This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
Heterometallic aluminates: alkali metals trapped by an aluminium aryloxide claw.

Mª Teresa Muñoz, Tomás Cuenca* and Marta E. G. Mosquera*

In the heterometallic species prepared \([\text{AlMM}\{2,6-(\text{MeO})_2\text{C}_6\text{H}_3\text{O}\}_2]\)\(_n\) (M = Li, Na and K), the \(\{\text{AlM}\{2,6-(\text{MeO})_2\text{C}_6\text{H}_3\text{O}\}_2\}\) moiety acts as a claw that grasp alkali metals of very different sizes.
Heterometallic aluminates: alkali metals trapped by an aluminium aryloxide claw.

Mª Teresa Muñoz, Tomás Cuenca* and Marta E. G. Mosquera.*

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

A series of heterometallic aluminium-alkali metal species [AlMMe₂{2,6-(MeO)₃C₆H₃O}₂]ₙ have been isolated for lithium, sodium and potassium. These compounds can be generated by the reaction of [AlMe₂{2,6-(MeO)₃C₆H₃O}]₂ with the metallated phenol [M{2,6-(MeO)₂C₆H₅}]₂ or through the reaction of the mixture of AlMe₂ and the appropriate alkali metal alkyl base with two equivalents of 2,6-dimethoxyphenol. In the heterometallic species obtained, the [AlMe₂{2,6-(MeO)₂C₆H₃O}]₂⁺ moiety is observed and could be described as a claw which fixes the alkali ion by the phenoxide oxygen atoms while the methoxy groups help to stabilize their coordination sphere. All compounds have been characterized by NMR spectroscopy and X-ray diffraction methods. Catalytic studies reveal that these compounds are active in ring-opening polymerization of ε-lactide.

Introduction

Aluminium organometallic compounds are well known for their remarkable structures and unique reactivity.¹ These derivatives participate in many organic transformations such as nucleophilic additions to carbonyl compounds,² cross coupling reactions with organic halides,³ hydro and carboaluminations to unsaturated species,⁴ conjugative addition to Michael acceptors⁵ and many others.⁶ In addition, they are active in numerous catalytic polymerization processes of a variety of substrates such as olefines,⁷ or functionalized monomers like epoxides⁸ and cyclic esters.⁹ In these processes those species containing Al-O bonds are particularly active.¹⁰

The reactivity of aluminium organometallics stems either from the acid character of the metal or from the carbanionic nature of the organic group bonded to it.¹¹ This dual Lewis character confers great versatility to the chemical behaviour of these compounds. A kind of derivatives where this multi Lewis character is particularly evident is in group 1 aluminates where an alkali metal and the aluminium are placed in close proximity.¹²

For these heterometallic systems the presence of two metals of different nature, one very electropositive alkali metal and a π-block metal, could provide valuable synergic effects, so reactivities and selectivities different from the homometallic counterparts can be expected.¹³ In fact, the interest in heterometallic “ate” species has increased exponentially since the beginning of the century due to the remarkable reactivity that they have shown.¹⁴ As such, these species have revolutionized the metallating reactions, outperforming the traditional single metal metallating agent such as alkyl lithium compounds.¹⁵

Although “ate” derivatives have been tested in many organic transformations, studies on their ability as polymerization catalysts are scarce.¹⁶ Hence it is of interest to evaluate the activity of aluminate species in such processes, especially considering that aluminium is a key metal in the preparation of active species for catalytic polymerizations.

In this context, our research is oriented to the preparation of aluminium derivatives active in polymerization processes.¹⁷ Particularly we are interested in studying derivatives with functionalized aryloxide groups since the additional functionalities in the ring can influence the structure and reactivity of the species formed.¹⁸,¹⁹ Surprisingly there are few studies of functionalized phenols as ligand precursors even though they are cheap, readily available chemicals.

