Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

Coordination preference of hexa(2-pyridyl)benzene with copper(II) directed by hydrogen bonding

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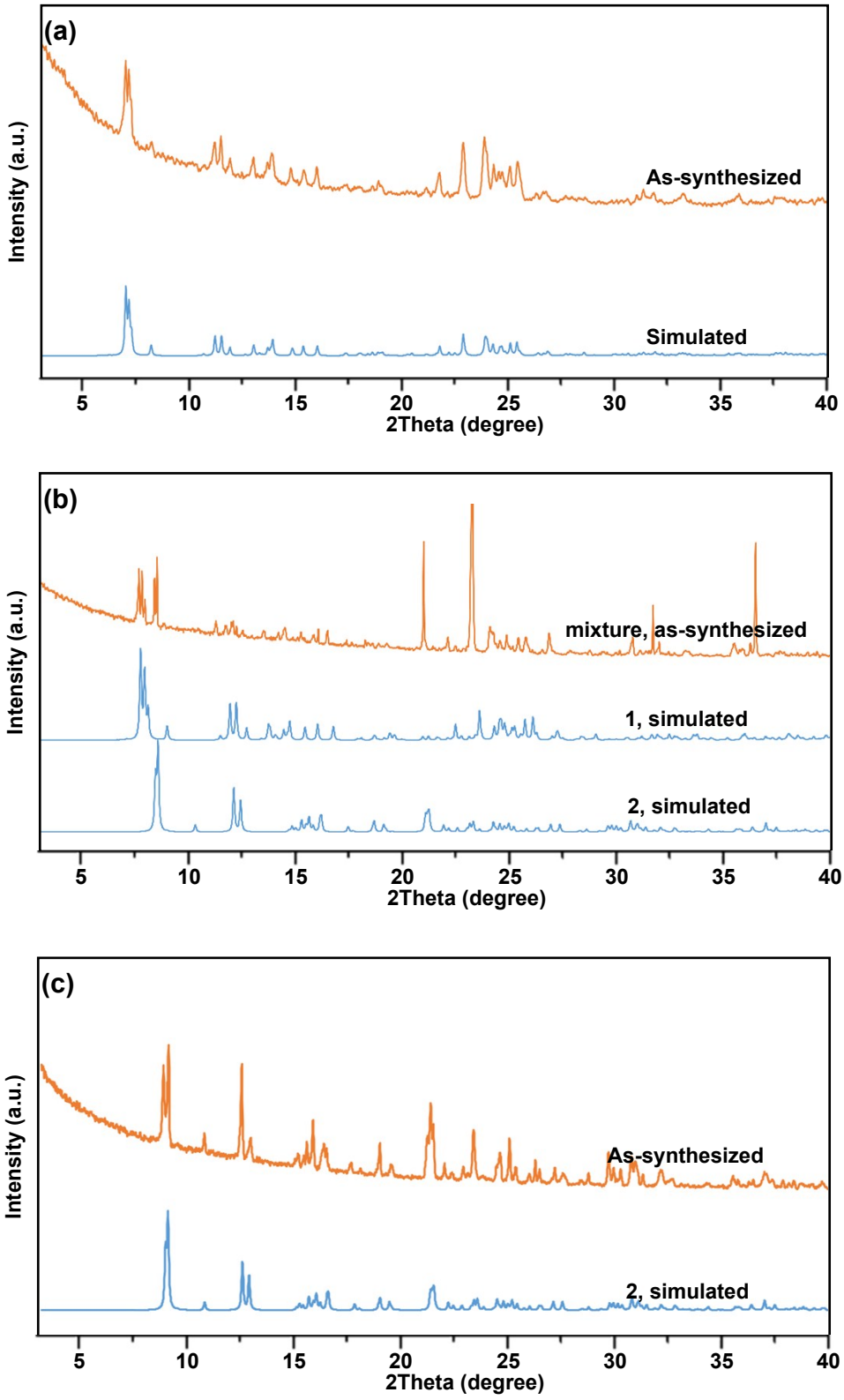
1. General Information

Reagents. 2-phenylpyridine, triphenylphosphine, potassium carbonate, 2-bromopyridine, copper(I) chloride and triethylamine were purchased from commercial sources and used as received without further purification. $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ was synthesized following the procedure described in literature.[1] *N*-methyl-2-pyrrolidone (NMP) was dried over molecular sieves (3 Å) prior to use. Tetrahydrofuran (THF) was distilled from sodium/benzophenone and stored over molecular sieves (3 Å) prior to use. Acetonitrile and d_3-acetonitrile were distilled from P_2O_5 and stored over molecular sieves (4 Å) prior to use.

Experiment equipment. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker DRX spectrometer operating at 500 MHz and 125 MHz for ^1H and ^{13}C acquisitions, respectively. Elemental analysis (EA) for C, H, and N was conducted using Truspec Micro (Leco). Single crystal X-ray diffraction (SC-XRD) data were collected on a Bruker D8 VENTURE diffractometer equipped with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) or synchrotron radiation of 2D-SMC at the Pohang Accelerator Laboratory (PAL, Korea) using an ADSC Quantum-210 detector furnished with a silicon (111) double crystal monochromator (DCM) at 100 K.

X-Ray Crystallography. Using Olex2[2], the structures were solved by ShelXT[3] using Intrinsic Phasing and refined by ShelXTL[4] using Least Squares minimization. For all four compounds, all the non-hydrogen atoms were refined anisotropically and hydrogen atoms were added on their ideal positions.

