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Tetrahedron 59 (2003) 5849–5854

TETRAHEDRON

Thiophosphorylated cavitand: structure and affinity towards soft metal ions

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Received 23 January 2003; revised 27 May 2003; accepted 16 June 2003

Abstract—The *iiii* stereoisomer of the tetrathiophosphonate-calix[4]resorcinarene host **1** exhibited excellent extraction properties towards soft metal ions, with a better affinity for Ag^+ (91%), than for Tl^+ (38%) and Hg^{2+} (16%). The extraction of other picrate salts (Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}) was not detected. The stoichiometry and the structure of the Hg^{2+}, Tl^+ and Ag^+ complexes were studied by NMR in solution and gave respectively 1:1, 1:1 and 1:2 host–guest complexes. The formation of the self-assembled $\mathbf{1}_2{\cdot}(AgPic)_4$ complex was independent on the anion and only observed with silver(I) ion.

1. Introduction

The phosphorylated cavitands, which combine an aromatic lipophilic cavity with phosphorylated binding sites, are particularly good ligands for metal and ammonium cations. While phosphonate P(O) derivatives have proved to be efficient extractants for hard cationic species,[1] different and interesting properties are expected for the thio-phosphonate P(S) derivatives towards soft metal cations. The P=S thiophosphoryl group was attached to the resorc[4]arene skeleton to produce the thiophosphorylated cavitand **1** by using a two-step synthesis, which allowed mainly the formation of the [*iiii*] stereoisomer with the four P=S bonds oriented towards the molecular cavity. This was not expected since six stereoisomers can be formed depending on the inward or outward orientation of the P=S groups. The formation of the [*iiii*] isomer is particularly important to favor the formation of intracavity complexes with metal ions. The affinity of this molecular host for Ag^+ and its ability to generate dimeric species in acetone solution by metal coordination has been previously reported.[2] From ^1H and ^{31}P NMR titration experiments, we have shown that cavitand **1** extracted quantitatively Ag^+ ions from water to organic solution, and in presence of an excess of silver picrate in acetone, the $\mathbf{1}_2{\cdot}(AgPic)_4$ complex was spontaneously obtained. An X-ray structure analysis revealed that the dimeric structure was stabilized through metal ion coordination and efficient π-stacking interactions of the P-phenyl groups with the picrate anions. It was thus interesting to explore the possibilities of **1** to complex other cations of environmental interest like mercury and lead. We report here the structural features of cavitand **1** and its affinity for other metal ions like Tl^+ and Hg^{2+} in solution. They formed 1:1 complexes, and exhibited a general behavior different from that of the Ag^+ cation. Furthermore, we will show that the formation in solution of the $\mathbf{1}_2{\cdot}(AgPic)_4$ structure was not essentially due to π–π interactions and did not depend on the anion.

2. Results and discussion

2.1. Synthesis of host 1

Cavitand **1** was synthesized from the previously reported tetraphosphonitocavitand **3**, obtained by reacting resorc[4]-arene **2**[3] with dichlorophenylphosphine.[4] Thiophosphato-cavitands were previously obtained by reaction of the parent phosphite compounds with sulfur. This reaction proceeded with the same stereoselectivity on the four phosphorus atoms to yield the [*iiii*] stereoisomer.[5] In the same way, the addition of sulfur to a solution of **3** led to the formation of cavitand **1** in 52% yield after chromatography. The stereochemistry of host **1** was established from the ^1H, ^{13}C and ^{31}P NMR spectra, which revealed a C_{4v} molecular symmetry,[2] and its solid state structure determination undoubtedly proved the [*iiii*] configuration (Scheme 1).

Keywords: cavitand; thiophosphorylated ligand; complexation; supramolecular chemistry; X-ray structure.

