

Inclusion of Two PhP(O)(OH)₂ Guest Molecules into the Cavity of the Macrocyclic Cavitand Cucurbit[8]uril

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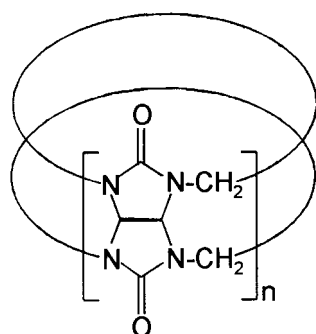
Key words: crystal structure, cucurbit[8]uril, inclusion compounds, phenylphosphonic acid

Abstract

A new inclusion compound which is a supramolecular adduct of cucurbit[8]uril with two guest molecules of phenylphosphonic acid, PhP(O)(OH)₂, included into the cavity as “two guests in host” is reported. The guests match both size and hydrophilicity/hydrophobicity requirements. Two phenyl groups of molecules of PhP(O)(OH)₂ are directed toward the center of the large hydrophobic cavity whereas the PO(OH)₂ groups are outward-looking and bound with each hydrophilic portal of cucurbit[8]uril by a short hydrogen bond.

Introduction

Selective inclusion of guest molecules in the host cavity is a very important problem of modern chemistry. Numerous complexes generated by such host macrocyclic organic molecules as crown ethers [1], cryptands [2], calixarenes [3] or cyclodextrins [4] are presently available. The encapsulation of inert gases, metal ions or organic molecules into the cavities of these molecules gives rise to stable compounds with unusual structures and interesting properties. Cucurbit[*n*]urils (*n* = 5–10) [C₆H₆N₄O₂]_{*n*} are also known to include suitable size guests. They can be described as barrel-shaped macrocyclic



cucurbit[*n*]uril

molecules with an internal cavity and a rigid structure. They have two identical portals on each side of the ‘barrel’ which are fringed by *n* carbonyl groups. The dimensions of the cavity vary with *n*. The cavity is hydrophobic, but the portals

are hydrophilic. This means that guests must match both size and hydrophilicity/hydrophobicity requirements [5].

Recently obtained cucurbit[8]uril (*n* = 8) has the largest cavity ($V = 479 \text{ \AA}^3$), $d_{\text{cavity}} = 8.8 \text{ \AA}$, $d_{\text{portal}} = 6.9 \text{ \AA}$, $h_{\text{cavity}} = 9.1 \text{ \AA}$. Thus the cavity size of cucurbit[8]uril allows to include rather bulky molecules, for example such macrocycles as 1,4,7,10-tetraazacyclododecane (cyclen) and 1,4,8,10-tetraazacyclotetradecane (cyclam). These inclusion compounds are stabilized primarily through van der Waals interactions between the inner macrocycle (guest) and outer cavitand (host) [6].

Large cavity cucurbit[8]uril can include even two guest molecules, for example, two such bulky molecules as 2,6-bis(4,5-dihydro-1H-imidazol-2-yl)naphthalene can be accommodated. Here, not only van der Waals interactions and the hydrophobic effect but also hydrogen bonding between the protonated dihydroimidazole substituents and the portal oxygen atoms of cucurbit[8]uril play an important role in the formation of inclusion compound [7]. Two naphthalene rings within the cavity are located parallel to each other at a distance of about 3.4 Å, which is indicative of π - π interactions between these rings [8].

The encapsulation of two or more guest molecules into the cavity of cucurbit[8]uril is of great interest in the view of the unique possibility of studying new types of stereoisomerism, bimolecular reactions and the behavior of the molecules in the microenvironment. The ability of cucurbit[8]uril to accommodate two closely spaced guests located in a forced orientation allows one to use it as the synthetic molecular container in which bimolecular reactions between specially selected guests can proceed with high regio- and stereoselectivity. Thus, photodimerisation of 4,4’-

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diammoniostilbene encapsulated into the cavity proceeds with a much higher rate and high stereoselectivity [9, 10].

In this paper we report a new inclusion compound having two PhP(O)(OH)₂ molecules in the cucurbit[8]uril cavity.

