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Examination of the Coordination Sphere of Al^{III} in Trifluoromethyl-Heteroarylalkenolato Complex Ions by Gas-Phase IRMPD Spectroscopy and Computational Modelling

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A series of aluminium complex ions with trifluoromethyl-heteroarylalkenolato (TMHA) ligands are studied by gas-phase infrared multiphoton-dissociation (IRMPD) spectroscopy and computational modelling. The selected series of aluminium TMHA complex ions are promising species for the initial study of intrinsic binding characteristics of Al^{III} cations in the gas phase as corresponding molecular ions. They are readily available for examination by (+) and (-) electrospray ionization mass spectrometry (ESI-MS) by spraying of $[AI^{3+} \cdot (L^{-})_3]$ solutions. The complex ions under investigation contain trivalent AI^{3+} cations with two chelating anionic enolate ligands, $[AI^{3+} \cdot (L^{-})_2]^+$, providing insights in the nature of the heteroatom-Al

bonds. Additionally, the structure of a deprotonated benzimidazole ligand, L^{-} , and an anionic complex ion of AI^{III} with two doubly deprotonated benzimidazole ligands, $[AI^{3+}(L^{2-})_2]^-$, are examined by (–)ESI-IRMPD spectroscopy. Experimental and computational results are highly consistent and allow a reliable identification of the ion structures. In all complex ions examined the planar TMHA ligands are oriented perpendicular to each other around the metal ion, leading to a tetrahedral coordination sphere in which aluminium interacts with the enolate oxygen and heteroaryl nitrogen atoms available in each of the bidentate ligands.

1. Introduction

Aluminium is the most abundant neurotoxic metal on earth which is exclusively found in oxygen-containing compounds (e.g. as oxide, hydroxide but also as silicate, sulphate or phosphate) as trivalent Al³⁺, because of its strong affinity to oxygen.^[1] Recent research showed that aluminium, which is widely bioavailable to humans, is toxic to the central nervous system as evidenced by the fact that it has been detected in both senile plaques and neurofibrillary tangle bearing neurons in the brains of patients suffering from Alzheimer's Disease (AD).^[2-4] In addition, aluminium has been shown to influence acetylcholine esterase activity.^[2] Especially for the research in the context of AD it is still a matter of scientific debate whether Al^{III} causes the disease, or possesses only a strong affinity for the fibrillar amyloid proteins.^[3] Therefore, basic research is needed to understand the interactions of such a highly charged and polarizing main group metal cation with Lewisbasic heteroatom functionalities to ultimately explain the nature of aluminium-biomolecule complexes. So far, only the structure of aluminium(III)-flavonoid complexes (e.g. hydroxyflavones, flavonoid 3-O-glycosides etc.) with exclusively oxygen metal-binding sites have been examined in solution by electronic (UV), Raman, and NMR spectroscopy and in the gas phase by tandem mass spectrometry and theory.^[5-11] In these studies the chelating properties of different oxygen containing functionalities such as phenolic hydroxyl and carbonyl groups of flavonoids could be evaluated.^[5-11]

Beyond the current status of research, herein the structure of charged complexes of trivalent Al^{III} are investigated in the gas phase by electrospray ionization infrared multiphoton-dissociation ESI-IRMPD spectroscopy and computational model-

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ling. For the first time this strategy was applied to study intrinsic properties^[12-14] of a triply charged main group metal ion in solvent free complexes. It is worth noting that the complex forming ligands provide a number of different electron-rich moieties for coordination to the metal, similar to those found in biomolecules, such as proteins and peptides.

The trifluoromethyl-heteroarylalkenolato (TMHA) compounds selected as ligands (L) strongly prefer their alkenole tautomers in solution as a consequence of both the strong electron-withdrawing properties of the trifluoromethyl group and the possibility of stabilizing the enole tautomer by intramolecular hydrogen bonding between nitrogen and the hydroxyl proton, as suggested by NMR studies (Scheme 1).^[15] In solution neutral



Scheme 1. Keto-enol tautomerisation equilibrium of the trifluoromethyl-heteroarylalkenole compounds.

