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Versatile structures of group 13 metal halide complexes with 4,4′-bipy: from 1D coordination polymers to 2D and 3D metal-organic frameworks

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Abstract

A systematic structural study of complexes formed by aluminium and gallium trihalides with 4,4′-bipyridine (bipy) in a 2:1, 1:1, and 1:2 stoichiometric ratio has been performed. Molecular structures of 11 complexes in the solid state have been determined for the first time. Complexes of 2:1 composition are molecular, while complexes of 1:1 composition form metal-organic frameworks of different kinds: ionic 3D network (three interpenetrated **lvt** nets for $AlCl_3bipy$), ionic 2D network for $AlBr_3bipy$ and $GaBr_3bipy$ and 1D coordination polymer in the case of $GaCl_3bipy$. Thus, the nature of the Lewis acid plays a critical role on the structural type of the complex in the solid state. Incorporation of excess bipy molecules into $(GaCl_3bipy)_\infty$ (formation of crystallosolvate) leads to an unprecedented change of the molecular structure from non-ionic 1D coordination polymer to ionic 2D metal organic framework $[GaCl_2bipy_2]^+[GaCl_4]^-$ ·2bipy. As indicated by temperature-dependent XRD study, removal of bipy by heating in vacuum restores non-ionic 1D structure. Quantum chemical computations for simple cluster model systems (up to eight Al and Ga atoms) reveal that ionic forms are slightly favourable, although the energy differences between the ionic and non-ionic structures are not large. These theoretical predictions are in good agreement with experimental findings. Thus, even relatively simple cluster models may be used to indicate the structural preferences in the solid state. Both experimental and computational IR frequency shifts of the in-plane ring bending mode of bipy upon complexation correlate well with the M-N bond distances in the complexes.

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Introduction

Metal-organic frameworks (MOFs) attracted much attention in the recent past due to their use in different areas of chemistry and technology, including heterogeneous catalysis,[1] solid state luminescence,[2] adsorbents for gas storage and separation.[3] Complexes of group 13 metal halides MX_3 feature a central atom in a different coordination environment (coordination numbers 4, 5, 6) depending on complex composition, the nature of the metal halide and the basicity of the donor ligand.[4] The structural variety is potentially useful for constructing MOFs. However, until now there are only a few examples of MOFs based on group 13 halide complexes. In case of indium, several MOFs have been reported,[2,5,6] including one with 4,4'-bipyridine (bipy).[7] A search of the CSD database revealed only a few examples of gallium-containing[6,8] and aluminium-containing[9] MOFs and several Ga^{3+} oligomers with octahedral coordination (c.n. 6) of gallium.[10] To construct such oligomers, bulky organic ligands bearing multiple donor and acceptor centres and a relatively flexible backbone have been employed. The use of relatively simple rigid ligands, such as pyrazine (pyz) and bipy, is less common. Known examples include non-ionic 1D coordination polymers which are realized in 1:1 stoichiometry complexes $(MX_3pyz)_\infty$ where Al and Ga atoms possess coordination number 5 (trigonal bipyramidal environment).[11,12] Interestingly, in case of In, the complex of other stoichiometry $InCl_3pyz_{1.5}$ is formed, in which additional pyz molecules link –In-pyz-In- chains to complete octahedral coordination of In atom.[11] Usage of longer bridging ligand, such as 4,4′-bipy, may lead to a construction of coordination polymer networks with larger pores, which could potentially serve as hosts for different molecules and new functional materials. Crystal structure analysis of InF_3bipy[7] revealed a neutral 2D coordination network. The coordination number of In equals 6; bipy and one of the fluorine atoms serve as bridging ligands. It is of interest if the network structures are also possible for complexes of lighter group 13 metal halides with 4,4′-bipy. Complexes of aluminum and gallium halides with 4,4′-bipy have been studied before by mass-spectrometry and quantum chemical computations,[13] but no structural information is available.

Competition between molecular and ionic structures is a crucial factor in determining the possibility of MOF formation for group 13 element halides. Molecular-ionic interplay in group 13 element complexes is well documented, starting from the molecular ammonia borane BH_3NH_3 and its ionic counterpart diammoniate diborane $[BH_2(NH_3)_2]^+ [BH_4]^-$.[14] Lewis acidity of group 13 acceptor has a significant impact on the structures of the complexes with bidentate ligands en and tmen. Weak Lewis acids (group 13 element hydrides and organometallic derivatives) form molecular complexes $ER_3·LL·ER_3$ (E = B, Al, Ga; R = H, CH_3; LL = en, tmen).[15] Strong Lewis acids (group 13 metal halides) adopt ionic structures in the solid state

[EX$_2$LL]$^+$[EX$_4$]$^-$.[16] Complexes of aluminum and gallium trihalides with chelating bidentate donor 2,2'-bipy are ionic: [AlCl$_2$(2,2′-bipy)$_2$]$^+$Cl$^-$·CH$_3$CN,[17] [GaX$_2$(2,2-bipy)$_2$]$^+$[GaX$_4$]$^-$ for X = Cl, Br and [GaI$_2$(2,2'-bipy)]I,[18] as well as complexes with monodentate donor pyridine in 1:2 ratio [MCl$_2$py$_4$]$^+$[MCl$_4$]$^-$ (M = Al, Ga).[19,20]

More recently, molecular-ionic interplay was studied by Gandon et al[21,22] on the example of GaX$_3$ complexes with N-heterocyclic carbenes as monodentate ligands. It was shown that the donor strength of the carbene has significant influence on the structure of the complex. With the weaker donor dime-IMD only molecular 1:1 adducts GaX$_3$L (X = Cl, Br, I) are formed. The stronger donor IBioxMe$_4$ favors an ionic structure [GaX$_2$L$_2$]$^+$[GaX$_4$]$^-$ in the case of X = Cl, but molecular complexes are formed for X = Br, I. All studied complexes with the strongest donor dime-MDI are ionic. Thus, both Lewis acidity of group 13 halide and Lewis basicity of carbene play an important role for the structural type of the compound in the solid state. Authors explained observed trends in structural preferences on the basis of kinetics reasons.[22]

Thermodynamic stability is also expected to be an important factor. However, theoretical prediction of the structural type (ionic or molecular) of the complex in the solid state is still a challenging task. In the present report, we demonstrate that the gas phase quantum chemical computations on relatively small cluster models are sufficient to predict preferable structural types of the group 13 metal halide complexes with rigid donors 4,4′-bipy and pyrazine in the solid state. We evaluate the validity of our computational predictions via the systematic structural study of MX$_3$ complexes with 4,4′-bipy of different composition. The complexes were characterized by X-ray diffraction analysis and by IR spectroscopy. Moreover, we demonstrate that in the case when the computed energy difference between the ionic and molecular structures is small, structural transformation between these types of structures can be induced by the excess of 4,4'-bipy ligand.

Results and discussion

Computational studies.

In order to model infinite coordination polymers and ionic networks, simple finite cluster model was employed. Two formal structural isomers of the M$_8$X$_{24}$L$_{12}$ composition have been considered (Figure 1): molecular 4(MX$_3$)$_2$L$_3$ and ionic [M$_4$X$_8$L$_{12}$]$^{4+}$([MX$_4$]$^-$)$_4$ (M = Al, Ga; X = Cl, Br; L = pyz, 4,4′-bipy). The latter structure represents the part of the 2D infinite ionic framework. Both molecular and ionic isomers have the same number of M-N bonds and the same number of non-bonded nitrogen atoms. Therefore, the reaction energy of process (1) may serve as an indicator of the energetic preference of ionic or non-ionic structure.

$$4\ (MX_3)_2L_3\ =\ [M_4X_8L_{12}]^{4+}([MX_4]^-)_4 \qquad\qquad (1)$$

The obtained results (Table 1) indicate that for pyz complexes the reaction energy is always positive (the non-ionic chain motif is favored by 46-126 kJ mol^{-1}), which is in qualitative agreement with known experimental structures of pyrazine complexes (non-ionic 1D coordination polymers $(MX_3pyz)_\infty$ (M = Al, Ga; X = Cl, Br)[11,12] or simple monomeric adduct GaI_3pyz[12]). In contrast, in case of 4,4′-bipy, the computed reaction energies are negative (Table 1), indicating energetic preference of the ionic structure. In order to experimentally verify our predictions, complexes of MX_3 with 4,4′-bipy have been synthesized and structurally characterized.

