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Toward Coordination Polymers Based on Fine-Tunable Group 13 Organometallic Phthalates

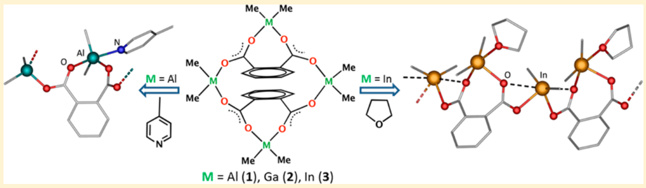
Iwona Justyniak,*,[†] Wojciech Bury,[‡] Daniel Prochowicz,[‡] Katarzyna Wójcik,[†] Janusz Zachara,[‡] and Janusz Lewiński*,[†,‡]

[†]Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland

[‡]Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warsaw, Poland

Supporting Information

ABSTRACT: A family of group 13 organometallic macrocyclic phthalates $[(\mathrm{MMe_2})_2(\mu\text{-}\mathrm{O_2C})_2\text{-}1,2\text{-}\mathrm{C_6H_4}]_2$ (where M = Al (**1**), Ga (**2**), In (**3**)) is prepared, and the reactivity of these homologous carboxylates toward various monodentate Lewis bases is investigated. The studies provide the first structurally characterized methylindium $[\{(\mathrm{Me_2In})(\mu\text{-}\mathrm{O_2C})_2\text{-}1,2\text{-}\mathrm{C_6H_4}\}\{\mathrm{Me_2In(THF)}\}]_n$ (**4**) and methylaluminum $[\{(\mathrm{Me_2Al})(\mu\text{-}\mathrm{O_2C})_2\text{-}1,2\text{-}\mathrm{C_6H_4}\}\{\mathrm{Me_2Al(py\text{-}Me)}\}]_n$ (**5**) 1D coordination polymers stabilized by dicarboxylate ligands as a result of disruption of the parent tetranuclear macrocyclic structural motifs in **3** and **1** by the incoming donor ligands. The molecular and crystal structures of the reported compounds are examined by spectroscopic studies and single-crystal X-ray diffraction.



INTRODUCTION

A range of group 13 organometallic carboxylates has been reported in the past two decades. Particularly intriguing examples are those making use of additional functionality within the carboxylate ligand to produce multinuclear macrocyclic aggregates or extended structures in the solid state.[1] The generation of new architectures based on group 13 organometallic carboxylates requires fine control over reactivity and self-assembly processes and a nuanced understanding of the factors that influence the formation of one structure over another.

Early works focused on the use of monofunctional carboxylic acids and the synthesis of $[\mathrm{R_2M}(\mu\text{-}\mathrm{O_2CR'})]_2$ complexes. In the case of diorganoaluminum and gallium monocarboxylates, the formation of $[(\mathrm{R_2M}(\mu\text{-}\mathrm{O_2CR'})]_2$ (where M = Al, Ga) dimeric complexes has been observed. These complexes feature a central eight-membered $\mathrm{M_2O_4C_2}$ ring in a chairlike conformation.[2] There is only one known dialkylgallium carboxylate complex with a carboxylate group terminally coordinating in a chelating manner to a Ga center, which is likely determined by both the character of the carboxylate ligand and the steric demand of the substituents bonded to the metal.[3] In contrast, diorganoindium carboxylates $[(\mathrm{R_2In}(\mu\text{-}\mathrm{OAc})]_n$ (R = Me or Et) have been isolated as polymeric chains where the indium atoms are six-coordinate and the carboxylate ligand is both chelating and bridging.[4] In 1987, Trotter et al.[5] reported the first molecular structure of a mononuclear diorganogallium derivative of a carboxylic acid with amine termini. In turn, our group[6] and others[7] have synthesized a series of group 13 organometallic mono- and multinuclear compounds derived from bifunctional aromatic and aliphatic carboxylic acids. Molecular structures of these compounds are determined by various factors such as reagent stoichiometry and the properties of both metal centers and organic residues. For example, the reaction of 2 equiv of $\mathrm{Me_3Al}$ with aromatic bifunctional carboxylic acids, such as salicylic, anthranilic, and phthalic, produces the corresponding tetraaluminum compounds $[(\mathrm{AlMe_2})_2(\mu\text{-}\mathrm{O_2C})\mathrm{C_6H_4}\text{-}2\text{-}\mathrm{X}]_2$ (where X = O, NH, or $\mathrm{CO_2}$ anionic subunit) with a central 16-membered ring structure.[6] In contrast, the reactions of $\mathrm{Me_3Al}$ with diphenylglycolic acid and the amino acid 2,2-diphenylglycine led to remarkable macrocyclic structures, the 16-membered ring compounds $\{\{[\mathrm{Ph_2C(X)(CO_2)}]_2(\mathrm{Me_2Al})(\mathrm{MeAl})\}(\mathrm{AlMe_2})\}_2$ (X = O or NH) that contain six aluminum centers, and the nonsymmetrical 32-membered ring complex $\{\{[\mathrm{Ph_2C(NH)(CO_2)}]_2(\mathrm{Me_2Al})(\mathrm{MeAl})\}(\mathrm{AlMe_2})\}_4$ incorporating 12 aluminum centers.[7b] Surprisingly, the formation of coordination polymers containing group 13 organometallics derived from either dicarboxylic or other bifunctional carboxylic acids has not been observed.

