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A *p*-Sulfonatothiacalix[4]arene Supramolecular Capsule Containing a Dinuclear Copper(II) Complex

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The reaction of tetrasodium *p*-sulfonatothiacalix[4]arene (Na₄H₄TCAS), copper(II) nitrate and pyridine N-oxide (PNO) afforded a yellow copper(II)-*p*-sulfonatothiacalix[4]arene complex. X-ray diffraction analysis displays that it is an interesting dimeric supramolecular capsule, [Cu₂(PNO)₂(H₂O)₆]⁴⁺ ⊂ [(H₆TCAS)₂]⁴⁻·22H₂O, in which two PNO molecules bridge the two Cu^{II} ions in the O,O'-μ₂ mode and the hydrophobic aromatic rings point into the cavities of the thiacalixarenes. Interestingly, the thiacalixarenes pack themselves into the closed pores through π···π interactions in *ab* plane, and these pores further link to each other through hydrogen bonding to construct infinite hydrophilic tunnels, which fill with the disordered water molecules as the guests.

Keywords: *p*-Sulfonatothiacalix[4]arene; Copper; Supramolecular capsule; Crystal structure

INTRODUCTION

Recently, design and investigation of self-assembled molecular capsules have attracted considerable interests in supramolecular chemistry because of their abilities of molecular substrates inclusion by means of various intermolecular forces and the great importance of biological systems for the mimicry of the catalytic efficiency of enzymes and the drug delivery [1–9]. Generally, rigid nonplanar molecules with curved or bowl-like micro-environments have the abilities to assemble into capsules and cages through supramolecular interactions. Among these multifarious building blocks, water-soluble sulfonatocalix[4,5]arenes have been proved to be productive for their pre-organized cone-like cavities,

which can shroud various guest molecules such as crown ethers [10–13], tetra-protonated cyclam [14], di-protonated [2,2,2] cryptand [15], H₂SO₄ [16], amino acids [17,18] and protonated 2,2'-bipyridine [19,20]. For larger water-soluble calixarene such as sulfonatocalix[6]arenes, they can adopt the so-called double cone conformation and confine two tetraphenylphosphonium cations in their cavities to form a molecular capsule-like arrangement [21]. Though there are several examples that capsules based on calixarenes host mononuclear species such as metal-crown ether complexes [22–26], capsules containing dinuclear and polynuclear species are rare [27]. Herein, we wish to report the preparation and x-ray crystallographic characterization of a dimeric supramolecular capsule, which contains a dinuclear Cu^{II} unit in the solid state. More interestingly, the capsules construct water-filled tunnels along the crystallographic *c* direction through π···π interactions and hydrogen bonding interactions.

RESULTS AND DISCUSSION

Yellow crystalline blocks of complex **1** were obtained by mixing copper(II) nitrate, pyridine N-oxide (PNO) and tetrasodium *p*-sulfonatothiacalix[4]arene (Na₄H₄TCAS) in an aqueous solution with the pH = 1. The single crystal X-ray diffraction study reveals that complex **1** crystallizes in the space group *Pbcn* and features a capsule with C_i symmetry (see Fig. 1). The capsule consists of two H₆TCAS²⁻ ions, two coordinated Cu^{II} cations, and two PNO. Each Cu^{II} ion is coordinated directly by one oxygen atom

