Benzo-15-crown-5-Aluminium Chloride Complexes of Unusual Stability

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Among twelve crown ethers of 12, 15, 18, and 21 rings only benzo-15-crown-5 and those with an electron-releasing substituent formed the complexes with aluminium chloride which were stable in methanol.

The halides of group III elements, such as boron trifluoride and aluminium chloride, are typical Lewis acids and known to form stable adducts with ether and tertiary amine in nonpolar solvents. The common feature of the ether adducts so far known is easy exchange of the donated ether molecule(s) with other donative molecule (Eq. 1) or substitution of the halide ion by protic molecule such as methanol (Eq. 2).1) Though the extent of the processes depends on the nature of

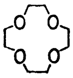
$$R_2O\rightarrow AlX_3 + R_2'O \longrightarrow R_2'O\rightarrow AlX_3 + R_2O \quad (1)$$

$$R_2O\rightarrow AlX_3 + R'OH \longrightarrow R'OAlX_2 + HX + R_2O \quad (2)$$

the halide and the donating molecule, there is no ether–aluminium halide adduct (or complex) which is stable in protic solvent as far as we know.

In the course of our study to introduce various substituents into the benzene ring of benzocrown ethers, attempted Friedel-Crafts acylation catalyzed by aluminium chloride was proved to be unpractical. The failure of the reaction can be reasonably explained in terms of the formation of a stable crown ether adduct with the aluminium chloride, and resulting deactivation of the catalyst.2) However, this study led us to a novel finding that a complex containing aluminium chloride was obtained even after usual hydrolysis of the reaction mixture and successive recrystallization from methanol. The unusual feature of the complex has prompted us to study behavior of typical Lewis acids to various crown ethers (**1** to **8**). It should be noted that despite of a large number of studies on the chemistry of the crown ether complexes with group I and II element cations as well as ammonium-type ions there have been few papers concerned with those of group III element halides.3)

This paper described a specific feature of benzo-15-crown-5 and some of its derivatives with an electron-releasing group, those ethers which afford stable 1:1 complexes with aluminium chloride in methanol. Though elucidation of the relationship between their structures and the unusual stability has to await X-ray crystallography, the present observations would shed light to the study for the crown ether complexes with neutral Lewis acids.



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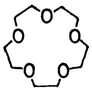

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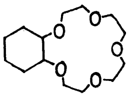

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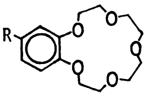
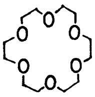


R = H : 4a
CH_3 : 4b
t-C_4H_9 : 4c
NO_2 : 4d
$COCH_3$: 4e



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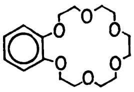

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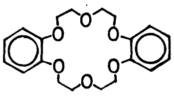

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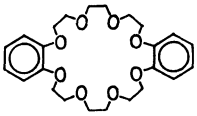

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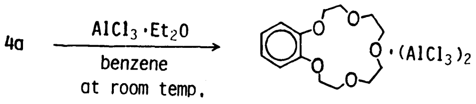
Results and Discussion

Slow addition of benzo-15-crown-5 (**4a**) (3 mmol) in benzene into an ethereal aluminium chloride (6 mmol) produced white precipitates (**9**) in a quantitative yield (>95%), which proved to be an 1:2 adduct of the crown ether and aluminium chloride (Eq. 3). The same adduct was obtained even when the ratio of the starting materials was changed to 1:1. The reaction in more donative solvent, THF or nitromethane, afforded viscous oil, which offered difficulty for further treatment. The adduct **9** was sparingly soluble in methanol, and attempted recrystallization from the solvent gave a complex (**10**), white powders, mp 147—148 °C, in 77% yield (Eq. 4). Longer heating of **9** in methanol brought about slow decomposition to liberate the crown ether. The interaction between

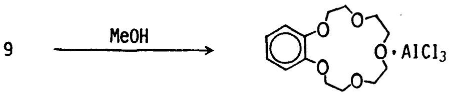


(3)

9

EA: calcd for $C_{14}H_{20}O_5Al_2Cl_6$:

	C%	H%
Found	31.02	3.90
Calcd	31.42	3.74



(4)

10

EA: calcd for $C_{14}H_{20}O_5AlCl_3$:

