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The First Organoaluminum Derivative of a Hydroxy Carboxylic Acid. Molecular Structure of the Tetranuclear $[Et_2Al]_4[(\mu\text{-}O_2C)C_6H_4\text{-}2\text{-}\mu\text{-}O]_2$ Adduct

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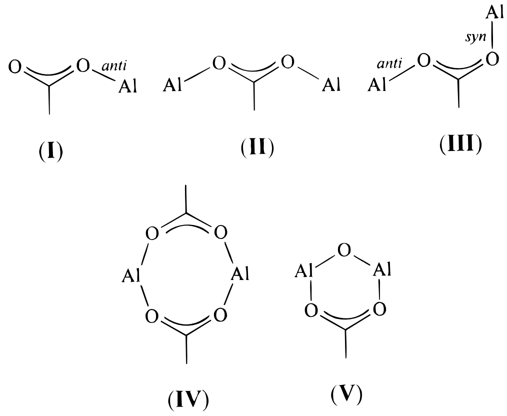
Summary: The reaction of triethylaluminum with salicylic acid in a 2:1 molar ratio results in the formation of the novel tetranuclear diethylaluminum aryloxide carboxylate adduct $[Et_2Al]_4[(\mu\text{-}O_2C)C_6H_4\text{-}2\text{-}\mu\text{-}O]_2$ *(**1**). Compound **1** has been characterized by elemental analysis and* ^{1}H *and* ^{27}Al *NMR and IR spectroscopy, and its molecular structure has been determined by X-ray crystallography. The molecule is a centrosymmetric cluster with a skeleton framework consisting of three fused heterocycle rings, one 12- and two 6-membered. The two diethylaluminum units symmetrically join the two salicylic acid dianions by the formation of bridges between the aryloxide oxygen atom and one carboxylate oxygen atom of the second ligand. The two other diethylaluminum units are chelated by the aryloxide and second carboxylate oxygen atoms of each ligand. The carboxylate groups display a bidentate coordination mode with syn−anti conformation. The binding mode of the carboxylate and alkoxide ligands to metal centers is also discussed.*

Introduction

Recently, there has been much renewed interest in the interactions of aluminum alkyls with carboxylic acids. This is due to the application of organoaluminum carboxylates as precursors of alumina fibers.[1] On the other hand, the knowledge about the structure and reactivity of organoaluminum carboxylates is rather scant. Although the carboxylate anion is a common ligand in metal coordination chemistry, only ionic organoaluminum carboxylates and carboxylate-substituted alumoxanes have been crystallographically characterized.[2,3] Very recently, we reported the synthesis and structure characterization of the first examples of organoaluminum derivatives of mono- and dicarboxylic acids, the dimeric dinuclear and tetranuclear dimethylaluminum carboxylates $[Me_2AlO_2CPh]_2$[4a] and $[Me_2AlO_2CC_6H_4CO_2AlMe_2]_2$,[4a,b] respectively. For the latter we found additionally that the most likely location of the aluminum center relative to the *O,O*-bidentate carboxylate group is the *anti* direction.[4b] The carboxylate anion acts as a bridging bidentate ligand in these organoaluminum complexes and only for the ionic $[Me_3AlO_2CCH_3]^-$ adduct as a monodentate ligand[2a] (Chart 1).

Chart 1. Observed Coordination Modes in Organoaluminum Carboxylates[a]



[a] Legend: (**I**) for $[Me_3AlO_2CCH_3]^-$;[2a] (**II**) for $[(Me_3Al)_2O_2CCH_3]^-$;[2b] (**III**) for $[Me_2AlO_2CC_6H_4CO_2AlMe_2]_2$;[4b] (**IV**) for $[R_2AlO_2CPh]_2$;[4a,5] (**V**) see ref 3.

