



鉍物ベーマイト ($[\text{AlO}(\text{OH})]_n$) と有機配位子の直接反応による アルミニウム配位化合物の合成

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The First Example of the Synthesis of Six-coordinate Aluminum(III) Compounds via the Direct Reactions of the Mineral Boehmite ($[\text{AlO}(\text{OH})]_n$) with Ligands

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内容概要

ベーマイトはボーキサイト中に含まれる天然鉍物で、Al, O, Hの三種類の元素からなる無色の粉末として廉価で市販されている。ベーマイトは規則的な構造を有し、アルミニウム原子ひとつに対して6つの酸素原子が配位しているため、焼成によりアルミナを作る原料としてもさかんに用いられている。ベーマイト中のアルミニウムは Al^{3+} イオンとして存在していると考えられるため、定量的な Al^{3+} 供給源と見做す事ができる。本稿では新しい合成方法としてベーマイトを使った有機アルミニウム化合物の直接合成する方法を初めて紹介する。酸素や窒素が配位したアルミニウム化合物であるアルミニウム(III)アセチルアセトン, aluminum (III) acetylacetonate ($\text{Al}(\text{acac})_3$), やトリスヒドロキノリンアルミニウム, tris(8-quinolinato) aluminum (III) (Alq_3) は従来アルミニウムの硫酸塩や硝酸塩を出発物質として合成されてきた。また、塩化アルミニウムを原料とした合成にはクロロホルムなどの有機溶媒を用いる必要があった。今回我々が開発した方法は、ベーマイトとアセチルアセトンあるいは8-ヒドロキノリノールなどの有機化合物を水中に懸濁したまま直接反応させることにより、1段階で高効率に合成する方法である。さらに本反応副生成物として水分子を放出するだけであり精製が非常に容易である点、また従来法のように酸や有機溶媒を用いない環境にやさしい手法である点で優れている。様々な錯体合成の出発物質となり得るアセチルアセトン錯体を簡便かつ高収率で合成できる本方法は実用的に価値の高いものと期待される。また、 Alq_3 は近年注目される有機ELの発光層に用いられる物質で、ユニークな発光特性を示すことで知られる。今後その重要性が産業界を中心にさらに高まるであろう Alq_3 を大量かつ安価に高純度合成する方法としては本報告が最初の例である点は注目に値する。

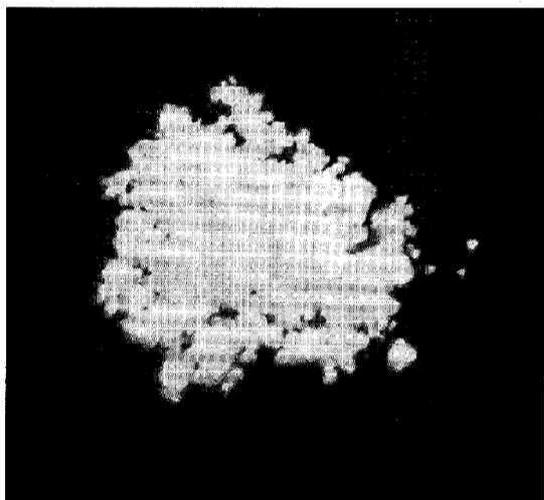
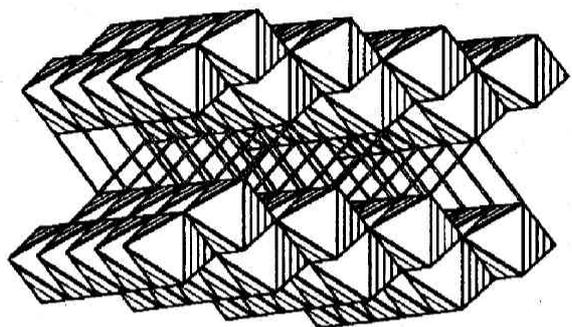
本稿では上記ふたつの合成反応を中心に、それぞれの合成方法と生成物のキャラクタリゼーション(核磁気共鳴、質量分析、熱分析、粉体X線結晶構造、元素分析、蛍光スペクトル)ならびに反応機構について詳細を述べた。今後、この手法を発展させさらに多様かつ複雑な構造を有する有機アルミニウム化合物の簡便な合成法を見出して行きたい。

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1. Introduction

Boehmite is a naturally occurring mineral with the structure consists of double chains of edge-shared AlO_6 octahedra, in which the Al atom is surrounded by five oxide and one hydroxide anions². (Scheme. 1)



Scheme 1. Schematic representation of the layer structure of a mineral boehmite (top) and a picture of the commercial boehmite powder (bottom).

