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# THE STUDY OF COORDINATIVE INTERACTION IN THE ORGANOALUMINIUM DERIVATIVES OF SUBSTITUTED PHENOLS

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## Summary

Intramolecular coordination in dimethylaluminium phenoxides (with an *ortho*-substituted ring) was investigated. Only strongly donating groups in the phenoxy ring (COOMe) displayed strong intramolecular coordination. All compounds investigated formed donor—acceptor complexes with hexamethylphosphoramide (HMPA). Dimethylaluminium methylsalicilate coordinated HMPA without splitting the intramolecular carbonyl oxygen—aluminium bond, which suggests formation of the pentacoordinated aluminium atom.

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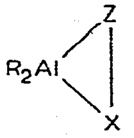
Association of organoaluminium compounds or intermolecular complexation has been up till now the subject of many investigations [1,2].

Less information however is available on the ability of these compounds to coördinate with donor atom X of the same molecule (intramolecular coordination).



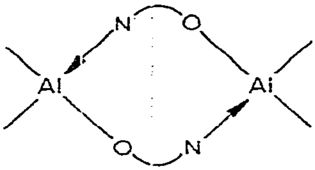
$Z = (CH_2)_n$, $S(CH_2)_{n-1}$ or $N(CH_2)_{n-1}$; $n = 3$ or 4

$X =$ S(ref. 3), N(refs. 4–10) or O(refs. 4,5,7)

(A)

A few examples of such coordination have been shown to exist, mainly by cryoscopic investigations. The compounds A have been shown to be monomeric, in contrast to other organoaluminium derivatives which are normally associated. In some cases these compounds were thermally stable and the ability of the metal and X to participate in intermolecular coordination was considerably low.

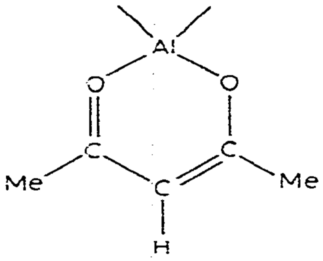
When this bonding takes place via oxygen, as in $R_2AlO{-}(CH_2)_n{-}NR'_2$ ($n = 2, 3$) or in dialkylaluminium 8-quinolinate [11], such compounds are dimers (B) with no intramolecular coordination.



(B)

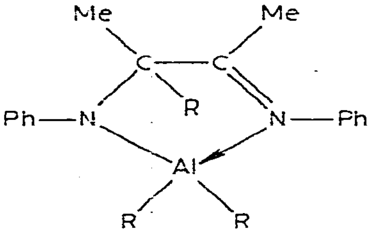
Other authors [12] suggest a monomeric structure with intramolecular coordination for dialkylaluminium 8-quinolinate.

The existence of a chelate structure (C) in dimethylaluminium acetylacetonate is not the only explanation of the C—Me group equivalence in its PMR spectrum [13], but it is the most likely one although it could also be due to the fast migration of the $Me_2Al$ group from one oxygen to another.



(C)

At present there is no spectroscopic evidence of intramolecular coordination in the literature mentioned above, with the exception of [10]. Intramolecular coordination was demonstrated in the derivative D which was a monomer in benzene with the C=N band shifted by 25 $cm^{-1}$ towards the lower frequencies as compared with 2-methyl-3-phenylaminobutanone-2 anyl, owing to the coordination of nitrogen with aluminium.



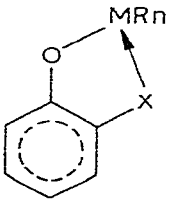
(D)

In the case of organometallic compounds of other Main Group metals studies of intramolecular coordination were performed using *ortho*-substituted phenoxy and thiophenoxy groups as one of the substitutents [14,15,16].

