One-step Synthesis of Aluminum Acetylacetonate from $[AlO(OH)]_n$ (Boehmite) in Water

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Aluminum acetylacetonate, $Al(acac)_3$, was prepared in the reaction between the mineral boehmite, $[AlO(OH)]_n$, and acetylacetone (2,4-pentanedione; Hacac) in water. In this one-step synthesis, the pale yellow crystalline product precipitated out of the solution. Characterization of the recrystallized crystal by mass spectrometry, thermogravimetric/differential thermal analysis (TG/DTA), ^1H NMR, and the X-ray diffraction (XRD) was consistent with $Al(acac)_3$. This is the first example of the preparation of the six-coordinate aluminum compound from boehmite.

Boehmite[1] 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 anions.[2] These chains share a further two edges to form puckered sheets (Figure 1). These sheets are bound to each other through 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, boehmite can be regarded as a rich source of the Al^{3+} ions in the form of the cluster of six-coordinate oxides poised to be employed in the synthesis of six-coordinate aluminum compounds. We set out to investigate if the water dispersed boehmite would react with organic reagents to yield water insoluble aluminum coordination compounds in situ. In addition, this research may uncover a unique chemistry by the mineral boehmite.

In this report, we employed Hacac as a reactant. Hacac is slightly water soluble and can exist in the keto and enol forms. If Hacac is able to extract the Al^{3+} ion in boehmite, the reaction should yield $Al(acac)_3$, which is a chemically well-defined, hydrolytically stable and lipophilic pale yellow compound. It has been extensively used as catalyst in, for example, olefin polymerization,[4] epoxy curing,[5] and silane polymerization.[6] Recently, $Al(acac)_3$ is used in fabrication of the superhydrophobic surface.[7] Typically, $Al(acac)_3$ is prepared in the reaction of Hacac with $Al_2(SO_4)_3 \cdot 17H_2O$ or $Al(NO_3)_3 \cdot 9H_2O$ in water in the presence of ammonia.[8,9] $AlCl_3$ is employed when the reaction was accomplished in chloroform.[10] All these methods are, however, accompanied by the acid by-products. Meanwhile, the proposed reaction produces water as the sole by-product that renders the product isolation/purification processes simple. This method can be the environmentally friendly alternative route to the production of the aluminum coordination compounds.

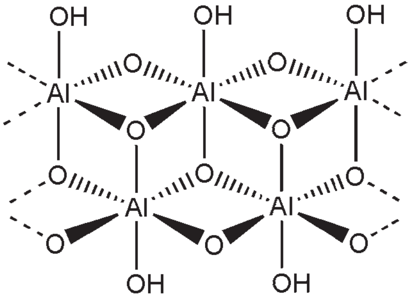


Figure 1. Structure of a part of boehmite showing an array of edge-shared AlO_6 octahedra in a sheet of $[AlO(OH)]_n$.

Acetone (Wako Chemical) was distilled prior to use. Boehmite (Wako Chemical) and Hacac (Tokyo Kasei) were used as received. Mass spectra data were 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 G8120 instrument using air as a carrier gas. XRD data were collected on a Rigaku Multiflex diffractometer. ^1H NMR spectrum was obtained in $CDCl_3$ on a JEOL ECA-500 spectrometer.

To a dried powder of boehmite (1.00 g, 16.7 mmol) was added four equiv. of Hacac (6.67 g, 66.7 mmol).[11] A colorless powder of boehmite spontaneously turned pale orange yellow upon contact with neat Hacac. The mixture was covered by 30 mL of deionized water and boiled under vigorous stir.[12] Initial pale orange color of the reaction solution gradually intensified as the reaction proceeds for the next few hours then no visible change was recognized. Eventually the reaction was discontinued after 12 h. The contents were filtered using a glass filter and the deposit was rinsed with 5 mL of cold water for three times prior to bring it to dryness under vacuum. The deposit had crystalline glare with distinctive granular appearance ($<$1 mm in diameter). The crude crystalline deposit was dissolved and recrystallized from hot acetone. Spectroscopic characterizations and TG/DTA data of the product agree well with those of $Al(acac)_3$.[13] The reaction yield was 69.5% (3.75 g) based on boehmite. Comparison of the XRD patterns of the product and the standard sample of $Al(acac)_3$ showed that the two substances are essentially identical (Figure 2).

