

Group 13 Metal Halide Based Coordination Polymers of Al, Ga, In and 2,4,6-Tri(4-pyridyl)-1,3,5-triazine

Thomas Schäfer,^[a] Alexander E. Sedykh,^[a] Jonathan Becker,^[a] and Klaus Müller-Buschbaum^{*[a,b]}

Dedicated to Prof. Bernd Harbrecht on the Occasion of his 70th Birthday

Abstract. Four isotopic one-dimensional coordination polymers (CP) were synthesized using the group 13 metal halides AlBr_3 , GaCl_3 , GaBr_3 , and InI_3 and the tridentate ligand 2,4,6-tri(4-pyridyl)-1,3,5-triazine (tpt) serving as bidentate linker. The neutral one-dimensional CPs $\frac{1}{3}[\text{AlBr}_3(\text{tpt})]$, $\frac{1}{3}[\text{GaCl}_3(\text{tpt})]$, $\frac{1}{3}[\text{GaBr}_3(\text{tpt})]$, and $\frac{1}{3}[\text{InI}_3(\text{tpt})]$ are constituted by zigzag-shaped chains in the crystal structure, in which

one coordination site of the tpt ligand remains uncoordinated. All CPs were characterized by SCXRD, PXRD, simultaneous DTA/TG, elemental-analysis and IR spectroscopy. Furthermore, three complexes of the composition $[(\text{AlBr}_3)_3(\text{tpt})]$, $[(\text{GaCl}_3)_3(\text{tpt})]$, and $[(\text{GaBr}_3)_3(\text{tpt})]$ were structurally characterized by SCXRD, being preliminary and side products of the formation of the coordination polymers.

Introduction

The investigation of coordination polymers (CP) and metal-organic frameworks (MOF)^[1] has become a strongly investigated field in chemical research in the last two decades,^[2–4] since those compounds can possess a variety of outstanding features, such as luminescence,^[5,6] porosity,^[7] optical,^[8] and magnetic^[9] properties, which are the result of a combination of the properties originating from the inorganic and organic building blocks. A specific combination of these components leads to materials with intriguing properties.

As for most MOFs and CPs, the most common organic linkers for coordination polymers and MOFs based on group 13 metals are carboxylate based.^[10–12] Whereas N-donor based ligands are not so frequent, most compounds constituting from group 13 metal halides together with pyrazine ($\frac{1}{\infty}[\text{GaCl}_3(\text{pyz})]$),^[13] 4,4'-bipyridine ($\frac{2}{\infty}[(\text{InF}_3)(\text{bipy})]$),^[14] and 1,2-bis(4-pyridyl)ethylene ($\frac{2}{\infty}[\text{Ga}_2\text{Cl}_4(\text{bpe})_5]$),^[1] $\frac{1}{\infty}[\text{GaCl}_2(\text{bpe})_3]_2[\text{GaCl}_4]_4 \cdot 3\text{bpe}$)^[15] as organic linkers.^[13–19] Especially, for the tridentate 2,4,6-tri(4-pyridyl)-1,3,5-triazine (tpt), which is employed in combination with transition metals^[20] in a large variety of scientific studies, only

one polymeric structure in combination with group 13 metal halides has been reported until now, being ${}^3_{\infty}[\text{InCl}_3]_3(\text{tpt})_2$.^[21]

However, tpt is a tridentate linker and despite the reported compounds seems to be a promising candidate for establishing coordination polymers especially in combination with group 13 metal halides. The respective metal ions feature several coordination numbers (CN = 4, 5, 6) in their complexes, which is suitable for constructing CPs and MOFs.^[18] In this work, we present four one-dimensional coordination polymers $\frac{1}{3}[\text{AlBr}_3(\text{tpt})]$, $\frac{1}{3}[\text{GaCl}_3(\text{tpt})]$, $\frac{1}{3}[\text{GaBr}_3(\text{tpt})]$, and $\frac{1}{3}[\text{InI}_3(\text{tpt})]$, synthesized under solvothermal conditions by the reaction of the respective metal halide with 2,4,6-tri(4-pyridyl)-1,3,5-triazine in *m*-xylene and naphthalene as solvent. Furthermore, the byproducts $[(\text{AlBr}_3)_3(\text{tpt})]$, $[(\text{GaCl}_3)_3(\text{tpt})]$, and $[(\text{GaBr}_3)_3(\text{tpt})]$, which also form, in the presented reactions are structurally characterized.

Results and Discussion

The synthesis of the four isotypic, neutral, one-dimensional coordination polymers $\frac{1}{z}[\text{MX}_3(\text{tpt})]$ [$\text{M} = \text{Al}$, $\text{X} = \text{Br}$ (**1**); $\text{M} = \text{Ga}$, $\text{X} = \text{Cl}$ (**2**); $\text{M} = \text{Ga}$, $\text{X} = \text{Br}$ (**3**); $\text{M} = \text{In}$, $\text{X} = \text{I}$ (**4**)] is performed under solvothermal conditions using *m*-xylene and naphthalene as solvent. An illustrative depiction of the crystal structure on the basis of $\frac{1}{z}[\text{AlBr}_3(\text{tpt})]$ is shown in Figure 1 (see also **1–4** crystallize in the orthorhombic crystal system in the space group *Pnma*. The structure consists of one-dimensional zigzag-chains, stacking alternately along the crystallographic *a*-axis in a sinusoidal shape. The one-dimensional chains are constituted by trigonal bipyramidal coordinated metal centers, in which the central metal atom is coordinated by three equatorial halide ligands and two axial N atoms of tpt ligands. The one-dimensional zigzag-chains extend along the crystallographic *b*-axis, with the third coordination site, pointing in direction of the crystallographic *c*-axis, remains uncoordinated. An illustrative depiction of the extended coordination of the metal atoms is given in Figure 2 for

* Prof. Dr. K. Müller-Buschbaum
E-Mail: Klaus.mueller-buschbaum@anorg.chemie.uni-giessen.de

[a] Institute of Inorganic and Analytical Chemistry
Justus-Liebig University Gießen
Heinrich-Buff-Ring 17
35392 Gießen, Germany

[b] Center for Materials Research (LaMa)
Justus-Liebig University Gießen
Heinrich-Buff-Ring 16
35392 Gießen, Germany

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$\frac{1}{2}[\text{AlBr}_3(\text{tpt})]$ (**1**). Since CPs based on group 13 metal halides are not common, discrete examples for CPs and MOFs based on MX_3 and N-donor ligands adopting a trigonal bipyramidal coordination for the central metal atom have been, to the best of our knowledge, not yet reported for AlBr_3 , GaBr_3 , and InI_3 . Because of cracking of crystals upon cooling, the crystallographic data for the different compounds were partly collected at 200 K and partly at 100 K. Discussion of interatomic distances and the relating comparison with the literature has to consider this influence. The interatomic Al–Br distances determined by single crystal X-ray structure analyses as 232.45(1) pm and 233.39(1) pm for CP **1** are close to the interatomic distances found for the complex $[\text{AlBr}_3(\text{py})]$ (Al–Br: 226.7–227.9 pm)^[13] However, the interatomic Al–N distance of 211.43(1) pm is elongated by about 17 pm (Al–N: 193.5 pm).^[13]

