Supporting information for

Synthesis, crystal structure and optical properties of $Me(OH)(HCOO)_2$ (Me = Al, Ga)

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Table 1. Structural data for $Me(OH)(HCOO)_2$ (Me = Al, Ga)

	$Al(OH)(HCOO)_2$[a]	$Ga(OH)(HCOO)_2$[b]
Space group, #	*C*2, 5	*C*2, 5
The number of formula units, *Z*	8	8
Cell constants:		
a, Å	8.8629(2)	8.8746(1)
b, Å	9.9890(2)	10.3291(1)
c, Å	10.2411(1)	10.27870(9)
β, °	106.223(1)	105.7565(6)
V, Å^3	870.56(3)	906.81(2)
D_x, g/cm^3	2.045	2.589
wRp (X-ray/Neutron1/Neutron2), %	2.51/1.92/-	2.81/1.23/0.66
Rp (X-ray/Neutron1/Neutron2), %	1.86/1.51/-	2.02/0.99/0.53
$R(F^2)$ (X-ray/Neutron1/Neutron2), %	2.60/8.79/-	2.82/5.28/1.64
χ^2	2.644	2.124
χ^2 for space group *C*2/*c*, 15	3.077	2.505

a - CCDC 1547303
b - CCDC 1547304

Table 2. Atomic coordinates and isotropic thermal parameters ($U_{iso} \times 100$, Å^2) for $Al(OH)(HCOO)_2$ and $Ga(OH)(HCOO)_2$ (given in Italic)

Atom	Wyckoff	*x/a*	*y/b*	*z/c*	U_{iso}*100
Me(1)	4*c*	-0.0018(11)	0.2194(8)	0.2490(8)	1.67(6)
		-0.0020(8)	*0.2477(7)*	*0.2484(6)*	*1.60(3)*
Me(2)	4*c*	0.2502(10)	-0.0331(10)	0.2478(7)	2.48(7)
		0.2454(7)	*-0.0063(7)*	*0.2501(5)*	*1.87(4)*
O(1)	4*c*	0.4193(12)	0.0380(8)	0.1935(8)	1.84(3)
		0.4275(9)	*0.0715(8)*	*0.1839(7)*	*1.59(3)*
O(2)	4*c*	0.3623(12)	-0.1792(11)	0.3211(7)	1.84(3)
		0.3760(17)	*-0.1470(13)*	*0.3323(12)*	*1.59(3)*
O(3)	4*c*	0.0647(10)	-0.1193(8)	0.2952(8)	1.84(3)
		0.0611(9)	*-0.0800(8)*	*0.2888(8)*	*1.59(3)*
O(4)	4*c*	0.1225(12)	0.1120(12)	0.1696(7)	1.84(3)
		0.1318(17)	*0.1436(13)*	*0.1737(12)*	*1.59(3)*
O(5)	4*c*	0.1647(10)	0.2344(6)	0.4227(11)	1.84(3)
		0.1583(10)	*0.2537(8)*	*0.4287(11)*	*1.59(3)*
O(6)	4*c*	0.5933(10)	-0.1251(6)	0.2064(6)	1.84(3)
		0.5839(12)	*-0.0967(6)*	*0.1747(9)*	*1.59(3)*
O(7)	4*c*	0.3105(10)	0.0511(8)	0.4259(9)	1.84(3)
		0.3239(10)	*0.0926(6)*	*0.4197(8)*	*1.59(3)*
O(8)	4*c*	-0.0783(11)	0.0570(6)	0.3198(7)	1.84(3)
		-0.0963(12)	*0.0850(6)*	*0.3014(8)*	*1.59(3)*
O(9)	4*c*	-0.1499(10)	0.2256(6)	0.0754(11)	1.84(3)
		-0.1779(10)	*0.2376(8)*	*0.0753(11)*	*1.59(3)*
O(10)	4*c*	-0.3267(9)	0.3818(8)	0.0809(9)	1.84(3)
		-0.3114(10)	*0.4239(6)*	*0.0648(8)*	*1.59(3)*
C(1)	4*c*	-0.0460(11)	-0.0662(6)	0.3322(8)	1.84(3)

