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Aluminum hippurate and diglycolate as multinuclear metal carboxylates

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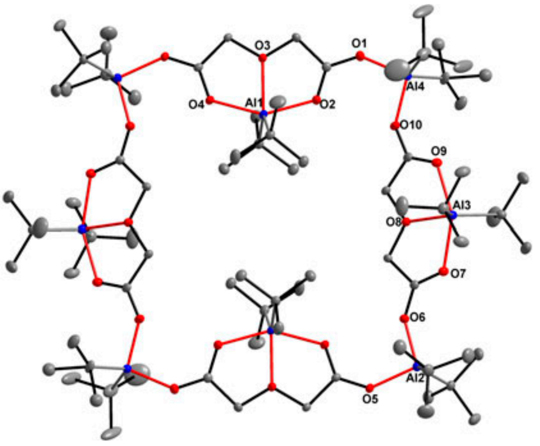

Reactions of functionalized carboxylic acids with tri-*tert*-butyl aluminum were studied. Multinuclear aluminum carboxylates $^t\text{Bu}_8\text{Al}_4[\text{NC(O)(Ph)CH}_2\text{CO}_2]_2$ (**1**) and $^t\text{Bu}_{16}\text{Al}_8[\text{O}_2\text{C(CH}_2\text{)O(CH}_2\text{)CO}_2]_4$ (**2**) were synthesized in reactions of $^t\text{Bu}_3\text{Al}$ with hippuric and diglycolic acids, respectively. A molecule of **1** consists of four aluminums and two hippurate moieties, which form three fused heterocyclic rings as a skeleton framework. Compound **2** is an octanuclear complex consisting of five fused heterocyclic rings, one $\text{Al}_8\text{O}_{14}\text{C}_{12}$ 34-membered one and four AlO_3C_4 eight-membered ones.

Keywords: Aluminum; Hippuric acid; Diglycolic acid; Multinuclear complexes; X-ray diffraction study

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1. Introduction

Carboxylic acids with additional functional groups COOH, OH, or NHR have attracted attention as precursors of multidentate ligands in the chemistry of group 13 metals due to the possibility of various coordination modes [1–16]. Multicarboxylate ligands are good candidates for the construction of metal organic frameworks (MOFs) that display rich structural diversity [17, 18]. Lately, we have reported the reaction of trialkylaluminum compounds with diphenic acid in a 2:1 M ratio resulting in formation of dialkylaluminum dicarboxylates, $[Et_4Al_2(OOCC_{12}H_8COO)]_3$, and $[i\text{-}Bu_4Al_2(OOCC_{12}H_8COO)]_2$ [19]. Recently, the hexanuclear complex $Et_{12}Al_6[CH(COO)_2]_2(THF)_2$ has been obtained in the reaction of triethylaluminum with malonic acid [20]. Our studies have shown that using functionalized carboxylic acids having additional oxygens leads to the formation of multinuclear complexes in reactions with trialkylaluminum. In this article, we extend our study to the synthesis and characterization of alkylaluminum hippurate and diglycolate bearing carboxylate ligands having additional NHR and COOH groups, respectively.

Hippuric (benzoylaminoethanoic) and diglycolic (oxydiacetic) acids are ubiquitous ligands in coordination chemistry of transition metals (see for example [21–34]), whereas only a few examples of main group metal diglycolates have been published [35, 36]. Reactions of hippuric and diglycolic acids with group 13 metal trialkyls have not been investigated.

2. Experimental

2.1. *Materials and instrumentation*

All manipulations were carried out using standard Schlenk techniques under an inert gas atmosphere. Solvents were distilled over the blue benzophenone-K complex. $^tBu_3Al{\cdot}OEt_2$ was synthesized as described [37]. ^1H NMR spectra were obtained on a Mercury-400BB spectrometer. Chemical shifts were referenced to the residual proton signals of $CDCl_3$ (7.26 ppm). Elemental analyses were obtained on a PerkinElmer 2400 analyzer.