Experimental

All reactions were carried out in air. Stock solutions of [Mo₃(PdCl)S₄(H₂O)₉]³⁺ in 2 M HCl were prepared by the published procedure [11] and made up to required [H⁺] with 12 M HCl. Cucurbit[8]uril was made according to Day et al. [12]. PhP(O)(OH)₂ was of commercial quality (Aldrich). The ³¹P NMR spectra were measured with a Bruker 250 MHz spectrometer using 85% H₃PO₄ as external standard.

Synthesis of (H₃O)₄[Mo₃S₄(H₂O)₄Cl₅]₂Cl₂·(2C₆H₅PO(OH)₂ · C₄₈H₄₈N₃₂O₁₆)·8H₂O (I). 5 mg of PhP(O)(OH)₂ was added to 1 ml of 7 mM solution of [Mo₃(PdCl)S₄(H₂O)₉]³⁺ in 6M HCl. The color of the reaction mixture has changed from green to brown in 3 h. Then 0.1 ml of 6 mM cucurbit[8]uril solution in 6 M HCl was added. The reaction mixture was stirred and left for 5 months at room temperature. Dark green crystals of **1** were collected by filtration and dried in air. Yield: 6 × 10⁻⁴ g (20%).

Crystallography. The data were collected on a Nonius Kappa CCD diffractometer using Collect [13] and HKL2000 [14] programs. Crystallographic data are given in Table 1. The structure was solved by direct methods and refined anisotropically for non-hydrogen atoms (except for disordered O atoms in free water molecules) by full-matrix least squares on Fo² using SHELX-97 package [15]. Hydrogen atoms were located geometrically and refined in the rigid-body approximation. Phenyl group of PhP(O)(OH)₂ molecule is disordered over two position with relative weights of 0.506(18) and 0.494(18) for C(1X), C(2X), C(3X), C(4X), C(5X), C(6X) and C(1Y), C(2Y), C(3Y), C(4Y), C(5Y), C(6Y), correspondingly. The disordered carbon atoms were refined with equivalent anisotropic displacement parameters.

Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-217564. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) +44 (0) 1223/336033; E-mail: deposit@ccdc.cam.ac.uk].

Results and discussion

The macrocyclic cavitand cucurbit[8]uril can function as a host molecule. It combines a hydrophobic cavity with hydrophilic portals. This means that suitable guests must match both size and hydrophilicity/hydrophobicity requirements. Good candidates are therefore aromatic acids or amines. In this paper we present a new inclusion compound which contains a supramolecular adduct of cucurbit[8]uril with two guest molecules, PhP(O)(OH)₂, included in the cavity as "two guests in host" (Figure 1). This supermolecule has

Table 1. Crystal data and structure refinement for **1**

Empirical formula	C ₆₀ H ₁₀₆ Cl ₁₂ Mo ₆ N ₃₂ O ₄₂ P ₂ S ₈
Formula weight	3267.23
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C2/c
Unit cell dimensions	<i>a</i> = 40.7454(7) Å <i>b</i> = 12.9531(3) Å <i>c</i> = 23.6002(6) Å <i>β</i> = 110.8763(14)°
Volume	11638.0(4) Å ³
Z	4
Density (calculated)	1.865 g/cm ³
Absorption coefficient	1.167 mm ⁻¹
<i>F</i> (000)	6560
Crystal size	0.20 × 0.11 × 0.07 mm
Theta range for data collection	2.14 to 28.18°
Index ranges	-54 ≤ <i>h</i> ≤ 54, -16 ≤ <i>k</i> ≤ 17, -30 ≤ <i>l</i> ≤ 31
Reflections collected	105126
Independent reflections	14102 [<i>R</i> _{int} = 0.0747]
Absorption correction	None
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	14102/0/699
Goodness-of-fit on <i>F</i> ²	1.205
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0680, <i>wR</i> ₂ = 0.1833
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0806, <i>wR</i> ₂ = 0.1917
Largest diff. peak and hole	1.210 and -1.579 eÅ ⁻³

