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Structural diversity of dimethylgallium naphthalene-2,3-dicarboxylate/pyridine systems

Supporting information

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1. X-Ray Crystallography Data

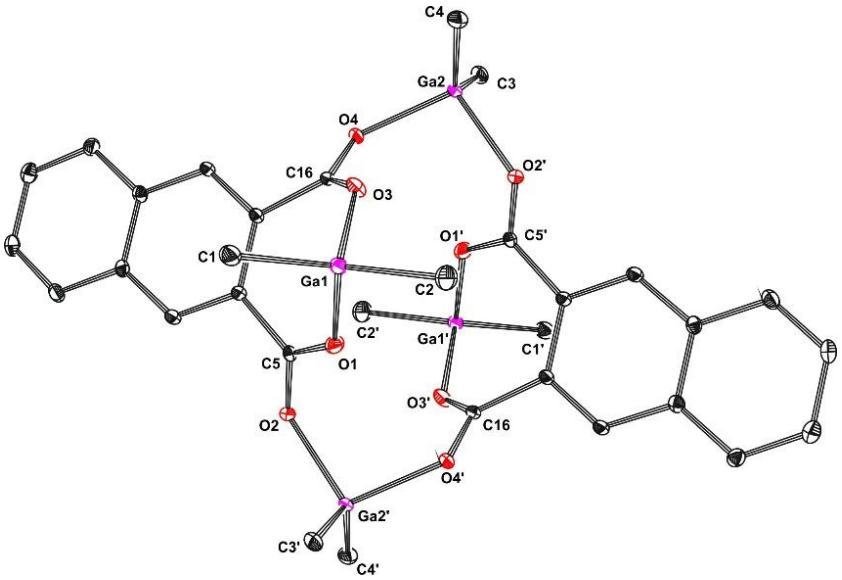

Fig. S1. The molecular structure of **1** with thermal ellipsoids set at 30% probability. Hydrogen atoms have been omitted for clarity. Operators for generated equivalent atoms: (*-x+1,-y+1,-z+2*), (*-x+1,-y+1,-z+1*).

Table S1. Crystallographic data and structure refinement parameters for **1.**

Empirical formula	$C_{33}H_{38}Cl_2Ga_4O_8$	
Formula weight	912.41	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 9.2021(2) Å	α = 83.711(2)°.
	b = 10.0945(3) Å	β = 86.881(2)°.
	c = 20.3227(3) Å	γ = 80.193(2)°.
Volume	1847.78(7) Å^3	
Z	2	
Density (calculated)	1.640 Mg/m^3	
Absorption coefficient	3.076 mm^{-1}	
F(000)	916	
Theta range for data collection	2.018 to 26.999°.	
Index ranges	-11<=h<=11, -12<=k<=12, -25<=l<=25	
Reflections collected	41567	
Independent reflections	8043 [R_{int} = 0.1231]	
Completeness to theta = 25.242°	99.9 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8043 / 0 / 432	
Goodness-of-fit on F^2	1.060	
Final R indices [I>2sigma(I)]	R_1 = 0.0339, wR_2 = 0.0930	
R indices (all data)	R_1 = 0.0379, wR_2 = 0.0982	
Largest diff. peak and hole	0.823 and -0.780 e. Å^{-3}	

$R1 = \Sigma||Fo| - |Fc||/\Sigma|Fo|$. [b] *$wR2 = [\Sigma w(Fo^2 - Fc^2)^2/\Sigma w(Fo^2)^2]^{1/2}$*

Table S2. Selected bond lengths (Å) and angles (deg) for **1**.

Bond Lengths (Å)					
Ga1-C1	1.951(2)	Ga2-O2’	1.991(1)		
Ga1-C2	1.939(2)	Ga2-O4	1.981(1)		
Ga2-C3	1.955(2)	C5-O1	1.263(3)		
Ga2-C4	1.950(2)	C5-O2	1.256(2)		
Ga1-O1	1.943(1)	C16-O3	1.260(3)		
Ga1-O3	1.943(2)	C16-O4	1.260(3)		
Bond Angles (deg)					
O1-C5-O2	120.94(19)	O1-Ga1-C1	108.36(8)	O4-Ga2-C4	110.47(8)
O3-C16-O4	121.27(19)	O1-Ga1-C2	103.73(9)	O2-Ga2’-C3’	108.02(8)
Ga1-O1-C5	132.13(14)	O3-Ga1-C1	111.13(9)	O2-Ga2’-C4’	102.38(9)
Ga2-O4-C16	121.54(14)	O3-Ga1-C2	101.25(10)		
O1-Ga1-O3	90.40(7)	O4-Ga2-C3	101.26(8)		

