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# Synthesis and Characterization of Selenophosphatocavitands

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**Abstract** Treatment of a series of substituted resorcin[4]arenes in pyridine with dichlorophenyl-phosphine followed by addition of selenium powder resulted in the formation of the corresponding selenophosphatocavitands  $[R_2CHC_6HR_1O_2PSePh]_4$  ( $R_1 = H$ ,  $R_2 = CH_2CH_2Ph$ , 1;  $R_1 = CH_3$ ,  $R_2 = CH_3$ , 2;  $R_1 = CH_3$ ,  $R_2 = C_2H_5$ , 3) in moderate yields. All compounds were spectroscopically characterized, of which the structure of **3**·CHCl<sub>3</sub> has been established by X-ray crystallography. The molecular structure of **3** shows that the selenophosphato-cavitand adopts  $C_{4v}$  bowl-shaped conformation with four P=Se bonds oriented toward the molecular cavity.

**Graphical Abstract** Three selenophosphatocavitands  $[R_2CHC_6HR_1O_2PSePh]_4$  ( $R_1 = H$ ,  $R_2 = CH_2CH_2Ph$ , **1**;  $R_1 = CH_3$ ,  $R_2 = CH_3$ , **2**;  $R_1 = CH_3$ ,  $R_2 = C_2H_5$ , **3**) were synthesized and spectroscopically characterized, of which the structure of **3**·CHCl<sub>3</sub> has been established by X-ray crystallography.



**Keywords** Resorcinarene · Selenium · Phosphatocavitand · Synthesis · Structure

## Introduction

Calix[4]resorcinarenes are cavity-containing macrocyclic compounds that attract considerable interest in the field of host–guest and supramolecular chemistry as three-dimensional building blocks for the design of selective cation receptors and carriers [1]. It is thus understood that the use of calix[4]resorcinarenes for the chemo- and stereo-selective recognition of carbohydrates is particularly important, of which phosphorus-containing calix[4]resorcinarenes have been of increasing interest in the past decades, mainly because of their ability to act as unusual *multi*-dentate ligands [2, 3]. Quite a few phosphorus-containing calix[4]resorcinarenes have been synthesized in which the phosphorus atoms adopts various coordination numbers

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and oxidation states. For examples, derivatives of calix[4]resorcinarenes with Ph<sub>2</sub>P, PhP, (Et<sub>2</sub>N)<sub>2</sub>P(=O), and (EtO)<sub>2</sub>P(=O) units show strong coordination ability with transition metals such as gold(I), platinum(II), silver(I), and copper(I), to give transition-metal rimmed bowl complexes, which have the potential to accept small guest molecules and ions [4–8]. The phosphoryl (P=O) or thiophosphoryl (P=S) groups were attached to the calix[4]resorcinarene skeleton to produce the typical phosphito- or thiophosphato-cavitand which may be prepared by using a two-step synthetic route. While the phosphito- and thiophosphato-cavitands were previously described and proved to be efficient extractants for metal cations, however, the analogous selenophosphatocavitands have not been reported to date. As a part of our interests on cavitand compound based upon calix[4]resorcinarenes, we have previously reported the tetrametallophosphonitocavitand complexes and their optical properties [9, 10]. In this paper, we wish to present synthesis and characterization of selenophosphatocavitands, which is expected to expand the pool of the supramolecular chemistry of the chalcogeno-phosphato-cavitands.

## **Experimental**

## General

All reagents, unless otherwise stated, were purchased as analysis grade and used without further purification. Calix[4]resorcinarenes were prepared by a modification of the literature method [11]. <sup>1</sup>H NMR and <sup>31</sup>P NMR spectra were recorded on a Bruker Avance-400 Fourier-transform spectrometer with reference to SiMe<sub>4</sub> and 85 % H<sub>3</sub>PO<sub>4</sub>, respectively, infrared spectra on a Nicolet 6700 FT-IR spectrophotometer. All elemental analyses were carried out using a Perkin-Elmer 2400 CHN analyzer.

