Electronic Supporting Information

All About That Base: Investigating the Role of Ligand Basicity in Pyridyl Complexes Derived from a Copper-Schiff Base Coordination Polymer

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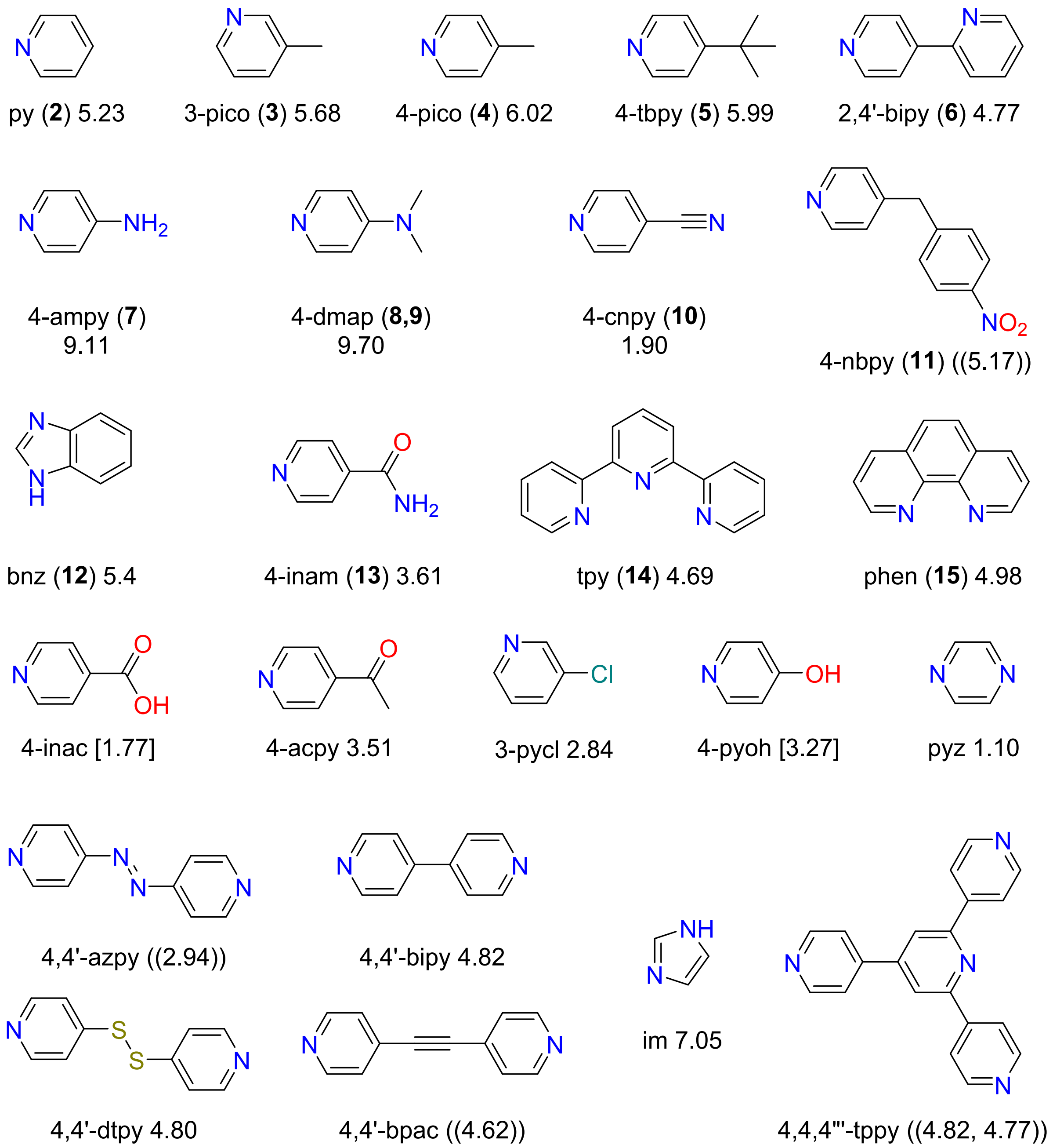
Ligands used in this work



Scheme S1 Ligands used in this study (py – 4,4′-azpy) and those from previous work (4,4′-bipy, 4,4′-dtdp, 4,4′-bpac and 4,4′,4″-tppy;[1] im[2]) along with their pK_a values. Numbers in bold refer to complexes formed with [Cu(**L**)] in this work. pK_a values in square brackets are that for more acidic protons (e.g. –OH and –COOH). Values in double parentheses are estimated pK_a value calculated from Hammett parameters or analogous phenyl compounds.

Synthesis of compounds 2-15

*Synthesis of [Cu(**L**)(py)] (2)*

{[Cu(**L**)]$_2$}$_n$ (27.5 mg, 0.05 mmol) was dissolved in 2 ml pyridine in a vial and 1 ml water added. The vial was placed in a container with a further 10 ml water and allowed to stand for seven days to give brown needle crystals of **2**. As noted by Pfeiffer *et al.*,[3] the crystals are prone to loss of pyridine on isolation.

Crystallisation of **2** can also be achieved as follows: {[Cu(**L**)]$_2$}$_n$ (27.5 mg, 0.05 mmol) was dissolved in 5 ml DMSO at a hotplate temperature of 170 °C and allowed to cool to room temperature. Pyridine (158 mg, 2.0 mmol, 162 µl) was added and the vial placed in a covered beaker of water for 12 days, after which, brown crystals of **2** formed.

*Synthesis of [Cu(**L**)(3-pico)$_2$] (3)*

{[Cu(**L**)]$_2$}$_n$ (27.5 mg, 0.05 mmol) was dissolved in 2 ml 3-picoline in a vial and 1 ml water added. The vial was placed in a container with a further 10 ml water and allowed to stand for seven days to give fine brown needle crystals of **3**. Yield 20 mg (43 %). As with compound **2**, the crystals are prone to loss of 3-picoline, preventing a reliable elemental analysis.

Crystallisation of **3** can also be achieved as follows: {[Cu(**L**)]$_2$}$_n$ (27.5 mg, 0.05 mmol) was dissolved in 5 ml DMSO at a hotplate temperature of 170 °C and allowed to cool to room temperature. 3-Picoline (186 mg, 2.0 mmol, 194 µl) was added and the vial placed in a covered beaker of water for 11 days, after which, large dark green-black crystals of **3** formed.

*Synthesis of [Cu(**L**)(4-pico)] (4)*

{[Cu(**L**)]$_2$}$_n$ (27.5 mg, 0.05 mmol) was dissolved in 2 ml 4-picoline in a vial and 1 ml water added. The vial was placed in a container with a further 10 ml water and allowed to stand for three days to give small black-brown needle crystals of **4**. Yield 16 mg (44 %). $C_{19}H_{16}CuN_2O_2$: Expected: C 62.03; H 4.38; N 7.61. Found: C 62.04; H 4.36; N 7.62.

Crystallisation of **4** can also be achieved as follows: {[Cu(**L**)]$_2$}$_n$ (27.5 mg, 0.05 mmol) was dissolved in 5 ml DMSO at a hotplate temperature of 170 °C and allowed to cool to room temperature. 4-Picoline (186 mg, 2.0 mmol, 194 µl) was added and the vial placed in a covered beaker of water for 10 days, after which, large dark green-black crystals of **4** formed.

*Synthesis of [Cu(**L**)(4-tbpy)$_2$] (5)*

{[Cu(**L**)]$_2$}$_n$ (27.5 mg, 0.05 mmol) was dissolved in 2 ml 4-*tert*-butylpyridine in a vial. 2 ml H_2O was added to the vial to form a biphasic mixture. The vial was then placed in a jar with 10 ml 2-propanol. After three days the solutions in the vial had become monophasic and large blackish-green crystals of **5** had formed. The crystals were filtered, washed with 1:1: MeOH:H_2O and left to dry in air. Yield 21 mg (39 %). $C_{22}H_{22}CuN_6O_8S_2$: Expected: C 68.28; H 6.47; N 7.71. Found: C 68.07; H 6.44; N 7.70.

Crystallisation of **5** can also be achieved as follows: {[Cu(**L**)]$_2$}$_n$ (27.5 mg, 0.05 mmol) was dissolved in 5 ml DMSO at a hotplate temperature of 170 °C and allowed to cool to room temperature. 4-*tert*-Butylpyridine (270 mg, 2.0 mmol, 292 µl) was added and the vial placed in a covered beaker of water for 5 days, after which, large dark green-black crystals of **5** formed.

*Synthesis of [Cu(**L**)(2,4'-bipy)] (**6**)*

{[Cu(**L**)]$_2$}$_n$ (27.5 mg, 0.05 mmol) and 2,4′-bipy (15.6 mg, 0.05 mmol) were dissolved in 7 ml DMSO at a hotplate temperature of 170 °C, allowed to cool and left open to air. Dark green-black crystals formed over two days which were filtered, washed with 2 x 2 ml 8:2 DMSO/H_2O and 2 x 2 ml water. Yield 28.9 mg (67 %). $C_{23}H_{17}CuN_3O_2$: Expected: C 64.10; H 3.98; N 9.75. Found: C 63.62; H 3.88; N 9.47.

*Synthesis of [Cu(**L**)(4-ampy)] (7)*

{[Cu(**L**)]$_2$}$_n$ (27.5 mg, 0.05 mmol) and 4-ampy (500 mg, 5.3 mmol) were dissolved in 7 ml DMSO at a hotplate temperature of 170 °C, allowed to cool and left open to air. Dark green-black crystals formed over seven days which were filtered, washed with 2 x 2 ml 8:2 DMSO/H_2O and 2 x 2 ml water. Yield 19.2 mg (52 %). $C_{18}H_{15}CuN_3O_2$: Expected: C 58.61; H 4.10; N 11.39. Found: C 58.36; H 4.00; N 11.29.

*Synthesis of [Cu(**L**)(4-dmap)$_2$] (**8** and **9**)*

{[Cu(**L**)]$_2$}$_n$ (27.5 mg, 0.05 mmol) and 4-dmap (500 mg, 4.1 mmol) were dissolved in 7 ml DMSO at a hotplate temperature of 170 °C, allowed to cool and left open to air. Dark green-black crystals formed over seven days which were filtered, washed with 2 x 2 ml 8:2 DMSO/H_2O and 2 x 2 ml water. Yield 37.5 mg (72 %). The sample was a mixture of the two polymorphs **8** and **9**. $C_{27}H_{29}CuN_5O_2$: Expected: C 62.47; H 5.63; N 13.49. Found: C 62.06; H 5.57; N 13.32.

*Synthesis of [Cu(**L**)(4-cnpy)] (**10**)*

{[Cu(**L**)]$_2$}$_n$ (27.5 mg, 0.05 mmol) and 4-cnpy (500 mg, 4.8 mmol) were dissolved in 7 ml DMSO at a hotplate temperature of 170 °C, allowed to cool and left open to air. Dark green-black crystals formed over seven days which were filtered, washed with 2 x 2 ml 8:2 DMSO/H_2O and 2 x 2 ml water. Yield 26.6 mg (70 %). $C_{19}H_{13}CuN_3O_2$: Expected: C 60.23; H 3.46; N 11.09. Found: C 59.93; H 3.37; N 10.91.

