



New aluminum 2,2'-methylenebis(4-chloro-3-methyl-6-(isopropyl)phenoxides): Structural characterization of an unusual ionic aluminum bisphenoxide $[Al(THF)_4(Cl)_2]^+ [Al(mcmip)_2]^- \cdot x THF$

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ABSTRACT

The synthesis and X-ray structure determination of an uncommon ionic aluminum bisphenoxide $[Al(THF)_4(Cl)_2]^+ [Al(mcmip)_2]^- \cdot 1.1 THF$ (**1**) and its neutral analogue $(mcmip)Al(CH_2CH_3)(THF)$ (**2**) are reported ($mcmipH_2$: 2,2'-methylenebis(4-chloro-3-methyl-6-(isopropyl)phenol). The ligand was reacted in THF with diethyl aluminum chloride, respectively triethyl aluminum, under liberation of ethane to yield crystalline aluminum bisphenoxides. Compound **2** exhibits the usual structural features found in neutral THF-aluminum bisphenoxides adducts whereas the ionic compound **1** consists of a cationic octahedral aluminum dichloride moiety, $[Al(THF)_4(Cl)_2]^+$, and an anionic di-bisphenoxide aluminate fragment $[Al(mcmip)_2]^-$ containing two 2,2'-methylenebis(4-chloro-3-methyl-6-(isopropyl)phenol) ligands. Both aluminum bisphenoxides were tested as catalysts in the copolymerization of cyclohexene oxide with CO_2 and displayed similar good catalytic activities although the carbonate amounts present in the copolymer remain low.

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Soluble aluminum compounds like organoaluminum compounds [1] or pure aluminum alkoxides [2] play an important role as homogeneous catalysts in organic synthesis. Molecular aluminum derivatives are well known to display variable molecular compositions ranging from monomeric to polymeric aggregates owing to the aluminum's ability to easily adopt tetrahedral, octahedral as well as the less abundant trigonal-bipyramidal coordination geometries [3]. For this reason collecting spectroscopic information on the active aluminum species involved in a catalytic process can be achieved most of the time only via a "simplification" of the investigated catalytic system. Considering more specifically the aluminum alkoxides used as Lewis acid catalysts [2], the utilization of an ancillary chelating alkoxy ligand can elegantly provide a structurally well-defined, "single-site" catalyst. Bulky 2,2'-methylene-bisphenols constitute a versatile and easy-to-handle "toolbox" for the coordination chemist as reported by many research groups [4]. The synthesis on a large scale of these chelating ligands from formaldehyde and the corresponding substituted phenols is relatively easy, allowing the rapid development of a ligand library [5]. During the course of our studies on new potential catalysts of the copolymerization of CO_2 and epoxides, we became interested in systems involving aluminum bisphenoxides and synthesized as well as structurally characterized different new aluminum compounds

[6]. Within this context, it was interesting to synthesize a "tailored" aluminum 2,2'-methylene-bisphenoxide having: i) a sterically demanding group at locations 6,6' to shield at some extent the active coordination site of the catalyst and so repress the formation of higher oligomeric aluminum bisphenoxides, ii) an alkyl substituent at locations 3,3' of the phenol rings in order to "twist" the bisphenol ligand via the mutual steric hindrance of these substituents and modify in that way the size of the coordination site, and iii) an electron withdrawing group (–I effect considered) at locations 4,4' to ensure a high Lewis acidity and compete with the steric/electronic influence of the substituents at locations 6 and 3. The synthesis of such a bisphenol was described as early as in the 50s and was the subject of several patents [7], the molecule showing an interesting potential as pulmonary antiseptic (biclotymol [CAS 15686-33-6]). The structural characterization of this particular bisphenol was performed by Rantsordas et al. [8] and the use as a chelating ligand in aluminum catalysts was firstly reported by C.-C. Lin and co-workers in 2001 [9]. Interestingly this ligand was newly reported in a patent dealing with zirconium-based catalysts used in the oligomerization of ethylene [10].

