Supplementary Information

Highly Efficient Electrochemiluminescence Based on Pyrazolecarboxylic Metal Organic Framework

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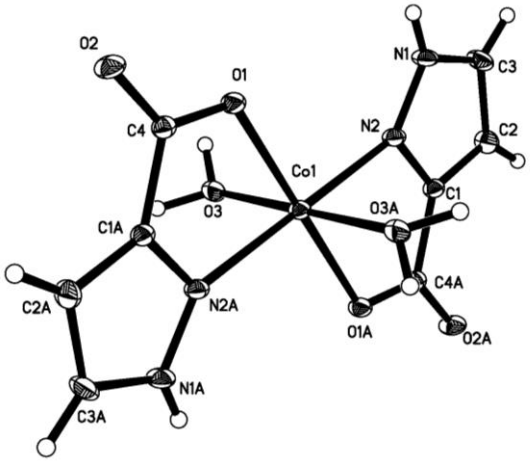

Figure S1 Molecular structure of **1**, with the atom-numbering scheme, showing displacement ellipsoids at the 30% probability level.

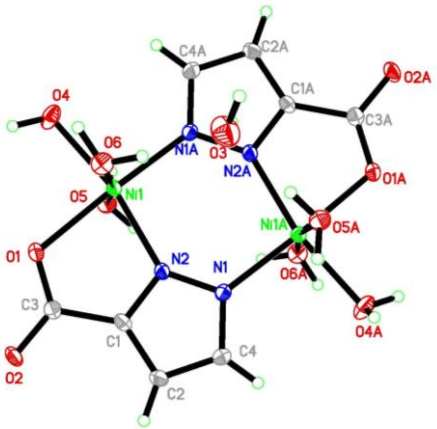

Figure S2 Molecular structure of **2**, with the atom-numbering scheme, showing displacement ellipsoids at the 30% probability level.

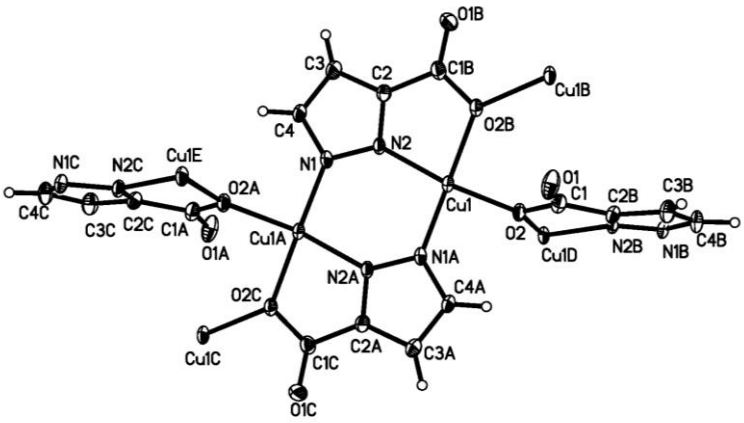

Figure S3 The coordination environment of Cu^{2+} in **3**.

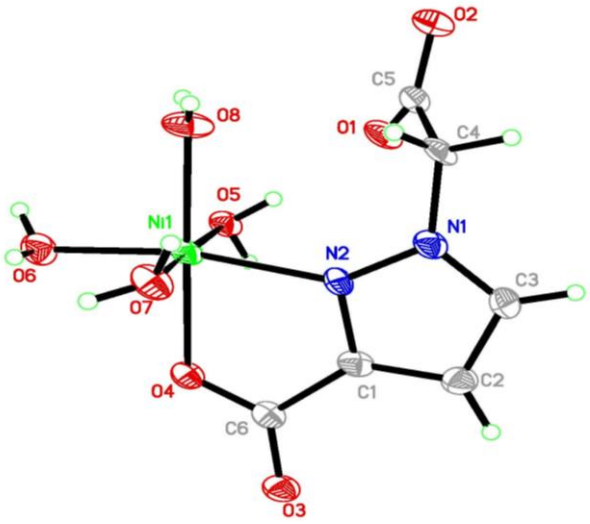

Figure S4 Molecular structure of **4** with thermal ellipse at the 30% probability level.