These chains share a further two edges to form puckered sheets (**Figure 1**). These sheets are bound to each other through

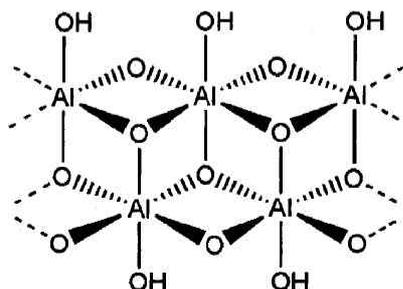
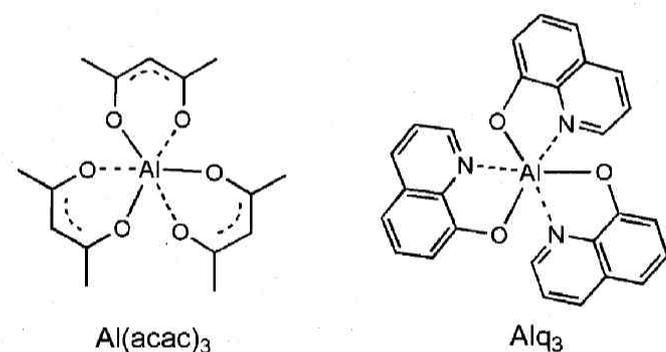


Figure 1. Structure of a part of boehmite showing an array of edge-shared AlO_6 octahedra in a sheet of $[\text{AlO}(\text{OH})]_n$.

hydrogen bonds forming a particle of several tens of micrometer in size. Boehmite is hydrophobic and its reactions include, for example, dehydration to form γ -alumina, and the surface derivatization with carboxylic acids.³ In addition to these reactions, boehmite can be regarded as a rich source of the aluminum atoms in the form of a cluster of six-coordinate oxides poised to be employed in the synthesis of six-coordinate aluminum compounds. We were intrigued if the water dispersed boehmite would react with organic reagents to yield water insoluble metal chelates in situ. In this study, we employed acetylacetonone (Hacac) and 8-hydroxyquinoline (8-Hq) as the ligands. Hacac is slightly water soluble and exists in the keto and enol forms. If Hacac is able to extract the metal in boehmite, the reaction would provide $\text{Al}(\text{acac})_3$. Typically, $\text{Al}(\text{acac})_3$ is prepared in the reaction of Hacac with $\text{Al}_2(\text{SO}_4)_3 \cdot 17\text{H}_2\text{O}$ or $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in water in the presence of ammonia.^{4,5} AlCl_3 is employed when the reaction was accomplished in chloroform.⁶ $\text{Al}(\text{acac})_3$ has been widely used as catalyst in, for example, olefin polymerization,⁷ epoxy curing,⁸ and silane polymerization.⁹ Recently, $\text{Al}(\text{acac})_3$ is used for the preparation of superhydrophobic surface.¹⁰ On the other hand, 8-hydroxyquinoline (8-Hq) has been known as achelate forming reagent, which precipitates many metals. For instance, 8-Hq readily forms a precipitate of tris(8-hydroxyquinolinato) aluminum(III) (Alq_3) with the Al^{3+} ion.¹¹ Given these conditions, we were intrigued by conducting the direct reaction between boehmite and 8-Hq that was anticipated to give Alq_3 in a single step under environmentally friendly conditions. Since the first application as the emission layer in the organic light emitting diodes (OLEDs) by Tang and Van Slyke, Alq_3 continues to attract attention and remains as one of the most widely studied Al coordination compounds.¹² Generally Alq_3 is prepared in the reaction between the Al^{3+} ion source, such as $\text{Al}(\text{NO}_3)_3$ and $\text{Al}_2(\text{SO}_4)_3$, and 8-Hq in water.¹³ A few solid state synthesis methods has been investigated, such as the reaction of aluminium isopropoxide with 8-Hq in an oven,¹⁴