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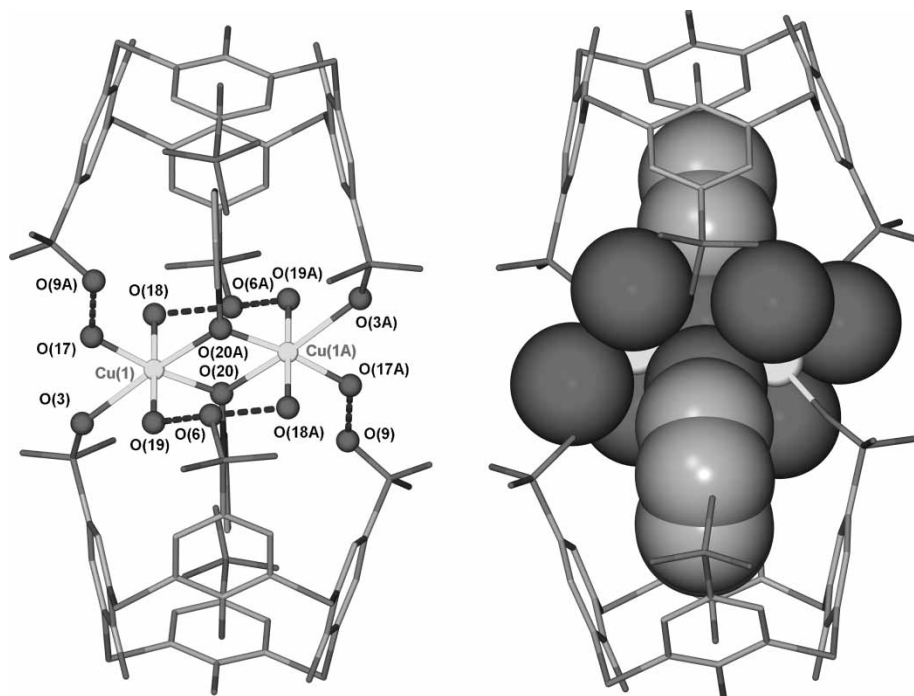


FIGURE 1 The coordination environments of Cu^{II} ions (left) and the space filling of the included part (right). All hydrogen bonds are in dashed lines.

of a sulfonate group in the axial position, and is further ligated by three aqua ligands in the equatorial position. In addition, two oxygen atoms from two PNO molecules tend to meet the demand of the Cu^{II} ion for its distorted octahedral O_6 environment, one in the axial position and the other in the equatorial position. The equatorial plane is a perfect plane (the mean deviation from plane is 0.039 Å), with Cu–O distances in the range of 1.951(4)–1.971(3) Å. The average Cu–O bond at the axis direction is 0.40 Å longer than that in the equatorial plane, where the top and bottom bonds

both stretch comparatively due to the John-Teller Effect. Interestingly, the two Cu^{II} ions are bridged by two μ_2 -oxygen from two PNO molecules, with the Cu···Cu separation of 3.50 Å. The H_6TCAS ions maintain the conventional cone conformations and adopt “head-to-head” fashions, each two to shroud a dinuclear Cu^{II} unit (Fig. 1). In order to contain the aromatic ring, H_6TCAS splay its phenyl rings from C_{4v} to C_{2v} symmetry. The separations between the centroid···centroid of the opposite phenyl rings are 7.663 Å and 6.288 Å. The hydrophobic part of the PNO molecule is embedded in the cavity of the

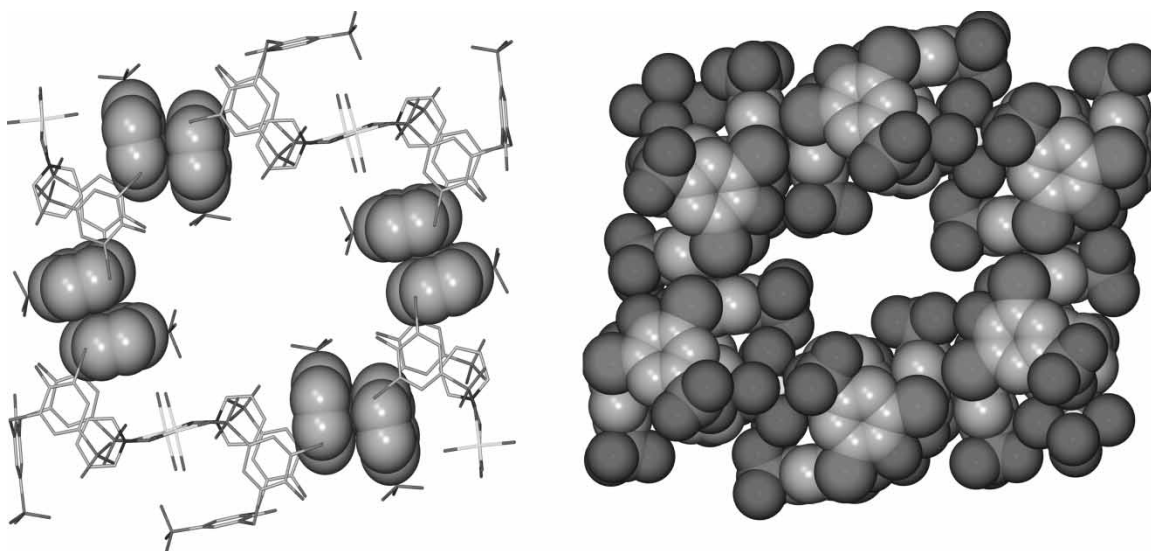


FIGURE 2 The π ··· π interactions between the thiacalixarenes (left) and space filling of the crown-like pore (right).