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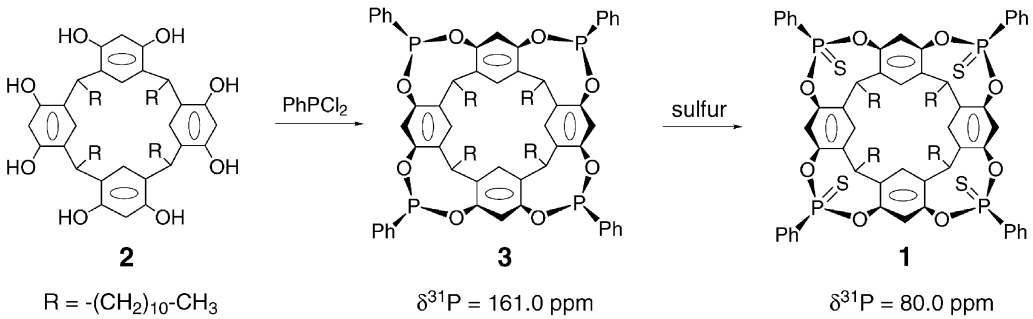
doi:10.1016/S0040-4020(03)00946-3



Scheme 1.

2.2. Crystal structure of the thiophosphonatocavitand 1

The X-ray crystal structure of cavitand **1** was obtained from a crystal grown from a dichloromethane/acetonitrile mixture. The host has the [*iiii*] configuration with the four P═S bonds oriented toward the molecular cavity and possesses an approximate C_{4v} symmetry (Fig. 1). The four aromatic cycles defining the cavity have about the same angle of inclination to the plane perpendicular to the C_4 axis of the molecule (56.7°±1.2).

The P═S bond lengths, mean value 1.908(1) Å, are significantly shorter than in the $\mathbf{1}_2$·$(AgPic)_4$ complex for which a mean value of 1.946(1) Å was observed. The four fused eight membered-rings adopt the boat–chair conformation as defined by the values of the endocyclic torsion angles (average values are 85, −5, −88, 88, 5, −85, 83 and −83°).[6] The P═S bonds and the phenyl substituents are in the axial and equatorial positions, respectively. The P-phenyl groups are coplanar with the adjacent P═S bond; the largest observed torsion angle is 15.6° for S43–P14–C57–C58.

The crystal contains three solvent molecules, one of which is disordered (see Section 4), and the two other ones make contacts with the ligand. Interestingly, one acetonitrile molecule was bound within the molecular cavity of the host and the second one was deeply embedded between the long chain substituents at the lower rim. The methyl carbon of the bound CH_3CN molecule is at an average distance of 4.0 Å from the plane of the four aromatic rings of the resorc[4]arene moiety, accounting for weak attractive CH···π interactions. It lies 1.27 Å below the plane defined by the sulfur atoms of the PS groups indicating a deep encapsulation of the guest [average S···C(301) (C301═carbon of the nitrile group) distances is 3.35 Å]. The nitrogen lies 1.33 Å above this plane. The nitrogen of the second molecule of acetonitrile is oriented towards the lower rim of **1**.

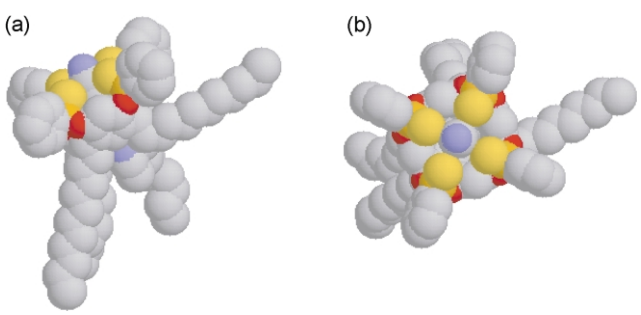


Figure 1. Space-filling model of the molecular structure of host **1** in the crystal. Only two molecules of solvent (CH_3CN) are shown (H atoms have been omitted for clarity); (a) side view; (b) top view.

