Electronic Supplementary Material (ESI) for Dalton Transactions

Auxiliary Ligand-Directed Synthesis of a Series of Cd(II)/Co(II) Coordination Polymers with Methylenebis(3,5-dimethylpyrazole): Syntheses, Crystal Structures, and Properties

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Experimental

Materials and measurements

Methylene bis(3,5-dimethylpyrazole) **(H_2MDP)** was prepared according to previously described methods[1] and other reagents and chemicals were purchased commercially and used as received without further purification. Elemental analyses (C, H, N) were performed on a Vario EL III elemental analyzer. Infrared spectra were measured as KBr disks on were on a Spectrum-One FT-IR Spectrophotometer. X-ray powder diffraction data were collected on a Miniflex2 diffractometer with Cu-*K*α radiation (ë=1.54184 Å) and scans were run for each sample over the range $5^o \leq 2\theta \leq 65^o$. Thermal gravimetric analyses were performed on a NETSCHZ STA-449C thermoanalyzer at a heating rate of 10^oC/min under nitrogen atmosphere. Magnetic data were obtained with a Quantum Design MPMS XL SQUID magnetometer. Fluorescence spectra were measured with an Edinburgh Analytical instrument FLS920.

Preparation of the compounds 1–6

{[Cd(H_2MDP)(OPh)](H_2O)}$_n$ (1)

A mixture of $Cd(NO_3)_2 \cdot 4H_2O$ (0.2 mmol, 60 mg), H_2MDP (0.2 mmol, 40 mg), H_2OPh (0.2 mmol, 33 mg), and H_2O (10 mL) was sealed in a 25 mL Teflon-lined bombs, heated at 130^{o}C for 72 h, and then cooled slowly at 2 ^{o}C/h to room temperature, affording pale yellow lamellar crystals of **1** in 71% yield (based on H_2MDP). Anal. Calcd for $C_{19}H_{22}CdN_4O_5$: C, 45.71; N, 11.23; H, 4.41. Found: C, 45.63; N, 11.28, H, 4.49. IR (KBr, cm^{-1}): 3235 (m), 1548 (s), 1401 (s), 1285 (m), 856 (m), 752 (w), 648 (w).

{[Cd(H_2MDP)(MPh)](H_2O)$_{1/10}$}$_n$ (2)

Yellow block crystals of **2** were obtained through a procedure similar to that of **1** except using H_2MPh instead of H_2OPh (48% yield based on H_2MDP). Anal. Calcd for $C_{19}H_{20.2}CdN_4O_{4.1}$: C, 47.24; N, 11.60; H, 4.18. Found: C, 47.07; N, 11.72, H, 4.21. IR (KBr, cm^{-1}): 3192 (w), 1608 (m), 1556 (m), 1357 (m), 890 (w), 752 (m), 719 (m), 658 (w).

{[Cd(H_2MDP)(PPh)](H_2O)$_{3/2}$}$_n$ (3)

Colorless block crystals of **3** were obtained through a procedure similar to that of **1** except using H_2PPh instead of H_2OPh (56 % based on H_2MDP). Anal. Calcd for $C_{19}H_{23}CdN_4O_{5.50}$: C, 44.90; N, 11.02; H, 4.53. Found: C, 44.74; N, 10.97, H, 4.58. IR (KBr, cm^{-1}): 3349 (m), 1542 (m), 1381 (s), 839 (m), 732 (m), 615 (w).

{[Co(H_2MDP)(OPh)](H_2O)$_2$}$_n$ (4)

Purple rod crystals of **4** were obtained in moderate yields (63% based on H_2MDP) by a similar method as described for **1**, except using the corresponding $Co(OAc)_2 \cdot 4H_2O$ (0.25 mmol, 62 mg) instead of $Cd(NO_3)_2 \cdot 4H_2O$. Anal. Calcd for $C_{19}H_{24}CoN_4O_6$: C, 49.21; N, 12.09; H, 5.18. Found: C, 49.40; N, 11.93, H, 5.13. IR (KBr, cm^{-1}): 3265 (m), 1560 (m), 1392 (m), 874 (w), 832 (w), 760 (w), 702 (w), 660 (w).

