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The future of aluminum chemistry

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Abstract

This article represents a survey of current aluminum chemistry and some predictions regarding what type of aluminum chemistry will be conducted in the year 2000 and after. Because of the abundance and availability of aluminum in the earth, research incorporating this element will always be of importance to applications that impact on daily life. Indeed, applied chemistry is the primary goal of most aluminum research. It is likely that three broad areas of aluminum chemistry, catalysis, materials synthesis, and biological studies, will see substantial activity in the future. The use of aluminum in materials will continue in step with the growth of materials science, in general. In contrast, the use of aluminum compounds in catalysis and in effecting synthetic transformations will see a spectacular increase. This is a result of an increased understanding of the chemistry of aluminum, and the availability of a wide range of compounds containing aluminum, which has been achieved over the past few decades during a period of increased attention to Main Group chemistry. In the coming years a clear understanding of the influence of aluminum on biological systems will almost certainly be obtained based upon the quality and amount of effort that has focused on this area in recent times. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Aluminum; Catalysis; Materials; Biological

1. Introduction

It is difficult to predict the future, particularly with regards to research endeavors where a single discovery can revolutionize an entire field. The Nobel Prize rewards these types of breakthroughs. However, it is likely that most of the Nobel Laureates did not predict ahead of time the enormity of their discoveries. Indeed, absolute prescience probably does not exist, but owes acknowledgement to some past, foundational event. Even H.G. Wells, a remarkable intellect whose science fiction portrayed discoveries that would not be made for up to a century, based his ‘anticipations’ on the trends he observed in the technology of his day [1]. For example, his predictions regarding automobiles, roads, and bridges were clearly based upon developments that lead up to the combustion engine.

This present contribution, hardly comparable to Wells' remarkable predictions, will, nevertheless, follow an approach similar to Well's in trying to predict the future of aluminum chemistry. Key developments in aluminum chemistry will be examined for trends that will be developed in the new millennium. This article will have two advantages over the predictions of H.G. Wells. The first is that it is of much more limited scope. The second is that the article is focused on aluminum chemistry, and one thing is certain, that aluminum chemistry will always have a bright and expanding future. The availability and unique properties of the element will ensure that this is so.

It is likely that three broad areas of aluminum chemistry, catalysis, materials synthesis, and biological studies, will see substantial activity in the future. The use of aluminum in materials will continue in step with the growth of materials science, in general. In contrast, the use of aluminum compounds in catalysis and in effecting synthetic transformations will see a spectacular increase. This is a result of an increased understanding of the chemistry of aluminum, and the availability of a wide range of compounds containing aluminum, which has been achieved over the past few decades. In the coming years a clear understanding of the influence of aluminum on biological systems will almost certainly be

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obtained based upon the quality and amount of effort that has focused on this area in recent times.

2. Historical background

Aluminum is the third most abundant element in the earth's crust (82 g kg^{-1}, 8%) and the most abundant metal. Its presence there is exceeded only by oxygen (474 g kg^{-1}, 46%) and silicon (282 g kg^{-1}, 26%) [2]. The combination of this availability with the unique mechanical and electrical properties of the element makes it of supreme utility in a multitude of quotidian applications. For example, it is used extensively in cooking utensils, furniture and automobiles. However, this widespread utility is a relatively recent occurrence for mankind. As found in nature the metal is in combination with other elements such as oxygen and silicates. It would appear that the strong bonding of Al to O (and Si to O) in these materials has limited the use of Al in living systems [3].

The metal, originally named aluminium by Davy in 1807, was not isolated in recognizable form until the mid-1820s when Oersted and Wohler reduced aluminum(III)chloride with potassium. In 1854 Deville dramatically improved the process by substituting sodium for potassium as the reductant. With further improvements in the preparation of sodium the chemical aluminum industry, using the Deville–Castner process, was well underway by the 1880s. A key problem associated with the cost of aluminum at this point was the use of aluminum(III)chloride and the necessity of using highly reactive sodium metal as the reductant. Once electrolytic equipment became more commonplace, new ways of reducing aluminum to prepare other useful starting materials was explored. The best method, and the one that is now in use worldwide, was developed by Hall in 1886. In this process aluminum is produced by electrolyzing aluminum(III)oxide dissolved in cyrolite ($NaF–AlF_3$) [4].

Even as small quantities of aluminum were becoming available, early experiments demonstrated that organometallic complexes could be made [5]. Ethylaluminum sesquiiodide ($EtAlI_2–Et_2AlI$) was prepared by Hallwachs and Schafarik in 1859 by combining ethyliodide with aluminum metal. In 1865 Buckton and Odling prepared aluminum alkyls from mercury alkyls and aluminum metal. Despite the availability of alkylaluminums as key reagents to further the advance of organometallic aluminum chemistry, essentially nothing was done in this area for nearly a century. Eisch has proposed a good explanation for this occurrence [5]. These early alkylaluminum reagents were prepared in diethyl ether, a common solvent at the time for organometallic zinc and magnesium chemistry, but a solvent that reduces the activity of alkyl aluminum complexes through the formation of Lewis acid–base adducts. Thus, the problem may not have been the availability of aluminum reagents, but the misconception that such reagents were not very reactive due to their isolation as etherates. Whatever the reason, aluminum chemistry remained dormant for nearly 100 years.