*Synthesis of [Cu(**L**)(4-nbpy)] (**11**)*

{[Cu(**L**)]$_2$}$_n$ (27.5 mg, 0.05 mmol) and 4-nbpy (500 mg, 2.3 mmol) were dissolved in 7 ml DMSO at a hotplate temperature of 170 °C, allowed to cool and left open to air. Dark green-black crystals formed over seven days which were filtered, washed with 2 x 2 ml 8:2 DMSO/H_2O and 2 x 2 ml water. Yield 21 mg (41 %). $C_{25}H_{19}CuN_3O_4$: Expected: C 61.41; H 3.92; N 8.59. Found: C 61.45; H 3.85; N 8.68.

*Synthesis of [Cu(**L**)(bnz)] (**12**)*

{[Cu(**L**)]$_2$}$_n$ (27.5 mg, 0.05 mmol) and bnz (500 mg, 4.2 mmol) were dissolved in 7 ml DMSO at a hotplate temperature of 170 °C, allowed to cool and left open to air. Dark green-black crystals formed over seven days which were filtered, washed with 2 x 2 ml 8:2 DMSO/H_2O and 2 x 2 ml water. Yield 18.3 mg (47 %). $C_{20}H_{15}CuN_3O_2$: Expected: C 61.14; H 3.85; N 10.69. Found: C 60.62; H 3.71; N 10.45.

*Synthesis of [Cu(**L**)(4-inam)(H_2O)].DMSO (**13**)*

{[Cu(**L**)]$_2$}$_n$ (27.5 mg, 0.05 mmol) and 4-inam (244 mg, 2.0 mmol) were dissolved in 7 ml DMSO at a hotplate temperature of 170 °C, allowed to cool and left open to air. Dark green-black crystals formed over seven days which were filtered, washed with 2 x 2 ml 8:2 DMSO/H_2O and 2 x 2 ml water. The product was contaminated by unreacted {[Cu(**L**)]$_2$}$_n$ in each attempt at synthesis and thus a reliable elemental analysis could not be obtained.

*Synthesis of [Cu(**L**)(tpy)] (**14**)*

H_2**L** (50 mg, 2.0 mmol), tpy (55 mg, 0.23 mmol), $Cu(NO_3)_2.3H_2O$ (60 mg, 0.25 mmol) and K_2CO_3 (300 mg) were placed in a conical flask and MeOH (20 ml) carefully added to minimise dissolution of the contents. The flask was covered with parafilm and left to stand for one month to give dark green crystals in K_2CO_3 (modified from Bohle and Stasko[4]).

*Synthesis of [Cu(**SB-1**)(phen)].3MeOH (**15**)*

H_2**L** (50 mg, 2.0 mmol), 1,10-phenanthroline monohydrate (45 mg, 0.23 mmol), 0.23 mmol), $Cu(NO_3)_2.3H_2O$ (60 mg, 0.25 mmol) and K_2CO_3 (300 mg) were placed in a conical flask and MeOH (20 ml) carefully added to minimise dissolution of the contents. The flask was covered with parafilm and left to stand for one month to give dark green crystals in a larger amount of {[Cu(**L**)]$_2$}$_n$ and K_2CO_3.

Table S1 Crystallographic parameters for compounds 2-15

Compound	**2**	**3**	**4**	**5**	**6**
Ligand	py	3-pico	4-pico	4-tbpy	2,4′-bipy
Identification code	2015tdk064	2016tdk012	2016tdk017	2016tdk003	2016tdk005
Empirical formula	$C_{18}H_{14}CuN_2O_2$	$C_{25}H_{23}CuN_3O_2$	$C_{19}H_{16}CuN_2O_2$	$C_{31}H_{35}CuN_3O_2$	$C_{23}H_{17}CuN_3O_2$
Formula weight	353.85	461.00	367.88	545.16	430.93
Temperature/K	100(2)	100(2)	100(2)	100(2)	100(2)
Crystal system	orthorhombic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$Pna2_1$	$P2_1$	$P2_1/c$	$P2/c$	$P2_1/c$
a / Å	9.7594(4)	9.2782(4)	12.4100(8)	18.3414(5)	21.0789(10)
b / Å	11.4338(3)	18.5496(7)	4.7791(3)	12.3024(3)	3.83614(16)
c / Å	13.2116(5)	12.2910(4)	26.5274(18)	24.5778(8)	22.5607(9)
α / °	90	90	90	90	90
β / °	90	90.788(3)	102.191(7)	90.347(3)	103.128(4)
γ / °	90	90	90	90	90
Volume / Å^3	1474.24(9)	2115.16(14)	1537.83(18)	5545.7(3)	1776.62(14)
Z	4	4	4	8	4
ρ_{calc} / gcm^{-3}	1.594	1.448	1.589	1.306	1.611
μ / mm^{-1}	1.492	1.060	1.434	0.820	1.256
$F(000)$	724.0	956	756.0	2296.0	884.0
Crystal size / mm^3	0.073 × 0.040 × 0.020	0.078 × 0.054 × 0.030	0.222 × 0.035 × 0.01	0.264 × 0.128 × 0.084	0.233 × 0.032 × 0.005
2θ range for data collection / °	4.712 to 54.956	3.314 to 54.954	5.06 to 54.966	3.31 to 54.968	4.776 to 54.968
Index ranges	$-11 \leq h \leq 12$ $-14 \leq k \leq 14$ $-17 \leq l \leq 16$	$-12 \leq h \leq 12$ $-24 \leq k \leq 22$ $-15 \leq l \leq 15$	$-16 \leq h \leq 15$ $-6 \leq k \leq 6$ $-34 \leq l \leq 31$	$-23 \leq h \leq 23$ $-15 \leq k \leq 15$ $-31 \leq l \leq 31$	$-27 \leq h \leq 27$ $-4 \leq k \leq 4$ $-29 \leq l \leq 29$
Reflections collected	18404	27288	10086	70547	34552
Independent reflections	3367 [$R_{int} = 0.0797$, $R_{sigma} = 0.0596$]	9433 [$R_{int} = 0.0424$, $R_{sigma} = 0.0547$]	3525 [$R_{int} = 0.0412$, $R_{sigma} = 0.0420$]	12708 [$R_{int} = 0.0351$, $R_{sigma} = 0.0220$]	4032 [$R_{int} = 0.0510$, $R_{sigma} = 0.0244$]
Data/restraints/parameters	3367/343/207	9433/575/659	3525/1036/372	12708/1802/962	4032/1055/381
Goodness-of-fit on F^2	1.055	0.991	1.039	1.058	1.160
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0480$, $wR_2 = 0.0966$	$R_1 = 0.0432$, $wR_2 = 0.0808$	$R_1 = 0.0407$, $wR_2 = 0.0998$	$R_1 = 0.0542$, $wR_2 = 0.1572$	$R_1 = 0.0517$, $wR_2 = 0.1244$
Final R indexes [all data]	$R_1 = 0.0653$, $wR_2 = 0.1031$	$R_1 = 0.0619$, $wR_2 = 0.0868$	$R_1 = 0.0584$, $wR_2 = 0.1057$	$R_1 = 0.0928$, $wR_2 = 0.1849$	$R_1 = 0.0627$, $wR_2 = 0.1292$
Largest diff. peak/hole / e Å^{-3}	0.36/−0.38	0.56/−0.35	0.55/−0.28	1.00/−0.48	0.49/−0.54
CCDC number	1907282	1907268	1907270	1907281	1907279

Compound	**7a**	**7b**	**8**	**9**	**10**
Ligand	4-ampy 0.77 Å	4-ampy 0.4 Å	4-dmap (polymorph 1)	4-dmap (polymorph 2)	4-cnpy
Identification code	2015tdk065	TDK-SN2-052A	2015tdk108	2015tdk096	2015tdk107b
Empirical formula	$C_{18}H_{15}CuN_3O_2$	$C_{18}H_{15}CuN_3O_2$	$C_{27}H_{29}CuN_5O_2$	$C_{27}H_{29}CuN_5O_2$	$C_{19}H_{13}CuN_3O_2$
Formula weight	368.87	368.87	519.09	519.09	378.86
Temperature/K	100(2)	100(2)	100(2)	100(2)	100(2)
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	orthorhombic
Space group	$P2_1$/c	$P2_1$/c	$P2_1$/c	$P2_1$/c	*Pbca*
a / Å	15.5807(7)	15.51709(13)	12.2309(5)	35.0007(9)	7.7950(2)
b / Å	5.5244(2)	5.49923(6)	19.1471(6)	12.6364(4)	17.1368(6)
c / Å	17.5567(7)	17.54359(16)	11.1735(4)	16.9160(4)	23.0559(8)
α / °	90	90	90	90	90
β / °	90.031(4)	90.0016(8)	110.895(4)	94.861(3)	90
γ / °	90	90	90	90	90
Volume / Å^3	1511.17(11)	1497.03(2)	2444.59(17)	7454.7(4)	3079.83(17)
Z	4	4	4	12	8
ρ_{calc} / gcm^{-3}	1.621	1.637	1.410	1.388	1.634
μ / mm^{-1}	1.461	1.475	0.928	0.913	1.437
F(000)	756.0	756.0	1084.0	3252.0	1544.0
Crystal size / mm^3	0.099 × 0.024 × 0.011	0.300 × 0.030 × 0.010	0.099 × 0.082 × 0.035	0.209 × 0.087 × 0.034	0.178 × 0.037 × 0.036
2θ range for data collection / °	4.64 to 54.968	3.504 to 125.264	4.748 to 54.968	3.428 to 54.968	5.072 to 54.968
Index ranges	$-20 \leq h \leq 17$ $-7 \leq k \leq 7$ $-22 \leq l \leq 22$	$-37 \leq h \leq 37$ $-13 \leq k \leq 13$ $-39 \leq l \leq 43$	$-15 \leq h \leq 15$ $-24 \leq k \leq 21$ $-13 \leq l \leq 14$	$-45 \leq h \leq 45$ $-16 \leq k \leq 16$ $-21 \leq l \leq 21$	$-7 \leq h \leq 10$ $-12 \leq k \leq 22$ $-29 \leq l \leq 23$
Reflections collected	9657	211441	19122	54951	15176
Independent reflections	3440 [R_{int} = 0.0524, R_{sigma} = 0.0735]	24013 [R_{int} = 0.0637, R_{sigma} = 0.0252]	5600 [R_{int} = 0.0268, R_{sigma} = 0.0290]	16992 [R_{int} = 0.0523, R_{sigma} = 0.0580]	3526 [R_{int} = 0.0244, R_{sigma} = 0.0210]
Data/restraints/parameters	3440/0/217	24013/316/372	5600/344/462	16992/2311/1254	3526/877/374
Goodness-of-fit on F^2	1.016	1.032	1.038	1.128	1.094
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0499, wR_2 = 0.0921	R_1 = 0.0376, wR_2 = 0.0955	R_1 = 0.0341, wR_2 = 0.0814	R_1 = 0.0679, wR_2 = 0.1451	R_1 = 0.0334, wR_2 = 0.0756
Final R indexes [all data]	R_1 = 0.0757, wR_2 = 0.1014	R_1 = 0.0525, wR_2 = 0.1039	R_1 = 0.0445, wR_2 = 0.0857	R_1 = 0.1070, wR_2 = 0.1595	R_1 = 0.0419, wR_2 = 0.0791
Largest diff. peak/hole / e Å^{-3}	0.60/−0.81	1.03/−1.65	0.34/−0.33	0.85/−0.67	0.29/−0.41
CCDC number	1907269	1907280	1907271	1907278	1907273

