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Isoreticular Chemistry of Group 13 Metal–Organic Framework Compounds Based on V-Shaped Linker Molecules: Exceptions to the Rule?

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ABSTRACT: Following the concept of isoreticular chemistry, we carried out a systematic study on Ga-containing metal–organic frameworks (MOFs) using six V-shaped linker molecules of differing sizes, geometries, and additional functional groups. The linkers included three isophthalic acid derivatives (m-H₂BDC-R, R = CH₃, OCH₃, NHCOCH₃), thiophene-2,5-dicarboxylic acid (H₂TDC), and two 4,4'-sulfonyldibenzoic acid derivatives (H₂SDBA, DPSTA). The crystal structures of seven compounds were elucidated by a combination of model building, single-crystal X-ray diffraction



(SCXRD), three-dimensional electron diffraction (3D ED), and Rietveld refinements against powder X-ray diffraction (PXRD) data. Four new Ga-MOFs that are isoreticular with their aluminum counterparts, i.e. Ga-CAU-10-R (Ga(OH)(*m*-BDC-R); R = OCH₃, NHCOCH₃), Ga-CAU-11 (Ga(OH)(SDBA)), and Ga-CAU-11-COOH (Ga(OH)(H₂DPSTC)), were obtained. For the first time large single crystals of a MOF crystallizing in the CAU-10 structure type could be isolated, i.e. Ga-CAU-10-OCH₃, which permitted a detailed structural characterization. In addition, the use of 5-methylisophthalic acid and thiophene-2,5-dicarboxylic acid resulted in two new Ga-MOFs denoted Ga-CAU-49 and Ga-CAU-51, respectively, which are not isostructural with any known Al-MOF. The crystal structure of Ga-CAU-49 ([Ga₄(*m*-HBDC-CH₃)₂(*m*-BDC-CH₃)₃(OH)₄(H₂O)]) contains an unprecedented rod-shaped inorganic building unit (IBU) of the formula $\frac{1}{\infty}$ {Ga₁₆(OH)₁₈O₆₀}, composed of corner-sharing GaO₅ and GaO₆ polyhedra. In Ga-CAU-51 ([Ga(OH)(C₅H₂O₂S)]) chains of alternating *cis* and *trans* corner-sharing GaO₆ polyhedra form the IBU. A detailed characterization of the title compounds was carried out, including nitrogen gas and water vapor sorption measurements. Ga-CAU-11 was the only compound exhibiting porosity toward nitrogen with a type I isotherm, a specific surface area of $a_{S,BET} = 210 \text{ m}^2/g$, and a micropore volume of $V_{mic} = 0.09 \text{ cm}^3/g$. The new MOF Ga-CAU-51 exhibits exceptional water sorption properties with a reversible S-shaped isotherm and a high uptake around $p/p_0 = 0.38$ of $m_{ads} = 370 \text{ mg/g}$.

■ INTRODUCTION

The concept of isoreticular chemistry is well-known for metal– organic frameworks (MOFs), which are assembled by organic linker molecules and inorganic building units (IBUs).^{1–3} Such a modular construction leads to materials that crystallize in various framework topologies.⁴ In some cases, components can be chosen to intentionally create a framework structure with specific, desired properties. For example, the pore size can be tailored by substituting smaller for larger metal ions or linker molecules, e.g. in CAU-21⁵ and MOF-5,⁶ respectively, or the water sorption properties can be tuned by variation of the linker molecules.⁷ Hence, MOFs are materials of interest for drug delivery,⁸ gas storage,⁹ catalysis,¹⁰ and heat transformation¹¹ since these applications rely strongly on specific host–guest interactions that need to be optimized.^{12,13}

MOFs containing Al³⁺ ions have been intensely studied in the past decade due to the abundance of aluminum salts,¹⁴ their high thermal and chemical stability,⁷ and outstanding sorption properties.¹⁵ In contrast, MOFs built from Ga³⁺ ions have rarely been described.¹⁶ Important pioneering work was carried out by the group of Ferey and Loiseau, reporting almost the entirety of frameworks based on Ga³⁺ with carboxylate linkers.^{17–20} In most cases, Al- and Ga-MOFs form isoreticular frameworks.^{21–23} The ionic radii of group 13 elements Al³⁺, Ga³⁺, and In³⁺ with a coordination number (CN) of 6 are 0.675, 0.760, and 0.940 Å, respectively.²⁴ With a decrease in surface charge density of the metal center, from $[Al(H_2O)_6]^{3+}$ to $[Ga(H_2O)_6]^{3+}$ and $[In(H_2O)_6]^{3+}$, considerably higher exchange rates during synthesis are found for the latter metal ions.²⁵ A higher lability usually allows the synthesis

