

NMR Investigations on Supramolecular Assemblies of $[\text{Ru}(\text{bpy})_2\text{Cl}(\text{bpeb})]^+$ and β -Cyclodextrins: Aggregated Array and Inclusion Compound

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Abstract: In this work we are reporting the multi-assembly of the complex $[\text{Ru}(\text{bpy})_2\text{Cl}(\text{bpeb})]\text{Cl}$ (bpeb = *trans*-1,4-bis[2-(4-pyridyl)ethenyl]-benzene), which in D_2O solution forms either an aggregate held by π - π stacking interactions or an inclusion complex (host-guest). The latter is more stable than the stacked one, obtained by the addition of β -cyclodextrins (β -CD) to the aggregated ruthenium complex in solution. The aggregated array was investigated by variable temperature NMR, showing the breakage of this structure as temperature increased. Host-Guest interaction could be obtained by the addition of β -CD to the aggregated species. The novel inclusion compound was detected by NOESY experiments, showing correlation between internal protons (H_5 and H_3) of the β -CD and protons of the bpeb ligand.

Supramolecular self-assembled species may be achieved by means of the association of two or more molecular entities through weak interaction such as electrostatic forces, hydrogen bonding or van der Waals interactions, constituting examples of molecular recognition. The nature of host – host, host – solvent and host - guest interactions are the most important factor to understand the driving force to the formation of cyclodextrins (CD) inclusion compounds. Thus, NMR spectroscopy provides a powerful tool to characterise these noncovalent associations in solution.¹ In this work we are reporting the multi-assembly of the complex $[\text{Ru}(\text{bpy})_2\text{Cl}(\text{bpeb})]\text{Cl}$ (bpeb = *trans*-1,4-bis[2-(4-pyridyl)ethenyl]-benzene) which in D_2O solution forms either an aggregate held by π - π stacking interactions or an inclusion complex (host-guest). The latter is more stable than the stacked one, obtained by the addition of β -

cyclodextrins to the aggregated ruthenium complex in solution.

NMR experiments were recorded on a DRX 500MHz Bruker spectrometer, except the ^1H spectra used to construct the Job plots,² which were carried out in a INOVA1 300MHz Varian spectrometer. The signals of the $[\text{Ru}(\text{bpy})_2\text{Cl}(\text{bpeb})]^+$ complex were fully assigned based on NMR experiments, such as 1D ^1H and ^{13}C NMR, 2D ^1H - ^1H COSY and ^1H - ^{13}C HMQC in acetone [d_6] 10 mmol dm^{-3} solution as well as in D_2O solutions. Also, on results previously reported.³ The studies focusing on aggregation and inclusion phenomena were carried out in D_2O with solution concentrations ranging from 1 to 10 mmol dm^{-3} by means of ^1H NMR spectra acquisition in different temperatures and NOESY experiments.

In a 10 mmol dm⁻³ D₂O solution, [Ru(bpy)₂Cl(bpeb)]⁺ shows broad hydrogens signals. Nevertheless, the spectrum changes drastically as a function of temperature, as can be seen in Figure 1 (left). All aromatic protons signals undergo a narrowing with increasing temperature and the spectrum becomes resolved. These observations are consistent with the presence of a supramolecular aggregate formed due to the alternated π - π

stacking of complex [Ru(bpy)₂Cl(bpeb)]⁺, driven by hydrophobic interactions from the unsaturated and planar bpeb ligand. The rise of temperature and a dilution of the solution causes this aggregate to collapse, resulting in spectrum 1a. Accordingly, the addition of increasing amounts of β -cyclodextrins to D₂O solutions of [Ru(bpy)₂Cl(bpeb)]⁺ also resolves the ¹H NMR spectra, reflecting the breakage of the aggregated species (Figure 1, center).

