New Journal of Chemistry

Supplementary Material (ESI)

Copper(II) Complexes with Diethoxyphosphoryl-1,10-phenanthrolines: from Molecules to Infinite Supramolecular Arrays

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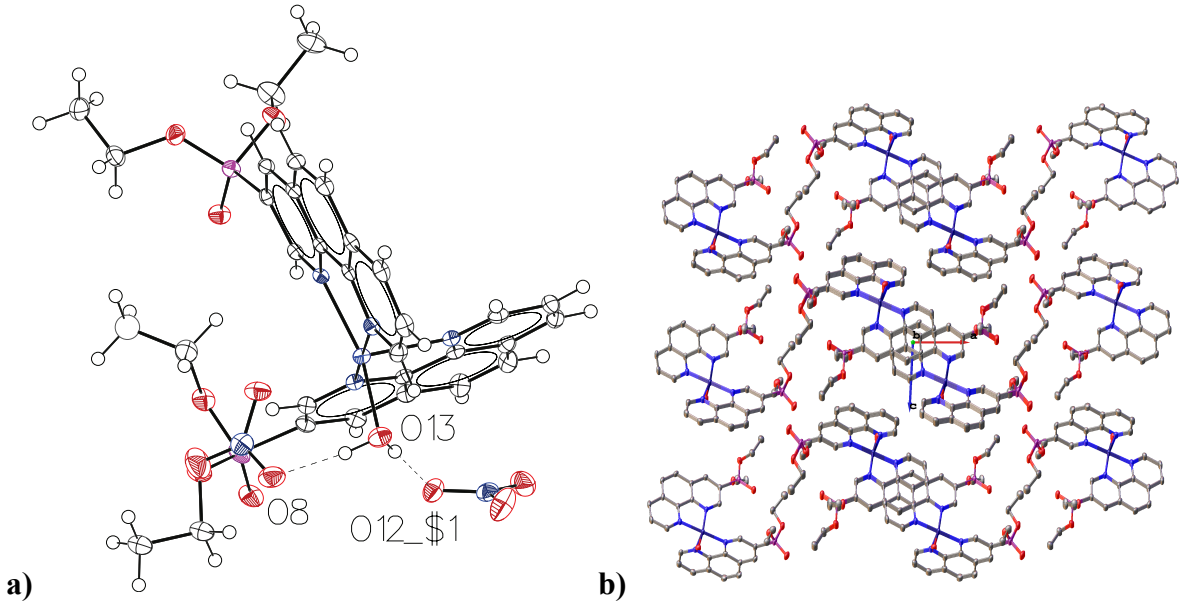


Figure S1. Crystal packing of [Cu(**3-Pphen**)$_2$(H_2O)(NO_3)](NO_3) (**1**) **(a)** View of hydrogen bonds between free nitrate anions and coordinated water molecules. Thermal ellipsoids are drawn at 50% probability. **(b)** View along *b* axis. Hydrogen atoms and nitrate counterions are omitted for clarity.

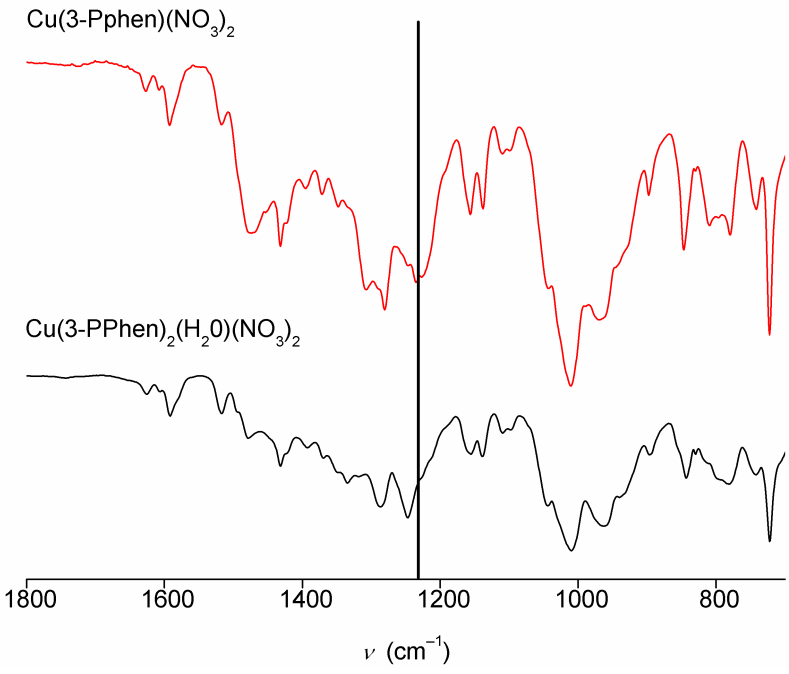
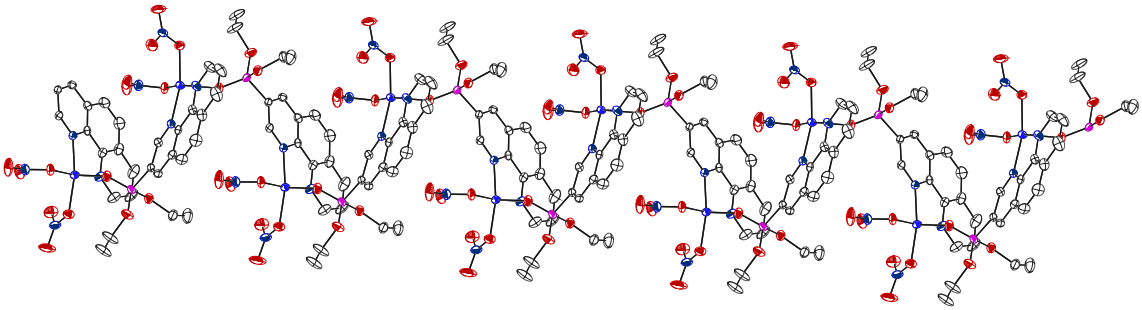


Figure S2. IR spectra of complexes **1** and **2**.

a)



b)

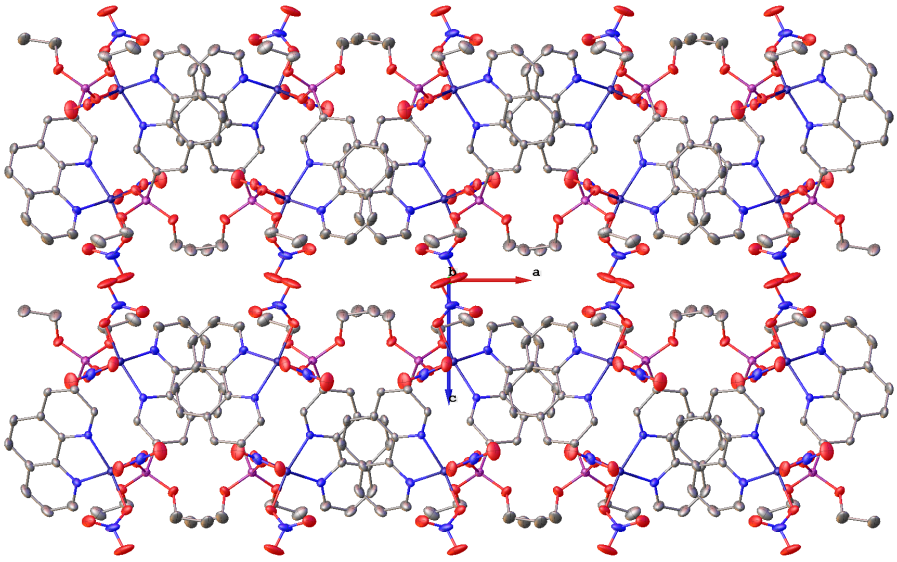


Figure S3. View of a polymeric chain of complex **2**. **(a)** View of coordination polymer. Hydrogen atoms and disordered atoms are omitted for clarity. Thermal ellipsoids are drawn at 50% probability. **(b)** Packing for complex **2** along *b* axis. The polymers are imbricated according to the *b* axis. Two layers of overlapping polymers are parallel to each other according to the *c* axis.

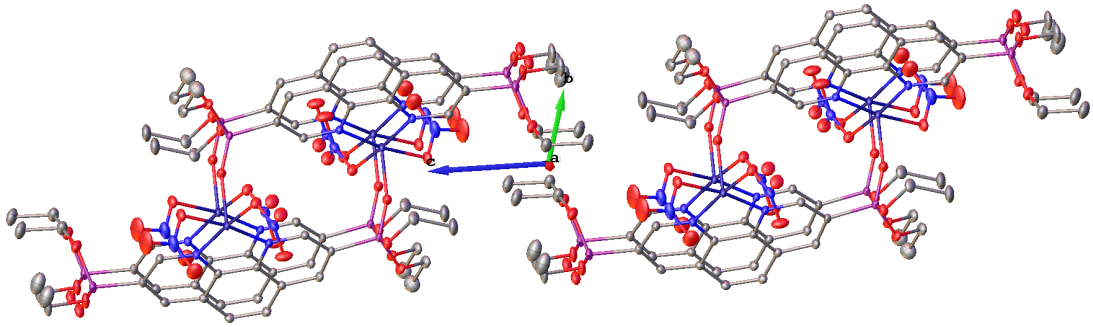
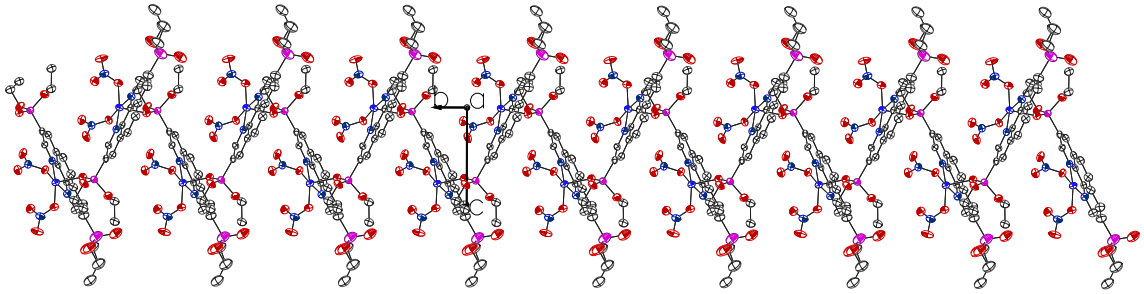
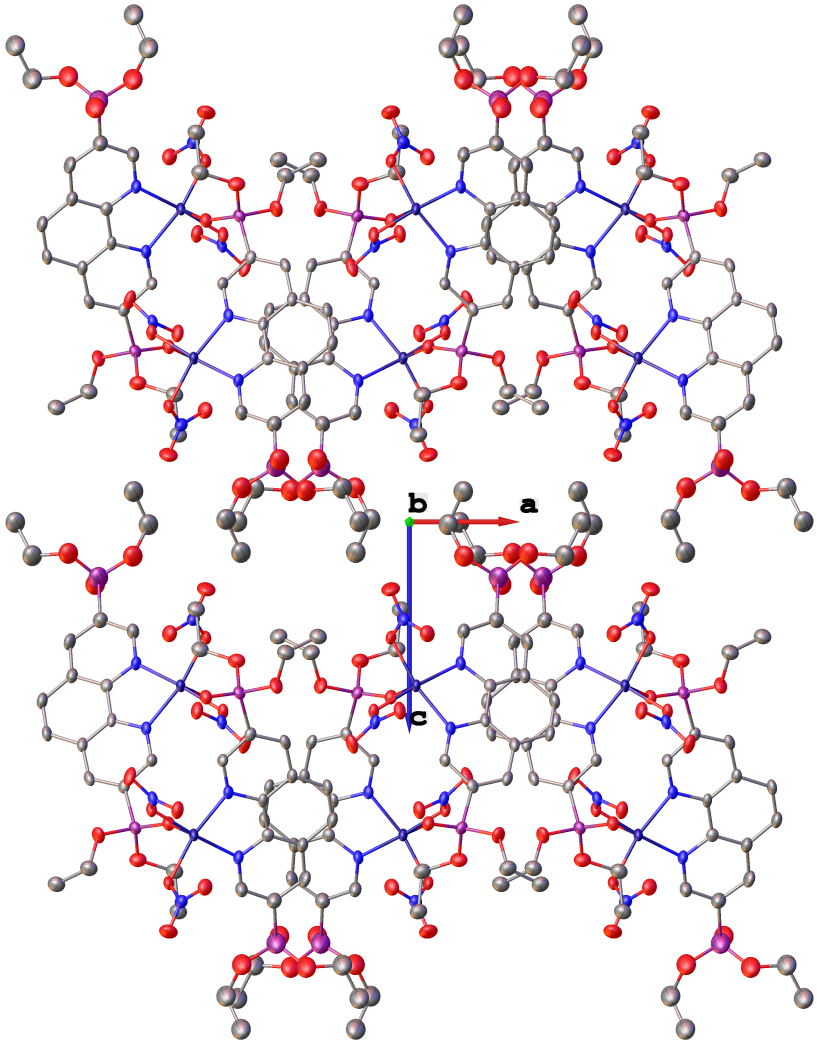


