Electronic Supplementary Information for CrystEngComm

Electronic Supplementary Information (ESI)

Syntheses, crystal structures and luminescent properties of Zn(II)/Cd(II) supramolecular complexes incorporating 4-sulfinobenzoate and its in situ oxidized ligand

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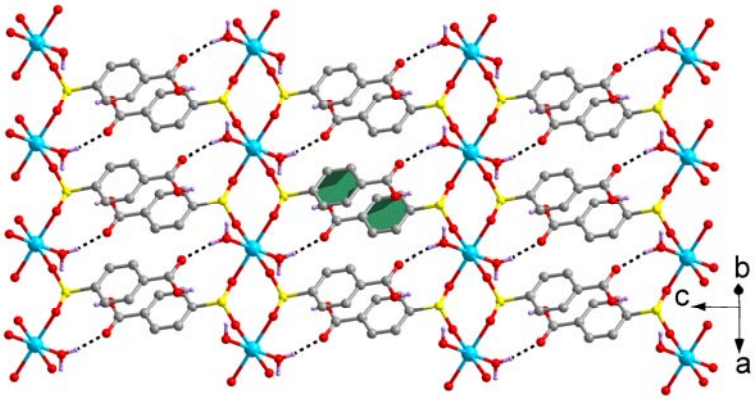


Fig. S1 2-D layer structure extended by hydrogen bonds with the π···π stacking interactions denoted as sea green planes.

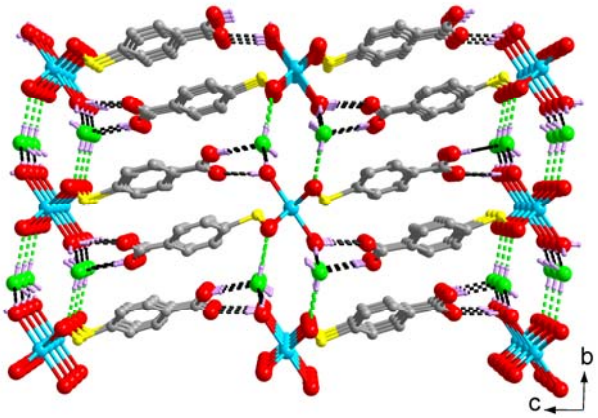


Fig. S2 3-D supramolecular network of complex **1** extended by hydrogen bonds (green dashed lines) with the lattice water molecules denoted as green balls.

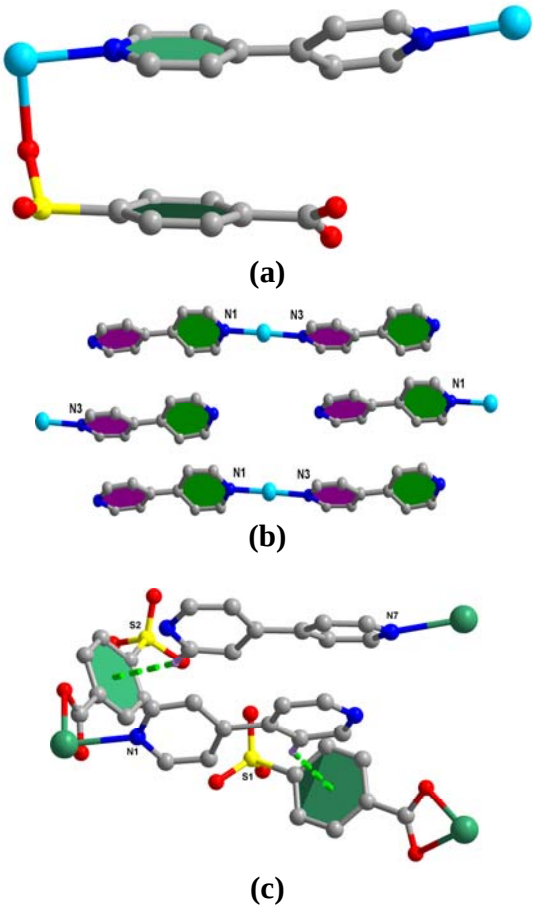


Fig. S3 C-H···π and π-π stacking interactions in complexes **4** (a), **5** (b) and **6** (c). The dihedral angles between the pyridyl rings were reported in the main text.