The literature concerning reactions of group 13 organometallic carboxylates with Lewis bases is very limited. Simple Lewis acid–base adducts between a mononuclear group 13 organometallic carboxylate moiety and Lewis base are lacking, and only very recently, the first dichloroaluminum and gallium adducts with γ-picoline (py-Me), $[\mathrm{Cl_2M}(\lambda_2\text{-}\mathrm{O_2CPh})(\text{py-Me})_2]$, which feature a nonbridging and M-chelating carboxylate ligand, were reported.[8] Similarly, the indium homologue forms $[\mathrm{Cl_2In}\text{-}(\lambda_2\text{-}\mathrm{O_2CPh})(\text{py-Me})_2]$.[9] Reactions between group 13 metal alkyl derivatives of bifunctional carboxylates and Lewis bases have been far less explored. Previously, we revealed that the macrocyclic tetranuclear organoaluminum anthranilate $[(\mathrm{AlEt_2})_2(\mu\text{-}\mathrm{O_2C})\mathrm{C_6H_4}\text{-}2\text{-}\mathrm{NH}]_2$ and related organogallium salicylate $[(\mathrm{GaMe_2})_2(\mu\text{-}\mathrm{O_2C})\mathrm{C_6H_4}\text{-}2\text{-}\mathrm{O}]_2$ react with

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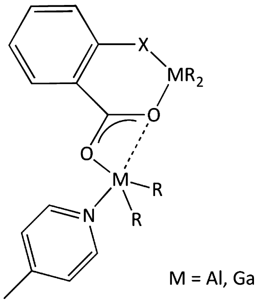
py-Me to form discrete dinuclear complexes of the type $[MR_2(\mu\text{-}O_2C)C_6H_4\text{-}2\text{-}X](py\text{-}Me)$ (**I**) as a result of the disruption of the parent macrocyclic tetranuclear structural motif by the added donor ligand (Scheme 1).[6c,10]

Scheme 1. Structure Representation of Dinuclear Complexes of the Type $[MR_2(\mu\text{-}O_2C)C_6H_4\text{-}2\text{-}X](py\text{-}Me)$ (I)



I

Intriguing results were obtained upon reacting the tetranuclear macrocycle $[(AlMe_2)_2(\mu\text{-}O_2C)_2\text{-}1,2\text{-}C_6H_4]_2$ (**1**), derived from Me_3Al and phthalic acid,[6b] with an excess of Me_3Al and subsequent addition of 1,2-bis(4-pyridyl)ethane (Scheme 2, path 1).[11] The latter reaction afforded the hexanuclear aggregate **II** with two tetramethylalumoxane moieties entrapped by a methylaluminumphthalate subunit, while the 1,2-bis(4-pyridyl)ethane ligand links the two alumoxane Al centers to form a 22-membered ring system and concomitant formation of 3,3-dimethyl-2-benzofuran-1(3*H*)-one. Interestingly, carrying out the same reaction using 4 equiv of Me_3Al afforded the tetramethylaluminoxane-bipyridine adduct **III**.

As an extension of our previous investigations of the chemistry of group 13 metal carboxylates,[4c,6,8a,11] and in the course of our studies exploiting fine-tunable structural features of metal carboxylates as versatile molecular building blocks for crystal engineering of extended metal−organic materials,[11,12] herein we report the synthesis of group 13 homologues of dimethylaluminum phthalate **1** and their reactivity with monodentate donor ligands. This study provides the first structurally characterized alkylaluminum coordination polymer stabilized by a dicarboxylate ligand and its alkylindium homologue, where both novel supramolecular structures are formed through disruption of the parent tetranuclear macrocyclic structural motif by the donor ligand.

