

One-dimensional ladder gallium coordination polymer

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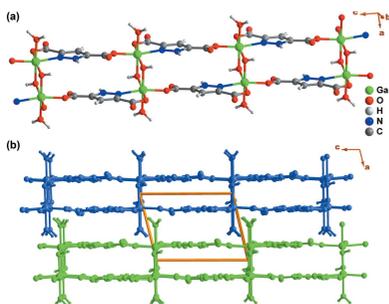
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A one-dimensional ladder-type coordination polymer, poly[[$(\mu_2$ -hydroxido)(μ_2 -1*H*-pyrazole-3,5-dicarboxylato)gallium(III)] monohydrate], [Ga(C₅H₂N₂O₄)(OH)(H₂O)]_n or [Ga(HPDC)(OH)(H₂O)]_n, **I**, isotypic with a V³⁺ coordination polymer previously reported by Chen *et al.* [*J. Coord. Chem.* (2008). **61**, 3556–3567] was prepared from Ga³⁺ and pyrazole-3,5-dicarboxylic acid monohydrate (H₃PDC·H₂O). Compound **I** was isolated using three distinct experimental methods: hydrothermal (HT), microwave-assisted (MWAS) and one-pot (OP) and the crystallite size should be fine-tuned according to the method employed. The coordination polymeric structure is based on a dimeric Ga³⁺ moiety comprising two μ_2 -bridging hydroxide groups, which are interconnected by HPDC²⁻ anionic organic linkers. The close packing of individual polymers is strongly directed by the supramolecular interactions, namely several O–H···O and N–H···O hydrogen-bonding interactions.

1. Chemical Context

Research on coordination polymers (CPs) and metal–organic frameworks (MOFs) remains a topical area in chemistry, particularly the study of their crystal structures (Cui *et al.*, 2016). These crystalline materials are typically obtained from a combination of metal ions and organic molecules, giving rise to one-, two- or three-dimensional structures (Chaplais *et al.*, 2009). A wide variety of synthetic methods have been reported for the preparation of CPs/MOFs (Stock & Biswas, 2012; Yuan *et al.*, 2018) ranging from ambient-temperature synthesis to conventional [hydrothermal (HT) and one-pot processes (OP)] and microwave (MWAS) synthesis. In addition, other less common techniques such as electrochemistry (EC), mechanochemistry (MC) and ultrasonic (US) synthesis can be used (Rubio-Martinez *et al.*, 2017; Stock & Biswas, 2012).

A large number of MOF-containing divalent transition-metal ions have been described (Stock & Biswas, 2012; Devic & Serre, 2014). Examples of CPs/MOFs containing main-group elements, such as Al³⁺, Ga³⁺, or In³⁺, remain scarce (Stock, 2014). A search in the Cambridge Structural Database unveils around 100 Ga³⁺-bearing CP/MOF structures, for example. Remarkably, most of these structures were solved using powder X-ray diffraction (PXRD) techniques (Reinsch & De Vos, 2014; Volkringer *et al.*, 2009). Such materials exhibit high thermal and chemical stability and are ideal candidates for a wide variety of applications (Silva *et al.*, 2015; Yuan *et al.*, 2018; Ajoyan *et al.*, 2018; Howarth *et al.*, 2016). As a result of the close similarity of the coordination chemistry of gallium



and aluminium, most of the Ga^{3+} -CP/MOFs published are isotypic with well-known Al^{3+} -CP/MOFs, and also with the much rarer In^{3+} -CP/MOFs (Schilling *et al.*, 2016). This may, in part, explain why most of the studies found in the literature of Ga^{3+} -CP/MOFs report only their structures. Furthermore, most of the applications that have been studied are related to those that are also found for Al^{3+} -CP/MOFs (Banerjee *et al.*, 2011; Zhang *et al.*, 2018; Reinsch & De Vos, 2014; Canivet *et al.*, 2014; Zhou *et al.*, 2012). For certain applications, Ga^{3+} -CP/MOFs excel, even surpassing the performance of the Al^{3+} -CP/MOFs (Coudert *et al.*, 2014; Ramaswamy *et al.*, 2017; Weber *et al.*, 2016; Gao *et al.*, 2014). Furthermore, gallium materials possess low toxicity and are found in applications such as gas and water adsorption, shock-absorber technology and semiconductors (Ramaswamy *et al.*, 2017; Coudert *et al.*, 2014; Schilling *et al.*, 2016)

