Electronic Supplementary Information (ESI)

Synthesis and Structural Diversity of d^{10} Metal Coordination Polymers Constructed from New Semirigid Bis(3-methyl-1H-pyrazole-4-carboxylic acid)alkane Ligands

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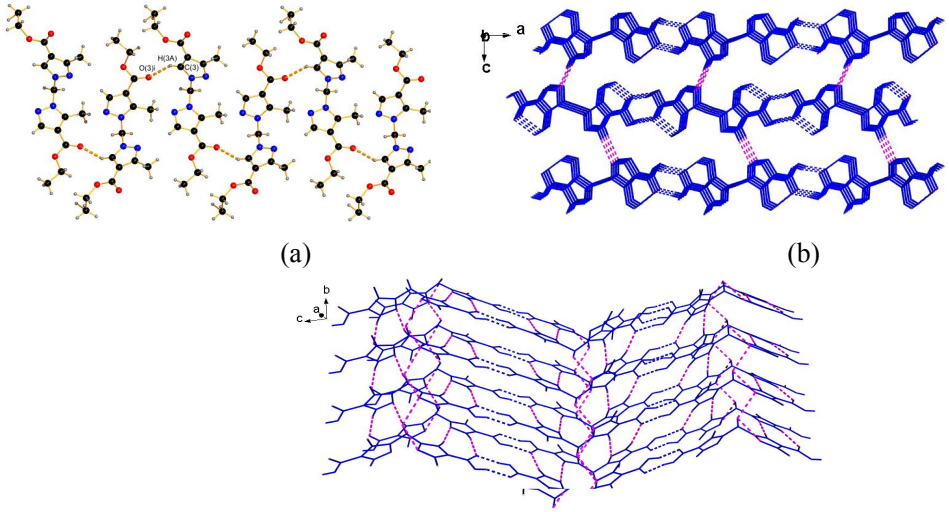
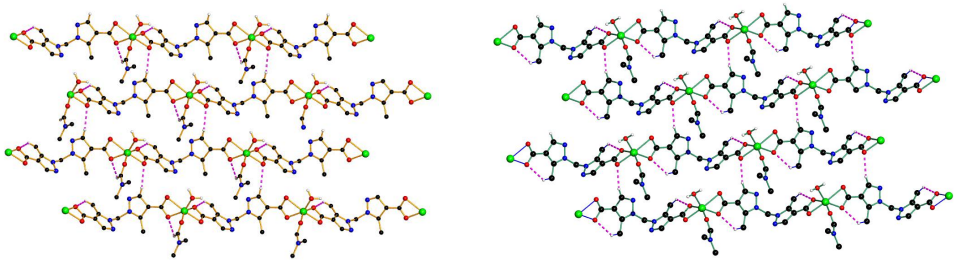
Table of Contents



(a) (b)

(c)

Figure S1 (a) The 1D chainlike structure of **2b**. (b) The 3D supramolecular network of $\mathbf{H_2L^1}$. (c) The 2D supramolecular structure of $\mathbf{H_2L^2}$. The hydrogen atoms not involved in hydrogen bonds are omitted for clarity. Hydrogen bonds are indicated by dashed line.



(a) (b)

Figure S2 2D layers construted by C–H···O hydrogen bonds in **3a** (a) and **3b** (b). The hydrogen atoms not involved in hydrogen bonds are omitted for clarity. Hydrogen bonds are indicated by dashed lines.

