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Coordination Chemistry Reviews
210 (2000) 1–10

COORDINATION CHEMISTRY REVIEWS

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Tetrametallic Group 13 'Mitsubishi' Molecules

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Received 26 July 1999; accepted 3 September 1999

Contents

Abstract

Under fairly disparate conditions tetrametallic aluminum complexes can be isolated that feature a central six-coordinate aluminum connected by bridging heteroatoms to three peripheral four-coordinate aluminum atoms. Based upon their striking resemblance to the Mitsubishi emblem these molecules will be given the name 'Mitsubishi™' [1]. This review will discuss the formation of these compounds and will seek to establish the guiding principles under which additional 'Mitsubishi™' compounds may be formed. The impact of these compounds on the formation of solid-state materials, particularly aluminum oxide, will be briefly discussed.

Keywords: Aluminum; Gallium; Lanthanide; Mitsubishi; Tetrametallic

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0010-8545/00/$ - see front matter
PII: S0010-8545(00)00314-3

1. Introduction

Several structural types persist for combinations between the Group 13 (M) and Group 16 (E) elements. Easily, the most populous class are those of formula $[R_mM(ER')_{3-m}]_n$ (with $m = 0–2$; R,R′ = hydrogen, alkyl, aryl). Based upon the degree of steric encumbrance incorporated into the R or R′ group, the resulting compounds can be monomeric ($n = 1$) [2], dimeric ($n = 2$) [3,4], trimeric ($n = 3$) [3] or tetrameric ($n = 4$, as a cyclic species [5], a cluster [6], or ladder [7]). Some of these species can readily undergo interconversion reactions in solution.

Less common are the compounds of formula $[RME]_n$ best represented by the cubic tetrameric molecules (with $n = 4$) [8]. As the nuclearity of these compounds increase, their resemblance to the solid-state material also increases. This has been dramatically demonstrated in the formation of large clusters such as $(RAlO)_{6,8,9}$ [9] and $(MesGaO)_9$ [10]. Compounds possessing four Group 13 atoms can also be isolated in conjunction with many other ligands. However, the rules governing the formation of these latter multi-metallic derivatives are not well established. Perhaps the most systematically studied of these compounds are those that incorporate open chain amines [11].

A rare but emerging class of tetrametallic derivatives are those which contain a central six-coordinate aluminum with three peripheral four-coordinate aluminum atoms. The skeleton of these compounds resembles the emblem of the Mitsubishi company. To differentiate them from other tetrametallic derivatives these are called simply 'Mitsubishi Molecules'(Fig. 1) [1] [12]. Several examples of this type of complex have appeared sporadically in the literature over the years. More recently, the controlled synthesis of a series of this type of molecule has been achieved [13]. Aside from their relatively unique structures these molecules may also be used as stoichiometric precursors to Al_2O_3 [14].

This review will survey what is known about the formation and structures of the Mitsubishi™ class of tetrametallic molecules. The most extensively developed groups are the homoleptic alkoxides, $[Al(OR)_3]_4$, the mixed-metal alkoxides, $[M\{(\mu\text{-}OR)_2Al(OR)_2\}_3]$ (M = lanthanide) and the alkyl alkoxides, $[Al\{(\mu\text{-}OR)_2AlR_2\}_3]$ (R = alkyl). The relevance of these molecules to materials synthesis will be briefly discussed.

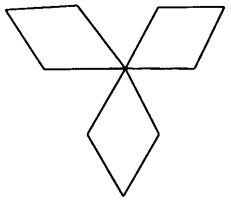
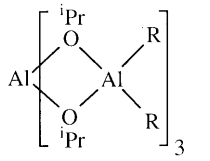


Fig. 1. The skeletal arrangement of atoms in a Mitsubishi™ molecule.



(R = 2 O^{i}Pr, 4 OSiMe$_3$)

Fig. 2. Derivatization of the terminal alkoxides of a Mitsubishi™ molecule.