 $[A]^{3+} \cdot (L^{-})_{3}]$ complexes of the trivalent aluminium metal cation are formed such that the $AI^{|||}$ is surrounded by three deprotonated anionic trifluoromethyl-heteroarylalkenolate ligand units. These ligands contain a number of different potential metal chelating sites, such as aromatic π systems as well as Lewisbasic heteroatoms like nitrogen, oxygen and sulphur.^[15]

Hence, a set of four representative TMHA aluminium complexes were selected for this study to elucidate the proximate coordination sphere of aluminium and in order to assess more thoroughly the competition between various functional groups (e.g. enolate oxygen, nitrogen, sulphur heteroatoms) to solvate such a strongly polarizing, hard,^[16,17] trivalent, main group metal cation (Scheme 2). In addition, these compounds



Scheme 2. Trifluoromethyl-heteroarylalkenole (TMHA) compounds 1–4 used as bidentate anionic (deprotonated) ligands L^- in cationic aluminium complex ions of the type $[A|^{3+} \cdot (L^-)_2]^+$ studied in the gas phase by (+)ESI-IRMPD. Doubly deprotonated benzimidazole-alkenole ligand 1 (L^{2-}) is forming the negatively charged $[A|^{3+} \cdot (L^-)_2]^-$ complex ion additionally examined by (-)ESI-IRMPD spectroscopy.

are interesting, because synthetic aluminium TMHA complexes^[15] are promising precursor candidates for chemical vapor deposition^[18] (CVD) processes, as they are insensitive to moisture and air stable as well as sufficiently volatile. For CVD applications the fundamental understanding of the decomposition mechanism is of vital interest. Therefore, the gas-phase structure analysis of intermediates is important to optimize size, morphology, and composition of the materials to be deposited. Along with tin,^[19] niobium,^[20] palladium and platinum,^[21] aluminium alkenolates are in the focus of ongoing research as they are attractive alternatives to alkoxides used for the growth of oxidic nanoparticles. Besides that TMHA compounds exhibit antimicrobial activity as inhibitors of a number of enzymes.^[22,23]

For a detailed structure elucidation $[AI^{3+}\cdot(L^{-})_{3}]$ complexes are transferred to the gas phase by ESI. Positively charged $[Al^{3+}\cdot(L^{-})_{2}]^{+}$ as well as negatively charged $[Al^{3+}\cdot(L^{2-})_{2}]^{-}$ aluminium complex ions, the latter ones comprise two doubly deprotonated ligands, serve as precursor ions for ESI-IRMPD spectroscopy and computational modelling (Scheme 2).^[24,25] IRMPD spectroscopy with a free electron laser (FEL) combined with theory has proven to be a powerful analytical strategy to elucidate ion structures, especially if those ions have only a limited number of oscillators, which exercise vibrations that obey harmonic approximations.^[26-30] As the electron density and geometry of a certain functional group is strongly influenced by its chemical environment, for example, a chelating interaction with a metal cation in a complex, characteristic intensity patterns in the IR fingerprint region can be obtained, which can be correlated to computed IR spectra of conformers as identified by theory. In doing so, the binding motifs in the coordination sphere can be precisely elucidated. Of special importance for our purpose are the abundant fingerprint absorption bands of, for example, C=N and carbonyl groups, which are characteristically shifted when the nitrogen of the former and the oxygen of the latter are involved in hydrogen bonding or are serving as Lewis-basic metal complexation sites.^[24,31-41] Recently, Williams and co-workers were the first to show that transicomplexes trivalent tion metal of lanthanides (La^{3+} , Ho^{3+} , Eu^{3+}) with peptide ligands can be successfully examined with IRMPD spectroscopy.^[42]

By measuring the IRMPD spectra of desolvated TMHA aluminium complexes in the gas phase, we aimed to elucidate the coordination sphere of the aluminium ion. As the mode of charge stabilization can be very sensitive to the identity of the charge carrier and the ligands, the TMHA aluminium complexes can serve as simplified models even for Al^{III}-biomolecule interactions. The instrumental setup used consisted of a combination of an FEL with a Fourier transform ion cyclotron resonance (FTICR) mass spectrometer equipped with an electrospray ion source allowing access to gas-phase molecular ions of a series of charged aluminium complexes (see Scheme 2). Their absorption behaviour in the infrared could then be examined subsequently by IRMPD spectroscopy. A 4.7 T FTICR mass spectrometer was used for the IRMPD experiments and has been described in detail elsewhere.^[24,43-46] The computational approach consisted of calculations on a series of isomers of the compounds to determine the most stable structure and its IR spectrum. The calculated spectra were subsequently compared to the experimental data for identification of a particular ion structure and to confirm the validity of the calculated conformer. For more details, see the following Section and refs. [24–26].

2. Results and Discussion

Benzimidazole Ligand 1 in Aluminium Complex lons: $[Al^{3+} \cdot (L^{-})_2]^+$

The cationic aluminium complex ions $[Al^{3+}(L^{-})_2]^+$ of deprotonated ligands 1–4 are found with predominant abundance in the gas phase as the (+)ESI-MS of the respective complex with ligand 1 illustrates (see Figure 1S in the Supporting Information).