Figure S4. Crystal packing of [Cu(**3,8-Pphen**)$(NO_3)_2]_2$ (**3-I**) along *a* axis, the complexes are arranged in parallel layers due to π–π stacking. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms are omitted for clarity.

a)





b)

Figure S5. View of a polymeric chain of complex **3-II**. **(a)** View of the coordination polymer along *a* axis. Hydrogen atoms and disordered atoms are omitted for clarity. Thermal ellipsoids are drawn at 50% probability. The polymeric chains are extended according to the *b* axis. **(b)** Packing for complex **3-II** along *b* axis. Two layers of overlapping polymers are parallel to each other according to the *a* axis.

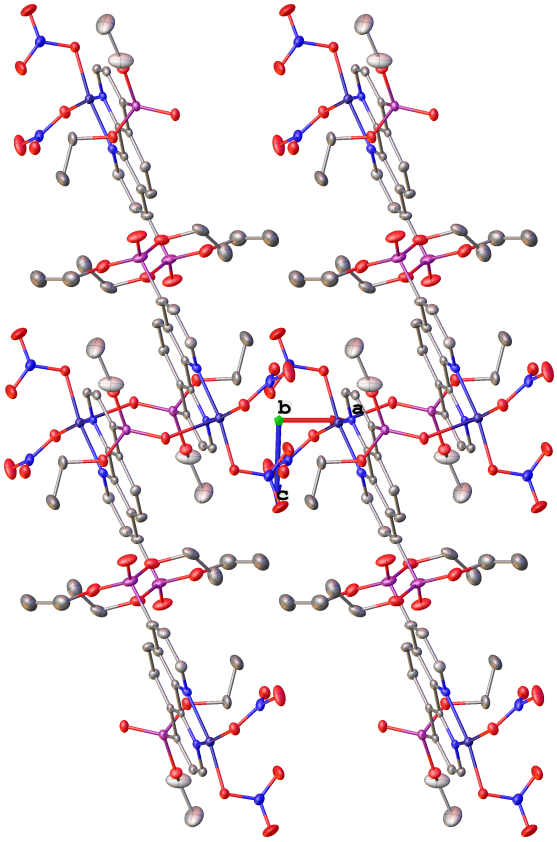


Figure S6. Crystal packing of [Cu(**4,7-Pphen**)$(NO_3)_2]_2$ (**4**) along *b* axis. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms are omitted for clarity.

Table S1. Crystal data and structure refinement for **1**.

Empirical formula	$C_{32}H_{36}CuN_6O_{13}P_2$
Formula weight	838.15
Temperature/K	115
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	18.6371(6)
b/Å	7.9394(2)
c/Å	23.7780(8)
α/°	90
β/°	92.779(2)
γ/°	90
Volume/Å^3	3514.23(19)
Z	4
ϱ_{calc}mg/mm^3	1.584
m/mm^{-1}	0.789
F(000)	1732.0
Crystal size/mm^3	0.12 × 0.1 × 0.1
2Θ range for data collection	5.41 to 55.206°
Index ranges	$-24 \le h \le 24$, $-10 \le k \le 10$, $-30 \le l \le 30$
Reflections collected	152871
Independent reflections	8162[R(int) = 0.0815]
Data/restraints/parameters	8162/5/490
Goodness-of-fit on F^2	1.079
Final R indexes [I>=2σ (I)]	$R_1 = 0.0403$, $wR_2 = 0.0966$
Final R indexes [all data]	$R_1 = 0.0567$, $wR_2 = 0.1055$
Largest diff. peak/hole / e Å^{-3}	0.88/-0.50

Table S2. Bond Lengths for **1**.

Atom	Atom	Length[Å]	Atom	Atom	Length[Å]
C1	C2	1.413(3)	C23	N4	1.358(3)
C1	N1	1.327(3)	C24	N3	1.361(3)
C2	C3	1.364(4)	O6A	C25A	1.462(4)
C3	C4	1.411(3)	O6A	P2	1.572(3)
C4	C5	1.433(3)	C25A	C26A	1.513(5)
C4	C12	1.409(3)	C28A	C27	1.505(8)
C5	C6	1.354(4)	O6B	C25B	1.468(15)
C6	C7	1.439(3)	O6B	P2	1.613(14)
C7	C8	1.402(3)	C25B	C26B	1.575(16)
C7	C11	1.402(3)	C28B	C27	1.470(7)
C8	C9	1.380(3)	C27	O4	1.465(3)
C9	C10	1.413(3)	C29	C30	1.486(4)
C9	P1	1.798(2)	C29	O1	1.455(3)
C10	N2	1.329(3)	Cu1	N1	2.0110(19)
C11	C12	1.435(3)	Cu1	N2	2.0647(19)
C11	N2	1.362(3)	Cu1	N3	2.203(2)
C12	N1	1.354(3)	Cu1	N4	2.0248(19)
C13	C14	1.401(4)	Cu1	O13	2.0057(18)
C13	N3	1.326(3)	Cu1	O7	2.538(2)
C14	C15	1.370(4)	C31	C32	1.497(4)
C15	C16	1.409(3)	C31	O3	1.461(3)
C16	C17	1.435(3)	O1	P1	1.5731(18)
C16	C24	1.402(3)	O2	P1	1.4632(18)
C17	C18	1.354(4)	O3	P1	1.5763(19)
C18	C19	1.434(3)	O4	P2	1.567(2)
C19	C20	1.408(3)	O5	P2	1.4675(18)
C19	C23	1.409(3)	N5	O10	1.237(3)
C20	C21	1.380(3)	N5	O11	1.250(3)
C21	C22	1.409(3)	N5	O12	1.260(3)
C21	P2	1.803(2)	N6	O7	1.272(3)
C22	N4	1.332(3)	N6	O8	1.244(3)
C23	C24	1.440(3)	N6	O9	1.234(3)

Table S3. Bond Angles for **1**.

Atom	Atom	Atom	Angle[°]	Atom	Atom	Atom	Angle[°]
N1	C1	C2	122.3(2)	N1	Cu1	N3	98.38(8)
C3	C2	C1	119.5(2)	N1	Cu1	N4	176.53(8)
C2	C3	C4	119.6(2)	N1	Cu1	O7	92.54(7)
C3	C4	C5	123.8(2)	N2	Cu1	N3	102.41(7)
C12	C4	C3	117.1(2)	N2	Cu1	O7	82.84(7)
C12	C4	C5	119.1(2)	N3	Cu1	O7	168.44(7)
C6	C5	C4	120.7(2)	N4	Cu1	N2	96.54(8)
C5	C6	C7	121.5(2)	N4	Cu1	N3	79.13(8)
C8	C7	C6	123.6(2)	N4	Cu1	O7	90.11(7)
C11	C7	C6	118.8(2)	O13	Cu1	N1	88.33(8)
C11	C7	C8	117.6(2)	O13	Cu1	N2	160.52(8)
C9	C8	C7	119.4(2)	O13	Cu1	N3	95.49(7)
C8	C9	C10	119.1(2)	O13	Cu1	N4	94.30(7)
C8	C9	P1	121.42(18)	O13	Cu1	O7	81.00(7)
C10	C9	P1	119.46(17)	O3	C31	C32	108.6(2)
N2	C10	C9	122.5(2)	C1	N1	C12	118.5(2)
C7	C11	C12	119.8(2)	C1	N1	Cu1	128.17(17)
N2	C11	C7	123.3(2)	C12	N1	Cu1	113.34(15)
N2	C11	C12	116.8(2)	C10	N2	C11	118.00(19)
C4	C12	C11	120.0(2)	C10	N2	Cu1	130.69(15)
N1	C12	C4	123.1(2)	C11	N2	Cu1	111.29(15)
N1	C12	C11	116.90(19)	C13	N3	C24	117.5(2)
N3	C13	C14	123.4(2)	C13	N3	Cu1	132.15(16)
C15	C14	C13	119.1(2)	C24	N3	Cu1	110.34(15)
C14	C15	C16	119.4(2)	C22	N4	C23	118.7(2)
C15	C16	C17	123.1(2)	C22	N4	Cu1	125.74(16)
C24	C16	C15	117.2(2)	C23	N4	Cu1	115.46(15)
C24	C16	C17	119.6(2)	C29	O1	P1	118.67(16)
C18	C17	C16	120.7(2)	C31	O3	P1	123.19(16)
C17	C18	C19	121.0(2)	C27	O4	P2	121.35(17)
C20	C19	C18	123.0(2)	O1	P1	C9	101.05(10)
C20	C19	C23	117.4(2)	O1	P1	O3	102.00(10)
C23	C19	C18	119.6(2)	O2	P1	C9	112.63(11)
C21	C20	C19	120.0(2)	O2	P1	O1	118.19(11)
C20	C21	C22	118.6(2)	O2	P1	O3	115.22(10)
C20	C21	P2	120.21(18)	O3	P1	C9	106.02(10)
C22	C21	P2	121.12(18)	O6A	P2	C21	105.85(13)
N4	C22	C21	122.7(2)	O6B	P2	C21	96.8(5)
C19	C23	C24	119.2(2)	O4	P2	C21	106.69(11)

N4	C23	C19	122.6(2)	O4	P2	O6A	99.99(12)
N4	C23	C24	118.3(2)	O4	P2	O6B	118.6(5)
C16	C24	C23	119.9(2)	O5	P2	C21	112.69(12)
N3	C24	C16	123.4(2)	O5	P2	O6A	118.49(13)
N3	C24	C23	116.8(2)	O5	P2	O6B	109.4(5)
C25A	O6A	P2	122.5(2)	O5	P2	O4	111.84(11)
O6A	C25A	C26A	106.3(3)	O10	N5	O11	122.9(2)
C25B	O6B	P2	117.4(11)	O10	N5	O12	119.1(2)
O6B	C25B	C26B	99.2(12)	O11	N5	O12	118.0(2)
O4	C27	C28A	110.2(3)	O8	N6	O7	119.0(2)
O4	C27	C28B	107.8(3)	O9	N6	O7	120.9(3)
O1	C29	C30	107.9(2)	O9	N6	O8	120.1(2)
N1	Cu1	N2	81.58(8)	N6	O7	Cu1	125.54(16)

Table S4. Hydrogen Bonds for **1**.