2.3. Metal salts extraction studies

The affinity of metal ions for **1** was evaluated by the biphasic extraction method of the metal picrate from an aqueous solution into a chloroform solution.[7] The percent of picrate extracted was determined for Ag^+ (91%), Tl^+ (38%), and Hg^{2+} (16%).[2] The extraction of other picrate salts like Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, was not detected. It is interesting to note that the ionic radius was not concerned in coordination with PS groups. For example, the Ag^+ and Pb^{2+} which have almost the same ionic radius (1.26 Å and 1.20 Å, respectively) behave differently, a consequence of the different softness of the metal ions relatively to the soft sulfur binding sites of the ligand. Due to the better solubility of the Tl^+ picrate in acetone, we followed the formation of the complex in this solvent by ^{31}P and ^1H NMR spectroscopy. The variation $\Delta\delta\,^{31}P$ as a function of added picrate, is depicted in Figure 2 and shows unambiguously that 1:1 complex was formed. We observed a lowfield shift for the formation of the complex ($\Delta\delta_{max}$=3.07 ppm). Similarly, in the ^1H NMR spectrum the H(1) and H(2) protons are the most sensitive to the addition of metal salt. A lowfield shift was observed for H(1) and H(2) with $\Delta\delta_{max}$=0.36 and 0.19 ppm, respectively, corresponding to the formation of the 1:1 complex (Table 1).

In the ^{31}P NMR spectra an important broadening of the resonance occurred by addition of the picrate salt. A narrow line was again observed when approaching the 1:1 ratio. This is indicative of a fast exchange process on the NMR time scale between free and complexed ligand. When 1 equiv. of salt was added only the 1:1 complex was observed indicating a large association constant which cannot be determined from the NMR data (K_a>10^4 M^{-1}).

Table 1. $\Delta\delta_{max}$ ($\delta_{complex}-\delta_{free}$) of ^{31}P and H(1) and H(2) chemical shifts of metal complexes of **1** in acetone solution

$\Delta\delta=\delta_c-\delta_f$	Tl^+·Pic^-	Hg^{2+}·$2Cl^-$	Ag^+·Pic^-	Ag^+·BF_4^-	Ag^+·Ts^-
^{31}P	3.07	−2.80	4.0	8.0	5.30[a]
H(1)	0.36	0.06	0.40	0.80	0.9[a]
H(2)	0.19	0.08	0.17	0.36	0.20[a]

[a] Values for [Ag]/[**1**]≈2.

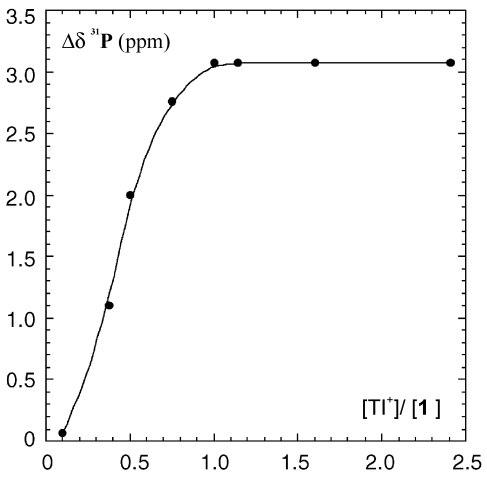


Figure 2. ^{31}P NMR chemical shifts for the NMR titration of **1** with $Tl^{+}Pic^{-}$ in d_6-acetone.

We thus conducted extraction experiments in $CHCl_3/H_2O$ to determine the association constant $K_a=5.2\times10^7\ M^{-1}$ ($\Delta G°=-43.9$ kJ mol^{-1}) from the UV spectra. It is noteworthy that the affinity of Tl^+ for host **1** is comparable to that observed with tetraphosphonatocavitands containing P=O binding sites towards hard metal cations.[1]

The picrate experiment was not successful with mercury. The decomposition of the host prevented any further complexation studies with Hg^{2+} picrate salt. However, the formation of the $HgCl_2$ complex in acetone solution was characterized by ^{31}P and ^{1}H NMR. A maximum shift $\Delta\delta\,^{31}P=-2.8$ ppm was observed for a 1:1 [Hg^{2+}]/[**1**] ratio. In this case the H(1) and H(2) protons are only slightly shifted (Table 1). This fact and the upfield shift of the ^{31}P resonance are probably indicating of a different coordination mode when compared to the picrate salts for which a lowfield shift was observed for the phosphorus resonance.

