Structural and thermodynamic properties of molecular complexes of aluminum and gallium trihalides with bifunctional donor pyrazine: decisive role of Lewis acidity in 1D polymer formation†

Tatiana N. Sevastianova,a Michael Bodensteiner,b Anna S. Lisovenko,a Elena I. Davydova,a Manfred Scheer,b Tatiana V. Susliakova,a Irina S. Krasnova,a and Alexey Y. Timoshkin*a

Solid state structures of group 13 metal halide complexes with pyrazine (pyz) of 2:1 and 1:1 composition have been established by X-ray structural analysis. Complexes of 2:1 composition adopt molecular structures MX3·pyz·MX3 with tetrahedral geometry of group 13 metals. Complexes of AlBr3 and GaCl3 of 1:1 composition are 1D polymers (MX3·pyz)∞ with trigonal bipyramidal geometry of the group 13 metal, while the weaker Lewis acid GaI3 forms the monomeric molecular complex GaI3·pyz, which is isostructural to its pyridine analog GaI3·py. Tensimetry studies of vaporization and thermal dissociation of AlBr3·pyz and AlBr3·pyz·AlBr3 complexes have been carried out using the static method with a glass membrane null-manometer. Thermodynamic characteristics of vaporization and equilibrium gas phase dissociation of the AlBr3·pyz complex have been determined. Comprehensive theoretical studies of (MX3)n·(pyz)m complexes (M = Al, Ga; X = Cl, Br, I; n = 1, 2; m = 1–3) have been carried out at the B3LYP/TZVP level of theory. Donor–acceptor bond energies were obtained taking into account reorganization energies of the fragments. Computational data indicate that the formation of (MX3·pyz)∞ polymers with coordination number 5 is only slightly more energetically favorable than the formation of molecular complexes of type MX3·pyz for X = Cl, Br. It is expected that on melting (MX3·pyz)∞ polymers dissociate into individual MX3·pyz molecules. This dovetails with low melting enthalpies of the (MX3·pyz)∞ complexes. Polymer stability decreases in the order AlCl3 > AlBr3 > GaCl3 > AlI3 > GaBr3 > GaI3. For Ml3·pyz complexes computations predict that the monomeric structure motif is more energetically favorable compared to the catena polymer. These theoretical predictions agree well with the experimentally observed monomeric complex GaI3·pyz in the solid state. Thus, the Lewis acidity of the group 13 halides may play a decisive role in the formation of 1D polymeric networks.

Introduction

Group 13 element trihalides are strong Lewis acids which form stable donor–acceptor complexes with nitrogen-containing bases.1–3 Volatile group 13–15 donor–acceptor complexes are prospective single-source precursors (SSP) for the chemical vapor deposition (CVD) of binary and composite nitrides.4,5 Volatility and the strength of the donor–acceptor bond are the two key characteristics of a successful SSP. Volatility of the solid adduct is determined by its sublimation enthalpy, which in turn depends on the structural properties of the compounds. Complexes which exhibit isolated molecules in their crystal structures have lower sublimation enthalpies and are usually more volatile than polymeric and ionic compounds.5 Complexes with large donor–acceptor bond energies and sufficient volatility, such as the pyridine adducts MX3·Py, reveal a significant concentration in vapors even at elevated (600–800 K) temperatures.6,7

Usually, complexes with monodentate donors, for example AlCl3·NH2tBu,5 are used as SSP for the synthesis of binary...
13–15 compounds. For generating ternary and composite nitrides SSP should have different group 13 elements in the same molecule. This may be achieved by the introduction of the bifunctional donors LL. Complexes with LL = ethylenediamine (en), tetramethylethylenediamine (tmen) containing organometallic derivatives MR₃ adopt molecular structures MR₃·LL-MR₃, but have weak donor–acceptor (DA) bonds and dissociate upon heating.² Both theoretical and experimental studies³,⁴,⁵,⁶ show that the substitution of organometallic acceptors by group 13 element halides strongly increases the DA bond energy of complexes with monodentate donors. It is natural to assume that such a trend will hold for the complexes with bifunctional donors as well. Our previous study of group 13 metal halide complexes with en and tmen⁷ showed that such complexes adopt ionic structures [M(LL)X₂]⁴⁺[MX₄]⁻, in which en and tmen serve as chelating bidentate ligands. It is expected that the use of non-chelating rigid bifunctional donors will be suitable for the formation of molecular mixed metal precursors.

