

Characterization of Cyclotrimeratrylene Inclusion Compounds by Means of Solid State ^{13}C NMR

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Abstract. Solid inclusion compounds of cyclotrimeratrylene (CTV) with benzene, toluene, acetone, tetrahydrofuran, acetic acid and chloroform, as well as two hydrated forms, were prepared and characterized by solid state ^{13}C NMR. The inclusion process for CTV appears to be quite selective, and in some instance depends critically on the presence or absence of water. A number of different structural types are indicated by the solid state ^{13}C NMR splitting patterns. For the guests listed above, ^1H NMR in solution indicated a guest to host ratio close to 0.5, except for chloroform, for which the ratio is closer to 2.

Key words: cyclotrimeratrylene, ^{13}C NMR magic angle spectra, clathrate, carbon chemical shift.

1. Introduction

Solvates of cyclotrimeratrylene (CTV) were first reported during the Fifties [1, 2], and on the basis of powder diffraction and infrared data it was suggested that these CTV complexes might be clathrates. Only one complete crystal structure is available for CTV complexes (3), that for $\text{CTV} \cdot 0.5 \text{ benzene} \cdot \text{H}_2\text{O}$. In this channel inclusion compound, benzene and water molecules reside in channels lined by four stacks of CTV molecules.

We have used NMR techniques to further investigate guest-host behaviour in CTV complexes. The existence of a guest-host complex can be confirmed by the observation of guest lines in the ^{13}C NMR spectrum by using solid state NMR techniques [4, 5]. Also, often the inclusion process has a pronounced effect on the ^{13}C NMR spectrum of the host lattice e.g. as in the case of the quinol clathrates [4, 6]. From the multiplicity of lines due to carbons normally equivalent in solution, information on the size of the asymmetric unit in the crystal cell can be obtained. Information on the composition of the inclusion complexes can be obtained by analysing the ^1H NMR spectrum of the dissolved material.

2. Experimental

Cyclotrimeratrylene was prepared by the dehydration of veratryl alcohol (3,4-dimethoxybenzyl alcohol) in glacial acetic acid in the presence of sulphuric acid [7].

The trimer was separated from the much less soluble tetramer by recrystallization from acetone, and was characterized by its ^1H NMR and mass spectrum [7–9]. Inclusion compounds were prepared either by slow evaporation or slow cooling of concentrated

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Table I. Carbon and Hydrogen Analyses

Observed		Calculated		Composition
C	H	C	H	
73.35	6.79	73.60	6.79	CTV · $\frac{1}{2}$ benzene
70.71	6.82	70.99	6.95	CTV · $\frac{1}{2}$ benzene · H ₂ O
71.69	6.89	71.58	7.04	CTV · $\frac{1}{2}$ THF
71.18	6.69	71.37	6.94	CTV · $\frac{1}{2}$ acetone
70.96	6.88	71.0	7.02	CTV · $\frac{1}{2}$ ethanol
53.52	5.0	54.37	5.04	CTV · $\frac{1}{2}$ CHCl ₃
70.69 ^a	6.81	69.20	6.88	CTV · H ₂ O
70.82 ^b	6.69	70.56	6.80	CTV · $\frac{1}{2}$ H ₂ O
		71.98	6.71	CTV

^a From toluene by slow evaporation.^b From wet acetic acid.

solutions of CTV. Solid state ¹³C NMR spectra were obtained at a frequency of 50.3 MHz on a Bruker CXP-200 pulsed NMR spectrometer, employing techniques described previously [5]. ¹H and ¹³C NMR spectra for solutions were obtained on Bruker WP-80 and WH-400 NMR spectrometers. Hexamethylbenzene was used as an external reference for the solid state experiments.

Analyses for carbon and hydrogen were performed on a number of the complexes and are given in Table I.