Figure 1. Experimental IRMPD spectrum of the cationic aluminium complex ion $[AI^{3+}(L^{-})_2]^+$ of deprotonated ligand 1 (a) compared to computed IR spectra of the four relevant ion structures identified by theory in (b–e). (B3LYP/6-311G**; scaling factor: 0.98; colored version of the Figure in the supporting Information).

The acquired IRMPD spectrum of the $[Al^{3+}(L^{-})_2]^+$ complex ion with two anionic benzimidazole ligands **1** is shown in Figure 1 a exhibiting rich patterns of well resolved and abundant features located between 800 and 1700 cm⁻¹.

All four tetrahedral ion structures of the $[A]^{3+}(L^{-})_2]^+$ complex ion identified by theory are largely similar, differing only in the binding patterns (Figure 1b–e). In all cases, the deprotonated bidentate benzimidazole ligands are connected to the Al cation through the enolate oxygen. The second binding site of the metal cation is varying as two different nitrogens are available for the interaction with aluminium. Either both imidazole nitrogens in position 3 (Figure 1b), or one of these nitrogens combined with the nitrogen in position 1, which carries the proton (Figure 1c), or both position 1 imidazole nitrogens are coordinated to the Al cation (Figure 1 d and e). The relative energies are given in Figure 1 as well.

The computed IR spectra of the isomeric structures exhibit striking similarities in the range between 1000 and 1300 wave numbers in which $C-C_{ring}$, $C-H_{ring}$, C-F motions and scaffold vibrations of the imidazole heterocycle are found. An inspection

of the theoretical spectra reveals differences in signal intensities in the range from 1300 to 1500 cm⁻¹ (C–C_{ring} and C–H_{ring} vibrations) and even more significantly in the range from 1500 to 1700 cm⁻¹ (1530 cm⁻¹: C=N_{Al} and C–O_{enolate}; 1620 cm⁻¹: C=C_{enolate}). The visual comparison of the experimental spectrum (Figure 1a) in relation to the computed ones in terms of peak positions and relative peak intensities, allows one to conclude that the spectrum of the [Al³⁺·(L⁻)₂]⁺ complex ion presented in Figure 1 b with both position 3 imidazole nitrogen atoms coordinated to the aluminium presents the best match. This conclusion corresponds well with the observation that this complex is significantly lower in energy than the other complexes, showing that the aluminium cation clearly prefers to interact with the benzimidazole nitrogens in position 3, presumably to

> minimize the interference on the aromatic system of the imidazole-heterocycle moiety.

$[Al^{3+}(L^{2-})_{2}]^{-}$

The (-)ESI-MS of the TMHA aluminium complex with ligand 1 is presented in the Figure 2S in the Supporting Information in which the negatively charged ligand 1 (m/z 227) and the corresponding $[Al^{3+}\cdot(L^{2-})_2]^-$ complex ion (m/z 479) of Al^{III} with two doubly deprotonated TMHA ligands are observed in high abundance. Both ions were selected for (-)ESI-IRMPD-analysis. Theory predicts only a single relevant ion structure of the [Al³⁺ $\cdot (L^{2-})_2]^-$ complex in which the doubly negatively charged ligands bind to the aluminium

cation through both the deprotonated enolate oxygen and the nitrogen of the benzimidazole moiety. The experimental (-)ESI-IRMPD spectrum of the anionic aluminium complex ion $[AI^{3+} \cdot (L^{2-})_2]^-$ is consistent with the computed IR spectrum of the tetrahedral ion structure identified by theory, as Figure 2 illustrates. However, three features of the computed spectrum differ slightly from the experimentally recorded spectra. Firstly, the two bands referring to C–C_{ring} and C–H_{ring} motions appear blue-shifted in the experimental spectrum (between 1100 and 1200 cm⁻¹) and secondly, the asymmetric stretching mode of the enolate C=C double bonds predicted to be at around 1640 cm⁻¹ is found substantially weaker and red-shifted in the experimental spectrum.

[L]⁻

In the (–)ESI-MS of the TMHA aluminium $[Al^{3+}\cdot(L^{-})_{3}]$ complex the signal of the deprotonated anionic trifluoromethyl-heteroarylalkenolato ligand **1** is found at *m/z* 227 (see Figure 2S in the Supporting Information). This ion was selected as the pre-



Figure 2. Experimental (–)ESI-IRMPD spectrum of the anionic aluminium complex ions $[AI^{3+}(L^{2-})_2]^-$ of doubly deprotonated ligand 1 compared to the computed IR spectrum of the ion structure identified by theory presented in the inset. (B3LYP/6-311G**; scaling factor: 0.98; colored version of the Figure in the Supporting Information).