2.4. Silver(I) complex

We have already reported the peculiar behavior of the silver(I) picrate salt in presence of host **1**. In this case, in addition to a fast exchange process between the free and complexed forms, we observed the formation of a second species, which was characterized as the $\mathbf{1}_2\cdot(AgPic)_4$ coordination compound in acetone solution as well as in chloroform. In acetone, a lowfield shift $\Delta\delta\,^{31}P=4.0$ ppm was measured, and the H(1) and H(2) protons were shifted by 0.40 and 0.17 ppm, respectively, (Table 1).

With $AgBF_4$, the ^{31}P NMR titration curve in acetone showed unambiguously the formation of a 1:2 host–guest complex (Fig. 3). Similarly, the resonances of the H(1) and H(2) protons depend on the [Ag^+]/[**1**] ratio and reach a maximum value after addition of approximately 2 equiv. of substrate (Fig. 4). However, in this case no complex precipitated from the solution as observed with the picrate salt. Moreover, an important downfield shift ($\Delta\delta=8.0$ ppm) of the ^{31}P NMR signal of the receptor was observed up to 2 equiv. of $AgBF_4$ as compared to the $\Delta\delta=4.0$ ppm observed with the AgPic complex. In return, the AgPic and $AgBF_4$ complexes have the same stoichiometry and dimeric structure, indicating that $\pi-\pi$ interactions of the P-phenyl groups with the picrate anion are not a prerequisite.

To elucidate the role of the aromatic anion, we performed a series of experiments with the tosylate salt (AgTs) in acetone. By adding AgTs to a solution of **1** in an NMR tube, increased chemical shifts were observed for each ^{1}H and ^{31}P resonances of the receptor indicating a fast exchange process on the NMR time-scale. Again, we observed a maximum lowfield shift of the ^{31}P resonance ($\Delta\delta\,^{31}P=5.3$ ppm) for a 2:1 [Ag]/[**1**] ratio, which evidenced the formation of a dimeric adduct. Like with $AgBF_4$, no crystalline material was recovered from the solution. However, even if the saturation plateau was reached after addition of approximately 2 equiv. of AgTs, the H(1) and H(2) proton chemical shifts, which are then shifted by 0.9 and 0.2 ppm, respectively, still deviate after the addition of more tosylate salt, although the $\delta\,^{31}P$ seems to slightly decrease (Figs. 3 and 4).

This features probably a surrounding effect of the tosyl group. In absence of structural data it is difficult to go further in the discussion, but an aromatic group induced shift effect could be considered. Nevertheless, the structure

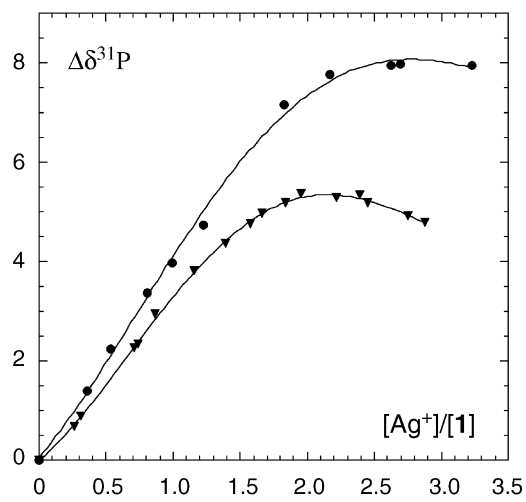


Figure 3. ^{31}P NMR spectral changes of **1** with added $AgBF_4$ (–●–) or AgTs (–▼–), in d_6-acetone.