In this study, a phenol bearing donor groups in ortho positions, 2,6-dimethoxyphenol, has been chosen as the ligand precursor. In our previous investigations we have isolated heterometallic ate species of different nuclearity, [AlLiMe₂{2,6-(MeO)₂C₆H₅}]₂ and [AlLiMe₂{2,6-(MeO)₂C₆H₅}]₃ from the reaction of the hexametallic lithium aryloxide cage [Li{2,6-(MeO)₂C₆H₅}]₆ and different aluminium precursors.¹⁹

We report here the extension of our work to potassium and sodium, using [AlMe₂{2,6-(MeO)₂C₆H₅}]₂ (2) as the aluminium precursor. These studies have allowed us to isolate the metallated phenols [M{2,6-(MeO)₂C₆H₅}]₂ (M = Na (1b), K (1c)) and the two new heterometallic ate compounds [AlMe₂{2,6-(MeO)₂C₆H₅}]₃ (M = Na (3b), K (3c)). Interestingly, compound 3c is the first potassium-aluminium derivative with aryloxide ligands bridging the metals. The structure of the heterometallic derivatives 3b and 3c was determined in the solid state and both show the structural motif [AlMe₄{2,6-(MeO)₂C₆H₅O}]₂, analogous to the one present in the lithium...
species previously described by our group. This fragment acts as a kind of claw that can grasp alkali metals of very different sizes such as lithium and potassium, without changing substantially its structural parameters (figure 1). The solid state structure of the species \(\text{[AlMe}_2\text{2,6-(MeO)C}_{6}\text{H}_3]_2\) \(2\) previously reported by us is also described.

![Figure 1. Aluminium phenoxide claw, \(M = \text{Li, Na, K}\).](image)

**Experimental Section**

**General Considerations.** All manipulations were carried out under an inert atmosphere of argon using standard Schlenk and glovebox techniques. All solvents were rigorously dried prior to use following standard methods. NMR spectra were recorded at 400.13 (\(^1\)H) and 100.62 (\(^13\)C) MHz on a Bruker AV400.

Chemical shifts (\(\delta\)) are given in ppm using C\(_6\)D\(_6\) as solvent. \(^1\)H and \(^13\)C resonances were measured relative to solvent peaks considering TMS \(\delta = 0\) ppm. Elemental analyses were obtained on a Perkin-Elmer Series II 2400 CHNS/O analyzer. Molecular weights of polymers were determined by gel permeation chromatography (GPC) in a Varian HPLC apparatus in THF at room temperature calibrated with respect to polystyrene standards and corrected with a factor of 0.58. L-lactide was purchased from Aldrich and then purified by recrystallization from toluene and sublimation under vacuum. All reagents were commercially obtained and used without further purification.

**Benzyl sodium**, \(^20\) benzyl potassium \(^20\) and \(\text{[AlMe}_2\text{2,6-(MeO)C}_{6}\text{H}_3]_2\) \(2\) were prepared according to reported methods.

**Synthesis of \(\text{[Na}_{2,6-(\text{MeO})}\text{C}_{6}\text{H}_3]_2\) \((1b)\).** To a solution of benzyl sodium (0.37 g, 3.21 mmol) in 10 mL of toluene, a solution of 2,6-dimethoxyphenol (0.50 g, 3.21 mmol) in 10 mL of toluene was added at 78 °C. The mixture was stirred for 10 min at low temperature and then allowed to reach room temperature, leaving it to stir for 3 hours, and the precipitation of a white solid was observed. Yield: 54\% (0.33 g, 1.73 mmol). \(^1\)H NMR (C\(_6\)D\(_6\)): \(\delta\) 3.13 (s, 6H, OCH\(_3\)), 6.41 (m, 3H, OAr-H). \(^13\)C (C\(_6\)D\(_6\)): \(\delta\) 54.54 (s, OCH\(_3\)), 104.22 (s, m-OAr-H), 109.38 (s, p-OAr-H), 150.98 (s, OAr). Anal. Calcd. (%) for KC\(_6\)H\(_3\)O\(_7\): 0.1C\(_6\)H\(_3\) (201.47 g/mol) C, 51.87; H, 4.90. Found: C, 52.71; H, 4.45.

