Notes

Structural Aspects of the Aluminum−Carboxylate Interaction. Molecular Structure of the Tetranuclear $[(AlMe_2)_2(\mu\text{-}O_2C)_2\text{-}1,2\text{-}C_6H_4]_2$ Adduct

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Introduction

Recently, there has been renewed considerable interest on the interactions of aluminum alkyls with carboxylic acids. This is due to the utilization of organoaluminum carboxylates as precursors of alumina fibers[1] or aluminum oxides[2] as well as to the relevance of aluminum carboxylates to alumoxanes[3] and aluminum biochemistry.[4,5] Although the carboxylate anion is a common ligand in the metal coordination chemistry, the aluminum chemistry of carboxylates remains largely unexplored.[6] Ionic organoaluminum carboxylates,[7] carboxylate-substituted alumoxanes,[8] and, very recently, dialkylaluminum carboxylates are the only crystallographically characterized aluminum carboxylates.[3,9] In this respect, the investigation on the synthesis, structure, and reactivity of aluminum derivatives of carboxylic acids is of both fundamental and practical importance.

Recent work in our laboratory has focused on the structure and reactivity of organoaluminum compounds derived from *O,O′*-bifunctional ligands,[10] and the organoaluminum chemistry of carboxylate ligands is an extension of this work. We report here the synthesis and structural characterization of the dimeric tetranuclear $[(AlMe_2)_2(\mu\text{-}O_2C)_2\text{-}1,2\text{-}C_6H_4]_2$ (**1**) compound derived from Me_3Al and phthalic acid. To our knowledge, this is the first examination of the organoaluminum coordination chemistry of a dicarboxylate ligand. When discussing the structural aspects of the metal ion−carboxylate interaction, we demonstrate that the anti direction is the most likely location of the aluminum center relative to the carboxylate group.

Experimental Section

All operations were carried out under nitrogen. Trimethylaluminum was distilled before use, and phthalic acid was used as supplied. Solvents were dried and distilled prior to use. NMR spectra were recorded on a Varian 300 VXL spectrometer. IR spectra were recorded on a Specord-75IR spectrometer.

Preparation of $[(AlMe_2)_2(\mu\text{-}O_2C)_2\text{-}1,2\text{-}C_6H_4]_2$ (1). To a solution of phthalic acid (4 mmol) in toluene (7 mL) was added Me_3Al (8 mmol) at −78 °C. The reaction mixture was then allowed to warm to room temperature. After stirring for an additional 1 h, the solution was evaporated to dryness in vacuo to afford a white solid. Yield: 95%. Anal. Calcd for $C_{24}H_{32}Al_4O_8$: C, 51.81; H, 5.80. Found: C, 51.7; H, 5.8. ^1H NMR (CD_2Cl_2): (20 °C) δ −1.42 (s, 6H, $Al(CH_3)$), −1.23 (s, 6H, $Al(CH_3)$), −0.64 (s, 12H, $Al(CH_3)_2$), 7.83 (m, 4H, CH), 8.05 (m, 4H, CH); (−70 °C) −1.51 (s, 6H, $Al(CH_3)$), −1.29 (s, 6H, $Al(CH_3)$), −0.71 (s, 12H, $Al(CH_3)_2$), 7.82 (m, 4H, CH), 8.04 (m, 4H, CH). ^{27}Al NMR (C_6D_6, 20 °C): δ 160 ($W_{1/2}$ = 4600 Hz). IR (CH_2Cl_2, cm^{-1}): 1610 (s), 1562 (s), 1504 (s), 1440 (s), 1418 (m), 1196 (m), 908 (w), 898 (w), 884 (w), 656 (w), 620 (m).

X-ray Structure Determination. Crystallographic data are summarized in Table 1. Colorless single crystals of **1** suitable for diffraction studies were grown from CH_2Cl_2 solutions at −15 °C, and one was mounted in a Lindemann glass capillary under an inert atmosphere. All diffraction data were collected on a Siemens P3 four-circle instrument at room temperature. An automatic search routine was used to locate up to 22 reflections which were used for the determination and least-squares refinement of the orientation matrix. Intensity data were recorded using the $\omega-2\theta$ scan technique and corrected for Lorentz and polarization effects. The structure was solved by direct methods using the SHELXS-86 program[11] and refined by the full-matrix least-squares method against F^2 values with SHELXL-93[12] program. All of the non-hydrogen atoms were refined with anisotropic thermal parameters. Methyl hydrogen atoms were introduced at geometrically idealized coordinates and refined as disordered groups with two positions rotated by 60° about the Al−C vector. The remaining hydrogen atoms for **1** were located from the difference Fourier map and isotropically refined. The final weighting scheme was $w^{-1} = \sigma^2(F_o)^2 + (0.0555P)^2 + 0.4508P$, where $P = {}^1/_3(F_o{}^2 + 2F_c{}^2)$. The largest positive and negative peaks on the final difference Fourier map have no significant chemical meaning, and the maximum shift/error ratios in final cycle of refinement were less than 0.001.