{Co(H_2MDP)(MPh)}$_n$ (5)

A mixture of $Co(NO_3)_2 \cdot 6H_2O$ (0.2 mmol, 59 mg), H_2MDP (0.2 mmol, 40 mg), H_2MPh (0.2 mmol, 33 mg), KOH (0.36 mmol, 20 mmg), and H_2O (10 mL) was placed in a 25 mL Teflon-lined stainless steel autoclave. The autoclave was sealed, heated to 160 ℃ in 2 h, and held at the temperature for 72 h. After the mixture had slowly cooled to room temperature at 3 ^{o}C/h, purple block crystals of **5** were obtained in 69% yield (based on the H_2MDP). Anal. Calcd for $C_{19}H_{20}CoN_4O_4$: C, 53.36; N, 13.10; H, 4.68. Found: C, 53.23; N, 12.92, H, 4.58. IR (KBr, cm^{-1}): 3204 (m), 1618 (s), 1560 (s), 1430 (m), 1360 (s), 806 (w), 737 (m), 702 (m), 660 (w).

{Co(H_2MDP)(HBTC)}$_n$ (6)

A mixture of $CoCl_2 \cdot 6H_2O$ (0.25 mmol, 59 mg), H_2MDP (0.2 mmol, 40 mg), H_3BTC (0.2 mmol, 42 mg), and H_2O (10 mL) was placed in a 25 mL Teflon-lined stainless steel autoclave. The autoclave was heated at 160^{o}C for 72 h, and then cooled slowly at 3^{o}C/h to room temperature, affording purple lamellar crystals of **6** in 41% yield (based on H_2MDP).Anal. Calcd for $C_{20}H_{20}CoN_4O_6$: C, 50.92; N, 11.88; H, 4.24. Found: C, 50.76; N, 11.96, H, 4.33. IR (KBr, cm^{-1}): 3209 (w), 1695 (s), 1627 (m), 1587 (m), 1350 (s), 1262 (m), 896 (w), 760 (m), 714 (m), 683 (m), 628 (w).

IR and Thermal Analyses

For compounds **1-5**, the absence of strong absorption bands around 1700 cm^{-1} indicates complete deprotonation of the carboxylic groups. While for compound **6,** the vibration band at 1695 cm^{-1} was observed, which indicates the incomplete deprotonation of the H_3BTC ligand.[2] To investigate the thermal stability of these complexes, the thermogravimetric analysis (TGA) experiments were carried out in the temperature range of 30-800 °C under a flow of nitrogen with a heating rate of 10 °C min^{-1} (Figure 7). Complex **2** lose little weight before 320 ^{o}C, and then decomposes at higher temperature. For complex **3**, the weight loss in the range of 30-240 ^{o}C corresponds to the departure of one and a half lattice water molecules (calcd, 5.31%; found, 5.14%), and then the framework undergoes decomposition at about 340 °C. As to **4**, weight loss of 7.66% was observed in the temperature range of 30-267 °C, which corresponds to the release of two lattice water molecules (calcd 7.78%), and then the framework was found to decompose at about 309 °C. Complexes **5** and **6** do not lose any weight before 375 and 340^{o}C, respectively, and then decompose rapidly on further heating.

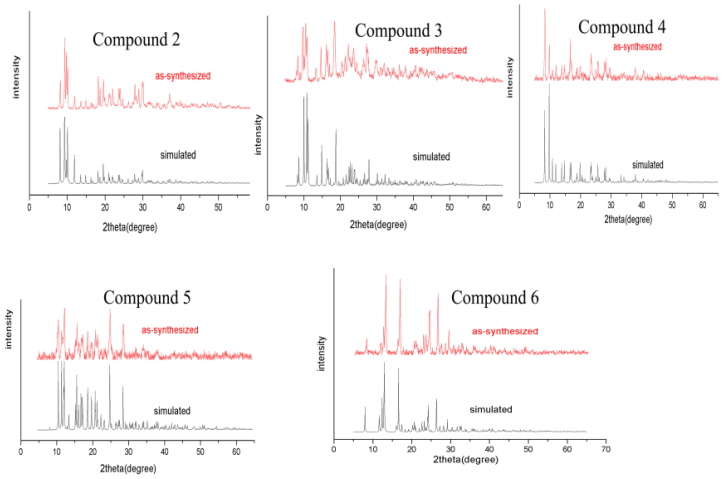

Figure S1. PXRD patterns of complexes **2-6.**

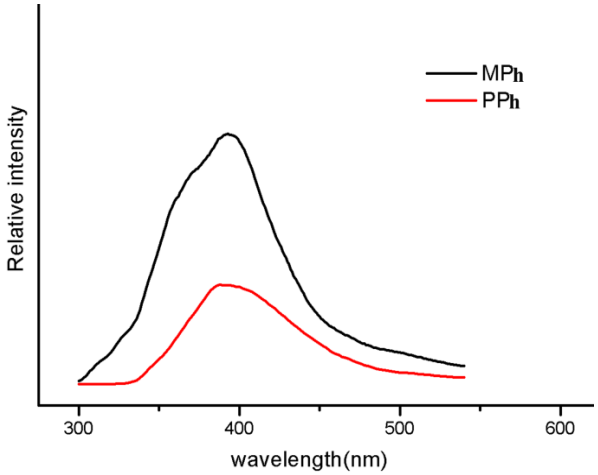

Figure S2. Emission spectra of ligands **H_2MPh** and **H_2PPh** in the solid state at room temperature.