Compound	**11**	**12**	**13**	**14**	**15**
Ligand	4-nbpy	bnz	4-inam	tpy	phen
Identification code	2015tdk104	2016tdk015	2015tdk102	2016tdk013	2016tdk010
Empirical formula	$C_{25}H_{19}CuN_3O_4$	$C_{20}H_{15}CuN_3O_2$	$C_{21}H_{23}CuN_3O_5S$	$C_{28}H_{20}CuN_4O_2$	$C_{25}H_{17}CuN_3O_2$
Formula weight	488.97	392.89	493.02	508.02	454.95
Temperature/K	100(2)	100(2)	100(2)	100(2)	100(2)
Crystal system	monoclinic	monoclinic	triclinic	monoclinic	triclinic
Space group	$P2_1$/c	$P2_1$/c	$P\bar{1}$	$C2$/c	$P\bar{1}$
a / Å	6.42037(13)	28.0625(17)	5.6328(2)	16.8283(9)	8.4913(2)
b / Å	28.6887(7)	4.88379(17)	12.7929(6)	13.7876(6)	11.1491(3)
c / Å	11.1669(2)	27.4855(17)	15.6440(9)	9.7394(5)	13.2268(3)
α / °	90	90	68.148(5)	90	101.462(2)
β / °	92.298(2)	118.305(8)	81.123(4)	103.090(5)	90.604(2)
γ / °	90	90	88.371(4)	90	98.979(2)
Volume / Å^3	2055.20(8)	3316.5(4)	1033.26(10)	2201.04(19)	1211.04(6)
Z	4	8	2	4	2
ρ_{calc} / gcm^{-3}	1.580	1.574	1.585	1.533	1.248
μ / mm^{-1}	1.103	1.337	1.198	1.028	0.925
F(000)	1004.0	1608.0	510.0	1044.0	466.0
Crystal size / mm^3	0.245 × 0.059 × 0.055	0.15 × 0.025 × 0.01	0.174 × 0.028 × 0.023	0.076 × 0.062 × 0.03	0.211 × 0.176 × 0.066
2θ range for data collection / °	4.624 to 54.962	4.356 to 54.974	5.206 to 54.962	4.97 to 54.96	5.384 to 55.08
Index ranges	$-8 \leq h \leq 7$ $-37 \leq k \leq 30$ $-14 \leq l \leq 14$	$-36 \leq h \leq 35$ $-6 \leq k \leq 6$ $-35 \leq l \leq 35$	$-7 \leq h \leq 7$ $-16 \leq k \leq 16$ $-20 \leq l \leq 20$	$-20 \leq h \leq 21$ $-11 \leq k \leq 17$ $-12 \leq l \leq 8$	$-11 \leq h \leq 10$ $-14 \leq k \leq 14$ $-17 \leq l \leq 17$
Reflections collected	14078	28075	13694	7198	15133
Independent reflections	4691 [R_{int} = 0.0217, R_{sigma} = 0.0192]	7601 [R_{int} = 0.0493, R_{sigma} = 0.0469]	4701 [R_{int} = 0.0296, R_{sigma} = 0.0366]	2515 [R_{int} = 0.0213, R_{sigma} = 0.0239]	5535 [R_{int} = 0.0138, R_{sigma} = 0.0136]
Data/restraints/parameters	4691/919/447	7601/1347/612	4701/718/345	2515/219/232	5535/777/411
Goodness-of-fit on F^2	1.183	1.097	1.039	1.135	1.062
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0412, wR_2 = 0.0949	R_1 = 0.0621, wR_2 = 0.1524	R_1 = 0.0331, wR_2 = 0.0696	R_1 = 0.0302, wR_2 = 0.0734	R_1 = 0.0337, wR_2 = 0.1038
Final R indexes [all data]	R_1 = 0.0443, wR_2 = 0.0961	R_1 = 0.0850, wR_2 = 0.1622	R_1 = 0.0408, wR_2 = 0.0725	R_1 = 0.0373, wR_2 = 0.0764	R_1 = 0.0349, wR_2 = 0.1048
Largest diff. peak/hole / e Å^{-3}	1.08/−0.41	1.51/−0.79	0.44/−0.37	0.37/−0.35	0.49/−0.31
CCDC number	1907272	1907274	1907275	1907276	1907277

Crystal structure descriptions

Compound **2** crystallises in the orthorhombic space group *Pna*2$_1$. The asymmetric unit consists of one Cu(II) ion, one doubly-deprotonated **L**$^{2-}$ ligand and one pyridine molecule. The Cu(II) ion is chelated by **L**$^{2-}$ with Cu−O$_{salicyl}$ = 1.899(14) Å, Cu−O$_{phenol}$ =1.922(13) Å and Cu−N$_{imine}$ = 1.949(8) Å. This [Cu(**L**)] unit is disordered along a 180° axis just off of the Cu−N bond and modelled with a 50:50 ratio. The pyridine molecule bonds to the Cu(II) ion with Cu−N$_{py}$ = 2.017(6) Å to give an *trans*-N$_2$O$_2$ square-planar coordination sphere. The short bonds in this plane indicate that the ligands are all coordinated through the $d_{x^2-y^2}$ orbital. There do not appear to be any further bonds to the Cu(II) ion in the d_{z^2}. This results in a planar [Cu(**L**)(py)] unit with the largest deviation from the mean plane of the complex being 0.470(12) Å. The [Cu(**L**)(py)] units then form stacks in the *a*-axis without any obvious π-stacking.

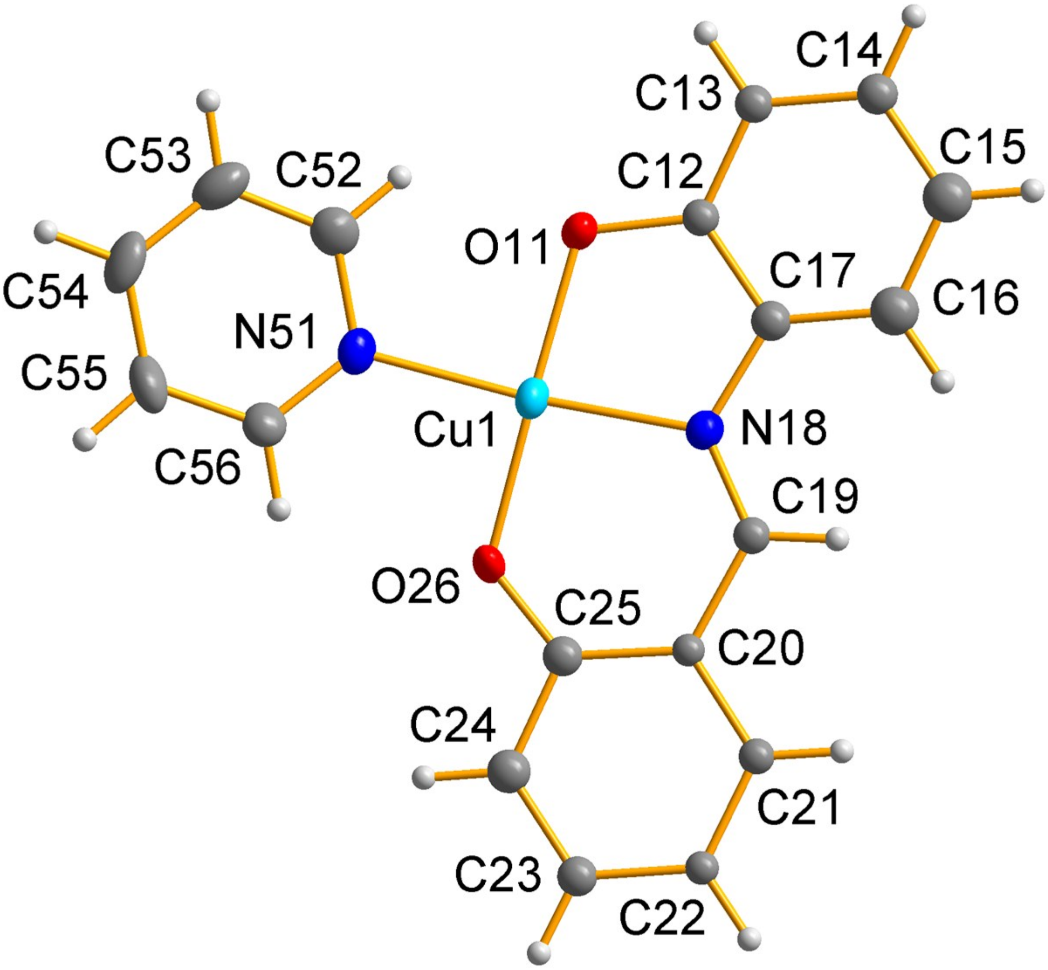


Figure S1 Asymmetric unit of compound **2**. Thermal ellipsoids are at 50 % probability. One component of the disordered [Cu(**L**)] group and hydrogen atom labels are omitted for clarity.

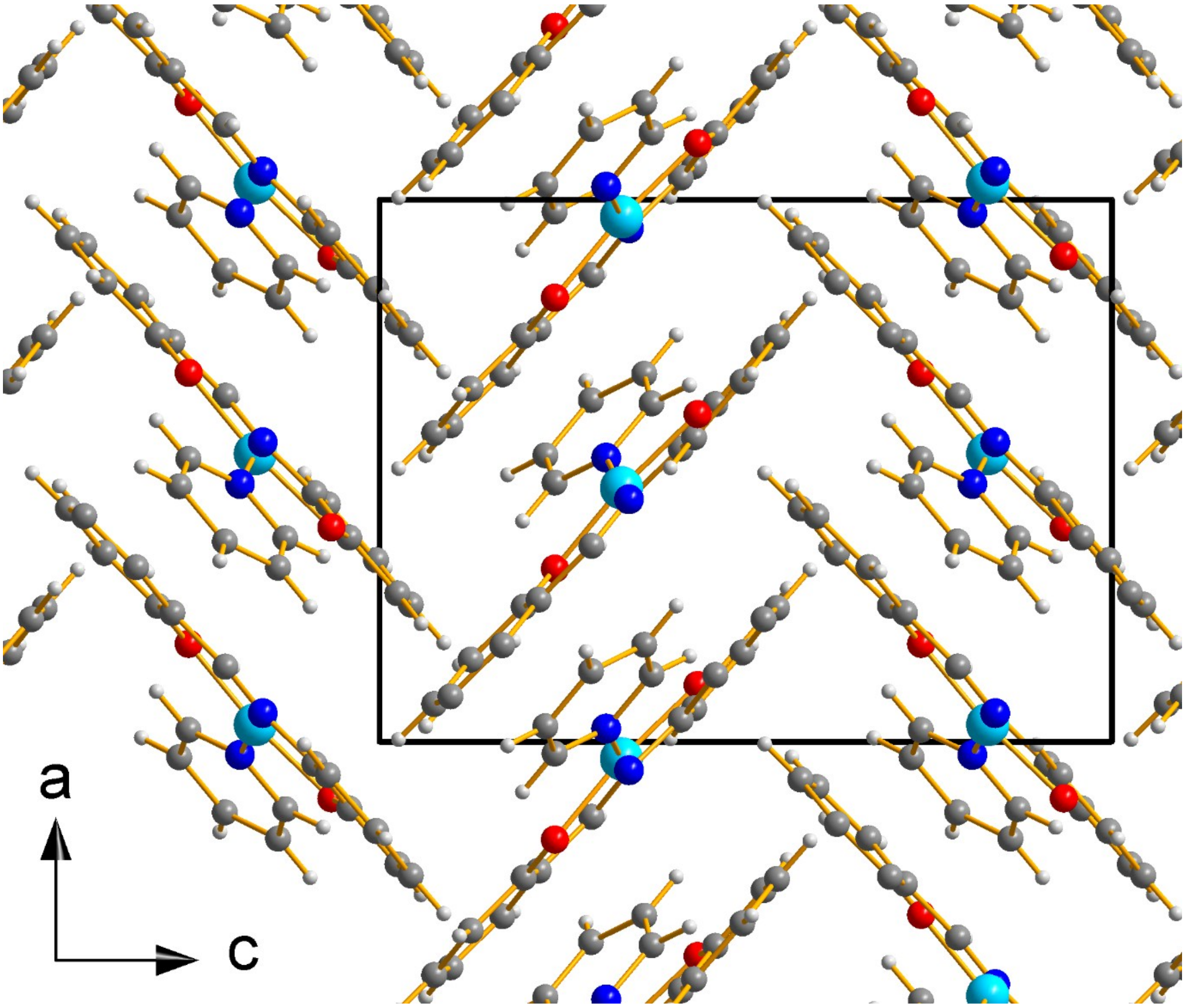


Figure S2 Packing of [Cu(**L**)(py)] units in compound **2** looking down the *b*-axis.

