

Bang-Tun Zhao,<sup>a\*</sup> Pu-Zhou Hu,<sup>a</sup>  
Jian-Ge Wang,<sup>a</sup> Lu-Fang Ma,<sup>a</sup>  
Li-Ya Wang<sup>a</sup> and Seik Weng Ng<sup>b</sup>

<sup>a</sup>Department of Chemistry, Luoyang Normal University, Luoyang 471022, People's Republic of China, and <sup>b</sup>Department of Chemistry, University of Malaya, 50603 Kuala Lumpur, Malaysia

Correspondence e-mail: zbt@lynu.edu.cn

#### Key indicators

Single-crystal X-ray study  
T = 295 K  
Mean  $\sigma(\text{C}-\text{C}) = 0.005 \text{ \AA}$   
Disorder in main residue  
R factor = 0.041  
wR factor = 0.130  
Data-to-parameter ratio = 16.0

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

## Bis[hexaaquacadmium(II)] 25,26,27,28-tetrahydroxy-2,8,14,19-tetrathiacalix[4]arene-5,11,17,23-tetra-sulfonate monohydrate clathrate

The title compound,  $[\text{Cd}(\text{H}_2\text{O})_6]_2(\text{C}_{24}\text{H}_{20}\text{O}_{16}\text{S}_8) \cdot \text{H}_2\text{O}$ , the bis[hexaaquacadmium(II)] salt of the *p*-sulfonatocalix[4]arene tetraanion, crystallizes as a hydrate; two symmetry-independent cations interact with the tetraanion *via* their coordinated water molecules. The Cd atoms and water O atom lie on special positions of site symmetry *m* and the complete calixarene anion is generated by mirror symmetry. The water molecule is weakly associated with the calixarene cavity by way of long  $\text{O}-\text{H} \cdots \text{O}$  hydrogen bonds.

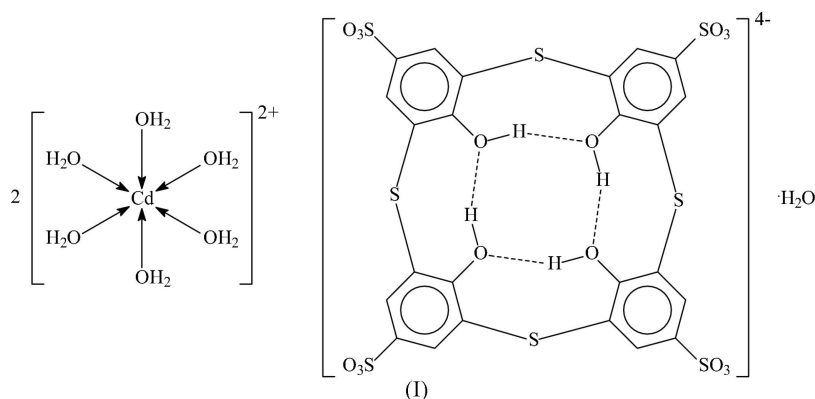
Received 5 September 2005

Accepted 7 September 2005

Online 14 September 2005

#### Comment

The *p*-sulfonatocalix[4]arene tetraanion (see scheme) adopts a bowl-shaped conformation, with the negatively charged sulfonate groups at the upper rim and the neutral/deprotonated hydroxyl groups at the lower rim. As such, it is capable of forming inclusion compounds through  $\pi$ -stacking, hydrogen-bonding and coordinative interactions (Atwood *et al.*, 2001). A manganese(II) derivative of this species has been described (Gao *et al.*, 2003) in which the hexaaquamanganese cations interact with the anionic *p*-sulfonatocalix[4]arene indirectly, *via* their coordinated water molecules. That compound was formulated as  $[\text{Mn}(\text{H}_2\text{O})_6]_2(\text{C}_{24}\text{H}_{20}\text{O}_{16}\text{S}_8) \cdot 0.5\text{H}_2\text{O}$ .



The present cadmium complex, (I) (Fig. 1), is essentially isostructural with the manganese analogue (similar cell dimensions and the same space group), but was modelled as  $[\text{Cd}(\text{H}_2\text{O})_6]_2(\text{C}_{24}\text{H}_{20}\text{O}_{16}\text{S}_8) \cdot \text{H}_2\text{O}$ , *i.e.* with full occupancy of the non-coordinated water molecule. The hexaaquacadmium(II) species possess typical geometrical parameters (Table 1).

An extensive network of  $\text{O}-\text{H} \cdots \text{O}$  hydrogen bonds (Table 2) helps to stabilize the crystal packing in (I). The non-coordinated water molecule (*O9w*) lies on a special position of site symmetry *m*; as it forms long hydrogen bonds [ $\text{H} \cdots \text{O} = 2.44(2) \text{ \AA}$ ] to neighbouring acceptor calixarene hydroxide O atoms, its displacement factor is relatively large.