In continuation of our studies on structures, volatility, and gas-phase stability of group 13 element halides with monodentate nitrogen-containing donors,² we turned our attention to complexes with rigid bifunctional donor pyrazine (pyz). Polymeric structures of GaCl₃·pyz and GaBr₃·pyz in the solid state were established in 2007 by Richards and co-workers.¹¹ Previous mass spectrometry and tensiometry studies of the complex formation in the GaCl₃·pyz system¹² confirmed the existence of the individual molecules (GaCl₃)₂·pyz and GaCl₃·pyz in the gas phase. Both complexes undergo reversibly thermal dissociation in the gas phase; GaCl₃·pyz is the dominant form in vapors, while the (GaCl₃)₂·pyz content is very low (0.2% at 383 K and only 0.05% at 673 K).¹² It is expected that the substitution of GaCl₃ by the stronger Lewis acid AlBr₃ will stabilize complexes of 2 : 1 composition in vapors. To test this hypothesis, vaporization and thermal stability of (AlBr₃)₂·pyz and AlBr₃·pyz complexes have been studied by the static tensiometric method. The structures of both complexes, as well as their GaCl₃ analogs, and the GaI₃·pyz adduct have been determined by X-ray structural analysis. In addition, results of comparative theoretical DFT studies of (MX₃)ₙ·(pyz)ₙ (M = Al,Ga; X = Cl,Br,I; n = 1,2; m = 1–3) are also reported.

Results and discussion

I. Structural studies

Let us first consider results of structural investigation of the complexes. Expected structural types of the molecular complexes are presented in Fig. 1 (M – group 13 metal, X – halogen, L – monodentate, LL – bifunctional donor ligand). Note that the group 13 metal can adopt both tetrahedral (Fig. 1a–c) and trigonal bipyramidal environments (Fig. 1d,e). LL serves either as a terminal monodentate ligand (Fig. 1b) or as a bridging ligand with formation of distinct molecules MX₃·LL-MX₃ (Fig. 1c) or infinite polymeric chains -LL-MX₃·LL-MX₃· (Fig. 1e).

We have been able to grow single crystals of complexes of the bifunctional donor pyz with 2 : 1 composition (AlBr₃)₂·pyz (1), (GaCl₃)₂·pyz (2), and 1 : 1 composition AlBr₃·pyz (3), GaCl₃·pyz (4), GaI₃·pyz (5). Experimental details of all complexes are presented in Table S1.] We will start our discussion with structural features of the complexes with a 2 : 1 composition.

Complexes (MX₃)₂·pyz. In contrast to en and tmen, which form ionic complexes [M(LL)X₂]⁴⁺[MX₄]⁻,¹⁰ pyrazine serves as a bridging ligand, coordinating two molecules of MX₃ with formation of molecular complexes MX₃·pyz-MX₃. 1 and 2 are isostructural, molecular structure of 1 is shown in Fig. 2, structure of 2 is available in the ESI.¹ In these complexes the central atom M adopts a usual tetrahedral environment with coordination number four. However, DA bond distances in 1 and 2 (1.999 and 2.044 Å, respectively) are noticeably larger compared to M–N distances in complexes with monodentate donor Py (1.935(3) and 1.966(2) Å for AlBr₃·Py and GaCl₃·Py, respectively).¹³

Complexes MX₃·pyz. The molecular structures of the compounds (AlBr₃·pyz)ₙ (3) and GaI₃·pyz (5) are given in Fig. 3–5. Data for (GaCl₃·pyz)ₙ, 4 are in good agreement with previously reported values by Samanamu et al.¹¹ (in their work¹¹ the complex was synthesized in tetrahydrofuran solution and recrystallized from diethyl ether). Note that in 3 and 4 pyrazine serves as a bridging ligand with formation of a polymeric chain in which the group 13 metal possesses the coordination number five. The halogen atoms always occupy equatorial, and the nitrogen atoms – axial positions. The MX₃ fragment remains essentially planar. Compounds 3 and 4 are isostructural and the bond distance M–N in 3 (2.133 Å) is by 0.07 Å shorter than in 4 (2.203 Å). Such a trend agrees well with the
changes of the covalent radii of Al and Ga.$^{14}$ Note that the M–N bond distances are elongated (by 0.13–0.16 Å) on going from complexes of 2:1 to 1:1 composition due to the change in the tetrahedral environment in compounds 1 and 2 to trigonal bipyramidal in 3 and 4. The packing of the polymer chains in a crystal of 3 is shown in Fig. 4. The closest inter-polymer H···Br contacts are 3.01 and 3.12 Å.

In contrast to the polymers 3 and 4, GaI$_3$pyz (5) exists in the solid state only as an individual molecule GaI$_3$pyz (Fig. 5), isostructural to the molecular complex GaI$_3$-Py.$^{23}$ The Ga–N bond distance in 5 is by 0.027 Å longer than in GaI$_3$-Py, which indicates lower donor ability of pyrazine compared to pyridine.

