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A new supramolecular assembly obtained from the combination of silver(I) cations with a thiophosphorylated cavitand

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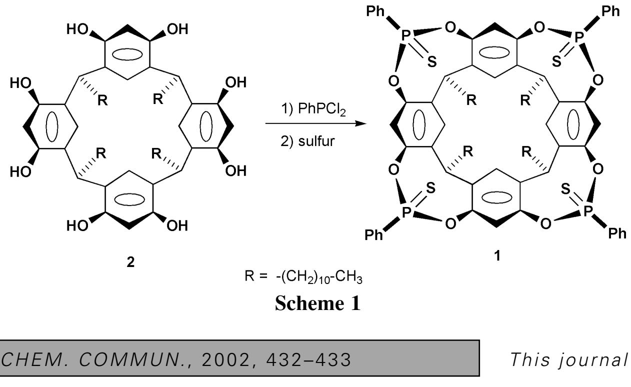
The new tetra-thiophosphonatocavitand 1 in its *iiii* configuration extracts quantitatively Ag$^+$ ions from aqueous solutions; the tetranuclear complex [1_2·Ag_4Pic_4] was selectively formed and characterized in the solid state by X-ray diffraction which revealed the formation of a new dimeric assembly through Ag$^+$ coordination.

Supramolecular assemblies obtained by self-association of molecular precursors have recently emerged as promising hosts for molecular recognition and are probably one of the best approaches to generate new materials in the fields of supramolecular catalysis and chemical sensors. In this way, giant molecular receptors offer the possibility to encapsulate one large guest or several guests within the confined room of a molecular chamber. Their host–guest properties will then depend on the size and nature of the inner space.[1] The formation of large synthetic molecular receptors arises essentially from the (self)association of well defined molecular hosts. For this purpose, the calixarenes and the resorcinol-based cavitands are very efficient building blocks.[1,2] Such assemblies can be achieved by the rim-to-rim covalent or non-covalent association of two cavitands. Among the different strategies involving non-covalent association, H-bonding[3] and self-assembly *via* metal ion coordination[4] are particularly attractive.

Recently we have demonstrated that phosphorylated cavitands, which combine an aromatic lipophilic cavity with four phosphorylated binding sites at the upper rim, are powerful ligands for cationic guests.[5] While P(O) derivatives bind efficiently hard cationic species, we could expect different and interesting properties for the P(S) derivatives towards soft metal cations. We thus disclose herein our first results on the preparation and binding properties of the thiophosphorylated cavitand **1**. The new dimeric structure that resulted from the self-assembly of **1** and silver cations is described and characterized by X-ray crystallography.

The first thiophosphorylated cavitands have been synthesized by Nifant'ev *et al.* from resorcinarene and $P(NMe_2)_3$ or $P(NEt_2)_3$ followed by addition of sulfur.[6] A modified route was used for the preparation of **1** as shown in Scheme 1. Resorcinarene **2** was obtained following the published procedure.[7] Reaction of **2** with $PhPCl_2$ in diethyl ether in the presence of pyridine afforded exclusively the tetra-phosphonitocavitand.[8] Its subsequent *in situ* oxidation with sulfur proceeded with retention of configuration at phosphorus, and led to the tetra-thiophosphonatocavitand **1** in 52% yield after column chromatography on silica gel.† The *iiii* stereoisomer with the four P=S bonds oriented inwards was selectively obtained and its structure was ascertained by NMR and mass spectrometry, and confirmed by an X-ray structure analysis.[9] This stereoselective synthesis is of prime importance as multicomponent mixtures are often obtained during the ring closure reactions of resorcinarenes with phosphorus reagents.[10]



Scheme 1

The ionophoric properties of **1** toward soft metal cations were evaluated by using the picrate extraction method.[11] Metal ions such as Ag$^+$ (91%), Tl$^+$ (38%) and Hg^{2+} (16%) were extracted efficiently with a maximum for Ag$^+$; Cd^{2+} and Pb^{2+} were not extracted. The better extractability of **1** toward silver(I) cation was attributed to the latter's high affinity for sulfur. By adding increasing quantities of silver picrate (AgPic) to an acetone solution of **1**, a downfield shift of the ^{31}P NMR resonance was observed ($\Delta\delta \approx 4$ ppm) corresponding to a fast exchange process on the NMR time scale between free and complexed **1** (Fig. 1). For an approximate guest to host ratio $G/H \geqslant 1$ a second signal appeared at δ 83.8 corresponding to a new complex which slowly precipitated from the solution. This new species was then recovered by filtration to give a quantitative yield of a 2:4 complex of formula $\mathbf{1}_2$·$(AgPic)_4$. A similar evolution of the ^{1}H NMR spectrum was observed and confirmed the formation of the new compound. This behaviour was also observed in $CHCl_3$ solution, where two equivalents of silver picrate were dissolved in presence of host **1**.

