Supplementary Material (ESI) for CrystEngComm

Supporting information

Encapsulated different forms of water molecules by Cu(II) complexes with diverse structures

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Table S1 Selected bond lengths (Å) and angles (°) for **1** − **3**[a]

Complex **1**			
Cu–N2	1.924(3)	Cu–N1	2.058(3)
Cu–O1	1.927(2)	Cu–O4$^{\#1}$	2.227(2)
Cu–N3	2.044(3)		
N2–Cu–O1	171.1(5)	N3–Cu–N1	157.4(8)
N2–Cu–N3	79.9(2)	N2–Cu–O4$^{\#1}$	101.5(9)
O1–Cu–N3	100.7(5)	O1–Cu–O4$^{\#1}$	86.7(8)
N2–Cu–N1	79.1(1)	N3–Cu–O4$^{\#1}$	105.6(4)
O1–Cu–N1	98.7(3)	N1–Cu–O4$^{\#1}$	86.5 (7)
Complex **2**			
Cu1–N5	1.910(3)	Cu2–N2	1.919(3)
Cu1–O4	1.937(2)	Cu2–O1	1.942(2)
Cu1–N4	2.036(3)	Cu2–N1	2.029(3)
Cu1–N6	2.050(3)	Cu2–N3	2.038(3)
Cu1–O6w	2.274(2)	Cu2–O4w	2.289(3)
N5–Cu1–O4	167.5 (1)	N2–Cu2–O1	164.7(9)
N5–Cu1–N4	80.0 (6)	N2–Cu2–N1	80.2 (8)
O4–Cu1–N4	99.1 (7)	O1–Cu2–N1	100.7 (4)
N5–Cu1–N6	80.0 (9)	N2–Cu2–N3	79.8 (2)
O4–Cu1–N6	99.7 (2)	O1–Cu2–N3	97.4 (7)
N4–Cu1–N6	160.0(1)	N1–Cu2–N3	159.7(4)
N5–Cu1–O6w	98.9(1)	N2–Cu2–O4w	101.0(1)
O4–Cu1–O6w	93.5(5)	O1–Cu2–O4w	94.1(5)
N4–Cu1–O6w	98.3(9)	N1–Cu2–O4w	92.1(1)
N6–Cu1–O6w	86.9(1)	N3–Cu2–O4w	95.3(6)
Complex **3**			
Cu–N3	1.935(2)	Cu–N2	2.025(2)
Cu–O2	1.942(2)	Cu–O1w	2.216(2)
Cu–N1	2.022(2)		
N3–Cu–O2	162.8(9)	N1–Cu–N2	159.5(2)
N3–Cu–N1	79.6 (9)	N3–Cu–O1w	104.5(9)
O2–Cu–N1	98.6(1)	O2–Cu–O1w	92.5(1)
N3–Cu–N2	79.9(2)	N1–Cu–O1w	94.3(0)
O2–Cu–N2	100.2(9)	N2–Cu–O1w	92.6(0)

[a] Symmetry codes: #1 x, −y+1/2, z−1/2.

Table S2 Geometrical parameter of hydrogen bonds in **1** − **3**[a]

D–H···A	D–H [Å]	H···A [Å]	D···A [Å]	D–H–A [°]

