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Utilizing Metal Melts of Low-Melting Metals as a Novel Approach for MOF Synthesis: The 3D-Imidazolate $3\infty[\text{Ga}_2(\text{Im})_6\text{ImH}]$ from Gallium and Imidazole

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**Utilizing Metal Melts of Low-Melting Metals as a Novel
Approach for MOF Synthesis: The 3D-Imidazolate
 $^3_\infty[\text{Ga}_2(\text{Im})_6\text{ImH}]$ from Gallium and Imidazole**

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3 **Utilizing Metal Melts of Low-Melting Metals as a Novel Approach for**
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6 **MOF Synthesis: The 3D-Imidazolate $\overset{3}{\infty}[\text{Ga}_2(\text{Im})_6\text{ImH}]$ from Gallium and**
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9 **Imidazole**

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13 Alexander Zurawski, Frauke Hintze and Klaus Müller-Buschbaum*

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17 München, Department Chemie der Ludwig-Maximilians-Universität

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22 *Dedicated to Prof. Rüdiger Kniep on the Occasion of his 65th Birthday*

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27 Received...

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31 **Abstract.** Metals with low melting points like gallium (mp. 30 °C) prove a new approach for
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33 the synthesis of MOFs. As the melting point of gallium is even lower than of the linker ligand
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35 imidazole, formation of the MOF $\overset{3}{\infty}[\text{Ga}_2(\text{Im})_6\text{ImH}]$, Im^- = imidazolate anion, ImH = imida-
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37 zole, can be achieved by reaction of a melt of the referring metal with a melt of the ligand.
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39 Gallium is oxidized in the reaction, and hydrogen gas and the imidazolate amide as colourless
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41 single crystalline product are formed. At the melting point of imidazole (mp. 88-90 °C) two
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43 liquid phases are observed. Phase separation lasts until the reaction, starting at 120 °C, con-
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45 sumes the liquid reagents. We consider this a reaction on the phase border between the liquid
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47 phases as no mixing is observed. $\overset{3}{\infty}[\text{Ga}_2(\text{Im})_6\text{ImH}]$ constitutes of a three-dimensional frame-
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49 work structure with a 3,6 topology that is built of two Kagome nets sharing common connec-
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51 tivity points. Each Ga^{3+} ion is octahedrally coordinated by six nitrogen atoms of imidazolate
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53 and imidazole ligands. The framework exhibits a limited porosity of 8.5 % of accessible space
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55 and a diameter of 376 - 509 pm for the pore windows.
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3 **Keywords:** MOFs; Coordination Polymers; Gallium; Imidazolates; Metal Melts
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20 **Introduction**

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22 Over the past years we developed a synthesis strategy for amide and amine coordination com-
23 pounds and polymers of the rare earth elements [1 – 2]. It derives from the oxidation of non-
24 noble metals with a melt of an amine R₂-NH and includes the formation of hydrogen gas and
25 amide ligands. No additional solvent is used, which proves an advantage for the oxophilic
26 lanthanides [3 – 7], especially as oxygen-containing solvents are avoided. First shown for
27 small molecular complexes from ^{tert}But substituted pyrazole [8], the absence of unwanted co-
28 ligands also proves a suitable strategy for unsubstituted aromatic N-heterocyclic ligands to
29 obtain 1D chain like coordination polymers [9], 2D networks [10] and 3D frameworks [11].
30 Because of the high melting points of the rare earth metals all reaction occurs between solid
31 metal and ligand melt. In order to elaborate our strategy further other non-noble metals in the
32 periodic table need to be utilized. Successful attempts were made with group 2 metals [12]. In
33 the third main group the element gallium attracted our attention because of its low melting
34 point (mp. 30 °C). This renders a new option accessible: metal melts for solvent free syntheses
35 of organic amides. With $\frac{3}{\infty}[\text{Ga}_2(\text{Im})_6\text{ImH}]$ we now present that low melting metal melts can
36 indeed be used as a new approach to such compounds. It can even be utilized for the synthesis
37 of MOFs [13] as the trend towards highly aggregated systems is not diminishing by the use of
38 molten gallium.
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Experimental

All manipulations were carried out under inert atmospheric conditions using glove box, ampoule as well as vacuum line techniques. The IR spectra were recorded using a BRUKER FTIR-IS66V-S spectrometer. For the IR investigations KBr pellets were used under vacuum. The thermal properties were studied using multiple simultaneous DTA/TG (SETARAM TG-DTA 92-16) on the reaction of gallium metal with imidazole and on single crystalline ${}^3_{\infty}[\text{Ga}_2(\text{Im})_6\text{ImH}]$. Samples were heated from 20 °C up to 800 °C in a constant He flow of 50 ml/min. 6.4 mg Ga were treated with 19.8 mg ImH at a heating rate of 5 °C/min, 19.0 mg of crystalline ${}^3_{\infty}[\text{Ga}_2(\text{Im})_6\text{ImH}]$ and 16.8 mg “Ga(Im)₃” were treated at a heating rate of 10 K/min. The micro analysis was carried out on a ELEMENTAR Vario El analyser.

