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Crystal structures of the tetrachloridoaluminates(III) of rubidium(I), silver(I), and lead(II)

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Abstract: The reactions of the binary metal chlorides AgCl, RbCl and $PbCl_2$ at $T = 180°C$ in the ionic liquid [BMIm]Cl · $4AlCl_3$ (BMIm = 1-*n*-butyl-3-methylimidazolium) yielded air-sensitive, colorless, high-quality crystals of their tetrachloridoaluminate(III) salts. Thereby, the obstructions that hinder proper crystallization of these compounds from pristine $AlCl_3$ melts were circumvented. X-ray diffraction on single-crystals revealed a monoclinic structure (space group $P2_1/c$) for $Ag[AlCl_4]$, which unexpectedly has a closer relation to $Cu[AlCl_4]_2$ than to $Cu[AlCl_4]$. $Rb[AlCl_4]$ crystallizes in the baryte structure type (orthorhombic, *Pnma*), and $Pb[AlCl_4]_2$ is isotypic to α-$Sr[GaCl_4]_2$ (orthorhombic, *Pbca*).

Keywords: crystal structure; ionic liquids; tetrachloridoaluminate.

Dedicated to: Professor Arndt Simon on the occasion of his 80th birthday.

1 Introduction

Ternary compounds of the type $M[AlCl_4]_n$, where M presents a main-group or transition metal in oxidation state n, have been known for several decades, starting with the determination of the crystal structure of $Na[AlCl_4]$ [1]. To date, a total of 34 different elements had their tetrachloridoaluminates synthesized and subsequently structurally characterized (Fig. 1) [1–34]. Among them is $Y[AlCl_4]_3$, which was published by Simon et al. in 1995 [31]. However, there are several cases of reported $M[AlCl_4]_n$ salts of which no crystal structure has been determined, although the compound itself has been known for years or even decades. $Ag[AlCl_4]$, one of the title compounds, first mentioned by Kendall et al. in 1923 [35] is such a case and has been cited in almost a dozen publications ranging from electrochemical studies [36] to possible applications as a gas-adsorbent material [37].

This lack of structural analysis can be attributed to the established preparation method of these ternary compounds. A commonly encountered method to synthesize tetrachloridoaluminates is heating a mixture of $AlCl_3$ with the corresponding metal chloride near the sublimation point of $AlCl_3$. The resulting homogeneous melts often crystallize as powders of poor crystallinity. Usually, this can be prevented through gas-phase reactions in which, depending on the melting point of the metal chloride, either $AlCl_{3(g)}$ acts as a transporting agent or dimeric $Al_2Cl_{6(g)}$ reacts with the gaseous species of the starting compound. However, this method yielded single-crystals of sufficient quality for a structural analysis for neither $Ag[AlCl_4]$ nor $Rb[AlCl_4]$. $Pb[AlCl_4]_2$ was synthesized by Müller in 2012 [34]. However, we found no mention of its crystal structure in any database or peer-reviewed journal. Here, we present the result of our syntheses in an ionic liquid (IL) alongside with the crystal structures of these three tetrachloridoaluminates.

2 Results and discussion

2.1 Preparative results and role of the ionic liquid

The dissolution of AgCl, RbCl, or $PbCl_2$ in the Lewis-acidic ionic liquid [BMIm]Cl · $4AlCl_3$ (BMIm = 1-*n*-butyl-3-methylimidazolium) at 180–200°C and subsequent cooling of the reaction mixture to room temperature resulted in the precipitation of colorless, air sensitive, plank-shaped crystals of $Ag[AlCl_4]$, $Rb[AlCl_4]$ or $Pb[AlCl_4]_2$. Crystals of the silver and rubidium compound were not obtained at all or only in insufficient quality for single-crystal measurements by reactions in pristine $AlCl_3$, whereas proper crystallization of the lead salt was also successful in an $AlCl_3$ melt. The role of the IL can be classified as that of a solvent,

