

Evidence for the *trans*-influence of axial substituents as a significant factor determining the structure and stability of five-coordinate complexes: molecular structure of the first simple five-coordinate dialkylaluminum *O,O'*-chelate complex

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Abstract

The addition of 4-methylpyridine to $\text{Me}_2\text{Al}[\text{OC}(\text{Me})\text{C}_6\text{H}_4\text{-2-O}]$ produced the relatively stable five-coordinate Lewis acid–base adduct $\text{Me}_2\text{Al}[\text{OC}(\text{Me})\text{C}_6\text{H}_4\text{-2-O}] \cdot (\gamma\text{-picoline})$. The resulting compound has been characterized by ^1H and ^{27}Al NMR spectroscopy and cryoscopic molecular weight measurements and the molecular structure has been confirmed by X-ray crystallography. X-ray structure analysis of this simple five-coordinate complex reveals that the *trans*-influence of axial substituents is a significant factor controlling the structure and stability of five-coordinate aluminum compounds. © 1999 Elsevier Science S.A. All rights reserved.

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In recent years it has been extensively demonstrated that pentacoordination plays a significant role in selective organic transformations mediated by organoaluminum compounds, however, the nature of the intermediates remains elusive [1–5]. Recent reports have also shown that pentacoordinate aluminum species are of potential importance in the ring-opening polymerization of heterocyclic monomers [6,7]. Despite this, less direct information has been gleaned about the nature of the bonding and reactivity of simple five-coordinate organoaluminum complexes. Structurally characterized five-coordinate aluminum alkyls are dominated by derivatives of macrocyclic or multidentate open-chain ligands [8,9], and fully characterized mononuclear compounds with mono- or bidentate ligands, which could serve as a useful structural model, are very scarce. To date there is only one structurally characterized trialkylaluminum complex with two monodentately bonded ligands, the polymeric chain structure of Me_3Al with the [12]ane S_4 ligand [10] and a few examples of intramolecularly coordinated neutral organoaluminum compounds [11–16]. Only recently have we succeeded in the isolation and structural characterization of the first simple five-coor-

dinate aluminum monoalkyl chelate complexes $\text{RAl}(\text{O},\text{X})_2$ (where *O,X* donates bidentate, monoanionic oxygen–oxygen or oxygen–nitrogen based ligands) [17,18], though first attempts to isolate this type of complex have been undertaken since the end of the sixties [19]. The observed tendency of dialkylaluminum chelate compounds derived from unsaturated α - or β -hydroxy carbonyl compounds to form five-coordinate $[\text{R}_2\text{Al}(\text{O},\text{O}')]_2$ adducts in the solid state has indicated that the metal center in the monomeric $\text{R}_2\text{Al}(\text{O},\text{O}')$ molecule is able to coordinate an additional ligand [20,21]. However, the reported attempts to isolate the simple five-coordinate $\text{R}_2\text{Al}(\text{O},\text{O}') \cdot \text{L}$ adduct, which could serve as a model compound for investigations of the structure and reactivity of five-coordinated aluminum species, have been unsuccessful [22–24]. In the course of our exploration of organoaluminum chelate complexes we report here the molecular structure of the first $\text{R}_2\text{Al}(\text{O},\text{O}') \cdot \text{L}$ -type adduct, and show that the *trans*-influence of axial substituents is a significant factor controlling the structure and stability of five-coordinate aluminum complexes.

The reaction of $\text{Me}_2\text{Al}(\text{hacac})$ (**1**) (where *hacac* = deprotonated 2'-hydroxyacetophenone) with 1 equiv. (or excess) of γ -picoline (py-Me) allows for the isolation of the Lewis acid–base adduct $\text{Me}_2\text{Al}(\text{hacac}) \cdot \text{py-Me}$ (**2**) quanti-