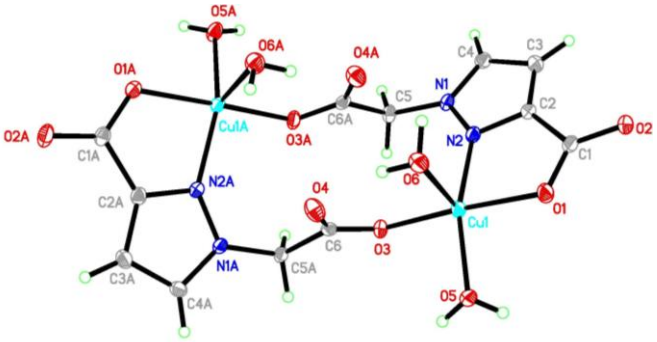

Figure S5 Molecular structure of **5** with thermal ellipse at the 30% probability level.

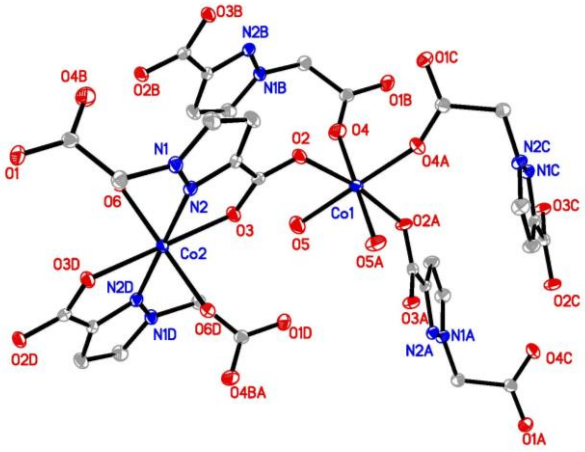

Figure S6 Coordination environments of the Co(II) atoms in **6**

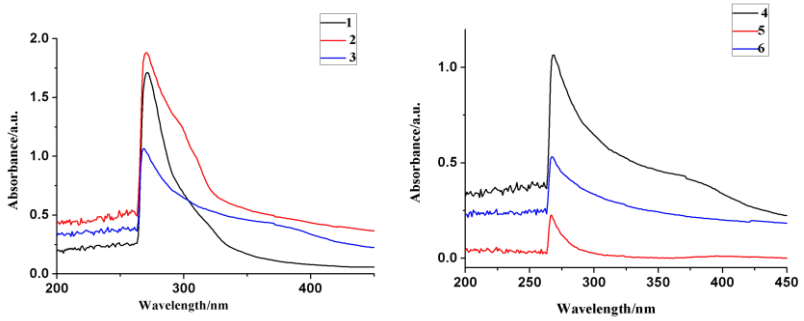

Figure S7 Liquid state UV-vis absorption spectra for **1**-**6** in DMF with 10^{-6} M at room temperature.

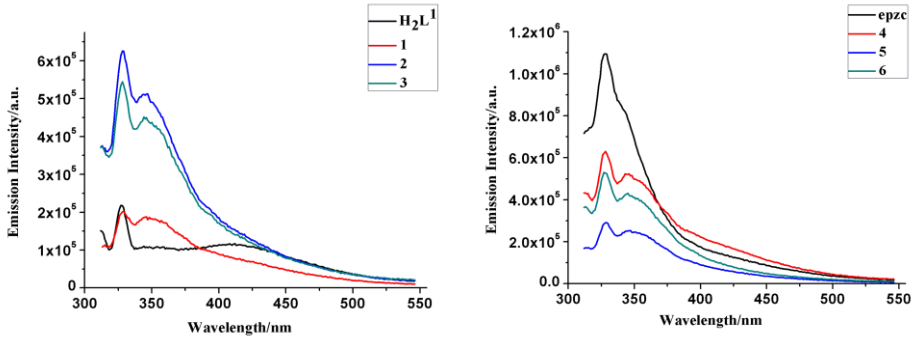

Figure S8 Emission spectra of **1**–**6** in the liquid state in DMF with 10^{-6}M at room temperature (λ_{ex} 271 nm for **1**, 270 nm for **2**, 268 nm for **3** and **4**, and 267 nm for **5** and **6** respectively).