Structural studies.

We have been able to grow single crystals and structurally characterize the following complexes: 1:1 composition: $AlCl_3bipy$ (**1**), $AlBr_3bipy$ (**2**), $GaCl_3\cdot bipy$(**3**), $GaBr_3bipy$ (**4**); 1:2 composition: $GaCl_3bipy_2\cdot 2bipy$ (**5**); 2:1 composition: $(AlCl_3)_2bipy$ (**6**), $(GaCl_3)_2bipy$ (**7**), heterobimetallic complex $AlGaCl_6bipy$ (**8**), $(AlBr_3)_2bipy$ (**9**), $(GaBr_3)_2bipy$ (**10**) and heterobimetallic complex $AlGaBr_6bipy$ (**11**). Experimental details on crystal structure for all complexes are presented in Tables S1-S4 (Supporting Information).

Complexes of 1:1 composition. In agreement with our predictions on the favorability of ionic structures, three out of four studied complexes of 1:1 composition are ionic: $[AlCl_2(bipy)_2]^+[AlCl_4]^-$ (**1**), $[AlBr_2(bipy)_2]^+[AlBr_4]^-$ (**2**), $[GaBr_2(bipy)_2]^+[GaBr_4]^-$ (**4**). Only the complex with gallium trichloride, for which computed energy difference is only 17 kJ mol^{-1} (Table 1) turned out to be non-ionic 1D polymer $[GaCl_3bipy]_\infty$ (**3**) similar to pyrazine analogs.[11,12]

In compounds **1**, **2**, **4** the bipy ligands play a role of long spacers that connect $\{AlCl_2\}^+$ nodes into positively charged 3D framework (**1**) or 2D layers (**2, 4**). Four nitrogen atoms of bipy ligands form a square around M atom, while two *trans*-Cl anions complete its coordination polyhedron to an octahedron (Figure 1a). According to the topological approach[23] these coordination polymers can be described as combination of squares (MN_4) connected by linear spacers (bipy). Due to the different size of MX_4^- counter ions the resulting simplified nets belong to different topological types. In the case of **1** the 3D uninodal 4-connected **lvt** net[24] is observed. Formal description of **lvt** net is given by Yaghi et al.[24a] The net takes 18th place among 20 most frequent underlying nets observed in 3D-polymeric structures containing organic ligands.[23b] Transition metal complexes with bipy also form 2D and 3D MOF (for selected examples of Fe^{2+}, Co^{2+}, Cu^{2+}, Cd^{2+} complexes see ref. 26 and references therein). Among them, only two bipy complexes are found with the same **lvt** topology[26(d,e)] (see also SI), but both of

them are two-interpenetrated. In **1,** three **lvt** nets interpenetrate into each other (Figure 1b). According to the classification proposed by Blatov and Proserpio[25] the case of **1** falls into *Class Ia* with full interpenetration vector of [1,0,0] (interlayer distance 7.08 Å).

Compounds **2** and **4** are isostructural (Figure 2a,b). Each metal ion achieves octahedral environment by coordinating four bipy ligands in the equatorial plane and two halide ions in the axial positions. In contrast to **1**, the resulting layers form planar **sql** net (Figure 2c). In **2** and **4** the interlayer distances are almost the same, 5.34 Å and 5.36 Å, respectively. M-N distances in **2** (2.049-2.070 Å) are by 0.04 – 0.06 Å shorter compared to gallium analog **4**. M-X distances in cations (c.n. 6) are by 0.15-0.19 Å longer compared to that in anions (c.n. 4).

In contrast, **3** forms non-ionic 1D coordination polymer $[GaCl_3bipy]_\infty$ with 4,4′-bipy molecules bridging nearly planar $GaCl_3$ units in infinite chain. Coordination environment of Ga^{3+} ion is trigonal pyramidal, with bipy ligands coordinated in the apical positions (Figure 3a). The infinite chains form double layers in which all chains are co-directional. The layers are packed in crystal structure with rotation for about 80 degrees (Figure 3b). Complexes of this type were observed for pyrazine analogs.[11,12]

However, when the reaction between $GaCl_3$ and 4,4'-bipy was carried out in large excess of 4,4'-bipy, the complex with 1:2 composition $[GaCl_2bipy_2]^+[GaCl_4]^-\cdot 2bipy$ (**5**) was isolated. X-ray structural analysis reveals that it adopts an ionic structure, featuring 2D cationic network (Figure 4a) analogous to one found for **2** and **4**, with $[GaCl_4]^-$ anions and free 4,4'-bipy molecules located between these quasi-2D sheets. Cationic **sql** layer in **5** is similar to that found in **2** and **4**, but in contrast the layers are separated not only by counter anions but also by two isolated bipy molecules per repeating unit of the polymeric structure to give larger interlayer distance of 8.17 Å. Formally, **5** can be described as crystallosolvate **3**·bipy, but it possesses completely different structure from **3**!

Structural changes in MOF upon incorporation of solvent molecules are also known, but they usually do not result in such drastic changes. It was reported that in the series of MOF formed by gallium dipyrrinato complexes with AgOTf, $AgSbF_6$ and $AgPF_6$, the formation of network topologies depends on the size of the anion.[6] Reversible shrinkage/expansion of the MIL-53(Ga){H_2O} structure ("breathing effect") was described.[8] However, in the present report incorporation of the excess of bipy molecules (formation of crystallosolvate) leads to reorganization of the molecular structure from non-ionic 1D coordination polymer to the ionic 2D MOF.

The temperature-dependent powder diffraction experiment have been performed by heating **5** in vacuum from 25 to 150 °C in 25 °C steps. Results indicate that structural

transformation from **5** to **3** in vacuum (process 2) begins at 125 °C and completes at 150 °C (Figure 6).

$$\textbf{5} \text{ (s)} = \textbf{3} \text{ (s)} + 4,4'\text{-bipy (g)} \quad (2)$$
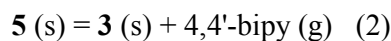
This correlates well with exponential increase of the intensity of bipy^{+} ion above 121 °C in temperature-dependent mass-spectrometry measurements of **5**. Note, that intensity of bipy^{+} ions in mass-spectrum of **3**, independently measured at the same conditions, is about two orders of magnitude lower than in mass-spectrum of **5** (Figure S14).

Vapor pressure over the **5** in the 160-210 °C range was estimated from the TG measurements (see SI for details). The vapor pressure of 4,4′-bipy over **5** is significantly lower than saturated vapor pressure of uncomplexed 4,4′-bipy. From the vapor-pressure temperature dependence the following thermodynamic characteristics of process (2) were obtained: $\Delta_{(2)}H°_{438}$ = 98±6 kJ mol^{-1} and $\Delta_{(2)}S°_{438}$ = 155±13 J mol^{-1} K^{-1}.