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of larger single crystals.²⁶ Therefore, the crystal structures of Ga- and In-MOFs are often elucidated by SCXRD, while the structures of Al-MOFs are most often determined from PXRD data.^{27,28} Structure determination from SCXRD data is preferable, as it is more straightforward and since a higher accuracy is achieved due to the lack of overlapping reflections.²⁹

In recent years we have intensely studied the influence of the linker size and geometry on the crystal structure of Al-MOFs.¹⁶ In particular, the use of V-shaped linker molecules has resulted in a rich structural chemistry and we were able to demonstrate that subtle changes in the linker lead to Al-MOFs with very different properties.³⁰ In line with these investigations and following our interest in the chemistry of group 13 MOFs, we have recently started a systematic investigation of Ga-MOFs. Thus, the use of various substituted naphthyldicarboxylic acids under similar reaction conditions resulted in the formation of isostructural Al- and Ga-MOFs.²¹

Herein we present our latest results on the systematic study on the use of V-shaped linker molecules, differing in size, linker geometry, and functional groups (Figure 1). In addition to



Figure 1. V-shaped linker molecules and their angles between the carboxylic acid groups as used in the synthesis of Al- and Ga-MOFs: 4,4'-sulfonyldibenzoic acid (H₂SDBA), thiophene-2,5-dicarboxylic acid (H₂TDC), 5-methoxybenzene-1,3-dicarboxylic acid (m-H₂BDC-OCH₃), 5-acetamidebenzene-1,3-dicarboxylic acid (m-H₂BDC-NHCOCH₃) and 5-methylbenzene-1,3-dicarboxylic acid (m-H₂BDC-CH₃).

establishing the synthesis parameters, chemical and physical properties, and crystal structures of one Al-MOF and five new Ga-MOFs, we compare the structural chemistry of Al- and Ga-MOFs.

EXPERIMENTAL SECTION

Materials. Gallium(III) nitrate heptahydrate (Ga(NO₃)₃·7H₂O, ABCR, 99.99% PURATREM), aluminum(III) nitrate nonahydrate (Al(NO₃)₃·9H₂O, Grüssing, reinst), 5-methoxybenzene-1,3-dicarboxylic acid (*m*-H₂BDC-OCH₃, TCI, >95%), 5-methylbenzene-1,3-dicarboxylic acid (*m*-H₂BDC-CH₃, ABCR, 98%), 4,4'-sulfonyldibenzoic acid (H₂SDBA, Sigma-Aldrich, >98%), 3,3',4,4'-diphenylsulfonetetracarboxylic acid (H₂TDC, TCI, >98%), and thiophene 2,5-dicarboxylic acid (*m*-H₂BDC-NTCI, >98%) are commercially available and were used without further purification. 5-Acetamidebenzene-1,3-dicarboxylic acid (*m*-H₂BDC-NHCOCH₃) was synthesized from 5-aminobenzene-1,3-dicarboxylic acid (*m*-H₂BDC-NHCOCH₃) was synthesized from 5-aminobenzene-1,3-dicarboxylic acid (*m*-H₂BDC-NHCOCH₃) are and characterized by ¹H-NMR spectroscopy (section 2 in the Supporting Information).

Methods. The reactions were carried out using either conventional heating or microwave-assisted heating. Syntheses in conventional ovens were performed in custom-made steel autoclaves equipped with Teflon liners with a total volume of 2 or 20 mL.³ For the microwave-assisted reactions in Biotage Initiator and Initiator + microwave systems, 20 mL glass reactors were employed. Initial characterization by PXRD was done on a STOE Stadi P-Combi diffractometer equipped with a MYTHEN 1K detector and using Cu $K\alpha_1$ radiation. PXRD data for structure determination and refinement were collected on a STOE Stadi MP instrument with a MYTHEN 1K detector and a flat sample spinner using Cu K α_1 radiation. SCXRD data were collected on a STOE imaging plate detector system (IPDS) using graphite-monochromated Mo K α radiation. The temperaturedependent PXRD data (TD PXRD) were collected with a STOE capillary furnace in 0.5 mm quartz capillaries. Humidity-dependent PXRD (HD PXRD) data were collected on a PANalytical Empyrean diffractometer (Cu K $\alpha_{1/2}$ radiation). IR spectra were recorded on a Bruker ALPHA-FT-IRA220/D-01 spectrometer equipped with an ATR unit. The thermogravimetric (TG) analyses were done using a NETZSCH STA 409 CD analyzer (air flow 75 mL/min, heating rate 4 K/min) and on a Linseis STA PT 1000 (nitrogen flow 80 mL/min or air flow 80 mL/min, heating rate 4 K/min). The carbon, hydrogen, nitrogen, and sulfur contents were determined by elemental analysis on a HEKAtech Euro EA Elemental Analyzer. The crystal structure database³³ (CSD) search was carried out in the MOF subset list³⁴ employing the programs ConQuest³⁵ and Mercury.³⁶ Calculations of pore diameters or theoretical specific surface areas were conducted using PLATON³⁷ or Zeo++.³⁸ Three-dimensional electron diffraction (3D-ED) data were collected on a JEOL JEM2100 instrument equipped with a Timepix detector from Amsterdam Scientific Instruments. Topological analyses were carried out using ToposPro³⁹ and Systre.⁴⁰