Modern aluminum organometallic chemistry began in earnest with the pioneering work of Ziegler in the 1950s. He was the first to synthesize alkylaluminum reagents directly from aluminum metal, olefins, and hydrogen. These reagents, in turn, react with olefins to produce longer-chain hydrocarbons. With hydrolysis, long-chain alcohols could be formed. With only modest changes, this reaction is still used industrially to manufacture detergents.

In the course of exploring the use of organoalkali reagents for oligomerizing ethylene, Ziegler discovered that lithium tetraethylaluminate was an active catalyst. While trying to determine how the presence of transition-metal salts affected this reaction, the Ziegler group discovered that titanium dramatically accelerated the reaction and produced polyethylene. Shortly thereafter (1963) Ziegler, along with Natta, who worked out the stereochemistry of the polymers, was awarded the Nobel Prize. This discovery that alkylaluminums could activate transition metals for the polymerization of olefins revolutionized polymer chemistry [6] and made researchers around the world suddenly aware of the utility and potential importance of aluminum chemistry. This is reflected in the fact that organoaluminum compounds were readily available by 1967 in 100 000 lb lots at a cost of $1 per pound [7].

Alkylaluminum reagents are readily prepared from oil by-products and are generally inexpensive. This makes them ideal for eventual commercial applications. Thus, a great deal of research in this area is directed towards the use of aluminum reagents as catalysts and for the preparation of solid-state materials. Much of the interest in aluminum chemistry is certain to remain in these two areas in the new millennium.

3. Current and future developments

3.1. Catalysis

3.1.1. Six-coordinate aluminum cations

My research group has been pursuing charged Group 13 compounds for a number of years. This includes both cationic [8] and anionic [9] Group 13 chemistry, two areas that had not previously received systematic attention. The applied chemistry we conducted with cationic aluminum relies on an ability to imbue the complex, either through changes in the ligand constituents, or in the geometry around the aluminum atom, with properties that may be optimized for the polymerization of oxiranes.

The first cations to be synthesized and described in the early literature were four-coordinate (as depicted generally in Fig. 1(b)) [10]. After a brief exploration of this class of cations, we determined that they were too reactive and labile to be used broadly in applications.

We, thus, began the development of a new class of six-coordinate cations supported by various salen ligands (Fig. 1(e)) [11]. These complexes present open axial coordination sites that attract Lewis-basic substrates. A related bonding arrangement results when one of the free bases is replaced by an additional Lewis-basic site within the ligand [12]. The cations are air stable, and can be made soluble in either polar or non-polar solvents. For catalytic purposes this means that the cations can be isolated and reused after the intended reaction has been conducted. This would reduce the amount of waste inherent to the process and increase the control a researcher has over the reaction of interest.

The use of six-coordinate cations in catalysis will certainly be broadened in the coming years. These cations will be of lower cost, based upon the availability of aluminum, and ^{27}Al NMR is a nice tool for exploring the coordination environment at the metal. Moreover, they will be far less reactive and more soluble in common solvents than conventional Lewis acids such as Me_3Al, Me_2AlCl, $MeAlCl_2$, and $EtAlCl_2$. The fact that none of the cations degrades in water hints at potential aqueous, and thereby environmentally benign, processes. Moreover, it is likely that Lewis acids of the form R_2AlX are in fact cationic in the presence of two-point Lewis-base substrates such as oxazolidinone [13]. We have previously shown that such species form cations in the presence of two Lewis-base molecules. Thus, in addition to their many positive attributes these cations may behave much like their neutral counterparts.

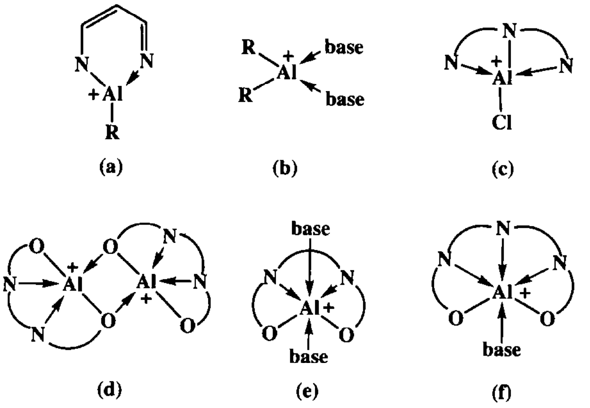


Fig. 1. A summary of the various types of cations that are mentioned in the text.

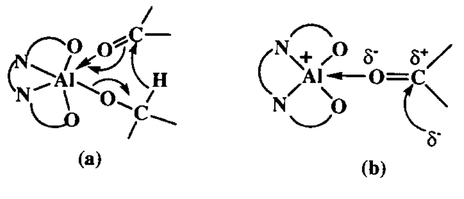
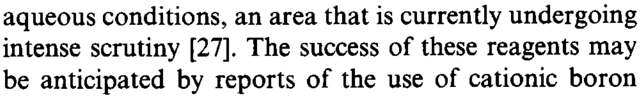


Fig. 2. A six-coordinate cation as a bidentate (a) and monodentate (b) catalyst.

3.1.1.1. Oxirane oligomerization. Our preliminary work has shown that the cations can be useful in initiating oxirane oligomerizations [11]. Initially we had hoped that these would prove to be living polymerization catalysts. However, our recent endeavors in this area appear to indicate that the polymerization proceeds through the Lewis-acid-initiated carbocationic mechanism [14]. Of related interest others have found, however, that chelated, four-coordinate complexes can be used in oxirane polymerization (Fig. 1(c)) [15]. The six-coordinate cations may also be useful in methacrylate polymerizations. In their use, they would behave in a manner similar to currently employed sterically hindered aluminum Lewis-acid catalysts [16].

