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Structure Investigations of Dichloroaluminum Benzoates: An Unprecedented Example of a Monomeric Aluminum Complex with a Chelating Carboxylate Ligand

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Dichloroaluminum benzoate and its adducts with Lewis bases show a large structural variety from molecular complexes to ionic species as indicated by X-ray diffraction, spectroscopic studies, and quantum-chemical calculations.

Although the carboxylate anion is one of the most abundant ligands in the coordination chemistry, the chemistry of aluminum carboxylates is largely an unexplored area. There have been many attempts to prepare discrete molecular aluminum carboxylate complexes with well-defined structures. In part, this is in view of the importance of such single molecular species as useful precursors in materials science,[1] structural models for functional materials based on aluminum carboxylates,[2] as well as valuable models for elucidation of the preferred coordination mode of a carboxylate ligand to the metal center.[3] Nevertheless, there is a relative paucity of structural data for simple aluminum-carboxylate systems. The first crystallographic evidence for organoaluminum carboxylate species was provided by Atwood and co-workers in their structural determinations of the $[MeCO_2(AlMe_3)_2]^-$ anion with the monodentate carboxylate ligand **I** (Scheme 1).[4] More recently, the structural characterization of a series of di-*tert*-butylaluminum carboxylates[5] and dimethylaluminum derivative of 2,4,6-triphenylbenzoic acid[6] confirmed dimeric, carboxylate-bridged structures of $[R_2Al(\mu\text{-}O_2CR')]_2$-type compounds in the solid state. Simultaneously, Barron suggested that a carboxylate-bridged structure **II** is preferred and that the chelate mode **III** is unavailable for carboxylates on aluminum because of the ring strain associated with the AlO_2C cycle, and this assumption was supported by theoretical calculations.[5] Worthy of note is also a number of crystallographically characterized alkylaluminum compounds derived from bifunctional carboxylic acids exhibiting a large structural variation.[2c,7]

All the mentioned efforts have focused on the synthesis and characterization of alkylaluminum species. Surprisingly, related aluminum halogen complexes have not been explored. Our interest in chloroaluminum carboxylates stems from the potential use of these derivatives as an anion trap in composite polymer electrolytes applied in lithium or lithium ion batteries.[8] Herein, we report on the solid state and solution structure investigations of dichloroaluminum benzoate and its adducts with 4-methylpyridine (*py-Me*), and provide the first structurally authenticated aluminum complex with a chelating carboxylate ligand. The addition of 1 molar equiv. of $MeAlCl_2$ to benzoic acid in CH_2Cl_2 results in the quantitative formation of dichloroaluminum benzoate which was isolated by crystallization from the postreaction solution as the dimeric adduct $[Cl_2Al(\mu\text{-}O_2CPh)]_2$ (**1**). The molecular structure of **1** consists of two Cl_2Al units bridged by benzoate groups (Figure 1). The Al−O bond lengths ($Al-O_{avg}$ = 1.766 Å) are slightly shorter than that in the aluminum alkyl analogues characterized previously (cf. $Al-O_{avg}$ = 1.810 Å),[5] reflecting the different Lewis acidity of the X_2Al species involved. A salient feature of the structure of **1** is the almost flat central eight-membered $Al_2O_4C_2$ ring in contrast to the chairlike conformation of $[{}^tBu_2Al(\mu\text{-}O_2CPh)]_2$.[5] Barron

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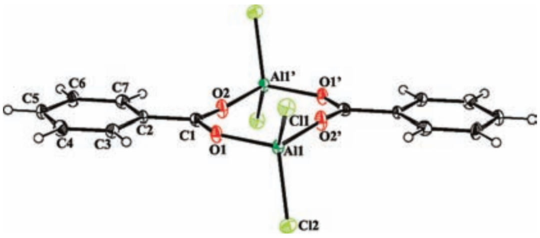


Figure 1. Molecular structure of **1** with thermal ellipsoids set at a 40% probability level.