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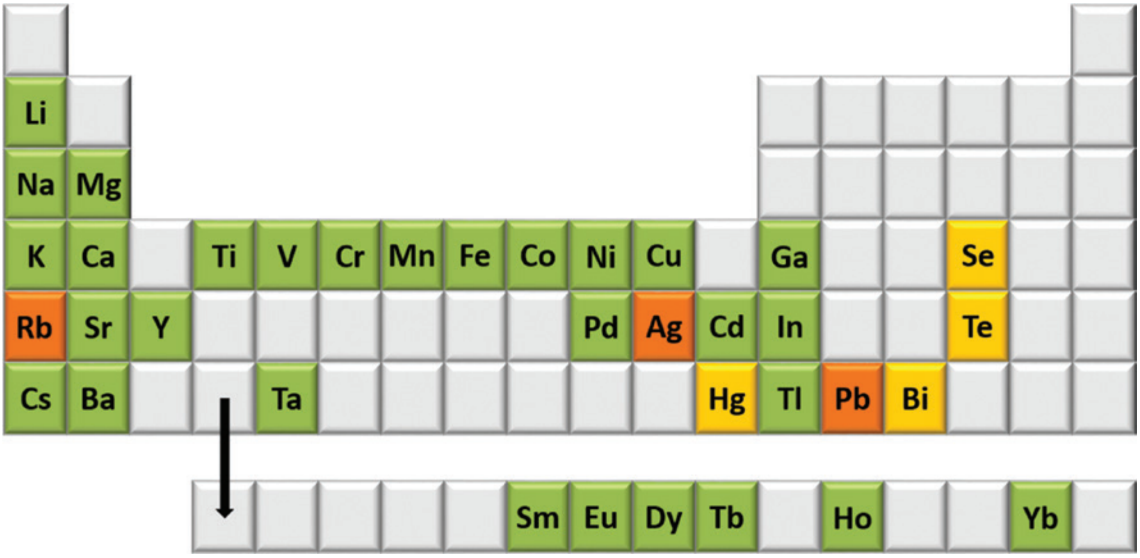

Fig. 1: Overview of elements with structurally characterized tetrachloridoaluminate salts. Green: ternary salts of the type $M[AlCl_4]_n$; yellow: ternary salts including polycations $M_y[AlCl_4]_x$; orange: discussed in this work.

supporting the crystal growth, as well as of a reagent, providing the $[AlCl_4]^-$ ions for all three compounds.

2.2 The crystal structure of $Ag[AlCl_4]$

X-ray diffraction analysis on a single crystal of silver(I)-tetrachloridoaluminate(III) revealed a monoclinic structure in the space group $P2_1/c$ (no. 14) with four formula units per unit cell and lattice parameters $a = 711.8(1)$, $b = 661.1(1)$, $c = 1343.4(2)$ pm and $\beta = 92.26(1)°$ at $T = 296(1)$ K. Atomic parameters and interatomic distances are listed in Tables S1 and S2 of the Supporting Information available online. In the structure of $Ag[AlCl_4]$, each silver atom is surrounded by two η^2- and two η^1-coordinating $[AlCl_4]^-$ tetrahedra, forming a distorted octahedral coordination sphere of chloride ions (Fig. 2). The coordination number of six is unusually high for silver(I) ions, as it is only found in about 4% of its coordination compounds, according to the Inorganic Crystal Structure Database (ICSD) [38].

The position of the silver ions in the structure of $Ag[AlCl_4]$ could not be determined reliably with the use of a second-order displacement tensor. It was necessary to introduce a second atomic position instead, to compensate for the irregular shape of the electron density, which can be attributed to an increased oscillation of the atom in the soft anionic structure of $[AlCl_4]^-$ tetrahedra. The Ag–Cl distances range from 262.3(3) to 305.2(3) pm, which deviates significantly from the 277.4(1) pm observed in AgCl [39]. When compared to the benzene stabilized C_6H_6-$Ag[AlCl_4]$ however, the interatomic distances match almost perfectly, with a range of 259(2)–304(3) pm observed in the organometallic compound [40]. The $[AlCl_4]^-$ tetrahedra are slightly distorted, with Al–Cl distances of 212.3(2)–215.1(2) pm. This distortion is a common phenomenon for compounds containing tetrahedral anions and has also been observed in other tetrachloridoaluminates, e.g. $Li[AlCl_4]$, $Na[AlCl_4]$, or $K[AlCl_4]$ [1, 17, 23]. Therefore, it will not be mentioned further in the following. When considering only silver(I) and aluminum(III) cations, the structure of $Ag[AlCl_4]$ can be regarded as a distorted derivate of the β-tin structure type (Fig. S2a). In $Ag[AlCl_4]$, two of these networks are