2. Homoleptic aluminum alkoxides

Aluminum triisopropoxide is prepared by combining either $AlCl_3$ or $AlMe_3$ with dry isopropanol [15]. It was first suggested to be tetrametallic by Bradley [16]. This was sometime later verified spectroscopically [17] and in a crystallographic investigation [18]. At that time it was shown that the tetrametallic (solid) interconverted with a trimetallic derivative ((*i*PrO)Al[(μ-O*i*Pr)$_2$Al(O*i*Pr)$_2$]$_2$ (which is a liquid) in solution and in the solid (Eq. (1)). More of the trimetallic forms as the temperature of the solution or solid is increased. The apparently five-coordinate central aluminum atom of the trimetallic compound forms adducts with amines while the tetrametallic derivative does not [19].

$$(O^{i}Pr)Al\{(\mu\text{-}O^{i}Pr)_2Al(O^{i}Pr)_2\}_2 \rightleftharpoons Al\{(\mu\text{-}O^{i}Pr)_2Al(O^{i}Pr)_2\}_3 \quad (1)$$

This original structure exemplifies the Mitsubishi™ motif found in this class of molecules [16]. It contains a central six-coordinate aluminum with three four-coordinate aluminum atoms occupying the periphery. The Al–O(bridging) distances for the central Al atom are ~1.94 Å while those on the periphery fall in the range 1.73–1.86 Å. The terminal alkoxide groups are somewhat shorter in the range 1.63–1.77 Å. The Al_2O_2 four-membered rings feature O–Al(six-coord)–O angles of 74 and 78°, while the same angle around the four-coordinate aluminum atoms are 82 and 84°. The RO–Al–OR angles are somewhat more obtuse in the range 97–102°.

Transesterification of [Al(O*i*Pr)$_3$]$_4$ with Me_3SiOAc results in a tetrametallic compound having four $OSiMe_3$ groups on the peripheral aluminum atoms (Fig. 2) [12]. Thus, the six-coordinate core of the starting material is apparently undisturbed in this reaction. Incorporation of an additional $OSiMe_3$ unit into the molecule results in a complex that is proposed to have the same structure as the trimetallic compound shown in Eq. (1). Addition of a third such unit causes the formation of the homoleptic siloxide dimer, [Al(OSiMe$_3$)$_3$]$_2$. This is the type of nuclearity that is common for homoleptic aluminum alkoxides. Thus, it appears that the *i*Pr group is unique in supporting a Mitsubishi formulation.

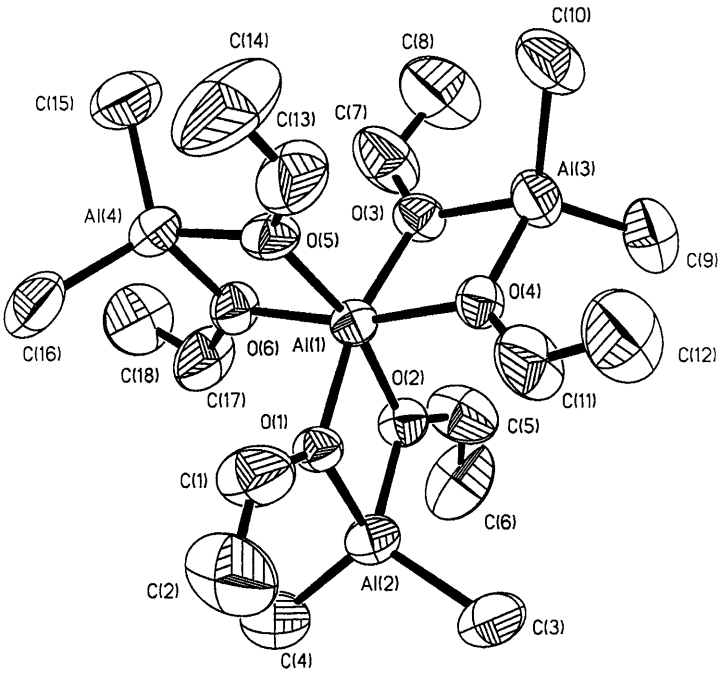


Fig. 3. ORTEP view of $[Al\{(\mu\text{-}OEt)_2AlMe_2\}_3]$.

3. Alkyl aluminum alkoxides

Several tetrametallic as well as dimeric species were proposed in combinations between $Al(O^iPr)_3$ and $AlMe_3$ [20]. Similarly, ethylaluminum diethoxide was shown, by ^{27}Al-NMR and mass spectroiscopy, to exist as a mixture of tetrametallic, $[Et_nAl_4(OEt)_{12-n}]$ and trimetallic $[Et_nAl_3(OEt)_{9-n}]$ compounds [21].

