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2,4-Pentanediolate as an Alkoxide/Diketonate “Hybrid” Ligand and the Formation of Aluminum and Zirconium Derivatives

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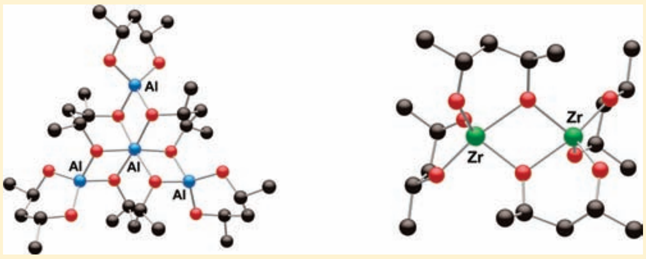
Supporting Information

ABSTRACT: When 2,4-pentanediol (2,4-H_2pd) is deprotonated, the resulting dianion (2,4-pd) serves as a type of “hybrid” ligand, i.e., an alkoxide that possesses structural features of a β-diketonate. 2,4-Pentanediol reacts with Al(O-*s*-Bu)$_3$ and Zr(O-*i*-Pr)$_4$ to form chelated multinuclear complexes. The aluminum-containing product is first isolated as the insoluble $[Al(2,4\text{-pd})(2,4\text{-Hpd})]_n$; on sublimation, a hydrocarbon-soluble mixture of polymetallic species is generated. Mass spectral evidence suggests that both $Al_4(2,4\text{-pd})_6$ and $Al_5(2,4\text{-pd})_7(2,4\text{-Hpd})$ are present. The zirconium complex is isolated as an adduct, $[Zr(2,4\text{-pd})_2]_2\cdot(2,4\text{-}H_2pd)$. The pentanediolates decompose on heating to form Al_2O_3 and ZrO_2. Unlike the mononuclear Al(acac)$_3$ and Zr(acac)$_4$ derivatives (acac = acetylacetonate), the formation of aggregates with the 2,4-pd ligand suggests that the latter has more coordinative flexibility. The geometries of several model aluminum complexes with oxygen donor ligands were studied with density functional theory methods. The optimized structures were used with the gauge, including atomic orbital (GIAO) method to calculate their ^{27}Al NMR magnetic shielding values for comparison with experiment.



INTRODUCTION

The β-diketones comprise a large class of molecules of the form $R_1C(—OH)C(—R_3)C(=O)R_2$, and the corresponding anions form thermally stable chelates with metals from across the periodic table.[1] In addition to the planar β-diketonates, such as the common acetylacetonate anion (acac), β-diketones can function as neutral ligands that form slightly puckered 6-membered rings (Figure 1).[2] Although they belong to a fundamentally different class of ligands, 2,4-diolates can also form 6-membered rings with bite angles similar to the β-diketonates. Those derived from 2,4-pentanediols even bear some geometric resemblance to acac ligands (Figure 1), as they both carry methyl groups on the carbons alpha to the oxygens; the pentanediols of course have the extra possibility of diastereomeric conformations.

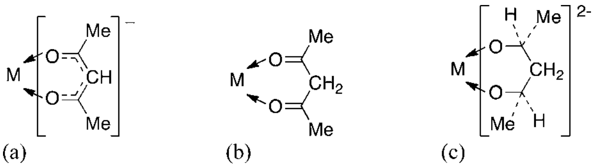


Figure 1. Schematic of the acetylacetonate (acac) anion (a), a β-diketone functioning as a neutral ligand (b), and a 2,4-pentanediolate dianion (c). In the latter, the carbon atoms bonded to the oxygens are chiral, and several diastereomers are possible.

Several alkyl,[3] halo,[4] and amino[5] pentanediolate complexes have been structurally characterized, but comparatively few examples exist of homoleptic pentanediolate complexes. The $[Ti(2,4\text{-dmpd})_2]_2$ (2,4-dmpd = 2,4-dimethylpentane-2,4-diolate) complex was prepared by alcoholysis of Ti(O-*i*-Pr)$_4$ with 2,4-dimethyl-2,4-pentanediol, and displays a dimeric structure both in the solid state and gas phase.[6] The same reaction of the diol with Zr(O-*i*-Pr)$_4$ yielded a trimetallic complex $Zr_3(\mu_3\text{-}O)(2,4\text{-dmpd})_4$ with an unexpected oxo ligand.[7] The focus of these studies was on structural and mass spectroscopic characterization; detailed thermal decomposition data were not reported.

The use of metal β-diketonates as precursors in MOCVD applications, especially when modified with R groups such as *t*-Bu or CF_3 to improve their volatility, is widespread.[8−10] As an alternative to the β-diketonates, metal alkoxides ($M(OR)_n$) have been used to produce high quality oxide films with MOCVD, often without an auxiliary oxygen source.[9,11] However, in certain cases poorer shielding of the metal centers than that provided by the metal β-diketonates limits the hydrolytic stability of alkoxides.[12,13] In the present study, 2,4-pentanediol (2,4-H_2pd) was used as a type of “blended” ligand, an alkoxide that possesses structural features of a β-diketonate. An investigation of the decomposition characteristics of its aluminum and zirconium derivatives was made to determine whether they would show promise as precursors to their respective metal oxides. These two metals form mononuclear Al(acac)$_3$ and Zr(acac)$_4$ derivatives, both of which have been investigated as MOCVD precursors.[10,14,15]