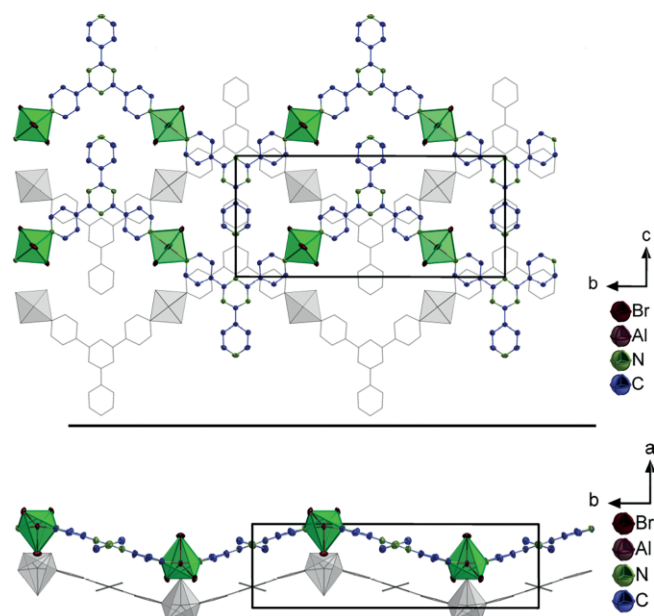


Figure 1. Crystal structure of coordination polymer $\frac{1}{2}[\text{AlBr}_3(\text{tpt})]$ (**1**) with a view along [100], illustrating the one-dimensional zigzag-chains (top) and excerpt of the crystal structure with a view along [00–1] (bottom). The coordination polyhedrons of Al are highlighted in green. For better clarity, all hydrogen atoms are omitted. Thermal ellipsoids are depicted at 50% probability level of the atoms.

In $[\text{AlBr}_3(\text{py})]$, Al^{3+} is coordinated by one N-donor ligand, whereas the metal center in CP **1** is coordinated by two ligands, increasing the coordination number from four to five.

The observed interatomic distances for Ga–N being 216.15(1) pm and for Ga–Cl 219.03(1)–220.26(3) pm for CP **2** and are in good agreement with the interatomic distances reported, e.g. for $\frac{1}{2}[\text{GaCl}_3(\text{bipy})]$ (Ga–N = 218.1–219.3 pm; Ga–Cl = 218.8–220.1 pm).^[18]

Comparison of CP **3** with CP **2** shows an increase of all interatomic distances (Ga–N: 219.92(1) pm; Ga–Br: 233.56(1)–234.47(0) pm; CP **3**), as expected. The interatomic Ga–Br-distances are slightly elongated with respect, e.g. to complex $[\text{GaBr}_3(\text{py})]$ (Ga–N: 197.9 pm; Ga–Br: 229.5–230.6 pm).^[13]

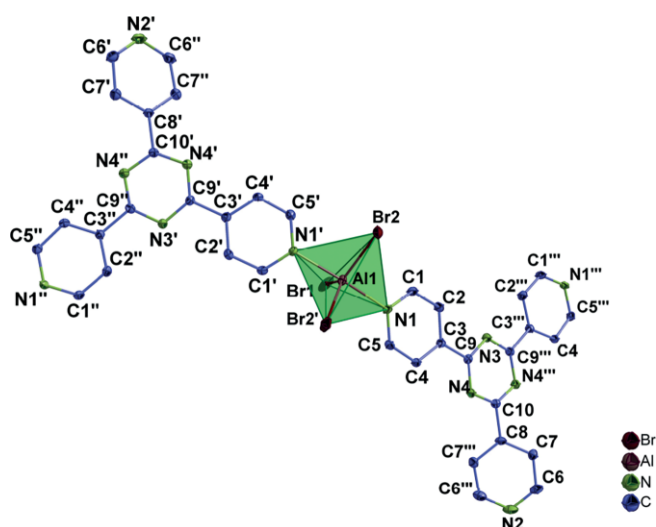


Figure 2. Extended coordination of Al^{3+} ions by tpt in coordination polymer $\frac{1}{2}[\text{AlBr}_3(\text{tpt})]$. Symmetry operations: I = $x, 0.5-y, 0.5-z$; II = $1.5-x, -0.5+y, 0.5-z$; III = $1.5-x, 1-y, z$. For better clarity, all hydrogen atoms are omitted. Thermal ellipsoids are depicted at 50% probability level of the atoms.

Comparison of the interatomic In–I distances determined by single crystal X-ray structure analysis cannot be carried out for $\frac{1}{2}[\text{InI}_3]_3(\text{tpt})_2$,^[21] although the latter is chemically closest, the structure was reported without information on interatomic distances. Therefore, comparison needs to be drawn with other complexes, such as $[\text{InI}_3(\text{py})_3]$, with pyridine as N-donor, although exhibiting an octahedral coordination of In^{3+} .^[22] The observed interatomic In–N distances of CP **4** (In–N: 241.20(1) pm; In–I: 270.19(1)–270.33(1) pm CP **4**) are in the region of distances reported for the complex with py (In–N: 230.9–232.3 pm; In–I: 283.9–286.7 pm)^[22] with respect to the different C–N.

Successful syntheses of the coordination polymers $\frac{1}{2}[\text{AlBr}_3(\text{tpt})]$ (**1**), $\frac{1}{2}[\text{GaCl}_3(\text{tpt})]$ (**2**), $\frac{1}{2}[\text{GaBr}_3(\text{tpt})]$ (**3**), and $\frac{1}{2}[\text{InI}_3(\text{tpt})]$ (**4**) were carried out under different solvothermal reaction conditions. Since group 13 metal halides are Lewis acids, most of the common polar and Lewis basic solvents, such as pyridine, DMF form complexes with the group 13 metal halides. Such solvents therefore compete with the coordination of the tpt ligand. Accordingly, all reactions were limited to non-coordinative solvents, such as benzene, toluene and *m*-xylene as well as liquid naphthalene in order to achieve multiple coordination of tpt.

Phase pure bulk materials are only accessible at temperatures between 180 °C and 250 °C in sealed Duran® glass ampoules using solvents under solvothermal conditions. In principle, the employed metal halides already react with the tpt ligand at room temperature in the presence of the respective solvents but with formation of a mixture of multiple reaction products that cannot be identified. Therefore, the herein described reactions are utilized to proceed to one thermodynamically stable bulk product. The solvothermal approach also shows limitations to achieve phase pure reaction products, as standard cleaning procedures, such as washing with boiling

solvents and sublimation of volatile impurities are not suitable. The formed byproducts as well as the tpt ligand are hardly soluble in the respective boiling solvents, and sublimation attempts at temperatures above 200 °C lead to lower purity than before. So, an additional procedure was applied using solvothermal conditions also for some part of the washing procedure. Under these conditions, byproducts, such as complexes, the tpt ligand, etc. can be dissolved, whereas the CP as main product remains in the solid state. This enables a separation of the reaction product from side phases by decanting of the liquid phase under solvothermal conditions.