		-0.0506(11)	*-0.0305(6)*	*0.3257(11)*	*1.59(3)*
C(2)	4*c*	0.2826(11)	0.1614(8)	0.4746(8)	1.84(3)
		0.2775(11)	*0.1848(8)*	*0.4798(8)*	*1.59(3)*
C(3)	4*c*	0.2693(11)	0.2951(8)	0.9808(9)	1.84(3)
		0.2797(13)	*0.3188(7)*	*0.9850(7)*	*1.59(3)*
C(4)	4*c*	0.4419(11)	-0.0029(6)	0.7912(9)	1.84(3)
		0.4416(10)	*0.0230(6)*	*0.8164(12)*	*1.59(3)*
H(1)	4*c*	0.613(3)	0.370(1)	0.616(4)	1.84(3)
		0.616(1)	*0.4068(9)*	*0.622(1)*	*1.59(3)*
H(2)	4*c*	0.364(3)	0.194(2)	0.572(3)	1.84(3)
		0.357(2)	*0.217(1)*	*0.5769(9)*	*1.59(3)*
H(3)	4*c*	0.334(3)	0.270(3)	0.087(1)	1.84(3)
		0.338(2)	*0.301(1)*	*0.0932(8)*	*1.59(3)*
H(4)	4*c*	0.351(1)	0.0720(8)	0.794(4)	1.84(3)
		0.350(1)	*0.0906(9)*	*0.829(1)*	*1.59(3)*
H(5)	4*c*	0.158(4)	0.282(3)	0.606(3)	1.84(3)
		0.125(3)	*0.321(1)*	*0.586(1)*	*1.59(3)*
H(6)	4*c*	0.396(2)	0.620(1)	0.9211(9)	1.84(3)
		0.379(2)	*0.643(1)*	*0.916(1)*	*1.59(3)*

Thermal parameters of oxygen, carbon and hydrogen atoms were constrained as a single variable.

Table 3. Selected interatomic distances *d* (Å) for $Al(OH)(HCOO)_2$ and $Ga(OH)(HCOO)_2$ (given in Italic)

Interatomic distances		Interatomic distances	
Me(1)-O(2)	1.876(12) *1.899(17)*	Me(2)-O(1)	1.877(11) *2.078(10)*
Me(1)-O(4)	1.878(12) *1.911(17)*	Me(2)-O(2)	1.807(11) *1.907(15)*
Me(1)-O(5)	1.975(13) *2.008(12)*	Me(2)-O(3)	2.032(11) *1.941(9)*
Me(1)-O(6)	1.876(11) *2.013(13)*	Me(2)-O(4)	1.875(12) *1.897(16)*
Me(1)-O(8)	1.973(11) *2.018(12)*	Me(2)-O(7)	1.943(13) *1.976(10)*
Me(1)-O(9)	1.893(14) *2.026(11)*	Me(2)-O(10)	1.859(13) *1.970(10)*
Average	**1.912**	**Average**	**1.899**
Average	***1.979***	***Average***	***1.962***

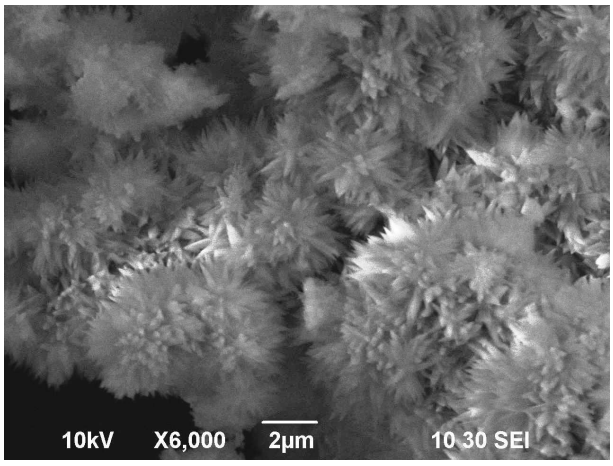


Fig. S1. The SEM image of the crystal aggregates of $Al(OH)(HCOO)_2$ produced by heating of aluminum nitrate solution in diluted formic acid at 80°C.

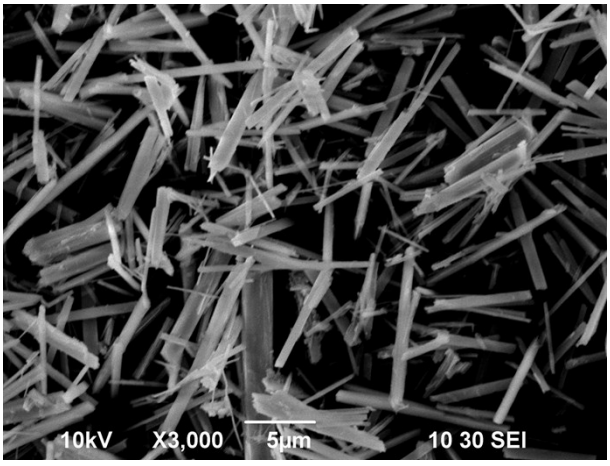


Fig. S2. The SEM image of $Ga(OH)(HCOO)_2$ crystals produced by evaporation of gallium nitrate solution in diluted formic acid at 60°C.

