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A hydrated co-crystal of bis(μ-oxo-κ^2O:O)-bis[aquaoxodichloromolybdenum(VI)] with cucurbit[6]uril

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Cucurbit[6]uril crystallizes with bis(μ-oxo-κ^2O:O)bis[aquaoxodichloromolybdenum(VI)] as the 10.5-hydrate, with the formula $[Mo_2O_4Cl_4(H_2O)_2]\cdot(C_{36}H_{36}N_{24}O_{12})\cdot10.5H_2O$. The molybdenum-bearing component interacts indirectly with two cryptands through the two coordinated water molecules, each outer-sphere-coordination cryptand forming only one hydrogen bond with each water molecule. The asymmetric unit has two cryptands, both of which lie on special positions of $\overline{1}$ site symmetry. One of them encapsulates a water molecule that is disordered over two general positions, whereas the other encapsulates one that lies on a centre of inversion. The solvent water molecules interact with the dinuclear complex and with both cucurbituril molecules to form a three-dimensional network structure.

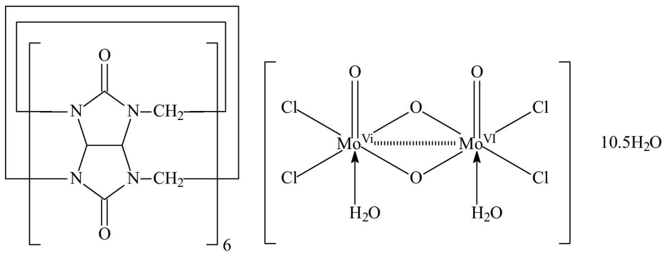
Key indicators

Single-crystal X-ray study
T = 173 K
Mean σ(C–C) = 0.005 Å
H-atom completeness 99%
Disorder in solvent or counterion
R factor = 0.046
wR factor = 0.139
Data-to-parameter ratio = 14.4

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

Comment

Our previous paper (Liu *et al.*, 2005) described the crystal structure of an adduct of cucurbit[5]uril, $C_{30}H_{30}N_{20}O_{10}$, in which the cryptand binds simultaneously to K and Zn ions. A water molecule is located within the barrel-shaped cryptand. Cucurbit[6]uril is the next larger member of this class of cryptands. The literature reports that molydenum as well as tungsten cluster compounds yield supramolecular compounds with cucurbit[*n*]urils (Dybtsev *et al.*, 2000; Fedin *et al.*, 2000, 2001, 2002). The present study was aimed at the synthesis of a large molybdenum cluster complex which would be stabilized through the capping of parts of the cluster by the cryptand molecules. Instead, in the reaction, the $[Mo_7O_{24}]^{6-}$ reagent was broken up into a dinuclear species which exists as a neutral complex. The title compound, (I), is a co-crystal of $[Mo_2O_4Cl_4(H_2O)_2]$ and cucurbit[6]uril, in which the two components are linked by hydrogen bonds, *i.e.* $[Mo_2O_4Cl_4(H_2O)_2]\cdot(C_{36}H_{36}N_{24}O_{12})\cdot10.5H_2O$.



(I)

In the dinuclear entity, the Mo atoms are linked by an Mo—Mo bond, the distance of which compares well with that [2.584 (1) Å] found in $[C_5H_5NH]_2[Mo_2H_2O_4Cl_4(H_2O)_2]\cdot H_2O$; the metal atom in that compound exists in a +5 oxidation state (Glowiak & Sabat, 1975).

