$[SbCl_2(\eta^2\text{-1,4-dt})(\mu_2\text{-1,4-dt})][AlCl_4]$: Ionic Liquid-based Synthesis of a Stibenium Cation (dt = dithiane)

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The reaction of antimony(III) chloride with 1,4-dithiane (1,4-dt) in the ionic liquid [BMIM]Cl ([BMIM]Cl: 1-butyl-4-methylimidazolium chloride) with an excess of the Lewis acid $AlCl_3$ results in the formation of a ligand-stabilized stibenium cation $[SbCl_2]^+$. 1,4-Dithiane simultaneously serves as a chelating η^2-ligand, exhibiting a boat-like conformation, as well as a bridging μ_2-ligand, exhibiting a chair-like conformation, with Sb^{3+} as the coordinating cation. Due to the bridging 1,4-dithiane ligands, a chain-like structural building unit $^1_\infty[SbCl_2(\eta^2\text{-1,4-dt})_{1/1}(\mu_2\text{-1,4-dt})_{2/2}]^+$ is formed.

Key words: Stibenium Cation, Ionic Liquid, Crystal Structure, 1,4-Dithiane

Introduction

Electron-rich pnictogen centers are known to react as Lewis acceptors although a lone pair is present at the main-group element [1, 2]. The resulting stibenium- or stibinidenium cations in the case of antimony, as well as comparable species of other pnictogens, are typically obtained as ligand-stabilized salts and lead to a wide range of different coordination compounds of the main-group elements. Stibenium cations most often form coordination compounds with group 15 elements, *i. e.*, N-, P-, As- or Bi-containing ligands [3 – 5]. In contrast, stibenium cations coordinated by group 16 elements are rare to date.

As a part of our studies concerning the benefit of ionic liquids (ILs) in inorganic synthesis, we studied their use in view of a coordination of chalcogen-containing ligands to pnictogen centers [6]. Lewis-acidic ionic liquids are known as suitable reaction media for the synthesis of inorganic compounds exhibiting novel structural building units and bonding situations [7]. This also includes cases of element-element bonding and low oxidation states of the main-group elements. Based on this strategy, the title compound $[SbCl_2(\eta^2\text{-1,4-dt})(\mu_2\text{-1,4-dt})][AlCl_4]$ was obtained that is constituted of a $[SbCl_2]^+$ stibenium cation. This stibenium cation is coordinated and interlinked by 1,4-dithiane (1,4-dt) as a ligand. Here, $[SbCl_2(\eta^2\text{-1,4-dt})(\mu_2\text{-1,4-dt})][AlCl_4]$ represents the first stibenium cation that is coordinated by group 16 elements. Surprisingly, 1,4-dt acts as a bidentate bridging ligand as well as a bidentate chelating ligand. Noteworthy, only three compounds of extended network structures with 1,4-dithiane as a linker have yet been reported. These examples comprise silver(I)- and indium(III)-based coordination compounds [8 – 10]. A simultaneous coordination of 1,4-dt as a bridging and chelating ligand is shown with the title compound for the first time.

Results and Discussion

$[SbCl_2(\eta^2\text{-1,4-dt})(\mu_2\text{-1,4-dt})][AlCl_4]$ was prepared by reaction of antimony(III) chloride and 1,4-dithiane in the Lewis-acidic ionic liquid $[BMIM][AlCl_4]$. The synthesis resulted in colorless crystals of the title compound. X-Ray structure analysis based on single crystals revealed $[SbCl_2(\eta^2\text{-1,4-dt})(\mu_2\text{-1,4-dt})][AlCl_4]$ to crystallize monoclinically in space group $P2_1/c$ with $Z = 4$ (Table 1). In addition to single-crystal structure analysis, the thermal behavior of the title compound was investigated by differential thermal analysis and thermogravimetry (DTA-TG).

