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COMMUNICATION

Dihalo bismuth cations: unusual coordination properties and inverse solvent effects in Lewis acidity

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A series of well-defined cationic hepta-coordinate bismuth halides [BiX₂(py)₅][B(3,5-(CF₃)₂-C₆H₃)₄] (X = Cl, Br, I), stabilized only by substitutionally labile solvent molecules, were synthesized and fully characterized. Their apparent *D*_{5h} symmetry with a lone pair at the central atom is unprecedented for main group compounds. The potential of BiX₃ to show unexpectedly high Lewis acidities in moderately polar solvents is likely due to the formation of [BiX₂(solv)₅]⁺ and related ionic species.

Highly-coordinated and (potentially) hypervalent main group compounds with simple monodentate ligands have been subject of intense scientific discussions due to challenging questions in coordination chemistry and bonding theory.^{1,2} This includes well-known examples such as SF₆, IF₇, and BiPh₅.³ However, the fundamental understanding of these compounds becomes more challenging when a lone pair is present at the central atom of a heavy main group coordination entity. The stereoactivity of lone pairs in heavy main group compounds is of fundamental importance for their coordination chemistry, which enables applications in photocatalysis,⁴ non-linear optics,⁵ and in the design of ferroelectrics.⁶

In order to study the stereochemical activity of a lone pair in well-defined molecular compounds, the model complex should ideally i) bear only one type of ligand (or at least only one type of ligand at symmetry-equivalent coordination sites), ii) bear only monodentate ligands without large steric bulk, iii) show no strong intermolecular interactions, and iv) show no strong interactions between two or more ligands. Overall, well-defined

molecular main group compounds which bear one to nine monodentate ligands in addition to a lone pair at the central atom E have been discussed and may be described with the general formula EX_nL_m (X/L = monoanionic/neutral monodentate ligand; n+m = 1-9).^{7,8-11} Some cases have been studied in great detail: investigations into the remarkable case of XeF₆, for example, revealed two energetically close-lying structures in the gas phase (*O_h* and *C_{3v}* symmetry) and yet another ionic structure “[XeF₅]F” in the solid state.¹²

The choice of suitable model compounds is more challenging, when species with a lone pair at the central atom and more than six ligands are to be studied. Since the maximum accessible valence of a main group element with a lone pair is six, mixed ligand sets consisting of neutral and anionic ligands must be used in order to generate neutral species. If charged species are targeted, interactions with the counterion should be minimized (*vide supra*), and the counterion must be designed accordingly. Thus, examples of compounds EX_nL_m with n + m = 7 and a lone pair at the central atom E are extremely rare. In the case of a stereochemically *active* lone pair, a coordination number of eight would lead to a cube or a square antiprism as the coordination polyhedron. With a stereochemically *inactive* lone pair, a coordination number of seven would give structures with *C_{2v}* (capped trigonal prism), *C_{3v}* (capped octahedron), or *D_{5h}* (pentagonal bipyramid) symmetry. In this context, the complex ion [XeF₇]⁻ in the compounds Cs[XeF₇] and [NO₂][Xe₂F₁₃] has been established as a textbook example.¹³ The analysis of its coordination chemistry is on one hand simplified by the fact that seven identical ligands are present. On the other hand, it is further complicated by the presence of F...Cs contacts in Cs[XeF₇] and F₆XeF...XeF₆ contacts in [NO₂][Xe₂F₁₃]. The coordination geometry around the seven-coordinate xenon atom in Cs[XeF₇] and [NO₂][Xe₂F₁₃] was found to be capped octahedral (*C_{3v}*) and capped trigonal prismatic (*C_{2v}*), respectively, which led to the conclusion “that the structure of [XeF₇]⁻ is chiefly determined by the lattice symmetry, evidently because energy differences between the different possible geometries of the free anion are marginal”.¹³

Bismuth(III) compounds appear to be ideal candidates to study the influence of lone pairs at the central atom on the coordination chemistry of high-coordinate molecular species,

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because bismuth atoms can readily adopt high coordination numbers due to their large atomic radius and sufficient Lewis acidity.^{2,14} With compounds such as $[\text{Bi}(\text{H}_2\text{O})_9][\text{OTf}]_3$,^{10,11} $[\text{Bi}(\text{dmsO})_8][\text{ClO}_4]_3$,¹⁰ $[\text{Bi}(\text{SePMe}_3)_6][\text{OTf}]_3$,⁸ and $[\text{Bi}(\text{dmf})_8][\text{Bi}_3]_{12}$,¹⁵ coordination numbers of up to nine have been realized. A number of intriguing examples with seven-coordinate bismuth compounds such as $[\text{BiCl}_3(\text{py})_4]$,^{9,16} $[\text{Bi}_2(15\text{-crown-5})][\text{Bi}_2\text{I}_7]$,¹⁷ and related species^{18–21} have been reported. Nevertheless, molecular main group compounds with a coordination number of seven that meet the above-mentioned criteria for the analysis of a (potentially) stereochemically active lone pair have not been published to date.

