

Cationic Clusters

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Why Do Five Ga⁺ Cations Form a Ligand-Stabilized [Ga₅]⁵⁺ Pentagon and How Does a 5:1 Salt Pack in the Solid State?

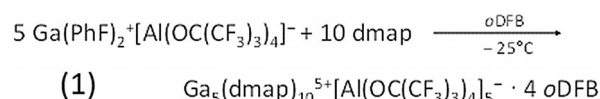
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Abstract: The reaction of the Ga⁺ source [Ga(PhF)₂]⁺[Al(OR^F)₄]⁻ with the neutral σ-donor ligand *dmap* (4-Me₂N-C₆H₄N) produces the unexpectedly large and fivefold positively charged cluster cation salt [Ga₅(*dmap*)₁₀]⁵⁺ ([Al(OR^F)₄]⁻)₅. It includes a regular and planar Ga₅ pentagon with strong metal–metal bonding. Additionally, the compound represents the first salt in which an ionic 1:5 packing is realized. We discuss the nature of this structure which results from the conversion of the non-bonding 4s² lone-pair orbitals into fully Ga–Ga-bonding orbitals and the solid-state arrangement of the ions constituting the lattice as an almost orthohexagonal AX₅ lattice, possibly the aristotype of any 5:1 salt.

The coordination chemistry of the Group-13-metal monocations Ga⁺ and In⁺ with ligands other than π-coordinating arenes^[1] is still rather in its infancy and that of Al⁺ is even unknown. In principle, the mixed-valence salts Ga⁺[GaX₄]⁻ (X = Cl, Br, I)^[2] appeared to be ideal starting materials for such chemistry. Yet, the introduction of neutral σ-donors led to undesired redox chemistry (comproportionation or disproportionation). In this respect, the facile access to an In[SO₃CF₃]⁻ salt^[3] was a step ahead and allowed for the characterization of the first In⁺ crown-ether complexes.^[4] However, related chemistry with Ga⁺ did not work and the only published compound which seemed likely to be a suitable starting material for coordination chemistry was the [Ga₂Cp*]⁺ cluster cation^[5]—with the complication of providing one surplus equivalent of neutral GaCp* per used Ga⁺ (Cp* = C₅Me₅). The subsequent facile access to arene complexes of In⁺ and Ga⁺ salts^[6,7] with the non-reactive weakly coordinating anion (WCA)^[8] [Al(OR^F)₄]⁻ opened a new starting point to interesting coordination chemistry with a variety of σ-donors including phosphines,^[6,7] carbenes,^[9] pyridines,^[10] and also crown ethers.^[11] In all of this, [Al(OR^F)₄]⁻ was very helpful^[12] for the elimination of cation–

anion interactions and allowed for a predictable reaction outcome. However, due to its considerable size (diameter 1.25 nm, V⁻ = 0.76 nm³) and the pseudo-gas-phase conditions that the anion provides,^[8,13] the overall charge of such coordination compounds was expected to be limited to +1. However, when changing to bidentate 2,2′-bipyridine (*bipy*) and phenanthroline (*phen*) as ligands, unexpectedly, the formation of indium-cluster-cation salts with planar triangles (for example, [In₃(*bipy*)₆]³⁺) and rhomboids (for example, [In₄(*phen*)₆]⁴⁺) that both feature strong In–In bonding was observed.^[14] Gallium, on the contrary, disproportionated in the presence of the same ligands. This was rationalized with the stronger reducing nature of Ga^I vs. In^I which, in the first case, led to reduced, non-innocent [*bipy*]⁻ ligands and only for In^I to clusters that retained the formal oxidation state of the metal.^[14] Concomitantly, Baines et al. reported^[15] the formation of strongly Ga–Ga-bonded, polyether-stabilized salts such as [(cryptand)Ga₂Cl₂]²⁺[(SO₃CF₃)⁻]₂ **A**. To shed light on the unclear oxidation states in materials like **A**, X-ray absorption spectroscopy^[16] and Auger-electron kinetic-energy^[17] measurements were conducted that assigned an intermediate chemical oxidation state of +II in **1**. Thus, the question remained if Ga⁺ clustering with a retention of the oxidation state +I is also possible, given the fact that an innocent strongly σ-donating ligand is used. This question was recently solved by using ^tBuNC as the ligand L, leading to the formation of the salt [Ga₄L₈]⁴⁺[(Al(OR^F)₄)⁻]₄ with a square-planar central Ga₄ ring. It represented the first univalent gallium-cluster cation.^[18]

