Electronic Supplementary Material (ESI) for Chemical Communications

Supporting information for A Microporous Metal-Organic Framework with High Stability for GC Separation of Alcohols from Water

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Experimental Section:

The ligand (S)-4,5,6,7-tetrahydro-1H-imidazo[4,5-c]pyridine-6-carboxylic acid was prepared according to the literature method. All chemicals employed were commercially available and used as supplied without further purification. The elemental analyses were carried on a Perkin-Elmer 240C elemental analyzer. The infrared (IR) spectra were recorded (400-4000 cm^{-1} region) on a Nicolet Impact 410 FT-IR spectrometer using KBr pellets. Thermogravimetric analyses (TGA) were performed under oxygen atmosphere with a heating rate of 10 °C/min using a Perkin-Elmer TGA 7 thermogravimetric analyzer. Low pressure gas and vapor adsorption measurements were performed with Autosorb-iQ2-MP-AG machine. Gas chromatographic measurements were performed on a GC-450 Bruker with a thermal-current detector (TCD).

Synthesis of JUC-110:

$Cd(NO_3)_2 \cdot 4H_2O$ (0.02 g, 0.065 mmol) and (S)-4,5,6,7-tetrahydro-3H-imidazo[4,5-c]pyridine-6-carboxylic acid hydrochloride (H_2thipc) (0.04g, 0.197 mmol) were dissolved in H_2O (2mL) and then DMF(6mL) and 150μL of TEA were added into the solution. The mixture was stirred at room temperature and then sealed in a 12mL Teflon-lined steel vessel and heated at 85 °C for 4 days. After cooled to the room temperature, colorless block-shaped crystals of JUC-101 (67%) were obtained. Elemental analyses: Anal Calcd for JUC-101: C 26.45%, H 4.72, N 13.23; Found: C 25.96%, H 4.84%, N 12.87%.

Single-crystal X-ray crystallographic study:

Diffraction intensities for two compounds were collected at 293K on Bruker Apex Ⅱ CCD area-detector diffractometer (Mo Kα, 0.71073 Å). An empirical absorption correction was applied to the date using the SADBAS program. The structure was solved with direct methods. Anisotropic thermal parameters were applied to the all

non-hydrogen atoms. Hydrogen atoms were fixed at calculated positions and refined by using riding mode. All calculations performed using the SHELEXTL program. Crystallographic data are summarized in Table 1, the selected bond lengths and bond angles of JUC-101 are listed in Table 2.

Low-pressure gas and vapor sorption measurements: The as-synthesized samples of JUC-110 were heated at 160 °C under vacuum for 17 h before the measurements. N_2 and CO_2 used were of 99.999% purity and the liquid such as water, methanol and ethanol used without further purification. N_2 and CO_2 adsorption measurements were performed at 77 K and 273 K respectively, and the vapor adsorption-desorption isotherms were measured at 298 K.

GC separation measurements: The packed-column (180 × 2 mm) was filled with samples of JUC-110. Argon (99.999 %) was used as the carrier gas. The temperature of carburettor was set to be 175 ºC. Before GC experiments, the column was activated at 160 ºC with the Ar flow for 120 min. The GC separation of ternary mixture was conducted with a temperature program consisting of three steps: 100 ºC for the first 4 min, than 170 ºC from 5 to 13 min and 190 ºC for the remainder of the measurement. The GC separation of binary mixtures of alcohols and water were performed with a temperature program: 100 ºC for the first 7.5 min, than ramp from 100 to 160 ºC within 0.5 min and 160 ºC for the remainder of the measurement. For a typical run 1μL of the mixture was manually injected to the injection port.