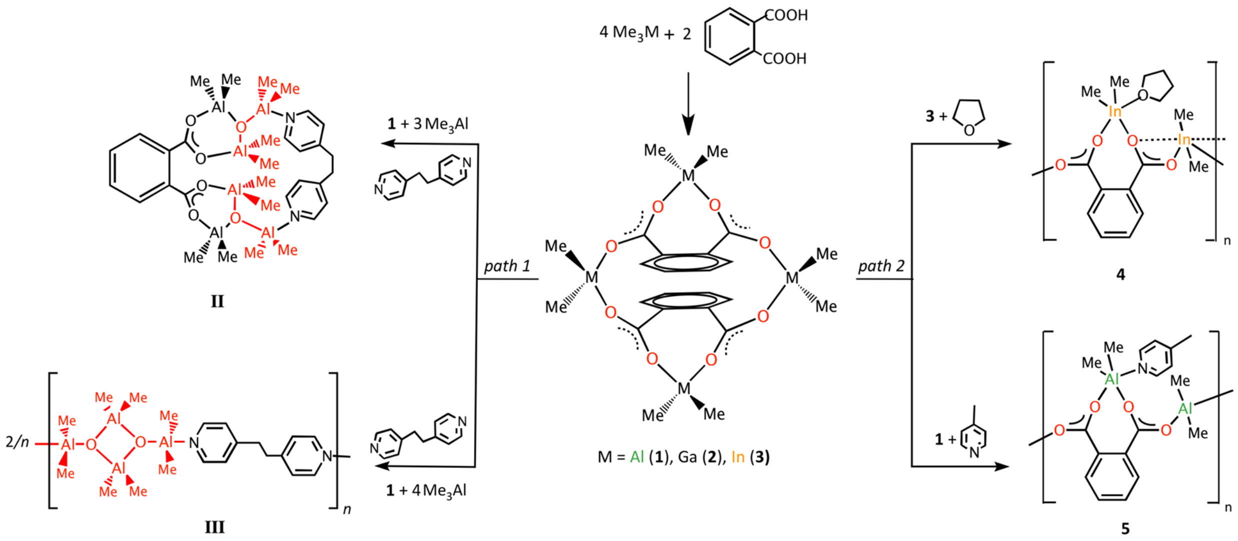
RESULTS AND DISCUSSION

As previously reported,[6b] the reaction of phthalic acid with 2 equiv of Me_3Al affords discrete tetranuclear aggregate $[(AlMe_2)_2(\mu\text{-}O_2C)_2\text{-}1,2\text{-}C_6H_4]_2$ (**1**). Similar treatment of phthalic acid with 2 equiv of Me_3Ga in toluene led to the formation of the related gallium homologue $[(GaMe_2)_2(\mu\text{-}O_2C)_2\text{-}1,2\text{-}C_6H_4]_2$ (**2**) in essentially quantitative yield. However, the analogous reaction involving Me_3In resulted in the formation of a product that was insoluble in nonpolar solvents with an anticipated composition of $[(InMe_2)_2(\mu\text{-}O_2C)_2\text{-}1,2\text{-}C_6H_4]_2$ (**3**) (vide infra). Compound **2** was characterized spectroscopically, and its identity was confirmed by single crystal X-ray diffraction.

The ^1H NMR spectrum of **2** shows similar pattern to that observed for **1**.[6b] There are three observed Ga−Me resonances: one singlet resonance was attributed to the equivalent protons in Me_2Ga units joining the two dicarboxylate ligands, and the remaining two singlets were assigned to the equivalent in pairs Ga−Me groups of the bridgehead Me_2Ga moieties; one Me group is situated toward and the second one away from the central macrocycle ring. The IR spectrum of **2** in CH_2Cl_2 solution shows bands at 1600 and 1575 cm^{-1}, characteristic for a bidentate carboxylate group, which are similar to those found in **1** (1610 and 1562 cm^{-1}). The IR spectrum of **3** exhibits the characteristic carboxylate bands at 1595 and 1510 cm^{-1}.

The molecular structure of **2** is isostructural with the aluminum analogue **1** (Figure 1).[6b] The centrosymmetric tetranuclear aggregate forms a skeleton framework with three fused distorted heterocyclic rings and one 16- and two 7-membered rings. The four carboxylate groups act as bidentate bridging ligands between the four dimethylgallium units, forming the distorted 16-membered $Ga_4(OCO)_4$ ring. In addition, we found that the most likely location of the gallium

Scheme 2. Synthetic Pathways Involving Me_3M (M = Al, Ga, In) and Phthalic Acid in the Presence of (Path 2) Mono- and (Path 1) Bidentate Lewis Bases



