Electronic Supplementary Information

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

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The collection of structural data was obtained through systematic search of the 5.22 version (October 2001) of the Cambridge Crystallographic Database (CSD) using CCDC software. First, the searches were performed for structures containing five-coordinate aluminium atom with the C_2AlO_3, C_2AlO_2N, or C_2AlO_2S central core. Second, structures listed formally in CSD as four-coordinate with the C_2AlO_2 core, having a contact less than 4.5Å to the closest oxygen, nitrogen or sulphur ligand were retrieved. Additional search was carried out for four-coordinate aluminium complexes with C_2AlON, C_2AlN_2, or C_3AlO core and a contact to O-donor at distance less than 4.5Å. Both intermolecular and intramolecular Al…X contacts (where X = O, N or S) were located in the searches using QUEST*3D* program. It was stated that the number of chemical bonds separating the Al and X atoms that are in nonbonded intramolecular contact should be greater or equal 4. The searches were restricted to non-charged complexes with aliphatic C(sp^3) atoms bonded to Al atom. The resulting subsets were then sorted and investigated manually. Subsequently, entries with the R-factor greater than 0.08 (with one exception for ALMEAL) and those with an error flag were rejected. Duplicate determinations of the same compound were retained when these represented different polymorphs or structures measured in different temperatures. The data retrieved from CSD was completed with structural data for 10 compounds of type **I** and **II** obtained from our recently determined structures (Comp. **1** - **10**, Supplementary References). Finally, the search revealed 68 compounds. The geometrical parameters defined below were recorded for each appropriate structural fragment in the structures retrieved, and the total data search obtained was of almost 200 data points.

The selected geometrical parameters used in analysis are sketched in Scheme 1. The position of the ligands relative to the C_2Al core are specified in spherical polar coordinates by two angles (θ and φ) and the distance d. The aluminium atom is placed in the origin. The vector Al–C_m defines the direction of the z-axis, where C_m represents the midpoint between C atoms.

The *y*-axis lies in the C_2Al plane and the *x*-axis is perpendicular to this plane. Since the C_2Al group has an idealised C_{2v} local point group symmetry, positions of the examined X-donor atoms are reflected into one quadrant. Therefore, the calculated values of φ and θ angles fall in the ranges (0°, 90°) and (0°, 180°), respectively. The dihedral angle φ is equal zero when the ligand lies on the σ_{xz} symmetry plane bisecting the C–Al–C angle and equal 90° when it is located on the *yz* plane defined by the C_2Al moiety.

For all complexes of type **I** and **II** a unified labelling scheme for the C_2AlO_2X structural unit was applied as presented on the Scheme 1. Of the three donor atoms the one with the longest Al…X distance (bonding or non-bonding) was labelled X^3 (O^3, N^3 or S^3), and the one in *trans* position to X^3 was labelled O^2. The remaining oxygen atom with the largest θ angle, which together with both carbon atoms in general defines equatorial plane of the distorted TBP, was labelled O^1. The umbrella displacement of the three equatorial ligands (two carbons and O^1 atom) from the basal plane can be described in a simple way by the angle θ_n between the normal to the C_2Al plane (*x*-axis) and Al–O^1 bond.

Besides, an appropriate standard bond length is necessary if deformations involving different donor atoms are to be compared directly. For our study, the average ligand-Al bond lengths and their standard deviations were calculated for each donor atom type from the structures containing four-coordinate Al centre with C_2AlX_2 core. The suitable data sets were obtained from the CSD files. The searches were restricted for crystal structures with $R < 0.05$ and without disorder. Moreover, the structures with aluminium centres that were not genuinely four-coordinated, that is, having short intra- or intermolecular contacts with potential donor atoms were rejected. The results are shown in Table S1. To unify the Al–X distances for the correlation analysis purpose the Al–N and Al–S distances were reduced by 0.109 and 0.518 Å, respectively, while the Al–O distances remained unchanged.

Table S1. Representative bond lengths in four coordinate Al complexes with C_2AlX_2 core.

X	No of observation	$\overline{d}_{Al–X}$ / Å	$\overline{\sigma}_{Al–X}$ / Å
O	64	1.846	0.032
N	212	1.954	0.037
S	56	2.364	0.031

Figure 2 shows the projection of the axial atoms positions on the σ_{xz} plane: O^2 (red crosses), O^3 (red circles), N^3 (blue diamonds) and S^3 (green triangles). The scatterplot contains 142 data calculated for type **I** and **II** complexes. Each structural C_2AlO_2X unit in the plot is

represented by two distinct points concerning positions of both axial ligands. For clarity location of the equatorial oxygen O^1 is depicted schematically. The skew dot-and-dash lines point the positions for which the values of θ angle are equal 135(6)°, that is a mean value of the θ angle calculated for tetrahedral complexes containing central C_2AlO_2 core. Structural data for those complexes were retrieved from the CSD as mentioned above.

