Synthesis of soluble aluminium carboxylates directly from aluminium hydroxide

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Water soluble aluminium carboxylates, of use as water based ceramic precursors and as starting materials for the synthesis of other metalloorganic materials, can be prepared in one or two steps from gibbsite [α-Al(OH)$_3$·3H$_2$O] and boehmite [Al(O)(OH)]$_n$. Both starting materials can be used to synthesize aluminium formate [Al(O$_2$CH)$_3$] and aluminium hydroxyformate [Al(OH)(O$_2$CH)$_2$]. These two compounds can be used to synthesize aluminium lactate [Al{O$_2$C(OH)CHCH$_3$}$_3$] and aluminium methoxyacetate [Al(OH)(O$_2$CCH$_2$OCH$_3$)$_2$·H$_2$O]. All of the compounds synthesized were characterized using XRD, TGA, DRIFTS, NMR and wet chemical techniques.

Introduction

Given alumina's widespread utility in ceramics manufacturing, continuous efforts are being made to develop new processing routes to high quality alumina based materials. These efforts are in part responsible for the development of chemical processing (*e.g.* sol–gel and polymer precursor) approaches, especially for advanced ceramic applications.

Chemical processing routes rely heavily on aluminium-containing metalloorganics that derive from aluminium metal.[1] Given that aluminium metal is produced using high energy, high temperature, high cost metallurgical processes, there is considerable impetus to develop new, low cost routes to aluminium metalloorganics. One potential alternative would be to make them directly from standard mineral sources, such as gibbsite [α-Al(OH)$_3$·3H$_2$O], bayerite [β-Al(OH)$_3$·3H$_2$O] or boehmite, [Al(O)(OH)]$_x$.
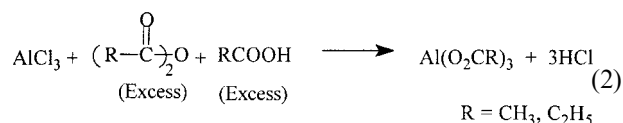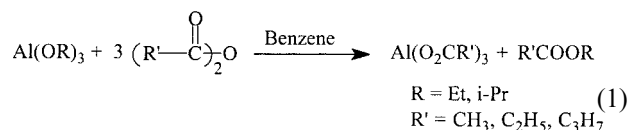
If it were possible to synthesize metalloorganics directly from aluminium hydroxide feedstock materials, it would be desirable to develop moisture and air stable materials that were soluble and/or melted easily to minimize processing problems. Such metalloorganics might then also be useful for making inorganic–organic hybrid materials.[2] Unfortunately, with the exception of the aluminium alkoxide alumatrane [N(CH$_2$CH$_2$O)$_3$Al][3] and some β-diketonates,[4] the only soluble and relatively moisture stable aluminium metalloorganics are the carboxylates, which are widely used in the textile, paper and pharmaceutical industries, and, recently, for ceramics processing.[5] For example, Al(O$_2$CH)$_3$ and Al(isobutyrate)$_3$ can be used as precursors to yttrium aluminium garnet.[6]

Aluminium carboxylates are currently made from aluminium-derived compounds, such as AlCl$_3$ and Al(OR)$_3$ (see below), rather than from aluminium hydroxides or oxyhydroxides. This then, represents the objective of the work presented here.
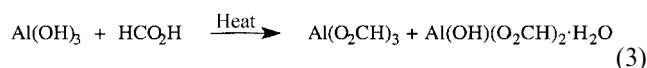
Note that the structural, physical and thermodynamic properties of the three feedstock aluminium sources listed above differ considerably and, hence, so do their chemical reactivities.[7] Gibbsite [α-Al(OH)$_3$·3H$_2$O] is the most common aluminium hydroxide mineral, accounting for >90 wt% of most bauxite. Bayerite [β-Al(OH)$_3$·3H$_2$O] is another very common aluminium hydroxide, produced in 10^6 tons y^{-1} quantities during the purification of bauxite.[1] Boehmite [Al(O)(OH)]$_x$ is the most stable and naturally abundant oxo-hydroxide.[7] High purity and high surface area gibbsite and boehmite are easily obtained and were used in the work reported here.

The history of aluminium carboxylate syntheses records considerable difficulties and contradictions. An early review casts doubt on the existence of aluminium carboxylates with carboxylate/Al ratios >2.[8] It was later proven that earlier failures in the synthesis of aluminium tricarboxylates were due to their hydrolytic instability.[9] The two major routes to aluminium carboxylates involve reaction of aluminium alkoxides with carboxylic acids/acid anhydrides, as in reaction 1,[9] or reaction of anhydrous AlCl$_3$ with acid anhydrides and/or carboxylic acids (reaction 2).[10]

$$\text{Al(OR)}_3 + 3\ \left(\text{R}'\!-\!\overset{\overset{\text{O}}{\|}}{\text{C}}\right)_{\!2}\!\text{O} \xrightarrow{\text{Benzene}} \text{Al(O}_2\text{CR}')_3 + \text{R}'\text{COOR}$$

$$\begin{array}{l} \text{R} = \text{Et, i-Pr} \\ \text{R}' = \text{CH}_3,\ \text{C}_2\text{H}_5,\ \text{C}_3\text{H}_7 \end{array} \quad (1)$$

$$\text{AlCl}_3 + \left(\text{R}\!-\!\overset{\overset{\text{O}}{\|}}{\text{C}}\right)_{\!2}\!\text{O} + \text{RCOOH} \longrightarrow \text{Al(O}_2\text{CR})_3 + 3\text{HCl}$$

$$\text{(Excess)} \quad \text{(Excess)} \qquad \text{R} = \text{CH}_3,\ \text{C}_2\text{H}_5 \quad (2)$$

A few reports describe the synthesis of aluminium formates directly from aluminium hydroxides. A 1933 Gmelin citation[11] reports that amorphous Al(OH)$_3$ reacts with formic acid as per reaction 3:

$$\text{Al(OH)}_3 + \text{HCO}_2\text{H} \xrightarrow{\text{Heat}} \text{Al(O}_2\text{CH})_3 + \text{Al(OH)(O}_2\text{CH})_2\cdot\text{H}_2\text{O} \quad (3)$$

Chaplygina *et al.* dispute these results, obtaining only Al(OH)(O$_2$CH)$_2$·H$_2$O.[12] More recent work confirms the Gmelin report.[13] Thus, one direct route exists. Unfortunately, according to these early reports, reaction 3 appears to work only with freshly prepared, amorphous Al(OH)$_3$, made from AlCl$_3$ or Al(O^{i}Pr)$_3$.[2] Thus, the real question is whether or not naturally occurring materials or those produced in multi-ton quantities can be used instead.

