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Structurally Diverse Copper(II) Complexes with Pyridazine-Integrated with Pyrazine- Schiff Base Ligand Featuring an Easily Lost Proton in the Hydrazone Backbone

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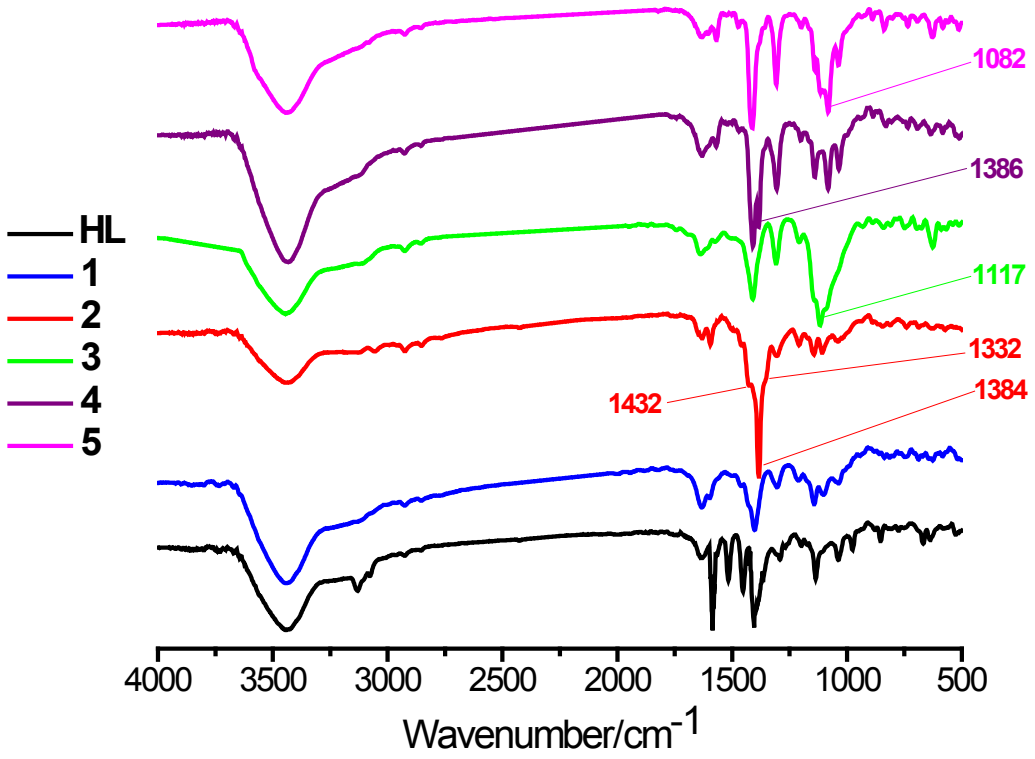

Fig. S1 The IR spectra of **HL** and **1-5**.

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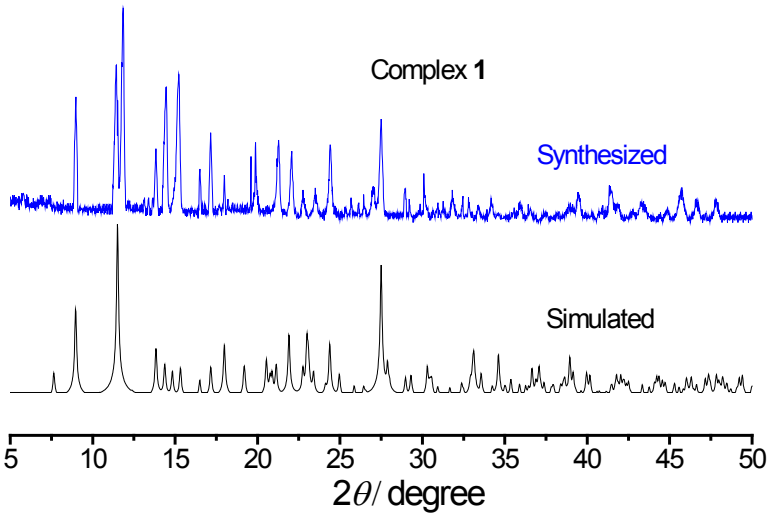