The X-ray crystal structure of the $\mathbf{1}_2$·$(AgPic)_4$ complex showed a supramolecular assembly made of two cavitands linked by their upper rim with four silver cations through P=S···Ag···S=P coordination (Fig. 2).‡ As expected cavitand **1** has the *iiii* configuration with the four P=S bonds oriented inwards.

The Ag$^+$ cations adopt a distorted tetrahedral geometry and are coordinated to two sulfur atoms of different cavitands with Ag–S distances in the range 2.470(1)–2.500(1) Å. There exist additional strong interactions with the phenolate oxygen

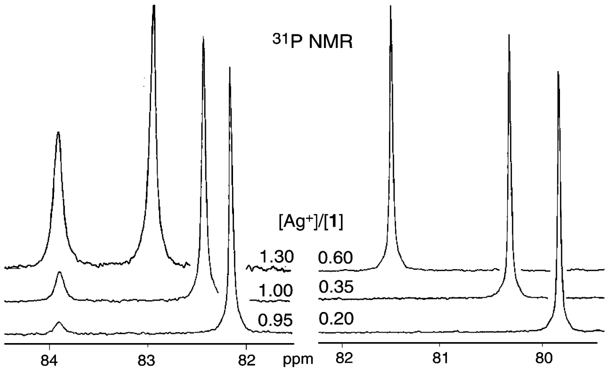


Fig. 1 ^{31}P NMR spectral changes of **1** with successive addition of silver(I) picrate in acetone-d_6 (300 K).

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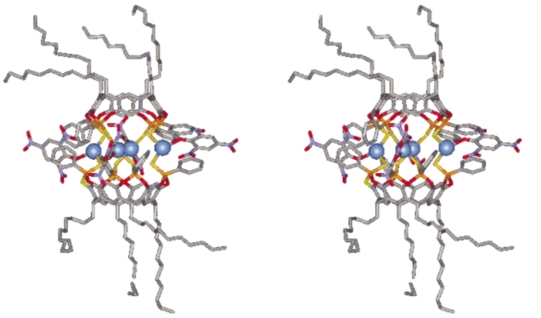

Fig. 2 Stereoview of the X-ray crystal structure of $\mathbf{1}_2$·(AgPic)$_4$. Hydrogen atoms and solvent molecules are omitted for clarity.

(average Ag–O distance 2.32 Å), and the oxygen of one *o*-nitro group of the picrate anion (average Ag–O distance 2.56 Å) (Fig. 3).

Efficient π-stacking of the P-phenyl groups with the picrate anions stabilises the supramolecular complex and favours the formation of the dimeric structure. The top view of the molecule (Fig. 4) shows the arrangement of the two cavitands aligned along their common C_4 axis and offset by about 45°, leading to a helical structure.

The $\mathbf{1}_2$·(AgPic)$_4$ complex crystallises with four molecules of acetone which do not establish specific interactions with the complex. It is noteworthy that no solvent or guest is present inside the molecular cavity. The internal volume of the capsule is defined by the two aromatic hemispheres separated by the P–S–Ag$^+$–S–P fragments in the *anti,anti* conformation. The inner space is reduced by the occupancy of the sulfur atoms, and there is probably just enough room to accommodate small guests in the two independent chambers defined by the aromatic cavities.

In summary, the stereoselective synthesis of the *iiii* stereoisomer of the thiophosphorylated cavitand **1** has been presented. The affinity of the new ligand towards soft metal ions was demonstrated with a particular selectivity for silver(I). Thus, we were able to generate the supramolecular complex $\mathbf{1}_2$·(AgPic)$_4$, stabilised through metal coordination and π-interactions, and characterised in solution and in the solid state. The properties of this new supramolecular assembly and other related systems are presently being pursued.