Recent work by Barron and co-workers suggests that boehmite [AlO(OH)]$_n$ may offer the required solution.[14,15] They report that boehmite reacts with carboxylic acids to

generate particles consisting of small "boehmite-like cores" decorated with carboxylate groups (reaction 4). The average formula for these "alumoxane" materials is given as $[Al(O)_x(OH)_y(O_2CR)_z]_n$.

$$[Al(O)(OH)]_n + zRCO_2H \xrightarrow{\text{reflux/xylenes/4d}} [Al(O)_x(OH)_y(O_2CR)_z]_n + zH_2O \tag{4}$$
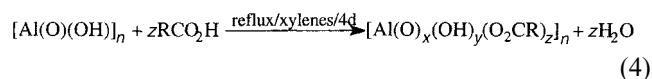
Analytical evidence indicates the presence of greater than one carboxylate unit per Al. IR reveals the presence of Al bound hydroxyl groups and a unique, bridging carboxylate. Reaction 4 is suggested to proceed by acid cleavage and replacement of hydrogen bonds between boehmite crystallite planes, basically causing exfoliation of the boehmite structure.

The longer chain acid modified alumoxanes; those with R = pentyl, heptyl or methoxyethyl, are soluble in organic solvents (*e.g.* THF, benzene, toluene, DMF), depending on the carboxylic acid group attached, and offer processability.[14] Preliminary molecular weight data suggest polymers with 20–30 kDa. The authors suggest that these alumoxanes form directly from boehmite without formation of small molecular species.[14] It is significant to note that the boehmite core structure is retained, *i.e.*, the Al–O network is not completely broken down during the formation of carboxylate alumoxanes from boehmite.[14,15]

We have explored this type of chemistry using a different approach. First, our recent work on the synthesis of processable aluminium isobutyrates, $Al(O_2C^iPr)_3$ indicates that these materials are highly susceptible to hydrolysis to form $Al(OH)(O_2C^iPr)_2$.[16] Recognizing that H_2O is a by-product of the synthesis reaction (*e.g.* reaction 4), efforts were made to scrupulously remove any water formed. This was done by using small amounts of acetic anhydride in reaction 4 or by slowly distilling the reactant carboxylic acid (bp $>100\,°C$) to codistill any H_2O generated during the reaction.

We report here the successful synthesis of several aluminium carboxylates directly from low-cost aluminium hydroxides and oxohydroxides.

Experimental procedures

General instrumental procedure

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). Fourier transform infrared spectra were obtained on a Mattson Galaxy Series 3020 bench adapted with a Harrick Scientific "Praying Mantis" diffuse reflectance accessory (DRA-2CO). The system was continuously purged with liquid N_2 boil off. Single crystal potassium bromide (KBr, ICL Inc.), powdered with an alumina mortar and pestle, was used as the non-absorbing medium. Samples were prepared using 0.3–0.5 wt% analyte rigorously mixed with the powdered KBr.

Thermogravimetric analyses (TGA). TGA of studies were performed using a 2950 thermal analysis instrument (TA instruments, Inc., New Castle, DE). Samples (10–20 mg) were placed in a platinum pan and heated under flowing, dry air ($60\,\text{cm}^3\,\text{min}^{-1}$), in "Hi-Res 4.0 mode" at $50\,°C\,\text{min}^{-1}$ to $1000\,°C$. The "Hi-Res 4.0 mode" decreases the heating rate as the rate of mass loss increases, to provide sharply defined thermal events. The TGA balance flow meter was set at $40\,\text{mL}\,\text{min}^{-1}\ N_2$, while the purge flow meter was adjusted to $60\,\text{mL}\,\text{min}^{-1}$ of synthetic air. Note that because all of the compounds produced here contain aluminium, which oxidizes in the TGA to alumina, TGA ceramic yields (loss on ignition) can be used to determine if the proposed chemical composition is that found more accurately than chemical analysis. Thus, TGA ceramic yields were used here as an alternative to chemical analysis for most of the compounds produced below.

Nuclear magnetic resonance (NMR) spectroscopy. All NMR spectra were recorded using a Bruker 360 MHz spectrometer. ^{27}Al NMR spectra were obtained with the spectrometer operating at 93.8 MHz and using a 41 000 Hz spectral width, a relaxation delay of 0.2 s and a pulse width of 13°. Samples were dissolved in dry, distilled CH_2Cl_2. D_2O in a sealed inner tube served as the lock solvent and a 1 M solution of $AlCl_3$ in $D_2O:H_2O$ (1:1) served as an external reference. ^1H and ^{13}C spectra were taken using $CDCl_3$ as solvent. $^{13}C\{^1H\}$ NMR spectra were obtained with the spectrometer operating at 90.5 MHz and using a 20 000 Hz spectral width, a relaxation delay of 0.2 s, a pulse width of 4.1° and 16 K data points.

Elemental analysis. Samples were submitted to the University of Michigan, Department of Chemistry Analytical Service for analysis of carbon, hydrogen and nitrogen contents. A Perkin Elmer (Norwalk, CT) 2400 CHN Elemental Analyzer was used, operating at $1075\,°C$, with He as the carrier gas. Powder specimens (1.5 mg) were loaded into tin capsules with powdered tin (6–10 mg) as a combustion aid. Acetanilide was used as a reference standard, and was analyzed in the same manner as the samples. Each powder was analyzed twice. Note that the accuracy of TGA analyses can actually exceed the accuracy of chemical analyses under certain conditions where there is an ash yield, as noted above. Consequently, TGA ceramic yields were deemed more reliable than chemical analyses for most of the compounds produced here.

Powder XRD studies. Samples (40–80 mg) were loaded in sample holders (glass plates) and a Rigaku Rotating Anode Goniometer (Rigaku Denki Co. Ltd., Tokyo, Japan) was used for data collection. The working voltage and current were 40 kV and 100 mA, respectively. Cu-Kα ($\lambda = 1.54$ Å) radiation with a Ni filter was used. Scans were continuous from 5–80° 2θ with a step scan of 10° $2\theta\,\text{min}^{-1}$ and increments of 0.05° 2θ. Products (peak positions and relative intensities) were characterized by comparison with standard JCPDS files.

Materials

Spacerite (Grade S11, Alcoa chemicals), Catapal d alumina (boehmite, Vista Chem. Co.), bauxite (Alcoa, Point Comfort, Texas), lactic acid (Fluka, 90%), formic acid (Fluka, 95–97%), methoxyacetic acid (Aldrich, 98%), and NaOH (Mallinckrodt, AR) were used as received. Physical and chemical analysis confirmed that both the Spacerite and Catapal were gibbsite and boehmite, respectively.