3. Results and Discussion

The solution ¹³C NMR spectrum of CTV is shown in Figure 1a. For the 27 carbons in the CTV molecule, only 5 lines are observed in the spectrum because of the high symmetry of the

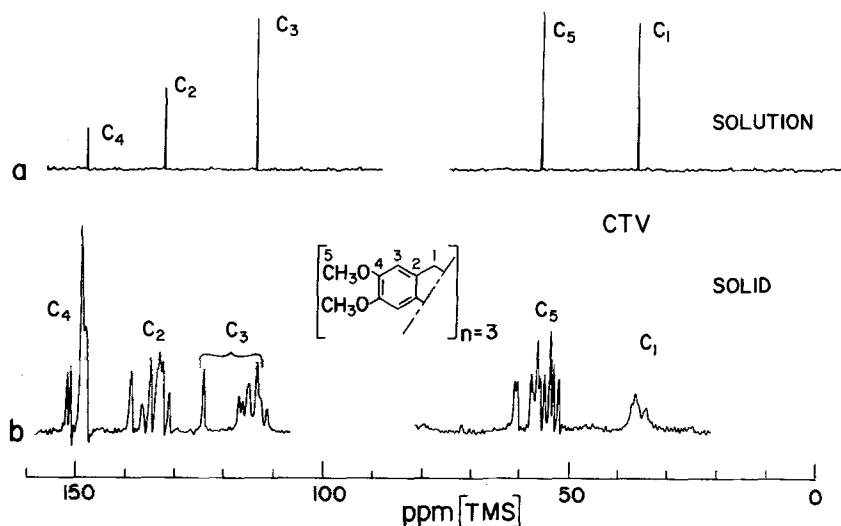


Fig. 1. (a) ¹³C NMR spectrum of CTV in chloroform solution. (b) ¹³C NMR spectrum of recrystallized, dried CTV.

molecule in solution. ^1H NMR results have shown that the molecule exists exclusively in the crown conformation of C_{3v} symmetry [7, 10]. The spectrum of guest-free CTV, obtained by recrystallization from acetone and drying at 150°C , (Figure 1b), shows multiples of lines, so that evidently in the solid the molecule has lost its high symmetry. For a completely asymmetric molecule, the lines for carbons 2, 3, 4 and 5 should be split into multiplets of 6 and the carbon 1 line should be a triplet. However, if we closely examine the methyl carbon resonance (C_5), 12 lines can be identified, so that the crystal contains 12 distinct methyl groups, and there must, therefore, be two molecules per asymmetric unit.

The spectrum shown in Figure 2a was obtained for the solid resulting from the slow cooling of a concentrated hot solution of CTV in dry benzene. A strong signal at 127 ppm reveals the presence of included benzene. On examining the splitting of the ^{13}C NMR lines, a multiplicity of twelve seems to be indicated so that the asymmetric unit must again consist of two molecules. This means that the inclusion compound is different from that for which a structure was reported [3], as the latter has only a single molecule per asymmetric unit. ^1H NMR of the dissolved material showed that benzene was the only guest material present, water being absent.

When a concentrated solution of CTV in benzene was allowed to evaporate slowly in air, with no attempts to exclude moisture, the well-formed crystals which resulted gave the spectrum shown in Figure 2b. Again there is a line due to included benzene, now at 129 ppm. The multiplicity of the C_3 , C_4 and C_5 lines is now more in keeping with there being one molecule per asymmetric unit. The ^1H NMR spectrum of the dissolved complex confirms the presence of water and benzene, so that this material most likely is the $\text{CTV} \cdot 0.5 \text{ benzene} \cdot \text{H}_2\text{O}$ complex for which the structure was reported [3]. It should be noted that this complex can also be prepared by stirring a solution of CTV in benzene together with water. The hydrated complex is insoluble in benzene and redissolves in benzene only after extensive heating. Presumably water must be driven off before dissolution can take place.