According to the crystal structure analysis, $[\mathrm{SbCl_2}(\eta^2\text{-1,4-dt})(\mu_2\text{-1,4-dt})][\mathrm{AlCl_4}]$ is constituted of $[\mathrm{SbCl_2}(\eta^2\text{-1,4-dt})(\mu_2\text{-1,4-dt})]^+$ cations and $[\mathrm{AlCl_4}]^-$ anions (Fig. 1). Antimony is coordinated by two chlorine atoms forming a stibenium cation $[\mathrm{SbCl_2}]^+$ (Fig. 2). Herein, the Sb–Cl distances are almost equal in length (237.1 and 239.6 pm) which is in agreement with values reported for comparable stibenium compounds, including the phosphane-stabilized compound $[\mathrm{SbCl_2(PPh_2)_2}][\mathrm{AlCl_4}]$ (Sb–Cl: 239.0 pm) [2]. The Cl–Sb–Cl angle in the title compound is near to a rectangular arrangement (91.7°) (Table 2), whereas comparable compounds show a somewhat wider angle (*e. g.*, ∠(Cl–Sb–Cl) in $[\mathrm{SbCl_2(PPh_2)_2}]^+$ with 96.5° [2]). In addition to the direct Sb–Cl bonding, long-ranging Sb–$\mathrm{Cl_{Al}}$ contacts (up to 380 pm) to neighboring $[\mathrm{AlCl_4}]^-$ anions are observed (Fig. 3). These Sb–$\mathrm{Cl_{Al}}$ contacts are below the sum of the van der Waals radii of antimony and chlorine ($d_{\mathrm{Sb+Cl}}$ = 400 pm) [11]. The $[\mathrm{AlCl_4}]^-$ counterions show a mean Al–Cl distance of 211 pm and a mean Cl–Al–Cl angle of 110°, indicating the expected distorted tetrahedral shape (Fig. 3). These data are well in accordance with those of known tetrachloridoaluminates(III) [12]. Two chlorine atoms of the $[\mathrm{AlCl_4}]^-$ anion (Cl5, Cl6) show somewhat increased parameters of thermal motion (Fig. 3). This finding can be explained by two sets of triple hydrogen bonding of these two chlorine atoms with the chelating 1,4-dt ligand.

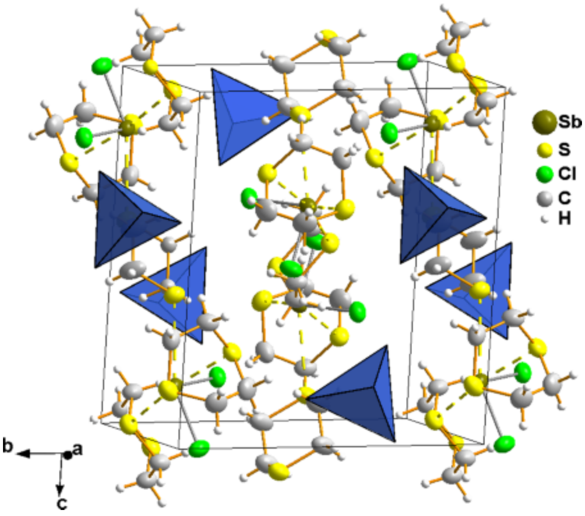

Fig. 1. Unit cell of $[\mathrm{SbCl_2}(\eta^2\text{-1,4-dt})(\mu_2\text{-1,4-dt})][\mathrm{AlCl_4}]$.

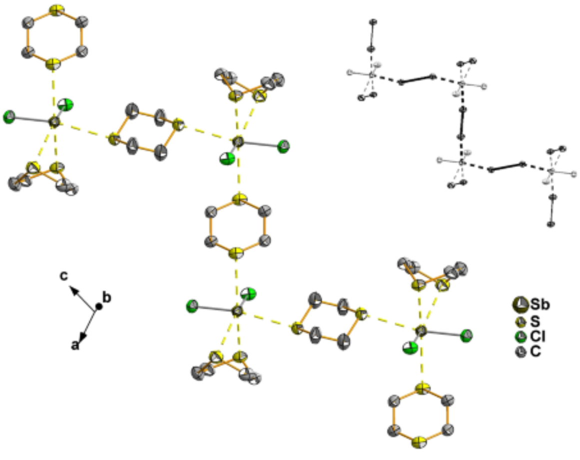

Fig. 2. Zig-zag-shaped arrangement of the $^1_\infty[\mathrm{SbCl_2}(\eta^2\text{-1,4-dt})_{1/1}(\mu_2\text{-1,4-dt})_{2/2}]^+$ cation (displacement ellipsoids with 50 % probability of finding).