General synthetic procedures

All reactions were carried out under a N_2 atmosphere. Synthetic procedures and TGA ceramic yields are reported for each product in this section. Additional analytical data are provided in the Results and discussion section.

Synthesis of aluminium formate $[Al(O_2CH)_3 \cdot H_2O]$ from Spacerite. Spacerite [200 g, 2.54 mol of $Al(OH)_3$] was mixed with *ca.* 1600 mL of formic acid in a 2 L Schlenk flask equipped with a stillhead, and heated to distill off *ca.* 1100 mL of formic acid–water azeotrope (26% H_2O) at $100\,°C$ in 2–3 h. The remaining solvent was removed by vacuum evaporation at $100\,°C$ over 8 h. The resultant dry solid weighed 392 g (85.7% yield of $Al(O_2CH)_3 \cdot H_2O$). TGA ceramic yield of the product was 27.3% (Fig. 1). Theoretical ceramic yield for $Al(O_2CH)_3 \cdot H_2O$ to Al_2O_3: 28.3%.

The product made above (25.0 g) was purified and made more soluble by boiling in *ca.* 250 mL of water and cooling to room temperature overnight. The white powder that settled on cooling was removed by filtering the solution through a 10 mm pad of celite. The filterate was concentrated to *ca.* 100 mL by
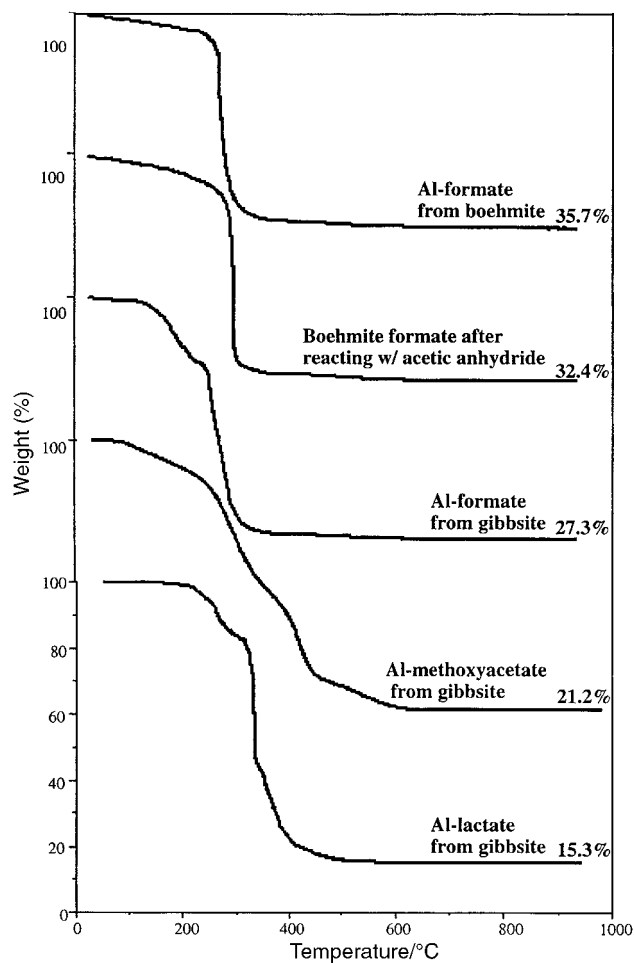
Fig. 1 TGAs of products from selected reactions.

distillation and the remaining water removed by vacuum evaporation at 100 °C over 8 h. The resultant white solid weighed 17.0 g (> 70% recovered yield) and had a TGA ceramic yield of 35.0%. Theoretical ceramic yield for $Al(OH)(O_2CH)_2 \cdot H_2O$ to Al_2O_3 is 33.5%. This material was completely soluble in hot water.

Synthesis of aluminium lactate [Al(O₂C(OH CHCH₃)₃)₃] from aluminium formate. Aluminium formate made from Spacerite (84.1 g, 467 mmol) was mixed with 200 mL (excess) lactic acid in a 1 L Schlenk flask and heated gently to 60 °C for 6 h. Then *ca.* 50 mL of ether was added to the reaction mixture and the solution filtered. The filtered white solid was boiled in *ca.* 1100 mL of boiling water, cooled to room temperature and filtered through a 10 mm celite pad to remove the small amount of insoluble white powder that settled to the bottom. The filtrate was concentrated to *ca.* 100 mL by distillation and the remaining water removed by vacuum evaporation at 100 °C over 8 h. The resultant off-white colored solid weighed 124 g (90.2% yield) and had a TGA ceramic yield of 15.3 wt% (Fig. 1). Theoretical ceramic yield for $Al[O_2C(OH)CHCH_3]_3$ to Al_2O_3 is 17.3 wt%. The material can be recrystallized by dissolution in hot water to give a supersaturated solution. Product is recovered by cooling. Note that excess lactic acid of recrystallization can be removed by sublimation at aspirator pressure and 100 °C.

Synthesis of aluminium formate [Al(O₂CH)₃·H₂O] from Catapal d. Catapal d (15.0 g, 112 mmol of Al_2O_3) was heated with 100 mL of formic acid in a 250 mL round bottom flask equipped with a stillhead, and *ca.* 50 mL of formic acid–water azeotrope was distilled off at 100 °C in about

1 h. The remaining solvent was vacuum evaporated at 100 °C for 6 h to yield a white powder. Yield: 26.8 g. TGA ceramic yield of the product was 35.7 wt% (Fig. 1). Theoretical ceramic yield for $Al(O_2CH)_3 \cdot H_2O$ to Al_2O_3 : 28.3%.

The product synthesized above (5.02 g, 37.4 mmol) was mixed with 100 mL of formic acid and 30 mL of acetic anhydride (excess) in a 250 mL Schlenk flask equipped with a stillhead, and heated to distill off the solvents, until the reaction mixture was concentrated to *ca.* 30 mL. The mixture was then dried under vacuum at 100 °C for 6 h, to yield 5.60 g of a white powder with a TGA ceramic yield of 32.4 wt% (Fig. 1). (See results and discussion section for analysis of TGA results).

The product with the ceramic yield of 35.7% synthesized above (10.0 g), was purified and made more soluble by boiling in 250 mL of water and cooling to room temperature overnight. The white powder that precipitated was removed by centrifuging the solution for 10 min and subsequent decanting. The decanted solution was concentrated to 100 mL by distillation and the remaining water was removed by vacuum evaporation at 100 °C over 8 h. The resultant white solid weighed 4.7 g and had a TGA ceramic yield of 35.2%. Theoretical ceramic yield for $Al(OH)(O_2CH)_2 \cdot H_2O$ to Al_2O_3 is 33.5%. (See results and discussion section for analysis of TGA results).