Scheme. S1 ligand H_2thipc

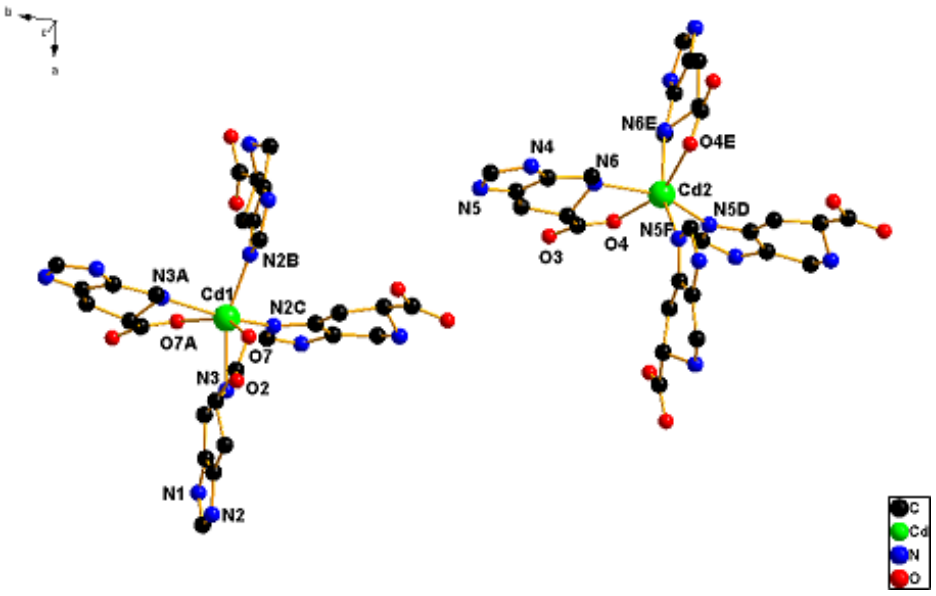

Figure S1. Coordination environment of two Cd ions in JUC-110, H atoms and water molecules were omitted for clarity. Symmetry transformations used to generate equivalent atoms: A: y, x, -z, B: -0.5+x, 1.5-y, -z, C: 1.5-y, -0.5+x, z, D: 0.5-x, -0.5+y, 1-z, E: -y, -x, 1-z, F: 0.5-y, -0.5+x, z

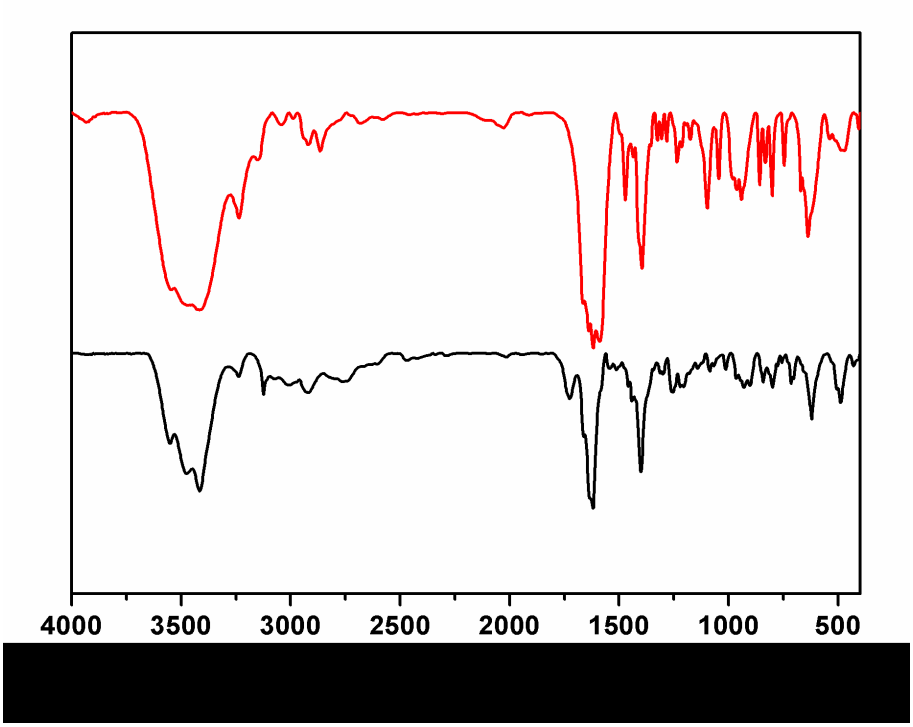

Figure S2. FT-IR spectra of ligand H_2thipc (black) and JUC-110 (red)

