Turova et al., 1979; Folting et al., 1991), $[(Pr^iOH)_2K(\mu-OPr)_2Al(\mu-OPr)_2]_n$ and

[C₆H₄O{CH=N(C₆H₅)}]₂Al(μ -OPr) $_2$ Al(OPr) $_2$ (Sharma et al., 2002). The crystal structure of **2** observed by us (Figure 2) is very similar to that reported earlier by Zhaoxiang and Wenfeng (2004).

The above studies suggest that [K{Al(OPr) $_4$ }] is not only an excellent synthon in common organic solvents but may also behave differently in coordinating solvents. It can easily catalyze the trimerization of anhydrous CH₃CN to aminopyramidine.

Experimental details

All the experimental manipulations were carried out under strictly anhydrous conditions. Solvents and reagents (RANKEM, India) were dried and purified by conventional methods and distilled/sublimed prior to use (Vogel, 1989). Due precautions were taken to handle hazardous chemicals like benzene. Aluminum(III) isopropoxide was synthesized and purified as reported in the literature (Bradley et al., 2001). The ¹H and ¹³C NMR data were collected on a Bruker 300 FT NMR spectrometer at 300.1 and 75.45 MHz, respectively, in a solution of DMSO-*d*₆ using TMS as internal standard. ESI mass spectra were performed on an Agilent 1100 LC/MSD SL quadrupole mass spectrometer (Agilent LC/MSD API-Electrospray SL G2708DA).

Preparation of [K{Al(OPr) $_4$ }THF] $_n$

Potassium metal (0.6088 g) was dissolved in dry PrOH (~50 mL). When hydrogen evolution had stopped, a solution of Al(OPr) $_3$ (3.1785 g in ~30 mL of anhydrous THF) was added. The mixture was heated to reflux. After being heated at reflux for 4 h, the mixture was allowed to cool at room temperature and filtered to remove a small amount of insoluble material. The clear filtrate was distilled to remove excess amount of azeotrope to about one fourth of its original volume. The resulting solution was concentrated *in vacuo* to give a white solid material (4.66 g, 94%). Re-crystallization of the latter from THF solution gave [(THF)K(μ -OPr) $_2$ Al(μ -OPr) $_2$] $_n$ as colorless crystals.

¹H NMR (300.13 MHz, DMSO-*d*₆, at 25°C, δ ppm): 3.91 (m, O-CH<, OPr); 1.16 (d, CH₃, OPr), 4.10 (m, O-CH₂, THF); 1.91 (m, -CH₂, THF). ¹³C: 61.47 (O-CH<, OPr); ¹³C: 25.38 (CH₃, OPr); ¹³C: 66.9 (OCH₂, THF); 28.38 (CH₂, THF). MS (ESI), 793 [K₂Al₃(OPr) $_8$ O(THF) $_2$] $^+$, 750.11 [K₂Al₂(OPr) $_8$ (THF) $_2$] $^+$, 720.11 [K₂Al₂(OPr) $_7$ CHO(THF) $_2$] $^+$, 632 [K₂Al₂(OPr) $_6$ (THF) $_2$] $^+$, 432.11 [KAl₂(OPr) $_4$ CHO(THF)] $^+$, 419 [KAl₂(OPr) $_4$ O(THF)] $^+$, 333.11 [KAl(OPr) $_3$ O(THF)] $^+$, 317.11 [KAl(OPr) $_3$ (THF)] $^+$, 302.11 [KAl(OPr) $_2$ C₆H₅CHO(THF)] $^+$, 287.11 [KAl(OPr) $_2$ CHO(THF)] $^+$, 231.11 [KAl(OPr)(THF)] $^+$, 201.11 [KAl(OPr)CHO(THF)] $^+$, 188.11 [KAl(OPr)O(THF)] $^+$, 172.11 [K(OPr)(THF)] $^+$, 129.11 [KO(THF)] $^+$, 303 [KAl(OPr) $_4$] $^+$, 288 [KAl(OPr) $_3$ CH₃CHO] $^+$, 229 [KAl(OPr) $_2$ CH₃CHO] $^+$, 215 [KAl(OPr)(CH₃CHO) $_2$] $^+$, 187 [KAl(OPr)(CH₃CHO)] $^+$, 185 [KAl(OPr)(CHCHO)] $^+$, 127 [KAl(OPr)] $^+$.

X-ray crystallography

The single crystal X-ray diffraction analyses were performed on a CCD-equipped Agilent Technology supernova diffractometer equipped

with a low-temperature attachment. Data were collected at 150(2) K using graphite-monochromated Mo-K α radiation (λ_{α} = 0.71073 Å). The strategy for the data collection was evaluated by using the CrysAlisPro CCD software. The data were collected by the standard ϕ - ω scan techniques and were scaled and reduced using CrysAlis Pro RED software. The structure was solved by direct methods using SHELXS-97 and refined by full matrix least squares with SHELXL-97, refining on F², giving R and Rw values of 0.0744 and 0.2092, respectively. The positions of all the atoms were obtained by direct methods. All non-hydrogen atoms were refined anisotropically. The remaining hydrogen atoms were placed in geometrically constrained positions and refined with isotropic temperature factors, generally 1.2 $\times$ 9 Ueq of their parent atoms. All the H-bonding interactions, mean plane analyses, and molecular drawings were obtained using the program Ortep. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge crystallographic data center (CCDC No. 1547839, 1548137). Symmetry transformations used to generate equivalent atoms were #1 x, -y + 1, z - 1/2, #2 x, -y + 1, z + 1/2.

The crystal data and refinement are summarized below:

^vCrystal data (**1**): C₆₄H₁₄₄Al₄K₄O₂₀, M = 1498.11, crystal size = 0.33 $\times$ 0.26 $\times$ 0.21 mm³, monoclinic, space group = C 2/c, U = 9217.6(8), a = 44.603(3) Å, b = 9.7009(3) Å, c = 25.9657(14) Å, α = 90°, β = 124.872°, γ = 90°, Z = 4, tetramer, Dc = 1.080 Mg m⁻³, μ (Mo-K α) = 0.71073; 30 783 reflections collected with 3.12 < 2 θ < 25.00° at 150(2) K, of these 30 783 were unique and 8114 which had F > 1.0325 were used in structural analysis.

^{vv}Crystal data (**2**): C₁₂H₁₈N₆, M = 246.32, crystal size = 0.90 $\times$ 0.80 $\times$ 0.60 mm³, monoclinic, space group = P2₁/n, U = 665.16(8) Å³, a = 7.4018(4) Å, b = 7.7991(6) Å, c = 11.6748(8) Å, α = 90°, β = 99.267(6)°, γ = 90°, Z = 2, Dc = 1.230 Mg m⁻³, μ (Mo-K α) = 0.71073; 4533 reflections collected with 3.8440 < 2 θ < 31.20 at 150(2) K, of these 4533 were unique and 1170 which had F > 1.195 were used in structural analysis.

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