Supporting Information

Water-capsule strategy in crystal engineering for water-solubility conversion from insoluble to soluble

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Experimental Section

Materials and General Methods. All chemicals were commercially purchased and used as supplied. The crystal structure of the resultant products was characterized by powder X-ray diffraction (XRD) by using a X'Pert-ProMPD (Holand) D/max-γAX-ray diffractometer with Cu Kα radiation (λ=0.154178 nm). The spectrograph uses 600 g mm^{-1} gratings and a 633 nm He–Ne laser. The TG analysis was carried out by Universal Analysis 2000 thermogravimetric analyzer (TGA) in N_2 with a heating rate of 10 °C /min. The X-ray diffraction data were collected on a Bruker X8 APEX-II CCD diffractometer with Mo Kα (λ = 0.71073 Å) by ω and θ scan mode at 150 K. The structure was solved by direct method and refined by full matrix least-squares technique with the *SHELXTL*-97 crystallographic software package. All non-H atoms were located from a difference Fourier map and refined anisotropically.

Synthesis of $[Na(H_2O)_4][H_4V^{V}_{10}V^{IV}_{8}O_{42}(V^{V}O_4)]\cdot 16H_2O$

The hydrothermal treatment of a mixture of NH_4VO_3 (0.20 g, 1.30 mmol), NaH_2PO_4

(0.08 g, 0.66 mmol) and H_2O (12 mL) at 160℃ in a Telon-lined stainless autoclave for 3 days resulted in black block crystals. Yield, 78% (based on V).

Dissolubility Experiment: Compound **1** was heated at 30, 50, 70, 90 and 110 ℃, respectively. Then the as-treated five samples were soaked into water solution in five plastic tubes.

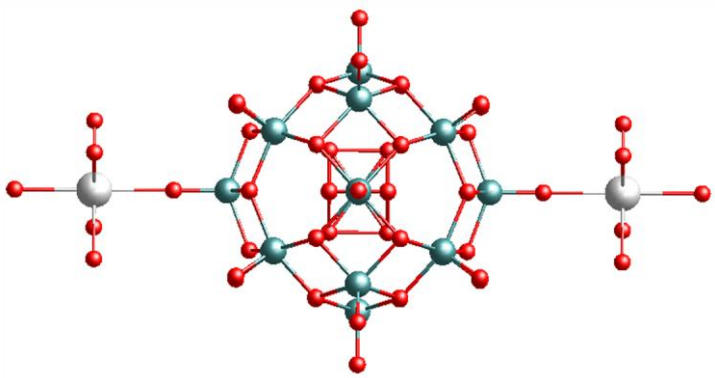

Fig. S1 Ball-stick view of the asymmetric unit of **1**. All hydrogen atoms and free lattice water molecules are omitted for clarity.

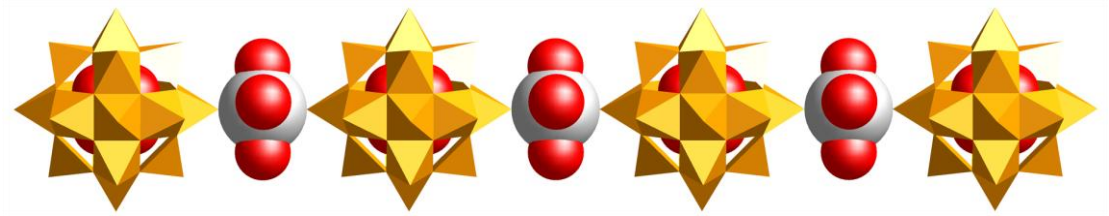

Fig. S2 Polyhedral and ball/stick view of the linear chain constructed by $[V_{18}O_{42}(VO_4)]$ clusters and six-coordinated sodium bridges.