**Coordination polymers of group 13 metal halides.** Examples of coordination polymer networks based on group 13 element halides are known. An interesting 3D polymer network was recently reported for InF$_3$·4,Hbta.$^{15}$ The formation of 1D polymeric chains with pyrazine was reported in 2007 for gallium halides,$^{11}$ while indium and thallium trihalides prefer ladder-type one-dimensional polymers.$^{11,16}$ In the present report we show that AlBr$_3$ with pyz in a 1:1 stoichiometry also forms a chain polymer (AlBr$_3$·pyz)$_2$, while GaI$_3$pyz exists in the form of individual molecules. Zig-zag chain polymers with 1,3-bis-(dimethylamino)propane were previously reported for AlH$_3$,$^{17}$ and GaH$_3$.$^{18}$ Other 1D polymers include catena complexes of AlCl$_3$ and GaCl$_3$ with the O-containing bidentate donor dioxane.$^{19,20}$ Interestingly, the complex AlCl$_3$-2diox adopts the polymeric structure (AlCl$_3$-diox)$_∞$-diox with “free” dioxane solvate molecules in between the polymeric chains.$^{19}$ Major structural parameters of known 1D polymers and nitrogen-containing MX$_3$·2L complexes of group 13 metal halides are summarized in Table 1. The Al–N distance in 3 is in the range of the reported values for AlX$_3$·2L complexes with bidentate nitrogen-donor ligands (2.021–2.166 Å). In the catena polymers, as well as in 3 and 4, the trigonal bipyramidal structure is distorted. As the criterion of structure distortion from the ideal trigonal bipyramid, the use of $\tau$-values was proposed by Addison et al.$^{21}$ It is defined by the formula $\tau = (\beta - \alpha)/60$, where $\alpha$, $\beta$ are the largest angles in the trigonal plane and along the principal axis (Fig. 1d,e). For the perfect trigonal bipyramid the $\tau$-value equals one, and for the perfect square pyramid the $\tau$ value equals zero. For all compounds listed in Table 1, the $\tau$-value is larger than 0.7, indicating essentially a trigonal bipyramidal environment. Interestingly, our computed $\tau$-values for the gas phase complexes MX$_3$·2pyz and (MX$_3$)$_2$·(pyz)$_3$ are very close to one (0.96–0.99), suggesting that there is very little distortion and strain is absent in the gas phase structures (Table 1). Structural changes are virtually independent of the size of the complex: valence angles and $\tau$-values are very similar for pyz-MX$_3$-pyz complexes with one trigonal bipyramidal center and for pyz-MX$_3$-pyz-MX$_3$-pyz with two trigonal bipyramidal centers. We conclude that the experimentally observed inequivalence of the X–M–X angles results from the intermolecular interactions in the solid state. The largest Cl–Ga–Cl angle in 1D polymer 4 (GaCl$_3$-pyz)$_∞$ (125.4 degrees) is close to 124.8° found in (GaCl$_3$-diox)$_∞$. The distortion of 3 (largest Br–Al–Br angle is 128.1°) is more pronounced and may result from the longer Al–Br distances, which are more affected by the packing strain. Worral and coauthors$^{20}$ noted that in catena (GaCl$_3$-diox)$_∞$ the Ga–Cl distances are shorter and the Ga–O distances are significantly longer than in other compounds with coordination number 5. Our results indicate that both Ga–N and Ga–Cl bond distances in 4 are by 0.03–0.04 Å longer compared to those in the benzotriazole (Hbta) complex GaCl$_3$·2Hbta.$^{30}$

We conclude that all studied complexes in the solid state exist either as individual molecules (1, 2, 5) or form 1D polymers (3, 4). With exception of GaI$_3$pyz (5), in all other studied complexes pyrazine serves as a bridging ligand. Especially noteworthy is the fact that in 3 and 4 the group 13 element adopts a trigonal bipyramidal environment, with pyrazine...
AlBr$_3$·2pyz

<table>
<thead>
<tr>
<th>Compound</th>
<th>R(M–N) (Å)</th>
<th>Max X–M–X (°)</th>
<th>N–M–N (°)</th>
<th>$r$ Value</th>
<th>Reference</th>
</tr>
</thead>
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<td>AlCl$_3$·2NMMe$_2$</td>
<td>2.1580(16); 2.1662(16)</td>
<td>121.08(2)</td>
<td>178.76(5)</td>
<td>0.96</td>
<td>22</td>
</tr>
<tr>
<td>AlCl$_3$·2NHMe$_2$</td>
<td>2.051(3); 2.073(3)</td>
<td>126.3(1)</td>
<td>176.5(1)</td>
<td>0.84</td>
<td>23</td>
</tr>
</tbody>
</table>

In the following the thermodynamic parameters for the dissociation processes of the complexes are considered. Computed proton affinities of Py and pyz are 937 and 881 kJ mol$^{-1}$, in good agreement with the experimental values of 929 ± 4 and 882 ± 4 kJ mol$^{-1}$ for Py and pyz, respectively. Based on these values, Py is the stronger donor compared to pyz. The computed second proton affinity of pyz is much smaller (403 kJ mol$^{-1}$), which may result from electrostatic repulsion in the pyrazinium dication HpyzH$_2^+$. Dissociation enthalpies of molecular complexes with group 13 element trihalides of 1 : 1 composition (Table 3) are considerably lower than proton affinities. Pyrazine complexes are by about 19 kJ mol$^{-1}$ weaker bound than pyridine ones, in accordance with proton affinity trends. Aluminum trichloride forms the most stable complexes. Acceptor ability of Lewis acids decreases in the order aluminum > gallium.
AlCl₃ > AlBr₃ > GaCl₃ > GaBr₃ which is in line with an increase of the DA bond distances. Stronger Lewis acids have larger values of charge transfer (equal to charge of the acceptor MX₃) and a larger negative charge on the nitrogen atom of the donor molecule (Table 4).