cursor ion for IRMPD spectroscopy to probe the structure of the free ligand $[L]^-$ in the gas phase and to scrutinize whether the ligand remains in the conformation found in the $[Al^{3+} \cdot (L^-)_2]^+$ complex ion, or whether the benzimidazole moiety rotates to establish a hydrogen bond for further stabilization. The computed IR spectra of the two isomeric structures

the gas phase after dissociation, the transition state for the rotation of the free deprotonated ligand **1** was determined. It turns out that the transition state between the isomers depicted in Figures 3 b,c lies 35.6 kJ mol⁻¹ above the structure depicted in Figure 3 c. If the dissociation energy of 549.1 kJ mol⁻¹ for a single ligand leaving $[AI^{3+}\cdot(L^{-})_{3}]$ without any rotation is

are strongly influenced by the presence (Figure 3b) or absence (Figure 3 c) of that additional hydrogen bond and exhibit significant differences. Especially, the asymmetric stretching mode of the enolate C=C double bond (Figure 3 c: 1550 cm^{-1}) and a strong C-O motion indicating a partial double bond character at 1660 cm⁻¹ dominate the IR spectrum at the blue end of the range in the absence of the hydrogen bonding between the imidazole N-H and the enolate oxygen. In the hydrogen bonded conformer (Figure 3b) the additional stabilization of the ion structure leads to a characteristic pattern of a set of three less dominant modes of similar origin also found in the experimental spectrum in that wave number range (Figure 3 a), allowing us to make a positive assignment. Additionally, a clearly resolved absorption at 1380 cm⁻¹ found in the experimental spectrum (Figure 3 a) is only observed in Figure 3b originating from C-H wagging modes. Overall, this suggests that the deprotonated ligand 1 rotates around the C-C bond connecting the



Figure 3. Experimental (–)ESI-IRMPD spectrum of the deprotonated anionic TMHA ligand 1 (m/z 227) (a) compared to the computed IR spectra of the two ion structures identified by theory: Anionic TMHA ligand 1 with hydrogen bonding (b) and without a hydrogen bonding (c). (B3LYP/6-311G**; scaling factor: 0.98; colored version of the Figure in the Supporting Information).



Figure 4. Three key structures in the dissociation of $[Al^{3+}(L^{-})_{3}]$ complexes with deprotonated TMHA ligand **1.** a) Starting complex. b) Transition state between (a) and (c). c) Final intermediate structure, which loses **1** to from $[Al^{3+}(L^{-})_{2}]^{+}$ [Figure 5 (a)], which was found in the gas phase by (+)ESI-IRMPD spectroscopy and confirmed by theoretical assignment. (Colored version of the Figure in the Supporting Information).

trifluoroenolate to the benzimidazole to establish a hydrogen bonded conformer during or after its release from the $[AI^{3+}\cdot(L^{-})_{3}]$ aluminium complex.

To establish the mechanism for this dissociation further, we performed a number of calculations.

We first investigated the most stable conformer for $[AI^{3+} \cdot (L^{-})_{3}]$. This turns out to be the isomer in which the imidazole nitrogens are arranged in a *mer*-type arrangement as depicted in Figure 4a and Scheme 3. Assuming first that the ligand rotates in

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$3 (\overset{\mathsf{CF}_{3}}{\underbrace{}}, \overset{\mathsf{CF}_{3}}{\underbrace{}, \overset{\mathsf{Al}(\mathsf{CH}_{3})_{3}}{\underbrace{}, \overset{\mathsf{Toluene,}}{-76 \, ^{\circ}\mathsf{C}}}, \overset{\mathsf{N}}{\underbrace{}, \overset{\mathsf{O}_{1,1}}{\underbrace{}, \overset{\mathsf{O}_{2,1}}{\underbrace{}, \overset{\mathsf{O}_{2$

Scheme 3. Synthesis of the neutral $[A^{13} \cdot (L^{-})_3]$ complexes. Detailed description of the synthesis and the conclusive spectroscopic data set on ligands 1–4 and the corresponding $[A^{13} \cdot (L^{-})_3]$ aluminium complexes is given elsewhere.^[15]

added to that, then this transition state lies 584.7 $kJ\,mol^{-1}$ above the $[Al^{3+}\cdot(L^{-})_{3}]$ minimum. If on the other hand it is assumed that dissociation and rotation of a single ligand into

the structure given in Figure 3b happens inside the ligand, then either the oxygen-aluminium bond or the imidazole nitrogenaluminium bond in $[AI^{3+}\cdot(L^{-})_{3}]$ will break first. In this case only the former process was considered, because in the formation of $[Al^{3+}\cdot(L^{-})_{3}]$ one would expect initial coordination to happen through the imidazole nitrogen, since this affects the the π system of the benzimidazole ligand least. Thus, in the reverse process, it can be expected that the oxygen-aluminium bond is