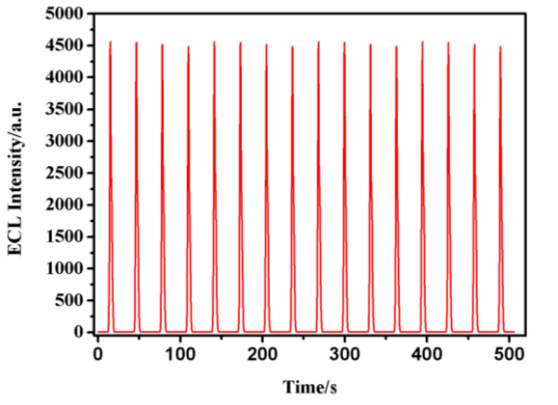

Figure S9 The electrochemiluminescence of $Ru(bpy)_3^{3+}$.

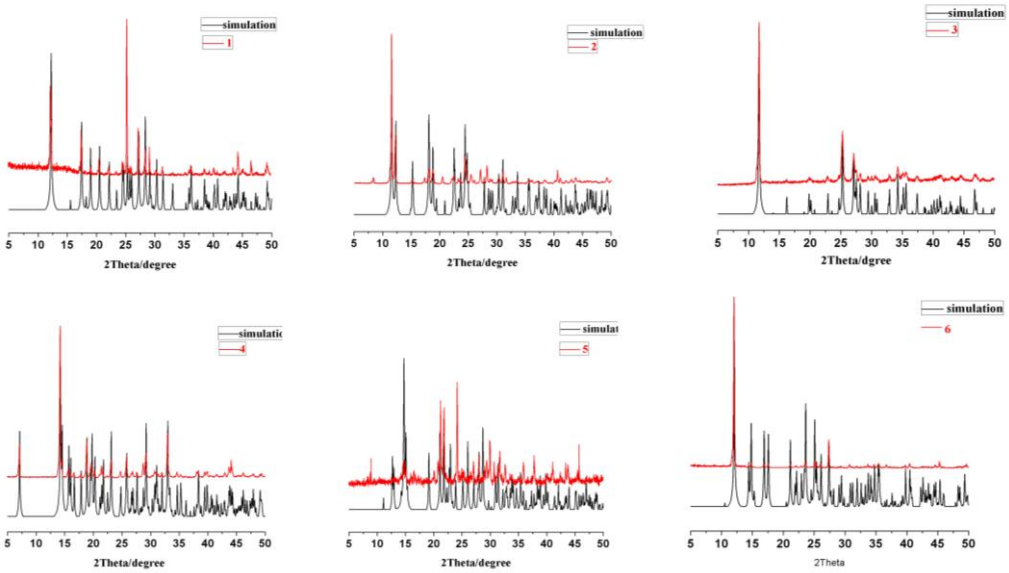

Figure S10 X-ray powder diffraction (PXRD) patterns of **1-6**.