Another useful criterion of the complex stability in the gas phase is the value of temperature at which the equilibrium constant for the complex dissociation process equals one. It may be estimated using standard dissociation enthalpies and entropies: \( T_{eq} = \Delta_{diss}H^{\ddagger} / \Delta_{diss}S^{\ddagger} \). This single criterion combines both energetic and entropy factors. According to \( T_{eq} \) values, complexes of 1:1 composition are most stable in vapors (\( T_{K=1} \) are in the range 660–940 K). The \( T_{K=1} \) values for 2:1, 1:2 and 2:3 complexes are significantly lower due to the entropy factor. Our theoretical results are in agreement with the experimental observations of complexes with a 1:1 composition in vapors.²,³,³³

**Estimation of the donor-acceptor bond energy.** In order to make a comparison between the stability of tetrahedral and trigonal bipyramidal complexes, the reorganization energy required for the pyramidalization of the acceptor MX₃ must be taken into account. Reorganization energies of group 13 metal trihalides from planar to perfectly pyramidal environment (tetrahedral XMX angle) are generally below 90 kJ mol⁻¹.¹,¹³ Since the XMX angles in complexes are larger than the tetrahedral ones, the reorganization energies upon complex formation are usually smaller (below 35 kJ mol⁻¹).³⁴,³⁵ In the present report we computed reorganization energies for the donor and acceptor fragments and obtained values of DA bond energy (Table 4): \( nE_{DA} = \Delta_{diss}H^{\ddagger} + kE_{reorg}(MX_3) + lE_{reorg}(pyz) \), where \( n \) – number of the DA bonds in the molecule, \( k, l \) – number of MX₃ and pyz fragments, respectively. The comparison with MX₃-Py analogs¹³ shows that DA bond energies of MX₃-pyz complexes are about 25 kJ mol⁻¹ smaller. These data are in good agreement with the increase of the M–N bond distances in pyz complexes compared to Py (Table 2). The formation of the DA bond with a second MX₃ molecule lowers the DA bond energy (for MX₃-pyz-MX₃ complexes by 25 kJ mol⁻¹ compared to MX₃-pyz). Changes in the partial charges of MX₃ fragments follow the energetic trends, suggesting that in MX₃-pyz-MX₃ two acceptors compete for the transferred charge. For complexes of 2:1 composition, mixed metal compounds MX₃-pyz-MX₃ (M,M’ = Al, Ga; X = Cl, Br) have been also studied theoretically (Table S5†). Dissociation enthalpies of mixed metal (heteronuclear) complexes can be obtained from values for homonuclear complexes using a simple additive scheme.

Much lower (by 60–70 kJ mol⁻¹) DA bond energies are observed for MX₃(pyz)₂ complexes with a trigonal pyramidal structure. Donor atoms occupy the axial positions which are energetically less preferable. However, in this case the charge transfer to the MX₃ fragment slightly increases, since now two pyz donor molecules provide the electron density for the acceptor.

Computed DA bond energies allow us to address the question about the most preferable structure of the 1:1 complexes. Values of the DA bond energies, derived from the (MX₃)₂(pyz)₃ compound, may be taken as a first approximation to the M–N bond energies in the catena polymer (MX₃-pyz)ₙ. Our computations predict that the DA bond is much stronger for the individual molecule MX₃-pyz (tetrahedral environment) than in the (MX₃-pyz)ₙ polymer with a trigonal bipyramidal environment. However, due to the fact that in the polymer two DA bonds are formed per one MX₃ unit, the total interaction energy slightly favors the formation of the catena polymer. The much lower reorganization energy of MX₃ in the polymer also facilitates the polymer formation. Formation of the polymeric structures in the gas phase is energetically favored by 21, 9, 11 kJ mol⁻¹ for AlCl₃, AlBr₃ and GaCl₃ acceptors, respectively. In the case of the weaker acceptor GaBr₃ computations predict almost equal Ga–N interaction energies for the formation of an individual molecule GaBr₃-pyz and (GaBr₃-pyz)ₙ polymer (the energy difference is less than 1 kJ mol⁻¹). Such small energetic differences between molecular and polymeric forms predicted for the gas phase structures imply that intermolecular interactions in the solid state can influence the preference of one or the other structural type.

