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Heterometallic Aluminum Alkoxides. The Characterization of $\{Mg[Al(OPr^i)_4]_2\}_n$ and $Mg_2Al_3(OPr^i)_{13}$

Juliane A. Meese-Marktscheffel, Ruth Fukuchi,
Melisa Kido, Glenn Tachibana,
Craig M. Jensen,* and John W. Gilje*

Chemistry Department, 2545 The Mall
University of Hawaii, Honolulu, Hawaii 96822

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Heterometallic alkoxides containing aluminum have been reported for a wide variety of metals.[1] The use of these compounds in CVD and hydrothermal materials syntheses has been suggested,[1] "double metal alkoxides" are marketed for use "in sol–gel and coatings applications"[2] and as precursors for "advanced ceramics",[3] "$Mg[Al(OPr^i)_4]_2$" has been used as a sol–gel precursor for spinel,[4] and we have employed it as a CVD source for glassy $MgAl_2O_4$.[5] However, there is little information on the actual molecular composition of this class of compounds, and even the chemical connectivity is uncertain. $Mo_2(O_2CH_3)_2[Al(OPr^i)_4]_2$,[6] which is atypical because it contains a metal–metal bond, and $\{Pr[Al(OPr^i)_4]_2(Pr^iOH)(\mu\text{-}Cl)\}_2$,[7] which contain an $Al(OR)_4$ unit, have been characterized by X-ray diffraction. After this communication had been submitted, we became aware of the very recently published structure of $Mg[Al(OPr^i)_4]_2{\cdot}2Pr^iOH$.[8] We are interested in these compounds and wish to report our preliminary results which include the crystal structure of $Mg_2Al_3(OPr^i)_{13}$ and a determination of some of the inter- and intramolecular kinetic processes which these molecules undergo.

Reactions of Mg with several stoichiometries of $Al(OPr^i)_3$ in isopropyl alcohol are reported to yield a single product, $Mg[Al(OPr^i)_4]_2$,[9,10] a volatile liquid which is monomeric in benzene.[10] We have repeated these reactions[11] and find the Mg–Al–OPr^i system to be more complicated. As previously described,[10] when Mg and $Al(OPr^i)_3$ in a 1:2 molar ratio are refluxed in isopropyl alcohol, high yields of liquid $Mg[Al(OPr^i)_4]_2$ may be obtained by distillation at reduced pressure. However, freshly distilled $Mg[Al(OPr^i)_4]_2$ does not remain liquid at room temperature; rather it becomes solid over several minutes. Mass spectra obtained at 50 °C contain only peaks for the relatively volatile $Mg[Al(OPr^i)_4]_2$, Im.[12] Spectra obtained at higher probe temperatures are typical of a mixture, with the most volatile component, Im, initially predominating but with higher mass peaks from $\{Mg[Al(OPr^i)_4]_2\}_2$, Id, growing in as Im is depleted.[13] These spectra indicate that I exists as a mixture of Im and Id. We interpret the slow solidification of freshly distilled I to be the result of the dimerization of Im to Id:

$$2\mathrm{Mg} + 4\mathrm{Al(OPr}^i)_3 \xrightarrow[\text{reflux}]{\mathrm{HOPr}^i} \underset{\mathrm{Im}}{2\mathrm{Mg[Al(OPr}^i)_4]_2} \rightleftharpoons \underset{\mathrm{Id}}{\{\mathrm{Mg[Al(OPr}^i)_4]_2\}_2}$$

Samples of I which are not totally pure do not solidify but remain as viscous homogeneous liquids at room temperature. (Which probably explains why this compound is reported in the literature to be a liquid.[10]) Over several weeks colorless crystals precipitate from these liquids.[14] An X-ray crystal structure,[15] Figure 1, shows these to be $Mg_2Al_3(OPr^i)_{13}$, II, and is first to be obtained on a nonsolvated, heterometallic aluminum alkoxide

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(3) Chemat Technology, Inc., PO Box 67E35, Los Angeles, CA 90067. 1991 Catalog.

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(11) All reactions and manipulations were carried out under dinitrogen using standard Schlenk and drybox techniques. Solvents were dried by appropriate means and distilled under dinitrogen before use. NMR spectra were in toluene-d_8 solutions using a GE-Omega-500 broadband spectrometer. I: A suspension of 13.236 g (64.8 mmol) of $Al(OPr^i)_3$ and 0.788 g (32.4 mmol) of Mg in 350 mL of isopropyl alcohol was refluxed in the presence of 0.05 g of Hg_2Cl_2 for 96 h. Excess isopropyl alcohol was removed by distillation at ambient pressure. Fractional distillation of the viscous residue at 105–109 °C/0.1–0.2 Torr yielded 15.90 g (89%) of Im, as a colorless liquid which slowly solidified over several minutes. II: A suspension of 21.857 g (107.0 mmol) of $Al(OPr^i)_3$, 1.734 g (71.3 mmol) of Mg, and 0.05 g of Hg_2Cl_2 in 350 mL of isopropyl alcohol was refluxed for 10 days. After distillation of excess isopropyl alcohol, the remaining light gray viscous residue was extracted with 50 mL of toluene, which was evaporated under vacuum to leave a viscous liquid (25.78 g, 81% if pure II), from which II crystallizes at room temperature over several weeks.