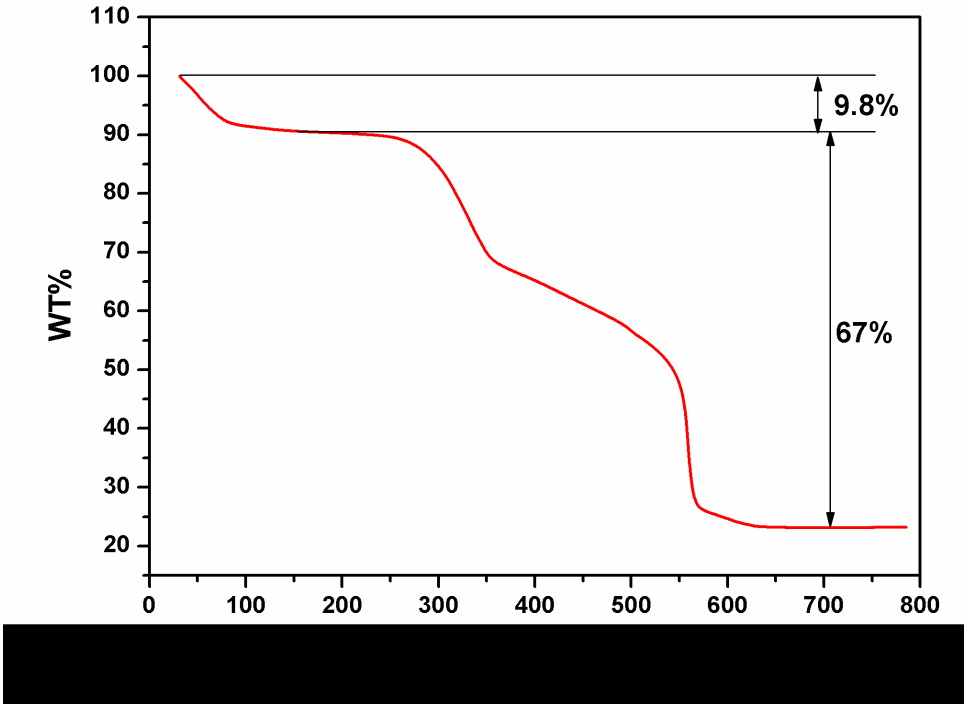

Figure S3. TGA isotherm of as-synthesized JUC-110

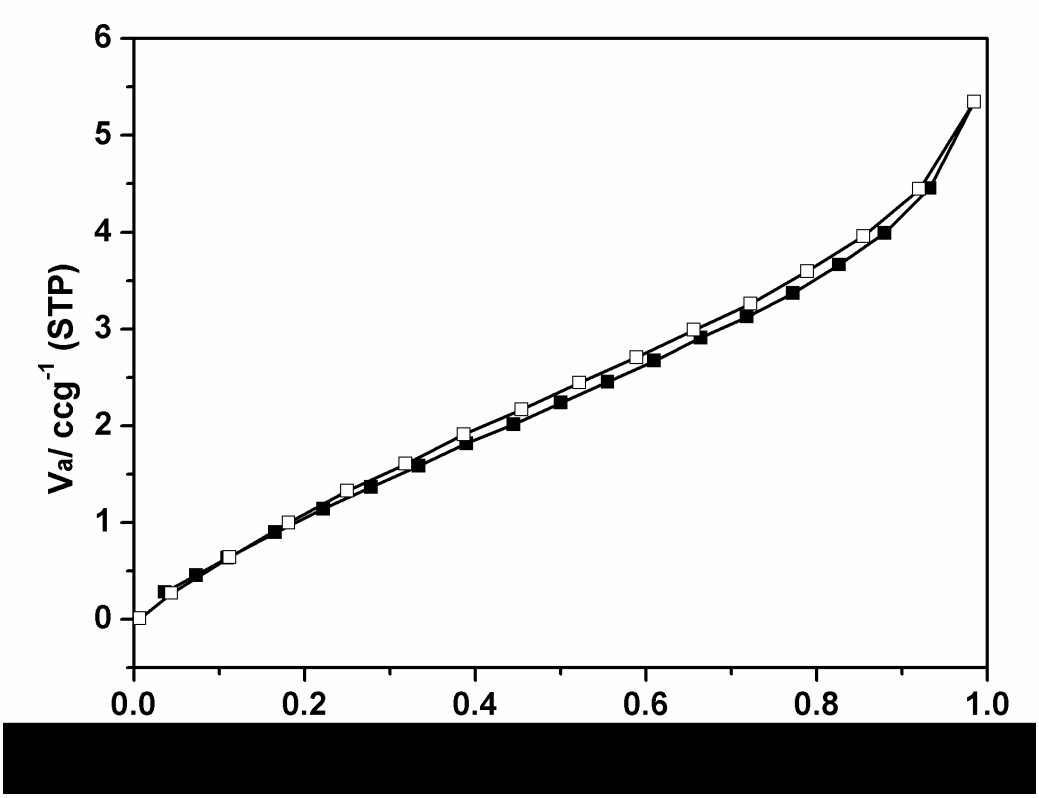

Figure S4. N_2 adsorption and desorption isotherm of JUC-110 at 77 K.