We report here the synthesis, isolation and characterization of $[\text{BiX}_2(\text{py})_5][\text{B}(3,5\text{-}(\text{CF}_3)_2\text{-C}_6\text{H}_3)_4]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$), the first series of well-defined cationic bismuth halides stabilized only by substitutionally labile solvent molecules, along with a detailed analysis of their coordination chemistry.

$[\text{BiCl}_2(\text{py})_5][\text{BArF}]$ (**1-Cl**) was obtained by reaction of BiCl_3 with one equivalent of $\text{Ti}[\text{BArF}]$ in pyridine in 70% yield (Figure 1a, $[\text{BArF}]^- = [\text{B}(3,5\text{-C}_6\text{H}_3(\text{CF}_3)_2)_4]^-$, $\text{py} = \text{pyridine}$). This synthetic route also gave access to $[\text{BiX}_2(\text{py})_5][\text{BArF}]$ (**1-X**, $\text{X} = \text{Br}, \text{I}$) in high yields (85–86%). The ^1H NMR spectra of **1-X** in CD_2Cl_2 show the expected signal pattern for the bismuth-bound pyridine ligands, with significantly downfield-shifted resonances ($\Delta\delta = 0.17\text{--}0.25$ (**1-Cl**), $0.17\text{--}0.36$ (**1-Br**), and $0.08\text{--}0.29$ ppm (**1-I**)) compared to non-coordinating pyridine. The ^1H , ^{11}B , and ^{19}F NMR spectra also indicate the presence of the $[\text{BArF}]^-$ anion without strong directional bonding interactions between cation and anion.

Material suitable for single-crystal X-ray diffraction analysis was obtained by layering a pyridine solution of **1-X** with toluene and storage at -30°C . **1-Cl** crystallized in the monoclinic space group $P2_1/n$ with $Z = 4$ (Figure 1c). For compounds **1-Br** and **1-I**, the quality of the single-crystal X-ray diffraction data does not allow for a detailed discussion of bond parameters, but establishes the same connectivity as observed for **1-Cl** (see Supp. Inf.). Within the scope of this work, further crystallization experiments of the bismuth halides BiX_3 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) were performed. Layering a saturated pyridine solution of BiBr_3 with hexane led to the formation of colorless blocks of $[\text{BiBr}_2(\text{py})_5][\text{BiBr}_4(\text{py})_2]$ (**1*-Br**), containing the same seven-coordinate bismuth cation as **1-Br** but a $[\text{BiBr}_4(\text{py})_2]^-$ counter anion (Figure 1b). Unfortunately, the data obtained for **1*-Br** does not allow for a detailed discussion of bond parameters (see S3), but emphasizes that the ligand-induced disproportionation of bismuth halides is relevant not only with highly polar solvents/ligands or chelating ligands,¹⁴ but also for solutions of BiX_3 in moderately polar solvents such as pyridine.