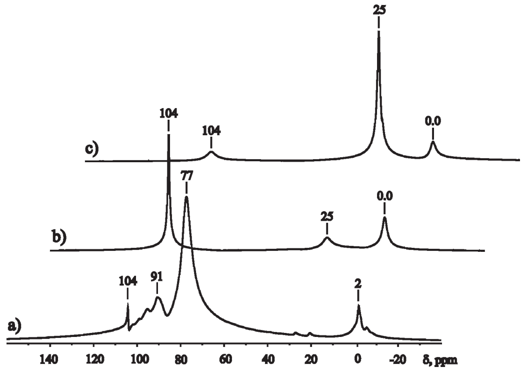
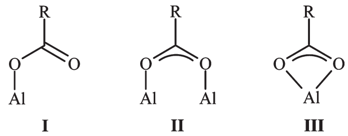


Figure 2. ^{27}Al NMR spectra of: (a) **1** in CD_2Cl_2, (b, c) **1** with added 2 or 4 equiv. of *py-Me* in thf-d_8, respectively.

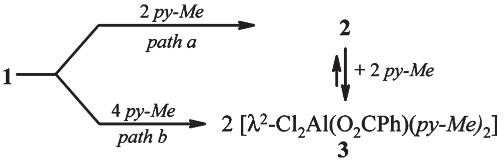
Scheme 1



observed for a series of [^{t}Bu$_2$Al(μ-O$_2$CR)]$_2$ complexes a correlation between the extent of the puckering of the $Al_2O_4C_2$ ring with the steric bulk of the carboxylate alkyl substituent.[5] The observed planar conformation of the central ring in **1**, i.e., the complex with reduced steric bulk on the metal centers in comparison to that in [^{t}Bu$_2$Al(μ-O$_2$CPh)]$_2$, indicate that electronic factors may significantly affects conformation of the $Al_2O_4C_2$ cyclic core. The similar IR spectra of **1** as a Nujol mull and a CH_2Cl_2 solution with bands at 1602 and 1564 cm^{-1} [ν_{asymm}(CO$_2$)],and 1454 and 1437 cm^{-1} [ν_{symm}(CO$_2$)] (see Figures S1 and S2) suggested the retention of the dimeric form in solution. Indeed, the ^{27}Al NMR spectrum of **1** in noncoordinating solvent (CD_2Cl_2) is dominated by the single resonance at 77 ppm[9] consistent with the four-coordinate dimeric structure along with a number of lower intensity resonances in the higher and lower field (Figure 2a). The presence of the latter signals indicate that the dimeric form of **1** is unstable in solution and rearrange to a number of likely neutral and ionic aluminum species with four- and six-coordinate aluminum centers.[10]

We were also curious as to how the addition of *py-Me* as a strong Lewis base might impact on the structure of chloroaluminum carboxylate species. Monitoring of the reaction of **1** with 2 equiv of *py-Me* in thf-d_8 (i.e., the Al:*py-Me* molar ratio equal to 1:1) by NMR and IR spectroscopies reveals quantitative formation of tentative ionic species **2** of as yet unidentified structure (Scheme 2, path a). For instance, the treatment of **1** by *py-Me* leads to disappearance of the ^{27}Al resonances due to **1** and to the appearance of a sharp signal at 104 ppm ($\omega_{1/2}$ = 105 Hz) characteristic of the [AlCl$_4$]$^-$ anion in addition to resonance at 0 ppm ($\omega_{1/2}$ = 320 Hz) associated with a six-coordinate cationic species (Figure 2b).[10] Surprisingly, there was a lack of a resonance indicative of the formation of a five-coordinate molecular adduct [Cl$_2$Al(λ^2-O$_2$CPh)(*py-Me*)] (**2′**). The IR spectrum of **2** in solution exhibits a relatively complex pattern in the range of the ν_{asymm}(CO$_2$) with a strong band at 1649 cm^{-1} and two weaker bands at 1631 and 1579 cm^{-1} (only one band is observed for ν_{symm}(CO$_2$) at 1441 cm^{-1}). These data indicate a nontrivial structure for **2** in a solution in which various coordination modes of the benzoate ligand are likely involved. An effort was taken to confirm the structure of **2** by X-ray crystallography. However, contrary to expectations, crystals of the unprecedented six-coordinate molecular adduct [Cl$_2$Al(λ^2-O$_2$CPh)(*py-Me*)$_2$] (**3**) were obtained.