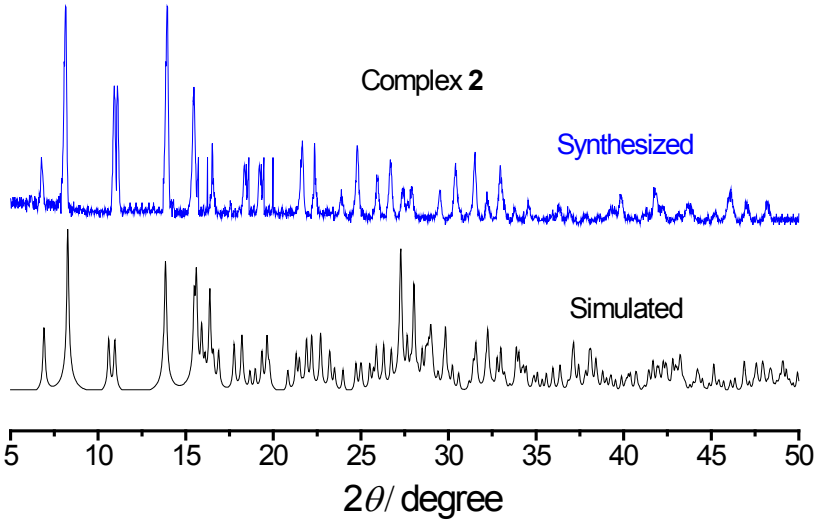

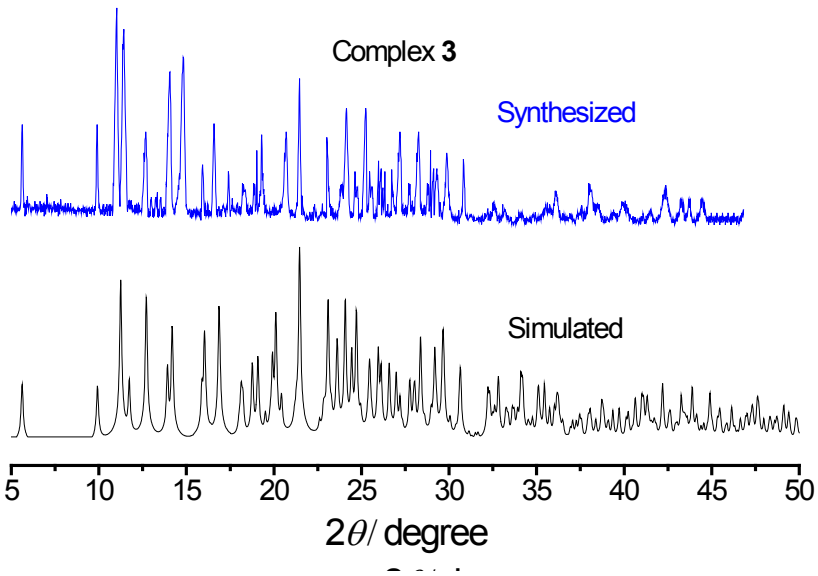

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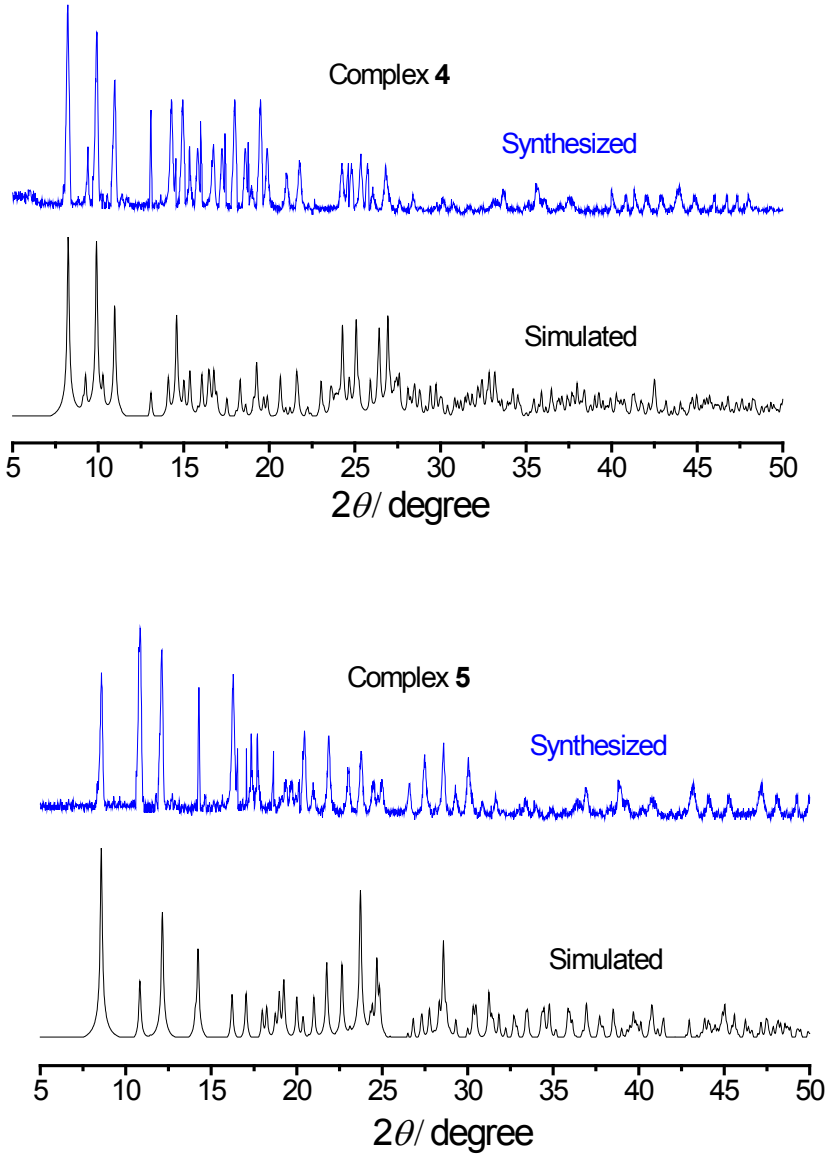

Fig. S2 As-synthesized (top) and simulated (bottom) PXRD patterns of **1-5**.

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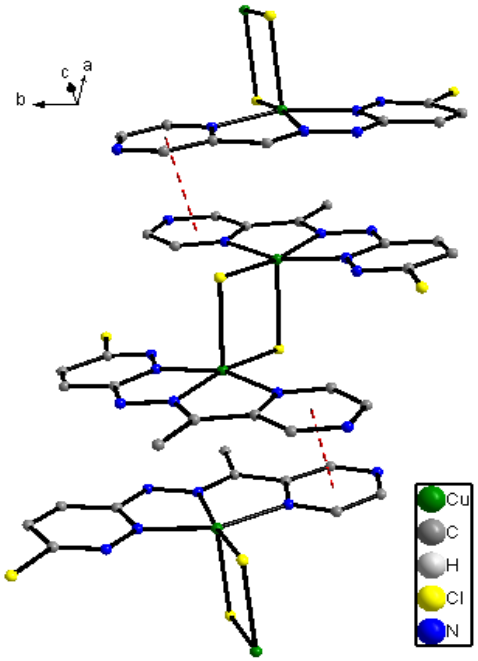

Fig. S3 The 1D supramolecular structure of **1** formed by the offset π...π stacking.