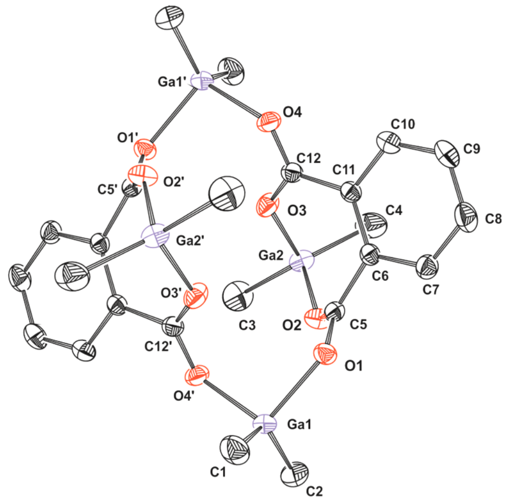


Figure 1. ORTEP diagram of the molecular structure of **2** with thermal ellipsoids set at 30% probability; hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ga1−O1, 1.983(2); Ga1−O4′, 1.979(2); Ga2−O2, 1.940(2); Ga2−O3, 1.946(2); Ga1−C1, 1.942(3); Ga1−C2, 1.938(3); Ga2−C3, 1.937(3); Ga2−C4, 1.943(4); C5−O1, 1.252(3); C5−O2, 1.260(3); C12−O3, 1.262(3); C12−O4, 1.250(3); O1−Ga1−O4′, 100.1(7); O2−Ga2−O3, 90.3(8).

center in **2** relative to the O,O-bidentate carboxylate group is the anti direction, as observed in **1**. The corresponding Ga−O distances to the bridgehead Ga(2) atom are shorter (average Ga−O_{anti} bond length is 1.943 Å) than those to the bridging Ga(1) atom (average Ga−O_{syn}, 1.981 Å) (for crystallographic details see the Experimental Section).

Discrete macrocyclic clusters **1**−**3** appeared to be excellent starting materials to probe their transformations into novel architectures in the presence of various monodentate Lewis bases (Scheme 2, path 2). After the addition of 1 equiv of THF to **1** and **2** in CH_2Cl_2 at ambient temperature, we did not observe any transformation of the macrocyclic metal−carboxylate core. In both cases, the IR spectrum of the postreaction mixture exhibits a pattern consistent with the parent tetranuclear structure of either **1** or **2**. The corresponding IR spectrum for a mixture of **3** and THF shows the presence of bands at 1539 and 1491 cm^{-1}, characteristic for carboxylate units; however, these vibrations are shifted from those observed in the parent aggregate **3** (vide infra). Thus, the structure of the complex was further examined by X-ray crystallography. From the postreaction mixture, colorless crystals of a 1D coordination polymer with the formula $[\{(Me_2In)(\mu\text{-}O_2C)_2\text{-}1,2\text{-}C_6H_4\}\{Me_2In(THF)\}]_n$ (**4**), the structure of which is detailed below, were isolated in high yield.

We were also curious as to how the addition of a pyridine-type ligand as a strong Lewis base might affect the structure of organoaluminum and -gallium phthalates **1** and **2**. The addition of 1 equiv of py-Me to **1** in CH_2Cl_2 at ambient temperature resulted in slow deposition of colorless crystals of the Lewis acid−base adduct $[\{(Me_2Al)(\mu\text{-}O_2C)_2\text{-}1,2\text{-}C_6H_4\}\{Me_2Al(\text{py-Me})\}]_n$ (**5**). For the similar reaction of py-Me with **2**, because of the low quality of the crystals formed, we were unable to obtain a proper data set to perform reliable X-ray analysis, so complex **6** was only characterized in solution by NMR and IR spectroscopy. The ^{1}HNMR and IR spectra of **6** have similar patterns to those observed for **5**.

Compounds **4** and **5** crystallize in monoclinic space groups $P2_1$ and $P2_1/n$, respectively. The structural analysis of **4** and **5** revealed that the addition of the corresponding Lewis base L disrupts the parent tetranuclear macrocyclic structural motif in **1** and **3** and leads to the formation of 1D coordination polymers based on asymmetric dinuclear $[\{(Me_2M)(\mu\text{-}O_2C)_2\text{-}1,2\text{-}C_6H_4\}\{Me_2M(L)\}]$ units (Figure 2). These coordination polymers are assembled from similar dinuclear molecular building units based on the phthalate ligand and two MMe_2 moieties, and their building units differ in the mode of both coordination and self-organization (Figure 2a,b). In both cases, one central five-coordinate MMe_2 moiety is chelated by the carboxylate groups of phthalate ligand, and its coordination sphere is completed by the monodentate L ligand. The second MMe_2 moiety is terminally bonded to one carboxylate group and acts as a connector, although its coordination mode is different in **4** and **5** (vide infra).