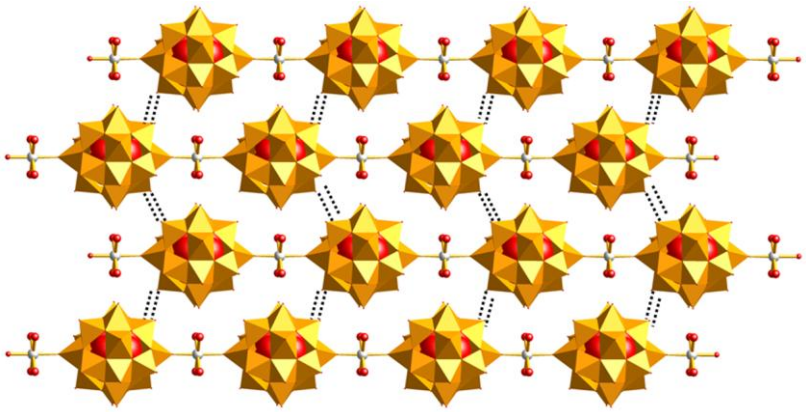

Fig. S3 2D netlike array of compound **1** via O-H···O hydrogen bonds (black-broken lines). All of the hydrogen atoms and lattice water molecules have been omitted for clarity.

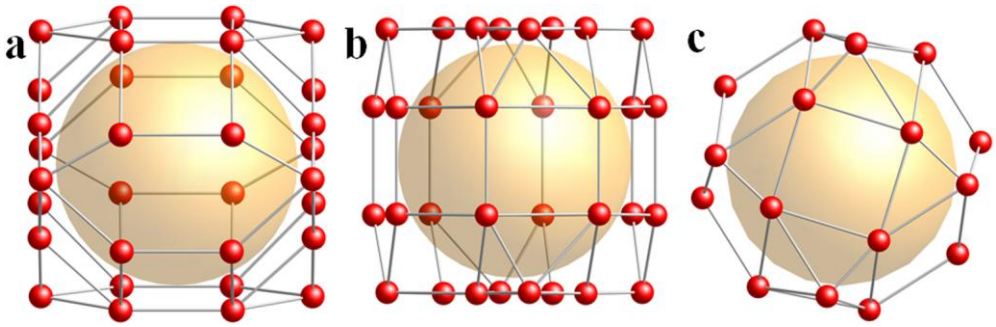

Fig. S4 Representation of the $(H_2O)_{32}$-shell constructed by 32 lattice water molecules along a (a), b (b) and c (c) axis, respectively. The yellow ball represented the $[V_{18}O_{42}(VO_4)]$ cluster.

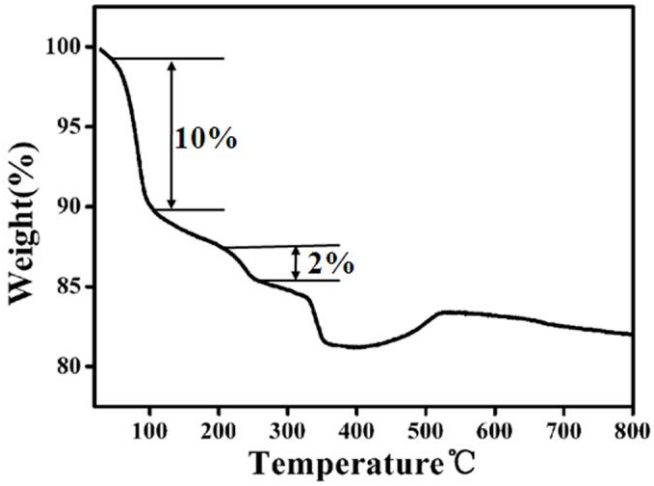

Fig. S5 TG curve of compound **1** recorded from 30 to 800 ℃ under flowing N_2. The first weight loss of 10.2% in 30-200 ℃ corresponds to the loss of 16 free water molecules. A second weight loss (about 2.6%) occurred between 200-280 ℃ and can be attributed to the loss of 4 coordination water molecules. The final step the maximum mass loss up to 300 °C is 5.52%, and the residue could be mixed-valence vanadium oxides V_3O_7/V_6O_{13} based on calculations, suggesting that a part of vanadium (V) atoms are deoxidized by NH_3 generated during the thermal composition.[1] Similar thermal decomposition behaviors have also been observed and reported in other polyoxovanadate compounds.[2-5]

1. L. Chen, Z. Z. Lin, F. L. Jiang, D. Q Yuan, M. C. Hong, *Chin. J. Struct. Chem.*, 2005, **24**, 1186–1192.

2. P. Román, R. Macías, A. Luque, C. Guzmán-miralles, *Thermochim. Acta*, 1992, **209**, 189–194.

3. A. S. J. Wery, J. M. Gutiérrez-Zorrila, A. Luque, P. Román, *Polyhedron*, 1996, **15**, 4555–4564.

4. P. P. Stander, C. P. J. Van-Vuuren, *Thermochim. Acta*, 1990, **157**, 347–355.

5. L. Chen, F. L. Jiang, M. Y. Wu, N. Li, W. T. Xu, C. F. Yan, C. Y. Yue, M. C. Hong, *Crystal Growth & Design*, 2008, **8**, 4093-4099.