Here we report on the reaction of the Ga⁺ source Ga^I(PhF)₂[Al(OR^F)₄] with the strong σ-donor but weak π-acceptor 4-(*N,N*-dimethylamino)pyridine (*dmap*) in *ortho*-difluorobenzene (*o*DFB). Reaction in a 2:1 ratio according to Equation (1) and storage for several weeks at –25 °C afforded



bright orange crystals (Figure S11 in the Supporting Information) suitable for single-crystal X-ray diffraction studies.^[27] Measurement, structure solution, and refinement revealed the unprecedented 5:1 salt [Ga₅(*dmap*)₁₀]⁵⁺ ([Al(OR^F)₄]⁻)₅ **1** (Figure 1a). The bright orange color of the solid is in good agreement with the TD-DFT-calculated UV/Vis spectrum of **1**⁵⁺ (see Supporting Information).

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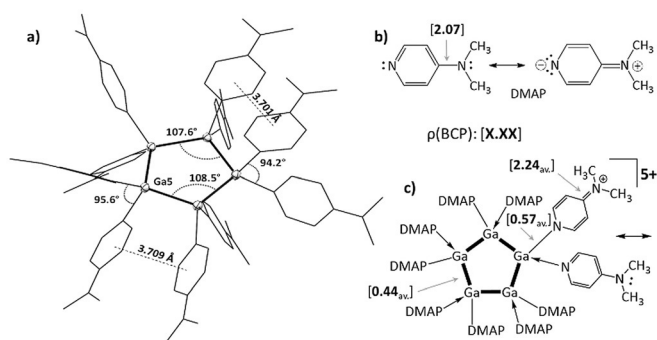


Figure 1. a) Molecular pentacation structure of the orange crystals of $[Ga_5(dmap)_{10}]^{5+}([Al(OR^F)_4]^-)_5$ **1**. The five $[Al(OR^F)_4]^-$ WCAs, the four co-crystallized *o*DFB molecules, and all hydrogen atoms were omitted for clarity. The Ga atoms are shown as ellipsoids with 50% probability level; the ligands are included as a wireframe model. b) Rationalization of the strongly σ -donating capacity of dmap. A larger contribution of the zwitterionic structure in (b) is in agreement with the experimentally observed structural parameters of the pentacation **1**⁵⁺. This is indicated by the selected resonance structure shown in (c). Selected AIM calculated electron densities ρ residing on the bond critical point (BCP) are given in brackets in $e^- \text{Å}^{-3}$.

Crystalline **1** forms reproducibly in good yield but is only stable at temperatures around or below -20 to -25°C , and is also highly sensitive to air and moisture. In one dedicated reaction, we isolated a yield of 29% orange crystals by always maintaining a cold chain. A powder-X-ray diffractogram of this orange material is in reasonable agreement with the simulation from the single-crystal data. The NMR spectra of *o*DFB solutions prepared according to Equation (1) detected at -20°C showed ^1H -, ^{13}C -, ^{19}F - and ^{27}Al -NMR signals of the intact ligands and anion but no $^{69/71}\text{Ga}$ resonance, probably due to the unsymmetrical environment of these quadrupolar nuclei. To elucidate possible aggregation reactions in solution, a DOSY-NMR study in *o*-DFB at -20°C with a stimulated-echo impulse sequence and including the non-reactive salt $\text{NBu}_4^+[Al(OR^F)_4]^-$ as a reference cation was performed. $[\text{NBu}_4]^+$ and (hypothetic) monomeric $[Ga(dmap)_2]^+$ have similar calculated cation volumes (0.379 vs. 0.376 nm^3 , see Table S1 in the Supporting Information) and should thus have comparable diffusion constants. A multicomponent analysis involving the reference signal at $\delta(^1\text{H}) = 3.12$ ppm showed two additional dmap-based diffusion coefficients to the $[\text{NBu}_4]^+$ reference velocity of $2.69 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ (Figure S9), with one of them being higher ($1.82 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$) and the other being lower ($6.93 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$) than the reference velocity. One may tentatively assign the first one to a free dmap ligand and the second one to an aggregate. Thus, the formation of the crystals is possibly a stepwise cycloligomerisation of monomeric $[Ga(dmap)_2]^+$ units. This conclusion is supported by electrospray-ionization mass spectra of solutions of **1** in *o*DFB, for example, with the isotopic pattern of the signals centered at $m/z = 425$ for mononuclear $[Ga(o\text{DFB})(dmap-H)_2]^+$ as well as of di- and trinuclear complexes such as $[Ga_2(o\text{DFB})_4(dmap)(dmap-H)]^+$ (m/z 837), $[(Ga_2(o\text{DFB})_5(dmap)_2-3H)]^+$ (m/z 949), and $[Ga_3(\text{PhF})(o\text{DFB})_2(dmap)_3(dmap-H)_2]^+$ (m/z

