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Account/Revue

Crystal chemistry of aluminium carboxylates: From molecular species towards porous infinite three-dimensional networks

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ABSTRACT

This account describes the crystal chemistry of aluminium in association with O-donor organic ligands, such as polycarboxylates. In this overview, molecular assemblies of aluminium-based species are discussed from the background knowledge of the polycationic species occurring in aqueous solution. The use of hydro/solvothermal synthetic route has led to the generation of novel crystalline extended three-dimensional networks, of metal-organic frameworks (MOFs) type, with consequent porosity properties. The first illustration of such materials was the aluminium-containing MIL-53 (Materials Institute Lavoisier – number 53), obtained from the hydrothermal reaction of aluminium salt source with terephthalic acid. This finding gave rise to the development of new series of porous aluminium MOF-like materials, some of which are now produced at the industrial scale. This review presents a description of various crystalline structures, from a classification based on the nuclearity of the aluminium-centered building units, involved in the construction of the framework.

1. Introduction

Since 1989 [1], the study of the association of metallic centers with chelating polydentate O- or N-donor organic linkers has led to a new and very topical class of solids, now known as metal-organic frameworks (MOF) or coordination polymers (or coordination network solids [2]). These solids, often three-dimensional and porous, are thermally stable and robust, and serve as host functionalized matrices for diverse applications, such as gas storage, molecular separation, drug delivery, catalytic reactors, batteries, thin films shaping… [3–6]. They conjugate the physical and chemical properties of both the inorganic and organic parts for providing multifunctional materials, and use in particular the pore geometry of the three-dimensional framework.

Almost all the metallic atoms of the periodic table can incorporate the framework. Historically, most of the early works reported the use of divalent transition metals (i.e. Zn^{2+}, Cu^{2+}…). It was further extended to tri-, tetra- and even pentavalent cations with the same success. Among them, trivalent metals were very promising, particularly the crystallized solids of the MIL-100/MIL-101 series [7–9], based on aluminium, chromium and iron which exhibited the first large mesoporous cavities in a framework. Among them, aluminium deserved a special attention due to its lightweight and its cheap cost, when thinking to industrial production for gas storage applications, for instance. For

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us, it was an opportunity to better understand the chemistry of aluminium from the knowledge of the species [7,8,10] which can exist, and which can be used to design novel three-dimensional topologies.

Aluminium is first one of the most abundant metallic elements on earth's crust (8.3% by weight) and is generally encountered in natural minerals, such as feldspars, zeolites, micas. The bauxite-type rocks are the most commonly source in the aluminium extraction process for producing the Al metal.

In aqueous solution, aluminium predominantly exists with the oxidation state of +3, complexed by anionic charged species, although the low valence state (+1) has also been explored with the discovery of a specific chemistry [11]. Depending on the pH values, the Al coordination ranges from six (octahedral at low pH) to four (tetrahedral at high pH). The intermediate five-fold coordination (trigonal bipyramid), less usual, is now well described in natural minerals (andalusite [12,13], grandedierite [14], yoderite [15], etc.), organic complexes [16,17] or organically templated open-framework aluminophosphates [18,19]. The recently observed [20] aqueous molecular form ($Al(OH)(H_2O)_4{}^{2+}$), specific to aluminium chemistry, is in contrast with other trivalent metals.

Due to their amphoteric behavior [21], aluminium hydroxides are generally dissolved in acidic solutions ($pH < 3$; $Al(H_2O)_6{}^{3+}$) or near-neutral and basic solutions ($pH > 8$; $Al(OH)_4{}^-$). Its trivalent charge associated to the small ionic radius (0.53 Å in tetrahedra, or 0.675 Å for octahedra [22]) leads to hard cations with a strong Lewis acid character. It implies a strong reactivity with Lewis bases, like OH^-, F^-, $PO_4{}^{3-}$, $SO_4{}^{2-}$, but also with organic O- or N-donor ligands (R-O^-, R-COO^- or R-NH_2...), with the formation of various species resulting from hydrolysis and/or complexation processes. Some recent works have reported calculations about the analyses of electronic structure of aluminium (or more generally group 13 elements) compared to those of trivalent transition metals [23]. In the case of the six-coordinate systems, they showed that the *p* elements exhibit electron-rich hypervalent bonding, without any role for the d orbitals, which the major difference with transition metals. Consequently, the Al-based compounds would be thermodynamically more stable and kinetically more reactive than those bearing neighbouring trivalent transition metals.