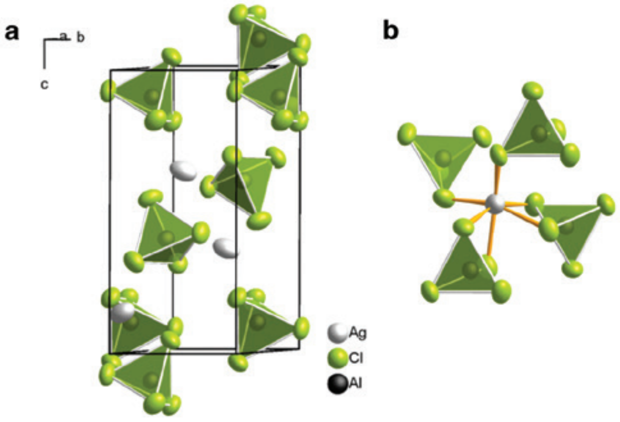

Fig. 2: (a) Crystal structure of $Ag[AlCl_4]$. (b) Distorted octahedral coordination of the silver ion formed by chloride ions of four $[AlCl_4]^-$ tetrahedra. Ellipsoids comprise 80% of the probability densities of the atoms at $T = 296$ K.

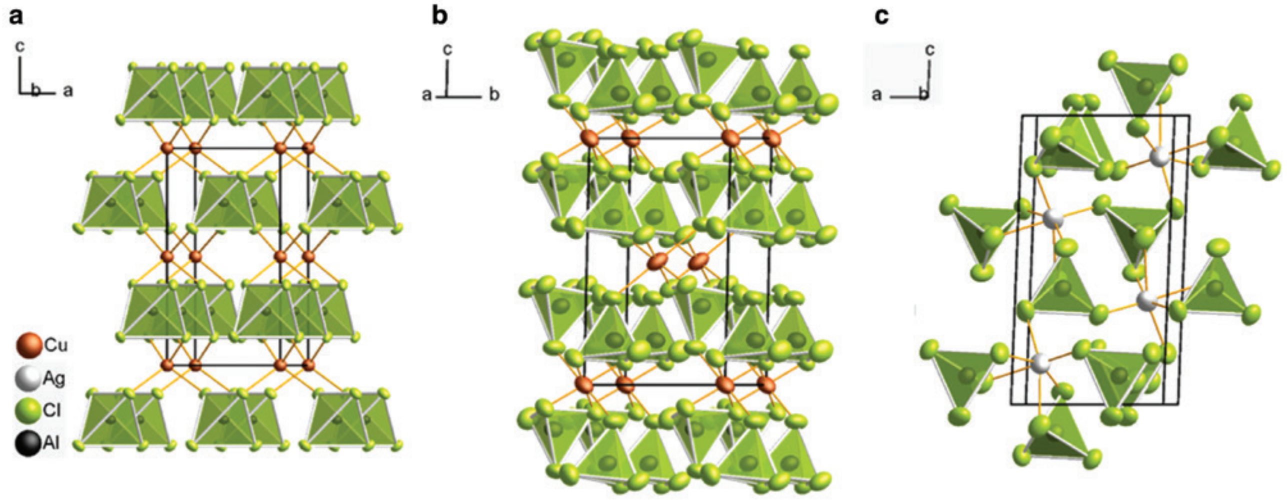

Fig. 3: Crystal structures of: (a) $Cu[AlCl_4]$, (b) $Cu[AlCl_4]_2$ and (c) $Ag[AlCl_4]$. Ellipsoids comprise 99.99% of the probability density of atoms at $T = 296$ K (a) or 80% at 296 K (b, c).

interwoven and inverted against each other (Fig. S2b). Alternatively, the structure can be described as a distorted hexagonal close packing of chloride ions whose hexagonal layers are parallel to the (101) plane. Silver(I) ions occupy 1/4 of the octahedral voids and aluminum atoms fill 1/8 of the tetrahedral voids, respectively (Fig. S2c).