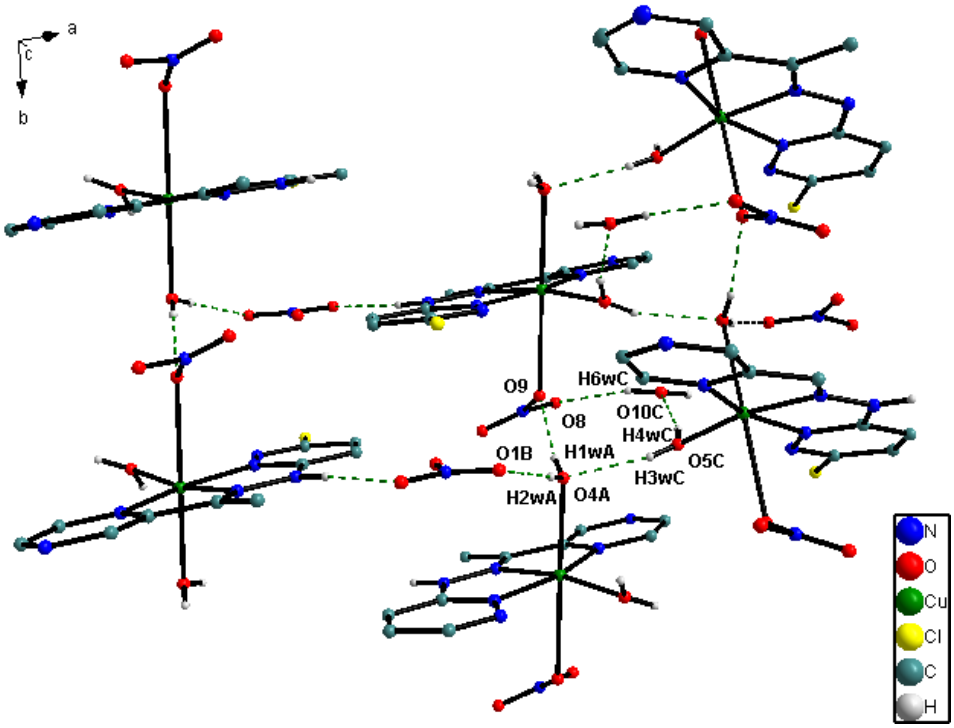

Fig. S4 The 2D supramolecular structure of **2** obtained by hydrogen-bond (O-H…O and N-H…O). Symmetry code: A: x, 1 + y, z; B: 1 - x, 1 - y, 1 - z; C: 3/2 - x, 1/2 + y, 3/2 - z.