Most of the works related to the aluminium chemistry concern three main application domains: formation of polycations, biochemistry of aluminium and preparation of alumina ceramics.

Polycationic moieties [24] are soluble molecular oligomeric compounds coming from the hydrolysis of the aquohydroxo species $[Al(OH)_h(H_2O)_{N-h}]^{(3-h)+}$ in water. An accurate control of their condensation gives rise to the formation of isolated nanoclusters with different nuclearities. In case of $h = 3$, the condensation leads to the precipitation of the hydroxide or oxyhydroxide phases. These researches were concentrated on the narrow range of existence of these polynuclear complexes because of specific properties of flocculation in water treatment processes. In particular, they act as efficient coagulants for the removal of some pollutants and turbidity. They can also be intercalated into layered clay-like solids, such as Montmorillonite with the production after heating treatment of pillared compounds used efficiently in heterogeneous catalysis. They are also found in antiperspirants, as adjuvants for vaccine formulation or dye mordants (see review article by Casey [24]).

The reactivity of aluminium in biological systems is also a significant field of research since Al is assumed to exhibit a neurotoxic activity [25–28]. This fact is due, for instance, to the observation of the abnormally high concentration of aluminium in brain tissues coming from patients developing an Alzheimer's disease or other degenerative neurologic processes, but its direct role into the mechanism of the formation of these specific diseases is still debating. Nevertheless, the role of aluminium in cellular systems is well documented and this leads to the exploration of biochemical models for which a large number of molecular complexes have been investigated.

In the last domain, different types of alumina are usually industrially produced from precipitation and calcination processes of forms of aluminium hydroxides. They find many applications as ceramics, composite materials or catalysts.

The knowledge of these different aspects of the aluminium chemistry was the starting point for attempting to build up extended infinite network with aluminium centers for potential areas of applications. This review will first present the state-of-the-art on the different molecular Al-based clusters which can be used as building blocks for the discovery of new MOF-type networks using various carboxylates linkers. They are described in the second part.

2. Aluminium polycationic species

Several reviews [24,29] have well described this aspect. One may just briefly summary this topic by listing the different aqueous species which have been isolated so far.

The cationic 'blocks' consist of several Al atoms connected to each other through oxo and hydroxo groups. The coordination of aluminium-center (usually 6) is often completed by aquo ligands in terminal positions. These species, very soluble in water, crystallize in the presence of counter anions (sulfates, selenates, etc.) for a certain degree of hydrolysis. Several types of oligomeric clusters have been discovered, mainly in the sixties, by Johansson [27].

The first cationic moiety is (Fig. 1a) the dinuclear unit $[Al_2(OH)_2(H_2O)_8]^{4+}$ (called Al_2J) [30]. It crystallizes with sulfates or selenates from slow evaporation of aqueous solutions. It contains two octahedrally coordinated aluminium atoms sharing a μ_2-OH edge. A second oligomer, more recently found (it took seven years for getting a crystal!), was obtained during the preparation of the dimeric species Al_2J with sulfates [31]. The octamer is composed of eight six-fold coordinated aluminium centers $[Al_8(OH)_{14}(H_2O)_{16}]^{10+}$ (Fig. 1b). Connections are ensured via two μ_3-OH and four μ_2-OH ligands. This central four-membered unit is corner-shared through μ_2-OH with four additional peripheral AlO_6 polyhedra.

The best known polycationic oligomer belongs to the Baker–Figgis–Keggin isomer family. In it, a central MO_4