Synthesis of ${}^3_{\infty}[\text{Ga}_2(\text{Im})_6\text{ImH}]$

Gallium (70 mg = 1 mmol) and imidazole (ImH, C₃H₃NNH; 204 mg = 3 mmol) were sealed in an evacuated DURAN glass ampoule. The reaction mixture was heated in 24 h to 120 °C and held at this temperature for 1850 h. The melt was cooled to room temperature in 1 h. The reaction gave a white crystalline product of trapezoidal crystals of ${}^3_{\infty}[\text{Ga}_2(\text{Im})_6\text{ImH}]$.

Yield (ImH): 181 mg (69 %). Shorter reaction times decrease the yield of the reaction. Higher reaction temperatures result in a different poorly crystalline product (see Discussion).

Analysis: C₂₁H₂₂N₁₄Ga₂, (M = 609.94 g·mol⁻¹): found C 41.76, H 3.79, N 32.17; calcd.: C 41.35, H 3.64, N 32.15 %.

Vibrational spectroscopy (C₂₁H₂₂N₁₄Ga₂): **MIR** (KBr): (3231 s, 3121 s, 3037 m, 3925 m, 2838 m, 2697 w, 2609 w, 1682 w, 1600 w, 1526 w, 1496 s, 1479 s, 1416 w, 1323 s, 1295 w, 1257 s, 1238 wsh, 1164 m, 1087 vs, 1062 vs, 949 s, 933 ssh, 907 w, 840 s, 764 ssh, 751 s, 664 vs, 615 m) cm⁻¹.

Crystal Structure Determination

A suitable crystal of ${}^3\infty[\text{Ga}_2(\text{Im})_6\text{ImH}]$ was selected for the single crystal X-ray analysis under glovebox conditions and sealed in a glass capillary. The data collection was carried out on a STOE IPDS-I diffractometer (Mo K_{α} radiation $\lambda = 0.7107 \text{ \AA}$) at 140 K. The structure was determined using direct methods [14]. All non-H atoms were refined anisotropically by least squares techniques [15]. The positions of the hydrogen atoms were also derived from the differential fourier card and refined isotropically. ${}^3\infty[\text{Ga}_2(\text{Im})_6\text{ImH}]$ crystallises in the monoclinic space group $C2/c$ (No. 15). The integrity of symmetry and geometry were checked with the program PLATON [16]. Crystallographic data are summarised in Table 1. Further information was deposited at the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223336033 or e-mail: deposit@ccdc.cam.ac.uk) and may be requested by citing the deposition number CCDC-xxxxxx, the names of the authors and the literature citation.

${}^3\infty[\text{Ga}_2(\text{Im})_6\text{ImH}]$ was also investigated on powder samples in sealed capillaries on a STOE Stadi P diffractometer with a focussed single crystal germanium monochromator (Cu $K_{\alpha 1}$ radiation, $\lambda = 1.540598 \text{ \AA}$ and Mo $K_{\alpha 1}$ radiation, $\lambda = 0.70930 \text{ \AA}$). Indexing of the powder confirms lattice and crystal system of the single crystal X-ray investigation [17]. The cell constants were refined on 11 reflections with the best possible resolution leading to a monoclinic unit cell without unindexed lines and an average $\delta(2^\circ)$ of 0.002° ($T = 293(2) \text{ K}$, $a = 2188.3(10) \text{ pm}$, $b = 1085.4(3)$, $c = 1219.5(10) \text{ pm}$, $\beta = 123.22(4)$, $V = 2423.1(20) 10^6 \text{ pm}^3$)

In addition an assumed high-temperature network “[Ga(Im)₃]” obtained at higher reaction temperatures as well as on the thermal analyser was also investigated by powder diffraction (Cu $K_{\alpha 1}$ radiation, $\lambda = 1.540598 \text{ \AA}$ and Mo $K_{\alpha 1}$ radiation, $\lambda = 0.70930 \text{ \AA}$). The low crystallinity of this product does not allow a reasonable indexing of the powder, so that at the current stage it can only be stated that larger differences in the d values of the main reflections be-

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3 tween ${}^3_{}[\text{Ga}_2(\text{Im})_6\text{ImH}]$ and “[Ga(Im)₃]” will have larger differences in their crystal structures
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6 [17].
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13 Discussion