2. PXRD data


(a)
Intensity (a.u.)
As-synthesized
Simulated
5
10
15
20
25
30
35
40
2Theta (degree)
(b)
Intensity (a.u.)
mixture, as-synthesized
1, simulated
2, simulated
5
10
15
20
25
30
35
40
2Theta (degree)
(c)
Intensity (a.u.)
As-synthesized
2, simulated
5
10
15
20
25
30
35
40
2Theta (degree)

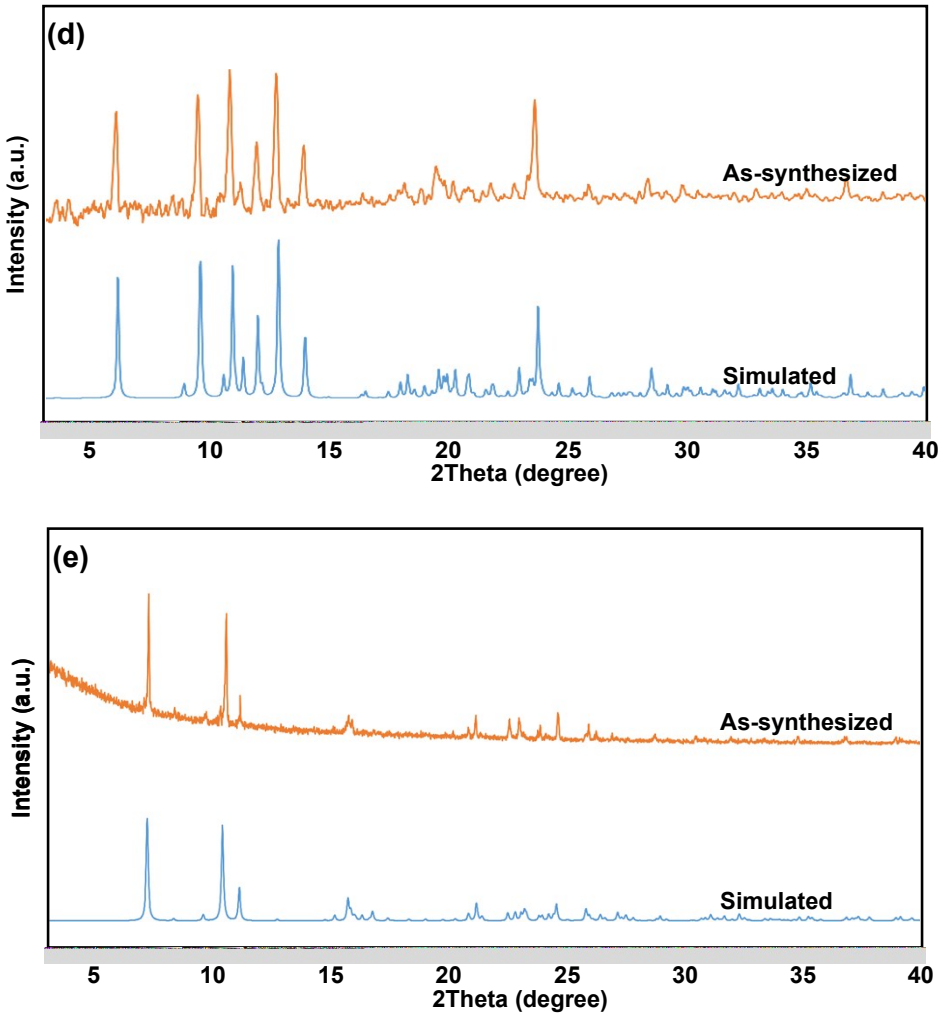


Figure S1. PXRD patterns of the complex **1** (a), the mixture of **1** and **2** (b), **2** (c), **3** (d) and [**4**] (e).

3. NMR data

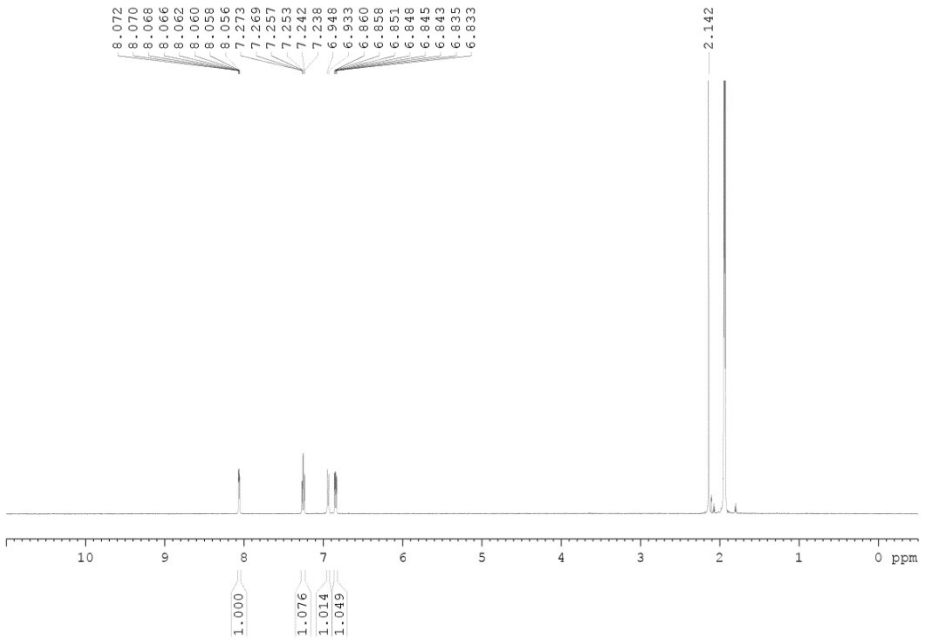


Figure S2. ^{1}H NMR spectrum of hexa(2-pyridyl)benzene (**2-HPB**) in CD_3CN.

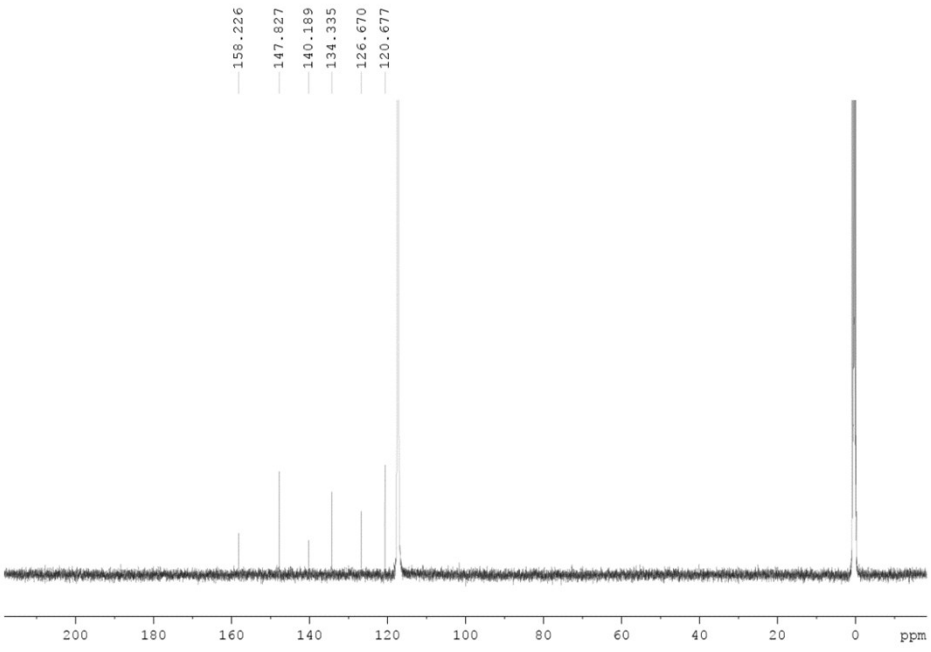


Figure S3. ^{13}C NMR spectrum of hexa(2-pyridyl)benzene (**2-HPB**) in CD_3CN.