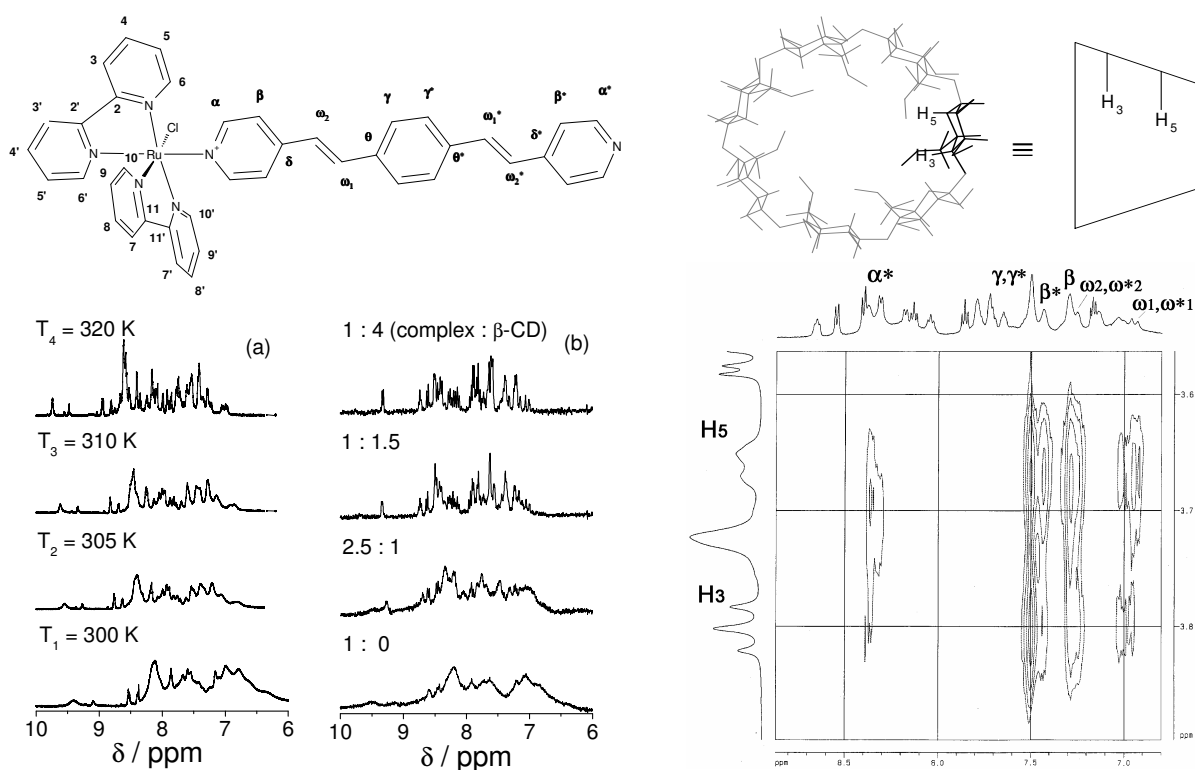


Figure 1. (a) temperature dependence of the ¹H NMR spectra , (b) β -CD titration of the ¹H NMR spectra and (c) NOESY of the inclusion compound.

It is reasonably to assign the observed effect to the formation of an inclusion compound, when we consider that the double

bonds of the bpeb ligand constitute a recognition site for hydrophobic interaction into the β -cyclodextrin cavity. It is thus is

reasonable to assign the observed effect to the formation of an inclusion compound. In fact, the NOESY spectrum (Figure 1 right) shows correlations between the inner protons H₃ and H₅ of the β-CD cavity with both, the aromatic protons α*, β, β*, γ, γ* and the double bonds protons ω₁, ω₁*, ω₂, ω₂*. The observed multiple correlation pattern might be attributed to the existence of a mixture of inclusion compounds, presumably the 1 : 1 and 1 : 2 complex : β-CD and of conformational isomers. To test the presence of more than one inclusion compound, Job plots were constructed based on the variations of δ values for either the bpeb or the H₃ and H₅ β-CD protons for the bpeb : β-CD and complex : β

-CD inclusion compounds. In all cases, we obtained plots slightly distorted, displaying maximum values between 0.5 and 0.6, which corresponds to 1 : 1 and 1 : 2 stoichiometries.²

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