Compound **3** crystallises in the monoclinic space group $P2_1$. The asymmetric unit consists of two [Cu(**L**)] units, as per compound **2**, except with no disorder in this moiety. A 3-picoline molecule completes the square plane of the coordination sphere of each Cu(II) ion. In this compound, each of the complexes in the asymmetric unit also has a disordered 3-picoline molecule coordinated in the d_{z^2} orbital (Cu1−N111 = 2.310(12) Å, Cu1−N121 = 2.262(17) Å, Cu3−N141 = 2.287(6) Å and Cu3−N151 = 2.33(2) Å) so that there are two [Cu(**L**)(3-pico)$_2$] complexes. The positional disorder in the two components is different with 52:48 for the Cu1 unit and 78:22 in Cu3's unit.

There are no obvious C−H···π or π···π interactions. Compound **3** appears to be close to a higher-symmetry form: the β-angle is 90.788(3) and the two units in the ASU appear to be related by a pseudo-2_1 rotation axis. The marked difference in disorder of the axial ligand shows that the $P2_1$ choice is likely correct and attempts to solve in an orthorhombic group result in a poor refinement.

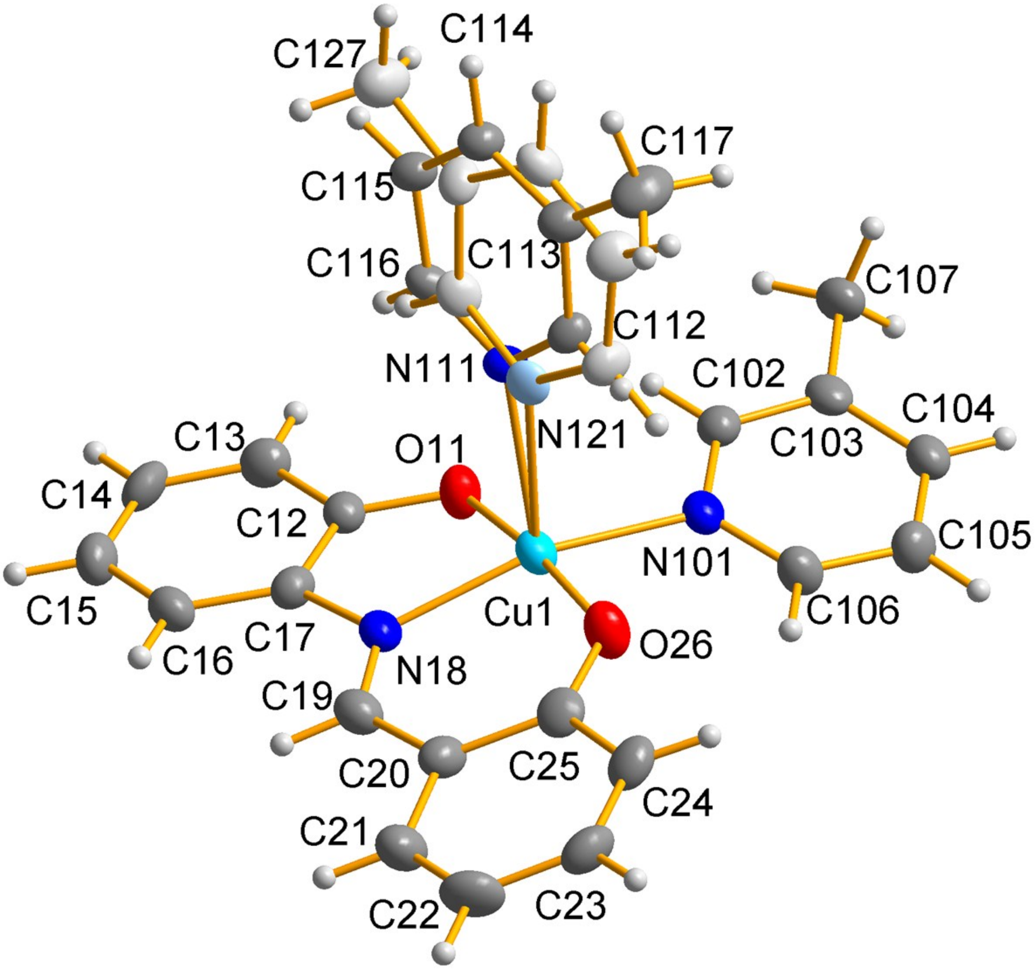


Figure S3 Partial asymmetric unit of compound **3** showing [Cu(**L**)(3-pico)] of Cu1. The Cu3 component is essentially similar to Cu1 and is related by a pseudo 2_1 axis running almost parallel to the O···O axis. The minor component of the disordered axial 3-pico unit (58:42) shown in pale. The disorder in the Cu3 component axial 3-pico is 78:22.

Compound **4** crystallises in the monoclinic space group $P2_1/c$. The asymmetric unit is essentially the same as compound **2**, but with 4-picoline replacing pyridine. The [Cu(**L**)(4-pico)] groups stack at 45° angles to the *b*-axis, alternately left and right while progressing down the *c*-axis, presenting a different packing to compound **2**.

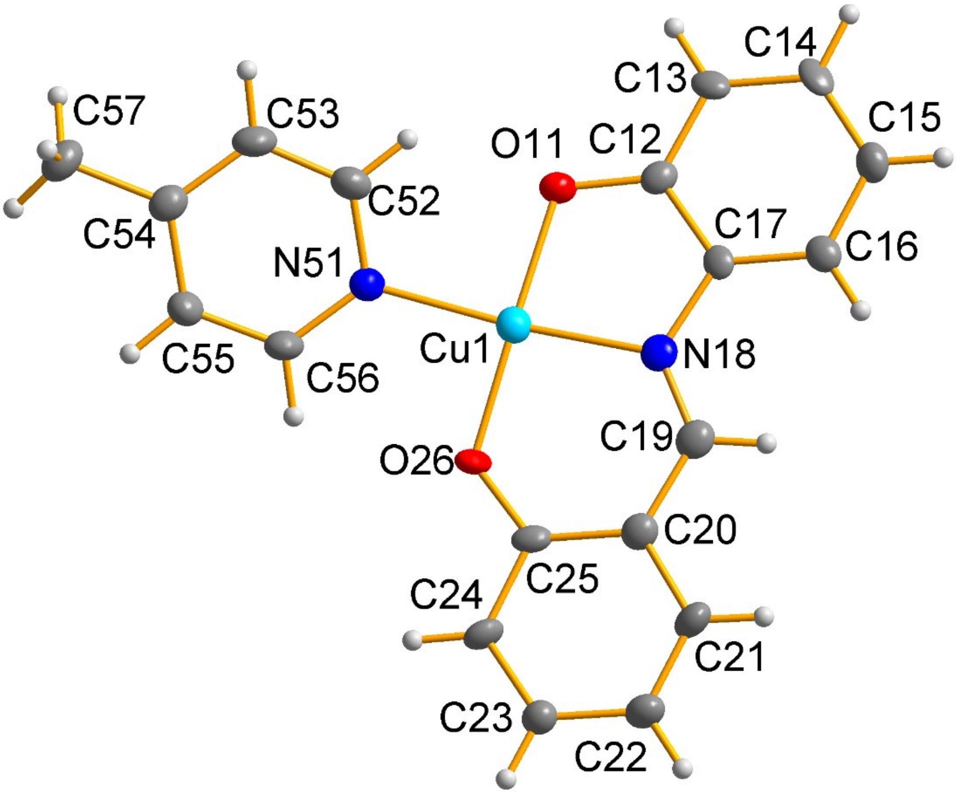


Figure S4 Asymmetric unit of **4**. Thermal ellipsoids are at 50 % probability. The minor component of the disordered [Cu(**L**)] group and hydrogen atom labels are omitted for clarity.

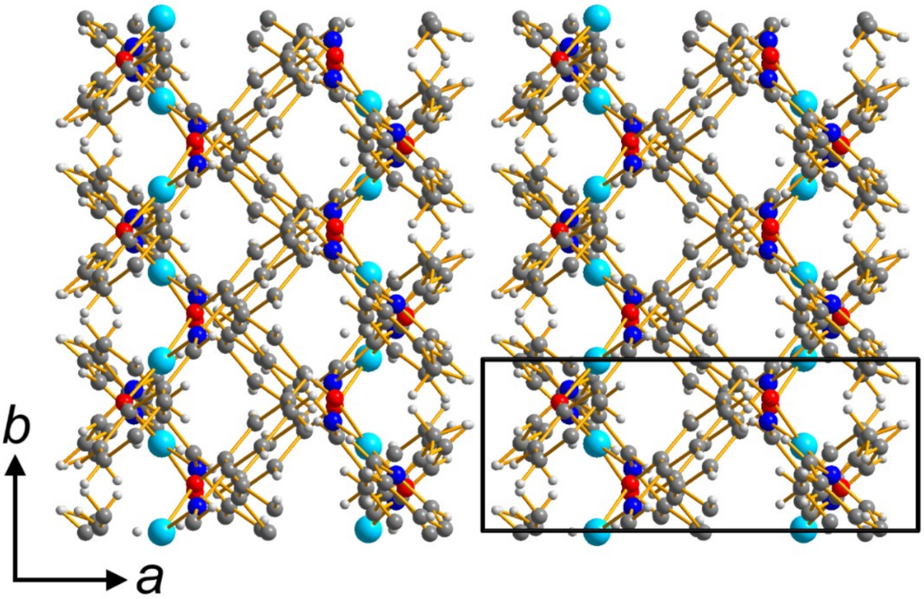


Figure S5 Packing of compound **4** viewed down the *c*-axis.

Compound **5** crystallises in the monoclinic space group *P*2/*c*. The asymmetric unit is similar to that of **3**, except the two 3-picoline ligands are replaced with 4-*t*-butylpyridine. In compound **5** the two independent [Cu(**L**)] units are positionally disordered, both showing a 65:35 ratio.