4. UV-VIS spectra

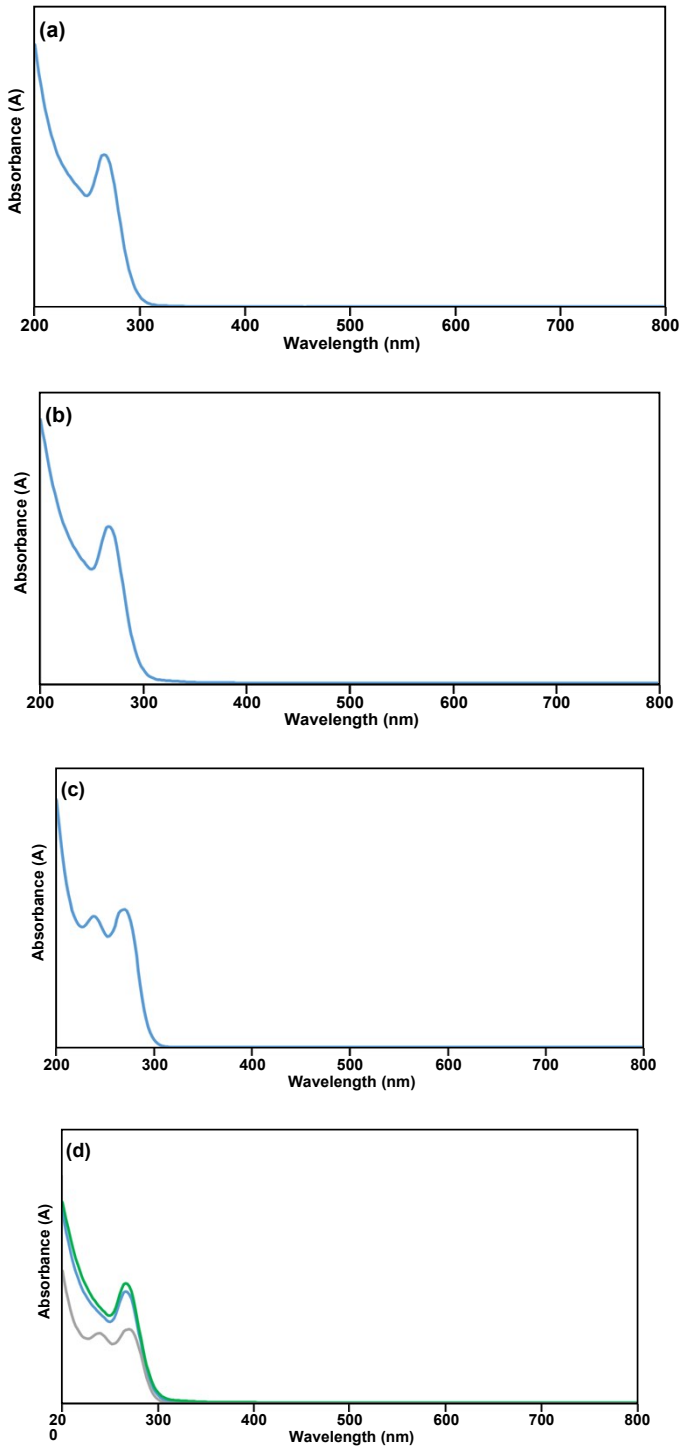


Figure S4. UV-Vis spectra of a 100 μM the complex **1** aqueous solution (a), a 100 μM **2** aqueous solution (b), 100 μM free ligand aqueous solution (**2-HPB**) (c) and the comparison of UV-Vis spectra (a) (blue), (b) (green) and (c) (gray) (d)