The bismuth atom in **1-Cl** is seven-coordinate and shows no directional bonding interactions with the $[\text{BArF}]^-$ counter anion. The $\text{Cl}\text{--}\text{Bi}\text{--}\text{Cl}$ axis is close to linear ($\text{Cl1}\text{--}\text{Bi1}\text{--}\text{Cl2}$, 174.4°), and the $\text{N}\text{--}\text{Bi}\text{--}\text{N}$ angles between neighboring pyridine ligands range between 69.9° and 75.2° . Thus, **1-Cl** adopts a very slightly distorted regular pentagonal bipyramidal coordination geometry with apparent D_{5h} symmetry. The chlorine atoms are located in the axial positions and the pyridine ligands are found in the equatorial plane with only minor deviations from the ideally expected bond angles of 180° ($\text{Cl1}\text{--}\text{Bi1}\text{--}\text{Cl2}$) and 72° ($\text{N}\text{--}\text{Bi}\text{--}\text{N}$), respectively. Notably, **1-Cl** shows no signs of a stereochemically active lone pair. This is in contrast to bismuth compounds with other coordination geometries, such as $\text{BiCl}_3(15\text{-crown-5})$,¹⁷ $[\text{BiCl}_2(18\text{-crown-6})_2][\text{Bi}_2\text{Cl}_8]$,²² $[\text{Bi}(\text{NiPr}_2)_2(\text{thf})_3][\text{BArF}]$,²³ and related compounds,^{24,25} for which the stereochemical activity of bismuth-centered lone pairs has frequently been discussed. It also contrasts with seven-coordinate $[\text{BiCl}_3(\text{py})_4]$, which bears one Cl ligand in the equatorial plane and shows significant deviations from a pentagonal bipyramidal coordination geometry, since angles between neighboring ligands in the equatorial plane range from 64.6° to 80.1° .⁹ Other seven-coordinate bismuth species contain chelating ligands and/or significant intermolecular interactions, which hamper the identification of the coordination geometry that would be preferred in the absence of such constraints.^{18–21} Thus, compound **1-Cl** represents – to the best of our knowledge – the first example of a main group compound in a regular pentagonal bipyramidal coordination geometry with a lone pair at the central atom. When put into context with the aforementioned complexes $\text{Cs}[\text{XeF}_7]$ (capped octahedral, C_{3v}) and $[\text{NO}_2][\text{Xe}_2\text{F}_{13}]$ (capped trigonal prismatic, C_{2v}),¹³ **1-Cl** with its apparent D_{5h} symmetry completes the series of energetically favorable coordination geometries of seven-coordinate compounds with a lone pair at the central atom.

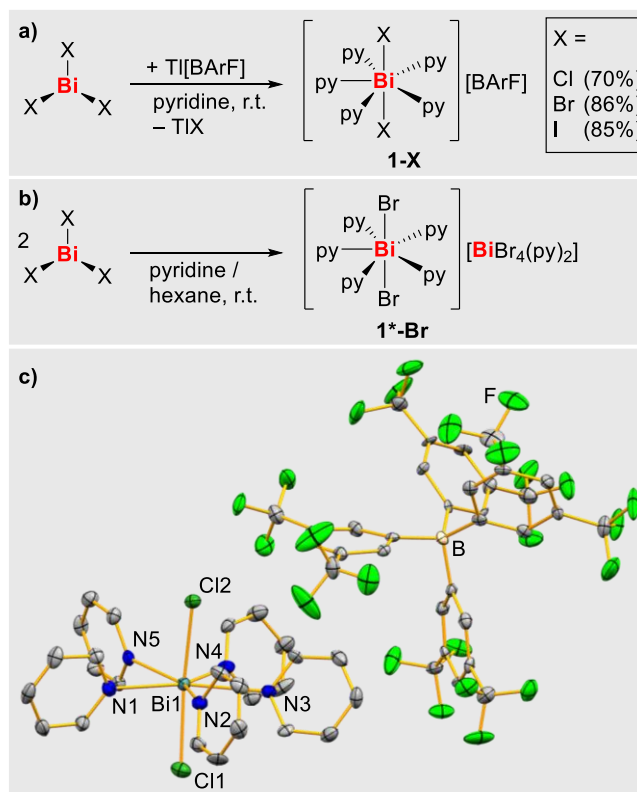


Figure 1. a) Reaction of BiX_3 with $\text{Ti}[\text{BArF}]$. $\text{X} = \text{Cl}, \text{Br}, \text{I}$. $[\text{BArF}]^- = [\text{B}(3,5\text{-C}_6\text{H}_3(\text{CF}_3)_2)_4]^-$, $\text{py} = \text{pyridine}$. b) Solvent induced disproportionation of BiBr_3 to form **1*-Br**. c) Molecular structure of **1-Cl** in the solid state. Displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms and split positions are omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$): $\text{Bi1}\text{--}\text{Cl1}$, 2.666(2); $\text{Bi1}\text{--}\text{Cl2}$, 2.626(2); $\text{Bi1}\text{--}\text{N1}\text{--}\text{N5}$, 2.539(7)–2.621(7); $\text{Cl1}\text{--}\text{Bi1}\text{--}\text{Cl2}$, $174.35(7)$; $\text{N1}\text{--}\text{Bi1}\text{--}\text{N2}$, $73.7(2)$; $\text{N1}\text{--}\text{Bi1}\text{--}\text{N5}$, $75.2(2)$; $\text{N2}\text{--}\text{Bi1}\text{--}\text{N3}$, $69.9(2)$; $\text{N3}\text{--}\text{Bi1}\text{--}\text{N4}$, $70.3(2)$; $\text{N4}\text{--}\text{Bi1}\text{--}\text{N5}$, $71.0(2)$.

