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# Quantum chemical studies on elementary fragments of three-coordinated methylaluminoxanes

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## Abstract

The molecular structures and relative stabilities of methylaluminoxanes (MAO) with three-coordinated aluminum centers were investigated by quantum chemical Hartree–Fock, MP2, and B3LYP methods. Linear and cyclic fragments of MAO were studied as a function of the degree of oligomerisation. The molecular structures are determined by the strain due to ring formation and/or by the stabilizing π-bonding interactions between the oxygen lone pairs and vacant p-orbitals of aluminums. The latter results in short Al–O distances, and in an Al–O–Al angle of 180° for linear MAO, with adjacent methyl groups perpendicular to each other. The relative stabilities of the cyclic MAO increase with the degree of oligomerisation. Smaller oligomers are destabilized due to the strain of the ring and reduced π-conjugation. Stabilities of the linear MAO show no variation with length of the fractions.

*Keywords:* Ab initio calculations; Aluminoxanes; Electronic effects; Stability; Structure elucidation

## 1. Introduction

Methylaluminoxanes (MAO) have attracted considerable interest ever since the discovery of the high activity of metallocene–MAO polymerization catalysts [1]. The main function of the MAO cocatalyst is to generate catalytic active species for olefin polymerization (Fig. 1). Dialkylation of the metallocene dichloride catalyst precursors is followed by abstraction of the methyl group resulting in a contact ion pair with the 14-electron metallocene cation, which has been demonstrated to be the catalytic active species [2]. The topic has been extensively reviewed [3].

The structural details of MAO remain unclear, despite the many experimental [4], theoretical [5], and combined [6,7] studies that have been carried out. The structure of MAO has been proposed to consist of a mixture of linear and cyclic oligomers (Fig. 2) with the degree of oligomerisation varying from 6 to 20 [8]. The object of the present work was to elucidate the structures and relative stabilities of three-coordinated elementary methylaluminoxane fragments. Hence, a systematic quantum chemical study for linear and cyclic MAO, representing different degrees of oligomerisation, was performed.

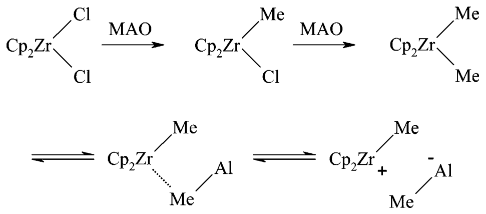

Fig. 1. Activation of zirconocene dichloride precursor by MAO.

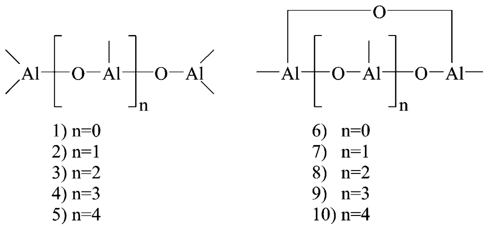

Fig. 2. Schematic structures of selected linear and cyclic methylaluminoxanes (MAO).

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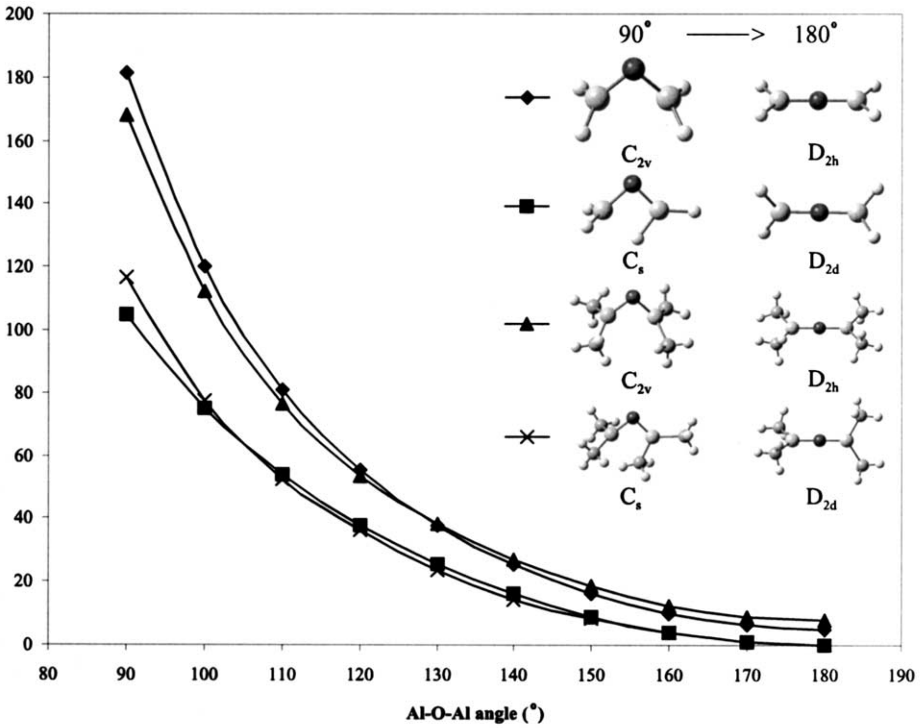