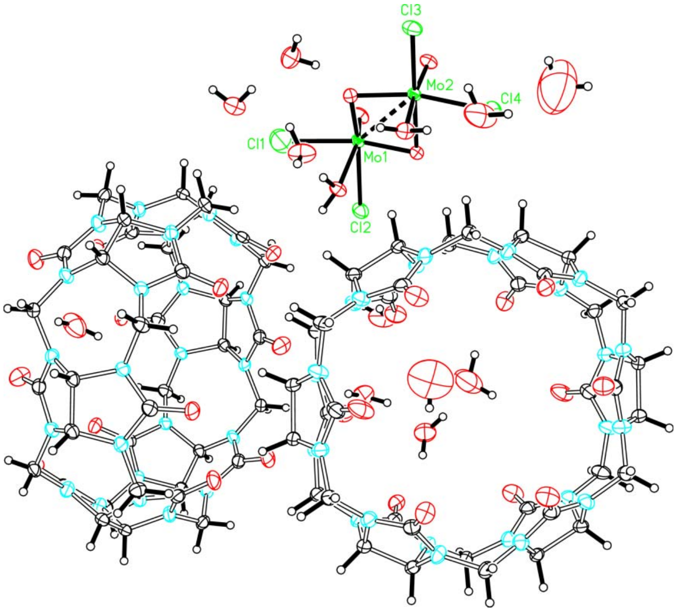


Figure 1
A view of the structure of (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. The disorder component is not shown, and only some atoms are labelled.

The coordinated water molecules interact with different cryptands in (I). This form of indirect bonding between the metal atom and the cryptand is similar to that found in the strontium complex of the cryptand (Gerasko *et al.*, 2003); such bonding occurs as a consquence of the polarity of the carbonyl groups (Gerasko *et al.*, 2004). Tetramethylcucurbit[6]uril is known to afford an inclusion complex with 4,4′-bipyridine (Zhao *et al.*, 2004).

Experimental

Ammonium heptamolybdate(VI) tetrahydrate, $[NH_4]_6[Mo_7O_{24}]\cdot 4H_2O$, (2.80 g, 2.30 mmol) and ammonium acetate (3.00 g, 38.9 mmol) were dissolved in acetic acid (15 ml) and water (160 ml). The mixture was heated to 353 K to dissolve the reagents; hydrazine hydrochloride, $N_2H_4\cdot 2HCl$ (0.30 g, 2.86 mmol), was then added. The mixture turned dark brown, and the brown compound that separated was collected by filtration and washed with ethanol. The compound (weighing 0.032 g) was then added to a solution of 0.018 *M* cucurbit[6]uril dissolved in water (5 ml). The mixture was heated for 10 min at 333 K. The title compound separated from the filtered solution as brown crystals after several days.

Crystal data

$[Mo_2O_4Cl_4(H2O)_2]\cdot(C_{36}H_{36}N_{24}O_{12})\cdot 10.5H_2O$
$M_r = 1619.77$
Triclinic, $P\bar{1}$
$a = 12.4125\ (5)$ Å
$b = 15.4864\ (6)$ Å
$c = 17.5542\ (7)$ Å
$\alpha = 106.082\ (1)°$
$\beta = 105.386\ (1)°$
$\gamma = 106.520\ (1)°$
$V = 2883.5\ (2)$ Å^3

$Z = 2$
$D_x = 1.866$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 8301 reflections
$\theta = 2.8–28.3°$
$\mu = 0.73$ mm^{-1}
$T = 173\ (2)$ K
Plate, brown
0.41 × 0.40 × 0.10 mm

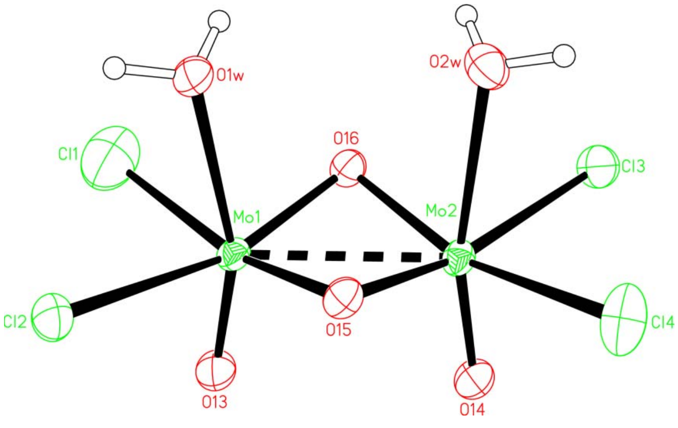


Figure 2
A plot of the $[Mo_2O_4Cl_4(H_2O)_2]$ complex in (I).

