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# COMPLEXES OF *p*-DIMETHOXYBENZENE WITH ORGANOALUMINIUM COMPOUNDS

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## SUMMARY

The complexes of *p*-dimethoxybenzene with dimethylaluminium chloride and trimethylaluminium have been studied in terms of IR and NMR spectra, cryoscopic molecular weights and composition determinations.

The data obtained have indicated that among the complexes of *p*-dimethoxybenzene with dimethylaluminium chloride and trimethylaluminium, only the 1/2 complexes formed by the two methoxy groups are stable. The 1/1 complexes exist at equilibrium with the 1/2 complexes and free *p*-dimethoxybenzene.

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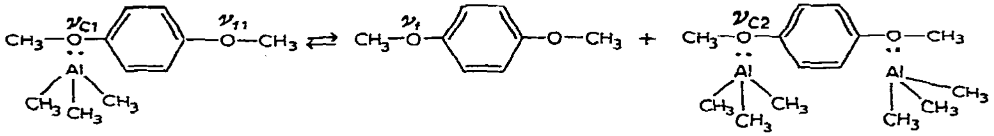
Complexes of organic polyfunctional donors with organoaluminium compounds have been studied by numerous investigators[1-3]. According to the structure of a given donor, such complexes can be formed by one or more functional groups. Thiele *et al.*[3] found that 1,2-dimethoxyethane forms with trimethylaluminium a stable 1/2 complex. A 1/1 complex of the two compounds is labile and, on heating, disproportionates to yield the free donors and the 1/2 complex.

Our earlier studies were concerned with the complexes of organoaluminium complexes with aromatic monofunctional donors such as anisole, benzonitrile, and ethyl benzoate[4,5,7]. In the present work complexes of aromatic bifunctional compounds are investigated. For these investigations *para*-substituted oxybenzene derivatives were chosen. In the first place, complexes of *p*-dimethoxybenzene (*p*-DMB) with methylaluminium chlorides were examined. Complexes of *p*-DMB with trimethylaluminium and dimethylaluminium chloride were studied in terms of IR and NMR spectra, cryoscopic molecular weights and composition determinations.

For studying the composition of the complexes in relation to the *p*-DMB/aluminium compound mole ratio, *p*-DMB–dimethylaluminium chloride complexes were isolated from the solutions containing the reactants in the ratios 1/1, 1/2, and 1/4. From the 1/2 and the 1/4 solutions, a solid 1/2 complex was isolated. Its composition was verified by quantitative analyses and molecular weight determinations.

After the solvent had been distilled from the 1/1 solution, there remained a liquid of composition and molecular weight corresponding to those of the 1/1 complex. The IR spectrum revealed, however, the presence of free *p*-DMB and the 1/2 and 1/1 complexes.

In benzene solutions of the 1/1 *p*-DMB–aluminium compound complex the presence of two types of free ethereal groups of related basicities indicates that an equilibrium is established between the 1/1 and 1/2 complexes and the free ligand.



An IR spectrum of such a mixture should exhibit four bands of C–O–C stretching vibrations. The frequencies of the bands found in the region 1100–1300 cm$^{-1}$ are listed in Table 1. Within this range the spectrum of the 1/1 *p*-DMB–dimethylaluminium chloride complex exhibits seven bands. A band at 1235 cm$^{-1}$ is attributable to free *p*-DMB. A band at 1152 cm$^{-1}$, also occurring as the only $\nu$(C–O–C) in the 1/2 complex spectrum, testifies to the presence of the 1/2 complex in the mixture. Bands at 1173 and 1255 cm$^{-1}$ are attributed to $\nu_{C_1}$ and $\nu_{f_1}$, respectively. Bands at 1217 and 1205 cm$^{-1}$ are assigned to deformation vibrations $\delta(CH_3)$ of the aluminium-borne $CH_3$ group.

TABLE 1

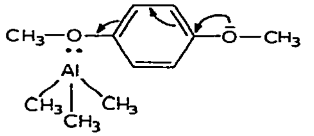
IR SPECTRA OF COMPLEXES OF *p*-DIMETHOXYBENZENE WITH $Me_2AlCl$ AND $Me_3Al$ IN THE REGION 1100–1300 cm$^{-1}$

The spectra were recorded on a Zeiss-UR-10 spectrophotometer in dilute benzene solutions.

