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SUPPORTING INFORMATION

ds-block metal ions catalyzed decarboxylation of pyrazine-2,3,5,6-tetracarboxylic acid and the complexes obtained from hydrothermal reactions and novel water clusters

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S1. Selected bond lengths (Å) and angles (°) for **1** and **2**

1		**2**	
Zn(1)-O(1)	2.108(4)	Zn(1)-O(3)	2.057(2)
Zn(1)-N(5)	2.123(4)	Zn(1)-N(3)	2.102(3)
Zn(1)-N(2)	2.129(4)	Zn(1)-N(4)	2.118(3)
Zn(1)-N(4)	2.148(4)	Zn(1)-N(2)	2.153(3)
Zn(1)-N(3)	2.152(4)	Zn(1)-N(5)	2.177(3)
Zn(1)-N(1)	2.230(4)	Zn(1)-N(1)	2.332(3)
O(1)-Zn(1)-N(5)	95.90(17)	O(3)-Zn(1)-N(3)	168.82(11)
O(1)-Zn(1)-N(2)	92.26(15)	O(3)-Zn(1)-N(4)	91.99(11)
N(5)-Zn(1)-N(2)	167.86(17)	N(3)-Zn(1)-N(4)	99.06(11)
O(1)-Zn(1)-N(4)	166.80(16)	O(3)-Zn(1)-N(2)	90.66(11)
N(5)-Zn(1)-N(4)	78.13(17)	N(3)-Zn(1)-N(2)	78.76(11)
N(2)-Zn(1)-N(4)	95.62(16)	N(4)-Zn(1)-N(2)	169.44(11)
O(1)-Zn(1)-N(3)	90.09(15)	O(3)-Zn(1)-N(5)	86.76(10)
N(5)-Zn(1)-N(3)	92.49(16)	N(3)-Zn(1)-N(5)	96.98(11)
N(2)-Zn(1)-N(3)	78.50(16)	N(4)-Zn(1)-N(5)	78.72(11)
N(4)-Zn(1)-N(3)	101.84(16)	N(2)-Zn(1)-N(5)	91.24(11)
O(1)-Zn(1)-N(1)	76.26(15)	O(3)-Zn(1)-N(1)	75.51(10)
N(5)-Zn(1)-N(1)	93.89(16)	N(3)-Zn(1)-N(1)	101.19(10)
N(2)-Zn(1)-N(1)	96.77(16)	N(4)-Zn(1)-N(1)	97.63(11)
N(4)-Zn(1)-N(1)	92.27(16)	N(2)-Zn(1)-N(1)	92.93(11)
N(3)-Zn(1)-N(1)	165.45(16)	N(5)-Zn(1)-N(1)	161.82(11)

S2. Selected bond lengths (Å) and angles (°) for **3** and **4**

3		**4**	
Zn(1)-O(1)	2.0680(14)	Cu(1)-N(5)	1.993(3)
Zn(1)-N(3)	2.1184(18)	Cu(1)-N(2)	2.007(3)
Zn(1)-O(4)^{i}	2.1188(15)	Cu(1)-N(3)	2.115(3)
Zn(1)-O(5)	2.1675(16)	Cu(1)-N(1)	2.189(3)
Zn(1)-N(2)	2.1761(18)	Cu(1)-N(4)	2.198(4)
Zn(1)-N(1)^{i}	2.2538(17)	Cu(1)-O(1)	2.255(3)
O(1)-Zn(1)-N(3)	94.96(6)	N(5)-Cu(1)-N(2)	170.86(14)
O(1)-Zn(1)-O(4)^{i}	171.15(6)	N(5)-Cu(1)-N(3)	92.16(13)
N(3)-Zn(1)-O(4)^{i}	87.69(6)	N(2)-Cu(1)-N(3)	80.82(13)
O(1)-Zn(1)-O(5)	88.89(6)	N(5)-Cu(1)-N(1)	92.32(12)
N(3)-Zn(1)-O(5)	102.84(7)	N(2)-Cu(1)-N(1)	96.05(12)
O(4)^{i}-Zn(1)-O(5)	82.29(6)	N(3)-Cu(1)-N(1)	163.46(13)
O(1)-Zn(1)-N(2)	97.16(6)	N(5)-Cu(1)-N(4)	79.44(14)
N(3)-Zn(1)-N(2)	77.04(7)	N(2)-Cu(1)-N(4)	96.48(13)
O(4)^{i}-Zn(1)-N(2)	91.66(6)	N(3)-Cu(1)-N(4)	103.93(13)
O(5)-Zn(1)-N(2)	173.94(6)	N(1)-Cu(1)-N(4)	92.55(13)
O(1)-Zn(1)-N(1)^{i}	102.34(6)	N(5)-Cu(1)-O(1)	95.95(13)
N(3)-Zn(1)-N(1)^{i}	160.85(6)	N(2)-Cu(1)-O(1)	89.76(12)
O(4)^{i}-Zn(1)-N(1)^{i}	76.46(6)	N(3)-Cu(1)-O(1)	88.61(12)
O(5)-Zn(1)-N(1)^{i}	85.81(6)	N(1)-Cu(1)-O(1)	75.09(12)
N(2)-Zn(1)-N(1)^{i}	92.55(7)	N(4)-Cu(1)-O(1)	166.71(11)