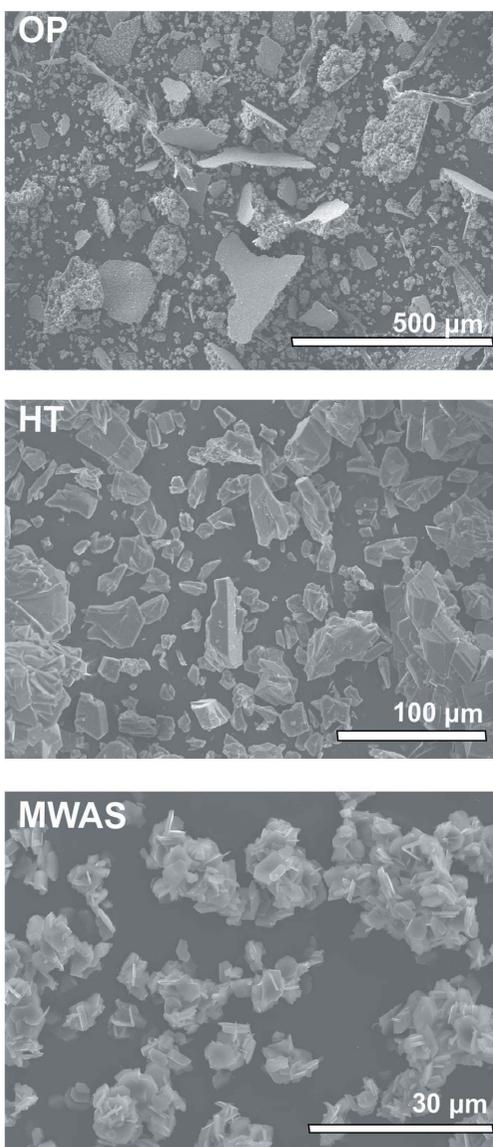
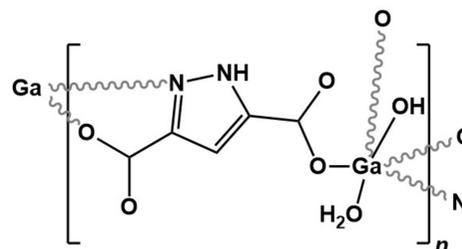


Figure 1
Scanning electron microscopy (SEM) images of bulk $[\text{Ga}(\text{HPDC})(\text{OH})(\text{H}_2\text{O})]$ (**I**) obtained by microwave-assisted synthesis (MWAS), hydrothermal synthesis (HT) and a one-pot process (OP).

Following our interest in CP/MOFs, we have attempted the preparation of MOF-303 (Fathieh *et al.*, 2018) with Ga^{3+} . In this crystallographic report we describe these studies, which culminated in the isolation of a compact one-dimensional ladder coordination polymer, $[\text{Ga}(\text{HPDC})(\text{OH})(\text{H}_2\text{O})]$ (**I**), prepared by the self-assembly of Ga^{3+} and the organic linker 3,5-pyrazoledicarboxylic acid monohydrate ($\text{H}_3\text{PDC}\cdot\text{H}_2\text{O}$). Compound **I** was obtained using a variety of methods (hydrothermal, microwave and a one-pot process) and a survey of the literature revealed that it is isotypic with a compound published in 2008 (Chen *et al.*, 2008), which is not unprecedented (Volkringer *et al.*, 2009; Finsy *et al.*, 2009; Volkringer *et al.*, 2008).



2. Crystal Morphology and Characterization

Compound **I** was prepared by hydrothermal (HT), microwave (MWAS) and one-pot (OP) synthesis. The general experimental conditions were similar (solvent, molar quantities and temperature). The compound is isotypic with $[\text{V}(\text{HPDC})(\text{OH})(\text{H}_2\text{O})]$ (Chen *et al.*, 2008), which was prepared using harsher conditions. Our attempts to obtain the analogous V^{3+} -bearing material using the conditions described here were unsuccessful.

MWAS produces phase pure coordination polymers much faster than the HT and OP approaches. PXRD studies have confirmed the same structural features (see Figure S1 in the supporting information). The crystal morphology, however, varied depending on the method employed (Fig. 1). Crystals typically exhibit irregular shapes. MWAS allowed a faster preparation of **I** when compared to the other methods (a reduction from 24 h to just 1 h) with a significantly smaller average crystal size (*ca* 3–5 μm) and a more uniform plate-like morphology. The HT method, on the other hand, afforded larger crystals (*ca* 15–65 μm) with a more block-type morphology, while the OP method resulted mainly in agglomerated particles with a plate-like morphology.

FT-IR spectroscopy supports the structural features revealed by the X-ray diffraction studies (Figure S2 in the supporting information). Compound **I** exhibits two broad bands centred at 3280 and 3159 cm^{-1} attributed to the O–H stretching vibrational modes from the coordinated water molecules and to the N–H stretching vibrations of the pyrazole ring. In the central region of the spectrum, between *ca* 1700 and 1300 cm^{-1} , it is possible to discern the typical C–O, C–C and C–N stretching vibrational modes arising from the pyrazole rings and the bending vibration of water molecules.

