SUPPORTING INFORMATION

Synthesis and structure of copper(II) complexes with an imine derived from 4-nitroaniline and 2-hydroxy-1-naphthaldehyde

Luka Fotović, Vinko Nemec* and Dominik Cinčić

Department of Chemistry, Faculty of Science, University of Zagreb, Horvatovac 102a, HR-10000 Zagreb, Croatia

Email: vnemec@chem.pmf.hr
Fax: +385 1 4606 341
Tel: +385 1 4606 373

Table of Contents

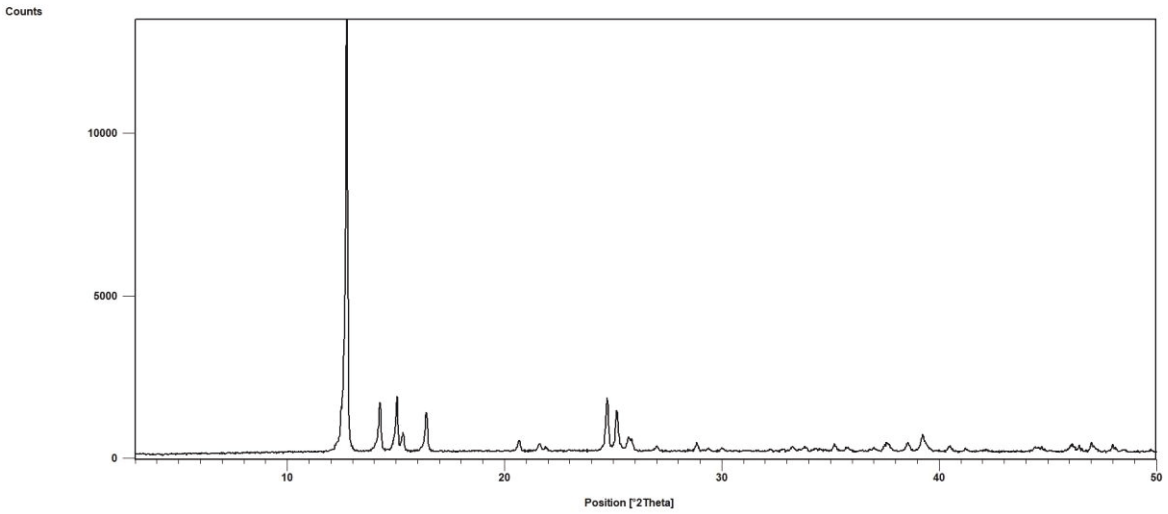

Figure S1. PXRD pattern of **CuOAc**.

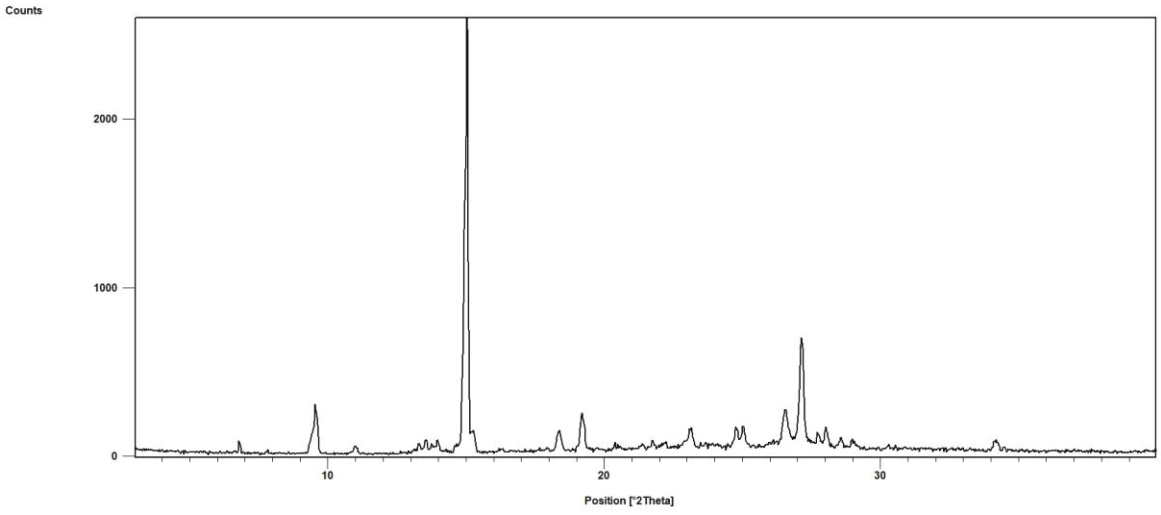

Figure S2. PXRD pattern of **n4noa**.