### Synthesis

#### General Synthesis of Selenophosphato-cavitand Compound

To a solution of substituted calix[4]resorcinarene (1.52 mmol) in 20 mL dry pyridine, dichlorophenylphosphine (0.85 mL, 6.08 mmol) was added slowly at room temperature. After stirring for 3 h at 80 °C, selenium powder (540 mg, 6.84 mmol) was added and the mixture was continuously stirred for 6 h. The solvent was removed under vacuum and the crude product was washed with water and dried under vaccum. Analytical pure product was obtained as white solid by recrystallization from acetone or chloroform. For 1: Yield: 1.63 g, 57.6 %. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 8.03 (dd, 8H, P(Se)Ph*H*<sub>o</sub>), 7.58 (m, 4H + 8H, P(Se)Ph*H*<sub>m</sub> + P(Se)Ph*H*<sub>p</sub>), 7.28 (s, 4H, Ar*H*), 7.22 (m, 20H, C<sub>6</sub>*H*<sub>5</sub>), 6.25 (s, 4H, Ar*H*<sub>upper</sub>), 4.75 (t, 4H, <sup>3</sup>*J* = 6.4 Hz, bridge C*H*), 2.34 (m, 16H, C*H*<sub>2</sub>C*H*<sub>2</sub>C<sub>6</sub>H<sub>5</sub>); <sup>31</sup>P NMR (CDCl<sub>3</sub>, 162 MHz):  $\delta$  (ppm) 80.67 (s); selected IR (KBr, cm<sup>-1</sup>): v(P–Ph) 1432.7, v(P–O) 1059.4, v(P=Se) 686.2. Anal. Calc. for C<sub>84</sub>H<sub>68</sub>O<sub>8</sub>P<sub>4</sub>Se<sub>4</sub>: C 61.32, H 4.17; found: C 61.30, H 4.18 %.

For **2**: Yield: 1.29 g, 48.2 %. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 8.23 (dd, 8H, P(Se)Ph*H*<sub>0</sub>), 7.54 (m, 4H + 8H, P(Se)Ph*H*<sub>m</sub> + P(Se)Ph*H*<sub>p</sub>), 7.17 (s, 4H, Ar*H*), 4.88 (q, 4H, <sup>4</sup>*J* = 7.8 Hz, bridge C*H*), 2.17 (s, 12H, ArC*H*<sub>3</sub>), 1.25 (d, 12H, <sup>2</sup>*J* = 6.4 Hz, C*H*<sub>3</sub>); <sup>31</sup>P NMR (CDCl<sub>3</sub>, 162 MHz):  $\delta$  (ppm) 79.39 (s); selected IR (KBr, cm<sup>-1</sup>): v(P-Ph) 1478.3, v(P-O) 1113.4, v(P=Se) 694.5. Anal. Calc. for C<sub>60</sub>H<sub>52</sub>O<sub>8</sub>P<sub>4</sub>Se<sub>4</sub>: C 52.75, H 3.91; found: C 52.73, H 3.96 %.

For **3**: Yield: 1.83 g, 66.3 %. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 8.21 (dd, 8H, P(O)PhH<sub>o</sub>), 7.60 (m, 4H + 8H, P(Se)PhH<sub>m</sub> + P(Se)PhH<sub>p</sub>), 7.15 (s, 4H, ArH), 4.75 (t, 4H, <sup>3</sup>J = 6.0 Hz, bridge CH), 2.75 (s, 12H, ArCH<sub>3</sub>), 2.15 (m, 8H, CH<sub>2</sub>CH<sub>3</sub>), 1.02 (t, 12H, <sup>3</sup>J = 7.2 Hz, CH<sub>2</sub>CH<sub>3</sub>); <sup>31</sup>P NMR (CDCl<sub>3</sub>, 162 MHz):  $\delta$  (ppm) 75.03 (s); selected IR (KBr, cm<sup>-1</sup>): v(P–Ph) 1478.3, v(P–O) 1121.7, v(P=Se) 686.7. Anal. Calc. for (C<sub>64</sub>H<sub>60</sub>O<sub>8</sub>P<sub>4</sub>Se<sub>4</sub>). (CHCl<sub>3</sub>): C 51.51, H 3.89; found: C 51.47, H 3.82 %.

