Crystal Structure and Formation of the Aluminium Hydroxide Chloride $[Al_{13}(OH)_{24}(H_2O)_{24}]Cl_{15} \cdot 13\ H_2O$

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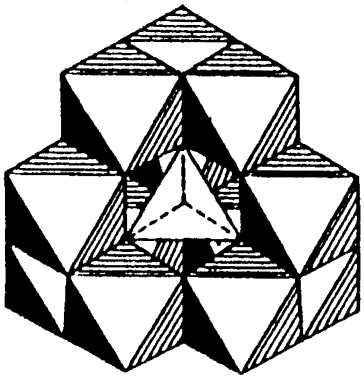
A basic aluminium chloride with high chlorine content (basicity 1.85) has been crystallized from a concentrated aqueous solution. Its crystal structure has been determined by X-ray structure analysis. The structure contains tridecameric cations of a novel type consisting only of interconnected AlO_6 octahedra. The formation of these polycations is discussed.

The structures of complex cations of basic aluminium chlorides, formed by hydrolysis and condensation, as well as the conditions of their formation, are of special interest because of their occurrence in natural water and their applications as antiperspirants and in water purification. Detailed information concerning the structures of similar complex cations has been provided by the crystal-structure analyses of basic aluminium sulfates and selenates carried out by Johansson and co-workers. They demonstrated the existence of a dimeric species[1] $[Al_2(OH)_2(H_2O)_8]^{4+}$, consisting of two octahedrally coordinated Al centres connected by a common edge (di-μ-OH^- bridge), and of a polycation $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ (Figure 1) with a Keggin-type structure.[2] The latter structure is characterized by a particular resonance shift in its ^{27}Al-NMR spectrum, even in solutions of basic aluminium chlorides,[3] caused by the tetrahedrally coordinated, central aluminium, which is surrounded by 12 other octahedrally coordinated Al atoms. Various crystalline basic aluminium chlorides have been prepared from solutions by Walter-Levy and Breuil.[4] The crystalline phases were characterized by means of X-ray powder analysis and their thermal decomposition was investigated. The powder diagrams of some of these crystalline phases were unambiguously indexed and the lattice constants were determined. This is also the case for a cubic phase prepared at Dow Chemical Co.[5] However, as far as we are aware, results of crystal structure analyses have hitherto not been reported.

In this paper, we report on a structure analysis of the most chlorine-rich of the basic aluminium chlorides described by Walter-Levy and Breuil.[4][6] These authors obtained the salt as a crystalline precipitate that formed after several days following dilution and storage of concentrated basic aluminium chloride solutions. Suitable monocrystals for our structure analysis were obtained serendipitously, in the course of studies on the colloid structures of basic aluminium chlorides. Colloid solutions with an Al:Cl ratio in the range 1−2 tend to form gels after evaporation of the solvent, and these were the subject of rheological and light-scattering investigations[7]. In basic aluminium chloride solutions, besides the aforementioned monomeric, dimeric and tridecameric species, further oligomeric and polymeric cations exist. To date, only vague statements have been made regarding their size and shape.[3] For comparison, we also studied solutions rich in chloride. It was known that crystalline phases could be precipitated from such media. After very slow evaporation of water from a concentrated solution of a basic aluminium chloride with an Al:Cl ratio of 0.7, besides very large crystals of $AlCl_3 \cdot 6H_2O$, crystals of another phase grew, which were the subject of our investigations.

Figure 1. Tridecameric cation after Johansson[2]



Results and Discussion

The lattice constants of the formed monocrystal were determined by means of single-crystal X-ray diffractometry. On the basis of the monoclinic unit cell obtained, the unindexed powder data reported by Breuil for the hydroxide chloride 5 $AlCl_3 \cdot 8\ Al(OH)_3 \cdot 37.5\ H_2O$[8] become indexable. Therefore, we conclude that a crystal of this phase was pre-