15 *Synthesis and Thermal Properties*

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18 In order to study the products of the reaction of gallium metal with imidazole (ImH =
19 C₃H₃NNH) a double strategy was followed. The reaction was carried out in glass ampoules in
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21 a glass tube oven (co. BÜCHI) that allows macroscopic observation. First both reagents melt
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23 (Ga: mp. 30 °C, imidazole: mp: 88-90 °C. The two liquid phases do not mix but retain a clear
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25 phase border between the colourless melt of the ligand (top) and the metallic melt of gallium
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27 (bottom). At 120 °C first reaction is observed in the glass tube oven by the appearance of a
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29 white milky shade at the phase border and low bubbling of H₂. During the reaction more and
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31 more of a white product is formed as colourless crystals of ${}^3_{}[\text{Ga}_2(\text{Im})_6\text{ImH}]$ at the phase bor-
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33 der up to yields of 70%. Non-stoichiometric investigations retain the excess of the referring
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35 reagent. Higher temperatures lead to microcrystalline material and finally a powder product of
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37 “[Ga(Im)₃]”.
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45 In addition the reaction was carried out on a thermal analyser (co. SETARAM) but is too slow
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47 to be followed by simultaneous DTA/TG. Therefore DTA/TG investigations on
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49 ${}^3_{}[\text{Ga}_2(\text{Im})_6\text{ImH}]$ and “[Ga(Im)₃]” were carried out (Figure 1). They exhibit four steps of ther-
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51 mal processes for ${}^3_{}[\text{Ga}_2(\text{Im})_6\text{ImH}]$ until complete decomposition, all endothermic and all
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53 combined to a mass loss. The first two steps at 300 and 380 °C reveal the release of imidazole.
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55 Due to the results from other aromatic amides [1 – 2, 9 – 11] we expect them to be identified
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57 with release of the neutral ligand prior to the release of anions from the system to give an as-
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59 sumed high temperature compound “[Ga(Im)₃]”. Further heating to 485 °C leads to decompo-
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sition of this high temperature phase (485 °C signal (3), 560 °C signal (4)) and yields amorphous products.

In order to prove the assumption of a high temperature phase the high temperature product initially from the glass oven experiment was also investigated by DTA/TG. It conforms the previous identifications as it only displays signals (3) and (4). They do not derive from ${}^3_{}[\text{Ga}_2(\text{Im})_6\text{ImH}]$ itself (see Figure 1, bottom), as also the powder pattern of the product of signal (2) “[Ga(Im)₃]” differs strongly from the pattern of ${}^3_{}[\text{Ga}_2(\text{Im})_6\text{ImH}]$, whereas the powder patterns of “[Ga(Im)₃]” from the glass tube oven experiment and the DTA/TG experiment show the same pattern. Unfortunately crystallinity of “[Ga(Im)₃]” is too low allow a successful structure resolution from X-ray powder techniques, which prove successful only for a certain crystallinity and at best high symmetry [18].

To the best of our knowledge this is the first example in which a metal melt was utilized for a MOF synthesis. It enlarges the range of our rather “extreme” reaction conditions that includes high temperature reactions in ligand melts [1, 2, 9 – 11], the use of microwaves [19], electric trides [20] and ball mill synthesis [21].

Crystal Structure

The crystal structure of ${}^3_{}[\text{Ga}_2(\text{Im})_6\text{ImH}]$ is a three-dimensional framework structure in which imidazolate anions link gallium(III) ions by alternating $\mu_2\text{-}\eta^1:\eta^1$ N-coordinations. The structure contains two different gallium sites that are both octahedrally coordinated but exhibit different linkage orders to other Ga atoms. Ga(1) is coordinated by six nitrogen atoms of five imidazolate anions and one imidazole molecule. Four imidazolate anions are $\mu_2\text{-}\eta^1:\eta^1$ linking to four other Ga atoms in two dimensions. Top and bottom of the coordination octahedron do not link to other gallium atoms, viz. one imidazolate anion and the imidazole molecule contribute as end-on ligands only. Ga(2) is coordinated by six nitrogen atoms of six imidazolate

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3 anions, which all link $\mu_2\text{-}\eta^1:\eta^1$ with the other nitrogen atom to six other Ga atoms in all three
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5 dimensions. Figure 2 displays the coordination of the gallium atoms figure 3 the framework
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7 structure of ${}^3_\infty[\text{Ga}_2(\text{Im})_6\text{ImH}]$.