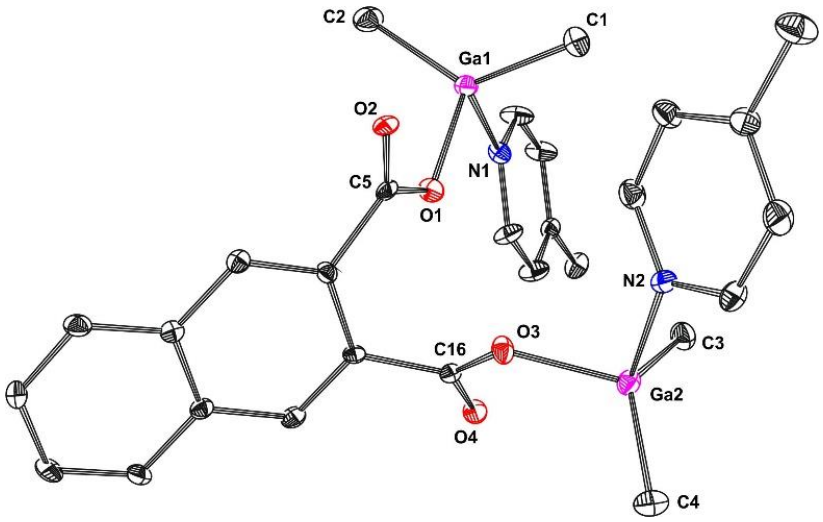

Fig. S2. The molecular structure of **2** with thermal ellipsoids set at 30% probability. Hydrogen atoms have been omitted for clarity.

Table S3. Crystallographic data and structure refinement parameters for **2.**

Empirical formula	$C_{28}H_{32}Ga_2N_2O_4$	
Formula weight	599.99	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 9.4740(4) Å	α = 83.380(2)°.
	b = 11.1300(5) Å	β = 75.285(2)°.
	c = 14.0500(6) Å	γ = 78.768(2)°.
Volume	1402.09(11) $Å^3$	
Z	2	
Density (calculated)	1.421 Mg/m^3	
Absorption coefficient	1.956 mm^{-1}	
F(000)	616	
Theta range for data collection	1.870 to 26.000°.	
Index ranges	-11<=h<=11, -13<=k<=13, -17<=l<=17	
Reflections collected	10407	
Independent reflections	5513 [R_{int} = 0.0841]	
Completeness to theta = 25.242°	99.7 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5513 / 0 / 331	
Goodness-of-fit on F^2	1.097	
Final R indices [I>2sigma(I)]	R_1 = 0.0774, wR_2 = 0.1445	
R indices (all data)	R_1 = 0.1224, wR_2 = 0.1633	
Largest diff. peak and hole	0.769 and -0.663 e. $Å^{-3}$	

$R1 = \Sigma||Fo| - |Fc||/\Sigma|Fo|$. [b] *$wR2 = [\Sigma w(Fo^2 - Fc^2)^2/\Sigma w(Fo^2)^2]^{1/2}$*

Table S4. Selected bond lengths (Å) and angles (deg) for **2**.

Bond Lengths (Å)					
Ga1-C1	1.955(8)	Ga2-O3	1.919(5)	C5-O1	1.300(8)
Ga1-C2	1.957(8)	Ga2-C3	1.962(8)	C5-O2	1.231(8)
Ga1-N1	2.068(6)	Ga2-C4	1.960(8)	C16-O3	1.303(8)
Ga1-O1	1.910(5)	Ga2-N2	2.083(6)	C16-O4	1.229(8)
Bond Angles (deg)					
O1-C5-O2	123.8(7)	N1-Ga1-C1	102.8(3)	O4-Ga2-C4	110.47(8)
O3-C16-O4	124.4(6)	N1-Ga1-C2	107.5(3)	O2-Ga2'-C3'	108.02(8)
Ga1-O1-C5	120.6(4)	N2-Ga2-O3	90.4(2)	O2-Ga2'-C4'	102.38(9)
Ga2-O3-C16	120.7(4)	N2-Ga2-C3	101.25(10)		
N1-Ga1-O1	90.1(2)	N2-Ga2-C4	101.26(8)		

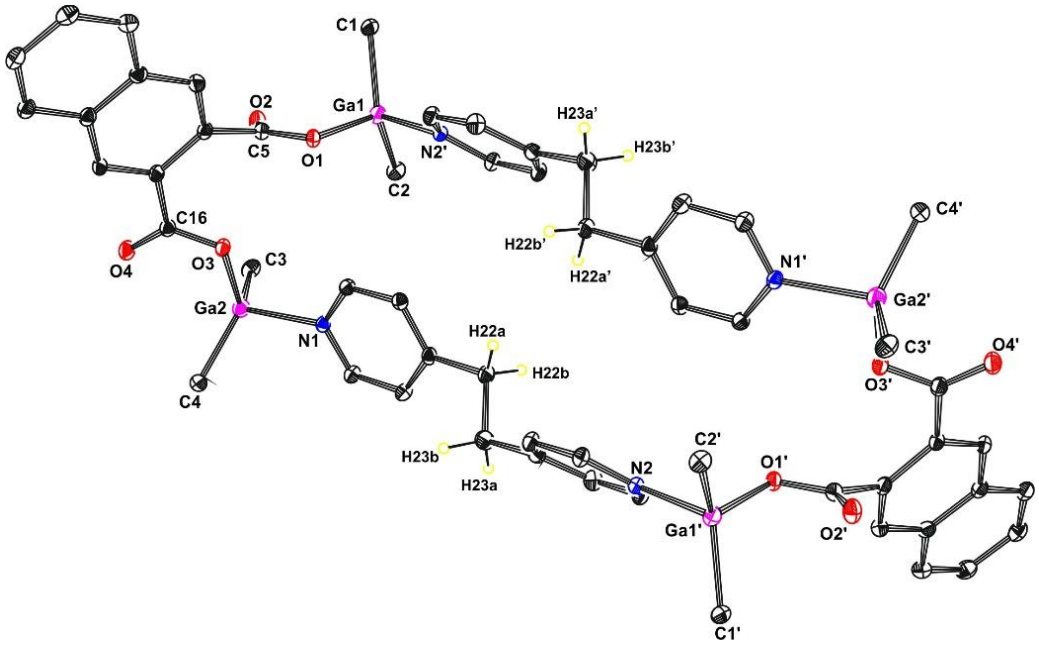

Fig. S3. The molecular structure of **3** with thermal ellipsoids set at 30% probability. Hydrogen atoms have been omitted for clarity. Operators for generated equivalent atoms: (*-x+1,-y+1,-z+1*).