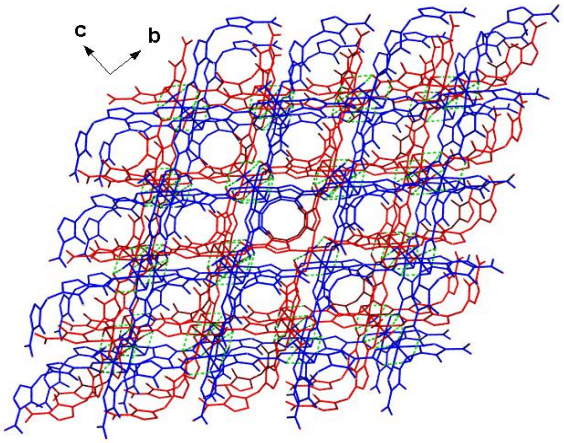
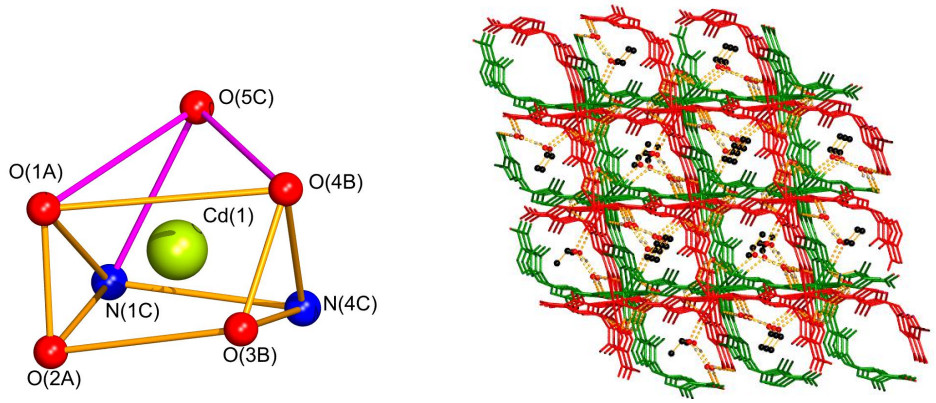


Figure S3 The 3D supramolecular structure of complex **4** viewing along the *a*-axis. The hydrogen atoms not involved in hydrogen bonds are omitted for clarity. Hydrogen bonds are indicated by dashed lines.



(a) (b)

Figure S4 (a) The distorted monocapped triangular prismatic geometry of Cd(II) in complex **6**. Symmetry code: A: 1 – *x*, 1/2 + *y*, 3/2 – *z*; B: –*x*, 1/2 + *y*, 3/2 – *z*; C: 2 – *x*, 1/2 + *y*, 3/2 – *z*. (b) The 3D supramolecular structure of complex **6** viewing along the *c*-axis. The hydrogen atoms not involved in hydrogen bonds are omitted for clarity. Hydrogen bonds are indicated by dashed lines.