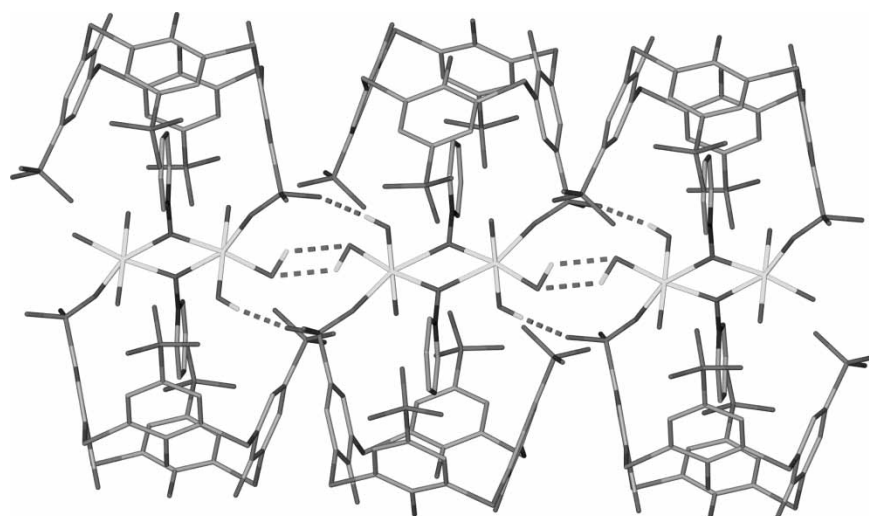
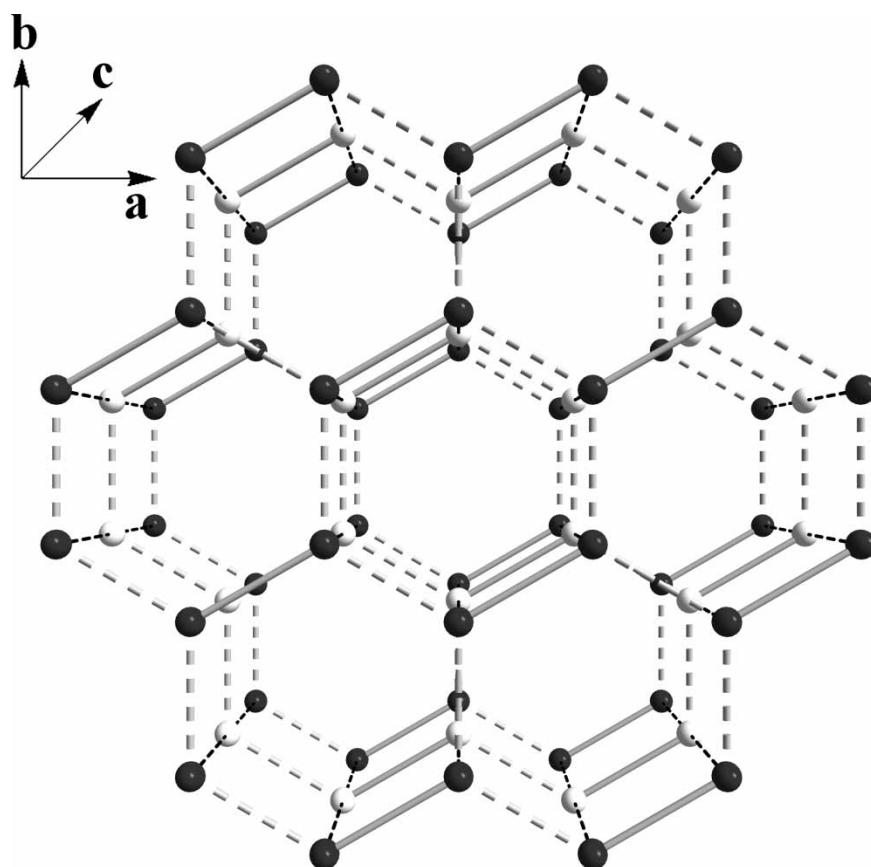


FIGURE 3 The hydrogen bonding interactions between the thiacalixarenes along the crystallographic c direction.