It might be assumed that $Cu[AlCl_4]$ has a crystal structure similar to that of $Ag[AlCl_4]$, however, the lighter homolog forms a tetragonal structure – space group $P\bar{4}2c$ – that shows a slightly distorted cubic close packing of chloride ions with copper ions occupying 1/4 of the tetrahedral voids (Fig. 3a). Unexpectedly, there is a high degree of similarity between the crystal structures of $Ag[AlCl_4]$ and $Cu[AlCl_4]_2$, i.e. the copper(II) salt (Fig. 3b). Both structures crystallize in the same space group type and both coinage metal ions are surrounded by six chloride ions, originating from four $[AlCl_4]^-$ units, in a distorted octahedral shape. The distortion in $Cu[AlCl_4]_2$ was attributed to the Jahn-Teller effect, resulting in an elongation of the axial Cu–Cl distances. Therefore, the η^2-coordinating $[AlCl_4]^-$ ions occupy the equatorial coordination plane while the axial ligands only bind by a vertex to the copper(II) ion. Contrary to that, there is no such ordered “functionality” of $[AlCl_4]^-$ ions in $Ag[AlCl_4]$; no distinction between equatorial and axial ligands can be made based on the coordination mode of the $[AlCl_4]^-$ ligands (Fig. 3c).

2.3 The crystal structure of $Rb[AlCl_4]$

Mairesse et al. analyzed the crystal structure of $Rb[AlCl_4]$ based on powder X-ray diffraction data in 1979 [7] and suspected it to belong to the baryte structure type [41]. However, they were unable to obtain single crystals for a full structural analysis, which has now been successful through the use of ILs.

Single-crystal X-ray diffraction experiments revealed the orthorhombic crystal structure of rubidium(I)-tetrachloridoaluminate in the space group *Pnma* (no. 62) with four formula units per unit cell and lattice parameters $a = 1114.8(2)$, $b = 708.9(1)$ and $c = 926.3(1)$ pm at 296(1) K. Atomic parameters and interatomic distances are listed in Tables S3 and S4 of the Supporting Information. The crystal structure of $Rb[AlCl_4]$ is composed of rubidium(I) cations and tetrahedral $[AlCl_4]^-$ anions (Fig. 4a). In fact, the assumption made by Mairesse et al. is correct: $Rb[AlCl_4]$ is isostructural to $BaSO_4$ (Fig. 4b). Therefore, its relation to other tetrachloridoaluminates of monovalent cations, such as $Cs[AlCl_4]$ [7] or $Tl[AlCl_4]$, [4] which also crystallize in the baryte structure type, is apparent.

Each rubidium atom is surrounded by 12 chloride ions in an irregular polyhedral sphere that can be described as a pentagon below and a capped hexagon above the central atom (Fig. 5). Both polygons are heavily distorted, as already reported for the baryte structure [42]. Corresponding to the high coordination number (c.n. = 12), the Rb–Cl distances in this coordination sphere range from 336.7(2) pm to 433.5(2) pm (average 374(32) pm), showing a significant increase compared to the 329.1(2) pm in RbCl (c.n. = 6) [43] and to that of other tetrachloridometalates, such as $Rb_2[ZnCl_4]$ (c.n. = 7; 8) or $Rb_2[CdCl_4]$ (c.n. = 9), in which the distances range from 321.8(1) to 386.1(1) pm [44, 45]. However, all interatomic distances in $Rb[AlCl_4]$ exceeding this previously observed range, are secondary bonds