To reduce high pressure inside the glass ampoules, naphthalene was applied according to its high boiling point of 218 °C. However, naphthalene reacts with the starting materials AlCl_3 , GaCl_3 , and GaBr_3 with formation of brownish to blackish insoluble impurities, and is only suitable for reactions with InI_3 . For all other reactions, *m*-xylene with a boiling point of 139 °C was used.

In the course of investigations, all obtained bulk materials were also examined by PXRD-investigations and elemental-

analysis. Without the described purification, all bulk powder patterns show reflections of the respective coordination polymer, the ligand, and, in some cases, additional reflections of side phases.

In the search for an alternative reaction pathway, to obtain phase pure coordination polymer **1–4**, also an in situ cyclotrimerization of 4-cyanopyridine yielding tpt in the presence of the group 13 metal halides was attempted, as it was described previously for the synthesis of $^3[\text{Bi}_2\text{Br}_6(\text{tct})]$ [tctp = 1,3,5-tris(4-cyanophenyl)triazine].^[23] Hereby, we found the monomeric complexes $[(\text{AlBr}_3)_3(\text{tpt})]$ (**5**), $[(\text{GaCl}_3)_3(\text{tpt})]$ (**6**), and $[(\text{GaBr}_3)_3(\text{tpt})]$ (**7**) that are side phases of the herein described synthesis of CP **1–4**, as depicted in Figure 3.

An illustrative depiction of the mentioned complexes is given in Figure 4 for complex **6** (see also Figures S13–S18, Supporting Information).

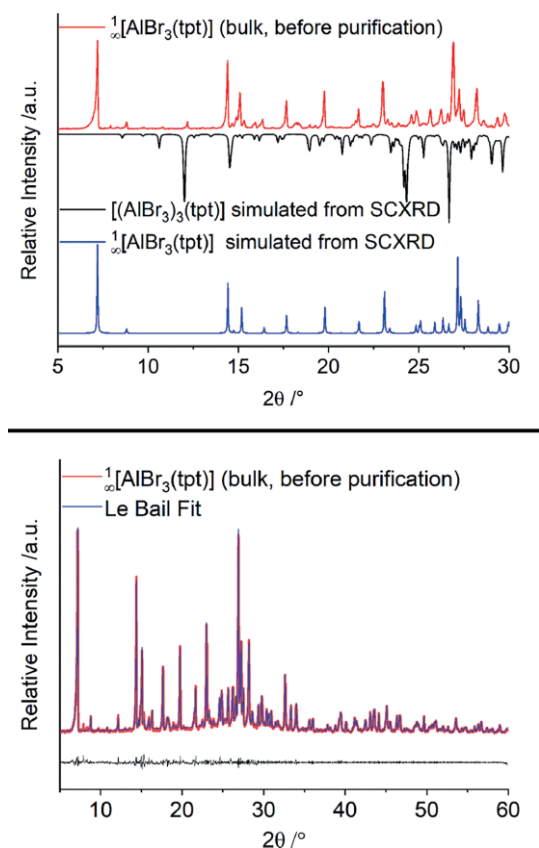


Figure 3. (top) Comparison of the experimental diffraction pattern of $^1[\text{AlBr}_3(\text{tpt})]$ (**1**) (red, top), the simulated diffraction patterns of $[(\text{AlBr}_3)_3(\text{tpt})]$ (**5**) (black, middle) and simulated diffraction pattern of $^1[\text{AlBr}_3(\text{tpt})]$ (**1**) (blue, bottom). Before purification, the complex **5** is found as side product of **1**; $\text{Cu-}K_{\alpha 1} = 154.1$ pm. All depictions represent excerpts of the powder patterns from 5° to 30° in 2θ . (bottom) Experimental powder-X-ray diffraction data for $^1[\text{AlBr}_3(\text{tpt})]$ (**1**) (red) and the Le Bail fit of CP **1**, complex (**5**), and the ligand tpt against the experimental data (blue) as well as the corresponding difference plot (black).

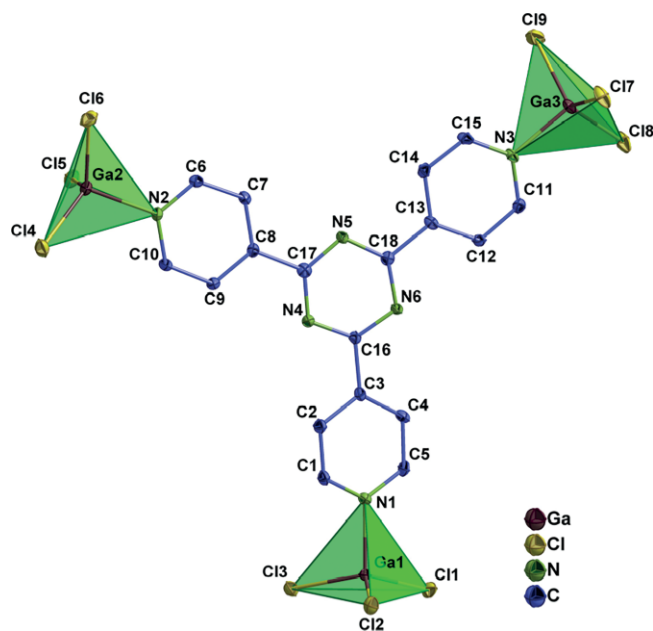


Figure 4. Extended coordination of Ga^{3+} ions by tpt in complex $[(\text{GaCl}_3)_3(\text{tpt})]$ (**6**). For better clarity, all hydrogen atoms are omitted. Thermal ellipsoids are depicted at 50% probability level of the atoms.