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■ RESULTS AND DISCUSSION

Synthesis of Aluminum Derivatives. The reaction of Al(O-*s*-Bu)$_3$ with 1.5 equiv of diastereomeric (*R,R* and *R,S*) 2,4-H$_2$pd in toluene generates a colorless solid that is effectively insoluble in a wide range of organic solvents, from acetone to hexane. Considerations of charge balance combined with elemental analysis suggest an average composition of [Al(2,4-pd)(2,4-Hpd)]$_n$; that is, a 1:1:1 ratio of aluminum to doubly and singly deprotonated pentanediol. The insolubility suggests that the product is extensively oligomerized, perhaps assisted by hydrogen bonding.[13] Nevertheless, the material can be sublimed on heating under vacuum, and the sublimed material is readily soluble in organic solvents. Evidently the sublimation largely completes the deprotonation of the pentanediol, as the results of NMR and mass spectroscopy (detailed below) indicate that the product contains a mixture of polynuclear species incorporating the fully deprotonated 2,4-pd dianion. The ^{1}H NMR spectrum in C$_6$D$_6$ contains poorly resolved peaks for the methyl and the methylene hydrogens; these were better resolved in the CDCl$_3$ spectrum but are still broadened. The ^{13}C NMR spectrum is similarly complex and contains multiple resonances reflecting the mixture of isomeric pentanediolates. At atmospheric pressure, the sublimed powder began to fuse as the temperature approached 40 °C; on continued heating, the solid lost its opacity and became transparent at 80 °C, and liquifaction was observed at 120 °C. Multiple attempts to obtain crystals suitable for X-ray crystallography were unsuccessful.

As a monoisotopic species with $I = 5/2$ and a wide chemical shift range (~400 ppm),[16] the ^{27}Al nucleus provides NMR spectra that are useful for studying coordination geometries, although the characteristic regions for different coordination numbers partially overlap.[17] Three resonances are observed in the ^{27}Al NMR spectrum of the sublimed pentanediolate (Figure 2): a sharp, narrow peak at δ 0.0, assigned to an octahedrally coordinated aluminum (cf., the shift at δ −0.9 ppm for the ^{27}Al NMR resonance of Al(acac)$_3$[18]), and two broad, heavily overlapped resonances (combined $w_{1/2} \approx 4900$ Hz) at δ 63.8 and 48.1 ppm, whose shifts are consistent with 4- and 5-coordinate aluminum.

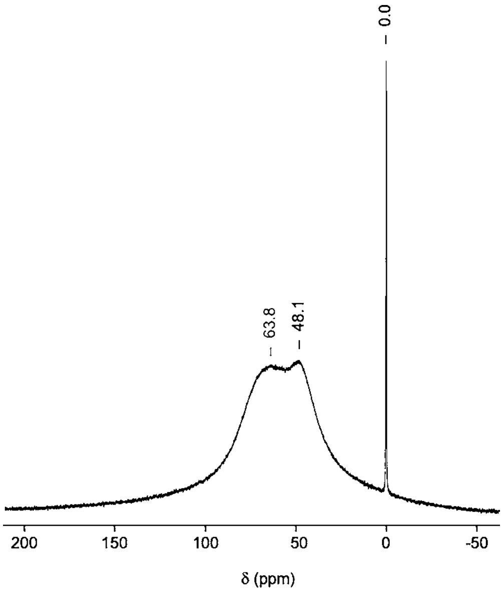
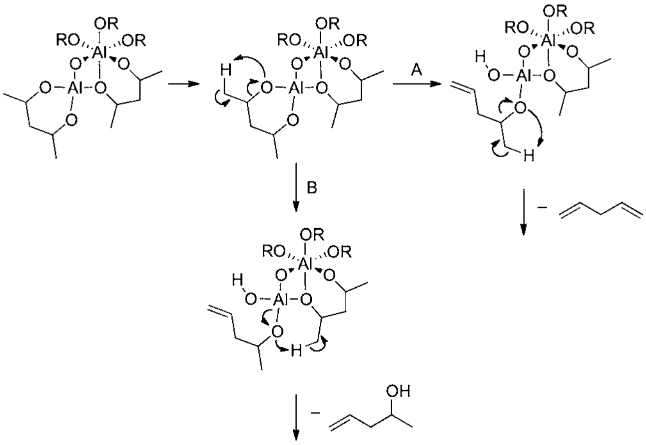


Figure 2. ^{27}Al NMR of the sublimed aluminum pentanediolate.

Thermal Decomposition and Mass Spectra. The 2,4-pd ligands in a metal complex could potentially undergo two different thermal decomposition routes, beginning with a *β*-hydrogen elimination. Such a step was proposed by Haanappel for the decomposition of Al(O-*s*-Bu)$_3$, during which an alkene and alcohol byproduct were formed.[19] One of the alkoxide oxygens abstracts a proton from the methyl carbons to form the first alkene and alcohol. The second step of the decomposition involves either the formation of penta-1,4-diene by an "internal" *β*-hydrogen elimination or pent-4-en-2-ol through an "external" *β*-hydrogen elimination. The compound would then undergo several more elimination steps until alumina was formed. These routes are designated "A" and "B" in Scheme 1, drawn in the context of a polynuclear aluminum pentanediolate species.