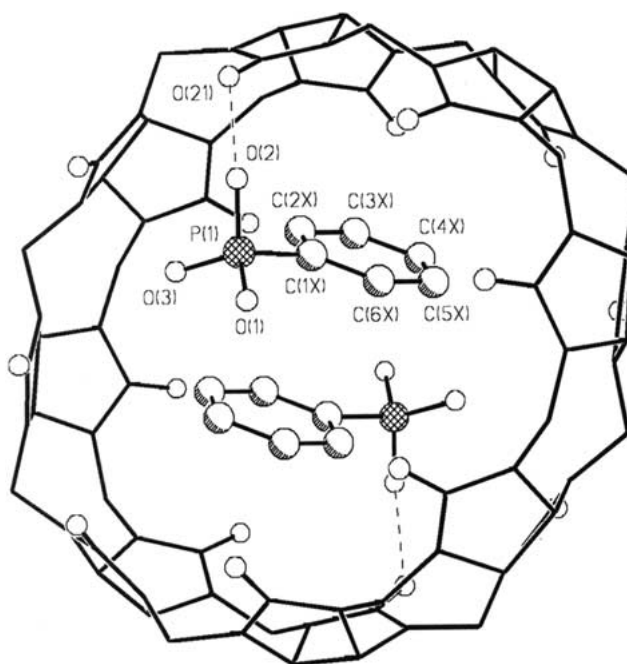
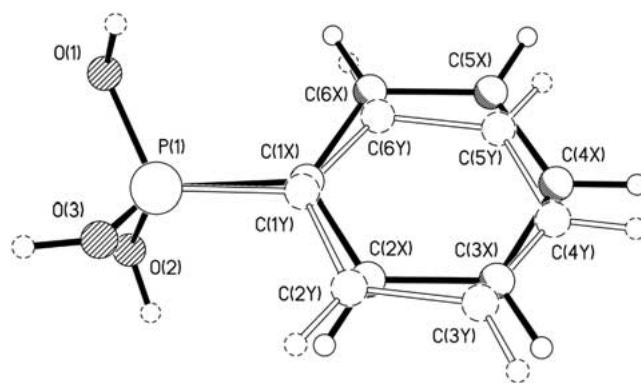
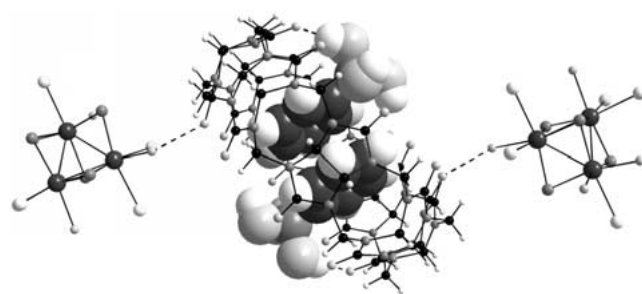
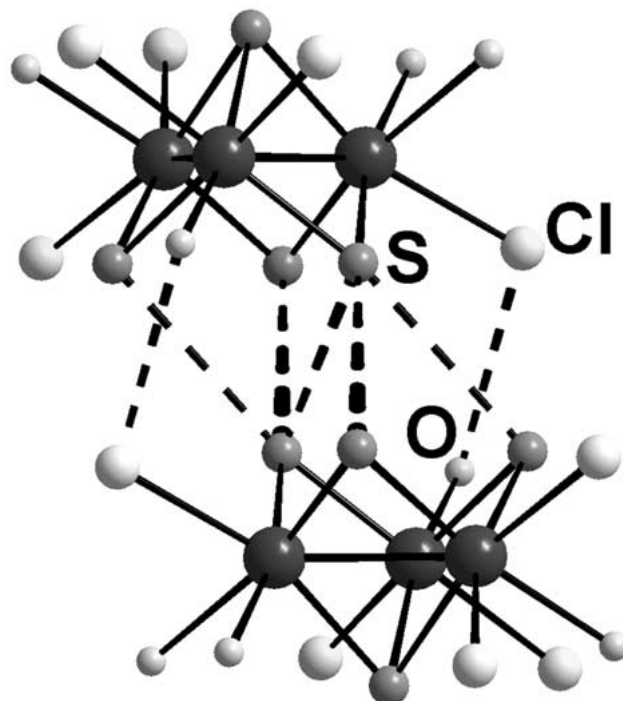