The materials showed similar thermal decomposition profiles between ambient temperature and *ca* 1000 K (Figure S3 in the supporting information). Between ambient temperature and *ca* 548 K, there is almost no weight loss, which is indicative of good thermal stability. The weight loss registered between *ca* 548 and 618 K is 14.9, 14.6 and 14.8% for the OP-, HT- and MWAS-derived materials, respectively, and is attributed to the release of the water of coordination and the decomposition of the hydroxyl group (theoretical weight loss 14.0%). The subsequent weight loss (*ca* 44.9%) is attributed to the decomposition of the ligand, resulting in the formation of Ga₂O₃.

3. Structural Commentary

Compound **I** was formulated by single-crystal X-ray diffraction as [Ga(HPDC)(OH)(H₂O)] from a crystal obtained using hydrothermal synthetic conditions (see *Experimental* section for further details). This compound crystallizes in the centrosymmetric *P*1̄ space group with the asymmetric unit

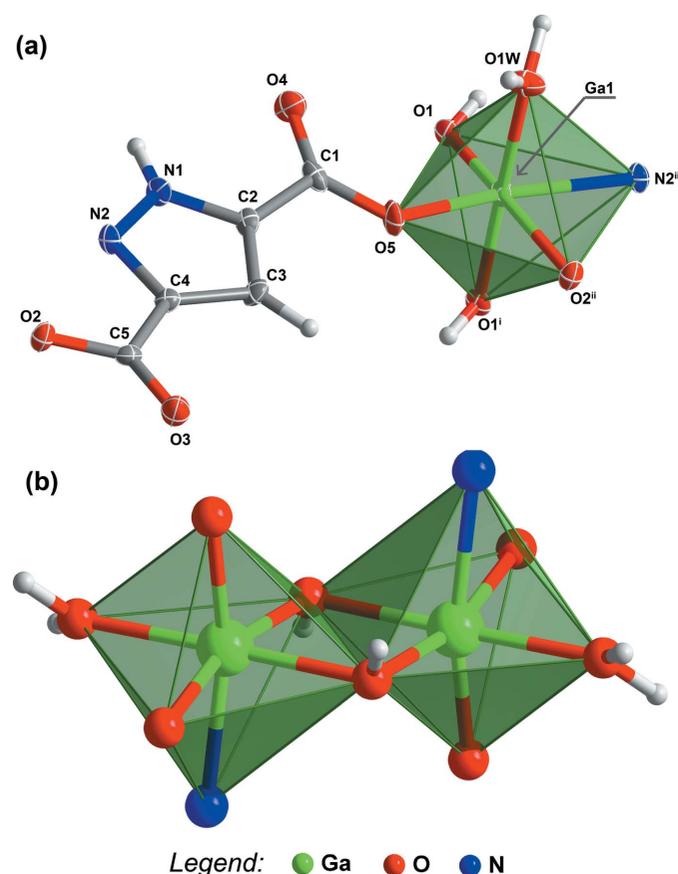


Figure 2
(a) Schematic representation of the asymmetric unit of [Ga(HPDC)(OH)(H₂O)] (**I**) showing all non-H atoms shown with displacement ellipsoids drawn at the 50% probability level and H atoms as small spheres with arbitrary radii. The coordination sphere of the crystallographically independent metal centre was completed by generating the remaining atoms through symmetry. [Symmetry codes: (i) $-x, -y, -z + 2$; (ii) $x, y, z + 1$] (b) Ga³⁺ dimer formed by two symmetry-related bridging hydroxyl groups.

Table 1
Selected geometric parameters (Å, °).

Ga1—O1	1.903 (3)	Ga1—O2 ⁱⁱ	1.987 (3)
Ga1—O5	1.932 (3)	Ga1—O1W	1.988 (3)
Ga1—O1 ⁱ	1.974 (3)	Ga1—N2 ⁱⁱ	2.112 (3)
O1—Ga1—O5	101.59 (12)	O1 ⁱ —Ga1—O1W	178.65 (12)
O1—Ga1—O1 ⁱ	79.94 (13)	O2 ⁱⁱ —Ga1—O1W	91.00 (11)
O5—Ga1—O1 ⁱ	93.13 (12)	O1—Ga1—N2 ⁱⁱ	93.94 (12)
O1—Ga1—O2 ⁱⁱ	166.31 (11)	O5—Ga1—N2 ⁱⁱ	164.18 (12)
O5—Ga1—O2 ⁱⁱ	87.28 (11)	O1 ⁱ —Ga1—N2 ⁱⁱ	92.49 (12)
O1 ⁱ —Ga1—O2 ⁱⁱ	89.26 (11)	O2 ⁱⁱ —Ga1—N2 ⁱⁱ	78.02 (11)
O1—Ga1—O1W	99.60 (12)	O1W—Ga1—N2 ⁱⁱ	86.27 (12)
O5—Ga1—O1W	88.20 (12)		

Symmetry codes: (i) $-x, -y, -z + 2$; (ii) $x, y, z + 1$.

being composed of one Ga³⁺ metal centre, one HPDC²⁻ anionic organic linker, one hydroxyl group and one coordinated water molecule, as depicted in Fig. 2a.