Synthesis. A summary of reaction parameters for the syntheses of all compounds is given in Table 1. It includes solvents, metal to linker molar ratio (M:L), reaction temperature (T) and time (t), as well as the heating method (MW, microwave-assisted reaction; conv, conventional heating). The synthetic procedure for every reaction started with weighing in the organic linker, and then the solvent was

Table 1. Overview of the Synthesis Parameters for Ga-CAU-10-OCH₃, Al-CAU-10-NHCOCH₃, Ga-CAU-10-NHCOCH₃, Ga-CAU-11, Ga-CAU-11-COOH, Ga-CAU-49, and Ga-CAU-51^{*a*}

compound	solvent	solvent ratio	$T/^{\circ}$ C, t/h	M:L ratio	heating
Ga-CAU-10-OCH ₃	water-toluene	1:9	140, 3	1:0.6	conv/MW
Al-CAU-10-NHCOCH ₃	water		160, 48	1:1	conv
Ga-CAU-10-NHCOCH ₃	water		120, 4	1:1	MW
Ga-CAU-11	water		120, 2	1:0.9	MW
Ga-CAU-11-COOH	water		180, 24	1:1.3	conv
Ga-CAU-49	water-toluene	1:0.8	120, 24	1:0.1	conv
Ga-CAU-51	water-AcOH	1:5	120, 4	1:1	MW

"Abbreviations: AcOH, acetic acid; DMF, *N*,*N*-dimethylformamide; MW, microwave-assisted heating; conv, conventional heating. Exact quantities of starting materials are provided in section 2 of the Supporting Information.

filled in the respective reactor. Subsequently, additives and the aqueous gallium(III) or aluminum(III) nitrate solution were added to the reaction mixture. Finally, the reaction vessel was closed and subjected to a temperature-time program in a conventional or microwave oven. The detailed synthesis procedures (including the exact amounts of starting materials), the results of the CHNS analyses, and synthesis yields can be found in section 2 in the Supporting Information.

Structure Determination of Ga-CAU-10-OCH₃ and Ga-CAU-49. The crystal structures of Ga-CAU-10-OCH₃ (Figure S3) and Ga-CAU-49 were determined by SCXRD. Single crystals of both compounds were selected under a polarizing microscope, and data collection was carried out at 293 K. The single-crystal structures were solved using the program SHELXT⁴¹ and refined with SHELXL⁴² using Olex2⁴³ as the GUI. All hydrogen atoms were added via AFIX instructions and refined using a riding model.

Structure Determination of M-CAU-10-NHCOCH₃ (M = AI^{3+} , Ga³⁺), Ga-CAU-11, Ga-CAU-11-COOH, and Ga-CAU-51. The crystal structures of Ga-CAU-11, M-CAU-10-NHCOCH₃ (M = Al^{3+} , Ga³⁺), and Ga-CAU-51 were determined from PXRD data. Structure models of Ga-CAU-11 and M-CAU-10-NHCOCH₃ (M = Al³⁺, Ga³⁺) were derived in Materials Studio⁴⁴ using crystallographic information on Al-CAU-11⁴⁵ and Al-CAU-10-OCH₃.⁷ After indexing of the PXRD patterns with TOPAS academic,⁴⁶ the unit cell dimensions were imposed in Materials Studio and Al³⁺ ions were substituted by Ga³⁺. The structure models were optimized using the universal force field as implemented in the software. A suitable structure model for Ga-CAU-51 was derived from 3D electron diffraction data recorded on small single crystals (ca. 1.5 μ m; section 4, Figure S3, and Table S2 in the Supporting Information). The structure refinement was performed using the Rietveld method implemented in the TOPAS academic software suit.⁴⁷ Details are provided in section 5 in the Supporting Information. The final Rietveld refinement plot of Ga-CAU-51 is shown in Figure 2, whereas all other Rietveld plots are presented in