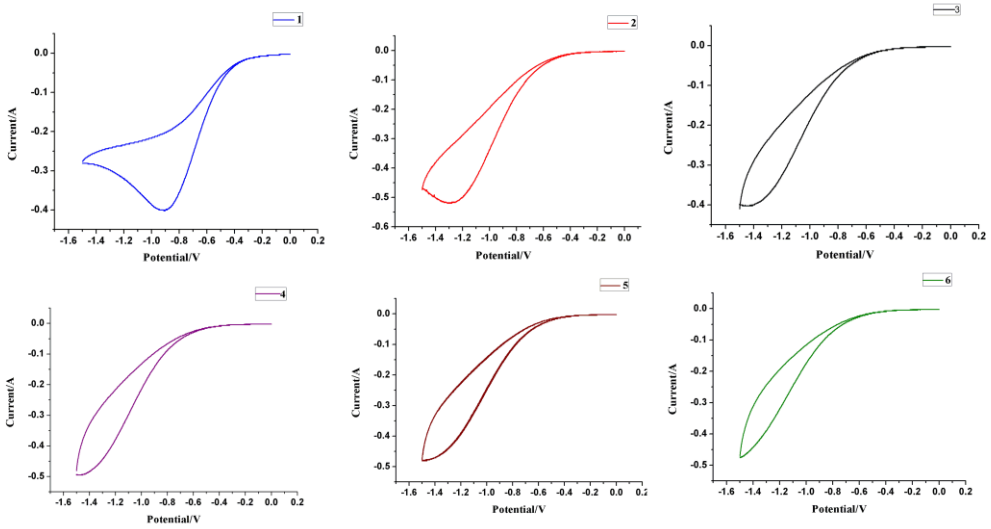

Figure S11 Cyclic Votammogram of **1-6** (1×10^{-6} mol L^{-1}) in DMF with 0.1 M K_2SO_8.

Table S1 Crystallographic data for **1-6.**

	1	**2**	**3**	**4**	**5**	**6**
Empirical formular	$C_8H_{10}CoN_4O_6$	$C_8H_{20}N_4Ni_2O_{12}$	$C_4H_2CuN_2O_2$	$C_6H_{12}NiN_2O_8$	$C_{12}H_{16}Cu_2N_4O_{12}$	$C_{12}H_{16}Co_2N_4O_{12}$
Formula weight	317.13	481.70	173.62	298.87	535.37	526.15
Crystal size/mm	0.25×0.20×0.13	0.22×0.20×0.15	0.3×0.24×0.2	0.22×0.22×0.20	0.25×0.23×0.23	0.21×0.18× 0.15
Temperature/K	293(2)	293(2)	293(2)	293(2)	296(2)	293(2)
λ(Mo-Kα)/ *Å*	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$	$C2/c$	$P2_1/c$	$C2/c$	$C2/c$
a / Å	5.1082 (3)	8.2122 (4)	15.4753 (9)	12.5491	13.0966	14.7287
b / Å	11.3902 (7)	9.1298 (4)	4.9036 (2)	7.1794	8.4245	7.2556
c / Å	9.3932 (7)	12.1575 (5)	12.9752 (5)	11.6227	16.766	16.8674
α/°	90	90	90	90	90	90
β /°	96.020 (7)	107.134 (5)	102.423 (5)	98.09(6)	108.240	95.253
γ/°	90	90	90	90	90	90
V / Å^3	543.51 (6)	871.06 (6)	961.56 (8)	1036.72	1756.9(4)	1794.97(15)
Z	2	2	4	4	4	4
D_{calc} /g·cm^{-3}	1.938	1.837	2.399	1.915	2.024	1.947
μ/ mm^{-1}	1.61	2.23	4.44	1.91	2.50	1.93
θ range/°	3.6 to 29.0	3.4 to 26.4	3.2 to 28.9	3.3 to 25	2.6 to 25	3.1 to 25
Reflections collected	2211	4036	2019	3718	5992	3344
Independent reflections	1253	1780	1104	1821	1542	1584
Observed reflections	1008	1488	934	1440	1428	1305
F(000)	322	496	680	616	1080	1064
S	1.07	1.10	1.06	1.02	1.00	1.07
wR_2	0.0358	0.1019	0.1097	0.165	0.063	0.081
$R_1[I>2\sigma(I)]$	0.0849	0.0390	0.0402	0.061	0.022	0.028
Largest diff. peak and hole/e·Å^{-3}	0.30 and -0.33	0.65 and -0.63	0.74 and -0.59	0.99 and -1.15	0.28 and -0.40	0.3 and -0.47

$R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

Table S2 Selected bond lengths (Å) and angles (°) for **1**-**6**.