Synthesis of aluminium methoxyacetate [Al(OH)(O₂C-CH₂OCH₃)₂·H₂O] from gibbsite. Spacerite (10.1 g, 124 mmol of Al) was mixed with 100 mL of methoxyacetic acid in a 250 mL Schlenk flask equipped with a stillhead, and heated to distil off 20 mL of the solvent in about 1 h, at which time, the reaction mixture became clear. The remaining solvent was removed by vacuum evaporation at 150 °C over 12 h. The resultant dry solid weighed 29.2 g {98.2% yield of [Al(OH)(O₂CCH₂OCH₃)₂·H₂O]} and had a TGA ceramic yield of 21.2%. The theoretical ceramic yield is 21.2%. Elemental analysis, found (calc.): C, 32.8 (32.4); H, 4.88 (4.99)%.

Results and discussion

As a first step, boehmite $[Al(O)(OH)]_n$ and gibbsite $[\alpha\text{-}Al(OH)_3 \cdot 3H_2O]$ were used as feedstock compounds and reacted with formic acid to produce aluminium formates. Then, an effort was made to prove that the formate ligand would exchange with other carboxylates, *e.g.* lactic and methoxyacetic acids. The starting materials, intermediate compounds and final products were all characterized by a variety of techniques.

The initial choice of formic acid is based on the fact that aluminium hydroxides dissolve readily in inorganic acids;[17] thus, concentrated formic acid, one of the strongest organic acids (pK_a of *ca.* 5 at 1 M), might be expected to promote a similar dissolution. The literature described above (and below) provide additional support for this choice.

The choice of lactic acid was predicated on the fact that aluminium lactate is stable and highly soluble in cold water. The choice of methoxyacetic acid was based on the results of Barron and co-workers, as described above.[14,15] The reaction chemistry described below complements the syntheses by Barron *et al.* of alumoxanes from minerals,[14] and offers the potential to produce a wide variety of aluminium-containing metalloorganics.

Characterization of the minerals used as aluminium sources

The XRD powder patterns for both aluminium hydroxide sources (Spacerite and Catapal d) are shown in Fig. 2. The standard ICDD file peaks are noted in the figure. Spacerite is found to be predominantly gibbsite and Catapal is primarily boehmite. This is in accord with their TGA ceramic yields (Fig. 3), which are 64.4% [*vs.* 65.3% for $Al(OH)_3 \cdot nH_2O$] and 76.5% [*vs.* 85.0% for $Al(O)(OH) \cdot nH_2O$ ($n=0$)], respectively. Henceforth, the minerals will be referred to by their common
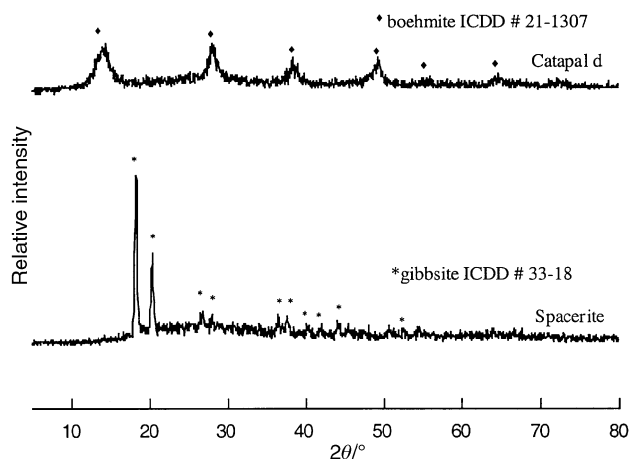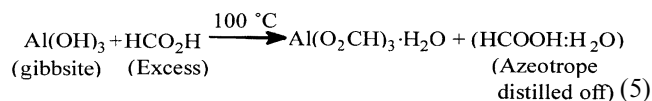
Fig. 2 XRD analyses of aluminium hydroxide sources.

Fig. 3 TGA traces of gibbsite and boehmite.

names (gibbsite and boehmite) rather than commercial names (Spacerite and Catapal). DRIFT spectra of both materials were also taken for comparison with those of the aluminium carboxylates and are shown below in the relevant sections.

Synthesis of aluminium carboxylates [Al(OH)$_x$(O$_2$CR)$_{3-x}$]

Aluminium formate [Al(OH)$_x$(O$_2$CH)$_{3-x}$]. In the reported syntheses of aluminium formate, a variety of hydrate products, as well as Al(OH)(O$_2$CH)$_2$ were obtained, depending on reaction conditions and on what temperature water was removed at.[12,13] The synthesis of Al(O$_2$CH)$_3$ has been deemed difficult because of its hydrolytic instability, therefore, most commercial material contains small to considerable amounts of Al(OH)(O$_2$CH)$_2$.[4]

The route shown in reaction 5 converts inexpensive aluminium hydroxides directly to Al(O$_2$CH)$_3$·H$_2$O without much difficulty and can be easily run at 100 g scales. However, the source (gibbsite or boehmite) played a significant role in the nature of the product, as seen below. The analytical results for the aluminium formates produced here are compared below, with those of a commercial sample.

$$Al(OH)_3 + HCO_2H \xrightarrow{100\ °C} Al(O_2CH)_3·H_2O + (HCOOH:H_2O)$$
(gibbsite) (Excess) (Azeotrope distilled off) (5)

Aluminium lactate [Al(O$_2$CCH(OH)CH$_3$)$_3$]. Attempts to synthesize aluminium lactate directly from gibbsite or boehmite failed. However, aluminium lactate could be obtained in high yields by reacting aluminium formate with excess lactic acid:

$$Al(O_2CH)_3 + CH_3CH(OH)COOH \xrightarrow[2-3\ h]{60\ °C} Al(O_2CCH(OH)CH_3)_3 + HCOOH$$
(Excess)
(6)
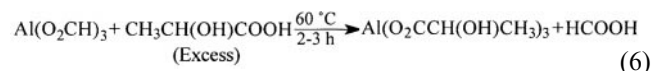
Aluminium methoxyacetate [Al(OH)(O$_2$CCH$_2$OCH$_3$)$_2$·H$_2$O]. Gibbsite reacts directly with methoxyacetic acid to give the aluminium hydroxydimethoxyacetate product in quantitative yield (reaction 7). The ceramic yield of 21.2 wt% found is also the theoretical ceramic yield.