D	H	A	d(D-H[Å]	d(H-A)(Å)	d(D-A)(Å)	D-H-A[°]
O13	H13A	O8	0.89	1.83	2.704(3)	169.7
O13	H13B	O12[1]	0.88	1.77	2.641(3)	167.7

[1]1-X,1/2+Y,3/2-Z

Table S5. Crystal data and structure refinement for **2**

Empirical formula	$C_{16}H_{17}CuN_4O_9P$
Formula weight	503.85
Temperature/K	115.0
Crystal system	orthorhombic
Space group	Pbca
a/Å	15.6819(7)
b/Å	10.5814(5)
c/Å	25.5715(14)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	4243.2(4)
Z	8
ϱ_{calc}mg/mm^3	1.577
m/mm^{-1}	1.161
F(000)	2056.0
Crystal size/mm^3	0.3 × 0.15 × 0.15
2Θ range for data collection	5.632 to 55.016°
Index ranges	-20 ≤ h ≤ 12, -8 ≤ k ≤ 13, -33 ≤ l ≤ 29
Reflections collected	20472
Independent reflections	4863[R(int) = 0.0334]
Data/restraints/parameters	4863/6/283
Goodness-of-fit on F^2	1.030
Final R indexes [I>=2σ (I)]	R_1 = 0.0362, wR_2 = 0.0803
Final R indexes [all data]	R_1 = 0.0572, wR_2 = 0.0889
Largest diff. peak/hole / e Å^{-3}	0.86/-0.54

Table S6. Bond Lengths for **2**.

Atom	Atom	Length[Å]	Atom	Atom	Length[Å]
Cu1	O1	1.9803(18)	N2	C10	1.326(3)
Cu1	O4	1.9681(16)	N2	C11	1.357(3)
Cu1	O7	2.1807(16)	C1	C2	1.410(3)
Cu1	N1	2.0310(19)	C2	P1[2]	1.795(2)
Cu1	N2	1.991(2)	C2	C3	1.378(3)
P1	O7	1.4684(17)	C3	C4	1.403(3)
P1	O8	1.5621(17)	C4	C5	1.444(3)
P1	O9	1.5587(18)	C4	C12	1.398(3)
P1	C2[1]	1.795(2)	C5	C6	1.346(4)
O1	N3	1.297(3)	C6	C7	1.423(4)
O2	N3	1.226(3)	C7	C8	1.409(4)
O4	N4	1.298(3)	C7	C11	1.403(3)
O5	N4	1.241(3)	C8	C9	1.366(4)
O8	C13	1.468(3)	C9	C10	1.398(4)
O9	C15	1.471(4)	C11	C12	1.425(3)
O9	C15A	1.470(7)	N4	O6	1.213(3)
O3	N3	1.216(3)	C13	C14	1.493(4)
N1	C1	1.317(3)	C15	C16	1.486(5)
N1	C12	1.367(3)	C15A	C16A	1.459(8)

[1]-X,-1/2+Y,1/2-Z; [2]-X,1/2+Y,1/2-Z

Table S7. Bond Angles for **2**.

Atom	Atom	Atom	Angle[°]	Atom	Atom	Atom	Angle[°]
O1	Cu1	O7	92.58(7)	O3	N3	O2	122.6(2)
O1	Cu1	N1	163.91(7)	N1	C1	C2	122.9(2)
O1	Cu1	N2	95.83(8)	C1	C2	P1[2]	117.54(17)
O4	Cu1	O1	89.55(8)	C3	C2	P1[2]	123.30(18)
O4	Cu1	O7	85.98(6)	C3	C2	C1	119.1(2)
O4	Cu1	N1	92.88(7)	C2	C3	C4	119.3(2)
O4	Cu1	N2	174.57(8)	C3	C4	C5	124.1(2)
N1	Cu1	O7	103.45(7)	C12	C4	C3	117.6(2)
N2	Cu1	O7	93.05(7)	C12	C4	C5	118.3(2)
N2	Cu1	N1	82.13(8)	C6	C5	C4	120.8(2)
O7	P1	O8	109.28(10)	C5	C6	C7	121.7(2)
O7	P1	O9	117.19(10)	C8	C7	C6	125.0(2)
O7	P1	C2[1]	111.06(10)	C11	C7	C6	118.7(2)
O8	P1	C2[1]	108.57(10)	C11	C7	C8	116.3(2)
O9	P1	O8	108.41(10)	C9	C8	C7	120.1(3)
O9	P1	C2[1]	101.88(10)	C8	C9	C10	119.7(3)
N3	O1	Cu1	115.99(14)	N2	C10	C9	122.0(3)
N4	O4	Cu1	112.69(15)	N2	C11	C7	123.4(2)
P1	O7	Cu1	147.39(11)	N2	C11	C12	116.7(2)
C13	O8	P1	121.54(16)	C7	C11	C12	120.0(2)
C15	O9	P1	123.4(2)	N1	C12	C4	123.2(2)
C15A	O9	P1	118.7(5)	N1	C12	C11	116.4(2)
C1	N1	Cu1	130.41(15)	C4	C12	C11	120.4(2)
C1	N1	C12	117.94(19)	O5	N4	O4	117.7(2)
C12	N1	Cu1	111.47(15)	O6	N4	O4	118.2(2)
C10	N2	Cu1	128.37(18)	O6	N4	O5	124.1(2)
C10	N2	C11	118.5(2)	O8	C13	C14	107.9(2)
C11	N2	Cu1	113.09(15)	O9	C15	C16	105.1(3)
O2	N3	O1	119.7(2)	C16A	C15A	O9	123.5(10)
O3	N3	O1	117.7(2)				

[1]-X,-1/2+Y,1/2-Z; [2]-X,1/2+Y,1/2-Z

Table S8. Torsion Angles for **2**.

A	B	C	D	Angle[°]	A	B	C	D	Angle[°]
Cu1	O1	N3	O2	12.4(3)	C2[2]	P1	O8	C13	66.1(2)
Cu1	O1	N3	O3	-167.5(2)	C2[2]	P1	O9	C15	174.4(3)
Cu1	O4	N4	O5	-2.1(3)	C2[2]	P1	O9	C15A	136.1(7)
Cu1	O4	N4	O6	177.5(2)	C2	C3	C4	C5	-177.1(2)
Cu1	N1	C1	C2	-172.72(17)	C2	C3	C4	C12	1.6(3)
Cu1	N1	C12	C4	174.77(17)	C3	C4	C5	C6	178.7(3)
Cu1	N1	C12	C11	-5.7(2)	C3	C4	C12	N1	-0.9(3)
Cu1	N2	C10	C9	-179.4(2)	C3	C4	C12	C11	179.6(2)
Cu1	N2	C11	C7	-179.03(19)	C4	C5	C6	C7	0.7(4)
Cu1	N2	C11	C12	0.4(3)	C5	C4	C12	N1	177.9(2)
P1	O8	C13	C14	-170.29(19)	C5	C4	C12	C11	-1.6(3)
P1	O9	C15	C16	-157.8(3)	C5	C6	C7	C8	179.9(3)
P1	O9	C15A	C16A	160.9(11)	C5	C6	C7	C11	0.3(4)
P1[1]	C2	C3	C4	-176.95(18)	C6	C7	C8	C9	-178.5(3)
O7	P1	O8	C13	-172.67(18)	C6	C7	C11	N2	177.4(2)
O7	P1	O9	C15	53.0(3)	C6	C7	C11	C12	-2.0(4)
O7	P1	O9	C15A	14.7(7)	C7	C8	C9	C10	0.2(5)
O8	P1	O7	Cu1	40.3(2)	C7	C11	C12	N1	-176.9(2)
O8	P1	O9	C15	-71.2(3)	C7	C11	C12	C4	2.7(3)
O8	P1	O9	C15A	-109.5(7)	C8	C7	C11	N2	-2.1(4)
O9	P1	O7	Cu1	-83.5(2)	C8	C7	C11	C12	178.4(2)
O9	P1	O8	C13	-43.9(2)	C8	C9	C10	N2	-0.5(5)
N1	C1	C2	P1[1]	175.28(18)	C10	N2	C11	C7	1.9(4)
N1	C1	C2	C3	-1.2(4)	C10	N2	C11	C12	-178.7(2)
N2	C11	C12	N1	3.6(3)	C11	N2	C10	C9	-0.5(4)
N2	C11	C12	C4	-176.8(2)	C11	C7	C8	C9	1.0(4)
C1	N1	C12	C4	-0.9(3)	C12	N1	C1	C2	2.0(3)
C1	N1	C12	C11	178.7(2)	C12	C4	C5	C6	0.0(4)
C1	C2	C3	C4	-0.7(3)	C15	O9	C15A	C16A	53.0(12)
C2[2]	P1	O7	Cu1	160.07(18)	C15A	O9	C15	C16	-65.5(10)

[1]-X,1/2+Y,1/2-Z; [2]-X,-1/2+Y,1/2-Z

Table S9. Crystal data and structure refinement for **3-I**.

Empirical formula	$C_{40}H_{52}Cu_2N_8O_{24}P_4$
Formula weight	1279.85
Temperature/K	115.0
Crystal system	triclinic
Space group	P-1
a/Å	7.7003(6)
b/Å	9.8407(8)
c/Å	17.8602(16)
α/°	105.813(2)
β/°	92.591(3)
γ/°	90.967(2)
Volume/Å^3	1300.23(19)
Z	1
ϱ_{calc}g/cm^3	1.635
μ/mm^{-1}	1.033
F(000)	658.0
Crystal size/mm^3	0.1 × 0.1 × 0.07
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.454 to 55.686
Index ranges	-10 ≤ h ≤ 10, -12 ≤ k ≤ 12, -23 ≤ l ≤ 23
Reflections collected	50096
Independent reflections	6099 [R_{int} = 0.0490, R_{sigma} = 0.0312]
Data/restraints/parameters	6099/0/356
Goodness-of-fit on F^2	1.039
Final R indexes [I>=2σ (I)]	R_1 = 0.0319, wR_2 = 0.0792
Final R indexes [all data]	R_1 = 0.0471, wR_2 = 0.0867
Largest diff. peak/hole / e Å^{-3}	0.63/-0.64

Table S10. Bond Lengths for **3-I**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	C2	1.498(3)	C17	C18	1.496(3)
C1	O1	1.459(2)	C17	O5	1.456(3)
C3	C4	1.503(3)	C19	C20	1.490(4)
C3	O3	1.477(2)	C19	O6	1.459(2)
C5	C6	1.416(3)	N1	Cu1	2.0152(16)
C5	C7	1.377(3)	N2	Cu1	2.0229(16)
C5	P1	1.792(2)	N3	O7	1.292(3)
C6	N1	1.326(2)	N3	O8	1.242(3)
C7	C8	1.408(3)	N3	O9	1.228(3)
C8	C9	1.401(3)	N4	O10	1.303(2)
C8	C10	1.435(3)	N4	O11	1.236(2)
C9	C13	1.432(3)	N4	O12	1.230(2)
C9	N1	1.357(2)	O1	P1	1.5679(14)
C10	C11	1.351(3)	O2	P1	1.4681(15)
C11	C12	1.435(3)	O2	Cu1[1]	2.1584(14)
C12	C13	1.402(3)	O3	P1	1.5602(15)
C12	C16	1.409(3)	O4	P2	1.4638(15)
C13	N2	1.362(2)	O5	P2	1.5760(16)
C14	C15	1.410(3)	O6	P2	1.5699(16)
C14	N2	1.328(2)	O7	Cu1	1.9944(14)
C15	C16	1.379(3)	O10	Cu1	1.9643(14)
C15	P2	1.795(2)	Cu1	O2[1]	2.1584(14)