5. TGA data

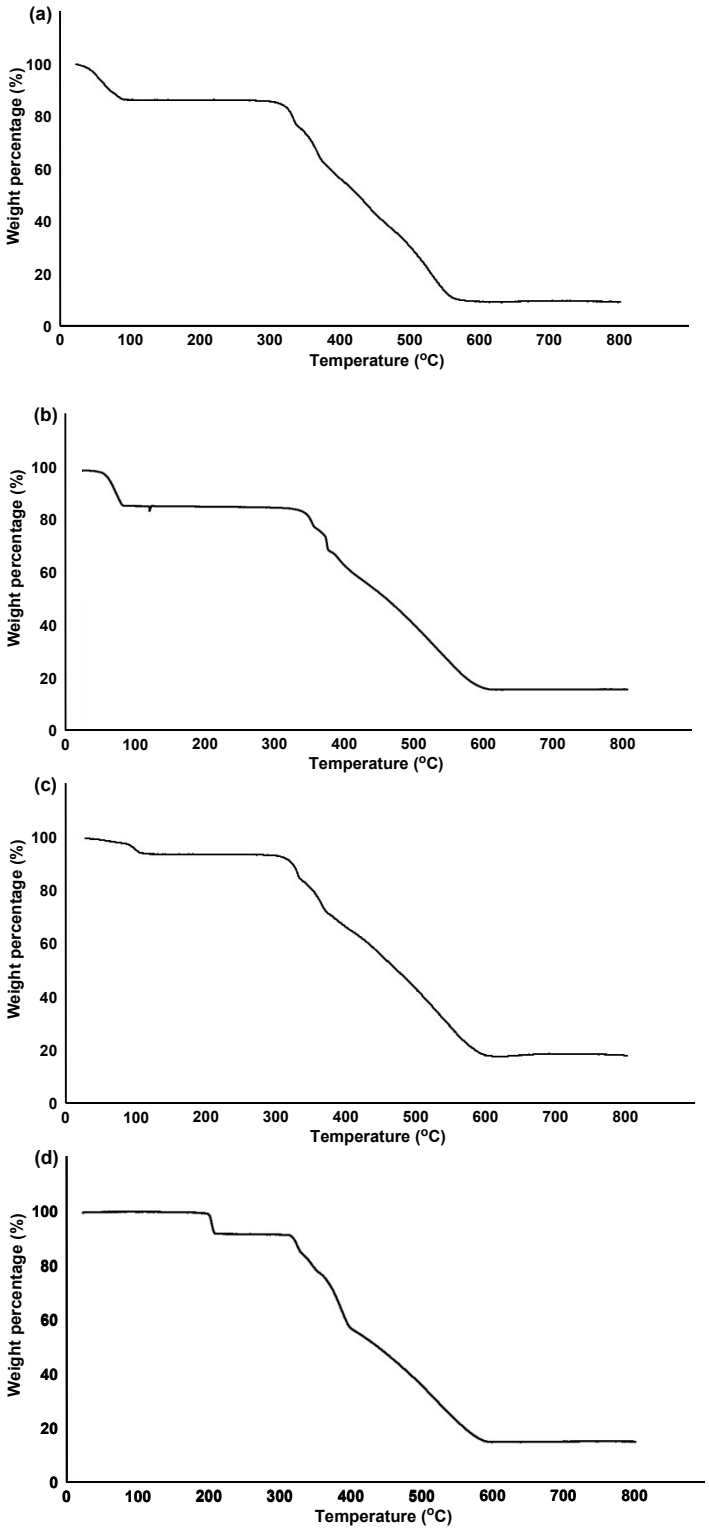


Figure S5. TGA of (a) **1**, (b) **2**, (c) **3** and (d) **4**.

6. X-ray Crystallographic Analysis

CCDC 1552123, 1552124, 1846816, and 1552125 contains the supplementary crystallographic data for **1**, **2**, **3**, and **4** respectively. These data can be obtained free of charge via www.ccdc.cam.ac.uk/cgibin/catreq.cgi (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CD21EZ, UK; fax (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk). For all six compounds, all the non-hydrogen atoms were refined anisotropically and hydrogen atoms were added to their ideal positions.

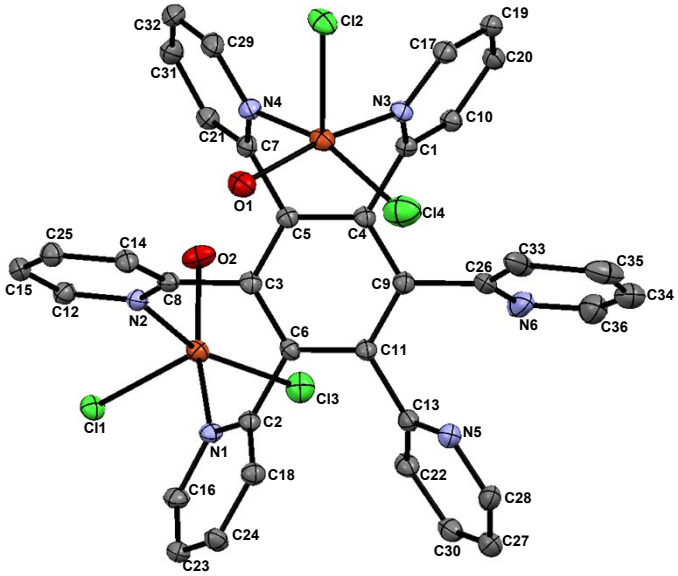


Figure S6. ORTEP diagram of (A,B)(C,D)-*trans*-$Cu_2Cl_4(H_2O)_2$(2-HPB)·4.75H_2O (**1**), ellipsoids are shown at 25% probability level.

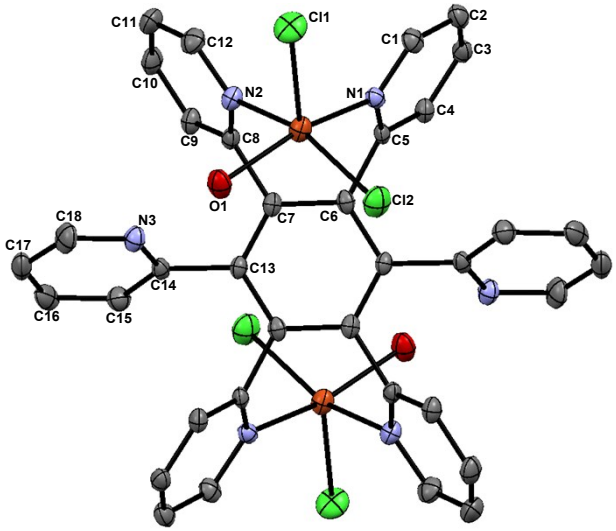


Figure S7. ORTEP diagram of (A,B)(D,E)-*trans*-$Cu_2Cl_4(H_2O)_2$(2-HPB)·5.5H_2O (**2**), ellipsoids are shown at 50% probability level.