To demonstrate the influence of the axial ligands interaction on the distortion of the equatorial substituents in type **I** and **II** complexes, the scatterplot of the θ_n angle (between the normal to the C_2Al plane and $Al–O^1$ bond) *versus* the $Al–O^2/Al–O^3$ distance (red circles) is shown in Figure S1. Appropriately corrected data for $Al–N^3$ distances are represented by blue crosses, those for $Al–S^3$ by green triangles. Horizontal dot-and-dash lines at 45° and 135° denote boundary of the θ_n angle and match the mean value observed for tetrahedral complexes. The dotted line at 90° refers to the planar conformation of the equatorial ligands.

The correlation between the $Al–O^2$ bond length and $Al–X^3$ distance [where $X^3 = O^3$ (circles), N^3 (blue crosses) and S^3 (green triangles)] for type **I** and **II** complexes is shown in Figure S2. The Al–N and Al–S distances were appropriately reduced by 0.109 and 0.518 Å, respectively.

A list of reference codes, selected geometrical parameters and ligand atom numbering are presented in Tables S2 and S3.

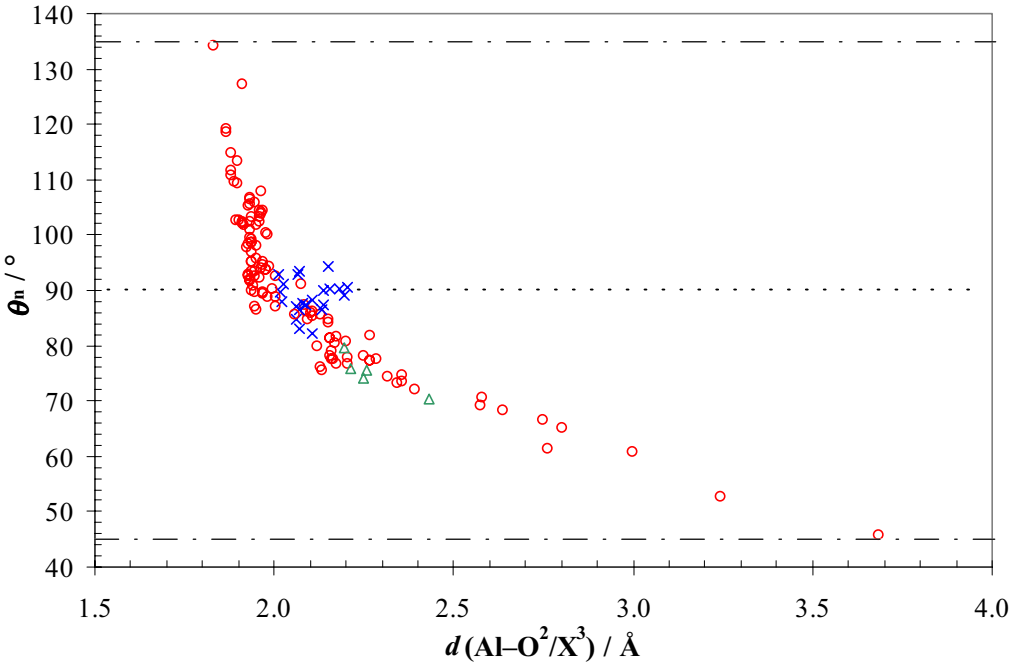

Figure S1. Scatterplot of the θ_n angle *versus* Al–O^2/Al–O^3 distance (red circles). The data for Al–N^3 (blue crosses) and Al–S^3 (green triangles) distances were appropriately corrected for the differences in standard radii. Horizontal dot-and-dash lines match the mean θ_n values (45° and 135°) observed for tetrahedral complexes with the C_2AlO_2 core.