A much lower Ga–N bond stability in the GaBr₃-pyz polymer may explain the relatively low melting point of (GaBr₃-pyz)ₙ (88–90 °C)¹¹ compared to the isostructural compounds (GaCl₃-pyz)ₙ (178–180 °C)¹³ and (AlBr₃-pyz)ₙ (circa 266 °C, present work). Derived from tensimetry studies melting enthalpies increase from GaCl₃-pyz (12 ± 6 kJ mol⁻¹)¹² to AlBr₃-pyz (64 ± 3 kJ mol⁻¹). Note that the melting points of polymers

<table>
<thead>
<tr>
<th>Compound</th>
<th>M–N</th>
<th>M–X1</th>
<th>M–X2</th>
<th>Reference</th>
</tr>
</thead>
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<tr>
<td>AlBr₃-py</td>
<td>1.935(3)</td>
<td>2.268(1)</td>
<td>2.277(1), 2.280(1)</td>
<td>13 This work</td>
</tr>
<tr>
<td>AlBr₃-pyz-AlBr₃ (1)</td>
<td>1.999(6)</td>
<td>2.253(18)</td>
<td>2.267(2), 2.246(3)</td>
<td>11 This work</td>
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<tr>
<td>(AlBr₃-pyz)ₙ (5)</td>
<td>2.133(2)</td>
<td>2.309(15)</td>
<td>2.325(8)</td>
<td>13 This work</td>
</tr>
<tr>
<td>GaCl₃-py</td>
<td>1.966(2)</td>
<td>2.150(7)</td>
<td>2.158(7), 2.159(7)</td>
<td>11 This work</td>
</tr>
<tr>
<td>GaCl₃-pyz-GaCl₃ (2)</td>
<td>2.044(7)</td>
<td>2.135(2)</td>
<td>2.147(2)</td>
<td>11 This work</td>
</tr>
<tr>
<td>(GaCl₃-pyz)ₙ (4)²</td>
<td>2.203(5)</td>
<td>2.174(2)</td>
<td>2.185(14)</td>
<td>11 This work</td>
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<tr>
<td>(GaCl₃-pyz)ₙ (4)³</td>
<td>2.211(15)</td>
<td>2.175(8)</td>
<td>2.182(6)</td>
<td>11 This work</td>
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<tr>
<td>GaI₃-py</td>
<td>2.000(4)</td>
<td>2.510(6)</td>
<td>2.519(7), 2.524(6)</td>
<td>13 This work</td>
</tr>
<tr>
<td>GaI₃-pyz (5)</td>
<td>2.027(6)</td>
<td>2.305(7)</td>
<td>2.304(9), 2.309(9)</td>
<td>13 This work</td>
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</table>

² 123 K.³ 293 K.
increase along with the increase of the M-N bond energy (DA bond energies are 64, 77 and 85 kJ mol\(^{-1}\) for GaBr\(_3\), GaCl\(_3\) and AlBr\(_3\), respectively). In our opinion, this indicates a destruction of the \(MX_3\)-pyz polymers upon melting.

It should be noted that according to our experimental results, GaI\(_3\)-pyz (5) does not form a polymeric structure in the solid state (Fig. 5). Interestingly, numerous attempts on geometry optimization of \([\text{GaI}_3\text{pyz}]_2\) (starting from pyz-GaI\(_3\)-pyz-GaI\(_3\)-pyz geometry) failed due to a dissociation of the middle Ga-N bonds in course of geometry optimization. Optimization always converged to two GaI\(_3\)-pyz complexes and free pyz. This theoretical result is in excellent agreement with experimental observation of the monomeric molecular structure of 5 in the solid state. Taking the Ga-N bond energy derived from GaI\(_3\)-pyz as the mean Ga-N bond energy in the hypothetical gaseous polymer \([\text{GaI}_3\text{pyz}]_n\) we conclude that the monomeric complex GaI\(_3\)-pyz is by 12 kJ mol\(^{-1}\) more stable than the polymer. The monomeric AlI\(_3\)-pyz is by 7 kJ mol\(^{-1}\) more preferable than the polymer (AlI\(_3\)-pyz)\(_n\). 1-D polymer stability decreases in line with the decrease of Lewis acidity: AlCl\(_3\) > AlBr\(_3\) > GaCl\(_3\) > AlI\(_3\) > GaBr\(_3\) > GaI\(_3\). Thus, the Lewis acidity of group 13 halides plays a decisive role in the formation of 1D polymeric arrangement.

III. Tensimetry studies in the AlBr\(_3\)-pyz system

In order to obtain thermodynamic parameters for vaporization and gas phase dissociation of 1 and 3, a series of vapor pressure--temperature measurements have been performed with the static tensimetry method with a glass membrane null-manometer. Such a technique can be used to study both heterogeneous and (after complete vaporization of the substance) homogeneous gas phase equilibria. Detailed description of the method and its application to several case studies can be found in a recent review.\(^1\) Summary of the experiments, carried out for the AlBr\(_3\)-pyz system, is given in Table S6.\(^1\) Since in analogy with \([\text{GaCl}_3\text{pyz}]_2\) it is expected that complex (AlBr\(_3\))-pyz will undergo dissociation into AlBr\(_3\)-pyz upon heating, vaporization and the thermal stability of individual complex AlBr\(_3\)-pyz was studied first.