(12) Electron impact mass spectra of I obtained 3 and 6 weeks after distillation at a 50 °C source temperature: m/e (int) = 550 (Im, 8%), 535 (Im – CH_3, 89%), 491 (Im – OC_3H_7, 10%), 477 (Im – CH_3 – OC_3H_6, 100%), 449 (Im – OC_3H_7 – C_3H_6, 20%), 435 (Im – CH_3 – OC_3H_6 – C_3H_6, 54%), 389 (Im – CH_3 – $AlO_2C_6H_{15}$, 98%), 375 (Im – $AlO_2C_6H_{15}$ – C_2H_5, 54%), 331 (Im – CH_3 – $Al(OC_3H_7)_3$, 35%), 273 (Im – CH_3 – $Al(OC_3H_7)_3$ – OC_3H_6, 32%), 231 (Im – CH_3 – $Al(OC_3H_7)_3$ – OC_3H_6 – C_3H_6, 10%), 187 (Im – $Al(OC_3H_7)_3$ – OC_3H_7 – OC_3H_6 – C_3H_6, 6%). Each of these occurs in an isotope cluster typical of a fragment which contains a single magnesium. MW (calc) = 550.

(13) For example, at 150 °C the predominate masses which occur above m/e = 550 are 677, 837, 939, and 1041. These can be assigned to Id – $2Al(OC_3H_7)_3$ – CH_3, Id – $Al(OC_3H_7)_4$, Id – $2OC_3H_7$ – C_3H_7, and Id – OC_3H_7, respectively.

(14) NMR spectra show I to be the predominant species with minor impurities often being $HOPr^i$ and $[Al(OPr^i)_3]_4$. The amount of $[Al(OPr^i)_3]_4$ typical increases with time as II precipitates. Samples of I which originally are solid will become liquid if trace decomposition occurs.

(15) Structure determination summary: X-ray data were collected at 25 °C using a Nicolet P_1 diffractometer and Mo Kα radiation. $C_{39}H_{91}Al_3Mg_2O_{13}$ belongs to the monoclinic space group $P2_1/c$ (a = 15.927(4) Å, b = 18.239(7) Å, c = 19.914(7) Å, β = 91.34(2)°, V = 5783(3) Å^3, Z = 4). 3873 reflections were collected and merged to 3676 independent reflections (R_{int} = 3.00%). The structure was solved by direct methods, and initial least-squares analysis was carried out using the SHELXTL PLUS Program Package and 2098 data with $I > 3\sigma(I)$. Mg and Al could not be differentiated crystallographically but were assigned on the basis of M–O distances. (Distances in $Mg[Al(OPr^i)_4]_2{\cdot}2HOPr^i$ are nearly identical to analogous bonds in II.[8]) During the final cycles of refinement the C–C bonds were restrained to 1.54 Å, the C–O bonds to 1.43 Å, and the C geometry to tetrahedral, allowing a standard deviation of 0.01 Å on the various distances. Hydrogen atoms were added at calculated positions and refined using the "riding model". In view of the large thermal parameters associated with the isopropyl groups, a "rigid bond" restraint was applied to the anisotropic thermal parameters within the isopropoxide groups using SHELX92. (We thank Prof. George Sheldrick for his hospitality and his permission to do these calculations at the University of Goettingen.) SHELX92 refines against F^2 and the final wR^2 = 0.313 ($w = 1/[\sigma^2(F_o^2) + (0.1789P)^2 + (5.79P)]$) where $P = [\max(F_o^2,0) + 2F_c^2]/3$ and GOF = 1.182 for all 3676 data for comparison with more usual refinements against F, the conventional R^1 = 0.096 for 2437 $I > 2\sigma(I)$. Difficulties in obtaining good X-ray structures on the soft "plastic" crystals typically encountered in the metal alkoxides and found for II have previously been commented upon, as has the desirability of obtaining data at low temperature. (See, for example: Coan, P. S.; Hubert-Pfalzgraf, L. G.; Caulton, K. G. *Inorg. Chem.* **1992,** *31,* 1262. Drake, S. R.; Streib, W. E.; Folting, K.; Chisholm, M. H.; Caulton, K. G. *Inorg. Chem.* **1992,** *31,* 3205.) Unfortunately, we have not been able to collect such data.