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tatively¹. The formation of stable adducts is not observed when a weaker Lewis base such as Et₂O or THF was used. Hence it appears that only relatively strong Lewis bases may coordinate to the tetrahedral metal center in dialkylaluminum chelate complexes to form stable adducts. Compound **2** is stable as a solid under inert atmosphere, however, in solution it slowly disproportionates to Me₃Al·py-Me and MeAl(hacet)₂ at ambient temperature. Compounds **1** and **2** have been characterized by NMR spectroscopy and cryoscopic molecular weight measurements in benzene and the molecular structure of **2** has been confirmed by X-ray crystallography². It should also be added that we have previously reported the structural investigations of the dimethylaluminum chelate compound derived from the related hydroxyacetophenone ligand, 2-aceto-4-chlorophenol, and our studies have revealed that the latter compound exists as a monomeric, four-coordinated molecule in solution and as the five-coordinated dimer [Me₂Al(μ-OC₆H₃(Cl)-2-C(Me)-O)]₂ (**3**) in the solid state [20].

The spectroscopic data of **1** and **2** show no complexity, however, the ²⁷Al NMR data are noteworthy. A comparison of the δ²⁷Al values of the four-coordinate Me₂Al(hacet) (**1**) (δ 152 ppm) and its Lewis acid–base adduct with py-Me (**2**, δ 118 ppm) shows a magnitude of the shielding effect on the five-coordinate adduct formation (Δδ 34 ppm). Further, the chemical shift of the monomeric complex **2** is close to those observed for the dimeric five-coordinated dialkylaluminum derivatives of saturated hydroxycarbonyl compounds [25] or alkoxy- and amine-functionalized alcohols (for this group of compounds the chemical shift range is approximately from 135 to 110 ppm) [26]. Thus, the degree of association or the

nature of a chelating ligand does not significantly affect the aluminum nuclei shielding in the neutral five-coordinated dialkylaluminum complexes. A more pronounced change in the shielding at aluminum results by replacing an alkyl group in the dialkylaluminum chelate derivatives by a more electronegative substituent, which is indicated by the δ²⁷Al values of the RAl(O,X) chelate complexes, MeAl(mesal)₂ (68 ppm; mesal = deprotonated methyl salicylate) [17] and MeAl(amket)₂ (67 ppm; amket = deprotonated 2'-aminoacetophenone) [18]. Since simple five-coordinated organoaluminum complexes are usually unstable and/or highly reactive, it is apparent from the above data that ²⁷Al NMR spectroscopy is a powerful tool for the characterization of these species in solution.

As illustrated in Fig. 1, the aluminum atom in **2** is five-coordinate and its coordination sphere geometry can be described as a distorted trigonal bipyramid. The equatorial plane, defined by the two carbon atoms and the aryloxy oxygen, is planar with bond angles involving Al in this plane ranging from 115.39(9) to 125.41(11)° (Σ(X–Al–Y) = 359.9°). The axial positions are occupied by the oxygen atom of the chelating carbonyl group and the pyridine nitrogen atom with the O(2)–Al–N(1) angle of 172.67(6)°. The apical Al–N(1) bond length (2.135(2) Å) is similar to that found for the five-coordinate adduct derived from 2-pyridylmethanol, [tBu₂Al(μ-OCH₂-2-C₅H₄N)]₂ (2.130(5) Å) [27]. The equatorial Al–O(1) distance (1.797(2) Å) is substantially shorter and the apical Al–O(2) bond (2.066(2) Å) is significantly longer than the corresponding Al–O bond distances found for the binuclear five-coordinate dimethylaluminum compound derived from the related hydroxyacetophenone ligand, [Me₂Al(μ-OC₆H₃(Cl)-2-C(Me)O)]₂ (**3**) (1.851(2) and 1.965(2) Å, respectively) [20]. Further, the conformation of the six-membered AlOCCCO ring in **2** may be described as an open envelope with a planar acetylphenoxide core and folded along the AlO₂ plane (structure