**Tensimetry studies of complex of a 1 : 1 composition.** In the first two experiments, the individual complex 3, purified by sublimation in a vacuum, was studied. Data obtained in two independent experiments 1 and 2 agree well with each other. In experiment 1, 36.2 mg of AlBr\(_3\)-pyz were sublimed into the system (volume 27.40 ml). Three heating–cooling cycles (up to temperature 765 K) with the heating range of about 1–2 °C per minute were performed. After heating above 674 K, very minor
decomposition of the organic ligand was evident as light darkening on the walls of the glass system. Measured vapor pressure–temperature dependence in experiment 1 is shown in Fig. 6 (data for the first two runs are shown). Several temperature zones have been identified.

**Saturated vapor pressure range.** Zone (a) corresponds to vaporization of some impurity (appearance of the so called “parasitic” gas), which undergoes thermal expansion in zone (b). This residual parasitic gas has negligible vapor pressure at room temperature, indicating that it condenses, adsorbs or chemically reacts with \( \mathrm{AlBr_3-pyz} \). The low apparent vaporization enthalpy of \( 10 \pm 2 \text{ kJ mol}^{-1} \) (obtained from linear \( \ln(P/P^\circ) = f(1/T) \) dependence in zone (a)) hints to the physisorption process. The origin of this impurity is unclear, but we must note that it was present in separately synthesized samples used in experiments 1 and 2. The molar fraction of evolved “parasitic” gas is 12% (experiment 1) or 16% (experiment 2) with respect to the amount of the introduced sample. Assuming that at high temperatures this parasitic gas is unreactive, saturated and unsaturated vapor pressures of the \( \mathrm{AlBr_3-pyz} \) complex were obtained by subtraction from the total pressure the partial pressure of the evolved parasitic gas, taking into account its thermal expansion. Joint treatment of the obtained partial pressures of gaseous \( \mathrm{AlBr_3-pyz} \) over solid (zone c) and liquid (zone d) \( \mathrm{AlBr_3-pyz} \) allowed us to establish thermodynamic characteristics for the sublimation and vaporization processes. The plot of \( \ln(P/P^\circ) = f(1/T) \) dependence is given in Fig. 7. The good agreement between the data obtained in two independent experiments 1 and 2 confirms our assumption about the inertness of the parasitic gas at elevated temperatures.

**Unsaturated vapor pressure range.** Zone (e) corresponds to the unsaturated vapor pressure range. In this zone, only gaseous products are present in the system. At the point of exit into the unsaturated vapor range, the estimated molecular mass of the vapors agrees well with the computed one for the monomeric molecules \( \mathrm{AlBr_3-pyz} \), indicating that it is the dominant form in vapors. Upon temperature increase, the \( P/T \) values (which are proportional to the quantity of gaseous moles in the system: \( P/T = nR/V \)) slightly increase, which may be attributed to a homogeneous gas phase thermal dissociation of the \( \mathrm{AlBr_3-pyz} \) complex upon heating:

\[
\mathrm{AlBr_3 \cdot pyz (g)} = \mathrm{AlBr_3 (g)} + \mathrm{pyz (g)} \tag{1}
\]

The good agreement between the data obtained in subsequent heating/cooling runs suggests that the true equilibrium state is achieved in the system, and no irreversible side processes occur. However, the maximal partial pressure of dissociation products is less than 10 torr (dissociation degree is lower than 6%). Low partial pressures of dissociation products lead to large errors in the determination of the equilibrium constant. Joint treatment of all obtained data in the unsaturated vapor region (experiments 1 and 2, 156 experimental points in total), taking into account dimerization of \( \mathrm{AlBr_3} \) (cf.\(^\text{26}\)), allowed us to estimate the dissociation enthalpy and entropy of gaseous \( \mathrm{AlBr_3-pyz} \) (Table 5). Larger uncertainty is due to the smaller dissociation degree of the complex. Nevertheless, the present experimental estimation of the dissociation enthalpy as \( 126 \pm 14 \text{ kJ mol}^{-1} \) within the experimental errors agrees with the theoretically computed value of 118 kJ mol\(^{-1}\) and is comparable to the experimental dissociation enthalpy for the \( \mathrm{GaCl_3-pyz} \) complex (124.2 ± 2.8 kJ mol\(^{-1}\)).