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10 With a Niggli formula of ${}^3_\infty[\text{Ga}(\text{Im})_{6/2}\text{Ga}(\text{Im})_{4/2}(\text{Im})_{1/1}(\text{ImH})_{1/1}]$ and a metal : ligand ratio of 2 :
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12 7 the structure does not adopt a simple known structure type. However a careful look into de-
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14 tail of the two-dimensional subnets of ${}^3_\infty[\text{Ga}_2(\text{Im})_6\text{ImH}]$ reveals that they can be derived from
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16 Kagome nets. They exhibit a network topology that consists of small three-membered rings
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18 and large six-membered rings consisting of two 2D nets, both having a (3,4) topology. Both
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20 Kagome nets have common connectivity centres in Ga2 (with Ga1 having a connectivity of
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22 four and Ga2 of six). ${}^3_\infty[\text{Ga}_2(\text{Im})_6\text{ImH}]$ has an overall network topology of (3,6). The two 2D
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24 coordinations, ${}^3_\infty[\text{Ga}_2(\text{Im})_6\text{ImH}]$ cannot be a zeolite analogue. The topology and relation with a
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26 Kagome net are depicted in Figure 4.
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43 The interatomic distances in ${}^3_\infty[\text{Ga}_2(\text{Im})_6\text{ImH}]$ corroborate the expectations for octahedral
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45 $\text{Ga}^{\text{III}}\text{-N}$ [23]: They range from 204.7(2) to 209.8(3) pm. For comparison, in
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47 $[\text{Ga}(\text{pypepH})_2]\text{Cl}\cdot 2\text{H}_2\text{O}$ the $\text{Ga}^{\text{III}}\text{-N}$ distances observed range from 200.7(2) to 215.2(2) pm
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49 [24] and in $[(5\text{-mpyr})_4\text{GaCl}_2][\text{GaCl}_4]$ they are 207(2) and 209(2) pm [25]. For cubic GaN (oc-
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51 tahedral coordination sphere of Ga) the referring distances are 199.2 and 199.3 [26], being
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53 shorter due to the high charge of the nitride ion. For a tetrahedral Ga – N coordination even
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55 shorter distances would be expected like 194.1 and 195.0 pm in the hexagonal GaN [27].
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No gallium imidazolate was structurally characterized prior to this investigation.
 $[\text{GaCl}(\text{Im})_2(\text{H}_2\text{O})]$ and $[\text{Ga}(\text{Im})_4\text{Cl}_2]\text{Cl}$ were reported but without any structure data [28, 25].

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3 Furthermore Ga_2O_3 was reacted with imidazole by milling and reported to react slowly upon
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5 “intensive grinding” [29]. But the investigation also does neither provide any structure deter-
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7 minations nor a product formula, only IR bands are given. For relevant interatomic distances
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9 and angles of $^3[\text{Ga}_2(\text{Im})_6\text{ImH}]$ presented here, see Table 2.
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13 The crystal structure of $^3[\text{Ga}_2(\text{Im})_6\text{ImH}]$ furthermore exhibits voids of 200 \AA^3 per unit
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15 cell equalling 8.5% free space regarding the size of a guest molecule like water and the van-
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17 der-Waals spheres of the framework atoms [16]. This should be sufficient for sorption proc-
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19 esses of guest atoms and small molecules, so that the framework classifies as a MOF struc-
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21 ture. Furthermore the network exhibits critical channel windows of $3.8 - 5.1 \text{ \AA}$ diameters as
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23 possible paths for sorption processes (see Figure 2, bottom). First BET investigations were
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25 carried out observing the adsorption of N_2 gas at 77K. They exhibit a low porosity of 12.5
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27 cm^3/g N_2 sorption for the micropores. Possible discrimination of adsorbents was reported with
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29 window sizes of the pores of the same dimension for $\text{Cu}(\text{FMA})(4,4'\text{-Bpe})_{0.5}$ (FMA = fumarate,
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31 $4,4'\text{-Bpe} = 4,4'\text{-Bpe} = \textit{trans}$ -bis(4-pyridyl)ethylene) [30], and nitrogen being the least favour-
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33 able of the two to three atom molecules H_2 , N_2 , CO , CO_2 , H_2O investigated. Therefore multi-
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35 ple gas BET investigations with different adsorbents are also planned for $^3[\text{Ga}_2(\text{Im})_6\text{ImH}]$ to
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37 investigate if it is also an adsorbent selective MOF that shows higher porosity for other ad-
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51 52 **Conclusion**

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55 With the synthesis of $^3[\text{Ga}_2(\text{Im})_6\text{ImH}]$ we present a framework that utilizes a melt of the low
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57 melting gallium metal together with molten imidazole as linker. To the best of our knowledge
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59 this is the first example in the literature that describes the use of a metal melt for MOF synthe-
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sis. Furthermore this is also the first report of a crystal structure of a gallium imidazolate.

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Legends for Figures

Scheme 1 The amine imidazole = ImH (left) and the crucial M – ligand – M angle of the imidzolate ligand = Im⁻ (right).

Figure 1 The thermal analysis of ${}^3_{\infty}[\text{Ga}_2(\text{Im})_6\text{ImH}]$ (top) and of “[Ga(Im)₃]” (bottom). ${}^3_{\infty}[\text{Ga}_2(\text{Im})_6\text{ImH}]$ undergoes transformation into a high-temperature phase that is assumed to be “[Ga(Im)₃]” upon the two step release of imidazole (signals (1) and (2)). The high temperature phase decomposes at 485 °C. This is corroborated by the absence of signals (1) and (2) in the investigation of “[Ga(Im)₃]”. Its decomposition is also a two step process that ends in an amorphous residue.