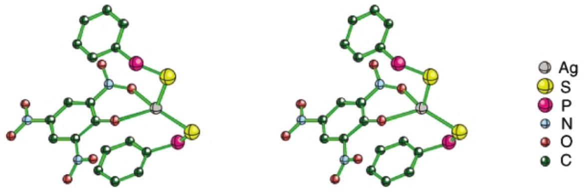

Fig. 3 Stereoview of the local coordination environment of the Ag$^+$ ions in $\mathbf{1}_2$·(AgPic)$_4$. Selected bond distances (Å): Ag(1)–O(810) 2.530(3), Ag(1)–O(807) 2.343(2), Ag(1)–S(41) 2.491(1), Ag(1)–S(241) 2.496(1), Ag(2)–O(609) 2.537(3), Ag(2)–O(607) 2.336(2), Ag(2)–S(42) 2.479(1), Ag(2)–S(242) 2.470(1), Ag(3)–O(707) 2.292(3), Ag(3)–O(716) 2.573(3), Ag(3)–S(43) 2.500(1), Ag(3)–S(243) 2.498(1), Ag(4)–O(507) 2.317(2), Ag(4)–O(516) 2.583(3), Ag(4)–S(44) 2.487(1), Ag(4)–S(244) 2.473(1).

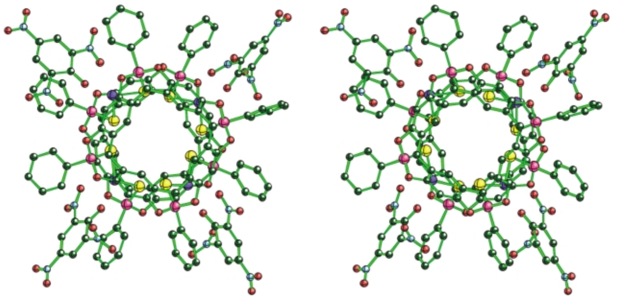

Fig. 4 Top stereoview of $\mathbf{1}_2$·(AgPic)$_4$. Hydrogen atoms and long chain substituents are omitted for clarity.

Notes and references

† Compound **1** gave mass spectrometric and elemental analytical data consistent with its structure. *Selected data* for **1**: mp 216 °C; δ_P(CDCl$_3$) 80.03. δ_H(CDCl$_3$) 0.86 (t, ^3J 6.5, 12H, CH$_3$), 1.25–1.47 (m, 72H, CH$_2$), 2.35 (m, 8H, CH$_2$), 4.78 (t, ^3J 7, CH), 6.97 (t, ^4J 2, ArH), 7.31 (s, 4H, ArH), 7.50 (m, 8H, P–ArH), 7.60 (t, ^3J 7, 4H, P–ArH), 8.03 (dd, ^3J 8, ^3J 14.5, 8H, P–ArH). δ_C(CDCl$_3$) 14.10 (CH$_3$), 22.68, 28.03, 29.40, 29.72, 31.26, 31.94 (CH$_2$), 36.05 (CH), 120.05, 122.12 (ArC), 128.23, (^3J 16, P–ArC), 131.09 (^2J 12.2, P–ArC), 131.96 (^1J 162.2, P–ArC), 132.61 (P–ArC), 135.03 (ArC), 146.47 (^2J 12.2, ArC).

‡ *Crystal data* for $\mathbf{1}_2$·(AgPic)$_4$(Me$_2$CO)$_4$: $C_{228}H_{280}Ag_4N_{12}O_{48}P_8S_8$, M = 4892.35, triclinic, space group $P\bar{1}$, a = 23.095(9), b = 23.507(9), c = 24.193(9) Å, α = 67.75(2), β = 74.05(2), γ = 83.99(2)°, V = 11688(8) Å^3, T = 100 K, Z = 2, D_c = 1.390 Mg m^{-3}, $F(000)$ = 5096, μ(Mo-Kα) = 0.533 mm^{-1}. Reflections collected/unique = 295890/44486 (R_{int} = 0.051), parameters: 2978, final R_1 = 0.0568, wR_2 = 0.1614 (all data), GoF = 1.02, max/min residual electron density 1.41/−0.97 e Å^{-3}, solution and refinement using SHELXL 97.[12] CCDC reference number 173834. See: http://www.rsc.org/suppdata/cc/b1/b110698h/ for crystallographic data in CIF or other electronic format.

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