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Table 1. Crystallographic Data and Structure Refinement for $[(AlMe_2)_2(\mu\text{-}O_2C)_2\text{-}1,2\text{-}C_6H_4]_2$ (**1**)

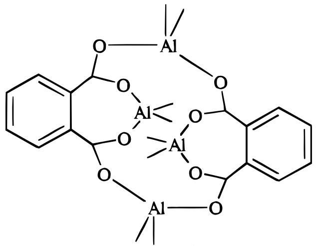
empirical formula	$C_{24}H_{32}Al_4O_8$
fw	556.44
T, °C	20(2)
λ, Å	Mo Kα (0.710 73)
crystal system	monoclinic
space group	$C2/c$ (No. 15)
a, Å	19.046(3)
b, Å	12.024(2)
c, Å	14.139(2)
β, deg	109.946(12)
volume, Å^3	3043.8(8)
Z	4
D_{calcd}, g cm^{-3}	1.214
μ(Mo Kα), cm^{-1}	1.93
F(000)	1168
crystal size, mm	0.50 × 0.42 × 0.26
2θ range, deg	4.6 to 50.1
index ranges	$0 \le h \le 22, 0 \le k \le 14, -16 \le l \le 15$
no. of reflcns collcd	2770
no. of independent rflcns	2676 ($R_{int} = 0.0149$)
refinement method	full-matrix least-squares on F^2
no. of data/restraints/parameters	2675/0/191
goodness-of-fit on F^2	1.041
final R indices [$I > 2\sigma(I)$], %[a]	$R1 = 0.0323$, w$R2 = 0.0859$
R indices (all data), %	$R1 = 0.0414$, w$R2 = 0.0952$
ρ_{max}/ρ_{min}, e Å^{-3}	0.171/−0.161

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, w$R2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma(F_o^2)^2]^{1/2}$.

Results and Discussion

The addition of 2 molar equiv of Me_3Al to phthalic acid in toluene resulted in the formation of the tetranuclear adduct **1** in nearly quantitative yields (eq 1). Compound **1** is stable as a solid and in solution under an inert atmosphere. However, it is oxygen and moisture sensitive. The molecular structure of **1** has been determined by X-ray crystallography, and the solution structure has been confirmed by NMR and IR spectroscopy. The molecular structure of **1** and the atom-numbering scheme are shown in Figure 1. Selected bond lengths and angles for **1** are presented in Table 2. The crystal structure of **1** reveals that the molecule is a centrosymmetric tetranuclear adduct with a skeleton framework consisting of three fused distorted heterocycle rings and one sixteen- and two seven-membered rings. The four carboxylate groups occur as bidentate ligands and act as a three-center bridge between the four dimethylaluminum units, which results in the formation of the highly distorted sixteen-membered $Al_4(OCO)_4$ ring. The two aluminum atoms, Al(2) and Al(2′), join symmetrically the two dicarboxylate ligands being bonded in the syn direction to one oxygen atom of each ligand. The remaining aluminum atoms, Al(1) and Al(1′), bridge between the carboxylate groups within the phthalate ligands (being bonded in the anti direction of the carboxylate ligand) with the formation of additional two seven-membered heterocycle rings; these two bridgehead aluminum atoms lie in positions opposite the central macrocycle ring. Thus, in the title adduct each carboxylate group displays a syn−anti conformation (Chart 1).

$$4Me_3Al + 2C_6H_4\text{-}1,2\text{-}(COOH)_2 \xrightarrow{-\,MeH}$$



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(1)

The mean O−C−O angle in the coordinated carboxylate is 120.5° and corresponds to the related bond angle in a free acid (123.29(8)°).[13] The aluminum atoms deviate from the planes of both carboxylate groups—for the C(7) group in the same direction (0.179(1) and 0.451(1) Å) and for the plane of the second C(8) group in opposite direction (0.299(1) and 0.036(1) Å), which may be attributed to the sterically encumbered nature of the phthalate ligand. Both carboxylate groups are rotated about the C−C bond relative to the plane defined by the aromatic ring with corresponding dihedral angles 42.2(1) and 31.4(1)° for the group bonded to C(1) and C(2) atoms, respectively. It is reasonable to assume that the significant different arrangement of carboxylate groups in relation to the