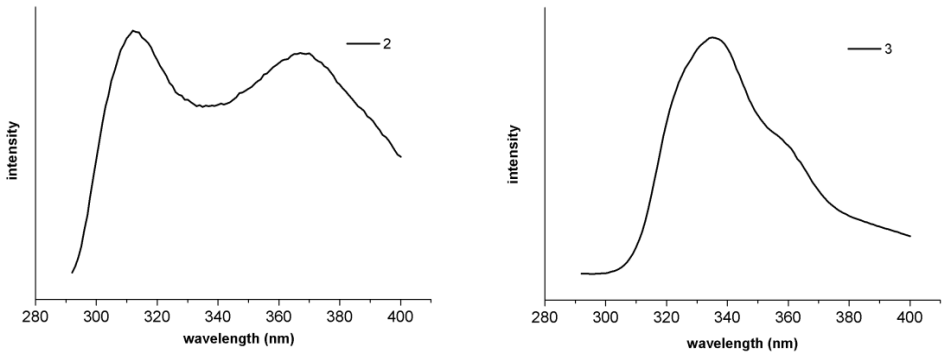

Figure S3. Excitation spectra of complexes **2** and **3** in the solid state at room temperature.

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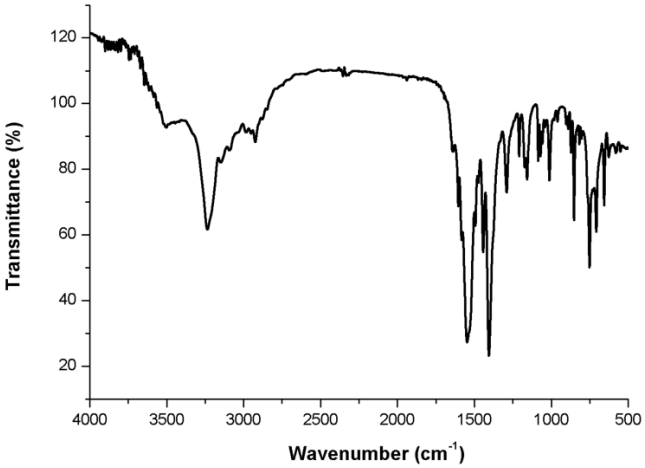

Figure S4. The IR spectrum of complex **1**.

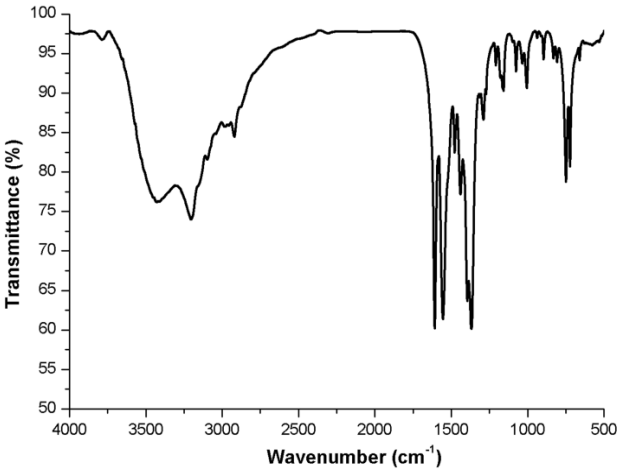

Figure S5. The IR spectrum of complex **2**.