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sent. The results of its X-ray structure analysis confirmed this assertion, although not all the positions of the hydrogen atoms could be determined. The water content in the formal unit was found to be slightly lower than reported, being consistent with the composition 5 $AlCl_3 \cdot 8\ Al(OH)_3 \cdot 37\ H_2O$. The cell contains 4 formal units. The atomic positions determined in the structure analysis show two analogous types of large units, built up from connected AlO_6 octahedra (Figure 2). Two of each kind are present in the unit cell. The chlorine atoms are situated outside of these complex units, along with the oxygen and hydrogen atoms obviously belonging to water molecules. Considering the charges (Al^{3+}, Cl^-), the large units must be viewed as polycations. Each polycation consists of 13 octahedra (Figure 3): a central one, 6 further octahedra surrounding the central unit and connected to it by common edges, and finally 6 peripherally arranged octahedra, with each one joined to the inner ring by two common corners. The Al^{3+} ion in the central octahedron lies at an inversion centre of the space group, and thus the polycations are centrosymmetric. The central Al^{3+} and the 6 Al^{3+} of the ring are coplanar and together form a centred, almost regular, hexagon. The oxygen positions correspond to octahedra with varying degrees of distortion. The Al−O distances in the central octahedron are virtually equal (188−189 pm), and the O−Al−O angles are approximately equal (97°), but differ from the octahedral ideal of 90°. The ring octahedra are distorted to a greater extent. The peripheral octahedra occupy alternate positions above and below the plane of the hexagon. Accordingly, they show a certain degree of deformation; the Al−O distances to the free corners are obviously longer than those to the corners that are shared with the adjacent octahedra. Since not all of the hydrogen atom positions could be determined, the question remains as to which oxygen atoms the hydrogen atoms should be assigned so as to form hydroxide ions or water molecules. Consideration of the charges may elucidate this matter. In the polycation, we find 13 Al^{3+} ions with 39 positive charges. On the other hand, there are 15 Cl^- ions, giving 15 negative charges per polycation. This leaves 39 − 15 = 24 negative charges in the polycation to account for. This number corresponds to the number of linkage oxygen atoms. We can thus assume that these oxygen atoms belong to hydroxide ions. Water molecules must then be present at the 24 free corners of the peripheral octahedra. An additional 13 water molecules are situated outside of the polycation. The basic aluminium chloride investigated can therefore be assigned the formula $[Al_{13}(OH)_{24}(H_2O)_{24}]Cl_{15} \cdot 13\ H_2O$.

Hence, a further tridecameric cation species has been detected in addition to Johansson′s tridecamer. The new species is characterized by a single resonance of octahedrally coordinated Al in its ^{27}Al-NMR spectrum and needs to be formally distinguished from the previously identified species. The notation Al_{13} is no longer unambiguous. It seems reasonable to distinguish the two tridecameric species by using an auxiliary index that denotes the different coordination of the central aluminium: $Al_{13}{}^t$ (t: tetrahedral) for the Johansson species and $Al_{13}{}^o$ (o: octahedral) for the new structure. The two tridecamers have OH^- ($Al_{13}{}^o$) or O^{2-} groups ($Al_{13}{}^t$) that form a common vertex of three octahedra. Therefore, Brown et al.[9] and Baes and Mesmer[10] discuss the formation of $Al_{13}{}^t$ in terms of the assembly of trimers $[Al_3(\text{tri-}\mu\text{-}OH)(OH)_3(H_2O)_9]^{5+}$ (Figure 4), which are in turn formed by the condensation of a dimer $[Al_2(OH)_2(H_2O)_8]^{4+}$ with a monomer $[Al(OH)(H_2O)_5]^{2+}$. It has been assumed that the Keggin tridecamer is formed by the reaction of the hydroxide ions of an $[Al(OH)_4]^-$ anion with the nucleophilic tri-μ-OH^- of trimeric units, building up a tetrahedral arrangement of linking oxygen ions with the liberation of water. In our tridecamer $Al_{13}{}^o$, there are OH^- groups that connect three octahedra. The central Al^{3+} is surrounded by six tri-μ-OH^-. The formation of this polycation structure can also be envisaged as starting from trimers, formed by condensation of dimeric and monomeric

Figure 2. Crystal structure of $[Al_{13}(OH)_{24}(H_2O)_{24}]Cl_{15} \cdot 13\ H_2O$; section of the unit cell: polycations with centres in $z = 1/2$