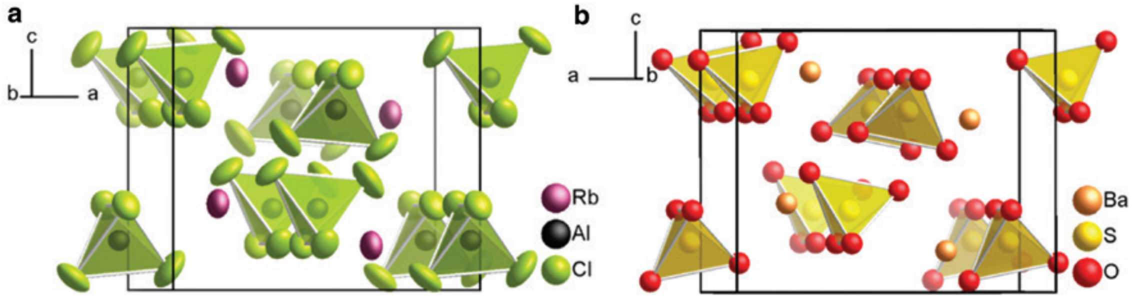

Fig. 4: Isotypic crystal structures of: (a) Rb[$AlCl_4$] and (b) $BaSO_4$ [41]. Ellipsoids comprise 70% of the probability density of atoms at 296 K. For $BaSO_4$, no anisotropic displacement parameters were given.

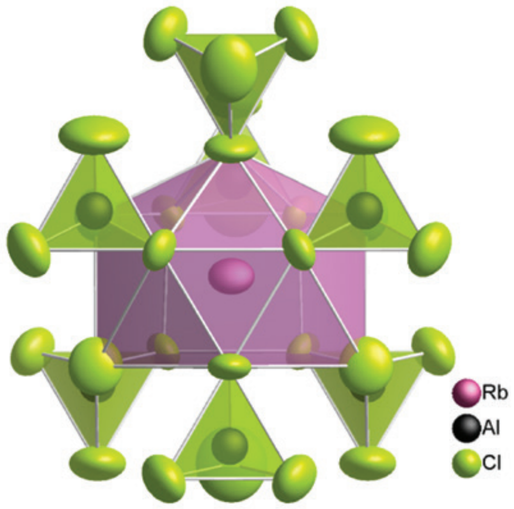

Fig. 5: The irregular coordination environment around the $[RbCl_{12}]^{11-}$ core unit built from seven $[AlCl_4]^-$ ions in Rb[$AlCl_4$]. Ellipsoids comprise 70% of the probability density of atoms at $T = 296$ K.

to chloride ions that belong to an already coordinating $[AlCl_4]^-$ ion, rendering it a bidentate chelating ligand.

2.4 The crystal structure of Pb[$AlCl_4$]$_2$

In 2012, Müller successfully crystallized Pb[$AlCl_4$]$_2$ from a pristine $AlCl_3$ melt [34]. Single-crystal diffraction performed on these crystals revealed an orthorhombic structure that he categorized to be isotypic to α-Sr[$GaCl_4$]$_2$. X-ray analysis of single crystals that precipitated from IL confirmed the structure model by Müller. Thus, the ionic liquid has no influence on the crystal structure and simply acts as a solvent and reactant. The crystal structure of lead(II)-bis(tetrachloridoaluminate) is orthorhombic with the space group *Pbca* (no. 61), eight formula units per unit cell and lattice parameters $a = 1220.2(1)$, $b = 1034.4(1)$ and $c = 2022.0(2)$ pm at 296(1) K. Atomic parameters and interatomic distances are listed in Tables S5 and S6 of the Supporting Information. In the crystal structure each Pb^{2+} ion is surrounded by nine chloride ions belonging to one η^1- and four η^2-coordinating $[AlCl_4]^-$ tetrahedra. The coordination of the lead cation can be described as a significantly distorted variant of either a tricapped trigonal prism or a capped square-antiprism (Fig. 6b). The Pb–Cl distances in Pb[$AlCl_4$]$_2$ range from 286.1(1) to 345.3(1) pm, which is very similar to the distance range in $PbCl_2$ (286(4)–364(4) pm) [46]. Moreover, the two coordination polyhedra of the lead cations are almost identical, with somewhat reduced distortion of the tricapped trigonal prism in $PbCl_2$ (Fig. 6c).