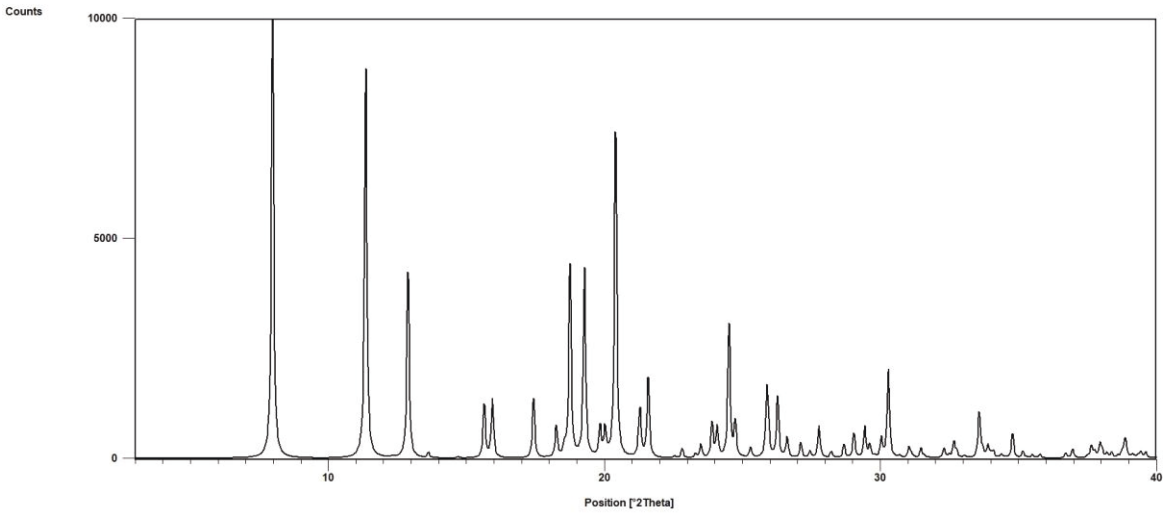

Figure S3. Calculated PXRD pattern of the Cu(**n4noa**)$_2$ complex.

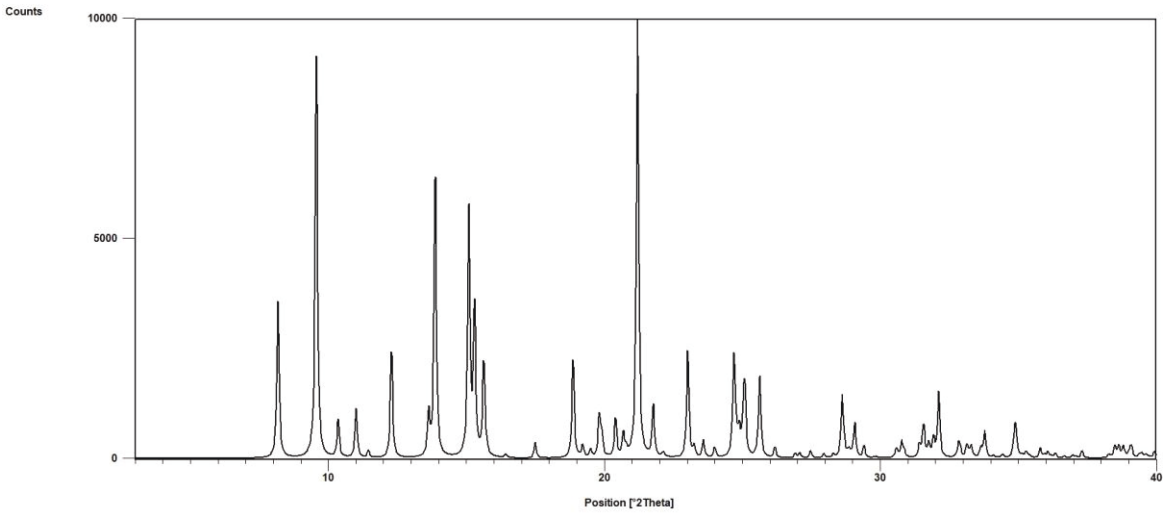

Figure S4. Calculated PXRD pattern of Cu(**n4noa**)$_2$(**py**)$_2$ adduct.