3.1.1.2. Organic transformations. Some additional catalytic reactions that these cations might be useful for include Meerwein–Ponndorf–Verley reductions (MPV) [17], Friedel–Crafts reactions [18], Oppenaur oxidation, Tishchenko reactions [19], the ene reaction [20], mixed-aldol condensation [21], Diels–Alder reactions (DA) [22], dipolar cycloadditions, Claisen rearrangements [23], and the cyclotrimerization of isocyanates to isocyanurates [24]. In each case the cation is acting as a soluble Lewis acid that binds through two sites (a two-point catalyst) (Fig. 2(a)) or a single site (one-point catalyst) (Fig. 2(b)). As an example, a two-point system is thought to be active in the MPV reaction (Eq. (1)) [25].



$$R-\overset{\overset{O}{\|}}{C}-R' + Me-\underset{H}{\overset{OH}{C}}-Me \xrightleftharpoons{\text{catalyst}} R-\underset{H}{\overset{OH}{C}}-R' + Me-\overset{\overset{O}{\|}}{C}-Me \qquad (1)$$

Furthermore, the cations, unlike the majority of aluminum reagents used in synthesis [26] or catalysis, are not air or moisture sensitive and should not degrade under the reaction conditions. For instance, it might be possible to use the cations as DA catalysts under aqueous conditions, an area that is currently undergoing intense scrutiny [27]. The success of these reagents may be anticipated by reports of the use of cationic boron compounds [28], and cationic transition metal complexes [29] in DA catalysis.

3.1.2. Low-coordinate aluminum cations

Following an earlier precedent with two-coordinate cations [30], recent work has shown that three-coordinate alkylaluminum cations (Fig. 1(a)) are promising

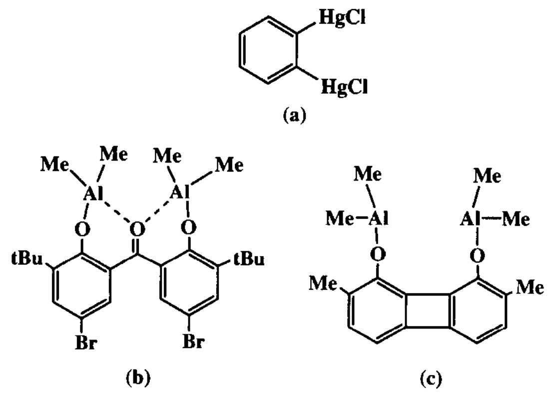


Fig. 3. Bifunctional Lewis acids.

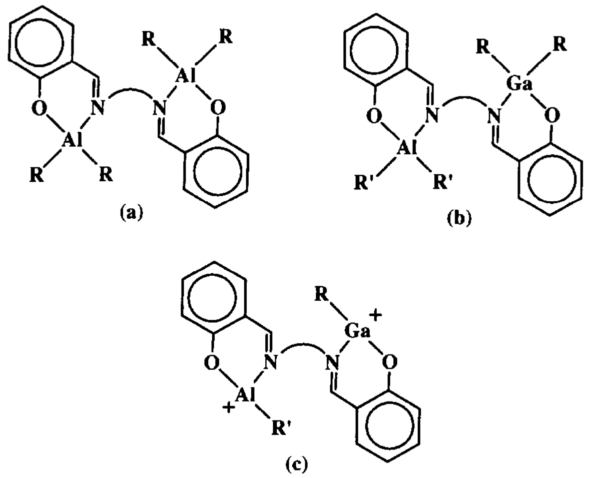


Fig. 4. Bimetallic salen-supported compounds.

catalysts for the polymerization of ethylene [31]. This has led to an explosion of interest in cationic alkyl aluminum compounds that is only now emerging in the literature. This focus will originally involve the design and synthesis of ligands that are bidentate and uni-negative. However, once the patent literature is established for these systems (if it is not already), researchers will begin exploring other geometries for cationic aluminum. One promising development in this area will be the formation of five-coordinate compounds where an alkylaluminum cation is in a geometry that leaves a coordination site open. This type of complex should be less air sensitive and more easily made monomeric. This might also include compounds (like those shown generally in Fig. 1(d)) whose coordination number is increased by oligomerization in the solid but that would be monomeric in solution [32].

These compounds should also be able to be supported on a polymer for heterogeneous applications. This is one area of work that will accelerate in the new millenium. Indeed, this area is already being explored from an organic synthetic viewpoint [33]. It should be cautioned, however, that the properties of the attached cations will probably differ from that of their free state. This has been observed in supported transition-metal catalysts.

3.1.3. Bidentate Lewis acids

While multidentate Lewis basic ligands and compounds are commonplace, the analogous chemistry with Lewis acids remains relatively unexplored. This is despite the tremendous potential of such compounds in catalysis, synthesis and molecular recognition. For example, multidentate Lewis acids may be useful in the development of anion binding agents [34]. Additionally, there are a number of biologically important reactions that are mediated by two Lewis-acidic metals in close proximity. This is an important feature in the hydrolysis of phosphate ester bonds, for instance [35]. Currently, there are no simple, model systems that will effect this bond cleavage as well as enzymes (such as alkaline phosphatase). Clearly, these reactions will be improved and a wide range of other applications will be found once the synthesis and characterization of the multidentate Lewis-acid compounds has been achieved.