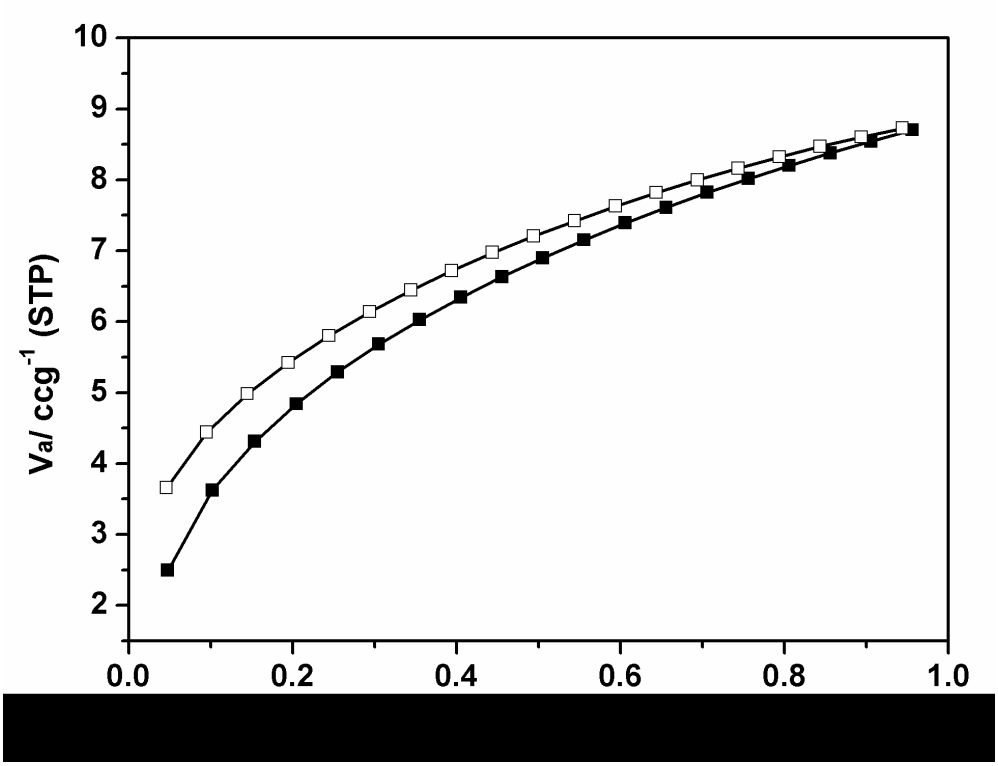

Figure S5. CO_2 adsorption and desorption isotherm of JUC-110 at 273 K.

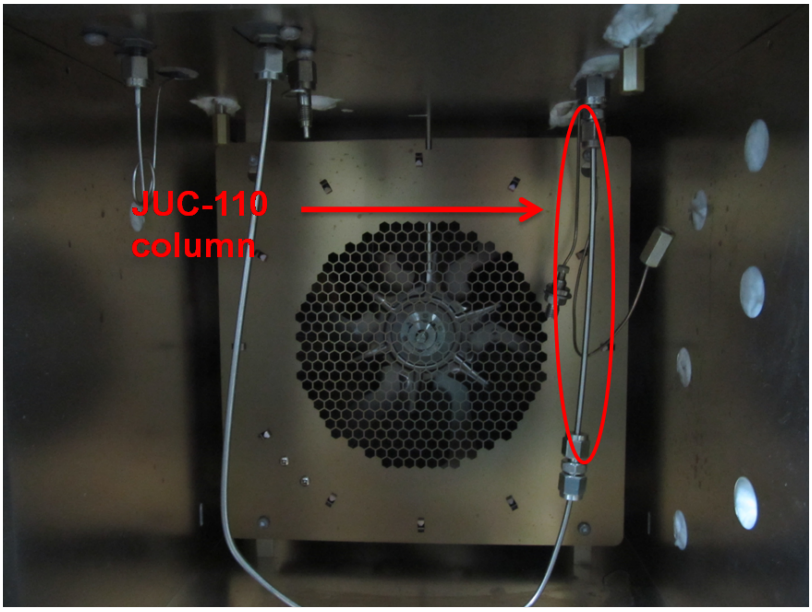

Figure S6. A view of the GC apparatus equipped with a JUC-110 packed column (18 mm long × 2 mm i.d.) using the TCD detector.