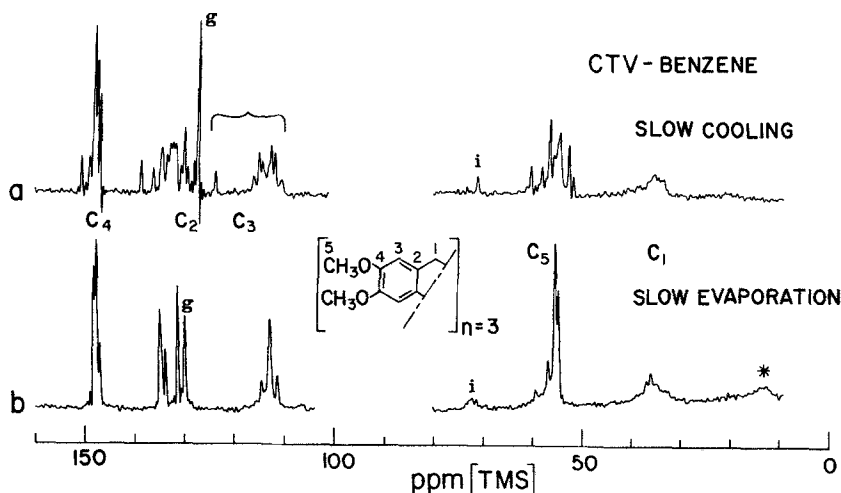


Fig. 2. (a) ^{13}C NMR spectrum of the solid CTV-benzene inclusion compound obtained by slow cooling of a hot concentrated solution. (b) ^{13}C NMR spectrum of solid CTV-benzene-water inclusion compound obtained by slow evaporation of a benzene solution; g marks guest molecule resonance, i marks impurity.

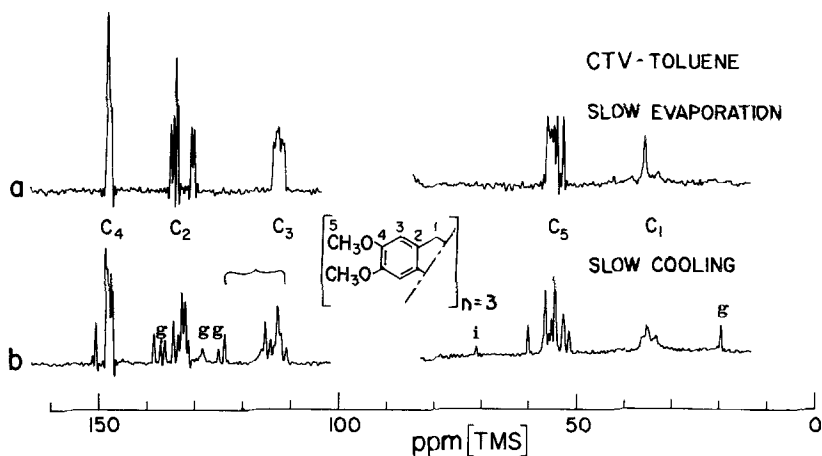


Fig. 3. (a) ^{13}C NMR spectrum of solid hydrated CTV obtained by evaporation of toluene solution. (b) ^{13}C NMR spectrum of solid CTV-toluene inclusion compound obtained by slow cooling of a hot concentrated toluene solution; g marks guest resonances, i marks impurity.

In order to see if this type of behaviour was more general, toluene was substituted for benzene. The spectrum shown in Figure 3b was obtained for the compound obtained by slow cooling of a hot, concentrated toluene solution of CTV. The lines due to guest toluene are clearly visible, so that the material is indeed an inclusion compound. Also, there is considerable similarity of the CTV host lattice spectrum with that obtained for the anhydrous benzene compound, so that again there probably are two CTV molecules per asymmetric unit.

On leaving a toluene solution of CTV to evaporate in air, the crystals obtained yielded the spectrum shown in Figure 3a. The CTV C_2 and C_5 lines clearly show a multiplicity of six so that in this case there is only one molecule per asymmetric unit. Note that there is no evidence of included toluene in this instance. This was confirmed by ^1H NMR of the dissolved material, which showed that only water was present as guest material.