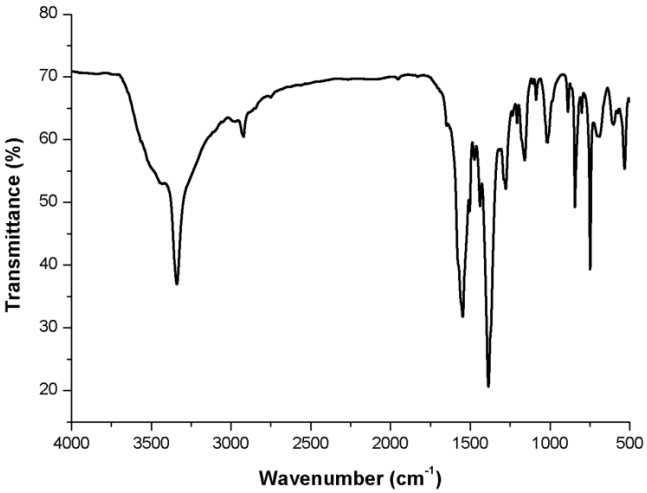

Figure S6. The IR spectrum of complex **3**.

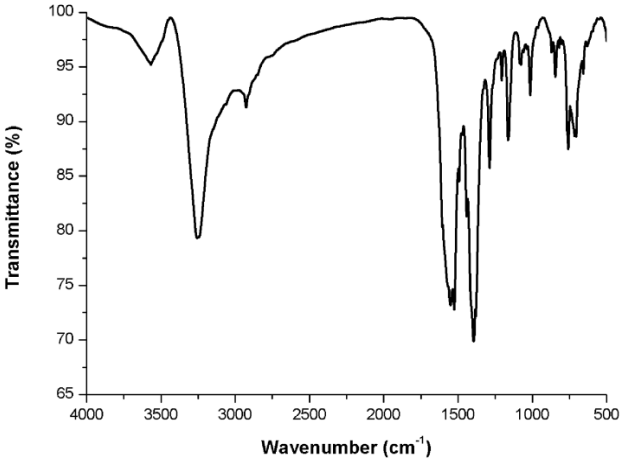

Figure S7. The IR spectrum of complex **4**.