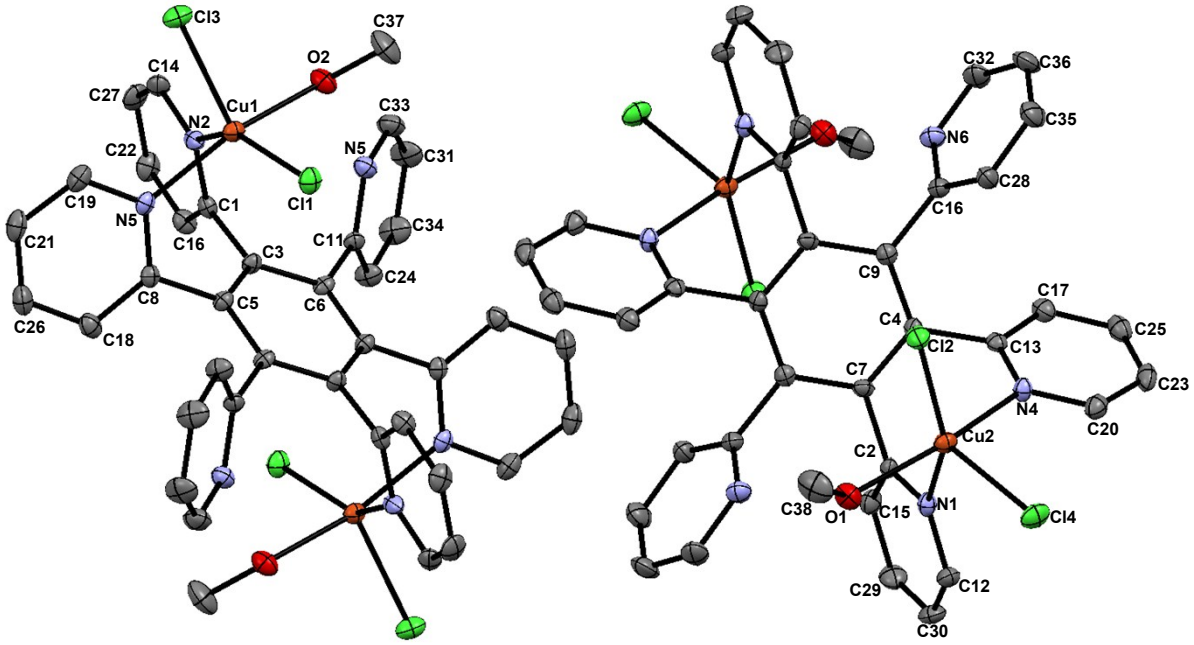


Figure S8. ORTEP diagram of (A,B)(D,E)-*trans*-$Cu_2Cl_4(MeOH)_2$(2-HPB) (**3**), ellipsoids are shown at 50% probability level.

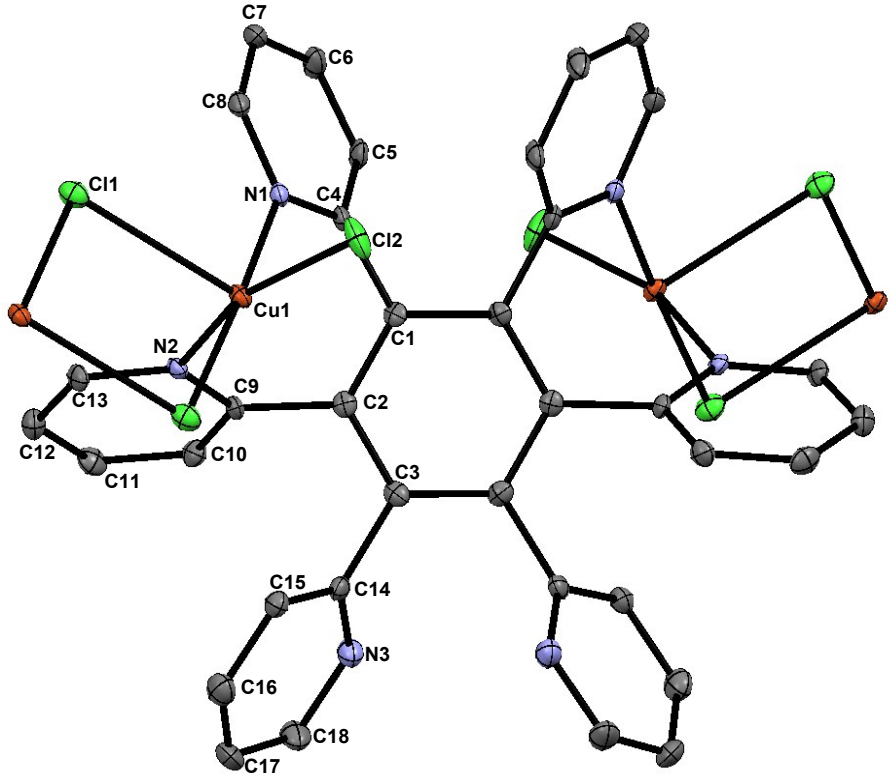


Figure S9. ORTEP diagram of [(A,B)(C,D)-*trans*-Cu_2Cl_4(2-HPB)·DMF]$_n$ ([**4**]$_n$), ellipsoids are shown at 50% probability level.