Table S5. Crystallographic data and structure refinement parameters for **3.**

Empirical formula	$C_{56}H_{60}Ga_4N_4O_8$	
Formula weight	1195.96	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 10.5847(3) Å	α = 90°.
	b = 18.5066(3) Å	β = 100.876(2)°.
	c = 13.8257(3) Å	γ = 90°.
Volume	2659.63(11) Å	
Z	4	
Density (calculated)	1.493 Mg/m^3	
Absorption coefficient	2.062 mm^{-1}	
F(000)	1224	
Theta range for data collection	1.860 to 25.652°.	
Index ranges	-12<=h<=12, -22<=k<=21, -16<=l<=11	
Reflections collected	19640	
Independent reflections	5002 [R_{int} = 0.0326]	
Completeness to theta = 25.242°	100.0 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5002 / 0 / 329	
Goodness-of-fit on F^2	1.044	
Final R indices [I>2sigma(I)]	R_1 = 0.0359, wR_2 = 0.0996	
R indices (all data)	R_1 = 0.0410, wR_2 = 0.1041	
Largest diff. peak and hole	0.486 and -0.510 e. $Å^{-3}$	

R1 = Σ||Fo| − |Fc||/Σ|Fo|. [b] *wR2 = [Σw(Fo² − Fc²)²/Σw(Fo²)²]^1/2*

Table S6. Selected bond lengths (Å) and angles (deg) for **3**

Bond Lengths (Å)

Ga1-C1	1.966(3)	Ga2-O3	1.9142(18)	C5-O1	1.294(3)
Ga1-C2	1.962(3)	Ga2-C3	1.959(3)	C5-O2	1.224(3)
Ga1-N2’	2.081(2)	Ga2-C4	1.966(3)	C16-O3	1.293(3)
Ga1-O1	1.9334(18)	Ga2-N1	2.078(2)	C16-O4	1.225(3)

Bond Angles (deg)

O1-C5-O2	124.2(2)	N2’-Ga1-O1	88.89(8)	N2’-Ga1-C2	104.46(11)
O3-C16-O4	124.7(3)	O1-Ga1-C1	104.71(10)	N1-Ga2-C3	110.75(11)
Ga1-O1-C5	109.95(17)	O1-Ga1-C2	115.70(11)	N1-Ga2-C4	102.60(11)
Ga2-O3-C16	116.45(17)	N2’-Ga1-C1	107.92(11)		

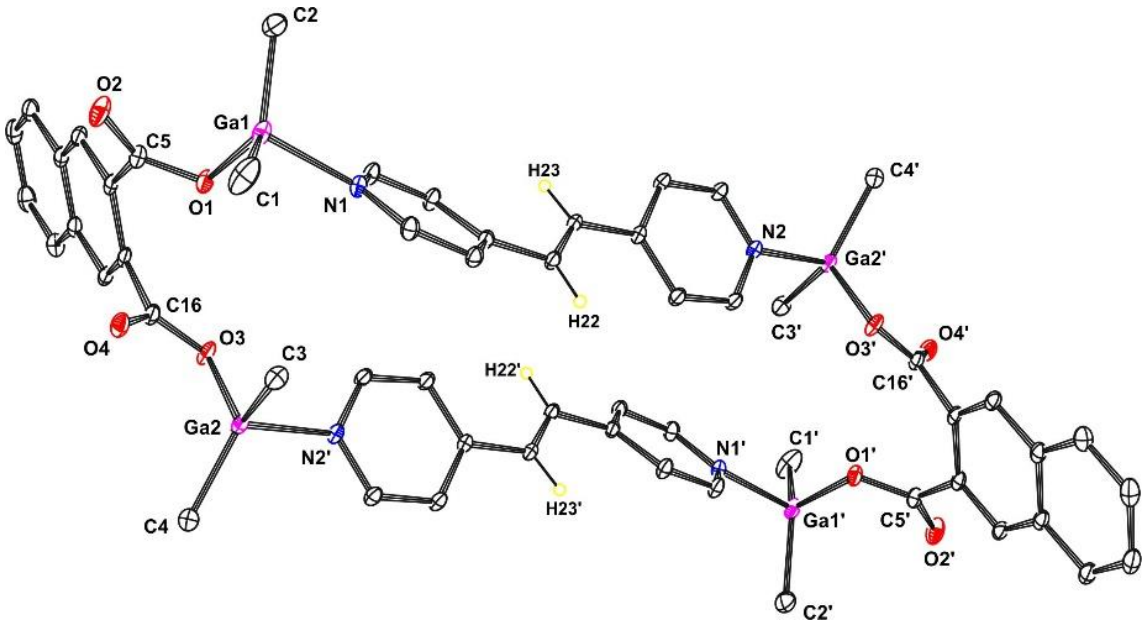

Fig. S4. The molecular structure of **4** with thermal ellipsoids set at 30% probability. Hydrogen atoms have been omitted for clarity. Operators for generated equivalent atoms: (*-x+3/2,-y+3/2,-z+1*).