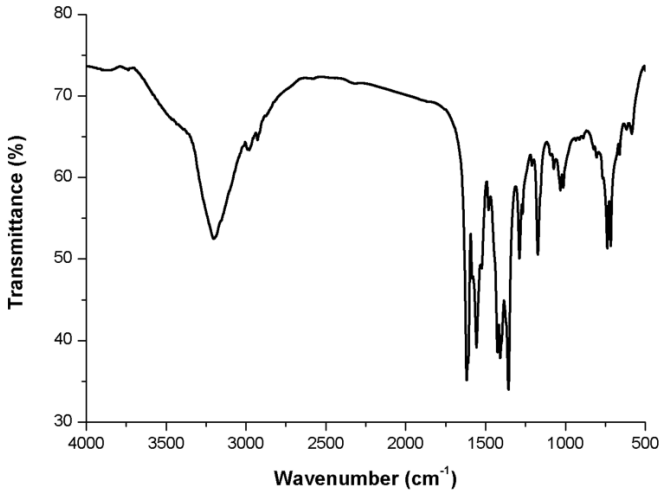

Figure S8. The IR spectrum of complex **5.**

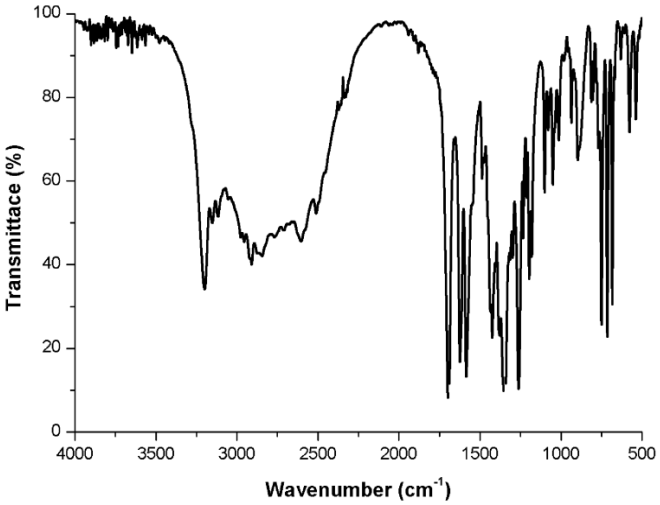

Figure S9. The IR spectrum of complex **6.**

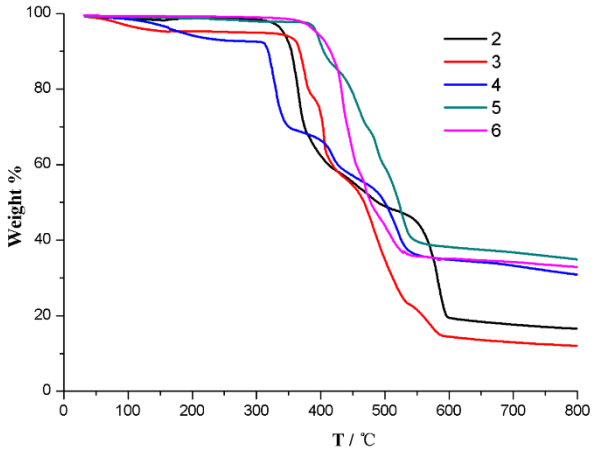

Figure S10. TGA curves for complexes **2-6.**

Table S1 Selected Bond Lengths (Å) and Bond Angles (°) for **1**

Bond	Dist	Bond	Dist
Cd(1)-N(1)#1	2.268(3)	Cd(1)-O(4)	2.331(3)
Cd(1)-O(1)#2	2.260(3)	Cd(1)-O(3)	2.444(3)
Cd(1)-N(3)	2.273(3)	Cd(1)-O(2)#2	2.518(3)
Angle	(°)	Angle	(°)
N(1)#1-Cd(1)-O(1)#2	114.53(13)	N(3)-Cd(1)-O(4)	95.95(13)
N(1)#1-Cd(1)-N(3)	107.29(13)	N(1)#1-Cd(1)-O(3)	82.87(11)
O(1)#2-Cd(1)-N(3)	96.44(12)	O(1)#2-Cd(1)-O(3)	159.22(12)
N(1)#1-Cd(1)-O(4)	130.75(12)	N(3)-Cd(1)-O(3)	88.44(12)
O(1)#2-Cd(1)-O(4)	104.88(12)	N(3)-Cd(1)-O(2)#2	148.61(11)
O(4)-Cd(1)-O(3)	54.43(10)	O(4)-Cd(1)-O(2)#2	83.17(11)
N(1)#1-Cd(1)-O(2)#2	96.44(11)	O(3)-Cd(1)-O(2)#2	115.20(11)

Symmetry codes: #1) x-1/2, -y+1/2, z-1/2; #2) -x+1/2, y+1/2,-z+1/2;

Table S2 Selected Bond Lengths (Å) and Bond Angles (°) for **2**

Bond	Dist	Bond	Dist
Cd(1)-O(4)#1	2.205(4)	Cd(1)-N(4)	2.363(6)
Cd(1)-O(3)	2.216(5)	Cd(1)-O(4)#3	2.695(5)
Cd(1)-N(2)#2	2.255(5)		
Angle	(°)	Angle	(°)
O(4)#1-Cd(1)-O(3)	132.34(19)	O(4)#1-Cd(1)-O(4)#3	75.56(19)
O(4)#1-Cd(1)-N(2)#2	114.36(19)	O(3)-Cd(1)-O(4)#3	86.50(17)
O(3)-Cd(1)-N(2)#2	105.82(19)	N(2)#2-Cd(1)-O(4)#3	81.47(19)
O(4)#1-Cd(1)-N(4)	107.71(19)	N(4)-Cd(1)-O(4)#3	176.82(16)
O(3)-Cd(1)-N(4)	91.1(2)	C(19)-O(4)-Cd(1)#4	112.0(4)
N(2)#2-Cd(1)-N(4)	97.2(2)	C(12)-O(3)-Cd(1)	103.1(4)

Symmetry codes: #1) x, y-1, z: #2) -x+1,-y,-z) -x+1,-y+1,-z+1.

Table S3 Selected Bond Lengths (Å) and Bond Angles (°) for **3**

Bond	Dist	Bond	Dist
Cd(1)-O(4)	2.235(6)	Cd(1)-O(2)	2.307(5)
Cd(1)-N(1)#1	2.241(7)	Cd(1)-O(1)	2.464(7)
Cd(1)-N(3)	2.299(5)	Cd(1)-O(3)	2.710(7)
Angle	(°)	Angle	(°)
O(4)-Cd(1)-N(1)#1	124.8(3)	N(1)#1-Cd(1)-O(2)	134.21(17)
O(4)-Cd(1)-N(3)	111.38(19)	O(4)-Cd(1)-N(1)#1	124.8(3)
N(1)#1-Cd(1)-N(3)	100.07(17)	O(4)-Cd(1)-N(3)	111.38(19)
O(4)-Cd(1)-O(2)	95.6(3)	N(1)#1-Cd(1)-N(3)	100.07(17)
N(3)-Cd(1)-O(2)	81.3(2)	O(4)-Cd(1)-O(2)	95.6(3)
O(4)-Cd(1)-O(1)	92.52(18)	N(1)#1-Cd(1)-O(2)	134.21(17)
O(4)-Cd(1)-O(3)	51.9(2)	N(1)#1-Cd(1)-O(3)	78.8(2)
N(3)-Cd(1)-O(3)	101.3(2)	O(2)-Cd(1)-O(3)	146.4(2)
O(1)-Cd(1)-O(3)	125.7(2)		

Symmetry codes: #1) $-x+2, -y, -z+1$.