To the best of our knowledge, the only other compound containing lead(II) ions coordinated to complex chloridometalate anions is the isostructural Pb[$GaCl_4$]$_2$, which was also mentioned by Müller [34]. All Pb–Cl distances in the crystal structure of the gallium compound are up to 10 pm shorter than in the aluminum analog, while still giving rise to the same coordination environment. The Ga–Cl distances are about 4–5 pm longer than the Al–Cl distances, and the unit cell volume differs by less than 2%. Therefore, the differences between the aluminate and the gallate can be interpreted as a shift of the chloride ions, caused by the lower electronegativity of aluminum (Pauling values: Pb 1.9, Ga 1.8, Al 1.6). As mentioned before, Pb[$AlCl_4$]$_2$ is isotypic to α-Sr[$GaCl_4$]$_2$, [34] which also means that it is a derivative of the cuprite structure type. The aluminum atoms, representing the center of the anionic tetrahedra, replace the copper(I) ions, whereas the lead(II) ions take the positions of the oxide anions. In accordance with the lower symmetry, the packing is slightly distorted, but the two interwoven cristobalite networks can still be recognized within the structure of Pb[$AlCl_4$]$_2$ (Fig. S3). It might be somewhat surprising that Pb[$AlCl_4$]$_2$ is isotypic to α-Sr[$GaCl_4$]$_2$ rather than to RT-Sr[$AlCl_4$]$_2$ [15, 25]. Both strontium compounds crystallize in the orthorhombic space group type *Pbca*.

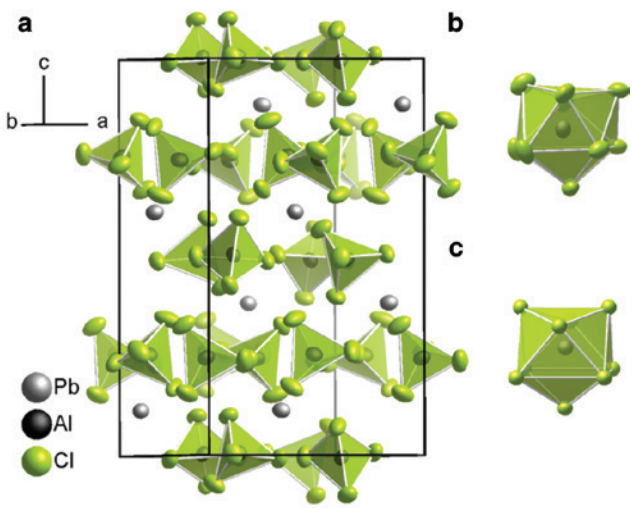

Fig. 6: (a) Crystal structure of $Pb[AlCl_4]_2$. (b) and (c) Coordination of nine chloride ions in a distorted tricapped prism around a lead(II) cation in the crystal structure of 3 and $PbCl_2$, respectively. Ellipsoids comprise 90% of the probability density of atoms at 296 K. No anisotropic displacement parameters were given for $PbCl_2$ [46].

However, the aluminate shows a coordination environment for the strontium(II) ions that comprises four η^2-coordinating $[AlCl_4]^-$ tetrahedra with the next nearest chloride ligand lying over 450 pm away from the central atom, making a nine-fold coordination, as described for the lead compound, improbable. Furthermore, the room-temperature modification of $Sr[AlCl_4]_2$ is derived from a tetragonal high-temperature structure – space group $I4_1/acd$ – that exists above 180°C [25]. As a result, the unit cell of RT-$Sr[AlCl_4]_2$ shows only minimal deviation from tetragonal metrics with $\Delta(a{-}b) = 15$ pm compared to the $\Delta(a{-}b) = 186$ pm observed for the unit cell of $Pb[AlCl_4]_2$, which makes finding a direct structural relation between those two compounds difficult. It might be argued that the lone pair of lead(II) plays a role in that.