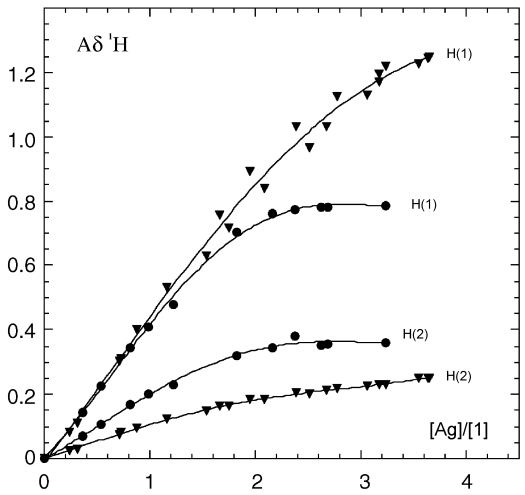


Figure 4. H(1) and H(2) ^{1}H NMR spectral changes of **1** with added $AgBF_4$ (–●–) or AgTs (–▼–) in d_6-acetone.

of the 1:2 host–guest complex in solution can be unambiguously assigned, and confirms that the participation of the picrate anion in the stabilization of the complex as viewed in the solid state structure of the $\mathbf{1}_2\cdot(AgPic)_4$ complex, is not necessary. The formation in solution of the silver(I) cation complex is not anion dependent. The picrate anion probably intervenes only to stabilize the crystalline structure.

3. Conclusion

The thiophosphorylated cavitand **1** derived from the resorc[4]arene **2** and functionnalized at the upper rim with four thiophosphonate bridging groups, was structurally characterized in the solid state. Its affinity for soft metal cations Ag^+, Hg^{2+} and Tl^+, was characterized in solution and the dimeric structure observed with the silver(I) complex was not detected with other metal ions, which showed the formation of 1:1 complexes. In the solid state, the anion contribute to the stability of the $\mathbf{1}_2\cdot(AgPic)_4$ complex. However, the participation of the picrate anion to the structure is not a prerequisite in the formation of the complex. The $AgBF_4$ as well as the AgTs salt led to the dimeric structure in solution, and indicate that the predominance of the strong affinity of the sulfur for the silver ion is the main contribution to the stabilizing of the complex.

4. Experimental

4.1. General

All manipulations involving air-sensitive species were carried out under dry argon. Unless otherwise noted, all reagents were purchased from commercial suppliers and used without further purification. Diethyl ether was distilled from Na and pyridine was distilled from KOH prior to use. Reactions were monitored by ^{31}P NMR and thin layer chromatography (Merck Kieselgel 60F254). Silica gel used for column chromatography was Merck Kieselgel 60 (0.040–0.063 mm). Elemental analyses and electrospray mass spectra were performed by the Service Central d'Analyses CNRS and the Centre de Spectrométrie de Masse, University of Lyon. Melting points were measured with a DSC7 Perkin Elmer calorimeter. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on Varian Unity$^{\oplus}$ 500 and Bruker DPX 200 spectrometers. Chemical shifts are in δ values from Me_4Si (^{1}H, ^{13}C) or H_3PO_4 85% (^{31}P). ^{31}P NMR spectra are proton decoupled. UV spectra were recorded on Varian Cary 219 spectrometer. Picrate salts were already available or prepared according to well known procedures.[8] Resorc[4]arene **2** was synthesized according to the literature procedures.[3]