**Synthesis of \(\text{[AlNa}_{2,6-(\text{MeO})}\text{C}_{6}\text{H}_3]_2\) \((3b)\).** To a mix of 0.10 g (0.568 mmol) of \(1b\) and 0.12 g (0.284 mmol) of \(\text{[AlMe}_2\text{2,6-(MeO)C}_{6}\text{H}_3]_2\) was added 10 mL of toluene at -78 °C. The mixture was stirred for 10 min at low temperature and then allowed to reach room temperature, and the precipitation of a white solid was observed. The suspension was stirred for 2 hours at room temperature. The solid was dissolved after a brief reflux. Storage of the solution at room temperature for a day allowed the formation of white crystals of compound \(3b\) Yield: 60\% (0.13 g, 0.34 mmol). \(^1\)H NMR (C\(_6\)D\(_6\)): \(\delta\) -0.49 (s, 3H, AlCH\(_3\)), 3.40 (s, 6H, OCH\(_3\)), 6.29 (d, 2H, J\(_{HH}\) = 8 Hz, m-OAr-H), 6.56 (t, 1H, J\(_{HH}\) = 8 Hz, p-OAr-H). \(^13\)C (C\(_6\)D\(_6\)): \(\delta\) -10.33 (s, AlCH\(_3\)), 55.72 (s, OCH\(_3\)), 105.60 (t, m-OAr-H), 116.33 (p, m-OAr-H), 140.44 (s, o-OAr), 150.57 (s, i-OAr). Anal. Calcd. (%) for Na\(_2\)Al\(_2\)C\(_{30}\)H\(_{48}\)O\(_{12}\) (772.58 g/mol) C, 55.96; H, 6.26. Found: C, 55.71; H, 6.59.

**Synthesis of \(\text{[AlK}_{2,6-(\text{MeO})}\text{C}_{6}\text{H}_3]_2\) \((3c)\).** A solution of 2,6- dimethoxyphenol (0.50 g, 3.21 mmol) in toluene (10 mL) was added to 0.42 g (3.21 mmol) of KBr in 10 mL of toluene at -78 °C, and the mixture was stirred for 10 minutes. Then the solution was allowed to reach room temperature. After stirring for 2 hours, a grey solution with solid was formed. 0.68 g (1.60 mmol) of \(\text{[AlMe}_2\text{2,6-(MeO)C}_{6}\text{H}_3]_2\) heated to a brief reflux in 20 mL of toluene were added to the suspension and stirred for 10 minutes. When the reaction mixture reached room temperature the white solid formed was dissolved by heating while 25 mL of THF were added giving a pale yellow solution. After one day of storage at room temperature, white crystals of compound \(3c\) were observed. Yield: 52\% (0.68 g, 1.68 mmol). \(^1\)H NMR (THF-d\(_2\)): \(\delta\) -1.10 (s, 3H, AlCH\(_3\)), 3.71 (s, 6H, OCH\(_3\)), 6.38 (m, 1H, p-OAr-H), 6.45 (m, 2H, m-OAr-H). \(^13\)C (THF-d\(_2\)): \(\delta\) -0.50 (s, 3H, AlCH\(_3\)), 3.35 (s, 6H, OCH\(_3\)), 6.30 (m, 2H, m-OAr-H), 6.48 (m, 1H, p-OAr-H). \(^13\)C (C\(_6\)D\(_6\)): \(\delta\) -9.00 (s, AlCH\(_3\)), 55.36 (s, OCH\(_3\)), 104.17 (s, m-OAr-H), 105.64 (s, p-OAr-H), 138.10 (s, o-OAr), 151.23 (s, i-OAr). Anal. Calcd. (%) for KAlC\(_{30}\)H\(_{48}\)O\(_{12}\) (402.46 g/mol) C, 53.72; H, 6.01. Found: C, 52.93; H, 5.51.

**Polymerization of L-lactide.** In a glovebox, a Schlenk flask was charged with 26 μmol of the desired complex and 26 μmol of benzyl alcohol. 2.5 mL of dry toluene was added. This solution was added to 2.6 mmol (373 mg) of L-lactide dissolved in 2.5 mL of dry toluene and the mixture was heated in an oil bath at 125 °C. Small portions were removed with a pipette to determine the conversion by \(^1\)H NMR. After 5h, polymerization was quenched with hexane, then it was purified with dichloromethane and, finally, the polymer was precipitated with an excess of hexane. The white solid was filtrated and dried under vacuum to constant weight.