Fig. 3. Potential energy surfaces of dialuminoxane and tetramethyldialuminoxane (**1**).

## 2. Computational details

Geometry optimizations were performed at the HF/3-21G* level, which has been demonstrated to provide realistic structures for organoaluminium compounds. Furthermore, neither increasing the size of the basis set nor inclusion of electron correlation at the MP2 level has significant influence on the geometries [9]. B3LYP/6-31G*, MP2/6-31G*, and MP2/6-311G** calculations were performed to confirm the relative stability order of the MAO studied. The geometry minima were confirmed by frequency calculations. All calculations were carried out by the GAUSSIAN 94 program package [10].

## 3. Results and discussion

### *3.1. The origin of the equilibrium geometries in three-coordinated aluminoxanes*

The structural characteristics of the basic aluminoxane, the dialuminoxane, have been demonstrated to arise from the π-interaction between aluminum and oxygen [5c]. This interaction is due to donation of the oxygen lone pairs to the unoccupied p-orbital of aluminum, leading to short Al–O bonds and linear Al–O–Al arrangements. The similar Al–O π-interaction has been found to be the reason for the observed structures of aluminum alkoxides, which have short Al–O bonds and large Al–O–C angles [11]. While the presence of such π-interaction is natural for group III elements, the strength of the interaction has not been rigorously determined. The π-interaction has been suggested to be relatively weak but sufficient for determining the expected ground state geometries for this type of compounds [12].

The strength of the Al–O π-interaction was investigated for the dialuminoxane, and for its tetramethyl-substituted analogue (complex **1**). The main task in determining the strength of the π-interaction is to find a reference model, in which this particular interaction has been removed. However, the construction of such 'π-interaction free' structure is not straightforward, since the two lone pairs of oxygen can interact with the vacant p-orbitals of aluminum's in various orientations. The complexes were constrained to four positions (Fig. 3), of which $D_{2d}$-, $D_{2h}$-, and $C_s$-symmetric species show variable degrees of π-interaction, whereas only the $C_{2v}$-symmetric is 'π-interaction free' (Fig. 4).

Fig. 3 demonstrates that the $D_{2d}$-symmetry is preferred by both dialuminoxane and tetramethyldialuminoxane. The energy difference to the $D_{2h}$-structure is small, less than 10 kJ mol$^{-1}$ for both compounds. It should be emphasized that this energy difference does not describe the strength of the π-interaction, since the interaction is strongly present in both orientations (Fig. 4), even though the interaction is slightly stronger in $D_{2d}$-symmetry. Neither does the bending from the $D_{2d}$ to the $C_s$-symmetry describe the strength of the π-interaction, because the interaction is still present in between