TABLE 1

ANALYTICAL DATA FOR ALUMINIUM FOR THE $ArOAlMe_2$ COMPOUNDS

| No. | Compound | % Al | |
|---|---|---|---|
| | | Found | Calculated |
| I | $2\text{-}CH_3C_6H_4OAlMe_2$ | 12.36 | 12.46 |
| II | $2\text{-}CH_3OC_6H_4OAlMe_2$ | 14.71 | 15.00 |
| III | $2\text{-}ClC_6H_4OAlMe_2$ | 15.23 | 15.18 |
| IV | $2\text{-}CH_3O\overset{O}{\overset{\|}{C}}C_6H_4OAlMe_2$ | 12.89 | 12.98 |
| V | $3,4\text{-}Cl_2C_6H_3OAlMe_2$ | 12.24 | 12.23 |



M = Hg, Sn, Pb (refs. 14,15)

(E)

From the point of view of coordination chemistry of the organometallic compounds of nontransition metals it was of considerable interest to compare the dependances obtained earlier with the results obtained for organometallic groups containing the lighter nontransition organometallic groups (such as $AlR_2$). With this aim we undertook studies of intramolecular coordination in the organoaluminium derivatives of *ortho*-substituted phenols with a lone electron pair.

## Results

### *Proton magnetic resonance*

Table 2 lists the PMR data for the benzene solutions of compounds I—V (Tab. 1) and their 1 : 1 complexes with hexamethylphosphoroamide (HMPA). The PMR spectra of compounds I—V show one signal for the methyl groups attached to Al. The spectra of compounds I and II also contain a singlet for the $C—CH_3$ and $C—O—CH_3$ groups respectively. The PMR spectrum of compound IV contains two methyl signals for the carbomethoxy group: an intensive line at 3.04 ppm and a weak signal at 3.45 ppm (with an intensity ratio of 10 : 1). The total integrated intensity of these two signals is 0.5 that of the methyl group bonded to aluminium.

Addition of HMPA to the benzene solutions of compounds I—V changes somewhat the chemical shifts of both $Al—CH_3$ protons and *ortho*-substituent methyl protons. Only one signal for the carbomethoxygroup is observed in the mixture of compound IV and HMPA. Furthermore, the chemical shift of the $N—CH_3$ groups in the mixtures differs negligibly from that in the pure hexamethylphosphoramide (HMPA) solution.

TABLE 2

CHEMICAL SHIFTS ($\delta$, ppm) OF THE METHYL GROUP PROTONS OF COMPOUNDS I—V AND THEIR 1 : 1 MIXTURES WITH HMPA (0.1 *M* BENZENE SOLUTION)

| Compound | $\delta$(Al—Me) | $\delta(CH_3)$ | Compound/HMPA (1 : 1) | | | | |
|---|---|---|---|---|---|---|---|
| | | | $\delta$(Al—Me) | $\Delta_1$ [a] | $\delta(CH_3)$ | $\delta(N—CH_3)$ | $\Delta_2$ [b] |
| HMPA | | | | | | 2.24 | 0 |
| I | —0.40 | 2.30 | —0.23 | 0.17 | 2.52 | 2.16 | —0.08 |
| II | —0.24 | 3.25 | —0.20 | 0.04 | 3.66 | 2.23 | —0.01 |
| III | —0.21 | | —0.26 | —0.05 | | 2.21 | —0.03 |
| IV | —0.13 | 3.45, 3.04 | —0.30 | —0.17 | 3.54 | 2.20 | —0.04 |
| V | —0.45 | | —0.37 | 0.08 | | 2.09 | —0.13 |

[a] $\Delta_1 = \delta$(Al—Me) (compound/HMPA) — $\delta$(Al—Me) (compound). [b] $\Delta_2 = \delta$(N—Me) (compound/HMPA) — $\delta$(N—Me) (HMPA).

### *IR spectroscopy*

Table 3 shows the frequencies of the most characteristic bands in the spectra of the benzene solutions of the compounds investigated and their mixtures with HMPA. It is seen from this table that with the exception of IV the C—O stretching frequencies for the Ar—O—Al fragment of all compounds appear in the region of 1222—1238 cm$^{-1}$. In compound IV this band is considerably lower (1166 cm$^{-1}$). Two very intensive bands, the stretching C—O—C and C=O modes of the ester group at 1370 and 1628 cm$^{-1}$ respectively (with a shoulder at 1641 cm$^{-1}$) were also observed in IV. The former had much higher and the latter had lower wave numbers than in free *o*-metoxymethylbenzoate.