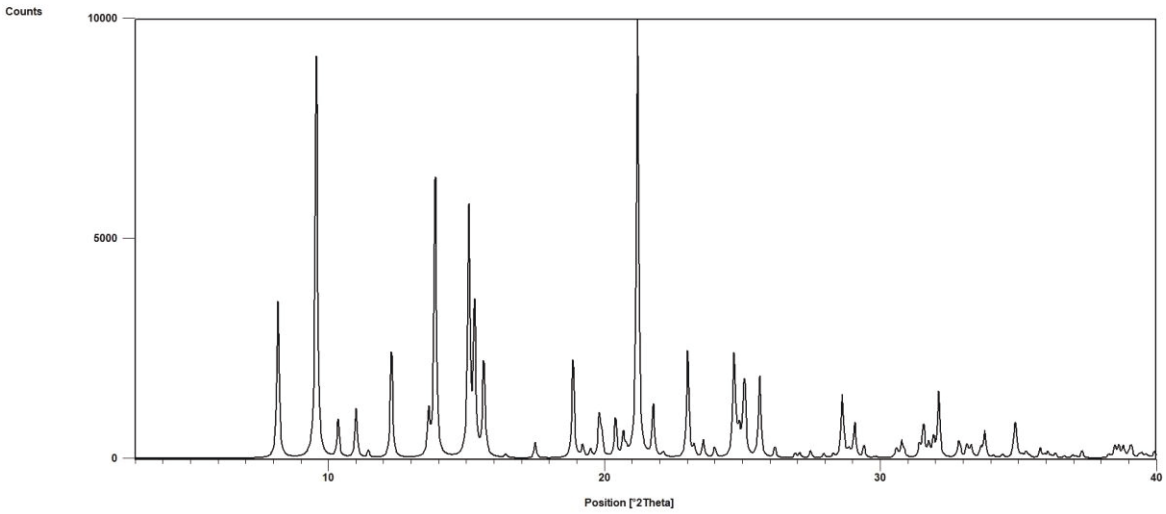

Figure S5. Calculated PXRD pattern of Cu(**n4noa**)$_2$(**thf**)$_2$ adduct.

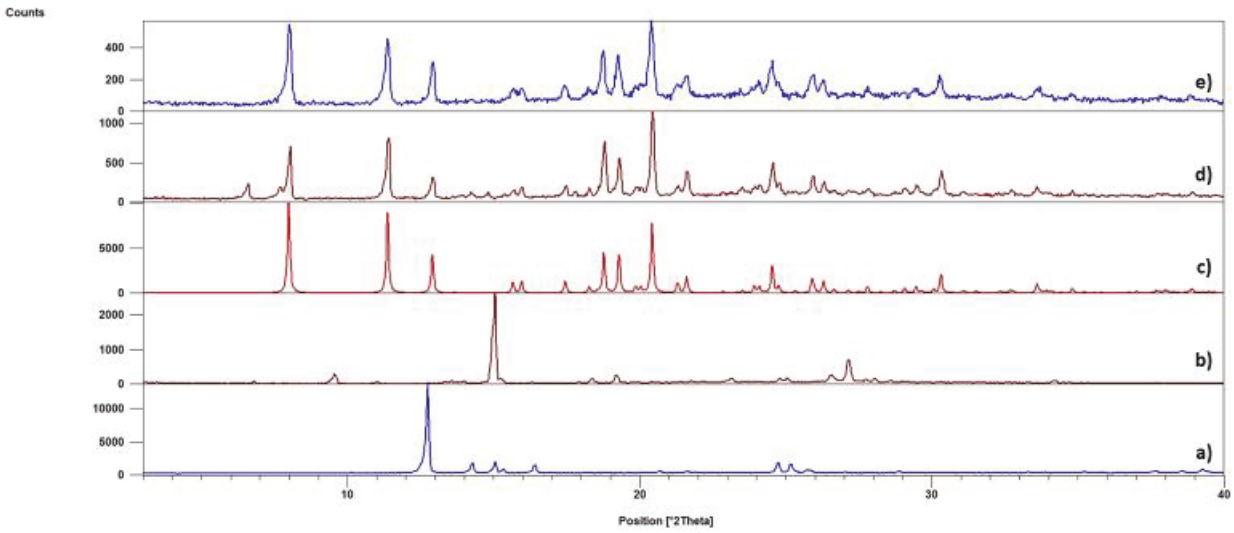

Figure S6. PXRD patterns of: a) **CuOAc**, b) **n4noa**, c) calculated PXRD pattern from Cu(**n4noa**)$_2$ single crystal data, d) product obtained by reflux heating **CuOAc** and **n4noa** in a 1:2 stoichiometric ratio, e) product obtained by liquid-assisted grinding **CuOAc** and **n4noa** in a 1:2 stoichiometric ratio along with stainless steel balls 7 mm in diameter.