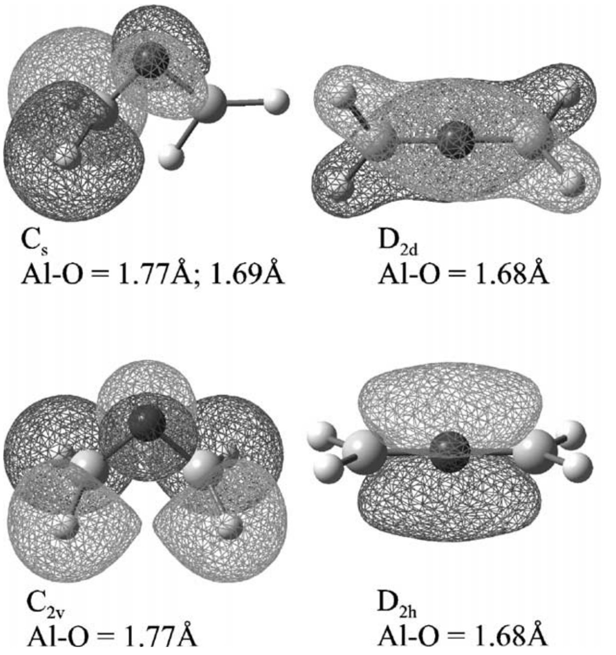
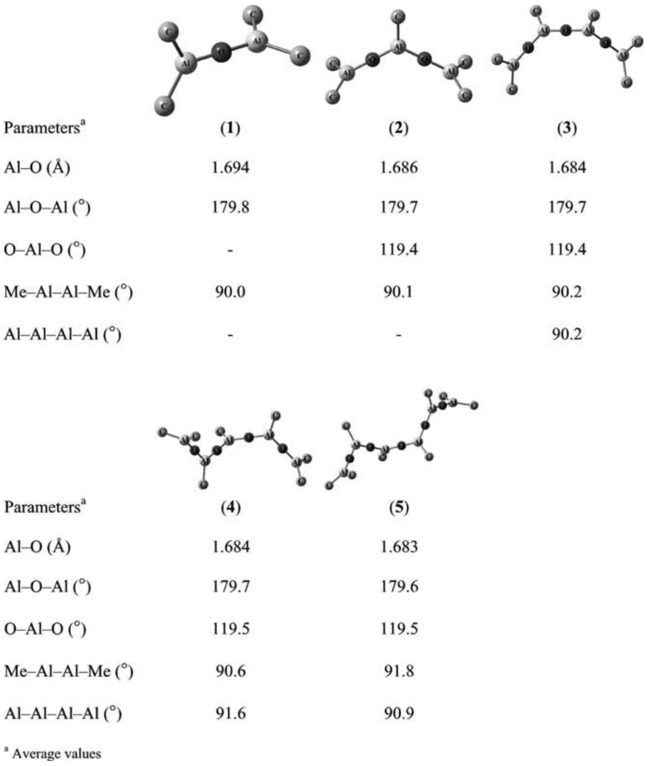


Fig. 4. Highest bonding molecular orbitals of dialuminoxane with respect to Al and O, $C_s$ (HOMO); $D_{2d}$ (HOMO-3); $C_{2v}$ (HOMO) and $D_{2h}$ (HOMO-3). It should be noted that three highest HOMOs of $D_{2d}$- and $D_{2h}$-symmetric species constitute mainly of bonding orbitals between Al and H.

the oxygen and one of the two aluminum atoms. The 'π-interaction free' structure is, however, attainable by bending the $D_{2h}$-symmetric species to $C_{2v}$. The consequences of losing the π-interaction can be observed in Fig. 3. The difference in energy between the two bent forms, $C_s$ (π-interaction) and $C_{2v}$ (no π-interaction) becomes relevant when the Al–O–Al bending angle is considerably decreased, i.e. when the π-interaction is removed.

While the linear Al–O–Al arrangement is evidently preferred owing to the π-interaction between Al and O, the reasons behind the unusually short Al–O distances [13] are less straightforward. In addition to the π-interaction, also the strongly cationic character of three-coordinated aluminums shortens the Al–O bonds. The influence of the π-interaction can be, however, seen from Fig. 4, where the Al–O distances are presented for the four orientations of dialuminoxane. The 'π-interaction free' structure, $C_{2v}$, has slightly shorter distances than what is common to compounds containing Al–O bonds, 1.77 Å. Apparently, this shortening is due to the strong ionic character of aluminum [14]. The $C_s$-symmetric species, containing both 'π-interaction free' and 'π-interaction induced' bonds, clearly demonstrates the shortening influence of the π-interaction by further decreasing the Al–O bond from 1.77 to 1.69 Å. The $D_{2d}$- and $D_{2h}$-symmetric structures, in which the π-interaction contributes to both Al–O bonds, possess the very short distances of 1.68 Å.



| Parameters[a] | (1) | (2) | (3) |
|---|---|---|---|
| Al–O (Å) | 1.694 | 1.686 | 1.684 |
| Al–O–Al (°) | 179.8 | 179.7 | 179.7 |
| O–Al–O (°) | - | 119.4 | 119.4 |
| Me–Al–Al–Me (°) | 90.0 | 90.1 | 90.2 |
| Al–Al–Al–Al (°) | - | - | 90.2 |

| Parameters[a] | (4) | (5) |
|---|---|---|
| Al–O (Å) | 1.684 | 1.683 |
| Al–O–Al (°) | 179.7 | 179.6 |
| O–Al–O (°) | 119.5 | 119.5 |
| Me–Al–Al–Me (°) | 90.6 | 91.8 |
| Al–Al–Al–Al (°) | 91.6 | 90.9 |

[a] Average values

Fig. 5. HF/3-21G* optimised structures of linear methylaluminoxane fragments with $n = 0–4$. Hydrogens are omitted for clarity.