In the polymeric chain structure of **4**, two independent dinuclear $[\{(Me_2In)(\mu\text{-}O_2C)_2\text{-}1,2\text{-}C_6H_4\}\{Me_2In(THF)\}]$ units are present and self-assemble side by side. They differ slightly in the geometrical parameters, and only one unit is described in further detail. The asymmetric $[\{(Me_2In)(\mu\text{-}O_2C)_2\text{-}1,2\text{-}C_6H_4\}\{Me_2In(THF)\}]$ unit consists of one central five-coordinate and one remote six-coordinate indium atom. The coordination sphere of the central five-coordinate $Me_2In(1)$ moiety is completed by two carboxylate oxygen atoms of a phthalate ligand and a THF molecule (Figure 2a). The geometry of the In(1) atom can be described as a highly distorted trigonal bipyramid. The equatorial plane comprising the two carbon atoms and carboxylate oxygen O(1) is planar with bond angles involving indium in this plane in the range of 102.7(2)−109.7(2)°. The axial positions are occupied by the carboxylate oxygen O(1) atom and solvated THF molecule with an O(1)−In(1)−O(9) angle of 163.5(1)°. The In(1)−O(1) and In(1)−O(3) bond lengths are 2.339(3) and 2.181(3) Å, respectively. The primary coordination sphere of the second $Me_2In(2)$ moiety can be described as distorted tetragonal with two strong In−$O_{carboxylate}$ bonds and angles in the range of 82.3(1)−144.9(2)°. A secondary interaction between the second carboxylate oxygen of the carboxylate group and indium atom (average In−$O_{carboxylate}$ bond lengths of 2.812 Å) results in an increase of the coordination number to six. The primary In−$O_{carboxylate}$ bond lengths are essentially equal (average length of 2.247 Å) and are shorter than those for the five-coordinate indium atom (average: 2.383 Å).

The polymeric chain structure of **5** is assembled by the alternating asymmetric dinuclear unit $[\{(Me_2Al)(\mu\text{-}O_2C)_2\text{-}1,2\text{-}C_6H_4\}\{Me_2Al(\text{py-Me})\}]$. The coordination sphere of the central five-coordinate $Me_2Al(1)$ moiety is completed by two carboxylate oxygen atoms of a phthalate ligand and py-Me molecule (Figure 2b,d).

The four-coordinate $Me_2Al(2)$ moiety acts as a connector and joins two adjacent units by terminal carboxylate oxygen atoms, which results in the polymeric chain structure. The axial positions of the five-coordinate aluminum atom are occupied by the nitrogen atom N(1) and the carboxylate oxygen atom O(1) with a N(1)−Al(1)−O(1) angle of 165.5(2)°. The axial Al(1)−N(1) distance is 2.151(5) Å, which is comparable to the length of the analogous bond in the first structurally characterized five-coordinate dimethylaluminum O,O-chelate complex $[Me_2Al(O,O')(\text{py-Me})]$ (2.135(2) Å) (where *O,O′* = 2′-hydroxyacetophenone).[13] The equatorial Al(1)−O(3) bond length (1.863(4) Å) is quite short compared with that observed