	C%	H%
Found	41.74	5.06
Calcd	41.86	5.02

the ether oxygens and aluminium in both **9** and **10** was shown by bathochromic shift in the IR absorptions of ether linkages (Fig. 1). The adduct **9** was also proved to be transformed easily into **10** on dissolution in methanol, and thus **9** and **10** gave the same NMR spectrum in methanol-d_4 (Fig. 2). The larger down-field shift in methylene signals ($\Delta\delta$ 0.4—0.6 ppm) than those of aromatic protons ($\Delta\delta$ *ca.* 0.32 ppm)

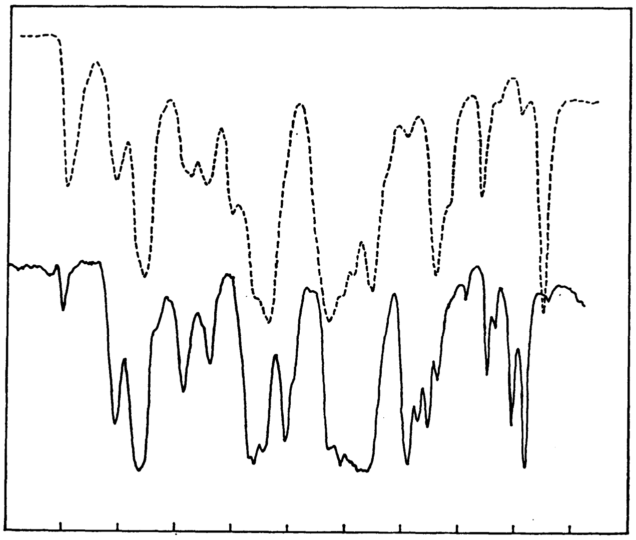


Fig. 1. Infrared spectra of benzo-15-crown-5 and complex **10**. ----: Benzo-15-crown-5, ——: complex **10**.

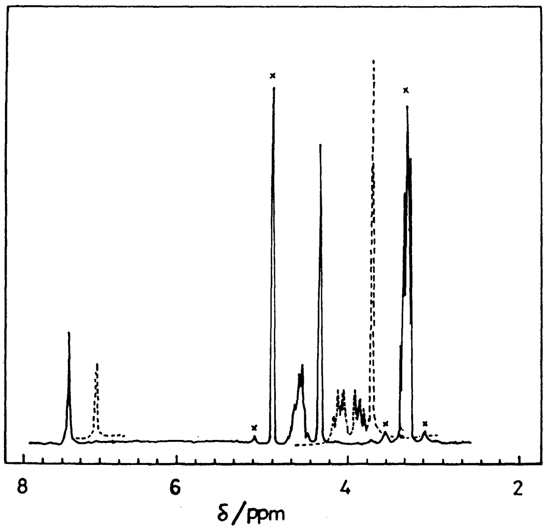


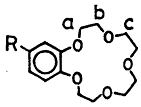
Fig. 2. ^1H NMR (90 MHz) spectra of benzo-15-crown-5 and complex **10** in methanol-d_4.
----: Benzo-15-crown-5, ——: complex **10**, ×: impurities in methanol-d_4.

is indicative of the preferential coordination of aluminium with the ether oxygens. The fact that the similar treatment of **9** with ethanol gave **10** (NMR and EA; Found: C, 41.55; H, 5.00%) reasonably ruled out the possibility that **10** was one of the products derived by substitution of the chloride ion(s) by the alcohols. The complex **10** is insoluble in most solvents but shows a small solubility in methanol (*ca.* 6×10^{-3} mol/l). Molecular weight determination by means of vapor pressure depression technique gave an average value of 403±10 (calcd for $C_{14}H_{20}O_5AlCl_3$: 401.3), indicating that **10** was monomeric in methanol. None of useful information was obtained in MS analysis. The reactions of **4a** with boron trifluoride etherate, aluminium bromide and indium chloride under the similar conditions gave white precipitates, but on dissolution in methanol they liberated the crown ether. Thus, the following experiments were conducted with use of aluminium chloride. Aluminium chloride adducts of **1**, **5**, **6**, and **8** were again proved to decompose in methanol and **7** did not afford any solid adduct. Although **2** and **3** seem to be favorable ligands than **4a** in terms of their increased basicity of the ether oxygens, the methanol-d_4 solutions of their 1 : 2 adducts showed the NMR spectra coincided with those of the free crown ethers.