[1]-X,1-Y,-Z

Table S11. Bond Angles for **3-I**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	C1	C2	108.73(18)	O9	N3	O7	118.1(2)
O3	C3	C4	110.73(18)	O9	N3	O8	123.8(2)
C6	C5	P1	118.96(15)	O11	N4	O10	119.22(17)
C7	C5	C6	119.40(17)	O12	N4	O10	118.06(17)
C7	C5	P1	121.64(14)	O12	N4	O11	122.71(18)
N1	C6	C5	121.67(17)	C1	O1	P1	124.05(13)
C5	C7	C8	119.74(17)	P1	O2	Cu1[1]	161.01(9)
C7	C8	C10	124.04(17)	C3	O3	P1	120.50(13)
C9	C8	C7	116.73(18)	C17	O5	P2	122.50(14)
C9	C8	C10	119.23(17)	C19	O6	P2	120.72(14)
C8	C9	C13	119.36(17)	N3	O7	Cu1	108.95(12)
N1	C9	C8	123.64(17)	N4	O10	Cu1	117.50(12)
N1	C9	C13	117.00(16)	O1	P1	C5	103.44(9)
C11	C10	C8	121.09(18)	O2	P1	C5	114.91(9)
C10	C11	C12	121.03(18)	O2	P1	O1	113.66(8)
C13	C12	C11	118.65(17)	O2	P1	O3	113.99(8)
C13	C12	C16	116.89(17)	O3	P1	C5	102.58(9)
C16	C12	C11	124.46(18)	O3	P1	O1	107.07(8)
C12	C13	C9	120.54(17)	O4	P2	C15	113.68(9)
N2	C13	C9	115.95(17)	O4	P2	O5	115.26(9)
N2	C13	C12	123.51(17)	O4	P2	O6	117.80(9)
N2	C14	C15	122.22(18)	O5	P2	C15	106.64(9)
C14	C15	P2	120.17(15)	O6	P2	C15	100.06(9)
C16	C15	C14	119.27(18)	O6	P2	O5	101.53(9)
C16	C15	P2	120.54(15)	N1	Cu1	N2	81.79(6)
C15	C16	C12	119.70(18)	N1	Cu1	O2[1]	93.25(6)
O5	C17	C18	110.13(19)	N2	Cu1	O2[1]	94.48(6)
O6	C19	C20	108.4(2)	O7	Cu1	N1	171.19(6)
C6	N1	C9	118.74(16)	O7	Cu1	N2	90.38(6)
C6	N1	Cu1	128.90(13)	O7	Cu1	O2[1]	91.37(6)
C9	N1	Cu1	112.32(12)	O10	Cu1	N1	99.17(6)
C13	N2	Cu1	112.43(13)	O10	Cu1	N2	172.33(6)
C14	N2	C13	118.38(17)	O10	Cu1	O2[1]	93.06(6)
C14	N2	Cu1	129.09(13)	O10	Cu1	O7	88.05(6)
O8	N3	O7	118.09(18)				

[1]-X,1-Y,-Z

Table S12. Torsion Angles for **3-I**.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C1	O1	P1	C5	124.51(16)	C12	C13	N2	C14	-1.6(3)
C1	O1	P1	O2	-0.77(18)	C12	C13	N2	Cu1	175.05(15)
C1	O1	P1	O3	-127.57(16)	C13	C9	N1	C6	-177.22(17)
C2	C1	O1	P1	-123.21(18)	C13	C9	N1	Cu1	4.9(2)
C3	O3	P1	C5	-147.01(14)	C13	C12	C16	C15	-0.4(3)
C3	O3	P1	O1	104.46(15)	C14	C15	C16	C12	-0.8(3)
C3	O3	P1	O2	-22.14(17)	C14	C15	P2	O4	176.60(16)
C4	C3	O3	P1	-73.3(2)	C14	C15	P2	O5	48.47(19)
C5	C6	N1	C9	-0.1(3)	C14	C15	P2	O6	-56.89(18)
C5	C6	N1	Cu1	177.42(14)	C15	C14	N2	C13	0.2(3)
C5	C7	C8	C9	-0.2(3)	C15	C14	N2	Cu1	-175.82(15)
C5	C7	C8	C10	-179.80(19)	C16	C12	C13	C9	-177.90(18)
C6	C5	C7	C8	2.3(3)	C16	C12	C13	N2	1.7(3)
C6	C5	P1	O1	163.05(15)	C16	C15	P2	O4	-4.9(2)
C6	C5	P1	O2	-72.47(18)	C16	C15	P2	O5	-133.02(17)
C6	C5	P1	O3	51.79(17)	C16	C15	P2	O6	121.62(18)
C7	C5	C6	N1	-2.3(3)	C17	O5	P2	C15	102.20(17)
C7	C5	P1	O1	-17.65(19)	C17	O5	P2	O4	-24.99(19)
C7	C5	P1	O2	106.83(17)	C17	O5	P2	O6	-153.50(16)
C7	C5	P1	O3	-128.91(17)	C18	C17	O5	P2	100.3(2)
C7	C8	C9	C13	177.35(18)	C19	O6	P2	C15	176.69(18)
C7	C8	C9	N1	-2.3(3)	C19	O6	P2	O4	-59.6(2)
C7	C8	C10	C11	-177.41(19)	C19	O6	P2	O5	67.24(18)
C8	C9	C13	C12	0.3(3)	C20	C19	O6	P2	-146.35(19)
C8	C9	C13	N2	-179.37(17)	N1	C9	C13	C12	179.94(18)
C8	C9	N1	C6	2.4(3)	N1	C9	C13	N2	0.3(3)
C8	C9	N1	Cu1	-175.46(15)	N2	C14	C15	C16	1.0(3)
C8	C10	C11	C12	-0.1(3)	N2	C14	C15	P2	179.52(15)
C9	C8	C10	C11	3.0(3)	O8	N3	O7	Cu1	0.3(2)
C9	C13	N2	C14	178.03(17)	O9	N3	O7	Cu1	-179.63(18)
C9	C13	N2	Cu1	-5.3(2)	O11	N4	O10	Cu1	27.2(2)
C10	C8	C9	C13	-3.0(3)	O12	N4	O10	Cu1	-154.03(14)
C10	C8	C9	N1	177.35(18)	P1	C5	C6	N1	177.02(15)
C10	C11	C12	C13	-2.6(3)	P1	C5	C7	C8	-176.95(15)
C10	C11	C12	C16	177.84(19)	P2	C15	C16	C12	-179.35(15)
C11	C12	C13	C9	2.5(3)	Cu1[1]	O2	P1	C5	-19.6(3)
C11	C12	C13	N2	-177.85(18)	Cu1[1]	O2	P1	O1	99.3(3)
C11	C12	C16	C15	179.10(19)	Cu1[1]	O2	P1	O3	-137.6(3)

[1]-X,1-Y,-Z

Table S13. Crystal data and structure refinement for **3-II**.

Empirical formula	$C_{20}H_{26}CuN_4O_{12}P_2$
Formula weight	639.93
Temperature/K	100
Crystal system	orthorhombic
Space group	Pbca
a/Å	16.2508(6)
b/Å	9.2040(4)
c/Å	34.9028(15)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	5220.5(4)
Z	8
ϱ_{calc}g/cm^3	1.628
μ/mm^{-1}	2.971
F(000)	2632.0
Crystal size/mm^3	0.14 × 0.1 × 0.05
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	7.432 to 136.926
Index ranges	-19 ≤ h ≤ 7, -10 ≤ k ≤ 11, -40 ≤ l ≤ 42
Reflections collected	26677
Independent reflections	4744 [R_{int} = 0.0371, R_{sigma} = 0.0286]
Data/restraints/parameters	4744/70/331
Goodness-of-fit on F^2	1.181
Final R indexes [I>=2σ (I)]	R_1 = 0.0994, wR_2 = 0.2459
Final R indexes [all data]	R_1 = 0.1029, wR_2 = 0.2480
Largest diff. peak/hole / e Å^{-3}	1.14/-1.46

Table S14. Bond Lengths for **3-II**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	C2	1.441(11)	C17A	C18A	1.471(14)
C1	O1	1.394(12)	C17A	O5	1.458(13)
C1	O1A	1.434(13)	C19	C20	1.475(14)
C3	C4	1.463(16)	C19	O5	1.448(12)
C3	O3	1.444(14)	C19A	C20A	1.468(15)
C3A	C4A	1.457(15)	C19A	O6	1.435(13)
C3A	O3A	1.450(14)	N1	Cu1	2.018(6)
C5	C6	1.371(11)	N2	Cu1	2.025(5)
C5	C16	1.398(11)	N3	O7	1.235(7)
C5	P1	1.800(12)	N3	O8	1.295(7)
C5	P1A	1.794(11)	N3	O9	1.225(7)
C6	C7	1.414(11)	N4	O10	1.240(8)
C7	C8	1.440(10)	N4	O11	1.300(8)
C7	C15	1.407(10)	N4	O12	1.211(8)
C8	C9	1.340(11)	O1	P1	1.562(13)
C9	C10	1.449(9)	O1A	P1A	1.544(12)
C10	C11	1.388(10)	O2	P1	1.450(14)
C10	C14	1.403(9)	O2A	P1A	1.493(13)
C11	C12	1.384(9)	O3	P1	1.557(13)
C12	C13	1.400(9)	O3A	P1A	1.536(12)
C12	P2	1.794(7)	O4	P2	1.476(5)
C13	N2	1.306(9)	O4	Cu1[1]	2.201(5)
C14	C15	1.417(9)	O5	P2	1.560(5)
C14	N2	1.364(8)	O6	P2	1.558(5)
C15	N1	1.354(9)	O8	Cu1	1.966(5)
C16	N1	1.332(9)	O11	Cu1	1.991(5)
C17	C18	1.481(14)	Cu1	O4[2]	2.201(5)
C17	O6	1.480(12)			