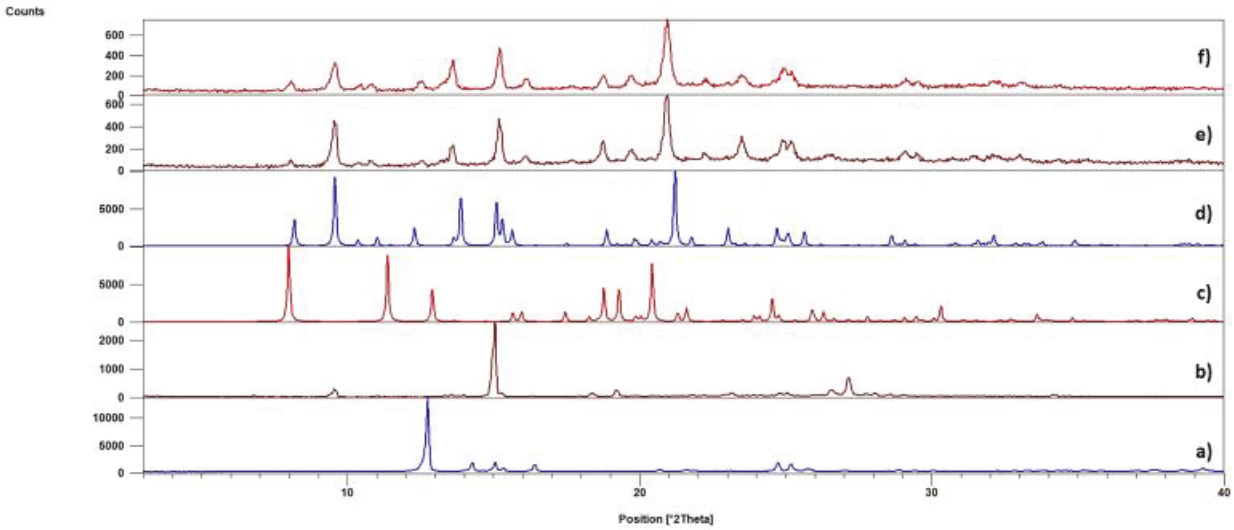

Figure S7. PXRD patterns of: a) **CuOAc**, b) **n4noa**, c) calculated PXRD pattern fromCu(**n4noa**)$_2$ single crystal data, d) calculated PXRD pattern from Cu(**n4noa**)$_2$(**py**)$_2$ single crystal data, e) product obtained by liquid-assisted grinding Cu(**n4noa**)$_2$ and **py** in a 1:2 stoichiometric ratio along with stainless steel balls 7 mm in diameter f) product obtained by liquid-assisted grinding **CuOAc**, **n4noa** and **py** in a 1:2:2 stoichiometric ratio along with stainless steel balls 7 mm in diameter.