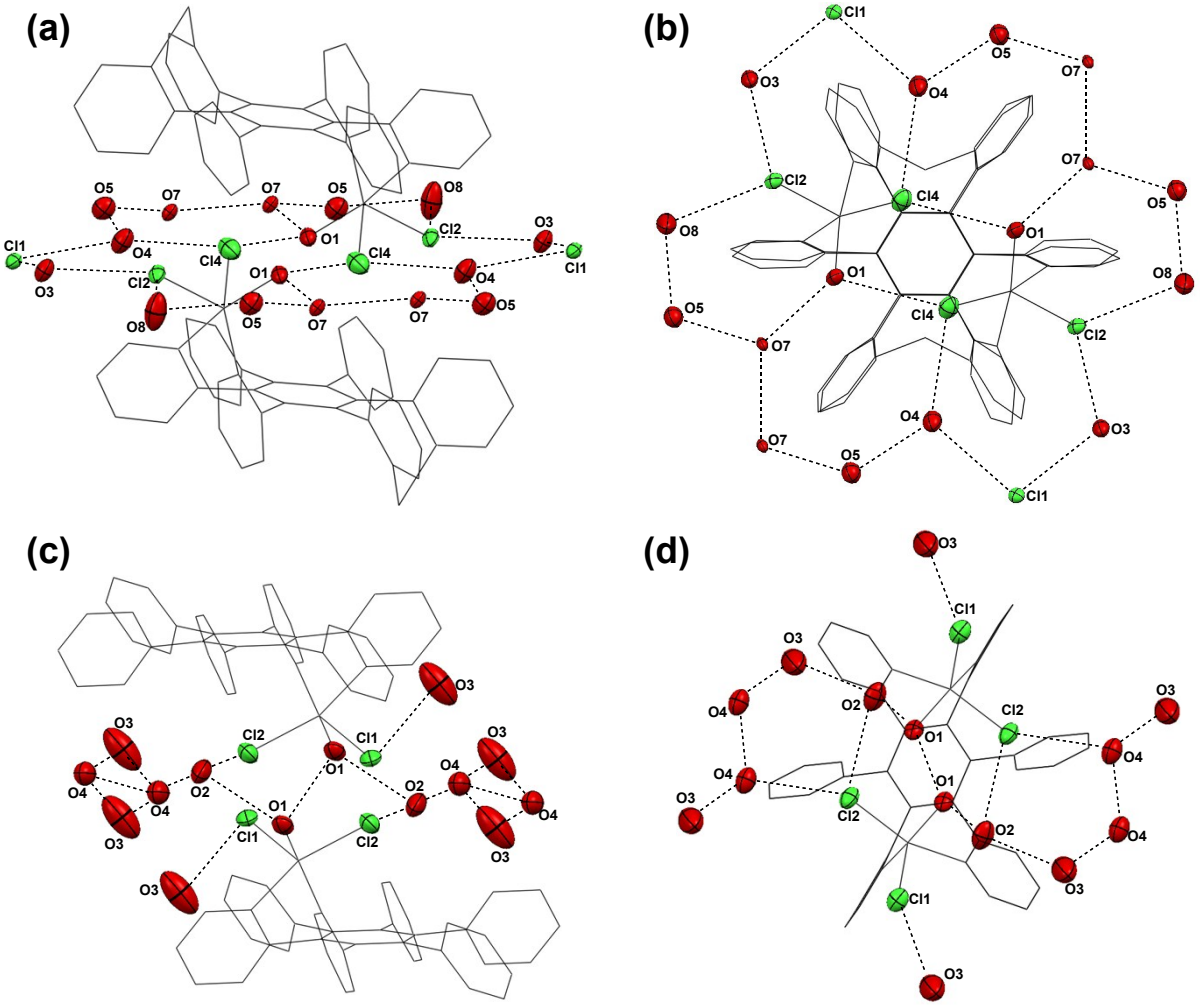


Figure S10. Molecular structure of complexes **1** (a) side view, (b) top view and **2** (c) side view, (d) top view.

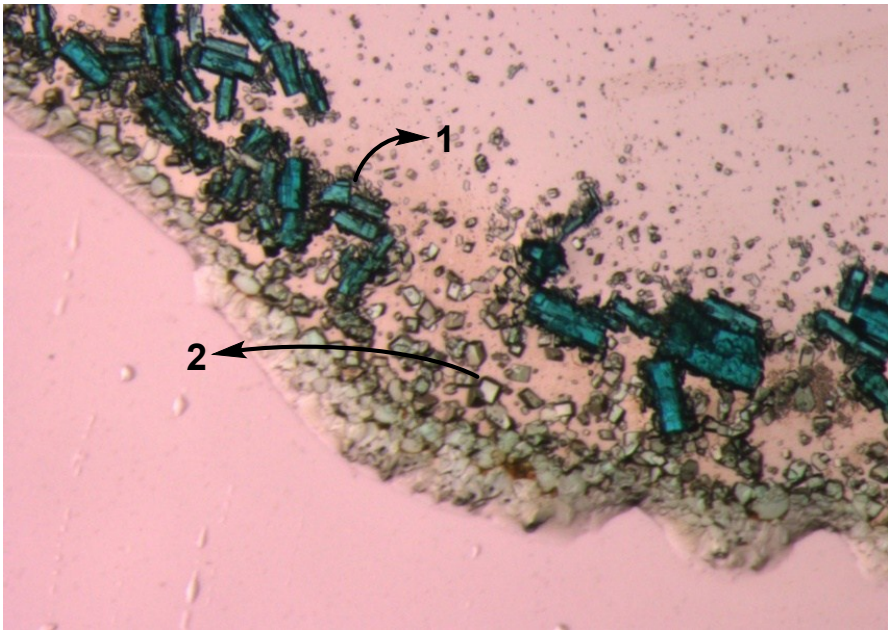
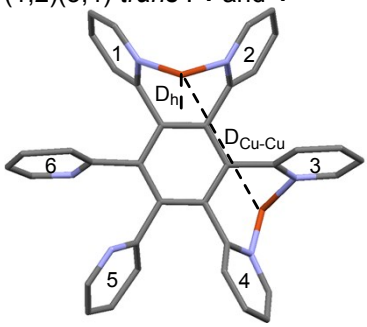
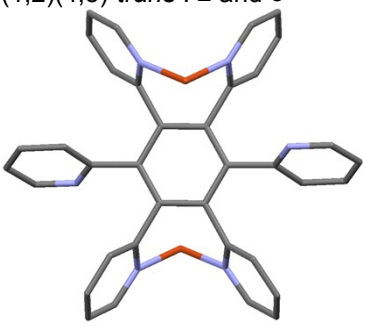


Figure S11. Optical microscope image of **1** (blue crystals) and **2** (green crystals). The crystals of **1** were added deliberately for comparison.

(1,2)(3,4)-*trans* : **1** and **4**



(1,2)(4,5)-*trans* : **2** and **3**



	D_h	D_{Cu-Cu}	$\angle_1$	$\angle_2$	$\angle_3$	$\angle_4$	$\angle_5$	$\angle_6$	$\angle_{av}$
1	2.442	7.229	64.72	64.58	64.18	68.87	64.30	58.85	64.25
2	2.459	7.285	66.23	68.24	60.12	66.23	68.24	60.12	64.86
3	2.430	7.407	58.58	65.27	62.35	58.58	65.27	62.35	62.07
4	2.348	7.202	60.33	62.15	61.12	60.33	62.35	61.12	61.27

* D_h : Distance between the copper atom and the plane defined by the central benzene (Å)
* D_{Cu-Cu} : Distance between the two copper centers (Å)
* $\angle_n$: angle between the plane of nth pyridine and the plane of central benzene(°)
* $\angle_{av}$: average value for angles $\angle_1$ - $\angle_6$(°)

Figure S12. Details concerning angles and distances in **1**, **2**, **3** and **4**.