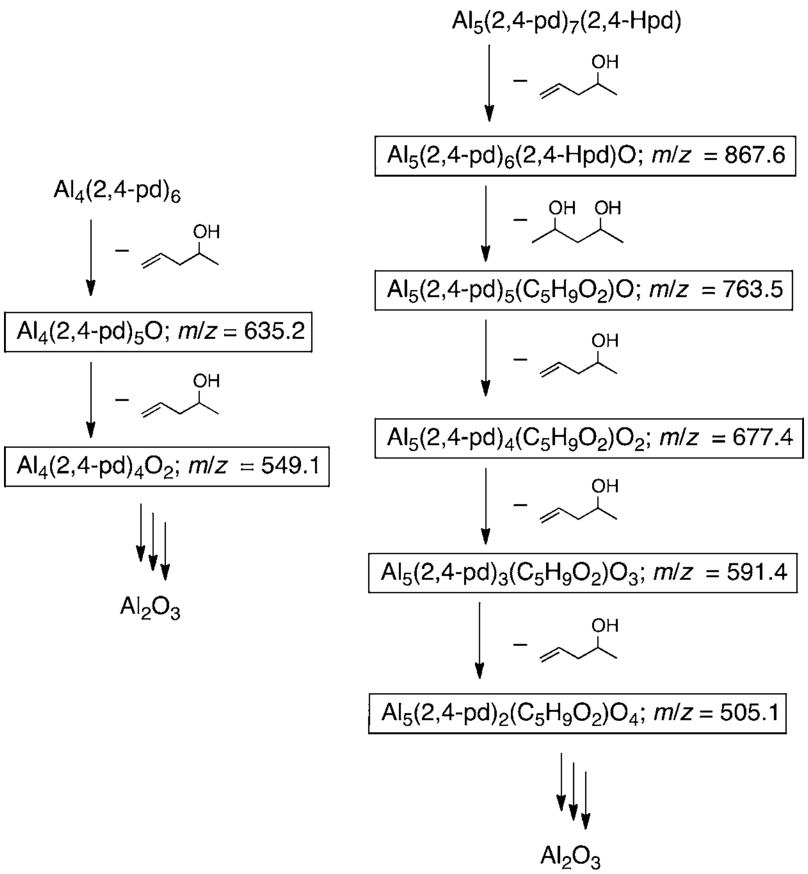
Scheme 1. Decomposition of a Pentanediolate by *β*-Hydrogen Elimination Reactions



Evidence for the operation of route B was provided by the results of APCI mass spectrometry on a sample of the sublimed aluminum pentanediolate dissolved in hexane. The spectra were collected in both positive and negative ion mode, and gave evidence for the presence of two polynuclear species, Al$_4$(2,4-pd)$_6$ and Al$_5$(2,4-pd)$_7$(2,4-Hpd). Although signals corresponding to the molecular ions for the complexes were not observed, [M + H]$^+$ peaks consistent with the successive elimination of pentenol (mass 86.1 g mol^{-1}) from Al$_4$(2,4-pd)$_6$ were located at *m/z* 635.2 and 549.1 (calcd 635.3 and 549.2 for [Al$_4$(2,4-pd)$_5$O + H]$^+$ and [Al$_4$(2,4-pd)$_4$O$_2$ + H]$^+$, respectively). Similarly, a prominent peak is present at *m/z* 867.6 that corresponds to the loss of pentenol from Al$_5$(2,4-pd)$_7$(2,4-Hpd) (calc. 867.4 for [Al$_5$(2,4-pd)$_6$(2,4-Hpd)O + H]$^+$); the related peak at *m/z* 865.6 was observed in negative ion mode (calc. 865.4). A step down in mass from this is a signal at *m/z* 763.5, which reflects the loss of protonated 2,4-H$_2$pd (calc. 763.3). Additional peaks at *m/z* 677.4, 591.4, and 505.1 (negative ion mode for the last) are consistent with the loss of three additional pentenols; the decomposition is summarized in Scheme 2. There is no clear evidence for other polymetallic species in the spectra.[20]

In the absence of more structural data, it is not possible to be definitive about the structures of the pentanediolates. However, the ^{27}Al NMR spectrum of the tetrameric alkoxide [Al(O-*i*-Pr)$_3$]$_4$ displays a narrow peak in the octahedral region at δ −0.1 ppm[21] and a single broad peak at 60.3 ppm for the three tetrahedrally coordinated aluminums. A related structure for

Scheme 2. Decomposition Scheme for $Al_4(2,4\text{-pd})_6$ and $Al_5(2,4\text{-pd})_7(2,4\text{-Hpd})$[a]



[a] Species detected with mass spectrometry are in boxes; the m/z ratios are the observed values, and correspond to (molar mass + H), except for $Al_5(2,4\text{-pd})_2(C_5H_9O_2)O_4$, which corresponds to (molar mass − H).

$Al_4(2,4\text{-pd})_6$ that possesses three terminal 2,4-pd ligands on three aluminum centers bridged to an octahedrally coordinated central aluminum (Figure 3), i.e., a "Mitsubishi" structure,[22,23] would be consistent with the ^{27}Al NMR spectrum. A similarly symmetric structure is not possible for $Al_5(2,4\text{-pd})_7(2,4\text{-Hpd})$, and a number of arrangements were considered for it, subject to the constraint that the aluminum centers were either 4-, 5-, or 6-coordinate. Computational modeling (see below) narrowed the possibilities further, and the structure depicted in Figure 3, based on a 10-membered $(Al{-}O)_5$ ring, was found to be computationally stable, and a minimum on the potential energy surface. It was adopted as a working model for further studies.