Table S1. The band valance sum calculations[6,7] for compound **1**.

Compound **1**	V site	V1	V2	V3	V4	V5
	BVS	5.023	4.613	4.554	4.481	4.714
	Assigned O.S.	+5	+5	+5	+4	+5

6. A. Müller, *Inorg. Chem.*, 1997, **36**, 5239.

7. I. D. Brown, D. Altermatt, *Acta Crystallogr. B.*, 1985, **41**, 244.

Table S2. Crystal Data and Structure Refinement of compound **1**.

Empirical formula	$H_{40}NaO_{66}V_{19}$
Formula weight	2087.17
Temperature	150(2) K
Wavelength	0.71073 Å (Mo Kα)
Crystal system	Tetragonal
Space group	I4/m
Unit cell dimensions	a = 13.3146(10) Å α = 90°
	b = 13.3146(10) Å
	c = 15.8763(3) Å
Volume ($Å^3$)	2814.4(5)
Z	2
Density (Mg/m^3)	2.463
Absorption coefficient (mm^{-1})	3.133
F(000)	2032
Crystal size (mm)	0.10 × 0.15 × 0.25
Theta range for data collection (°)	2.00 to 24.99
Index ranges	–15 <= h <= 15, –15 <= k <= 15, –18 <= l <= 18
Reflections collected	18536
Independent reflections	1284 [R_{int} = 0.0225]
Completeness to theta = 24.99°	98.8%
Max. and min. transmission	0.7447 and 0.5081
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1284 / 0 / 113
Goodness-of-fit on F^2	1.114
Final *R* indices [|I| > 2sigma(I)]	R_1 = 0.0586, wR_2 = 0.1575

R indices (all data)	R_1 = 0.0606, wR_2 = 0.1592
Largest diff. peak and hole ($e.Å^{-3}$)	0.735 and -3.269

Table S3. Selected Bond Lengths (Å) and Angles (º) of compound **1**.