1139; see Figure S4–S6 and discussion about the energy below).

The main and hitherto unprecedented structural element of the pentacation **1** (hereafter: **1**⁵⁺; Figure 1a) is a five-membered Ga_5 ring that includes two dmap ligands attached to each gallium atom. With rather short Ga–Ga distances of 248.75(9)–250.1(1) pm (average: 249.5(6) pm), it forms an essentially planar pentagon. Five dmap ligands are located above the plane of the ring and five below; the average Ga–N separation amounts to 2.033(4) pm (range: 2.012(5) to 2.067(4) pm) and is significantly shorter than other reported Ga^I –N distances of this kind, for example, in the univalent pyrazine complex $Ga(\text{pyrazine})_3^+[Al(OR^F)_4]^-$ (average: 233.0 pm).^[10] This indicates a heavy involvement of DMAP in the bonding, as indicated by the resonance structures in Figure 1b,c. The neutral digallane(4) ($\text{disil})_2Ga-Ga(\text{disil})_2$ ($d_{Ga-Ga} = 254$ pm; $\text{disil} = -C(H)(SiMe_3)_2$)^[19] and the dumbbells of elemental α -gallium (246 pm) hold similar Ga–Ga distances to **1**⁵⁺. Additionally, the recent $[Ga_4\text{BuNC}_8]^{4+}([Al(OR^F)_4]^-)_4$ (**2**) with a C_i -symmetric square-planar four-membered gallium ring also has an average Ga–Ga-separation of 246 pm.

In agreement with the selected resonance structure shown in Figure 1c, the C–N distances between the pyridine ring and the dimethylamino group are, at $d_{C-N} = 133.8(8)$ pm, about three pm shorter on average than in free dmap.^[20] This suggests considerable charge transfer and iminium ion character (Figure 1b,c). The Ga–Ga–Ga angles in the regular and planar pentagon range from 107.05(3) to 108.49(3)° with an average of 107.93(3)°; the N–Ga–N angles are about 96.5(2)° on average. Two pairs of dmap ligands of adjoining gallium atoms are oriented in a π -stacking fashion with an average distance of 370.5(1) pm between the centroids of the pyridine planes, which places the interaction at the limit of the sums of the carbon van-der-Waals radii (340 pm). The cation structure is undistorted and shows only very few weak contacts to the anions as shown by the Hirshfeld plot in Figure S10. The pentacation structure of **1** is related to the known $(SiX_2)_5$ pentamers ($X = \text{Cl}, \text{Br}, \text{I}$), which, in contrast, hold a folded Si_5 ring.^[21] However, it was shown that this ring may easily flatten.^[22] Related phenomena were observed for the puckered $(SiCl_2)_6$ hexamer and its planar $[Si_6Cl_{14}]^{2-}$ chloride adduct.^[23] The flattening was attributed to the pseudo-Jahn–Teller effect.^[24] It is noteworthy that the analogues $(GeX_2)_5$, directly isoelectronic to **1**, are unknown.