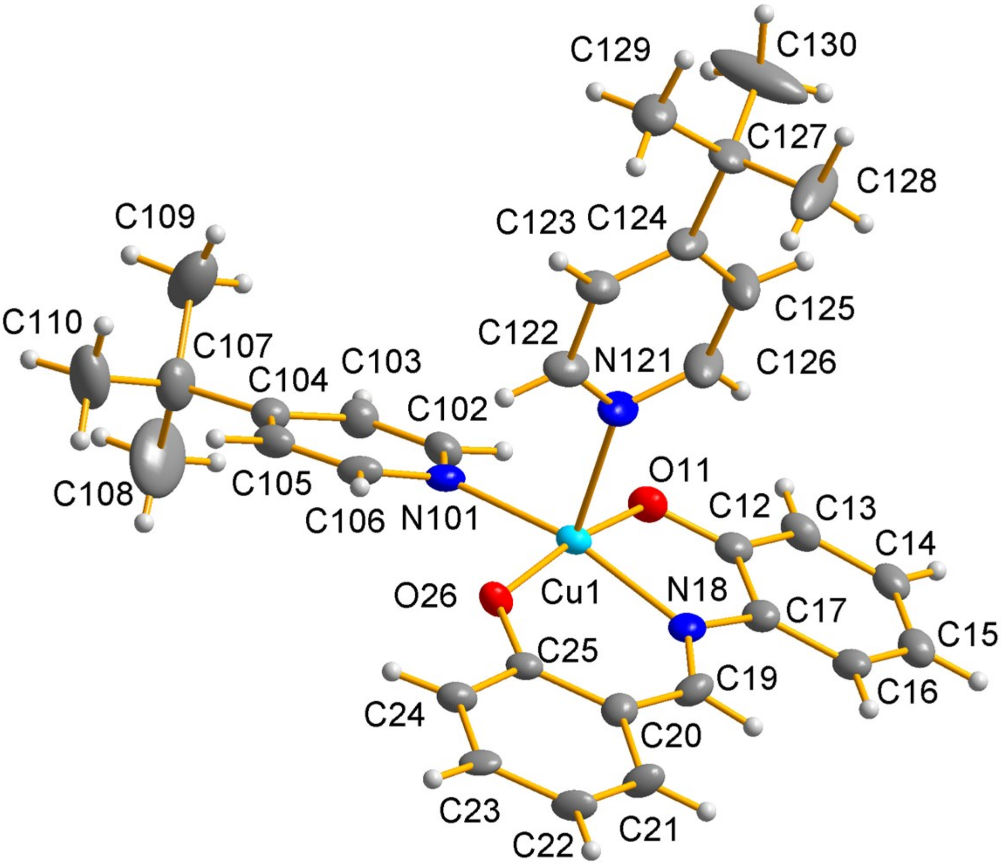


Figure S6 Partial asymmetric unit of **5**. Thermal ellipsoids are at 50 % probability. The minor component of the disordered [Cu(**L**)] group and hydrogen atom labels are omitted for clarity.

Compound **6** crystallises in the monoclinic space group *P*2$_1$/*c*. The asymmetric unit is similar to compound **2** consisting of one 70:30 disordered [Cu(**L**)] unit and a 2,4′-bipyridine ligand. The 2,4′-bipyridine ligand shows a 50:50 rotational disorder in the 2-pyridine ring. The [Cu(**L**)(2,4′-bipy)] units form stacks in the *b*-axis.

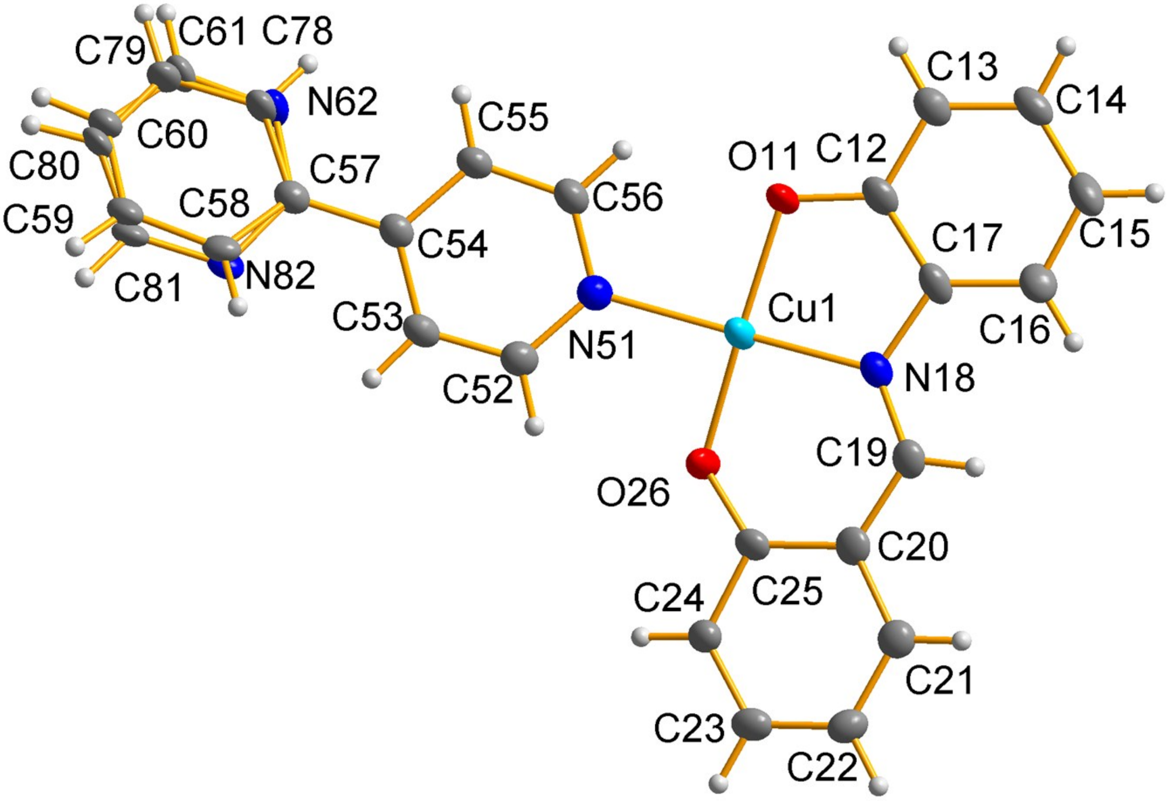


Figure S7 Asymmetric unit of compound **6**. Thermal ellipsoids are at 50 % probability. The minor component of the disordered [Cu(**L**)] group and hydrogen atom labels are omitted for clarity.

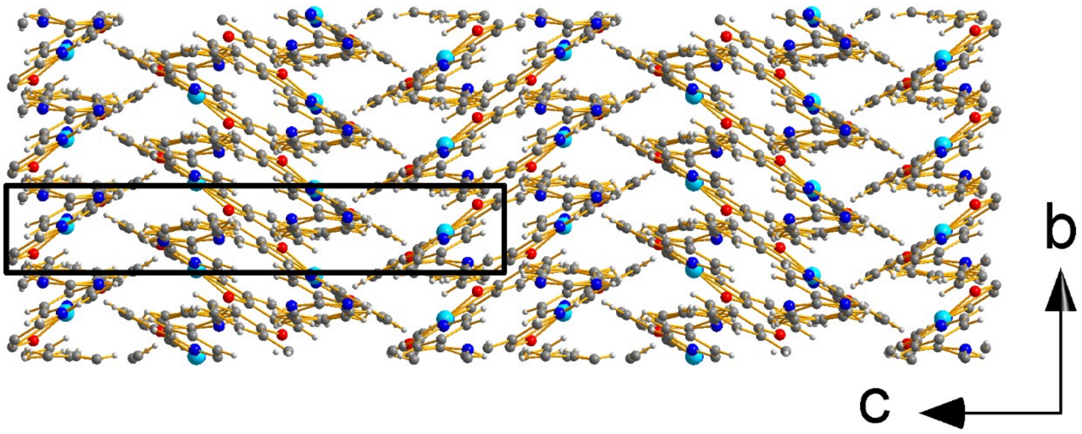


Figure S8 Stacking of [Cu(**L**)(2,4′-bipy)] complexes in compound **6**, looking down the *a*-axis.

Compound **7** crystallises in the monoclinic space group $P2_1/c$. The asymmetric unit is similar to compound **2** with 4-aminopyridine replacing pyridine. At a resolution of 0.77 Å, there is no apparent disorder in the [Cu(**L**)] unit, but on collection to 0.4 Å, a 96:4 disorder can be seen. The [Cu(**L**)(4-ampy)] complexes form stacks in the *b*-axis. The cell of compound **7** has a *β*-angle of 90.031(4)°, but does not display any pseudo symmetry associated with a possible phase transition.

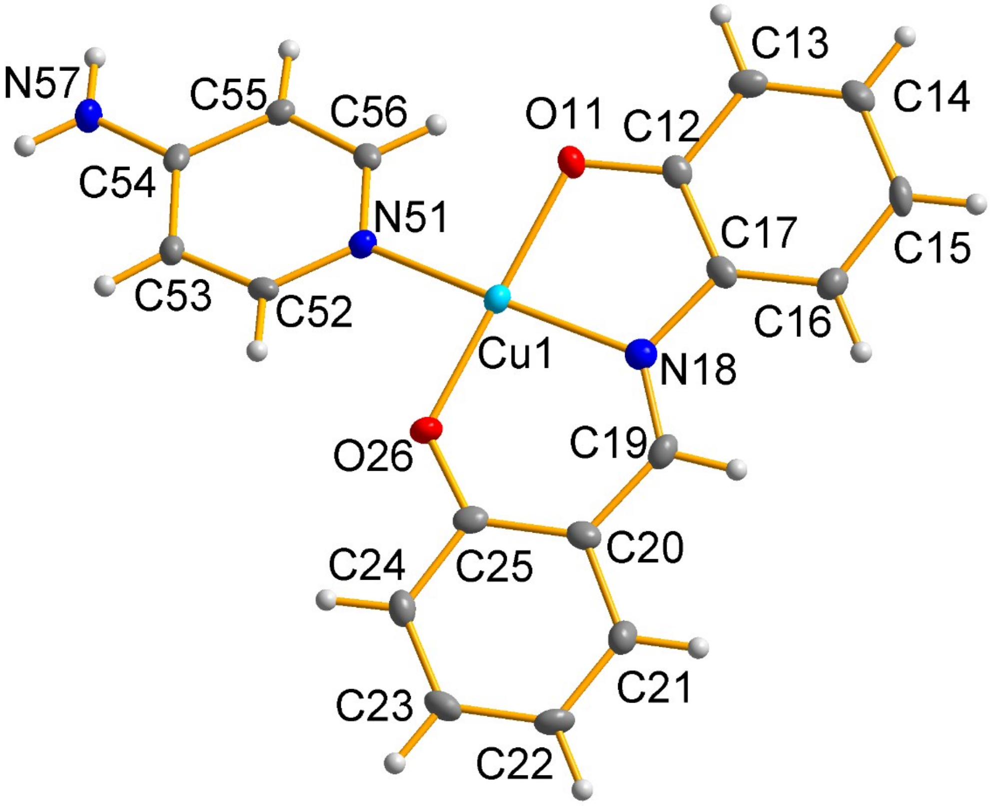


Figure S9 Asymmetric unit of **7**. Thermal ellipsoids are at 50 % probability. Structure shown is the 0.77 Å collection.