1			
Co1–O3^{i}	2.0866 (19)	Co1–O1	2.0946 (17)
Co1–O3	2.0866 (19)	Co1–N2	2.125 (2)
Co1–O1^{i}	2.0946 (17)	Co1–N2^{i}	2.125 (2)
O3^{i}–Co1–O3	180.0	N1–N2–Co1	143.03 (16)
O3^{i}–Co1–O1^{i}	91.10 (7)	N2–Co1–N2^{i}	180.00 (12)
O3–Co1–O1^{i}	88.90 (7)	O1–Co1–N2^{i}	78.13 (7)
O3^{i}–Co1–O1	88.90 (7)	O1^{i}–Co1–N2^{i}	101.87 (7)
O3–Co1–O1	91.10 (7)	O3–Co1–N2^{i}	91.09 (8)
O1^{i}–Co1–O1	180.0	O1^{i}–Co1–N2	78.13 (7)
O3^{i}–Co1–N2	91.09 (8)	O3–Co1–N2	88.91 (8)
O1–Co1–N2	101.87 (7)	O3^{i}–Co1–N2^{i}	88.91 (8)
Symmetry code: (i) −*x*+2, −*y*+1, −*z*+1.			
2			
Ni1–N1^{i}	2.024 (3)	Ni1–O1	2.115 (2)
Ni1–N2	2.038 (3)	Ni1–O5	2.158 (3)
Ni1–O4	2.064 (2)	N1–Ni1^{i}	2.024 (3)
Ni1–O6	2.077 (3)	O1–Ni1–O5	86.68 (10)
N1^{i}–Ni1–N2	98.05 (11)	O6–Ni1–O5	168.72 (10)
N1^{i}–Ni1–O4	93.02 (11)	O4–Ni1–O5	84.38 (10)
N2–Ni1–O4	168.68 (12)	N2–Ni1–O5	92.75 (11)
N1^{i}–Ni1–O6	93.36 (11)	N1^{i}–Ni1–O5	92.39 (11)
N2–Ni1–O6	96.04 (11)	O6–Ni1–O1	88.01 (10)
O4–Ni1–O6	85.64 (11)	O4–Ni1–O1	89.60 (10)
N1^{i}–Ni1–O1	177.13 (10)	N2–Ni1–O1	79.29 (10)
Symmetry code: (i) −x+2, −y+1, −z+1.			
3			
Cu1–N1^{iii}	1.929 (4)	Cu1–O2^{i}	2.010 (3)
Cu1–N4	1.948 (3)	N1–Cu1^{iii}	1.929 (3)
Cu1–O2	1.993 (3)	O2–Cu1^{ii}	2.010 (3)
N4–Cu1–O2	162.00 (13)	C4–N4–Cu1	114.2 (3)
N1^{iii}–Cu1–O2^{i}	169.73 (14)	N1^{iii}–Cu1–N4	98.30 (13)
N4–Cu1–O2^{i}	81.36 (12)	N1^{iii}–Cu1–O2	91.44 (13)
O2–Cu1–O2^{i}	91.70 (7)	N4–N1–Cu1^{iii}	124.2 (3)
Symmetry code: (i) −*x*+1/2, *y*−1/2, −*z*+1/2; (ii) −*x*+1/2, *y*+1/2, −*z*+1/2; (iii) −*x*+1/2, −*y*+5/2, −*z*.			
4			
N2–Ni1	2.080(4)	Ni1–O8	2.024(3)
Ni1–O4	2.037(3)	Ni1–O7	2.058(3)
Ni1–O6	2.070(4)	Ni1–O5	2.117(3)
O8–Ni1–O7	91.18(14)	O4–Ni1–O7	90.24(13)
O8–Ni1–O6	92.19(15)	O4–Ni1–O6	88.32(14)
O7–Ni1–O6	93.08(14)	O8–Ni1–N2	100.33(15)
O4–Ni1–N2	79.07(14)	O7–Ni1–N2	90.23(15)