symmetry code: ^{i} x, y, z+1

S3. Selected bond lengths (Å) and angles (°) for **5** and **6**

5				**6**	
Cu(1)-O(7)	1.974(4)	Cu(2)-O(4)^{ii}	1.946(4)	Cu(1)-N(3)	1.993(3)
Cu(1)-O(1w)	1.985(5)	Cu(2)-N(3)	2.022(5)	Cu(1)-N(2)	2.006(3)
Cu(1)-N(6)	1.996(5)	Cu(2)-N(4)	2.024(5)	Cu(1)-N(1)	2.177(3)
Cu(1)-N(5)	2.030(5)	Cu(2)-N(1)	2.093(5)	Cu(1)-O(3)	2.203(3)
Cu(1)-O(5)^{i}	2.271(4)	Cu(2)-O(1)	2.300(4)	Cu(1)-O(1)	2.294(3)
		Cu(2)-O(8)	.547(8)	Cu(1)-O(5)	1.966(3)
O(7)-Cu(1)-O(1w)	90.52(18)	N(3)-Cu(2)-N(4)	80.4(2)	O(5)-Cu(1)-N(2)	90.82(13)
O(7)-Cu(1)-N(6)	94.3(2)	O(4)^{ii}-Cu(2)-N(1)	91.81(18)	N(3)-Cu(1)-N(2)	81.35(14)
O(1w)-Cu(1)-N(6)	174.7(2)	N(3)-Cu(2)-N(1)	97.5(2)	O(5)-Cu(1)-N(1)	89.25(12)
O(7)-Cu(1)-N(5)	151.59(18)	N(4)-Cu(2)-N(1)	168.23(19)	N(3)-Cu(1)-N(1)	98.39(13)
O(1w)-Cu(1)-N(5)	93.6(2)	O(4)^{ii}-Cu(2)-O(1)	97.54(16)	N(2)-Cu(1)-N(1)	175.42(13)
N(6)-Cu(1)-N(5)	81.1(2)	N(3)-Cu(2)-O(1)	89.07(18)	O(5)-Cu(1)-O(3)	90.29(12)
O(1w)-Cu(1)-O(5)^{i}	93.06(17)	N(4)-Cu(2)-O(1)	116.11(18)	N(3)-Cu(1)-O(3)	94.47(13)
N(6)-Cu(1)-O(5)^{i}	87.36(18)	N(1)-Cu(2)-O(1)	75.28(17)	N(2)-Cu(1)-O(3)	111.28(13)
N(5)-Cu(1)-O(5)^{i}	99.24(17)	O(4)^{ii}-Cu(2)-N(4)	89.6(2)	N(1)-Cu(1)-O(3)	73.30(11)
		N(3)-Cu(2)-O(8)	92.29(19)	O(5)-Cu(1)-O(1)	91.87(12)
		N(3)-Cu(2)-O(4)	169.73(24)	N(3)-Cu(1)-O(1)	88.01(13)
		N(4)-Cu(2)-O(8)	96.86(18)	N(2)-Cu(1)-O(1)	103.75(12)
		N(1)-Cu(2)-O(8)	71.60(15)	N(1)-Cu(1)-O(1)	71.67(11)
		O(4)-Cu(2)-O(8)	86.47(16)	O(3)-Cu(1)-O(1)	144.87(10)
		O(1)-Cu(2)-O(8)	146.75(14)	O(5)-Cu(1)-N(3)	171.90(12)

symmetry code:^{i} -x+1,-y+1,-z+2; ^{ii}-x+1,-y+1,-z+1.