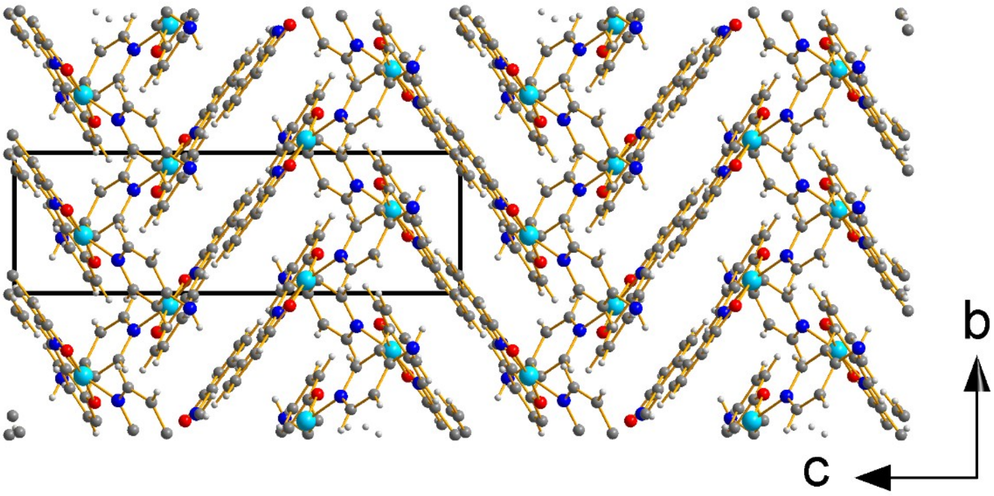


Figure S10 Packing of [Cu(**L**)(4-ampy)] complexes in compound **7**, looking down the *a*-axis.

Compound **8** crystallises in the monoclinic space group $P2_1/c$. The asymmetric unit is similar to compound **3** with 4-*N,N*-dimethylaminopyridine replacing pyridine. The disorder in the [Cu(**L**)] unit is 70:30 while the 4-dmap ligands are ordered. The axial 4-dmap ligand is unusual in this family of compounds in that the plane of the pyridyl ring is rotated roughly 90° so that is coplanar with the N−Cu−N axis rather than the O−Cu−O axis as seen in compounds **3**, **5**, **8** and **9**.

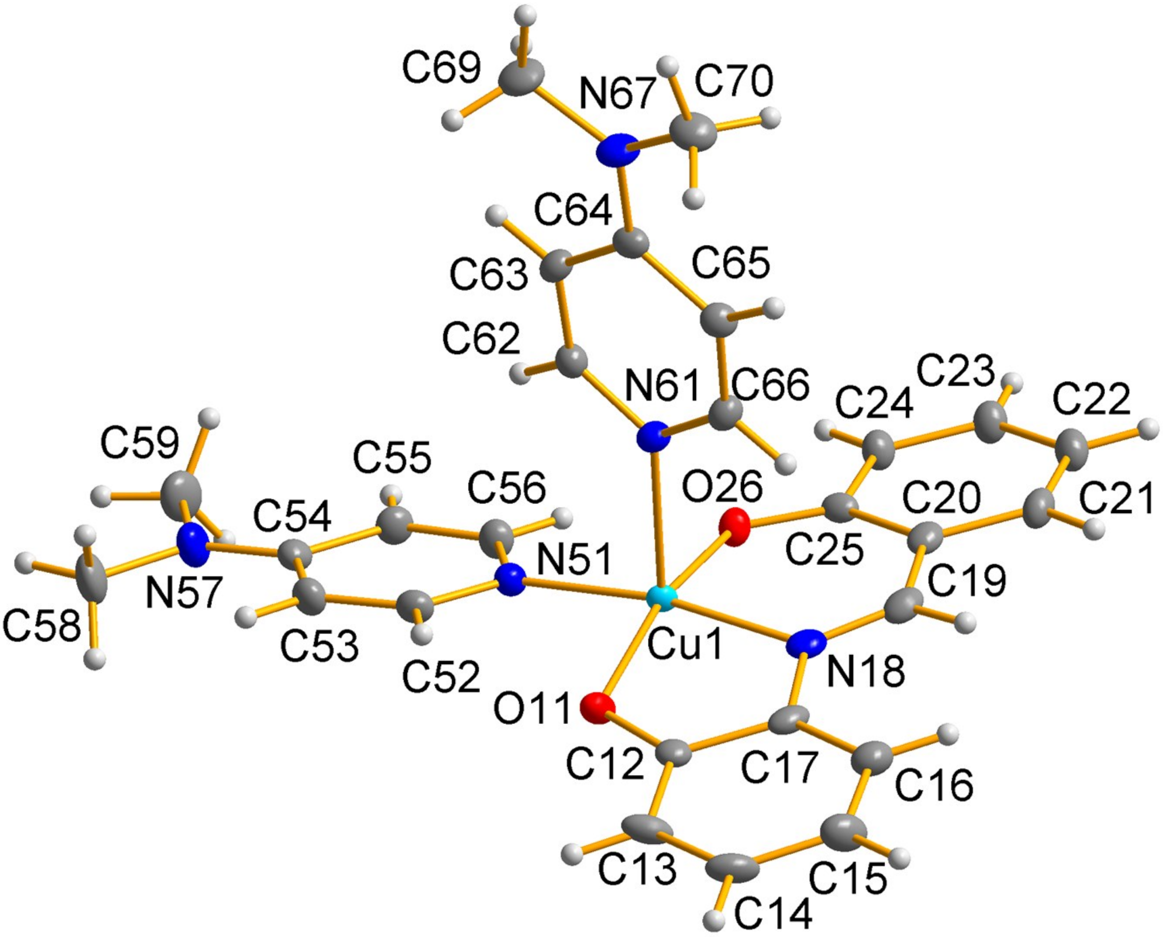


Figure S11 Asymmetric unit of compound **8**. Thermal ellipsoids are at 50 % probability. The minor component of the disordered [Cu(**L**)] group and hydrogen atom labels are omitted for clarity.

Compound **9** crystallises in the monoclinic space group $P2_1/c$. The asymmetric unit consists of three [Cu(**L**)(4-dmap)$_2$] complexes. Unlike in compound **8**, the plane of the pyridyl rings of the axial 4-dmap ligands are coplanar with the O−Cu−O axis. Each of the rings has a tilt angle compared to the plane of the [Cu(**L**)] unit and each is different (see main text for more details). Each [Cu(**L**)] unit shows a different degree of disorder: Cu11/12: 55:45; Cu21/22: 66:34; Cu31/32: 70:30.

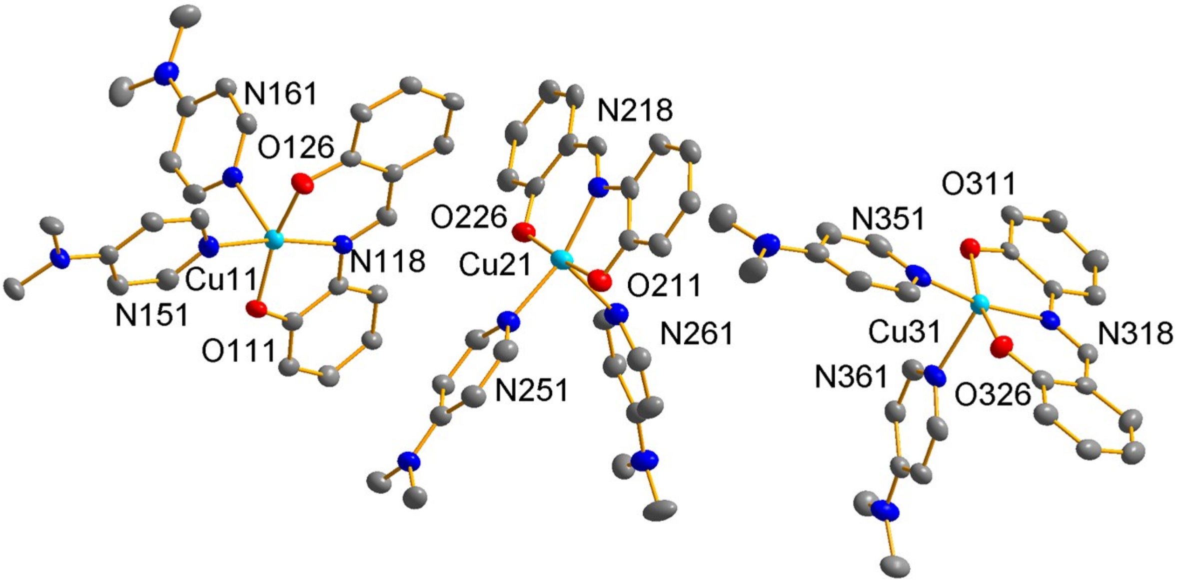


Figure S12 Asymmetric unit of compound **9**. Thermal ellipsoids are at 50 % probability. The minor component of the disordered [Cu(**L**)] groups, hydrogen atoms and the majority of atom labels are omitted for clarity.

Compound **10** crystallises in the orthorhombic space group *Pbca*. The asymmetric unit is similar to that of 2, but with 4-cyanopyridine replacing pyridine. The [Cu(**L**)] unit is disordered with a 58:42 ratio. The [Cu(**L**)(4-cnpy)] complexes dimerise through interaction of Cu1 with O11 of the neighbouring complex through the d_{z^2} orbital (Cu1−O11 = 2.367(11) Å).

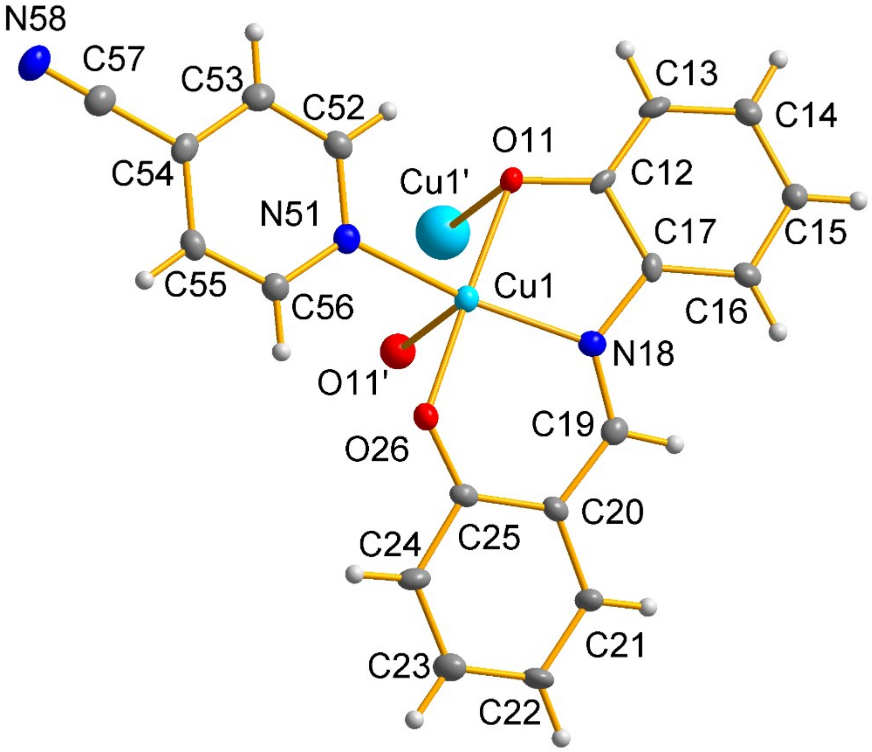


Figure S13 Asymmetric unit and selected symmetry equivalents of compound **10**. Thermal ellipsoids are at 50 % probability. The minor component of the disordered [Cu(**L**)] group and hydrogen atom labels are omitted for clarity. Symmetry codes: *i*) 2−*x*, 1−*y*, 1−*z*.