Figure 1. Supramolecular adduct 2PhP(O)(OH)₂ · C₄₈H₄₈N₃₂O₁₆. Hydrogen bonds are indicated by dashed lines.

an inversion center. Two phenyl groups of two disordered over two positions (Figure 2) molecules of PhP(O)(OH)₂ are directed inside the center of the large hydrophobic cavity whereas the PO(OH)₂ groups are outward-looking and bound with each hydrophilic portal of cucurbit[8]uril by one short hydrogen bond (O(2) ... O(21) 2.586 Å). Two phenyl rings within the cavity are located strictly parallel to each other at an interplanar distance of 3.881 Å,

Table 2. Selected bond lengths [Å] and angles [°] for **1**

Bond	d(Å)	Bond	d(Å)
Mo(1)–Mo(2)	2.7575(6)	O(1)–H(1)	0.8200
Mo(1)–Mo(3)	2.7524(6)	O(2)–H(2)	0.8200
Mo(1)–S(1)	2.3354(14)	O(3)–H(3)	0.8200
Mo(1)–S(2)	2.2724(15)	C(1X)–C(2X)	1.4398
Mo(1)–S(3)	2.2863(15)	C(1X)–C(6X)	1.4397
Mo(1)–O(1M)	2.197(4)	C(2X)–H(2XA)	0.9300
Mo(1)–O(2M)	2.396(4)	C(2X)–C(3X)	1.4396
Mo(1)–Cl(1)	2.5245(15)	C(3X)–H(3XA)	0.9300
Mo(2)–Mo(3)	2.7533(6)	C(3X)–C(4X)	1.4395
Mo(2)–S(1)	2.3234(14)	C(4X)–H(4XA)	0.9300
Mo(2)–S(2)	2.2870(14)	C(4X)–C(5X)	1.4398
Mo(2)–S(4)	2.2814(15)	C(5X)–H(5XA)	0.9300
Mo(2)–O(3M)	2.218(4)	C(5X)–C(6X)	1.4396
Mo(2)–Cl(2)	2.4892(18)	C(6X)–H(6XA)	0.9300
Mo(2)–Cl(3)	2.5527(15)	C(1Y)–C(2Y)	1.4398
Mo(3)–S(1)	2.3443(14)	C(1Y)–C(6Y)	1.4397
Mo(3)–S(3)	2.2643(14)	C(2Y)–H(2YA)	0.9300
Mo(3)–S(4)	2.2746(14)	C(2Y)–C(3Y)	1.4396
Mo(3)–O(4M)	2.252(4)	C(3Y)–H(3YA)	0.9300
Mo(3)–Cl(4)	2.5373(17)	C(3Y)–C(4Y)	1.4397
Mo(3)–Cl(5)	2.4775(15)	C(4Y)–H(4YA)	0.9300
P(1)–O(1)	1.504(7)	C(4Y)–C(5Y)	1.4396
P(1)–O(2)	1.528(8)	C(5Y)–H(5YA)	0.9300
P(1)–O(3)	1.480(8)	C(5Y)–C(6Y)	1.4397
P(1)–C(1X)	1.739(9)	C(6Y)–H(6YA)	0.9300
Angle	ε(°)	Angle	ε(°)
Mo(3)–Mo(1)–Mo(2)	59.962(16)	Mo(1)–Mo(3)–Mo(2)	60.112(16)
S(1)–Mo(1)–Mo(2)	53.51(4)	S(1)–Mo(3)–Mo(1)	53.82(4)
S(1)–Mo(1)–Mo(3)	54.12(4)	S(1)–Mo(3)–Mo(2)	53.50(4)
S(1)–Mo(1)–O(2M)	86.37(10)	S(1)–Mo(3)–Cl(4)	163.82(6)
S(1)–Mo(1)–Cl(1)	161.45(5)	S(1)–Mo(3)–Cl(5)	86.34(5)
S(2)–Mo(1)–Mo(2)	53.03(4)	S(3)–Mo(3)–Mo(1)	53.15(4)
S(2)–Mo(1)–Mo(3)	97.48(4)	S(3)–Mo(3)–Mo(2)	97.50(4)
S(2)–Mo(1)–S(1)	105.38(5)	S(3)–Mo(3)–S(1)	106.02(5)
S(2)–Mo(1)–S(3)	93.91(6)	S(3)–Mo(3)–S(4)	94.21(5)
S(2)–Mo(1)–O(2M)	91.90(12)	S(3)–Mo(3)–Cl(4)	86.11(6)
S(2)–Mo(1)–Cl(1)	88.41(5)	S(3)–Mo(3)–Cl(5)	95.24(5)
S(3)–Mo(1)–Mo(2)	96.85(4)	S(4)–Mo(3)–Mo(1)	97.74(4)