The complexes **5** and **7** are isotypic and crystallize in the orthorhombic crystal system in the space group *Pbca*, whereas complex **6** crystallizes in the orthorhombic crystal system in the space group *Pca2*₁. In the monomeric complexes, all coordination sites of the tpt ligand are coordinated to one group 13 metal trihalide, whereas M^{3+} is coordinated by three halide ligands and one tpt ligand forming a slightly distorted tetrahedron. The interatomic distances (Al–N: 193.74(1)–194.95(1) pm, Al–Br: 225.94(1)–227.33(1) pm for **5**; Ga–N: 198.51(3)–200.21(2) pm, Ga–Cl: 214.22(2)–215.72(3) pm for **6**; Ga–N: 199.47(2)–200.57(1) pm; Ga–Br: 228.68(2)–230.41(2) pm for **7**) and angles, determined by single crystal X-ray investigations, are in good accordance with the literature (Al–N = 193.5 pm, Al–Br = 226.7–227.9 pm for $[\text{AlBr}_3(\text{py})]$; Ga–N = 196.6 pm, Ga–Cl = 215.7–216.0 pm for $[\text{GaCl}_3(\text{py})]$; Ga–N = 197.9 pm, Ga–Br = 229.5–230.6 pm for $[\text{GaBr}_3(\text{py})]$) (see Tables S12–S14, Supporting Information).^[13]

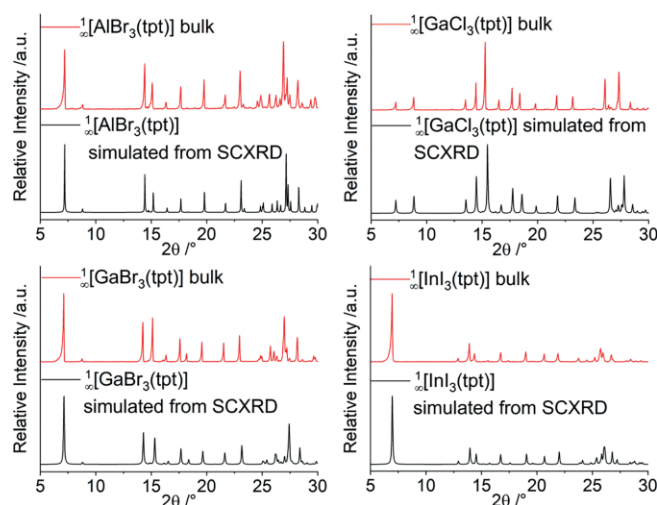


Figure 5. Comparison of the experimental (red, top) and simulated (black, bottom) diffraction patterns of $\frac{1}{3}[\text{AlBr}_3(\text{tpt})]$ (**1**) (top, left), $\frac{1}{3}[\text{GaCl}_3(\text{tpt})]$ (**2**) (top, right), $\frac{1}{3}[\text{GaBr}_3(\text{tpt})]$ (**3**) (bottom, left), and $\frac{1}{3}[\text{InI}_3(\text{tpt})]$ (**4**) (bottom, right); $\text{Cu}-K_{\alpha 1} = 154.1 \text{ pm}$. All depictions represent excerpts of the powder patterns from 5° to 30° in 2θ (see also Figures S19–S22, Supporting Information).

The obtained bulk materials of the coordination polymers **1–4** were also investigated by X-ray powder diffraction, which reveal a good accordance of the obtained diffraction patterns with the diffraction patterns simulated from single crystal data, as depicted in Figure 5 (see also Figures S19–S22, Supporting Information). In addition, all coordination polymers were investigated by elemental-analysis, confirming the composition of all bulk materials.

The IR spectra of CP **1–4** illustrate successful coordination of tpt to M^{3+} , e.g. by a shift of the $\nu(\text{C}=\text{N})$ ring vibration mode

from 1592 cm^{-1} for the free tpt ligand to higher values for the coordinated pyridyl sites, by 17.5 cm^{-1} – 26.5 cm^{-1} [$\nu(\text{C}=\text{N})$: 1618.5 cm^{-1} , CP **1**; 1614.0 cm^{-1} , CP **2**; 1616.8 cm^{-1} , CP **3**; 1609.5 cm^{-1} , CP **4**].^[24]

Coordination to the metal halides induces a positive polarization of the nitrogen atom of the respective pyridyl sites. If we look at the MO diagram of pyridine in C_{2v} symmetry, this polarization affects and therefore stabilizes the HOMO-1 and HOMO-2 resulting in a lowering of the aromatic conjugation within the pyridyl ring. Thus electrons are more localized and the $\text{C}=\text{N}$ -bond gets stronger. This causes the observed hypsochromic shift of the respective $\nu(\text{C}=\text{N})$ ring vibration mode. A comparison of this shift for the herein reported CPs **1–4** indicates a dependency according to the metal halide being coordinated to tpt and reveals an increase of this shift in the order: $\text{InI}_3 < \text{GaCl}_3 < \text{GaBr}_3 < \text{AlBr}_3$.

The $\nu(\text{C}=\text{N})$ ring vibration for the uncoordinated pyridyl site was found to be at 1602.2 cm^{-1} (CP **1**), 1597.9 cm^{-1} (CP **2**), 1603.6 cm^{-1} (CP **3**), and 1593.7 cm^{-1} (CP **4**) (see also Figures S23–S26, Supporting Information).

Thermal investigations by simultaneous DTA/TG analysis reveal good temperature stability for coordination polymers **1–4**, as shown in Figure 6. $\frac{1}{3}[\text{InI}_3(\text{tpt})]$ (**4**) exhibits the highest decomposition temperature of 415°C and is the most temperature stable of these one-dimensional coordination polymers, followed by $\frac{1}{3}[\text{GaCl}_3(\text{tpt})]$ (**2**) (315°C), $\frac{1}{3}[\text{AlBr}_3(\text{tpt})]$ (**1**) (305°C), and $\frac{1}{3}[\text{GaBr}_3(\text{tpt})]$ (**3**) (295°C) (see also Figures S27–S30, Supporting Information).

Furthermore, the TG-curves for CP **1** and **4** show initial mass losses correlating with no detectable DTA-signal at lower temperatures than the decomposition temperature, indicating a certain volatility of the compounds at temperatures close to

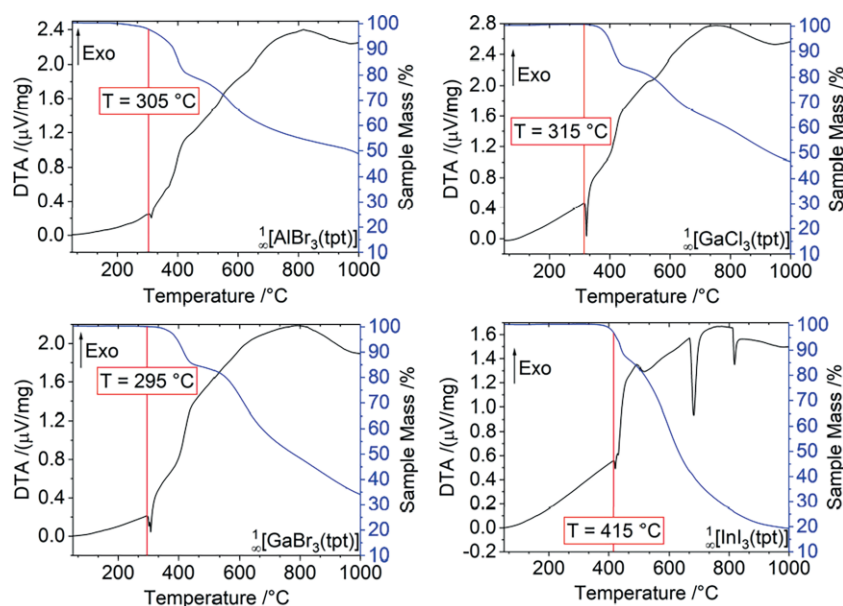


Figure 6. Simultaneous DTA/TG of coordination polymer $\frac{1}{3}[\text{AlBr}_3(\text{tpt})]$ (**1**), (top, left), polymer $\frac{1}{3}[\text{GaCl}_3(\text{tpt})]$ (**2**) (top, right), polymer $\frac{1}{3}[\text{GaBr}_3(\text{tpt})]$ (**3**) (bottom, left), and polymer $\frac{1}{3}[\text{InI}_3(\text{tpt})]$ (**4**) (bottom, right). All investigations were performed in a constant argon flow of $50 \text{ mL} \cdot \text{min}^{-1}$ with a heating rate of $5 \text{ K} \cdot \text{min}^{-1}$ from room temperature to 1000°C . The red lines mark the onset temperature for the endothermic decomposition of the respective coordination polymer.