S4. Selected bond lengths (Å) and angles (°) for **7** and **8**

7		**8**	
Cd(1)-O(5)	2.294(4)	Cd(1)-N(1)	2.239(2)
Cd(1)-O(6)	2.304(4)	Cd(1)-N(3)	2.285(2)
Cd(1)-N(1)	2.351(4)	Cd(1)-N(4)	2.315(2)
Cd(1)-N(3)	2.374(4)	Cd(1)-O(6)	2.3638(17)
Cd(1)-N(4)	2.393(4)	Cd(1)-O(5)	2.3895(16)
Cd(1)-O(1)	2.458(3)	Cd(1)-O(1)	2.4214(16)
Cd(1)-O(3)	2.469(4)	Cd(1)-O(3)	2.5341(16)
O(5)-Cd(1)-O(6)	170.93(12)	N(1)-Cd(1)-N(3)	143.49(7)
O(5)-Cd(1)-N(1)	89.15(13)	N(1)-Cd(1)-N(4)	144.82(7)
O(6)-Cd(1)-N(1)	81.86(14)	N(3)-Cd(1)-N(4)	71.63(7)
O(5)-Cd(1)-N(3)	104.35(14)	N(1)-Cd(1)-O(6)	82.19(6)
O(6)-Cd(1)-N(3)	83.77(15)	N(3)-Cd(1)-O(6)	90.38(6)
N(1)-Cd(1)-N(3)	143.56(15)	N(4)-Cd(1)-O(6)	99.73(7)
O(5)-Cd(1)-N(4)	89.06(14)	N(1)-Cd(1)-O(5)	89.73(6)
O(6)-Cd(1)-N(4)	97.62(14)	N(3)-Cd(1)-O(5)	96.14(6)
N(1)-Cd(1)-N(4)	144.95(14)	N(4)-Cd(1)-O(5)	86.89(7)
N(3)-Cd(1)-N(4)	70.17(15)	O(6)-Cd(1)-O(5)	171.92(5)
O(5)-Cd(1)-O(1)	85.06(13)	N(1)-Cd(1)-O(1)	67.73(6)
O(6)-Cd(1)-O(1)	92.48(13)	N(3)-Cd(1)-O(1)	76.82(7)
N(1)-Cd(1)-O(1)	67.19(13)	N(4)-Cd(1)-O(1)	146.51(6)
N(3)-Cd(1)-O(1)	80.22(14)	O(6)-Cd(1)-O(1)	91.32(6)
N(4)-Cd(1)-O(1)	147.32(14)	O(5)-Cd(1)-O(1)	85.55(6)
O(5)-Cd(1)-O(3)	93.96(12)	N(1)-Cd(1)-O(3)	67.80(6)
O(6)-Cd(1)-O(3)	81.52(13)	N(3)-Cd(1)-O(3)	146.55(6)
N(1)-Cd(1)-O(3)	67.16(12)	N(4)-Cd(1)-O(3)	77.63(6)
N(3)-Cd(1)-O(3)	142.69(13)	O(6)-Cd(1)-O(3)	81.96(6)
N(4)-Cd(1)-O(3)	78.06(13)	O(5)-Cd(1)-O(3)	95.06(5)
O(1)-Cd(1)-O(3)	134.35(12)	O(1)-Cd(1)-O(3)	135.52(6)

S5: Hydrogen-bonding contacts (Å, º) in complex **1**.

D-H···A[a]	*d*(D-H)	*d*(H···A)	*d*(D···A)	∠(DHA)
O6-H6A···O10[i]	0.850	2.025	2.781	147.74
O6-H6B···O9[i]	0.852	1.958	2.807	174.42
O7-H7B···O6[ii]	0.856	1.928	2.774	169.75
O8-H8A···O7[iii]	0.854	2.065	2.913	171.57
O8-H8B···O10	0.856	2.016	2.865	171.76
O9-H9A···O7[iii]	0.850	2.005	2.816	159.57
O9-H9B···O8[iii]	0.852	1.988	2.800	159.11

[a] D = donor; A = acceptor.