S(3)–Mo(1)–Mo(3)	52.42(4)	S(4)–Mo(3)–Mo(2)	52.93(4)
S(3)–Mo(1)–S(1)	105.59(5)	S(4)–Mo(3)–S(1)	105.30(5)
S(3)–Mo(1)–O(2M)	164.75(10)	S(4)–Mo(3)–Cl(4)	83.98(6)
S(3)–Mo(1)–Cl(1)	85.34(5)	S(4)–Mo(3)–Cl(5)	162.35(6)
O(1M)–Mo(1)–Mo(2)	138.46(12)	O(4M)–Mo(3)–Mo(1)	137.96(11)
O(1M)–Mo(1)–Mo(3)	95.73(12)	O(4M)–Mo(3)–Mo(2)	91.24(11)
O(1M)–Mo(1)–S(1)	85.03(12)	O(4M)–Mo(3)–S(1)	84.76(12)
O(1M)–Mo(1)–S(2)	166.40(13)	O(4M)–Mo(3)–S(3)	168.84(12)
O(1M)–Mo(1)–S(3)	91.58(13)	O(4M)–Mo(3)–S(4)	85.51(12)
O(1M)–Mo(1)–O(2M)	79.87(17)	O(4M)–Mo(3)–Cl(4)	82.77(12)
O(1M)–Mo(1)–Cl(1)	79.64(12)	O(4M)–Mo(3)–Cl(5)	82.35(12)
O(2M)–Mo(1)–Mo(2)	97.91(10)	Cl(4)–Mo(3)–Mo(1)	139.26(5)
O(2M)–Mo(1)–Mo(3)	140.49(9)	Cl(4)–Mo(3)–Mo(2)	136.88(5)
O(2M)–Mo(1)–Cl(1)	80.73(10)	Cl(5)–Mo(3)–Mo(1)	99.86(5)
Cl(1)–Mo(1)–Mo(2)	141.43(4)	Cl(5)–Mo(3)–Mo(2)	139.80(5)
Cl(1)–Mo(1)–Mo(3)	137.55(4)	Cl(5)–Mo(3)–Cl(4)	81.83(6)
Mo(3)–Mo(2)–Mo(1)	59.926(16)	Mo(1)–S(1)–Mo(3)	72.05(4)
S(1)–Mo(2)–Mo(1)	53.91(4)	Mo(2)–S(1)–Mo(1)	72.58(4)
S(1)–Mo(2)–Mo(3)	54.20(4)	Mo(2)–S(1)–Mo(3)	72.29(4)
S(1)–Mo(2)–Cl(2)	89.16(6)	Mo(1)–S(2)–Mo(2)	74.43(4)
S(1)–Mo(2)–Cl(3)	84.95(5)	Mo(3)–S(3)–Mo(1)	74.43(4)
S(2)–Mo(2)–Mo(1)	52.54(4)	Mo(3)–S(3)–Mo(2)	74.36(4)
S(2)–Mo(2)–Mo(3)	97.10(4)	O(1)–P(1)–O(2)	100.8(4)
S(2)–Mo(2)–S(1)	105.30(5)	O(1)–P(1)–C(1X)	112.1(5)
S(2)–Mo(2)–Cl(2)	89.96(7)	O(2)–P(1)–C(1X)	108.1(5)
S(2)–Mo(2)–Cl(3)	166.89(5)	O(3)–P(1)–O(1)	109.9(5)
S(4)–Mo(2)–Mo(1)	97.43(4)	O(3)–P(1)–O(2)	115.1(5)
S(4)–Mo(2)–Mo(3)	52.71(4)	O(3)–P(1)–C(1X)	110.5(5)
S(4)–Mo(2)–S(1)	105.76(5)	C(2X)–C(1X)–P(1)	115.9(3)
S(4)–Mo(2)–S(2)	94.49(6)	C(6X)–C(1X)–P(1)	124.1(3)
S(4)–Mo(2)–Cl(2)	162.62(6)	C(6X)–C(1X)–C(2X)	120.0
S(4)–Mo(2)–Cl(3)	90.42(5)	C(1X)–C(2X)–H(2XA)	120.0
O(3M)–Mo(2)–Mo(1)	140.28(11)	C(3X)–C(2X)–C(1X)	120.0
O(3M)–Mo(2)–Mo(3)	133.91(12)	C(4X)–C(3X)–C(2X)	120.0
O(3M)–Mo(2)–S(1)	164.28(12)	C(3X)–C(4X)–C(5X)	120.0
O(3M)–Mo(2)–S(2)	87.84(12)	C(6X)–C(5X)–C(4X)	120.0
O(3M)–Mo(2)–S(4)	81.27(12)	C(5X)–C(6X)–C(1X)	120.0
O(3M)–Mo(2)–Cl(2)	82.12(13)	C(6Y)–C(1Y)–C(2Y)	120.0
O(3M)–Mo(2)–Cl(3)	80.89(12)	C(3Y)–C(2Y)–C(1Y)	120.0
Cl(2)–Mo(2)–Mo(1)	98.61(5)	C(2Y)–C(3Y)–C(4Y)	120.0
Cl(2)–Mo(2)–Mo(3)	143.29(5)	C(5Y)–C(4Y)–C(3Y)	120.0
Cl(2)–Mo(2)–Cl(3)	81.92(6)	C(4Y)–C(5Y)–C(6Y)	120.0
Cl(3)–Mo(2)–Mo(1)	138.75(4)	C(5Y)–C(6Y)–C(1Y)	120.0
Cl(3)–Mo(2)–Mo(3)	95.55(4)		

