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Directionality and borderline distance of secondary bonding on the fifth coordinate site in aluminium alkoxides†

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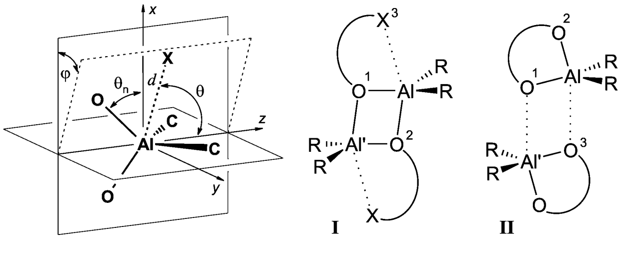
A survey of the Cambridge Structural Database for alkylaluminium alkoxides has been used to determine the borderline distances and angular distributions of secondary interactions on the fifth coordinate site, and map out the minimum-energy pathways in associative reactions.

Pentacoordinate aluminium complexes have recently often been implicated as operative intermediates in various stoichiometric and catalytic organic syntheses[1] and polymerisation processes.[2] However, the question of bonding distance between the metal centre and Lewis base in hypercoordinate complexes and the strength of the bond on the fifth coordination site have not received a definite answer in the literature until now. Little is also known about the way in which tetrahedral metal centres interact to form weak dative bonds with electron donors. The purpose of our investigation is to examine, by means of structure correlation,[3] the borderline distances and angular distributions of secondary interactions, and map out the minimum-energy pathways in associative reactions for aluminium alkoxides.

We performed systematic structure analyses on two groups of alkoxide/aryloxide compounds that share some structural similarities in the solid state and exhibit substantial inter- or intra-molecular donor–acceptor interactions. The basic structure types **I** and **II** are illustrated in Scheme 1, where the dotted lines express potential interactions between the Al centre and the fifth donor site. One group comprises the dimeric dialkylaluminium alkoxides **I** derived from alcohols consisting of an X-donor functionality (X = O, N or S; R = Me, Et, ^{i}Bu or ^{t}Bu); the metal centres are held together by the bridging alkoxide bonds and the terminal donor centres interact on the fifth coordinate site by secondary bonding.[4] The second group that we examined are the *O,O'*-chelate complexes **II** which occur as four-coordinate monomers in solution and five-coordinate dimers in the solid state.[5]

The structural data were taken from the Cambridge Structural Database[6] and additionally from recently obtained results.[7] For each compound with a four- or five-coordinate metal centre (as defined in the CSD), the search was subjected to the following constrains: Al–O distances (bonded or non-bonded, inter- or intra-molecular) up to 4.50 Å in length, *R*-factor less than 0.08, and error free. An idealised C_2AlO_2 coordination sphere would have C_{2v} local point symmetry, with σ_{xz} and σ_{yz} symmetry planes. Therefore, the position of the fifth ligand was specified relative to the C_2Al core in spherical polar coordinates by two angles (θ and φ) and the distance *d*. Finally, the search revealed 68 compounds and the total data set used for the correlation analysis was of almost 200 data points. The coordinate system, the atom labelling scheme and the resulting geometric parameters used in our analysis are sketched in Scheme 1.



Scheme 1

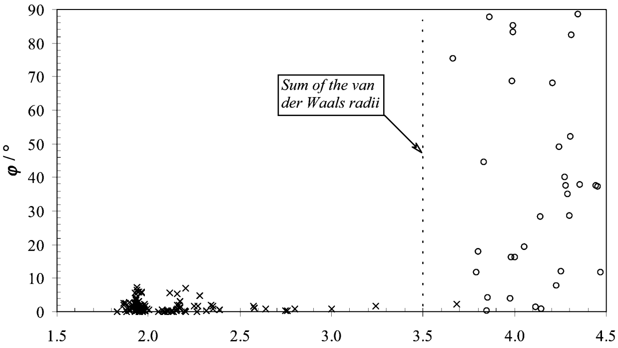
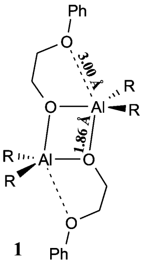


Fig. 1 Scatterplot of the φ angle *vs.* the Al–O distance. The presented data are calculated for the oxygen O^2 and O^3 atoms of type **I** and **II** complexes (×). Additionally, 32 points (○) representing angular positions of the oxygen atoms that are in contact with the tetrahedral aluminium centre in the structures containing four-coordinate C_2AlON, C_2AlN_2, or C_3AlO central core, are included.

Fig. 1 shows a plot of the φ angle for O^3 and O^2 atoms *vs.* Al–O distances. The distribution of the resulting data points appears to be grouped into two distinct sets. One group of the Al–O distances, 1.85–3.25 Å, was found to lie essentially in one plane, the symmetry plane σ_{xz}, with a very small deviation (φ < 7°).[8] At the long distance end, this data set approaches gradually the van der Waals (vdW) surface at 3.5 Å.[9] The directional properties of these contacts clearly indicate that these are real secondary attractive interactions. It should be noted at this point that borderline cases represented by compounds **1**[10] and **2**[11] have not been interpreted as evidence for bonded interactions in the literature. The second group beyond the vdW surface is distributed statistically. The isotropic angular distribution beyond 3.6 Å corresponds essentially to non-attractive interactions. However, in this long distance region one can find points which have angular characteristics similar to those from