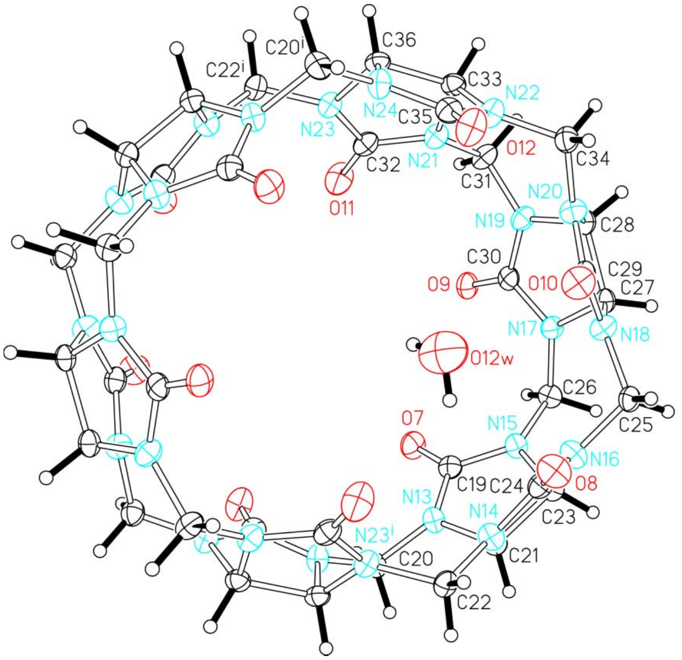


Figure 3
A plot of one of the $C_{36}H_{36}N_{24}O_{12}$ cryptands encapsulating a disordered water molecule that lies on a general position. The second disorder component is not shown. [Symmetry code (i): $2 - x, 2 - y, 2 - z$.]

Data collection

Bruker APEX CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
$T_{min} = 0.701$, $T_{max} = 0.930$
24 428 measured reflections