As an extension of our research on the structure and reactivity of alkylaluminum O,O′-chelate complexes, including the methyl salicylate anion as an O,O′-bidentate ligand,[6,7] we report the results on the synthesis and structural characterization of the tetranuclear diethylaluminum carboxylate $[Et_2Al]_4[(\mu\text{-}O_2C)C_6H_4\text{-}2\text{-}\mu\text{-}O]_2$ adduct derived from salicylic acid and triethylaluminum. To our knowledge, no reaction of alkylaluminum compounds with hydroxy carboxylic acids has been studied. Morever, the title compound contains in the framework structure two bridging carboxylate groups and two bridging aryloxide oxygen atoms related by symmetry, and we propose on the basis of comparison of the binding mode of carboxylate and alkoxide ligands to metal centers that that the bridging three-centered M−O−C−O−M carboxylate group and the bridging monocentered M−O−M alkoxide group can be considered as isomorphic ligands. Indeed, the structural aspects of the aluminum ion-carboxylate interaction are of biological interest.[8]

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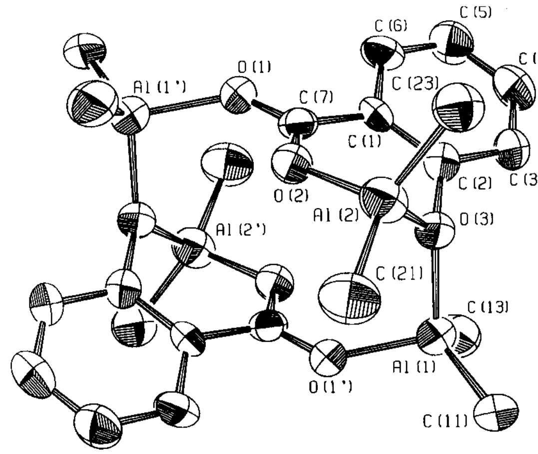
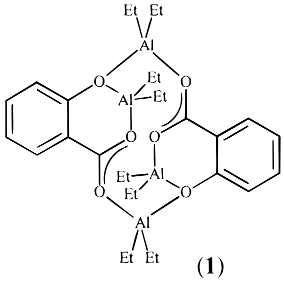


Figure 1. ORTEP view of $[Et_2Al]_4[(\mu\text{-}O_2C)C_6H_4\text{-}2\text{-}\mu\text{-}O]_2$ (**1**) with atom-numbering scheme. Thermal ellipsoids are shown at the 20% probability level. Methyl groups of the ethyl substituents and hydrogen atoms are omitted for clarity.

Results and Discussion

The addition of 2 molar equiv of Et_3Al to salicylic acid results in the evolution of ethane and formation of the tetranuclear adduct $[Et_2Al]_4[(\mu\text{-}O_2C)C_6H_4\text{-}2\text{-}\mu\text{-}O]_2$ (**1**; eq 1). Compound **1** is stable as a solid and in solution under an inert atmosphere but 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 and cryometric molecular weight determination.

$$4Et_3Al + 2HOC_6H_4CO_2H \longrightarrow$$



$$+ 4EtH \qquad (1)$$

(**1**)