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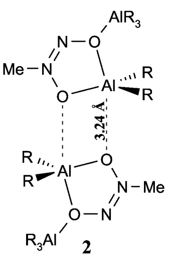

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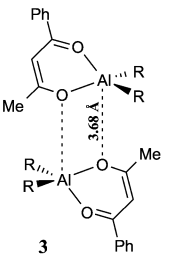

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† Electronic supplementary information (ESI) available: details concerning data retrieval from CSD files, list of CSD refcodes with references, selected geometrical parameters, ligand atom numbering, Figs. S1 and S2. See http://www.rsc.org/suppdata/cc/b2/b204555a/

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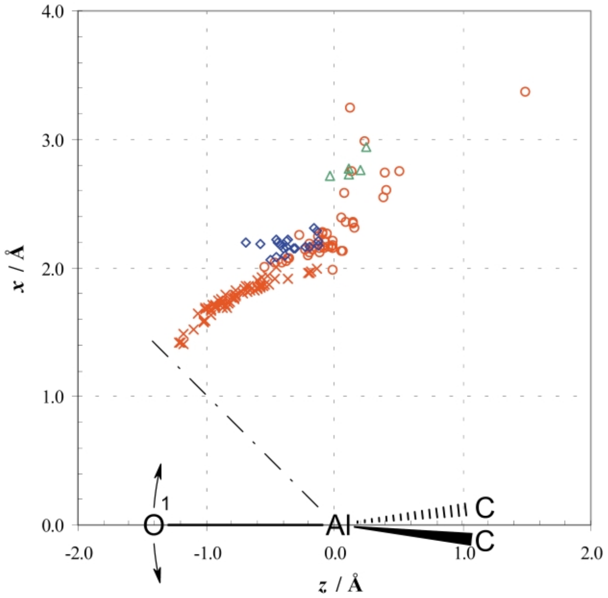

Fig. 2 Distribution of the axial atoms positions for complexes of type **I** and **II** projected on the *xz* plane: O^2 (red crosses), O^3 (red circles), N^3 (blue diamonds) and S^3 (green triangles). The skew dot-and-dash line points the mean value of the θ angle [135(6)°], calculated for genuine four-coordinate complexes containing a central C_2AlO_2 core.

the first group (*e.g.* compound **3**[12]). Although the position of some points is due to conformational adjustments or the intrinsic nature of corresponding compounds, the directionality of others may result from the electrostatic attractive force between the metal and donor centre. We note that the simple electrostatic attractive force may be substantial at greater distances than the short range vdW interactions (electrostatic interactions are relatively long range and fall off as $-r^{-1}$, and vdW interactions fall off as $-r^{-6}$). In this way we envisage that the outer cut-off Al–O distance should not be a strict value. In general, secondary bonds encompass a wide scale of strengths and in regard to this issue we also strongly recommend the discussion published in this Journal between Cotton *et al.*[13] and Steiner and Desiraju[14] on the distinction between weak hydrogen bonds and vdW interactions. As we demonstrated recently, there is a strong relationship between hydrogen bonds and secondary donor-acceptor bonds in the group 13 complexes.[15]

The obtained results indicate that there is a strongly preferred trajectory for the approaching ligand on the fifth coordinate site. In view of this we suspected that the type **I** and **II** compounds are suitable structural models for the S_N2 reaction. A survey of available crystal structures shows (see below) that the observed distortions do indeed follow the plots similar to those found for interconversions of five-coordinate species of Si,[16] Sn,[17] Zn[18] or Cd,[19] and essentially map out the minimum-energy pathway in the associative (*e.g.*, S_N2 at tetrahedral Al^{III}) reaction.

The distribution of the axial ligand positions (Fig. 2) indicates that the trajectory for oxygen donors is very narrow for the short and moderate Al–O distances and spreads out for weakly bonded ligands. However, positions of nitrogen donors contrast with the trajectory observed for oxygen ligands. A careful inspection of the molecular structures of *O*,*N*-chelate complexes clearly indicate that distinct behaviour results from steric factors brought about by alkyl substituents on amine functionalities. The comparison of general trends observed for both oxygen and nitrogen donors nicely demonstrates how steric factors may affect the trajectory of the approaching ligand. Moreover, as the ligating atom of the donor group approaches the metal centre, a concomitant umbrella type distortion of the angles between the equatorial substituents and the two axial ones is observed. The corresponding scatter plot of the angle θ_n between the normal to the C_2Al plane and Al–O^1 bond *vs.* Al–O^2/Al–X^3 distance is shown in Fig. S1 (ESI†). Simultaneously, as the Al–X^3 distance becomes shorter, the Al–O^2 distance tends to become longer (corresponding scatterplot is shown in Fig. S2 of ESI†). The reaction path leads from the tetrahedron to a trigonal-bipyramidal transition state with axial Al–O distances of 2.03(5) Å and the latter structure resembles a point on the reaction profile where the extent of bond formation is equivalent to that of bond breaking. Thus, the formation of the secondary bond leads to weakening of the primary bond which is in accord with the structural *trans*-effect.[20] The revealed direction of a ligand approach to the metal centre is toward the centre of the C_2O face, *i.e.*, opposite to the primary Al–O dative bond. This is fully consistent with our recent investigation of the reactivity of alkylaluminium model complexes with molecular oxygen.[21] Further reports upon the implications of discussed phenomena will follow in due course.

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