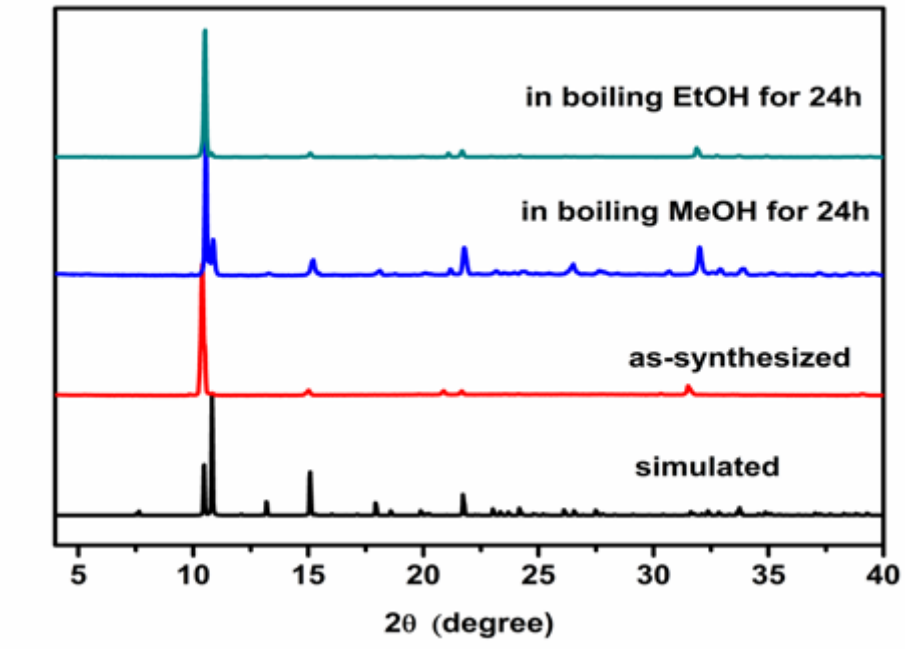

Figure S7. PXRD patterns of JUC-110: simulated (black), as-synthesized (red), treated in boiling MeOH for 24h (blue), and treated in boiling EtOH for 24h (cyan).

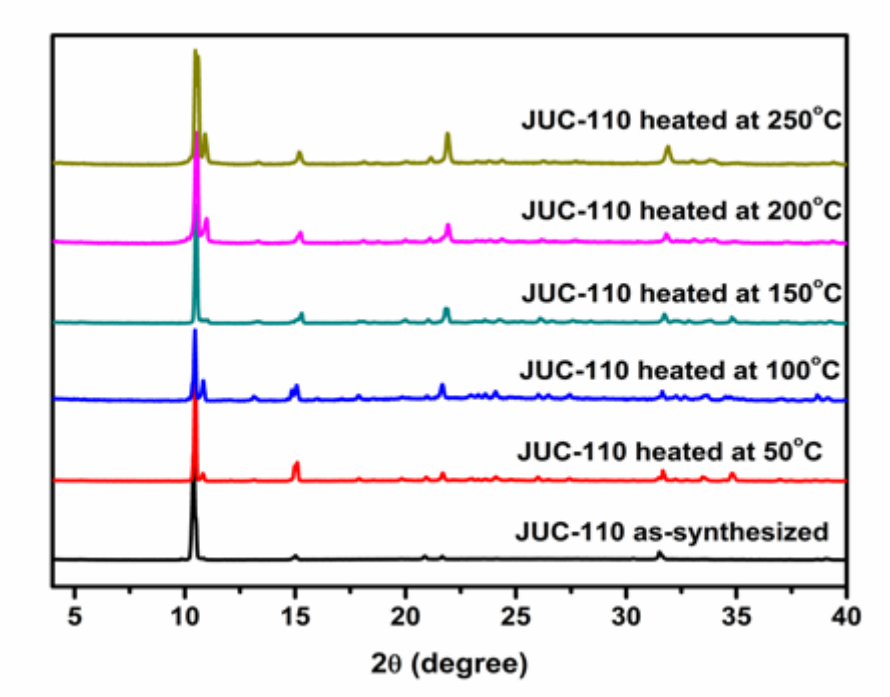

Figure S8. TXRPD patterns of JUC-110 bulk sample: as-synthesized (black), heated at 50 °C (red), heated at 100 °C (blue), heated at 150 °C (cyan), heated at 200 °C (magenta) and heated at 250 °C (dark yellow).