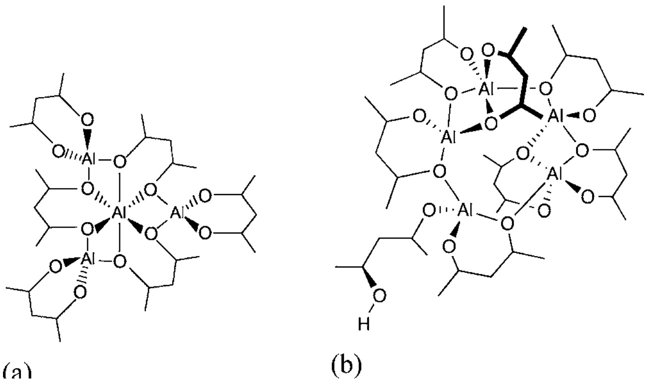
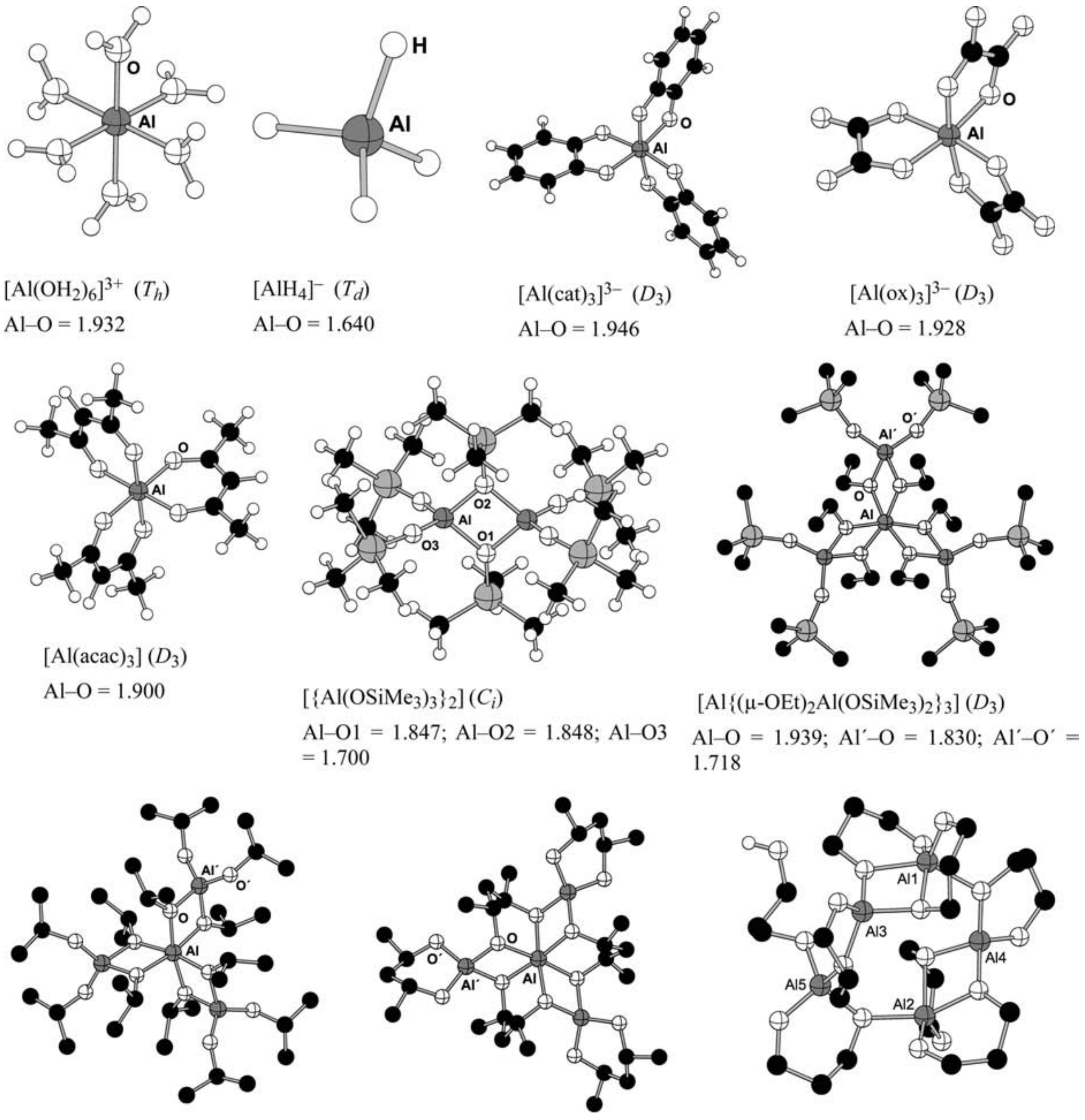


Figure 3. Suggested structures for $Al_4(2,4\text{-pd})_6$ (a) and $Al_5(2,4\text{-pd})_7(2,4\text{-Hpd})$ (b).