Interestingly, the relevance of π-interaction can be observed also by comparing the dialuminoxane to its tetramethylated congener. The electron-donating methyl substituent decreases the cationic nature of aluminum by providing more electron density than hydrogen does. This has two consequences. First, the Al–O bonds become somewhat elongated. Secondly, the energy differences between the π-interaction containing $C_s$ and the 'π-interaction free' $C_{2v}$ is decreased. Consequently, the π-interaction should be stronger for complexes with electron-withdrawing substituents bonded to aluminum.

### 3.2. The structures of three-coordinated methylaluminoxanes

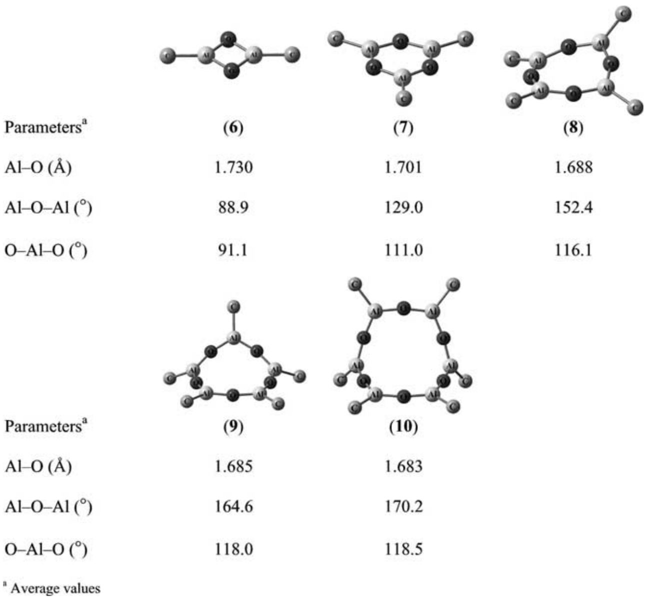
Schematic structures of the selected three-coordinated linear and cyclic MAO are presented in Fig. 2. Chain lengths were increased up to $n = 4$, where $n = 0$ represents the shortest possible linear and cyclic fragments. The structures and relative stabilities of structures **1**–**10** were analyzed as a function of the degree of oligomerisation.

The optimised structures of linear fragments with $n = 0–4$ are presented in Fig. 5. The same structural characteristics apply to all oligomers. The Al–O distances are short, ca. 1.68 Å, owing to the conjugation of the two lone pairs of oxygen with the vacant p-orbital of aluminum. For the same reason, the Al–O–Al angle is 180° and the methyl groups bonded to adjacent aluminums are perpendicular to each other. It should be noted that the structures with more than four aluminums (**4** and **5**) are ambiguously determined because the dihedral angle formed by four aluminums next to each other can adopt either 90 or −90° orientation. This results in two unique conformational isomers for **4** and three isomers for **5**. The structures of Fig. 5 represent the lowest energy conformations.

Experimental structure characterizations are not available for the studied compounds. However, the structural analogue of complex **1** with R=$CH(SiMe_3)_2$ has been determined [4h]. Unexpectedly, the compound crystallizes in the slightly less favorable $D_{2h}$-symmetry. As discussed by Volatron et al. [5c], this result may be due to the steric influence of the bulky substituent, together with crystal packing effects.

The optimised structures for cyclic 3-coordinated MAO with $n$ ranging from 0 to 4 are presented in Fig. 6. The two smallest fragments are planar, **6** is of $C_{2h}$ and **7** is of $C_{3h}$ symmetry, whereas the larger fragments **8** and **10** are of $C_{2v}$ while **9** is of $C_s$ symmetry [15]. The reasons for these structural changes become evident in a consideration of the bonding angles of sp$^2$-hybridized aluminum. The strain due to the cyclic structure in **6** and **7** constrains the O–Al–O angle below the optimal ca. 120°. Further increase in the size of the ring would require a planar compound to have an O–Al–O angle greater than 120°. In compounds **8**–**10** this is avoided by breaking the planar arrangement.