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 1. The unit cell contains two unique molecules which reside on the centers of inversion and are essentially identical. Therefore, the structure of only one representative molecule (molecule *a*), with smaller esd's, is discussed. The crystal structure of **1** reveals that the molecule is a tetranuclear adduct with a framework consisting of three fused distorted heterocycle rings, one 12- and two 6-membered. The two diethylaluminum units join the two salicylic acid dianions via bridges between the aryloxide oxygen atom and one carboxylate oxygen atom of the second ligand (which gives a highly distorted 12-membered ring). The two other diethylaluminum units are chelated by the aryloxide and second carboxylate oxygen atoms of each ligand; these bridgehead aluminum atoms lie in an opposite position relative to the central macrocycle ring. The carboxylate group is rotated about the C−C bond relative to the aromatic ring by 20.7(3)°, and the O(2)−Al(2)−O(3) bite angle is 91.2(2)°. It is interesting to note that the carboxylate groups display a bidentate coordination mode with *syn−anti* conformation (see **III**, Chart 1) and both bonded aluminum atoms slightly deviate in the opposite direction from the plane of the carboxylate group (0.43(1) and 0.22(1) Å for the Al(1) and Al(2) atoms, respectively). The aryloxide oxygen atom has an approximately planar geometry with bond angles 109.9−124.9° and lies 0.199(5) Å above the plane defined by the Al_2C environment. The aluminum atoms are in a distorted-tetrahedral environment with widened C−Al−C bond angles (average 122°) and narrowed O−Al−O bond angles. Although the O(3)−Al(1)−O(1′) (95.6(2)°) and O(2)−Al(2)−O(3) (91.2(2)°) angles are significantly different due to the nature of the framework structure, these values are very close to the corresponding bond angles observed for the related tetranuclear organoaluminum compound derived from dicarboxylic acid, $[Me_2AlO_2CC_6H_4CO_2\text{-}AlMe_2]_2$.[4b] It is worth noting that compound **1** has a framework structure related to the $[Me_2AlO_2CC_6H_4CO_2\text{-}AlMe_2]_2$ adduct[4b] in such a way that the two related by symmetry carboxylate groups in the skeleton of the latter are replaced by aryloxide oxygen atoms; i.e., the two three-atom bridge centers in the latter were reduced to two one-atom bridge centers in the former. Thus, the monocentered M−O−M bridging alkoxide group can be considered as a compressed three-centered M−O−C−O−M bridging carboxylate group. In this respect the O,O-bidentate carboxylate group can be described as an isomorphic Lewis base center with an alkoxide group. Other aspects concerning the structural relation of the carboxylate, alkoxide, and oxo ligands will be published separately.

Table 1. Selected Bond Distances (Å) and Bond Angles (deg) for the Two Crystallographically Independent Molecules of $[Et_2Al]_4[(\mu\text{-}O_2C)C_6H_4\text{-}2\text{-}\mu\text{-}O]_2$ (1)[a]

molecule a		molecule b	
	Bond Distances (Å)		
Al(1)−O(1′)	1.854(5)	Al(3)−O(4″)	1.839(6)
Al(1)−O(3)	1.875(4)	Al(3)−O(6)	1.873(6)
Al(1)−C(11)	1.949(6)	Al(3)−C(31)	1.97(2)
Al(1)−C(13)	1.969(11)	Al(3)−C(33)	1.98(2)
Al(2)−O(2)	1.835(5)	Al(4)−O(5)	1.826(6)
Al(2)−O(3)	1.879(4)	Al(4)−O(6)	1.885(6)
Al(2)−C(21)	1.931(7)	Al(4)−C(41)	1.97(2)
Al(2)−C(23)	1.95(2)	Al(4)−C(43)	1.935(11)
O(1)−C(7)	1.256(7)	O(4)−C(57)	1.236(9)
O(2)−C(7)	1.267(7)	O(5)−C(57)	1.290(10)
O(3)−C(2)	1.402(7)	O(6)−C(52)	1.399(10)
C(1)−C(7)	1.488(9)	C(51)−C(57)	1.475(12)
	Bond Angles (deg)		
O(1′)−Al(1)−O(3)	95.6(2)	O(4″)−Al(3)−O(6)	97.3(3)
O(2)−Al(2)−O(3)	91.2(2)	O(5)−Al(4)−O(6)	90.2(3)
Al(1)−O(3)−Al(2)	124.9(3)	Al(3)−O(6)−Al(4)	124.4(4)
C(7)−O(1)−Al(1′)	130.8(5)	C(57)−O(4)−Al(3″)	131.8(7)
C(7)−O(2)−Al(2)	123.3(5)	C(57)−O(5)−Al(4)	124.3(7)
C(2)−O(3)−Al(1)	121.1(4)	C(52)−O(6)−Al(3)	121.4(6)
C(2)−O(3)−Al(2)	109.9(4)	C(52)−O(6)−Al(4)	108.7(6)
O(1)−C(7)−O(2)	121.5(8)	O(4)−C(57)−O(5)	120.7(11)
O(1)−C(7)−C(1)	117.9(8)	O(4)−C(57)−C(51)	118.6(11)
O(2)−C(7)−C(1)	120.5(8)	O(5)−C(57)−C(51)	120.7(10)

[a] Atoms labeled with a prime and a double prime belong to the centrosymmetric counterpart of the dimeric units with symmetry codes (−*x*, −*y*, −*z*) and (−*x* + 1, −*y* + 1, −*z* + 1), respectively.