the decomposition without melting congruently. The ongoing decomposition of the polymers is complex, the mass loss continuing above 1000 °C and without distinct chemical products identified.

Conclusions

Four new, isotypic one-dimensional coordination polymers were synthesized originating from the group 13 metal halides AlBr_3 , GaCl_3 , GaBr_3 , and InI_3 and the tridentate ligand 2,4,6-tri(4-pyridyl)-1,3,5-triazine (tpt). $[\text{AlBr}_3(\text{tpt})]$ (**1**), $[\text{GaCl}_3(\text{tpt})]$ (**2**), and $[\text{GaBr}_3(\text{tpt})]$ (**3**) were synthesized via a solvothermal approach using stoichiometric reaction conditions and *m*-xylene as solvent, whereas $[\text{InI}_3(\text{tpt})]$ (**4**) was successfully synthesized using naphthalene under solvothermal conditions as solvent. All CPs consist of neutral one-dimensional zigzag-chains, in which all M^{3+} ions are coordinated by three halide ligands in equatorial positions and two tpt-ligands in axial positions forming slightly distorted trigonal-bipyramidal coordination. Simultaneous DTA/TG analysis of the coordination polymers reveals fair temperature stability of all compounds (295 °C, CP **3**; 305 °C, CP **1**; 315 °C, CP **2**), with $[\text{InI}_3(\text{tpt})]$ (**4**) showing the highest stability of 415 °C. All CPs were characterized by SCXRD, PXRD, simultaneous DTA/TG, elemental-analysis and IR spectroscopy. Furthermore, three monomeric complexes were identified as side products, being $[(\text{AlBr}_3)_3(\text{tpt})]$ (**5**), $[(\text{GaCl}_3)_3(\text{tpt})]$ (**6**), and $[(\text{GaBr}_3)_3(\text{tpt})]$ (**7**), which were also structurally characterized.

Experimental Section

Because of the air and moisture sensitivity of the investigated group 13 metal halides and the obtained reaction products, all reactions and manipulations were carried out under inert gas atmosphere in Duran® glass ampoules, using vacuum line, Schlenk and glovebox techniques (MBraun, Labmaster SP, and Innovative Technology, Pure Lab). The reactions in Duran® glass ampoules were performed in a Büchi glass-furnace as well as in heating furnaces based on Al_2O_3 tubes with Kanthal wire resistance and NiCr/Ni temperature elements. The heating programs were applied using Eurotherm 2416 control units. The starting materials AlBr_3 (anhydrous, 99.999 %, Sigma–Aldrich), GaCl_3 (anhydrous, 99.999 %, Sigma–Aldrich), GaBr_3 (anhydrous, 99.999 %, Sigma–Aldrich), InI_3 (anhydrous, 99.998 %, Sigma–Aldrich), 2,4,6-tri(4-pyridyl)-1,3,5-triazine (97.0 %, TCI), 4-cyanopyridine (98.0 %, TCI) were used as purchased. Naphthalene (99 %, Sigma–Aldrich) was purified by sublimation in a temperature gradient from 70 °C to room temperature under reduced pressure ($p = 1.0 \times 10^{-3}$ mbar) prior to reactions. Toluene (99.85 %, extra dry, Acros Organics) and *m*-xylene (99 %, extra dry, Acros Organics) were degassed and stored over activated molecular sieves (4 Å) for 3 days prior to use. Benzene was dried by distillation in a dry argon atmosphere from sodium and stored over activated molecular sieves (4 Å).

Microanalyses were carried out on a Thermo FlashEA – 1112 series analyser. IR spectra were recorded with a Bruker VERTEX70 / Platinum spectrometer in transmission mode using an ATR-unit. Thermal properties were determined by simultaneous DTA/TG (NETZSCH STA 409-PC) in a constant argon flow of $50 \text{ mL} \cdot \text{min}^{-1}$ with a heating rate of $5 \text{ K} \cdot \text{min}^{-1}$ from room temperature to 1000 °C.

X-ray Crystallography: Single crystal X-ray determinations of $[\text{AlBr}_3(\text{tpt})]$ (**1**), $[\text{GaCl}_3(\text{tpt})]$ (**2**), $[\text{GaBr}_3(\text{tpt})]$ (**3**), and $[(\text{AlBr}_3)_3(\text{tpt})]$ (**5**) were performed on a BRUKER AXS Smart Apex 1 diffractometer with graphite monochromator (Mo-K_α radiation; $\lambda = 0.71073 \text{ Å}$). The single-crystal X-ray determinations of $[\text{InI}_3(\text{tpt})]$ (**4**), $[(\text{GaCl}_3)_3(\text{tpt})]$ (**6**), and $[(\text{GaCl}_3)_3(\text{tpt})]$ (**7**) were performed on a BRUKER AXS D8 Venture diffractometer equipped with dual $\text{CuK}\alpha$ microfocus sources, a PHOTON100 detector and an OXFORD CRYOSYSTEMS 700 low temperature system. The data collections for the compounds **2**, **3**, **4**, **5**, and **6** were performed at 100 K whereas data collection for compound **1** and **7** was performed at 200 K. Measurements at 200 K were carried out due to the cracking of the respective single crystals upon cooling to 100 K. The structures were solved by direct methods, refined with the least-square method by ShelXL^[25–27] and expanded using Fourier techniques, all within the OLEX2 software suite.^[28] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned to idealized geometric positions and included in structure factors calculations. Depictions of the crystal structures were created using DIAMOND.^[29]

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-1986831 (**1**), CCDC-1986832 (**2**), CCDC-1986833 (**3**), CCDC-1986834 (**4**), CCDC-1986835 (**5**), CCDC-1986836 (**6**), and CCDC-1986837 (**7**) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, <http://www.ccdc.cam.ac.uk>).