$$Al(OH)_3 + CH_3OCH_2CO_2H \xrightarrow{200\ °C} Al(OH)(O_2CCH_2OCH_3)_2$$
(gibbsite) (Excess) $+ CH_3OCH_2CO_2H + H_2O$ (7)
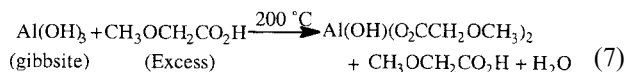
In contrast, boehmite gives a product with a 52.0 wt%, ceramic yield, suggesting formation of an alumoxane rather than a molecular material, in agreement with Barron et al., who report a value of ca. 30 wt%.[14] Note that in the work of Barron et al., the ceramic yield depended on the reaction time. A reaction time of 24 h was suggested to result in incomplete
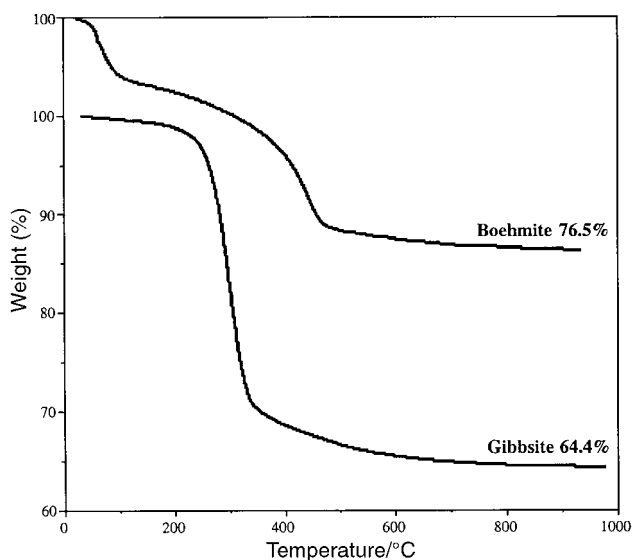
reaction (forming the alumoxane), whereas longer reaction times led to gelation. No gelation was seen in the current studies with gibbsite.

XRD analysis of aluminium carboxylates

The XRD patterns for the formates (Fig. 4) differ significantly from those of the starting materials (Fig. 2), indicating a breakdown of the mineral crystal structure. The commercial aluminium formate sample (Pfaltz & Bauer) is amorphous, as suggested by the poorly resolved diffraction pattern (Fig. 4). The few weak peaks observed in the XRD pattern of the commercial aluminium formate sample do not correspond to
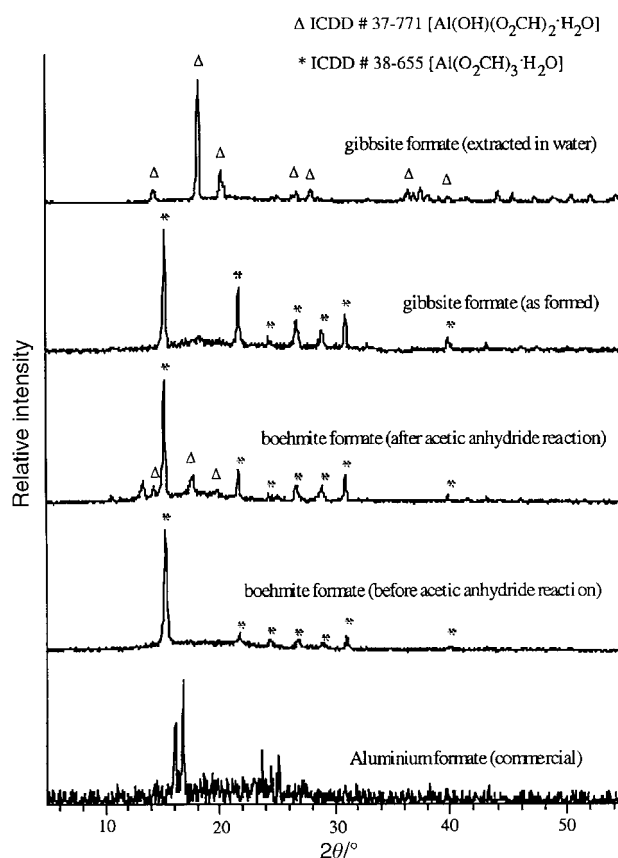

Fig. 4 XRD analyses of aluminium formates.

any known aluminium formate ICDD files (Fig. 4). Thus, proper comparison cannot be made. However, the XRD patterns of formates made here correspond to those of standard ICDD files for aluminium formates, as described below.

Gibbsite-derived aluminium formate. The XRD pattern (Fig. 4) matches that of $Al(O_2CH)_3 \cdot H_2O$ (ICDD# 38-655) quite well. It does not match the characteristic XRD patterns of anhydrous $Al(O_2CH)_3$ (ICDD# 38-583), $Al(OH)(O_2CH)_2$ (ICDD# 38-584) or $Al(OH)(O_2CH)_2 \cdot H_2O$ (ICDD# 37-771). It should be noted that the XRD patterns of formates prepared from $AlCl_3$[12] or aluminium *sec*-butoxide,[16] match each other but do not agree with any standard ICDD file patterns for aluminium formates.

Boehmite-derived formate. The XRD pattern of the product obtained after reaction with formic acid only suggests that the product is $Al(O_2CH)_3 \cdot H_2O$ (ICDD# 38-655) (Fig. 4), though the intensities of the peaks are weaker than those from the gibbsite reactions. This may be because of incomplete conversion of boehmite to aluminium formate, as suggested by the low yield of water soluble aluminium formate from this reaction (see Experimental).

However, upon reaction with acetic anhydride and formic acid, the resulting product appears to be a mixture of $Al(O_2CH)_3 \cdot H_2O$ (ICDD# 38-655) and $Al(OH)(O_2CH)_2 \cdot H_2O$ (ICDD# 37-771). Therefore, we conclude that removal of by-product water by acetic anhydride is essential in converting boehmite to aluminium formate. The presence of some $Al(OH)(O_2CH)_2 \cdot H_2O$ can be explained by incomplete reaction or partial hydrolysis of the triformate during sample handling.