The anionic organic linker HPDC²⁻ has two distinct coordination modes: forming a *N,O*-chelate with the crystallographically independent Ga³⁺ metal centre [bite angle of 78.02 (11)°], and bridging with an adjacent metal centre through a *syn* interaction involving the carboxylate group, imposing a Ga···Ga intermetallic distance of *ca* 8.52 Å (*i.e.* the length of the *c* axis of the unit cell). The octahedral {GaNO₅} coordination sphere is completed by one water molecule and two-symmetry related μ_2 -bridging hydroxyl groups, which are the responsible for the formation of a centrosymmetric dimer, as depicted in Fig. 2b (intermetallic distance of *ca* 2.97 Å).

The Ga—O bond lengths range between 1.903 (3) and 1.988 (3) Å and the Ga—N distance is 2.112 (3) Å (Table 1), in good agreement with those reported for other carboxylate-based materials as witnessed by a search in the Cambridge Structural Database (CSD version of 2019; Groom *et al.*, 2016): mean value of 1.988 Å for the Ga—O bond (CSD

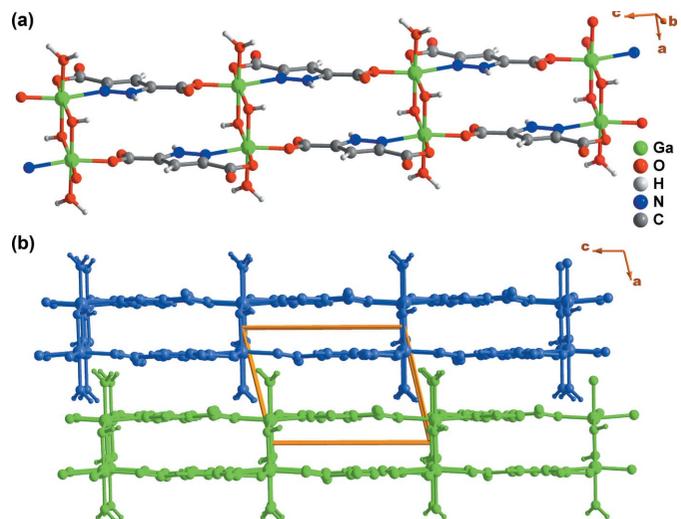


Figure 3
Schematic representation of the (a) one-dimensional ladder-type coordination polymer present in **I**, and (b) the close packing of the polymers viewed along the [010] direction of the unit cell.

Table 2
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$O1W-H1X\cdots O4^{iii}$	0.94	1.73	2.643 (4)	164
$O1W-H1Y\cdots O2^{iv}$	0.94	1.89	2.803 (4)	165
$O1-H1\cdots O3^v$	0.77	1.99	2.751 (4)	175
$N1-H1N\cdots O3^{vi}$	0.88	1.96	2.773 (4)	152

Symmetry codes: (iii) $-x+1, -y, -z+2$; (iv) $-x+1, -y+1, -z+1$; (v) $x, y-1, z+1$; (vi) $x, y-1, z$.

range, 1.832–2.475 Å) and 2.023 Å for the Ga–N bond (CSD range 1.798–3.275 Å).

The aforementioned connectivity promotes the formation of a one-dimensional ladder-type coordination polymer along the [001] direction (Fig. 3a), which close pack in a parallel fashion in the *ab* plane of the unit cell mediated by various supramolecular contacts (see the following section). Although the organic linkers are stacked within these ladders, the inter-centroid distance is 4.442 (3) Å, indicating the absence of significant π – π supramolecular interactions.

4. Supramolecular Features

Compound **I** contains several functional groups that can promote the formation of various hydrogen-bonding interactions (Fig. 4, Table 2). The coordinated water molecule is engaged in two strong and directional O–H \cdots O hydrogen-bonding interactions with neighbouring carboxylate groups from adjacent one-dimensional chains: $d_{D\cdots A}$ distances of 2.643 (4) and 2.803 (4) Å and $\angle(DHA)$ angles in the 164–165°