Figure 2. Disorder of the phenyl group of PhP(O)(OH)₂ over two positions.Figure 3. The cucurbituril supramolecular adduct bound with two incomplete cuboidal cluster aqua-complexes [Mo₃S₄(H₂O)₄Cl₅]²⁻. Hydrogen bonds are indicated by dashed lines.Figure 4. Dimer of [Mo₃S₄(H₂O)₄Cl₅]²⁻. Hydrogen bonding and S...S interactions are indicated by dashed lines.

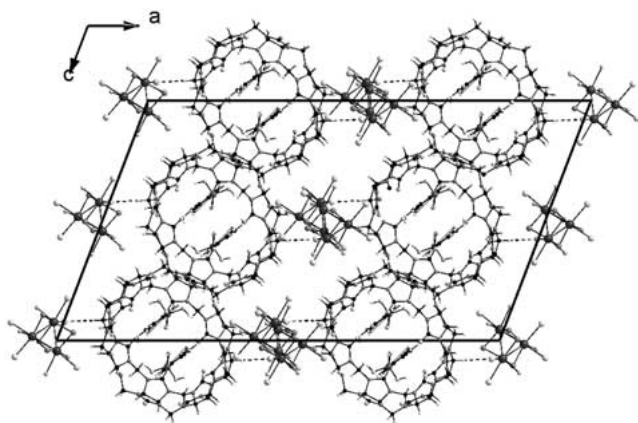
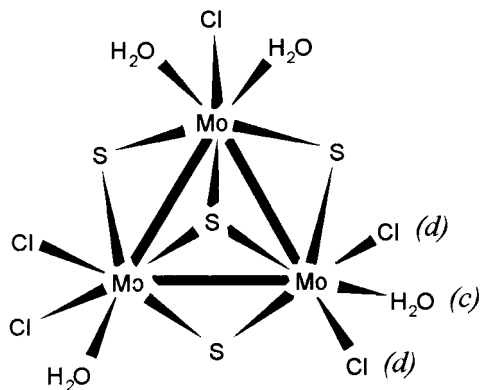