Complexes of 2:1 composition. We have also been able to grow single crystals of complexes of 2:1 composition which form two isostructural series. Chlorides (AlCl$_3$)$_2$bipy **(6)**, (GaCl$_3$)$_2$bipy (**7**) and the heterometallic complex AlCl$_3$GaCl$_3$bipy (**8**) belong to the orthorhombic structural type, while bromides (AlBr$_3$)$_2$bipy (**9**), (GaBr$_3$)$_2$bipy (**10**), and AlBr$_3$GaBr$_3$bipy (**11**) adopt the monoclinic structural type. Bipy serves as bridging ligand, forming MX$_3$bipyMX$_3$ molecules analogous to complexes with pyrazine.[12] All complexes **6-11** adopt similar molecular structures with coordination number 4 on group 13 metal (Table 2). As an example, the structure of (AlCl$_3$)$_2$bipy is given in Figure 7a. Substitution of Cl by Br leads to the change of the structural type from orthorhombic to monoclinic, and is accompanied by a substantial change of molecular packing (Figure 7b). In crystal structures of chlorides the molecules are packed co-directionally, while in bromides they form herring-bone packing. The nonequivalence of M1-N1 and M2-N2 distances in complexes (MX$_3$)$_2$bipy is small but noticeable (0.0067±0.0018 Å in **6**, 0.0036±0.0018 Å in **7**, 0.003±0.009 Å in **9**, 0.019±0.006 Å in **10**) and arises from rotation of two pyridine fragments due to the packing effects. X…X intermolecular contacts shorter than doubled van der Waals radii of X are observed in both structural types. The substitution of Cl by Br has minor effect on the M-N bond distances in the solid adducts (Table 2).

According to the X-ray data, the structures of **8** and **11** contain Al and Ga in the same crystallographic positions. The Al/Ga content was refined and gave the same ratio 0.45(1)/0.55(1) for both compounds. The structures can be interpreted as heterobimetallic molecular complexes (Al$_{1.1}$Ga$_{0.9}$X$_3$)$_2$bipy or as a result of co-crystallization of isostructural (AlX$_3$)$_2$bipy and (GaX$_3$)$_2$bipy (X=Cl, Br) molecules in the given ratio. Observation of AlGaX$_5$bipy^{+} ions in the mass-spectra indicate that heterobimetallic molecules are existing in vapors above the complexes.[13] A comparison of structural parameters of studied complexes with

pyz[11,12] and py[27,28] analogs is given in Table 3. The M-N distances increase from Al to Ga. The M-N distances increase in the order py < bipy < pyz (Table 3). This clearly shows the larger donor ability of 4,4′-bipy compared to pyz.

IR studies. The shift of characteristic vibrational bands of 4,4′-bipy ligand is a useful tool for the characterization of the complex formation.[29] We have found, that the bands of 4,4′-bipy at 608(s) (in-plane ring bending), 806(vs) (δC-H), 989m (ring) and 1589s cm^{-1} (C-C, C-N) are sensitive to the complex formation. We note, that in the IR spectra of **5**, bands corresponding to both complexed and free (not complexed) bipy have been observed, in agreement with experimental X-ray structure of the compound in the solid state [GaCl$_2$bipy$_2$]$^+$[GaCl$_4$]$^-$·2bipy. The largest shifts upon complexation (from 27 cm^{-1} for **3** up to 56 cm^{-1} for **7**) were observed for the strong band at 608 cm^{-1} (in-plane ring bending), since this mode involves significant changes in both N-C bond distances and CNC bond angle, which are quite sensitive to the complex formation.[30] The observed IR shifts of this band $\Delta v = v_{complex} - v_{bipy}$ correlate well with the M-N bond length for all studied complexes: the larger the distance, the smaller the shift (Figure 8). Similar correlation is also observed between optimized M-N distances and harmonic vibrational frequency shifts computed for the gas phase molecules with bridging bipy units at RI-BP86/def2-SVP level of theory (Figure 8). In case of complexes with only terminal bipy ligands, the computed IR frequency shift (13-27 cm^{-1}) is about two times smaller compared to that of bridging bipy (27-55 cm^{-1}). Taking into account that experimental bond distances in the condensed phase are shorter than in the gas phase,[4b,31] experimental and computed data are in reasonable agreement with each other. The observed Δv-R(M-N) correlation can be compared with the relationship between structural and thermodynamic properties of molecular complexes, presented by Romm et al.[32]

Conclusions

The nature of the group 13 metal halide strongly affects the structure of their complexes with 4,4′-bipy, allowing the formation of 1D coordination polymers, 2D and 3D ionic networks.

Quantum chemical computations for the simple cluster models in the gas phase reveal that in case of pyz, 1D coordination polymers are energetically preferable, while in case of 4,4′-bipy the energy difference between structural types is not large and ionic forms are slightly favorable. Despite the used computational approach completely neglects the packing effects (which may have significant impact on the favorability of structural type in the solid state), computational predictions are in qualitative agreement with experimentally observed ionic structures of **1**, **2**, **4**, **5** in the solid state and molecular structures of known pyz complexes.[11,12] Both experimental and computed IR shifts of the in-plane bending band of 4,4′-bipy ligand at

608 cm^{-1} correlate well with the M-N bond distances for all studied complexes. Note, that in the case of complexes between $GaCl_3$ and bipy the computed energy difference in the gas phase is only 17 kJ mol^{-1} in favor of the ionic structural motif. This small difference indicates the possibility of competition between the two structures. Indeed, coordination polymer **3** is formed in stoichiometric 1:1 ratio, while in the excess of 4,4′-bipy the ionic structure **5** is realized. We demonstrate that the interplay between non-ionic 1D polymer $(GaCl_3bipy)_\infty$ **3** and ionic 2D network $[GaCl_2bipy_2]^+[GaCl_4]^-\cdot2bipy$ **5** can be induced by the excess of the bipy, which remains essentially free between these 2D layers. Removal of this excess of the uncomplexed bipy upon heating **5** in vacuum results in rather unique structural transformation back to 1D coordination polymer **3**. Thus, computational data on simple finite cluster models may serve as first indication of the preferred type of structure of the complex in the solid state.

Experimental

Synthetic procedures. In order to exclude hydrolysis, all operations have been carried out in wholeglass apparatus sealed under vacuum, analogously to the procedures described earlier.[12,13,27] Group 13 element halides were synthesized from elements and purified by multiple (not less than 4 times) resublimations in vacuum. All complexes have been synthesized by direct interaction of group 13 element trihalides with 4,4'-bipy under vacuum. Either stoichiometric amounts of components were used, or slight excess of one component was employed. The excess component was removed after the synthesis by sublimation. As an example, two synthetic procedures for $AlCl_3bipy$ **(1)** are given below. Synthesis 1: $AlCl_3$ (126.0 mg, 0.945 mmol) was sublimed at circa 90 ℃ to bipy (151.8 mg, 0.972 mmol). The initial $AlCl_3$ to bipy ratio was 1:1.03. The system was stored at 160 ℃ for several days and the excess component was not removed. Single crystals suitable for the X-ray analysis have been grown by slow sublimation of the complexes in vacuum at circa 190-200 ℃ during several weeks. Synthesis 2: bipy (279.6 mg, 1.790 mmol) was sublimed at circa 90℃ to $AlCl_3$ (204.6 mg, 1.534 mmol). The initial $AlCl_3$ to bipy ratio was 1:1.17. The system was stored at 120-160 ℃ for several days. After that, an excess of bipy was sublimed (150-170 ℃, several days) into a special compartment and sealed off. Single crystals, suitable for X-ray structural analysis, were grown by sublimation at 220-230 ℃ during several weeks. IR (KBr pellet): 429m, 489vs, 533m, 583m, 649vs, 812s, 816s, 821s, 1019m, 1075m, 1222m, 1422s, 1490m, 1535m, 1619vs. Calculated: C 41.48; H 2.79; N 9.68. Found: C 41.72 ± 0.24; H 2.98 ± 0.19; N 9.61 ± 0.07. The syntheses of other complexes were carried out analogously (see Supporting Information for details). It should be noted that due to very high halogen content and high sensitivity towards

water, we have encountered serious instrument-based problems upon CHN analysis, which precluded use of the CHN analysis for other compounds. Their identity was unambiguously derived from the X-ray structural analysis. Homogeneity of the samples was controlled by X-ray powder diffraction.   In case of **1**, measurements from two single crystals from the two independent syntheses have been performed and resulted in virtually identical results.