In the spectrum of the benzene solution of the IV/HMPA mixture the positions of these bands (1362 and 1632 cm$^{-1}$) change negligibly, the latter band appearing in the form of a rather narrow signal without a shoulder. Table 3 also shows that in the spectra of benzene solutions of the equimolar mixtures of all compounds with HMPA the positions of the characteristic bands of the N—P=O fragment in HMPA change noticeably, the largest change being observed for compounds I and V while the smallest shifts take place for compound IV. The N—P stretching mode shifts towards higher frequencies (compared with pure HMPA in benzene) while the P=O stretching vibration is observed at lower wave number. For excess HMPA with respect to dimethylaluminium phenoxide the spectrum of the 1 : 1 mixture overlaps that of free HMPA.

### *Cryoscopic measurements*

Table 4 lists the molecular weights and degrees of association of compounds I—IV (0.1 *M* concentrations in benzene) measured 3 and 24 h after dissolving the organoaluminium compounds in benzene. It can be see from the Table that the molecular weights of compounds I and III measured after 3 h correspond to the mixture of a dimer and a trimer. After 24 h the molecular weight of compound I corresponded to the trimer. Compound II is dimeric in solution, while compound IV is mainly monomeric.

TABLE 3

THE FREQUENCIES OF THE MOST CHARACTERISTIC BANDS OF COMPOUNDS I—V AND THEIR 1 : 1 MIXTURES WITH HMPA (0.1 *M* BENZENE SOLUTION)

| Compound | Free compound | | | Compound/HMPA (1 : 1) | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | $\nu$(C—O—Al) | *o*-substituent | | *o*-substituent | | $\nu$(N—P) | | $\nu$(P=O) | |
| | | $\nu$(C—O—C) | $\nu$(C=O) | $\nu$(C—O—C) | $\nu$(C=O) | $\nu$ | $\Delta\nu$ | $\nu$ | $\Delta\nu$ [a] |
| HMPA | | | | | | 988 | 0 | 1217 | 0 |
| I | 1232 | | | | | 1005 | 17 | 1170 | —47 |
| II | 1218 | 1260 | | [b] | | 1000 | 12 | 1180 | —37 |
| III | 1237 | | | | | 1002 | 14 | 1175 | —42 |
| IV | 1166 | 1370 | 1628 (1641) | 1362 | 1632 | 995 | 7 | 1190 | —27 |
| V | 1222 | | | | | 1005 | 17 | 1168 | —49 |

[a] $\Delta\nu = \nu(\text{complex}) - \nu(\text{free compound})$. [b] Assignments of the bands uncertain in this region.

TABLE 4

MOLECULAR WEIGHTS AND DEGREES OF ASSOCIATION OF COMPOUNDS I—IV, 3 AND 24 h AFTER DISSOLVING IN 0.1 *M* BENZENE SOLUTION

| Compound | Calculated molecular weight | | | Degree of association found | |
|---|---|---|---|---|---|
| | Monomer | Dimer | Trimer | After 3 h | After 24 h |
| I | 164 | 328 | 492 | 2.4 ± 0.2 | 3.0 ± 0.1 |
| II | 180 | 360 | 540 | 2.1 ± 0.2 | 2.2 ± 0.1 |
| III | 184.5 | 369 | 553.5 | 2.7 ± 0.2 | [a] |
| IV | 208 | 416 | 624 | 1.2 ± 0.05 | 1.3 ± 0.05 |

[a] Compound III is unstable when kept for a longer time in benzene solution.