Compound **1**			
V(1)-O(1)^{a}	1.513(8)	V(1)-O(1)^{b}	1.513(8)
V(1)-O(1)^{c}	1.513(8)	V(1)-O(1)^{d}	1.513(8)
V(1)-O(1)^{e}	1.513(8)	V(1)-O(1)^{f}	1.513(8)
V(1)-O(1)	1.513(8)	V(1)-O(1)^{g}	1.513(8)
V(2)-O(2)	1.614(7)	V(2)-O(6)^{c}	1.917(5)
V(2)-O(6)	1.917(5)	V(2)-O(7)^{b}	1.916(5)
V(2)-O(7)^{g}	1.916(5)	V(2)-V(3)^{b}	2.893(2)
V(2)-V(4)^{g}	2.8978(15)	V(2)-V(4)^{b}	2.8978(15)
V(2)-V(3)	2.903(2)	V(3)-O(3)	1.600(7)
V(3)-O(7)^{c}	1.932(5)	V(3)-O(7)	1.932(5)
V(3)-O(6)	1.933(5)	V(3)-O(6)^{c}	1.933(5)
V(3)-V(2)^{a}	2.893(2)	V(4)-O(4)	1.605(5)
V(4)-O(8)^{e}	1.935(5)	V(4)-O(6)^{e}	1.938(5)
V(4)-O(7)	1.940(5)	V(4)-O(8)	1.942(5)
V(4)-V(5)	2.8967(16)	V(4)-V(2)^{a}	2.8978(15)
V(5)-O(5)	1.613(10)	V(5)-O(8)^{e}	1.905(5)
V(5)-O(8)^{b}	1.905(5)	V(5)-O(8)	1.905(5)
V(5)-O(8)^{d}	1.905(5)	V(5)-V(4)^{e}	2.8967(16)
V(5)-V(4)^{b}	2.8967(16)	V(5)-V(4)^{d}	2.8967(16)
Na(1)-O(9)^{h}	2.345(8)	Na(1)-O(9)^{i}	2.345(8)
Na(1)-O(9)	2.345(8)	Na(1)-O(9)^{b}	2.345(8)
Na(1)-O(5)	2.389(10)	Na(1)-O(5)^{i}	2.389(10)
O(1)-O(1)^{e}	1.743(12)	O(1)-O(1)^{b}	1.743(12)
O(1)-O(1)^{c}	1.757(17)	O(6)-V(4)^{b}	1.938(5)
O(7)-V(2)^{a}	1.916(5)	O(8)-V(4)^{b}	1.935(5)
O(1)^{a}-V(1)-O(1)^{b}	180.000(2)	O(1)^{a}-V(1)-O(1)^{c}	70.3(3)
O(1)^{b}-V(1)-O(1)^{c}	109.7(3)	O(1)^{a}-V(1)-O(1)^{d}	109.7(3)
O(1)^{b}-V(1)-O(1)^{d}	70.3(3)	O(1)^{c}-V(1)-O(1)^{d}	180.000(2)
O(1)^{a}-V(1)-O(1)^{e}	71.0(6)	O(1)^{b}-V(1)-O(1)^{e}	109.0(6)
O(1)^{c}-V(1)-O(1)^{e}	109.7(3)	O(1)^{d}-V(1)-O(1)^{e}	70.3(3)
O(1)^{a}-V(1)-O(1)^{f}	70.3(3)	O(1)^{b}-V(1)-O(1)^{f}	109.7(3)
O(1)^{c}-V(1)-O(1)^{f}	109.0(6)	O(1)^{d}-V(1)-O(1)^{f}	71.0(6)
O(1)^{e}-V(1)-O(1)^{f}	109.7(3)	O(1)^{a}-V(1)-O(1)	109.7(3)
O(1)^{b}-V(1)-O(1)	70.3(3)	O(1)^{c}-V(1)-O(1)	71.0(6)
O(1)^{d}-V(1)-O(1)	109.0(6)	O(1)^{e}-V(1)-O(1)	70.3(3)
O(1)^{f}-V(1)-O(1)	180.0(5)	O(1)^{a}-V(1)-O(1)^{g}	109.0(6)
O(1)^{b}-V(1)-O(1)^{g}	71.0(6)	O(1)^{c}-V(1)-O(1)^{g}	70.3(3)
O(1)^{d}-V(1)-O(1)^{g}	109.7(3)	O(1)^{e}-V(1)-O(1)^{g}	180.0(6)
O(1)^{f}-V(1)-O(1)^{g}	70.3(3)	O(1)-V(1)-O(1)^{g}	109.7(3)