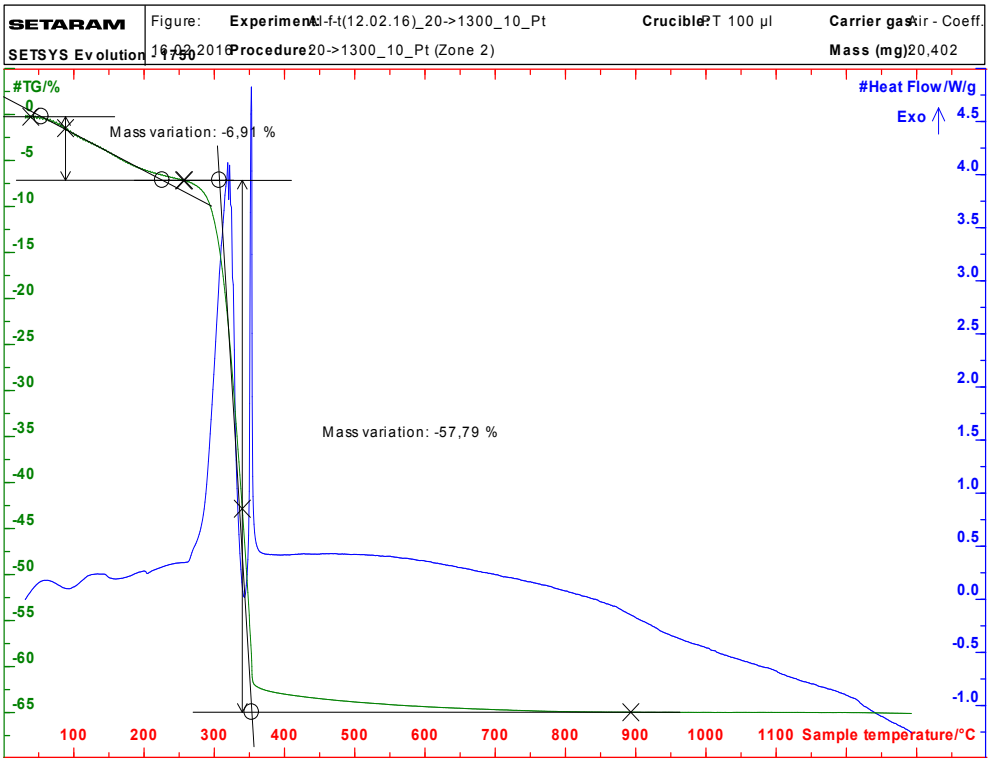


Fig. S3. The thermogravimetric analysis (TG, DTA) of hydrated basic aluminum formate $Al(OH)(HCOO)_2 \cdot 0.5H_2O$.

