

Dalton Transactions

Accepted Manuscript



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Synthesis, Structure, and Properties of Dialumane Supported by Pyrazolate Ligands

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Abstract:

The dialumane $[\text{Al}_2][\text{Na}(\text{Ph}_2\text{pz})_3]_2$ (**1**) has been prepared by the reaction of $\text{Na}(\text{Ph}_2\text{pz})$ with a metastable solution of AlCl_3 . The structure of **1** contains two hydrotris(pyrazolyl)borate-like $\text{Na}(\text{Ph}_2\text{pz})_3^{2-}$ moieties that are coordinated each Al atom of the dialumane in a $\kappa^2, \kappa^1\text{-N,N,N}$ fashion and several π -stacking interactions are present between the pyrazolate and phenyl rings. In solution the pyrazolate ligands in **1** are in dynamic exchange, even at -80°C , which shows the lability of these ligands to the low-valent aluminum centers.

Introduction:

Dialumanes have been of recent interest due to their role as reactive intermediates, their ability to act as two-electron reducing agents, and their potential to serve as building blocks for metalloid aluminum clusters.¹ These clusters may be isolated by kinetically trapping the disproportionation products of aluminum(I) compounds by using ligands such as 1,2,3,4,5-pentamethylcyclopentadienide and $[\text{N}(\text{SiMe}_3)_2]^-$.² The largest of these clusters, $\text{Al}_{77}[\text{N}(\text{SiMe}_3)_2]_{22}^{2-}$, represents an intermediate between molecular clusters and nanoparticles, and contains a central aluminum atom surrounded by concentric shells of aluminum atoms that increase in molecular character as they extend towards the surface of the cluster.^{2a} The cluster is capped by twenty two “ $\text{Al}[\text{N}(\text{SiMe}_3)_2]$ ” units which protect the cluster from further disproportionation into bulk aluminum.

More recently, the PtBu₂ ligand has been shown to stabilize clusters of aluminum and gallium.^{3,4} Al₄(PtBu₂)₆ has been isolated, which is the first structurally characterized analog of the highly energetic Al₄H₆ molecule^{4a-c} and is the first example of a low-valent aluminum complex containing a bridging ligand. Crystallographic and computational analyses of PtBu₂ bridging modes within two Al₂(PtBu₂)₄ isomers have also provided insight into the process of Al-Al bond formation.^{3d} Additionally, large gallium clusters have been structurally characterized that contain between sixteen and fifty-one metal atoms in the cluster core.⁴ These recent results have inspired our lab to investigate ligands that adopt various bridging modes, however, reaction mixtures of AlX (X = Cl, Br, I) with PR₂ (R = Ph, tBu) often lead to P-C bond cleavage and metal oxidation due to the highly reducing nature of the AlX solutions.⁵ Among the oxidized aluminum products from these reactions are K[Al₄(PPh₂)₇PPh],^{5b} which contains a PhP²⁻ ligand and two Al²⁺ dimers, and Al₃P(tBu₂P)₄Cl₂,^{5a} which contains a naked P³⁻ and three Al³⁺ metal centers.

To continue our investigation into ligands that may stabilize metalloid clusters, the pyrazolate ligand system was selected due to its propensity to span metal centers in varying coordination modes that include μ - η^1 : η^1 and μ - η^2 : η^2 and their robust nature due to the aromaticity of the pyrazolate ring.⁶ Several low-valent gallium⁷ and indium⁸ hydrotris(3,5-disubstitutedpyrazolyl)borate [HB(R₂pz)₃]⁻ species have been reported, yet there are no structurally characterized species of low-valent aluminum compounds containing pyrazolate or HB(R₂pz)₃⁻ ligands. Herein we report the synthesis, characterization, and solution properties of a pyrazolate-stabilized dialumane.

Results and Discussion:

The reaction of aluminum(I) chloride·diethyl etherate [AlCl·(OEt₂)_n] with sodium(tetrahydrofuran) 3,5-diphenylpyrazolate {[Na(THF)][Ph₂pz]}₄ produced an orange-brown reaction mixture. Heating-induced crystallization is common for low-valent aluminum and gallium clusters^{2,4} and also proved successful here. The toluene extract of the {[Na(THF)][Ph₂pz]}₄ and