## Discussion

It is known that alkoxy derivatives of dialkylaluminium are associates in inert solvents. E.g. dimethylaluminium phenoxyde was found to be a mixture of dimer and trimer in hydrocarbons, the reaction to the right being slightly exothermic [17]:

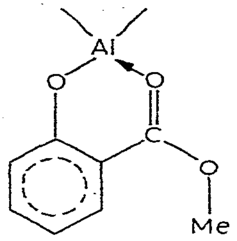
$$\text{C (dimer)} \rightleftharpoons \text{B (trimer)}$$

Investigation of the structures of sublimed organoaluminium derivatives of phenol [18] showed that immediately after dissolving in benzene they are dimers and are slowly converted to trimers (after about 24 h). We observed the same behaviour for the solution of dimethylaluminium *o*-cresoxide (I) in benzene. One may thus conclude that the steric effects of one *o*-methyl group do not affect the degree of association in these derivatives.

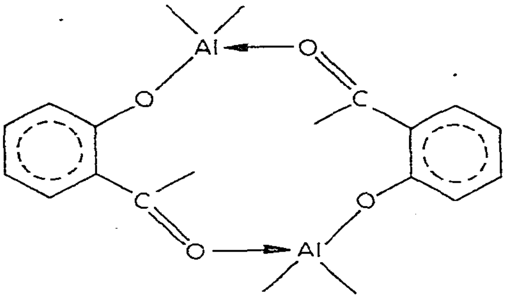
Moreover, as the compounds contain *ortho*-substituents with lone electron pairs in the phenyl ring one could expect two means of association. The metal atom may either take part in an intermolecular association with the oxygen of another molecule of the organoaluminium compound, or can form an intramolecular coordinative bond with the *ortho*-substituent. In the complexes of organoaluminium compounds with monodentate ligands the metal is most often characterized by coordination number 4 with $sp^3$ hybridization [1], and one might a priori expect that the stronger intramolecular coordination by the bidentate substituent in these compounds would lead to a lower ability of organoaluminium phenoxide to associate and thus to a lower association degree. In a border case when the strength of the intramolecular coordination is higher than intermolecular association the monomer may exist.

It follows from the data in Table 4 that a replacement of the $CH_3$ group in compound I by the $OCH_3$ groups results in a decrease of degree of association in solution of compound II from 3 to 2.2. The carbonyl oxygen of the ester group in the *ortho* position in IV is a stronger donor than that of the Al—O—Ph bond. As a result IV is nearly entirely monomeric with intramolecular coordination. In the PMR spectrum of this compound one signal of the Al—$CH_3$ group is present, along with two signals from the $COOCH_3$ groups of the higher (monomer IV) and lower (dimer) intensities. This assignment is confirmed by the fact that the degree of association of the compound determined from the ratio of signals intensities coincides with the value obtained cryoscopically.

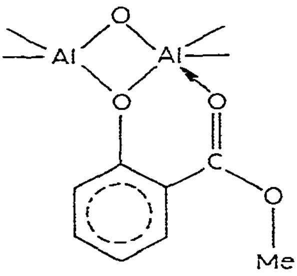
One can expect the existence of many types of coordination of which the following four are considered.



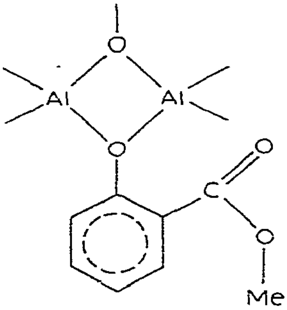
(IVa)



(IVb)



(IVc)



(IVd)

Monomeric IVa is identified by molecular weight measurements and PMR spectra but these indicate also the existence of another coordination of aluminium. IR spectra are in full agreement with the presence in solution of IVa together with IVb. Strong complexation of the carbonyl group is shown by IR spectra both for monomeric and associated species in solution, the observed frequency [20] of $\nu$(C=O) corresponding to that of stable complexes *. A strong $\nu$(C=O) band at 1628 $cm^{-1}$ has to be attributed to IVa and a shoulder at 1641 $cm^{-1}$ confirms a weaker Al ← O bond in IVb but excludes IVc. The presence of only one band at 1166 $cm^{-1}$ of $\nu$(C—O—Al) supports the existence of uncomplexed oxygen in C—O—Al but rules out the C—O=$Al_2$ group whose frequency should appear at about 1220 $cm^{-1}$ [17]. This evidence supports only the existence of structures IVa and IVb.