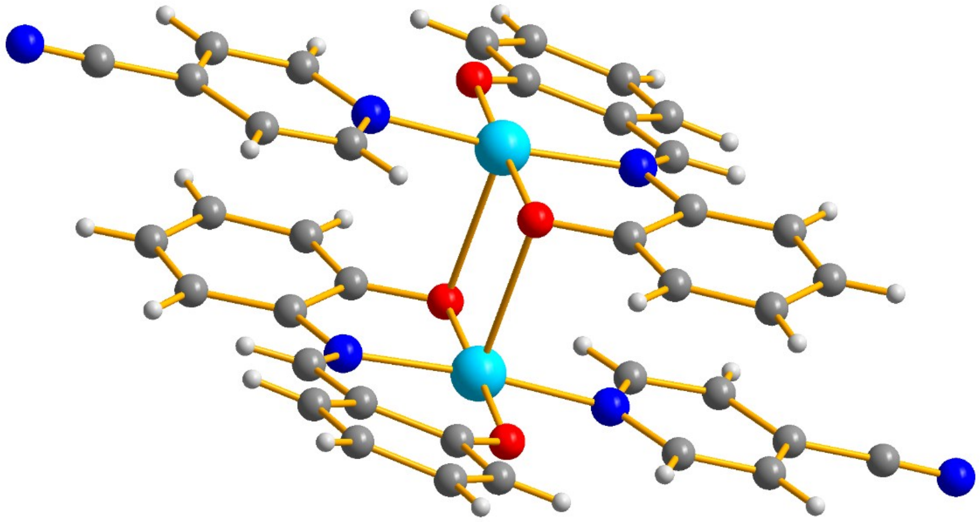


Figure S14 Dimer of [Cu(**L**)(4-cnpy)] complexes.

Compound **11** crystallises in the monoclinic space group *P*2_1/*c*. The asymmetric unit is similar to compound **2** but with 4-(4−nitrobenzyl)pyridine (4-nbpy) replacing pyridine. The degree of disorder in the [Cu(**L**)] unit is 80:20. The [Cu(**L**)(4-nbpy)] groups stack along the *a*-axis.

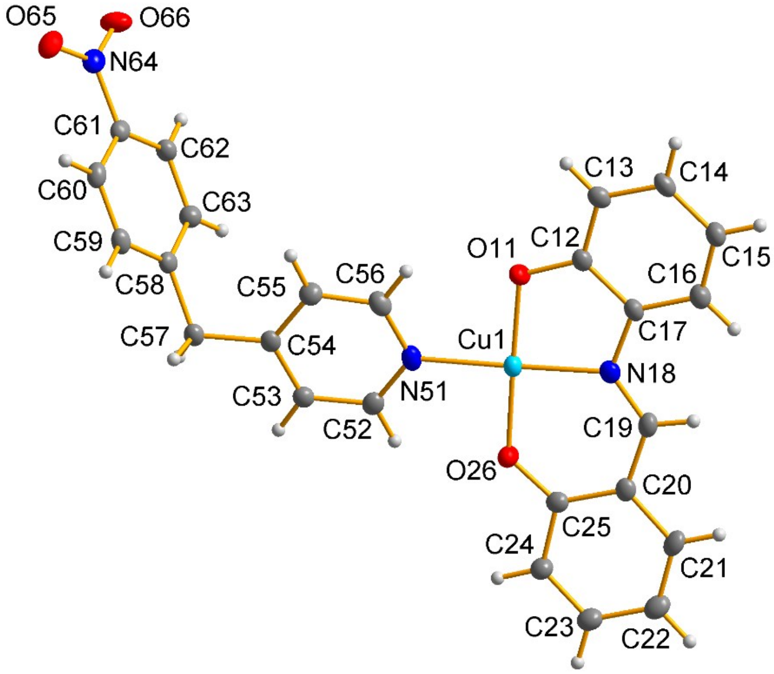


Figure S15 Asymmetric unit of compound **11**. Thermal ellipsoids are at 50 % probability. The minor component of the disordered [Cu(**L**)] group and hydrogen atom labels are omitted for clarity.

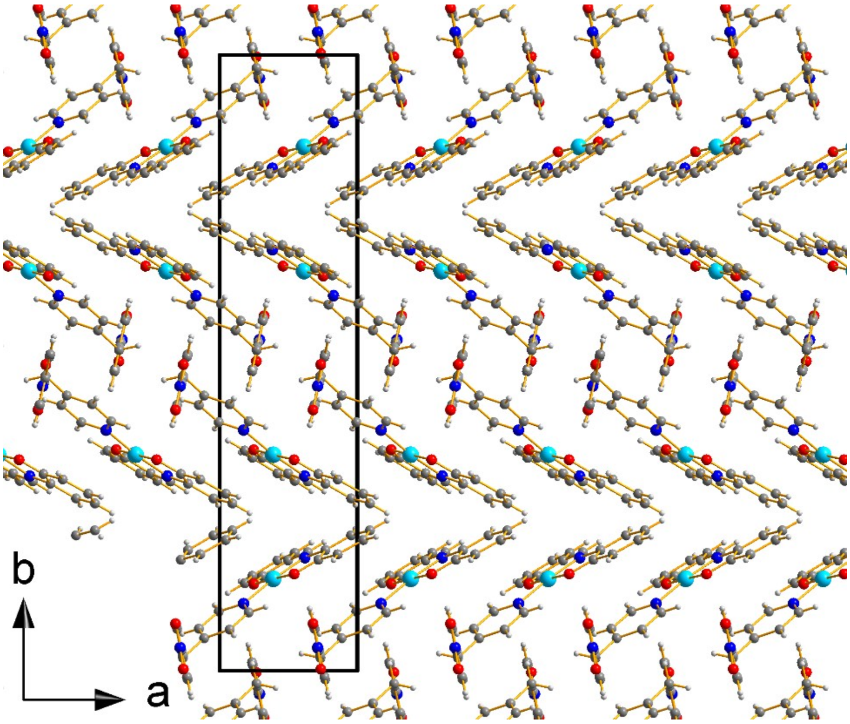


Figure S16 Packing of [Cu(**L**)(4-nbpy)] units along the *a*-axis in compound **11**, looking down the *c*-axis.

Compound **12** crystallises in the monoclinic space group $P2_1/c$. The asymmetric unit consists of two [Cu(**L**)(bnz)] complexes. The disorder in the two [Cu(**L**)] units is 78:12 for Cu1/Cu2 and 85:15 for Cu3/Cu4. Each benzimidazole ligand hydrogen bonds to a phenolic oxygen of a neighbouring [Cu(**L**)(bnz)] complex, forming hydrogen-bonded chains in the *c*-axis. Each chain consists of one group from the ASU only (i.e. a chain of Cu1 groups and a chain of Cu3 groups).

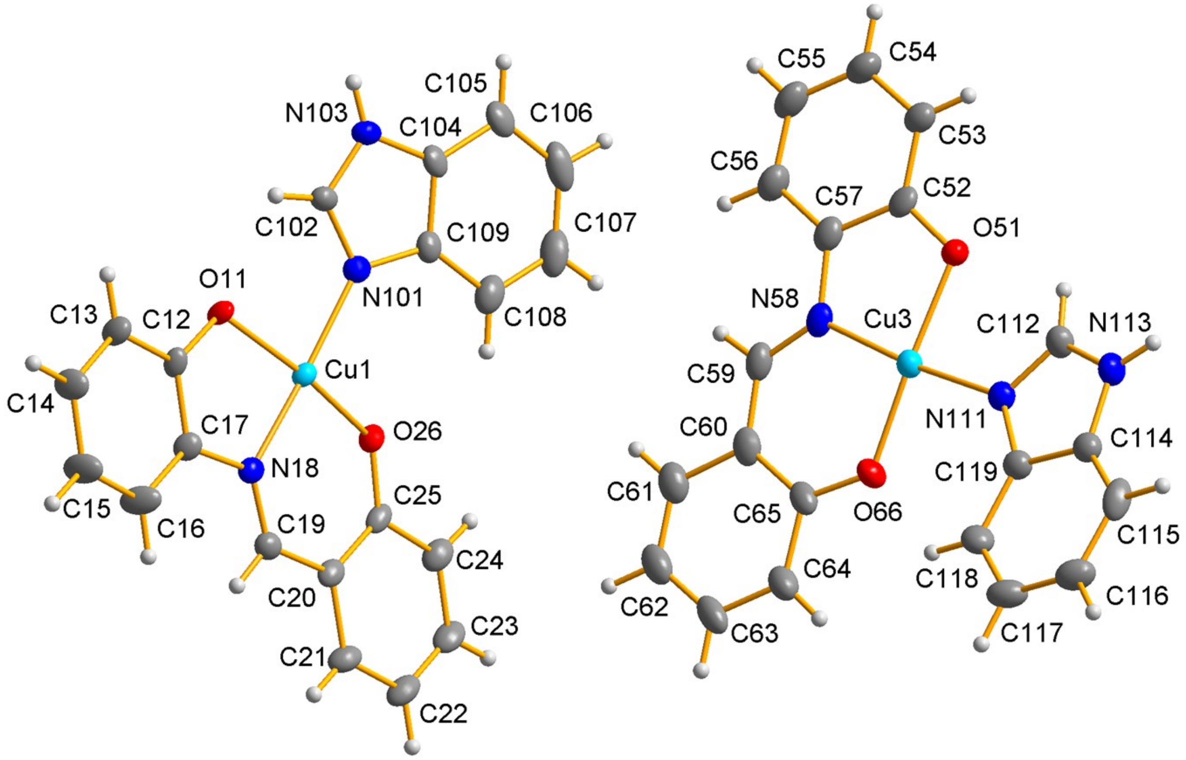


Figure S17 Asymmetric unit of compound **12**. Thermal ellipsoids are at 50 % probability. The minor component of the disordered [Cu(**L**)] groups and hydrogen atom labels are omitted for clarity.

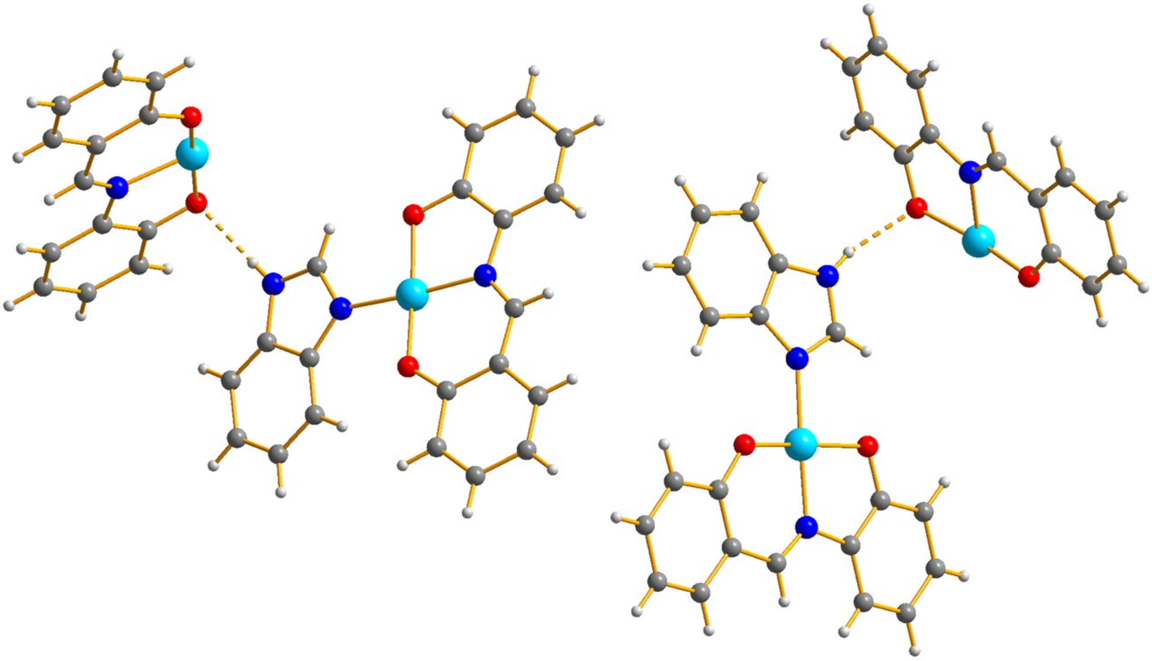


Figure S18 Hydrogen bonding in compound **1**.