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The Al−O bond distances to the aryloxide group in **1** range from 1.875(4) to 1.879(4) Å and are longer than those to the carboxylate ligand. For the latter, the Al−O bond distances situated in an *anti* direction with respect to the carboxylate group (1.854(5) Å) are longer than those in the *syn* direction (1.835(5) Å), which is consistent with the differentiation observed between the Al−O_{anti} and Al−O_{syn} distances in the related dicarboxylic acid organoaluminum derivative $[Me_2AlO_2CC_6H_4CO_2AlMe_2]_2$.[4b] The distinction in the C−O distances observed among the carboxylate groups in **1** probably results from the *syn*−*anti* coordination mode of these groups to aluminum.

It is interesting to note that the aluminum(III) derivatives of glycolic and lactic acids, isolated from aqueous solutions, consist of monodeprotonated hydroxy carboxylic acid molecules which act as bidentate ligands and these anions are coordinated to aluminum by a hydroxy and a carboxylate oxygen atoms.[9,10]

The tetranuclear structure of compounds **1** is retained in solution. This follows from the cryometric molecular weight determinations in benzene. The ^{1}H and ^{27}Al NMR and IR spectra of **1** are consistent with the structures found in the solid state. The ^{1}H NMR consists of four well-separated pairs of the Al−CH_2CH_3 resonances. These four pairs of ethyl group multiplets attribute to the pairwise equivalent ethyl groups of the diethylaluminum moieties joining the two deprotonated salicylate ligands and the bridgehead diethylaluminum moieties. The ^{27}Al NMR spectrum of **1** shows one broad resonance at 152 ppm (the observed broadening is possibly due to the overlapping of the two resonances of different diethylaluminum moieties), and this chemical shift is similar to that observed for other four-coordinated dialkylaluminum complexes with O,O′-bidentate ligands.[4b,7,11] The IR spectrum of **1** in CH_2Cl_2 solution shows the ν(C−O) bands at 1608 and 1592 cm^{-1}, characteristic of bidentate carboxylate groups.[12]

Experimental Section

All operations were carried out under nitrogen. Triethylaluminum was distilled before use, and salicylic 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.

Synthesis and Characterization of $[Et_2Al]_4[(\mu\text{-}O_2C)C_6H_4\text{-}2\text{-}\mu\text{-}O]_2$ (1). To a suspension of salicylic acid (0.96 g, 7.2 mmol) in dichloromethane (15 mL) was added Et_3Al (1.64 g, 14.4 mmol) dropwise at −78 °C. The reaction mixture was warmed to room temperature. After it was stirred for an additional 1 h, the solution was concentrated and then cooled to −15 °C for 1 day to yield colorless crystals of **1** (0.90 g, 41%). Anal. Calcd for $C_{30}H_{48}O_6Al_4$: C, 58.82; H, 7.90. Found: C, 59.1; H, 8.0. Molecular weight (cryoscopically in benzene): calcd (found) 612.6 (610). ^{1}H NMR (C_6D_6, 25 °C): δ −0.21 [q, 4H, Al(CH_2CH$_3$)]; −0.02 [q, 4H, Al(CH_2CH$_3$)]; 0.18 [q, 4H, Al(CH_2CH$_3$)]; 0.56 [q, 4H, Al(CH_2CH$_3$)]; 0.83 [t, 6H, Al(CH$_2$$CH_3$)]; 0.97 [t, 6H, Al(CH$_2$$CH_3$)]; 1.11 [t, 6H, Al(CH$_2$$CH_3$)]; 1.52 [t, 6H, Al(CH$_2$$CH_3$)]; 6.62 (t, 2H, CH); 6.72 (d, 2H, CH); 6.90 (m, 2H, CH); 7.65 (d, 2H, CH). ^{27}Al NMR (C_6D_6, 25 °C): δ 152 ($w_{1/2}$ = 4800 Hz). IR (CH_2Cl_2, cm^{-1}): 1608 (vs), 1592 (vs), 1552 (s), 1460 (vs), 1430 (s), 1224 (m), 1208 (m), 1145 (w), 1156 (w), 1100 (m), 984 (m), 956 (w), 920 (w), 877 (w), 888 (w), 828 (m), 804 (m), 652 (s), 558 (w), 520 (w), 468 (w), 412 (w), 420 (w), 350 (m).