Table S7. Crystallographic data and structure refinement parameters for **4.**

Empirical formula	$C_{56}H_{56}Ga_4N_4O_8$	
Formula weight	794.62	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	*C*2/c	
Unit cell dimensions	*a* = 18.8661(3) Å	*α* = 90°.
	b = 13.2599(2) Å	*β* = 94.2370(10)°.
	c = 21.6552(2) Å	*γ* = 90°.
Volume	5402.51(13) $Å^3$	
Z	4	
Density (calculated)	1.465 Mg/m^3	
Absorption coefficient	2.030 mm^{-1}	
F(000)	2432	
Theta range for data collection	2.138 to 30.118°.	
Index ranges	-26<=*h*<=26, -18<=*k*<=18, -30<=*l*<=30	
Reflections collected	64560	
Independent reflections	7581 [R_{int} = 0.0309]	
Completeness to theta = 25.242°	99.8 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7581 / 0 / 329	
Goodness-of-fit on F^2	1.109	
Final R indices [I>2sigma(I)]	R_1 = 0.0337, wR_2 = 0.0878	
R indices (all data)	R_1 = 0.0434, wR_2 = 0.0925	
Largest diff. peak and hole	1.164 and -0.658 e.$Å^{-3}$	

R1 = Σ||Fo| − |Fc||/Σ|Fo|. [b] *wR2 = [Σw(Fo² − Fc²)²/Σw(Fo²)²]^1/2*

Table S8. Selected bond lengths (Å) and angles (deg) for **4**

Bond Lengths (Å)

Ga1-C1	1.948(3)	Ga2-O3	1.9363(14)	C5-O1	1.293(2)
Ga1-C2	1.965(3)	Ga2-C3	1.957(2)	C5-O2	1.224(3)
Ga1-N1	2.0616(16)	Ga2-C4	1.953(2)	C16-O3	1.291(2)
Ga1-O1	1.9163(15)	Ga2-N2’	2.0861(16)	C16-O4	1.231(2)

Bond Angles (deg)

O1-C5-O2	124.8(2)	N1-Ga1-O1	88.66(6)	C3-Ga2-C4	125.98(10)
O3-C16-O4	123.60(18)	O1-Ga1-C1	115.10(12)	O3-Ga2-C3	113.34(8)
Ga1-O1-C5	118.38(13)	O1-Ga1-C2	107.13(10)	O3-Ga2-C4	112.30(9)
Ga2-O3-C16	110.76(13)	N1-Ga1-C1	105.96(9)	O3-Ga2-N2’	88.31(6)

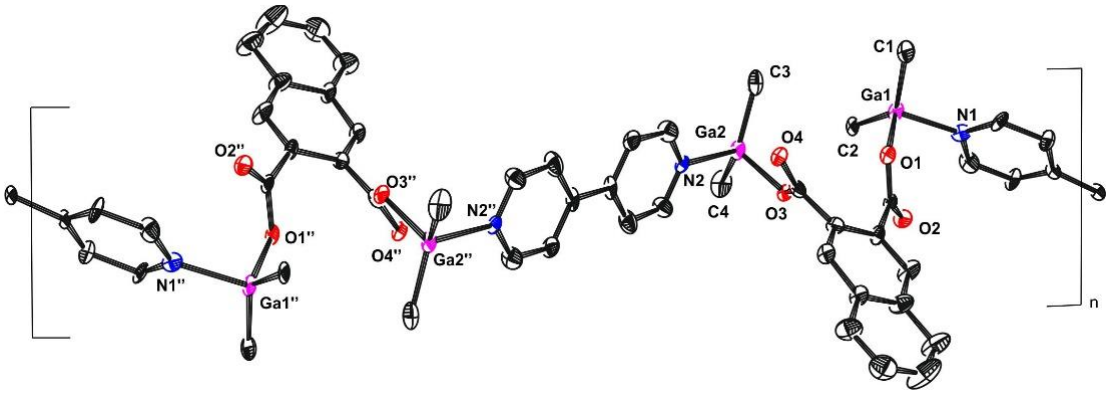

Fig. S5. The molecular structure of **5** with thermal ellipsoids set at 30% probability. Hydrogen atoms have been omitted for clarity. Operators for generated equivalent atoms: (*-x,-y+1,-z+1*), (*-x+2,-y+1,-z*)

Unfortunately, due to the poor quality of the crystals and disorder of the DCM molecules, a fully satisfactory refinement of the crystal structure of **5** could not be achieved, precluding a detailed discussion of metrical parameters. Modification of the synthesis and crystallization conditions by employing other solvents did not better results.