To our knowledge, an ionic AX_5 lattice constructed from an isolated pentacation A^{5+} and five univalent counterions X^- is hitherto unknown. Formally, such structures may exist, but as exemplarily shown for the compound $[P_3N_3(dmap)_6]Cl_6$ ^[25] that contains a formal hexacation $[P_3N_3(dmap)_6]^{6+}$, such formally highly charged systems do accommodate many of the counterions in a host–guest assembly; in this example, five out of six chloride ions. So essentially, the ion packing in the $[P_3N_3(dmap)_6]Cl_6$ salt is that of a 1:1 salt as in $[P_3N_3(dmap)_6(Cl_5)]Cl$. By contrast, **1** forms a truly ionic lattice. All ions in **1** are arranged in a hexagonal primitive lattice that is slightly distorted due to the larger size of the pentacation (Figure 2). In every layer, one out of six ions is a pentacation (see Figure 2a). Thus, each pentacation is surrounded by six anions in the plane and one anion each above and below the

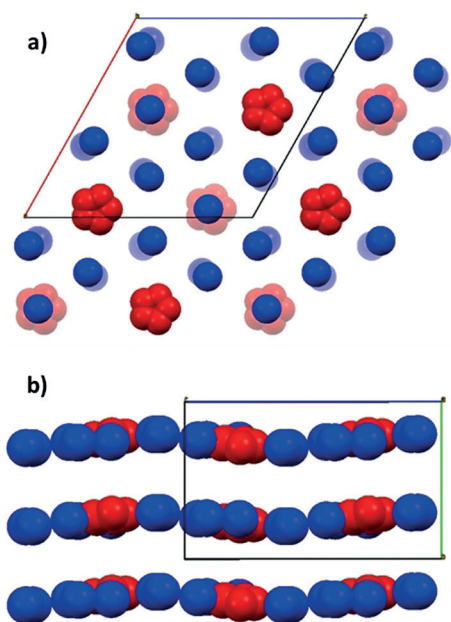


Figure 2. Primitive hexagonal packing of the ions in **1**. View a) along the *b* axis and b) along the *a* axis.

ring plane (see also Figures S11 and S12). To the best of our knowledge, not even a theoretical investigation exists that deals with the question how pentacations should pack with monoanions in an ionic lattice.

By using the General Utility Lattice Program (GULP),^[26] an equivalent periodic AX_5 array of +5 and -1 point charges with the +5 charges located in the center of the Ga_5 ring and the -1 charges located at the Al positions was constructed (Figure 3a). This array would have an electrostatic interaction energy of $-2740 \text{ kJ mol}^{-1}$. This is only 21 kJ mol^{-1} less stable than a perfect orthohexagonal arrangement with the same volume (Figure 3b), which gives a Madelung constant of 4.18. With the nearest Al-Ga₅-centroid distances in the experimental structure of **1** being between 9.6 and 12.4 \AA , the $[Ga_5]^{5+}Al_5^{-}$ point-charge arrangement gives a Madelung constant of 3.78. On this basis, we suggest the orthohexagonal

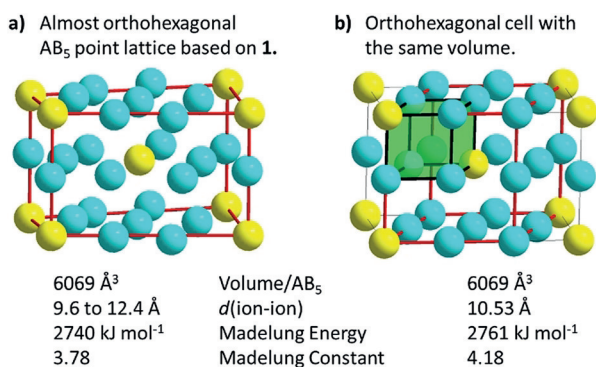


Figure 3. Almost orthohexagonal arrangement of the ions of **1** in the lattice (a) and the theoretical arrangement of one 5+ and five 1- ions in a comparable cell with the same volume (b). The yellow colored spheres represent the positions of the centroid of the Ga_5 ring and the light blue colored spheres the aluminum atoms of the anion.

structure, describing a hexagonal system with orthorhombic axes in a fixed ratio ($\approx 1:\sqrt{3}$), as the archetype of the AX_5 structure of this radius ratio.