Figure 2. Final Rietveld refinement plot for Ga-CAU-51. The observed curve is shown in black, the calculated curve in red, the difference curve in blue, and the positions of allowed reflections are shown as black ticks.

the Supporting Information. For Ga-CAU-11-COOH only a Pawley fit was performed (Figure S11 and Table S8). Results of the crystal structure refinements are summarized in Table 2. In addition to the Ga compounds, structural data information on the isostructural Al-MOFs is also included. The asymmetric units and bond lengths are given in section 5, Figures S4–S18, and Tables S3–S14 in the Supporting Information. The CCDC entries 2067831–2067836 contain the full crystallographic data for Al-CAU-10-NHCOCH₃, Ga-CAU-10-OCH₃, Ga-CAU-51, Ga-CAU-10-NHCOCH₃, Ga-CAU-49, and Ga-CAU-11, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

RESULTS AND DISCUSSION

Seven new group 13 MOFs containing Al^{3+} or Ga^{3+} ions and V-shaped linker molecules differing in size, linker geometry, and additional functional groups (Figure 1) have been obtained by solvothermal syntheses (Table 1) employing conventional as well as microwave-assisted heating. Reactions were carried out using the metal nitrates and the solvents water, acetic acid, and toluene. The Ga-CAU-11 type compounds, containing the larger, more flexible linker molecules, i.e. 4,4'-sufonyldibenzoic acid H_2 SDBA and DPSDA, were synthesized under hydrothermal reaction conditions similar to those reported for Al-CAU-11 by Reimer et al. in 2015.⁴⁵

When the more rigid and smaller isophthalic acid derivatives $(m-H_2BDC-X, X = CH_3, OCH_3, NHCOCH_3)$ were used, MOFs exhibiting different crystal structure types, depending on the metal ion employed, were obtained. While the reactions with Al³⁺ salts exclusively led to the formation of CAU-10 type structures, a larger structural variability was observed for the Ga-MOFs. Thus, we were able to obtain the first Ga-CAU-10 type compounds with m-H₂BDC-NHOCH₃ and m-H₂BDC-OCH₃, while the use of *m*-H₂BDC-CH₃ resulted in a new, more complex crystal structure (Ga-CAU-49). The use of toluene proved to be advantageous in these syntheses, although we can only speculate on its role during the crystallization. Thus, it could influence the solubility of the starting materials or the final MOFs. It is worth mentioning that the Ga-CAU-49 and Ga-CAU-10-OCH₃ syntheses resulted in coarse crystalline products containing single crystals of suitable size for structure determination by SCXRD. This observation is in line with previous reports on the synthesis of Al- and Ga-MOFs showing that larger crystals are more frequently obtained with Ga^{3+} salts.^{48,49} This phenomenon is related to the higher lability of Ga³⁺ complexes in comparison to Al³⁺ complexes.²⁵

When H_2TDC was employed, a small, rigid linker with a larger opening angle between the two carboxylate groups in comparison to m-H₂BDC-X (148 vs 120°) another new, highly porous Ga-MOF, denoted Ga-CAU-51, could be isolated from an acetic acid and water (5/1) mixture under solvothermal reaction conditions. Further details on the synthesis of each title compound are given in section 2 in the Supporting Information).

The crystal structure determinations of the title compounds were carried out from single-crystal and powder diffraction data. A comparison of the structures of Al- and Ga-MOFs obtained with the same linker molecules reveals that isostructural compounds, i.e. CAU-10 and CAU-11, were observed when the linker molecules m-H₂BDC-OCH₃, m-H₂BDC-NHCOCH₃, and H₂SDBS were used (Figure 3). However, when linker molecules m-H₂BDC-CH₃ and H₂TDC were employed, compounds with distinct, new framework structures, denoted Ga-CAU-49 and Ga-CAU-51, respectively, were obtained.

Since the structures of CAU-11 and CAU-10 have been reported previously, their structural descriptions are given in section 5 in the Supporting Information. The focus of the following sections will be on the new crystal structures of Ga-CAU-49 and Ga-CAU-51.