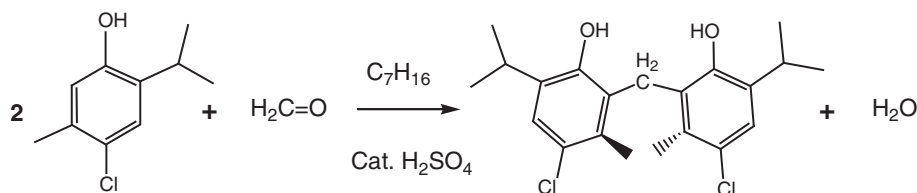
The title ligand, 2,2'-methylenebis(4-chloro-3-methyl-6-(isopropyl)phenol), was synthesized from the reaction of paraformaldehyde with 4-chloro-3-methyl-6-(isopropyl)phenol in heptane in the presence of catalytic amounts of sulphuric acid following the general synthetic method reported in the literature [7,9] (Scheme 1).

A solution of diethyl aluminum chloride in THF was added dropwise to a cold suspension of the substituted phenol. The suspension was allowed to warm up to room temperature to become a colorless

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¹ Dedicated to the memory of Dr. Jakub Konrad Sypień.



Scheme 1. Synthesis and structure of 2,2'-(methylenebis(4-chloro-3-methyl-6-(isopropyl)phenol)) (mcmipH₂).

solution whereas an evolution of ethane was observed. After a couple of hours THF was evaporated to yield a pale waxy compound which solidified after a couple of hours. The aluminum bisphenoxide **1** was dissolved again in THF and left a couple of weeks at $-25\text{ }^{\circ}\text{C}$; a small amount of colorless single crystals suitable for an X-ray structural determination [11] could be eventually isolated, these crystals are stable at low temperatures, slowly deteriorating above $0\text{ }^{\circ}\text{C}$. Surprisingly, we observed that, instead of displaying an usual neutral adduct structure of type (bisphenoxide-*O,O'*)Al(Cl)(THF), the isolated aluminum bisphenoxide presented an uncommon dinuclear ionic structure $[\text{Al}(\text{THF})_4(\text{Cl})_2]^+ [\text{Al}(\text{mcmip})_2]^- \cdot 1.1\text{ THF}$. Crystals of the compound **1** are monoclinic, crystallizing in the space group $P2(1)/n$ (no. 14) [12].

The ORTEP diagram of the ionic aluminum bisphenoxide is illustrated in Fig. 1. Selected bonds and angles are listed in the Supplementary material. The molecular structure of **1** consists of discrete $[(\text{mcmip})_2\text{Al}]^-$ aluminate anions containing two bisphenoxides bound in an almost symmetrical way to the aluminum center and of symmetrical $[\text{AlCl}_2(\text{THF})_4]^+$ cations with apical chlorine atoms with no short interionic contacts. The complex co-crystallized with 1.1 molecules of THF per unit: 0.5 plus 0.6 being disordered. Considering the cation, the aluminum atom is situated at the center of an almost perfect octahedron, with Al–Cl distances of $2.225(3)\text{ \AA}$ (Al2–Cl6) and $2.246(3)\text{ \AA}$ (Al2–Cl5) and Al–O distances ranging from $1.944(5)\text{ \AA}$ (Al2–O6) to $1.955(5)\text{ \AA}$ (Al2–O5 and Al2–O7), comparable to the distances found in the literature for other $[\text{AlCl}_2]$ -fragment-containing ionic compounds [13]. The angles measured within the octahedron slightly diverge from the ideal values with a Cl6–Al2–Cl5 angle of $178.90(13)$ and the different perpendicular $\text{O}(x)\text{--Al--O}(y)$ angles ranging from $88.5(2)$ to $91.3(2)\text{ }^{\circ}$. The anion contains two bisphenoxides bound to the aluminum center in such a way that the aluminum center is completely shielded by these ligands. The different aluminum–oxygen distances are all within a