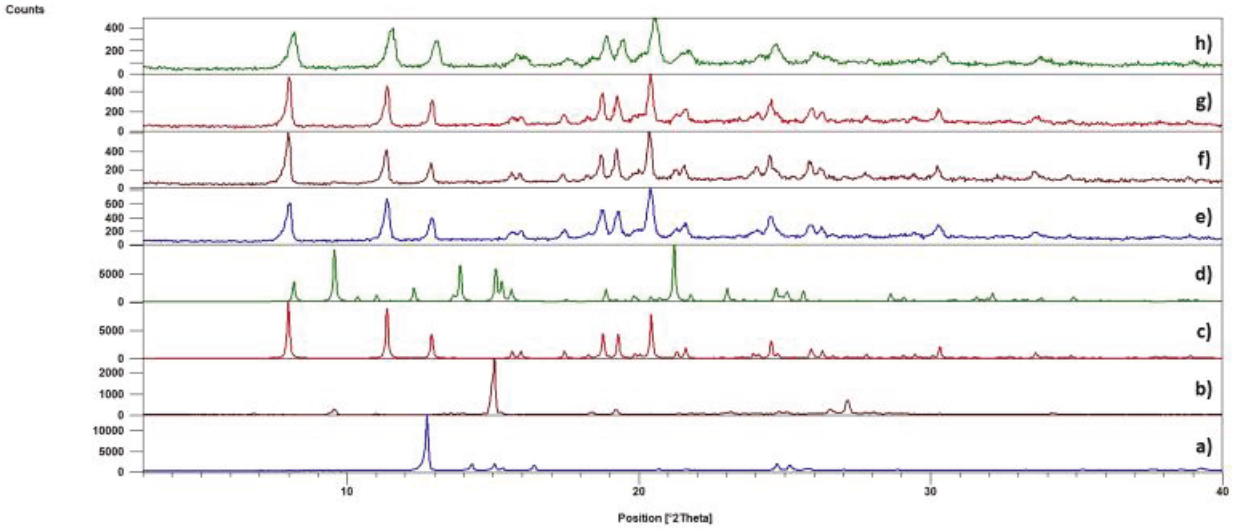

Figure S8. PXRD patterns of: a) **CuOAc**, b) **n4noa**, c) calculated PXRD pattern from Cu(**n4noa**)$_2$ single crystal data, d) calculated PXRD pattern from Cu(**n4noa**)$_2$(**thf**)$_2$ single crystal data, e) product obtained by liquid-assisted grinding Cu(**n4noa**)$_2$ and **thf** in a 1:2 stoichiometric ratio along with stainless steel balls 7 mm in diameter, f) product obtained by liquid-assisted grinding **CuOAc**, **n4noa** and **thf** in a 1:2:2 stoichiometric ratio along with stainless steel balls 7 mm in diameter, g) product obtained by liquid-assisted grinding **CuOAc**, **n4noa** and **thf** in a 1:2:2 stoichiometric ratio with catalytic amount of triethylamine along with stainless steel balls 7 mm in diameter, h) product obtained by liquid-assisted grinding **CuOAc**, **n4noa** and **thf** in a 1:2:2 stoichiometric ratio with catalytic amount of triethylamine along with stainless steel balls 10 mm in diameter.

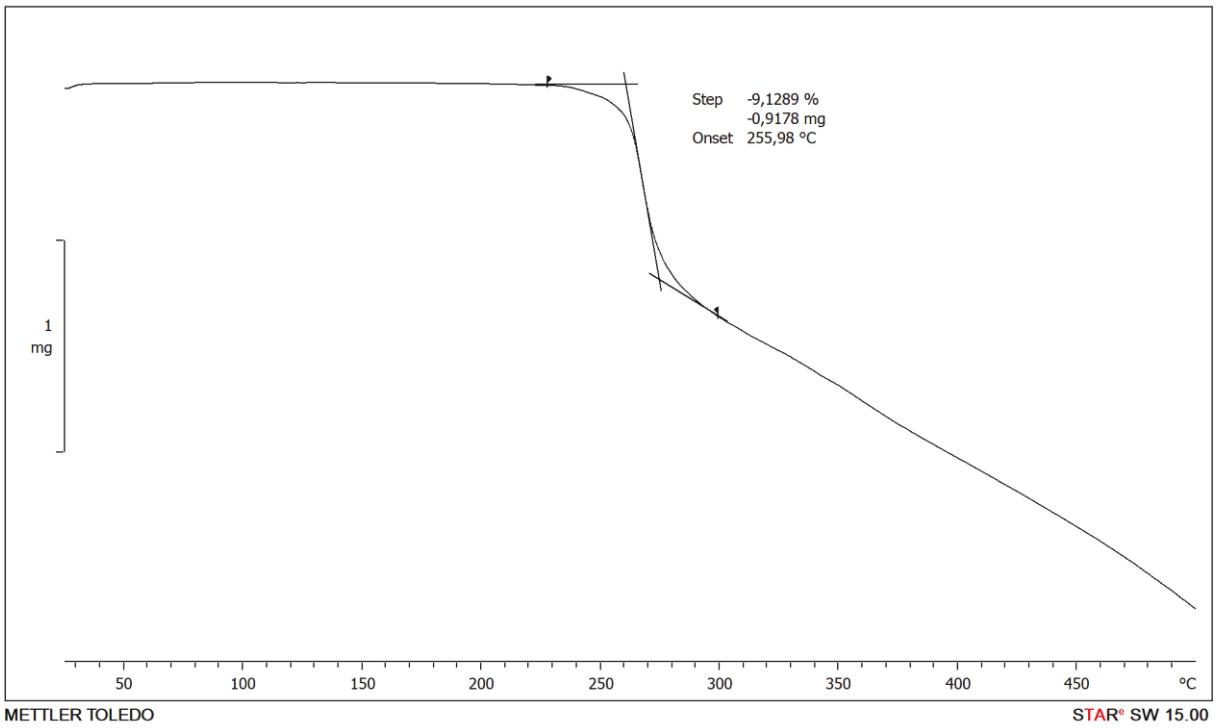

Figure S9. TG curve of Cu(**n4noa**)$_2$(**py**)$_2$.