X-ray crystal structure analyses. Crystals of **1-11** were taken from a sealed tube in the glove box and covered with perfluorinated Fomblin$^®$ oil. The single crystals were taken to the pre-centered goniometer head with CryoMount$^®$ and directly attached to the diffractometer into a stream of cold nitrogen. The data were collected on an Agilent Technologies Gemini R-Ultra diffractometer equipped with Ruby CCD detector and an Enhanced Ultra CuK$_\alpha$ sealed tube (λ = 1.54178 Å) and fine-focus MoK$_\alpha$ (λ = 0.71073 Å) sealed tube. The data for **1-6** and **8-11** were collected using CuK$_\alpha$ radiation and 1° ω scans, for **7** MoK$_\alpha$ radiation and 0.5° ω scans were used. All measurements were performed at 123 K, except for crystal of **8** which was measured at 150 K.   Either semi-empirical[33] or analytical absorption corrections from crystal faces[34] were applied. Crystallographic data and details of the diffraction experiments are given in Table 1S (Supporting Information). The structures were solved by direct methods with *SHELXS-97*[35] (**1**), *SUPERFLIP*[36] (**3**) or *SIR*-97[37] (**2, 4-10**) and refined by full-matrix least-squares method against $|F|^2$ in anisotropic approximation using *SHELXL-97*[38] or the multiprocessor and variable memory version *SHELXL2013*. All non-hydrogen atoms were refined anisotropically, while the hydrogen atoms were refined riding on pivot atoms. CCDC 1026689-1026699 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from   the   Cambridge   Crystallographic   Data   Center   via http://www.ccdc.cam.ac.uk/products/csd/request/.

The crystal of **1** proved to be a racemic twin in space group *Fdd*2. The refined ratio between two components is 0.60(2)/0.40(2). Two crystallographically independent [AlCl$_4$]$^-$ anions in **1** appeared to be severely disordered around 2-fold axis running along *z* axis. One of them, based on Al(2), is orientationally disordered over 2 positions. Another one is positionally and rotationally disordered over 3 positions. Disordered terminal chlorine atoms at Al(3), Al(4) were located from difference Fourier map. Refinement in anisotropic approximation resulted in severely elongated a.d.p. ellipsoids. After that Cl positions were additionally split resulting in total 8 positions with site occupancy factors of 0.125 each. These positions were finally included into refinement in isotropic approximation.

The compounds **2** and **4** were found to be isostructural according to their unit cell parameters, as well as compounds **6-8** and **9-11** that form two isostructural series.   The refinement of Al and Ga in mixed metal positions in **8** and **11** was performed as follows. The

coordinates of metal atoms were set equal as well as their constrained displacement parameters. The ratio between Al and Ga was refined and then fixed in the resulting 0.55(1)/0.45(1) values that are found to be equal in both metal positions for both structures to give the composition $C_{10}H_8N_2Al_{1.10}Cl_6Ga_{0.90}$ (**8**) and $C_{10}H_8N_2Al_{1.10}Br_6Ga_{0.90}$ (**11**). It appeared to be not possible to separate the positions of Al and Ga, because it led to unreasonable bond lengths. Therefore, the constraints on coordinates and displacement parameters were kept, and an anisotropic approximation was used for the further refinement. In **5** the $[GaCl_4]^-$ anion is disordered over two close positions with ratio of 0.5/0.5 refined in the same way as described for **8** and **11**.

Analysis of crystal packing in **1** and **2** and the series of molecular complexes **6-11** were done using ADS routine within TOPOS 4.0 Professional programs set.[39]

Powder diffraction measurements were performed on the powder diffractometer Bruker «D2 Phaser» at SPbSU Research Centre for X-ray Diffraction Studies. The thermal behavior of **5** upon heating in vacuum was studied on the high-temperature X-ray powder diffractometer Rigaku Ultima IV (CuKα1+2 radiation, 40 kV/30 mA, Bragg-Brentano geometry, PSD D-Tex Ultra) with a thermo-attachment in the 50-150 °C temperature range with the temperature step 25 degrees.

Mass-spectrometry measurements have been carried out at Thermoscientific ISQ mass-spectrometer with direct insertion probe (DIP) controller. Ionization energy 70 eV. Samples were placed in the thin glass capillaries (circa 2x10 mm) and inserted into the MS via DIP. Each sample was heated from 50 to 200 °C with 10 °C/min heating rate, with registration of two spectra per second. Data processing was carried out using Excalibur 2.1 package.

Computational details. All computations have been performed using TurboMole[40] (v. 6.1 and 6.3.1). Full geometry optimizations with subsequent vibrational analysis have been carried out at the RI-BP86/def2-SVP level of theory.[41-45] This approach has been used before for studying model aluminum trichloride complexes with bipy and pyz.[46] In case of ionic $[M_4Br_8bipy_{12}]^{4+}([MBr_4]^-)_4$ (M=Al, Ga) and molecular $(GaBr_3)_3(bipy)_2$ compounds (M = Al, Ga) optimizations converged to high order stationary points. Reoptimization attempts failed due to the flatness of the potential energy surface, as indicated by the low imaginary frequencies of $12i$, $6i$ cm^{-1} for $[Al_4Br_8bipy_{12}]^{4+}([AlBr_4]^-)_4$; $8i$, $4i$, $2i$ cm^{-1} for $[Ga_4Br_8bipy_{12}]^{4+}([GaBr_4]^-)_4$; and $1i$ cm^{-1} for $(GaBr_3)_3(bipy)_2$. The energy difference between these higher order stationary points and the respective minima on PES is expected to be very small and out of chemical consequence.

Acknowledgements

Supplementary Data

Electronic supplementary information (ESI) available: Synthetic procedures, crystallographic tables, listings of optimized xyz coordinates and total energies, structure drawings (69 pages). This material is available free of charge via the Internet.

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Table 1. Computed gas phase reaction energies (kJ mol^{-1}) for the process (1). RI-BP86/def2-SVP level of theory.

L\MX$_3$	AlCl$_3$	AlBr$_3$	GaCl$_3$	GaBr$_3$
pyz	60	118	46	126
4,4′-bipy	-35	-50[a]	-17	-13[a]

[a] High-order stationary point.

Table 2. Selected bond distances (in Å) for **6-11.**

Compound	X = **Cl**			X= **Br**		
	6	**7**	**8**[a]	**9**	**10**	**11**[a]
	(AlCl$_3$)$_2$bipy	(GaCl$_3$)$_2$bipy	(Al$_{1.1}$Ga$_{0.9}$Cl$_3$)$_2$bipy	(AlBr$_3$)$_2$bipy	(GaBr$_3$)$_2$bipy	(Al$_{1.1}$Ga$_{0.9}$Br$_3$)$_2$bipy
M1—X1	2.1079 (8)	2.1506 (7)	2.1265 (13)	2.271 (3)	2.2963 (10)	2.2725 (10)
M1—X2	2.1109 (8)	2.1476 (6)	2.1326(12)	2.269 (3)	2.3034 (10)	2.2830 (10)
M1—X3	2.1091 (9)	2.1457 (6)	2.1392(12)	2.273 (3)	2.2989 (10)	2.2908 (10)
M2—X4	2.1102 (8)	2.1590 (6)	2.1315(14)	2.263 (3)	2.2918 (10)	2.2824 (10)
M2—X5	2.1209 (8)	2.1461 (7)	2.1268(12)	2.269 (3)	2.3028 (10)	2.2906 (10)
M2—X6	2.1147 (9)	2.1540 (7)	2.1251(11)	2.282 (3)	2.3078 (10)	2.2766 (10)
M1—N1	1.9489 (18)	1.9924 (18)	1.973(3)	1.941 (9)	2.000 (5)	1.969 (4)
M2—N2	1.9422 (18)	1.9888 (18)	1.983(3)	1.938 (9)	1.981 (6)	1.978 (4)
X...X	3.47-4.30	3.46-4.26	3.50-4.28	3.77-4.74	3.79-4.69	3.77-4.71

[a] The distances are averaged because of Al/Ga mixed crystallographic positions.