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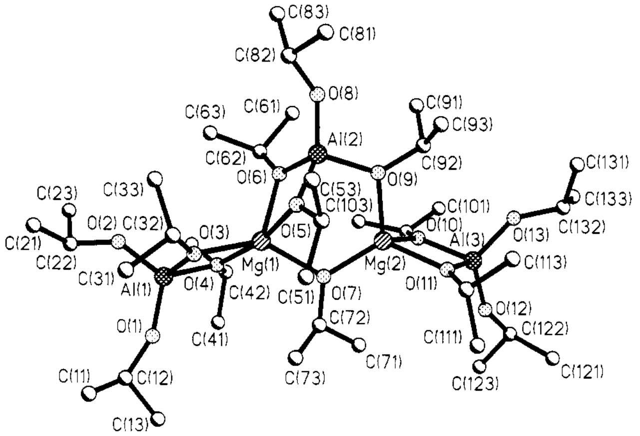


Figure 1. Molecular structure of $Mg_2Al_3(OPr^i)_{13}$ (II). Average bond distances (Å): Al–O (terminal) = 1.65(1), Al–O (bridging) = 1.77(1). The Mg–O bonds show greater variation: Mg(1)–O(3) = 2.005(8), Mg(1)–O(4) = 2.077(8), Mg(1)–O(5) = 2.136(9), Mg(1)–O(6) = 2.019(8), Mg(1)–O(7) = 1.999(8), Mg(2)–O(7) = 1.910(8), Mg(2)–O(9) = 1.989(8), Mg(2)–O(10) = 1.949(9), Mg(2)–O(11) = 1.980(9).

$M_xAl_y(OR)_z$. In the molecule each magnesium is coordinated to a terminal $Al(OPr^i)_4$ group via double OPr^i bridges. The two magnesiums are joined by a bridging OPr^i group and by an $Al(OPr^i)_4$, which is doubly OPr^i bridged to one magnesium and singly bridged to the second. The molecule is unsymmetrical with both a tetrahedral and a five-coordinate magnesium. This structure is important to the general area of heterometallic aluminum alkoxide chemistry as it establishes a heretofore unrecognized triply bridging coordination mode for the $Al(OPr^i)_4$ moiety and is the first unambiguous characterization of an $Al(OPr^i)_4$ unit bridging two nonbonded metals.

While II forms from I by

$$\underset{\text{I}}{\{\text{Mg}[\text{Al}(\text{OPr}^i)_4]_2\}_n} \rightarrow n/2\underset{\text{II}}{\text{Mg}_2\text{Al}_3(\text{OPr}^i)_{13}} + n/2\text{Al}(\text{OPr}^i)_3$$

it can be prepared in good yield by[11]

$$2\text{Mg} + 3\text{Al}(\text{OPr}^i)_3 \xrightarrow[\text{reflux}]{\text{HOPr}^i} \underset{\text{II}}{\text{Mg}_2\text{Al}_3(\text{OPr}^i)_{13}}$$

However, the reaction requires over a week. II cannot be purified by distillation, rather it decomposes at about 120 °C and 0.1 Torr:

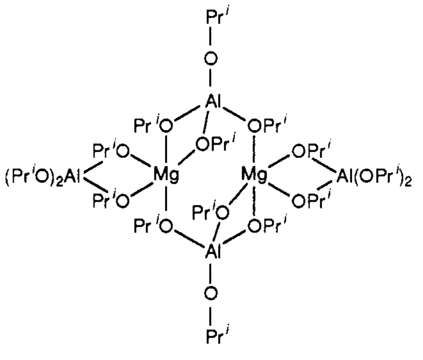
$$\underset{\text{II}}{\text{Mg}_2\text{Al}_3(\text{OPr}^i)_{13}} \rightarrow \underset{\text{Im}}{\text{Mg}[\text{Al}(\text{OPr}^i)_4]_2} + \text{uncharacterized nonvolatile materials}$$

which may be the reason $Mg_2Al_3(OPr^i)_{13}$ was not detected earlier.