Table 2. X-ray Data Collection and Structure Analysis Parameters for $[Et_2Al]_4[(\mu\text{-}O_2C)C_6H_4\text{-}2\text{-}\mu\text{-}O]_2$ (1)

mol formula	$C_{30}H_{48}Al_4O_6$
fw	612.63
temp, K	293(2)
cryst size, mm	0.16 × 0.30 × 0.42
wavelength (λ, Å)	Mo Kα (0.710 73 Å)
cryst syst	triclinic
space group	$P\bar{1}$ (No. 2)
a, Å	10.885(2)
b, Å	11.127(2)
c, Å	16.897(3)
α, deg	77.783(14)
β, deg	80.950(15)
γ, deg	65.275(14)
V, Å^3	1811.3(6)
Z	2
calcd density, g cm^{-3}	1.123
linear abs coeff, mm^{-1}	0.164
F(000)	656
2θ range, deg	4.0−47.1
no. of rflns collected	4097
no. of indep rflns	3787 (R_{int} = 0.042)
refinement method	full-matrix least squares on F^2
no. of data/restraints/params	3575/72/478
goodness of fit on F^2	0.941
final *R* values ($I > 2\sigma(I)$)	R1 = 0.0611, wR2 = 0.0840
R index (all data)	wR2 = 0.1259
residual extreme, e Å^{-3}	+0.12/−0.13

X-ray Structure Determination. A single crystal of **1**, suitable for X-ray diffraction studies, was placed in a thin-walled capillary tube (Lindemann glass 0.5 mm) under an inert atmosphere. The tube was plugged with grease and then flame-sealed and mounted on a goniometer head of a four-circle P3 (Siemens AG) diffractometer. The selected crystallographic data, the parameters of data collections, and refinement procedures are presented in Table 2. The crystal class and the orientation matrix were obtained from the least-squares refinement of 30 well-centered reflections randomly selected in the 2θ range 11.6−25.6°. The intensities were collected in the ω−2θ mode. A meaningful crystal decay of 41.8% was noticed. After correction for the Lorentz−polarization effect and crystal decomposition, the equivalent reflections were averaged. The structure was solved by direct methods using the *SHELXS-86* program,[13a] which revealed the positions of the aluminum and oxygen atoms and a majority of the C atoms. The distribution of the peaks showed that compound **1** crystallizes with two crystallographically independent half-molecules in the asymmetric unit, resulting in a *Z* value of 2. Full-matrix least-squares refinement method against F^2 values was carried out by using the SHELXL-93 program.[13b] Neutral-atom complex scattering factors were employed.[13c] All non-hydrogen atoms were refined with anisotropic displacement parameters. The H atoms were refined with fixed geometry, riding on their carrier atoms, with a fixed isotropic displacement parameter equal to 1.2 or 1.5 (methyl group) times the value of the equivalent isotropic displacement parameter of the parent carbon. Difference Fourier maps, calculated at a late stage of the refinement, indicated disorder of ethyl groups in both independent molecules. Final results with *R* = 0.061

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were obtained with a restraint model in which atoms of the ethyl groups were disordered over two sets of positions with adjusted occupancy factors (the final SOF values being in the range 0.58(2)−0.75(2) for major conformers) and chemically equivalent Al−C and C−C distances restrained to be equal. Because of the disorder and large libration coefficients, some of the C−C distances are less accurately determined (especially for molecule b). The somewhat high *R* value is mainly due to the disorder and crystal decomposition. The final weighting scheme for **1** was $w^{-1} = \sigma^2(F_o^2) + (0.0380P)^2$, where $P = {}^1/_3(F_o^2 + 2F_c^2)$.

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Supporting Information Available: Listings of crystallographic data, atomic parameters, anisotropic thermal parameters, and complete bond distances and angles for **1** (9 pages). Ordering information is given on any current masthead page.

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