Crystal Structures. *Ga*-*CAU*-49. The reaction of gallium-(III) nitrate with m-H₂BDC-CH₃ in toluene and water (1/1) results in the compound Ga-CAU-49 with the composition

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Table 2. Crystallographic Parameters of Ga-CAU-10-OCH₃, Al-CAU-10-NHCOCH₃, Ga-CAU-10-NHCOCH₃, Ga-CAU-11, Ga-CAU-49, and Ga-CAU-51 (tw = This Work)

	M-CAU	J-10-OCH ₃	M-CAU-1	0-NHOCH ₃	M-CA	AU-11		
							Ga-CAU-49	Ga-CAU-51
metal ion (M)	Al ^{3+ 7}	Ga ³⁺ (tw)	Al ³⁺ (tw)	Ga ³⁺ (tw)	Al ^{3+ 45}	Ga ³⁺ (tw)	Ga ³⁺ (tw)	Ga ³⁺ (tw)
refinement from (data)	PXRD	SCXRD	PXRD	PXRD	PXRD	PXRD	SCXRD	3DED/ PXRD
cryst syst	tetragonal	tetragonal	tetragonal	orthorhombic	orthorhombic	orthorhombic	monoclinic	monoclinic
space group	$I4_1/a$	I4 ₁ /a	I4 ₁ /a	I4 ₁ /a	Pnma	Pnma	C2/c	$P2_{1}/c$
a/Å	21.3609(3)	21.570(3)	21.4594(4)	21.7251(3)	6.6111(5)	6.7288(4)	37.335(8)	12.5726(8)
b/Å	21.3609(3)	21.570(3)	21.4594(4)	21.7251(3)	12.888(1)	12.8292(9)	11.524(2)	15.777(1)
c/Å	10.5699(2)	10.790(2)	10.7902(4)	10.8522(3)	20.020(1)	20.4174(18)	24.123(5)	14.025(1)
β /deg							97.11(3)	102.538(7)
$V/Å^3$	4822.9(2)	5020.2(2)	4968.9(2)	5122.0(2)	10300(4)	1705.8(5)	1762.5(2)	2715.7(4)
R _{wp}	7.6		5.8	3.8		7.7	5.4	4.3
R _{Bragg}	4.3		4.1	2.9		1.4	2.8	1.7
GOF	2.0		6.1	3.8		not reported	3.1	2.7
no. of rflns collected		20185					43557	
no. of indep rflns		2822					11577	
R indices $(I > 2\sigma(I))$		R1 = 0.0524					R1 = 0.0647	
		wR2 = 0.1356					wR2 = 0.1520	
R indices (all data)		R1 = 0.0555					R1 = 0.0944	
		wR2 = 0.1377					wR2 = 0.1681	
no. ofdata/restraints/ params		2822/0/159					11577/0/705	
GooF		1.079					1.036	
Linker: H_2 SDBS <i>m</i> - H_2 BDC-X H_2 TDC		DC						
Al ³⁺ A	I-CAU-1	1 Al-CAU	-10-X		Al-MI	L-53	Al-CAU	J -23
			A.	*		5		1
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Figure 3. Overview of the group 13 MOFs obtained in this study (AlO₆ polyhedra are displayed in gray). Isostructural compounds (CAU-10 and CAU-11) are observed when the linker molecules H₂SBDS, *m*-H₂BDC-OCH₃, and *m*-H₂BDC-NHCOCH₃ are employed (MO₆ polyhedra, $M = Al^{3+}$, Ga³⁺ is displayed in green), while distinct, new framework structures are observed with *m*-H₂BDC-CH₃ and H₂TDC as linker molecules. The latter MOFs are denoted Ga-CAU-49 and Ga-CAU-51, respectively (GaO₆ polyhedra and GaO₅ polyhedra displayed in pale blue and pink, respectively).

 $[Ga_4(m-HBDC-CH_3)_2(m-BDC-CH_3)_3(OH)_4(H_2O)]$. Ga-CAU-49 crystallizes in a new and very complex crystal structure containing an unprecedented IBU of the formula ${}_{\infty}^1{Ga_{16}(OH)_{18}O_{60}}$, composed of corner-sharing GaO₅ and GaO₆ polyhedra. This is, to the best of our knowledge, the first time a trigonal-bipyramidal coordination geometry has been observed in a Ga-MOF, while for coordination polymers and complexes this coordination geometry is well-known.^{50,51} The hexagonal arrangement of the IBUs is shown in Figure 4. Five symmetry-independent Ga³⁺ ions and linker molecules are observed in the asymmetric unit, and the Ga³⁺ ions form ${}_{\infty}^1{Ga_{16}(OH)_{18}O_{60}}$ chains, which are extending along the *ac* diagonal of the unit cell (Figure 4d). In contrast to other Aland Ga-MOFs the IBU contains 5-fold-coordinated Ga^{3+} ions. The IBU is formed by corner-sharing GaO_5 and GaO_6 polyhedra shown in pink and blue, respectively, in Figure 4. Each IBU is connected through the linker molecules to six other IBUs, which leads to a heptanodal 3,3,4,4,4,5,5-c net (Figure S24). The choice of nodes when deconstructing the inorganic building units of Ga-CAU-49 and Ga-CAU-51 was made as described by O'Keeffe and Yaghi,⁵² where the point of extension of each linker was used as a node. Elaborate structural details can be found in section 5 in the Supporting Information. Water molecules are represented by O6 and O7