Figure 2 Depiction of the framework structure of ${}^3_{\infty}[\text{Ga}_2(\text{Im})_6\text{ImH}]$ as a view on the [110] plane and with coordination polyhedra of N atoms around the Ga atoms (top). N-N-connection lines mark only the coordination polyhedra and do not represent bonds. The framework exhibits its voids with pore windows in the critical 4.5 Å region. Paths for sorption cannot be not linear illustrated by transparent Van-der-Waals spheres, as the overlay is only about half of the window diameters in a straight line along the c axis (bottom).

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2
3 **Figure 3** The coordination spheres of the atoms Ga1 and Ga2 of $\overset{3}{\infty}[\text{Ga}_2(\text{Im})_6\text{ImH}]$ as a depiction of the thermal ellipsoids of the atoms representing a probability density level of the atoms of 50%. Symmetry operations: i: 0.5-x, 0.5-y, 1-z; ii: -x, 1-y, 1-z; iii: -0.5+x, 0.5-y, -0.5+z; iv: 0.5-x, 0.5+y, 1.5-z.

15 **Figure 4** Topological drawings of the 3,6 framework structure of $\overset{3}{\infty}[\text{Ga}_2(\text{Im})_6\text{ImH}]$ consisting of two (3,4) nets. Each of the two-dimensional nets adopts a Kagome net of triangles around a six-fold ring. Both Kagome nets have common connectivity points.

Table 1. Crystallographic data for ${}^3[\text{Ga}_2(\text{Im})_6\text{ImH}]$. Deviations are given in brackets.

Formula	$\text{C}_{21} \text{H}_{22} \text{N}_{14} \text{Ga}_2$
Formula weight / (g mol)	609.94
Cell constants, (a,b,c)/pm	a = 2185.7(4) b = 1082.1(2) c = 1216.9(2) $\beta = 123.3(1)$
Volumina / 10^6 pm^3	2405.3(8)
Z	4
$d_{\text{calc.}} / (\text{g cm}^{-3})$	1.682
Temperature / K	173(2)
X-ray radiation	Mo- $\text{K}\alpha$, $\lambda = 71.073 \text{ pm}$
Diffractometer	STOE IPDS I
Crystal system, space group	monoclinic, $C2/c$
Data range	$6.70 \leq 2\theta \leq 60.80$; $-31 \leq h \leq 27$; $-15 \leq k \leq 15$; $-15 \leq l \leq 15$
Diffractometer setup	$0 \leq \omega \leq 180^\circ$, $\varphi = 0^\circ$, $\Delta\omega = 0.7$
Measured reflections	12711
No. unique reflections; R_{int}	3365; 0.0535
No. of parameters	213
Ratio refl. /parameters	16
μ / cm^{-1}	22.83
R_1 for n reflections with $F_o > 4\sigma(F_o)$; n	$R_1^a = 0.038$; 2694
R_1 for all reflections	$R_1 = 0.051$
wR_2 for all reflections	$wR_2^b = 0.113$
Remaining electron density / ($e/(10^6 \text{ pm}^3)$)	+0.92 / -0.84

$$^a R_1 = \sum [|F_o| - |F_c|] / \sum [|F_o|], \quad ^b wR_2 = (\sum w (F_o^2 - F_c^2)^2 / (\sum w (F_o^4)))^{1/2}. \quad [15]$$

Table 2. Selected interatomic distances and angles in ${}^3_{\infty}[\text{Ga}_2(\text{Im})_6\text{ImH}]$. Deviations are given in brackets.

atoms	distances / pm	atoms	angles / °
Ga1 - N1	204.7(2)	N1 - Ga1 - N3	90.6(1)
Ga1 - N3	209.8(3)	N1 - Ga1 - N3 ⁱ	89.4(1)
Ga1 - N5	208.3(2)	N1 - Ga1 - N5	90.5(1)
Ga2 - N2	208.7(2)	N1 - Ga1 - N5 ⁱ	89.5(1)
Ga2 - N4 ⁱⁱⁱ	208.9(2)	N1 ⁱ - Ga1 - N1	180.0
Ga2 - N7	206.7(3)	N2 - Ga2 - N4 ⁱⁱⁱ	90.4(1)
N - C (range)	133.4(4) - 138.4(4)	N2 - Ga2 - N4 ^{iv}	89.6(1)
C - C (range)	135.7(7) - 136.7(4)	N4 ⁱⁱⁱ - Ga2 - N4 ^{iv}	180.0(1)
		N5 - Ga1 - N3	89.2(1)
		N7 - Ga2 - N2	91.3(1)
		N7 - Ga2 - N2 ⁱⁱ	88.7(1)
		N7 - Ga2 - N4 ⁱⁱⁱ	89.1(1)
		N7 - Ga2 - N4 ^{iv}	90.9(1)

Symmetry operations: i: 0.5-x, 0.5-y, 1-z; ii: -x, 1-y, 1-z; iii: -0.5+x, 0.5-y, -0.5+z; iv: 0.5-x, 0.5+y, 1.5-z.