3 Conclusions

Single crystals of $Ag[AlCl_4]$, $Rb[AlCl_4]$, and $Pb[AlCl_4]_2$ have become accessible by an ionothermal approach in ILs. The determination of the crystal structure of $Ag[AlCl_4]$ revealed unexpected similarities to $Cu[AlCl_4]_2$ rather than to $Cu[AlCl_4]$. $Rb[AlCl_4]$ has been confirmed to belong to the baryte structure type, as was suspected by previous work of Mairesse et al. based on powder diffraction analysis. $Pb[AlCl_4]_2$ is isotypic to α-$Sr[GaCl_4]_2$, as had been demonstrated by Müller before. Since previous as well as our attempts to grow single crystals of sufficient quality from $AlCl_3$ melts failed for two of the three title compounds, it can be concluded, that the use of the ionic liquid as a solvent, reactant and crystallizing agent is crucial. The chloride ions of the $[AlCl_4]^-$ groups are poorer donors than isolated chloride ions, resulting in significantly longer *M*–Cl distances than in the binary chlorides and, consequently, in high coordination numbers of the *M* cations.

4 Experimental

4.1 Synthesis

All compounds were handled in an argon-filled glove box (M. Braun; $p(O_2)/p^0 < 1$ ppm, $p(H_2O)/p^0 < 1$ ppm). The reactions were carried out in silica ampoules with a length of 120 mm and a diameter of 14 mm. The syntheses took place in the ionic liquid $[BMIm]Cl \cdot 4AlCl_3$, which acted as solvent and reactant.

For the synthesis of $Ag[AlCl_4]$, the ampoule was loaded with 97.4 mg AgCl (0.68 mmol, 99.998%, Alfa Aesar), 151.6 mg [BMIm]Cl (0.87 mmol, 98%, Sigma Aldrich, dried under vacuum at 100°C), and 454.1 mg $AlCl_3$ (3.4 mmol, sublimed three times). The evacuated and sealed ampoule was heated at 180°C for 60 h.

$Rb[AlCl_4]$ was obtained from a mixture of 82.0 mg RbCl (0.68 mmol, 99%, abcr), 150.6 mg [BMIm]Cl (0.86 mmol, 98%, Sigma Aldrich, dried under vacuum at 100°C), and 450.9 mg $AlCl_3$ (3.38 mmol, sublimed three times). The evacuated and sealed ampoule was heated at 180°C for 60 h.

The synthesis of $Pb[AlCl_4]_2$ was realized by mixing 186.6 mg $PbCl_2$ (0.67 mmol, 98%, Sigma Aldrich), 150.0 mg [BMIm]Cl (0.86 mmol, 98%, Sigma Aldrich, dried under vacuum at 100°C), and 450.0 mg $AlCl_3$ (3.38 mmol, sublimed three times). The evacuated and sealed ampoule was heated at 200°C for 24 h.

The mixture was cooled to room temperature at $\Delta T/t = -6$ K h^{-1}. All title compounds were obtained as colorless, plank shaped, air sensitive crystals alongside with recrystallized hexagonal $AlCl_3$ platelets. The IL was removed by washing the products with dry dichloromethane under inert gas conditions three times. The product of the $Ag[AlCl_4]$ synthesis could not be treated under these conditions as the crystals decayed upon contact with dichloromethane. All products were obtained in an estimated yield of 50–60%, being contaminated only by a recrystallized of $AlCl_3$ present in excess. Respective powder diffractograms can be found in Figs. S4–S6 of the Supporting Information.

4.2 EDX analysis

Energy dispersive X-ray (EDX) spectroscopy was employed to check the chemical composition of the crystals, using a SU8020 (Hitachi) SEM equipped with a Silicon Drift Detector (SDD) X-Max^N (Oxford). However, several problems impeded the interpretation of the measured data. Since the samples could not be polished due to their high sensitivity to moisture, the surface of the crystals was uneven and the crystals themselves tilted. Furthermore, the compound partially decomposes in the high-energetic electron beam ($U_a = 25$ kV) that is necessary to activate the metal atoms for this measurement. EDX analysis was therefore mainly used as a qualitative analysis to confirm the suspected composition. In that regard, we were able to confirm the examined crystals to be ternary compounds containing aluminum, chlorine and the respective second metal. Impurities in the form of oxygen were also detected, which can be attributed to the carbon pad used for preparation of the single crystals under inert atmosphere. These pads are known to trap large amounts of oxygen, which we were unable to remove under dynamic vacuum even after long treatment times.