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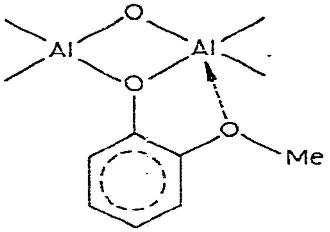
* The $\nu$(C=O) frequency observed is nowhere near that of the free compound which appears at 1714 and 1732 $cm^{-1}$ (the splitting observed is due to conformation transition upon rotation about the C—C bond). Such a large frequency change can neither be due to the electronic effect of the OAlMe$_2$ group nor to weak interaction but is caused by a strong O → Al bond. The difference in the C=O stretching frequencies for p-nitro- and p-methoxymethylobenzoate i.e. for very different electronic systems is only 14 $cm^{-1}$ [19]. For weak interaction like hydrogen bonding in acetic acid $\nu$(C=O) shifts only ca. 30 $cm^{-1}$ towards the lower frequency.

Dimethyl (*o*-methoxyphenoxyaluminium (II) has a lower degree of association than I. This is due to steric hindrance of the O—$CH_3$ group but one can also suppose it is caused by the interaction in IIa as shown.



The donor abilities of methoxy oxygen are poor [25] compared to that of the carbonyl group in IV or of oxygen in the Al—O bond. The wave number of $\nu(COC)_{as}$ is that of the uncomplexed methoxy group. One can expect that if any interaction exists, it is not stronger than that of hydrogen bonding.

The second indication, but one that is not too significant, for the presence of IIa is the great change in the chemical shift of the $OCH_3$ protons (0.4 ppm) observed when HMPA is added to the solution of (II). This can indicate a change in aluminium—methoxy oxygen interaction. The above evidence supports indirectly only very weakly the supposition for the existence of structure IIa with weak intramolecular interaction.

The degree of association does not change in compound III compared to compound I. The chlorine atom in the C—Cl bond is a very poor electron donor and thus if the intracoordination of Al takes place it is very weak [21].

We succeeded in showing more detailed differences in the strength of the intramolecular coordination of aluminium with an *ortho*-substituent, depending on the nature of the substituent, by investigating the spectra of benzene solutions of the equimolar mixtures of the respective compounds with HMPA. The complexation of HMPA with organoaluminium compounds such as trialkylaluminium and organoaluminium halides has been previously studied [22]. HMPA was found to coordinate with aluminium via the P=O oxygen. The value of the P=O IR band shift was used as a measure of the strength of the coordinative bond.

It can be seen from the data in Table 3 that in all cases the expected shift of the P=O and P—N modes is observed. These results allow us to state that complex formation with HMPA takes place with all compounds investigated. The magnitude of this shift depends however on the nature of the substituent in the phenyl ring of the organoaluminium compound and increases in the following order (included also are some data of other aluminium compounds [22]):

$$IV < II < III = Me_3Al < V < I < AlCl_3$$

*Ortho*-substituents may affect the coordinating ability of aluminium due to the following three factors.

*The electronic effect*

This is transmitted through the bonds chain to the metal. One could have expected the electron donor group to decrease and the electron acceptor group to increase the aluminium acidity. However, the values $\nu$(P=O) and $\nu$(N—P) are practically equivalent in compounds I and V. Thus even the mutual electron attracting action of two chlorines from positions 3 and 4 is insufficient to change considerably the metal—oxygen bond formed by coordination with HMPA. Assuming a monotonous character for the influence of electronic effects on the aluminium acidity one may suggest no considerable change of the metal acceptor ability in the presence of donors.