Calculated ^{27}Al NMR Chemical Shifts. To estimate the reasonableness of the proposed pentanediolate structures, several known complexes of aluminum with anionic oxygen donor ligands, and for which ^{27}Al NMR spectra have been reported, were optimized with density functional theory methods (Figure 4). Theoretical shifts were calculated by subtracting the absolute shielding of the complexes from that of a calculated reference, which for ^{27}Al NMR is the aquated Al^{3+} ion, assigned a formula of $[Al(OH_2)_6]^{3+}$. With the HF/6-311+G(2d,p)//B3LYP/6-311G(2d,p) protocol, all calculated shifts for anionic complexes are within 4 ppm of the experimental values (Table 1). The neutral complexes display somewhat larger errors; the amount of shielding is consistently underestimated, up to a value of ∼15 ppm for the 4-coordinate aluminums in $[\{Al_4(O\text{-}i\text{-}Pr)_3\}_4]$. Compared to the window of ^{27}Al NMR shifts (∼400 ppm), the maximum deviations represent errors of ≤4%.

Given the 10−15 ppm chemical shift error range for neutral complexes, the two resonances calculated for $[Al_4(2,4\text{-pd})_6]$ at δ 10.2 and 89.1 are reasonably consistent with the resonances observed at δ 0.0 and approximately δ 50−65 ppm. The tentative structure for $[Al_5(2,4\text{-pd})_7(2,4\text{-Hpd})]$ contains both 4- and 5-coordinate aluminum, and the resonances calculated at δ 44−45 and 75−77 ppm, respectively, would also fall under the broad reasonances of the ^{27}Al NMR spectrum.



$[Al(OH_2)_6]^{3+}$ (T_h)
Al–O = 1.932

$[AlH_4]^-$ (T_d)
Al–O = 1.640

$[Al(cat)_3]^{3-}$ (D_3)
Al–O = 1.946

$[Al(ox)_3]^{3-}$ (D_3)
Al–O = 1.928

[Al(acac)$_3$] (D_3)
Al–O = 1.900

$[\{Al(OSiMe_3)_3\}_2]$ (C_i)
Al–O1 = 1.847; Al–O2 = 1.848; Al–O3 = 1.700

$[Al\{(\mu\text{-}OEt)_2Al(OSiMe_3)_2\}_3]$ (D_3)
Al–O = 1.939; Al′–O = 1.830; Al′–O′ = 1.718

$[\{Al_4(O\text{-}i\text{-}Pr)_3\}_4]$ (D_3)
Al–O = 1.954; Al′–O = 1.818; Al′–O′ = 1.727

$[Al_4(pd)_6]$ (D_3)
Al–O = 1.963; Al′–O = 1.822; Al′–O′ = 1.736

$[Al_5(2,4\text{-}pd)_7(2,4\text{-}Hpd)]$
Al(1,2)–O = 1.75–1.99; Al(3,4,5)–O = 1.72–1.86

Figure 4. Geometry optimized structures of aluminum complexes and selected bond lengths (Å). Symmetry constraints (if any) applied during optimization are listed in parentheses. For clarity, hydrogens atoms are omitted from the structures of $[Al\{(\mu\text{-}OEt)_2Al(OSiMe_3)_2\}_3]$, $[\{Al_4(O\text{-}i\text{-}Pr)_3\}_4]$, $[Al_4(pd)_6]$, and with the exception of the terminal OH, $[Al_5(2,4\text{-}pd)_7(2,4\text{-}Hpd)]$.

Thermogravimetric Analysis of Aluminum Pentanediolates. Samples of the sublimed pentanediolate were analyzed under flowing nitrogen and air (Figure 5). Under either gas stream, weight was lost even before 100 °C was attained; the weight loss that was displayed by the end of a hold at 110 °C for 10 min suggests that some decomposition was already occurring. The temperature was then ramped by 10 °C every minute until 600 °C was reached. Under N_2, weight loss continues gradually until ca. 290 °C (71%), after which there is a large mass decrease from 300 to 330 °C. Under air, decomposition is initially more rapid, and over half the weight is lost by 260 °C. The weight remaining at 329 °C (N_2) or 365 °C (air) (37–38%) reflects the elimination of nearly all organic species, and could represent an $Al_nO_{n-1}(OH)_{n+2}$ intermediate. Under air, the final weight loss at 589 °C is consistent with complete dehydration to Al_2O_3 (calc. 28% from $Al_4(2,4\text{-}pd)_6$; 27% from $Al_5(2,4\text{-}pd)_7(2,4\text{-}Hpd)$). Further heating to 589 °C under N_2 results in only 4% additional weight loss, approximating to $[AlO(OH)]_n$ (calcd 33% for $n = 4$, starting from $Al_4(2,4\text{-}pd)_6$; 31% for $n = 5$, starting from $Al_5(2,4\text{-}pd)_7(2,4\text{-}Hpd)$). The general pattern is that observed for the dehydration of boehmite.[28,29] A sample of unsublimed $[Al(2,4\text{-}pd)(2,4\text{-}Hpd)]_n$ was also examined with TGA, and under N_2 its decomposition curve (not shown) is broadly similar to that of the sublimed material. Its final weight loss at 589 °C (27%)