**Experiments with excess amounts of pyz.** It is expected that the introduction of the free pyz ligand should prevent complex dissociation by shifting the equilibrium (1) to the left. In order
to check the validity of the used model, after experiment 2, 21.3 mg of pyz were introduced into the system via one of the branches, after this the volume of the system decreased to 30.6 ml. Three subsequent heating-cooling runs up to the temperature of 660 K were performed (experiment 3). Decomposition of the organic ligand pyz was observed at high temperatures, and the results of the successive heating/cooling cycles are not reproducible. Therefore, only data for the first heating run were analyzed. The vapor-pressure temperature dependence is shown in Fig. 8. Zone (a) corresponds to the vaporization of an excess pyz, followed by its thermal expansion in zone (b). The exponential pressure increase in zone (c) suggests liberation of chemically bound pyz, thus, formation of a complex with excess pyz (estimated complex composition AlBr$_3·$1.5pyz). This complex completely decomposes into solid AlBr$_3·$pyz and gaseous pyz above 414 K followed by vaporization of AlBr$_3·$pyz (zone d). In the unsaturated vapor region of experiment 3 (zone e), the complex dissociation was largely suppressed suggesting that the chosen model is correct.

From the tensimetry study we conclude that complex AlBr$_3·$pyz vaporizes in the form of monomeric molecules AlBr$_3·$pyz, which are stable in vapors below 600 K and undergo reversible thermal dissociation into gaseous AlBr$_3$ and pyz above this temperature.

**Tensimetry study of complex of 2 : 1 composition.** Two tensimetry experiments have been performed, one with the separately prepared complex Al$_2$Br$_6·$pyz (experiment 4), and with a separate introduction of Al$_2$Br$_6$ and pyz into the system (experiment 5). In both experiments, a partial irreversible decomposition of the organic ligand was evidenced upon heating above 580 K (black coloring on the walls of the system), leading to irreproducibility of subsequent heating–cooling runs. However, X-ray structural analysis of a single crystal grown after experiment 4 confirmed the existence of 1 in the solid state, indicating the incompleteness of the pyrolytic process. Small partial pressures of the dissociation products and irreversible pyrolysis make it impossible to establish thermodynamic characteristics of the complex dissociation. The estimated complex dissociation degree at 575 K is 8 ± 7%. It indicates that the Al$_2$Br$_6·$pyz complex is less stable in vapors than AlBr$_3·$pyz, which is in agreement with our computational results and also in line with the order of stability found for Ga$_2$Cl$_6·$pyz and GaCl$_3·$pyz complexes.\(^{12}\)

**Conclusions**

The formation of 1D polymers of group 13 metal halides with pyrazine is dependent on the Lewis acidity of the MX$_3$ moiety. While AlBr$_3$ and GaCl$_3$ form 1D polymers (MX$_3·$pyz)$_\infty$, the weakest Lewis acid (GaI$_3$) does not afford a polymeric structure at all. GaI$_3$ forms the monomeric molecular complex Ga$_2$I$_6·$pyz, which is isostructural to its pyridine analog Ga$_2$I$_6·$py. Comprehensive theoretical studies at the B3LYP/TZVP level of theory reveal that (MX$_3·$pyz)$_\infty$ polymer stability decreases in order AlCl$_3$ > AlBr$_3$ > GaCl$_3$ > AlI$_3$ > GaBr$_3$ > GaI$_3$. Upon heating the 1D polymers vaporize in the form of monomeric molecules MX$_3·$pyz. It is assumed that dissociation of the polymer into monomers occurs upon melting of compounds. Much lower donor properties of the second nitrogen center of the bifunctional donor pyz results in lower stability of M$_2$X$_6·$pyz complexes in the gas phase compared to MX$_3·$pyz complexes. An excess of MX$_3$ catalyzes the thermal destruction of the organic
ligand in the complexes, lowering the decomposition temperature of \( \text{M}_2\text{X}_3\cdot\text{pyz} \) complexes by about 100 °C.

**Experimental**

**Synthesis of adducts**

Group 13 element halides were synthesized from elements and purified by multiple (not less than 4 times) sublimation in a vacuum. Due to easy hydrolysis of metal halides, all complexes have been synthesized by direct interaction of group 13 element trihalides with pyrazine in whole glass apparatus under vacuum. Analogous to the procedure described in the work, a small excess (up to circa 10%) of the donor ligand was used for synthesis of 1 : 1 complexes MX\(_3\)·pyz. Similarly, a small excess of MX\(_3\) was used for the synthesis of (MX\(_3\))\(_2\)·pyz complexes with a 2 : 1 composition. In each case the excess component was removed by heating in a vacuum and its amount was determined. Single crystals suitable for the X-ray structural analysis have been grown by slow sublimation of the complexes in a vacuum. As typical examples, the synthesis of (AlBr\(_3\))\(_2\)·pyz (1), AlBr\(_3\)·pyz (3), and GaI\(_3\)·pyz (5) complexes will be described below. Synthesis and tensimetry studies of (GaCl\(_3\))\(_2\)·pyz (2) and GaCl\(_3\)·pyz (4) were described in ref. 12.