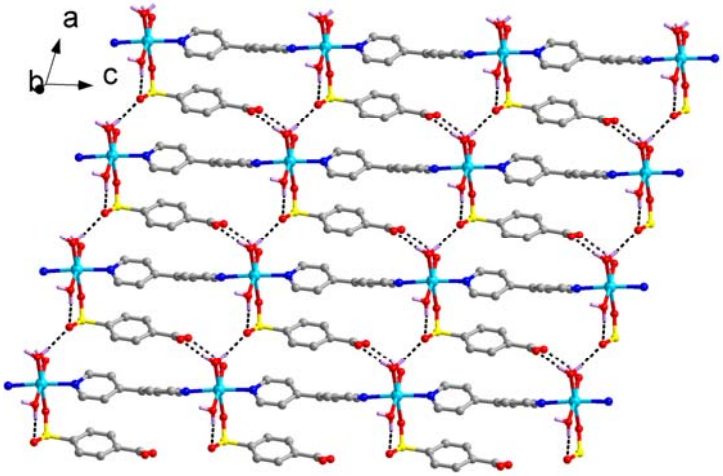


Fig. S4 2-D layer structure stabilized by hydrogen bonds.

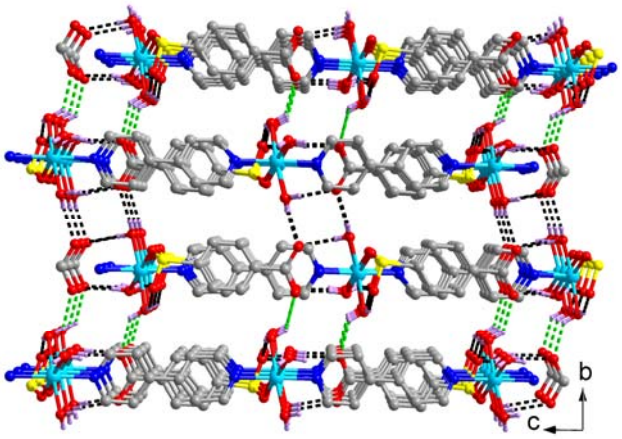
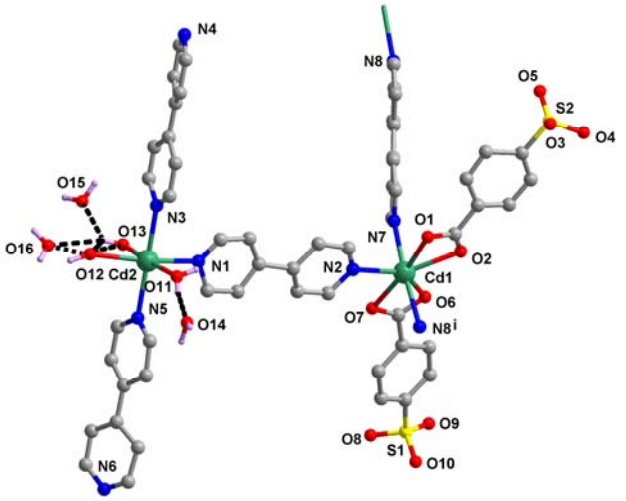
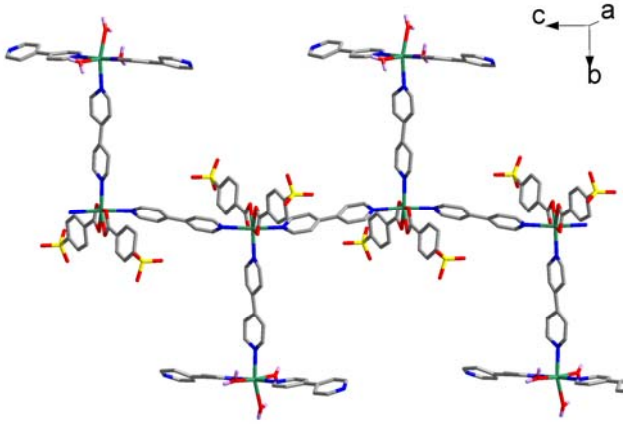