When acetic acid was used as the crystallizing solvent, again distinct materials were obtained depending on whether the acetic acid was anhydrous or not. In the case of anhydrous acetic acid, the acid molecule was found to be the only guest. In the case of wet acetic acid, a hydrated complex resulted, with water as the only guest. This hydrated complex yielded a different ^{13}C NMR spectrum from that obtained for the hydrate from toluene, so that the two hydrates must have different structures.

On the other hand, when THF was the solvent, the inclusion compound obtained contained only THF, regardless of the dryness of the solvent. The solid state ^{13}C NMR spectrum of this material resembled those obtained for the anhydrous benzene and toluene inclusion compounds.

The CTV-acetone inclusion compound gave the nicely resolved spectrum shown in Figure 4b. The multiplicity of the lines is six, so that there is only one molecule per unit cell. A second CTV-acetone preparation, containing slightly less acetone, gave the spectrum shown in Figure 4a. Note that most of the lines are slightly broader, and that several new lines are apparent. It is likely that these spectral differences reflect relaxation of the CTV host lattice around vacant guest sites. A compound with a sufficient number of vacancies in the channel could well give a spectrum very different in appearance from that for the compound with completely filled channels.

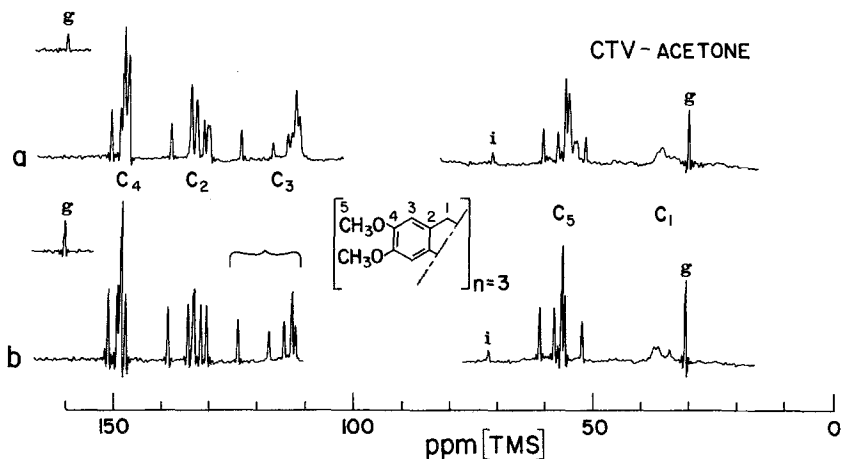


Fig. 4. (a) ^{13}C NMR spectrum of solid CTV-acetone inclusion compound. (b) same as (a), with lower acetone content; g marks guest resonances, i marks impurity.

CTV is not very soluble in ethanol, so that in an attempt to make an ethanol inclusion, CTV was recrystallized from a benzene-ethanol mixture. The spectrum for the inclusion compound which resulted shows that only ethanol is included as guest (Figure 5b). Again the CTV host lattice spectrum resembles those obtained for the benzene, toluene and THF inclusion compounds.

As a final example of a CTV inclusion compound spectrum, Figure 5a shows that obtained for the chloroform compound. The multiplicity of six for the C₂ carbon suggests that there is one molecule per asymmetric unit. The chloroform carbon line is unusually broad, and probably reflects partially averaged carbon-chlorine dipolar coupling.

Table II lists the CTV complexes identified, including the preparative method, approximate composition and the number of CTV molecules per asymmetric unit in the unit cell. Except