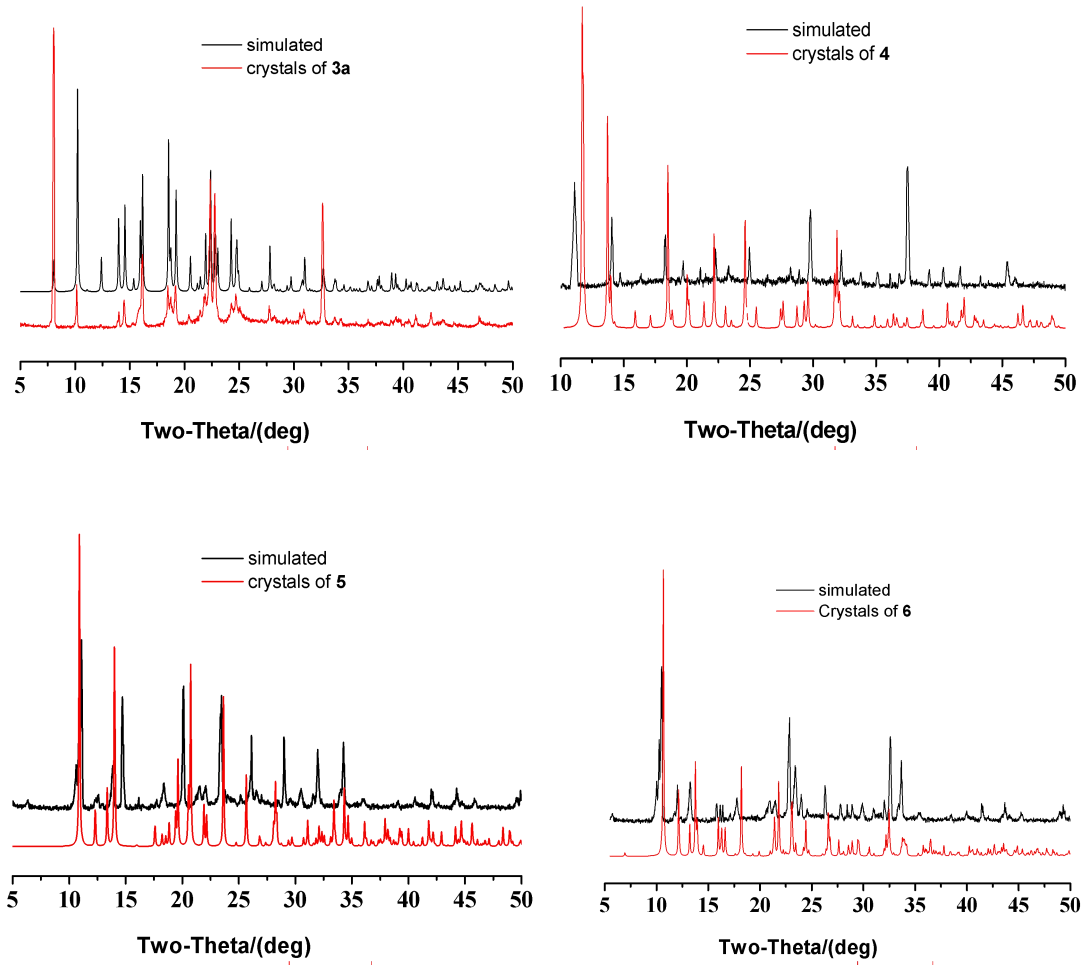


Figure S5. The PXRD Patterns of CPs **3**–**6**.

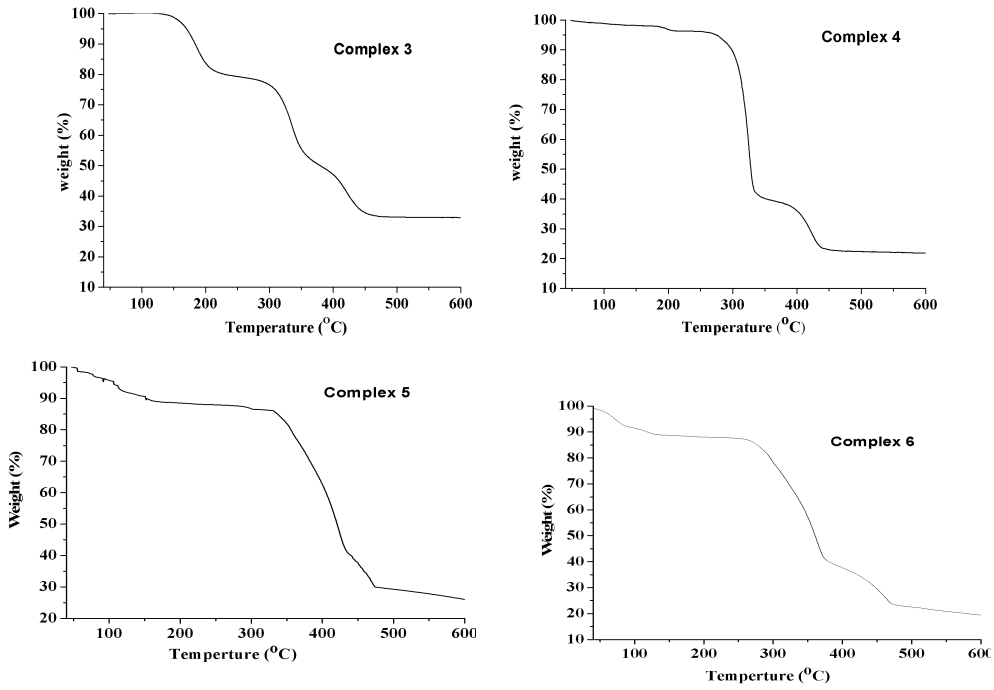


Figure S6 The TG-traces for CPs **3**–**6**.