**Circular dichroism (CD).** Measurements were performed by...
using a JASCO-715 spectropolarimeter. Recorded spectra were the average of 2 scans taken at the speed of 50 nm min⁻¹ with a 0.125 s time response. The sensitivity and resolution were fixed at 20 mdeg and 0.5 nm respectively. Measurements were carried out in 1 cm path quartz cells at 25 °C. The sample was measured in toluene at several concentrations. No CD spectrum was obtained for any of the solutions whatever the concentration was.

#### Results and discussion

The approach to achieve the formation of heterometallic species may be oriented in two ways; one would imply the initial reaction of the 2,6-dimethoxyphenol with the alkali metal alkyl base MR and then the treatment of the metallated phenol with the aluminium precursor [AlMe₃][2,6-(MeO)₂C₆H₄O] (2). In the other synthetic approach the initial step would be to generate an alkali metal-aluminium heterometallic species by mixing AlMe₃ and MR that would then react with the right stoichiometric amount of 2,6-dimethoxyphenol.

Starting with the first strategy, in order to prepare the sodium and potassium derivatives [M(OAr)]₃, 2,6-dimethoxyphenol was reacted with benzyl sodium and benzyl potassium, giving the species [M{2,6-(MeO)₂C₆H₄O}₃] (M = Na (1b), K (1c)) (see Scheme 1).

### Scheme 1. Synthesis of 1.

Compounds 1b and 1c are air sensitive and should be stored under argon. They were characterized by analytical and spectroscopic methods. The formation of 1 was confirmed by the disappearance of the signal for the alcohol group in the ¹H NMR spectra, where similar resonances are observed for 1b-1c in comparison to the previously reported lithium derivative [Li{2,6-(MeO)₂C₆H₄O}] (2). As such, we observe one singlet at 3.24 (1b) and 3.13 (1c) ppm for the methoxy group hydrogen atoms, being at 3.16 ppm for the lithium derivative. The resonances for the aromatic ring also appear at close shift values for these compounds, a multiplet at 6.51 (1b) and 6.14 (1c) ppm, being slightly different in the lithium case, which shows a doublet at 6.48 ppm and a triplet at 6.56 ppm for meta and para protons respectively.

The reaction of compounds 1 and [AlMe₃][2,6-
(MeO)₂C₆H₄O]₂ (2) led to the formation of the heterometallic derivatives 3b and 3c that were isolated as colourless crystals (see scheme 2). The potassium species 3e is barely soluble in toluene so it was necessary to use a donor solvent such as THF to dissolve it and achieve the formation of crystals.

![Image: Chemical structure of 3b and 3c.]

**Scheme 2. Synthesis of 3.**

When we perform the synthesis of the heterometallic species using the second strategy, that is, by mixing initially the metallic precursors AlMe₃ and MR and then adding two equivalents of 2,6-dimethoxyphenol, the corresponding heterometallic compounds 3 were also generated, although the yields are lower and the formation of other species is observed in the NMR spectra.

Compounds 3 are air sensitive and should be stored under argon, but for short periods of time remain unchanged in air. They were characterized in solution by multinuclear NMR spectroscopy. In the ¹H NMR spectra in C₆D₆, [AlLiMe₂[2,6-(MeO)₂C₆H₄O]₂] and compounds 3 show a resonance for the methyl groups bound to aluminium at similar values, (δ ca. -0.50) indicating an analogous electronic environment for those methyl groups in the three compounds. The other hydrogen atoms in the structure appear also at similar shifts for the three derivatives, (δ 3.35-3.40 (OMe range), 6.23-6.30 (m-OAr-H range) and 6.48-6.56 (p-OAr-H range)). These data suggest that the methyl groups have the same acidic character and the different alkali metals have a little effect on the shielding of those protons. However, there is an important change in comparison to the precursor [AlMe₂{2,6-(MeO)₂C₆H₄O}₂] (2), in that, the signal for the methyl group bonded to the aluminium moves significantly to higher field values, from -0.27 ppm in 2 to -0.50 ppm in 3 signifying a more shielded environment for the methyl groups in the aluminates.