and intercalation of 8-Hq in the interlayers of Al-smectites.¹⁵ However, these procedures are either accompanied by the environmentally harmful byproducts or unfit for quantitative formation of chemically pure Alq_3 . Meanwhile, boehmite has been chemically functionalized by carboxylic acids¹⁶ to prepare the inorganic-organic hybrid materials.¹⁷ Despite interesting property of the resulting carboxylatoalumoxanes, the coordination mode of the carboxylate group to boehmite are not fully understood. Our research may contribute to understand the new aspects of the coordination chemistry of boehmite.



2. Reaction of boehmite with acetylacetone

2.1 Experiments Acetone (Wako Chemical) was distilled prior to use. Boehmite (Wako Chemical) and Hacac (Tokyo Kasei) were used as received. Mass spectra analysis was obtained on a Hitachi M-2000 mass spectrometer with an electron beam energy of 70 eV for EI mass spectra. TG/DTA analyses were obtained on a Rigaku G 8120 instrument using air as a carrier gas. An XRD sample is prepared by mounting grounded powders on glass slides prior to analysis. Data were collected on a Rigaku Multiflex diffractometer.

A dried powder of boehmite (1.00 g, 16.7 mmol) was added by four equiv. of Hacac (6.67 g, 66.7 mmol). Here we added an excess amount of Hacac from the following reason. Although the molar number of boehmite was determined using $\text{AlO}(\text{OH})$ ($= 60 \text{ g} \cdot \text{mol}^{-1}$) as a unit, since the commercial boehmite is hydrated by unidentified number of

water ($\text{AlO}(\text{OH}) \cdot n\text{H}_2\text{O}$). In order to ensure the complete consumption of boehmite an excess amount of Hacac was added. Boehmite turned pale orange yellow upon contact with neat Hacac. Then, the mixture was covered by 30 mL of deionized water and boiled under vigorous stir. Initial pale orange color of the reaction solution gradually intensified as the reaction proceeds for the next few hours until no visible change was recognized. In order to ensure the completion of the reaction, the solution mixture was left to reflux overnight and the reaction was discontinued after 12 hours. The contents were filtered using a glass filter and the products were rinsed with 5 mL of cold water for three times prior to dry under vacuum. The products had crystalline glare with granular appearance ($< 1 \text{ mm}$ in diameter), which was obviously different from a fine powder of boehmite. These crude crystals were dissolved and recrystallized from hot acetone prior to analyses. Its mass spectroscopic and TG/DTA data agrees well with those of $\text{Al}(\text{acac})_3$.¹⁸ The reaction yield was 69.5% (3.75 g) based on boehmite. A photographic image of the recrystallized product ($\text{Al}(\text{acac})_3$) is shown in Figure 2.

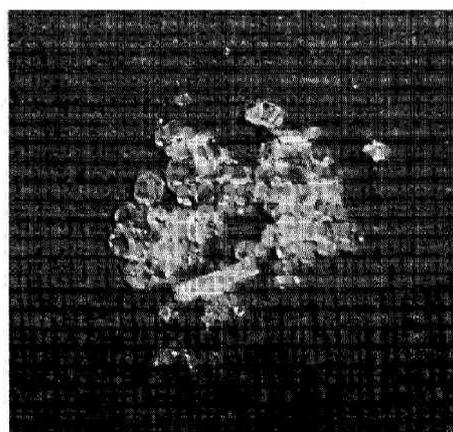


Figure 2. Photographic image of the recrystallized $\text{Al}(\text{acac})_3$. ^1H NMR of CDCl_3 solution exhibits two singlets at $\delta = 1.99$ (6H, s, $\text{C}(\text{O})\text{CH}_3$), and 5.48 (1H, s, $\text{C}(\text{O})\text{CHC}(\text{O})$) that are consistent with the chelating acetylacetonato ligands.