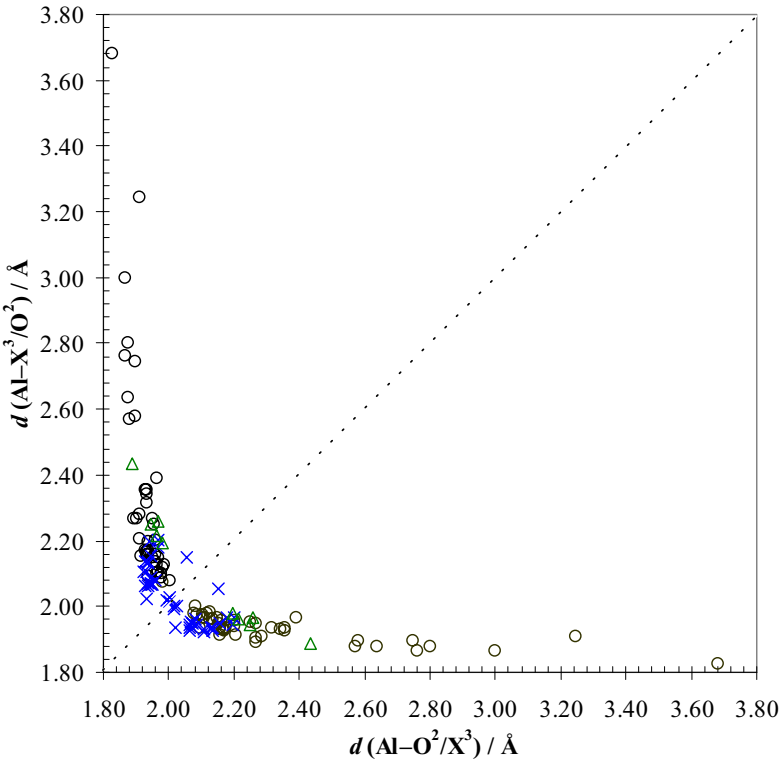

Figure S2. The correlation between the Al–O^2 bond length and Al–X^3 distance [where X^3 = O^3 (circles), N^3 (blue crosses) and S^3 (green triangles)] for complexes of type **I** and **II**. The Al–N and Al–S distances were appropriately corrected.

Table S2. Reference codes, ligand atom numbering, and selected geometrical parameters (in Å) for compounds of type **I** and **II**.

Refcode	O^1	O^2	X^3	d(Al–O^1)	d(Al–O^2)	d(Al–X^3)
ALMEAL	O1%	O2%	O1	1.882	1.909	3.243
BAQPAK	O1	O1A	O2	1.845	1.933	2.166
BAQPAK	O3	O3A	O4	1.842	1.931	2.158
CATBEE	O1	O1B	O2	1.826	1.891	2.268
COQGOE	O1	O1A	O2	1.828	1.864	2.999
COQHEV	O1	O1A	O2	1.832	1.877	2.801
HOZJAH	O1	O1B	O2	1.821	1.895	2.747
HOZJEL	O1A	O1	O2A	1.840	1.909	2.283
JIZDEB	O1B	O1	O2B	1.859	1.952	2.249
JIZDIF	O1B	O1	O2B	1.861	1.949	2.267
KECQIS	O1	O4	O2	1.842	1.915	2.155
KECQIS	O4	O1	O5	1.836	1.948	2.151
KECQOY	O1	O4	O2	1.811	1.931	2.169
KECQOY	O4	O1	O5	1.875	1.928	2.172
LIDJOX	O1A	O1	O2A	1.846	1.903	2.268
NOKBIY	O1	O1B	O2	1.817	1.864	2.761
NORQIU	O1A	O2A	O1	1.851	1.965	2.103
NORQIU	O3A	O4A	O3	1.854	1.975	2.088
NORQOA	O1A	O2A	O1	1.902	1.936	2.093
QEFZEG	O1	O4	O2	1.864	1.934	2.315
QEFZEG	O10	O7	O11	1.875	1.929	2.355
QEFZEG	O4	O1	O5	1.874	1.934	2.355
QEFZEG	O7	O10	O8	1.872	1.931	2.344
RIRHEF	O3	O3F	O1	1.848	1.936	2.157
RIRHEF01	O3	O3D	O1	1.848	1.936	2.157
RUHYOI	O1A	O2A	O1	1.850	2.003	2.082
TEVNOX	O1	O1B	O2	1.821	1.880	2.572
TEVNOX01	O1	O1B	O2	1.821	1.877	2.638
TEVNUD	O1A	O1	O2A	1.858	1.938	2.199
WANVIQ	O1B	O1	O2B	1.876	1.965	2.390
DEYKIB	O1A	O1	N1A	1.852	1.934	2.130
HOZKUC	O1B	O1	N1B	1.833	1.931	2.216
HOZLEN	O1B	O1	N1B	1.868	1.922	2.216
JADKAA	O1	O2	N1	1.868	2.003	2.135
JADKAA	O2	O1	N2	1.862	1.993	2.126
JIQQIJ	O1A	O1	N1A	1.879	2.003	2.123
KAYBAN	O1D	O1	N1D	1.864	1.946	2.196
MAZYOB	O1	O2	N1	1.849	1.935	2.245
MAZYOB	O2	O1	N4	1.845	1.947	2.265
NEKSOL	O1	O2	N1	1.818	1.967	2.289
NEKSOL	O2	O1	N2	1.826	1.946	2.174
NEKSOL01	O1	O2	N1	1.831	1.951	2.177
NEKSOL01	O2	O1	N2	1.805	1.968	2.311
NEKSUR	O1A	O1	N1A	1.842	1.927	2.171
NEWCUN	O1	O2	N1	1.852	1.926	2.245
NEWCUN	O2	O1	N2	1.856	1.935	2.241