¹ Me₂Al[OC(Me)C₆H₄-2-O] (**1**) was prepared according to the previously reported synthesis of the related derivative of 2-aceto-4-chlorophenol [22]. ¹H NMR (C₆D₆): δ –1.90 (6H, s, Al-CH₃), 1.60 (3H, s, CH₃), 6.20 (1H, m, CH_{arom}), 6.83 (1H, m, CH_{arom}), 6.99 (2H, m, CH_{arom}). ²⁷Al NMR: δ 152 ppm. Me₂Al[OC(Me)C₆H₄-2-O]·(γ-picoline) (**2**): to a solution of **1** (1.40 g, 7.0 mmol) in hexane (5 cm³), γ-picoline (0.65 g, 7.0 mmol) was added at room temperature. After stirring for 5 min, solvent and excess of γ-picoline were removed in vacuo to leave quantitatively a yellow solid which was then recrystallized from toluene/hexane. Molecular weight (benzene): found 284, calc. 285.31. ¹H NMR (C₆D₆): δ –1.93 (6H, s, Al-CH₃), 1.77 (3H, s, CH₃), 1.71 (3H, s, CH₃), 6.30 (1H, m, CH_{arom}), 6.53 (2H, d, C-H), 6.83 (1H, m, CH_{arom}), 7.08 (2H, m, CH_{arom}), 8.56 (2H, d, CH_{arom}). ²⁷Al NMR: δ 118 ppm.

² Crystal data for **2**: C₁₆H₂₀AlNO₂, *M* = 285.31, crystal dimension 0.5 × 0.4 × 0.3 mm, monoclinic, *P*2(1)/*n*, yellow; *a* = 8.615(2), *b* = 7.499(1), *c* = 23.746(5) Å; β = 93.12(3)°; *V* = 1531.8(5) Å³; *Z* = 4; *R*₁ = 0.0501; *T* = 173 K. A single crystal of **2** was sealed in a glass capillary under an inert atmosphere. Data collection was performed using a KM4 (KUMA Diffraction) four-circle diffractometer with graphite monochromator (λCuKα = 1.54178 Å) using ω–2θ scan technique. Unit cell was determined from 66 reflections. Three standard reflections were monitored every 100 measurements. Lorentz-polarization corrections were made but absorption was ignored. The structure was solved by direct methods (SHELXS-86 [33]) and refined by a full-matrix least-squares procedure (SHELXL-93 [34]) on *F*². All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in calculated positions and then refined as isotropic. Final *R* = 0.037, *wR*₂ = 0.115 with *w* = 1/[σ²(*F*_o) + (*aP*)² + *bP*], *P* = *F*_o² + 2*F*_c²/3, *a* = 0.1024, *b* = 0.5885.

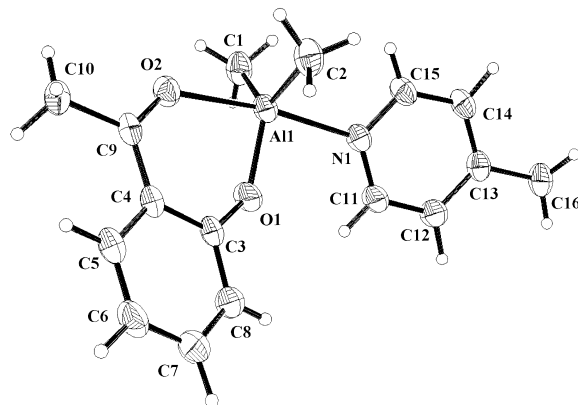
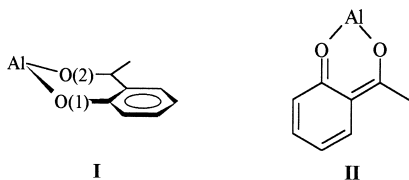


Fig. 1. ORTEP diagram of Me₂Al[OC(Me)C₆H₄-2-O]·(γ-picoline) (**2**) showing 50% probability thermal ellipsoids for non-hydrogen atoms. Selected bond lengths (Å) and angles (°): Al(1)–O(1), 1.797(2); Al(1)–O(2), 2.066(2); Al(1)–N(1), 2.066(2); Al(1)–C(1), 1.967(2); Al(1)–C(2), 1.977(2); O(1)–Al(1)–C(1), 119.10(9); O(1)–Al(1)–C(2), 115.39(9); C(1)–Al(1)–C(2), 125.41(11); O(2)–Al(1)–N(1), 172.67(6).