Aluminium formates made from either gibbsite or boehmite can be converted to more water soluble $Al(OH)(O_2CH)_2 \cdot H_2O$ upon boiling in water, as seen by the XRD patterns presented in Fig. 4, and as confirmed by TGA ceramic yields (see experimental). This material is soluble in hot water, despite reports that it is insoluble.[12]

Thermogravimetric analysis of aluminium carboxylates

Gibbsite-derived formate. The TGA ceramic yield of 27.3 wt% found is close to theory (28.3 wt%) for $Al(O_2CH)_3 \cdot H_2O$. The decomposition pattern (Fig. 1) shows two distinct mass loss regions that correspond to those reported for $Al(O_2CH)_3 \cdot 3H_2O$.[12] The initial mass loss of *ca.* 20% (calc. 16%) below 210 °C, is attributed to the formation of $Al(OH)(O_2CH)_2 \cdot H_2O$ by loss of CO (reaction 8).[12]

$$Al(O_2CH)_3 \cdot H_2O \xrightarrow{\leq 210\ ^\circ C} Al(OH)(O_2CH)_2 \cdot H_2O + CO \qquad (8)$$

The second mass loss of *ca.* 53% (calc. 56.1%) seen above 210 °C arises from:[12,16]

$$2\ Al(OH)(O_2CH)_2 \cdot H_2O \xrightarrow{340\ ^\circ C} Al_2O_3 + 4\ CO + 5\ H_2O \qquad (9)$$

Boehmite-derived formate. The higher 35.7 wt% ceramic yield for the boehmite/HCO_2H reaction product (Fig. 1) *vs.* the 28.3 wt% calculated for $Al(O_2CH)_3 \cdot H_2O$ suggests incomplete conversion to aluminium formate, perhaps due to the formation of alumoxane. This possibility is also suggested by the TGA decomposition pattern, as the mass loss below 210 °C is much less than seen for gibbsite-derived formate. If $Al(O_2CH)_3 \cdot H_2O$ formation is incomplete, a higher ceramic yield would be expected. After reacting the initial product formed with excess acetic anhydride and formic acid, the ceramic yield drops to 32.4% [theory is 33.5% for $Al(OH)(O_2CH)_2 \cdot H_2O$], in accord with the supposition that some unreacted, amorphous material remains initially.

Reaction with acetic anhydride not only reduces the ceramic yield of the product, but increases the mass loss seen below

210 °C (Fig. 1). As with the gibbsite-derived formate, the mass loss below 210 °C is attributed to decomposition of $Al(O_2CH)_3 \cdot H_2O$ to $Al(OH)(O_2CH)_2 \cdot H_2O$ (reaction 8). It is, therefore, suggested that addition of acetic anhydride leads to further conversion, to more $Al(O_2CH)_3 \cdot H_2O$, and hence the increased mass loss below 210 °C. However, the mass loss below 210 °C, is still less than that observed for the gibbsite-derived formate and the ceramic yield is still higher than that calculated for $Al(O_2CH)_3 \cdot H_2O$. These facts along with the XRD analysis above, suggest that the product is a mixture of $Al(O_2CH)_3 \cdot H_2O$ and $Al(OH)(O_2CH)_2 \cdot H_2O$. Alternatively, a mixture of the latter two compounds and an alumoxane may be the source of the higher than expected ceramic yields.

It is interesting to note that the final water of hydration appears to be resistant to reaction with acetic anhydride, even at 100 °C, the boiling point of the formic acid–water azeotrope.

The TGA decomposition patterns of all the formates prepared as above (Fig. 1) differ greatly from their respective sources (Fig. 3), suggesting a breakdown of the Al–O–Al network. This is in contrast to the reported TGA patterns of alumoxanes, where the Al–O–Al core structure is retained.[14]

Gibbsite-derived lactate. The TGA profile shown in Fig. 1 exhibits a 20% mass loss below 200 °C not seen in a commercial aluminium lactate sample (Aldrich) and the final ceramic yield is 20% less than that calculated. This could arise due to either traces of hydrates or solvent of crystallization. If one lactic acid of crystallization is assumed $[Al(O_2C(OH)CHCH_3)_3 \cdot CH_3CH(OH)COOH]$, then the calculated ceramic yield matches that found exactly. Other analyses, especially NMR, reported below, confirm the formation of aluminium lactate. The lactic acid of recrystallization can be removed by sublimation (see Experimental).

Gibbsite-derived methoxyacetate. The TGA ceramic yield found (Fig. 1), exactly matches that calculated for $[Al(OH)(O_2CCH_2OCH_3)_2 \cdot H_2O]$. The elemental analysis (see Experimental) also confirms its formation. It is significant to note that methoxyacetic acid, upon reaction with boehmite, results in alumoxane,[14] while reaction with gibbsite yields the aluminium hydroxybismethoxyacetate $[Al(OH)(O_2CCH_2OCH_3)_2 \cdot H_2O]$.

Thus, our study extends the synthesis of soluble alumina precursors from minerals, beyond alumoxanes, to well-defined 'small molecule' carboxylates. The 'top-down' approach suggested for the synthesis of alumoxanes[14] can be extended to prepare aluminium carboxylates by replacing boehmite with gibbsite. In later work, we will show that functionalized derivatives of methoxyacetate, *e.g.* $[Al(OH)(O_2CCH_2OCH_2CH=CH_2)_2]$, can be prepared and polymerized to give stable organic–inorganic hybrids.

DRIFTS analysis of aluminium carboxylates

Carboxylates can act as mono-, bi-, tri- and tetradentate ligands, depending on the coordination with the metal ion.[18] Two types of carboxylate coordination with Al have been reported in the literature. In "type a" coordination, one aluminium binds to a bidentate carboxylate, as shown below.[19] In "type b" coordination, a bidentate carboxylate group bridges two Al atoms, as shown below.[14] Both coordination types were reported to be present in aluminium trilaurate, according to solution IR studies.[20] However, these findings were later disputed, and only "type a" coordination was found to occur.[21]

Type a   Type b

Carboxylate alumoxanes, are reported to have "type b"
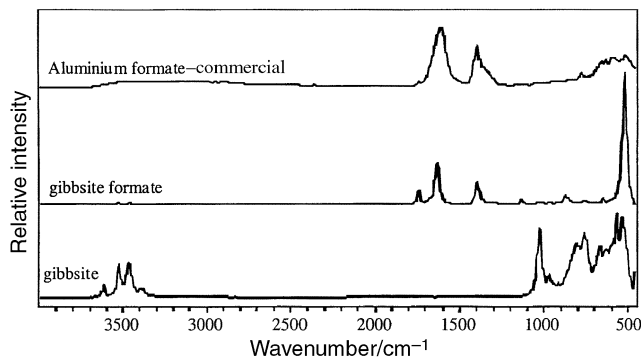
Fig. 5 DRIFTS of gibbsite-derived formate.

Fig. 7 DRIFTS of gibbsite-derived lactate.

coordination, *i.e.* carboxylate groups bridging two Al centers.[14] However, other metal carboxylates [(M(O$_2$CR)$_x$; M = Al, Ga, In, Bi, Sb)] are reported to have only "type a" coordination.[18,19] The νC=O bands for both coordination types are quite different and, hence, easily distinguishable. The aluminium carboxylates prepared here exhibit "type a" coordination, in accordance with the literature[19] which serves to differentiate them from the carboxylate alumoxanes.[14]

Gibbsite-derived formate. The DRIFT spectrum is shown in Fig. 5.