Since these experiments led us to the presumption that the ability of forming stable complex with aluminium chloride was limited to benzo-15-crown-5 structure, we proceeded to examine whether the feature was common among substituted benzo-15-crown-5 ethers. The adducts obtained from **4d** and **4e** bearing an electron-withdrawing group were found to liberate the corresponding crown ether in methanol-d_4, even when the amount of aluminium chloride was increased to 10 molar excess taking account of possible donation of the substituent to the halide. **4b** and **4c** with an electron-releasing group gave semi-solid and viscous oil, respectively, in the reaction with 2 equivalents of aluminium chloride. White powders were obtained by evaporation of the solvent, and their NMR spectra in methanol-d_4 demonstrated the formation of the complexes which showed the similar signals to that of **10**. However, attempts to isolate them as crystals failed. The down-field deviation of ^1H signals in the three complexes in the solvent at room temperature are summarized in Table 1. From these data it could be deduced that the aluminium atom in the complexes does not equally interact with the five ether oxygens, but preferentially does with the three located remote from the benzene ring. The deduction is also in line with the less basicity of the phenol ether oxygens than other aliphatic ones.

It is noteworthy that the formation of the crown ether–aluminium chloride complexes which are stable in methanol is limited only to benzo-15-crown-5 and

TABLE 1. THE DOWN-FIELD SHIFTS OF ^1H SIGNALS OF BENZO-15-CROWN-5–ALUMINIUM CHLORIDE IN METHANOL-d_4



R	$\Delta(\delta_{complex}-\delta_{free})$/ppm[a]				
	Aromatic proton	Methylene proton			
		a	b	c	d
H	0.32	0.42	0.62	0.59	0.59
CH_3	0.33	0.43	0.63	0.60	0.60
t-C_4H	0.29 0.31	0.44	0.62	0.59	0.59

a) δ_{free} and $\delta_{complex}$ stand for chemical shifts of free crown ethers and their aluminium chloride complexes, respectively.

those with an electron-releasing group. Moreover, there is no precedent of such peculiar properties among known ether–aluminium chloride adducts (or complexes). The stability of various crown ether complexes with cation is known to be determined principally by the basicity of crown ethers and matching of their cavities with the size of a guest cation. The present results, however, seem to indicate that the similar generalization does not necessarily hold for the aluminium chloride complex, a complex with neutral species, in view of the behaviors that the adducts of **2** and **3** are more susceptible to the decomposition. The presence of the benzo moiety might be one of the reasons for the increased stability of **10** and the complexes of **4b** and **4c**, leading to increased conformational rigidity of the crown ether ring and the resulting steric hindrance toward the attack by methanol.

Experimental

Materials. 12-Crown-4, 15-crown-5, and 18-crown-6 were of commercial origin (Bokusuy Brown Co.). 4′-Acetobenzo-15-crown-5 (mp 94.2—95.4 °C) was obtained by acetylation of **4a** with acetic anhydride in polyphosphoric acid–acetic acid mixture. Other crown ethers were prepared according to the published procedures[4] (lit, 5 for **4d**). Indium chloride (extra pure) was used as received, and other Lewis acids used were purified by the known procedure: sublimation for aluminium chloride and distillation for aluminium bromide and boron trifluoride etherate. Solvents were dehydrated over sodium–potassium alloy and distilled under nitrogen.

General Procedure. The preparations of the adducts and the complex (**10**) were carried out in a closed system and under nitrogen. ^{1}H NMR spectra in methanol-d_4 were recorded using Brucker WH 90 FT spectrometer (90 MHz) at room temperature. The following procedure for the preparation of **9** and **10** was also used in the other combinations of the Lewis acid and the crown ether. To a solution of **4a** (3 mmol) in benzene (6 ml) aluminium chloride (6 mmol) in ether (3 ml) was slowly added. The adduct (**9**) precipitated was collected and thoroughly washed with ether, and dried under vacuum. The treatment of **9** with methanol (or ethanol) gave **10**.

References

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