Table S1. Crystal and Structure Refinement of JUC-110

Parameter	**JUC-110**
Empirical formula	C_{14} H_{28} Cd N_6 O_{10}
Formula weight	552.83
Temperature, K	293(2)
Wavelength, Å	0.71073
Crystal system	Tetragonal
Space group	P4212
a, Å	16.3498(3)
b, Å	16.3498(3)
c, Å	16.8924(7)
α, deg	90
β, deg	90
γ, deg	90
V, Å ^{3}	4515.6(2)
Z	8
$\rho_{calc,}$ mg/m^3	1.626
μ, mm^{-1}	1.028
F(000)	2256.0
Refl. collected	28701
Independent refl.	5706
Refinement method	Full-matrix
	least-squares on F2
Final R indices (R1)	0.0314
[I>2sigma(I)] wR2	0.0760
R indices (R1)	0.0405
(all data) wR2	0.0786
GOOF	1.031

Table S2. Selected bond lengths (Å) and angles (deg) for JUC-110

Cd(1)-N(2)#1	2.262(3)	Cd(2)-N(5)#4	2.283(2)
Cd(1)-N(2)#2	2.262(3)	Cd(2)-N(5)#5	2.283(2)
Cd(1)-O(7)#3	2.352(2)	Cd(2)-O(4)#6	2.336(2)
Cd(1)-O(7)	2.352(2)	Cd(2)-O(4)	2.336(2)
Cd(1)-N(3)	2.366(3)	Cd(2)-N(6)	2.392(3)
Cd(1)-N(3)#3	2.366(3)	Cd(2)-N(6)#6	2.392(3)
N(2)-Cd(1)#7	2.262(3)	N(5)-Cd(2)#8	2.283(2)
N(2)#1-Cd(1)-N(2)#2	92.2(3)	N(5)#4-Cd(2)-N(5)#5	90.22(14)
N(2)#1-Cd(1)-O(7)#3	86.12(9)	N(5)#4-Cd(2)-O(4)#6	113.14(10)
N(2)#2-Cd(1)-O(7)#3	115.75(10)	N(5)#5-Cd(2)-O(4)#6	84.78(8)
N(2)#1-Cd(1)-O(7)	115.75(10)	N(5)#4-Cd(2)-O(4)	84.78(8)
N(2)#2-Cd(1)-O(7)	86.12(9)	N(5)#5-Cd(2)-O(4)	113.14(10)
O(7)#3-Cd(1)-O(7)	149.33(13)	O(4)#6-Cd(2)-O(4)	155.28(14)
N(2)#1-Cd(1)-N(3)	87.61(12)	N(5)#4-Cd(2)-N(6)	154.87(9)
N(2)#2-Cd(1)-N(3)	152.30(11)	N(5)#5-Cd(2)-N(6)	93.60(10)
O(7)#3-Cd(1)-N(3)	91.89(11)	O(4)#6-Cd(2)-N(6)	91.95(10)
O(7)-Cd(1)-N(3)	69.22(9)	O(4)-Cd(2)-N(6)	70.88(8)
N(2)#1-Cd(1)-N(3)#3	152.30(11)	N(5)#4-Cd(2)-N(6)#6	93.60(10)
N(2)#2-Cd(1)-N(3)#3	87.61(12)	N(5)#5-Cd(2)-N(6)#6	154.87(9)
O(7)#3-Cd(1)-N(3)#3	69.22(9)	O(4)#6-Cd(2)-N(6)#6	70.87(8)
O(7)-Cd(1)-N(3)#3	91.88(11)	O(4)-Cd(2)-N(6)#6	91.95(10)
N(3)-Cd(1)-N(3)#3	105.05(19)	N(6)-Cd(2)-N(6)#6	93.39(16)

Symmetry transformations used to generate equivalent atoms:

#1 -y+3/2,x-1/2,z; #2 x-1/2,-y+3/2,-z; #3 y,x,-z; #4 -x+1/2,y-1/2,-z+1; #5 -y+1/2,x-1/2,z;

#6 -y,-x,-z+1; #7 y+1/2,-x+3/2,z; #8 y+1/2,-x+1/2,z.