O(2)-V(2)-O(6)^{c}	110.6(3)	O(2)-V(2)-O(6)	110.6(3)
O(6)^{c}-V(2)-O(6)	82.5(3)	O(2)-V(2)-O(7)^{b}	110.5(3)
O(6)^{c}-V(2)-O(7)^{b}	138.9(3)	O(6)-V(2)-O(7)^{b}	83.1(2)
O(2)-V(2)-O(7)^{g}	110.5(3)	O(6)^{c}-V(2)-O(7)^{g}	83.1(2)
O(6)-V(2)-O(7)^{g}	138.9(3)	O(7)^{b}-V(2)-O(7)^{g}	82.9(3)
O(2)-V(2)-V(3)^{b}	118.0(3)	O(6)^{c}-V(2)-V(3)^{b}	114.89(17)
O(6)-V(2)-V(3)^{b}	114.89(17)	O(7)^{b}-V(2)-V(3)^{b}	41.45(16)
O(7)^{g}-V(2)-V(3)^{b}	41.45(16)	O(2)-V(2)-V(4)^{g}	118.78(4)
O(6)^{c}-V(2)-V(4)^{g}	41.55(15)	O(6)-V(2)-V(4)^{g}	114.05(17)
O(7)^{b}-V(2)-V(4)^{g}	114.36(18)	O(7)^{g}-V(2)-V(4)^{g}	41.59(16)
V(3)^{b}-V(2)-V(4)^{g}	77.00(4)	O(2)-V(2)-V(4)^{b}	118.78(4)
O(6)^{c}-V(2)-V(4)^{b}	114.05(17)	O(6)-V(2)-V(4)^{b}	41.55(15)
O(7)^{b}-V(2)-V(4)^{b}	41.59(16)	O(7)^{g}-V(2)-V(4)^{b}	114.36(18)
V(3)^{b}-V(2)-V(4)^{b}	77.00(4)	V(4)^{g}-V(2)-V(4)^{b}	122.45(7)
O(2)-V(2)-V(3)	119.2(3)	O(6)^{c}-V(2)-V(3)	41.27(16)
O(6)-V(2)-V(3)	41.27(16)	O(7)^{b}-V(2)-V(3)	114.02(17)
O(7)^{g}-V(2)-V(3)	114.02(17)	V(3)^{b}-V(2)-V(3)	122.73(8)
V(4)^{g}-V(2)-V(3)	76.33(4)	V(4)^{b}-V(2)-V(3)	76.33(4)
O(3)-V(3)-O(7)^{c}	102.1(3)	O(3)-V(3)-O(7)	102.1(3
O(7)^{c}-V(3)-O(7)	82.1(3)	O(3)-V(3)-O(6)	101.4(3)
O(7)^{c}-V(3)-O(6)	156.5(3)	O(7)-V(3)-O(6)	93.4(2)
O(3)-V(3)-O(6)^{c}	101.4(3)	O(7)^{c}-V(3)-O(6)^{c}	93.4(2)
O(7)-V(3)-O(6)^{c}	156.5(3)	O(6)-V(3)-O(6)^{c}	81.6(3)
O(3)-V(3)-V(2)^{a}	106.3(3)	O(7)^{c}-V(3)-V(2)^{a}	41.04(16)
O(7)-V(3)-V(2)^{a}	41.04(16)	O(6)-V(3)-V(2)^{a}	130.22(16)
O(6)^{c}-V(3)-V(2)^{a}	130.22(16)	O(3)-V(3)-V(2)	106.4(3)
O(7)^{c}-V(3)-V(2)	129.47(16)	O(7)-V(3)-V(2)	129.47(16)
O(6)-V(3)-V(2)	40.84(16)	O(6)^{c}-V(3)-V(2)	40.84(16)
V(2)^{a}-V(3)-V(2)	147.27(8)	O(4)-V(4)-O(8)^{e}	101.3(3)
O(4)-V(4)-O(6)^{e}	100.2(3)	O(8)^{e}-V(4)-O(6)^{e}	94.5(2)
O(4)-V(4)-O(7)	102.1(3)	O(8)^{e}-V(4)-O(7)	156.6(3)
O(6)^{e}-V(4)-O(7)	81.9(2)	O(4)-V(4)-O(8)	102.5(3)
O(8)^{e}-V(4)-O(8)	81.3(3)	O(6)^{e}-V(4)-O(8)	157.3(3)
O(7)-V(4)-O(8)	93.1(2)	O(4)-V(4)-V(5)	106.8(2)
O(8)^{e}-V(4)-V(5)	40.64(16)	O(6)^{e}-V(4)-V(5)	130.74(16)
O(7)-V(4)-V(5)	129.26(16)	O(8)-V(4)-V(5)	40.67(16)
O(4)-V(4)-V(2)^{a}	105.6(2)	O(8)^{e}-V(4)-V(2)^{a}	130.90(17)
O(6)^{e}-V(4)-V(2)^{a}	40.98(16)	O(7)-V(4)-V(2)^{a}	40.97(16)
O(8)-V(4)-V(2)^{a}	129.87(17)	V(5)-V(4)-V(2)^{a}	147.59(6)
O(5)-V(5)-O(8)^{e}	110.40(19)	O(5)-V(5)-O(8)^{b}	110.40(19)
O(8)^{e}-V(5)-O(8)^{b}	139.2(4)	O(5)-V(5)-O(8)	110.40(19)
O(8)^{e}-V(5)-O(8)	83.02(12)	O(8)^{b}-V(5)-O(8)	83.02(12)
O(5)-V(5)-O(8)^{d}	110.40(19)	O(8)^{e}-V(5)-O(8)^{d}	83.02(12)
O(8)^{b}-V(5)-O(8)^{d}	83.02(12)	O(8)-V(5)-O(8)^{d}	139.2(4)