Refcode	O^1	O^2	X^3	d(Al–O^1)	d(Al–O^2)	d(Al–X^3)
NEWDAU	O1	O2	N2	1.851	1.936	2.181
NEWDAU	O2	O1	N1	1.857	1.935	2.172
QEDHUC	O1F	O1	N1F	1.852	1.943	2.306
TALWIM	O1B	O1	N1B	1.853	2.055	2.259
TEPZUJ	O1	O2	N1	1.851	1.947	2.181
TEPZUJ	O2	O1	N2	1.852	1.960	2.190
HOZKAI	O1	O1a	S1	1.840	1.889	2.951
JIZCOK	O1	O2	S1	1.856	1.979	2.714
JIZCOK	O2	O1	S2	1.865	1.964	2.733
JIZCOK	O3A	O3	S3A	1.865	1.946	2.767
JIZDAX	O1	O1a	S1	1.870	1.966	2.778
Comp. **1**	O1	O2	O1A	1.832	1.828	3.682
Comp. **2**	O2	O1	O2A	1.856	1.980	2.076
Comp. **3**	O1	O1A	O2	1.830	1.895	2.578
Comp. **4**	O1	O3	O2	1.892	1.959	2.160
Comp. **4**	O3	O1	O4	1.889	1.958	2.203
Comp. **5**	O11	O21	O12	1.911	1.960	2.135
Comp. **5**	O21	O11	O22	1.909	1.963	2.127
Comp. **6**	O1	O1A	O2	1.848	1.912	2.206
Comp. **7**	O2	O2A	O1	1.895	1.981	2.118
Comp. **8**	O2	O1	O2A	1.849	1.968	2.107
Comp. **9**	O1	O3	O2	1.890	1.967	2.150
Comp. **9**	O3	O1	O4	1.885	1.984	2.127
Comp. **9**	O6	O6A	O5	1.886	1.977	2.104
Comp. **10**	O1	O1A	O2	1.853	1.935	2.173

Table S3. Reference codes, ligand atom numbering, and selected geometrical parameters (in Å) for compounds containing four-coordinate C_2AlO_2 (not representing type **I** or **II**), C_2AlN_2, C_2AlON, or C_3AlO central core and a contact to the closest oxygen (O^3) ligand less than 4.5Å

CSD Refcode	X	Y	O^3	*d*(Al–X)	*d*(Al–Y)	*d*(Al–O^3)
HAGJAA	O3	O2	O5	1.844	1.843	3.789
HAGJAA	O1	O3	O5	1.850	1.837	3.803
RITRER	O1	O2	O3	1.806	1.837	3.850
RITRER	O5	O6	O7	1.767	1.835	3.851
NIKKAT	O1	O1A	O2	1.830	1.847	3.978
CPWMAL10	O1%	O2%	O3	1.822	1.794	3.981
PEXTUH	O3	O1	O8	1.841	1.837	3.989
PEXTUH	O3	O1	O5	1.841	1.837	3.991
ZOWHEY	O1	O2	O4	1.823	1.823	4.004
ZOWHEY	O1	O2	O3	1.828	1.816	4.052
ZOWHEY	O1	O2	O4	1.828	1.816	4.117
ZOWHEY	O1	O2	O3	1.823	1.823	4.146
NIKKAT	O1	O1A	O2	1.847	1.830	4.228
NUSLIW	O1	O3	O4	1.819	1.824	4.305
NIBSUM	O3	O2	O2A	1.880	1.835	4.311
NIBSUM	O6	O5	O5A	1.884	1.826	4.346
NUSLIW	O1	O3	O2E	1.819	1.824	4.453
CPWMAL10	O1%	O2%	O1	1.822	1.794	4.513
PUJXEX	N1	N2	O1	1.944	2.011	3.664
PUJXEX	N1	N2	O2	1.944	2.011	4.287
PUJXAT	N1	N3	O2	1.988	2.015	3.985
PUJXAT	N1	N3	O1	1.988	2.015	4.206
BOKCIN10	O1	N1	O2	1.841	1.935	3.861
DEKNUC	O1	C7	O2	1.976	1.958	4.301
JIFLUF	O2	C12	O1	2.000	1.958	4.243
JIFLUF	O2	C12	O3	2.000	1.958	4.254
YUWZEV	O2	C12	O3	1.988	1.955	4.442
CUDVEC	O2	C12	O3	1.987	1.964	4.467
BOYVEQ	O2	C13	O3	1.966	1.942	4.140
CUDVAY	O2	C26	O3	2.024	1.972	3.831
VADTID	O3	C13	O2	1.960	2.009	4.277
CUDVAY	O4	C29	O5	1.972	1.954	4.276
VADTID	O6	C26	O5	1.935	2.006	4.354

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