broken first. This assumption was investigated further, when the dissociation of $[A|^{3+}\cdot(L^{-})_2]^+$ was studied. The resultant structure for $[A|^{3+}\cdot(L^{-})_3]$ is given in Figure 4 c. This structure is 81.0 kJ mol⁻¹ higher in energy than the global minimum in Figure 4a. The transition state between these two structures (depicted in Figure 4b) is 154.3 kJ mol⁻¹ higher in energy than the global minimum in Figure 4a. However, the total dissociation energy is 487.9 kJ mol⁻¹, which means that this barrier is actually a submerged barrier with respect to the dissociated product. As a consequence, rotation around the C–C bond before complete dissociation of the complex is energetically more favourable than rotation after dissociation by 98.6 kJ mol⁻¹.

To investigate whether this description of the break-up of the $[Al^{3+} \cdot (L^{-})_3]$ complex is unique, we also studied the dissociation of the $[Al^{3+} \cdot (L^{-})_2]^+$ ligand into $[Al^{3+} \cdot (L^{-})]^{2+}$ and L^- . In this case both initial dissociation of the oxygen-aluminium bond and initial dissociation of the imidazole nitrogen-aluminium bond were considered. Initial dissociation of the imidazole nitrogen-aluminium bond does not form a stable complex and leads to the loss of a fluoride ion, which subsequently attaches itself to the aluminium cation. On the other hand, as in the case of the break-up of $[Al^{3+} \cdot (L^{-})_3]$, dissociating the oxygenaluminium bond first leads to a stable structure. Thus, the conclusion needs to be drawn that the oxygen-aluminium bond dissociates first, as indeed could be expected, since this least affects the π system of the benzimidazole ligand as mentioned previously. The energy of this structure, depicted in Figure 5 c, lies 295.2 kJ mol⁻¹ above the global minimum, depicted in Figure 5 a. Interestingly, there is also a local minimum halfway between the structures in Figures 5 a, c, lying 189.8 kJ mol⁻¹ above the global minimum. This structure is depicted in Figure 5 b. The corresponding structure is not present as a minimum in the dissociation pathway for $[Al^{3+}\cdot(L^{-})_{3}]$, but as a transition state. This intermediate structure has the β carbon to oxygen coordinated to the aluminium cation. This structure is further stabilized by a hydro-

gen bond between the carbonyl oxygen and a C–H of the other benzimidazole ligand. Rotation of the benzimidazole unit from his structure, depicted in Figure 5 b, towards the structure

Figure 5. Three key structures in the dissociation of $[Al^{3+} \cdot (L^{-})_2]^+$ complexes. a) Starting complex, found in the gas phase by (+)ESI-IRMPD spectroscopy and confirmed by theoretical assignment. b) Intermediate structure. c) Final intermediate structure, which loses 1 to form $[Al^{3+} \cdot (L^{-})]^{2+}$. (Colored version of the Figure in the Supporting Information).

in Figure 5a has a barrier of 30.7 kJmol⁻¹. Rotation towards the structure depicted in Figure 5c has a barrier of 107.9 kJmol⁻¹, which means that this process only has a barrier lying 2.5 kJmol⁻¹ above the energy needed to obtain the structure depicted in Figure 5c, from which dissociation occurs. Thus, the dissociation of 1 from $[Al^{3+} \cdot (L^{-})_2]^+$ to form $[Al^{3+} \cdot (L^{-})]^{2+}$ will happen in a similar fashion to the dissociation of 1 from $[Al^{3+} \cdot (L^{-})_3]$ in a process, which is endothermic, but essentially barrierless. The loss of the final ligand to form Al^{3+} was not investigated. However, given the similarities between losing one or two ligands from $[Al^{3+} \cdot (L^{-})_3]$ there is no reason to assume that a similar process will not be in operation here as well.

Benzoxazole Ligand 2 in Aluminium Complex lons: $[Al^{3+}\cdot(L^{-})_{2}]^{+}$

Similar to the discussion of the corresponding $[AI^{3+} \cdot (L^{-})_2]^+$ complex ion of ligand 1, three tetrahedral ion structures with benzoxazole-enolato ligands 2 were identified by theory (see structures in Figure 6b–d). Besides the enolate oxygen, which is connected to the Al cation in all complex ions, the second binding site to the metal cation can either be occupied by the oxazole nitrogen or the second oxygen.