The nucularity in the solid state for compounds 3 were determined by single-crystal X-ray diffraction studies since appropriate crystals were isolated. Also for comparison purposes the study of structure of the aluminium precursor [AlMe₂{2,6-(MeO)₂C₆H₄O}₂] (2) was also performed.

As shown in figure 2, compound 2 is a dinuclear derivative where the aryloxide group acts as a bridging ligand. In this compound, the aluminium centres show a typical tetrahedral environment, being bonded to two aryloxide ligands and two methyl groups. There is also a non-covalent interaction between the oxygen atoms from the MeO moieties and the aluminium, Al⋯OMe 2.59 Å and 2.54 Å, giving a pseudo-octahedral environment for the metal. The central core AlO₂ and the two phenyl rings are co-planar, this disposition is probably affected by the presence of these Al⋯OMe interactions. In fact, a CSD (Cambridge Structural Database) search showed that the most frequent arrangement for derivatives bearing the fragment (AlOAr)₂ is when the central AlO₂ plane and the phenyl rings are placed at an angle bigger than 40°. For those cases where the angle is close to planarity, in the vast majority of the compounds there is a substituent in ortho position that establishes an interaction with the metal directing this co-planar disposition, as in 2. For this kind of (AlOAr)₂ derivatives a clear tendency in the Al-O distance is also observed, being shorter for those compounds with a coplanar arrangement of the AlO₂ plane and the phenyl rings (see ESI).

![Image: ORTEP plot of 2 showing thermal ellipsoid plots (30% probability).]

**Figure 2.** ORTEP plot of 2 showing thermal ellipsoid plots (30% probability).

In figure 3, an ORTEP view for the asymmetric unit of 3b along with the atom-labelling schemes is shown. In this unit, the presence of one aluminium atom and one sodium atom bridged by two phenoxide groups is observed. The aluminium center completes its coordination sphere with two methyl groups. The sodium atom is bonded to a {AlMe₂[2,6-(MeO)₂C₆H₄O]₂}⁻ fragment that grabs the alkali ion.

![Image: ORTEP plot of 3b asymmetric unit showing thermal ellipsoid plots (30% probability).]

**Figure 3.** ORTEP plot of 3b asymmetric unit showing thermal ellipsoid plots (30% probability).

This {AlMe₂[2,6-(MeO)₂C₆H₄O]₂}⁻ moiety is also present in compound 2, although in this case would be binding a {Al(CH₃)}⁻ fragment. When comparing the bond distances and angles in this fragment for 2 and 3b, a shortening of the Al-O
bonds lengths and an increase of the O-Al-O angle are observed for the heterometallic derivative (table 2). However, the Al-C distances do not change significantly.

Table 2. Selected bond lengths (Å) and angles (deg) for 2, [AlLiMe$_2$(2,6-(MeO)$_2$C$_6$H$_4$)$_2$], 3b and 3c

<table>
<thead>
<tr>
<th></th>
<th>Bond lengths</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2</td>
<td>[AlLi]</td>
<td>3b</td>
</tr>
<tr>
<td>Al1-O1</td>
<td>1.892(2)</td>
<td>Al1-O1</td>
<td>1.852(1)</td>
</tr>
<tr>
<td>Al1-O1#1</td>
<td>1.898(2)</td>
<td>Al1-O2</td>
<td>1.799(2)</td>
</tr>
<tr>
<td>C11-C11</td>
<td>1.368(3)</td>
<td>O1-C11</td>
<td>1.359(2)</td>
</tr>
<tr>
<td>C11-C12</td>
<td>1.382(4)</td>
<td>C11-C12</td>
<td>1.390(3)</td>
</tr>
<tr>
<td>C12-O3</td>
<td>1.358(5)</td>
<td>C12-O3</td>
<td>1.372(3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O2-C21</td>
<td>1.346(2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O2-C22</td>
<td>1.351(3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C11-C13</td>
<td>1.388(4)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C13-O2</td>
<td>1.359(3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C13-O2#3</td>
<td>1.385(4)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>All-C1</td>
<td>1.956(3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>All-C2</td>
<td>1.957(2)</td>
</tr>
</tbody>
</table>

Symmetry transformations: #1 x+1,-y,-z+1.