H_6TCAS with the depth of 4.15 \AA according to Atwood's definition [28]. There are non-classical hydrogen bonding interactions ($C-H \cdots$ aromatic ring interaction) between the PNO molecule and the H_6TCAS^{2-} ion, with the closest $C \cdots$ aromatic ring centroid distance of 3.323 \AA . In addition to the

coordination bonds, this superanion capsule is also stabilized by the hydrogen bonding. There are hydrogen bonds between coordinated water molecules and the oxygen atoms of the sulfonate groups, and the $O \cdots O$ separations range from $2.665\text{--}2.771 \text{ \AA}$. Around the capsule, there are twenty two disordered



SCHEME 1 The schematic representation of formation of tunnels through supramolecular interactions. The black and white solid balls, thiacalixarenes in different layers; the gray solid lines, coordination bonds; the gray thick dashed lines, $\pi \cdots \pi$ interactions; the black thin dashed lines, the hydrogen bonding interactions.

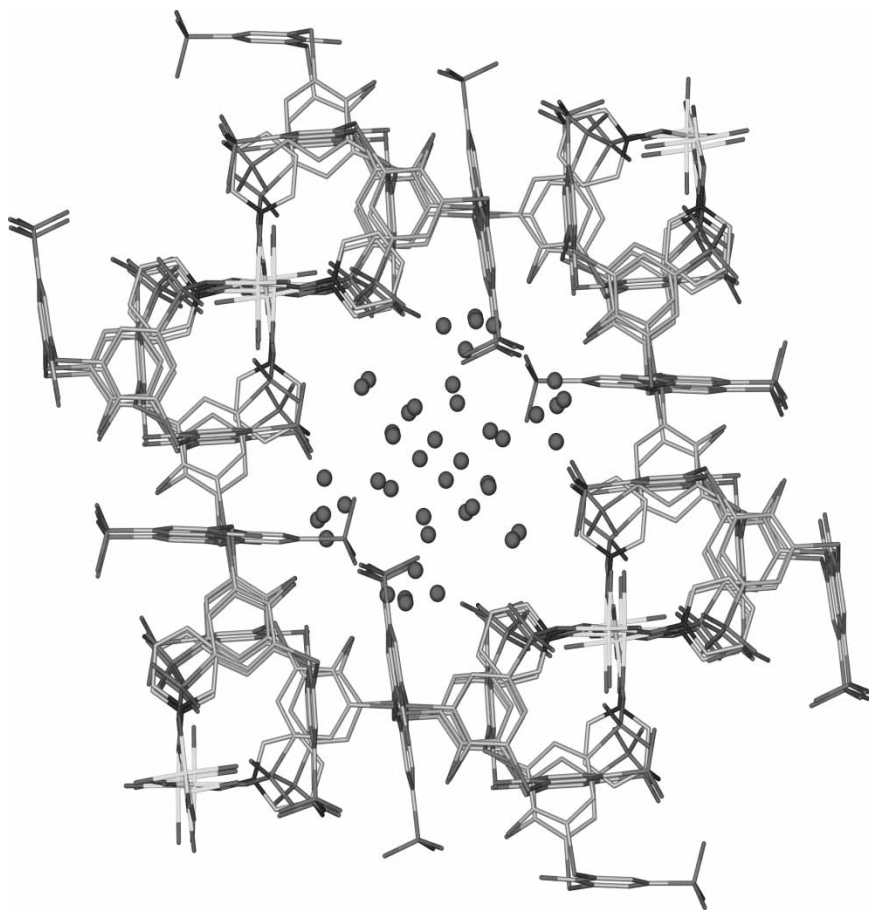


FIGURE 4 Viewing of the water-filled tunnels along the crystallographic *c* direction.

lattice water molecules occupying twenty six positions.