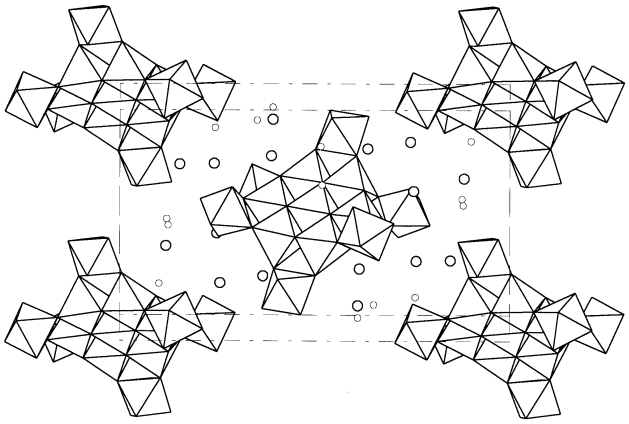
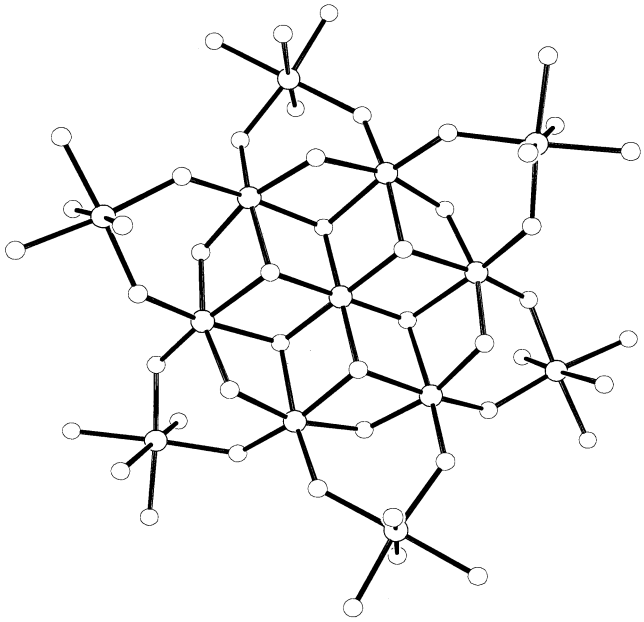


Figure 3. Structure of the polycation $[Al_{13}(OH)_{24}(H_2O)_{24}]^{15+}$; large circles: aluminium; small cirder: oxygen



units. However, in this case, the process continues with the addition of other dimers, which condense together after further protolysis and form the ring surrounding the central atom. The peripheral octahedra could clearly be attached subsequently by the condensation of monomer units with the compact planar core.

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Experimental Section

General: The Al_{13}° hydroxide chloride was crystallized from a basic aluminium chloride solution with an Al/Cl ratio of 0.7. The solution was prepared by dissolution of partially thermally decomposed $AlCl_3 \cdot 6\ H_2O$ in hot water (80°C) at a mass ratio of solid material/water of 1:1. The thermal decomposition of the starting material was carried out at about 180°C in a whirling air stream. The solution was placed in an open dish at ambient temperature. After 4 months, well-grown crystals of suitable dimensions for X-ray structure analysis were obtained. The quality of separated crystals was tested by polarization microscopy. Solid-state ^{27}Al-NMR analysis was performed with a Bruker MSL300 instrument at a frequency of 15 KHz.

X-ray Crystallographic Study: T = 295°C; crystal size 0.20 × 0.20 × 0.15 mm, formula weight 1957.27, monoclinic, space group $P2_1/c$, a = 13.901(1), b = 23.483(3), c = 22.345(2) Å, β = 90.36(1)°, V = 7294.1(12) Å^3, Z = 4, $D_{calcd.}$ = 1.782 g cm^{-3}. Enraf-Nonius CAD4 diffractometer, graphite-monochromated Cu-K_α radiation (λ = 1.5418 Å), F(000) = 4040, μ = 7.736 cm^{-1}, ω-2θ scan, scan range (θ) 2.73−74.73°, *hkl* range +17, +29, ±27, no. of unique reflections 14942, no. of observed reflections 11292 with $I > 2\sigma(I)$, refined parameters 903, $R1$ for observed reflections 0.00527, $R1$ for all reflections 0.0776, $wR2$ for observed reflections 0.1341, $wR2$ for all reflections 0.1497, GooF = 1.077 for the observed and GooF = 1.025 for all reflections, residual electron density 0.80/−0.62 e Å^{-3}. The structure was solved by direct methods (SHELXS-86) and refined by full-matrix least-squares methods with SHELXL-93. DIFABS was used for empirical absorption correction. Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany) on quoting the depository number CSD-408095.

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