O6–Ni–N2	166.98(14)	O8–Ni–O5	87.91(13)
O4–Ni1–O5	90.64(13)	O7–Ni1–O5	176.58(13)
O6–Ni1–O5	90.25(13)	N2–Ni1–O5	86.70(14)
O8–Ni1–O4	178.46(15)		

Symmetry codes: (i) *x*, −*y*−1/2, *z*+1/2; (ii) *x*, −*y*+1/2, *z*+1/2; (iii) −*x*+1, −*y*, −*z*+1; (iv) *x*, −*y*+1/2, *z*−1/2.

5

Cu1–O1	1.9561(16)	Cu1–O5	1.9589(15)
Cu1–N2	1.9947(17)	Cu1–O6	2.3934(16)
O3–Cu1–O1	174.21(7)	O3–Cu1–O5	89.01(6)
O1–Cu1–O5	89.00(7)	O3–Cu1–N2	98.23(7)
O5–Cu1–N2	157.66(7)	O3–Cu1–O6	96.35(6)
O1–Cu1–O6	89.34(6)	O5–Cu1–O6	99.63(6)
N2–Cu1–O6	100.52(6)		

Symmetry codes: (ii) −*x*+3/2, *y*−1/2, −*z*+3/2; (iii) −*x*+3/2, −*y*+1/2, −*z*+1; (iv) −*x*+1, −*y*+1, −*z*+1.

6

Co1–O5	2.0772(18)	Co–O5^{iii}	2.0772(18)
Co1–O2^{iii}	2.1827(17)	Co1–O2	2.1827(18)
Co2–O6	2.0799(16)	Co2–N2	2.1334(18)
Co2–N2^{iv}	2.1334(18)	Co–O3	2.1437(15)
Co2–O3^{iv}	2.1437(15)	Co1–O4^{i}	2.0271(19)
Co–O4^{ii}	2.0271(19)	O4–Co1^{ii}	2.0271(19)
O5–Co1–O2	87.12(7)	O5^{iii}–Co1–O2	86.91(7)
O2^{iii}–Co1–O2	171.10(8)	O6^{iv}–Co2–O6	180.00(8)
O6^{iv}–Co2–N2	92.82(7)	O6–Co2–N2	87.18(7)
O6–Co2–N2^{iv}	92.82(7)	O6^{iv}–Co2–N2^{iv}	87.18(7)
N2–Co2–N2^{iv}	180.00 (8)	O6^{iv}–Co2^{V}–O3	89.77 (7)
O6–Co2–O3	90.23 (7)	N2–Co2–O3	76.17 (6)
N2^{iv}–Co2–O3	103.83 (6)	O6^{iv}–Co2–O3^{iv}	90.23 (7)
O6–Co2–O3^{iv}	89.77 (7)	N2–Co2–O3^{iv}	103.83 (6)
N2^{iv}–Co2–O3^{iv}	76.17 (6)	O3–Co2–O3^{iv}	180.000 (1)
O4^{i}–Co1–O4^{ii}	93.94 (12)	O4^{i}–Co1–O5	177.87 (7)
O4^{i}–Co1–O5	85.21 (9)	O4^{i}–Co1–O5^{iii}	85.21 (9)
O4^{ii}–Co1–O5^{iii}	177.87 (7)	O5–Co1–O5^{iii}	95.70 (12)
O4^{i}–Co1–O2^{iii}	91.22 (7)	O4^{ii}–Co1–O2^{iii}	94.85 (7)
O5–Co1–O2^{iii}	86.91 (7)	O5^{iii}–Co1–O2^{iii}	87.12 (7)
O4^{i}–Co1–O2	94.85 (7)	O4^{ii}–Co1–O2	91.22 (7)

Symmetry codes: (i) *x*, −*y*+2, *z*−1/2; (ii) −*x*+1, −*y*+2, −*z*+1; (iii) −*x*+1, *y*, −*z*+1/2; (iv) −*x*+1, −*y*+1, −*z*+1.