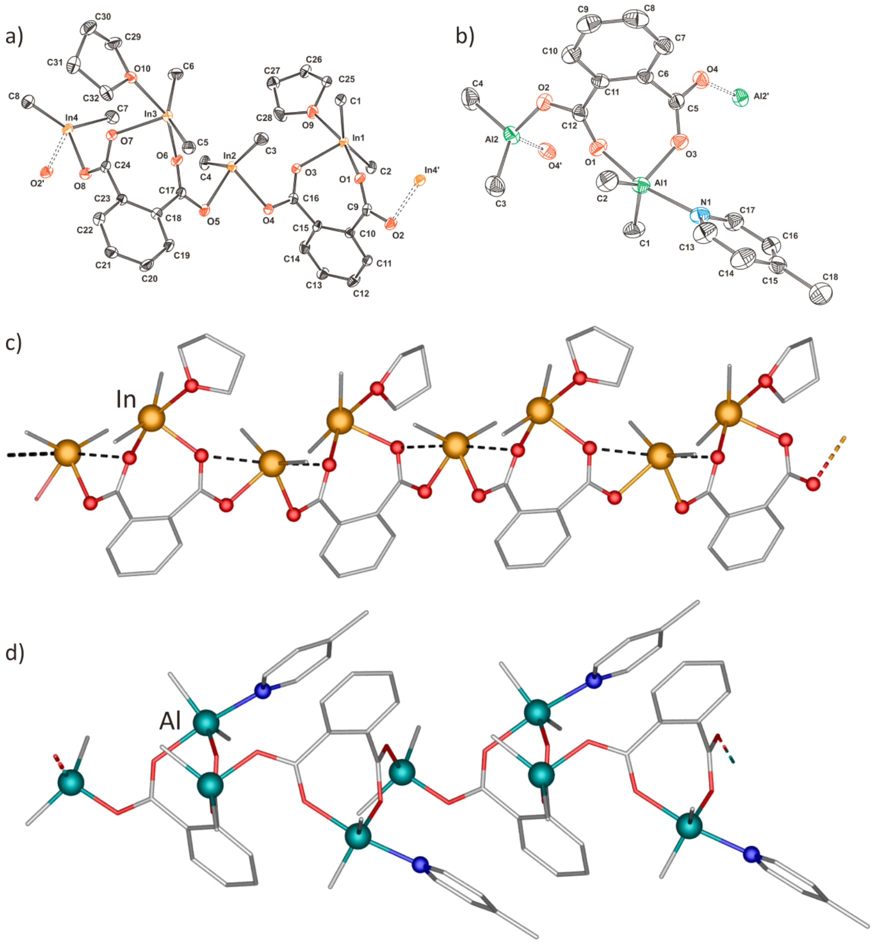


Figure 2. (a) ORTEP diagram of the asymmetric unit of building blocks in **4** with thermal ellipsoids set at 30% probability. Selected bond lengths (Å) and angles (deg): In1−O1, 2.339(3); In1−O3, 2.181(3); In1−O9, 2.402(4); In2−O3, 3.004(3); In2−O4, 2.242(3); In2−O5, 2.251(3); In2−O6, 2.619(3); In3−O6, 2.392(3); In3−O7, 2.218(3); In3−O10, 2.388(3); In4−O7, 3.086(3); In4−O8, 2.206(3); O1−In1−O3, 80.2(1); O9−In1−O3, 163.5(1); O4−In2−O5, 82.3(1); O3−In2−O6, 172.5(1); O10−In3−O7, 79.8(1); O6−In3−O7, 76.0(1). (b) ORTEP diagram of the asymmetric unit of building blocks in **5** with thermal ellipsoids set at 40% probability. Selected bond lengths (Å) and angles (deg): Al1−O1, 2.053(5); Al1−O3, 1.863(4); Al1−N1, 2.151(5); Al2−O2, 1.813(4); C5−O3, 1.260(6); C5−O4, 1.263(7); C12−O1, 1.256(7); C12−O2, 1.272(6); O1−Al1−O3, 82.6(2); O1−Al1−N1, 165.5(2). (c) View of the crystal structure of **4** along the *c* axis and (d) view of the crystal structure of **5** along the *c* axis. Hydrogen atoms are omitted for clarity.

for the axial position Al(1)−O(1) (2.053(5) Å). The geometry of the four-coordinate aluminum atom in **5** is a distorted tetrahedral with angles in the range of 103.3(2)−121.2 (3)°. The Al(2)−O(2) and In(2)−O(4) bond lengths are 1.813(4) and 2.242(3) Å, respectively.

The observed diversity in the coordination abilities of the Al atoms can seem surprising (the basic environment of the Al atom in both cases is identical, C_2AlO_2). However, we previously showed that the strength of Al−O bonds is related to the position of the Al atom relative to the carboxylate group and the anti direction is the most likely location of the Al center relative to the carboxylate group.[6b] In **5**, the $Al-O_{carboxylate}$ bonds for four- and five-coordinate Al atoms are differently situated in relation to the carboxylate groups, which probably considerably differentiates the Lewis acidity of the aluminum centers, so only one aluminum atom is additionally coordinated by py-Me.

■ CONCLUSIONS

We have demonstrated that the use of isostructural tetranuclear adducts $[(MMe_2)_2(\mu\text{-}O_2C)_2\text{-}1,2\text{-}C_6H_4]_2$ (where M = Al or In) in the presence of different monodentate Lewis bases leads to the generation of new organometallic coordination polymers based on a dicarboxylic unit. Further studies on the use of group 13 organometallic carboxylates with bidentate Lewis to construct new solid-state systems are in progress.

■ EXPERIMENTAL SECTION

All manipulations were conducted under a nitrogen atmosphere by using standard Schlenk techniques. All reagents were purchased from commercial vendors. Compound **1** was obtained according to the previously describe method in the reaction of phthalic acid with 2 equiv of Me_3Al.[6b] Solvents were dried and distilled prior to use. NMR spectra were acquired on a Varian Mercury 400 spectrometer. IR spectra were recorded on a Specord-75 IR spectrometer.

Synthesis of 2. To a solution of phthalic acid (0.664 g, 4 mmol) in toluene (7 mL) was added Me_3Ga (0.918 g, 8 mmol) at −78 °C, and the reaction mixture was allowed to warm to ambient temperature. After a stirring period of 1 h, the solution was evaporated to dryness in vacuum to afford a white solid. Yield: 1.38 g, 95%. Anal. Calcd for $C_{24}H_{32}Ga_4O_8$: C, 39.59; H, 4.39. Found: C, 39.54; H, 4.33. ^1H NMR (C_6D_6, 400.10 MHz, 298 K): $\delta = -0.70$ (s, 6H, Ga−CH_3), −0.34 (s, 6H, Ga−CH_3), 0.34 (s, 12H, Ga−CH_3), 6.87 (m, 4H, Ar), 7.55 (m, 4H, Ar). IR (CH_2Cl_2, cm^{-1}): 1600 (s), 1575 (s), 1500(s), 1450 (s), 1430 (s), 1200 (m), 1090 (m), 970 (w), 890 (m), 865 (m), 650 (m), 608 (m).