2.2. *Synthesis of $^tBu_8Al_4[NC(O)(Ph)CH_2CO_2]_2$ (1)*

A solution of $^tBu_3Al{\cdot}OEt_2$ (1.360 g, 5 mM) in CH_2Cl_2 (10 cm^3) was added dropwise into a solution of hippuric acid (0.448 g, 2.5 mM) in CH_2Cl_2 (30 cm^3) at –76 °C. The reaction mixture was allowed to warm slowly to room temperature. The solvent was removed *in vacuo*. A viscous yellow product was obtained. Pure **1** was obtained after crystallization from the $n\text{-}C_6H_{14}\text{-}CH_2Cl_2$ solution at 7 °C (Yield: 0.515 g, 0.560 mM, 45 wt%). Compound **1** undergoes decomposition at 285 °C. Anal. Calcd for $C_{50}H_{86}Al_4N_2O_6$ (%): C, 65.28; H, 9.36. Found: C, 64.91; H, 9.52.

^1H NMR ($CDCl_3$) δ: 7.80 (4H, m, H_{aromat}), 7.67 (2H, m, H_{aromat}), 7.57 (4H, m, H_{aromat}), 4.64 (4H, s, $C\underline{H}_2$), 0.90 [36H, s, $(C\underline{H}_3)_3CAl$], 0.80 [36H, s, $(C\underline{H}_3)_3CAl$] ppm. Due to a very low solubility of the compound, it was not possible to measure the ^{13}C NMR spectrum.

2.3. *Synthesis of $^tBu_{16}Al_8[O_2C(CH_2)O(CH_2)CO_2]_4$ (2)*

A solution of $^tBu_3Al{\cdot}OEt_2$ (1.360 g, 5 mM) in CH_2Cl_2 (10 ml) was added dropwise into a suspension of diglycolic acid (0.335 g, 2.5 mM) in CH_2Cl_2 (20 cm^3) at –76 °C. The reaction mixture was allowed to warm slowly to room temperature. The solvent was removed *in vacuo* and a viscous colorless product was obtained. Pure **2** precipitated after addition of *n*-hexane to the reaction product (Yield: 1.295 g, 0.625 mM, 80 wt%). X-ray-quality crystals were obtained from the n-C_6H_{14}-CH_2Cl_2 solution at –20 °C. Compound **2** undergoes decomposition at 280 °C. Anal. Calcd for $C_{80}H_{160}Al_8O_{20}$ (%): C, 57.90; H, 9.65. Found: C, 57.56; H, 9.90.

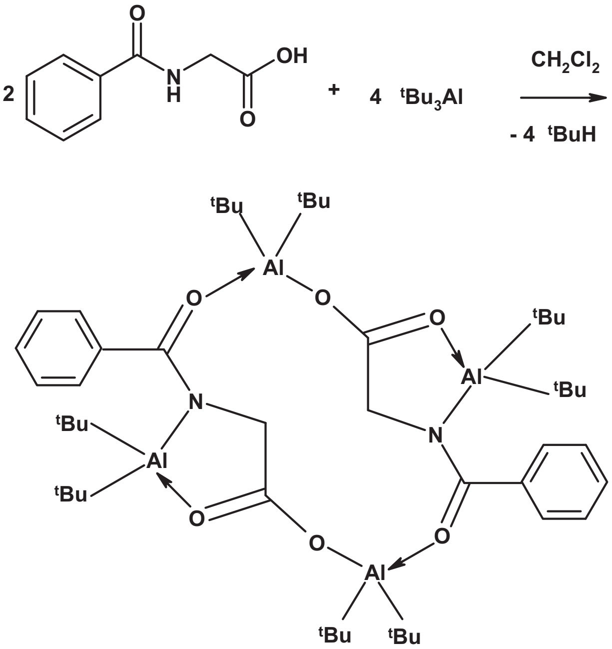
^{1}H NMR ($CDCl_3$) δ: 4.53 (16H, s, $C\underline{H}_2$), 0.90 [72H, s, $(C\underline{H}_3)_3CAl$], 0.83 [72H, s, $(C\underline{H}_3)_3CAl$] ppm. Due to a very low solubility of the compound, it was not possible to measure the ^{13}C NMR spectrum.