Scheme 1

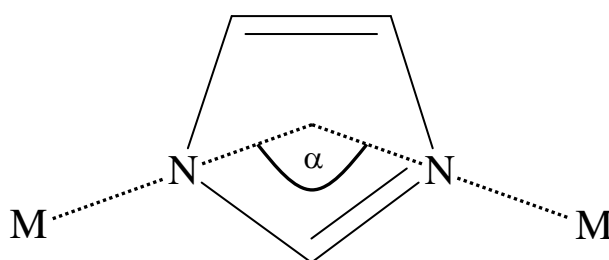
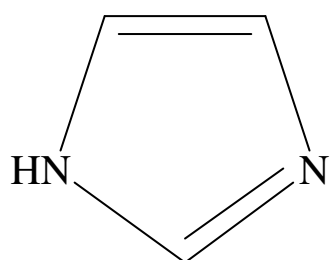


Figure 1

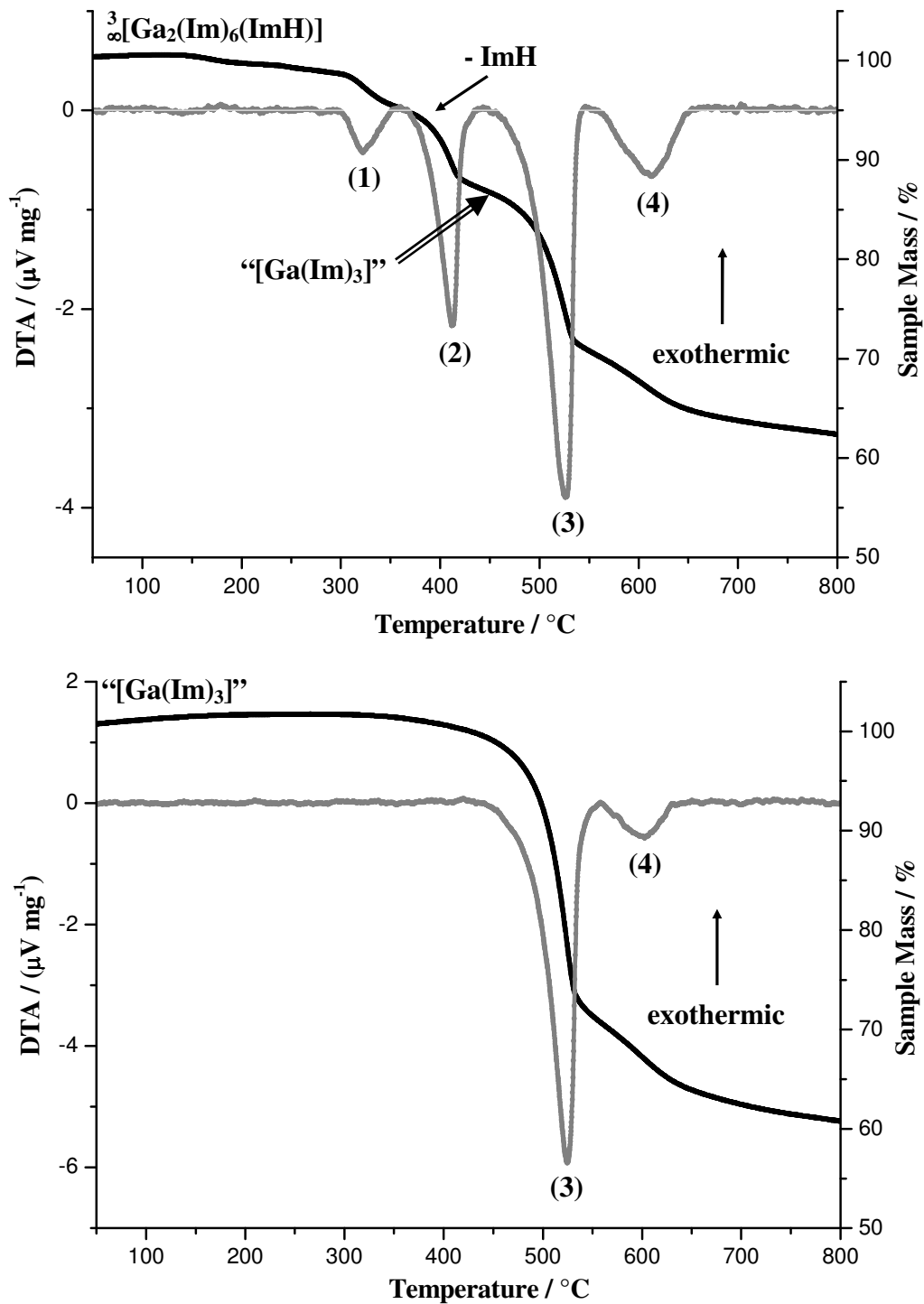


Figure 2

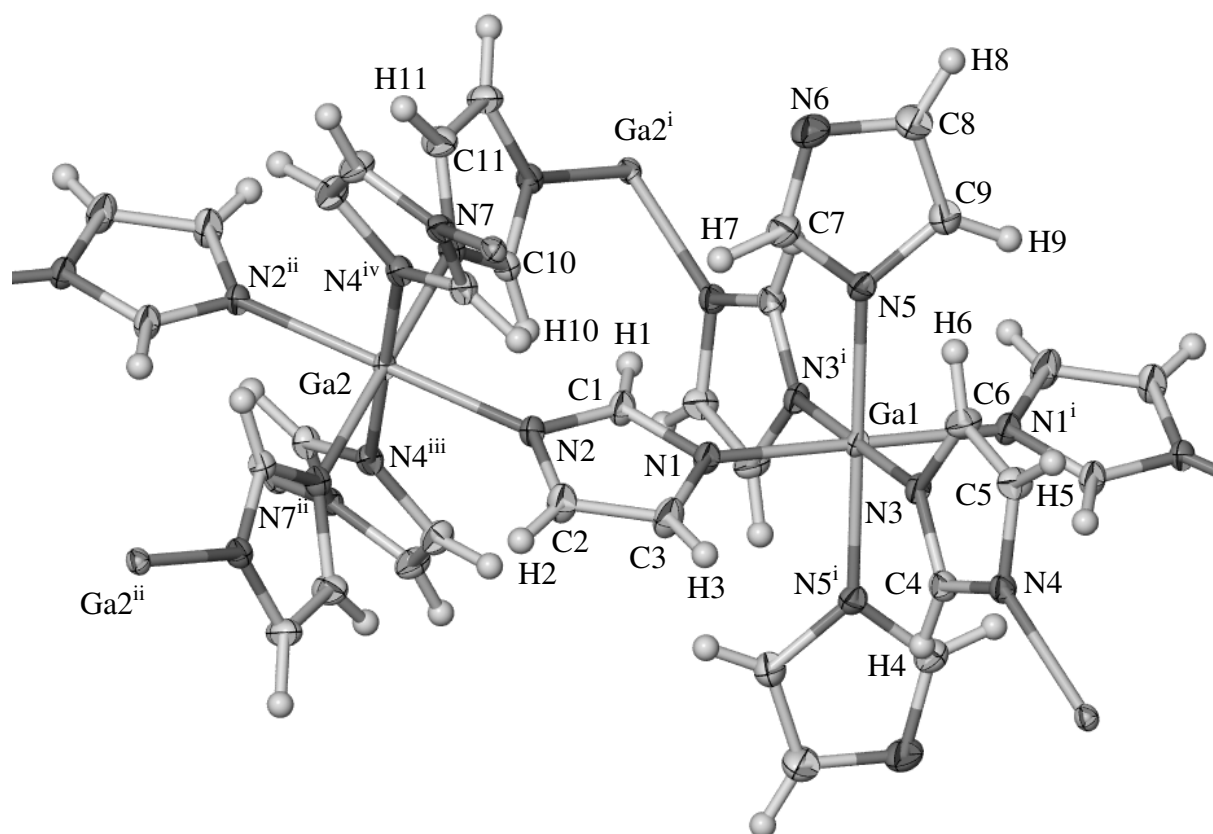