Complex **1**				
O5–H5···O3$^{\#2}$	0.92(5)	1.53(5)	2.453(3)	177(5)
O6w–H6a···O2$^{\#1}$	0.84(0)	2.06(5)	2.897(4)	171(5)
O6w–H6b···O1$^{\#3}$	0.84(2)	2.16(2)	2.991(4)	168(4)
Complex **2**				
O4w–H4a···O9w	0.83(0)	2.18(3)	2.946(4)	153(4)
O4w–H4b···O7w	0.83(6)	1.94(2)	2.773(4)	171(4)
O6w–H6b···O10w	0.83(1)	1.92(2)	2.747(4)	173(4)
O6w–H6a···O5$^{\#1}$	0.83(5)	2.04(2)	2.854(3)	165(4)
O10w–H10a···O6$^{\#2}$	0.85(2)	1.86(2)	2.703(4)	172(5)
O10w–H10b···O11w	0.84(7)	1.97(3)	2.795(4)	163(5)
O11w–H11a···O2$^{\#3}$	0.86(4)	1.92(2)	2.781(4)	172(6)
O11w–H11b···O8w	0.84(1)	2.04(3)	2.796(4)	150(6)
O13w–H13a···O6w	0.90(2)	1.90(3)	2.790(5)	170(8)
O13w–H13b···O6$^{\#2}$	0.89(2)	2.28(5)	3.053(6)	144(8)
O13w–H13b···O12w$^{\#4}$	0.89(2)	2.56(6)	3.304(8)	142(7)
O7w–H7a···O2w	0.84(2)	2.38(4)	3.050(4)	138(5)
O7w–H7a···O1$^{\#5}$	0.84(2)	2.44(5)	3.018(4)	127(5)
O7w–H7b···O5w$^{\#5}$	0.84(2)	1.94(2)	2.767(4)	167(5)
O9w–H9a···O2w	0.82(6)	2.05(3)	2.837(4)	159(5)
O9w–H9b···O5$^{\#6}$	0.84(0)	1.95(3)	2.746(4)	158(5)
O5w–H5a···O9w	0.85(8)	1.91(2)	2.760(4)	169(5)
O5w–H5b···O3w$^{\#2}$	0.84(2)	1.92(2)	2.755(4)	172(5)
O2w–H2a···O12w	0.81(4)	2.09(2)	2.902(5)	172(5)
O2w–H2b···O3$^{\#5}$	0.83(0)	2.05(2)	2.882(4)	174(5)
O12w–H12a···O2w	0.83(2)	2.31(6)	2.902(5)	129(7)
O12w–H12b···O6$^{\#7}$	0.85(2)	1.87(2)	2.717(4)	172(8)
O1w–H1a···O12w	0.83(8)	2.00(2)	2.820(5)	166(5)
O1w–H1b···O5$^{\#8}$	0.84(2)	2.01(2)	2.856(4)	178(5)
O3w–H3a···O5w$^{\#5}$	0.85(0)	2.06(3)	2.872(4)	159(5)
O3w–H3b···O1w	0.84(5)	1.95(3)	2.757(4)	159(5)
O8w–H8a···O4$^{\#3}$	0.83(2)	2.30(4)	3.027(4)	146(5)
O8w–H8a···O13w$^{\#3}$	0.83(2)	2.63(4)	3.249(7)	132(5)
O8w–H8b···O11w$^{\#3}$	0.83(2)	2.36(4)	3.055(5)	142(5)
Complex **3**				
O6w–H6b···O4$^{\#1}$	0.86(5)	2.00(2)	2.851(4)	170(6)
O1w–H1a···O5$^{\#2}$	0.81(9)	2.09(3)	2.825(3)	150(5)
O6w–H6a···O7w$^{\#1}$	0.87(2)	2.00(2)	2.823(4)	157(5)
O1w–H1b···O3$^{\#3}$	0.85(5)	1.86(2)	2.711(3)	171(6)
O7w–H7b···O4$^{\#2}$	0.88(5)	2.03(2)	2.915(4)	174(6)
O7w–H7a···O6w	0.87(7)	1.87(2)	2.736(5)	169(5)
O8–H8a···O5$^{\#4}$	0.88(2)	1.70(2)	2.575(3)	171(6)

[a] Symmetry codes for complex **1**: #1 x, −y+1/2, z+1/2; #2 −x+1, −y+1, −z; #3 x, y, z+1. Symmetry codes for complex **2**: #1 −x, −y+1, −z+1; #2 x+1, y, z; #3 −x+1, −y+1, −z+1; #4 x+1, y, z−1; #5 −x, −y, −z+2; #6 −x, −y+1, −z+2; #7 x, y, z+1; #8 −x−1, −y+1, −z+2. Symmetry codes for complex **3**: #1 x, −y+1/2, z +1/2; #2 x, y, z+1; #3 −x+1, −y+1, −z; #4 x, −y+3/2, z+1/2.