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 1). The spontaneous development of the pale orange yellow color is indicative of the presence of the chelating ligand, suggesting immediate formation of the first chelate ligand subsequent to the cleavage of the oxo-ligands. Then the second Hacac will protonate the oxo-ligand to a new hydroxy group and essentially the alumoxane framework should decompose by this event. The third Hacac will substitute the hydroxy group in the manner similar 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. Unlike the Hacac substitution, the alumoxane framework is preserved in carboxlatoalumoxanes.[3,14] It is considered that the geometric difference between the two ligands is mostly

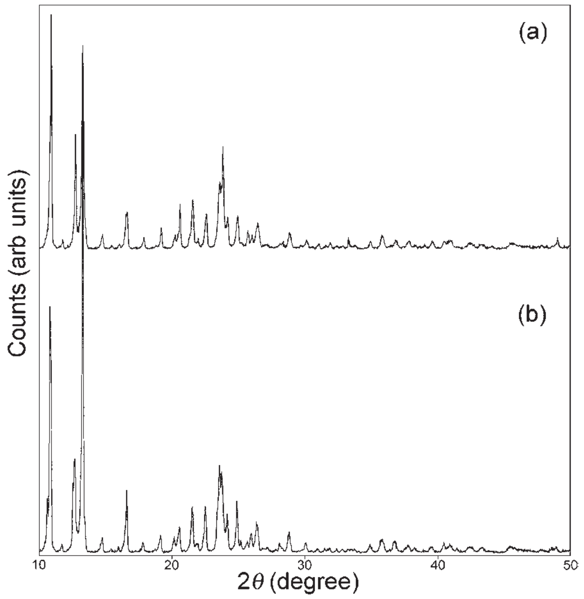
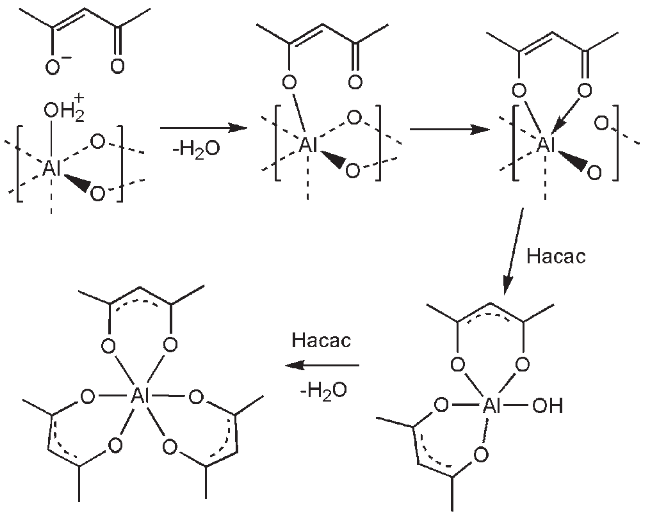


Figure 2. Comparison of the XRD patterns (Cu Kα radiation, $\lambda = 1.54056$ Å) of the standard sample of Al(acac)$_3$ (a), and the product (b).



Scheme 1. Proposed steps for Hacac coordination to boehmite and the Al^{3+} extraction.

responsible for the difference in reactivities of boehmite. 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. When the bridging ligand is formed the ligand replaces only the surface hydroxy groups, thus the alumoxane framework remains intact. On the other hand, the chelating ligand requires the oxo-lignad cleavage, which must be induced only when the ligand is capable of chelation. Detail of the reaction mechanisms will be discussed in the future publications.

We have demonstrated the first example of the synthesis of the six-coordinate mononuclear aluminum compound, Al(acac)$_3$ using boehmite as a source of the Al^{3+} ions in an aqueous solution. This method enables a large scale preparation of the analogous compounds under "green" conditions. It is highly interesting to see if the similar method can be applied to the preparation of various six-coordinate aluminum compounds using O- and N-donor bidentate ligands, such as 8-quinolinol.

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References and Notes

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11 The number of mol was calculated for AlO(OH), although the commercial boehmite is hydrated by unidentified number of water (AlO(OH)$\cdot n$H$_2$O). In order to ensure the thorough consumption of boehmite, an excess amount of Hacac was added when stoichiometry required three equiv.
12 It is noteworthy that when the volume of water was increased by ten times, the reaction was severely retarded.
13 ^{1}H NMR (CDCl$_3$): δ 5.48 (1H, s, C(O)CHC(O)), 1.99 (6H, s, C(O)CH_3). MS (EI, %) m/z 324 (M$^+$, 100), 225 (M$^+$ − CH$_3$COCHCOCH$_3$, 88), 126 [M$^+$ − (CH$_3$COCHCOCH$_3$)$_2$, 80]. 99.6% of the product vaporizes between 180 and 250 °C with DTA peak at 196.2 °C (Al(acac)$_3$: mp 194.6 °C). See: Ref. 2.
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