Comparison of the experimental spectrum (Figure 6a), especially the wave number range from 1500 to 1800 cm⁻¹ with the computed ones, allows an unambiguous structure assignment, whereby the lowest energy conformer presented in Fig-



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of aluminium for oxygen, which is best expressed by the fact that most important minerals in the earth's crust are Al^{III}oxides^[49] and that aluminium-oxo compounds are stable leaving groups in many synthetic operations.^[50]

Dimethyloxazole Ligand 3 in Aluminium Complex Ions: [Al·L₂]⁺

In analogy to the $[Al^{3+} \cdot (L^{-})_2]^+$ complex ion of ligand **2** three tetrahedral ion structures of the respective complex ion with two dimethyloxazoline-enolato ligands **3** were identified by

Figure 6. Experimental IRMPD spectrum of the cationic aluminium complex ion $[Al^{3+}\cdot(L^{-})_2]^+$ of deprotonated TMHA ligand **2** (a) compared to computed IR spectra of the three relevant ion structures identified by theory in (b–d). (B3LYP/6-311G**; scaling factor: 0.98; colored version of the Figure in the Supporting Information).

ure 6b is the best match to the experimental spectrum (1520 cm⁻¹: C=N_{Al} and C-O_{enolate}; around 1610 cm⁻¹: C=C_{enolate}). This assignment is additionally supported by the fact that the

theory (see structures in Figure 7 b–d). Besides the enolate oxygen, which is involved in the Al complexation of all potential isomers another binding site is to be occupied by either an oxazole nitrogen or oxygen.

IR spectra of the conformers with one (Figure 6c) or two benzoxazole oxygens (Figure 6 d) coordinated to aluminium show a prominent band at 1700 cm⁻¹ (vas: C=Cenolate and C=Cbenzoxazole) which is absent in the recorded spectrum (Figure 6a). Thus, analogous to the results found for the benzimidazole analogues, the aromaticity of the oxazole moiety, which would be strongly perturbed by the interaction of the oxygen with the metal cation, governs the selection of coordination sites interacting with aluminium. This is further supported by the fact that the highest electron density is found at the enolate oxygen and the enaminolate nitrogen, which can be attributed to the comparably



Figure 7. Experimental IRMPD spectrum of the cationic aluminium complex ion $[Al^{3+} \cdot (L^{-})_2]^+$ of deprotonated TMHA ligand **3** (a) compared to computed IR spectra of the three relevant ion structures identified by theory in (b–d). (B3LYP/6-311G**; scaling factor: 0.98; colored version of the Figure in the Supporting Information).

low aromaticity of oxazoles and benzoxazoles in general.^[47] Due to the electron donating effect of the ring-oxygen atom to keep aromaticity, the remaining electron density at this possible coordinating site becomes considerably lower, favouring the electron-rich heterocyclic-nitrogen atom becoming the favoured coordinating site. This finding is further supported by solid-state structures of two related derivatives also showing N,O coordination to Al³⁺ centres as six-membered rings of related benzoxazole ligands in five-coordinated or distorted octahedral complexes.^[48]

While this conclusion appears to be straightforward, it is still remarkable as it contradicts the well documented preference

The experimental IRMPD spectrum acquired by irradiation of the $[Al^{3+} \cdot (L^{-})_2]^+$ precursor ion of ligand **3** (*m/z* 439) is presented in Figure 6a. Again, the vibrational bands in the wave number range from 1500 to 1750 cm⁻¹ are important for the structure assignment as the significantly different signal patterns of the three isomers allow selective identification. The computed IR spectrum of the $[Al^{3+} \cdot (L^{-})_2]^+$ complex ion with both oxazole nitrogens coordinated to the aluminium is presented in Figure 7b. The strong bands around 1500 cm⁻¹ and around 1610 cm⁻¹, which are attributed to the asymmetric stretching modes of the C=N double bond in the oxazole and the enolate double bond, match the experimental IRMPD spec-

trum best (Figure 7a) This assignment is in line with the results found for the other $[AI^{3+} \cdot (LL^{-})_2]^+$ complex ions and the relative energetics of the different isomers.

Dimethylthiazole Ligand 4 in Aluminium Complex lons: $[Al\cdot L_2]^+$

The recorded IRMPD spectrum of the $[Al^{3+}\cdot(L^{-})_2]^+$ precursor ion with two deprotonated ligands **4** (*m*/*z* 471) is presented in Figure 8a.



Figure 8. Experimental IRMPD spectrum of the cationic aluminium complex ion $[Al^{3+}(L^{-})_{2}]^{+}$ with deprotonated TMHA ligands **4** (a) compared to computed IR spectra of the three relevant ion structures identified by theory in (b–d). (B3LYP/6-311G**; scaling factor: 0.98; colored version of the Figure in the Supporting Information).