An early start in the synthesis of 1,2-ethanediylbis(difluoroborane) [36] was not substantiated in subsequent years although this field is currently being developed by a growing number of researchers [37]. For example, interesting acid–base complexes form when two Lewis-acidic mercury atoms are positioned *ortho* to one another (Fig. 3(a)) [38]. Mercury is also useful in preparing compounds with multiple Lewis-acidic sites [39]. Regarding aluminum, the known compounds are designed to orient two closely spaced low-coordinate aluminum alkyls pointing in one direction (examples are shown in Fig. 3(b) and (c)) [40]. Based upon the amount of effort and expertise being expended in preparing neutral bidentate aluminum-containing Lewis-acids, it is certain that some useful and important compounds will result in the near future.

A complimentary area of research that looks promising is the formation of bidentate dicationic compounds. These will be derived from an emerging class of neutral bimetallic Group 13 compounds that are supported by the salen ligands (Fig. 4(a) and (b)) [41]. Through various synthetic methods it should be possible to prepare the dicationic species, with either two aluminum atoms, or better yet, one aluminum and one gallium atom (Fig. 4(c)) [42]. These dicationic compounds should bind strongly to anionic guests (in a *cis* fashion), as well as those containing electron-rich atoms. Furthermore, the backbone of the salen ligands (the connection between the two nitrogens) may be manipulated to control the distance between the Lewis-acidic sites. This allows the possibility of binding substrates having a range of sizes with one easily manipulated system. As an example, a phosphodiester may be bound in a bidentate manner by using three methylene units in the ligand backbone (Fig. 5(a)). In this type of complex the diester would be hydrolyzed by an external base molecule. Alternatively, the backbone may be lengthened such that only one Lewis-acid site is in contact with the substrate so that a water molecule may be bound and activated by the second acidic site (Fig. 5(b)). This type of complex would model an internal base-hydrolysis mechanism. Based upon the cost, availability and the many ways in which a salen ligand may be derivatized, it is expected that these types of compounds will be developed extensively in the coming years. It is likely that the best varieties will be those incorporating either boron or gallium, which will not hydrolyze as readily as those containing aluminum.

3.2. Materials

Materials research has increased dramatically in the past decade, due in part to a growing awareness that the juncture of organic, inorganic and materials chemistry offers unique opportunities for the preparation of materials that will directly impact daily life. Furthermore, materials chemistry is viewed as a strategic area for a country's national defense [43]. These new developments will necessarily employ aluminum. The organometallic areas that are likely to do so can be divided into two categories, electronic and structural materials. These are broad areas and it makes common sense to believe that work will be done in these areas in the new millennium. Some specific areas I think will see intense focus include nanoparticulate materials, intermetallics, new routes to alumina, and building-block routes to silicates and phosphates.

3.2.1. Electronic materials

Three uses of aluminum in electronic materials will see increased activity in the coming years. The first is the formation of nanoparticulate electronic materials. A second related area is the formation of intermetallic materials either in thin-film or nanoparticulate form. The third area is broad and involves the use of precursor molecules that incorporate both the appropriate stoichiometry of the elements and the framework of the solid-state structure.

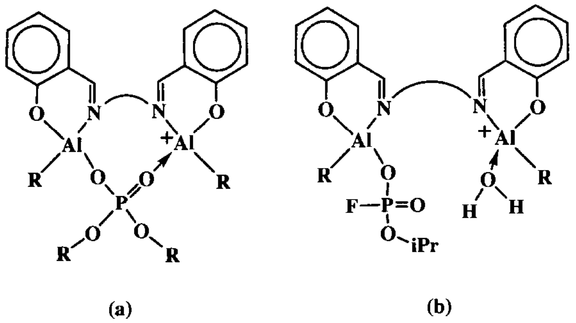


Fig. 5. Bimetallic dicationic complexes of a phosphodiester (a) and nerve agent sarin (b).

3.2.1.1. Aluminum nitride nanoparticulates.

There has been a tremendous upsurge in interest in solid-state electronic materials containing Main Group elements [44]. For AlN this is due to a wide range of possible applications including use as an insulating, passivating, or cladding layer, and as one component in blue–green lasers made from Group 13–nitride solid solutions. Organometallic routes to this material have generally involved the gas-phase decomposition of individual molecules containing the elements desired in the materials [45]. These routes require high temperatures and are, thereby, somewhat limited in application. A recent development to lower the temperature needed to form the material involves the design and synthesis of molecules possessing the appropriate stoichiometry and bonding between the elements desired in the solid-state material [46]. This unimolecular precursor approach has been used to some effect in the production of Group 13–15 solid-state materials, such as the nitrides of Al, Ga, In [47] and in solid-solutions containing AlP or AlAs [48]. It will continue to be of importance in materials synthesis, but will probably not be used to prepare bulk quantities of materials. This is due, in part, to new, favorable developments in the formation of AlN through engineering techniques such as molecular beam epitaxy [49], vapor phase epitaxy [50] and sputtering [51]. Rather, materials having unique properties and niche applications will increasingly be the targets of organometallic routes.