#### X-ray Crystallography

X-ray diffraction intensity data for a single-crystal of **3**·CHCl<sub>3</sub> (0.11 mm  $\times$  0.13 mm  $\times$  0.17 mm) were collected at 293(2) K on a Bruker SMART Apex 1000 areadetecting diffractometer equipped with graphite monochromated MoK $\alpha$  radiation ( $\lambda = 0.71073$  Å) by using an  $\omega$ scan technique  $(2.37^{\circ} < \theta < 27.55^{\circ})$ . The collected frames were processed with the software SAINT [12]. The data were corrected for absorption using the program SADABS [13]. Structures were solved by Direct Methods and refined by full-matrix least-squares on  $F^2$  using the SHELXTL software package [14]. All non-hydrogen atoms were refined anisotropically. The positions of all hydrogen atoms attached on carbon were generated geometrically  $[C(sp^3)-$ H = 0.96 Å and  $C(sp^2)-H = 0.93$  Å] and allowed to ride on adjacent carbon atoms before the final cycle of refinement. One carbon atom C(40) was treated with disorder. The final refined values of the multiplicities are 0.5 for C(40) and 0.5 for C(40a). The crystallographic data and details of the structure refinement are given in Table 1. Selected bond lengths and bond angles of  $3 \cdot CHCl_3$  are given in Table 2.

Table 1 Crystallographic data for selenophosphato-cavitand compound  $3\cdot CHCl_3$ 

Compound	$3 \cdot \text{CHCl}_3$	
Empirical formula	$C_{65}H_{60}O_8Cl_3P_4Se_4$	
Formula weight	1515.20	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
<i>a</i> , Å	15.856(11)	
b, Å	18.610(13)	
<i>c</i> , Å	23.785(16)	
α, °	90	
β, °	107.413(11)	
γ, °	90	
$V, Å^3$	6697(8)	
Z	4	
Т	293	
$\mu$ (MoK $\alpha$ ), mm <sup>-1</sup>	2.458	
$D_{\rm c}$ , g cm <sup>-3</sup>	1.503	
Reflections collected	34,195	
Independent reflections/R(int)	11,761/0.1332	
Final R1, wR2 $[I \ge 2\sigma(I)]$	0.0755, 0.1714	
[all data]	0.2203, 0.2297	
Goodness-of-fit on $F^2$	0.975	
Residual $\rho$ , e Å <sup>-3</sup>	+1.117/-0.693	

Table 2 Selected bond lengths (Å) and bond angles (°) for $3 \cdot CHCl_3$			
Se(1)–P(1)	2.051(3)	O(1)–P(1)–Se(1)	115.1(2)
Se(2)-P(2)	2.051(3)	O(8)–P(1)–Se(1)	114.9(2)
Se(3)–P(3)	2.050(3)	C(41)–P(1)–Se(1)	119.4(3)
Se(4)-P(4)	2.055(3)	O(2)–P(2)–O(3)	104.4(3)
P(1)–O(1)	1.616(6)	O(2)–P(2)–C(47)	101.3(4)
P(1)–O(8)	1.621(6)	O(3)–P(2)–C(47)	100.3(5)
P(1)-C(41)	1.792(9)	O(2)–P(2)–Se(2)	114.8(2)
P(2)–O(2)	1.607(6)	O(3)–P(2)–Se(2)	115.2(2)
P(2)–O(3)	1.609(6)	C(47)-P(2)-Se(2)	118.6(4)
P(2)-C(47)	1.757(10)	O(5)–P(3)–Se(3)	115.7(2)
P(3)–O(5)	1.613(6)	O(4)–P(3)–Se(3)	115.5(2)
P(3)–O(4)	1.617(6)	C(53)–P(3)–Se(3)	119.6(3)
P(3)–C(53)	1.774(9)	O(7)–P(4)–Se(4)	116.0(2)
P(4)–O(7)	1.601(5)	O(6)–P(4)–Se(4)	115.4(2)
P(4)-O(6)	1.605(6)	C(59)-P(4)-Se(4)	119.4(3)
P(4)–C(59)	1.785(9)	C(1)-O(1)-P(1)	121.6(4)