Contrary to the results discussed above, in this case the computed spectra of the three isomeric ion structures under examination are largely similar but exhibit significant differences in the absorption pattern in the range from 1220 to 1360 cm⁻¹. Decisive for the assignment is a strong band at 1300 cm⁻¹ (Figure 8a) which only finds a counterpart in the computed spectrum of the $[Al^{3+} \cdot (L^{-})_2]^+$ complex ion with both thiazole nitrogens coordinated to the aluminium presented in Figure 8b. This band was predicted to originate from an asymmetric stretching of the F₃C-Carbon bond. Additionally, the band at 1230 cm⁻¹ is found in panel Figure 8c and d but is missing in panel b. It is noted that the experimental spectrum is slightly blue-shifted compared to the computed spectra for example, Figure 8b which somewhat hampers the structure identification. Beside these minor aspects the calculated IR spectrum presented in Figure 8b shows a good agreement with the experimental data set, justifying the structure assignment, which is consistent with the results of the other IRMPD analyses. It is interesting that exchanging oxygen in ligand 3 by sulphur in ligand 4 has a significant effect. Whereas in Figure 7 all isomers feature essentially planar ligands, the sulphur atoms when bound to the Al cation show significant pyramidalization (see Figure 8). A direct consequence of this is that the S-bound isomers are higher in energy with respect to the lowest energy isomer than the O-bound isomers in Figure 7.

3. Conclusions

The IRMPD spectroscopic results combined with a careful computational analysis of the gas-phase ion structures allowed an unambiguous structure elucidation of aluminium TMHA complex ions. According to our results cationic $[AI^{3+}\cdot(L^{-})_2]^+$ and anionic $[AI^{3+}\cdot(L^{2-})_2]^-$ species adopt tetrahedral arrangements with two planar bidentate ligands arranged around the central main group metal cation. In the examined complex ions the negatively charged enolate oxygen is coordinated to alumini-

> um, however, experimental evidence suggests that the second binding site of the bidentate ligands is determined by the aromatic character of the heterocycle that is, imidazole, oxazole and thiazole of the ligands. We only found those Lewis-basic nitrogens interacting with Al[™] whose free electron pairs are not directly involved in the delocalized aromatic π system. Although this straightforward explanation served well to understand the complete outcome of this study, it is remarkable that the aromaticity of the heterocycles governs the Al coordination sphere and outweighs the strong affinity of aluminium to oxvaen.

To the best of our knowledge this is the first time that the coordination sphere of such a highly charged, small and strongly polarizing, main group metal ion as Al^{III} has been investigated in the gas phase. The spectroscopic data set interpreted on the basis of in-depth computations provided a detailed view on the structure and the nature of cationic and anionic aluminium complexes, which could serve as a blueprint for other hard main group metal cations with Lewis-basic ligands of any kind, for example, bio-molecules, such as proteins.

Experimental Section

Materials

The TMHA compounds **1–4** were prepared using the general methods previously reported.^[15,19–21] Experimental details for the preparation, additional information on the materials used, and analytical data of compounds **1–4**, including ¹H and ¹³C NMR spectra, are presented in ref. [15]. Corresponding neutral $[AI^{3+}(L^{-})_{3}]$ complexes of TMHA ligands **1–4** were obtained in a quantitative yield from a reaction with trimethyl aluminium in toluene (see Scheme 3).

Mass Spectrometry

The aluminium complexes $[Al^{3+}\cdot(L^{-})_2]^+$ of ligands 1-4 were generated in the gas phase by (+)ESI-MS (Figure 1S in the Supporting Information). Additionally, (-)ESI-MS of a solution of $[Al^{3+}\cdot(L^{-})_3]$

complexes with ligand 1 showed signals referring to the deprotonated ligand 1 (L^- at m/z 227) and to a negatively charged aluminium complex ion $[\mathrm{AI}^{3+}{\cdot}(\mathrm{L}^{2-})_2]^-$ (see ion at m/z 479 in Figure 2S in the Supporting Information). Together with the cations both these anions were subjected to IRMPD-spectroscopic analysis. All precursor ions selected for IRMPD-MS were found in the gas phase with high abundances after phase transfer with ESI (see for example, Figure 1S in the Supporting Information). For the ESI-IRMPD-MS experiments and tandem MS experiments neutral [Al³⁺·(L⁻)₃] complexes were dissolved in CH₃CN in mM concentrations. Collision induced dissociation (CID) experiments with monoisotopic precursor ion selection were performed in the EB part of a Finnigan MAT 900 instrument with an EB-Quadrupole Ion Trap (QIT) configuration (ThermoFisher, Bremen, Germany) and have been described in detail elsewhere.^[24,45] Exact ion mass measurements were conducted on a LTQ-Orbitrap XL instrument (ThermoFisher Scientific) equipped with an ESI ion source (external calibration; resolution > 20000 fwhm). All exact ion masses reported were determined with an experimental error \leq 3 ppm.^[24,45]