Scheme 2



In fact, **3** was isolated essentially quantitatively from the reaction of **1** with 4 equiv of *py-Me* (Scheme 2, path b).

The spectroscopic data for **3** are in accordance with the proposed formulation, which is confirmed by a single-crystal X-ray diffraction study. The IR spectrum of **3** in Nujol shows bands at 1627 cm^{-1} [ν_{asymm}(CO$_2$)] and 1451 cm^{-1} [ν_{symm}(CO$_2$)] consistent with the monomeric chelate structure. The ^{27}Al NMR spectrum of **3** in thf-d_8 revealed the presence of a single strong resonance at 25 ppm ($\omega_{1/2}$ = 165 Hz) consistent with a six-coordinate aluminum center,[10] along with significantly lower intensity resonances corresponding to **2** (Figure 2c), which indicates that the molecular adduct **3** is in equilibrium with the ionic form **2** in a solution. It is interesting to note that dichloroaluminum benzoate and its reactions with *py-Me* exhibit a number of features that are consistent with those observed previously for dichloroaluminum acetylacetonate complex, [Cl$_2$Al(*acac*)],[11] i.e., both compounds form labile molecular species which readily equilibrate with ionic species in solution,[11a] and form ionic species in the presence of Lewis bases[11b,c] or even molecular adducts, cf. [Cl$_2$Al(*acac*)(*py-Me*)$_2$].[11b]

The molecular structure of **3** consists of a discrete mononuclear unit with the aluminum atom in a distorted octahedral configuration (Figure 3). Strikingly, the carboxylate group acts as a symmetrical chelating ligand (O−Al−O = 66.4(1)° and O−C−O = 115.8(3)°). The pyridine ligands are mutually trans (N−Al−N = 174.1(1)°) with coplanar aromatic rings, and the Cl1−Al−Cl2 angle of 101.41(5)°). Both the Al−O (1.975(1) Å) and the Al−Cl (2.232(1) Å) distances

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[9] This chemical shift is similar to that observed for the chemically closely related four-coordinate [Cl$_2$Al(*acac*)] complex exhibiting the ^{27}Al resonances at 88 ppm (see refs 10 and 11a).

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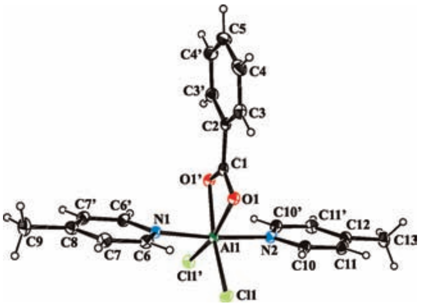

Figure 3. Molecular structure of **3** with thermal ellipsoids set at a 40% probability level.