small range indicating that the negative charge is delocalized over the aluminate anion (Al1–O1: $1.726(4)\text{ \AA}$; Al1–O2: $1.739(4)\text{ \AA}$; Al1–O4: $1.746(4)\text{ \AA}$; Al1–O3: $1.747(4)\text{ \AA}$). The angles and interatomic distances found within the bisphenoxide ligands are comparable to those found in the complexes reported by Lin [9]. The interatomic distances measured within the two distinct bisphenoxide ligands of the anion are quite similar whereas the overall geometries of the two ligand/aluminum sub-units are subtly different. This can be clearly seen considering the two eight-membered rings formed by the ligand backbones and the aluminum center [14] which display via the steric hindrance of the methyl substituents a distorted *boat–boat* conformation. The angles involving the two eight-membered rings (O1--Al1--O2 108.3 and O3--Al1--O4 105.7°) are clearly distinct, being nevertheless within the range usually found for monomeric tetrahedrally coordinated aluminum bisphenoxides [4,9,14]. The unusual dinuclear structure found in our case markedly differs from similar Al(mcmip) bisphenoxides isolated and structurally characterized by Lin and co-workers after reaction of the same ligand with trimethyl aluminum. In that particular case the compound displayed standard neutral donor–acceptor features of the type (mcmip)AlCH₃(THF) [9]. In order to corroborate these results, we ran a similar reaction with triethyl aluminum and could, following the same general procedure, isolate and characterize an analogous neutral complex (mcmip)Al(CH₂CH₃)(THF), **2**. The ORTEP diagram of compound **2** is on the whole comparable to the structure reported by Lin and co-workers [9] as it can be taken from Fig. 2 and will not be discussed in detail in this contribution. Crystals of neutral aluminum bisphenoxide **2** are also monoclinic, space group $P2(1)/c$ (no. 14) [15]. Selected bonds and angles are listed in the Supplementary material.

Trying to elucidate the formation of the isolated ionic compound **1** and to connect this to the already reported coordination chemistry involving the mcmip ligand is quite complicated. Although

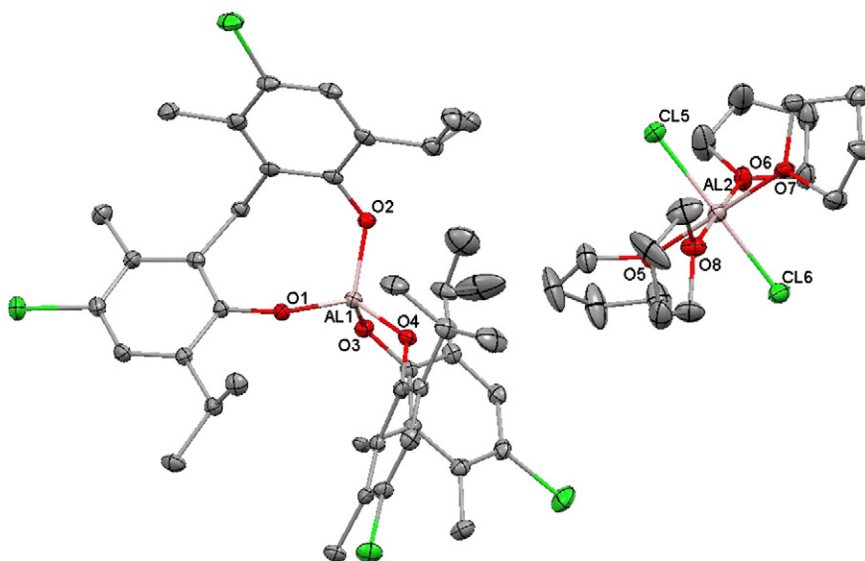


Fig. 1. A perspective view of $[\text{Al}(\text{THF})_4(\text{Cl})_2]^+ [\text{Al}(\text{mcmip})_2]^- \cdot 2\text{ THF}$, with atom-numbering scheme within the coordination sphere. Displacement ellipsoids are drawn at the 20% probability level, H atoms and crystal's THF molecules have been omitted.

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