[AlCl·(OEt₂)_n] reaction mixture was heated to 60 °C, yielding [Al₂][Na(Ph₂pz)₃]₂·toluene (**1**·toluene) as highly air-sensitive, pale yellow crystals, which have been characterized by ¹H and ¹³C{¹H} NMR spectroscopy, X-ray crystallography, and elemental analysis. Complex **1** is soluble in THF but is insoluble in hexanes, toluene, and diethyl ether. Vigorous gas evolution occurs when **1** is exposed to ethanol, water, and methylene chloride and attempts to dissolve **1** in pyridine and acetonitrile resulted in formation of insoluble precipitates. The +2 formal oxidation state of the aluminum centers in **1** may be the result of comproportionation of Al⁺ with Al³⁺ impurities in solution, as previously reported by Schnöckel et. al.⁹ However, reactions between the AlCl solutions and AlCl₃ plus six equivalents {[Na(THF)][Ph₂pz]}₄ did not yield crystalline material of **1**. Crystalline samples of **1** have been isolated several times in a reproducible 5% crystalline yield by following this gentle heating procedure.

Complex **1** crystallizes in the space group P $\bar{1}$ and perspective views are shown in Figure 1. The complex displays virtual C_{2h} point symmetry with a crystallographically imposed center of inversion at the midpoint of the Al-Al bond. Complex **1** can be viewed as a dialumane [Al₂(Ph₂pz)₄] to which two Ph₂pz donors are added resulting in Al-Al bond distance of 2.5794(6) Å, which is within the range of other dialumanes [2.527(6) – 2.751(2) Å].^{1a, 1c, 5b, 9, 11} The Al-N distances are 1.9088(9), 1.9192(9), and 1.9430(9) Å and Na-N distances are 2.325(1), 2.339(1), and 2.354(1) Å. The N-Al-N and N-Al-Al angles are between 100.68(4) and 112.10(4)° [avg = 105.26(7)°] and 107.79(3) and 121.73(3)° [avg = 113.58(5)°], respectively, resulting in distorted tetrahedral Al environments. There are several intramolecular interactions present in the solid-state structure of **1**, which include two η²-Na:Ph interactions with Na-C distances of 3.043(1) and 3.076(1) Å, two Ph:pz:Ph π-stacking interactions, and two Ph:pz π-stacking interactions (see Supporting Information). The centroid to centroid distances of the Ph:pz:Ph and Ph:pz π-systems are 3.562 and 3.621 Å, and 3.929 Å, respectively.

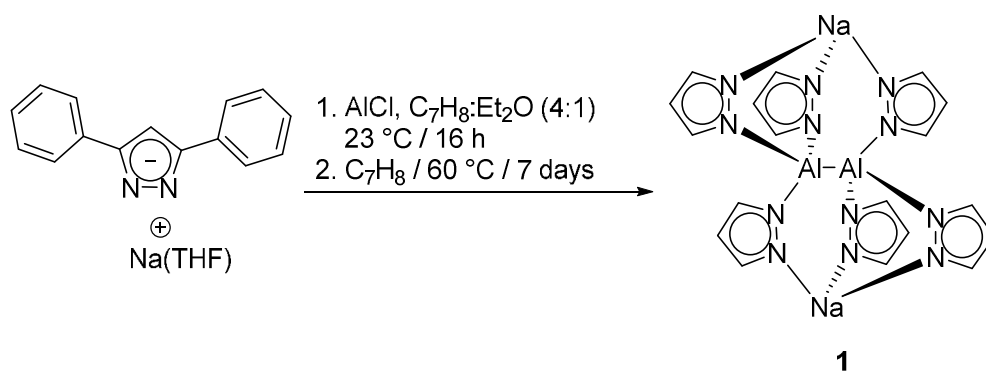
Complex **1** can be viewed as a staggered $\text{Al}_2\text{N}_6^{2-}$ ethane-like molecule in which each Ph_2pz ligand is bound in a terminal η^1 -fashion to the Al atoms of the dialumane. The second N atom on each Ph_2pz ligand is coordinated to one of the two sodium ions above and below the Al-Al bond. Each sodium ion participates in a π -interaction with one phenyl ring of a coordinated Ph_2pz ligand. The $[\text{Na}(\text{Ph}_2\text{pz})_3]^{2-}$ moieties are reminiscent of the $\text{HB}(\text{R}_2\text{C}_3\text{N}_2)_3^-$ ligands in which the Na^+ ion formally replaces the “ HB^{2+} ” fragment. From this perspective **1** can be viewed as an $[\text{Al}_2][\text{Na}(\text{Ph}_2\text{pz})_3]_2$ complex in which the $\text{Na}(\text{Ph}_2\text{pz})_3^{2-}$ ligands are coordinated in a $\kappa^2, \kappa^1\text{-N,N,N}$ fashion. Intramolecular interactions are prevalent in the solid state structure of **1** and most likely influence the $\kappa^2, \kappa^1\text{-N,N,N}$ -coordination mode of the structure. Similar $\kappa^2, \kappa^1\text{-N,N,N}$ bonding has been observed in $[\text{Cu}_2][\text{Tp}^*]_2$ [$\text{Tp}^* = \text{HB}(\text{Me}_2\text{pz})_3^-$] and $[\text{Cu}_2][\text{HB}(3\text{-CF}_3, 5\text{-CH}_3\text{pz})_3]$, however, the geometries of the copper centers are distorted trigonal pyramidal and do not resemble the distorted tetrahedral geometry of the aluminum centers in **1**.¹² The distorted tetrahedral metal centers in $\{[\text{Ga}_2][\text{Tp}^*]_2\}^{2+}$ and $[\text{Zn}_2][\text{Tp}^*]_2$ are isoelectronic to **1** but have $\kappa^3\text{-N,N,N-Tp}^*$ coordination to each metal center. A $\kappa^2, \kappa^1\text{-N,N,N}$ -coordination mode would likely result in structural deviations from the idealized tetrahedral geometry of these metal centers and would destabilize the complexes.^{7b, 13} However, the long Na-N bond distances [avg = 2.339(2) Å] in **1**, relative to the B-N bond distances of the $\text{HB}(\text{R}_2\text{pz})_3$ ligands (avg \approx 1.55 Å), allows tetrahedral coordination of the $[\text{Na}(\text{Ph}_2\text{pz})_3]^{2-}$ moiety while maintaining the $\kappa^2, \kappa^1\text{-N,N,N}$ -coordination to each Al atom of the dialumane. Additionally, several π -stacking interactions result from the $\kappa^2, \kappa^1\text{-N,N,N}$ -coordination mode which would be absent in the $\kappa^3\text{-N,N,N}$ -coordination mode.