Fig. S5 3-D supramolecular network extended by hydrogen bonds (green dashed lines) between coordinated water molecules and carboxyl groups.



(a)



(b)

Fig. S6 Molecular structure (a) and 1-D linear chain structure (b) of the reported $\{[Cd_2(SB)_2(4,4'\text{-bipy})_4(H_2O)_3]_n \cdot 3nH_2O\}$.

PXRD Analysis. Powder X-ray diffraction (PXRD) patterns for solid samples of complexes **1-6** are measured at room temperature as illustrated in Fig. S7. The patterns are highly similar to their simulated ones (based on the single-crystal X-ray diffraction data), indicating that the single-crystal structures are really representative of the bulk of the corresponding samples.

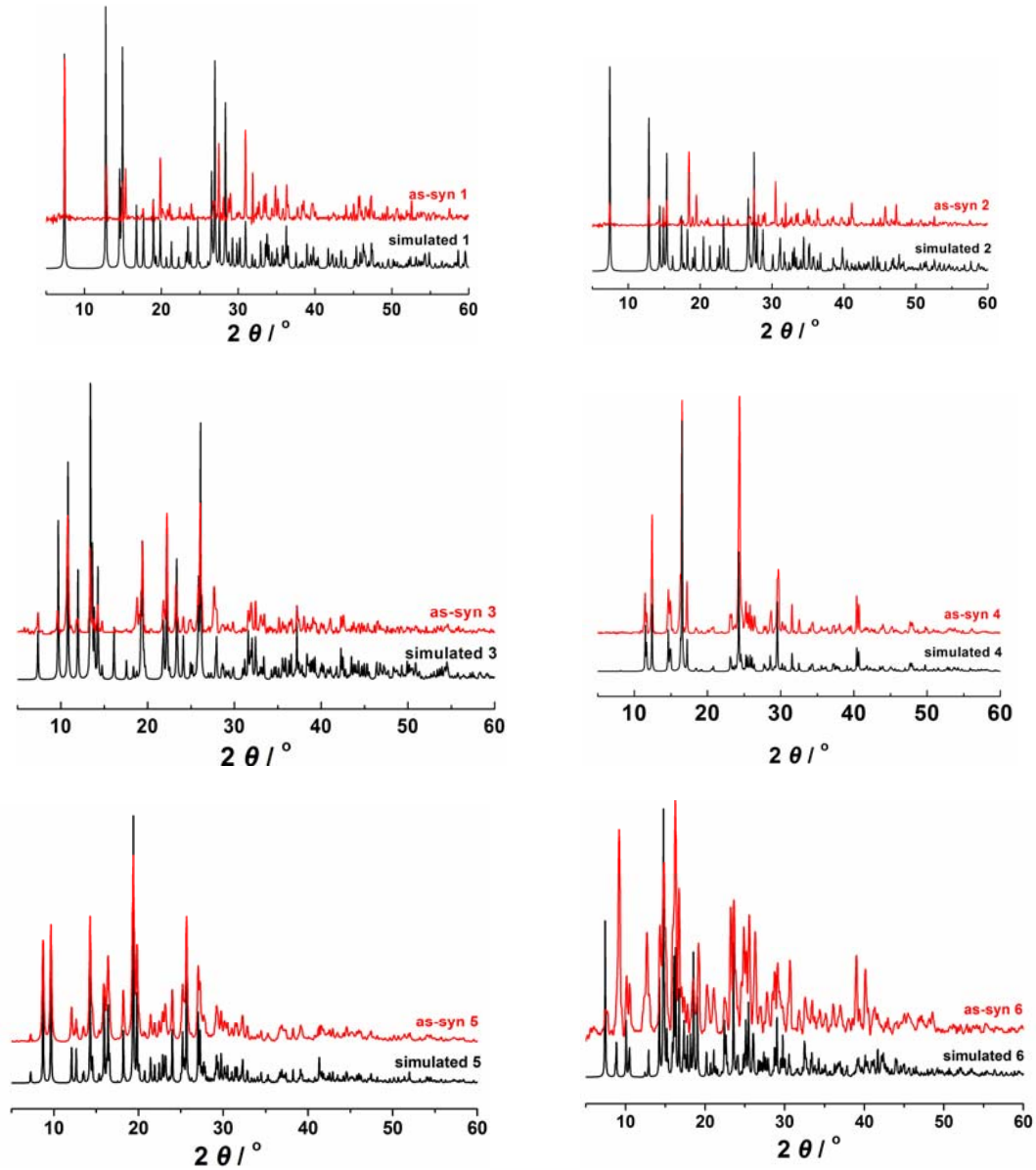


Fig. S7 PXRD patterns for complexes **1-6**.

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Thermogravimetric analysis

To examine the thermal stability of the complexes, in this study, their stabilities were analyzed on crystalline samples by thermogravimetric analyses (TGA) from room temperature to 900 °C at a rate of 10 °C min^{-1}, under N_2 atmosphere. As shown in Fig. S8, the TGA curve indicates that complex **1** loses the lattice and coordinated water molecules from 40 to 160 °C with the observed weight loss of 13.98% (calcd 14.19%). The following gradually weigh losses correspond to the loss of the organic components occurs in the temperature range 160-580 °C. The remaining component is ZnO (obsd 16.25%, calcd 16.03%). Complex **2** exhibits the similar loss