One key problem with the formation of solid-state nitride-containing materials through organometallic or conventional high-temperature routes is that N_2 is preferentially eliminated during the high temperatures needed to make the material. This problem could be avoided or lessened by conducting the material formation in solution at lower temperatures [52]. Moreover, it is likely that a solution-state route would naturally lead to a nanoparticulate form of the material. This is observed, for instance, in the solution synthesis of GaAs and GaP from separate sources [53]. Importantly, the size of the particles can be manipulated by the addition of chelating ligands. Nanoparticulate materials have physical properties, such as stress, shear resistance, and reduced thermal expansion that are superior to thin films. The electronic properties of the material are dependent on the size of the particles [54,55]. Furthermore, nanoparticles are readily sintered in the formation of composites and alloys. Thus, they are an important target for research efforts in the new millenium.

AlN nanoparticles are known and can be made by combining aluminum metal with ammonia at elevated temperatures [56] and through a sol–gel route employing separate sources of the reactants [57]. Precursor-polymer approaches, utilizing $\{M(NH)_{3/2}\}_n$ in the presence of chelating ligands, have been used to prepare

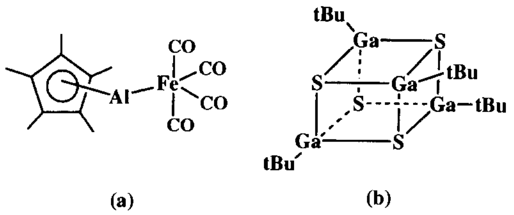


Fig. 6. An intermetallic complex (a) and a cubic precursor molecule (b).

nanoparticulate GaN [31], AlN and GaN–AlN composites (particle sizes ~ 20 nm) [58]. A key problem to be addressed by all of the attempted syntheses is to be able to achieve size homogeneity. This may be solved by the use of unimolecular precursors, particularly those with a framework like the solid-state material. However, the use of such a precursor has yet to be explored although it is likely that there are aluminum amide compounds currently available that could be used in this manner. A solution-state route to nanoparticles of aluminum–Group 15 combinations will undoubtedly be developed in the near future. Moreover, these routes may prove relevant to CVD processes [59].

One additional application that may be realized for AlN depends more on the strength of the material rather than the electronic properties. This application is as a strengthening agent in SiC–AlN solid solutions [60] and other composite ceramics such as TiN–AlN [61]. Such ceramics are envisioned to have lower densities and superior high-temperature properties by comparison to metallic alloys. Separate-source [62] and precursor-polymer [63,64] approaches have been made to obtain these composites. However, an optimal synthesis has yet to be obtained. I believe the new millenium will see the emergence of a new class of nanoparticulate AlN materials, including composites with SiC, TiN and many other ternary and quaternary combinations such as Si_3N_4–AlN and related systems.

3.2.1.2. Intermetallics. Recently, intermetallic precursor molecules, possessing bonding between transition metals and the Group 13 elements, have been synthesized and used to prepare intermetallic solid-state alloys [65]. Apparently the intermetallic bonds remain in place during the decomposition process. These bonds are fairly strong, ~ 50 kcal mol^{-1} in $[(\eta^5\text{-}C_5Me_5)\text{-}Al\text{-}Fe(CO)_4]$, for example (Fig. 6(a)). It should be noted, however, that intermetallic precursor molecules do not have to contain pre-existing metal Group 13 bonds [66] to be used in alloy formation, although such bonding is clearly favorable. The alloys that are formed with these precursors (and many others with Ga and In) have an increasing applicability. For example, Ni/Al and Mn/Al may be used as epitaxial contact metals in 13/15 electronic devices [67] and have favorable high-temperature properties [68]. The intermetallic $NbAl_3$ is being examined as a possible turbine blade material [69].

Better still is the use of molecules having the appropriate stoichiometry and arrangement of the atoms in a structure that approximates the structure of the solid-state material. This approach to materials is somewhat rare, and requires the researcher to be able to exercise control over the steric and electronic effects of the reactants to obtain the desired structure. This is an area that will see a great deal of future development, since these molecules, once prepared, can be used to access solid-state materials, often in metastable phases, at significantly reduced temperatures. A striking example of this approach is the use of a tetrametallic, cubic molecule, $[t\text{-BuGaS}]_4$ in the formation of cubic, metastable, GaS (Fig. 6(b)) [70]. It is clear that the structure of the molecule has a structure-directing influence on the nature of the solid-state material. Moreover, the *c*-GaS is useful as a much-needed passivation agent for GaAs [71]. As yet, however, this type of approach has not been proven for materials containing aluminum.

3.2.2. Aluminum oxide

An important feature of metallic aluminum is the fact that it auto-oxidizes to form a corrosion-resistant surface coating of alumina, Al_2O_3 [72]. Alumina is an unreactive thermally stable ceramic. There are several common forms of this material, each with its own set of unique applications [73]. In bulk these include use as corrosion-resistant barriers and as catalyst supports. Both of these applications involve the use of high-temperature processing. Films of the material have a number of applications [12] including uses as dielectric insulators for semiconductor devices [74], reinforcing materials [75] and, more commonly, as corrosion resistant coatings. Furthermore, nanoparticulate forms have improved resistance to mechanical and thermal shock [76]. There are two important phases of this material, α-$Al_2O_3$and γ-Al_2O_3. The α, or high-temperature, form (corundum) is preferred as a protective coating while the γ form has the advantage of lattice matching with Si(100). A stoichiometric unimolecular precursor to either form of this material has yet to be developed, although numerous separate source routes are available [77]. The same is true for mullite, $3Al_2O_3{\cdot}2SiO_2$ [78]. Lower-energy routes to these materials would broaden their range of applications as well as lower the cost of their preparation. Moreover, the lower decomposition temperatures, combined with a structural bias within the molecule, may lead to the formation of new metastable alumina phases. While most of the materials development will involve the design and use of molecular components, it should be noted that new innovative developments are still possible with 'old' materials. One example is the solubilization of boehmite to form composites; in essence a 'materials to molecules to composite' approach [79].