2.4. *Crystallographic data*

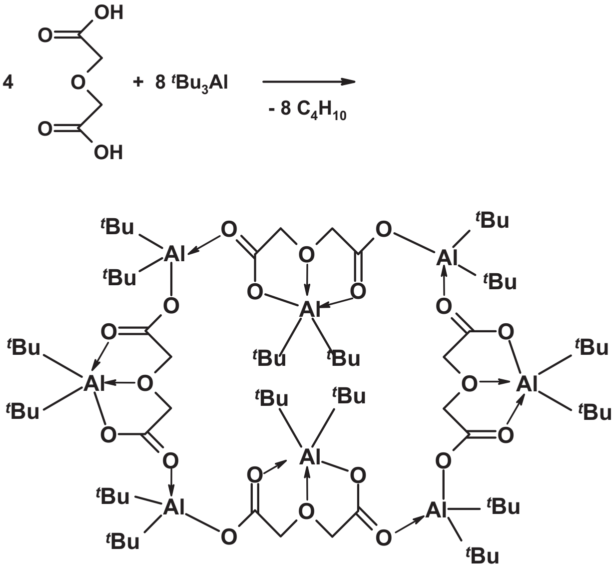
Single crystal data for **1** and **2** were collected at 100(2) K using graphite-monochromated Mo/Kα radiation ($\lambda = 0.7107$ Å). Experiments were performed on an Xcalibur Opal CCD κ-axis (Oxford Diffraction) and a Gemini A Ultra (Agilent Technologies) diffractometers, respectively. The CrysAlis^{Pro} program [38] was used for data collection, cell refinement, data reduction, and the empirical absorption corrections using spherical harmonics, implemented in a multiscan scaling algorithm. The structures were solved using direct methods and refined with full-matrix least-squares using the SHELXS97 and SHELXL97 programs, respectively [39], both implemented in the OLEX2 program [40]. For **2**, a preliminary model with all non-hydrogen atoms refined with anisotropic temperature factors indicated disordered *tert*-butyl groups bonded to Al4 as well as high residual electron density distributed throughout channels along the [101] direction. The calculated total solvent accessible volume per unit cell amounted to 5460.2 Å^3 (~12%) pointing to a severely disordered solvent molecule (a void volume of 145 Å^3). This could not be resolved into any meaningful atomic positions and was treated, therefore, using the MASK procedure [41] implemented in the OLEX2 program [40]. The electron density was estimated to be 103 electrons per unit cell, and the correction of the F_{obs} data to remove its contribution resulted in R_1 falling to 6.30%, wR_2 falling to 16.16%, and the residual electron density falling to well below 0.45 e/Å^3. In the final model, all non-hydrogen atoms were refined with anisotropic temperature factors (also in the case of one *tert*-butyl group bonded to Al4, where a multisite model was applied and refined to s.o.f. of 0.782(5) for a major component). In the case of **1**, the final model with all non-H atoms refined anisotropically gave $R_1 = 4.61\%$ and $wR_2 = 12.28\%$. In both cases, the hydrogens were introduced in geometrically idealized positions and refined with a riding model with U_{iso}(H) values of $1.2 \times U_{eq}$(C) or $1.5 \times U_{eq}$(C) for methyl groups.

3. Results and discussion

The treatment of hippuric and diglycolic acids with two molar equivalents of ^{t}Bu$_3$Al in OEt_2 produces $^tBu_8Al_4[NC(O)(Ph)CH_2CO_2]_2$ (**1**) and $^tBu_{16}Al_8[O_2C(CH_2)O(CH_2)CO_2]_4$ (**2**), respectively, as shown in schemes 1 and 2. The pure compounds obtained after crystallization from the n-C_6H_{14}-CH_2Cl_2 solutions were examined by X-ray crystallography, NMR spectroscopy, and elemental analysis. The molecular structures of the compounds were determined on the basis of X-ray diffraction studies and are shown in figures 1 and 2. The



Scheme 1. Synthesis of $^t\mathrm{Bu}_8\mathrm{Al}_4[\mathrm{NC(O)(Ph)CH_2CO_2}]_2$ (**1**).