steps as complex **1** with the loss of the lattice and coordinated water molecules occurring between 40 and 156 °C (obsd 12.75%, calcd 12.99%). The following weight loss completes at 610 °C, corresponding to CdO (obsd 23.41%, calcd 23.15%). Complex **3** loses the coordinated water molecules from 50 to 120 °C with the observed weight loss of 7.58% (calcd 7.37%). Then, the following weight loss with the decomposing of organic components occurs in the temperature range 260-580 °C, and the final remaining component is CdO (obsd 25.98%, calcd 26.27%). The weight loss of the coordinated water molecules in complex **4** occurs between 55 and 115 °C (obsd 11.53%, calcd 11.76%). The following weight loss with the decomposing of organic components occurs in the temperature range 230-485 °C. The remaining component is ZnO (obsd 14.42%, calcd 14.80%). Complex **5** loses the lattice and coordinated water molecules from 35 to 120 °C with the observed weight loss of 19.71% (calcd 19.96%). Then, the following weight loss with the decomposing of organic components occurs in the temperature range 310-675 °C, and the final remaining component is ZnO (obsd 11.52%, calcd 11.27%). Complex **6** loses the lattice and coordinated water molecules from 35 to 130 °C with the observed weight loss of 8.05% (calcd 7.96%). Then, the following weight loss with the decomposing of organic components occurs in the temperature range 130-670 °C, and the final remaining component is CdO (obsd 19.03%, calcd 18.91%).