Our own interest in this area began with attempts to prepare alumina through low-temperature molecular routes. In collaboration with Praxair Surface Technologies, Inc., we designed and prepared organometallic molecules having the ideal stoichiometry and symmetry for alumina production (Fig. 7(a) with M = Al) [80]. While our compounds were stoichiometric for Al_2O_3, they were structurally similar to the, now historic, homoleptic aluminum *iso*-propoxides that were the first to demonstrate the tetrametallic C_3-symmetric motif (Fig. 7(b) with M = Al) [81]. Because the Al–O cores of these molecules are arranged in a fused tri-diamond shape that is reminiscent of the emblem of the Mitsubishi company, they were named Mitsubishi molecules [82]. For this reason we describe our efforts in this area as 'Mitsubishi to materials' [83]. These molecules are useful for the low-temperature deposition of pure Al_2O_3 under a wide variety of conditions [84].

The Mitsubishi motif can be changed to incorporate different metals at either the peripheral or central sites. For example, with the appropriate reaction stoichiometry a molecule having peripheral gallium atoms may be obtained (Fig. 7(a) with M = Ga). This is an unusual molecule since, in the all-alkoxide derivatives the newly introduced heavy elements such as transition metals [85] and lanthanide elements prefer the central six-coordinate site (Fig. 7(b) with M = La) [86]. These type of molecules have demonstrated use in the formation of materials such as $LaAlO_3$ through sol–gel routes [87]. This and related materials are currently being incorporated into automobile catalytic converters. The stoichiometric derivatives may be used in a like manner and offer the advantage of possessing the same ratio of metal to oxyen as the desired material. Future uses of these molecules will focus on the formation of metastable phases of alumina, and on nanoparticulate materials.

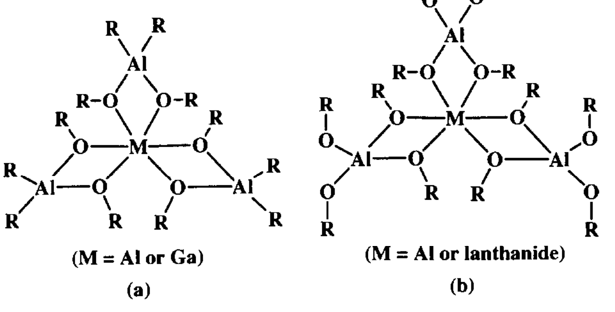


Fig. 7. New stoichiometric alumina precursors (a) and their historical analogues (b).

3.2.3. Silicates and phosphates of aluminum

Nanoporous [88] or open-framework [89] aluminosilicate [90] and phosphate [91] materials have far-ranging applications in catalysis, separations and many other areas. There is perhaps not a single aspect of modern life that is not impacted on in a substantial manner by these materials, particularly the aluminosilicates. Examples of most of these materials may be obtained naturally in the form of zeolites and clays. However, molecular routes, either through direct reactions or more usually sol–gel or hydrothermal syntheses, allow a broader range of these materials to be prepared in a controlled manner and in greater purity. This has been amply demonstrated in the preparation of synthetic zeolites as well as newer phosphate materials [92] including layered phosphates [93]. Some of the aluminophosphate materials are unique, with no precedence in zeolite chemistry [94]. Researchers are also discovering unique applications for these materials, such as in the catalystic oxidation of cyclohexane in air [95]. Moreover, the phosphate materials have generally larger pore volumes than the silicates. This chemistry is in its infancy and will continue to grow for both academic and industrial reasons.

A new approach to these materials, and one that may also use sol–gel techniques, is through the use of molecular building blocks. Here the framework of the desired material is designed into the molecular architecture. As for the building-block approach to semiconductors (see Section 3.2.1.2 above), the idea is that the molecular units will combine, under less strenuous conditions, to form the open-framework material. Another important quality of this route is that soluble precursor molecules may be employed.

3.2.3.1. Aluminum silicates. The Al–O–Si linkage has an almost overwhelming tendency to oligomerize unless bulky groups are employed either on the Al or Si atom [96]. Through the use of exceedingly bulkyl silanetriols molecules containing the framework of zeolitic materials can be obtained. The first of these molecules (Fig. 8(a)) contains the same eight-membered, $Al_2Si_2O_4$, ring as the mineral gismondine [97]. Under different conditions the same reagents (as well as other combinations) unite to form a cage framework similar to zeolite A (Fig. 8(b)). When $LiAlH_4$ is used as the source of Al, tetra-anionic cages, having the same framework, are formed. It is certain that these types of molecular approaches will lead to the discovery of new zeolitic materials. For instance, it is likely that these materials are representative of structural types of silicates that can withstand the substitution of many other elements into the framework. This has already been demonstrated in the synthesis of a titanosiloxane framework (Fig. 8(c)). Although prepared with entirely different reagents, this framework is the same as that shown in

