Structure investigation of a dimethylaluminium derivative of ethyl *rac*-lactate in the solid state and solution. First evidence for stereoselective association of a dialkylaluminium *O,O′*-chelate complex

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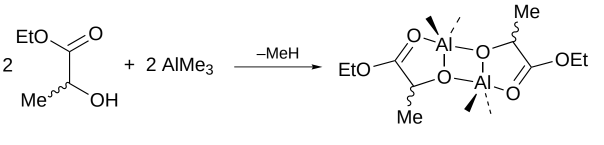
The reaction of $AlMe_3$ with an equimolar amount of ethyl *rac*-lactate (Helac) affords *rac*-$[Me_2Al\{(S^*)\text{-elac}\}]_2$; the X-ray structure shows that the adduct is formed in a highly stereoselective manner and variable-temperature ^1H NMR spectra indicates that the five-coordinated complex is non-rigid in solution.

Organoaluminium derivatives of *O,O′*-bifunctional ligands have been under investigation for many years owing to their practical and fundamental importance. For example, these compounds have been reported as organometallic intermediates in carbon–carbon bond formation reactions,[1] as precursors of catalysts in polymerisation processes[2,3] or precursors for MOCVD.[4] Although five-coordination in diorganoaluminium chelate complexes has been frequently postulated and as early as 1972 the $[R_2Al(O,O')]_2$-type adduct has been reported as the first crystallographically characterised five-coordinated organoaluminium compound,[3a] there are not many examples of structurally characterised $[R_2Al(O,O')]_2$-type complexes.[3a,4,5] Recently, we have described the structure characterisation of the first simple monomeric five-coordinate monoalkyaluminium chelate complex.[6] Due to the potential utility of organoaluminium derivative of *O,O′*-bifunctional ligands in organic synthesis and polymerisation processes, the investigation into the chemistry of organoaluminium chelate compounds, especially complexes bearing chiral centres,[7] has become an important challenge. The results concerning the structure of the dimethylaluminium derivative of racemic ethyl lactate are presented here as part of our studies on the structure of dialkylaluminium chelate compounds in solid state and solution. We report here that the formation of the $[R_2Al(O,O')]_2$ adduct is a stereoselective reaction and show that this type of five-coordinated complex is non-rigid in solution.

The interaction of Me_3Al with an equimolar amount of ethyl *rac*-lactate (Helac) results in quantitative evolution of methane and formation of *rac*-$[Me_2Al\{(S^*)\text{-elac}\}]_2$ **1** (Scheme 1).†

The molecular structure of **1** has been determined by X-ray diffraction‡ and its solution structure has been characterised by ^1H and ^{27}Al NMR as well as cryoscopic molecular mass determination.§ The molecule is a dimer with two five-coordinate aluminium atoms (Fig. 1). The monomeric units are bonded *via* alkoxide oxygen atoms O(1) and O(1′) with the formation of a central four-membered ring $Al_2(\mu\text{-}O)_2$. The ethyl lactate anions form two five-membered chelate rings with aluminium, which lie approximately in one plane with a central bridging ring. The root mean square deviation of the atoms from this plane is 0.086 Å. The geometry of the aluminium atom coordination sphere can be described as a distorted trigonal bipyramid. The equatorial plane is defined by the C(6) and C(7) carbon atoms and the alkoxide oxygen. The axial positions are occupied by the O(2) oxygen atom of the carbonyl group and the alkoxide O(1′) oxygen atom of the second monomeric unit. The angle between the axial substituents is 164.74(6)°. As is shown in Fig. 1, the methyl groups bonded to the chiral C atom in the chelating ligand lie on the same side of the plane outlined by three fused heterocyclic rings, and the dimer molecule has C_2 symmetry. This indicates that only monomeric units of the same configuration as the chiral centre in the chelating ligand associate with each other giving exclusively (*R,R*) and (*S,S*) diastereoisomers. Thus, the formation of the dimeric five-coordinate complex **1** is a stereoselective reaction.