In the extended structure, a peculiar feature of this complex is that the thiocalixarenes pack themselves into closed pores. In the crystallographic *ab* plane six thiocalixarenes from four capsules $\pi \cdots \pi$ interact with each other, with the aromatic ring centroid \cdots centroid distances of 3.557 Å (see Fig. 2). They thus form closed pores of 10.195 Å \times 7.252 Å (The closed distances between the oxygen atoms of the sulfonate groups). The hydrophilic sulfonate groups and phenolic groups both point inside the pore. Along the crystallographic *c* direction, each thiocalixarene exploits four sets of hydrogen bondings to link the thiocalixarene in the adjacent layer (see Fig. 3). These pores in different layers display an {ABAB...}-type packing motif and construct hydrophilic tunnels (see Scheme 1). The disordered water molecules are filled in the tunnel as guest molecules (see Fig. 4).

The power XRD patterns for **1** were collected to check the purity of the polycrystalline sample. The diffraction peaks on the patterns of the experiment and simulated from the single-crystal X-ray data correspond well in position, suggesting the phase

purity of the polycrystalline sample (see Supporting Information, S1).

To study its stability, thermogravimetric analysis (TGA) for **1** was performed in N₂ atmosphere from 30°C to 800°C. TGA reveals that the weight loss from 30°C to 250°C is 20.68%, corresponding to 22 moles of H₂O per formula unit (calcd. 20.58%). When the temperature is above 250°C, **1** begins to burn the organic compounds and then to decompose. (see Supporting Information, S2).

In conclusion, we have synthesized and characterized a supramolecular capsule, which contains a dinuclear Cu^{II} unit in the solid state. These capsules interact with each other through $\pi \cdots \pi$ interactions and hydrogen bonding interactions to form hydrophilic tunnels, which are occupied by disordered water molecules.

EXPERIMENTAL SECTION

General

Elemental analyses were performed on a German Elementary Vario EL III instrument. The FT-IR spectra were recorded on a Nicolet Magna 750

FT-IR spectrometer using KBr pellets in the range of 4000–400 cm^{-1} . The X-ray power diffraction experiment was carried out on a DMAX 2500 instrument. The thermogravimetric analysis was performed using a NETZSCH STA 449C instrument in flowing N_2 with a heating rate of $10^\circ\text{C min}^{-1}$ in the range of 30–800°C.

Material

Tetrasodium *p*-sulfonatothiacalix[4]arene was synthesized by literature methods [29]. All other reagents were commercially available and used without further purification.

Preparation of Copper(II)-thiacalixarene Complex, 1

Copper(II) nitrate (24 mg, 0.1 mmol), Pyridine N-oxide (10 mg, 0.1 mmol), and tetrasodium *p*-sulfonatothiacalix[4]arene (48 mg, 0.05 mmol) were dissolved in 5 ml distilled water and the pH value of the solution was adjusted by the 0.1 mol/L HNO_3 to 1.0. Yellow prisms of **1** were deposited from the solution after slow evaporation for several weeks. For **1**, yield 20 mg, 34.81% based on *p*-sulfonatothiacalix[4]arene. *Anal. Calc.* for **1** ($\text{C}_{58}\text{H}_{94}\text{Cu}_2\text{N}_2\text{O}_{62}\text{S}_{16}$): C, 28.42%; H, 3.86%; N, 1.14%. *Found:* C, 28.48%; H, 3.84%; N, 1.15%. IR (KBr disk, $\nu \text{ cm}^{-1}$): 3339.23 (s), 1628.16 (m), 1475.30 (s), 1449.02 (s), 1388.18 (m), 1199.47 (s), 1040.85 (s), 738.22 (s), 614.19 (s).