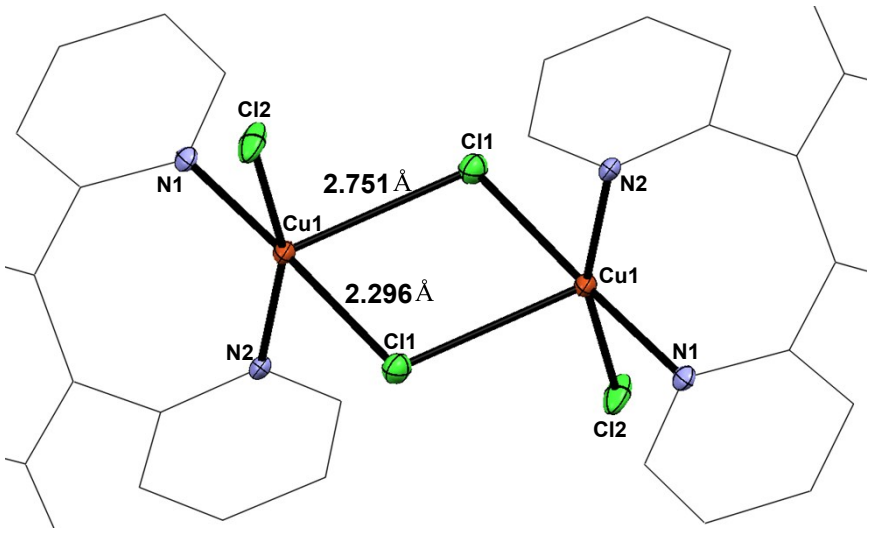


Figure S13. The Cu_2Cl_4 cluster composed of $[Cu_2(\mu\text{-}Cl)_2]$ core and two chlorides in **4**.

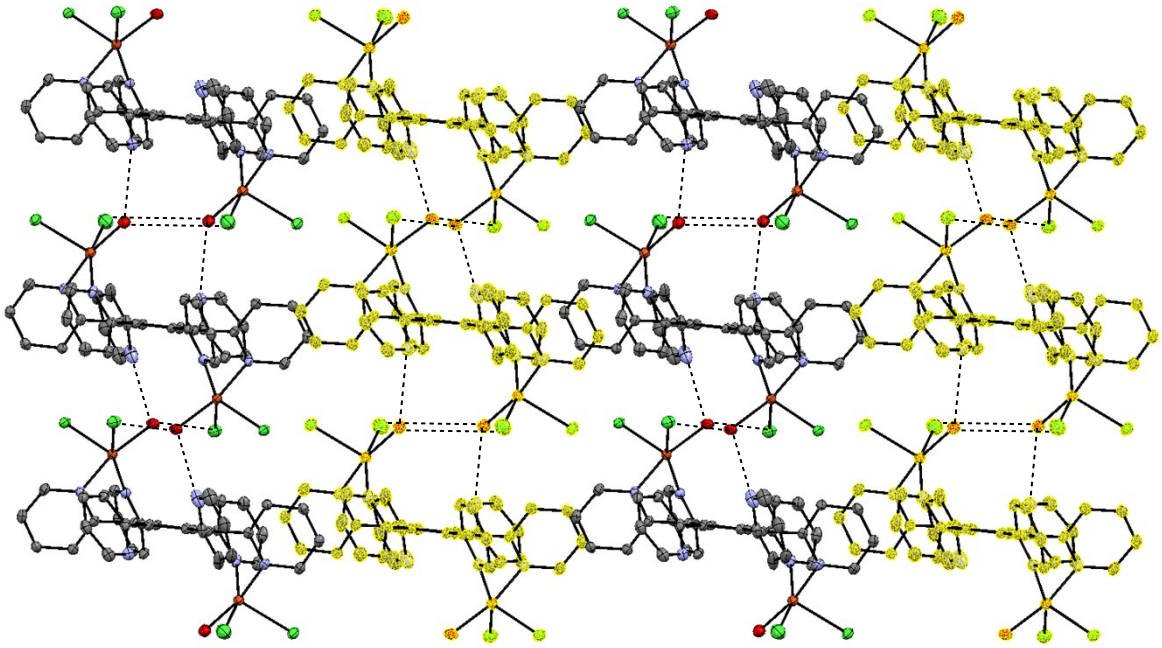


Figure S14. Perspective view of the packing in the crystal structure of **1**. Ellipsoids are shown at 25% probability level. Hydrogen atoms and lattice solvent molecules are omitted for clarity. The hydrogen bonds are descripted as dotted lines.

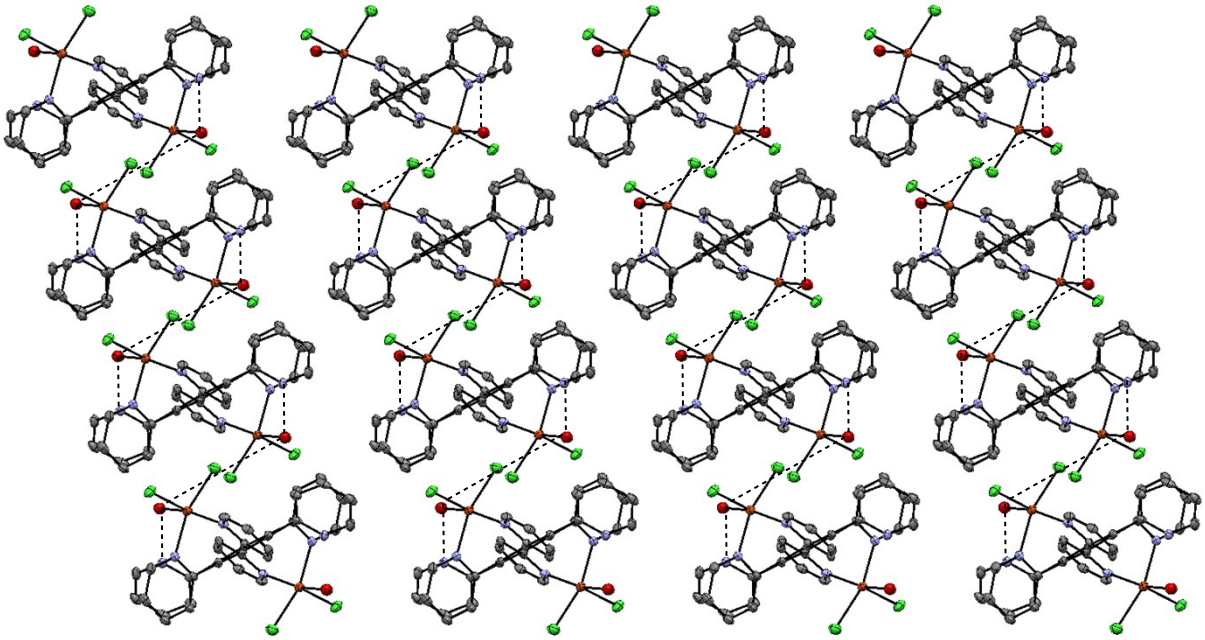


Figure S15. Perspective view of the packing in the crystal structure of **2**. Ellipsoids are shown at 25% probability level. Hydrogen atoms and lattice solvent molecules are omitted for clarity. The hydrogen bonds are descripted as dotted lines.