Crystal Data for Coordination Polymer 1: ($\text{C}_{18}\text{H}_{12}\text{Br}_3\text{AlN}_6$) ($M = 579.05 \text{ g} \cdot \text{mol}^{-1}$, colorless needle): orthorhombic, space group *Pnna* (no. 52), $a = 7.1643(3) \text{ Å}$, $b = 24.5476(1) \text{ Å}$, $c = 10.9907(4) \text{ Å}$, $a = \beta = \gamma = 90^\circ$, $V = 1932.89(1) \text{ Å}^3$, $\rho_{\text{calc}} = 1.990 \text{ g} \cdot \text{cm}^{-3}$, $T = 200 \text{ K}$, $\mu(\text{Mo-K}_\alpha) = 6.324 \text{ mm}^{-1}$, 31515 reflections measured ($3.318^\circ \leq 2\theta \leq 62.924^\circ$), 3020 unique ($R_{\text{int}} = 0.0553$, $R_{\text{sigma}} = 0.0365$), used in all calculations. GOF: 1.026. Final $R_1 = 0.0306$ [$I > 2\sigma(I)$] and $wR_2 = 0.0593$ (all data).

Crystal Data for Coordination Polymer 3: ($\text{C}_{18}\text{H}_{12}\text{Cl}_3\text{GaN}_6$) ($M = 488.41 \text{ g} \cdot \text{mol}^{-1}$, colorless needle): orthorhombic, space group *Pnna* (no. 52), $a = 6.9762(9) \text{ Å}$, $b = 24.452(2) \text{ Å}$, $c = 10.9335(1) \text{ Å}$, $a = \beta = \gamma = 90^\circ$, $V = 1865.1(3) \text{ Å}^3$, $\rho_{\text{calc}} = 1.739 \text{ g} \cdot \text{cm}^{-3}$, $T = 100 \text{ K}$, $\mu(\text{Mo-K}_\alpha) = 1.923 \text{ mm}^{-1}$, 14486 reflections measured ($6.234^\circ \leq 2\theta \leq 51.336^\circ$), 1780 unique ($R_{\text{int}} = 0.0976$, $R_{\text{sigma}} = 0.0572$) used in all calculations. GOF: 0.912. Final $R_1 = 0.0355$ [$I > 2\sigma(I)$] and $wR_2 = 0.1008$ (all data).

Crystal Data for Coordination Polymer 4: ($\text{C}_{18}\text{H}_{12}\text{Br}_3\text{GaN}_6$) ($M = 621.79 \text{ g} \cdot \text{mol}^{-1}$, colorless needle): orthorhombic, space group *Pnna* (no. 52), $a = 7.0755(2) \text{ Å}$, $b = 24.7686(9) \text{ Å}$, $c = 10.9661(4) \text{ Å}$, $a = \beta = \gamma = 90^\circ$, $V = 1921.81(1) \text{ Å}^3$, $\rho_{\text{calc}} = 2.149 \text{ g} \cdot \text{cm}^{-3}$, $T = 100 \text{ K}$, $\mu(\text{Mo-K}_\alpha) = 7.687 \text{ mm}^{-1}$, 30018 reflections measured ($4.062^\circ \leq 2\theta \leq 59.294^\circ$), 2709 unique ($R_{\text{int}} = 0.0589$, $R_{\text{sigma}} = 0.0294$) used in all calculations. GOF: 1.060. Final $R_1 = 0.0233$ [$I > 2\sigma(I)$] and $wR_2 = 0.0480$ (all data).

Crystal Data for Coordination Polymer 4: ($\text{C}_{18}\text{H}_{12}\text{I}_3\text{InN}_6$) ($M = 807.86 \text{ g} \cdot \text{mol}^{-1}$, yellow block): orthorhombic, space group *Pnna* (no. 52), $a = 7.4556(2) \text{ Å}$, $b = 25.3615(8) \text{ Å}$, $c = 11.6608(4) \text{ Å}$, $a = \beta = \gamma = 90^\circ$, $V = 2204.88(1) \text{ Å}^3$, $\rho_{\text{calc}} = 2.434 \text{ g} \cdot \text{cm}^{-3}$, $T = 100 \text{ K}$, $\mu(\text{Mo-K}_\alpha) = 5.289 \text{ mm}^{-1}$, 27676 reflections measured ($3.844^\circ \leq 2\theta \leq 56.562^\circ$), 2736 unique ($R_{\text{int}} = 0.0427$, $R_{\text{sigma}} = 0.0199$) used in all calculations. GOF: 1.143. Final $R_1 = 0.0208$ [$I > 2\sigma(I)$] and $wR_2 = 0.0359$ (all data).

Crystal Data for Complex 5: ($C_{18}H_{12}Br_9Al_3N_6$) ($M = 1112.47$ g·mol⁻¹, colorless plate): orthorhombic, space group *Pbca* (no. 61), $a = 12.5099(7)$ Å, $b = 14.0929(7)$ Å, $c = 36.420(2)$ Å, $\alpha = \beta = \gamma = 90^\circ$, $V = 6420.8(6)$ Å³, $\rho_{calc} = 2.302$ g·cm⁻³, $T = 100$ K, $\mu(Mo-K\alpha) = 11.341$ mm⁻¹, 76005 reflections measured ($2.236^\circ \leq 2\theta \leq 51.362^\circ$), 6087 unique ($R_{int} = 0.0965$, $R_{sigma} = 0.0440$) used in all calculations. GOF: 1.038. Final $R_1 = 0.0307$ [$I > 2\sigma(I)$] and $wR_2 = 0.0649$ (all data).

Crystal Data for Complex 6: ($C_{18}H_{12}Cl_9Ga_3N_6$) ($M = 840.55$ g·mol⁻¹, colorless plate): orthorhombic, space group *Pca2₁* (no. 29), $a = 13.9080(2)$ Å, $b = 11.7214(2)$ Å, $c = 17.902(3)$ Å, $\alpha = \beta = \gamma = 90^\circ$, $V = 2918.4(7)$ Å³, $\rho_{calc} = 1.913$ g·cm⁻³, $T = 100$ K, $\mu(Mo-K\alpha) = 3.596$ mm⁻¹, 58234 reflections measured ($4.544^\circ \leq 2\theta \leq 56.560^\circ$), 6953 unique ($R_{int} = 0.0552$, $R_{sigma} = 0.0355$) used in all calculations. GOF: 1.071. Final $R_1 = 0.0238$ [$I > 2\sigma(I)$] and $wR_2 = 0.0413$ (all data).

Crystal Data for Complex 7: ($C_{18}H_{12}Br_9Ga_3N_6$) ($M = 1240.69$ g·mol⁻¹, orange block): orthorhombic, space group *Pbca* (no. 61), $a = 12.6053(1)$ Å, $b = 14.2261(1)$ Å, $c = 36.731(3)$ Å, $\alpha = \beta = \gamma = 90^\circ$, $V = 6586.8(1)$ Å³, $\rho_{calc} = 2.502$ g·cm⁻³, $T = 200$ K, $\mu(Mo-K\alpha) = 13.376$ mm⁻¹, 64846 reflections measured ($4.436^\circ \leq 2\theta \leq 50.700^\circ$), 6020 unique ($R_{int} = 0.0416$, $R_{sigma} = 0.0199$) used in all calculations. GOF: 1.141. Final $R_1 = 0.0347$ [$I > 2\sigma(I)$] and $wR_2 = 0.0774$ (all data).