Table 3. Major bond distances R, Å of group 13 metal complexes (MX$_3$)$_x$L with pyridine-based ligands bipy, pyz and py (tetrahedral environment on group 13 center). Complex composition 2:1 for bidentate donors (x=2) and 1:1 for py (x=1).

Acceptor	R$_{(M-N)}$			R$_{(M-X)}$		
	4,4′-bipy	pyz	py	4,4′-bipy	pyz	py
AlCl$_3$	1.9489(18); 1.9422(18)		1.930(2)[a]	2.1079(8)- 2.1209(8)		2.1166(9)- 2.126(1)[a]
AlBr$_3$	1.941(9); 1.938(9)	1.999(6)[b]	1.935(3)[c]	2.263(3)- 2.282(3)	2.2463(16)- 2.267(2)[b]	2.2677(10)- 2.2796(10)[c]
GaCl$_3$	1.9924(18); 1.9888(18)	2.044(7)[b]	1.966(2)[c]	2.1457(6)- 2.1590(6)	2.135(2)- 2.147(2)[b]	2.1503(7) - 2.1598(7)[c]
GaBr$_3$	2.000(5); 1.981(6)		1.979(2)[c]	2.2918(10)- 2.3078(10)		2.2948(5)- 2.3060(5)[c]

[a] ref. 28; [b] ref. 12; [c] ref. 27.

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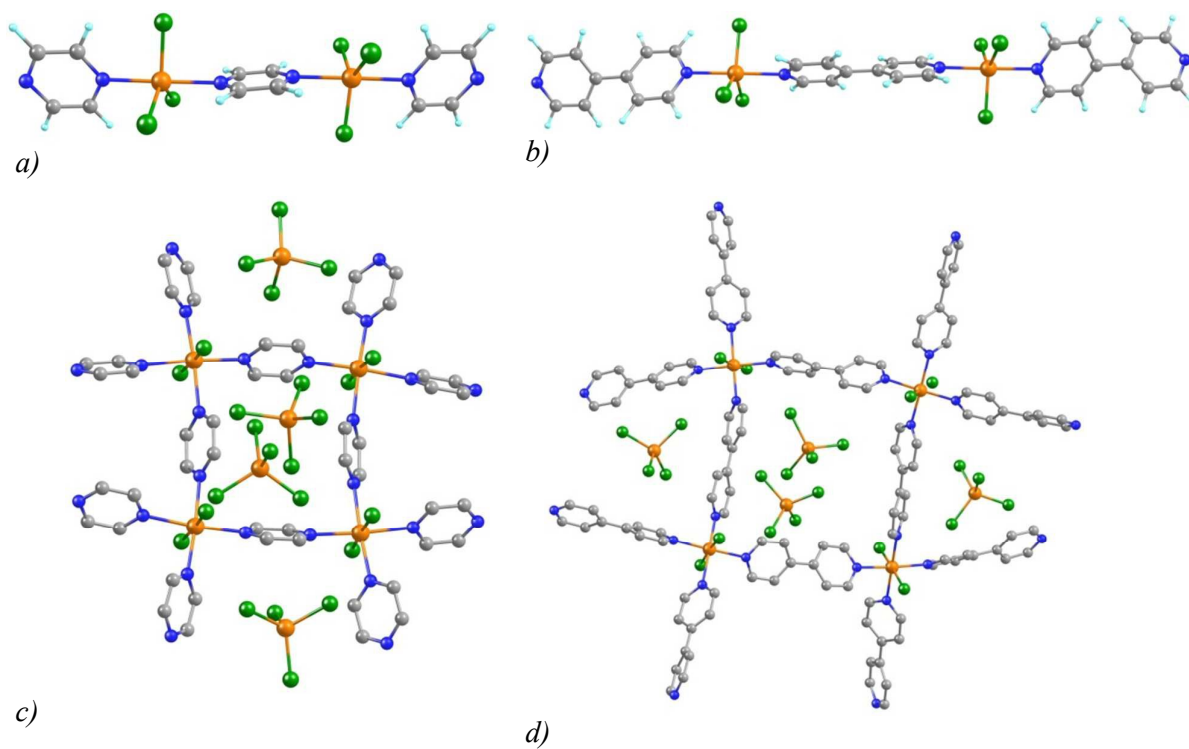
Figure 1. Optimized structures of the molecular $(GaCl_3)_2L_3$ a) L = pyz; b) L = bipy; and ionic $[Ga_4Cl_8L_{12}]^{4+}([GaCl_4]^-)_4$ compounds c) L = pyz; d) L = bipy.
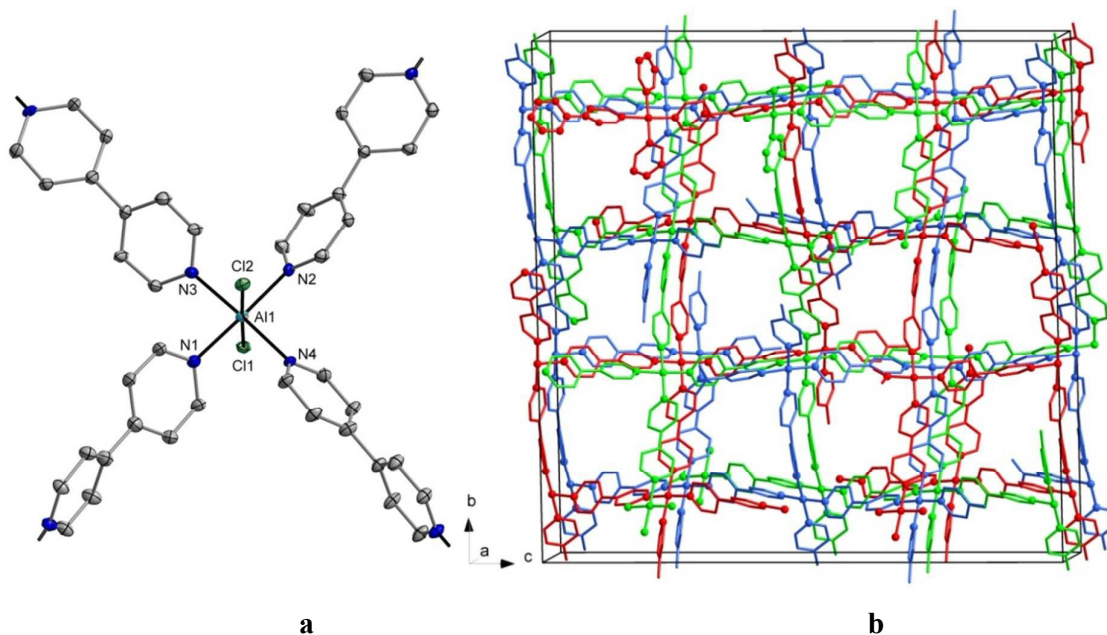
a　　　　　　　　　　　　　　　　　　**b**