It should be noted that the Al–O distances within the central $Al_2(\mu\text{–}O)_2$ ring in **1** [Al(1)–O(1) 1.848(2) Å and Al(1)–O(1′) 1.936(2) Å] differ significantly despite the fact that the same bridging oxygen atoms are bonded to the equivalent aluminium atoms. It is apparent that this results from the geometry of the dimeric five-coordinate molecules, which imposes that each bridging oxygen atom is in the equatorial position of one



Scheme 1

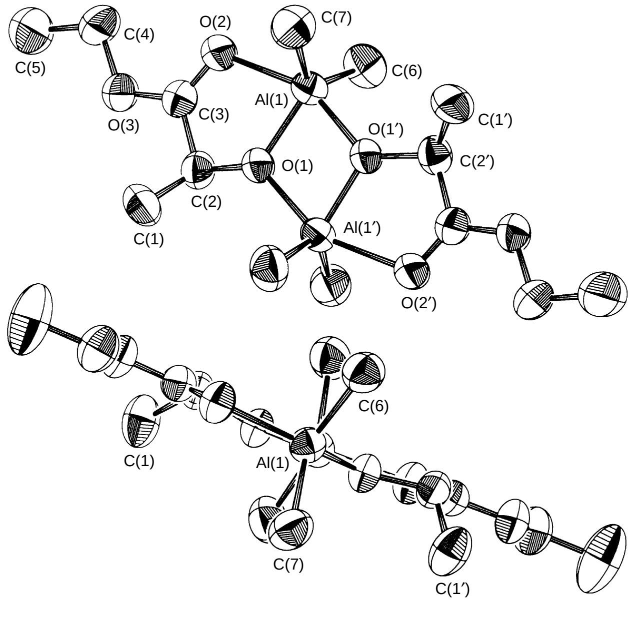


Fig. 1 ORTEP view of the molecular structure of $[Me_2Al\{(S)\text{-elac}\}]_2$ **1** with thermal ellipsoids drawn at 50% probability level. Bottom: view of the molecule along a mean plane formed by heterocyclic rings. Selected bond lengths (Å) and angles (°): Al(1)–O(1) 1.848(2), Al(1)–O(1′) 1.936(2), Al(1)–O(2) 2.157(2), Al(1)–C(6) 1.954(4), Al(1)–C(7) 1.956(4), O(2)–C(3) 1.224(3), O(1)–C(2) 1.405(3), O(1)–Al(1)–O(1′) 75.6(1), O(1)–Al(1)–C(6) 117.9(2), O(1)–Al(1)–C(7) 117.0(2), C(6)–Al(1)–C(7) 124.3(2), O(1)–Al(1)–O(2) 78.20(9), O(1′)–Al(1)–O(2) 153.8(1), C(3)–O(2)–Al(1) 111.4(2), C(2)–O(1)–Al(1) 122.9(2), Al(1)–O(1)–Al(1′) 104.2(1), O(1)–C(2)–C(3) 106.0(3), O(2)–C(3)–C(2) 120.4(3). Atoms labelled with a prime belong to the counterpart of dimeric units generated by two-fold axis (y, x, $-z$).

aluminium atom and in the axial position with respect to the other. Although non-equivalence of Al–O distances within the $Al_2(\mu\text{-}O)_2$ ring is usually noted in the description of structural data of compounds consisting of such a symmetrical four-centred bridging system, it is commonly interpreted as resulting from the different characters of these bridging bonds; for example, one Al–O bond is of a covalent and the other of a donor–acceptor or partial dative/covalent character.[8,9] We would like to emphasise at this point that the Al–O bonds in the $Al_2(\mu\text{-}O)_2$ ring are of the same character (σ two-centre–two-electron bonds) and the differences in the bridging Al–O bonds length are due to the different geometrical locations in the coordination sphere of the Al atoms.

The dimeric structure of **1** is retained in solution as found from a cryometric molecular mass determination in benzene. The NMR spectra of **1** are consistent with the structure found in the solid state. The ^{27}Al NMR spectrum of **1** consists of a single resonance at δ 114 indicative of five-coordinate aluminium.[5a,10] The ^1H NMR spectrum of **1** in CD_2Cl_2 solution at 20 °C displays a single resonance for the Al–CH_3 protons, and a doublet and quartet for the C–CH_3 and C–H protons, respectively, associated with the chiral centre as well as two resonances of the ester ethyl group; the methylene protons of the ethyl group are diastereotopic giving rise to an eight-line pattern. As the temperature is decreased the resonance associated with Al–CH_3 protons broadens (*ca.* −80 °C) and splits into two well separated resonances at −93 °C. This result can be best interpreted in terms of a dissociative process in which the Al–O chelate bond undergoes cleavage giving rise to the interchange of the chelating groups between the two aluminium centres and permitting the Al–CH_3 groups to become equivalent on the NMR timescale.