Figure 4. Crystal structure architecture of Ga-CAU-49 with its IBU in different perspective views (a-c) and the repetitive sequence of Ga³⁺ ions in the IBU marked in pink for CN = 5 and blue for CN = 6 as well as (d) the hexagonal connection pattern between the IBUs. Linker molecules are deleted for reasons of simplicity. GaO₅ trigonal bipyramids are shown in pink, and GaO₆ octahedra are shown in blue.

in the crystal structure of Ga-CAU-49 (Figure S16). Since there are various distances in the range of $d(O\cdots O) = 2.64(3)-3.04(2)$ Å between O6, O7 and adjacent oxygen atoms, H-bonding is anticipated.

Ga-CAU-51. Employing H₂TDC and gallium(III) nitrate in an acetic acid and water (5/1) mixture led to the crystallization of the new compound Ga-CAU-51 ([Ga(OH)(TDC)]). The crystal structure of Ga-CAU-51 contains chains of alternating cis, trans corner-sharing GaO₆ polyhedra as the IBU (Figure 5a). These chains are interconnected by thiophene-2,5dicarboxylate ions, forming square-shaped one-dimensional channels along [100] with a diameter of ca. 6.2 Å. This IBU has been described once for another Ga-MOF⁵³ and was also reported for the Al compounds MOF-303 and MOF-573, of composition [Ga(OH)(PzDC)], with $PzDC^{2-} = 1H-3,5$ pyrazoledicarboxylate.^{54,35} Further details on the structure and structure determination are given in (section 5 and Table S15 in the Supporting Information. A topological analysis of the framework gives the previously described tetranodal 5,5,5,5-c net **xhh**.³

Table 3 and Figure 3 summarize the structural details of MOFs based on the V-shaped linker molecules presented in Figure 1: i.e., framework name, IBU, and topology. For most of the linker molecules isostructural products are observed when Al³⁺ ions are replaced by Ga³⁺. Due to the different ionic radii $(r(Ga^{3+}) = 0.620 \text{ Å}, r(Al^{3+}) = 0.535 \text{ Å}), \text{ larger metal-oxygen}$ distances and unit cell parameters are found for the Ga-MOFs. The Ga–O (1.90(2)-2.05(6) Å) and Al–O (1.84(2)-1.86(2) Å) distances of the title compounds are in good agreement with the values reported in the literature (Figures S27 and S28), and the Al³⁺ and Ga³⁺ ions are found prevalently in an octahedral (CN = 6) coordination geometry. However, with Ga-CAU-49 and Ga-CAU-51, Ga-MOFs were discovered that do not have isostructural Al-MOFs. The use of *m*-H₂BDC-CH₃ results, as expected, in the formation of Al-CAU-10-CH₃, which contains chains of *cis* corner-sharing AlO₆ polyhedra, while in Ga-CAU-49 an unprecedented IBU with Ga³⁺ ions in octahedral and trigonal-bipyramidal coordination geometries is observed. With H₂TDC, i.e. the linker with the largest angle



Figure 5. Crystal structure of Ga-CAU-51 ([Ga(OH)(TDC)]) with (a) the arrangement of its *cis,trans* corner-sharing polyhedra, which are connected through thiophene-2,5-dicarboxylate ions to form the framework structure (b) containing square-shaped channels along [100] with a channel diameter of ca. 6.2 Å, and (c, d) pore walls in the crystal structure of Ga-CAU-51 depicted as Connolly surface models in Materials Studio.⁴⁴ GaO₆ octahedra are shown in blue, oxygen atoms in red, carbon atoms in black, and sulfur atoms in yellow.