X-ray Crystallographic Study

The X-ray density data of **1** were collected at 298(2) K on a Siemens Smart CCD diffractometer with graphite monochromated Mo- $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) using the ω -scan mode, and were corrected with the SADABS program [30]. The structure solution by direct methods [31], and the full matrix least-squares refinement was carried out using the SHELXL-97 software package with anisotropic thermal parameters for all non-hydrogen atoms [32]. The organic hydrogen atoms were generated geometrically (C–H bond fixed at 0.96 \AA), and allowed to ride on their parent atoms before the final cycle of refinement. The hydrogen atoms of the coordinated water molecules are calculated by WinGX software package [33]. Given the overall charge balance, two of the four sulfonate groups of each thiacalixarene are necessarily protonated. However, these protons were not found crystallographically. In addition, the sulfonate group coordinating to the metal centre is disordered and the atoms are split into two partial atomic positions with a refined occupancy of 0.5. CCDC—614683 for **1** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

SUPPORTING INFORMATION

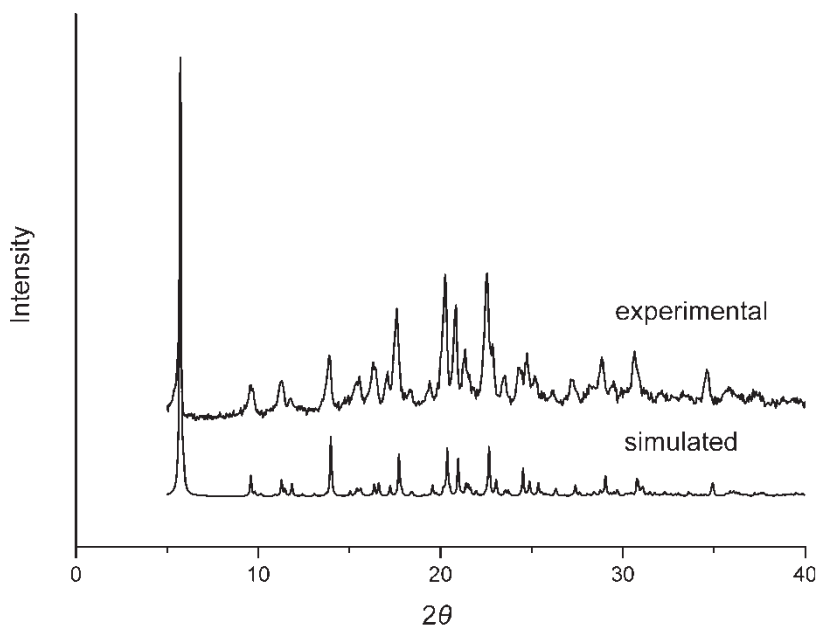


FIGURE S1 Experimental and simulated X-ray power diffraction patterns of **1**.

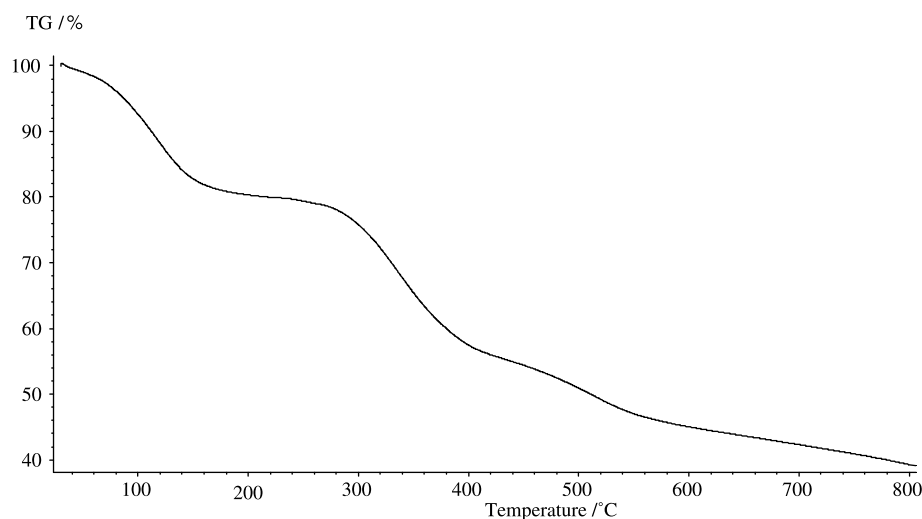


FIGURE S2 Thermogravimetric curve of complex 1.