I; the AlO(1)CC and AlO(2)CC torsion angles are 28.1(3) and $-9.2(3)^\circ$, respectively), contrary to the planar con-



formation of analogous heterocyclic rings in **3**. Although the marked change of the equatorial Al–O bond lengths in **2** and **3** is consistent with the different coordination number of the aryloxy oxygen atoms, the observed elongation of the apical Al–O bond and the envelopelike conformation of the $\overline{\text{AlOCCCCO}}$ ring in **2** are worth noting. Recently when discussing the molecular structure of **3**, we have shown that the π -interaction of the aryloxy oxygen lone pair with the acetylphenoxide extended π system substantially weakens the Lewis basicity of the bridging oxygen and simultaneously strengthens the basicity of the chelating carbonyl oxygen [20]. Therefore one would expect that in the structure of **2**, which has a two-coordinate aryloxy oxygen, the contribution of the resonance form II will be even more significant when compared to the dimeric structure of **3**; this was indeed observed for monomeric four-coordinate aluminum chelate complexes derived from related bifunctional ligands: $[\text{Me}(\text{RO})\text{Al}(\text{bhmap})]$ [28] (bhmap = deprotonated 3-tert-butyl-2-hydroxy-5-methyl-acetophenone) and $\text{Me}_2\text{Al}(\text{amket})$ [29] (amket = deprotonated 2'-aminoacetophenone) (it is notable that the heterocyclic rings in both compounds are essentially planar). However, the enhanced Lewis basicity of the acetyl group in **2** would significantly weaken the axial Al–N bond, and eventually would lead to the dissociation of γ -picoline; the structural *trans*-influence of the axial substituents was clearly observed by us in the five-coordinate $[\text{R}_2\text{Al}(\text{O},\text{O}')_2]$ compounds [20]. Hence, it is reasonable to assume that the envelopelike conformation of the heterocyclic ring in **2**, in the absence of steric hindrances, results from the *trans*-influence of the axial substituents. Such a distortion makes the aryloxy oxygen lone pair staggered with respect to the acetylphenoxide π conjugated bond system and presumably diminishes the electron delocalization from the aryloxy oxygen to the acetyl group. Additionally, in the observed conformation the aluminum atom is moved out of the carbonyl π nodal plane³. Thus, the electron density on the carbonyl O(2) atom and the orbital overlap between O(2) and Al(1) atoms in **2**, i.e. the strength of the interaction of the chelating group and the metal center, are controlled by the conformation of the $\overline{\text{AlOCCCCO}}$ ring. Given this stabilization, the simple five-coordinate complex **2** is relatively stable. We also conclude that in the case of analogous deriv-

atives of bidentate ligands with the extended π -interaction stronger as compared with the hydroxyacetophenolate ligand, e.g. acetylacetonate ligand, the stabilization by conformational changes within the chelate is not sufficient and therefore the corresponding five-coordinate Lewis acid–base adducts are unstable (see for example Refs. [22–24]). At this point it should be noted that the experimental observation of the *trans*-influence normally concerns the bond weakening effect [32]. However, the reported results clearly demonstrate that the *trans*-influence of the axial substituents is a significant factor determining the structure and stability of five-coordinate aluminum chelate complexes.

The chemistry of mononuclear five-coordinate complexes is directly relevant to the demonstrated intermediacy in a number of organic transformations and catalytic processes where intermediates are usually rationalized solely on the basis of the chemical outcome. Our study shows that the *trans*-influence is a significant factor determining the stability of five-coordinate organoaluminum complexes, however, the intramolecular coordination or multidentate ligands may successfully stabilize the pentacoordination by electronic or geometrical changes within the ligands. Hence, the reported results should lead to a better understanding of the structure and bonding of intermediates and transition states encountered in reactions proceeding via pentacoordinated species. We are currently investigating the structure of simple five-coordinated organoaluminum complexes derived from various bifunctional ligands, and their reactivity with a variety of substrates.

Supplementary material

Crystal structure data for **2** (tables of crystal data, structure solution and refinement, atomic coordinates and anisotropic thermal parameters, and complete bond lengths and angles) have been deposited at the Cambridge Crystallographic Data Center.

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³ This rare example of a bent-nonplanar mode of bonding was found for the only one structurally characterized aluminum organic carbonyl complex [30]. For the mode of coordination of organic carbonyls to aluminum compounds see Ref. [31].

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