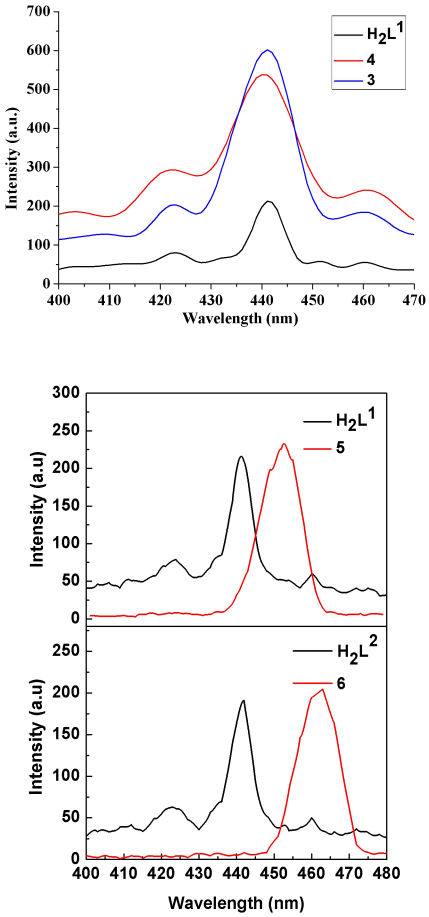


Figure S7 Solid-state emission spectra for ligands $\mathbf{H_2L^1}$, $\mathbf{H_2L^2}$, CPs **3**, **4** (λ_{ex} = 220 nm), and **5**, **6** (λ_{ex} = 224 nm) at room temperature.

Table S1 Selected bond lengths (Å) and angles (°) in **2b**, **H_2L^1**, **H_2L^2** and CPs **3**–**6.**

2b			
C(5)–O(1)	1.210(4)	C(5)–O(2)	1.330(4)
C(13)–O(3)	1.210(3)	C(13)–O(4)	1.326(3)
N(1)–N(2)	1.366(3)	N(3)–N(4)	1.368(3)
C(8)–N(1)	1.448(3)	C(8)–N(3)	1.446(3)
O(1)–C(5)–O(2)	122.3(4)	O(3)–C(13)–O(4)	123.3(2)
N(3)–C(8)–N(1)	112.5(2)		
H_2L^1			
C(2)–N(2)	1.362(6)	C(4)–O(1)	1.235(6)
C(4)–O(2)	1.300(6)	C(5)N(1)	1.324(6)
C(6)–N(2)	1.443(6)	C(6)–N(3)	1.453(6)
C(8)–N(3)	1.361(6)	C(10)–O(4)	1.241(7)
C(10)–O(3)	1.296(7)	C(11)–N(4)	1.320(6)
N(1)–N(2)	1.360(6)	N(3)–N(4)	1.360(6)
O(2)–C(4)–O(1)	123.1(4)	O(4)–C(10)–O(3)	123.5(4)
N(3)–C(6)–N(2)	112.4(3)		
H_2L^2			
C(4)–O(2)	1.248(3)	C(4)–O(1)	1.297(3)
C(10)–O(4)	1.241(3)	C(10)–O(3)	1.287(3)
C(6)–N(3)	1.436(3)	C(6)–N(2)	1.445(3)
N(1)–N(2)	1.369(3)	N(3)–N(4)	1.369(2)
O(2)–C(4)–O(1)	122.7(2)	O(4)–C(10)–O(3)	124.0(2)
N(3)–C(6)–N(2)	113.0(2)		
3a			
Zn(1)–O(1)	2.0882(19)	Zn(1)–O(2)	2.255(2)
Zn(1)#1–O(3)	2.385(2)	Zn(1)#1–O(4)	2.033(2)
Zn(1)–O(5)	2.073(2)	Zn(1)–O(6)	1.995(2)
Zn(1)–O(3)#2	2.385(2)	Zn(1)–O(4)#2	2.033(2)
O(6)–Zn(1)–O(4)#2	145.58(8)	O(5)–Zn(1)–O(6)	93.41(9)
O(4)#2–Zn(1)–O(5)	91.78(10)	O(6)–Zn(1)–O(1)	98.31(8)
O(4)#2–Zn(1)–O(1)	115.86(8)	O(5)–Zn(1)–O(1)	88.21(9)
O(5)–Zn(1)–O(2)	99.13(9)	O(3)#2–Zn(1)–O(2)	94.69(9)
O(5)–Zn(1)–O(2)	147.05(9)	O(1)–Zn(1)–O(2)	59.97(7)
O(6)–Zn(1)–O(3)#	87.68(7)	O(4)#2–Zn(1)–O(3)#2	58.50(8)
O(5)–Zn(1)–O(3)#2	108.43(9)	O(1)–Zn(1)–O(3)#2	162.04(8)
O(2)–Zn(1)–O(3)#2	102.45(8)	N(2)–C(6)–N(3)	110.7(2)°
#1: $x + 1, y + 1, z$; #2 $x - 1, y - 1, z$.			
3b			
Zn(1)–O(6)	1.950(4)	Zn(1)#1–O(4)	2.041(4)
Zn(1)–O(5)	2.047(4)	Zn(1)–O(1)	2.128(4)
Zn(1)–O(2)	2.257(4)	Zn(1)#1–O(3)	2.318(4)