Table S9. Crystallographic data and structure refinement parameters for **5.**

Empirical formula	$C_{57}H_{56}Cl_{10}Ga_4N_4O_8$	
Formula weight	1558.43	
Temperature	100(2) K	
Wavelength	1.54184 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 10.2423(18) Å	α = 102.112(19)°.
	b = 12.817(3) Å	β = 107.393(18)°.
	c = 15.306(3) Å	γ = 101.202(17)°.
Volume	1802.3(7) Å^3	
Z	1	
Density (calculated)	1.436 Mg/m^3	
Absorption coefficient	5.518 mm^{-1}	
F(000)	784	
Theta range for data collection	3.669 to 61.482°.	
Index ranges	-11<=h<=9, -10<=k<=14, -17<=l<=14	
Reflections collected	8871	
Independent reflections	5301 [$R_{(int)}$ = 0.1362]	
Completeness to theta = 61.482°	94.7 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5301 / 72 / 392	
Goodness-of-fit on F^2	1.491	
Final R indices [I>2sigma(I)]	R_1 = 0.1792, wR_2 = 0.4417	
R indices (all data)	R_1 = 0.2320, wR_2 = 0.4768	
Largest diff. peak and hole	2.756 and -1.664 e.Å^{-3}	

R1 = Σ||Fo| − |Fc||/Σ|Fo|. [b] *wR2 = [Σw(Fo² − Fc²)²/Σw(Fo²)²]^1/2*

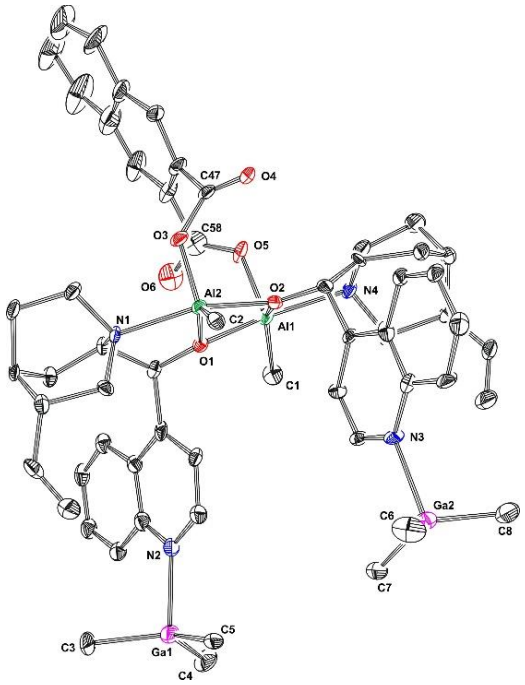

Fig. S6. The molecular structure of **6** with thermal ellipsoids set at 30% probability. Hydrogen atoms have been omitted for clarity.

Table S10. Crystallographic data and structure refinement parameters for **6.**

Empirical formula	$C_{274}H_{334}Al_8Ga_8N_{16}O_{24}$	
Formula weight	5009.15	
Temperature	100(2) K	
Wavelength	1.54184 Å	
Crystal system	Triclinic	
Space group	*P*1	
Unit cell dimensions	*a* = 14.0030(4) Å	*α* = 83.921(3)°.
	b = 20.4774(7) Å	*β* = 75.537(3)°.
	c = 26.4863(10) Å	*γ* = 71.123(3)°.
Volume	6956.0(4) Å^3	
Z	2	
Density (calculated)	1.196 Mg/m^3	
Absorption coefficient	1.584 mm^{-1}	
F(000)	2634	
Theta range for data collection	2.821 to 70.153°.	
Index ranges	-17<=*h*<=16, -24<=*k*<=22, -31<=*l*<=32	
Reflections collected	32273	
Independent reflections	32273 [R_{int} = 0.0565]	
Completeness to theta	99.8 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	32270 / 3 / 3009	
Goodness-of-fit on F^2	1.103	
Final R indices [I>2sigma(I)]	R_1 = 0.0961, wR_2 = 0.1173	
R indices (all data)	R_1 = 0.2596, wR_2 = 0.2798	
Largest diff. peak and hole	1.790 and -1.368 e.Å^{-3}	

R1 = Σ||Fo| − |Fc||/Σ|Fo|. [b] *wR2 = [Σw(Fo² − Fc²)²/Σw(Fo²)²]^1/2*

Table S11. Selected bond lengths (Å) and angles (deg) for **6**

Bond Lengths (Å)

Al1-C1	1.965(13)	Al2-O2	1.929(8)	Ga2-N3	2.140(10)
Al1-O1	1.944(8)	Al2-O3	1.772(9)	O3-C47	1.342(15)
AL1-O2	1.849(8)	Al2-C2	1.972(13)	O4-C47	1.195(16)
Al1-O5	1.822(9)	Al2-N1	2.111(9)	O5-C58	1.266(19)
Al1-N4	2.169(11)	Al2-O3	1.772(9)	O6-C58	1.30(2)
Al2-O1	1.850(8)	Ga1-N2	2.151(12)		

Bond Angles (deg)

C1-Al1-O1	96.3(5)	Al1-O1-Al2	102.3(4)	C2-Al2-O3	117.9(5)
C1-Al1-O2	140.8(6)	Al1-O2-Al2	102.9(4)	C2-Al2-N1	97.8(5)
C1-Al1-O5	119.4(6)	C2-Al2-O1	139.1(5)	O3-C47-O4	124.2(11)
C1-Al1-N4	98.3(5)	C2-Al2-O2	98.0(5)	O5-C58-O6	123.0(16)