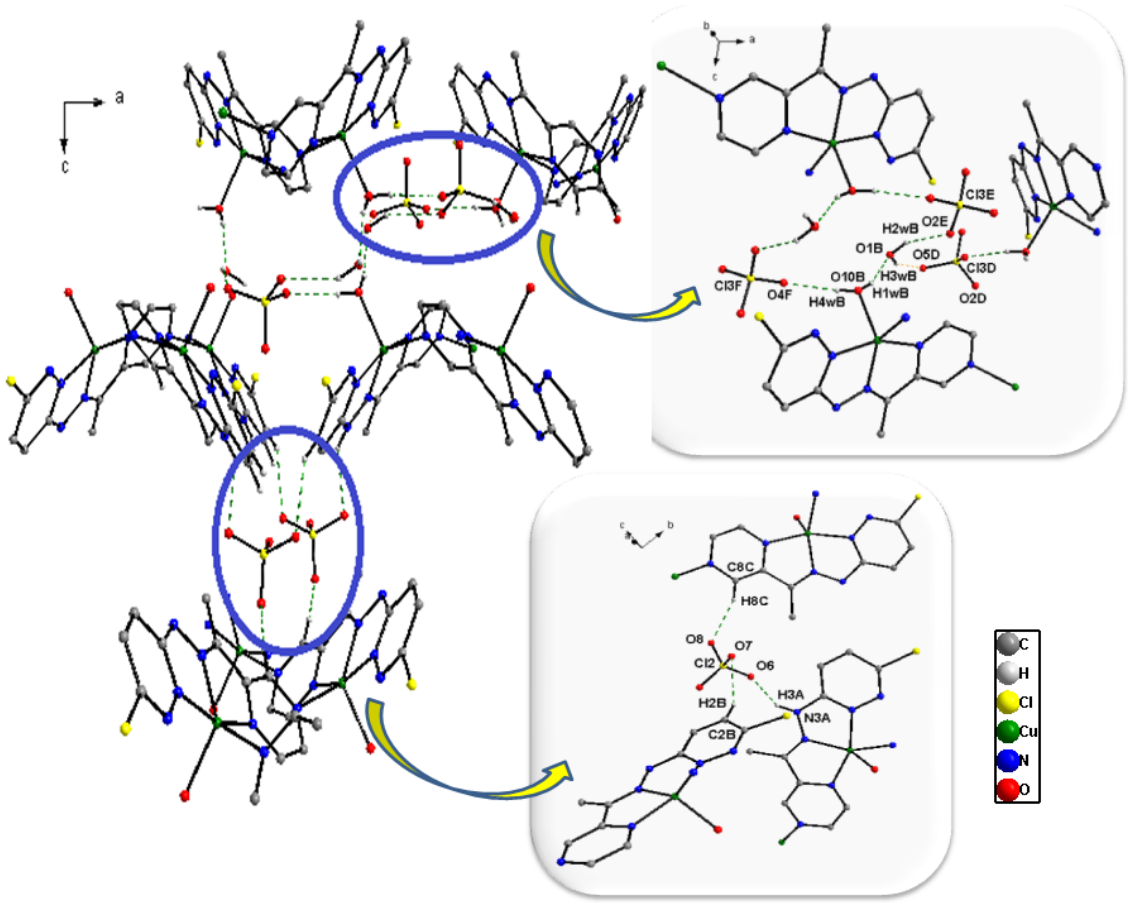

Fig. S5 The 3D supramolecular structure of **3** formed by hydrogen-bond (N-H…O, C-H…O and O-H…O). Symmetry code: A: -1 - x, y, z; B: 3/2 - x, -1/2 + y, z ; C: 1 - x, 1/2 + y, 3/2 – z; D: 1 - x, - y, 1 - z ; E: 1/2 + x, 1/2 - y, 1 – z; F: 1/2 - x, 1/2 + y, z.

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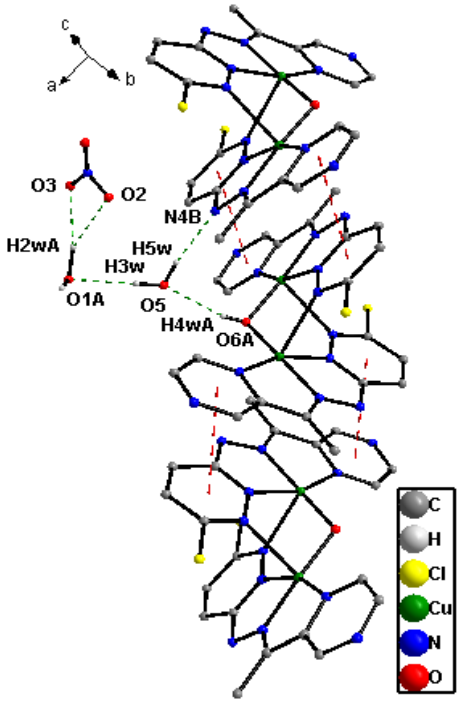

Fig. S6 The 1D supramolecular structure of **4** formed by the offset π...π stacking and hydrogen-bond (O-H…N and O-H…O). Symmetry code: A: 1 - x, 1 - y, 1 – z; B: -1 + x, y, z.