Scheme 2. Synthesis of $^t\mathrm{Bu}_{16}\mathrm{Al}_8[\mathrm{O_2C(CH_2)O(CH_2)CO_2}]_4$ (**2**).

crystal data as well as the details of the data collection and refinement are listed in table 1. A molecule of **1** consists of two hippurate units bonded to four, four-coordinate aluminum ions. The carboxylate groups are bidentate bridging between the carboxylates to form

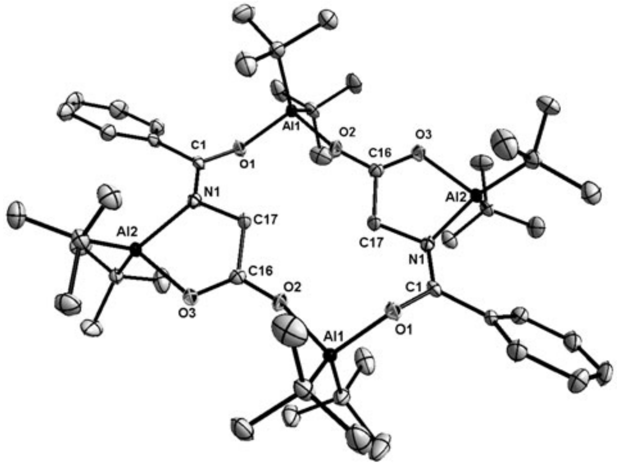


Figure 1. Molecular structure of ${}^{t}Bu_8Al_4[NC(=O)(Ph)CH_2CO_2]_2$ (**1**) with atomic displacement parameters set at the 50% level. Hydrogens are omitted for clarity. Selected interatomic distances (Å) and angles (°): Al1–O1 1.815 (2), Al1–O2 1.834(2), Al2–O3 1.899(2), Al2–N1 1.968(2), C16–O2 1.253(3), C16–O3 1.260(3), C1–O1 1.290(3), C1–N1 1.318(3), O2–C16–O3 125.2(2), O2–C16–C17 117.0(2), O3–C16–C17 117.8(2), C1–N1–C17 114.5(2), C1–N1–Al2 133.2(2), C17–N1–Al2 110.7(2), O1–C1–N1 122.5(2), O1–C1–C2 118.2(2), N1–C1–C2 119.2(2).

bridges containing Al(1), whereas Al(2) ions are involved in the formation of five-membered C_2NOAl chelate rings. Each aluminum is bonded to two ${}^{t}Bu$ groups and two heteroatoms.

A skeleton framework of a molecule of **1** consists of three fused heterocyclic rings with all the ${}^{t}Bu$ groups and the aromatic rings situated outside of the central $Al_2O_4N_2C_6$ ring. The shortest and the longest interatomic distances in this central empty ring are O(2)-C(17), 3.185(3) Å and O(1)-O(1), 6.593(3) Å, respectively. The sums of the angles around the atoms, [Σ(N1) = 358.4], [Σ(C16) = 360.0], and [Σ(C1) = 359.9], show the sp^2 hybridization of the atoms. The values of the torsion angles, O(2)-C(16)-O(3)-Al(2) – 176.8(2)° and O (2)-C(16)-C(17)-N(1) – 179.2(2)°, indicate that O(2) and the C_2NOAl ring are situated almost on the same plane. A delocalized structure within the carboxylate groups is shown by almost the same bond lengths: C(16)-O(2) – 1.253(3) Å and C(16)-O(3) – 1.260(3) Å. Similarly, a delocalized structure within the amidate groups is also observed: [C(1)-N(1) – 1.318(3) Å, C(1)-O(1) – 1.290(3) Å]. The ${}^{1}H$ NMR spectrum of **1** revealed two singlets at 0.80 and 0.90 ppm of ${}^{t}BuAl$ group protons, which indicated the inequivalence of these groups due to the two different Al sites.