4.1.1. 1,21,23,25-Tetra-*n*-decyl-5,9,13,17-tetraphenyl-2,20:3,19-dimetheno 1*H*,21*H*,23*H*,25*H*-bis[1,3,2]dioxaphosphocino[5,4-i:5′,4′-i′]benzo[1,2-d:5,4-d′]bis[1,3,2]benzodioxaphosphocin-5,9,13,17-tetrasulfide (1). Dichlorophenyl-phosphine (1.13 mL, 8.1 mmol) was added dropwise to a suspension of tetraresorcinol **2** (2.21 g, 2 mmol) and freshly distilled pyridine (2.5 mL) in diethylether (160 mL) at −40°C. The resultant mixture was stirred at −40°C for 4 h and then at room temperature for 24 h. Sulfur (0.32 g, 10 mmol) was then added and the reaction mixture was heated to reflux temperature for 2 days. After cooling to room temperature the white precipitate was filtered and the yellowish filtrate was concentrated under vacuum. The resulting beige waxy solid was purified by silica gel column chromatography (dichloromethane/hexane 2:3) to give the [*iiii*] stereoisomer **1** (1.72 g, 1.04 mmol, 52%). Mp 216°C (recrystallized from acetonitrile/$CHCl_3$); ^{1}H NMR (499.83 MHz, 293 K, $CDCl_3$) δ 0.86 (t, 12H, ^3J=6.5 Hz, CH_3), 1.25–1.47 (m, 72H, $CH_2(CH_2)_9CH_3$), 2.35 (m, 8H, $CH_2(CH_2)_9CH_3$), 4.78 (t, 4H, ^3J=7 Hz, C*H*), 6.97 (s, 4H, ArH), 7.31 (s, 4H, ArH), 7.50 (m, 8H, P–ArH), 7.60 (t, 4H, ^3J=7 Hz, P–ArH), 8.03 (dd, 8H, ^3J=8 Hz, $^3J_{PH}$=14.5 Hz, P–ArH); ^{13}C NMR (50.32 MHz, 300K, $CDCl_3$): δ 14.10 (*C*H$_3$), 22.68, 28.02, 29.40, 29.72, 31.26, 31.94 (*C*H$_2$), 36.05 (*C*H), 120.05, 122.12 (Ar*C*H), 128.23 (^3J=16.0 Hz, P–Ar*C*H), 131.09 (^2J=12.2 Hz, P–Ar*C*H), 131.96 (^1J=162.2 Hz, P–Ar*C*), 132.61 (P–Ar*C*H), 135.03 (Ar*C*q), 146.47 (^2J=12.2 Hz, Ar*C*q); ^{31}P NMR (81.02 MHz, 300K, $CDCl_3$): δ 80.03; ESI MS m/z 1658.7 $[M+H]^+$, 1677 $[M+H+H_2O]^+$. Anal. Calcd for $C_{96}H_{124}O_8P_4S_4$: C, 69.54; H, 7.54; P, 7.47; S, 7.73. Found: C, 69.19; H, 7.73; P, 7.31; S, 7.81.

4.1.2. Complex $\mathbf{1}_2\cdot(AgPic)_4$. The addition of an excess of silver picrate (>2 equiv.) to an acetone solution (6×10^{-3} M) of **1** led to the quantitative formation of the complex which precipitated from the solution. The solid was recovered by filtration and recristallized from acetone solution. ^{1}H NMR (499.83 MHz, 293 K, $CDCl_3$) δ 0.86 (t, 24H, ^3J=6.5 Hz, CH_3), 1.21–1.38 (m, 128H, $CH_2CH_2(CH_2)_8CH_3$), 1.43 (m, 16H, $CH_2CH_2(CH_2)_8CH_3$), 2.30 (m, 16H, $CH_2CH_2(CH_2)_8CH_3$), 4.58 (t, 8H, ^3J=7 Hz, C*H*), 7.12 (m, 16H, P–ArH), 7.26 (t, 8H, ^3J=7.5 Hz, P–ArH), 7.30 (s, 8H, ArH), 7.45 (s, 8H, ArH), 8.03 (dd, 16H, ^3J=7.5 Hz, $^3J_{PH}$=15.5 Hz, P–ArH), 8.36 (s, 8H, Pic) ^{31}P NMR (81.02 MHz, 300K, $CDCl_3$): δ 84.6. Anal. Calcd for $C_{216}H_{256}N_{12}O_{44}P_8S_8Ag_4$: C, 55.67; H, 5.54; P, 5.32; S, 5.50; Ag, 9.26. Found: C, 55.26; H, 5.47; P, 5.23; S, 5.69; Ag, 9.14.