Figure 2. (a) A fragment of the cationic $\{[AlCl_2bipy_2]^+\}_\infty$ net in **1** (ellipsoids of 50% probability). Selected bond distances (Å): Al1–Cl1 2.260(3), Al1–Cl2 2.280(4), Al1–N1 2.055(8), Al1–N2 2.050(7), Al1–N3 2.062(8), Al1–N4 2.055(8); Bond angles (°) Cl1–Al1–Cl2 178.39(15), N2–Al1–N3 89.8(3), N2–Al1–N4 93.2(3), N1–Al1–N3 88.5(3), N1–Al1–N4 88.6(3). (b) Three-interpenetrated **lvt** nets in the crystal structure of **1**. $[AlCl_4]^-$ counter ions are omitted for clarity.

a

b

c
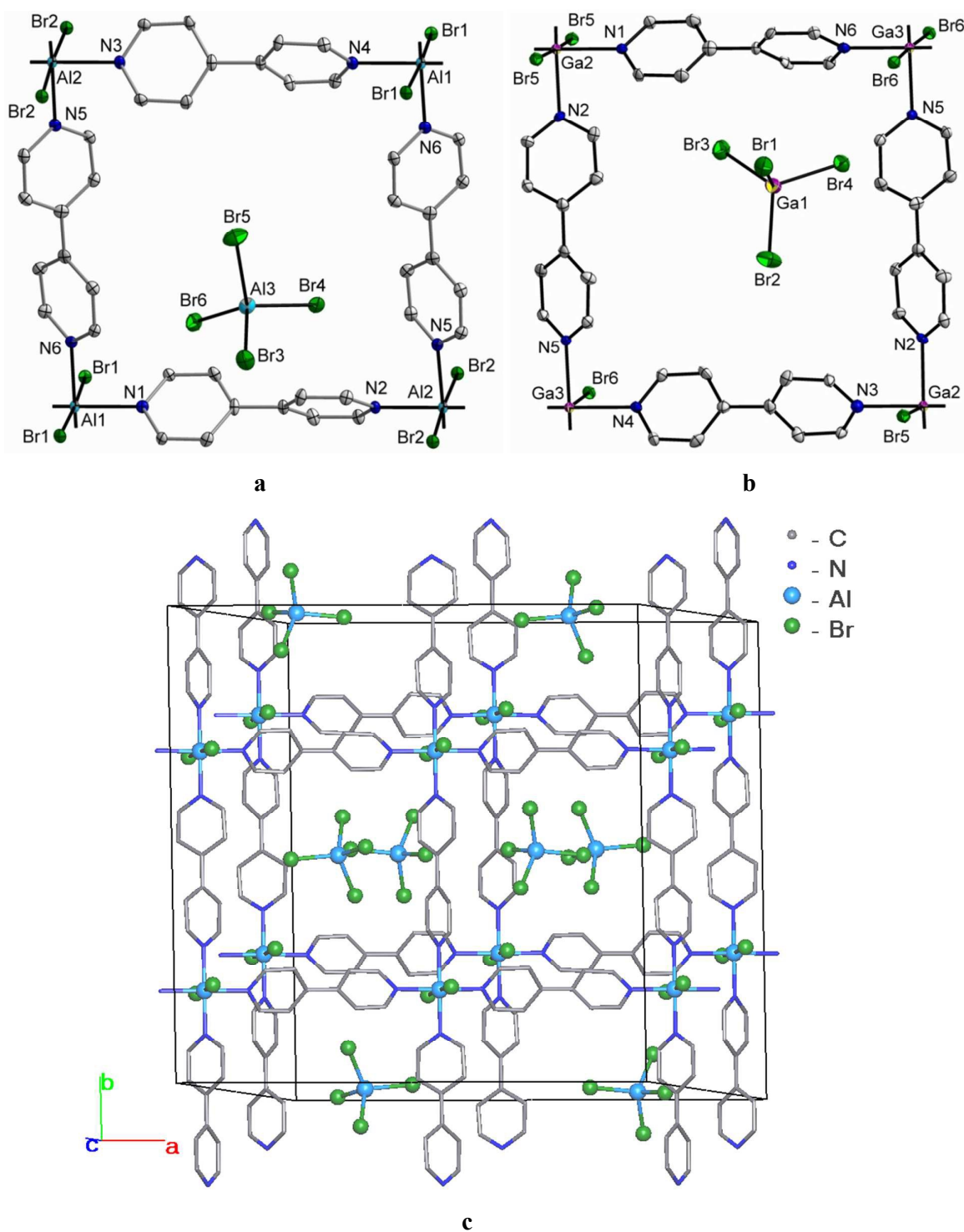
Figure 3. (a) A fragment of the 2D polymeric structure of $[AlBr_2(bipy)_2]^+[AlBr_4]^-$ (**2**) (ellipsoids of 50% probability). Selected bond distances (Å): Br1–Al1 2.4658(2), Br2–Al2 2.4708(2), Br3–Al3 2.3120(9), Br4–Al3 2.2960(9), Br5–Al3 2.3104(9), Br6–Al3 2.2893(10), Al1–N4 2.051(3), Al1–N6 2.058(2), Al1–N1 2.070(3), Al2–N2 2.049(3), Al2–N3 2.050(3), Al2–N5 2.054(2); Bond angles (°): Br1–Al1–N1 88.50(2), Br1–Al1–Br1 177.00(5), N1–Al1–N6 90.40(6), N4–Al1–N6 89.60(6), Br2–Al2–Br2 176.95(5), N2–Al2–N5 91.02(6), N3–Al2–N5 88.98(6). (b) A fragment of 2D polymeric structure of $[GaBr_2(bipy)_2]^+[GaBr_4]^-$ (**4**) (ellipsoids of 50% probability). Selected bond distances (Å): Ga2–N2 2.111(4), Ga2–N3 2.104(6), Ga2–N1 2.088(6), Ga3–N4 2.127(6), Ga3–N5 2.109(4), Ga3–N6 2.091(6); Bond angles (°): Br5–Ga2–