The molecules of **2** crystallized with the solvent molecules occupying approximately 12% of the unit cell volume. The presence of the signal at 5.30 ppm in the ${}^{1}H$ NMR spectrum indicated dichloromethane as a solvent present in the crystal structure. X-ray diffraction studies revealed severe disorder of the solvent, indicating its weak interactions with molecules of **2**. The centrosymmetric molecule of the aluminum diglycolate **2** consists of four diglycolate units bonded to four, four-coordinate, and four, five-coordinate aluminum ions. Four-coordinate aluminum bridges between two different diglycolate units, whereas five-coordinate aluminums are bonded to two ${}^{t}Bu$ groups and three oxygens of the same diglycolate units.

The skeleton framework of the molecule consists of five fused heterocyclic rings, one $Al_8O_{14}C_{12}$ 34-membered one and four AlO_3C_4 eight-membered ones. Due to the presence

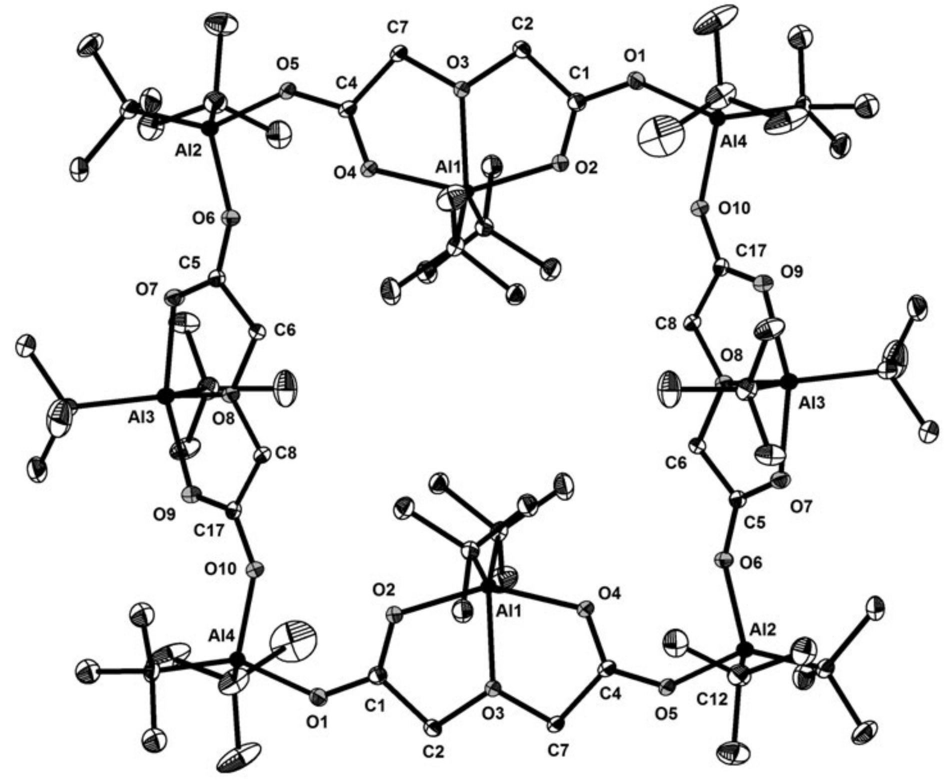


Figure 2. Molecular structure of $^{t}\mathrm{Bu}_{16}\mathrm{Al}_8[\mathrm{O}_2\mathrm{C}(\mathrm{CH}_2)\mathrm{O}(\mathrm{CH}_2)\mathrm{CO}_2]_4$ (**2**) with atomic displacement parameters set at the 20% level. Hydrogens are omitted for clarity. One ^{t}Bu group bonded to the Al4 atom is disordered. Selected interatomic distances (Å) and angles (°): Al1–O2 1.974(2), Al1–O3 2.022(2), Al1–O4 1.978(2), Al1–C9 1.992(3), Al1–C10 1.993(3), Al2–O5 1.857(2), Al2–O6 1.827(2), Al2–C12 1.973(4), Al2–C11 1.982(3), Al3–O7 1.999(2), Al3–O8 1.999(2), Al3–O9 2.022(2), Al3–C14 1.988(3), Al3–C13 1.988(3), Al4–O1 1.845(2), Al4–O10 1.829(2), Al4–C15 1.962(3), Al4–C16 