Table 1. Predicted Shielding Constants (σ_{calcd}) and Chemical Shifts (δ_{calcd}) in ppm

complex	σ_{calcd}	δ_{calcd}	δ_{exp} (solvent)	$\Delta\delta^{a}$	CN^{b}	ref
$[Al(OH_2)_6]^{3+}$	613.03	0.0	0.0 (D_2O)		6	this work
$[AlH_4]^-$	516.86	96.2	98 (THF)	−1.8	4	24
$[Al(cat)_3]^{3-}$	579.99	33.0	31.3 (aq)	1.7	6	25
$[Al(ox)_3]^{3-}$	592.89	20.1	16.2 (aq)	3.9	6	26
$[Al(acac)_3]$	604.93	8.1	−0.9 (C_6D_6)	9.0	6	18
$[\{Al(OSiMe_3)_3\}_2]$	547.95	65.1	59 (toluene)	6.1	4	27
$[Al\{(\mu\text{-OEt})_2Al(OSiMe_3)_2\}_3]$	602.22	10.8	5.3 ($CDCl_3$)^{c}	5.5	6	23
	545.21	67.8	58.3	9.5	4	
$[\{Al_4(O\text{-}i\text{-}Pr)_3\}_4]$	606.74	6.3	−0.1 (tol-D_8)	6.4	6	21
	537.34	75.7	60.3	15.4	4	
$[Al_4(2,4\text{-pd})_6]$	602.82	10.2			6	this work
	523.97	89.1			4	
$[Al_5(2,4\text{-pd})_7(2,4\text{-Hpd})]$	569.00	44.0			5	this work
	568.37	44.7				
	537.99	75.0			4	
	536.74	76.3				
	536.04	77.0				

$^{a}\Delta\delta = \delta_{calcd} - \delta_{exp}$. ^{b}Formal coordination number. ^{c}Experimental values are for the triphenylsilyl complex.

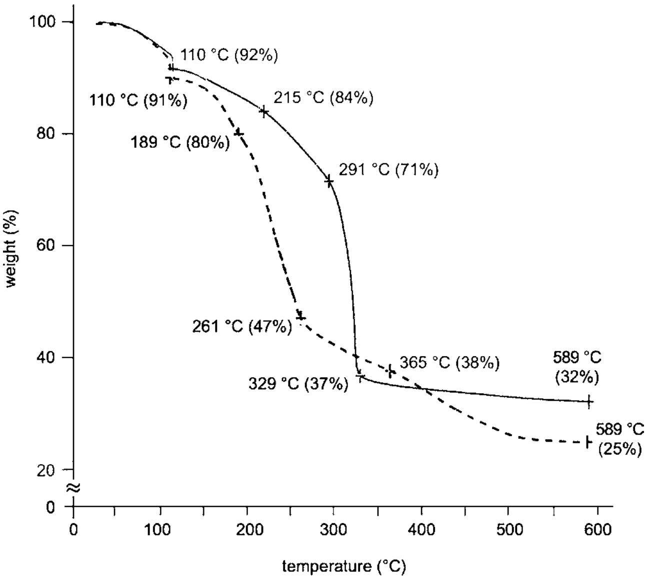


Figure 5. TGA of the sublimed aluminum pentanediolate under N_2 (solid line) and air (dashed line).

suggests that decomposition to Al_2O_3 is not yet complete, which would require a final mass of 22%.

Zirconium Derivative. A brief study with a zirconium derivative of the 2,4-pd ligand was conducted. Zirconium was selected as a metal with a higher valence than aluminum, but that also forms a mononuclear $M(acac)_n$ complex. There is also precedence for a dinuclear Ti derivative[6] and trinuclear Zr derivative[7] with the bulkier 2,4-dmpd ligand. Whether the use of the larger Zr center would form a structurally analogous derivative was not immediately obvious. The reaction of $Zr(O\text{-}i\text{-}Pr)_4\cdot HO\text{-}i\text{-}Pr$ with 2,4-H_2pd in toluene generates a white solid that is slightly soluble in THF and chloroform, but repeated attempts at crystallization failed to produce crystals suitable for single crystal X-ray analysis. The determination of the compound's structure was consequently based upon elemental analysis, NMR, and TGA data.

^{1}H NMR data indicate that the complex is fluxional in solution; the peaks are broadened at room temperature, and cooling a sample to −64 °C causes shifts in their relative intensities, but does not produce a limiting spectrum. Depending on how rigorously the product is dried, the amount of 2,4-H_2pd differs somewhat from preparation to preparation, but the ratio confirmed with elemental analysis is one pentanediol for four pentanediolates. A dinuclear bridged structure, that is, $[Zr(2,4\text{-pd})_2]_2\cdot 2,4\text{-}H_2pd$ (Figure 6) would be consistent with the related crystallographically characterized titanium dimer reported by Walters and co-workers,[6] which uses 2,4-dmpd as the basis for the alkoxide ligand. Geometric optimization of an idealized structure of $[Zr(2,4\text{-pd})_2]_2$ (C_2 symmetry) found it to be computationally stable (see Supporting Information), and a minimum on the potential energy surface.

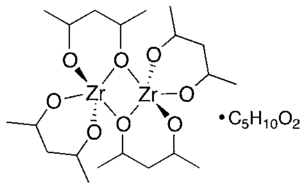


Figure 6. Suggested structure of $[Zr(2,4\text{-pd})_2]_2\cdot 2,4\text{-}H_2pd$.