Additionally, we chose ethyl lactate for structure investigation in the expectation that IR spectroscopy could be a sensitive probe for detecting an equilibrium between five- and four-coordinate dimeric organoaluminium species with chelated and dangling *O,O′*-bifunctional ligand carbonyl groups. However, the IR spectrum of **1** in CH_2Cl_2 solution shows only one carbonyl group stretching vibration at 1690 cm^{-1}. The observed decrease in comparison to that in free Helac (1728 cm^{-1}) is consistent with the coordination of the carbonyl group to aluminium. Furthermore, the presence of the strong band of the chelate carbonyl group and lack of uncoordinated carbonyl groups bands can be interpreted in terms of dangling ligands being present at non-detectable concentrations or that intermediate species involving dangling ligands have different geometry and corresponding bands occur with non-appreciable intensities.

Further studies are required in order to determine the nature of five-coordinate $[R_2Al(O,O')]_2$ adduct formation in a highly stereoselective manner and the structural characterisation of this type of adducts derived from AlR_3 and racemic *O,OH* bifunctional ligands is currently in progress.

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Footnotes and References

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† *Preparation* of **1**: ethyl *rac*-lactate (7.0 mmol) was dissolved in toluene (10 cm^3) and $AlMe_3$ (7.0 mmol) was added dropwise at −78 °C. After the addition was complete the reaction mixture was allowed to warm to room temp. The solvent was then removed under vacuum, leaving a white solid that was crystallised from toluene–hexane at 0 °C. The yield was essentially quantitative.

‡ *Crystal data* for **1**: $C_{14}H_{30}Al_2O_6$: tetragonal, space group $P4_12_12$ (no. 92) and $P4_32_12$ (no. 96) for (*S,S*) and (*R,R*) diastereoisomers, respectively; $Dc = 1.137$ g cm^{-3}, $Z = 4$, $a = 7.6188(7)$, $c = 35.055(6)$ Å, $U = 2034.8(4)$ Å^3, $T = 20$ °C, Mo-Kα radiation ($\lambda = 0.71073$ Å), $\mu = 1.64$ cm^{-1}, Siemens P3 diffractometer, $2\theta_{max} = 50°$, θ–2θ scans, 4171 reflections collected (1801 unique, $R_{int} = 0.0694$). The structure was solved by direct methods[11] in the $P4_12_12$ space group and was refined by full-matrix least-squares on F^2.[12] Hydrogen atoms were included in idealised positions and refined isotropically. Refinement converged at $wR_2 = 0.1082$ for 1697 data and 112 parameters [$R_1 = 0.0477$ for 1021 unique reflections with $F_o > 4\sigma(F_o)$]. Absolute structure could not be determined reliably due to the high e.s.d. for the refined Flack *x* parameter 0.3(4).[13] A weighting scheme $w = [\sigma^2(F_o^2) + (0.0280P)^2]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$ was used in the final stage of refinement. Residual electron density $= +0.17, -0.16$ e Å^{-3}. CCDC 182/529.

§ *Selected data* for **1**: ^1H NMR (CD_2Cl_2, 20 °C), δ −0.72 (12H, s, $AlCH_3$), 0.94 (6H, t, CH_2CH_3), 1.35 (6H, d, $CHCH_3$), 3.90 (4H, qd, CH_2CH_3), 4.40 (1H, q, $CHCH_3$); (−90 °C), −0.62 (6H, s, $AlCH_3$), −0.56 (6H, s, $AlCH_3$), 0.78 (6H, t, CH_2CH_3), 1.32 (6H, d, $CHCH_3$), 3.61 (4H, q, CH_2CH_3), 4.33 (1H, q, $CHCH_3$), ^{27}Al NMR (C_6D_6, 20 °C) δ 114 ($\Delta H_{\frac{1}{2}} = 5780$ Hz); molecular mass (cryoscopy in benzene): found 350, calc. 348.4.

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