When equimolar amounts of AlR_3 (R = Me, Et, ^{i}Bu) and $Al(OEt)_3$ are combined single products are obtained [13]. They are first isolated as oils. These convert slowly to crystalline solids over a period of days to months depending on how much solvent (toluene) they contain. The solids can be converted back to the oils by the addition of a small amount of solvent (about 1 molecule of solvent per 100 tetrametallics). The ^{1}H-NMR can be interpreted in terms of the maintenance of the tetrametallic units in solution.

Two of the compounds have been structurally characterized (one is shown in Fig. 3). The structures differ little from $[Al(O^iPr)_3]_4$. For instance, the Al–O distances are fairly consistent. Moreover, the Al–C distances are standard for four-coordinate aluminum alkyl complexes.

Solution studies indicate that the addition of $AlMe_3$ to $[Al(O^iPr)_3]_4$ causes replacement of the terminal alkoxide groups with methyls [22]. After all six of the alkoxides have been substituted with Me (to form the ^{i}OPr derivative of the compound shown in Fig. 3) the tetrametallic redistributes to form the dimeric alkoxide-bridged species (Eq. (2)).

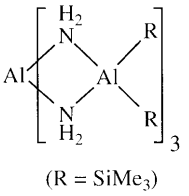


Fig. 4. Amido-bridged Mitsubishi molecule.

$$[Al\{(\mu\text{-}O^iPr)_2AlMe_2\}_3] \xrightarrow{2\ AlMe_3} 3\ [Me_2Al\{(\mu\text{-}O^iPr)]_2 \quad (2)$$

The most unusual alkoxide used to form an alkylaluminum alkoxide tetrametallic is 2-thiophenemethanol. It is incorporated in the compound, $[Al[\{2\text{-}(OCH_2)SC_4H_3)_2\}_2AlMe_2]_3]$ [23]. The average Al–O and Al–C distances are 1.873 and 1.968 Å, respectively.

4. Alkyl aluminum molecules with nitrogen ligands

Ammonia promotes an alkane elimination reaction when combined with R_3Al in a 1:1 stoichiometry to yield the common class of compounds $[R_2AlNH_2]_n$ ($n = 2, 3$). In a 2:1 ratio with $Al(SiMe_3)_3{\cdot}OEt_2$,however, a tetrametallic Mitsubishi derivative forms (Fig. 4) [24]. Higher yields are obtained when an N:Al ratio of 3:2 is used. The ^{1}H-NMR is very straightforward with a single peak for the $SiMe_3$ groups and a broad peak for the NH_2 groups.

In the structure the N–Al(six-coordinate) distances (2.022(4)–2.017(5) Å) are larger than the N–Al(four-coordinate) distances (1.923(5)–1.936(9) Å). The N–Al–N angles range from $\sim$83–93° while the Al–N–Al angles are $\sim$94°.

A multidentate amine ligand (cyclam) supports the formation of a unique tetrametallic compound containing bridging nitrogen and chloride atoms (Fig. 5). In the structure there is a two-fold axis of symmetry bisecting the central aluminum

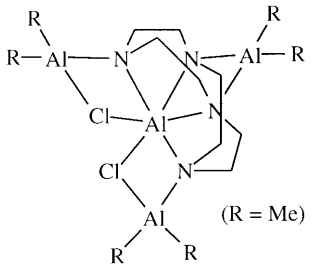


Fig. 5. Mitsubishi molecule incorporating a cyclam ligand.

and the aluminum atom containing only nitrogen bridges. The Al–N distances are 1.952(3) Å (to the $AlMe_2$ unit) and 1.981(3) Å (to the Me_2AlCl unit). As expected the Al–Cl distances are longer to the central aluminum (2.509(2) Å) than to the peripheral aluminum (2.258(2) Å). There are three singlets in the ^{1}H-NMR for the Al–Me protons (δ −0.687, −0.561, −0.531 ppm).

