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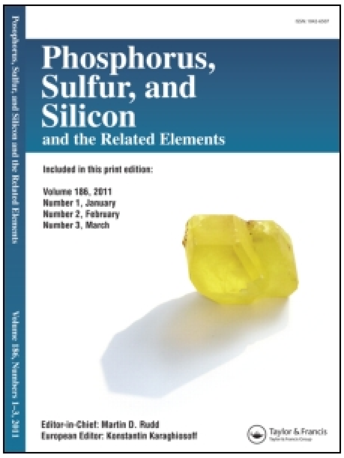

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Supramolecular Assemblies of Phosphorylated Cavitands

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SUPRAMOLECULAR ASSEMBLIES OF PHOSPHORYLATED CAVITANDS

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The recent results in the chemistry of cavitands have proved that they are very efficient molecular receptors and potential precursors of molecular devices. In this context, we have investigated the synthesis and binding properties of phosphorylated cavitands. The stereoselective synthesis and the structural studies of the new compounds showed that these bowl-shaped molecules possess a well defined aromatic cavity surrounded by four phosphoryl groups (P=O or P=S). They are very efficient ligands for metal and organic cations. They are able to encapsulate cationic species by cooperative effect of the preorganized aromatic cavity and the four phosphorylated groups. Moreover, the upper and lower rim functionalitics can lead to the formation of molecular capsules and supramolecular assemblies whose properties and structures have been investigated by X-ray diffraction and NMR studies in solution.

Keywords: Cation complexation; cavitands; phosphorus ligands; supramolecular chemistry

INTRODUCTION

The cavitands were first synthesized from resorc[4]arenes by D. J. Cram in the early 1980s and have been suitably substituted at their upper or lower rim to give a new family of molecular containers.[1] The bowl shape molecules possess a rigid structure with an aromatic cavity defined by four resorcinol moieties. The ring closure reaction that leads to the preorganized ligands could be achieved using various reagents, and the

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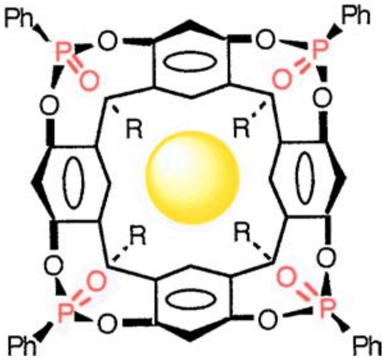

FIGURE 1 Tetraphosphonatocavitand.

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use of phosphorus groups allowed the formation of phosphocavitands containing four P(III)[2] or P(IV)[3] phosphorus binding sites (Figure 1). We recently reported about the synthesis and binding properties of tetraphosphonatocavitands bearing four P(O)Ph groups, which exhibited interesting complexing properties towards metal ions and ammonium cations.[4]

The results presented herein feature the possibilities for the phosphocavitands and their complexes to form supramolecular assemblies.

SYNTHESIS OF PHOSPHORYLATED CAVITANDS

The molecules are mainly obtained as their *iiii* stereoisomer with the four P=O oxygen atoms directed toward the center of the aromatic cavity. The quasi-exclusive formation of this isomer is attributed to the effect of the solvent/amine pair used during the reaction. When the reaction is run in a low-donating solvent, the *iiii* configuration is predominant. In a more polar solvent like acetone, a mixture of isomers is generally obtained as a result of a dramatic lack of selectivity, and no *iiii* derivatives were detected.

In toluene, the *all in* (*iiii*) structure is favored by a template effect involving the ammonium salt formed during the reaction. An average yield of 50% is obtained whatever are the R substituents at the lower rim of the cavitand.

ASSEMBLY OF PHOSPHORYLATED CAVITANDS THROUGH CATION COMPLEXATION

The powerful binding properties of the phosphorylayed cavitands towards ammonium cations were used to encapsulate the paraquat

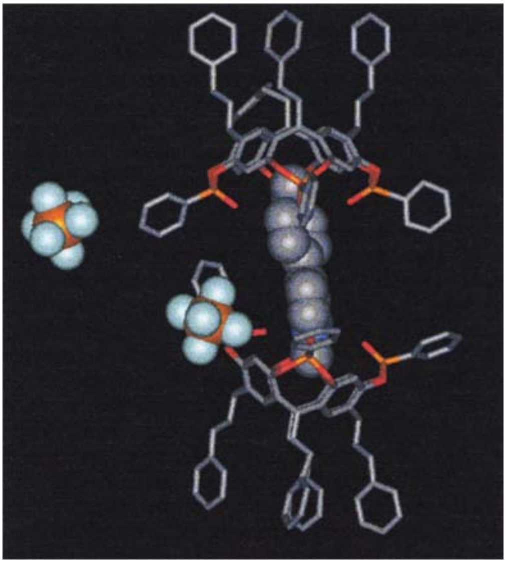

FIGURE 2 X-ray structure of the (P-cavitand)$_2$·paraquat(PF$_6$)$_2$ complex.

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dication. The X-ray structure of the complex showed that the 2:1 complex is formed (Figure 2). The complex is stable in solution and the NMR data are consistent with the formation of the 2:1 complex. The complex is stable in solution and an upfield shift of 3.8 ppm is observed for the signal of the methyl protons of the bis-pyridinium guest.

THIOPHOSPHORYLATED CAVITANDS: FORMATION OF A NANOSCALE MOLECULAR CAPSULE

The sulfur analog of the phosphocavitand was synthesized in its *iiii* configuration with the four P=S bonds oriented inwards. This new ligand exhibited quantitative extraction of Ag^+ ion from water to organic solution.^{5} In presence of an excess of silver ions, the new supramolecular complex [(PS-cavitand)$_2$·Ag$_4$Pic$_4$] was formed and isolated as a crystalline compound whose molecular structure is depicted in Figure 3.

The supramolecular assembly is stable in solution and forms a molecular capsule with empty space large enough to trap small guests. Further studies are in progress to isolate and characterize such complexes.

The phosphorylated cavitands in their *iiii* configuration are now easily accessible by a simple route from resorc[4]arene. Novel supramolecular architectures were obtained by complexation of cationic guests. Besides their evident esthetical aspect, the new complexes are of

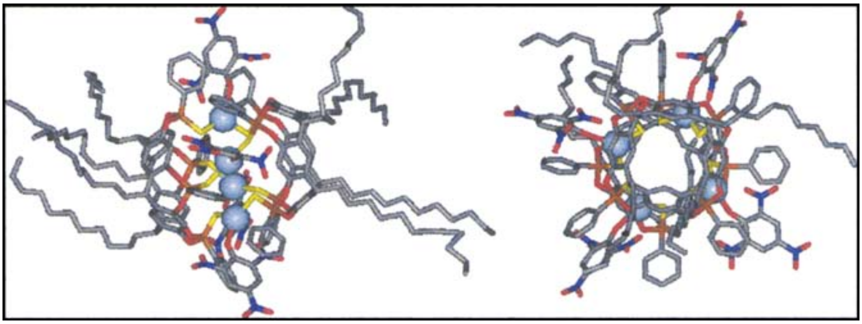

FIGURE 3 X-ray structure of the [(PS-cavitand)$_2$·Ag$_4$Pic$_4$] complex.

considerable interest as possible precursors for the design of new molecular devices, featuring further applications.

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