PXRD Analysis: PXRD analyses were carried out with a STOE STADI P diffractometer with focusing Ge(111) monochromator and a Dectris MYTHEN 1 K strip detector in Debye–Scherrer setup. Powder samples were prepared in Lindemann glass capillaries with 0.5 mm diameter in an inert gas atmosphere. Because of the high absorption of Cu- $K\alpha$ radiation, samples of coordination polymer **1**, **3**, and **4** were measured in a 1:5 mass ratio with quartz glass powder. The samples were measured in transmission geometry using Cu- $K\alpha$ radiation ($\lambda = 1.54056$ Å). A Le Bail Fit was carried out using the Topas-Academic V6 software suite.^[30] The crystallographic data of CP **1**, complex **5** and tpt were used for the refinement.^[31] The cell parameters were refined to: CP **1** (*Pnna*): $a = 7.238(1)$ Å, $b = 24.609(4)$ Å, $c = 11.005(2)$ Å, $\alpha = \beta = \gamma = 90^\circ$; Complex **5** (*Pbca*): $a = 12.573(3)$ Å, $b = 14.055(6)$ Å, $c = 36.547(10)$ Å, $\alpha = \beta = \gamma = 90^\circ$; Ligand tpt (*C2/c*): $a = 12.948(11)$ Å, $b = 11.156(11)$ Å, $c = 10.748(8)$ Å, $\alpha = \gamma = 90^\circ$, $\beta = 111.19(6)$. $R_{wp} = 7.28$ and $GoF = 1.43$.

General Synthesis Procedure. The herein reported syntheses and washing procedures were carried out in Duran® glass ampoules. All solid reagents and components were mixed in a mortar and sealed together with liquid solvents, if used, in an ampoule under reduced pressure ($p = 1.0 \times 10^{-3}$ mbar). If a liquid solvent was used, the solvent was frozen using liquid nitrogen before applying vacuum to the ampoule as well as for sealing of the ampoule. If the mixture consists only of solid components, the sealing of the ampoule under reduced pressure occurs at room temperature. The prepared reaction mixtures using liquid solvents were treated in an ultrasonic bath for 30 min before they were placed in an oven, where a heating program was applied. Once, the oven has finished the last step of the temperature program, the solvent or naphthalene was separated from the solid raw product by decanting under solvothermal conditions. This step was accomplished by fast and carefully turning of the ampoule outside the oven. During this step, the solvent must never start to boil until the ampoule has reached room temperature. Otherwise, the solid and liquid phase will be again mixed together. For reactions using liquid solvents, the ampoule was then cracked, and the obtained solid raw product was washed three times with 1 mL boiling toluene and dried at room

temperature under reduced pressure ($p = 1.0 \times 10^{-3}$ mbar). For reactions as well as additional cleaning procedures using naphthalene serving as solvent, the remaining naphthalene after the decanting step was removed from the raw product in a temperature gradient from 130 °C to 77 K in 2 h. The resulting raw product was washed three times with 1 mL boiling toluene.

Synthesis of $\frac{1}{3}[AlBr_3(tpt)]$ (1**):** **1** was achieved according the general procedure using 80 mg (1 equiv., 300 μ mol) $AlBr_3$, 94 mg (1 equiv., 301 μ mol) tpt and 1 mL *m*-xylene. The ampoule was placed in a Büchi glass-furnace and heated to 250 °C within 2 h. This temperature was kept for 24 h. Then, the ampoule was cooled to 220 °C within 20 min. Since the obtained bulk product was not phase pure after the washing process, a further cleaning procedure using 600 mg naphthalene was carried out. Therefore the prepared ampoule was placed in a Büchi-glass oven, heated to 250 °C in 20 min and this temperature was held for 12 h. The naphthalene was removed at 250 °C by decanting and the raw product was washed. The obtained colorless, crystalline product was characterized by powder-X-ray diffraction analysis, IR spectroscopy as well as CHN-analysis. Yield: 85 mg (49%). The product is air and moisture sensitive. $AlBr_3C_{18}H_{12}N_6$: calcd. C: 37.34%, H: 2.09%, N: 14.51%; found: C: 36.36%, H: 2.07%, N: 13.71%. **FT-IR** (ATR): $\tilde{\nu} = 3052.8$ (w), 1618.5 (w), 1602.2 (w), 1570.0 (w), 1510.0 (s), 1420.2 (w), 1371.2 (s), 1316.2 (m), 1219.7 (w), 1057.1 (m), 1018.2 (m), 873.9 (w), 848.4 (w), 806.5 (s), 755.8 (w), 735.9 (m), 699.7 (w), 688.3 (w), 655.8 (m), 643.6 (s), 520.0 (s), 481.5 (w) cm⁻¹.

Single Crystals of $\frac{1}{3}[AlBr_3(tpt)]$ (1**):** Single crystals were obtained according the general procedure, using 62 mg (3 equiv., 232 μ mol) $AlBr_3$, 48 mg (2 equiv., 153 μ mol) tpt and 600 mg naphthalene serving as solvent. The reaction mixture was placed in a Büchi glass-furnace and heated to 250 °C within 20 min. This temperature was held for 48 h. Afterwards, the reaction mixture was cooled to 200 °C within 20 min. After 8 h at this temperature, the liquid naphthalene was removed at 200 °C by decanting and remaining naphthalene was sublimed. This procedure results in a brownish to blackish reaction mixture with colorless single crystals of coordination polymer **1**.

Synthesis of $\frac{1}{3}[GaCl_3(tpt)]$ (2**):** **2** was achieved according the general procedure using 44 mg (1 equiv., 250 μ mol) $GaCl_3$, 79 mg (1 equiv., 253 μ mol) tpt and 1 mL *m*-xylene. The ampoule was placed in a Büchi glass-furnace and heated to 250 °C within 2 h. This temperature was held for 24 h. Now, the reaction mixture was cooled to 220 °C within 20 min. After decanting of the solvent, the raw product was washed and no additional cleaning procedure was needed. The obtained colorless, crystalline product was characterized by powder-X-ray diffraction analysis, IR spectroscopy as well as CHN-analysis. Yield: 101 mg (83%). The product is air and moisture sensitive. $GaCl_3C_{18}H_{12}N_6$: calcd. C: 44.27%, H: 2.48%, N: 17.21%; found: C: 43.61%, H: 2.10%, N: 16.60%. **FT-IR** (ATR): $\tilde{\nu} = 3049.7$ (w), 1614.0 (w), 1597.9 (w), 1569.9 (w), 1514.1 (s), 1418.7 (w), 1370.1 (s), 1314.8 (m), 1215.7 (w), 1158.0 (w), 1108.2 (w), 1057.4 (m), 1013.2 (w), 990.3 (w), 872.0 (w), 846.7 (w), 804.3 (s), 754.5 (w), 734.8 (m), 687.6 (w), 665.6 (w), 652.5 (m), 642.0 (s), 516.1 (s), 478.3 (w) cm⁻¹.