Triethanolamine can be used to form what are called alumatranes and gallatranes (Fig. 6) [25]. They can be prepared by transligation of the respective azatrane with triethanolamine or by combination of the ligand with trialkyl or trisamido Group 13 derivatives. The resulting compounds have been described as having unusual solution and gas phase redistribution behavior. While various oligomers have been proposed it appears that there is a preponderance of evidence for the tetrametallic Mitsubishi compound in both the solution [26] and solid state [27] for aluminum and the existence of the the tetrametallic gallatrane in the gas phase only [28]. The derivative in which the $-CH_2CH_2-$ linkages have been replaced by an aryl group are tetrameric in solution but dimeric in the solid [29].

The structurally characterized alumatrane features an Al–N distance for the central aluminum of 2.239(3) Å while for the peripheral aluminum atoms that distance is 2.069(5) Å. The bridging oxygen atoms average a distance of $\approx$1.8 Å to the central aluminum and $\approx$1.7 Å to the peripheral ones. The remaining two oxygen distances for the peripheral aluminum atoms fall in the range 1.75 Å.

5. Molecules containing two different metals

It is relatively easy to prepare compounds in which the central aluminum atom of a Mitsubishi™ tetrametallic has been replaced with a heavier element. For example, the compounds with In as the central atom surrounded by Al and Ga units have been prepared [30,31]. Additionally, there is one structurally characterized example, $[Al\{(\mu\text{-}OEt)_2GaMe_2\}_3]$ (Fig. 7), wherein the heavier element occupies the peripheral, four-coordinate sites in the Mitsubishi framework [13]. This is unusual since all of the other heterobimetallics have the heavier element in the central position (see below). This is apparently a consequence of the larger elements being able to better accommodate a six-coordinate rather than four-coordinate

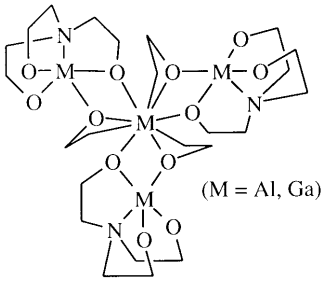


Fig. 6. Alumatrane and gallatrane Mitsubishi molecules (viewed along the M–N axis).

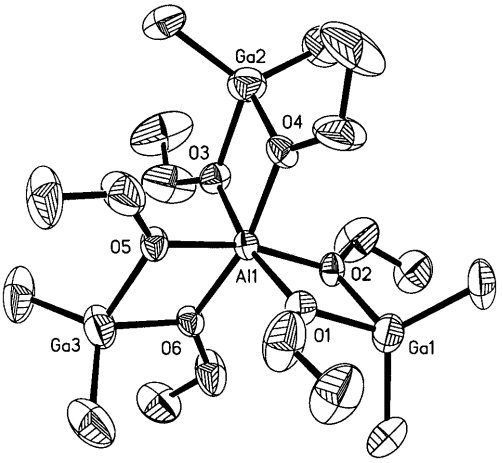
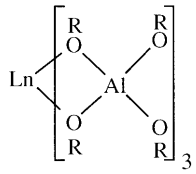


Fig. 7. ORTEP view of $[Al\{(\mu\text{-}OEt)_2GaMe_2\}_3]$.

geometry. For the gallium compound this is further evidence supporting the notion that Ga and B form predominantly covalent, and consequently, four-coordinate compounds. The Al–O distances (ave. 1.9 Å) are similar to what was observed in the all-aluminum derivatives. However, the O–Ga distances (ave. 1.92 Å) are somewhat longer. A similar occurrence was recently observed in the structurally characterized Mitsubishi™ compound, $[Al\{(\mu\text{-}H)_2Zr(Me_3Si\text{-}Cp)_2ZrH\}_3]$ [32]. Here the Zr atoms are prevented by the Cp groups from adopting a six-coordinate geometry.