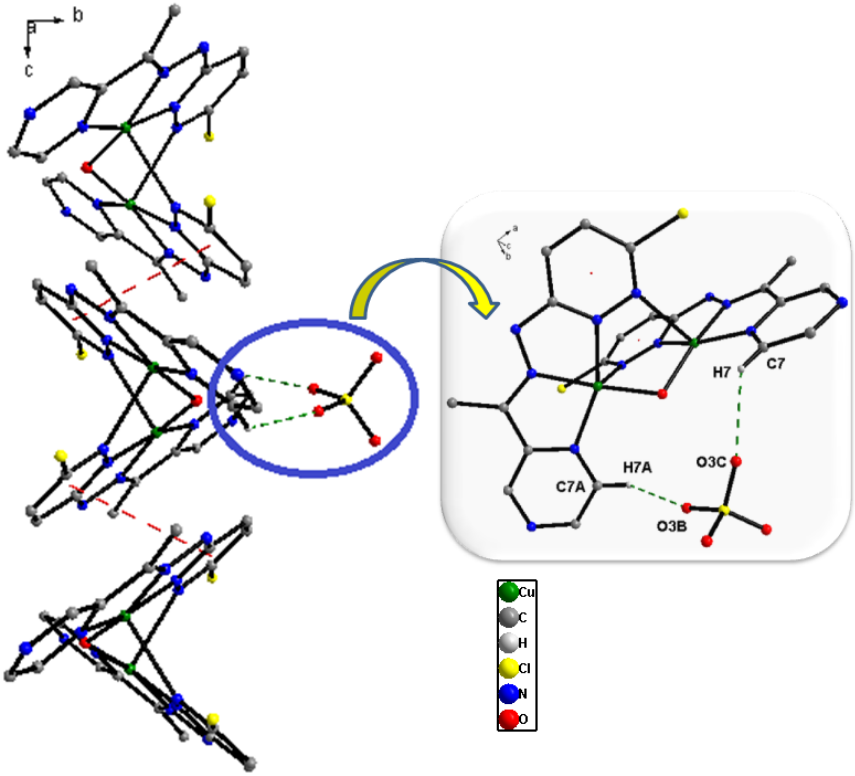

Fig. S7 The 1D supramolecular structure of **5** formed by the offset π...π stacking and hydrogen-bond (C-H…O). Symmetry code: A: 2 - x, y, 1/2 - z; B: 2 - x, 1 + y, 1/2 - z; C: x, 1 + y, z.

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Table S1. The geometrical parameters of hydrogen bonding for complexes **2-5**.

D-H…A	D-H (Å)	H…A (Å)	D…A (Å)	D-H…A (°)	Symmetry code
Complex **2**					
O10C-H6wC…O8	0.81	2.22	2.97	154	
O4A-H1wA…O9	0.82	1.94	2.73	162	
O4A-H2wA…O1B	0.82	2.07	2.88	167	A: x, 1 + y, z B: 1 - x, 1 - y, 1 - z C: 3/2 - x, 1/2 + y, 3/2 - z
O5C-H4wC…O10C	0.82	1.84	2.64	166	
O5D-H3wC…O4A	0.81	2.03	2.71	141	
Complex **3**					
C2B-H2B…O7	0.94	2.50	3.36	152	
N3A-H3A…O6	0.87	2.14	2.84	137	
C8C-H8C…O8	0.94	2.31	3.21	160	A: -1 - x, y, z B: 3/2 - x, -1/2 + y, z C: 1 - x, 1/2 + y, 3/2 - z D: 1 - x, - y, 1 - z E: 1/2 + x, 1/2 - y, 1 - z F: 1/2 - x, 1/2 + y, z
O10B-H4wB…O4F	0.80	2.00	2.79	172	
O10B-H1wB…O1B	0.83	1.84	2.64	160	
O1B-H3wB…O5D	0.82	2.37	3.15	158	
O1B-H2wB…O2E	0.86	2.27	3.04	151	
Complex **4**					
O5-H3w…O1A	0.85	2.05	2.88	164	
O5-H5w…N4B	0.85	2.05	2.90	165	

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O6A-H4wA…O5	0.74	2.07	2.78	162	A: 1 - x, 1 - y, 1 - z B: -1 + x, y, z
O1A-H2wA…O2	1.04	2.06	3.00	147	
O1A-H2wA…O3	1.04	2.07	3.09	163	
Complex **5**					
C7-H7…O3C	0.93	2.80	3.63	149	C: x, 1 + y, z

Table S2. The geometrical parameters of π…π interactions in complexes **1**, **4** and **5**.

Complex	*Z* (Å) [I]	*d* (Å) [II]	*Θ* (°) [III]
1 (*Cg*$_1$-*Cg*$_1$ [a])	3.97	3.40	1.42
4 (*Cg*$_1$-*Cg*$_2$ [b])	3.70	3.30	2.28
5 (*Cg*$_2$-*Cg*$_2$ [c])	4.14	3.54	0.00

[I] the centroid-centroid distance; [II] the interplanar spacing; [III] the dihedral angle. Detailed annotation information of the graph setting see M. David Curtis et al.[1] C_g1 = pyrazinyl ring, C_g2 = pyridazinyl ring, symmetry code: [a] = 2 - x, y, 3/2 - z; [b] = 1 - x, 2 - y, 1 - z; [c] = 2 - x, 1 - y, 1 - z.