It was rather unexpected to observe this pentacation structure with a non-ligand-bridged central Ga_5 ring. Arranging five +1 point charges in the same manner as the formal Ga^+ cations in the pentagon reveals an enormous Coulomb repulsion energy of 4506 kJ mol^{-1} . BP86-D3(BJ)/TZVP calculations give an overall interaction energy in the naked $[Ga_5]^{5+}$ of $+3930 \text{ kJ mol}^{-1}$, which is more favorable than the point-charge arrangement by 576 kJ mol^{-1} (Figure 4). Divided over five Ga-Ga bonds, this suggests a covalent interaction energy of at least 115 kJ mol^{-1} per bond (Figure 4). Yet, the monocations are still favored by thousands of kJ mol^{-1} . Thus, it appears that the coordination of the dmap ligand lifts the non-bonding $4s^2$ electron pair at Ga^+ to a level inducing an efficient Ga-Ga bond formation. Additionally, dmap coordination allowed for the delocalization of the unfavorable charge residing on the individual Ga^+ cations to the ligands (see Figure 1 b,c), apparently to a degree so that the Coulomb explosion of 1^{5+} into five monocations $[Ga(\text{dmap})_2]^+$ is overcompensated. This was investigated step by step in the next section.

Atoms-in-molecules (AIM) analyses on 1^{5+} and free dmap agree with this picture: The AIM charge residing on the Ga_5 basin amounts to +2.90 and that on the ten dmap ligands in 1^{5+} to +2.10, indicating heavy charge transfer. Concomitantly, the charge density on the bond critical point $\rho_{\text{BCP}}(\text{CNMe}_2)$ increases from $2.07 \text{ e}^- \text{\AA}^{-3}$ in free dmap to an average of $2.24 \text{ e}^- \text{\AA}^{-3}$ in 1^{5+} . Interestingly, the charge densities $\rho_{\text{BCP}}(\text{GaN})$ (average: $0.57 \text{ e}^- \text{\AA}^{-3}$) and $\rho_{\text{BCP}}(\text{GaGa})$ (average: $0.44 \text{ e}^- \text{\AA}^{-3}$) reside on a considerably elliptic bond path with average bond ellipticities ϵ of 0.07 (GaN) and 0.06 (GaGa). For comparison, $\epsilon(\text{CNMe}_2)$ is 0.13 for free, and 0.15, on average, for dmap in 1^{5+} . Apparently, charge delocalization through hyperconjugation is an important contribution to the bonding in the pentacation. Interestingly, the charge density $\rho_{\text{BCP}}(\text{GaGa})$ is higher on 1^{5+} than that on an isolated Ga_2 unit calculated on the same level: (0.44 (average) vs. $0.30 \text{ e}^- \text{\AA}^{-3}$). Moreover, we note that, compared to 1^{5+} , the Si-Si bond in $[\text{Si}_6\text{Cl}_{14}]^{2-}$ has a slightly higher charge density ($0.62 \text{ e}^- \text{\AA}^{-3}$) but much lower ellipticity (0.01).

The reaction energetics ($\Delta_r H^\circ$) of the components of 1^{5+} were calculated with BP86-D3(BJ)/TZVP starting from five Ga^+ cations, ten dmap ligands, and four *o*DFB solvent molecules as the zero point of energy (Figure 4). A first reaction that gives five monomeric complexes $[Ga(\text{dmap})_2]^+$ and four non-bonded *o*DFB molecules delivers 2272 kJ mol^{-1} . If two of these $[Ga(\text{dmap})_2]^+$ monomers are connected to form a dimer dication $[Ga_2(\text{dmap})_4]^{2+}$, $\Delta_r H^\circ$ rises by 74 kJ mol^{-1} . The more monomeric units are connected and the more the charge of the aggregate ions increases, the less favored the complex becomes (stepwise energy changes: +146 to +285 kJ mol^{-1} ; Figure 4). Yet, the pentacation arrangement becomes more stable by -265 kJ mol^{-1} when four solvent molecules *o*DFB, as observed in the asymmetric unit of the crystal structure of **1**, were added. However, from all starting points, five monocations $[Ga(\text{dmap})_2]^+$ (and four non-coordinated *o*DFB solvent molecules) are the most