12 659 independent reflections
11 649 reflections with $I > 2\sigma(I)$
$R_{int} = 0.016$
$\theta_{max} = 27.5°$
$h = -16 \rightarrow 16$
$k = -20 \rightarrow 20$
$l = -22 \rightarrow 22$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.139$
$S = 1.03$
12 659 reflections
879 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0814P)^2 + 8.1614P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.75$ e Å^{-3}
$\Delta\rho_{min} = -1.70$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Mo1—O13	1.678 (2)	Mo2—O14	1.680 (2)
Mo1—O15	1.921 (2)	Mo2—O15	1.933 (2)
Mo1—O16	1.937 (2)	Mo2—O16	1.938 (2)
Mo1—O1*w*	2.266 (2)	Mo2—O2*w*	2.353 (2)
Mo1—Cl1	2.390 (2)	Mo2—Cl3	2.485 (1)
Mo1—Cl2	2.485 (1)	Mo2—Cl4	2.462 (1)
O13—Mo1—O15	107.3 (1)	O14—Mo2—O15	104.8 (1)
O13—Mo1—O16	106.3 (1)	O14—Mo2—O16	108.4 (1)
O13—Mo1—O1*w*	161.5 (1)	O14—Mo2—O2*w*	166.1 (1)
O13—Mo1—Cl1	90.0 (1)	O14—Mo2—Cl3	91.4 (1)
O13—Mo1—Cl2	91.2 (1)	O14—Mo2—Cl4	92.8 (1)
O15—Mo1—O16	92.9 (1)	O15—Mo2—O16	92.5 (1)
O15—Mo1—O1*w*	86.0 (1)	O15—Mo2—O2*w*	85.4 (1)
O15—Mo1—Cl1	162.4 (1)	O15—Mo2—Cl3	163.0 (1)
O15—Mo1—Cl2	85.9 (1)	O15—Mo2—Cl4	82.2 (1)
O16—Mo1—O1*w*	85.3 (1)	O16—Mo2—O2*w*	80.0 (1)
O16—Mo1—Cl1	85.0 (1)	O16—Mo2—Cl3	87.2 (1)
O16—Mo1—Cl2	162.0 (1)	O16—Mo2—Cl4	158.8 (1)
O1*w*—Mo1—Cl1	76.42 (7)	O2*w*—Mo2—Cl3	77.8 (1)
O1*w*—Mo1—Cl2	76.78 (7)	O2*w*—Mo2—Cl4	79.1 (1)
Cl1—Mo1—Cl2	90.72 (4)	Cl3—Mo2—Cl4	91.95 (4)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*w*—H11···O9	0.84	2.03	2.835 (3)	161
O1*w*—H12···O3*w*	0.84	1.77	2.599 (4)	168
O2*w*—H21···O4$^{\rm i}$	0.83	2.39	3.080 (4)	142
O2*w*—H21···O3*w*	0.83	2.40	3.105 (4)	143
O2*w*—H22···O6*w*	0.83	1.91	2.731 (4)	168
O3*w*—H31···O2$^{\rm i}$	0.84	1.91	2.738 (4)	169
O3*w*—H32···O4*w*	0.84	2.11	2.874 (4)	152
O4*w*—H42···O6$^{\rm i}$	0.84	2.06	2.842 (4)	157
O4*w*—H41···O16	0.84	1.96	2.738 (4)	154
O5*w*—H51···Cl1$^{\rm ii}$	0.85	2.44	3.050 (7)	130
O5*w*—H52···O4*w*	0.84	1.78	2.624 (6)	175
O6*w*—H61···O12$^{\rm iii}$	0.84	2.32	2.831 (4)	120
O7*w*—H71···Cl4$^{\rm iv}$	0.88	2.27	2.60 (1)	102
O8*w*—H82···O6$^{\rm v}$	0.84	2.06	2.835 (5)	153
O8*w*—H81···O13*w*$^{\rm v}$	0.85	2.42	2.90 (2)	116
O9*w*—H91···Cl2$^{\rm vi}$	0.84	2.46	3.264 (4)	159
O9*w*—H92···O1	0.84	2.06	2.819 (4)	149
O10*w*—H101···O5	0.84	1.84	2.638 (4)	159
O10*w*—H102···O8*w*	0.83	1.70	2.511 (5)	164
O11*w*—H112···O10*w*	0.84	1.69	2.485 (5)	156
O11*w*—H111···O3	0.84	1.89	2.619 (4)	144
O12*w*—H122···O11$^{\rm vii}$	0.83	2.42	3.012 (7)	129

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x+1, -y+1, -z+2$; (iii) $x-1, y-1, z-1$; (iv) $-x+1, -y, -z+1$; (v) $-x+2, -y+1, -z+1$; (vi) $-x+2, -y+1, -z+2$; (vii) $-x+2, -y+2, -z+2$.

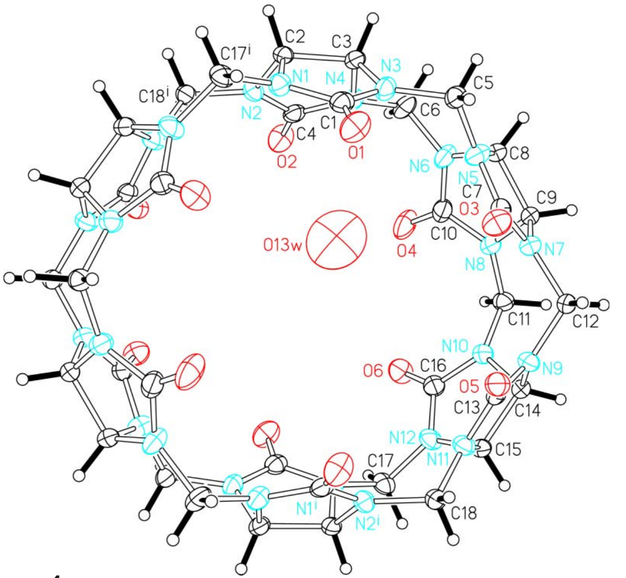


Figure 4
A plot of one of the $C_{36}H_{36}N_{24}O_{12}$ cryptands encapsulating the water molecule that lies on a special position. The disordered water component is not shown. [Symmetry code (i): $2-x, 1-y, 1-z$.]