The $[\mathrm{SbCl_2}]^+$ stibenium cations are interlinked *via* three molecules of 1,4-dithiane (Fig. 2). Together with the chlorine atoms, thus a pseudo-octahedral coordination of the central antimony atom is observed (Fig. 3). Although ligand-stabilized stibenium cations are known, such species most often exhibit phosphorus- or nitrogen-containing ligands [13–15]. As an additional feature, the 1,4-dithiane ligand in $[\mathrm{SbCl_2}(\eta^2\text{-1,4-dt})(\mu_2\text{-1,4-dt})]^+$ serves as both, a bidentate bridging ligand as well as a bidentate chelating ligand (Figs. 2, 3). While the chelating 1,4-dt exhibits a boat-type conformation, the bridging 1,4-dt shows a chair-type conformation. Noteworthy, two orientations of the bridging 1,4-dt are present and cause a certain displacement of the sulfur atoms (Fig. 3). This disorder was tackled by split-atom positions that were refined with non-fixed site occupation factors, resulting in an occupation of 83 % (S2A) and 17 % (S2B). 1,4-dt has been frequently described to act as a bidentate, bridging ligand (*e. g.*, in $[\mathrm{RuCl_2(dpb)(1,4\text{-}dt)}]$ and $\{[\mathrm{Ag_2(1,4\text{-}dt)_3}][\mathrm{CF_3SO_3}]_2\}_\infty$) [10, 16]) and typically exhibits a chair-like conformation between two metal centers similar to the situation in the title compound. Compounds with 1,4-dt as a bidentate, chelating ligand are known for altogether five compounds [16–20]. A simultaneous combination of both types of coordination – bridging and chelating – to the best of our knowledge has not yet been observed for 1,4-dt as

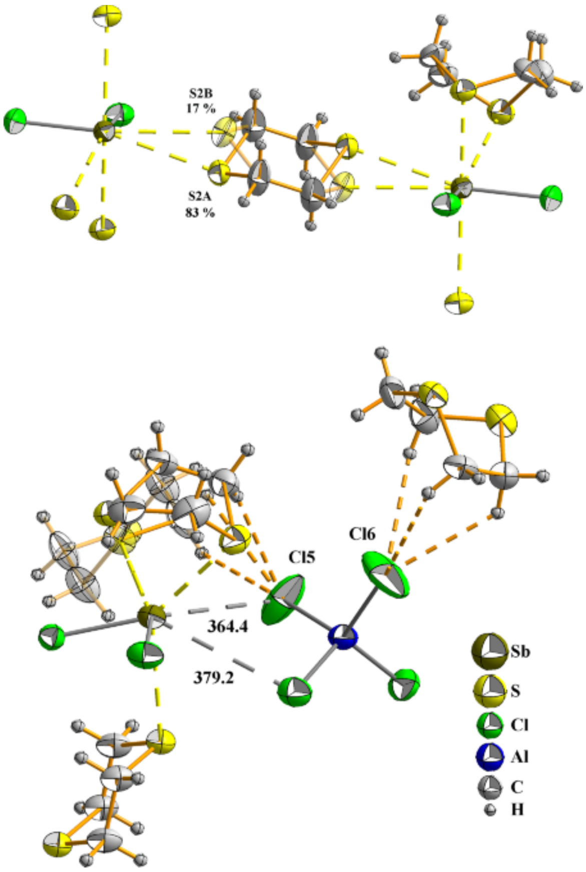

Fig. 3. Structure and distances of the ${}^{1}_{\infty}[\mathrm{SbCl_2}(\eta^2\text{-1,4-dt})_{1/1}(\mu_2\text{-1,4-dt})_{2/2}]^+$ cation (with displacement of the 1,4-dt ligand) and of the $[\mathrm{AlCl_4}]^-$ anion (all distances in pm; displacement ellipsoids with 50 % probability of finding).

a ligand. This finding can be ascribed to the absence of alternative ligands for coordination as well as to the weakly coordinating properties of the ionic liquid.

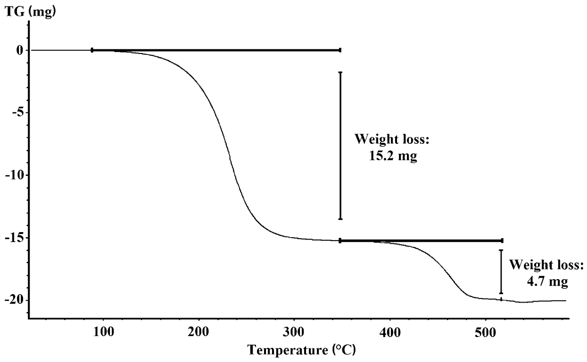

Fig. 4. Thermal decomposition of $[\mathrm{SbCl_2}(\eta^2\text{-1,4-dt})(\mu_2\text{-1,4-dt})][\mathrm{AlCl_4}]$ (total sample weight 20.1 mg).