Experimental

Tetrasodium *p*-sulfonatocalix[4]arene (Gao *et al.*, 2003; Iki *et al.*, 1998) (0.18 g, 0.2 mmol) was dissolved in water (10 ml) and cadmium nitrate (0.08 g, 0.4 mmol) was added to the solution. The filtered solution was set aside for several days resulting in the growth of colourless plates of (I).

Crystal data

[Cd(H<sub>2</sub>O)<sub>6</sub>]<sub>2</sub>(C<sub>24</sub>H<sub>2</sub>O<sub>16</sub>S<sub>8</sub>)·H<sub>2</sub>O  
*M<sub>r</sub>* = 1271.82  
 Monoclinic, *P*2<sub>1</sub>/*m*  
*a* = 13.1183 (5) Å  
*b* = 14.2581 (6) Å  
*c* = 13.1854 (5) Å  
 $\beta$  = 113.563 (1)°  
*V* = 2260.6 (2) Å<sup>3</sup>  
*Z* = 2

*D<sub>x</sub>* = 1.868 Mg m<sup>-3</sup>  
 Mo *K*α radiation  
 Cell parameters from 8025 reflections  
 $\theta$  = 2.8–28.4°  
 $\mu$  = 1.40 mm<sup>-1</sup>  
*T* = 295 (2) K  
 Block, colourless  
 0.35 × 0.33 × 0.27 mm

Data collection

Bruker APEX2 area-detector diffractometer  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)  
*T<sub>min</sub>* = 0.556, *T<sub>max</sub>* = 0.703  
 19302 measured reflections

5380 independent reflections  
 5106 reflections with *I* > 2σ(*I*)  
*R<sub>int</sub>* = 0.019  
 $\theta_{max}$  = 27.5°  
*h* = -17 → 17  
*k* = -18 → 18  
*l* = -17 → 17

Refinement

Refinement on *F*<sup>2</sup>  
*R* [*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.041  
*wR* (*F*<sup>2</sup>) = 0.130  
*S* = 1.11  
 5380 reflections  
 337 parameters  
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0599P)^2 + 6.3407P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 ( $\Delta/\sigma$ )<sub>max</sub> = 0.001  
 $\Delta\rho_{max} = 1.76 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{min} = -1.74 \text{ e } \text{Å}^{-3}$

Table 1 Selected bond lengths (Å).

Cd1—O1w	2.243 (5)	Cd2—O5w	2.272 (5)
Cd1—O2w	2.243 (5)	Cd2—O6w	2.245 (5)
Cd1—O3w	2.288 (3)	Cd2—O7w	2.275 (3)
Cd1—O4w	2.279 (4)	Cd2—O8w	2.287 (3)

Table 2 Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1w—H1w1...O6 <sup>iii</sup>	0.85 (1)	1.92 (1)	2.767 (4)	172 (3)
O2w—H2w1...O7	0.84 (1)	1.90 (1)	2.732 (4)	169 (4)
O3w—H3w1...O8	0.85 (1)	1.97 (1)	2.817 (4)	176 (5)
O3w—H3w2...O3 <sup>iv</sup>	0.85 (1)	1.91 (1)	2.754 (4)	171 (5)
O4w—H4w1...O4 <sup>v</sup>	0.85 (1)	1.91 (2)	2.746 (4)	168 (7)
O4w—H4w2...O8 <sup>iii</sup>	0.85 (1)	1.93 (1)	2.775 (5)	174 (7)
O5w—H5w1...O4 <sup>v</sup>	0.85 (1)	1.98 (1)	2.814 (4)	172 (6)
O6w—H6w1...O3	0.85 (1)	1.94 (1)	2.786 (4)	175 (4)
O7w—H7w2...O5	0.85 (1)	1.93 (1)	2.764 (4)	169 (5)
O7w—H7w1...O7	0.85 (1)	1.96 (2)	2.781 (4)	162 (6)
O8w—H8w1...O5 <sup>v</sup>	0.85 (1)	1.94 (1)	2.788 (4)	176 (5)
O8w—H8w2...O6 <sup>v</sup>	0.85 (1)	1.96 (1)	2.798 (4)	170 (5)
O9w—H9w1...O8w	0.86 (1)	2.44 (2)	3.188 (12)	146 (3)
O1—H11...O1 <sup>ii</sup>	0.85	2.23	2.864 (7)	132
O1—H12...O2	0.85	2.45	3.066 (5)	130
O2—H21...O1	0.85	2.48	3.066 (4)	127
O2—H22...O2 <sup>ii</sup>	0.85	2.33	2.940 (4)	129

Symmetry codes: (ii) *x*, -*y* + ½, *z*; (iii) -*x* + 1, -*y* + 1, -*z* + 1; (iv) *x* - 1, *y*, *z*; (v) -*x* + 2, -*y* + 1, -*z* + 1.