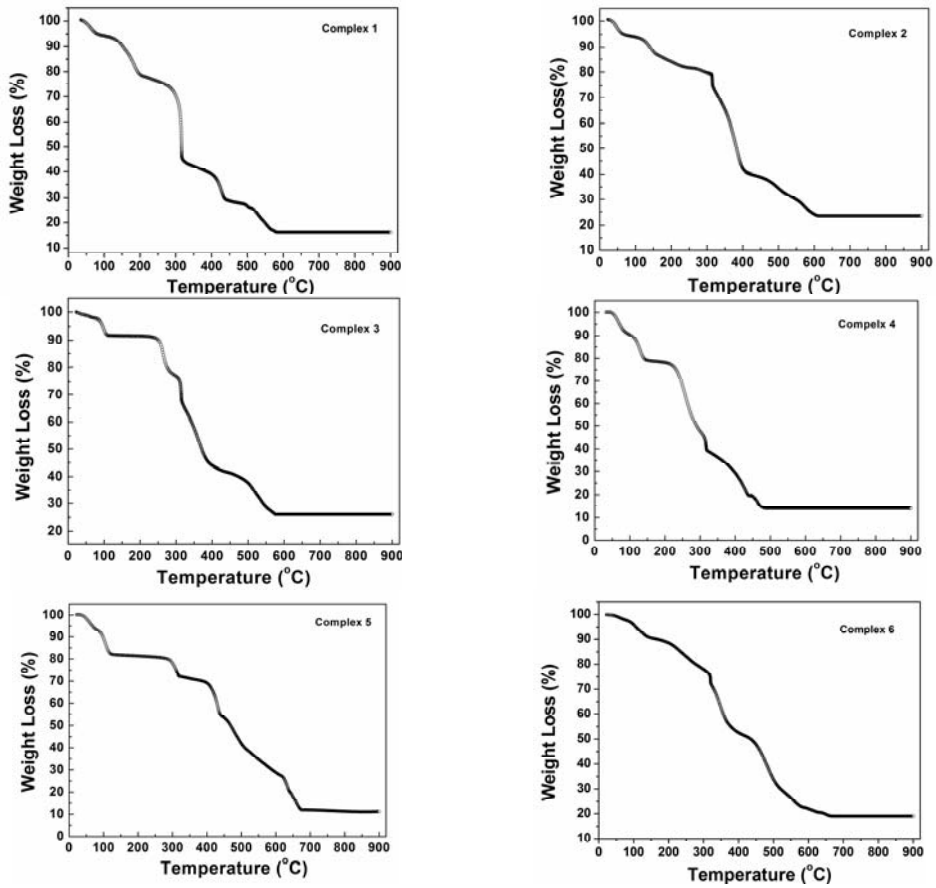

Fig. S8 TG curves of complexes **1-6**.

Table S1 Selected bond lengths (Å) data of complexes **1-6**[a]

Complex 1			
Zn(1)-O(4)^{i}	2.0740(19)	Zn(1)-O(1W)^{i}	2.116(2)
Zn(1)-O(4)	2.0740(19)	Zn(1)-O(3)^{ii}	2.152(2)
Zn(1)-O(1W)	2.116(2)	Zn(1)-O(3)^{iii}	2.152(2)
Complex 2			
Cd(1)-O(3)^{i}	2.261(4)	Cd(1)-O(1W)	2.282(5)
Cd(1)-O(3)	2.261(4)	Cd(1)-O(4)^{ii}	2.318(4)
Cd(1)-O(1W)^{i}	2.282(5)	Cd(1)-O(4)^{iii}	2.318(4)
Complex 3			
Cd(1)-O(2W)	2.318(3)	Cd(1)-O(1)^{i}	2.390(3)
Cd(1)-O(3)	2.341(2)	Cd(1)-N(2)	2.414(3)
Cd(1)-N(1)	2.365(3)	Cd(1)-O(1W)	2.432(3)
Cd(1)-O(2)^{i}	2.476(3)		
Complex 4			
Zn(1)-O(2W)	2.112(6)	Zn(1)-O(3W)	2.155(6)
Zn(1)-O(1)	2.129(6)	Zn(1)-N(1)	2.160(6)
Zn(1)-N(2)^{i}	2.143(5)	Zn(1)-O(1W)	2.167(6)
Complex 5			
Zn(1)-O(2W)	2.109(5)	Zn(1)-N(1)	2.140(5)
Zn(1)-O(3W)	2.115(5)	Zn(1)-N(3)	2.147(5)

Zn(1)-O(1W)	2.119(5)	Zn(1)-O(4W)	2.159(5)