Thermogravimetric Analysis. A sample of $[Zr(2,4\text{-pd})_2]_2\cdot 2,4\text{-}H_2pd$ was analyzed under flowing nitrogen (Figure 7). Weight was lost even before 100 °C was attained; after the temperature was held at 110 °C for 10 min, it was then ramped by 10 °C every minute until 600 °C was reached. A 10% weight loss had occurred at the end of the 110 °C hold, but loss corresponding to the removal of all the 2,4-H_2pd (calcd 85%) does not occur until about 240 °C. Elimination of a pentadiene (e.g., route "A" in Scheme 1) is suggested by the 9% drop in mass (calcd 10%) that occurs by 300 °C, but then decomposition is rapid, and by 326 °C, only 40% of the initial weight remains. This reflects the loss of all organic species, and could represent a $ZrO_{1+x}(OH)_{2-2x}$ intermediate (calcd 41% for $x = 0$).[30] The final weight loss at 589 °C represents close to complete conversion to ZrO_2 (calcd 35.5%).[31]

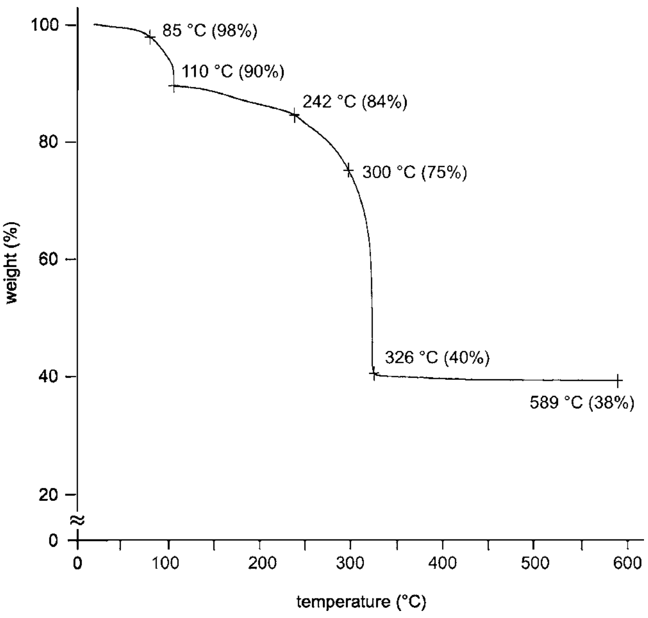


Figure 7. TGA of $[Zr(2,4\text{-}pd)_2]_2 \cdot 2,4\text{-}H_2pd$ under N_2.

CONCLUSIONS

Despite some similarities to β-diketonate ligands, the 2,4-pentadiolate dianion provides a considerably different coordination environment. The bridging abilities of the 2,4-pd ligand give it flexibility that is missing from the structurally rigid acac, for example. In contrast to the mononuclear $Al(acac)_3$ and $Zr(acac)_4$ derivatives, the 2,4-pd ligand supports the generation of polynuclear aggregates; in the case of aluminum, tetra- and pentanuclear complexes can form. The same tendency to aggregate also reduces volatility, however, and unlike the acac derivatives,[14] in their present form the usefulness of the 2,4-pentanediolate complexes for CVD applications appears limited. Nevertheless, as the parent pentanediolate ligand offers multiple sites of substitution, modified derivatives could profitably be combined with monodentate alkoxides to extend the structural possibilities in this class of compounds.

EXPERIMENTAL SECTION

General Considerations. Syntheses were performed with the rigorous exclusion of air and moisture using high vacuum, Schlenk, or drybox techniques. Proton NMR spectra were obtained on Bruker NR-300 or DRX-500 spectrometers at 300 and 500 MHz, respectively; ^{13}C NMR were obtained at 75.5 MHz. Aluminum (^{27}Al) NMR was obtained on a Bruker NR-400 spectrometer at 104 MHz and was referenced to $Al(H_2O)_6^{3+}$ (1 M $Al(NO_3)_3$ in D_2O, 0 ppm). Infrared data were measured using KBr pellets as previously described.[32] Elemental analysis was performed by Desert Analytical Laboratory, Tucson, AZ or Atlantic Microlab, Atlanta, GA. Thermogravimetric analysis was done on a Hi-Res TGA 2950 Thermogravimetric Analyzer (TA Instruments). Mass spectrometry measurements were done on a Finnigan MAT atmospheric pressure chemical ionization spectrometer.

Materials. Aluminum sec-butoxide ($Al(O\text{-}s\text{-}Bu)_3$) and zirconium isopropoxide ($Zr(O\text{-}i\text{-}Pr)_4 \cdot HO\text{-}i\text{-}Pr$) were used as received from Strem Chemicals. 2,4-pentanediol (2,4-H_2pd, mixture of *R,R* and *R,S* diasteriomers) (ACROS Chemical) was degassed by freeze−pump−thaw cycles before use. Solvents used for reaction and NMR were dried and distilled under nitrogen.

Reaction of $Al(O\text{-}s\text{-}Bu)_3$ and 2,4-H_2pd. $Al(O\text{-}s\text{-}Bu)_3$ (1.833 g, 7.44 mmol) and 2,4-H_2pd (1.184 g, 11.4 mmol) were added to a 125 mL Schlenk flask equipped with a stirring bar. Toluene (30 mL) was added and the mixture was stirred for 3 h under N_2 on a Schlenk line. The *sec*-butanol byproduct was removed by distillation at 98−101 °C at atmospheric pressure under nitrogen. The toluene was removed under vacuum, leaving a colorless solid that was washed with hexanes and then dried under vacuum. Yield: 1.15 g (87%), mp 257−260 °C. The unsublimed solid is insoluble in a variety of organic solvents, including THF, toluene, hexane, chloroform, methylene chloride and acetone. The material is hygroscopic, and gains 18% in mass after 5 h exposure to air. Principal IR bands (KBr, cm^{-1}): 644 (m), 943 (s), 1130 (s), 1135 (s), 1375 (s), and 2928 (s). Anal. Calcd (%) for $C_{10}H_{21}AlO_4$ (Al(2,4-pd)(2,4-Hpd)): C, 51.71; H, 9.11; Al, 11.6. Found C, 50.24; H, 8.53; Al, 11.1. Although the experimental values are low, the molar C/H/Al ratios are 10.1: 20.5: 1.0.