[1]1-X,1/2+Y,3/2-Z; [2]1-X,-1/2+Y,3/2-Z

Table S15. Bond Angles for **3-II**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	C1	C2	117.4(10)	O10	N4	O11	117.7(6)
O1A	C1	C2	118.5(11)	O12	N4	O10	123.9(7)
O3	C3	C4	109.0(18)	O12	N4	O11	118.4(7)
O3A	C3A	C4A	112.1(16)	C1	O1	P1	119.8(13)
C6	C5	C16	120.1(7)	C1	O1A	P1A	131.5(11)
C6	C5	P1	120.0(7)	C3	O3	P1	125.7(15)
C6	C5	P1A	119.5(7)	C3A	O3A	P1A	115.2(15)
C16	C5	P1	119.9(7)	P2	O4	Cu1[1]	144.6(3)
C16	C5	P1A	119.5(7)	C17A	O5	P2	120.1(15)
C5	C6	C7	119.2(7)	C19	O5	P2	125.5(13)
C6	C7	C8	124.7(7)	C17	O6	P2	118.8(8)
C15	C7	C6	117.1(6)	C19A	O6	P2	131.1(11)
C15	C7	C8	118.1(7)	N3	O8	Cu1	119.3(4)
C9	C8	C7	121.4(7)	N4	O11	Cu1	109.6(4)
C8	C9	C10	121.3(6)	O1	P1	C5	107.7(9)
C11	C10	C9	124.0(6)	O2	P1	C5	109.8(9)
C11	C10	C14	117.9(6)	O2	P1	O1	117.6(12)
C14	C10	C9	118.1(6)	O2	P1	O3	117.1(13)
C12	C11	C10	119.2(6)	O3	P1	C5	104.5(9)
C11	C12	C13	118.9(6)	O3	P1	O1	98.8(10)
C11	C12	P2	122.7(5)	O1A	P1A	C5	109.2(8)
C13	C12	P2	118.4(5)	O2A	P1A	C5	111.4(8)
N2	C13	C12	123.1(6)	O2A	P1A	O1A	110.3(10)
C10	C14	C15	120.5(6)	O2A	P1A	O3A	113.7(12)
N2	C14	C10	122.4(6)	O3A	P1A	C5	102.4(8)
N2	C14	C15	117.0(6)	O3A	P1A	O1A	109.6(10)
C7	C15	C14	120.5(6)	O4	P2	C12	110.9(3)
N1	C15	C7	122.6(6)	O4	P2	O5	118.2(3)
N1	C15	C14	116.9(6)	O4	P2	O6	112.9(3)
N1	C16	C5	121.7(7)	O5	P2	C12	100.1(3)
O6	C17	C18	111.7(12)	O6	P2	C12	109.8(3)
O5	C17A	C18A	114.9(19)	O6	P2	O5	103.9(3)
O5	C19	C20	107.8(16)	N1	Cu1	N2	81.9(2)
O6	C19A	C20A	104.3(13)	N1	Cu1	O4[2]	92.4(2)
C15	N1	Cu1	112.4(4)	N2	Cu1	O4[2]	103.0(2)
C16	N1	C15	119.2(6)	O8	Cu1	N1	175.5(2)
C16	N1	Cu1	128.4(5)	O8	Cu1	N2	94.4(2)
C13	N2	C14	118.4(6)	O8	Cu1	O4[2]	86.0(2)
C13	N2	Cu1	129.9(5)	O8	Cu1	O11	92.4(2)

C14	N2	Cu1	111.6(4)	O11	Cu1	N1	91.8(2)
O7	N3	O8	118.9(5)	O11	Cu1	N2	164.9(2)
O9	N3	O7	123.0(6)	O11	Cu1	O4[2]	90.9(2)
O9	N3	O8	118.0(6)				

[1]1-X,1/2+Y,3/2-Z; [2]1-X,-1/2+Y,3/2-Z

Table S16. Torsion Angles for **3-II**.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C1	O1	P1	C5	89.6(14)	C11	C12	P2	O5	32.8(6)
C1	O1	P1	O2	-35.1(18)	C11	C12	P2	O6	-76.1(6)
C1	O1	P1	O3	-162.0(13)	C12	C13	N2	C14	0.9(10)
C1	O1A	P1A	C5	-69.0(15)	C12	C13	N2	Cu1	-175.5(5)
C1	O1A	P1A	O2A	168.2(13)	C13	C12	P2	O4	-20.4(6)
C1	O1A	P1A	O3A	42.3(17)	C13	C12	P2	O5	-146.0(5)
C2	C1	O1	P1	122.5(13)	C13	C12	P2	O6	105.1(6)
C2	C1	O1A	P1A	-124.2(13)	C14	C10	C11	C12	-2.2(10)
C3	O3	P1	C5	-163.8(17)	C14	C15	N1	C16	-177.1(7)
C3	O3	P1	O1	85(2)	C14	C15	N1	Cu1	1.2(8)
C3	O3	P1	O2	-42(2)	C15	C7	C8	C9	3.6(12)
C3A	O3A	P1A	C5	-156.6(11)	C15	C14	N2	C13	178.8(6)
C3A	O3A	P1A	O1A	87.7(15)	C15	C14	N2	Cu1	-4.2(7)
C3A	O3A	P1A	O2A	-36.3(16)	C16	C5	C6	C7	1.8(14)
C4	C3	O3	P1	-94(2)	C16	C5	P1	O1	121.5(11)
C4A	C3A	O3A	P1A	-96(2)	C16	C5	P1	O2	-109.2(12)
C5	C6	C7	C8	-179.7(8)	C16	C5	P1	O3	17.1(14)
C5	C6	C7	C15	1.1(12)	C16	C5	P1A	O1A	171.0(9)
C5	C16	N1	C15	1.1(12)	C16	C5	P1A	O2A	-66.9(12)
C5	C16	N1	Cu1	-177.0(6)	C16	C5	P1A	O3A	54.9(12)
C6	C5	C16	N1	-3.0(14)	C17	O6	P2	C12	-99.0(10)
C6	C5	P1	O1	-58.8(12)	C17	O6	P2	O4	25.4(10)
C6	C5	P1	O2	70.5(13)	C17	O6	P2	O5	154.7(9)
C6	C5	P1	O3	-163.2(11)	C17A	O5	P2	C12	-164.4(14)
C6	C5	P1A	O1A	-20.0(12)	C17A	O5	P2	O4	75.1(14)
C6	C5	P1A	O2A	102.1(11)	C17A	O5	P2	O6	-50.9(14)
C6	C5	P1A	O3A	-136.1(11)	C18	C17	O6	P2	-135.9(13)
C6	C7	C8	C9	-175.6(8)	C18A	C17A	O5	P2	108(2)
C6	C7	C15	C14	176.0(7)	C19	O5	P2	C12	-170.2(13)
C6	C7	C15	N1	-3.1(11)	C19	O5	P2	O4	69.3(14)
C7	C8	C9	C10	-2.2(12)	C19	O5	P2	O6	-56.7(13)
C7	C15	N1	C16	2.0(11)	C19A	O6	P2	C12	-109.4(12)
C7	C15	N1	Cu1	-179.6(5)	C19A	O6	P2	O4	15.0(13)
C8	C7	C15	C14	-3.2(11)	C19A	O6	P2	O5	144.2(12)
C8	C7	C15	N1	177.6(7)	C20	C19	O5	P2	118.7(16)
C8	C9	C10	C11	178.3(7)	C20A	C19A	O6	P2	-112.3(15)
C8	C9	C10	C14	0.3(11)	N2	C14	C15	C7	-177.1(6)
C9	C10	C11	C12	179.8(7)	N2	C14	C15	N1	2.1(9)
C9	C10	C14	C15	0.1(10)	O7	N3	O8	Cu1	12.4(7)

C9	C10	C14	N2	178.6(6)	O9	N3	O8	Cu1	-165.5(5)
C10	C11	C12	C13	3.2(10)	O10	N4	O11	Cu1	-0.2(7)
C10	C11	C12	P2	-175.5(5)	O12	N4	O11	Cu1	-178.7(6)
C10	C14	C15	C7	1.5(10)	P1	C5	C6	C7	-177.9(8)
C10	C14	C15	N1	-179.3(6)	P1	C5	C16	N1	176.7(7)
C10	C14	N2	C13	0.2(9)	P1A	C5	C6	C7	-167.1(7)
C10	C14	N2	Cu1	177.2(5)	P1A	C5	C16	N1	165.9(7)
C11	C10	C14	C15	-178.1(6)	P2	C12	C13	N2	176.2(5)
C11	C10	C14	N2	0.5(10)	Cu1[1]	O4	P2	C12	-135.8(5)
C11	C12	C13	N2	-2.6(10)	Cu1[1]	O4	P2	O5	-21.1(7)
C11	C12	P2	O4	158.3(6)	Cu1[1]	O4	P2	O6	100.4(5)

[1]1-X,1/2+Y,3/2-Z

Table S17. Crystal data and structure refinement for **4**.

Empirical formula	$C_{40}H_{52}Cu_2N_8O_{24}P_4$
Formula weight	1279.85
Temperature/K	115
Crystal system	triclinic
Space group	P-1
a/Å	9.6399(12)
b/Å	12.1111(14)
c/Å	12.1162(16)
α/°	77.046(6)
β/°	88.932(6)
γ/°	77.832(6)
Volume/Å^3	1347.0(3)
Z	1
ϱ_{calc}g/cm^3	1.578
μ/mm^{-1}	0.997
F(000)	658.0
Crystal size/mm^3	0.35 × 0.25 × 0.25
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.452 to 55.314
Index ranges	-12 ≤ h ≤ 12, -15 ≤ k ≤ 15, -15 ≤ l ≤ 15
Reflections collected	34624
Independent reflections	6260 [R_{int} = 0.0527, R_{sigma} = 0.0392]
Data/restraints/parameters	6260/0/356
Goodness-of-fit on F^2	1.050
Final R indexes [I>=2σ (I)]	R_1 = 0.0336, wR_2 = 0.0756
Final R indexes [all data]	R_1 = 0.0495, wR_2 = 0.0813
Largest diff. peak/hole / e Å^{-3}	0.56/-0.47

Table S18. Bond Lengths for **4**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cu1	O2	1.9766(14)	O8	C15	1.477(3)
Cu1	O10[1]	2.2428(14)	O3	N17	1.226(2)
Cu1	N7	2.0185(17)	N16	C6	1.360(2)
Cu1	O5	1.9698(15)	N16	C12	1.326(2)
Cu1	N16	2.0094(16)	C5	C4	1.402(3)
P2	O12	1.5601(15)	C5	C6	1.434(3)
P2	O10	1.4723(14)	C3	C4	1.427(3)
P2	O11	1.5597(15)	C3	C2	1.381(3)
P2	C10	1.8073(19)	C4	C7	1.438(3)
P1	O9	1.5752(17)	C9	C10	1.426(3)
P1	O7	1.4626(16)	C9	C6	1.401(3)
P1	O8	1.5677(17)	C9	C8	1.435(3)
P1	C3	1.812(2)	O6	N18	1.218(3)
O12	C19	1.456(3)	C11	C10	1.375(3)
O2	N17	1.301(2)	C11	C12	1.404(3)
O10	Cu1[1]	2.2428(14)	N18	O4	1.219(2)
N7	C5	1.360(2)	C8	C7	1.356(3)
N7	C1	1.328(3)	C1	C2	1.398(3)
O1	N17	1.236(2)	C17	C18	1.490(4)
O5	N18	1.300(2)	C15	C16	1.495(4)
O9	C13	1.458(3)	C13	C14	1.508(4)
O11	C17	1.470(2)	C19	C20	1.454(4)