Table 1. Crystallographic data of $[\mathrm{SbCl_2}(\eta^2\text{-1,4-dt})(\mu_2\text{-1,4-dt})][\mathrm{AlCl_4}]$.

Empirical formula	$\mathrm{SbS_4Cl_6AlC_8H_{16}}$
Crystal system	monoclinic
Space group	$P2_1/c$
Lattice parameters	$a = 14.879(3)$ Å $b = 10.825(2)$ Å $c = 13.509(3)$ Å $\beta = 109.17(3)°$ $V = 2055.2(7)$ Å^3
Formula units per cell	$Z = 4$
Calculated density	$\rho = 1.94\ \mathrm{g\,cm^{-3}}$
Measurement device	image plate diffractometer IPDS II (Stoe, Darmstadt) $\lambda(\mathrm{Mo}K_\alpha) = 0.71073$ Å; $T = 200$ K
Measurement limits	$2.9° \le 2\theta \le 58.6°$ $0 \le h \le 20$, $-14 \le k \le 14$, $-18 \le l \le 17$
Linear absorption coefficient	$\mu = 2.6\ \mathrm{mm^{-1}}$
Crystal size	$0.17 \times 0.12 \times 0.04\ \mathrm{mm^3}$
Absorption correction	numerical (T_{min}: 0.49; T_{max}: 0.80)
Number of reflections	10034 measured; thereof 5191 independent
Data averaging	$R_{\mathrm{int}} = 0.023$
Structure refinement	full matrix least-squares on F_0^2, anisotropic displacement parameters for all non-hydrogen atoms
Number of parameters	192
Figures of merit	$R1 = 0.055$ $R1$ (3818 $F_0^2 > 2\,\sigma F_0^2$) $= 0.041$ $wR2 = 0.120$ (all data) GooF $= 0.98$
Residual electron density	$-0.91/+0.82$ e Å^{-3}

The Sb–S distances confirm a coordinative bonding between $[\mathrm{SbCl_2}]^+$ and 1,4-dt. Thus, distances in a range of 269.5 to 323.2 pm are observed (Table 2, Fig. 3) that are significantly elongated in comparison to those in binary compounds such as $\mathrm{Sb_2S_3}$ (Sb–S: 249 pm) or antimony thiolates (Sb–S: 241 pm) [21, 22]. Considering the coordinative Sb–S interactions, a chain-like arrangement of the cationic building unit ${}^{1}_{\infty}[\mathrm{SbCl_2}(\eta^2\text{-1,4-dt})_{1/1}(\mu_2\text{-1,4-dt})_{2/2}]^+$ becomes obvious (Fig. 2). Within these chains, the bridging 1,4-dt molecules are linking *via* their S atoms which are located at the equatorial positions of $\mathrm{Sb^{3+}}$. This coordination results in a zig-zag-shaped chain. Some C–H groups of the 1,4-dt ligand are involved in various intermolecular hydrogen bonding interactions to chlorine atoms of neighboring $[\mathrm{SbCl_2}(\eta^2\text{-1,4-dt})(\mu_2\text{-}$

Table 2. Selected bond lengths and angles of the [SbCl$_2$(η^2-1,4-dt)(μ_2-1,4-dt)]$^+$ cation.

Atoms	Distance (pm)	Atoms	Angle (deg)
Sb1–Cl1	237.1(1)	Cl1–Sb1–Cl2	91.7(1)
Sb1–Cl2	239.6(1)	Cl1–Sb1–S1	84.8(1)
Sb1–S1	302.3(1)	S1–Sb1–S2	108.5(1)
Sb1–S2	323.2(1)	S4–Sb1–Cl2	82.5(1)
Sb1–S3	300.2(1)	S3–Sb1–Cl1	79.3(1)
Sb1–S4	269.5(1)	C1–S1–C2	100.5(1)

1,4-dt)]$^+$ cations and [AlCl$_4$]$^-$ anions. The C–H···Cl distances range between typical values of 267 to 333 pm [23].