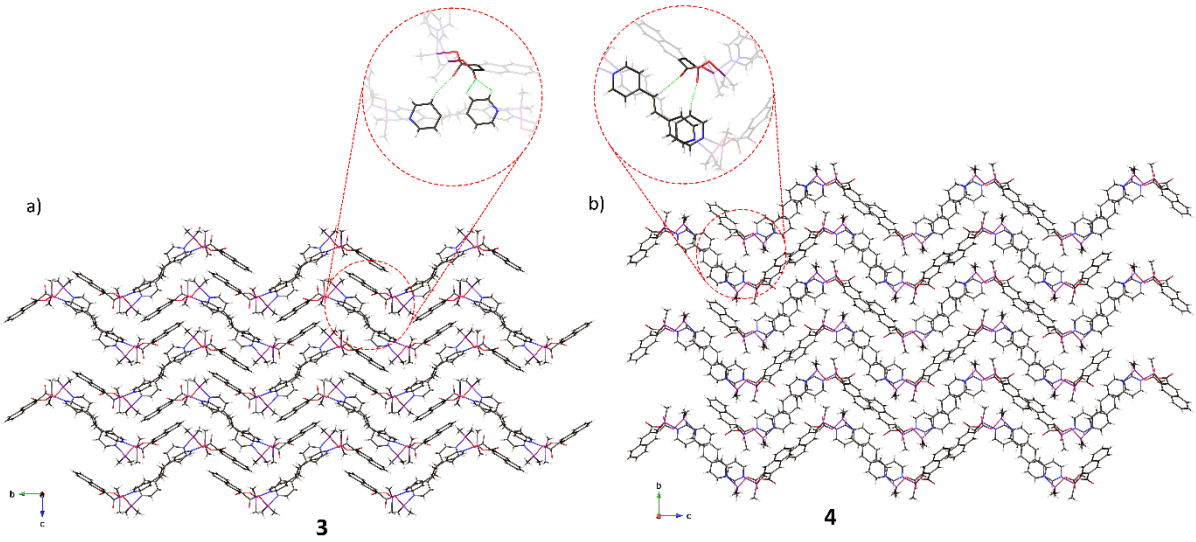

Fig. S7. Comparison of the crystal packing motifs in compounds **3** and **4**.

2. Analysis of Coordination Environments by Continuous Shape Measurements

The Continuous Shape Measurement (CShM) parameters were calculated using the SHAPE software.[1] The closer the calculated CShM value is to zero, the closer the coordination environment is to the corresponding ideal geometry.[2] CShM values were analyzed for complexes **1-4** and **6** considering the closest four and five donor atoms in the coordination spheres of the metal centers (Table S7). For complex **1**, the CShM values indicate a tetrahedral coordination geometry around the Ga centers, which is significantly more distorted for the chelated Ga centers (Ga1 and Ga3) than for the bridging ones (Ga2 and Ga4). In complexes **2-4**, the CShM values likewise point to predominantly tetrahedral coordination geometries at the metal centers. In these cases, the CShM values calculated assuming five nearest donor atoms are relatively high, consistent with the absence of a significant interaction at the fifth coordination site. In contrast, for complex **6**, CShM values calculated assuming four-coordinate Al centers indicate a vacant trigonal-bipyramidal geometry of coordination sphere, in agreement with the presence of an additional interaction occupying the fifth position. The CShM values calculated assuming a five-coordinate coordination sphere are comparable for trigonal-bipyramidal and square-pyramidal reference geometries, indicating a coordination environment that deviates substantially from ideal geometries. This distortion from an ideal trigonal-bipyramidal geometry is likely imposed by ligand-related geometric constraints, like the formation of AlNCCO macrocycles by chelating CN ligands and the specific conformation of bridging naphtha ligands.

Table S12. Calculated CShM parameters for complexes **1-4** and **6** considering four- and five-coordinate metal environments. CShM(T_d) and CShM(C_{3v}) correspond to tetrahedral and vacant trigonal-bipyramidal geometries for four-coordinate centers, respectively, while CShM(D_{3h}) and CShM(C_{4v}) correspond to trigonal-bipyramidal and square-pyramidal geometries for five-coordinate centers, respectively.

Metal center	four-coordinate environment	CShM(T_d)	CShM(C_{3v})	Fifth donor center	CShM(D_{3h})	CShM(C_{4v})
Complex **1**						
Ga1	C1 C2 O1 O3	1.760	2.551			
Ga2	C3 C4 O2 O4	0.997	2.861			
Ga3	C17 C18 O5 O7	1.555	2.392			
Ga4	C19 C20, O6 O8	0.939	2.793			
Complex **2**						
Ga1	C1, C2, O1, N1	1.229	2.041	O2	7.964	9.035
Ga2	C3, C4, O3, N2	1.316	1.816	O4	8.720	7.247
Complex **3**						
Ga1	C1 C2 O1 N2	1.455	2.434	O2	5.440	6.618
Ga2	C3 C4 O3 N1	1.256	2.585	O4	7.059	6.370
Complex **4**						
Ga1	C1 C2 O1 N1	1.433	2.011	O2	7.633	7.884
Ga2	C3 C4 O3 N2	1.312	1.718	O4	6.128	5.684
Complex **6**						
Al1	C1 O1 O2 O5	6.427	3.233	N4	3.600	2.405
Al2	C2 O1 O2 O3	6.011	2.751	N1	2.866	2.867
Al3	C59 O7 O8 O9	6.084	2.887	N7	3.000	2.930
Al4	C60 O7 O8 O11	7.062	3.870	N5	3.962	1.924
Al5	C118 O13 O14 O15	6.610	3.371	N11	3.468	2.428
Al6	C119 O13 O14 O17	6.815	3.899	N9	3.969	1.987
Al7	C176 O19 O20 O00L	6.272	3.170	N15	3.392	2.723
Al8	C177 O19 O20 O00S	5.802	2.575	N13	2.785	3.063