O(5)-V(5)-V(4)	118.82(4)	O(8)^{e}-V(5)-V(4)	41.41(16)
O(8)^{b}-V(5)-V(4)	114.46(18)	O(8)-V(5)-V(4)	41.64(16)
O(8)^{d}-V(5)-V(4)	114.29(18)	O(5)-V(5)-V(4)^{e}	118.82(4)
O(8)^{e}-V(5)-V(4)^{e}	41.64(16)	O(8)^{b}-V(5)-V(4)^{e}	114.29(18)
O(8)-V(5)-V(4)^{e}	114.46(18)	O(8)^{d}-V(5)-V(4)^{e}	41.41(16)
V(4)-V(5)-V(4)^{e}	76.56(4)	O(5)-V(5)-V(4)^{b}	118.82(4)
O(8)^{e}-V(5)-V(4)^{b}	114.29(18)	O(8)^{b}-V(5)-V(4)^{b}	41.64(16)
O(8)-V(5)-V(4)^{b}	41.41(16)	O(8)^{d}-V(5)-V(4)^{b}	114.46(18)
V(4)-V(5)-V(4)^{b}	76.56(4)	V(4)^{e}-V(5)-V(4)^{b}	122.36(9)
O(5)-V(5)-V(4)d	118.82(4)	O(8)^{e}-V(5)-V(4)^{d}	114.46(18)
O(8)^{b}-V(5)-V(4)^{d}	41.41(16)	O(8)-V(5)-V(4)^{d}	114.29(18)
O(8)^{d}-V(5)-V(4)^{d}	41.64(16)	V(4)-V(5)-V(4)^{d}	122.36(9)
V(4)^{e}-V(5)-V(4)^{d}	76.56(4)	V(4)^{b}-V(5)-V(4)^{d}	76.56(4)
O(9)^{h}-Na(1)-O(9)^{i}	90.000(1)	O(9)^{h}-Na(1)-O(9)	90.000(2)
O(9)^{i}-Na(1)-O(9)	180.000(2)	O(9)^{h}-Na(1)-O(9)^{b}	180.000(1)
O(9)^{i}-Na(1)-O(9)^{b}	90.000(1)	O(9)-Na(1)-O(9)^{b}	90.000(1)
O(9)^{h}-Na(1)-O(5)	90.000(1)	O(9)^{i}-Na(1)-O(5)	90.0
O(9)-Na(1)-O(5)	90.0	O(9)^{b}-Na(1)-O(5)	90.000(1)
O(9)^{h}-Na(1)-O(5)^{i}	90.000(1)	O(9)^{i}-Na(1)-O(5)^{i}	90.0
O(9)-Na(1)-O(5)^{i}	90.0	O(9)^{b}-Na(1)-O(5)^{i}	90.000(1)
O(5)-Na(1)-O(5)^{i}	180.000(1)	V(1)-O(1)-O(1)^{e}	54.85(16)
V(1)-O(1)-O(1)^{b}	54.85(16)	O(1)^{e}-O(1)-O(1)^{b}	90.000(1)
V(1)-O(1)-O(1)^{c}	54.5(3)	O(1)^{e}-O(1)-O(1)^{c}	90.000(1)
O(1)^{b}-O(1)-O(1)^{c}	90.000(1)	V(5)-O(5)-Na(1)	180.0
V(2)-O(6)-V(3)	97.9(2)	V(2)-O(6)-V(4)^{b}	97.5(2)
V(3)-O(6)-V(4)^{b}	135.6(3)	V(2)^{a}-O(7)-V(3)	97.5(2)
V(2)^{a}-O(7)-V(4)	97.4(2)	V(3)-O(7)-V(4)	137.2(3)
V(5)-O(8)-V(4)^{b}	98.0(2)	V(5)-O(8)-V(4)	97.7(2)
V(4)^{b}-O(8)-V(4)	135.6(3)		

Symmetry code for **1**: a: y-1, -x+1, -z; b: -y+1, x+1, z; c: x, y, -z; d: -x, -y+2, z; e: y-1, -x+1, z;

f: -x, -y+2, -z; g: -y+1, x+1, -z; h: y-1, -x+1, -z+1; i: -x, -y+2, -z+1.

Table S4. Hydrogen bonds geometry (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
O1W—H1WB···O7	0.85	2.05	2.89	179
O2W—H2WA···O6	0.85	2.08	2.88	159
O9—H9A···O2	0.85	2.40	3.20	158
O9—H9A···O2W	0.85	2.47	2.80	104