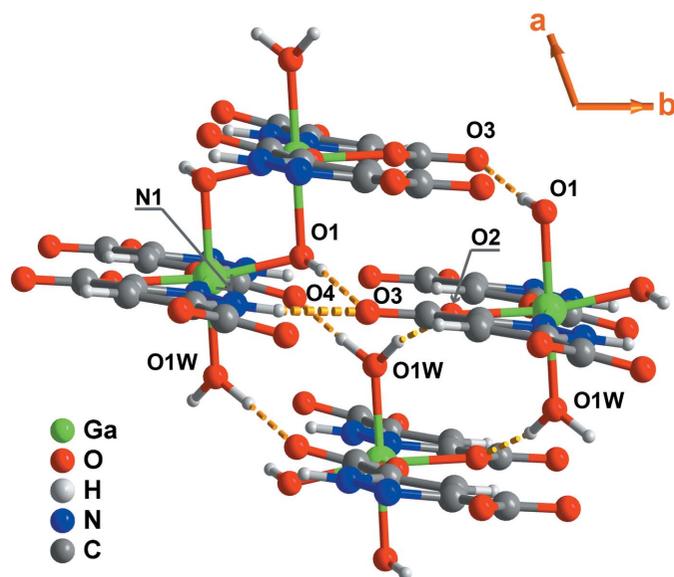


Figure 4
Schematic representation of a portion of the crystal packing of [Ga(HPDC)(OH)(H₂O)] (**I**) depicting the O–H \cdots O and N–H \cdots O supramolecular contacts (orange dashed lines) between ladder-type polymers. For geometrical details on the represented interactions see Table 2 (the symmetry codes used to generate equivalent atoms have been omitted for clarity).

range (Fig. 4, Table 2). These interactions may be described by the graph set motifs, $R_2^2(12)$ and $R_2^2(20)$. The independent μ_2 -bridging hydroxyl group also donates a hydrogen atom to a neighbouring carbonyl group (from the *N,O*-chelated moiety) in a strong interaction: $d_{D\cdots A}$ distance of 2.751 (4) Å and $\angle(DHA)$ angle of 175°. This contact leads to the formation of a supramolecular chain $C_1^1(10)$ across neighbouring polymers. Like the μ_2 -bridging hydroxyl group, the pyrazole ring is involved in a N–H \cdots O interaction with a *N,O*-chelated ligand, leading to the formation of a distinct type of supramolecular chain, $C_1^1(6)$ [$d_{D\cdots A}$ distance of 2.773 (4) Å and $\angle(DHA)$ angle of 152°].

These supramolecular interactions lead to a close packing of individual polymers and to a compact crystal structure of **I**, as shown in Fig. 5.

5. Synthesis and Crystallization Procedures

Chemicals were purchased from commercial sources (Merck and TCI) and used without any further purification. The methods and molar quantities described here were based on a methodology described by Yaghi and coworkers for the preparation of MOF-303 (Fathieh *et al.*, 2018).

Compound **I** was prepared by dissolving 147 mg (0.57 mmol) of gallium nitrate hexahydrate (Ga(NO₃)₃·6H₂O) and 100 mg (0.57 mmol) of 3,5-pyrazoledicarboxylic acid monohydrate (H₃PDC·H₂O) in 9.6 mL of water in the corresponding vessel (autoclave for hydrothermal synthesis, microwave vial for microwave synthesis and a round-bottom flask equipped with a condenser for the one-pot approach). Subsequently, the vessels were heated at 373 K for 24 h (hydrothermal and one-pot synthesis) or 1 h (microwave synthesis). The resulting white precipitates were separated by filtration, washed three times with water and three times with

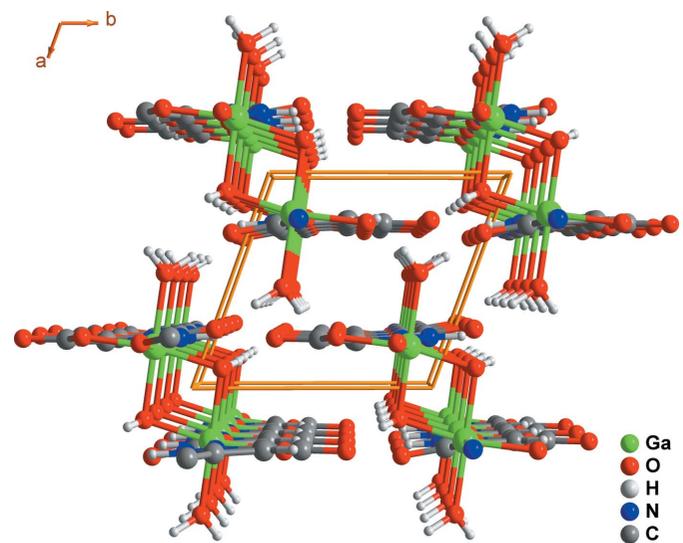


Figure 5
Crystal packing of [Ga(HPDC)(OH)(H₂O)] (**I**) viewed along the [001] direction of the unit cell.

Table 3
Experimental details.