 \angle (O₂C,C,CO₂) = 148° within the study, two Al-MOFs are known, the framework polymorphs Al-MIL-53-TDC⁵⁷ and CAU-23.⁵⁸ The former exhibits low long-range ordering, which was proven by NMR spectroscopy.⁵⁷ In contrast CAU-23 is a highly crystalline material containing chains of $(trans)_4(cis)_4$ corner-sharing AlO₆ polyhedra.⁵⁸ In combination with the larger Ga³⁺ ions only a highly crystalline compound was observed with chains of alternating *cis*-*trans* corner-sharing GaO₆ polyhedra. The crystal structure of Ga-CAU-51 resembles somewhat those of MOF-303 and MOF-573,^{54,55} which were recently reported but for which no detailed crystallographic information was presented.

Thermal analysis. The temperature-dependent properties of all title compounds were investigated by thermogravimetric (TG) and temperature-dependent (TD) PXRD analyses. The TG curves are presented in Figures S37–S43 and in Figure 6. The presence of solvent molecules in the crystal structures of Ga-CAU-49, Ga-CAU-10-OCH₃, and Ga-CAU-51 was confirmed, and all compounds decompose above 350 °C, leading to the formation of crystalline β -Ga₂O₃ or X-ray amorphous Al₂O₃ (Table S23). As has previously been described, the Al-MOFs exhibit higher thermal stabilities in comparison to their isostructural Ga-MOFs.²¹ This trend is also confirmed by TD PXRD measurements (Figures S44–S50). Figure 6 shows a correlation between the TG (left) and TD PXRD measurements (right) of Ga-CAU-51. The initial mass loss in the TG curve, up to a temperature of ca. 100 °C, is attributed to the

Table 3. V-Shaped Linker Molecules Used in This Study and Their Corresponding Al and Ga Compound Framework Type Structures, IBUs, and Topological Net Symbols⁴

		framework type/IBU/net symbol		
linker molecule	angle between carboxylate groups (deg)	Al compound	Ga compound	
H ₂ SDBS	102	Al-CAU-11/trans/sql	Ga-CAU-11/trans/sql	
<i>m</i> -H ₂ BDC-OCH ₃	120	Al-CAU-10/cis/lzh	Ga-CAU-10/cis/lzh	
<i>m</i> -H ₂ BDC-NHCOCH ₃	120	Al-CAU-10/cis/lzh	Ga-CAU-10/cis/lzh	
<i>m</i> -H ₂ BDC-CH ₃	120	Al-CAU-10/cis/lzh	Ga-CAU-49/cis,trans/-	
2,5-H ₂ TDC	148	Al-MIL-53/trans/sra	Ga-CAU-51/cis,trans/xhh	
		Al-CAU-23/(trans) (cis) /-		

^{*a*}For CAU-23 and Ga-CAU-49 no net symbols (three-letter names) have yet been assigned.



Figure 6. TG curve (left) and TD PXRD measurement (right) of Ga-CAU-51, with major events marked by red lines at ca. 100 and 350 °C.

desorption of water molecules from the framework. This correlates well with the first major event detected by TD PXRD, seen as a change in relative intensities and a slight shift in reflection positions. Ga-CAU-51 decomposes above ca. 350 $^{\circ}$ C, as confirmed by both techniques.

Sorption Measurements. All of the title compounds were studied regarding their sorption properties with nitrogen or water at 77 and 298 K, respectively (Table S25). The nitrogen isotherms are presented in Figures S51–S57. No considerable nitrogen uptake was detected except for Ga-CAU-11, which shows a type I shaped isotherm, which is typical for microporous materials (Figure S54).⁵⁹ Ga-CAU-11 exhibits a specific surface area of $a_{s,BET} = 210 \text{ m}^2/\text{g}$ and a micropore volume of $V_m = 0.09 \text{ cm}^3/\text{g}$.

Water sorption isotherms of all title compounds and their PXRD patterns after the sorption measurements are presented in Figures S59–S64 and Figures S65–S71 in the Supporting Information, respectively. In the following paragraphs, only the results of Ga-CAU-51 and Ga-CAU-10-NHCOCH₃ are presented in Figures 7 and 8, since they exhibit the highest H₂O uptake and the most distinct structural changes, respectively. For Ga-CAU-51 a sigmoidal-shaped isotherm with a steep rise at $p/p_0 = 0.38$ and a high maximum uptake of $m_{\rm ads} = 370 \text{ mg/g}$ is found (calculated by PLATON, ³⁷ $m_{\rm ads} = 402 \text{ mg/g}$).