The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **1** in $\text{THF-}d_8$ at 23 °C shows peaks consistent with Ph_2pz ligands and toluene. The ^1H NMR of **1** has broad, overlapping peaks between δ 6.93 and 7.82 that were confirmed as the *ortho*-, *meta*-, and *para*-phenyl protons by heteronuclear single quantum coherence (HSQC) analysis. The ring-core CH of the pyrazolate ring is observed at δ 6.34 and is very broad at room temperature, which suggests that a rapid site exchange process occurs on the NMR timescale for the

Ph₂pz ligand. Additionally, the ¹³C{¹H} NMR spectrum of **1** at 23 °C shows only one type of pyrazolate carbon substituent, which is inconsistent with the solid state structure, demonstrating that the 3- and 5-substituents of the Ph₂pz ligands are in fast exchange on the NMR timescale. Similar pyrazolate exchange processes have been observed for [Na(THF)][AlMe(tBu₂pz)₃] and [Li(THF)][AlH(R₂pz)₃] (R = Ph, *i*Pr).¹⁰ Variable temperature ¹H NMR of **1** were recorded from -80 to 23 °C in THF-*d*₈, however, even at -80 °C the ¹H NMR spectrum of **1** is complicated and the mechanism of the exchange processes could not be elucidated. The ¹³C{¹H} NMR spectrum of **1** in THF-*d*₈ at -80 °C shows at least four different types of pyrazolate 4-CH confirming that slow and complex exchange processes occur at this temperature.

In conclusion, we have prepared a dialumane containing pyrazole-based ligands. Complex **1** has two [Na(Ph₂pz)₃]²⁻ moieties bound in a κ²,κ¹-N,N,N-fashion to the Al₂⁴⁺ center and the complex is stabilized by several π-stacking interactions in the solid state. Unlike other κ²,κ¹-N,N,N-coordinated metal dimers, the aluminum centers in **1** have distorted tetrahedral geometries. ¹H and ¹³C{¹H} NMR experiments have shown that dialumane species are labile and have rapid ligand exchange in solution at room temperature. Intramolecular interactions influence ligand bonding in **1** and tailoring new ligands to maximize these interactions may be key to generating unique metal clusters.

Scheme 1. Synthesis of **1**. Phenyl rings omitted for clarity.