about 7.20 ppm, which is similar to that in related thiophosphorylated cavitand [8]. The <sup>31</sup>P NMR spectra of **1–3** showed a singlet at  $\delta$  80.67, 79.39, and 75.03 ppm, respectively, indicative of the same environment of the four phosphorous atoms. The FT-IR spectra of **1–3** showed the characteristic peaks for P–O and P=Se stretching vibrations at around 1110 and 690 cm<sup>-1</sup>, respectively, and the P–Ph stretching vibrations were observed at about 1470 cm<sup>-1</sup>, indicating of P(V) moieties in **1–3**.

## **Results and Discussion**

Treatment of series substituted resorcin[4]arene in pyridine solution with dichlorophenylphosphine followed by addition of selenium powder resulted in the formation of the phosphorylated (P=Se) cavitand in moderate yields (see Scheme 1). These complexes are air stable in both the solid and solution. The chemical shifts of the bridging CH in 1–3 appeared at around 4.80 ppm, and the upper aryl proton in compound 1 showed a singlet at 6.25 ppm, while the lower aryl proton in compounds 1–3 also showed a singlet at

The molecular structure of **3** is shown in Fig. 1a. The packing mode of **3** shows its alternating configuration (Fig. 1b). Complex **3** crystallizes in monoclinic space group  $P2_1/n$  with one molecule of selenophosorylated cavitand and a solvent molecule of CHCl<sub>3</sub> in the unit cell. In the solid state, the molecule adopts  $C_{4v}$  bowl-shaped conformation with four P=Se bonds oriented toward the molecular cavity. The P=Se bonds and the phenyl substituents are in the axial and equatorial positions,



Scheme 1 Syntheses of selenophosphatocavitands 1-3



Fig. 1 a Molecular structure of compound 3; b  $\pi$ -packing mode of compound 3

respectively. The P=Se bond lengths (2.050(3) -2.055(3) Å) are a little longer than P=S bond lengths in the phosphorylated (P=S) cavitands (mean value 1.908(1) Å) [7, 8]. The average P–O bond length in 3 is 1.611(6) Å, which is similar to that in the thiophosorylated cavitand (average 1.610 Å) [8] and the phosphonate cavitand (average 1.593 Å) [3]. The four fused eight membered-rings adopt the bowl-shaped conformation as defined by the values of the *endo*-cyclic torsion angles (93.04°, -88.62°, -92.20°, 88.94°, 90.28°, -88.65°, 89.28° and -88.67°). The P-phenyl groups are in different orientations with the adjacent P=Se bond; the least observed torsion angle is 8.99° for Se3-P3-C53-C54 and the largest observed torsion angle is 149.67° for Se1-P1-C41-C45. The ethyl fragments connected to the bridging carbon atoms in 3 acts as four-legged piano stool. The adjacent selenium atoms have approximately equal distance (av. 4.381(3) Å), forming claw-like squareness conformation.

Three selenophosphatocavitands with different substituents are synthesized and characterized. Single-crystal diffraction analysis of **3** shows that the selenophosphatocavitand adopts  $C_{4v}$  bowl-shaped conformation with four P=Se bonds oriented toward the molecular cavity. The P=Se bond lengths ranging from 2.050(3) to 2.055(3) Å and only one <sup>31</sup>P NMR signal was observed for the three compounds, indicating their symmetrical structures.

## **Supplementary Material**

Crystallographic data for **3**·CHCl<sub>3</sub> have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1405666. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (+44)1233-336-033; e-mail: deposit@ccdc.cam.ac.uk].

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