Single Crystals of $\frac{1}{3}[GaCl_3(tpt)]$ (2**):** Single crystals were obtained by a reaction of 41 mg (3 equiv., 233 μ mol) $GaCl_3$ with 48 mg (2 equiv., 138 μ mol) tpt. The solid reagents were mixed in a mortar and sealed in a Duran® glass ampoule. The ampoule with the reaction mixture was placed in a preheated Büchi glass-furnace at 320 °C. After 48 h, the oven was cooled to room temperature within 1 h. This procedure results in a colorless reaction mixture with colorless single crystals of coordination polymer **2**.

Synthesis of $\frac{1}{2}[(\text{GaBr}_3(\text{tpt}))]$ (3): 3 was achieved according the general procedure using 57 mg (1 equiv., 184 μmol) GaBr_3 , 61 mg (1 equiv., 195 μmol) tpt and 1 mL *m*-xylene. The mixture was placed in a Büchi glass-furnace and heated to 180 °C within 20 min. This temperature was held for 24 h. Afterwards, the solvent was removed by decanting and the raw product was washed. No additional cleaning procedure was needed. The obtained colorless, crystalline product was characterized by powder-X-ray diffraction analysis, IR spectroscopy as well as CHN-analysis. Yield: 95 mg (83 %). The product is air and moisture sensitive. $\text{GaBr}_3\text{C}_{18}\text{H}_{12}\text{N}_6$: calcd. C: 34.77 %, H: 1.95 %, N: 13.52 %; found: C: 35.67 %, H: 1.78 %, N: 13.54 %. **FT-IR** (ATR): $\tilde{\nu}$ = 3054.0 (w), 1616.8 (w), 1603.6 (w), 1574.2 (w), 1517.3 (s), 1421.7 (w), 1410.2 (w), 1372.9 (s), 1316.5 (m), 1216.8 (w), 1159.9 (w), 1110.4 (w), 1058.9 (m), 1018.6 (w), 991.7 (w), 873.9 (w), 848.7 (w), 806.7 (s), 735.8 (w), 697.7 (w), 688.6 (w), 665.9 (m), 654.9 (s), 643.8 (s), 519.0 (s) cm^{-1} .

Single Crystals of $\frac{1}{2}[(\text{GaBr}_3(\text{tpt}))]$ (3): Single crystals were obtained by a reaction of 72 mg (3 equiv., 233 μmol) GaBr_3 with 48 mg (2 equiv., 154 μmol) tpt. The solid reagents were mixed in a mortar and sealed in a Duran® glass ampoule. The ampoule with the reaction mixture was placed in a preheated Büchi glass-furnace at 320 °C. After 48 h, the oven was cooled to room temperature within 1 h. This procedure results in a colorless reaction mixture with also colorless single crystals of coordination polymer 3.

Synthesis of $\frac{1}{2}[(\text{InI}_3(\text{tpt}))]$ (4): 4 was achieved according the general procedure using 99 mg (1 equiv., 200 μmol) InI_3 , 65 mg (1 equiv., 208 μmol) tpt and 600 mg naphthalene. The reaction mixture was placed in a Büchi glass-furnace and heated to 250 °C within 20 min. The temperature was kept for 12 h. Afterwards, the naphthalene was separated from the solid raw product and the raw product was washed. No additional cleaning procedure was needed. The obtained light orange, crystalline product was characterized by single crystal- and powder-X-ray diffraction analysis, IR spectroscopy as well as CHN-analysis. Yield: 127 mg (85 %). The product is air and moisture sensitive. $\text{InI}_3\text{C}_{18}\text{H}_{12}\text{N}_6$: calcd. C: 26.76 %, H: 1.50 %, N: 10.40 %; found: C: 25.78 %, H: 1.36 %, N: 9.98 %. **FT-IR** (ATR): $\tilde{\nu}$ = 3045.0 (w), 1609.5 (w), 1593.7 (w), 1571.6 (w), 1513.8 (s), 1417.7 (w), 1369.5 (s), 1312.2 (m), 1213.3 (w), 1056.0 (m), 1009.9 (w), 868.1 (w), 800.4 (s), 750.4 (w), 731.6 (w), 692.7 (w), 666.5 (m), 650.1 (s), 642.3 (s), 510.0 (m) cm^{-1} .

Single Crystals of $[(\text{AlBr}_3)_3(\text{tpt})]$ (5): Single crystals were obtained by reaction of 62 mg (3 equiv., 232 μmol) AlBr_3 with 24 mg (1 equiv., 77 μmol) tpt. The solid reagents were mixed in a mortar and sealed in a Duran® glass ampoule. The ampoule with the reaction mixture was placed in a preheated Büchi glass-furnace at 320 °C. After 48 h, the oven was cooled to room temperature within 1 h. This procedure resulted in a colorless reaction mixture with single crystals of complex 5.

Single Crystals of $[(\text{GaCl}_3)_3(\text{tpt})]$ (6): Single crystals were achieved by reaction of 176 mg (1 equiv., 1.00 mmol) GaCl_3 with 104 mg (1 equiv., 1.00 mmol) 4-cyanopyridine in 0.5 mL toluene. The solid reagents were mixed in a mortar and sealed together with the solvent in a Duran® glass ampoule. The ampoule with the reaction mixture was placed in a tubular furnace and a heating program with 3 steps was applied, starting with heating to 200 °C in 1 h. The temperature was maintained for 72 h followed by cooling to room temperature within 12 h. The toluene was removed at room temperature and the colorless raw product was washed three times with 1 mL boiling benzene. This procedure resulted in a colorless reaction mixture with single crystals of complex 6.

Single Crystals of $[(\text{GaBr}_3)_3(\text{tpt})]$ (7): Single crystals were achieved by reaction of 309 mg (1 equiv., 1.00 mmol) GaBr_3 with 309 mg (1 equiv., 1.00 mmol) 4-cyanopyridine in 0.5 mL toluene. The solid reagents were mixed in a mortar and sealed in a Duran® glass ampoule. The ampoule with the reaction mixture was placed in a tubular furnace and a heating program with 3 steps was applied starting with heating to 200 °C in 1 h. The temperature was maintained for 72 h followed by cooling to room temperature within 12 h. The toluene was removed at room temperature and the colorless raw product was washed three times with 1 mL boiling benzene. This procedure resulted in a colorless reaction mixture with single crystals of complex 7.

Supporting Information (see footnote on the first page of this article): 30 figures and 14 tables on crystallographic data, IR spectroscopy and thermal analysis.

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