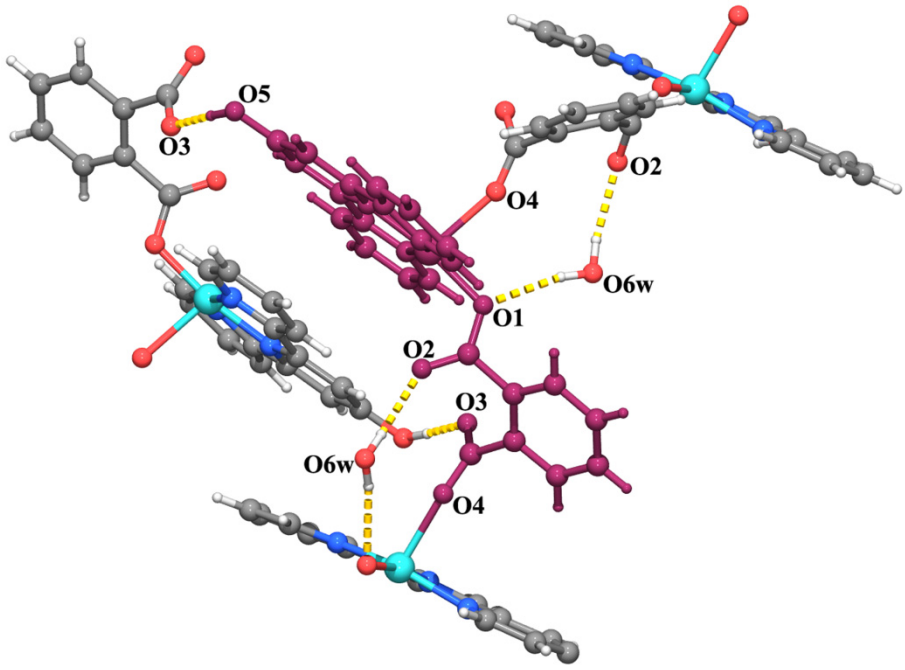

Fig. S1 Hydrogen bonding interactions in complex **1**. Purple color representation of the repeat units in the 1D chain.

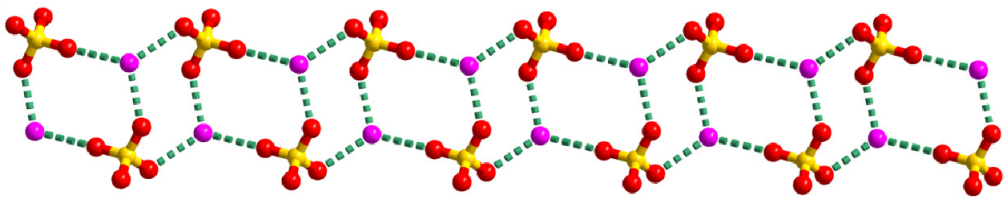

Fig. S2 Representation of O1w–H1b···O3 hydrogen-bonding interactions giving 2D double layers in **3**. Hydrogen atoms are omitted for clarity.

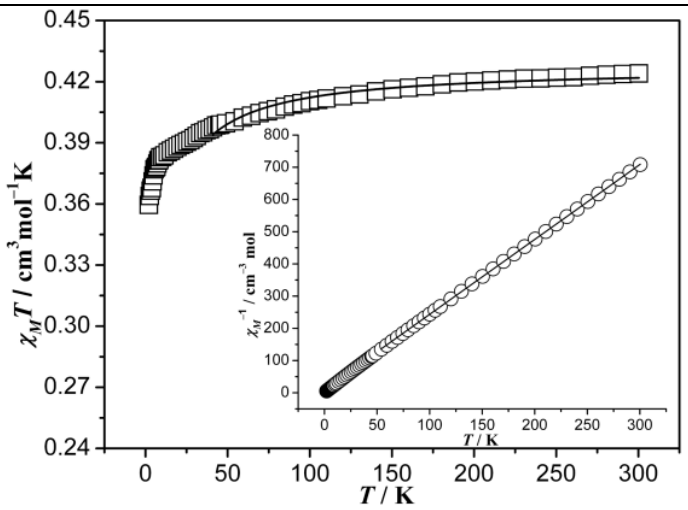

Fig. S3 Plot of $\chi_M T$ versus T for **1**. Insert: Plot of χ_M^{-1} versus T. The solid black line is the theoretical fit of the data using the parameters given in the text.