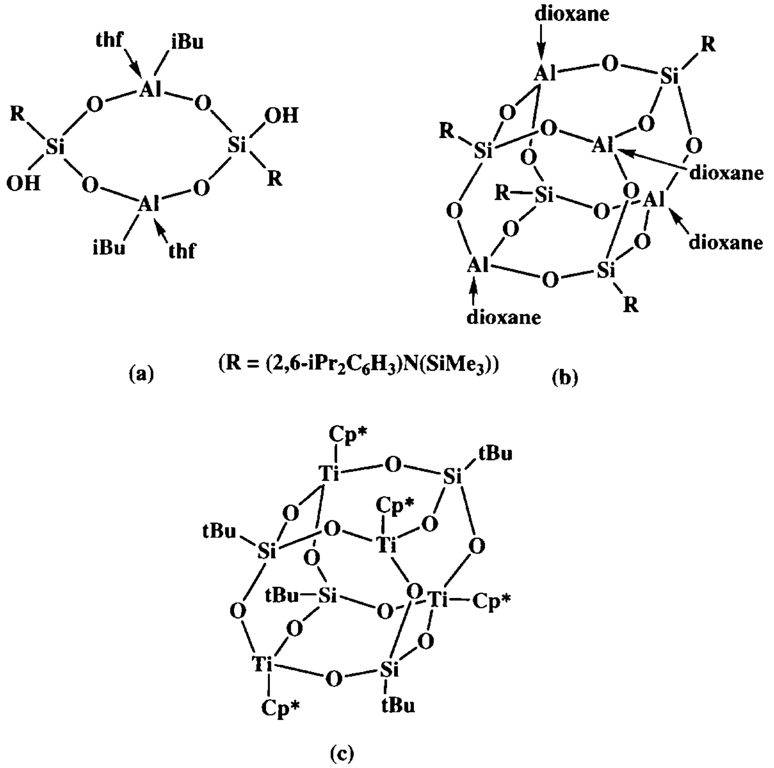


Fig. 8. Molecular frameworks for the formation of silicate materials.

Fig. 8(b) but with Ti substituted for Al. The scope of the materials that can be accessed using these molecular building blocks is virtually limitless. However, a key step in realizing this goal will be the conversion of these molecules (or more simple derivatives with the present examples serving as models) into real materials.

A further extension of this chemistry that should occur in the coming years is to use these molecular precursors to prepare ceramic composite materials such as mullite [52]. The molecular nature of the precursors will prevent problems seen in traditional sol–gel preparations, such as phase separation, from occurring. The control that can be exercised over the decomposition reaction may also allow the formation of organic–inorganic composite materials related to those observed in the structural materials of living systems.

3.2.3.2. Aluminum phosphates (and phosphonates). Following the precedent set by the silicate precursor molecules described above, aluminophosphate (AlPO) and gallophosphate (GaPO)[98] precursor molecules can also be made [99]. In their most simple manifestation they are dimeric (Fig. 9(a)) [100]. However, tetrametallic (cubic) [101] and hexametallic compounds can also be designed, which are models of the 'secondary building unit' in the three-dimensional structures of the materials. Two examples of these 'units', prepared by combining *t*-butylphosphonic acid with trimethylaluminum [102], are shown in Fig. 9(b) and (c). While the majority of these molecules have yet to be converted to a solid-state material, they still provide an important insight into structure and bonding in these types of materials. Presaging the important discoveries to be made in this area, dimeric and tetrameric aluminophosphate molecules (like those shown in Fig. 9(c) and (d)) were successfully decomposed in an organic solvent to form xerogels [100]. While there is a great deal of research left to be done in this area, it is apparent that new materials, and new forms of old materials can be accessed using the molecular (SBU) route. Future work will also involve more complicated molecules, such as those containing Al and a transition metal in the formation of new materials [103].

3.3. Biological activity of aluminum

3.3.1. Interactions with living systems

A wide variety of metals are necessary for the normal functioning of the human body. However, no biochemical role has been assigned to aluminum as yet and probably never will be. However, as aluminum is the most abundant metal present in the earth's crust, environmental exposure to Al is unavoidable; it is found in many processed foods, medicines, and other commercial products.

Biological systems cannot reduce aluminum ions to the metal state [104]. In aqueous solutions, Al^{3+} ions bind to a wide variety of anions including F^-, OH^-,

HPO_4^-, and citrate. There are also a large number of proteins that can bind to Al^{3+}, for example osteocalin, phosphophoryn, phosvitin, and chrome azurol [105]. Aluminum has been shown to be toxic to organisms. It causes inhibition of root formation in plants, abnormal development in fish, and neurological, bone tissue, and hematological disorders in man [106]. Despite the active role of Al^{3+} in living cells, not much is known about the biochemical mechanisms of aluminum toxicity. It is proposed that aluminum interferes with calcium and iron metabolism, and binds to cellular membrane components. It has been demonstrated that aluminum impairs cellular iron uptake in the human erythroleukemia cell line K562, thus affecting cell differentiation [107]. High concentrations of aluminum have been found in the plasma of rats that were orally administered aluminum citrate. This suggests that the kidneys do not completely remove absorbed Al^{3+} from the body. Thus it is possible for Al to accumulate in tissues [108]. The predominant aluminum species in blood plasma is Al transferase, and the major small-molecular-weight species is aluminum citrate. When introduced into systemic circulation both species can enter into the brain. Studies in rats have shown that oral ingestion of Al increases the concentration of Al in the brain [109]. Aluminum enters the brain through the blood–brain barrier where it can remain over a long period of time [110].