2.2 Results and Discussion The XRD spectrum of the resulting solid was compared with that of boehmite (Figure 3). A characteristic sharp diffraction pattern was indicative of the product to consist of only crystalline components. The XRD pattern of the product was compared with that of a commercially available $\text{Al}(\text{acac})_3$ (Figure 4). Two XRD patterns are essentially identical and confirmed our conclusion. It is noteworthy that when the reaction was conducted for 24 hours, the pale yellow crystalline grain grew larger in size ranging from 2 to 4 μm .

Mechanistically, we propose that the enol form of Hacac protonates the hydroxy group on the Al atom and consequently the acac^- coordinates concurrent with the water dissociation (Scheme 2).

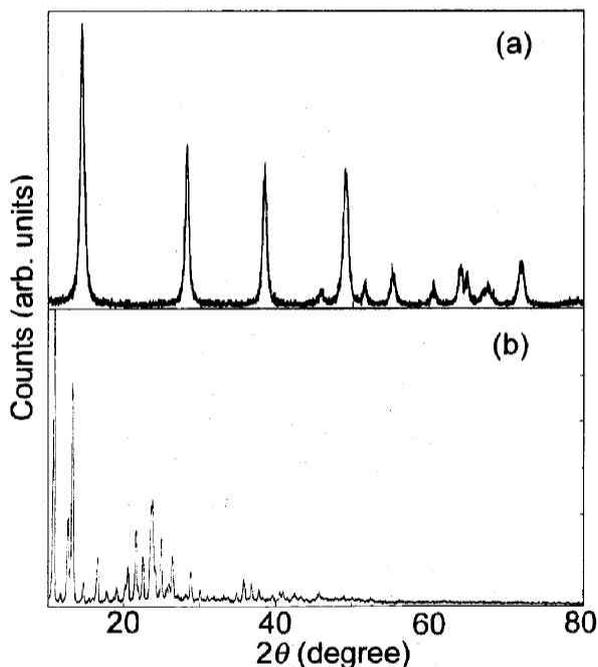


Figure 3. XRD patterns ($\text{CuK}\alpha$ radiation, $\lambda = 1.54056$) of boehmite (a) and the reaction product (b), showing the crystalline component.

Because the spontaneous development of the pale orange yellow color indicates the presence of the chelating ligand, the first chelation is considered to happen instantaneously subsequent to the cleavage of the oxo-ligands. Then the second Hacac will protonate the oxo-ligand to a new hydroxy group and, by this point, essentially the alumoxane framework should decompose. The third Hacac will

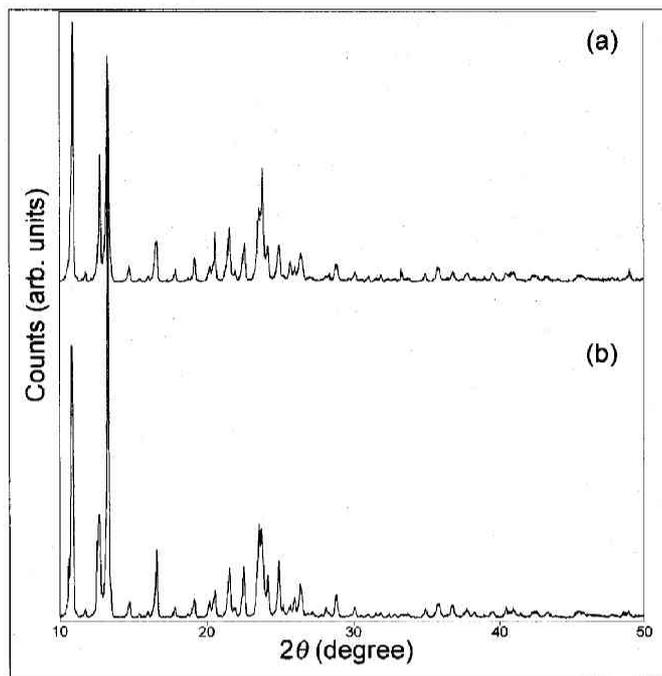


Figure 4. XRD patterns if a standard sample of $\text{Al}(\text{acac})_3$ (a) and the product (b).

substitute the hydroxy group similarly to the first Hacac substitution.