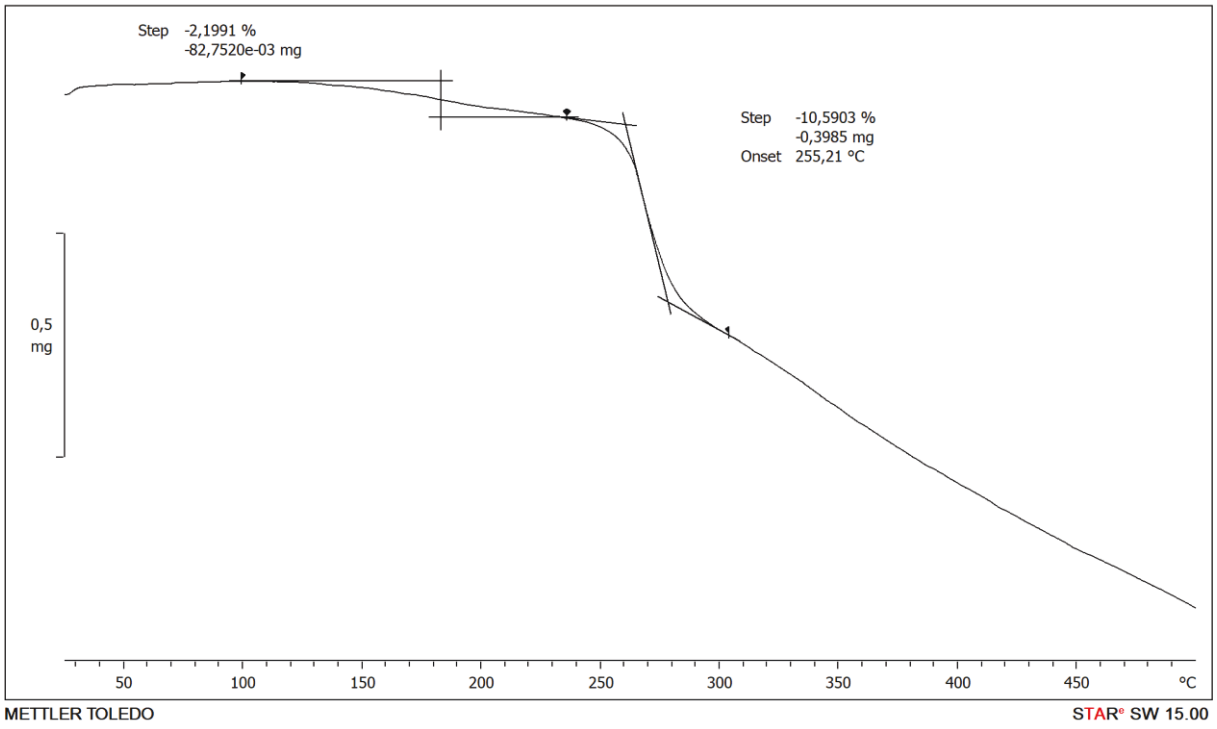

Figure S10. TG curve of Cu(**n4noa**)$_2$(**thf**)$_2$.

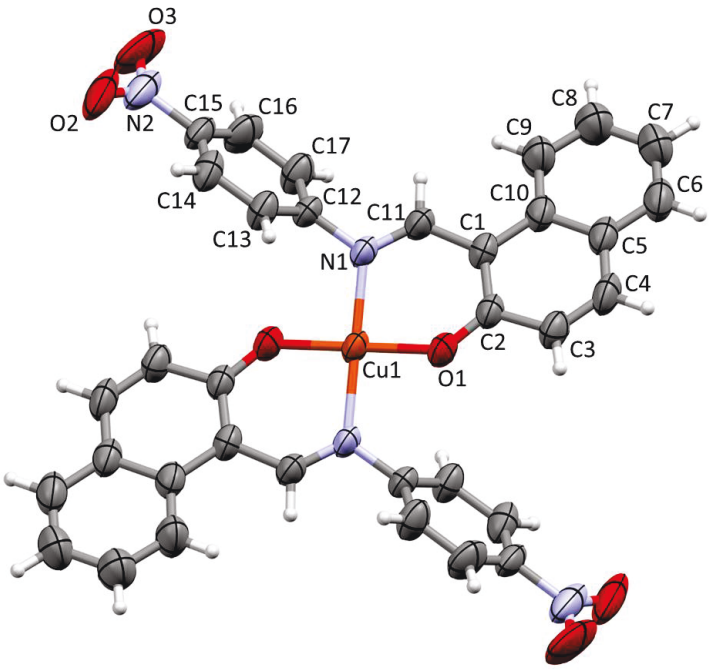

Figure S11. Molecular structure of Cu(**n4noa**)$_2$ showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50 % probability level, and H atoms are shown as small spheres of arbitrary radius.