Mitsubishis™ with a central lanthanide are more readily available [33]. This has been amply demonstrated in the formation of a wide range of 'double' alkoxides having the formula $Ln[M(O^iPr)_4]_3$ with Ln = Sc, Y, La and all of the other stable lanthanides and M = Al and Ga (Fig. 8). There are three general routes to these compounds. Two of them involve salt eliminations with anhydrous $LnCl_3$ and the third is by mixing the respective metal alkoxides in ^{i}PrOH. The tetrametallic nature of these compounds was established by solution molecular weight determinations, ^{1}H-NMR data, and by analogy to the homoleptic aluminum isopropoxides. The ^{1}H-NMR of many of these compounds indicates that the



(Ln = Sc, Y, La-Yb;
M = Al, Ga; R = ^{i}Pr)

Fig. 8. The broad range of Mitsubishi molecules that contain a lanthanide element.

bridging ^{i}PrO groups are either non-equivalent or diastereotopic. The result is three doublets that can be assigned to the Me_2C– groups.

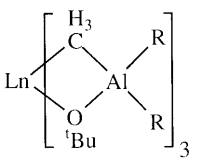
The proposed structures of these compounds has been confirmed by a crystallographic analysis of the erbium derivative [34]. In the structure the Er–O distances average 2.244 Å while the Al–O(bridging) distances average 1.792 Å. The terminal Al–O distances average 1.674 Å.

The transition metal derivative, $Cr[Al(O^{i}Pr)_4]_3$ is prepared by a salt elimination reaction similar to what was used for the lanthanides [35]. It undergoes an extensive reaction chemistry with alcohols such as CH_3OH, C_2H_5OH, n-C_4H_9OH and CF_3CH_2OH [36]. These reactions result in unique bimetallic tetraalkoxy aluminates in which the Mitsubishi™ framework of the starting material has remained intact. Mixed-ligand complexes are also possible, including some with acac groups on the peripheral aluminum atoms.

A series of lanthanide containing Mitsubishi compounds of a different sort can be isolated from the combination of three moles of $AlMe_3$ with the lanthanide alkoxide (Fig. 9). The compounds contain three bridging methyl groups and three bridging alkoxides. In the structures of the Y and Nd derivatives the Ln–O distances are 2.2–2.3 Å while the Ln–C distances are $\sim$2.7 Å. The Al–O distances are $\sim$1.8 Å and the Al–C (bridging) distances are marginally longer than the Al–C(terminal) distances ($\sim$2.0 versus 1.9 Å).

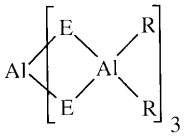
6. Mitsubishi routes to materials

It is important to note that the minerals Gibbsite or Bayerite contain an infinite network of Mitsubishi units. Thus, the incorporation of this framework into a molecule may prove to be useful in materials synthesis. Indeed, the compounds of formula $[Al\{(OEt)_2AlR_2\}_3]$ have been shown to be useful precursors to relatively pure Al_2O_3. They can be decomposed by heating as low as 180°C to form films of the material. At higher temperatures the decomposition proceeds more cleanly as indicated by a drop in carbon incorporation at higher temperatures ($<1\%$ C and H). At 600°C $\{(Me_3Si)_2Al(NH_2)_2\}_3Al$ eliminates Me_3SiH and CH_4 to form a mixture of SiC and AlN [37].



(Ln = Pr, Nd, Y; R =Me)

Fig. 9. Mixed-metal Mitsubishis with bridging methyl groups.



(R = alkyl, aryl, alkoxide, etc;
E = NH_2, PH_2, OH, SH, etc)

Fig. 10. The forecasted range of Mitsubishi molecules.

7. Conclusions

Tetrametallic Mitsubishi compounds readily form when the appropriate stoichiometry of fairly specific reagents is combined. The majority of these compounds do not undergo interconversion to other species in solution. Furthermore, the peripheral alkyl or alkoxide groups can be used in alkane and transesterification reactions without disturbing the overall morphology of the molecule. In cases where interconversion occurs the formation of symmetrical compounds containing four- and six-coordinate aluminum atoms is preferred over unsymmetrical ones containing five-coordinate aluminum. This follows the general trend observed for the Group 13 elements.

It would appear that a wider range of these molecules may be accessible. For instance, other derivatives containing the $-NH_2$ should be available (Fig. 10). Furthermore, it should also be possilbe to form the hydroxide, sulphide, etc. derivatives as well. These could be important as materials precursors since they feature a M:E ratio of 2:3, a combination that is currently rare for Group 13/15 and 13/16 combinations. The number of mixed-metal derivatives may be easily expanded by using other Ln alkoxides.

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