The NMR spectra of $Mg_2Al_3(OPr^i)_{13}$ can be interpreted in terms of the crystal structure. At 25 °C resonances can be assigned to the two terminal $Al(OPr^i)_4$ groups {^1H: 4.27 ppm (8H, CH); 1.36 ppm (48H, CH_3). ^{13}C: 64.34 ppm (CH); 27.49 ppm (CH_3)}, the three (OPr^i) groups which bridge an Al and a Mg {^1H: 4.32 ppm (3H, CH); 1.35 ppm (18H, CH_3). ^{13}C: 65.81 ppm (CH); 26.72 ppm (CH_3)}. Two additional signals {^1H: 4.32 ppm (1H, CH). ^{13}C: 64.23 ppm (CH) and ^1H: 4.36 ppm (1H, CH). ^{13}C: 64.27 ppm (CH)} are observed in the methine region as are two methyl resonances {1.40 ppm (6H, CH_3). ^{13}C: 28.20 ppm (CH_3) and 1.27 ppm (6H, CH_3). ^{13}C: 27.54 ppm (CH_3)} while it was not possible to assign these resonances more fully, one methine and one methyl resonance must arise from the terminal OPr^i attached to the Al(2), and the other set from the OPr^i which bridges Mg(1) and Mg(2).[16] Thus, at room temperature there is rapid exchange of all of the OPr^i groups within the two terminal $Al(OPr^i)_4$ groups and of the three OPr^i groups which bridge an Al and a Mg within the core of the molecule. On the NMR time scale further OPr^i exchange is slow to at least 90 °C.

All of the chemical shifts in the ^1H spectrum of II vary somewhat with temperature. In addition, the methine peak arising from the terminal $Al(OPr^i)_4$ groups broadens and passes through a coalescence point at −55 °C, and two resonances of equal intensity reappear as temperature decreases. Most likely this reflects slowing of exchange between terminal and bridging OPr^i groups. By −85 °C these two resonances occur at 4.16 (4H) and 4.51 ppm (4H) and can be assigned to terminal and bridging OPr^i groups, respectively, since terminal isopropoxides resonate at higher field than bridging ones in several other aluminum alkoxides.[17] From the 122-Hz separation of these peaks, the barrier to the exchange of the OPr^i groups within these two $Al(OPr^i)_4$ moieties can be estimated as $\Delta G^{\ddagger}_c$ = 10 kcal/mol.[18] This is the first kinetic datum for alkoxide migrations within heterometallic aluminum alkoxides. Also at −85 °C the three bridging OPr^i attached to Al(2) (4.25 ppm, 3H) are still rapidly exchanging. The terminal OPr^i on Al(2) and the one which bridges Mg(1) and Mg(2) give rise to resonances at 4.32 ppm (1H) and 4.38 ppm (1H).

While X-ray data are not available on Im or Id, the −85 °C ^1H NMR spectrum of I can be analyzed in terms of the predominant species being Id, whose structure, is derived



Id

from II by replacing the OPr^i group which bridges the two magnesiums by an $Al(OPr^i)_4$ group. In this structure the two halves of the molecule are equivalent, but each magnesium is chiral. Since mirror planes cannot pass through a chiral center, all eight OPr^i groups within each half of the molecule are nonequivalent and the methyl groups within each Pr^i group are diastereotopic. Consistent with this structure and slow OPr^i exchange, the methine region of the ^1H spectrum at −85 °C contains

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(16) Each of the methine and methyl resonances appeared as the expected septet and doublet, respectively, with J_{HCCH} = 6.0 Hz. While some overlap of peaks occurred in each region, ^{13}C and ^1H signals could be unambiguously correlated using 2D methods and, with the exception of the two methine resonances which occur at 4.32 and 4.36 ppm, the assignment of methyl and methine resonances within Pr^i groups was confirmed by double resonance experiments.

(17) Mehrotra, A.; Mehrotra, R. C. *J. Chem. Soc., Chem. Commun.* **1972**, 189.

(18) Calculated using the Eyring equation and $k_r = (2^{-0.5}\pi)(\Delta\nu)$ at a coalescence temperature of 220 K and the chemical shift separation at slow exchange of 122 Hz.

eight resonances of equal intensities: 4.87, 4.78, 4.72, 4.71, 4.41, 4.20, 4.14, and 3.99 ppm, each of which is a broad, partially resolved septet.

As temperature is raised several of the peaks in the spectrum of I undergo coalescence due to the speeding of exchange between various OPr^i sites in the molecule. In addition, the relative intensities of the peaks due to Id decrease while new peaks begin to grow in. By ambient temperature, where I is known to be monomeric in solution,[10] the ^1H NMR spectrum, consists of a sharp methyl doublet (1.30 ppm, $J_{HCCH} = 6.0$ Hz) and a methine septet (4.24 ppm, $J_{HCCH} = 6.0$ Hz), indicating time average equivalence of the OPr^i groups within monomeric Im.[19] Thus, the variable-temperature spectra indicate that Im and Id are in equilibrium, that the rate of dimerization and of dissociation, at least at the lower temperatures, are slow on the NMR time scale, and that Im is favored at high and Id at low temperatures.

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Supplementary Material Available: Perspective drawing of II showing thermal ellipsoids and tables of bond lengths and angles, atomic positional and displacement parameters, and calculated hydrogen positions for II (8 pages); list of observed and calculated structure factors for II (23 pages). Ordering information is given on any current masthead page.

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(19) ^{13}C Data for I (25 °C): 64.44 (CH), 27.46 ppm (CH_3).