[1]-X,-Y,1-Z

Table S19. Bond Angles for **4**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O2	Cu1	O10[1]	100.47(6)	C6	N16	Cu1	113.24(12)
O2	Cu1	N7	93.17(6)	C12	N16	Cu1	128.01(14)
O2	Cu1	N16	162.37(6)	C12	N16	C6	118.68(16)
N7	Cu1	O10[1]	88.04(6)	N7	C5	C4	123.58(18)
O5	Cu1	O2	93.84(6)	N7	C5	C6	115.81(17)
O5	Cu1	O10[1]	84.61(6)	C4	C5	C6	120.61(17)
O5	Cu1	N7	170.65(6)	C4	C3	P1	122.91(15)
O5	Cu1	N16	93.57(6)	C2	C3	P1	118.53(16)
N16	Cu1	O10[1]	96.13(6)	C2	C3	C4	118.56(19)
N16	Cu1	N7	81.46(7)	C5	C4	C3	116.95(17)
O12	P2	C10	100.80(9)	C5	C4	C7	118.04(18)
O10	P2	O12	115.90(8)	C3	C4	C7	125.01(19)
O10	P2	O11	108.67(8)	C10	C9	C8	125.01(17)
O10	P2	C10	113.53(8)	C6	C9	C10	116.93(18)
O11	P2	O12	109.73(8)	C6	C9	C8	118.06(17)
O11	P2	C10	107.77(8)	C10	C11	C12	120.32(18)
O9	P1	C3	106.17(9)	C9	C10	P2	120.12(15)
O7	P1	O9	116.50(10)	C11	C10	P2	121.18(15)
O7	P1	O8	117.80(10)	C11	C10	C9	118.70(17)
O7	P1	C3	110.78(10)	O6	N18	O5	118.34(19)
O8	P1	O9	98.70(9)	O6	N18	O4	123.7(2)
O8	P1	C3	105.49(9)	O4	N18	O5	118.00(18)
C19	O12	P2	121.25(15)	N16	C6	C5	116.24(17)
N17	O2	Cu1	110.54(11)	N16	C6	C9	123.44(18)
P2	O10	Cu1[1]	137.47(9)	C9	C6	C5	120.31(18)
C5	N7	Cu1	113.19(13)	C7	C8	C9	121.75(18)
C1	N7	Cu1	128.49(14)	C8	C7	C4	121.17(19)
C1	N7	C5	118.28(18)	N7	C1	C2	122.47(18)
N18	O5	Cu1	114.01(12)	N16	C12	C11	121.91(18)
C13	O9	P1	120.17(17)	C3	C2	C1	120.14(19)
C17	O11	P2	122.86(14)	O11	C17	C18	106.56(19)
C15	O8	P1	119.11(14)	O8	C15	C16	110.75(19)
O1	N17	O2	118.72(16)	O9	C13	C14	108.4(2)
O3	N17	O2	118.02(18)	C20	C19	O12	109.9(2)
O3	N17	O1	123.25(19)				

[1]-X,-Y,1-Z

Table S20. Torsion Angles for **4**.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Cu1	O2	N17	O1	3.1(2)	O7	P1	C3	C4	178.62(18)
Cu1	O2	N17	O3	-176.19(15)	O7	P1	C3	C2	-1.5(2)
Cu1	N7	C5	C4	179.60(15)	O8	P1	O9	C13	-171.27(18)
Cu1	N7	C5	C6	0.1(2)	O8	P1	C3	C4	-52.9(2)
Cu1	N7	C1	C2	-178.15(15)	O8	P1	C3	C2	127.05(17)
Cu1	O5	N18	O6	179.42(18)	C5	N7	C1	C2	-0.5(3)
Cu1	O5	N18	O4	-0.7(2)	C5	C4	C7	C8	1.8(3)
Cu1	N16	C6	C5	-2.7(2)	C3	P1	O9	C13	79.72(19)
Cu1	N16	C6	C9	178.55(15)	C3	P1	O8	C15	-64.78(17)
Cu1	N16	C12	C11	-177.88(14)	C3	C4	C7	C8	-178.4(2)
P2	O12	C19	C20	175.2(2)	C4	C5	C6	N16	-177.75(17)
P2	O11	C17	C18	-148.30(19)	C4	C5	C6	C9	1.0(3)
P1	O9	C13	C14	170.56(19)	C4	C3	C2	C1	0.3(3)
P1	O8	C15	C16	115.4(2)	C9	C8	C7	C4	0.3(3)
P1	C3	C4	C5	-179.43(15)	C10	P2	O12	C19	-166.3(2)
P1	C3	C4	C7	0.8(3)	C10	P2	O10	Cu1[1]	-48.58(15)
P1	C3	C2	C1	-179.58(16)	C10	P2	O11	C17	50.24(17)
O12	P2	O10	Cu1[1]	67.43(14)	C10	C9	C6	N16	-0.5(3)
O12	P2	O11	C17	-58.66(17)	C10	C9	C6	C5	-179.19(17)
O12	P2	C10	C9	179.20(15)	C10	C9	C8	C7	178.55(19)
O12	P2	C10	C11	-1.02(18)	C10	C11	C12	N16	0.1(3)
O10	P2	O12	C19	70.7(2)	C6	N16	C12	C11	-1.2(3)
O10	P2	O11	C17	173.67(15)	C6	C5	C4	C3	177.80(18)
O10	P2	C10	C9	-56.18(18)	C6	C5	C4	C7	-2.5(3)
O10	P2	C10	C11	123.59(16)	C6	C9	C10	P2	179.27(14)
N7	C5	C4	C3	-1.7(3)	C6	C9	C10	C11	-0.5(3)
N7	C5	C4	C7	178.08(18)	C6	C9	C8	C7	-1.7(3)
N7	C5	C6	N16	1.8(2)	C8	C9	C10	P2	-1.0(3)
N7	C5	C6	C9	-179.47(17)	C8	C9	C10	C11	179.19(18)
N7	C1	C2	C3	-0.5(3)	C8	C9	C6	N16	179.76(17)
O9	P1	O8	C15	-174.34(16)	C8	C9	C6	C5	1.1(3)
O9	P1	C3	C4	51.3(2)	C1	N7	C5	C4	1.6(3)
O9	P1	C3	C2	-128.84(18)	C1	N7	C5	C6	-177.92(17)
O11	P2	O12	C19	-52.9(2)	C12	N16	C6	C5	-179.92(17)
O11	P2	O10	Cu1[1]	-168.49(11)	C12	N16	C6	C9	1.4(3)
O11	P2	C10	C9	64.24(17)	C12	C11	C10	P2	-179.08(15)
O11	P2	C10	C11	-115.99(16)	C12	C11	C10	C9	0.7(3)
O7	P1	O9	C13	-44.1(2)	C2	C3	C4	C5	0.7(3)
O7	P1	O8	C15	59.43(19)	C2	C3	C4	C7	-179.1(2)

[1]-X,-Y,1-Z

Table S21. Continuous Shape Measure values ($S_{Q(P)}$) calculated for the coordination polyhedra of complexes **1**, **2**, **3-I**, **3-II** and **4**. Limiting values corresponding to the ideal reference geometries are also included.[a]

Polyhedron (Q)	S_Q(HP-6)	S_Q (PPY-6)	S_Q (OC-6)	S_Q (TPR-6)	S_Q (JPPY-6)
1	32.467	23.631	**1.813**	12.232	26.679
Polyhedron (Q)	S_Q (PP-5)	S_Q (vOC-5)	S_Q (TBPY-5)	S_Q (SPY-5)	S_Q (JTBPY-5)
2	30.167	**1.206**	4.019	1.474	6.741
3-I	30.372	**0.529**	6.019	1.044	8.083
3-II	29.173	**1.105**	4.295	1.503	6.883
4	31.524	**1.422**	3.176	1.789	5.967

[a] Bold-faced numbers correspond to the lowest $S_Q(P)$ values calculated according to Equation (1) by the Shape 2.1 program. Taken into account ideal reference geometries (P) are: the Hexagon (HP), the Pentagonal pyramid (PPY), the Octahedron (OC), Trigonal prism (TPR), Johnson pentagonal pyramid (JPPY), Pentagon (PP), Vacant octahedron (vOC), Trigonal bipyramid (TBPY), Spherical square pyramid (SPY) and Johnson trigonal bipyramid (JTBPY).

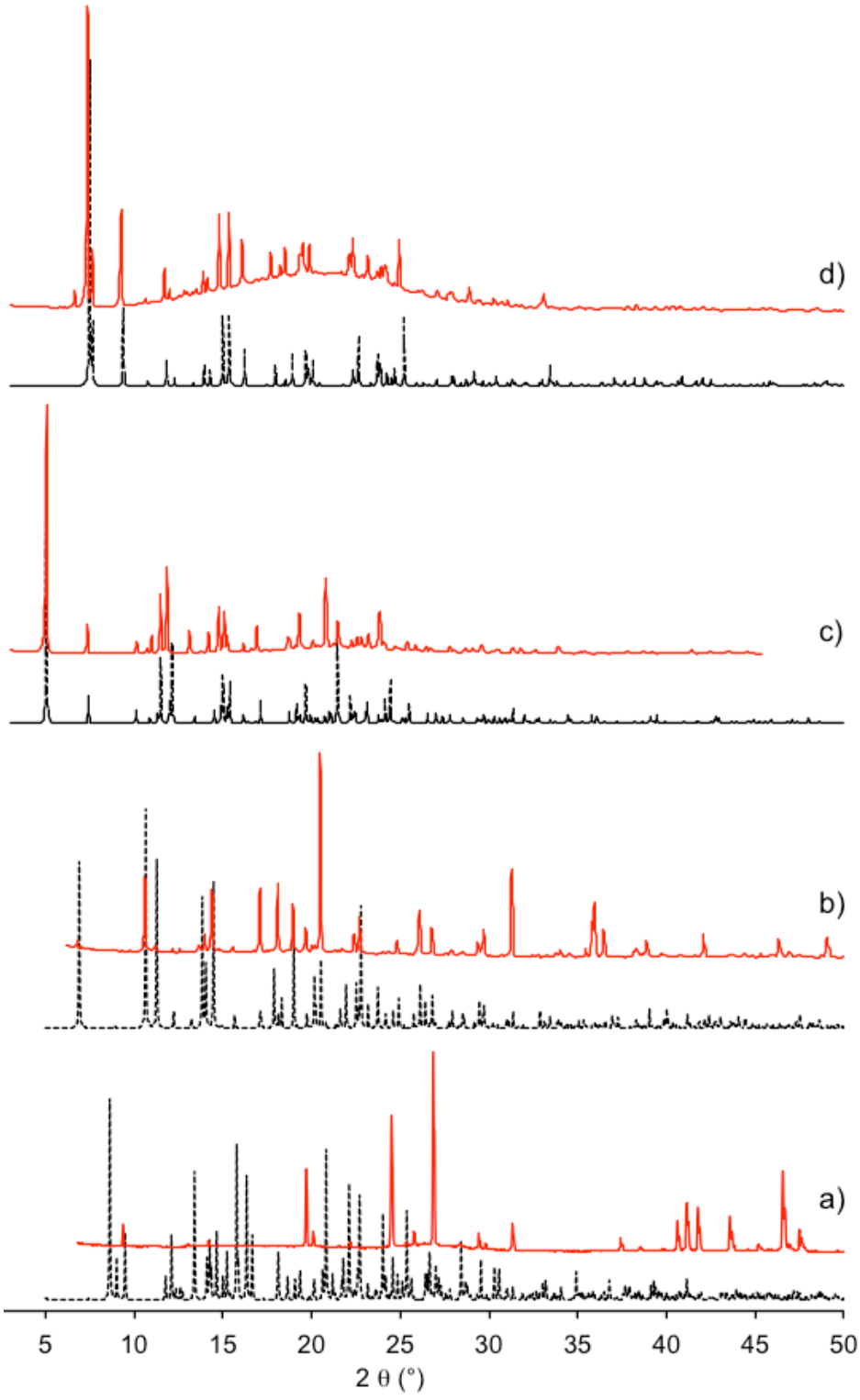


Figure S7. Experimental PXRD patterns (red) recorded at 298 K for a) **1**, b) **2**, c) **3-II** and d) **4** compared to the simulated ones (black dashed).[1]

[1] Discrepencies between experimental and simulated data observed for **1** and **3** arise from a possible preferential orientation of the microcrystals on the flat Kapton foil.