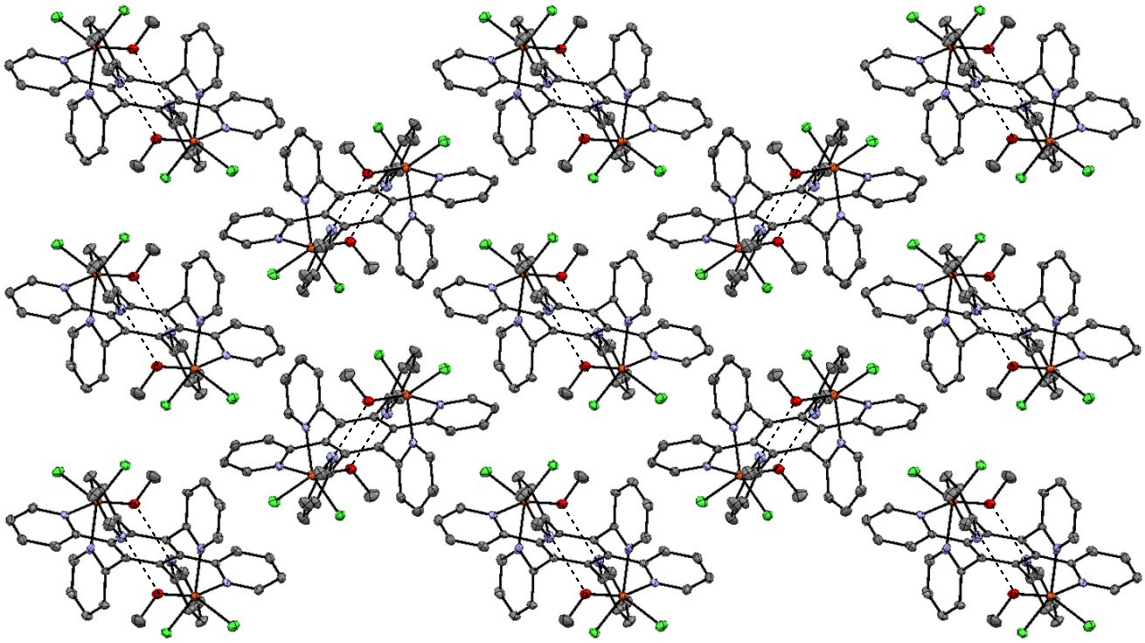


Figure S16. Perspective view of the packing in the crystal structure of **3**. Ellipsoids are shown at 25% probability level. Hydrogen atoms and lattice solvent molecules are omitted for clarity. The hydrogen bonds are descripted as dotted lines.

Table S1. Hydrogen Bonding Contact Distances (Å) and Angles (°) in **1** and **2**[a]

1 (DH···A)	r(D···A) (Å)	r(H···A) (Å)	∠DH···A (°)	**2** (DH···A)	r(D···A) (Å)	r(H···A) (Å)	∠DH···A (°)
O1H1A···Cl4$^{\#1}$	3.421	2.549	162.11	O1H1B···O2	2.771	2.124	130.27
O1H1B···N5$^{\#1}$	2.753	1.822	168.02	O1H1A···N3$^{\$1}$	2.799	1.807	158.92
O2H2A···Cl3$^{\#2}$	3.136	2.256	168.95	O2H2A···Cl2$^{\$2}$	3.227	2.178	167.74
O2H2B···N6$^{\#2}$	2.892	2.081	146.27	O2H2B···O3	2.743	1.981	132.2
O3H3A···Cl2$^{\#3}$	3.032	2.067	164.96	O3H3B···O4	2.63	1.72	171.27
O3H3B···Cl1	3.137	2.252	164.51	O3H3A···Cl1$^{\$4}$	3.182	2.342	169.45
O4H4A···Cl4$^{\#3}$	3.336	2.504	166.73	O4H4A···Cl2$^{\$5}$	3.244	2.37	134.52
O4H4B···Cl1	3.247	2.408	169.33	O4H4B···O4$^{\$3, b}$	2.717	1.743	172.86
O5H5A···O8$^{\#4}$	2.713	1.833	156.22	O1···O1$^{\$2}$	2.797		
O5H5B···O4$^{\#5}$	2.814	1.98	166.84				
O6H6A···O3$^{\#6}$	2.644	1.783	161.38				
O6H6B···O2	2.9	1.95	167.76				
O7H7A···O1	2.905	2.071	167.04				
O7H7B···O5$^{\#7}$	2.74	1.783	168.73				
O8H8A···Cl2	3.375	2.821	124.51				
O8H8A···Cl3$^{\#8}$	3.235	2.426	159				
O6···O6$^{\#6}$	2.727						
O7···O7$^{\#1}$	2.95						

[a] Symmetry transformations to generate equivalent atoms : in **1**, #1, (-X, -Y, 1-Z), #2 (1-X, 1-Y, 2-Z), #3, (1+X, Y, 1+Z), #4, (-1+X, Y, -1+Z), #5, (-1+X, Y, -1+Z), #6, (2-X, 1-Y, 2-Z), #7, (1+X, Y, Z), #8, (X, Y, -1+Z), in **2**, $1, (1-X, 1-Y, 1-Z), $2, (-X, 1-Y, 1-Z), $3, (-1-X, -Y, -Z), $4, (-X, -Y, 1-Z), $5, (-1+X, -1+Y, -1+Z)

[b] O4 atom is located at two site with occupancy factor 0.5 due to disorder

Reference

(1) Scrase, T. G.; O'Neill, M. J.; Peel, A. J.; Senior, P. W.; Matthews, P. D.; Shi, H. Y.; Boss, S. R.; Barker, P. D. Selective Lability of Ruthenium(II) Arene Amino Acid Complexes. *Inorg. Chem.* **2015**, *54*, 3118.

(2) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Cryst.* **2009**, *42*, 339.

(3) Millan, C.; Sammito, M.; Garcia-Ferrer, I.; Goulas, T.; Sheldrick, G. M.; Uson, I. Combining phase information in reciprocal space for molecular replacement with partial models. *Acta Crys.D* **2015**, *71*, 1931.

(4) Sheldrick, G. M. SHELXT - Integrated space-group and crystal-structure determination *Acta Cryst. A* **2015**, *71*, 3-8.