νO–H: the broad, low intensity peaks seen at *ca.* 3400 cm^{-1} are assigned to water of hydration rather than νAl–OH of Al(OH)(O$_2$CH)$_2$, as the latter appears as a much sharper peak at 3670 cm^{-1} for both Al(OH)(O$_2$C^{i}Pr)[16] and Al(OH)-(O$_2$CH)$_2$.[12]

νC–H: a low intensity peak around 2900 cm^{-1} is seen, as expected.[12]

νC=O: the characteristic peaks for the antisymmetric (1620 cm^{-1}) and symmetric (1390 cm^{-1}) stretching of the carboxylate ligand are present and match literature values.[13,19] The peak at 1730 cm^{-1} arises from traces of formic acid, since this band decreases in intensity on further vacuum drying.

The gibbsite-derived formate DRIFT spectrum does not correspond to that of the commercial sample in Fig. 5, except for a similarity in the carboxlyate stretching vibration region. But the commercial sample is water soluble, whereas in the present studies (see Experimental), only Al(OH)(O$_2$CH)$_2$ was found to be water soluble. The TGA ceramic yield of the commercial sample (34.1%) also suggests that it is Al(OH)-(O$_2$CH)$_2$·H$_2$O, the ceramic yield for which is calculated to be 33.5%.

Boehmite-derived formate. The DRIFT spectrum is shown in Fig. 6.

νO–H: the absence of significant bands in the 3400 to 3600 cm^{-1} range (attributed to water of hydration) differentiates this compound from gibbsite formate. Small νO–H peaks
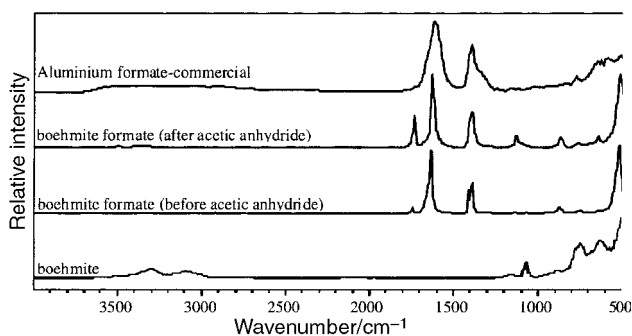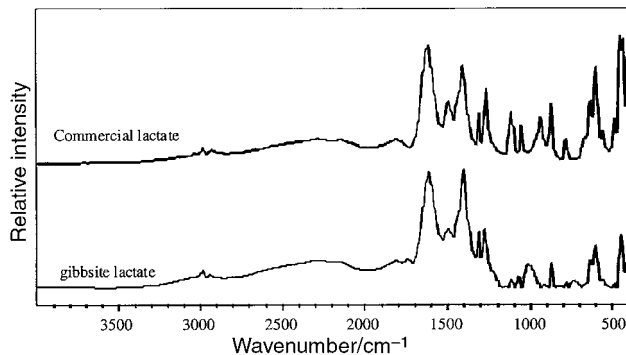
are seen that suggest that the presence of some water and a hydroxyl group, as expected for Al(OH)(O$_2$CH)$_2$·H$_2$O.[12]

The fact that, after reaction with acetic anhydride, the product has a DRIFT spectrum similar to that of gibbsite-derived formate, corroborates the conclusion, based on the TGA and XRD analyses, that it is indeed mostly Al(O$_2$CH)$_3$·H$_2$O.

νC=O: the peaks at 1620 cm^{-1} (antisymmetric C=O stretching) and at 1400 cm^{-1} (symmetric C=O stretching) are present in the as-produced material, in accordance with the literature.[12,19]

It is significant that the C=O stretching frequencies in all the aluminium formates made above, differ from those of carboxylate alumoxanes prepared from boehmite, which exhibit antisymmetric C=O stretches in the 1600 to 1580 cm^{-1} range, indicating a bridging coordination mode for the carboxylic acid groups (type b).[14] The corresponding values for the formates synthesized here are around 1620 cm^{-1}, in accord with the values reported for Al(O$_2$CH)$_3$,[12,19] indicating that the carboxylate group acts as a bidentate ligand on the same aluminium center (type a). Therefore, the breakdown of the boehmite network to form small molecule aluminium compounds is again suggested, unlike what was seen in the formation of carboxylate alumoxanes.[14]

Gibbsite-derived lactate. The DRIFT spectrum with peaks at 2990 cm^{-1} (C–H), 1610 cm^{-1} (antisymmetric C=O stretching), and 1400 cm^{-1} (symmetric C=O stretching), closely matches that of the commercial sample (Fig. 7).

Gibbsite-derived methoxyacetate. The DRIFT spectrum (Fig. 8) exhibits peaks at 2900 cm^{-1} (C–H), 1614 cm^{-1} (antisymmetric C=O stretching), and 1476 cm^{-1} (symmetric C=O stretching). It is significant to note that the values are similar to those of other aluminium carboxylates discussed above and are different from the reported alumoxane, prepared by the reaction of methoxyacetic acid with boehmite.[15]
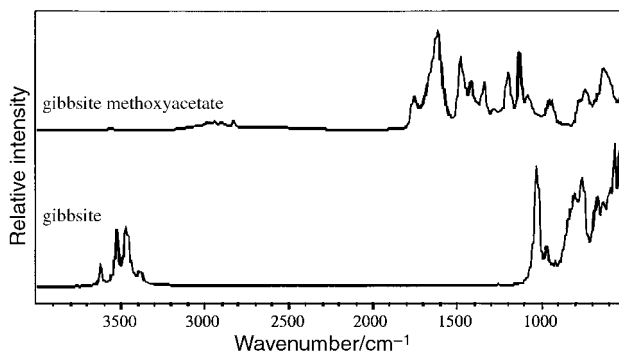

Fig. 6 DRIFTS of boehmite-derived formate.

Fig. 8 DRIFTS of gibbsite-derived methoxyacetate.