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Table S3. Crystal Data and Structure Refinement for **1-5**.

complexes	**1**	**2**	**3**	**4**	**5**
Identification code	878699	878698	878697	929082	929081
formula	$C_{20}H_{16}Cl_4Cu_2N_{12}$	$C_{10}H_{15}ClCuN_8O_9$	$C_{10}H_{13}Cl_3CuN_6O_{10}$	$C_{20}H_{21}Cl_2Cu_2N_{13}O_6$	$C_{20}H_{17}Cl_3Cu_2N_{12}O_5$
M/g mol^{-1}	693.33	490.29	547.15	737.48	738.89
T/K	293(2)	293(2)	248(2)	293(2)	296(2)
crystal system	Monoclinic	Monoclinic	Orthorhombic	Triclinic	Monoclinic
space group	C2/c	C2/c	Pbca	P-1	C2/c
a/Å	14.870(6)	32.804(3)	10.812(1)	11.2535(6)	14.641(7)
b/Å	19.709(8)	6.6637(6)	11.148(1)	11.921(1)	14.569(7)
c/Å	8.759(3)	21.391(2)	31.445(3)	12.0912(9)	12.478(6)
α/deg	90	90	90	92.170(7)	90
β/deg	106.423(4)	128.802(5)	90	115.524(6)	94.490(4)
γ/deg	90	90	90	107.005(6)	90
V/Å^3	2462.3(16)	3644.1(6)	3790.3(6)	1374.30(17)	2653(2)
Z	4	8	8	2	4
d_{cal}/g cm^{-3}	1.870	1.787	1.918	1.806	1.850
F(000)	1384	1992	2200	744	1480
Limiting indices	-13 <= h <= 18, -22 <= k <= 23, -9 <= l <= 10	-37 <= h <= 38, -7 <= k <= 7, -25 <= l <= 18	-13 <= h <= 14, -13 <= k <= 14, -41 <= l <= 40	-13 <= h <= 13, -14 <= k <= 14, -14 <= l <= 9	-17 <= h <= 16, -17 <= k <= 17, -14 <= l <= 15
Reflections collected / unique	5731/2268 [*R(int)* = 0.0319]	9586/3199 [*R(int)* = 0.0241]	25525/4705 [*R(int)* = 0.0373]	9121/5114 [*R(int)* = 0.0188]	9482/2472 [*R(int)* = 0.0363]
Data/restraints/parameters	2268/0/173	3199/9/281	4705/6/285	5114/3/395	2472/1/194
Goodness-of-fit on F^2	1.054	1.035	1.020	1.035	1.027
Final *R* indices [$I>2\sigma(I)$]	R_1 = 0.0354 wR_2 = 0.0650	R_1 = 0.0404 wR_2 = 0.1085	R_1 = 0.0358 wR_2 = 0.0938	R_1 = 0.0374 wR_2 = 0.0896	R_1 = 0.0341 wR_2 = 0.0799
R indices (all data)	R_1 = 0.0620 wR_2 = 0.0736	R_1 = 0.0455 wR_2 = 0.1133	R_1 = 0.0477 wR_2 = 0.1004	R_1 = 0.0462 wR_2 = 0.0964	R_1 = 0.0492 wR_2 = 0.0883

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Largest diff. peak, hole in e Å^3	0.492, -0.381	0.696, -0.498	0.608, -0.376	0.771, -0.764	0.415, -0.411

Table S4. Selected bond distances (Å), angles (°) and valence sum calculations of **1-5**.

Complex **1**		
N1-Cu1-N3 = 79.8(1)	N1-Cu1-N5 = 156.8(1)	N5-Cu1-N3 = 78.5(1)
N1-Cu1-Cl2 = 97.53(9)	N5-Cu1-Cl2 = 102.51(9)	N3-Cu1-Cl2 = 170.22(9)
N1-Cu1-Cl2A = 92.64(9)	N5-Cu1-Cl2A = 98.32(9)	N3-Cu1-Cl2A = 97.84(9)
Cl2-Cu1-Cl2A = 91.66(4)	Cu1-Cl2 = 2.257(1)	Cu1-Cl2A = 2.666(1)
Cu1-N1 = 2.011(3)	Cu1-N3 = 1.954(3)	Cu1-N5 = 1.957(3)
$\sum S$(Cu1) = 2.1		