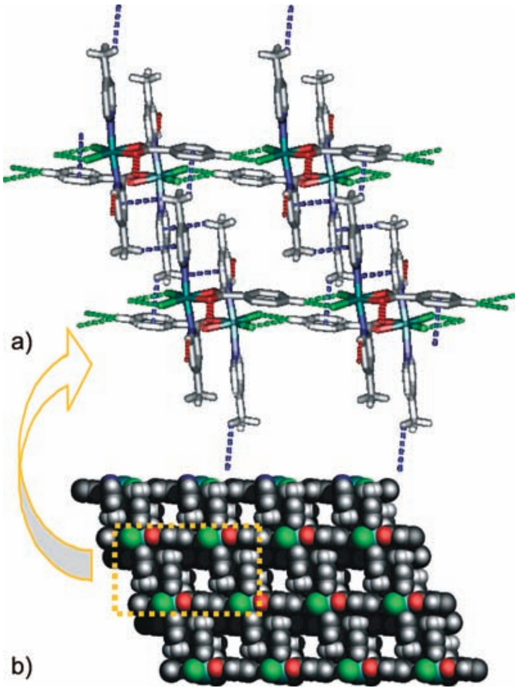

Figure 4. Crystal structure of **3**: (a) complementary C$-$H$_{ar}\cdots$O (red), C$-$H$_{ar}\cdots$Cl (green), and C$-$H$_{aliph}\cdots\pi$ (blue) interactions in rectangular meshes, (b) space-filling model of the crystal lattice viewed along the *b* axis.

are slightly longer than those observed for the four-coordinate dimer **1**, and the axial Al$-$N distances are 2.057(3) and 2.065(3) Å. Compound **3** represents the first monomeric aluminum carboxylate to be structurally characterized as well as the first observation of a chelating carboxylate ligand in an aluminum complex.

Interestingly, analysis of the crystal structure of **3** revealed that the monomeric units self-assemble via C$-$H$_{aliph}$...π and C$-$H$_{ar}$...Cl interactions to produce a 2D grid structure with rectangular meshes of dimensions 7.4 × 9.2 Å (Figure 4 and Figure S5 in the Supporting Information). These 2D grids are further organized by comple-mentary C$-$H$_{ar}\cdots$O interactions into 3D network featuring open channels directed along the *b* axis (Figure 4b).

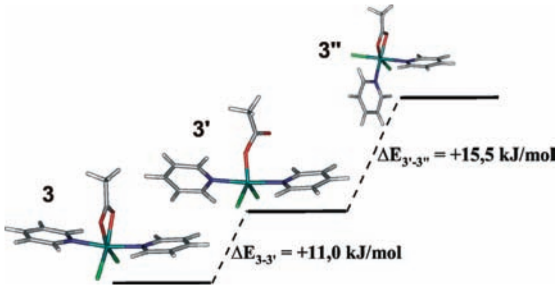

Figure 5. DFT calculated geometries of compounds **3**, **3**′, and **3**″.

To provide a fuller basis for discussion of the relative stability of dichloroaluminum carboxylate adducts with pyridine-type ligands and preferences for monodentate or chelating carboxylate density functional theory (DFT) calculations were carried out using Gaussian 03 program package.[12] The DFT calculations for model acetate compounds were obtained at B3LYP/cc-pVTZ level of theory (see Figure S6 in the Supporting Information).[12] These calculations on the corresponding systems show that stability in these systems can be readily understood in terms of the relative energetics of the reactants and products. Model calculations of the reaction of **1** with 2 equiv. of pyridine (*py*) (ΔE_{ZPC} = $-$22.7 kJ/mol, Scheme 2 path a and Scheme S1a in the Supporting Information) demonstrated that this process is far less exothermic than that of the reaction of **1** with 4 equiv. of *py* with overall energy gains of ΔE_{ZPC} = $-$92.4 kJ/mol (Scheme 2, path b and Scheme S1c in the Supporting Information). These calculations are in agreement with experimental data and confirm that the formation of the putative five-coordinate molecular adduct **2**′ or the ionic species **2** is less favorable than the formation of the thermodynamically stable six-coordinate molecular complex **3**. The determined total energies for **3** and its cis isomer **3**′ shows that the former complex is strongly favored (Figure 5). The comparison of relative energies for **3** and the five-coordinate adduct **3**″ featuring a monodentate carboxylate ligand indicates that the chelating mode for a carboxylate ligand is stabilized by 13.2 kJ/mol.

In conclusion, the study has revealed a complex nature of chloroaluminum benzoates featuring both molecular and ionic forms with different coordination numbers of the metal center and various coordination modes of the carboxylate ligand.

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Supporting Information Available: Details of syntheses, crystal data, and computational data (PDF and CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[12] For full details of the theoretical calculations (with additional B3LYP/6-311+G(d,p) calculations) see the Supporting Information.