C-bound H atoms were placed in calculated positions, with C—H = 0.96 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C), and were included in the refinement in the riding-model approximation. Three of the solvent water molecules are disordered over two positions each (O5*w*/O5′, O12*w*/O12′ and O13*w*/O13′); the occupancies of the first two were refined. The O13*w*/O13′ atom pair, which is encapsulated by one of the cyptand host molecules, lies on a special position of $\overline{1}$ site symmetry. The special position constraints were suppressed to allow the pair of atoms to refine over the symmetry element; however, as the molecule is probably more extensively disordered inside the cage, the refinement of the occupancy did not lead to any meaningful outcome. Instead, the occupancy for each portion was fixed as 0.25. The water molecule encapsulated in the other cage (O12*w*) is also disordered; the occupancy was refined. The occupancy of O5*w* was 0.54 (1) and that of O12*w* was 0.71 (1). Water H atoms were placed in chemically sensible positions on the basis of the hydrogen-bonding interactions but were not refined; their $U_{\rm iso}$(H) values were all fixed at 0.05 Å^2. For the disordered O5*w*/O5′ and O12*w*/O12′ water molecules, H atoms were placed on the major component only. As the O13*w*/O13′ pair of atoms do not form hydrogen bonds, the H atoms could not be placed in any position. The final difference Fourier map had a large peak at about 1.9 Å from the O12′ disorder component. The peak could not be refined as a third disorder component associated with atom O12*w*. The map also featured a large hole at about 0.5 Å from Cl1. This atom had a relatively large atomic displacement parameter compared with those of the other Cl atoms; however, attempts to refine atom Cl1 with a disorder model failed to improve the residual index. The structure does not have any voids large enough to hold a water molecule, as verified by *PLATON* (Spek, 2003).

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; 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*.

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References

Bruker (2002). *SADABS*, *SAINT* and *SMART*. Bruker AXS, Inc., Madison, Wisconsin, USA.

Dybtsev, D. N., Gerasko, O. A., Virovets, A. V., Sokolov, M. N. & Fedin, V. P. (2000). *Inorg. Chem. Commun.* **3**, 345–349.

Fedin, V. P., Sokolov, M. N., Dybtsev, D. N., Gerasko, O. A., Virovets, A. V. & Fenske, D. (2002). *Inorg. Chim. Acta*, **331**, 31–38.

Fedin, V. P., Sokolov, M. N., Lamprecht, G. J., Molina, R. H., Seo, M. S., Virovets, A. V., Clegg, W. & Sykes, A. G. (2001). *Inorg. Chem.* **40**, 6598–6603.

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Fedin, V. P., Virovets, A. V., Sokolov, M. N., Dybtsev, D. N., Gerasko, O. A. & Clegg, W. (2000). *Inorg. Chem.* **39**, 2227–2230.

Gerasko, O. A., Sokolov, M. N. & Fedin, V. P. (2004). *Pure Appl. Chem.* **76**, 1633–1646.

Gerasko, O. A., Virovets, A. V., Samsonenko, D. G., Tripol'skaya, A. A., Fedin, V. P. & Fenske, D. (2003). *Russ. Chem. Bull.* **52**, 585–593.

Glowiak, T. & Sabat, M. (1975). *J. Cryst. Mol. Struct.* **5**, 247–256.

Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Oak Ridge, Tennessee, USA.

Liu, J.-X., Long, L.-S., Huang, R.-B., Zheng, L.-S. & Ng, S. W. (2005). *Acta Cryst.* E. Submitted.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

Zhao, Y.-J., Xue, S.-F., Zhu, Q.-J., Tao, Z., Zhang, J.-X., Wei, Z.-B., Long, L.-S., Hu, M.-L., Xiao, H.-P., & Day, A. I. (2004). *Chin. Sci. Bull.* **49**, 1111–1116.