Complex **2**		
O5w-Cu1-N4 = 169.6(1)	O5w-Cu1-N1 = 96.1(1)	N4-Cu1-N1 = 79.6(1)
O5w-Cu1-N5 = 104.2(1)	O5w-Cu1-O4w = 87.9(1)	N4-Cu1-N5 = 79.8(1)
N1-Cu1-N5 = 159.4(1)	N4-Cu1-O4w = 101.7(1)	N1-Cu1-O4w = 92.9(1)
N5-Cu1-O4w = 91.3(1)	O5w-Cu1-O9 = 90.4(1)	N4-Cu1-O9 = 79.9(1)
N1-Cu1-O9 = 86.2(1)	N5-Cu1-O9 = 90.2(1)	

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Cu1-N1 = 1.988(3)	Cu1-N4 = 1.954(4)	Cu1-N5 = 2.030(3)
Cu1-O4w = 2.3822(2)	Cu1-O5w = 1.926(3)	Cu1-O9 = 2.593(4)
∑*S*(Cu1) = 2.3		

Complex **3**

N2-Cu1-N4 = 79.25(8)	N2-Cu1-N5 = 158.30(8)	N4-Cu1-N5 = 79.44(8)
N4-Cu1-O1w = 128.27(9)	N2-Cu1-O1w = 96.24(8)	N54-Cu1-O1w = 100.10(8)
N4-Cu1-N6A = 137.64(8)	N2-Cu1-N6A = 91.61(8)	N5-Cu1-N6A = 101.45(8)
N6-Cu1-O1w = 93.62(8)	Cu1-N2 = 1.98(2)	Cu1-N4 = 1.953(2)
Cu1-N5 = 2.018(2)	Cu1-N6A = 2.120(3)	Cu1-O1w = 2.045(2)
∑*S*(Cu1) = 2.3		

Complex **4**

O6-Cu1-N10 = 168.9(1)	O6-Cu1-N8 = 93.0(1)	N10-Cu1-N8 = 78.0(1)
O6-Cu1-N11 = 107.8(1)	N10-Cu1-N11 = 80.8(1)	N8-Cu1-N11 = 158.8(1)
O6-Cu2-N3 = 172.5(1)	O6-Cu2-N5 = 96.6(1)	N3-Cu2-N5 = 78.5(1)
O6-Cu2-N1 = 104.6(1)	N3-Cu2-N1 = 80.1(1)	N1-Cu2-N5 = 158.5(1)
O6-Cu2-N7 = 84.75(9)	N3-Cu2-N7 = 100.4(1)	N7-Cu2-N5 = 85.2(1)

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N7-Cu2-N1 = 100.1(1)	Cu1-N6 = 2.497(4)	Cu1-N8 = 1.980(2)
Cu1-N10 = 1.950(2)	Cu1-N11 = 2.031(3)	Cu1-O6 = 1.898(2)
Cu2-N1 = 2.045(3)	Cu2-N3 = 1.946(3)	Cu2-N5 = 1.986(4)
Cu2-N7 = 2.452(2)	Cu2-O6 = 1.908(2)	
∑*S*(Cu1) = 2.3	∑*S*(Cu2) = 2.3	

Complex **5**		
O1-Cu1-N4 = 166.64(9)	O1-Cu1-N2 = 93.9(1)	N4-Cu1-N4 = 78.6(1)
O1-Cu1-N5 = 105.4(1)	N5-Cu1-N5 = 80.8(1)	N2-Cu1-N5 = 159.1(1)
O1-Cu1-N1A = 85.62(9)	N4-Cu1-N1A = 105.2(1)	N2-Cu1-N1A = 89.4(1)
N5-Cu1-N1A = 99.6(1)	Cu1-N2 = 1.957(3)	Cu1-N4 = 1.938(3)
Cu1-N5 = 2.001(3)	Cu1-N1A = 2.441(3)	Cu1-O1 = 1.895(2)
∑*S*(Cu1) = 2.4		

References

1 M. D. Curtis, J. Cao, J. W. Kampf, *J. Am. Chem. Soc*. 2004, **126**, 4318.