When 3b asymmetric unit is grown, a tetrametallic Na$_2$Al$_2$ derivative is revealed (see figure 4a). In this structure the two aryloxide oxygen atoms, O1 and O2, are bridging the aluminum and sodium atoms composing two four-membered rings that are attached to the central Na$_2$O$_2$ core by sharing the Na1-O2 edge. The Na-O distances in this central cycle are quite different from each other (2.272(4) and 2.466(4) Å). The disposition of the aryl groups projected above and below the Na$_2$O$_2$ plane prevents the cycles from stacking and the three four-membered rings associate laterally in a cradle disposition.

Figure 4. a) Ball and stick plot of compound 3b. b) Central core.

In 3b the sodium atoms are pentacoordinated, bonded to three aryloxide groups and two methoxy moieties. The interactions observed between the sodium and the methoxy groups are asymmetric, Na···Ome 2.310 and 2.903 Å, and help to stabilise the coordination sphere of the alkali metal. In a similar way as in 2, the close disposition of two methoxy groups in relation to the aluminium atoms suggests the presence of weak interactions.

Another noteworthy difference is that 3b crystallises in a chiral space group and it is enantiomerically pure. Considering that none of the reactants were chiral, the chirality must come from the central core conformation. As depicted in figure 4b, the three rings that compose the central core are arranged helicoidally as a dextro rotatory helix. In solution no chirality is observed, as shown by a circular dichroism study. In order to gain further insight into the structure of 3b in solution, Diffusion-Ordered Spectroscopy (DOSY) NMR experiments were carried out. Following the methodology applied by several groups, we used three reference compounds and plotted the diffusion coefficients in logarithm to the logarithm of the molecular weights (see ESI). The correlation points towards a formulation [AlNaMe$_2$(2,6-(MeO)$_2$C$_6$H$_4$)$_2$] solvated with one solvent molecule. This result will be in agreement with the lack of chirality in solution since it indicates that the central core Na$_2$O$_2$ is not present when dissolved.

Figure 5. Ball and stick model for a) Molecular structure of 2, b-d) Asymmetric units for [AlLiMe$_2$(2,6-(MeO)$_2$C$_6$H$_4$)$_2$], 3b and 3c respectively.

The structure in the solid state for compound 3c shows the same asymmetric unit as 3b where the potassium is again bonded to a [AlMe$_2$(2,6-(MeO)$_2$C$_6$H$_4$)$_2$]$^+$ fragment (figures 5d and 6d). However in this case, there is a striking difference due to the bigger size of potassium and, as shown in figure 6d, the metal stacks out leaving the moiety [AlMe$_2$(2,6-(MeO)$_2$C$_6$H$_4$)$_2$]$^+$ nearly coplanar and with a symmetric coordination to the alkali metal. As such, the dihedral angles between the central AlO$_2$ core and the phenyl rings are 14.32° and 15.14°, being the Al···Ome distances 2.819 Å and 2.869 Å respectively. For the sodium species 3b, the coordination of the alkali metal to the aryloxide fragment distorts this arrangement and only one phenyl ring is coplanar with the AlO$_2$ core (distance Al···Ome 2.836 Å) being the dihedral angle to the other aromatic ring 42.51°, that places the OMe group further apart from the aluminium (distance...
Al···OMe 3.263 Å). For the lithium compound this asymmetry is more evident and the dihedral angles between the central core AlO₂ and the aromatic rings are 12.37° and 50.17°, being the Al···OMe distances 2.838 Å and 3.255 Å respectively.

In 3c the disposition of the aromatic rings’ substituents being nearly coplanar to the central core allows the stacking of the units, and instead of the formation of a discrete cradle core, the units pile along the a axis, generating a polymeric structure where the potassium atoms act as the connecting nexus (figure 7) of the \{AlMe₂(2,6-(MeO)₂C₆H₃O)₂\}⁺ fragments that place themselves in alternating positions above and below the potassium chain. The K···K distance is 3.6673 Å, shorter than in potassium metal (4.54 Å) and much smaller than double the van der Waals radius of potassium ($r_{vdW}$ = 2.75 Å). Actually this distance is quite short for a polymeric potassium structure being more often observed in dinuclear derivatives.