Crystal data	
Chemical formula	[Ga(C ₃ H ₂ N ₂ O ₄)(OH)(H ₂ O)]
<i>M_r</i>	258.83
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	150
<i>a</i> , <i>b</i> , <i>c</i> (Å)	6.6055 (13), 6.8830 (16), 8.5178 (19)
α , β , γ (°)	94.804 (8), 101.306 (7), 108.596 (7)
<i>V</i> (Å ³)	355.44 (14)
<i>Z</i>	2
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	3.88
Crystal size (mm)	0.13 × 0.10 × 0.07
Data collection	
Diffraction	Broker D8 QUEST
Absorption correction	Multi-scan (<i>SADABS</i> ; Bruker, 2001; Krause <i>et al.</i> 2015)
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	5768, 1303, 1182
<i>R</i> _{int}	0.034
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.603
Refinement	
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.031, 0.074, 1.11
No. of reflections	1303
No. of parameters	136
No. of restraints	3
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	0.65, -0.47

Computer programs: *APEX3* (Bruker, 2016), *SAINT* (Bruker, 2015), *SHELXT2014* (Sheldrick, 2015a), *SHELXL2018* (Sheldrick, 2015b), *PLATON* (Spek, 2009) and *DIAMOND* (Brandenburg, 1999).

ethanol, and dried overnight at ambient temperature (yields: 49, 47 and 60% for the one-pot, hydrothermal and microwave-assisted syntheses, respectively).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. Hydrogen atoms bound to carbon and nitrogen were placed at idealized positions using the HFIX 43 instruction in *SHELXL2018/3* and included in subsequent refinement with C–H = 0.95 Å and N–H = 0.88 Å with the isotropic thermal displacement parameters fixed at 1.2*U*_{eq} of the atom to which they are attached.

Hydrogen atoms from the coordinated water molecule and the hydroxyl group were directly located from difference-Fourier maps and included in the final structural models with the O–H and H...H distances restrained to 0.95 (1) and 1.55 (1) Å, respectively, in order to ensure a chemically reasonable environment. These hydrogen atoms were modelled with the isotropic thermal displacement parameters fixed at 1.5*U*_{eq}(O).

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supporting information

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Computing details

Data collection: *APEX3* (Bruker, 2016); cell refinement: *SAINTE* (Bruker, 2015); data reduction: *SAINTE* (Bruker, 2015); program(s) used to solve structure: *SHELXT2014* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018* (Sheldrick, 2015b); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *SHELXL2018* (Sheldrick, 2015b) and *PLATON* (Spek, 2009).

Poly[[$(\mu_2$ -hydroxido)(μ_2 -1*H*-pyrazole-3,5-dicarboxylato)gallium(III)] monohydrate]

Crystal data

[Ga(C₅H₂N₂O₄)(OH)(H₂O)]

$M_r = 258.83$

Triclinic, $P\bar{1}$

$a = 6.6055$ (13) Å

$b = 6.8830$ (16) Å

$c = 8.5178$ (19) Å

$\alpha = 94.804$ (8)°

$\beta = 101.306$ (7)°

$\gamma = 108.596$ (7)°

$V = 355.44$ (14) Å³

$Z = 2$

$F(000) = 256$

$D_x = 2.418$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 3255 reflections

$\theta = 2.5$ – 25.4 °

$\mu = 3.88$ mm⁻¹

$T = 150$ K

Block, colourless

$0.13 \times 0.10 \times 0.07$ mm

Data collection

Bruker D8 QUEST
diffractometer

Radiation source: Sealed tube

Multi-layer X-ray mirror monochromator

Detector resolution: 10.4167 pixels mm⁻¹

ω / φ scans

Absorption correction: multi-scan

(SADABS; Bruker, 2001; Krause *et al.* 2015)

5768 measured reflections

1303 independent reflections

1182 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.034$

$\theta_{\text{max}} = 25.4$ °, $\theta_{\text{min}} = 3.7$ °

$h = -7 \rightarrow 7$

$k = -8 \rightarrow 8$

$l = -10 \rightarrow 10$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.031$

$wR(F^2) = 0.074$

$S = 1.11$

1303 reflections

136 parameters

3 restraints

Hydrogen site location: mixed

H atoms treated by a mixture of independent
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0292P)^2 + 1.2151P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.001$