1.969(4), Al4–C26 1.986(12), O1–C1 1.265(3), O2–C1 1.245(3), O4–C4 1.247(3), O5–C4 1.257(3), O3–C2 1.434(3), O3–C7 1.434(3), O9–C17 1.247(3), O10–C17 1.260(3), O6–C5 1.261(3), O7–C5 1.247(3), O8–C6 1.433(3), O8–C8 1.426(3), O2–Al1–O3 75.0(1), O2–Al1–O4 149.9(1), O2–Al1–C9 94.8(1), O2–Al1–C10 96.7(1), O4–Al1–O3 74.9(1), O4–Al1–C9 98.2(1), O4–Al1–C10 96.9(1), C9–Al1–O3 117.5(1), C9–Al1–C10 127.2(1), C10–Al1–O3 115.3(1), C2–O3–Al1 120.9(2), C7–O3–Al1 121.0(2), C7–O3–C2 117.7(2), C6–O8–Al3 120.8(2), C8–O8–Al3 121.7(2), C8–O8–C6 116.4(2).

of Al1-O3 and Al3-O8 coordinate bonds, all $\mathrm{AlO}_3\mathrm{C}_4$ rings were subdivided to two $\mathrm{AlO}_2\mathrm{C}_2$ fused rings. Two Al1 ions and four ^{t}Bu groups are situated inside, whereas Al2, Al3, and Al4 together with twelve ^{t}Bu groups are placed outside of the $\mathrm{Al}_8\mathrm{O}_{14}\mathrm{C}_{12}$ ring. The large 34-membered ring is rare in group 13 carboxylate chemistry; a 32-membered ring complex obtained in the reaction of $\mathrm{Me}_3\mathrm{Al}$ with amino acid 2,2-diphenylglycine is the only example with a large ring [8].

The similar C–O bond length in the carboxylate groups [1.261.(3) to 1.247.(3) Å] indicates delocalized structure within these groups. All the Al1-O and Al3-O bonds [Al1-O2 1.974(2), Al1-O4 1.978(2), Al1-O3 2.022(2), and Al3-O7 1.999(2), Al3-O9 1.999(2), Al3-O8 2.022(2) Å] are significantly longer than Al–O bonds in ethyl aluminum malonate [1.824(1) to 1.901(1) Å], ethyl aluminum diphenate [1.806(3) to 1.847(3) Å], *iso*-butyl aluminum diphenate [1.831(1) to 1.849(1) Å], and methyl aluminum phthalate [1.818(1) to