Figure 3

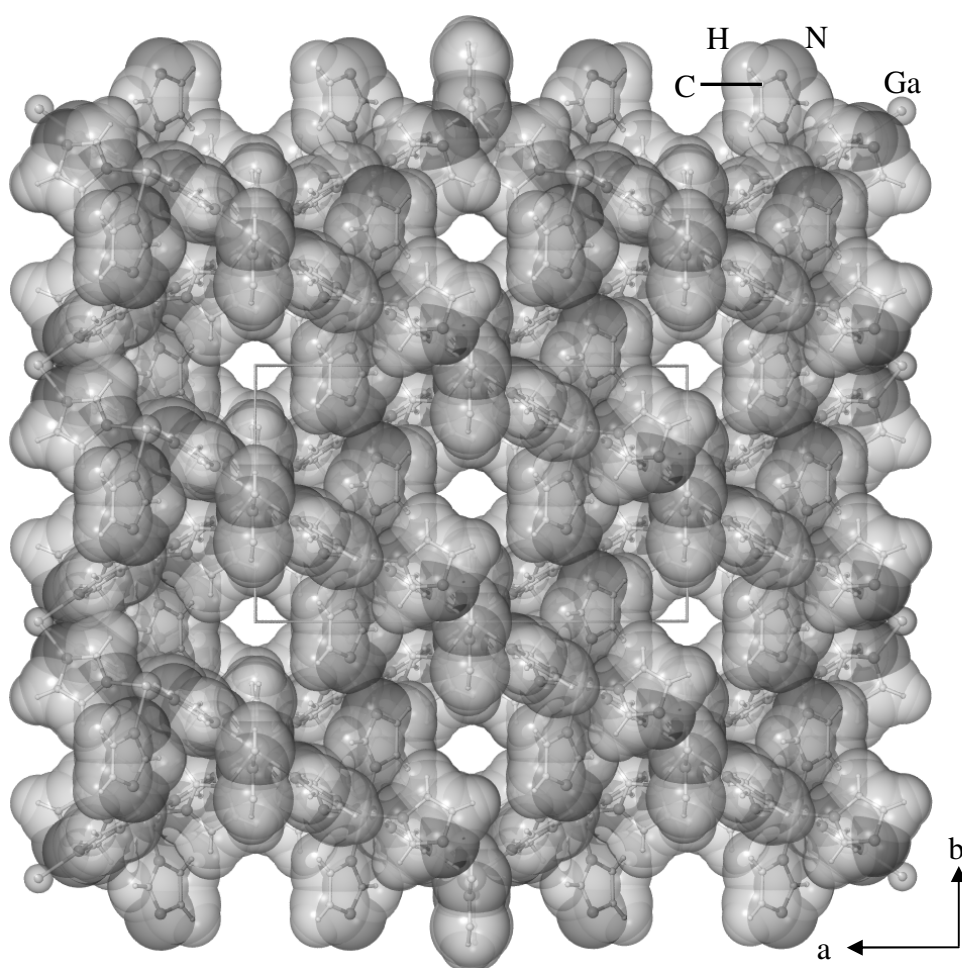
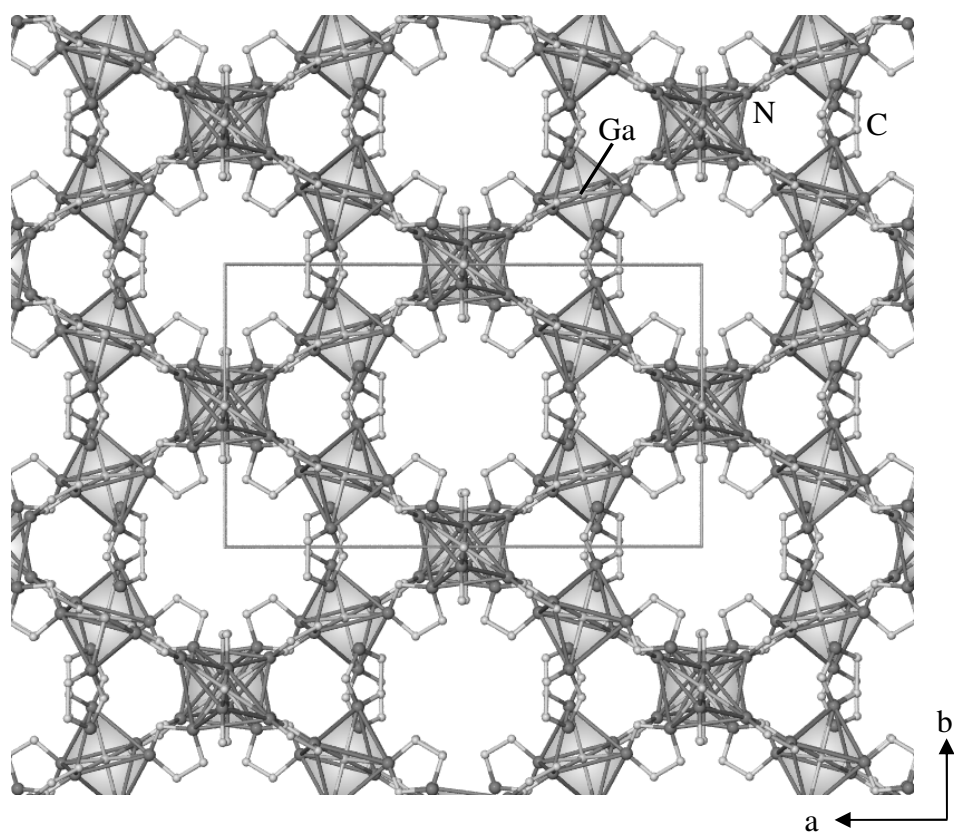


Figure 4