O(6)–Zn(1)–O(4)#1	145.54(15)	O(6)–Zn(1)–O(5)	90.57(17)
O(4)#2–Zn(1)–O(5)	91.85(17)	O(6)–Zn(1)–O(1)	97.77(15)
O(4)#2–Zn(1)–O(1)	116.65(16)	O(5)–Zn(1)–O(1)	88.50(16)
O(6)–Zn(1)–O(2)	100.09(16)	O(4)#1–Zn(1)–O(2)	95.05(16)
O(5)–Zn(1)–O(2)	149.43(16)	O(1)–Zn(1)–O(2)	61.84(14)
O(6)–Zn(1)–O(3)#1	87.71(14)	O(4)#2–Zn(1)–O(3)#1	59.08(14)
O(5)–Zn(1)–O(3)#1	108.87(16)	O(1)–Zn(1)–O(3)#1	161.80(15)
O(2)–Zn(1)–O(3)#1	100.17(15)	N(2)–C(6)–N(3)	110.9(4)
#1: *x* – 1, *y* + 1, *z*.			
4			
Zn(1)–O(1)	2.090(3)	Zn(1)–N(1)#1	2.199(3)
Zn(1)–O(3)	2.105(4)	Zn(1)–O(4)	2.082(4)
O(4)–Zn(1)–O(1)	93.11(12)	O(1)#2–Zn(1)–O(1)	97.12(19)
O(4)–Zn(1)–O(3)	178.23(18)	O(1)–Zn(1)–O(3)	85.72(12)
O(4)–Zn(1)–N(1)#1	87.41(14)	O(1)–Zn(1)–N(1)#1	173.44(13)
O(1)#2–Zn(1)–N(1)#1	89.39(13)	O(3)–Zn(1)–N(1)#1	93.91(14)
N(1)#1–Zn(1)–N(1)#3	84.10(18)	N(2)-C(6)-N(2)#2	110.8(5)
#1: –*x* + 1/2, *y* – 1/2, *z* – 1/2; #2: *x*, –*y* + 3/2, *z*; #3: –*x* + 1/2, –*y* + 2, *z* – 1/2.			
5			
Cd(1)–O(1)#1	2.276(2)	Cd(1)–O(4)#2	2.277(2)
Cd(1)–O(5)	2.294(2)	Cd(1)–N(4)	2.303(2)
Cd(1)–O(2)#1	2.423(2)	Cd(1)–N(1)	2.444(2)
O(1)#1–Cd(1)–O(4)#2	107.19(8)	O(1)#1–Cd(1)–O(5)	89.69(8)
O(4)#2–Cd(1)–O(5)	93.24(8)	O(1)#1–Cd(1)–N(4)	160.83(8)
O(4)#2–Cd(1)–N(4)	91.87(8)	O(5)–Cd(1)–N(4)	87.16(8)
O(1)#1–Cd(1)–O(2)#1	55.45(8)	O(4)#2–Cd(1)–O(2)#1	88.17(7)
O(5)–Cd(1)–O(2)#1	143.54(8)	N(4)–Cd(1)–O(2)#1	129.24(8)
O(1A)–Cd(1)–N(1)	82.27(8)	O(4)#2–Cd(1)–N(1)	159.98(8)
O(5)–Cd(1)–N(1)	104.62(8)	N(4)–Cd(1)–N(1)	80.26(8)
O(2)#1–Cd(1)–N(1)	82.82(8)	N(2)-C(6)-N(3)	111.2(2)
#1 –x + 1, y + 1/2, –z + 3/2; #2 –x + 1, y + 1/2, –z + 5/2.			
6			
Cd(1)–O(5)	2.2977(16)	Cd(1)–O(1)#1	2.3267(15)
Cd(1)–N(4)	2.3497(17)	Cd(1)–O(3)#2	2.3727(16)
Cd(1)–N(1)	2.4498(15)	Cd(1)–O(2)#1	2.4505(14)
Cd(1)–O(4)#2	2.4536(16)	O(5)–Cd(1)–O(1)#1	92.35(6)
O(5)–Cd(1)–N(4)	93.09(7)	O(1)#1–Cd(1)–N(4)	172.84(6)
O(5)–Cd(1)–O(3)#2	133.96(6)	O(1)#1–Cd(1)–O(3)#2	95.56(6)
N(4)–Cd(1)–O(3)#2	83.99(6)	O(5)–Cd(1)–N(1)	84.15(6)
O(1)#1–Cd(1)–N(1)	97.43(5)	N(4)–Cd(1)–N(1)	78.51(6)
O(3)#2–Cd(1)–N(1)	138.99(6)	O(5)–Cd(1)–O(2)#1	137.84(6)
O(1)#1–Cd(1)–O(2)#1	54.73(5)	N(4)–Cd(1)–O(2)#1	118.25(6)
O(3)#2–Cd(1)–O(2)#1	80.17(5)	N(1)–Cd(1)–O(2)#1	76.16(5)