The Bi–Cl distances of 2.626(2)–2.666(2) Å in cationic **1-Cl** are on average (2.646(2) Å) and within the limit of the double standard deviation only marginally shorter than the corresponding Bi–Cl^{axial} bonds in neutral [BiCl₃(py)₄] (2.656(3)–2.658(3) Å, average: 2.662(3) Å).⁹ In comparison, the Bi–N bonds in **1-Cl** (2.539(7)–2.621(7) Å, average: 2.585(7) Å) are considerably shorter than those in [BiCl₃(py)₄] (2.539(12)–2.816(14) Å, average: 2.664(14) Å).⁹ The shortening of Bi–X bonds (X = C, N) upon cationization was ascribed to the higher Lewis acidity of the charged species and has previously been noted for carbon- and nitrogen-centered ligands in the coordination sphere of bismuth.¹⁴ These findings are confirmed by natural bond orbital (NBO) analyses, which revealed averaged interaction energies of 62.3 kcal·mol⁻¹ and 59.0 kcal·mol⁻¹ for the Bi–N interactions in **1-Cl** and [BiCl₃(py)₄], respectively (ESI).

In an attempt to experimentally determine and compare the Bi–Cl bond strengths in compounds BiCl₃, [BiCl₃(py)₄], and **1-Cl**, they were subjected to Raman spectroscopic investigations. Sufficiently well-resolved spectra with characteristic bands in the range of 225–310 cm⁻¹ were obtained (ESI). Furthermore, DFT calculations reproduced the overall experimental spectra well, but at the same time, indicated that Bi–Cl and Bi–N vibrations are strongly coupled in [BiCl₃(py)₄], and **1-Cl**, which excluded the reliable determination of Bi–Cl bond strengths through this approach.

In order to circumvent this problem and to investigate the influence of pyridine coordination on the Bi–Cl bond strengths, we calculated the heterolytic Bi–Cl bond dissociation energies (BDEs) of [BiCl₃(py)_n]⁺ (*n* = 0–4) compounds. The results indicate that pyridine coordination facilitates heterolytic Bi–Cl bond cleavage by decreasing the heterolytic Bi–Cl BDEs from 63.0 (*n* = 0) to 18.6 (*n* = 4) kcal mol⁻¹.

Aiming at the identification of a global minimum for [BiCl₂(py)_n]⁺ type complexes, possible coordination geometries were systematically investigated (*n* = 0–6, Figure S8). In this study, [BiCl₂(py)₅]⁺ was found to be the minimum energy species, confirming that the experimentally found structure is not a result of crystal packing effects in the solid state (Figure 2). Importantly, no indications for a stereochemical activity of the bismuth-centered lone pair were found for [BiCl₂(py)₅]⁺, which is in contrast to six-coordinate [BiCl₂(py)₄]⁺ (ESI) and previously reported for [Bi(N₃)₆]³⁻.²⁵ Thus, the steric pressure of seven ligands and positive charge in [BiCl₂(py)₅]⁺ suppress the stereochemical activity of the bismuth-centered lone pair.

Neutral bismuth halides BiX₃ (X = Cl, Br, I) have found widespread use in Lewis-acid catalysis of organic reactions such as the nucleophilic substitution of propargylic alcohols with amides, the ring closure of δ-trialkylsilyloxy aldehydes to give tetrahydropyrans, and addition/cyclo-isomerization sequences for the construction of fluorenes.²⁶ The fact that compound [BiBr₂(py)₅][BiBr₄(py)₂] (**1*-Br**) was formed from BiBr₃ by pyridine-induced disproportionation suggests that in fact ionic bismuth species rather than neutral BiX₃ may be key components in these Lewis acid catalyses. Furthermore, it would suggest an inverse solvent effect: commonly, polar solvents decrease the Lewis acidity of a species by competing