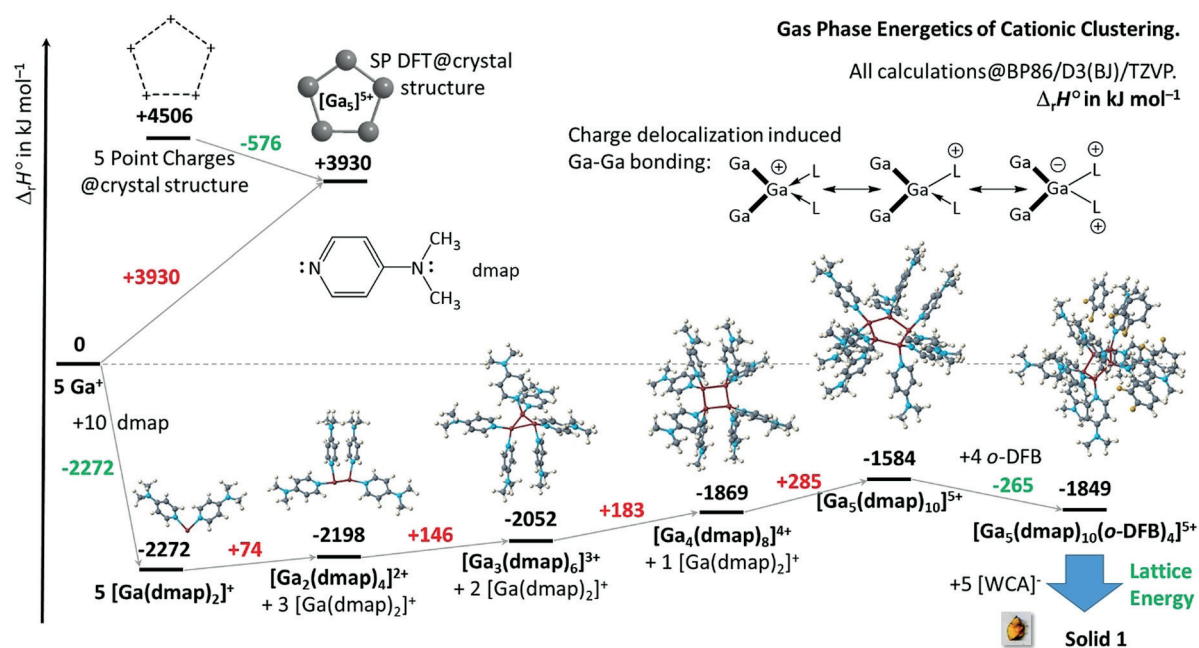


Figure 4. Investigation of the gas-phase thermodynamics of the step-by-step formation of the pentacation $[\text{Ga}_5(\text{dmap})_{10}]^{5+}$ and including the four molecules of co-crystallized *o*DFB.

favorable arrangement on thermodynamic grounds according to these $\Delta_r H^\circ$ calculations.

This trend will even be more pronounced if one considers $\Delta_r G^\circ$, which includes entropy loss upon aggregation. Still, one has to be reminded that these calculations are, by definition, performed in the gas phase. Investigations including Gibbs solvation energies calculated at the same level using the COSMO model and a dielectric constant of $\epsilon_r = 14.26$ for *o*DFB as the solvent suggest that an aggregation of n $[\text{Ga}(\text{dmap})_2]^+$ to $[\text{Ga}_n(\text{dmap})_{2n}]^+$ would be exergonic only for $n = 4$ (-63 kJ mol^{-1}) and 5 (-180 kJ mol^{-1} , see Supporting Information for details). This would be in agreement with the ambiguous situation observed in solution (DOSY-NMR, ESI-MS). At least the crystallization of the solid pentacation salt **1** is clearly favored: The high lattice energy of the AX_5 salt ($\approx 2740 \text{ kJ mol}^{-1}$, GULP), which is more than 1200 kJ mol^{-1} higher than the expected sum of the lattice energies of five hypothetical $[\text{Ga}(\text{dmap})_2]^+[\text{Al}(\text{OR}^f)_4]^-$ compounds of about $5 \times 300 \approx 1500 \text{ kJ mol}^{-1}$ (GULP), overcomes the Coulomb repulsion and favors the formation of solid **1**.

The unprecedented cluster-cation salt **1** includes a close relative to the possible aristotype lattice of any ionic AX_5 salt with an orthohexagonal arrangement. Enabled by efficient charge delocalization from the Ga^+ metal to the dmap ligand, even the strong Coulomb repulsion within the pentacation can be overcome by the large gain in AX_5 lattice energy. The formation of **1** clearly shows that strongly σ -donating but weakly π -accepting ligands have the potential to induce unexpected cationic-cluster formation. With this hitherto largest example, we suggest this to be a general construction principle.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: cationic clusters · density functional theory · gallium cations · main-group chemistry · weakly coordinating anions

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