4.2. Extraction experiments

The percent extraction of metal picrate salts from H_2O into $CHCl_3$ were determined by using a 10^{-3} M initial solution of host **1**. The stock solutions of the metal cations were prepared by dissolving the required amounts of the appropriate metal picrate (10^{-3} M) in water. Equal volumes (0.5 mL) of the organic and aqueous solutions were placed in a glass tube, centrifugated at room temperature for 1 mn, vortexed for 1 mn, and centrifugated for 10 mn. A 50 μL aliquot of the aqueous phase was pipetted out and diluted to 5 mL with acetonitrile. The absorbance A of the solution was measured at 380 nm on a UV spectrophotometer. For each cation a blank experiment was run with pure chloroform as organic phase, which allowed the determination of the A_o absorbance of the starting aqueous solution. The percentage %E of the cation extracted in the organic phase was defined as the ratio $100[(A_o - A)/A_o]$. The association constant for the $Tl^+ \cdot$**1** complex was determined by using the Cram procedure (Tl^+Pic^-: ε=17000; K_D=2.68×10^{-2}).[9]

4.3. NMR titration experiments

Silver tetrafluoroborate and silver tosylate were dried under vacuum in presence of P_2O_5 at room temperature for 48 h prior to use.

A 3.2×10^{-2} M $AgBF_4$ stock solution in d_6-acetone was first prepared. Ten NMR tubes containing identical quantity of host **1** (5 mg, 3 mmol) and increasing aliquots of the guest stock solution were then prepared. d_6-Acetone was added in each tube to give a total sample volume of 0.6 mL. This procedure gave a total of ten guest concentrations while concentration of host was kept constant. For each tube, guest and host concentrations [G] and [H] were calculated, and ^1H and ^{31}P NMR spectra were recorded.

In the case of AgTs, increasing quantities of AgTs were added to an initial solution of host **1** (10 mg) in d_6-acetone (0.5 mL). The [G]/[H] ratio was determined from the integration of the ^1H NMR resonances of the guest (tosyl) and host protons. Similarly, for Tl^+ and Hg^{2+} complexes, known increasing quantities of solid TlPic or $HgCl_2$ salt were added to a 10^{-2} M solution (0.5 mL) of host **1** in d_6-acetone. NMR spectra were then recorded for each sample.

4.4. X-Ray structure analysis of 1

Single crystals of **1** suitable for X-ray analysis were grown from dichloromethane/acetonitrile. Three crystals with approximate dimensions 0.4×0.4×0.3 mm^3, mounted in Lindemann glass capillaries were used for the data collection. The data were collected at 100 K on a MAR345 image plate detector using graphite-monochromated Mo K_α radiation (λ=0.71069 Å). The lattice parameters were refined from the data between 2θ=5 and 52°. Crystal data and structure refinement parameters are reported in Table 2. The structure was solved by direct methods and refined by full-matrix least squares on F^2 using SHELXS and SHELXL-97,[10] respectively. The positions of all the hydrogen atoms were calculated and included in the refinement with a common isotropic temperature factor (U=0.082 $Å^2$). One solvent molecule is disordered and it was quite difficult to interpret the electron density. Finally, it was interpreted as three parts: two acetonitrile molecules with different orientation and one