Infrared Multiphoton-Dissociation Spectroscopy

A 4.7 T FTICR mass spectrometer was used for the IRMPD experiments and has been described in detail elsewhere. $^{[24,43-46,51]}$

Tunable radiation for the photodissociation experiments was generated by the free electron laser for infrared experiments (FELIX).^[46] For the present experiments, spectra were recorded over the wavelength range from 800 to 1800 cm⁻¹. Pulse energies were around 50 mJ per macropulse of 5 μ s duration, although they fell off to about 20 mJ toward the blue edge of the scan range. The full width at half maximum (fwhm) bandwidth of the laser was typically 0.5% of the central wavelength. Positive and negative aluminium complex ions were formed by electrospray ionization using a Micromass Z-Spray source with diluted CH₃CN solutions (concentration 0.5 mm, flow rate 10 μ Lmin⁻¹) of the appropriate neutral aluminium complexes [Al³⁺·(L⁻)₃] generated with ligand compounds 1-4. Solution flow rates ranged from 15 to 30 µL min⁻¹ and the electrospray needle was generally held at a voltage of +4.3-4.4 kV in (+)ESI and -3.8 kV in (-)ESI. Ions were accumulated in a hexapole trap for about 3 s prior to being injected into the ICR cell through an rf-octopole ion guide. Electrostatic switching of the dc bias of the octopole allows ions to be captured in the ICR cell without the use of a gas pulse, thus avoiding collisional heating of the ions.^[44,45] All complex ions were irradiated for 3 s, corresponding to interaction with 30 macropulses.

The precursor ions exhibit similar but complex fragmentation patterns upon collision induced dissociation and IRMPD which are not yet fully understood (Table 1S and Scheme 1S–4S in the Supporting Information) The IRMPD spectra were recorded by monitoring the intensity of the most abundant product ions and the depletion of the respective precursor ion as a function of IR frequency over the 800–1800 cm⁻¹ range. The IRMPD yield was determined from the precursor (I_p) intensity and the intensity of the product ions (Σ $I_{product ions}$) after laser irradiation at each frequency [Eq. (1)]:

IRMPD Yield =
$$\Sigma I_{\text{product ions}} / (I_{\text{P}} + \Sigma I_{\text{product ions}})$$
 (1)

The yield was normalized linearly with laser power to take into account any changes in laser power as the photon energy was scanned. $^{\rm [26,45]}$

Computations

All calculations were performed using Gaussian 09, version A.02.^[52] Gaussian was compiled using the Portland compiler, version 8.0-6 applying the Gaussian-supplied versions of BLAS^[53] and ATLAS.^[53,54] In all our calculations we used the B3LYP^[55] functional of density functional theory (DFT), since we (and others) have found that this functional gives excellent results for organo-metal compounds.^[24,45,56] The 6-311G**^[57,58] basis set was used on all atoms. In all calculations we used ultrafine integrals. All computed relative energies were obtained from converged electronic energies. Errors in energies were not quantified, but given the overall similarities between the structures, we assumed that relative energies and resulting energetic ordering were reasonably accurate except where stated otherwise.

In all our calculations we used the following procedure. For a given molecular cation, we started our optimizations from a number of chemically feasible starting positions. After convergence, we calculated frequencies in the harmonic approximation to check whether a minimum was found. These frequencies were subsequently used to generate the vibrational spectra using our own software. Frequencies as calculated overestimate the observed frequencies, because of approximations made in the calculations, such as for example, neglecting anharmonicity or the incomplete description of correlation in DFT. The overestimation of the calculated frequencies was corrected using the standard scaling approach with a scaling factor of 0.98.^[24, 56, 59] The Lorentzian line shape functions used to convolute the calculated spectra have a fwhm of 15 cm⁻¹.

As signal intensities observed in experimental IRMPD spectra are influenced by laser power fluctuations and non-linear excitation and/or saturation effects and because linear absorption spectra predicted by theory do not include any instrument-dependent effects at all, the results are jointly presented with relative intensities, such that the relative intensities for the major peaks roughly match. For the transition state calculations, we used the QST2 algorithm as implemented in Gaussian 09. All transition states were confirmed to be true transition states by the presence of a single imaginary frequency. Their validity to the process in question was checked by visual inspection.

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Keywords: aluminium(III) complexes · computational chemistry · gas-phase coordination modes · infrared multiphoton dissociation spectroscopy · mass spectrometry

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