Complex 6

Cd(1)-O(6)	2.310(4)	Cd(2)-O(1W)	2.300(4)
Cd(1)-O(7)	2.655(4)	Cd(2)-O(2W)	2.314(4)
Cd(1)-N(1)	2.339(4)	Cd(2)-O(3W)	2.336(3)
Cd(1)-N(5)	2.339(4)	Cd(2)-N(7)	2.344(4)
Cd(1)-N(3)	2.358(4)	Cd(2)-N(4)	2.350(4)
Cd(1)-O(1)	2.422(3)	Cd(2)-N(6)^{i}	2.359(4)
Cd(1)-O(2)	2.475(3)		

[a] Symmetry operation: **For 1**, i -x,-y+2,-z+1; ii x-1,y,z; iii -x+1,-y+2,-z+1. **For 2**, i-x,-y+1,-z; ii -x+1,-y+1,-z; iii x-1,y,z. **For 3**, i -x+1,-y,-z. **For 4**, i x,y,z-1. **For 6**, x-1/2,-y+1/2,z+1/2.

Table S2 Hydrogen bond parameters for complexes **1-6**[a]

D-H···A	d(D···H)/Å	d(H···A)/Å	d(D···A)/Å	<(DHA)/°
		Complex 1		
O(1W)-H(1W1)...O(1)^{v}	0.85	1.87	2.720(3)	175.7
O(1W)-H(1W2)...O(2W)^{vi}	0.85	2.04	2.887(3)	175.7
O(2)-H(2B)...O(2W)	0.82	1.87	2.685(3)	173.1
O(2W)-H(2W1)...O(3)^{vii}	0.85	1.93	2.783(3)	177.9
		Complex 2		
O(1W)-H(1W1)...O(2W)^{v}	0.85(2)	2.04(2)	2.877(7)	169(8)
O(1W)-H(1W2)...O(1)^{vi}	0.85(2)	1.89(2)	2.721(6)	165(8)
O(2W)-H(2W1)...O(4)^{vii}	0.85(2)	1.97(2)	2.811(6)	177(8)
O(2W)-H(2W2)...O(4)^{viii}	0.85(2)	2.45(2)	3.283(6)	170(7)
O(2)-H(2A)...O(2W)	0.82	1.87	2.678(6)	169.5
		Complex 3		
O(1W)-H(1W1)...O(4)^{ii}	0.85(3)	1.93(3)	2.775(3)	176(4)
O(1W)-H(1W2)...O(2)^{iii}	0.85(3)	2.14(3)	2.960(4)	163(4)
O(2W)-H(2W1)...O(2)^{iii}	0.85(3)	2.15(2)	2.882(4)	145(3)
O(2W)-H(2W1)...O(4)^{iv}	0.85(3)	2.52(3)	2.934(3)	111(3)
O(2W)-H(2W2)...O(4)	0.85(3)	1.98(3)	2.777(3)	158(3)
		Complex 4		