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $[(AlMe_2)_2(\mu\text{-}O_2C)_2\text{-}1,2\text{-}C_6H_4]_2$ (**1**)[a]

Bond Distances			
Al(1)−O(71)	1.8184(13)	Al(2)−O(72′)	1.8527(12)
Al(1)−O(81)	1.8241(13)	Al(2)−O(82)	1.8704(13)
Al(1)−C(12)	1.927(2)	Al(2)−C(21)	1.940(2)
Al(1)−C(11)	1.933(2)	Al(2)−C(22)	1.943(2)
C(7)−O(72)	1.254(2)	C(8)−O(82)	1.261(2)
C(7)−O(71)	1.258(2)	C(8)−O(81)	1.258(2)
C(7)−C(1)	1.500(2)	C(8)−C(2)	1.488(2)
Bond Angles			
O(71)−Al(1)−O(81)	92.64(6)	O(72′)−Al(2)−O(82)	100.74(5)
O(71)−Al(1)−C(12)	112.14(10)	O(72′)−Al(2)−C(21)	112.34(9)
O(81)−Al(1)−C(12)	110.38(9)	O(82)−Al(2)−C(21)	105.36(8)
O(71)−Al(1)−C(11)	108.79(9)	O(72′)−Al(2)−C(22)	103.59(8)
O(81)−Al(1)−C(11)	105.48(9)	O(82)−Al(2)−C(22)	110.02(9)
C(12)−Al(1)−C(11)	122.98(11)	C(21)−Al(2)−C(22)	122.72(10)
C(7)−O(71)−Al(1)	134.70(11)	C(7′)−O(72′)−Al(2)	130.29(11)
C(8)−O(81)−Al(1)	135.72(11)	C(8)−O(82)−Al(2)	125.61(10)
O(72)−C(7)−O(71)	121.0(2)	O(81)−C(8)−O(82)	119.9(2)
O(72)−C(7)−C(1)	116.0(2)	O(82)−C(8)−C(2)	117.46(14)
O(71)−C(7)−C(1)	123.0(2)	O(81)−C(8)−C(2)	122.64(14)

[a] Symmetry transformations used to generate equivalent atoms denoted by prime: $^1/_2 - x$, $^1/_2 - y$, $-z$.

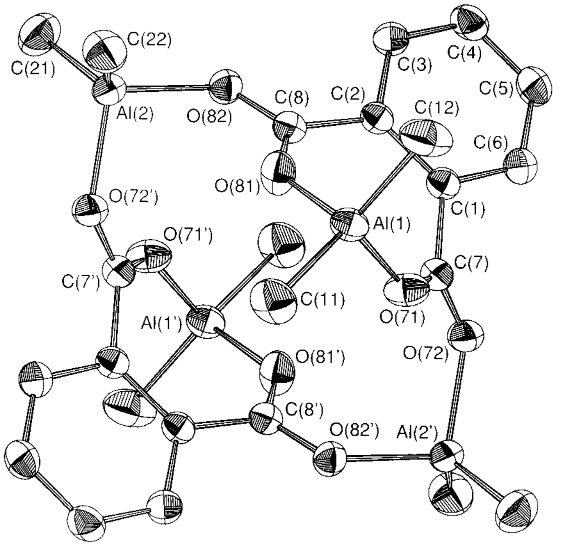

Figure 1. ORTEP plot of the crystal structure of $[(AlMe_2)_2(\mu\text{-}O_2C)_2\text{-}1,2\text{-}C_6H_4]_2$ (**1**) with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

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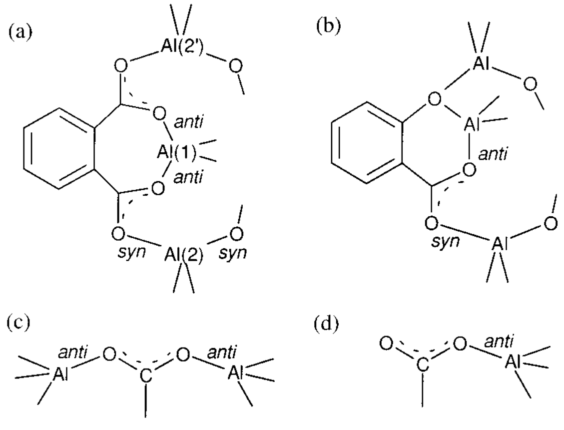
Chart 1. Schematic Representation of the Observed Coordination Modes in (a) $[(AlMe_2)_2(\mu\text{-}O_2C)_2\text{-}1,2\text{-}C_6H_4]_2$ (**1**), (b) $[(Et_2Al)_2(\mu\text{-}O_2C)C_6H_4\text{-}2\text{-}\mu\text{-}O]_2$,[9] (c) $[(Me_3Al)_2O_2CCH_3]^-$,[7b] and (d) $[Me_3AlO_2CCH_3]^-$ [7a]