Carboxylic acids also react with boehmite to yield carboxylatoalumoxanes.³ Spectroscopic studies indicate that the carboxylate group binds to the adjacent two Al atoms in the bridging mode. In addition, crystallographic evidence of the bridging coordination is obtained in the model reaction between the single isomer of alumoxane, $[(^t\text{Bu})\text{Al}(\mu_3\text{-O})_6]$, and benzoic acid, although the Al atoms in the resulting complex, $[\text{Al}_5(^t\text{Bu})_5(\mu_3\text{-O})_2(\mu_3\text{-OH})_2(\mu\text{-OH})_2(\mu\text{-O}_2\text{CPh})_2]$, were five-coordinate unlike boehmite.²¹ In carboxylatoalumoxane, unlike the outcome of Hacac substitution, the alumoxane framework is preserved in the product.³ This sharp contrast in the reactivities of boehmite must be attributed to the geometric difference between the two ligands. For the carboxylate group, in order to avoid the large ring strain, it prefers the bridging mode, while Hacac can readily form a six-membered ring. Thus, as long as the substitution replaces only the surface hydroxy groups, the alumoxane framework remains intact. On the other hand, the oxo-ligand cleavage must be induced only

when the chelate is formed on the Al atom as we proposed above. In order to study those phenomena, we are currently preparing computational works of the electronic structure of the ligands and boehmite.

It is worth noting that when the water to reactants ratio was increased by ten fold, exceeding amount of water retarded the reaction severely. We are currently investigating this phenomenon in association with the reaction mechanism.

3 Reaction of boehmite with 8-hydroxyquinoline

3.1 Experiments A dried boehmite powder (0.10 g, 1.7 mmol) was added by four equiv of 8-Hq (0.97 g, 6.7 mmol). The reaction mixture was covered by 30 mL of deionized water and this pale yellow suspension was boiled under vigorous stir. In the next few hours, the colour intensified gradually to greenish yellow and the reaction was discontinued after 24 h. The contents were filtered using a glass flit and the filtrates were rinsed with 5 mL of cold acetone for three times prior to dry under vacuum. The resulting greenish yellow solid 1, which readily dissolves in chloroform to provide yellow solution, was subject to analysis without further purification. The aromatic region of 1H NMR spectrum of complex 1 coincides with that of a standard sample of Alq_3 (Figure 5).

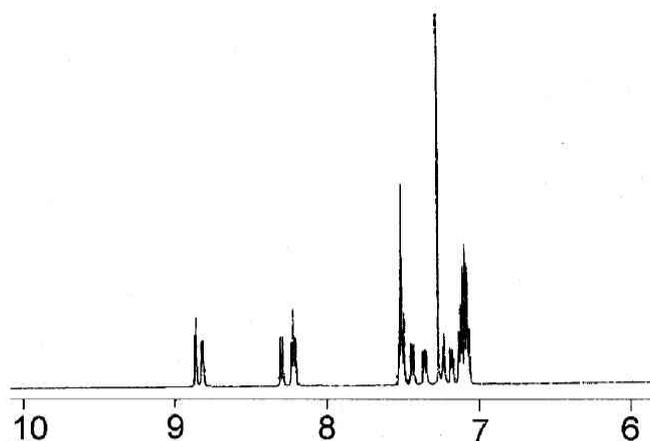
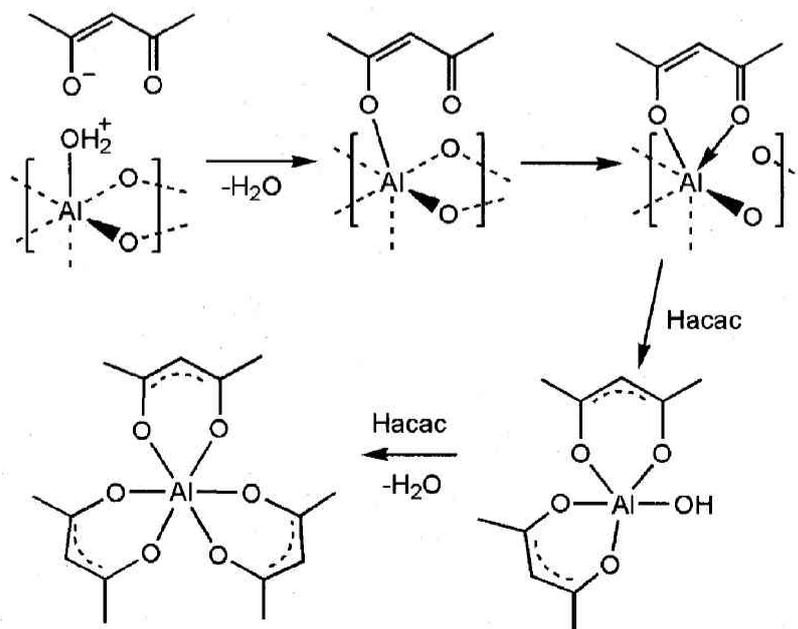