$\Delta\rho_{\text{max}} = 0.65$ e Å⁻³

$\Delta\rho_{\text{min}} = -0.47$ e Å⁻³

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Ga1	0.20874 (7)	0.17985 (7)	1.03804 (5)	0.00844 (15)
O1W	0.5321 (4)	0.2428 (4)	1.0908 (3)	0.0140 (6)
H1X	0.604 (6)	0.162 (6)	1.147 (5)	0.021*
H1Y	0.627 (5)	0.335 (5)	1.040 (5)	0.021*
O1	0.1126 (4)	-0.1152 (4)	1.0094 (3)	0.0100 (6)
H1	0.142 (8)	-0.167 (7)	1.082 (6)	0.015*
N1	0.2437 (5)	0.1027 (5)	0.4128 (4)	0.0102 (7)
H1N	0.249943	-0.023469	0.404671	0.012*
N2	0.2363 (5)	0.2116 (5)	0.2909 (4)	0.0088 (7)
C1	0.2537 (6)	0.1216 (6)	0.7048 (5)	0.0103 (8)
C2	0.2405 (6)	0.2131 (6)	0.5511 (4)	0.0089 (8)
C3	0.2296 (6)	0.4004 (6)	0.5154 (5)	0.0102 (8)
H3	0.223752	0.511146	0.586837	0.012*
C4	0.2289 (6)	0.3927 (6)	0.3507 (4)	0.0074 (8)
C5	0.2388 (6)	0.5450 (6)	0.2360 (5)	0.0087 (8)
O2	0.2500 (4)	0.4783 (4)	0.0937 (3)	0.0098 (6)
O3	0.2423 (5)	0.7207 (4)	0.2790 (3)	0.0137 (6)
O4	0.2886 (5)	-0.0428 (4)	0.7039 (3)	0.0149 (6)
O5	0.2257 (4)	0.2323 (4)	0.8208 (3)	0.0123 (6)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ga1	0.0123 (2)	0.0088 (2)	0.0059 (2)	0.00441 (17)	0.00399 (16)	0.00291 (15)
O1W	0.0120 (14)	0.0172 (16)	0.0176 (15)	0.0074 (13)	0.0071 (12)	0.0109 (12)
O1	0.0142 (14)	0.0097 (14)	0.0078 (14)	0.0050 (12)	0.0032 (11)	0.0044 (11)
N1	0.0164 (17)	0.0109 (16)	0.0069 (16)	0.0069 (14)	0.0057 (13)	0.0056 (13)
N2	0.0110 (17)	0.0093 (16)	0.0061 (15)	0.0025 (13)	0.0034 (13)	0.0029 (12)
C1	0.0076 (19)	0.014 (2)	0.0075 (19)	0.0009 (16)	0.0010 (15)	0.0034 (15)
C2	0.0073 (19)	0.012 (2)	0.0071 (19)	0.0018 (16)	0.0035 (15)	0.0016 (15)
C3	0.011 (2)	0.0117 (19)	0.0100 (19)	0.0053 (16)	0.0060 (16)	0.0018 (15)
C4	0.0066 (18)	0.0077 (18)	0.0084 (18)	0.0020 (15)	0.0034 (14)	0.0024 (15)
C5	0.0071 (19)	0.0087 (19)	0.0112 (19)	0.0040 (15)	0.0015 (15)	0.0018 (15)
O2	0.0158 (14)	0.0064 (13)	0.0086 (13)	0.0043 (11)	0.0048 (11)	0.0022 (10)
O3	0.0205 (16)	0.0120 (15)	0.0110 (14)	0.0084 (12)	0.0036 (12)	0.0033 (11)
O4	0.0203 (16)	0.0171 (16)	0.0125 (14)	0.0100 (13)	0.0076 (12)	0.0072 (12)
O5	0.0182 (15)	0.0139 (14)	0.0052 (13)	0.0050 (12)	0.0036 (11)	0.0028 (11)

Geometric parameters (Å, °)