Table S4 Selected Bond Lengths (Å) and Bond Angles (°) for **4**

Bond	Dist	Bond	Dist
Co(1)-O(3)#1	1.994(2)	Co(1)-N(3)#2	2.072(2)
Co(1)-N(1)	2.072(2)	Co(1)-O(2)	2.092(2)
Angle	(°)	Angle	(°)
O(3)#1-Co(1)-N(1)	99.85(10)	O(3)#1-Co(1)-O(2)	101.18(10)
O(3)#1-Co(1)-N(3)#2	111.61(11)	N(1)-Co(1)-O(2)	103.91(10)
N(1)-Co(1)-N(3)#2	107.19(11)	N(3)#2-Co(1)-O(2)	129.23(10)

Symmetry codes: #1) $-x+1/2, y+1/2, -z+1/2$; #2) $x-1/2, -y+3/2, z-1/2$.\

Table S5 Selected Bond Lengths (Å) and Bond Angles (°) for **5**

Bond	Dist	Bond	Dist
Co(1)-O(4)#1	1.9368(19)	Co(1)-N(3)#2	2.035(2)
Co(1)-O(2)	1.9552(18)	Co(1)-N(2)	2.051(2)
Angle	(°)	Angle	(°)
O(4)#1-Co(1)-O(2)	130.79(10)	O(4)#1-Co(1)-N(2)	92.43(9)
O(4)#1-Co(1)-N(3)#2	113.54(10)	O(2)-Co(1)-N(2)	111.86(9)
O(2)-Co(1)-N(3)#2	94.74(8)	N(3)#2-Co(1)-N(2)	114.77(9)

Symmetry codes: #1) $x+1/2, -y+1/2, z+1/2$; #2) $x-1/2, -y+1/2, z-1/2$.

Table S6 Selected Bond Lengths (Å) and Bond Angles (°) for **6**

Bond	Dist	Bond	Dist
Co(1)-O(6)#1	1.9244(17)	Co(1)-N(4)	1.997(2)
Co(1)-O(4)	1.9470(18)	Co(1)-N(3)#2	2.0213(19)
Angle	(°)	Angle	(°)
O(6)#1-Co(1)-O(4)	121.31(9)	O(6)#1-Co(1)-N(3)#2	101.59(9)

O(6)#1-Co(1)-N(4)	112.10(8)	O(4)-Co(1)-N(3)#2	100.06(8)
O(4)-Co(1)-N(4)	103.85(8)	N(4)-Co(1)-N(3)#2	118.23(8)

Symmetry codes: #1) $-x+1/2, y-1/2, -z+1/2$; #2) $-x-1/2, y-1/2, -z+1/2$.

Table S7. Hydrogen bond distance and angle data for **4-6**[a].

D–H/A	d(H···A)/ Å	D(D···A)/ Å	∠DHA/
For **5**			
N(1)-H(1A)···O(1)	2.08	2.843(3)	147
N(4)-H(4A)···O(1)#1	1.90	2.715(3)	157
For **6**			
N1-H1A···O3#2	1.94	2.796(3)	170
N2-H2A···O5#3	1.86	2.690(3)	161
O2-H2E···O1#4	1.64(5)	2.583(3)	161(4)

[a] Symmetry transformations to generate equivalent atoms: #1) 1 - *x*,1 - *y*,2 - *z*, #2) 1/2 - *x*,-1/2+*y*, 1/2 - z; #3) -1/2+*x*,1/2−*y*,1/2+*z*, #4) -*x*,1-*y*,1 - *z*.

Reference:
(1) P. E. Kruger, P. Moubaraki, G. D. Fallon, K. S. Murray, *J. Chem. Soc. Dalton Trans.,* 2000, 713.
(2) (a) W. Q. Kan, J. Yang, Y.Y. Liu, J. F. Ma, *Polyhedron,* 2011, **30**, 2113; (b) Y. Y. Liu, J. Li, Ma, J. F.; J. C. Ma, J. Yang, *CrystEngComm,* 2012, **14**, 169.