O(5)–Cd(1)–O(4)#2	80.20(6)	O(1)#1–Cd(1)–O(4)#2	97.87(6)
N(4)–Cd(1)–O(4)#2	87.65(6)	O(3)#2–Cd(1)–O(4)#2	53.80(6)
N(1)–Cd(1)–O(4)#2	158.49(6)	O(2)#1–Cd(1)–O(4)#2	125.21(5)
N(2)-C(6)-N(3)	111.33(16)		
#1: –x + 1, y + 1/2, –z + 3/2;#2: –x, y + 1/2, –z + 3/2.			

Table S2 Hydrogen bond distances (Å) and angles (°) in **2b**, **H_2L^1**, **H_2L^2** and CPs **3**–**6**.

D–H•••A	D–H	H•••A	D•••A	D–H•••A
2b				
C(3)–H(3A)•••O(3)i	0.93	2.43	3.258(3)	148
Symmetry code: i: x – 1/2, y, –z + 3/2.				
H_2L^1				
O(2)–H(2)•••O(4)i	0.82	1.81	2.608(6)	164
O(3)–H(3)•••O(1)ii	0.82	1.88	2.667(5)	161
C(1)–H(1B)•••O(1)	0.96	2.51	3.108(6)	120
C(5)–H(5)•••N(4)iii	0.93	2.48	3.410(6)	178
C(7)–H(7B)•••O(4)	0.96	2.44	3.076(6)	123
i:1/2 + x, –1/2 – y, z; ii –1/2 + x, –1/2 – y, z; iii 1/2 –x, –1/2 + y, 1/2 + z.				
H_2L^2				
O(1)–H(1)•••O(4)i	0.82	1.84	2.630(3)	162
O(3)–H(3)•••O(2)ii	0.82	1.82	2.636(3)	171
C(7)–H(7B)•••O(4)	0.96	2.56	3.093(4)	115
C(5)–H(5)•••N(4)iii	0.93	2.61	3.510(4)	164
C(6)–H(6B)•••N(1)iv	0.97	2.61	3.368(3)	135
C(11)–H(11)•••O(2)v	0.93	2.43	3.350(4)	168
i: –1/2 + x, 3/2 – y, –1/2 + z; ii: 1/2 + x, 3/2 – y, 1/2 + z; iii: 1/2 – x, –1/2 + y, 1/2 – z; iv: x, –1 + y, z; v: 1/2 – x, 1/2 + y, 1/2 – z.				
3a				
O(6)–H(6X)•••O(3)i	0.89	1.81	2.693(3)	172
O(6)–H(6Y)•••O(1)ii	0.94	1.85	2.740(3)	158
C(11)–H(11)•••O(1)iii	0.93	2.52	3.414(3)	162
C(1)–H(1B)•••O(2)	0.96	2.50	3.131(4)	124
C(7)–H(7B)•••O(4)	0.96	2.38	3.052(3)	127
i: –1/2 + x, 5/2 – y, –z; ii: –1/2 + x, 3/2 – y, –z; iii: x, 1 + y, z.				
3b				
O(6)–H(6X)···O(3)i	0.96	2.25	2.764(6)	113
O(6)–H(6Y)···O(1)ii	0.96	2.31	2.710(6)	104
C(1)–H(1B)•••O(2)	0.96	2.53	3.203(7)	127
C(11)–H(11)•••O(1)iii	0.93	2.57	3.470(7)	163
C(12)–H(12)•••O(4)iv	0.93	2.60	3.090(6)	114
i: –1/2 + x, –1/2 – y, –z; ii: –1/2 + x, 1/2 – y, -z; iii: x, –1 + y, z; iv: –1 + x, 1 + y, z.				