Ga1—O1	1.903 (3)	N1—H1N	0.8800
Ga1—O5	1.932 (3)	N2—C4	1.326 (5)
Ga1—O1 ⁱ	1.974 (3)	C1—O4	1.224 (5)
Ga1—O2 ⁱⁱ	1.987 (3)	C1—O5	1.276 (5)
Ga1—O1W	1.988 (3)	C1—C2	1.499 (5)
Ga1—N2 ⁱⁱ	2.112 (3)	C2—C3	1.369 (6)
Ga1—Ga1 ⁱ	2.9716 (10)	C3—C4	1.399 (5)
O1W—H1X	0.943 (10)	C3—H3	0.9500
O1W—H1Y	0.939 (10)	C4—C5	1.487 (5)
O1—H1	0.77 (5)	C5—O3	1.225 (5)
N1—N2	1.333 (4)	C5—O2	1.284 (5)
N1—C2	1.355 (5)		
O1—Ga1—O5	101.59 (12)	Ga1—O1—H1	118 (4)
O1—Ga1—O1 ⁱ	79.94 (13)	Ga1 ⁱ —O1—H1	107 (4)
O5—Ga1—O1 ⁱ	93.13 (12)	N2—N1—C2	110.6 (3)
O1—Ga1—O2 ⁱⁱ	166.31 (11)	N2—N1—H1N	124.7
O5—Ga1—O2 ⁱⁱ	87.28 (11)	C2—N1—H1N	124.7
O1 ⁱ —Ga1—O2 ⁱⁱ	89.26 (11)	C4—N2—N1	106.8 (3)
O1—Ga1—O1W	99.60 (12)	C4—N2—Ga1 ⁱⁱⁱ	112.3 (2)
O5—Ga1—O1W	88.20 (12)	N1—N2—Ga1 ⁱⁱⁱ	140.7 (3)
O1 ⁱ —Ga1—O1W	178.65 (12)	O4—C1—O5	129.1 (4)
O2 ⁱⁱ —Ga1—O1W	91.00 (11)	O4—C1—C2	118.2 (3)
O1—Ga1—N2 ⁱⁱ	93.94 (12)	O5—C1—C2	112.7 (3)
O5—Ga1—N2 ⁱⁱ	164.18 (12)	N1—C2—C3	107.5 (3)
O1 ⁱ —Ga1—N2 ⁱⁱ	92.49 (12)	N1—C2—C1	119.5 (3)
O2 ⁱⁱ —Ga1—N2 ⁱⁱ	78.02 (11)	C3—C2—C1	133.0 (4)
O1W—Ga1—N2 ⁱⁱ	86.27 (12)	C2—C3—C4	104.8 (3)
O1—Ga1—Ga1 ⁱ	40.86 (8)	C2—C3—H3	127.6
O5—Ga1—Ga1 ⁱ	99.50 (8)	C4—C3—H3	127.6
O1 ⁱ —Ga1—Ga1 ⁱ	39.08 (8)	N2—C4—C3	110.3 (3)
O2 ⁱⁱ —Ga1—Ga1 ⁱ	127.84 (8)	N2—C4—C5	115.1 (3)
O1W—Ga1—Ga1 ⁱ	140.45 (9)	C3—C4—C5	134.4 (3)
N2 ⁱⁱ —Ga1—Ga1 ⁱ	94.18 (9)	O3—C5—O2	124.3 (4)
Ga1—O1W—H1X	124 (2)	O3—C5—C4	121.2 (3)
Ga1—O1W—H1Y	123 (2)	O2—C5—C4	114.5 (3)
H1X—O1W—H1Y	110.8 (16)	C5—O2—Ga1 ⁱⁱⁱ	118.6 (2)
Ga1—O1—Ga1 ⁱ	100.06 (13)	C1—O5—Ga1	129.9 (3)
C2—N1—N2—C4	0.2 (4)	N1—N2—C4—C5	175.1 (3)
C2—N1—N2—Ga1 ⁱⁱⁱ	-173.6 (3)	Ga1 ⁱⁱⁱ —N2—C4—C5	-9.2 (4)
N2—N1—C2—C3	0.2 (4)	C2—C3—C4—N2	0.7 (4)
N2—N1—C2—C1	-178.4 (3)	C2—C3—C4—C5	-173.7 (4)
O4—C1—C2—N1	7.0 (5)	N2—C4—C5—O3	-177.0 (3)
O5—C1—C2—N1	-173.1 (3)	C3—C4—C5—O3	-2.8 (7)
O4—C1—C2—C3	-171.2 (4)	N2—C4—C5—O2	1.0 (5)

O5—C1—C2—C3	8.7 (6)	C3—C4—C5—O2	175.2 (4)
N1—C2—C3—C4	-0.5 (4)	O3—C5—O2—Ga1 ⁱⁱⁱ	-173.3 (3)
C1—C2—C3—C4	177.8 (4)	C4—C5—O2—Ga1 ⁱⁱⁱ	8.8 (4)
N1—N2—C4—C3	-0.5 (4)	O4—C1—O5—Ga1	-4.2 (6)
Ga1 ⁱⁱⁱ —N2—C4—C3	175.2 (2)	C2—C1—O5—Ga1	175.8 (2)

Symmetry codes: (i) $-x, -y, -z+2$; (ii) $x, y, z+1$; (iii) $x, y, z-1$.

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
O1 <i>W</i> —H1 <i>X</i> \cdots O4 ^{iv}	0.94	1.73	2.643 (4)	164
O1 <i>W</i> —H1 <i>Y</i> \cdots O2 ^v	0.94	1.89	2.803 (4)	165
O1—H1 \cdots O3 ^{vi}	0.77	1.99	2.751 (4)	175
N1—H1 <i>N</i> \cdots O3 ^{vii}	0.88	1.96	2.773 (4)	152

Symmetry codes: (iv) $-x+1, -y, -z+2$; (v) $-x+1, -y+1, -z+1$; (vi) $x, y-1, z+1$; (vii) $x, y-1, z$.