aromatic ring plane would affect the bond delocalization in the conjugated bond system within the ligand and cause nonequivalence of those groups associated with the C(1) and C(2) atoms. In fact, the C(1)−C(7) distance (1.500(2) Å) to the carboxylate group with more extended corresponding dihedral angles is longer than the related C(2)−C(8) distance (1.488(2) Å). Furthermore, nonequivalence of both carboxylate groups is reflected by the observed differences in the corresponding Al−O distances; the mean Al−O distances to the oxygen atoms associated with C(7) and C(8) atoms are 1.836 and 1.847 Å, respectively.[1]

The Al−O distances to the bridgehead Al(1) atom are shorter (average $Al-O_{anti}$ bond length is 1.821 Å) than those to the bridging Al(2) atom (average $Al-O_{syn}$, 1.862 Å). This indicates that for aluminum carboxylates the Al−O bond in the anti position is stronger than that in syn position.

It is notable that structural aspects of the metal ion−carboxylate interaction are of biological interest, and with respect to this numerous attempts are undertaken in order to determine which lone pair of oxygen atoms of the carboxylate group is preferred for metal ion binding.[14] The structure of **1** contains similar aluminum moieties bound to the oxygen atoms in syn−syn and anti−anti direction with respect to the carboxylate groups, respectively, and afford a direct comparison of basicity of the electrons lone pairs on carboxylate oxygen atoms. The results obtained indicate that the anti direction is the most likely location of the aluminum center relative to the carboxylate group. This conclusion is consistent with the conformation found for the bidentate $[(Me_3Al)_2O_2CCH_3]$ anion where both Me_3Al molecules are located in the anti positions, although authors suggested that it is favored primarily due to packing considerations,[7b] as well as with the observed coordination mode in the monodentate $[Me_3AlO_2CCH_3]$ anion.[7a] It should be noted that similar differentiation between the $Al-O_{anti}$ and $Al-O_{syn}$ distances to that in **1** we recently found in the related tetranuclear compound derived from the hydroxy carboxylic acid, salicylic acid[9] (Chart 1).

The NMR and IR spectra of the title compound are consistent with the structure found in the solid state. The ^1H NMR spectrum of **1** shows three $Al-CH_3$ resonances. One singlet corresponds to the equivalent protons in dimethylaluminum units joining the two dicarboxylate ligands, and the remaining two singlets are attributed to the equivalent in pairs methyl groups of the bridgehead dimethylaluminum moieties; one methyl group is situated toward and the second one away from the central macrocycle ring. It is interesting to note that the ^1H NMR spectrum patterns are similar at low temperature (−70 °C). The ^{27}Al NMR spectrum of **1** shows one broad resonance at 160 ppm, indicative of four-coordinated aluminum atoms.[15] The IR spectrum of **1** in CH_2Cl_2 solution shows bands at 1610 and 1562 cm^{-1} in the range of C═O stretching vibrations, which are characteristic for bidentate carboxylate groups.[3a,16]

Whereas the reaction of trialkylaluminum with dicarboxylic acid leads to the tetranuclear compound with all bidentate carboxylate groups, that of aluminum(III) gives the different type complexes. It is worth nothing that structurally characterized aluminum(III) complexes derived from dicarboxylic acids are also quite rare, and only two solid-state structures have been reported to date, the trischelate oxalate $[Al(ox)_3]^{3-}$ complex[17] and the bischelate malonate $[Al(malo)_2(H_2O)_2]^-$ complex.[18] In both cases fully deprotonated carboxylic acids form chelate complexes via monodentate carboxylate groups.

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Supporting Information Available: A listing of X-ray experimental details and crystallographic data, all atomic coordinates, anisotropic thermal parameters, and complete bond distances and angles for the crystal structure of **1** (4 pages). Ordering information is given on any current masthead page.

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