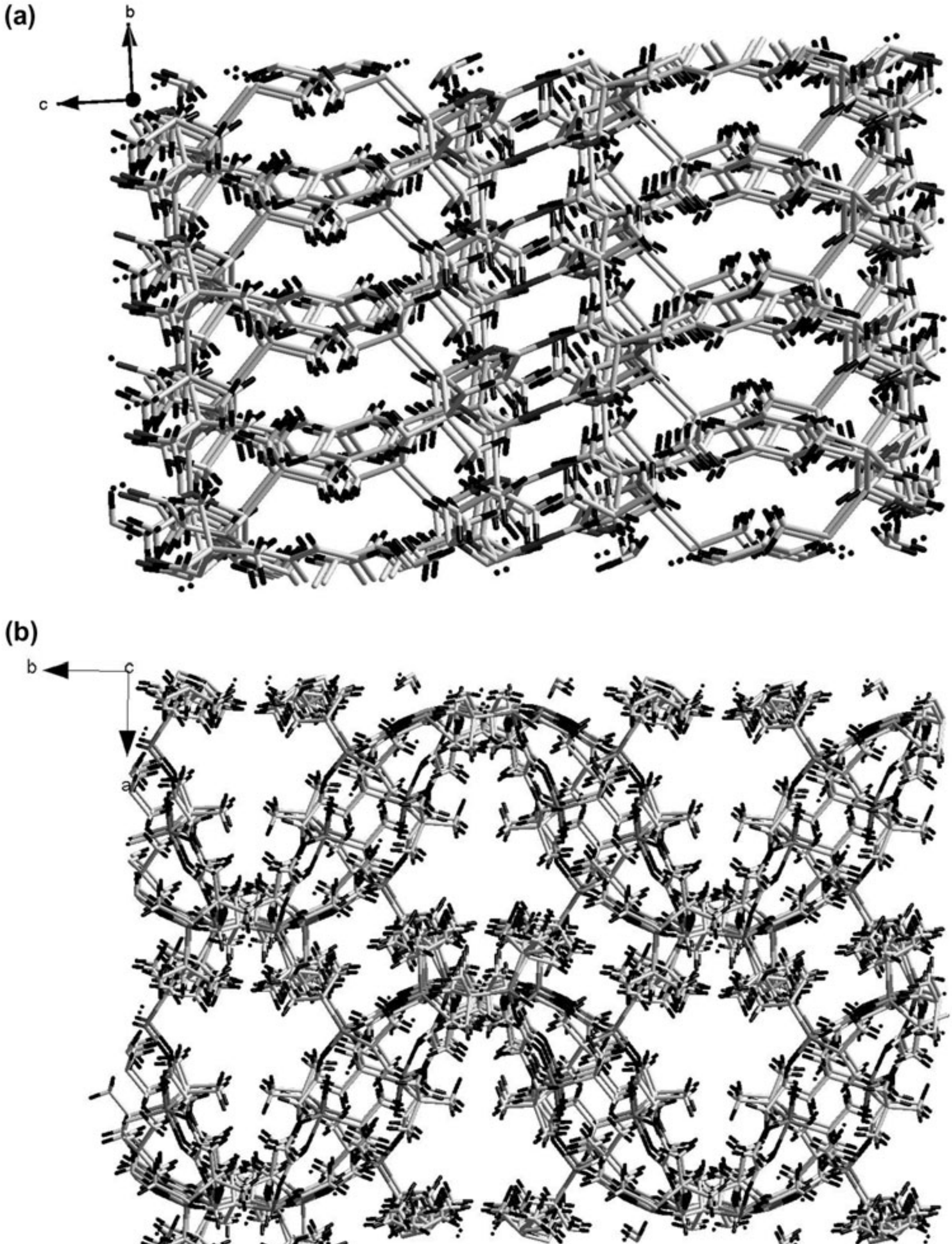


Figure 3. Crystal structures of **1** and **2** (hydrogens are included). (a) View along the *a* axis of the structure of **1**, (b) View along the *c* axis of the structure of **2**.

1.870(1) Å] [1a, 3, 4]. On the other hand, Al2-O and Al4-O bond lengths [Al2-O5 1.857 (2), Al2-O6 1.827(2), Al4-O1 1.845(2), and Al4-O10 1.829(2) Å] are similar to those of aluminum malonate, -diphenates, and -phthalate. Very probably, the lengthening of Al1-O

Table 1. Crystal data and data collection parameters for **1** and **2**.