3. NMR spectra

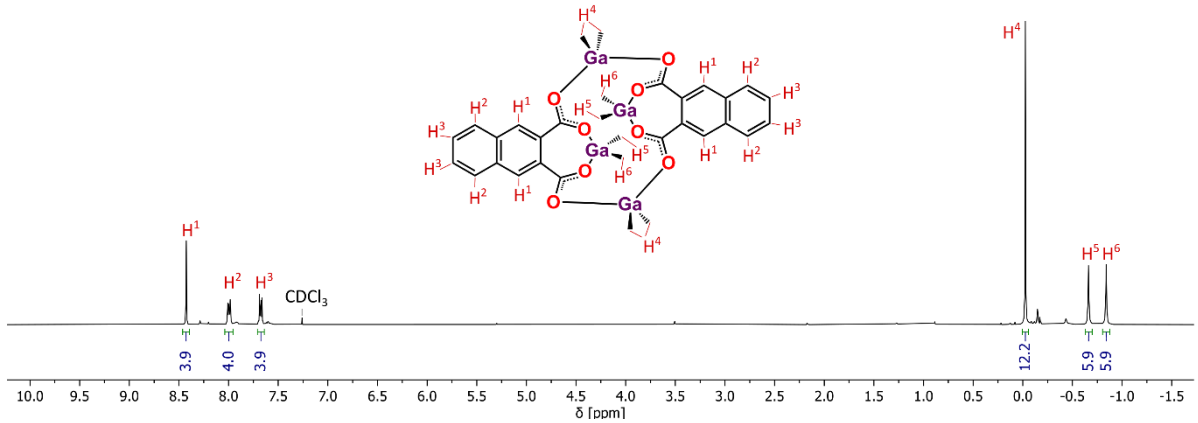

Fig. S8. ^{1}H NMR spectrum of **1** in $CDCl_3$.

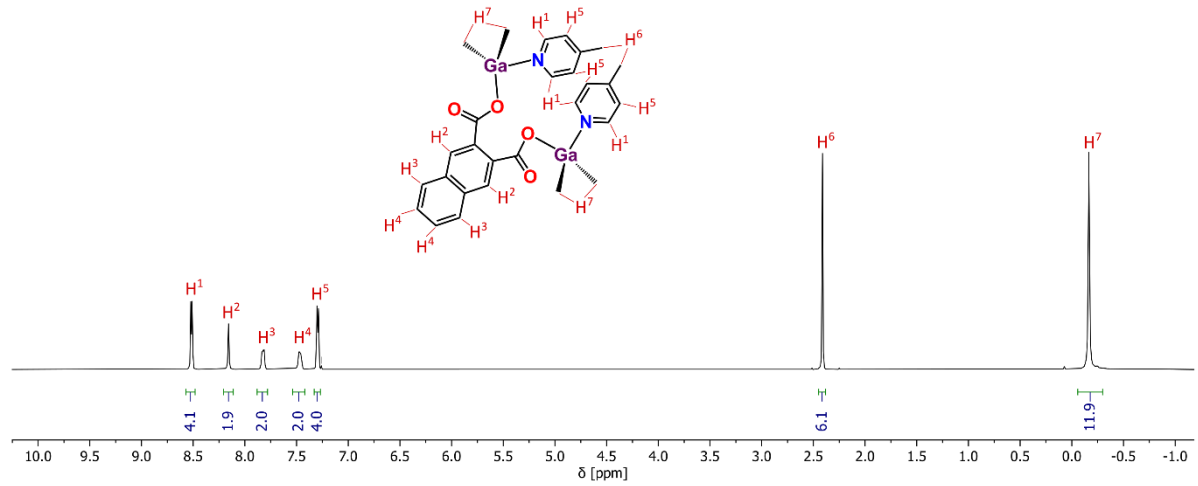

Fig. S9. ^{1}H NMR spectrum of **2** in $CDCl_3$.