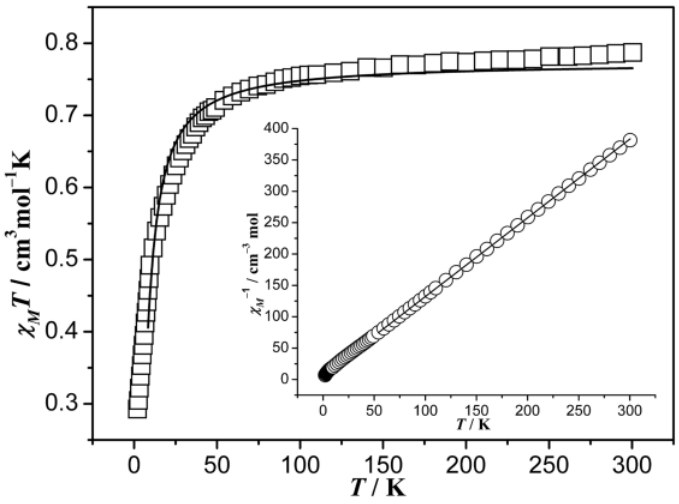

Fig. S4 Plot of $\chi_M T$ versus T for **2**. Insert: Plot of χ_M^{-1} versus T. The solid black line is the theoretical fit of the data using the parameters given in the text.

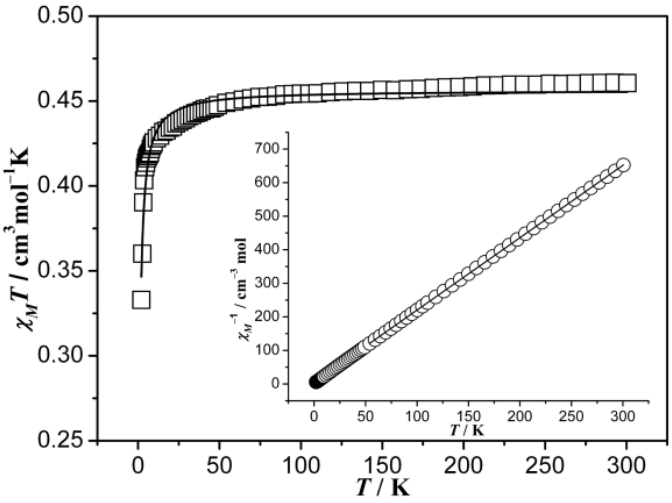

Fig. S5 Plot of $\chi_M T$ versus T for **3**. Insert: Plot of χ_M^{-1} versus T. The solid black line is the theoretical fit of the data using the parameters given in the text.

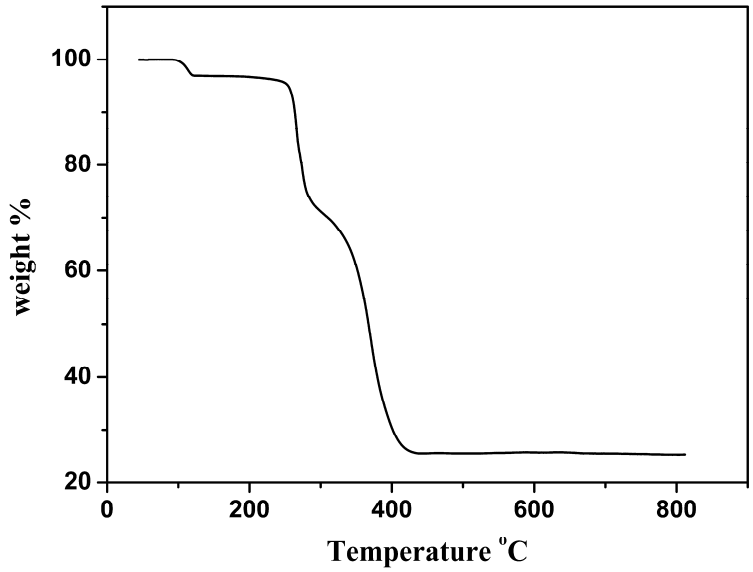

Fig. S6 TGA curves of complex **1**. Thermal gravimetric analysis of **1** with 2.830 mg sample shows onset of weight loss at 100˚C. Water removal continues up to 113˚C to give a total weight loss of 3.17%, which is equivalent to losing 1 mol H_2O per formula unit (calcd. value ~ 3.64%). The complete decomposition of the sample is achieved at 800 ˚C.