TABLE I Crystal data and data collection parameters for 1

Empirical formula	$C_{58}H_{94}Cu_2N_2O_{62}S_{16}$
Formula weight	2451.39
Temperature (K)	298(2)
Wavelength (Å)	0.71073
Crystal system, space group	Orthorhombic, <i>Pbcn</i>
Unit cell dimensions	$a = 29.850(18)$, $b = 18.007(8)$, $c = 18.423(8)$ Å
Volume (Å ³)	9902(8)
Z, calculated density (g cm ⁻³)	4, 1.644
Absorption coefficient (mm ⁻¹)	0.875
<i>F</i> (000)	5064
Crystal size	0.65 × 0.35 × 0.23
Range for data collection	1.72–27.48°
Limiting indices	−30 ≤ <i>h</i> ≤ 38, −23 ≤ <i>k</i> ≤ 23, −23 ≤ <i>l</i> ≤ 23
Reflections collected/unique	72268/ 11263 [<i>R</i> (int) = 0.0300]
Completeness to $\theta = 27.48^\circ$	99.1%
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.080
Final <i>R</i> indices [$I > 2\sigma(I)$]	$R1 = 0.0877$, $wR2 = 0.2433$
<i>R</i> indices (all data)	$R1 = 0.0932$, $wR2 = 0.2511$

TABLE II Selected bonds lengths and angles for 1 (Å, °)

Cu(1)–O(18)	1.951(4)	Cu(1)–O(17)	1.962(4)
Cu(1)–O(20)	1.965(3)	Cu(1)–O(19)	1.971(3)
Cu(1)–O(20) ^{#1}	2.369(3)	Cu(1)–O(3')	2.425(11)
Cu(1)–O(3)	2.300(5)		
O(18)–Cu(1)–O(17)	87.08(17)	O(18)–Cu(1)–O(20)	88.78(14)
O(17)–Cu(1)–O(20)	172.08(16)	O(18)–Cu(1)–O(19)	176.98(16)
O(17)–Cu(1)–O(19)	90.78(16)	O(20)–Cu(1)–O(19)	93.09(13)
O(18)–Cu(1)–O(3)	91.4(2)	O(17)–Cu(1)–O(3)	98.1(2)
O(20)–Cu(1)–O(3)	88.76(19)	O(19)–Cu(1)–O(3)	90.97(18)
O(18)–Cu(1)–O(20) ^a	92.45(15)	O(17)–Cu(1)–O(20) ^a	100.78(16)
O(20)–Cu(1)–O(20) ^a	72.65(12)	O(19)–Cu(1)–O(20) ^a	85.85(12)
O(3)–Cu(1)–O(20) ^a	160.90(18)	O(18)–Cu(1)–O(3')	100.8(3)
O(17)–Cu(1)–O(3')	75.4(3)	O(20)–Cu(1)–O(3')	112.0(3)
O(19)–Cu(1)–O(3')	80.7(3)	O(3)–Cu(1)–O(3')	25.1(3)
O(20) ^{#1} –Cu(1)–O(3')	165.9(3)	S(1)–O(3')–Cu(1)	139.5(5)

^aSymmetry transformations used to generate equivalent atoms: $-x, -y + 1, -z + 1$.

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References

- [1] Conn, M. M.; Rebek, J. Jr. *Chem. Rev.* **1997**, *97*, 1647.
- [2] Seidel, S. R.; Stang, P. J. *Acc. Chem. Res.* **2002**, *35*, 972.