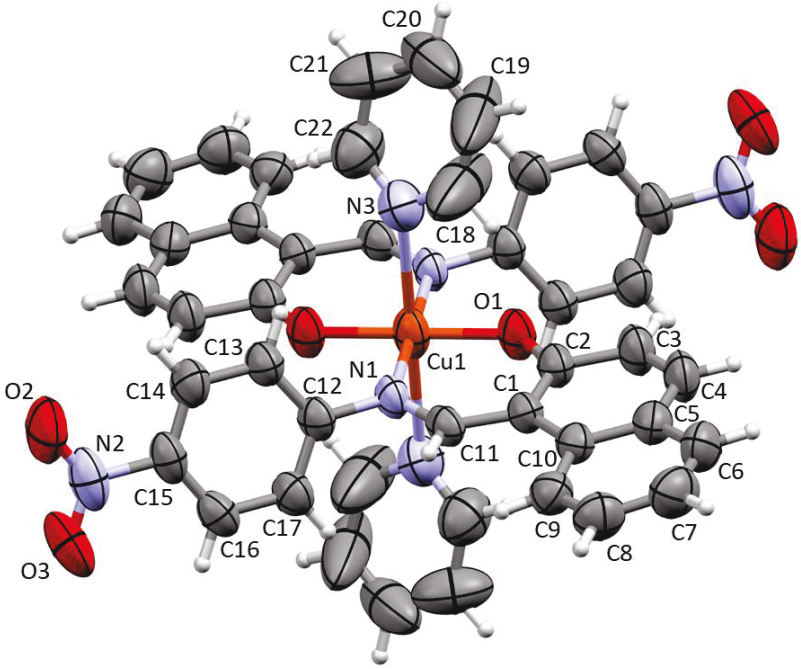

Figure S12. Molecular structure of Cu(**n4noa**)$_2$(**py**)$_2$ showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50 % probability level, and H atoms are shown as small spheres of arbitrary radius.

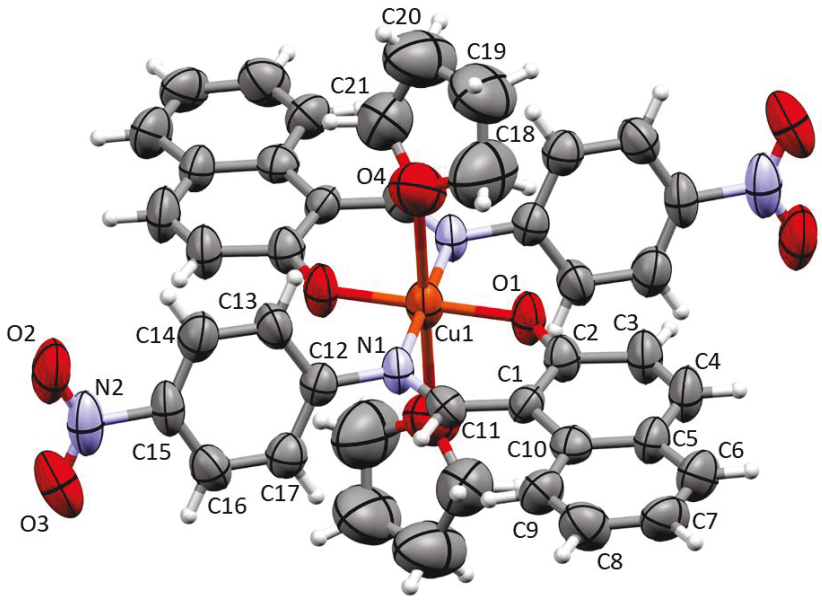

Figure S13. Molecular structure of Cu(**n4noa**)$_2$(**thf**)$_2$ showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50 % probability level, and H atoms are shown as small spheres of arbitrary radius.

Table S1. Crystal data and refinement details for the prepared compounds.

	Cu(**n4noa**)$_2$	Cu(**n4noa**)$_2$(**py**)$_2$	Cu(**n4noa**)$_2$(**thf**)$_2$
Molecular formula	$CuC_{34}N_4O_6H_{22}$	$CuC_{44}N_6O_6H_{32}$	$CuC_{42}N_4O_8H_{38}$
M_r	646.09	804.29	790.30
Crystal system	monoclinic	triclinic	triclinic
Space group	$P\,2_1/c$	$P\,\bar{1}$	$P\,\bar{1}$
Crystal data:			
a / Å	11.1022(5)	9.1696(6)	9.1721(13)
b / Å	9.4550(5)	9.4808(9)	9.5797(13)
c / Å	13.7613(7)	11.6801(8)	11.4448(15)
α / °	90	93.300(7)	96.138(11)
β / °	94.035(4)	108.738(6)	106.446(12)
γ / °	90	100.650(7)	101.543(12)
V / Å^3	1440.96(12)	937.54(13)	930.5(2)
Z	2	1	1
D_{calc} / g cm^{-3}	1.489	1.425	1.410
λ(MoK_α) / Å	0.71073	0.71073	0.71073
T / K	295	295	295
Crystal size / mm^3	0.28 x 0.24 x 0.20	0.26 x 0.21 x 0.16	0.18 x 0.16 x 0.14
μ / mm^{-1}	0.813	0.642	0.647
F(000)	662	415	411
Refl. collected/unique	12984 / 2525	6185 / 3274	7002 / 3241
Data/restraints/ parameters	209	263	254
$\Delta\rho_{max}$, $\Delta\rho_{min}$ / e Å^{-3}	0.821; –0.685	0.282; –0.344	0.413; –0.260
$R[F^2 > 4\sigma(F^2)]$	0.0540	0.0618	0.0767
w$R(F^2)$	0.1545	0.1490	0.2165
Goodness-of-fit, S	1.049	0.999	0.969

Table S2. List of experimental mechanochemical attempts for obtaining the Cu(**n4noa**)$_2$(**thf**)$_2$ adduct.