The buck-wheat plant has developed an aluminum resistance by using oxalic acid. Oxalic acid is released from the roots, and sequesters Al outside of the plant. Any aluminum that has entered the plant is deposited into the vacuoles of the leaves as $[Al(oxalate)_3]^{3-}$ [111]. In grasses and wheat, silicon has been shown to reduce the toxicity of Al in hydroponic cultures [112,113]. The interaction between Al and Si in plants will be an important area of research in the future [114]. It has been suggested that in humans, silicon may be the natural antidote to Al toxicity [115]. The most readily available source of Si to man is orthosilicic acid, $(Si(OH)_4)$, found in drinking water and other fluids (e.g. beer). Conflicting reports have arisen on the effect of Si on aluminum in the body. Reffitt et al. found no evidence that orthosilicic acid mobilized Al from body stores into urine [116]. However, Bella et al. reported significant increase in urinary elimination of Al after the ingestion of beer that contained silicic acid [117]. This difficulty in determining a causal relationship between Si and Al only serves to underscore the complexity of the problem. It is also an indicator of the depth of research that will be required in the future to solve this problem.

As a result of the increased bioavailability of aluminum, and the effects of aluminum on living systems (of which only a few were presented here), research to determine how Al^{3+} enter different cells, its effect on cell chemistry and morphology, the mechanism of its actions, and the fate of the Al^{3+} species will be an essential area of aluminum chemistry in the future. For human beings, in particular, exposure to aluminum is surely increasing as a result of the increasing average age of the population. It is likely that some remarkable and surprising interactions will be found in such a study. A more complete picture of the biological activity of aluminum will be developed in the coming years [118].

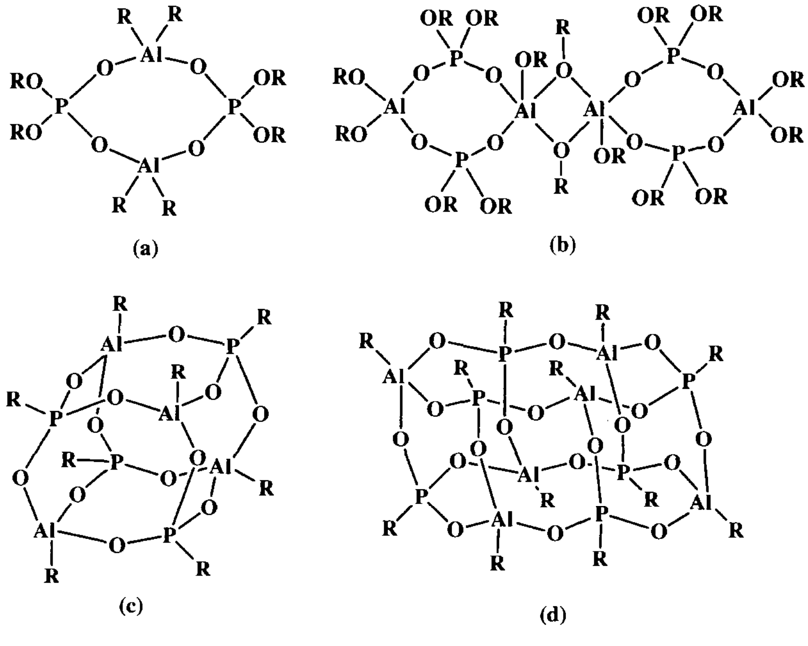

(a) (b) (c) (d)

Fig. 9. Phosphate clusters as potential materials precursors.

3.3.2. $[AlF_4]^-$ as phosphate mimic

Al–F bonds are very strong and do not degrade under physiological conditions. When bound by the oxygens of two phosphates the $[AlF_4]^-$ unit acts as a phosphate mimic whose bonds are difficult to cleave. Through this effect it apparently inhibits phospholipase D (PLD), which is an enzyme that hydrolyzes the terminal phosphodiester bonds of membrane phospholipids. It is proposed that inhibition is caused by the binding of $[AlF_4]^-$ to the phosphate binding site of the catalytic domain of PLD, which prevents the formation of a phosphatidyl–enzyme intermediate. PLD inhibition by $[AlF_4]^-$ has been demonstrated for mammalian [119] and plant [120] PLD. The phosphate mimicry may also be responsible for the observed activation of the G-protein by an $[AlF_4]^-$ containing subunit [121]. The activation is made more effective due to the slow rate of hydrolysis of the $[AlF_4]^-$ unit by comparison to normal phosphate-containing molecules.

There appears to be a great deal of medicinal chemistry possible with $[AlF_4]^-$, either to stop reactions from occurring or by promoting them to occur faster. Currently, the anion is formed from aqueous solutions of NaF and $AlCl_3$, and used on extracellular systems. A key difficulty that will have to be addressed before in vivo chemistry can be done is to find a way to introduce the $[AlF_4]^-$ group where needed. Once this problem has been successfully addressed a wide range of new medicinal applications will be accessible.

4. Conclusions

There is no doubt that aluminum will enjoy a prominent position in organometallic chemistry in the year 2000 and in subsequent years. The availability of the element in the actual dirt we walk upon, as well as its large-scale commercialization, means that researchers will have an inexpensive and ready supply of aluminum reagents to conduct imaginative research. The trend towards higher coordination numbers in aluminum compounds will lead to reagents that are of lessened air and moisture sensitivity and this, in turn, will lead to even newer applications. The future of aluminum chemistry is, indeed, very bright, and always will be.

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