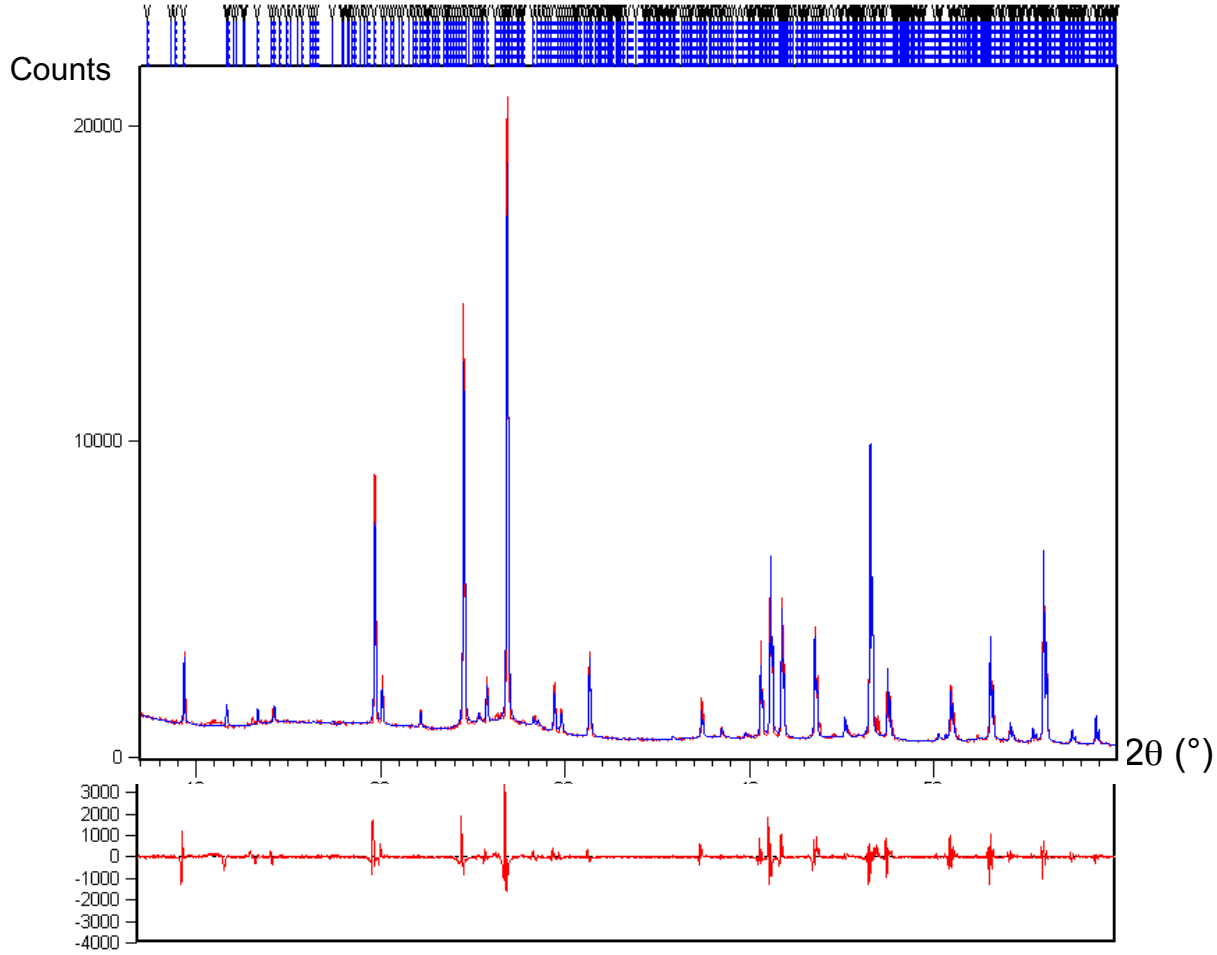


Figure S8. PXRD pattern for **1** (red) recorded at 298 K and view of the Lebail fit (blue).

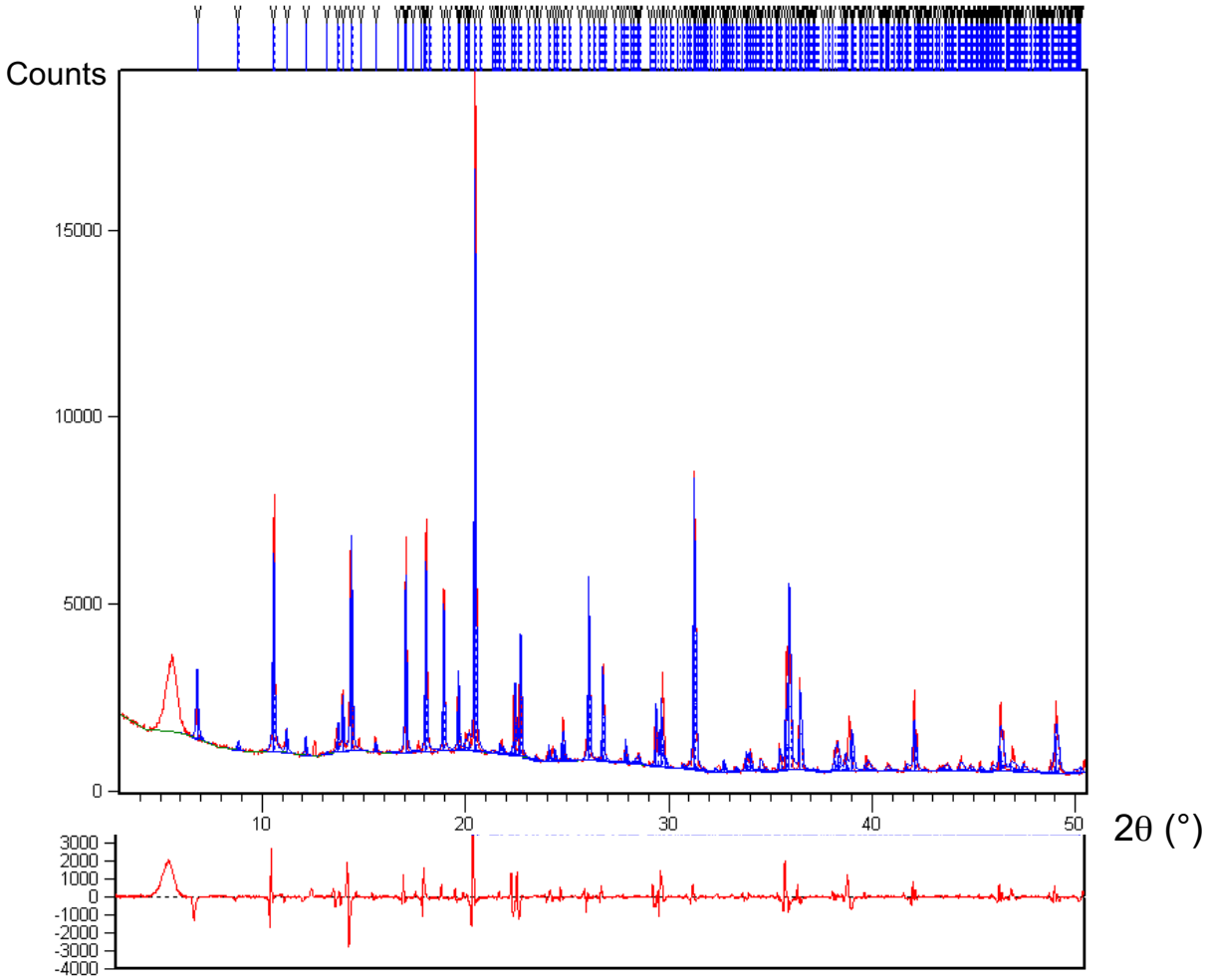


Figure S9. PXRD pattern for **2** (red) recorded at 298 K and view of the Lebail fit (blue).

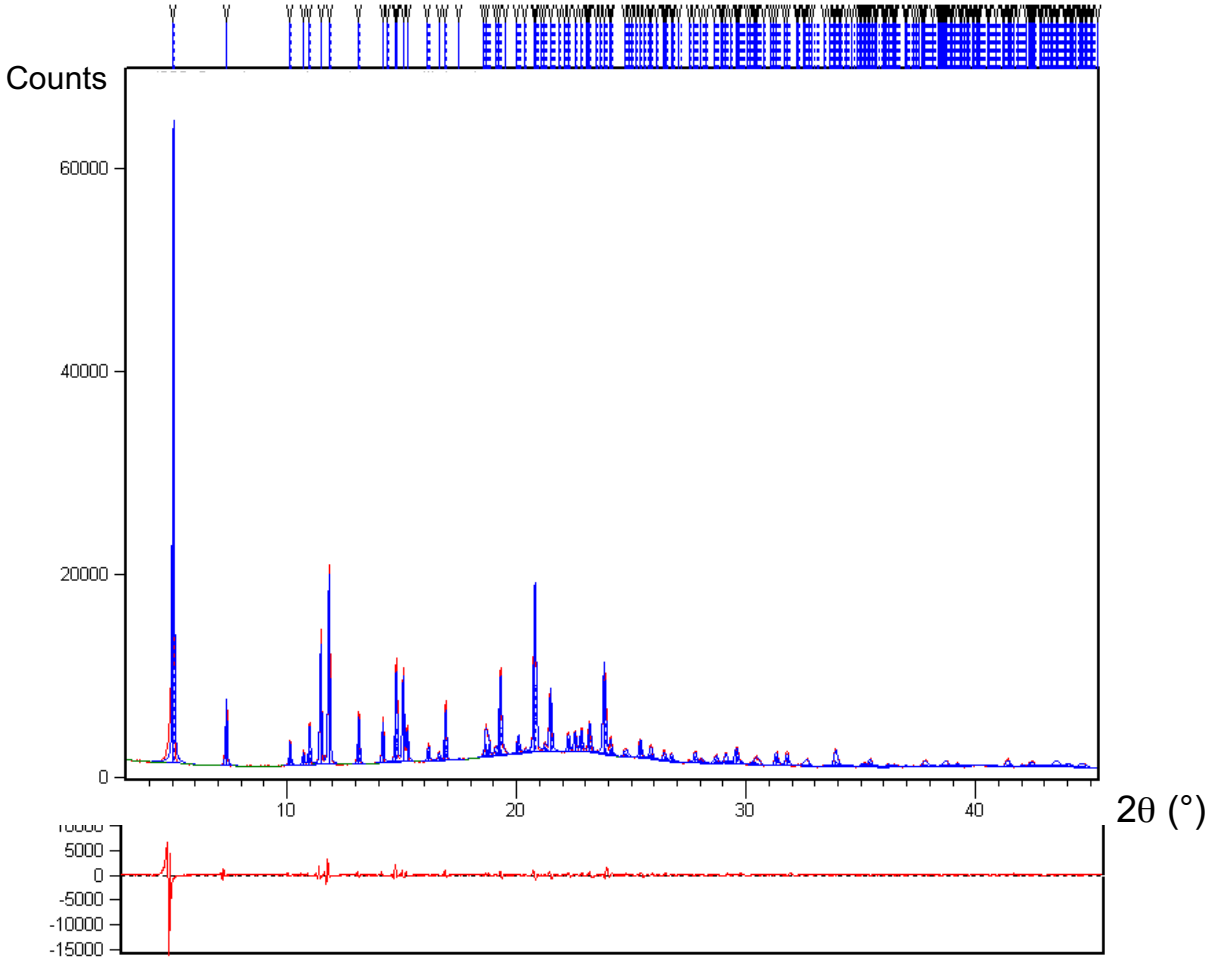


Figure S10. PXRD pattern for **3-II** (red) recorded at 298 K and view of the Lebail fit (blue).