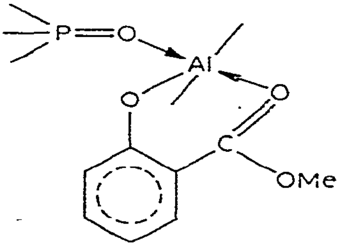
### *Steric effect*

Investigation of complex formation of the organoaluminium phenoxides with benzonitrile has demonstrated [23] that the metal ability to coordinate does not change noticeably on going from aluminium phenoxide to aluminium 2,6-dimethylphenoxide compound. Thus it may be assumed that the steric effects of *ortho*-substituents having the effective Van der Waals radius close to that of the methyl group will also display no influence on the coordinating ability of the metal by not hindering organic donors.

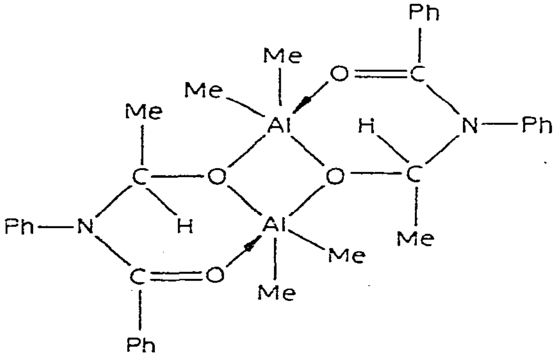
### *Intramolecular interaction*

It can therefore be suggested that the main factor responsible for the difference in aluminium ability for intramolecular coordination in the compounds investigated is the different strength of intramolecular interaction of the metal with the *ortho*-substituent in compounds II and III and intramolecular bond in IV. The fact that in compounds II and III the IR shift of P—N and P=O is lower than in compound I can suggest the intramolecular interaction of aluminium with the *ortho*-substituent. Comparing the IR and PMR shifts of compounds II and III with the *o*-Cl and *o*-OMe substituents one can see that the interaction, if it exists, is weaker for the former.

For the system IV + HMPA in benzene the very strong intramolecular coordination between C=O and the metal is retained since the respective IR bands of the ester group change negligibly compared with compound IV in benzene. At the same time the shift of $\nu$(P=O) and $\nu$(N—P) frequencies suggests coordination between aluminium and oxygen of HMPA although the strength of this bond is considerably lower than that in compounds I and V which contain no *ortho*-substituents with lone electron pair. Thus one may assume that in the equimolar mixture of compound IV with HMPA the structure VI with pentacoordinated aluminium exists.



(VI)



(VII)

For the organic compounds of aluminium in contrast to its inorganic derivatives the coordination number 5 is not characteristic, although according to the literature [24] the structure of complex $(Me_2AlOCPhNPh, MeCHO)_2$ (VII) contains the penta-coordinated metal atom with the ligand location corresponding to the partially distorted trigonal bipyramid.

The geometry of the coordinated ligand corresponds to the optimum geometry of $sp^3d$ or more probably $sp^2p$ hybridized aluminium.

Analysis of the molecular model of complex VI indicates that in this case the structure of the coordinated state of the metal atom corresponds closely to the trigonal bipyramidal location of the ligand around the aluminium atom.

## Experimental

Compounds I—V were prepared by careful action of 30% benzene solution of the respective substituted phenols on 30% solution of an equimolar quantity of trimethylaluminium in the same solvent at 5—8° C. After the completion of the reaction benzene was evaporated in a rotor evaporator, the white or pale yellow precipitate was washed with a small quantity of cold heptane, filtered and dried under vacuum. The products represent the white crystals which decompose rapidly in air. The purity of the compounds was controlled by analysis for Al and by means of PMR spectroscopy. All operations were performed under dry nitrogen. The molecular weights were determined cryoscopically for 0.1 *M* benzene solutions using the standard device modified so that investigations could be performed under dry nitrogen.

The PMR spectra were recorded on Jeol instrument at 100 MHz, the chemical shifts were measured with an outer stabilization with an accuracy of ±0.05 ppm.

The IR spectra were recorded in the region of 450—1800 $cm^{-1}$ on a Zeiss UR-10 instrument in a 0.12 mm cuvette modified for measurements in nitrogen atmosphere.

The work was performed at the Institute of Organic Chemistry and Technology of Warsaw Technical University.

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