4				
O(4)–H(4X)•••O(2)i	0.88	1.78	2.646(5)	169
O(3)–H(3X)•••O(2)ii	0.83	1.96	2.760(5)	161
C(6)–H(6B)•••O(5)iii	0.97	2.44	3.324(14)	152
C(6)–H(6B)•••O(5)iv	0.97	2.44	3.324(14)	152
O(5)–H(5Y)•••O(3)v	0.88	2.25	3.084(14)	158
i: x, –y + 3/2, z; ii: x + 1/2, –y +3/2, –z + 1/2; iii: x – 1/2, y + 1, –z + 1/2; iv: x – 1/2, –y + 3/2, –z + 1/2; v: –x + 1/2, –y + 1, z – 1/2.				
5				
O(5)–H(5D)•••O(6)	0.82	1.91	2.714(3)	167
O(5)–H(5C)•••O(3)i	0.82	2.00	2.738(3)	150
O(6)–H(6C)•••O(4)ii	0.82	2.32	2.966(3)	136
O(6)–H(6D)•••O(3)iii	0.82	2.09	2.868(3)	157
C(6)–H(6A)•••O(6)iv	0.97	2.54	3.419(4)	151
C(6)–H(6B)•••O(4)v	0.97	2.53	3.139(4)	120
C(11)–H(11)•••O(3)i	0.93	2.56	3.310(4)	138
i: 1 – x, 1/2 + y, 5/2 – z; ii: 1/2 – x, 1 – y, –1/2 + z; iii: –1/2 + x, 1/2 – y, 2 – z; iv: 1 + x, y, z; v: 3/2 – x, 1 – y, –1/2 + z.				
6				
O(8)–H(8X)•••O(6)	0.89	1.81	2.696(3)	171
O(5)–H(5Y)•••O(8)	0.82	1.98	2.790(3)	168
O(6)–H(6X)•••O(2)	0.86	1.97	2.830(2)	172
O(5)–H(5X)•••O(7)i	0.82	1.93	2.755(3)	178
O(6)–H(6Y)•••O(1)ii	0.84	1.93	2.768(2)	177
O(7)–H(7X)•••O(3)iii	0.82	2.07	2.795(3)	148
O(7)–H(7Y)•••O(4)iv	0.82	2.43	3.092(3)	139
C(1)–H(1C)•••O(2)	0.96	2.50	3.098(3)	121
C(7)–H(7C)•••O(4)	0.96	2.49	3.095(3)	121
i: 1 – x, 1 – y, 2 – z; ii: x, 1/2 – y, 1/2 + z; iii: 1 + x, y, z; iv: 1 + x, 1/2 – y, 1/2 + z.				