After sublimation at 238 °C at 240 mTorr, 0.511 g of a white solid was recovered. The sublimed material is soluble in all of the previously mentioned solvents. At atmospheric pressure, the sublimed powder begins to fuse near 40 °C; on continued heating, the solid becomes transparent at 80 °C, and melting is observed at 120 °C. ^1H NMR (300 MHz, $CDCl_3$, 298 K) (relative areas scaled to smallest resonance): δ 0.90−1.18 (br mult, 12H, CH_3), 1.18−1.86 (br mult, 26H CH_3, CH_2), 3.69−4.63 (br mult, 9H, CH), 4.85 (br s, 1H, CH, OH). ^{13}C NMR (75 MHz, C_6D_6, 298 K): δ 18.6 (CH_3), 21.4 (CH_3), 25.8 (CH_3), 27.1 (CH_3), 45.0 (CH_2), 63.4 (CH), 70.9 (CH). ^{27}Al NMR (104 MHz, C_6D_6, 298 K): δ 0.0 (sharp), 48.1 (br), 63.8 (br). Principal IR bands (KBr, cm^{-1}): 692(br), 957(s), 1133(s), 1371(s), 2924(s) and 2940(s). Anal. Calcd (%) for $C_{30}H_{60}Al_4O_{12}$ ($Al_4(2,4\text{-}pd)_6$: C, 50.0; H, 8.39; for $C_{40}H_{81}Al_5O_{16}$ ($Al_5(2,4\text{-}pd)_7(2,4\text{-}Hpd)$): C, 50.4; H, 8.57. Found: C, 49.9; H, 8.52.

Synthesis of Bis(2,4-pentanediolato)zirconium·2,4-Pentanediol, $[Zr(2,4\text{-}pd)_2]_2 \cdot H_2(2,4\text{-}pd)$. $Zr(O\text{-}i\text{-}Pr)_4 \cdot HO\text{-}i\text{-}Pr$ (2.21 g, 5.70 mmol) and 2,4-H_2pd (1.41 g, 13.5 mmol) were added to a 125 mL Schlenk flask equipped with a stirring bar. Toluene (30 mL) was added and the mixture was stirred for 24 h under N_2 on a Schlenk line. As the volatiles were removed under vacuum, a white precipitate formed. The solid residue was washed twice with 10 mL portions of hexane and then dried under vacuum, leaving $[Zr(2,4\text{-}pd)_2]_2 \cdot 2,4\text{-}H_2pd$ as a white powder, 0.71 g (38%). The powder sublimes at 230 °C at 300 mTorr. ^1H NMR (500 MHz, THF-d_8): δ 0.89 (CH_3), 1.08 (CH_3), 1.30 (br, CH_2), 1.40 (CH_2), 3.9−4.6 (br mult, CH, OH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 24.3 (CH_3), 46.5 (CH_2), 66.0 (CH), 69.1 (CH). Principal IR bands (KBr, cm^{-1}): 474(m), 525(m), 801(s), 934(m), 1094(s), 1120(s), 1367(s), 2923(s), 2965(s) and 3336(w). Anal. Calcd for $C_{25}H_{52}O_{10}Zr_2$: C, 43.20; H, 7.54. Found (unsublimed material): C, 42.95; H, 7.68.

Computational Methods. Geometry optimization and NMR shielding calculations were performed with the *Gaussian 03W* suite of programs[33] and the GIAO (gauge-including atomic orbitals) method.[34] A variation on a previously used protocol was adopted:[35] for geometry optimizations, the B3LYP functional, which incorporates Becke's three−parameter exchange functional[36] and the correlation functional of Lee, Yang, and Parr,[37] was used. For the shielding calculations, Hartree−Fock methods were employed. In the case of the crystallographically characterized $[Al\{(\mu\text{-}OEt)_2Al(OSiPh_3)_2\}_3]$,[23] the phenyl groups were replaced with methyl groups in order to make the molecule more computationally tractable. For the aluminum compounds, the standard Pople 6-311G(2d,p) basis set was used for all geometry optimizations except with $[Al\{(\mu\text{-}OEt)_2Al(OSiMe_3)_2\}_3]$ and $[Al_5(2,4\text{-}pd)_7(2,4\text{-}Hpd)]$, for which convergence difficulties were encountered; the smaller 6-31G(d,p) set was used in these cases. For the zirconium in $[Zr_2(2,4\text{-}pd)_4]$, the correlation-consistent cc-pVTZ-PP basis with an energy-consistent relativistic pseudopotential was used;[38] 6-311G(2d,p) was used for the other atoms. For the shielding calculations, a diffuse function was added to non-hydrogen atoms (i.e., with the 6-311+G(2d,p) basis set) for all compounds.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Coordinates of the geometry optimized structures, and a drawing and selected bond distances for $[Zr(2,4\text{-}pd)_2]_2$. These are available free of charge via the Internet at http://pubs.acs.org.

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