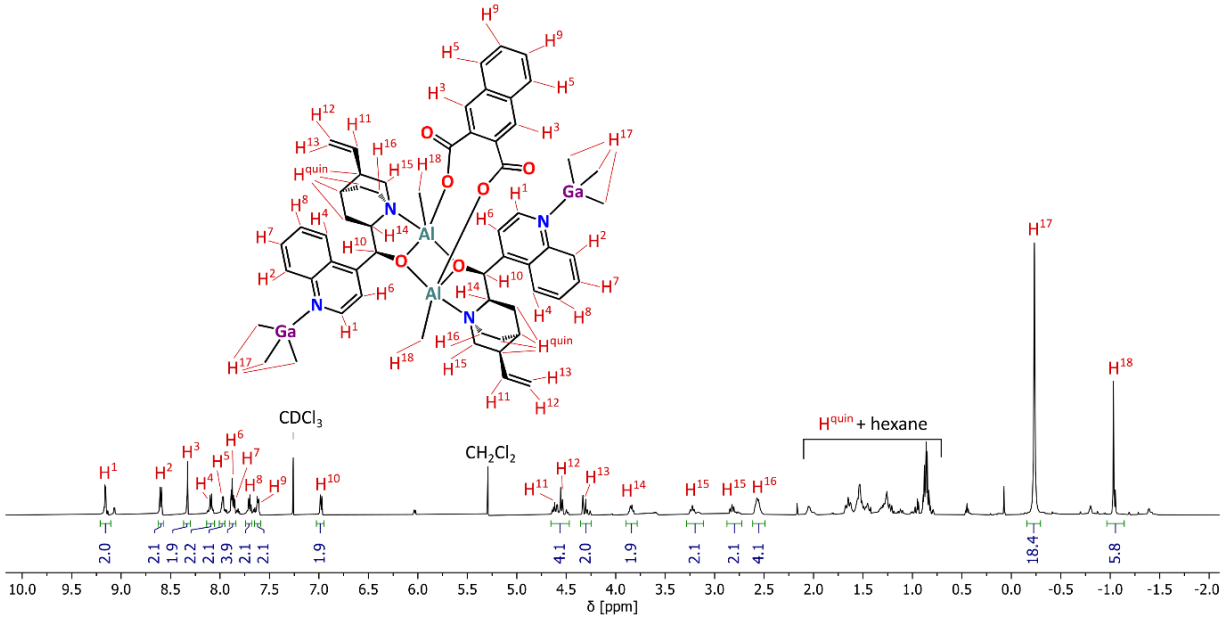

Fig. S10. ^{1}H NMR spectrum of **6** in $CDCl_3$.

4. FTIR spectra

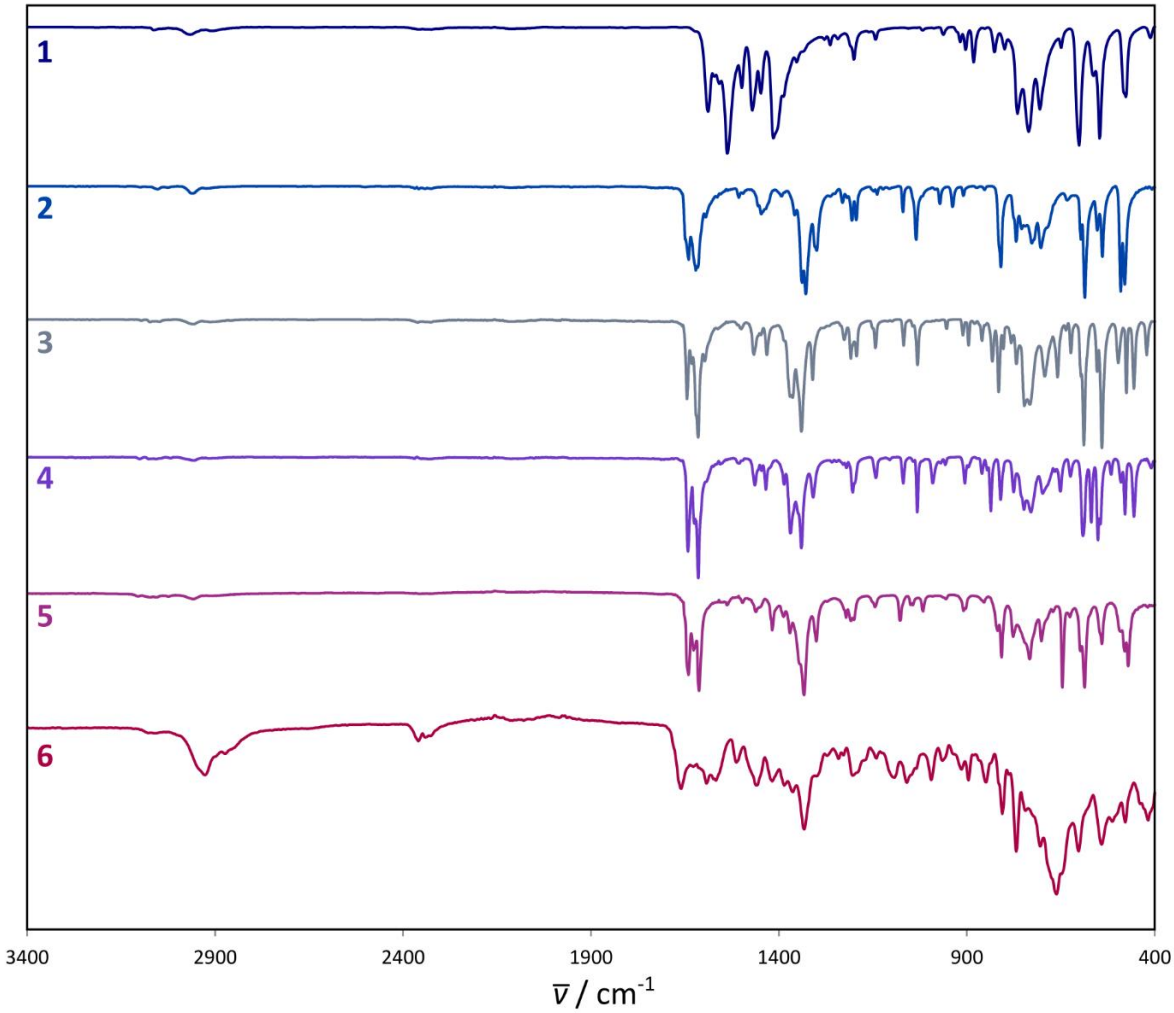

Fig. S11. Solid-state ATR FTIR spectra of compounds **1-6**.

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