As in the aluminium-lithium and aluminium-sodium derivatives, the presence of methoxy groups in ortho position seems to have a decisive effect on the stabilization of the alkali metals through the interactions between the oxygen and these metals. As such, potassium atoms show an octacoordinated arrangement with four bonds shared with phenoxide oxygen atoms and four with methoxy groups (figures 8 and 9). This behaviour is different for lithium and sodium species, which show a pentacoordinated arrangement and can be attributed to potassium’s bigger size. All the K-O distances in the compound are very similar, either from the bonds to the phenoxide groups, 2.921(4) and 2.939(4) Å, or from the methoxy groups, 2.917(4) and 2.971(4) Å.

All these interactions saturate the coordination sphere of the potassium atom and, although the crystallization took place in the presence of a donor solvent such as THF, no coordinated solvent molecules are present. The structure of this derivative was also analysed in solution by a Diffusion-Ordered Spectroscopy (DOSY) NMR experiment in thf-d₈. In this media the results indicate the presence of the heterobimetallic species \[\text{AlKMe}_2\{2,6-(\text{MeO})_2\text{C}_6\text{H}_3\text{O}\}_2\].

According to a search in the CSD, heterometallic aluminium potassium derivatives are not very numerous; those with a K-O-Al fragment being scarce. In particular, compound 3c is the first potassium-aluminium derivative where the metals are connected by aryloxide bridges.

In conclusion, in the series of compounds [AlMMe₂(2,6-(MeO)₂C₆H₃O)₂] (M = Li, Na (3b), K (3c)) the asymmetric units are isomorphous. In them, the alkali metals are chelated by a \{AlMe₂(2,6-(MeO)₂C₆H₃O)₂\}⁺ moiety. For the three compounds, bond distances and angles within this fragment are very similar (Al-O distances, 1.798(2)-1.852(1) Å range; C-O distances 1.314(4)-1.359(2) Å range; O-Al-O angles 86.39(13)-89.06(10)° range) (table 2). The main changes amongst the three are the modification of the dihedral angles between the phenyl groups and the AlO₂ central core to accommodate the different sizes of
the alkali ion. Hence, in these structures it can be considered that the phenoxide groups bind to aluminium until coordinative saturation, giving the \( \text{[AlMe}_2(2,6-(\text{MeO})_2\text{C}_6\text{H}_3\text{O})_2]^- \) moiety. This anion satisfies the coordinative needs of the approaching alkali metal cation and can be described as a claw which fixes the alkali metals to the framework by the phenoxide oxygen atoms while the methoxy groups help to stabilize the coordination sphere of the alkali metals. These bonding features, where the Al-O phenoxide bonds show an anchoring nature that provides the framework for the structure, while the alkali metals attach to it via ancillary bonds, are in good agreement with the well-established concept of anchoring/ancillary bonding in heterobimetallic chemistry.**

**Reactivity studies.**

The reactivity of the \([\text{AlMMe}_2(2,6-(\text{MeO})_2\text{C}_6\text{H}_3\text{O})_2]_2\) (M = Li, Na (3b), K (3c)) compounds towards \([\text{ZpCpCl}]_2\) was examined. When the reactions for the three compounds were monitored by \(^1\)H NMR spectroscopy, the apparition of two sets of resonances is observed. One group of signals at \( \delta = -0.27\) (s, 6H), 3.38 (s, 6H), 6.24 (d, 2H, \(^3\)I\(_{HH}\) = 8 Hz) and 6.65 (t, 1H, \(^3\)I\(_{HH}\) = 8 Hz) evidences the generation of derivative 2 in the reaction. The other set of signals at \( \delta = 6.72\) (t, 1H, \(^3\)I\(_{HH}\) = 8 Hz), 6.40 (d, 2H, \(^3\)I\(_{HH}\) = 8 Hz), 6.19 (s, 10H) and 3.45 (s, 6H) corresponds to the compound \([\text{ZpCpCl(OAr)}]_2\) indicating that the substitution of a Cl ligand for an arylxide ligand has taken place. A clear tendency of reactivity is observed, as such, after one day, the reaction had evolved to a greater extent for 3c than for the sodium and lithium counterparts (see ESI for NMR spectra). This behaviour indicates that the reactivity of these heterometallic species \([\text{AlMMe}_2(2,6-(\text{MeO})_2\text{C}_6\text{H}_3\text{O})_2]_2\) is highly influenced by the alkali metal and the ligand coordinated to it is transferred to the zirconium center, while the aluminum methyl groups remain unreactive.