Symmetry code: [i] x-1, y, z; [ii] x+1, y, z-1; [iii] x, -y+1/2, z+1/2.

S6: Hydrogen-bonding contacts (Å, º) in complex **2**.

D-H···A[a]	*d*(D-H)	*d*(H···A)	*d*(D···A)	∠(DHA)
O6-H6B···O7[i]	0.840	2.494	2.954	115.46
O7-H7A···O8	0.855	1.998	2.840	168.32
O7-H7B···O6[ii]	0.850	2.119	2.954	167.24
O8-H8A···O5[iii]	0.859	1.934	2.783	169.56
O9-H9A···O7[iv]	0.851	2.034	2.865	165.29
O9-H9B···O6[v]	0.850	1.963	2.808	172.59
O10-H10A···O8[vi]	0.861	2.029	2.864	163.21
O10-H10B···O9	0.855	1.996	2.792	154.50

[a] D = donor; A = acceptor.

Symmetry code: [i] x+1/2, y, -z+1/2; [ii] x-1/2, y, -z+1/2; [iii] -x+1/2, y+1/2, z; [iv] -x+1/2, y-1/2, z; [v] -x+3/2, y-1/2, z; [vi] -x+1, y-1/2, -z+1/2.

S7: Hydrogen-bonding contacts (Å, º) in complex **4**.

D-H···A[a]	*d*(D-H)	*d*(H···A)	*d*(D···A)	∠(DHA)
O7-H7A···O9[i]	0.848	2.001	2.848	176.01
O7-H7B···O8[i]	0.850	1.979	2.826	173.51
O8-H8A···O9[i]	0.851	2.085	2.911	163.41
O8-H8B···O6	0.853	2.045	2.855	158.30
O9-H9B···O10	0.851	1.979	2.811	165.51
O10-H10A···O7[ii]	0.851	2.005	2.848	171.24
O10-H10B···O6[ii]	0.850	1.984	2.798	160.04

[a] D = donor; A = acceptor.

Symmetry code: [i] x, -y+1/2, z+1/2; [ii] x, y, z-1.

S8: Hydrogen-bonding contacts (Å, º) in complex **5**.

D-H···A[a]	*d*(D-H)	*d*(H···A)	*d*(D···A)	∠(DHA)
O(1W)-H(1WA)···O(5W)[i]	0.851	1.917	2.758	169.09
O(2W)-H(2WA)···O(4W)[ii]	0.851	1.980	2.785	157.59
O(2W)-H(2WB)···O(5W)	0.850	2.035	2.883	175.12
O(3W)-H(3WB)···O(3W)[ii]	0.848	2.130	2.824	138.89
O(4W)-H(4WB)···O(3W)[ii]	0.850	1.892	2.740	175.03

[a] D = donor; A = acceptor.

Symmetry code: [i] -x+1, -y+1, -z+1; [ii] -x, -y+1, -z+1.

S9: Hydrogen-bonding contacts (Å, º) in complex **7**.

D-H···A[a]	*d*(D-H)	*d*(H···A)	*d*(D···A)	∠(DHA)
O5-H5A···O4[i]	0.848	1.852	2.699	175.90
O5-H5B···O2[ii]	0.850	1.945	2.721	151.30
O6-H6A···O2[iii]	0.849	2.009	2.768	148.38
O6-H6B···O3[i]	0.853	1.888	2.726	166.89

[a] D = donor; A = acceptor.