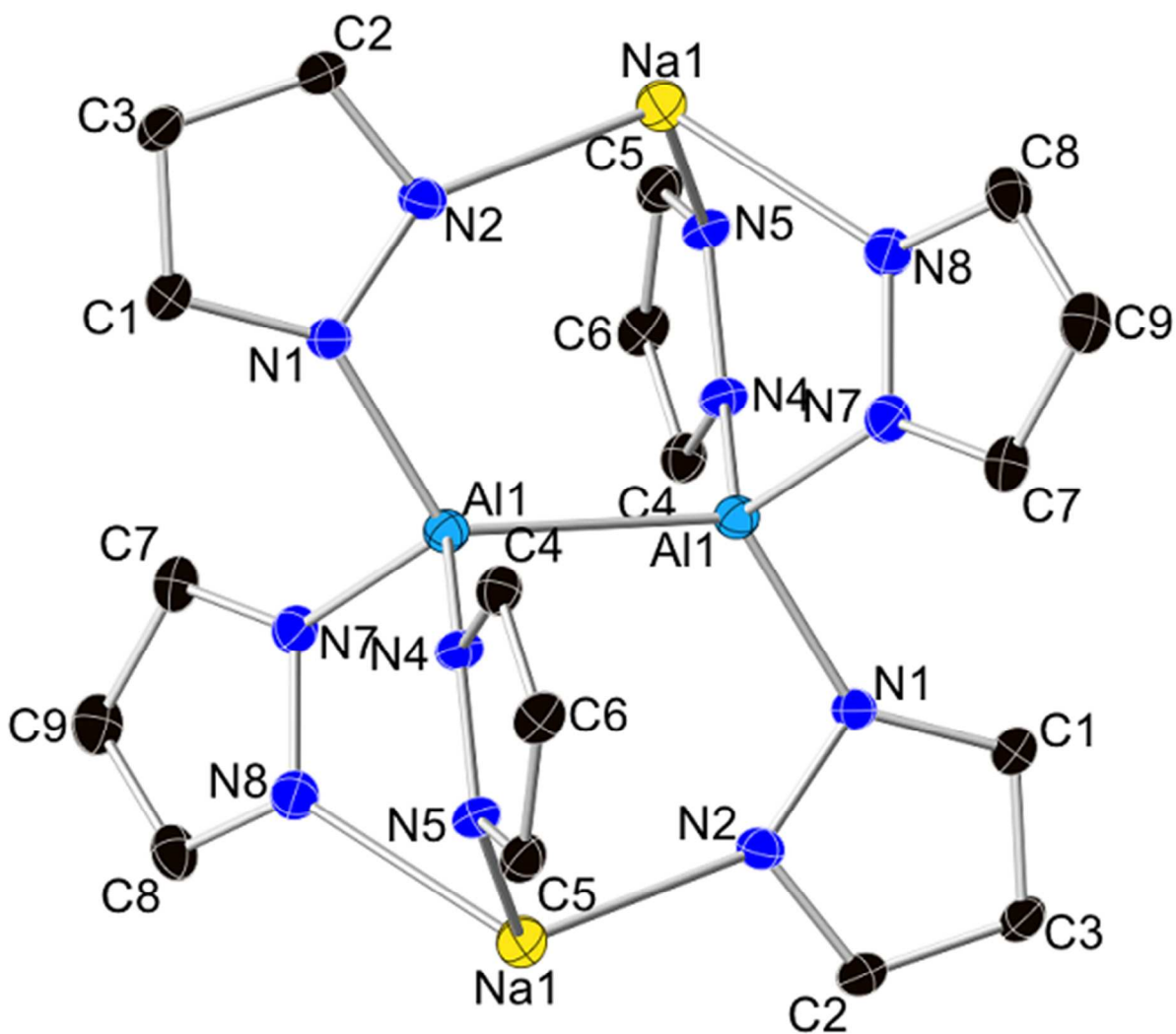


Figure 1. Perspective views of **1** with selected bond lengths (Å) and angles (deg): (top) Phenyl rings omitted for clarity; Al1-Al1 2.5794(6), Al1-N1 1.9088(9), Al1-N4 1.9430(9), Al1-N7 1.9192(9), Na1-N2 2.354(1), Na1-N5 2.339(1), Na1-N8, 2.325(1); N1-Al1-N7 100.68(4), N7-Al1-N4 112.10(4), N1-Al1-N4 103.00(4), N1-Al1-Al1 121.73(3), N4-Al1-Al1 107.79(3), N7-Al1-Al1 111.23(3), N8-Na1-N5 85.60(3), N8-Na1-N2 110.71, N5-Na1-N2 113.22.

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A dialumane supported by hydrotris(pyrazolyl)borate-like moieties that show dynamic behavior in solution has been prepared from an aluminum(I) chloride solution.