Synthesis of 3. The reaction was carried out according to the same procedure as described for **2** by using phthalic acid (0.664 g, 4 mmol) and Me_3In (1.278 g, 8 mmol). The resulting white solid was insoluble in nonpolar solvents. Anal. Calcd for $C_{24}H_{32}In_4O_8$: C, 31.74; H, 3.52. Found: C, 32.04; H, 3.58. Yield: 1.65 g, 91%. IR (cm^{-1}): 1595 (s), 1510(s), 1460 (s), 1420 (s), 1250 (m), 1090 (m), 970 (w), 880 (m), 875 (m), 750 (m), 608 (m)

Synthesis of 4. Me_3In (1.28 g, 8 mmol) was added to a solution of phthalic acid (0.664 g, 4 mmol) in toluene (7 mL) at −78 °C. The reaction mixture was allowed to warm to room temperature and was stirred for 2 h. Then, THF (0.576 g, 8 mmol) was added, and the solution was stirred for an additional 10 min. The solution stood overnight at 25 °C, and colorless square-shaped crystals formed. Anal. Calcd for $C_{32}H_{48}In_4O_{11}\cdot THF$: C, 38.43; H, 4.98. Found: C, 38.39; H, 4.96. Yield: 1.70 g, 75%. ^1H NMR (400 MHz, C_6D_6): 0.32 (s br, 24H, In−CH_3), 1.89 (m, 12H, CH_{2THF}), 3.86 (m, 12H, $-OCHH_{2THF}$), 6.59 (m, 4H, CH_{Ar}), 7.11 (m, 4H, CH_{Ar}). IR (cm^{-1}): 1539 (s), 1491 (s), 1450 (m), 1397 (s), 1297 (m), 1036 (m), 959 (w), 877 (m), 710 (m), 654 (m).

Synthesis of 5. Me_3Al (1.01 g, 14 mmol) was added to a solution of phthalic acid (1.16 g, 7 mmol) in CH_2Cl_2 (7 mL) at −78 °C. The reaction mixture was allowed to warm to room temperature and was stirred for 2 h. Then 4-methylpyridine (1.30 g, 14 mmol) was added, and the solution was stirred for an additional 10 min. The solution stood overnight at 25 °C, and colorless square-shaped crystals formed. Anal. Calcd for $C_{18}H_{23}Al_2NO_4$: C, 58.16; H, 6.19. Found: C, 58.19; H, 6.16. Yield: 1.60 g, 65%; ^1H NMR (400 MHz, C_6D_6): −0.72 (s br, 12H, Al−CH_3), 1.86 (s, 3H, py-Me), 6.59 (d, 2H, CH), 7.11 (s br, 2H, CH), 7.54 (s br, 2H, CH), 8.02 (d, 2H, CH). IR (nujol, cm^{-1}): 1625 (s), 1608 (s), 1575 (s), 1507(s), 1477 (s), 1360 (m), 1195 (m), 1170 (m), 870 (w), 835 (m), 757 (m), 625 (m).

Synthesis of 6. Me_3Ga (0.918 g, 8 mmol) was added to a solution of phthalic acid (0.664 g, 4 mmol) in toluene (7 mL) at −78 °C. The reaction mixture was allowed to warm to room temperature and was stirred for 2 h. Then 4-methylpyridine (0.745 g, 8 mmol) was added, and the solution was stirred for an additional 10 min. The solution stood overnight at 25 °C, and a white solid formed. Anal. Calcd for $C_{18}H_{23}Ga_2NO_4$: C, 47.32; H, 5.04, N, 3.06. Found: C, 47.41; H, 5.12, N, 3.11. Yield: 1.13g, 62%. ^1H NMR (400 MHz, C_6D_6): 0.15 (s, Ga−CH_3), 1.72 (s, 3H, py-Me), 6.62 (d, 2H, CH_{py}), 7.02 (m, 2H, CH_{ar}), 7.83 (m, 2H, CH_{ar}), 8.28 (d, 2H, CH_{py}). IR (nujol, cm^{-1}): 1621 (s), 1602 (s), 1562 (s), 1497(s), 1457 (s), 1380 (m), 1195 (m), 1070 (m), 970 (w), 835 (m), 737 (m), 655 (m).