4.3 X-ray crystal structure determination

Single-crystal X-ray diffraction was measured on a four-circle Kappa APEX II CCD diffractometer (Bruker) with a graphite(002) monochromator and a CCD detector at $T = 296(1)$ K. Mo$K\alpha$ radiation ($\lambda = 71.073$ pm) was used. After integration [47], a multi-scan absorption correction was applied by using SADABS [48] within the Bruker APEX3 software suite [49]. The initial structure solution was performed with SHELXT [50] and further refinement processed in SHELXL against F_o^2 [51, 52].

$Ag[AlCl_4]$: monoclinic; space group $P2_1/c$ (no. 14); $T = 296(1)$ K; $a = 711.8(1)$, $b = 661.1(1)$, $c = 1343.4(2)$ pm, $\beta = 92.26(1)°$, $V = 631.8(1) \times 10^6$ pm^3; $Z = 4$; $\rho_{calcd.} = 2.91$ g cm^{-3}; $\mu(MoK\alpha) = 4.9$ mm^{-1}; $2\theta_{max} = 51.8°$, $-5 \le h \le 8$, $-8 \le k \le 8$, $-16 \le l \le 16$; 7517 measured, 1227 unique reflections, $R_{int} = 0.047$, $R_\sigma = 0.030$; 65 parameters, R_1 [878 $F_o > 4\sigma(F_o)$] = 0.040, wR_2 (all F_o^2) = 0.083, GooF = 1.11, min./max. residual electron density: $-0.45/0.53$ e $\times 10^{-6}$ pm^{-3}. For atomic parameters see Tables S1 and S2 of the Supporting Information.

$Rb[AlCl_4]$: orthorhombic; space group $Pnma$ (no. 62); $T = 296(1)$ K; $a = 1114.8(1)$, $b = 708.9(1)$, $c = 926.3(1)$, $V = 732.0(2) \times 10^6$ pm^3; $Z = 4$; $\rho_{calcd.} = 2.31$ g cm^{-3}; $\mu(MoK\alpha) = 8.2$ mm^{-1}; $2\theta_{max} = 53.4°$, $-14 \le h \le 14$, $-8 \le k \le 5$, $-11 \le l \le 11$; 8344 measured, 846 unique reflections, $R_{int} = 0.049$, $R_\sigma = 0.024$; 34 parameters, R_1 [601 $F_o > 4\sigma(F_o)$] = 0.039, wR_2 (all F_o^2) = 0.098, GooF = 1.01, min./max. residual electron density: $-0.48/0.90$ e $\times 10^{-6}$ pm^{-3}. For atomic parameters see Tables S3 and S4 of the Supporting Information.

$Pb[AlCl_4]_2$: orthorhombic; space group $Pbca$ (no. 61); $T = 296(1)$ K; $a = 1220.2(1)$, $b = 1034.4(1)$, $c = 2022.0(2)$ pm; $V = 2551.9(3) \times 10^6$ pm^3; $Z = 8$; $\rho_{calcd.} = 2.84$ g cm^{-3}; $\mu(MoK\alpha) = 15.0$ mm^{-1}; $2\theta_{max} = 70.2°$, $-19 \le h \le 18$, $-15 \le k \le 16$, $-31 \le l \le 32$; 38501 measured, 5638 unique reflections, $R_{int} = 0.043$, $R_\sigma = 0.029$; 101 parameters, R_1 [3952 $F_o > 4\sigma(F_o)$] = 0.028, wR_2 (all F_o^2) = 0.038, GooF = 1.165, min./max. residual electron density: $-1.59/1.72$ e $\times 10^{-6}$ pm^{-3}. For atomic parameters see Tables S5 and S6 of the Supporting Information.

Further details of the crystal structure determination are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), E-mail: crysdata@fiz-karlsruhe.de, on quoting the deposition numbers CSD-1958743 ($Ag[AlCl_4]$), CSD-1958744 ($Rb[AlCl_4]$), and CSD-1958745 ($Pb[AlCl_4]_2$).

5 Supporting information

Additional crystal structure representations, powder diffractograms and atomic coordinates including displacement parameters are given as supplementary material available online (DOI: 10.1515/znb-2019-0162).

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