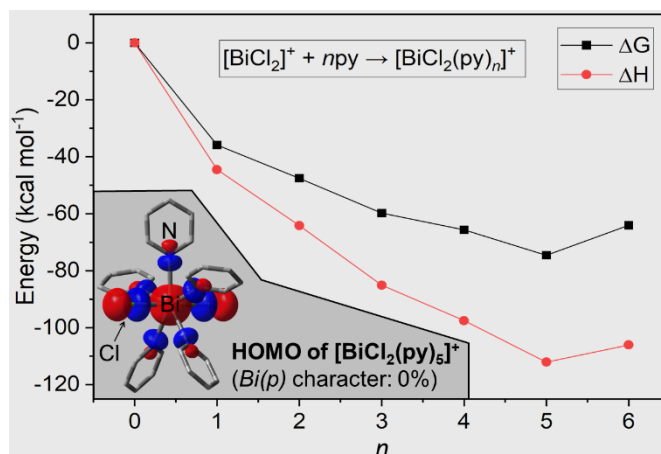


Figure 2. Graph: ΔH and ΔG values for the association of [BiCl₂]⁺ with pyridine. Inlay: HOMO of [BiCl₂(py)₅]⁺. These data were obtained from DFT calculations (ESI).

with a substrate for the Lewis acidic binding site. While this situation is still valid in solutions of BiX₃ in polar solvents, a polar reaction medium would also support the formation of ionic species through solvent-induced disproportionation, thereby generating more Lewis acidic bismuth cations such as **1*-Br**. In order to investigate the presence of charged species in solutions of BiX₃ in moderately polar solvents, conductivity measurements of BiX₃ in THF, acetonitrile, and pyridine were performed. Assuming that the reaction 2 BiX₃ ⇌ [BiX₂(L)_n][BiX₄(L)_m] dominates the generation of ionic species, the Stokes-Einstein and the Nernst-Einstein relation were employed to estimate the degree of dissociation of BiX₃ (Table 1, for details see ESI). While the formation of ionic species is small in THF (~1%), it is considerably large for the more polar solvents acetonitrile and pyridine (10–28%). Thus, there are two opposing trends for the Lewis acidity of BiX₃ in polar media: the potential of polar solvents to block Lewis acidic binding sites would decrease the Lewis acidity of BiX₃, while their ability to support the formation of ionic species would increase the Lewis acidity of BiX₃. In order to experimentally evaluate the Lewis acidity of BiX₃ in polar media, the Gutmann-Beckett method using OPET₃ as a hard donor and the modified Gutmann-Beckett method using EPMe₃ as softer donors (E = S, Se) were employed. In these methods, acceptor numbers (ANs) are determined from ³¹P NMR spectroscopic chemical shifts, where higher acceptor numbers suggest a higher Lewis acidity (ESI). While the formation of precipitates in some of the cases hampered a full quantitative interpretation of the experiments, especially BiBr₃ proved to show a remarkably increased Lewis acidity in acetonitrile (AN(OPET₃) = 68; AN(SPMe₃) = 83; AN(SePMe₃) = 78), when compared to dichloromethane as a less polar solvent^{8,27} (AN(OPET₃) = 30; AN(SPMe₃) = 17; AN(SePMe₃) = 11; ESI).

Table 1. Calculated degrees of dissociation [%] of BiX₃ (X = Cl, Br, I) solutions in pyridine, THF and MeCN according to 2 BiX₃ ⇌ [BiX₂(L)_n][BiX₄(L)_m] (L = THF, MeCN, Pyridine).

solvent	BiCl ₃	BiBr ₃	BiI ₃
THF	0.6	1.2	1.6
MeCN	10.9	11.2	..[a]
Pyridine	10.1	13.9	27.5

[a] No data are reported due to the poor solubility of BiI₃ in MeCN (ESI).

In summary, three distinct seven-coordinate bismuth cations of type $[\text{BiX}_2(\text{py})_5][\text{B}(\text{3,5}-(\text{CF}_3)_2\text{-C}_6\text{H}_3)_4]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) were synthesized and characterized. They show a pentagonal bipyramidal coordination geometry and a stereochemically inactive lone pair. This adds the missing example of D_{5h} symmetry to the series of compounds featuring seven-coordinate main group species with a lone pair at the central atom, such as $[\text{XeF}_7]^-$ with C_{3v} or C_{2v} symmetry. $[\text{BiBr}_2(\text{py})_5][\text{BiBr}_4(\text{py})_2]$ is formed from BiBr_3 in pyridine solution via ligand-induced disproportionation. This and related ionic species are suggested to be responsible for the unusual “inverse solvent effect” reported here, i.e. more polar solvents can increase the Lewis acidity of BiX_3 .

Conflicts of interest

There are no conflicts to declare.

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