Finally, the thermal behavior of [SbCl$_2$(η^2-1,4-dt)(μ_2-1,4-dt)][AlCl$_4$] was analyzed by performing thermogravimetry (Fig. 4). Upon heating to 600 °C, the title compound exhibits a significant weight loss of about 76 % between 120 and 300 °C. This can be attributed to an evaporation of SbCl$_3$ and 1,4-dithiane (calcd. 77.8 %). When increasing the temperature to more than 380 °C, a second decomposition step (weight loss: 23 %) occurred that can be ascribed to an evaporation of Al$_2$Cl$_6$ (calcd. 22.2 %). These findings match well with the respective boiling points of SbCl$_3$ (T_{bp}(SbCl$_3$): 223 °C) and the ligand (T_{bp}(1,4-dt): 200 °C). Evaporation of the AlCl$_3$ is observed at rather high temperatures, which can be ascribed to the interaction of this strong Lewis acid with Al$_2$O$_3$ as the crucible material.

Conclusions

[SbCl$_2$(η^2-1,4-dt)(μ_2-1,4-dt)][AlCl$_4$] consists of [SbCl$_2$]$^+$ stibenium cations that are interlinked to zig-zag chains *via* 1,4-dithiane as a ligand. [AlCl$_4$]$^-$ is positioned between the $^1_\infty$[SbCl$_2$(η^2-1,4-dt)$_{1/1}$(μ_2-1,4-dt)$_{2/2}$]$^+$ chains as a weakly coordinating anion. In general, stibenium cations that are stabilized by chalcogen-containing ligands are rare to date. The coordinative situation of the 1,4-dt ligand is unusual since it simultaneously serves as a bidentate chelating ligand as well as a bidentate bridging ligand. Both types of coordination are known but, till now, not realized in a single compound. Notably, chelating 1,4-dt exhibits a boat-like conformation, whereas bridging 1,4-dt shows a chair-like conformation. The formation of [SbCl$_2$(η^2-1,4-dt)(μ_2-1,4-dt)][AlCl$_4$] as a coordination compound is based on the ionic-liquid system and its weakly coordinating properties. Perspectively, this strategy of reaction could be used to realize many more coordination compounds of electron-rich pnictogen centers with unusual bonding and coordination situation.

Experimental Section

Materials and synthesis

The experiments were carried out under standard Schlenk and argon glove box techniques. Reactions were performed in argon-filled and sealed glass ampoules that were dried at 300 °C before use. The commercially available starting materials antimony(III) chloride (99.99 %, Sigma-Aldrich), aluminum(III) chloride (99.99 %, Sigma-Aldrich) and 1,4-dithiane (97 %, ABCR) were dried in vacuum for 24 h. To remove all traces of water, the commercially available ionic liquid [BMIM]Cl (Iolitec) was dried at 120 °C for two days in vacuum prior to use.

To synthesize [SbCl$_2$(η^2-1,4-dt)(μ_2-1,4-dt)][AlCl$_4$], 100 mg (0.44 mmol) of antimony(III) chloride, 105.4 mg (0.876 mmol) of 1,4-dithiane and 233.8 mg (1.75 mmol) of aluminum(III) chloride were reacted in the ionic liquid [BMIM]Cl at 75 °C for 5 days. Colorless crystals were obtained after cooling to room temperature with a rate of 1 K/h. These crystals were separated from the ionic liquid by filtration through a glass filter, followed by washing twice with 2 mL of dried diethyl ether. Finally, the title compound was dried in a vacuum overnight and obtained with a yield of about 70 %.

Characterization and analytical tools

For single-crystal structure analysis suitable crystals were chosen and fixed in glass capillaries with inert oil (KEL-F). Complete intensity data sets were collected with an IPDS II diffractometer (Stoe, Darmstadt) using MoK_α radiation (λ_α: 71.073 pm, graphite monochromator). Data reduction was performed using the program package X-AREA [24]. The structure was solved by Direct Methods using SHELXS-97 [25]. Anisotropic refinement on $2\sigma F^2$ was carried out for all non-hydrogen atoms by full-matrix least-squares methods using the program SHELXL-97 [26]. Disorder of the bridging ligand's sulfur atoms was observed and tackled by split atom positions with 83 and 17 % occupation (Fig. 3). The positions of the H atoms were modelled based on idealized C–H bonds using a riding model. A numerical absorption correction was applied using the program X-RED [27]. Crystallographic data and structure refinement details are summarized in Table 1. Selected bond lengths and angles of the title compound are listed in Table 2. Crystallographic illustrations were created with DIAMOND [28].

CCDC 937474 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Differential thermal analysis/thermogravimetry (DTA/TG) was performed with a Netzsch STA 409C instrument applying α-Al_2O_3 as a crucible material and reference. The samples were heated under N_2 flow to 600 °C with a rate of 10 K min^{-1}. The resulting data were baseline-corrected by subtracting the results of a measurement with an empty crucible.

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