**Synthesis of (AlBr\(_3\))\(_2\)·pyz (1)**

27.5 mg (0.343 mmol) of pyz was sublimated at 50 °C to 235.0 mg (0.881 mmol) of AlBr\(_3\) in the vacuumed reaction vessel (Fig. S7†). The reaction started immediately upon condensation of pyz. The system was stored at 140 °C for several days. After that, an excess of AlBr\(_3\) was quantitatively sublimed (2.7 mg, 0.034 mmol). The AlBr\(_3\) to pyz ratio was 1.99 ± 0.01, confirming the formation of complexes with a 2 : 1 composition. In each case the excess component was removed by heating in a vacuum and its amount was determined. Single crystals suitable for the X-ray structural analysis have been grown by slow sublimation of the complexes in a vacuum. As typical examples, the synthesis of (AlBr\(_3\))\(_2\)·pyz (1), AlBr\(_3\)·pyz (3), and GaI\(_3\)·pyz (5) complexes will be described below. Synthesis and tensimetry studies of (GaCl\(_3\))\(_2\)·pyz (2) and GaCl\(_3\)·pyz (4) were described in ref. 12.

**Synthesis of AlBr\(_3\)·pyz (3)**

14.3 mg (0.178 mmol) of pyz was sublimated at 50 °C to 38.1 mg (0.143 mmol) of AlBr\(_3\) in the vacuumed reaction vessel (Fig. S7†). The reaction started immediately upon condensation of pyz. The system was stored at 140 °C for several days. After that, an excess of pyz was sublimed (50–60 °C, 5 hours) into a special compartment, and sealed off, the mass was determined (2.7 mg, 0.034 mmol). The AlBr\(_3\) to pyz ratio was 0.99 ± 0.01, in agreement with the desired 1 : 1 complex composition. Single crystals, suitable for X-ray analysis, were grown by sublimation in a vacuum at 200–220 °C for 5 days. *m/z* (EI, 70 eV, 120 °C) 608–620 (M\(^+\), 0.1%), 529–539 (M\(^+\) – Br, <0.1%), 344–350 (M\(^+\) – AlBr\(_3\), 16), 265–269 (M\(^+\) – AlBr\(_3\), –Br, 100), 185–189 (AlBr\(_3\)\(^+\), 36), 106–108 (AlBr\(_3\), 6), 80 (pyz\(^+\), 41).

**Synthesis of GaI\(_3\)·pyz (5)**

66.7 mg (0.833 mmol) of pyz was sublimated at 50 °C to 370.5 mg (0.823 mmol) of GaI\(_3\) in the vacuumed reaction vessel (Fig. S7†). The reaction started immediately upon condensation of pyz. The system was stored at 100 °C for several days, after that the temperature was raised to 140–150 °C. Single crystals, suitable for X-ray structural analysis, were grown by sublimation in a vacuum at 200–220 °C for 5 days. *m/z* (EI, 70 eV, 120 °C) 530–532 (M\(^+\), 0.02%), 403–405 (M\(^+\) – I, 0.8), 323–325 (GaI\(_2\)\(^+\), 22.9), 196–198 (GaI\(^+\), 9.3), 80 (pyz\(^+\), 100).

**X-ray structure analysis of the complexes**

The crystal structure analyses were performed on an Oxford Diffraction Gemini R Ultra CCD. Either semi-empirical 35 or analytical absorption corrections from crystal faces 38 were applied. The structures were solved by direct and charge-flipping methods, respectively. Thereby the programs SIR-97 39 and Superflip 40 were employed. Full matrix least-squares refinements on \( F^2 \) in SHELXL-97 were carried out. 41 The hydrogen coordinates were partially refined. All pictures were created with Olex2. 42

Only one very large crystal of 2 could be obtained, which had to be broken. This procedure led to split reflections and caused the relatively large quality factors. CCDC-927394, -927395, -927396, -927397 and -927398, contain the supplementary crystallographic data for this paper.

**Quantum chemical computations**

These were performed using DFT hybrid functional B3LYP43 in conjunction with the triple zeta quality basis set with polarization functions. Ahlrich’s all electron TZVP basis set44 was used for Al, Ga, C, N, Cl, Br, effective core potential def2-TZVP basis set45,46 was used for I, standard 6-311G** basis set44 was used for H. The B3LYP method has been successfully applied for the complexes of group 13 metal halides with ammonia47 and provided good agreement with high temperature experimental data. Structures of all compounds were fully optimized and verified to be minima on their respective potential energy surfaces (PES). GAUSSIAN 03 program package45 was used throughout. Basis set superposition error (BSSE) was estimated by the counterpoise method48 realized in Gaussian03. BSSE was found to be less than 8 kJ mol\(^{-1}\) per donor–acceptor bond (Table S4, ESI†). In all cases the introduction of the BSSE correction does not change the order of the acceptor ability of MX\(_3\). Given the fact that the counterpoise method generally overestimates BSSE,46 in the following discussion we will use reaction energies, uncorrected for BSSE.

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References