Table 1 NMR chemical shifts (in ppm) for formates

Nucleus	Gibbsite formate	Boehmite formate	Aluminium formate (commercial)
^{1}H	8.3 [Al(O$_2$CH)$_3$]	8.3 [Al(O$_2$CH)$_3$]	8.2
^{13}C	165 [Al(O$_2$CH)$_3$]	166 [Al(O$_2$CH)$_3$]	166
^{27}Al	0.5 (sharp)	0.5 (sharp)	0.5 (sharp)
	4.7 (broad)	4.7 (broad)	4.7 (broad)
	55 (very broad)	55 (very broad)	

Table 2 NMR chemical shifts (in ppm) for gibbsite lactate and lactic acid

Nucleus	Gibbsite lactate	Lactic acid (commercial, 98%)
^{1}H	4.5 and 4.3 [–CH(OH)–],	5.1 (q) [OH]
	1.4 and 1.6 [–CH(OH)–CH_3],	4.4 (q) and 4.3 (q), 1H, [–CH(OH)–]
	5.3 [OH (?)].	1.3 (d) and 1.5 (d), 3H, [–CH(OH)–CH_3]
^{13}C	72.1 and 69.6 [–CH(OH)–],	67.0 and 63.6 [–CH(OH)–]
	22.1 and 21.2 [–CH(OH)–CH$_3$]	16.5 and 13.5 [–CH(OH)–CH$_3$]
	176.7 [COOAl]	175.5 [COOH]
^{27}Al	0.9 (sharp)	—
	16.9 (broad)	
	55.7 (very broad)	

NMR Analysis of aluminium carboxylates

Aluminium carboxylates hydrolyze in aqueous solutions to different extents, depending on the pH.[22–24] Thus, solution NMR spectra often provide ambiguous results. There is extensive literature on NMR studies of aluminium carboxylates (though not with HCO$_2$H).[22–24] All the studies indicate formation of different hydrolytic products [Al(OH)$_x$-(O$_2$CR)$_{3-x}$] at different pHs.[22–24]

Gibbsite-derived formate. The ^{1}H NMR spectrum has a single peak at 8.3 ppm, as expected (Table 1) (*cf.* 8.2 and 10.0 ppm for formic acid). The absence of a COOH peak cannot be considered significant, as it is highly dependent on temperature and concentration. The commercial aluminium formate sample also has only one peak at 8.2 ppm. The ^{13}C NMR is similar to that of the commercial sample (165–166 ppm) (Table 1), and differs from those of formic acid (181 ppm) and carboxylate alumoxanes (179–182 ppm). This further supports the "type a" coordination of the carboxylate ligands to the Al atom, and that the ligand does not bridge, as in carboxylate alumoxanes.[14]

The ^{27}Al NMR spectra of gibbsite and boehmite formates show 3 peaks each, attributable to different hydrolytic products, and are in agreement with the values reported for other aluminium carboxylates.[22–24] The commercial aluminium formate shows only two peaks. The very broad peak centered around 55 ppm seen in the gibbsite and boehmite formate samples is absent in the spectrum of the commercial aluminium formate sample. However, it is reported that the extent of hydrolysis in different samples depend on various factors, including pH and time, and therefore a direct comparison cannot be made.[24]

The pH dependency of the ^{27}Al NMR signals is obvious, as the ^{27}Al NMR peaks in all three formate samples collapse to one sharp peak (at 0.0 ppm), on acidification with conc. HCl. This suggests that the different ^{27}Al NMR peaks seen for the

various formates are due to different types of hydrolytic products only. Though the ^{27}Al NMR data on the aluminium formates made are inconclusive, due to the complications arising from hydrolysis, they still help to differentiate the products made here from the alumoxanes reported[14] and are in agreement with other aluminium carboxylate spectra reported.[22–24]

Boehmite formate. The NMR spectra are identical to those of gibbsite formate (Table 1). Thus, under the reaction conditions used here, formic acid reacts with boehmite to form 'small molecule' aluminium formate by breaking down the Al–O–Al network.

Gibbsite-derived lactate. The NMR spectrum matches exactly with that of a commercial sample (Aldrich). Two peaks (different intensities) are seen for each nucleus in both the ^{1}H and ^{13}C NMR spectra (Table 2). These can be attributed to association in solution, as seen for aluminium citrates.[23a] Simple solutions of lactic acid also show two peaks for each nucleus (Table 2). These multiple peaks are expected, given that chemical shift values for optical isomers (D- and L-lactic acids) differ when diastereomeric (solvent, dimeric or coordination) complexes form in solution.[25] The ^{13}C NMR chemical shift of the carboxylic carbon increases slightly (from 175 to 177 ppm) on complexation to Al, as seen in Al complexes of pyridone carboxylic acids.[23b] The three ^{27}Al NMR peaks are due to different hydrolytic species, as reported in the literature.[24]

Gibbsite-derived methoxyacetate. There are three distinct groups of resonances for each nucleus in the ^{1}H and ^{13}C spectra of aluminium methoxyacetate (Table 3). Similar spectra are seen for aluminium citrates, where a trimeric structure has been shown to form in solution. It seems reasonable to suggest that a similar structure forms here.[23a] The two peaks seen in the ^{27}Al NMR spectrum (Table 3) are similar to those seen in the literature for many other aluminium carboxylates.[22–25]

The carboxylic acid exchange reaction, demonstrated in the synthesis of aluminium lactate (reaction 6), establishes a method for producing aluminium carboxylates with tailored solubilities. All the aluminium carboxylates made above are water soluble. The formate derivatives are much less soluble than the lactate or methoxyacetate compounds, but can be used to generate spinnable YAG precursors.[4,17] The solubility of the products can be modified to provide organic solvent soluble materials. For example, we have successfully prepared toluene soluble aluminium allyloxypropanoate (AAP) *via* an exchange

Table 3 NMR chemical shifts (in ppm) for gibbsite methoxyacetate

Nucleus	Chemical shifts (ppm)
^{1}H	4.4, 4.0 and 3.8 [OCH_3]
	3.0, 3.2 and 3.1 [CH_2–O]
^{13}C	64.2, 63.8 and 62.9 [OCH$_3$]
	57.0, 55.2 and 52.9 [CH$_2$–O]
	170.7, 168.0 and 165.9 [COOAl]
^{27}Al	0.0 (sharp) and 10.0 (broad)

reaction using gibbsite-derived aluminium formate. AAP can be polymerized in toluene using AIBN as an initiator, as will be reported separately.[26]

Conclusions

Soluble aluminium carboxylates have been synthesized from readily available aluminium hydroxide and oxo-hydroxide sources in one or two highly efficient steps. The aluminium formates produced were characterized as $Al(O_2CH)_3 \cdot H_2O$, which hydrolyses in water to give moderately water soluble $Al(OH)(O_2CH)_2$. Based on previous studies, we find that for these reactions to be effective, water must be carefully removed to drive the reactions to completion to give true aluminium metalloorganics. Aluminium lactate produced in two steps from aluminium hydroxide and oxo-hydroxide sources can be used as a water soluble aluminium precursor for the preparation of aluminium-containing ceramics. The synthesis of aluminium formate from bauxite, the cheapest aluminium ore available, was also attempted, but the formic acid promoted dissolution of bauxite was not efficient and, hence, the process was not pursued further.

The process developed here can, in principle, be extended to other aluminium carboxylates, as facile and complete exchange of formate ligands with lactic and methoxyacetic acids has been demonstrated. The use of this exchange process to develop aluminium-containing polymers has been investigated and will be reported separately.[26]

Acknowledgements

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