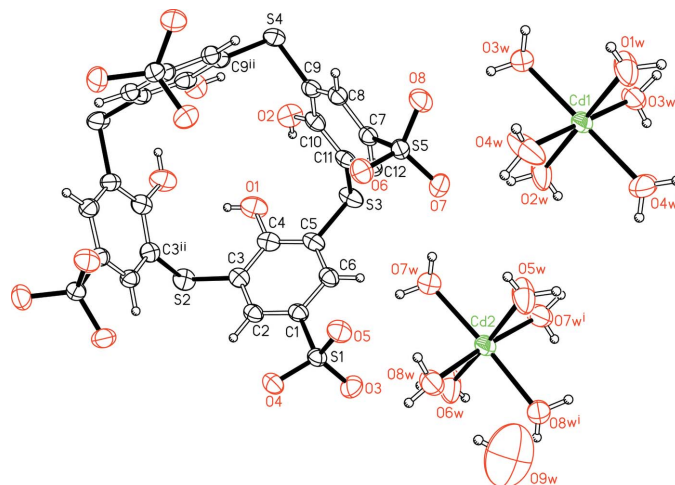


Figure 1 View of (I), showing 50% displacement ellipsoids (arbitrary spheres for H atoms). [Symmetry codes: (i) *x*, ½ - *y*, *z*; (ii) *x*, ½ - *y*, *z*.]

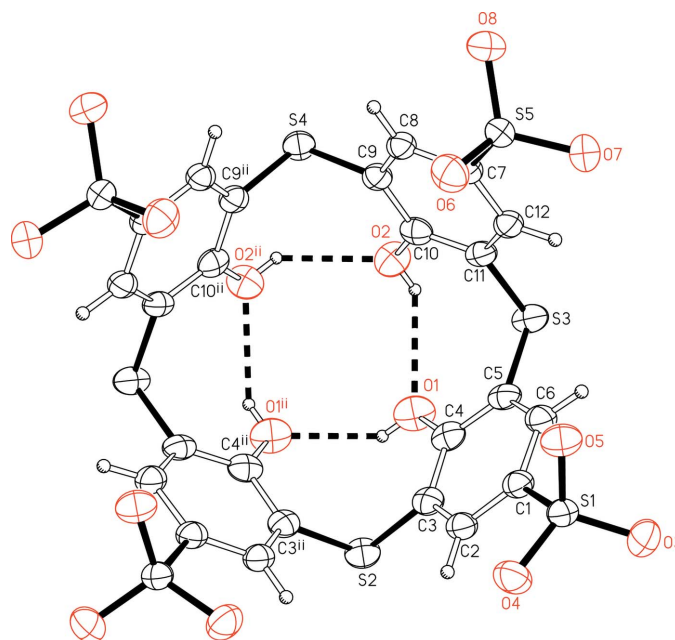


Figure 2 Detail of (I), showing one possible 'clockwise' cyclic arrangement of O—H...O hydrogen bonds within the calixarene anion. As a result of the positional disorder of the hydroxy H atoms (not shown), the hydrogen bonds can also propagate in the reverse (anticlockwise) sense.

The C-bound H atoms were positioned geometrically (C—H = 0.93 Å) and were included in the refinement in the riding-model approximation, with *U<sub>iso</sub>*(H) = 1.2*U<sub>eq</sub>*(C). The water H atoms were located in difference maps and were refined with the distance restraints O—H = 0.85 (1) Å and H...H = 1.39 (1) Å, and with *U<sub>iso</sub>*(H) = 1.2*U<sub>eq</sub>*(O). The two hydroxy H atoms of the anion are disordered over two positions. Two H-atom sites (H11 and H12 attached to O1 and H21 and H22 attached to O2), each of 50% occupancy, were generated for each O atom in idealized positions (O—H = 0.85 Å) and refined as riding with *U<sub>iso</sub>*(H) = 1.2*U<sub>eq</sub>*(O). This arrangement for the two orientations of the hydroxy groups leads to

the formation of either a clockwise or an anticlockwise ring of O—H...O hydrogen bonds (Fig. 2 and Table 2). The deepest difference hole is 0.65 Å from atom Cd1 and the highest difference peak is 2.77 Å from atom H8, in a possible solvent-accessible void. Attempts to refine the electron density as an O atom were unsuccessful.

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINTE* (Bruker, 2003); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

This work was supported by the Natural Science Foundation of Henan Province (grant Nos. 2004601012, 0511020100 and 234) and the University of Malaya.

## References

- Atwood, J. L., Barbour, L. J., Hardie, M. J. & Raston, C. L. (2001). *Coord. Chem. Rev.* **222**, 3–32.
- Bruker (2003). *SAINTE* and *SMART*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Gao, Q.-L., Zhu, W.-X., Dong, S.-J., Ma, S.-L. & Yan, X. (2003). *J. Mol. Struct.* **650**, 159–164.
- Iki, N., Fujimoto, T. & Miyano, S. (1998). *Chem. Lett.* pp. 625–626.
- Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.