Reactants (50 mg)	Volume of **thf** / μL	Added additive	Time / min	Grinding balls diameter /mm	Product
Cu(**n4noa**)$_2$	15.5	—	30	2×5	Cu(**n4noa**)$_2$
Cu(**n4noa**)$_2$	15.5	—	45	2×7	Cu(**n4noa**)$_2$
Cu(**n4noa**)$_2$	20	—	45	2×7	Cu(**n4noa**)$_2$
Cu(**n4noa**)$_2$	25	—	45	2×7	Cu(**n4noa**)$_2$
Cu(**n4noa**)$_2$	15.5	Acetone (10 μL)	45	2×5	Cu(**n4noa**)$_2$
Cu(**n4noa**)$_2$	15.5	Triethylamine (10 μL)	45	2×7	Cu(**n4noa**)$_2$
Cu(**n4noa**)$_2$	15.5	Triethylamine (10 μL)	45	10	Cu(**n4noa**)$_2$
Cu(**n4noa**)$_2$	15.5	Nitromethane (10 μL)	45	2×5	Cu(**n4noa**)$_2$
CuOAc + **n4noa**	15.5	—	30	2×5	Cu(**n4noa**)$_2$
CuOAc + **n4noa**	20	—	45	2×7	Cu(**n4noa**)$_2$
CuOAc + **n4noa**	15.5	Acetone (10 μL)	45	2×5	Cu(**n4noa**)$_2$
CuOAc + **n4noa**	15.5	Acetone (10 μL)	45	2×7	Cu(**n4noa**)$_2$
CuOAc + **n4noa**	15.5	Triethylamine (10 μL)	45	10	Cu(**n4noa**)$_2$
CuOAc + **n4noa**	15.5	Nitromethane (10 μL)	45	2×7	Cu(**n4noa**)$_2$

Table S3. Selected bond distances and angles for Cu(**n4noa**)$_2$, Cu(**n4noa**)$_2$(**py**)$_2$ and Cu(**n4noa**)$_2$(**thf**)$_2$.

d **(Å)**		**Angle (°)**	
Cu(**n4noa**)$_2$			
Cu1–O1	1.889(3)	O1–Cu1–N1	90.2(1)
Cu1–N1	1.977(3)	Cu1– O1–C2	129.2(2)
N1–C11	1.293(5)	Cu1– N1–C11	122.6(3)
O1–C2	1.277(4)	Cu1– N1–C12	120.8(2)
C1–C2	1.424(5)	C11– N1–C12	116.4(3)
N1–C12	1.424(4)	C11– C1–C2	119.4(3)
		N1–C11–C1	127.7(3)
		O1–C2–C1	124.1(3)
Cu(**n4noa**)$_2$(**py**)$_2$			
Cu1–O1	1.890(3)	O1–Cu1–N1	89.5(1)
Cu1–N1	2.016(3)	Cu1– O1–C2	132.3(3)
Cu1–N3	2.605(5)	Cu1– N1–C11	124.5(3)
N1–C11	1.291(6)	O1–Cu1–N3	91.7(1)
O1–C2	1.282(6)	N1–Cu1–N3	92.7(1)
C1–C2	1.411(6)	Cu1– N1–C12	118.8(2)
N1–C12	1.421(5)	C11– N1–C12	116.3(4)
		C11– C1–C2	119.6(4)
		N1–C11–C1	128.6(4)
		O1–C2–C1	125.0(4)
Cu(**n4noa**)$_2$(**thf**)$_2$			
Cu1–O1	1.879(4)	O1–Cu1–N1	89.2(2)
Cu1–N1	2.007(5)	Cu1– O1–C2	132.4(5)
Cu1–O4	2.600(8)	Cu1– N1–C11	125.5(4)
N1–C11	1.290(9)	O1–Cu1–O4	90.9(2)
O1–C2	1.275(9)	N1–Cu1–O4	86.9(2)
C1–C2	1.414(8)	Cu1– N1–C12	118.9(4)
N1–C12	1.443(8)	C11– N1–C12	116.3(4)
		C11– C1–C2	119.6(4)
		N1–C11–C1	128.6(4)
		O1–C2–C1	125.0(4)