Br5 176.99(5), N1–Ga2–N2 89.02(12), N2–Ga2–N3 90.98(12), Br6–Ga3–Br6 176.91(5), N4–Ga3–N5 90.32(11), N5–Ga3–N6 89.68(11). (c) a crystal packing of **2**.
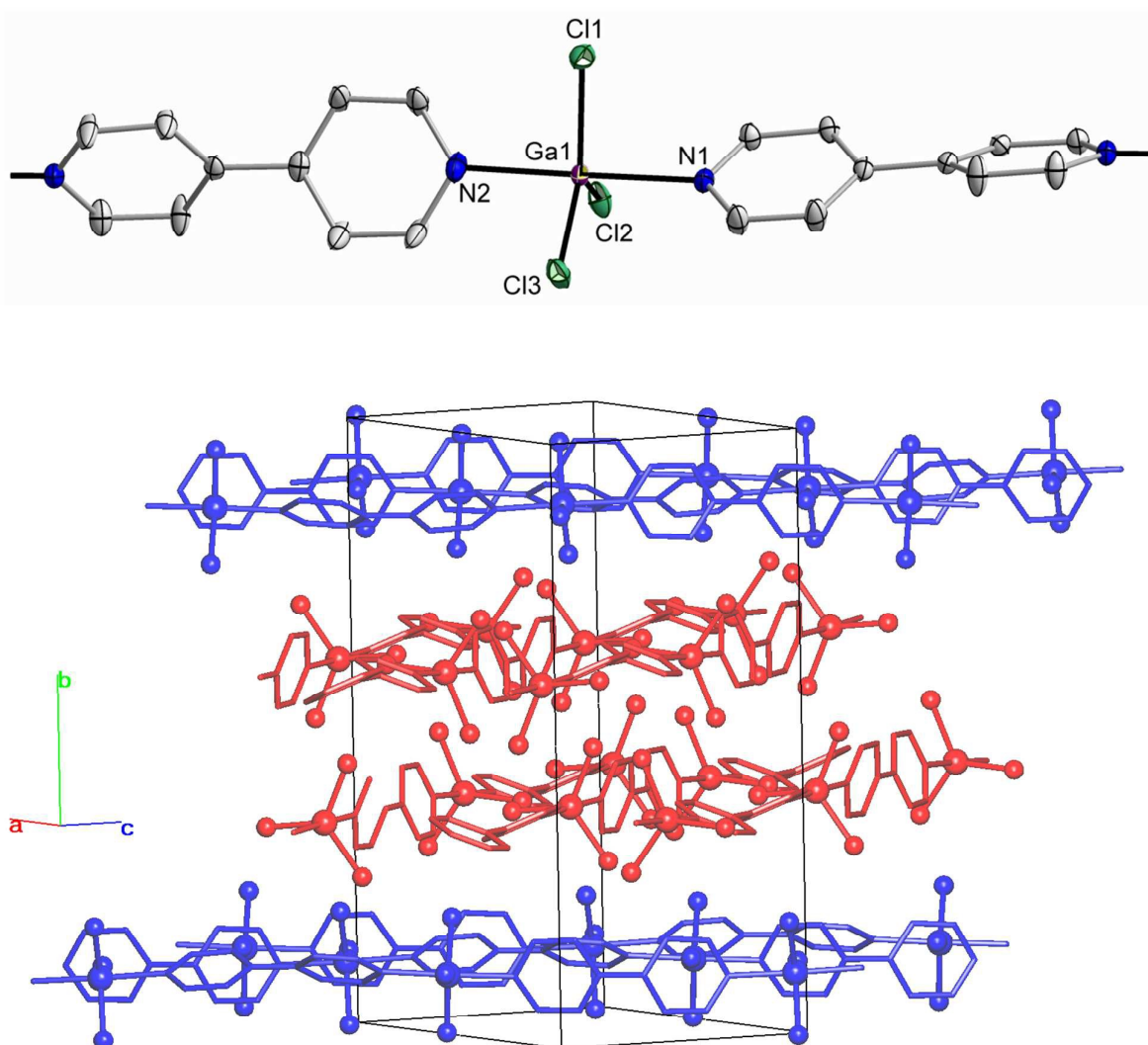

Figure 4. (a) A fragment of the polymeric chain (GaCl₃bipy)∞ in **3** (ellipsoids of 50% probability). Selected bond distances (Å): Ga1–Cl1 2.1880(6), Ga1–Cl2 2.2014(6), Ga1–Cl3 2.1947(6), Ga1–N1 2.1813(18), Ga1–N2 2.182(2); Bond angles (°) Cl1–Ga1–Cl2 121.26(3), Cl1–Ga1–Cl3 120.94(3), Cl2–Ga1–Cl3 117.80(3), N1–Ga1–N2 178.56(7).
(b) Packing of the chains.

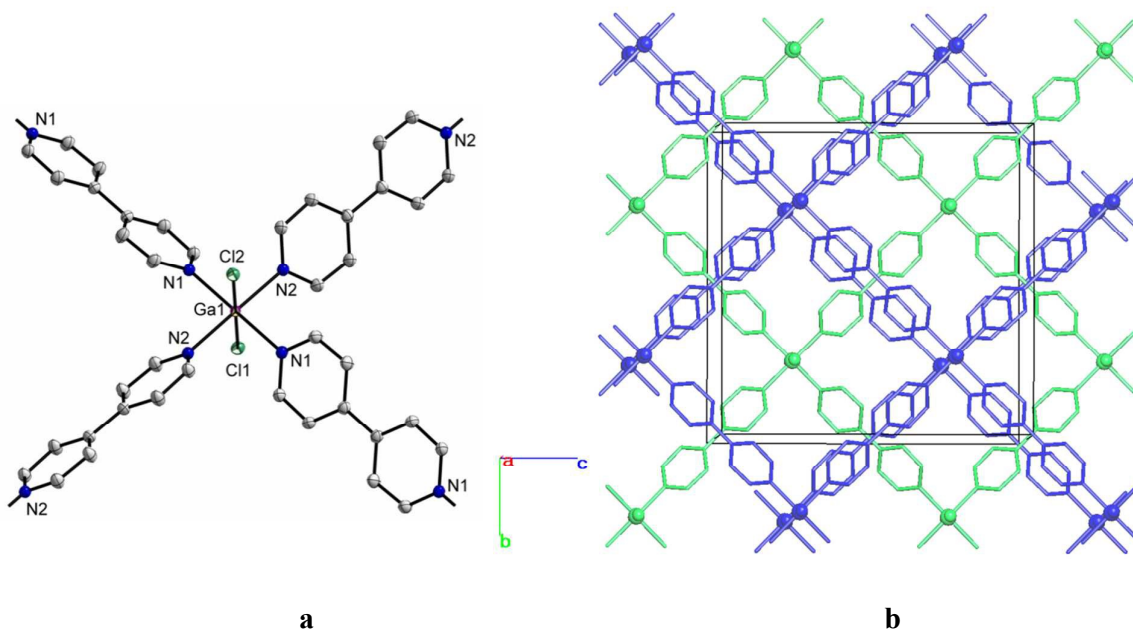**a**   **b**

Figure 5. (a) A fragment of the polymeric layer in **5** (ellipsoids of 50% probability). Selected bond distances (Å): Ga1–Cl1 2.3186(5), Ga1–Cl2 2.3006(5), Ga1–N1 2.1052(12), Ga1–N2 2.1061(12); Bond angles (°) Cl1–Ga1–Cl2 180.0, Cl1–Ga1–N1 89.92(3), Cl1–Ga1–N2 89.43(3), Cl2–Ga1–N1 90.08(3), Cl2–Ga1–N2 90.57(3), N1–Ga1–N2 89.97(5), N1–Ga1–N2 90.03(5). (b) the planar square nets **sql** in the crystal structure of **5** arranged in …ABAB… packing**.**
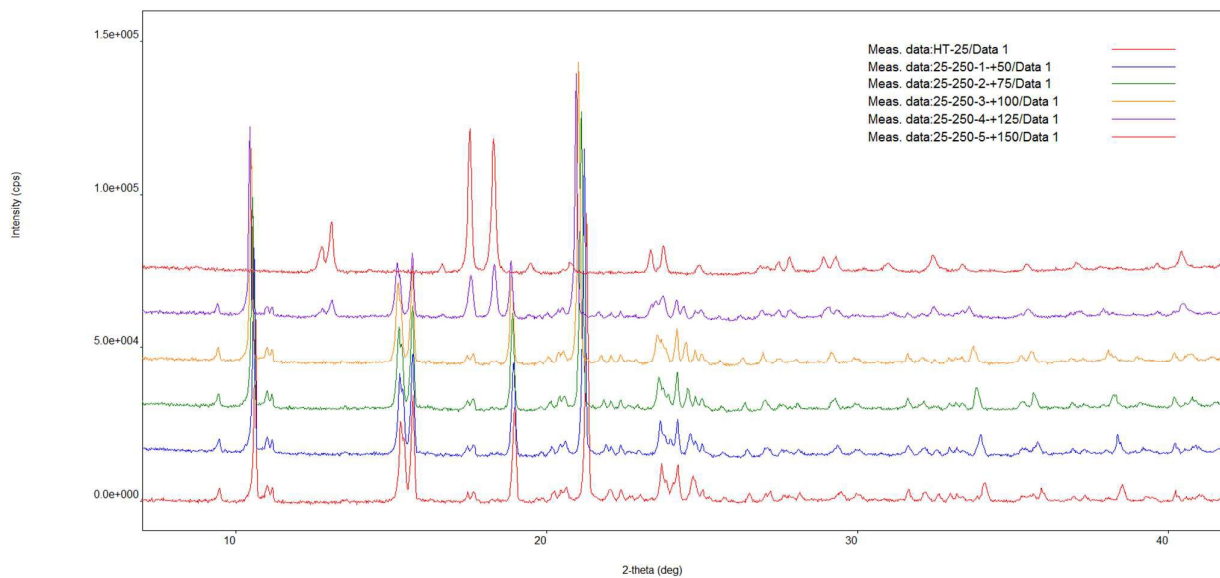
Figure 6. Temperature-dependent XRD patterns upon heating **5** in vacuum at 25-150 °C.