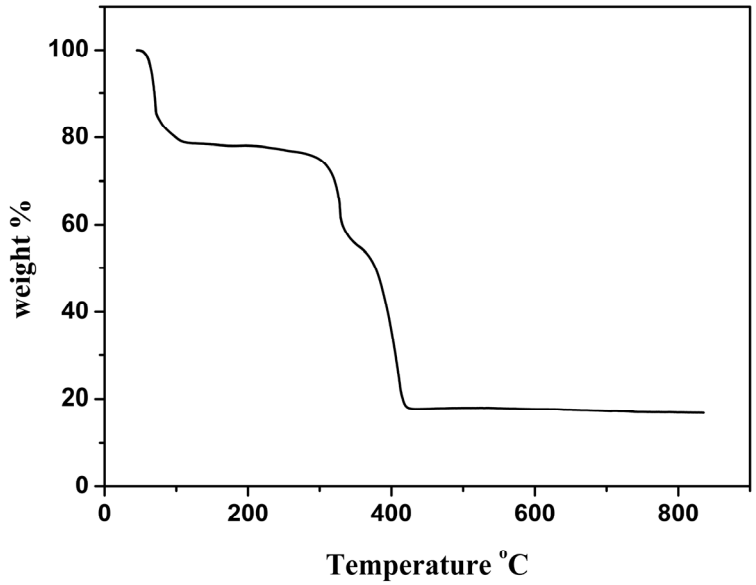

Fig. S7 TGA curves of complex **2**. Thermal gravimetric analysis of **2** with 2.287 mg sample shows onset of weight loss at 60˚C. Water removal continues up to 120˚C to give a total weight loss of 21.26%, which is equivalent to losing 13 mol H_2O per formula unit (calcd. value ~ 22.92%). The complete decomposition of the sample is achieved at 800 ˚C.

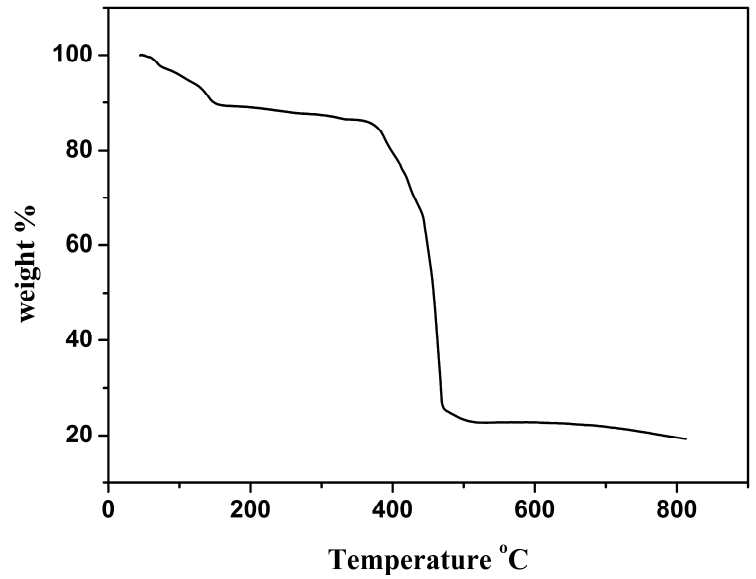

Fig. S8 TGA curves of complex **3**. Thermal gravimetric analysis of **3** with 1.707 mg sample shows onset of weight loss at 59˚C. Water removal continues up to 140˚C to give a total weight loss of 8.60%, which is equivalent to losing 3 mol H_2O per formula unit (calcd. value ~ 11.68%). The complete decomposition of the sample is achieved at 800 ˚C.