Table S3 Hydrogen bonds in **1-6.**

Complex	D–H···A	D–H (Å)	H···A (Å)	D···A(Å)	D–H···A (Å)
1	O3–H3A···Ol^{ii}	0.84	1.89	2.715 (3)	164
	N1–H1···O2^{iii}	0.83	2.05	2.809 (3)	152
	O3–H3B···O2^{iv}	0.91	1.83	2.731(3)	168
	Symmetry code: (ii) −*x*+1, −*y*+1, −*z*+1; (iii) −*x*+1, *y*+1/2, −*z*+1/2; (iv) *x*, −*y*+1/2, *z*+1/2.				
2	O4–H4*B*···O2^{ii}	0.86	1.91	2.680 (4)	148
	O4–H4*A*···O3^{iii}	0.86	2.17	2.906 (4)	144
	O5–H5*B*···O1^{ii}	0.86	1.87	2.725 (3)	172
	O5–H5*A*···O3^{i}	0.86	1.97	2.822 (4)	172
	O3–H3*B*···O2^{iv}	0.85	2.04	2.858 (4)	162
	O6–H6*B*···O3	0.86	1.90	2.756 (4)	171
	Symmetry code: (i) −*x*+2, −*y*+1, −*z*+1; (ii) −*x*+3/2, *y*+1/2, −*z*+1/2; (iii) *x*−1/2, −*y*+1/2, *z*−1/2; (iv) *x*−1/2, −*y*+1/2, *z*+1/2.				
3	C5–H5···O1^{iv}	0.93	2.50	3.278 (5)	142
	Symmetry code: (iv) *x*−1/2, −*y*+3/2, *z*−1/2.				
4	O5—H5*B*···O2^{i}	0.83	1.91	2.700 (5)	161
	O6—H6*A*···O2^{ii}	0.83	1.91	2.700 (5)	161
	O6—H6*B*···O1^{iii}	0.84	2.19	2.947 (5)	149
	O7—H7A···O2^{ii}	0.85	1.92	2.753 (5)	168
	O7—H7B···O3^{iv}	0.84	2.02	2.826 (5)	160
	O8—H8A···O4^{iv}	0.84	1.98	2.800 (4)	165
	O8—H8B···O5^{iii}	0.84	1.90	2.677 (5)	154
	Symmetry codes: (i) *x*, −*y*−1/2, *z*+1/2; (ii) *x*, −*y*+1/2, *z*+1/2; (iii) −*x*+1, −*y*, −*z*+1; (iv) *x*, −*y*+1/2, *z*−1/2.				
5	O5—H5*C*···O6^{ii}	0.81	1.97	2.772 (2)	169
	O5—H5*D*···O2^{iii}	0.79	1.96	2.737 (2)	166
	O6—H6*C*···O2^{iv}	0.82	2.01	2.819 (2)	168
	Symmetry codes: (ii) −*x*+3/2, *y*−1/2, −*z*+3/2; (iii) −*x*+3/2, −*y*+1/2, −*z*+1; (iv) −*x*+1, −*y*+1, −*z*+1.				
6	O5—H5···O3	0.82	1.99	2.734 (2)	151
	O6—H6···O2^{ii}	0.82	2.06	2.843 (2)	160
	O5—H5*W*···O1^{iv}	1.00 (4)	1.67 (4)	2.662 (3)	169 (3)
	O6—H6*W*···O1^{v}	0.89 (4)	1.78 (4)	2.670 (2)	172 (3)
	C3—H3···O1^{vi}	0.93	2.32	3.252 (3)	178
	Symmetry codes: (ii) −*x*+1, −*y*+2, −*z*+1; (iv) −*x*+1, −*y*+1, −*z*+1; (v) −*x*+1, *y*, −*z*+3/2; (vi) −*x*+3/2, *y*+1/2, −*z*+3/2.				