Figure 5. Aromatic regions of a 1H NMR spectrum of 1. NMR spectrum is observed in $CDCl_3$. Chemical shifts are reported with respect to TMS.

Electron ionization (EI) mass spectrum data of 1 shows a molecular ion peak at m/z value of 459 and a fragment peak at 315, corresponding to the Alq_3 with acquired H and $(Alq_3^+ - C_8H_5NO)$, respectively. The reaction yield was 96.4 % (0.739 g, 1.61 mmol) based on boehmite.¹⁹

3.2 Results and discussion In order to study stoichiometry of the reaction, boehmite was reacted with one and two equiv each of 8-Hq to obtain Alq_3 as the principal product with the production yields of 30 % and 58 %, respectively, based on boehmite. Therefore, it was postulated



that 8-Hq precipitates the Al^{3+} ion quantitatively from boehmite. Overall reaction can be written as shown in eqn. (1).



Fluorescence spectrum of 1 was also observed as a chloroform solution. When the solution was excited at 450 nm, a broad fluorescence, characteristic to Alq_3 was recorded (Figure 6).

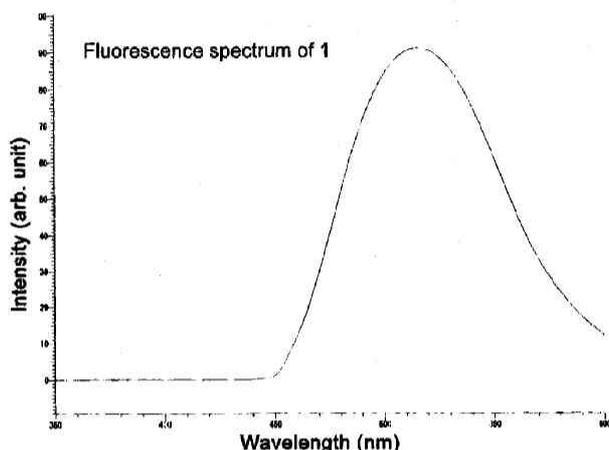
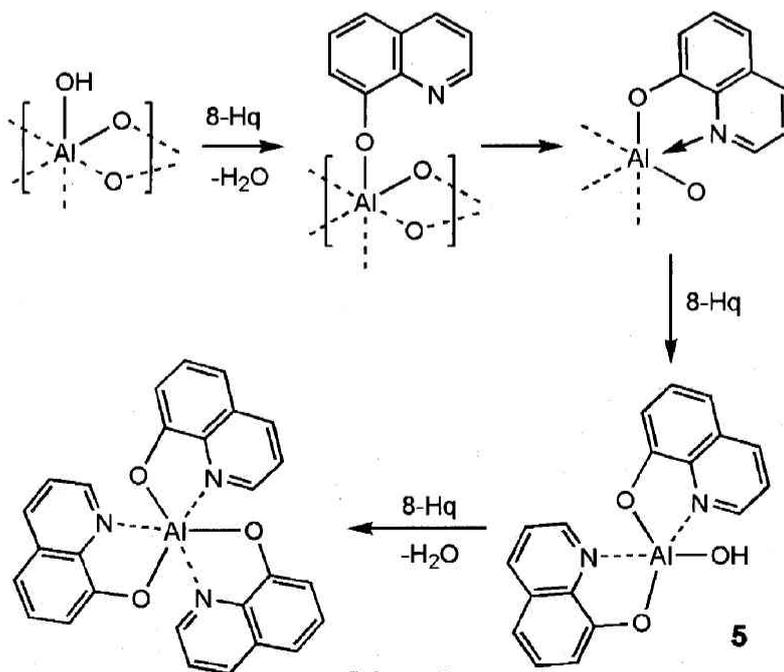


Figure 6. Fluorescence spectrum of 1 in CHCl_3 .