Figure 5. Layers formed by molecules of cucurbit[8]uril alternating with layers of the cluster complexes. Hydrogen bonds are indicated by dashed lines. All chloride anions and water molecules in the lattice are omitted for clarity.

which is more than twice the van der Waals radius of carbon (1.7 Å) and rules out any significant π - π interaction between the aromatic rings. It is interesting to note that in the crystal structure of free PhP(O)(OH)₂ [16] such interactions are equally lacking, but the mutual arrangement of molecules in the crystal is very different and thus the molecular 'pseudodimer' trapped inside the cucurbit[8]uril cavity in **1** cannot be regarded as a model for packing in the real crystal of PhP(O)(OH)₂. The host molecule in **1** is not absolutely rigid and undergoes a moderate distortion upon guest inclusion so that the difference between the larger and the smaller diameters (taken as the distance between two opposing CH₂ groups) is 0.321 Å. Each molecule of cucurbit[8]uril is bound with two incomplete cuboidal cluster aqua complexes [Mo₃S₄(H₂O)₄Cl₅]⁻ by hydrogen bonds (O(3M)···O(22), 2.66 Å) (Figure 3). Actually, a cluster chloro aqua complex of [M₃Q₄(H₂O)₄Cl₅]⁻ (M = Mo, W; Q = S, Se) stoichiometry can exist in 42 isomeric forms. Two of them were already found in the crystal structure of (H₃O)₂[Mo₃Se₄Cl₅(H₂O)₄]₂(C₃₆H₃₆N₂₄O₁₂)·15H₂O [17]. They differ in (a) the number of Cl and H₂O bound to each Mo atom and (b) coordinated ligand being *cis* or *trans* to



μ_3 -Q. Following established notation [17] the *cis*-ligands here are called *d*, and the *trans* - *c*. Thus the observed isomers can be written as c_2d_3 and c_1d_4 in respect to the number of Cl in the *c* and *d* positions. In the structure of

1 yet another possible ligand arrangement is found in the anion [Mo₃S₄(H₂O)₄Cl₅]⁻. It is also of the c_2d_3 type but differs in the unique Cl in the MoS₃Cl(H₂O)₂ unit being *trans* to μ_3 -S and not *cis*, as observed in the c_2d_3 -isomer of [Mo₃Se₄Cl₅(H₂O)₄]⁻. The clusters further form dimers held both by hydrogen bonding (O ... Cl: 3.15 Å) and S...S interactions (S...S: 2.92–3.40 Å) (Figure 4). The specific chalcogen–chalcogen contacts are routinely observed in the structures of M₃Q₄ clusters. They have recently been reviewed [18]. Both the cluster anion [Mo₃S₄(H₂O)₄Cl₅]⁻, and PhP(O)(OH)₂ are products of slow air oxidation of the cluster [Mo₃(Pd(PhP(OH)₂)₂)₄(H₂O)₉]⁴⁺ which originally forms from [Mo₃(PdCl)₄(H₂O)₉]³⁺ and PhP(H)(O)(OH) in 6 M HCl [19]. The layers formed by cucurbit[8]uril molecules alternate with layers of the cluster complexes in the *a* direction (Figure 5).

To probe the inclusion of molecules of aromatic acids into the cavity of a cucurbit[8]uril in solution we studied its reaction with PhP(H)(O)(OH) in 6M HCl by ³¹P NMR spectroscopy. In the spectrum of pure PhP(H)(O)(OH) the expected doublet of well defined triplets is observed (δ = 26.4 ppm, ¹J_{P-H} 595 Hz, ³J_{P-ortho-H} 13 Hz). In the presence of cucurbit[8]uril the well defined triplet structure disappears, ceding place to broad peaks. However, no new signals are observed and chemical shift remains the same. Since coupling is transmitted through the bonds and J depends *inter alia* on mutual orientation of the coupled atoms, the observed loss of triplet structure may be caused by the loss of the freedom of rotation around the P–C bond upon inclusion of the host molecule into the cucurbit[8]uril cavity.

Acknowledgements

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