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INCLUSION COMPLEXES OF A NOVEL HOST, 1,1,2,2-TETRAKIS(4-HYDROXYPHENYL)ETHANE, WITH VARIOUS GUESTS

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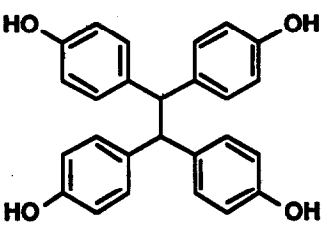
Key Words: Tetrakis(hydroxyphenyl)ethane, host molecule, inclusion, complexation, isolation

Abstract: It is found that 1,1,2,2-tetrakis(4-hydroxyphenyl)ethane, a novel host molecule, forms crystalline inclusion complexes with various n-donors in a definite ratio. Using this complexation, certain guest species are isolated from mixtures.

To date, in order to clarify specific interactive functions between host and guest at a molecular level, various types of organic hosts which form crystalline inclusion complexes with organic guests have been synthesized and studied by many researchers.[1-3] Among them, the host design based on phenolic species as simple building blocks is useful to this end.[4] During the course of our study on inclusion complexes to clarify the relationship between host molecules and their inclusion abilities, we found that 1,1,2,2-tetrakis(4-hydroxyphenyl)ethane (**1**) exhibited highly selective inclusion phenomena toward various n-donors. We describe here in detail the inclusion complexes of compound **1**.



1

Attempts to form the inclusion complexes of **1**[5] were carried out by recrystallization of **1** from various solvents. Compound **1** formed inclusion complexes with n-donors like alcohols, acetonitrile, cyclic ethers, carbonyl compounds, and nitrogen compounds, while it did not form complexes with haloalkanes such as carbon tetrachloride and chloroform or with π-donors like aromatic hydrocarbons. These results are summerized in Table 1 together with the host : guest ratios and infrared spectroscopic data. The results of

infrared spectroscopy showed that the νOH band of **1** (3546 and 3425 cm^{-1}) shifted toward lower frequencies. The bands in the 1745~1700 cm^{-1} region of acetone, ethyl acetate and benzaldehyde also shifted more than 13 cm^{-1} toward lower frequencies. These infrared spectroscopic studies indicate the existence of strong hydrogen bonds between **1** and n-donors that play an important role in forming inclusion complexes of **1**.[6]

Table 1. Molar ratio and IR spectra of the complex with **1**

Guest	Host:Guest molar ratio[a]	IR (cm^{-1})[b]	
		νOH	νCO
methanol	1 : 2		
ethanol	2 : 3[c]		
1-propanol	1 : 1[c]		
2-propanol	1 : 2		
acetonitrile	1 : 2	3350, 3253	
acetone	1 : 2	3363	1689
tetrahydrofuran	2 : 5[c]	3235	
1,4-dioxane	1 : 4	3289	
ethyl acetate	1 : 2	3340	1691
benzaldehyde	1 : 2	3314	1689
diethylamine	1 : 2		
pyridine	1 : 4	3326, 3225	
pyrrole	1 : 2		
carbon tetrachloride	—— [d]		
chloroform	——		
benzene	——		
toluene	——		
m-xylene	——		
p-xylene	——		

a) Determined by NMR integration. b) Measured by KBr disk method.
c) Recrystallized from aqueous solution. d) No complexation.

In order to study the inclusion complex formation of **1**, we carried out Differential Thermal Analysis (DTA) and Thermal Gravimetric Analysis (TGA) on the inclusion complexes of **1**. The thermal analysis was carried out at a ramp rate of 20 °C/min. During the run, nitrogen was passed through the cell at 200 ml/min. The results of the thermal analysis of the 1:2 methanol complex of **1** are shown in Fig. 1. The inclusion complex released the methanol guest molecules in a single step between 74 °C and 133 °C (Peak A on the DTA curve). This corresponds to a weight loss of 14% which is in good agreement with the required stoichiometry. Thereafter, melting of the host compound occurred between 289 °C and 329 °C, giving rise to the sharper B peak on the DTA curve. The thermograms obtained for the other inclusion complexes of **1** were similar to that in Fig. 1.

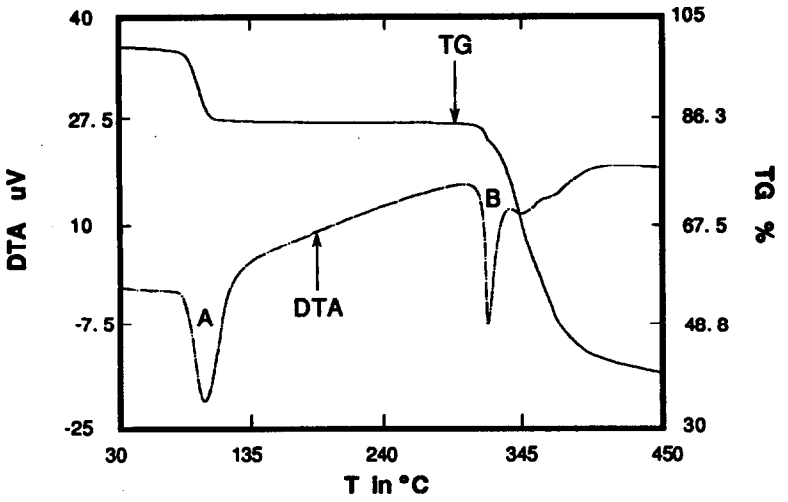


Fig. 1. DTA and TGA thermograms for 1:2 methanol complex of **1**.

Table 2 shows that the complexation with **1** is useful for isolation of certain guest species from mixtures, because **1** selectively combines with one of the components in the mixtures.

Table 2. Selective guest inclusion of **1** from two-component solvent mixtures

Entry	Recrystallization solvent mixture (I / II)[a]	Host : I : II molar ratio[b]
1	acetone / methanol	1 : 2 : 0
2	acetonitrile / methanol	1 : 2 : 0
3	acetonitrile / 2-propanol	1 : 2 : 0
4	pyridine / methanol	1 : 4 : 0
5	pyrrole / methanol	1 : 2 : 0
6	1-propanol / 2-propanol	1 : 0 : 2
7	methanol / ethanol	2 : 1 : 1

a) Equimolar ratio. b) Determined by NMR integration.

For example, **1** was dissolved in a 1:1 mixture of acetone and methanol by heating. The solution was kept at room temperature for 2 h. Colorless crystals of the 1:2 complex of **1** and acetone then gradually separated out. When **1** was dissolved in a 1:1 mixture of methanol and pyridine by heating and the mixture was kept at room temperature for 3 h, a 1:4 complex of **1** and pyridine was formed. Such a highly selective inclusion phenomenon of **1** was observed in combination with potential guests, which differed from each other in functional group characteristics (Entries 1, 2, 3, 4, and 5 in Table 2). Furthermore, in combination with

homologous and different branched compounds such as the solvent mixtures of 1-propanol and 2-propanol, a highly selective inclusion phenomenon of **1** was observed (Entry 6 in Table 2), while in combination with homologous compounds such as the solvent mixtures of methanol and ethanol, **1** did not separate them (Entry 7 in Table 2). This suggests that selectivity during inclusion formation of **1** is due to both chemical and steric interactions between the host and guest molecules.

Since compound **1** consists of two components : (1) aromatic rings that form lattice cavities, and (2) hydroxy groups that manage the coordination of the included guest molecules, it is appropriate to conclude that the molecular structure of **1** plays an important role in forming selectively included complexes and stabilizing them. The mechanistic details, scope and limitation are currently under investigation.

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