a

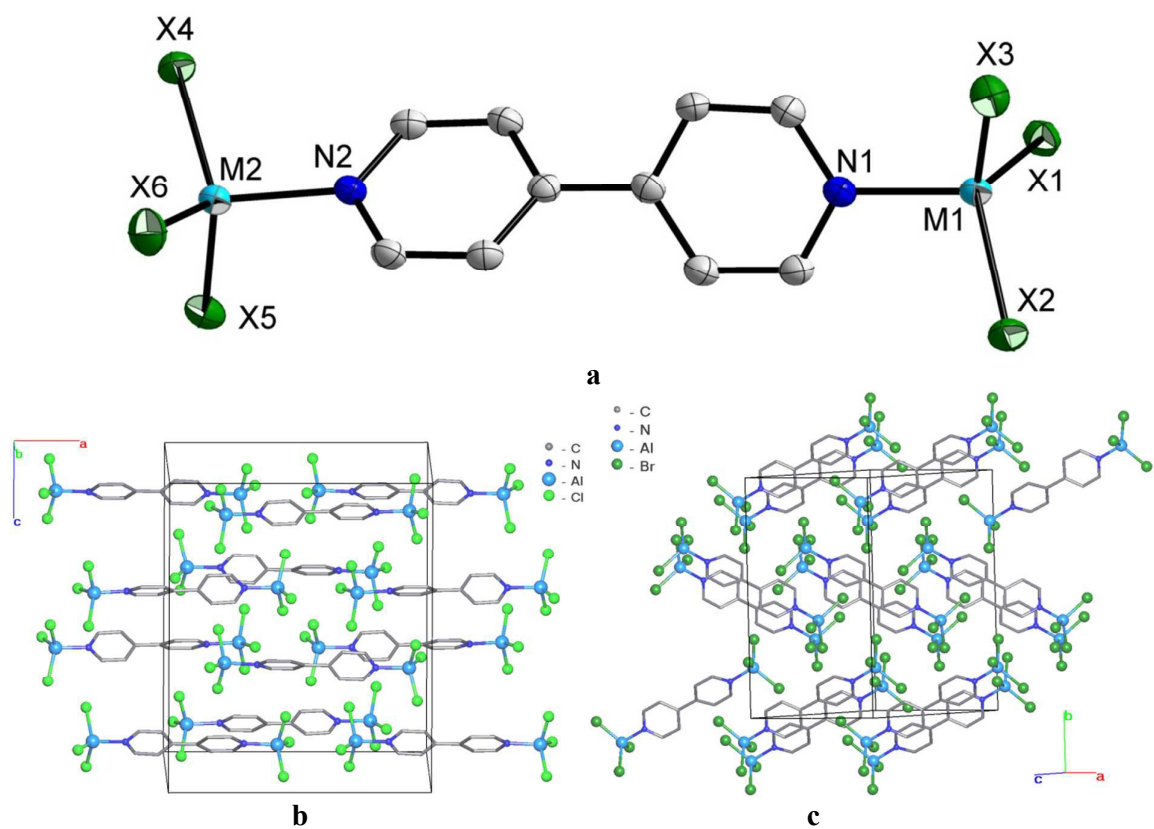**b**   **c**

Figure 7. (a) Molecular structure of $(MX_3)_2$bipy (**6-11**), M = Al, Ga; X = Cl, Br. Crystal packing for (b) $(MCl_3)_2$bipy (**6-8**) and (c) $(MBr_3)_2$bipy (**9-11**).

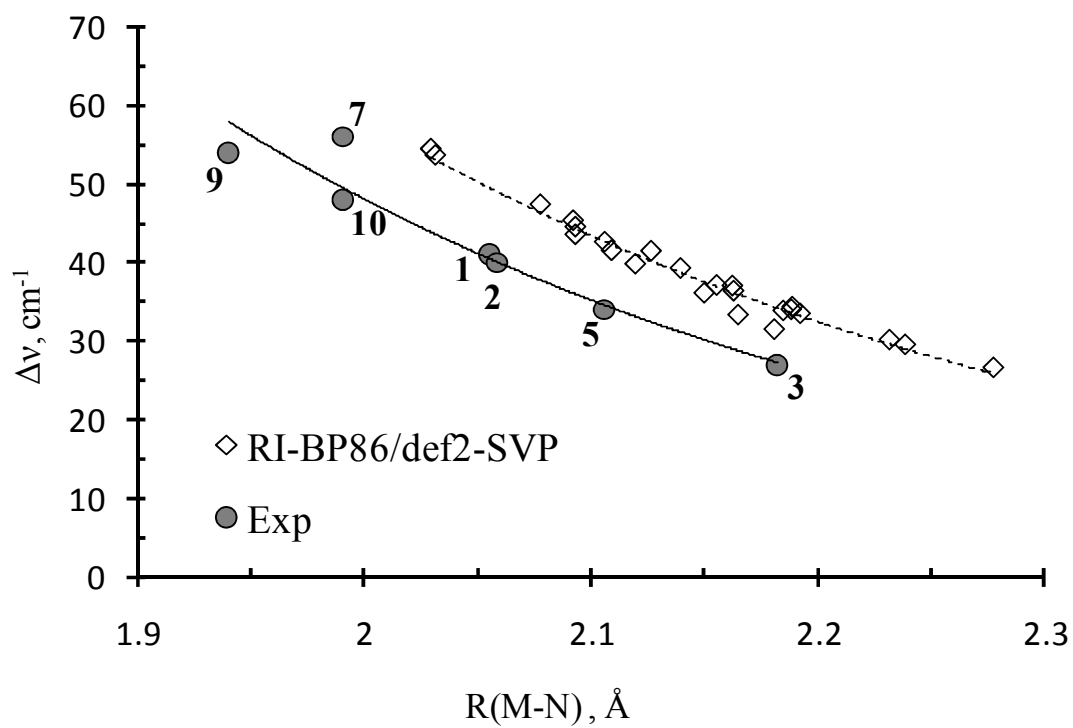**Figure 8.** Correlation between the M-N bond length R(M-N), Å and the shift Δv of the in-plane ring bending IR band of 4,4′-bipy. Experimentally studied compounds are indicated by numbers.

Table of content Synopsis:

The nature of the group 13 metal halide strongly affects the structure of their complexes with 4,4′-bipy, allowing the formation of 1D coordination polymers, 2D and 3D ionic networks. Excess of 4,4′-bipy leads to unique changes from the 1D non-ionic coordination polymer $(GaCl_3bipy)_\infty$ to the ionic 2D network $[GaCl_2bipy_2]^+[GaCl_4]^-\cdot 2bipy$. Computations using simple finite gas phase cluster models may serve as an indicator of the preferred structural type of the compound in the solid state.

Table of content Graphic:

1D

$$- 2n \text{ bipy} \quad \Big\Vert \quad + 2n \text{ bipy}$$

150 °C, vacuum

$$\Big([GaCl_2bipy_2]^+[GaCl_4]^- \Big)_n \cdot 2n \text{ bipy} \qquad \textbf{2D}$$

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