Table 2. Crystal data and refinement parameters for **1**

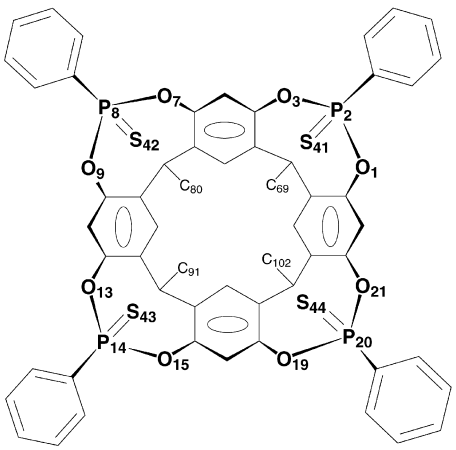
Formula	$C_{98}H_{124}O_8P_4S_4 \cdot 3CH_3CN$
Formula wt	1724.12
Crystal system	Triclinic
Space group	*P-1*
a (Å)	14.835(5)
b (Å)	15.034(5)
c (Å)	23.238(8)
α (deg.)	76.74(2)
β (deg.)	84.15(2)
γ (deg.)	89.95(2)
V ($Å^3$)	5017(3)
T (K)	100
D_x (g $cm_)^{-3}$	1.141
Z	2
F(000)	1842
μ (mm^{-1})	0.211
Crystal size (mm)	3 crystals: 0.60×0.20×0.05;0.5×0.5×0.5; 0.4×0.4×0.3
$2\theta_{max}$ (deg.)	53
Range of *hkl*	$0 \le h \le 18$ $-18 \le k \le 18$ $-28 \le l \le 29$
No of collected reflection	178617
No. of unique reflection (R_{int})	20368 (0.083)
Completeness	98.8%
No. of observed reflection [$I \ge 2\sigma(I)$]	18106
No. of parameters	1268
No. of restraints	170
Goodness of fit	1.020
R (R all data)	0.0823 (0.0877)
$WR2$	0.246
Extinction coefficient	0.019(1)
$\Delta\rho$(max, min) (eÅ×10^{-3})	1.175, −0.605

Table 3. Selected bond lengths (Å) and angles (deg.) in **1** with estimated standard deviation in parentheses

P2–S41:1.908(1)	P8–S42:1.906(1)	P14–S43:1.910(1)	P20–S44:1.909(1)
P2–C45:1.786(3)	P8–C51:1.793(3)	P14–C57:1.780(3)	P20–C63:1.787(3)
P2–O1:1.611(2)	P8–O7:1.607(2)	P14–O13:1.605(2)	P20–O19:1.617(2)
P2–O3:1.606(2)	P8–O9:1.613(2)	P14–O15:1.614(2)	P20–O21:1.613(2)
S41–P2–O1:114.5(1)	S42–P8–O7:115.7(1)	S43–P14–O15:115.4(1)	S44–P20–O19:115.0(1)
S41–P2–O3:115.7(1)	S42–P8–O9:114.9(1)	S43–P14–O13:115.5(1)	S44–P20–O21:115.5(1)
O1–P2–O3:104.6(2)	O7–P8–O9:104.6(1)	O15–P14–O13:104.3(1)	O19–P20–O21:104.5(1)
S41–P2–C45:119.1(1)	S42–P8–C51:118.9(1)	S43–P14–C57:119.4(1)	S44–P20–C63:119.1(1)
O1–P2–C45:100.5(1)	O7–P8–C51:100.0(1)	O15–P14–C57:99.3(1)	O19–P20–C63:100.3(1)
O3–P2–C45:100.0(1)	O9–P8–C51:100.3(1)	O13–P14–C57:100.3(1)	O21–P20–C63:99.8(1)

ethanol molecule with occupation factors of 0.45, 0.21 and 0.33, respectively. Some parts of the long alkyl chains are disordered. For example, all the carbon atoms of the chain from C81 to C90 occupy two positions with occupation factors of 0.55 and 0.45. Restraints have been applied on bond lengths and 1–3 non-bonded distances in the disordered parts of the alkyl substituents. The refinement converged to the final indices: R_1=0.082 for 20368 observed reflections, R_1=0.088 for all data. Scattering factors were taken from *The International Tables for X-ray Crystallography*.[11]

Selected bond distances and angles around the phosphorus atoms are compared in Table 3. Crystallographic data (excluding structure factors) for **1** have been deposited with the Cambridge Crystallographic Data Center as CIF files CCDC No. 199216.[12] Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.ac.uk].



Acknowledgements

We thank J.-C. Mulatier for helpful discussion and skillful experimental contribution.

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