Crystallographic Data. The X-ray data for complexes **2** and **5** were collected at room temperature on a Siemens P3 four-circle diffractometer using Mo Kα radiation (λ = 0.71073 Å). Suitable single crystals of **2** and **5** were placed in a thin-walled capillary (Lindemann glass) in an inert atmosphere. The crystal class and the orientation matrix were obtained from the least-squares refinement of randomly found reflections. The intensities were recorded in the ω-2θ scan mode and corrected for Lorentz and polarization effects. The structure was solved by direct methods using the SHELXS-97 program[14] and refined by the full-matrix least-squares method against F2 values with the SHELXL-93 program.[15] All of the non-hydrogen atoms were refined with anisotropic thermal parameters.

The X-ray data for complexes **4** were collected at 100(2) K on a Nonius Kappa CCD diffractometer[16] using graphite monochromated Mo Kα radiation (λ = 0.71073 Å). The crystal was mounted in a nylon loop in a drop of silicon oil. The unit cell parameters were determined from 10 frames, then refined on all data. The data were processed with DENZO and SCALEPACK (HKL2000 package).[17] The structure was solved by direct methods using the SHELXS-97 program and was refined by full matrix least−squares on F^2 using the program SHELXL-97. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were introduced at geometrically idealized coordinates with a fixed isotropic displacement parameter equal to 1.5 (methyl groups) times the value of the equivalent isotropic displacement parameter of the parent carbon.

Crystal Data for 2. $C_{24}H_{32}Ga_4O_8$: M = 727.38, monoclinic, space group $P2_1/c$ (no. 14), a = 9.2911(15) Å, b = 15.736(2) Å, c = 10.4345(17) Å, β = 96.099(13)°, U = 1516.9(4) $Å^3$, Z = 2, $F(000)$ = 728, D_c = 1.593 g cm^{-3}, T = 298(2) K, μ(Mo Kα) = 3.554 mm^{-1}, θ_{max} = 25.05°, 2655 unique reflections. Refinement converged at R1 = 0.0323, wR2 = 0.0677 for all data and 168 parameters (R1 = 0.0254, wR2 = 0.0652 for 2264 reflections with $I_o > 2\sigma(I_o)$). The goodness-of-fit on F^2 was 1.015. A weighting scheme of $w = [\sigma^2(F_0^2 + (0.0418P)^2 + 3.1964P]^{-1}$, where $P = (F_0^2 + 2F_c^2)/3$, was used in the final stage of refinement. The residual electron density was +0.34 /−0.35 e$Å^{-3}$.

Crystal Data for 4. $C_{36}H_{56}In_4O_{11}$: M = 1124.09, monoclinic, space group $P2_1$ (no. 4), a = 10.1160(2) Å, b = 16.0790(4) Å, c = 13.5500(4) Å, β = 98.300(2)°, U = 2180.89(9) $Å^3$, Z = 2, $F(000)$ = 1112, D_c = 1.712 g cm^{-3}, T = 100(2)K, μ(Mo Kα) = 3.554 mm^{-1}, θ_{max} = 25.35°, 7805 unique reflections. Refinement converged at R1 = 0.0364, wR2 = 0.0627 for all data and 168 parameters (R1 = 0.0292, wR2 = 0.0612 for 6962 reflections with $I_o > 2\sigma(I_o)$). The goodness-of-fit on F^2 was 1.003. A weighting scheme of $w = [\sigma^2(F_0^2 + (0.0418P)^2 + 3.1964P]^{-1}$, where $P = (F_0^2 + 2F_c^2)/3$, was used in the final stage of refinement. The residual electron density was +0.87 /−0.73 e$Å^{-3}$.

Crystal Data for 5. $C_{18}H_{23}Al_2NO_4$: M = 371.33, monoclinic, space group $P2_1/n$ (no. 14), a = 10.756(4) Å, b = 10.542(4) Å, c = 18.338(6) Å, β = 97.22(3)°, U = 2062.7(13) $Å^3$, Z = 4, $F(000)$ = 784, D_c = 1.196 g cm^{-3}, T = 298(2) K, μ(Mo Kα) = 0.161 mm^{-1}, θ_{max} = 21.96°, 2655 unique reflections. Refinement converged at R1 = 0.1239, wR2 = 0.1949 for all data and 231 parameters (R1 = 0.0665, wR2 = 0.1639 for 1486 reflections with $I_o > 2\sigma(I_o)$). The goodness-of-fit on F^2 was 1.027. A weighting scheme of $w = [\sigma^2(F_0^2 + (0.0418P)^2 + 3.1964P]^{-1}$, where $P = (F_0^2 + 2F_c^2)/3$, was used in the final stage of refinement. The residual electron density was +0.23 /−0.22 e$Å^{-3}$.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic data (CIF) for **2**, **4**, and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: lewin@ch.pw.edu.pl.
*E-mail: iwonaj@ichf.edu.pl.

Notes

The authors declare no competing financial interest.

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