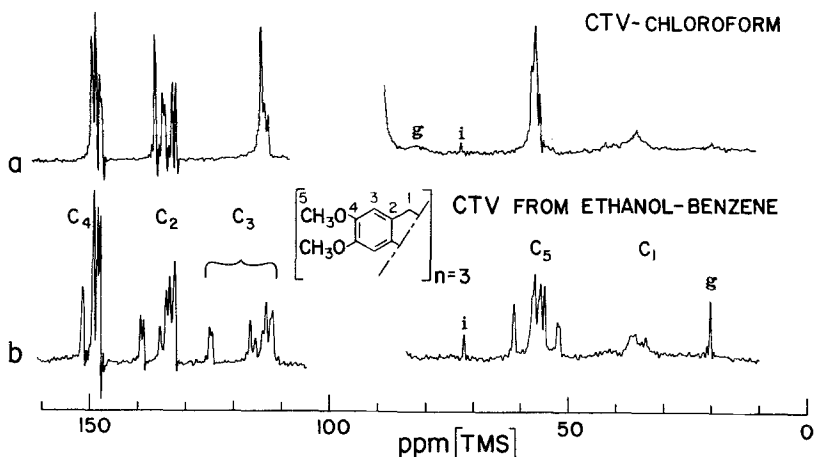


Fig. 5. (a) ^{13}C NMR spectrum of solid CTV-chloroform inclusion compound. (b) ^{13}C NMR spectrum of solid CTV-ethanol inclusion compound; g marks guest resonances, i marks impurity.

Table II. Cyclotrimeratrylene Inclusion Compounds

Solvent and technique ^a		Guest(s)	Host : guest Ratio	Mols/Asym. unit
Benzene	E	Benzene, H ₂ O	1 : 0.47 : 0.8	1
Benzene	SC	Benzene	1 : 0.59	2
Toluene	E	H ₂ O	1 : 0.35	1
Toluene	SC	Toluene	1 : 0.47	2
Acetic acid (dry)	SC	Acetic acid	—	1
Acetic acid (wet)	SC	H ₂ O	1 : 0.73	1
EtOH/Benzene	SC	EtOH	1 : 0.41	2
THF (wet or dry)	SC	THF	1 : 0.45	1
Acetone	E	Acetone	1 : 0.42	1
CHCl ₃	E	CHCl ₃	1 : 2.1	1

^a E = evaporation. SC = slow cooling.

for the CHCl₃ inclusion compound, and the complexes containing only water, the guest-host ratio is close to 0.5, as found in the X-ray study on the CTV-benzene-water inclusion compound. Analyses for carbon and hydrogen, given in Table I are in general agreement with this, although, because of the high host molecular weight, and low guest molecular weights, accurate compositions cannot be expected. The chloroform inclusion compound appears to be unique in that a guest-host ratio of ~1.5–2 is indicated. For the hydrated species, compositions not too far from half a water molecule per CTV host are indicated.

In general, the composition of the CTV complexes is not easily determined as many of the complexes are unstable, slowly losing guest material on standing. Hence, more complete composition studies are required.

The inclusion process for CTV is very selective. Table III lists the preferred guests in a number of cases where a choice of guest molecules was possible. Except in the case of THF, the preferred guest was always water where it was one of the possible guest materials. Therefore it is evident that polar guest molecules are preferred over non-polar ones, and guest molecules must play more than just a spacefilling role, as they do, for instance, in quinol and water clathrates.

From the solid state ¹³C NMR spectra, the anhydrous inclusion compounds of benzene, toluene, THF, and ethanol, as well as guest-free CTV, appear to have closely related structures. The spectra for the above materials as well as the acetone inclusion compound have an interesting spectral feature in common, namely the large splitting of the C₃ carbon line. The bulk of the multiplet occurs at 113 ± 5 ppm, yet one component appears consistently

Table III. Selectivity of inclusion process for CTV

Available guests	Preferred guest(s)
Benzene, Water	Benzene, Water
Toluene, Water	Water
Acetic Acid, Water	Water
Ethanol, Water	Water
Ethanol, Benzene	Ethanol
THF, Water	THF

at ~ 123 ppm. (This line was assigned as belonging to C_3 using the dipolar dephasing technique [11].) This has implications with regards to the detailed structure of the CTV molecules in the solid. More structural information is needed in order to correlate ^{13}C NMR chemical shift patterns with structural features, so that eventually it may be possible to assign structures on the basis of the solid state NMR spectrum.

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