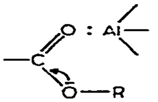
| Free compounds | | | Complexes | | | | Assignment | Notation |
|---|---|---|---|---|---|---|---|---|
| *p*-DMB[a] (cm$^{-1}$) | $Me_2AlCl$ | $Me_3Al$ | *p*-DMB/$Me_2AlCl$ mole ratio (cm$^{-1}$) | | *p*-DMB/$Me_3Al$ mole ratio (cm$^{-1}$) | | | |
| | | | 1/1 | 1/2 | 1/1 | 1/2 | | |
| | | | 1255s | | 1254s | | C–O–C free in the 1/1 | $\nu_{f_1}$ |
| 1235s | | | 1235s | | 1235s | | C–O–C in the free ether | $\nu_f$ |
| | 1205s | | 1217s | 1200–1210s | 1218s | 1195s | $CH_3$ deformation of MeAl | $\delta_{CH_3}$ |
| | | | 1205sh | | | 1214w | | |
| | | 1256w | | | | 1255w | | |
| | | | 1173s | | 1176s | | C–O–C in the 1/1<br>$\overset{\cdot\cdot}{\text{Al}}$ | $\nu_{C_1}$ |
| | | | 1152m | 1152s | 1159m | 1160s | C–O–C in the 1/2<br>$\overset{\cdot\cdot}{\text{Al}}$ | $\nu_{C_2}$ |

[a] p-Dimethoxybenzene; s- strong; w- weak; m- medium; sh- shoulder.

The addition of a molecule of the organoaluminium compound results in a lower density of the electron cloud on the complexing oxygen atom. The C–O–C bonds become longer and the frequency of the C–O–C stretching vibrations diminishes[6]. This reduction of frequency should be greater in the 1/2 than in the 1/1



complex because in the former complex the positive mesomeric effect of the free methoxy group no longer exists. The frequency of the C–O–C band of the free ethereal group should be higher in the 1/1 complex than in free *p*-DMB, because the complexed *para*-group acts as a class II substituent. This leads to a stronger *p*-conjugation and to elevation of the C–O bond order. A similar frequency rise has been recorded with



ester group complexes[7] in which the frequency of the C–O–R vibrations is much higher than in the free ester. The conjugated system is here shorter and therefore the increase of frequency higher.

The spectrum of the 1/2 *p*-DMB–dimethylaluminium chloride complex exhibited within the range investigated only two bands at 1152 and a broad one at 1200–1210 $cm^{-1}$. The bands were attributed to $\nu_{C_2}$ and $\delta_{CH_3}$, respectively.

In the NMR spectra of the 1/1 complexes of *p*-DMB with dimethylaluminium chloride and trimethylaluminium, the methoxy proton signal is shifted towards lower fields as compared with the ether. At room temperature the protons of the free and the complexed ether groups yield one signal. This is an averaged signal because of the rapid exchange of the organoaluminium compound. On the other hand, at a temperature of −60° C when the exchange is slowed down, two signals are produced, attributable to the protons of complexed and free methoxy groups.

The NMR spectra of the 1/2 complexes exhibit one signal of the methoxy group protons, both at room temperature and at −60° C.

The above data indicate clearly that, among the complexes of *p*-DMB with methylaluminium chlorides, the 1/2 complex formed by the two methoxy groups is stable. The 1/1 complex exists at equilibrium with free *p*-DMB and the 1/2 complex.

## REFERENCES

1 N. R. FETTER AND B. BARTOCHA, *Can. J. Chem.*, 40 (1962) 342.
2 K. H. THIELE AND W. BRÜSER, *Z. Anorg. Allgem. Chem.*, 384 (1966) 179.
3 K. H. THIELE, H. K. MÜLLER AND W. BRÜSER, *Z. Anorg. Allgem. Chem.*, 345 (1966) 194.
4 K. STAROWIEYSKI AND S. PASYNKIEWICZ, unpublished data.
5 K. STAROWIEYSKI, S. PASYNKIEWICZ AND M. BOLESŁAWSKI, *J. Organometal. Chem.*, 10 (1967) 393.
6 S. TAKEDA AND R. TARAO, *Bull. Chem. Soc. Japan.*, 38 (1965) 1568.
7 S. PASYNKIEWICZ AND K. STAROWIEYSKI, *Roczniki Chem.*, 41 (1967) 1139.