O(1W)-H(1W1)...O(2)	0.82	2.00	2.766(9)	156.1
O(1W)-H(1W2)...O(4)^{iii}	0.82	2.13	2.727(10)	129.4
O(2W)-H(2W1)...O(4)^{iv}	0.82	1.85	2.655(9)	167.8
O(2W)-H(2W2)...O(2)^{v}	0.82	2.04	2.812(9)	157.4
O(3W)-H(3W1)...O(3)^{vi}	0.82	2.00	2.761(9)	154.4
O(3W)-H(3W2)...O(3)^{iv}	0.82	2.05	2.860(9)	168.0
Complex 5				
O(1W)-H(1W1)...O(5W)	0.85(8)	2.04(5)	2.804(8)	149(10)
O(1W)-H(1W2)...N(2)^{i}	0.85(8)	1.96(4)	2.766(8)	157(10)
O(2W)-H(2W1)...O(5)	0.85(8)	1.87(3)	2.689(8)	162(9)
O(2W)-H(2W2)...O(5W)^{ii}	0.85(8)	1.94(2)	2.777(8)	166(8)
O(3W)-H(3W1)...O(3)^{iii}	0.85(8)	2.02(5)	2.790(7)	151(8)
O(3W)-H(3W2)...N(4)^{iv}	0.85(8)	2.07(5)	2.812(8)	147(8)
O(4W)-H(4W1)...O(3)^{v}	0.85(8)	2.38(8)	2.970(8)	127(8)
O(4W)-H(4W2)...O(6W)	0.85(8)	1.86(3)	2.688(9)	167(11)
O(5W)-H(5W1)...O(4)	0.85(8)	1.920(15)	2.769(9)	176(10)
O(5W)-H(5W2)...O(8W)^{vi}	0.85(8)	1.939(15)	2.792(10)	177(11)
O(6W)-H(6W1)...O(1)^{iii}	0.85	1.99	2.841(10)	176.1
O(6W)-H(6W2)...O(7W)^{vii}	0.85	1.72	2.570(13)	175.6
O(7W)-H(7W1)...O(8W)^{vi}	0.85	2.15	3.000(14)	176.7
O(7W)-H(7W2)...O(5)	0.85	1.73	2.579(11)	177.5
O(8W)-H(8W1)...O(2)	0.85(8)	1.90(2)	2.742(12)	172(13)

O(8W)-H(8W2)...O(6W)^{viii}	0.85(8)	2.13(8)	2.877(11)	146(12)
Complex 6				
O(1W)-H(1W1)...N(8)^{iii}	0.85	2.29	2.791(6)	118.3
O(1W)-H(1W2)...O(5W)^{iv}	0.86	2.40	3.261(7)	179.2
O(2W)-H(2W1)...O(7)^{v}	0.85	2.37	2.932(6)	124.4
O(2W)-H(2W2)...O(1W)	0.85	2.54	3.389(6)	179.6
O(3W)-H(3W1)...O(1W)	0.85	2.47	3.307(5)	168.8
O(3W)-H(3W2)...N(6)^{i}	0.85	2.34	3.180(5)	169.0
O(4W)-H(4W1)...O(5)^{vi}	0.85	2.26	2.880(9)	129.2
O(4W)-H(4W2)...O(10)	0.87	1.88	2.685(8)	153.7
O(5W)-H(5W1)...O(1)^{vii}	0.87	1.99	2.858(6)	178.7
O(5W)-H(5W2)...N(2)	0.85	1.93	2.754(6)	164.9
O(6W)-H(6W1)...O(4)	0.85	1.92	2.770(8)	174.4
O(6W)-H(6W2)...O(8)^{vii}	0.85	2.15	2.998(9)	174.8
O(1W)-H(1W1)...N(8)^{iii}	0.85	2.29	2.791(6)	118.3

[a] Symmetry operation: **For 1**, v -x+1,-y+2,-z+2; vi -x,-y+2,-z+2; vii -x+1,-y+1,-z+2. **For 2**, v x,y,z-1; vi x-1,y,z-1; vii -x+1,-y,-z+1; viii x,y,z+1. **For 3**, ii x+1,y,z; iii x,y+1,z; iv -x,-y+1,-z. **For 4**, iii -x+1,-y+1,-z+1; iv x+1,y,z-1; v x+1,y,z; vi -x+1,-y,-z+1. **For 5**, i x,y,z+1; ii x+1,y,z; iii -x+2,y-1/2,-z+1; iv x,y,z-1; v -x+1,y-1/2,-z+1; vi x-1,y,z-1; vii -x+1,y-1/2,-z; viii -x+1,y+1/2,-z+1. **For 6**, i, x-1/2,-y+1/2,z+1/2; iii, x,-y+1,z-1/2; iv, x+1/2,y+1/2,z+1; v, x,-y,z+1/2; vi, x+1/2,-y+1/2,z+1/2; vii, x,-y,z-1/2.