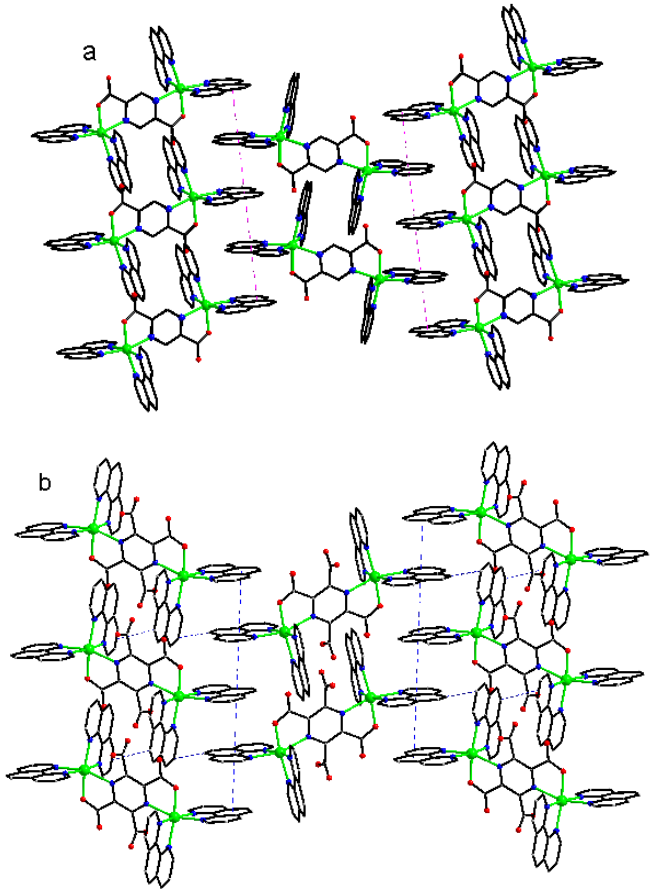
Symmetry code: [i] -x, -y+2, -z; [ii] -x, -y+1, -z; [iii] -x+1, -y+1, -z.

S10: Hydrogen-bonding contacts (Å, º) in complex **8**.

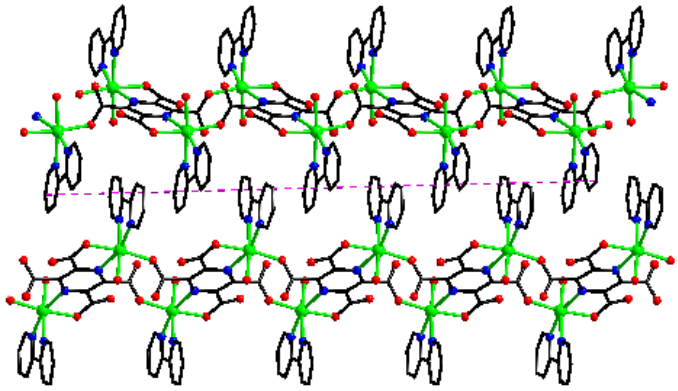
D-H···A[a]	*d*(D-H)	*d*(H···A)	*d*(D···A)	∠(DHA)
O5-H5A···O4[i]	0.858	1.814	2.670	176.20
O5-H5B···O2[ii]	0.857	1.744	2.594	171.44
O6-H6A···O2[iii]	0.836	1.859	2.686	169.69
O6-H6B···O3[iv]	0.845	1.922	2.759	171.22
O6-H6B···O4[iv]	0.845	2.645	3.299	135.30

[a] D = donor; A = acceptor.

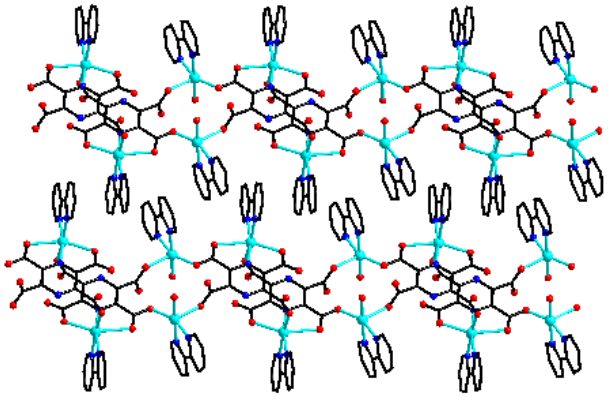
Symmetry code: [i] -x+1, -y, -z+2; [ii] -x+1, -y+1, -z+2; [iii] -x, -y+1, -z+2; [iv]-x, -y, -z+2.



S11: Crystal structures of **1** (a) and **2** (b) showing π···π interactions (dashed lines). The hydrogen atoms are not shown for clarity.



S12: Crystal structure of **3** showing π···π interactions (dashed lines). The hydrogen atoms are not shown for clarity.



S13: Crystal structure of **5** showing π···π interactions. The hydrogen atoms are not shown for clarity.