As described above, a characteristic feature of each molecule is a short Al–O bond due to π-bonding interactions. The Al–O distance decreases as a function of $n$ and is accompanied by increasing Al–O–Al angle. The inversely proportional correlation between the Al–O distance and the Al–O–Al angle can be explained by the stronger π-conjugation between the lone pairs of oxygen and the vacant p-orbital of aluminum as the Al–O–Al angle increases. On the other hand, also the strain in the small-sized rings may contribute to the elongated Al–O distances.



| Parameters[a] | (6) | (7) | (8) | (9) | (10) |
|---|---|---|---|---|---|
| Al–O (Å) | 1.730 | 1.701 | 1.688 | 1.685 | 1.683 |
| Al–O–Al (°) | 88.9 | 129.0 | 152.4 | 164.6 | 170.2 |
| O–Al–O (°) | 91.1 | 111.0 | 116.1 | 118.0 | 118.5 |

[a] Average values

Fig. 6. HF/3-21G* optimised structures of cyclic methylaluminoxane fragments with $n = 0$–4. Hydrogens are omitted for clarity.

The methylaluminoxane **7** is especially interesting, since it shows apparent similarities with benzene. The compound follows nominally the Hückel $4n+2\pi$-electron rule, it is planar, and it is cyclic. Therefore, it could be considered aromatic at first sight. The significant difference in electronegativity between Al and O, however, prevents the delocalisation of the electrons. Therefore, structure **7** cannot be considered aromatic but is similar to borazine, an inorganic analogue of benzene. Further evidence for the lack of aromatic stabilization of **7** is given in the following, where the relative stabilities of three-coordinated MAO are studied.

### *3.3. Relative stabilities of three-coordinated methylaluminoxanes*

The relative stabilities of the linear and cyclic compounds are presented in Table 1. The comparison between the cyclic structures is straightforward, since the energies can be given as a function of the AlOMe units. The comparison of relative stabilities of linear structures, and their comparison to cyclic structures, cannot be directly performed. The relative stabilities of all oligomers can be, however, qualitatively estimated by considering the following ring-opening reaction

$$(\mathrm{AlOMe})_x + \mathrm{TMA} \leftrightarrow (\mathrm{AlOMe})_x(\mathrm{TMA}) \tag{1}$$

In Eq. (1) $(\mathrm{AlOMe})_x$ represent the studied cyclic structures (**6**–**10**), TMA is trimethylaluminium, and $(\mathrm{AlOMe})_x(\mathrm{TMA})$ represent the studied linear structures (**1**–**5**). The relative stabilities of linear versus cyclic fragments can, therefore, be estimated by subtracting the energy of free TMA from the total energy of linear compounds.

The B3LYP and MP2 methods produce almost identical stabilities for all compounds, suggesting quantitative accuracy. The stabilities produced by the HF method deviate somewhat from the B3LYP and MP2 stabilities, suggesting a small overestimation by the HF method. The qualitative trends are, however, independent of the method.

The stabilities of linear aluminoxanes are independent of the degree of oligomerisation, whereas the stabilities of the cyclic compounds are influenced by the size of the ring. The smallest cyclic structure (**6**) is least stabilized, owing to the significant strain caused by the