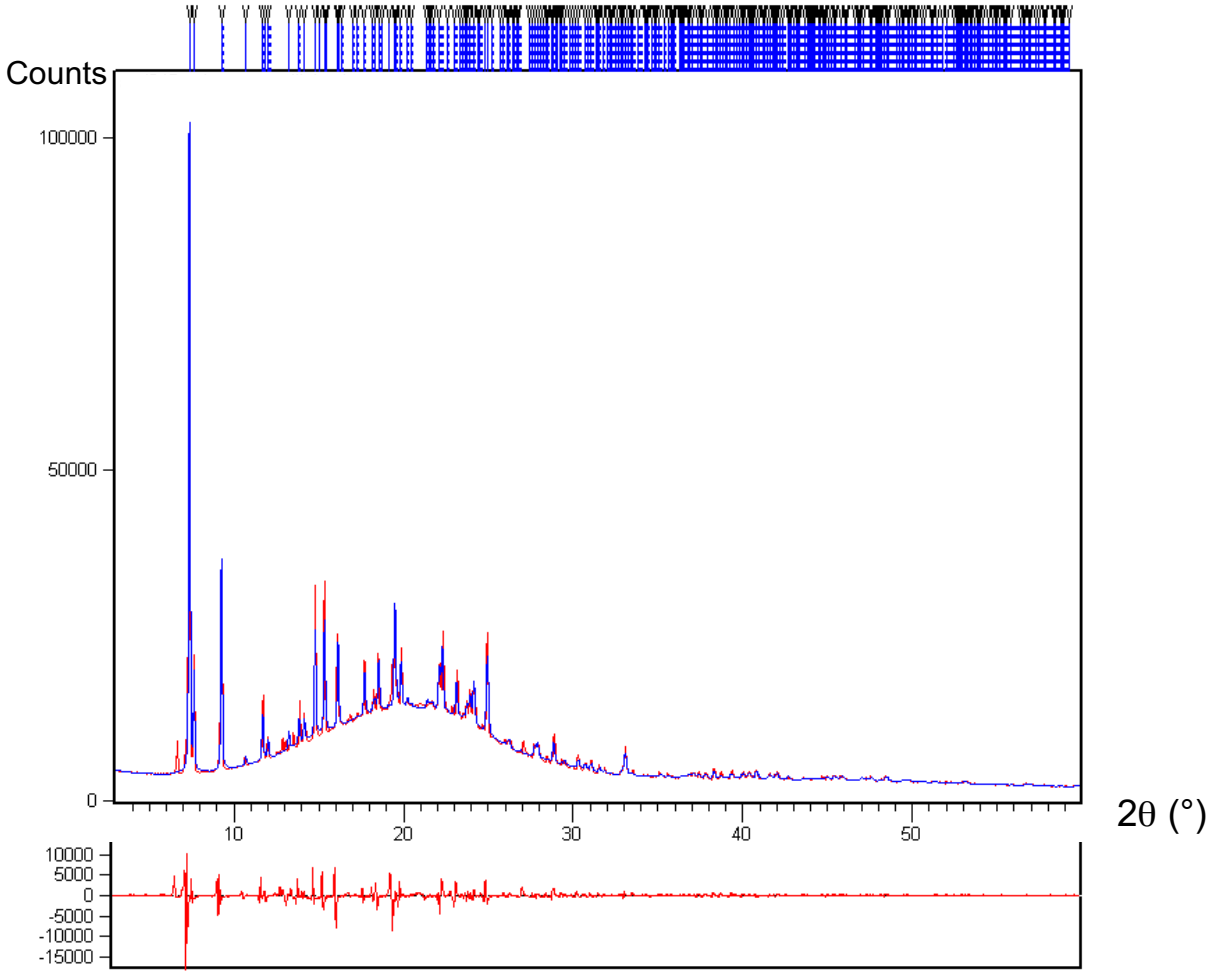


Figure S11. PXRD pattern for **4** (red) recorded at 298 K and view of the Lebail fit (blue).

Table S22. Single-crystal X-ray data and PXRD crystal data calculated using Lebail fit for **1**, **2**, **3-II** and **4**.

Unit cell parameters	**1**		**2**		**3-II**		**4**	
	SXRD[a]	PXRD[b]	SXRD[a]	PXRD[b]	SXRD[a]	PXRD[b]	SXRD[a]	PXRD[b]
Space group	$P2_1/c$	$P2_1/c$	Pbca	Pbca	Pbca	Pbca	P–1	P–1
a / Å	18.637	18.708	15.681	15.665	16.251	16.469	9.640	9.753
b / Å	7.939	7.929	10.581	10.571	9.204	9.550	12.111	12.128
c / Å	23.778	23.601	25.571	25.589	34.903	34.812	12.116	12.300
α / °	90	90	90	90	90	90	77.05	76.72
β / °	92.77	91.99	90	90	90	90	88.93	88.75
γ / °	90	90	90	90	90	90	77.83	77.77
R_{Bragg}		1.3%		1.8%		1.1%		2.3%

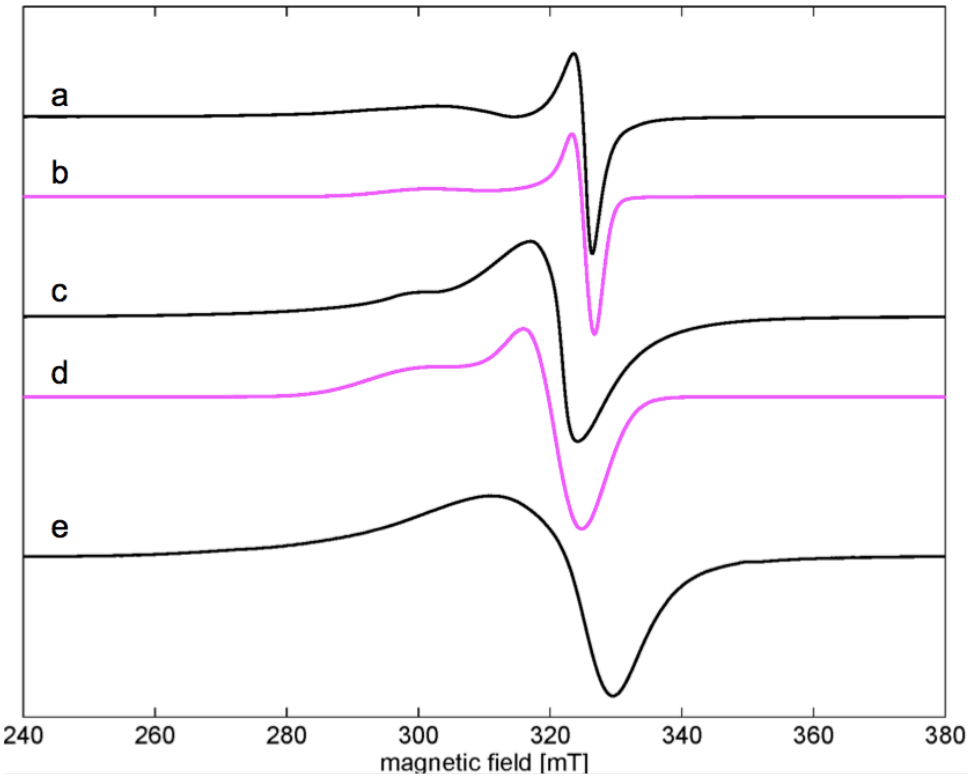


Figure S12. X-band EPR powder spectra recorded at 100 K for a) **3-II**, c) **2**, e) **4** and b), d) simulated spectra corresponding to **3-II** and **2**, respectively.

Table S23. X-Band EPR data for **2** and **3-II** in the solid state at 100 K.[a]

Complex	M : L	*g*			
		g_x	g_y	g_z	g_{iso} [b]
2	1:1	2.075	2.105	2.260	2.147
3-II	1:1	2.072	2.072	2.250	2.131

[a] Spectra were recorded in the solid state at 100 K. The simulation of g_i for compound **4** was not possible due to broadening of the signals (Figure S12). [b] Calculated values : $g_{iso} = (g_x + g_y + g_z)/3$.

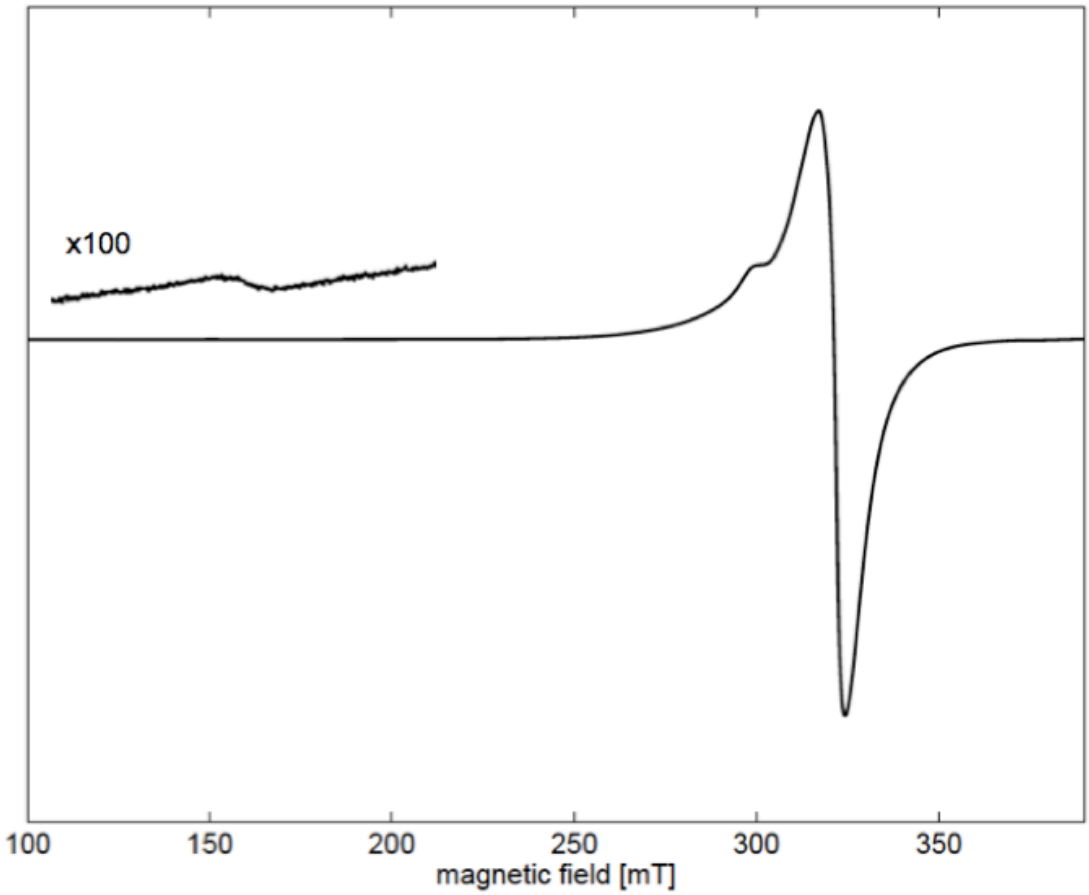


Figure S13**.** X-band EPR powder spectrum of complex **3** showing the half field forbidden transition (100 K).

Table S24. X-Band EPR data of copper(II) complexes **3-II** and **4** in the presence of methanol.[a]

Complex	M : L	*gb*				A^{Cu} x10^4 cm^{-1}			A^N x 10^4 cm^{-1}			g_z/A_z cm
		g_x	g_y	g_z	g_{iso}[b]	A_x	A_y	A_z	A'_x	A'_y	$'A_z$	
3-II	1:1	2.072	2.073	2.334	2.160	≈ 2	≈ 2	154.4	13.0	13.0	13.0	151
4	1:1	2.071	2.071	2.328	2.157	≈ 3	≈ 5	156.1	13.0	13.0	13.0	149

[a] in frozen CH_2Cl_2/toluene (3/1 v/v) solution containing 5 drops of CH_3OH.[b] g_i and A_i parameters were obtained by spectral simulation using Easyspin software.