In contrast, only a small water uptake is observed for Ga-CAU-10-NHCOCH₃, but two distinct steps are found, indicating a structural change in the framework upon water adsorption.⁵⁹ Therefore, humidity-dependent PXRD measurements were carried out, showing two major changes in the PXRD pattern of Ga-CAU-10-NHCOCH₃ as depicted in Figure 8. These changes are located at relative humidity values of ca. 30-40% and 60-70%, matching the starting points of



Figure 7. Water sorption isotherm of Ga-CAU-51 at 298 K. Filled symbols represent adsorption and empty symbols desorption.

the steep uptakes in the isotherm. Three framework forms were identified by PXRD measurements (Figure S73): the activated form of Ga-CAU-10-NHCOCH₃ (red), an intermediate wet form (blue), and the as-synthesized form (green). A structure determination could only be carried out for the activated form, as it exhibits a highly ordered framework. Thus, the deviation between calculated (calculated by PLATON $m_{ads} = 99 \text{ mg/g}$) and experimental uptakes ($m_{ads} = 55 \text{ mg/g}$) is related to structural changes upon water adsorption. Since the structural flexibility of CAU-10 MOFs has been studied quite extensively in the past, it is plausible to assume that rotation of the linker molecules occurs upon water sorption.³⁰

The syntheses, structure determinations, and full characterizations of one new Al-MOF and five Ga-MOFs containing different V-shaped linker molecules are reported. We were able

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Figure 8. (a) PXRD patterns at relative humidity values between 7 and 90%, measured at 298 K. Three colors represent PXRD data of the activated sample (red), an intermediate wet form (blue), and the as-synthesized phase (green). (b) Water sorption isotherm for Ga-CAU-10-NHCOCH₃ measured at 298 K. Filled symbols represent adsorption and empty symbols desorption. The color of the data points refers to the color used for the different structures of Ga-CAU-10-NHCOCH₃.

to confirm the previously reported high tendency of Ga-MOFs to crystallize in frameworks isoreticular with Al-MOFs. Thus, isostructural compounds were acquired in four out of six cases, i.e. Ga-CAU-10-R (R = OCH₃, NHCOCH₃), Ga-CAU-11, and Ga-CAU-11-COOH, while for the linker molecules *m*-H₂BDC-CH₃ and H₂TDC exceptions to this rule are observed. This led to the discovery of the new Ga-MOFs Ga₄(m-HBDC- $CH_3)_2(m-BDC-CH_3)_3(OH)_4(H_2O)$ (Ga-CAU-49) and Ga-(OH)(TDC) (Ga-CAU-51). Ga-CAU-49 exhibits an unprecedented, rod-shaped IBU ${}^{1}_{\infty}$ {Ga₁₆(OH)₁₈O₆₀} forming a complex 3D crystal structure with Ga³⁺ ions in an uncommon trigonal-bipyramidal coordination environment. Ga-CAU-10-R $(R = OCH_3, NHCOCH_3)$ are the first CAU-10 type compounds made from Ga³⁺ ions, which led to single crystals of suitable size for a structure determination through SCXRD in the case of Ga-CAU-10-OCH₃. Ga-CAU-51 exhibits exceptional water sorption properties with a maximum uptake of 370 mg/g. This work not only highlights the important role of isoreticular chemistry with regard to group 13 element MOFs but also shows how Ga^{3+} ions can be employed in solvothermal syntheses to discover compounds with new frameworks. Perhaps in the future the isostructural Al-MOFs will be synthetically accessible, but the right synthesis conditions must be found.

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ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.1c00767.

Thermogravimetric measurement of $Ga(NO_3)_3 \cdot xH_2O_1$ detailed synthesis procedures for Ga-CAU-10-OCH₃, 5acetamideisophthalic acid, Al-CAU-10-NHCOCH₃, Ga-CAU-10-NHCOCH₃, Ga-CAU-11, Ga-CAU-11-COOH, Ga-CAU-49, and Ga-CAU-51 and results of the CHNS analysis, SEM of Ga-CAU-10-OCH₃ single crystals, 3D electron diffraction measurements of Ga-CAU-51 ($[Ga(OH)(C_5H_2O_2S)]$), Rietveld and Pawley refinements, asymmetric units, and selected bond lengths for Ga-CAU-10-OCH₃, Al-CAU-10-NHCOCH₃, Ga-CAU-10-NHCOCH₃, and Ga-CAU-11, Le Bail refinement, asymmetric unit, and selected bond lengths for Ga-CAU-11-COOH, asymmetric unit and selected bond lengths for Ga-CAU-49, Rietveld refinement, asymmetric unit, and selected bond lengths for Ga-CAU-51, crystal structure descriptions of CAU-10, CAU-11, and Ga-CAU-49, CCDC database research, IR spectroscopy, thermogravimetric measurements, temperature-dependent PXRD, and sorption isotherms (PDF)

Accession Codes

CCDC 2067831–2067836 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

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