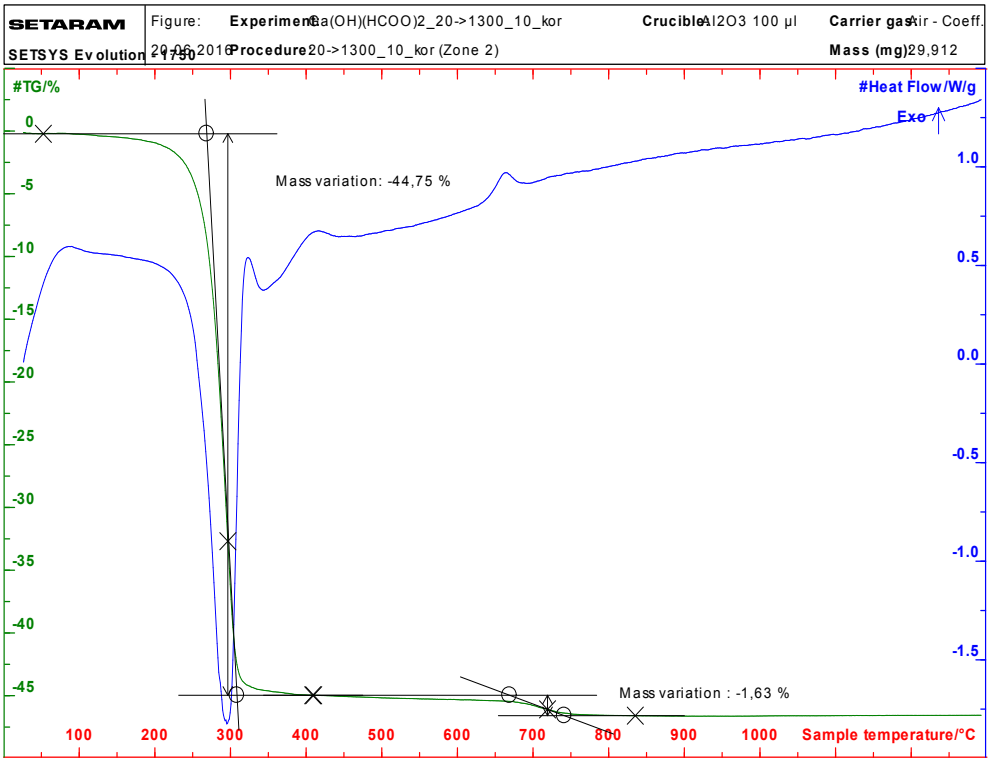
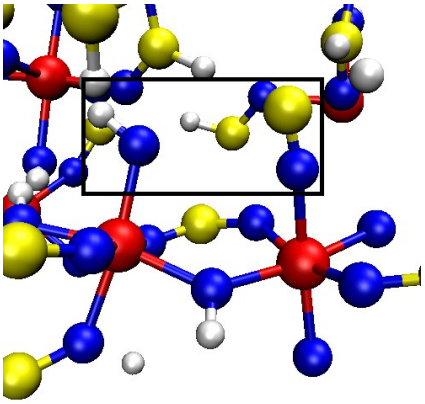
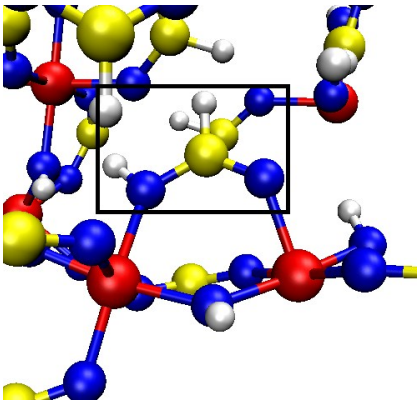


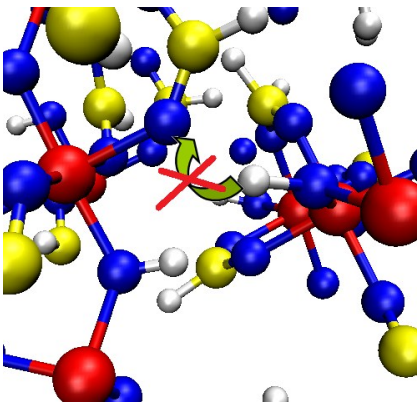
Fig. S4. The thermogravimetric analysis (TG, DTA) of the basic gallium formate $Ga(OH)(HCOO)_2$.



Movie 1 (separate file movie1.mpg or link https://youtu.be/FmbFAMaYYuk): Self-consistent charge density-functional tight-binding molecular dynamics simulation (MD using SCC-DFTB method) of the kinetic stability of defect I within the crystal of $Al(OH)(HCOO)_2$ at temperature 300 K during 0.2 ns. Only a fragment of crystal is shown with the defect on forefront (framed on the figure). The stable defect I is represented by formate anion decomposed after a possible **intra**chain H migration on OH group and CO molecule.



Movie 2 (separate file movie2.mpg or link https://youtu.be/w3z95fIoaPI): Self-consistent charge density-functional tight-binding molecular dynamics simulation (MD using SCC-DFTB method) of the kinetic stability of defect II within the crystal of $Al(OH)(HCOO)_2$ at temperature 300 K during 0.2 ns. Only a fragment of crystal is shown with the defect on forefront (framed on the figure). The stable defect II is represented by neutral molecule HCOOH after a possible **intra**chain H migration from the neighboring OH group. Molecule HCOOH acts mostly as a bidentate ligand, yet, a short-living (~ 40 ps) monodentate conformer can be registered using this MD simulation.



Movie 3 (separate file movie3.mpg or link https://youtu.be/ikOZo29aRmU): Self-consistent charge density-functional tight-binding molecular dynamics simulation (MD using SCC-DFTB method) of the kinetic stability of an unstable defect within the crystal of $Al(OH)(HCOO)_2$ at temperature 300 K during 0.2 ns. The defect is represented by neutral molecule HCOOH after possible **inter**chain H migration from the nearest OH group of neighboring molecular-like chain. The first 1 ps of the movie is slowed down to visualize the H migration from the defect, leading to the formation of perfect crystal lattice. A spontaneous **inter**chain H migration within perfect crystal is unlikely (crossed arrow on the figure).