Initial studies of the conduct of these derivatives in polymerization processes show that they are active in the ROP of \( \ell \)-lactide. We performed the experiments with a 100:1 monomer/initiator ratio in toluene, at 125°C, using BnOH as initiator and \([\text{AlMMe}_2(2,6-(\text{MeO})_2\text{C}_6\text{H}_3\text{O})_2]_2\) (M = Li, Na (3b), K (3c)) as catalysts. For comparison purposes, the activity of compound 2 was also analyzed. In these conditions, the most active catalysts were 2 and \([\text{AlLiMe}_2(2,6-(\text{MeO})_2\text{C}_6\text{H}_3\text{O})_2]_2\)_2 with a conversion of 78% and 75% respectively. The activity of the heterometallic catalysts reduces when moving from Li to Na and K, with conversion 48% for 3b and 20% for 3c. For the most active catalysts, 2 and \([\text{AlLiMe}_2(2,6-(\text{MeO})_2\text{C}_6\text{H}_3\text{O})_2]_2\)_2, the polymers obtained show narrow polydispersities, especially when using the lithium-aluminium derivative. Further studies on these polymerization processes are going.

**Conclusions**

A range of alkali metal \([\text{AlMMe}_2(2,6-(\text{MeO})_2\text{C}_6\text{H}_3\text{O})_2]_2\)_n derivatives have been isolated. In all the structures the presence of the \([\text{AlMe}_2(2,6-(\text{MeO})_2\text{C}_6\text{H}_3\text{O})_2]^-\) moiety is observed. This fragment could be described as a claw which fixes the alkali metals by the phenoxide oxygen atoms while the methoxy groups help to stabilize the coordination sphere of these metals. When moving from Li to Na and K this arylxide fragment does not change substantially the spectroscopic data or its structural parameters, only the dihedral angles between the central AlO plane and the phenyl rings modify to accommodate to the different alkali ions sizes. Preliminary polymerization studies indicate that the aluminium lithium species \([\text{AlLiMe}_2(2,6-(\text{MeO})_2\text{C}_6\text{H}_3\text{O})_2]_2\)_2 are active in \( \ell \)-lactide ROP giving polymers with narrower polydispersities than the homometallic counterpart 2.

**Acknowledgement.** Financial support from Facultad de Cristalización-Consolidación-Ingenio (CS2D2006-00015) and the Universidad de Alcalá (CCGG2013-EXP-061) are gratefully acknowledged. M.T.M. thanks the Universidad de Alcalá for a research fellowship. The authors thank Prof. Francisco Mencidetti and Thais Carmona for the CD measurements.

**Notes and references**

\(^*\) Departamento de Química Orgánica y Química Inorgánica, Universidad de Alcalá, Campus Universitario, E-28871 Alcalá de Henares, Spain. Fax: +34-918854683; Tel: +34-918854779. E-mail: martaeag.mosquera@uah.es.

† Electronic Supplementary Information (ESI) available: DOSY experiments for 3b and 3c, \(^1\)H NMR data for 2 and \([\text{ZpCpCl(OAr)}]_2\), scannerogram of Al-O distances and dihedral angles between Al-O plane and a phenyl ring for \([\text{AlOAr}]_2\) derivatives. See DOI: 10.1039/b000000x/

‡ Compound 2: M\(_n\) = 7951, polydispersity = 1.45; [AlLiMe\(_2(2,6-(\text{MeO})_2\text{C}_6\text{H}_3\text{O})_2]_2\): M\(_n\) = 5653, polydispersity = 1.23.


This journal is © The Royal Society of Chemistry [year]