Table 1
Relative stabilities of linear and cyclic methylaluminoxanes

| Method | $(MeAlO)_x$ | Linear | | | | | Cyclic |
|---|---|---|---|---|---|---|---|
| | | Compound | $E_x/x$ (a.u.) [a] | $\Delta E_x$ (kJ mol$^{-1}$) | Compound | $E_x/x$ (a.u.) | $\Delta E_x$ (kJ mol$^{-1}$) |
| HF/3-21G* | 1 | **1** | −354.675181 | 0.0 | | | |
| | 2 | **2** | −354.674827 | 0.9 | **6** | −354.621270 | 141.6 |
| | 3 | **3** | −354.674519 | 1.7 | **7** | −354.660459 | 38.7 |
| | 4 | **4** | −354.674358 | 2.2 | **8** | −354.668935 | 16.4 |
| | 5 | **5** | −354.674260 | 2.4 | **9** | −354.671741 | 9.0 |
| | 6 | | | | **10** | −354.673211 | 5.2 |
| B3LYP/6-31G*//HF/3-21G* | 1 | **1** | −357.702779 | 0.0 | | | |
| | 2 | **2** | −357.701876 | 2.4 | **6** | −357.665639 | 97.6 |
| | 3 | **3** | −357.701620 | 3.0 | **7** | −357.694789 | 21.0 |
| | 4 | **4** | −357.701442 | 3.5 | **8** | −357.698900 | 10.2 |
| | 5 | **5** | −357.701334 | 3.8 | **9** | −357.699895 | 7.6 |
| | 6 | | | | **10** | −357.700677 | 5.5 |
| MP2/6−31G*//HF/3-21G* | 1 | **1** | −356.879808 | 0.0 | | | |
| | 2 | **2** | −356.879155 | 1.7 | **6** | −356.842419 | 98.2 |
| | 3 | **3** | −356.878886 | 2.4 | **7** | −356.871932 | 20.7 |
| | 4 | **4** | −356.878745 | 2.8 | **8** | −356.875856 | 10.4 |
| | 5 | **5** | −356.878660 | 3.0 | **9** | −356.877189 | 6.9 |
| | 6 | | | | **10** | −356.877596 | 5.8 |
| MP2/6-311G**//HF/3-21G* | 1 | **1** | −356.975202 | 0.0 | | | |
| | 2 | **2** | −356.974458 | 2.0 | **6** | −356.936031 | 102.9 |
| | 3 | **3** | −356.974197 | 2.6 | **7** | −356.966706 | 22.3 |
| | 4 | **4** | −356.974069 | 3.0 | **8** | −356.971127 | 10.7 |
| | 5 | **5** | −356.973993 | 3.2 | **9** | −356.972699 | 6.6 |
| | 6 | | | | **10** | −356.973060 | 5.6 |

[a] The energy of free $AlMe_3$ has been subtracted from the total energy of linear compounds (see Eq. (1) and text).

ring formation as well as to a least optimal π-conjugation between oxygen and aluminum. The systematically increasing stability as a function of the number of AlOMe units is due to reduced strain accompanied by improving overlap between the p-orbitals of oxygen and aluminum. Compound **7**, the structural analogue of benzene, has no excess stabilization energy. This suggests that the molecule is not aromatic, owing to the high polarity of the Al–O bond.

Evidently, the stabilities of cyclic three-coordinated MAO are dependent on both strain caused by the ring formation and the degree of π-conjugation. In linear three-coordinated MAO, there is no strain and the degree of π-conjugation does not change with the number of fragments (see Fig. 5: Al–O distances as well as Al–O–Al angles are independent of the size of the fragment). The π-conjugation, and the absence of strain, is characteristic for the largest cyclic fragment (**10**) as well, and the geometry parameters and relative stability of **10** are nearly identical with those estimated for the linear fragments.

## 4. Conclusions

The structures and relative stabilities of linear and cyclic three-coordinated MAO were studied by quantum chemical methods. The compounds are characterized by a short Al–O distance due to π-bonding interaction between the oxygen lone pairs and vacant p-orbital of aluminum. Due to the π-conjugation, linear MAO prefer an Al–O–Al angle of 180° with adjacent methyl groups perpendicular to each other. The structures of cyclic MAO are determined by the strain due to the ring formation as well as by the π-conjugation.

The relative stabilities of linear fragments are constant, because the degree of π-conjugation does not change with the number of AlOMe units. The relative stability of cyclic MAO increases with the ring size. Small oligomers are destabilized by the strain of the ring formation as well as by the reduced π-bonding interaction between oxygen and aluminum. As a consequence, linear and large cyclic chains are preferred in three-coordinated MAO.

## Acknowledgements

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[14] Covalent bond order of the equilibrium structure ($D_{2d}$) with the strongest π-interaction was calculated to be only 0.28 between Al and O, which demonstrates very ionic bonding. Interestingly, the covalent border increases up to 0.32 for the $C_{2v}$ with no π-interaction, therefore, suggesting less ionic character for the 'π-interaction free' bond between Al and O.

[15] The crystal structure of the analogue of complex **8** (R = 2,4,6-tri-*t*-butylphenyl) has planar $Al_4O_4$ arrangement (4m). This planarity is probably due to accommodation of the molecule in the crystal lattice.