- [3] Hof, F.; Craig, S. L.; Nuckolls, C.; Rebek, Jr., J. *Angew. Chem., Int. Ed.* **2002**, *41*, 1488.
- [4] Rondelez, Y.; Rager, M. -N.; Duprat, A.; Reinaud, O. *J. Am. Chem. Soc.* **2002**, *124*, 1334.
- [5] Blanchard, S.; Le Clainche, L.; Rager, M.-N.; Chansou, B.; Tuchagues, J.-P.; Duprat, A. F.; Le Mest, Y.; Reinaud, O. *Angew. Chem., Int. Ed.* **1998**, *37*, 2732.
- [6] Corbellini, F.; Fiammengo, R.; Timmerman, P.; Crego-Calama, M.; Verslius, K.; Heck, A. J. R.; Luyten, I.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **2003**, *124*, 6569.
- [7] Kusakawa, T.; Fujita, M. *J. Am. Chem. Soc.* **2002**, *124*, 13576.
- [8] Arena, G.; Bonomo, R. P.; Contino, A.; Gulino, F. G.; Magri, A.; Sciotto, D. *J. Incl. Phenom. Macrocycl. Chem.* **1997**, *29*, 347.
- [9] Floriani, C.; Jacoby, D.; Chiesi-Villa, A.; Guastini, C. *Angew. Chem.* **1989**, *101*, 1430.
- [10] Hardie, M. J.; Johnson, J. A.; Raston, C. L.; Webb, H. R. *Chem. Commun.* **2000**, 849.
- [11] Atwood, J. L.; Barbour, L. J.; Dalgarno, S. J.; Hardie, M. J.; Raston, C. L.; Webb, H. R. *J. Am. Chem. Soc.* **2005**, *126*, 13170.
- [12] Wu, M. Y.; Yuan, D. Q.; Han, L.; Wu, B. L.; Xu, Y. Q.; Hong, M. C. *Eur. J. Inorg. Chem.* **2006**, 526.
- [13] Guo, Q. L.; Zhu, W. X.; Liu, Y. Ch.; Yuan, D. Q.; Zhang, J.; Ma, S. L. *Polyhedron* **2004**, *23*, 2055.
- [14] Airey, S.; Drljaca, A.; Hardie, S. J.; Raston, C. L. *Chem. Commun.* **1999**, 1137.
- [15] Hardie, S. J.; Raston, C. L. *Chem. Commun.* **2002**, 2216.
- [16] Hardie, S. J.; Makaha, M.; Raston, C. L. *Chem. Commun.* **1999**, 2049.
- [17] Nichols, P. J.; Raston, C. L. *Dalton Trans.* **2003**, 2923.
- [18] Atwood, J. L.; Ness, T.; Nichols, P. J.; Raston, C. L. *Cryst. Growth Des.* **2002**, *2*, 171.
- [19] Yu, L.; Guo, D. Sh.; Yang, E. C.; Zhang, H. Y.; Zhao, Y. L. *Eur. J. Org. Chem.* **2005**, 162.
- [20] Yuan, D. Q.; Wu, M. Y.; Wu, B. L.; Xu, Y. Q.; Jiang, F. L.; Hong, M. C. *Cryst. Growth Des.* **2006**, *6*, 515.
- [21] Makaha, M.; Raston, C. L.; Sobolev, A. N.; White, A. H. *Chem. Commun.* **2005**, 1962.
- [22] Atwood, J. L.; Barbour, L. J.; Dalgarno, S. J.; Hardie, M. J.; Raston, C. L.; Webb, H. R. *Dalton Trans.* **2002**, 4351.
- [23] Drljaca, A.; Hardie, S. J.; Raston, C. L.; Spiccia, L. *Chem. Eur. J.* **1999**, *5*, 2295.
- [24] Drljaca, A.; Hardie, S. J.; Ness, T. J.; Raston, C. L. *Eur. J. Inorg. Chem.* **2000**, 2221.
- [25] Ness, T. J.; Nichils, P. J.; Raston, C. L. *Eur. J. Inorg. Chem.* **2001**, 1993.
- [26] Drljaca, A.; Hardie, S. J.; Raston, C. L. *Dalton Trans.* **1999**, 3639.
- [27] Webb, H. R.; Hardie, M. J.; Raston, C. L. *Chem. Eur. J.* **2001**, *7*, 3616.
- [28] Atwood, J. L.; Orr, G. W.; Hamada, F.; Vincent, R. L.; Bott, S. G.; Robinson, K. D. *J. Am. Chem. Soc.* **1991**, *113*, 2760.
- [29] Yuan, D. Q.; Zhu, W. X.; Ma, S.; Yan, X. *J. Mol. Struct.* **2002**, *616*, 241.
- [30] Sheldrick, G. M. *SADABS, Program for Empirical Absorption Correction of Area Detector Data*; University of Göttingen: Göttingen.
- [31] Sheldrick, G. M. *ShELXL 97, Program for Crystal Structure Solution*; University of Göttingen: Göttingen, 1997.
- [32] Sheldrick, G. M. *Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, 1997.
- [33] Farrugia, L. J. *J. Appl. Cryst.* **1999**, *32*, 837.