	1	**2**
Empirical formula	$C_{50}H_{86}Al_4N_2O_6$	$C_{80}H_{160}Al_8O_{20}$
Formula weight	919.13	1657.92
Temperature (K)	100(2)	100(2)
Wavelength (Å)	0.71073	0.7107
Crystal system	Monoclinic	Monoclinic
Space group	*C2/c*	*P 1 21/n 1*
a (Å)	24.814(1)	13.595(1)
b (Å)	8.3837(6)	22.761(3)
c (Å)	27.805(2)	17.716(3)
α (°)	90	90
β (°)	102.736(6)	95.11(1)
γ (°)	90	90
V (Å^3)	5641.9(6)	5460(1)
Z	4	2
D_{calc} (g cm^{-3})	1.082	1.008
Absorption coefficient (mm^{-1})	0.126	0.128
F(0 0 0)	2000	1808
Crystal size (mm)	0.15 × 0.10 × 0.08	0.30 × 0.03 × 0.02
Θ range for data collection (°)	1.6794–28.9697	25.00–3.24
Index ranges	$-30 \le h \le 30$, $-9 \le k \le 10$, $-33 \le l \le 24$	$-16 \le h \le 16$, $-27 \le k \le 27$, $-21 \le l \le 21$
Reflections collected	9987	121,045
Independent reflections	5242 [R_{int} = 0.0342]	9596 [R_{int} = 0.0755]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	5242/0/292	9596/43/528
Goodness-of-fit on F^2	0.961	1.063
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0461$, $wR_2 = 0.1228$	$R_1 = 0.0630$, $wR_2 = 0.1616$
R indices (all data)	$R_1 = 0.0800$, $wR_2 = 0.1593$	$R_1 = 0.0788$, $wR_2 = 0.1714$
Max./min. residual electron density	0.369 to −0.319	0.436 to −0.232

and Al3-O bonds is caused by the higher coordination number for Al1 and Al3 in comparison with four-coordinate Al2 and Al4. The sums of the angles around O3 and O8 [Σ(O3) = 359.5, Σ(O8) = 358.8] show the absence of steric strain in the glycolate moieties. The glycolate moieties adopt highly distorted trigonal bipyramidal geometries around the five-coordinate aluminums, Al1 and Al3, with O2 and O4 and O7 and O9 occupying the axial positions [O2-Al1-O4 = 149.86°, O7-Al3-O9 = 150.38(9)°], and C9, C10, O3 for Al1, and C13, C14, O8 for Al3 defining the equatorial sites.

Recently, aluminum carboxylates have attracted attention owing to usefulness as MOFs [42]. To measure the applicability of **1** and **2** as porous materials, we have examined their crystal structures. Viewed along the *a* axis of the structure of **1** reveals small open channels with *ca.* 1.5–2.0 Å size, whereas open channels of *ca.* 3.5 Å diameters are shown in the crystal packing structure for **2** along the *c* axis (figure 3). In comparison with the pore sizes of known MOFs like MIL-53 (channel dimensions of 8.5 × 8.5 Å^2) [42] and WUT-1 (cavities of 6.2 and 10.4 Å diameter) [43], the channel sizes of **1** and **2** are relatively small.

4. Conclusion

We have reported the structural characterization of two macrocyclic and multinuclear di-*tert*-butylaluminum carboxylates, ^{t}Bu$_8$Al$_4$[NC(O)(Ph)CH$_2$CO$_2$]$_2$ (**1**) and ^{t}Bu$_{16}$Al$_8$[O$_2$C(CH$_2$)O(CH$_2$)CO$_2$]$_4$ (**2**), in reactions of hippuric and diglycolic acids with ^{t}Bu$_3$Al. These compounds may be described as soluble molecular analogs of MOF materials. The acids used are considered as functionalized carboxylic acids having an additional amidate function (hippuric acid) or carboxylate function and an oxygen donor (diglycolic acid). On the basis of the literature data [1–15, 19, 20] and our results, we conclude that the structure of the aluminum carboxylates depends strongly on the kind of additional functions present in the carboxylic acids. A suitable manipulation of the functional groups makes it possible to design metal carboxylate frameworks.

Supplementary material

CCDC 1015951 and 1015952 contain supplementary crystallographic data for **1** and **2**, respectively. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

The X-ray structure of **1** was determined in the Crystallographic Unit of the Physical Chemistry Laboratory at the Chemistry Department of the University of Warsaw. The X-ray structure of **2** was determined at the Faculty of Chemistry of the Warsaw University of Technology. We thank the Warsaw University of Technology for its financial support.

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