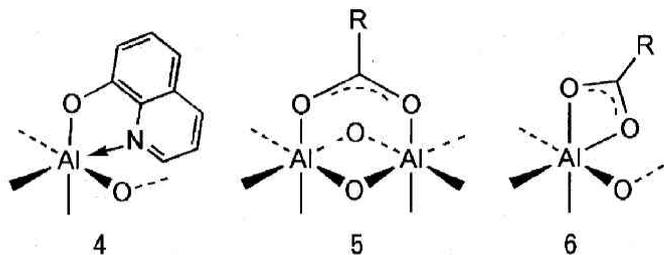
Mechanistically, due to Lewis acidity of the Al atom in boehmite, the surface hydroxy group is considered to undergo protonation by the entering 8-Hq and lose a water molecule concomitant with

the ligand substitution (Scheme 3).²⁰ Then, perhaps the second 8-Hq in the vicinity of the intermediate 2 protonates an oxo-ligand to generate a new hydroxy group (3), which would eventually be substituted by yet another 8-Hq to form Alq_3 .

It is worth noting that the analogous reaction observed between carboxylic acid and boehmite is also proposed to proceed via the substitution of surface hydroxy groups and protonation of an oxo-ligand.¹⁶ However, unlike 8-Hq, carboxylic acid is suggested to coordinate mostly in bridging fashion across two adjacent Al atoms. The carboxylic acids substitute only the surface hydroxy groups and the alumoxane core structure is kept intact, hence the resulting carboxylatealumoxane maintains the particle-like appearance with 50-100 nm in diameter.^{16,21} This is in sharp contrast with the result obtained in 8-Hq coordination, which apparently coordinates to the Al atom in boehmite as a chelate ligand and completely disassembles the core structure until the ligand is consumed. Geometrically, it is speculated that 8-Hq is conveniently arranged to form the five-membered ring (4) with the Al atom, while the carboxylate group is more suitable for the six-membered ring with the oxo-bridged Al atoms (5) and the ring strain is too large for chelate formation (6).²¹



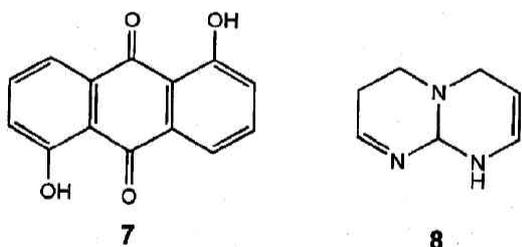
Scheme 3



4. Conclusion

This report described a novel use of boehmite as a solid-state, quantitative source of the Al³⁺ ions for the preparation of six-coordinate aluminum compounds.

This research demonstrated an innovative use of boehmite as a source of the Al atoms in the synthesis of a six-coordinate mononuclear alumoxane compound, Al(acac)₃ and Alq₃ in a heterogeneous aqueous mixtures. The method enables a large scale preparation of the Al³⁺ coordination compounds under "green" conditions. Syntheses using various oxygen- and nitrogen-donor bidentate ligands (7 and 8) are in progress as well as computational studies of the electronic structure of the ligands and boehmite.²²



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6. References and Notes

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- MS (EI, %) m/z 324 (M+, 100), 225 (M+ - CH₃COCHCOCH₃, 88), 126 [M+ - (CH₃COCHCOCH₃)₂, 80]. Mass loss of 99.6 % occurs between 180 and 250°C with DTA peak at 196.2 °C. Elemental analysis: Found (Calcd. for C₁₅H₂₁O₆Al); C 54.99 (55.54), H 6.48 (6.54).
- Elemental analysis: Found (Calcd. for C₂₇H₁₈N₃O₃Al); C 69.37 (70.59), H 3.94 (3.95), N 8.98 (9.15).
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