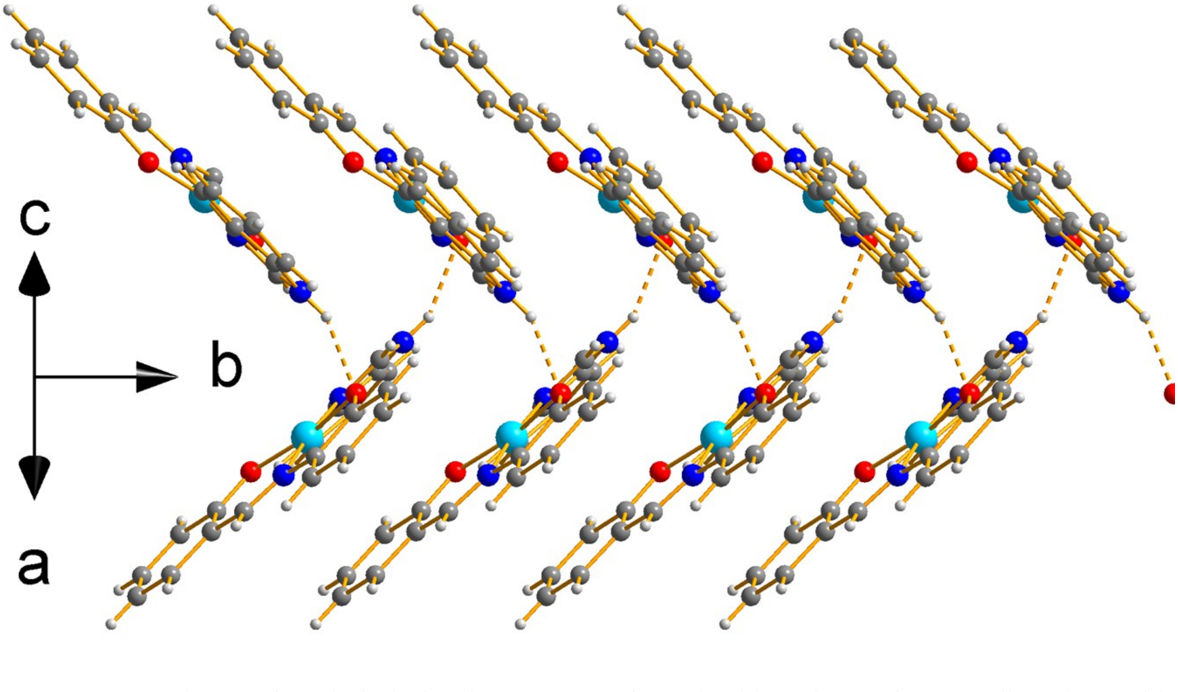


Figure S19 Hydrogen bonded chains in compound **12**, looking down the 101 direction. This chain consists of Cu3/Cu4 units.

Compound **13** crystallises in the triclinic space group $P\bar{1}$. The asymmetric unit consists of one disordered [Cu(**L**)] unit with a 4-isonicotinamide (4-inam) ligand taking the final square planar coordination site. A disordered water molecule is coordinated to the Cu(II) in the d_{z^2} orbital. While the water oxygen atom is disordered over two sites, the best model was obtained by fixing the hydrogen atoms of the two components onto a shared site so that the hydrogen bonds formed are the same for both components. A DMSO molecule is present in the ASU. The disorder in the [Cu(**L**)] unit and the water molecule is linked at 94:6.

Both the –NH_2 of the amide and the water molecule take part in hydrogen bonding. The water molecule bonds to O11 of two neighbouring [Cu(**L**)(4-inam)(H_2O)] complexes and a water of a further complex completes a symmetric eight-membered hydrogen bonded ring which builds up chains in the *a*-axis. The –NH_2 group of the imide similarly bonds to two DMSO oxygen atoms link the chains in the *c*-axis to give hydrogen-bonded sheets that then stack in the *b*-axis.

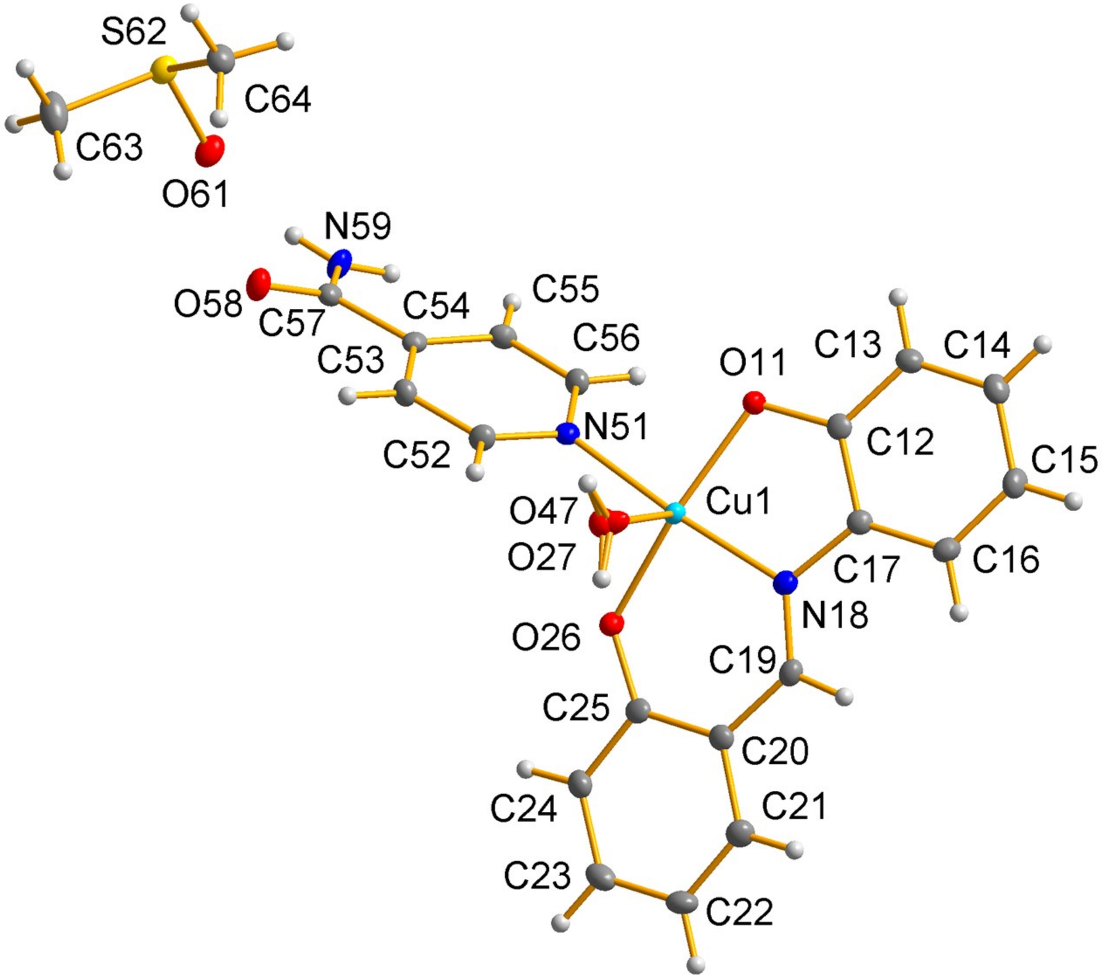


Figure S20 Asymmetric unit of compound **13**. Thermal ellipsoids are at 50 % probability. The minor component of the disordered [Cu(**L**)] groups and hydrogen atom labels are omitted for clarity.

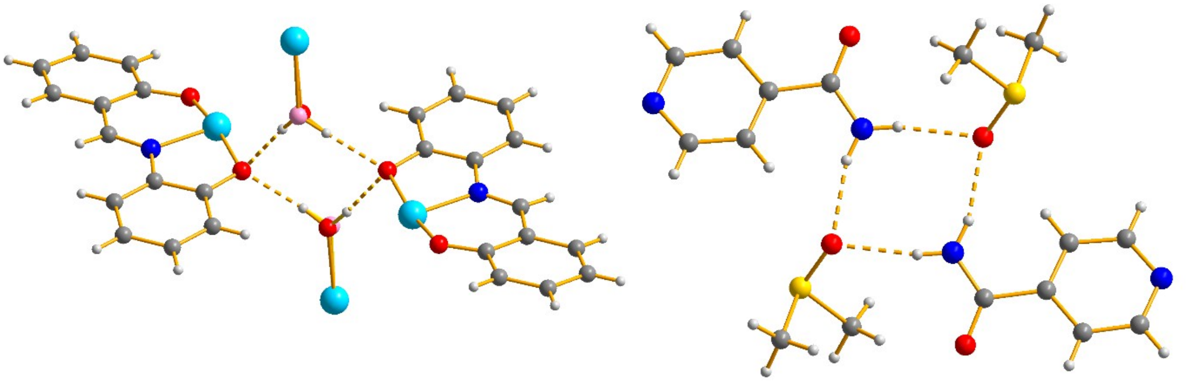


Figure S21 Left: symmetric hydrogen-bonded ring between four [Cu(**L**)(4-inam)(H_2O)] complexes. Right: similar motif between amide and DMSO groups. Each ring contains an inversion centre.

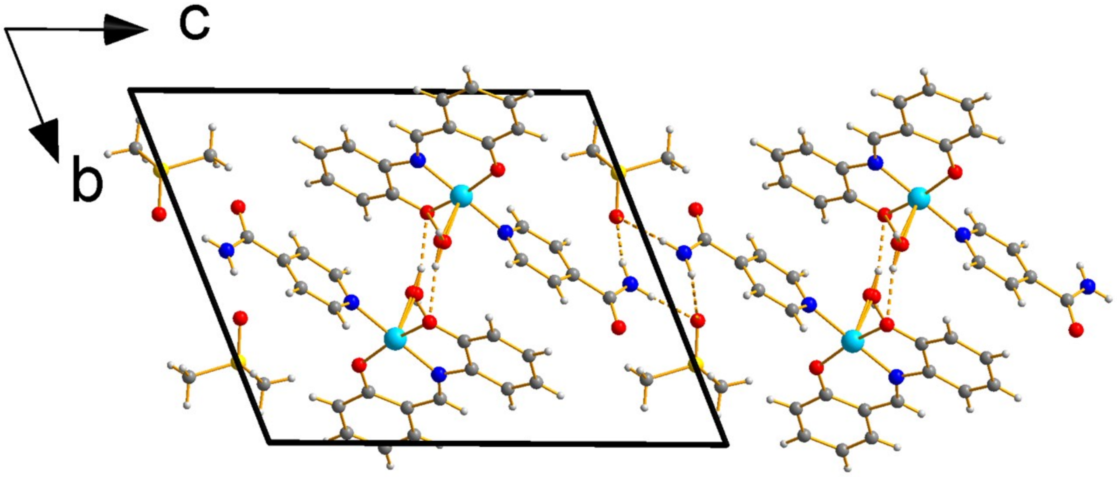


Figure S22 Packing of compound **13**, looking down the *a*-axis. Hydrogen-bonded chains run down the *a*-axis, bridged through water molecules while the chains are bonded into sheets through the amide groups in the *c*-axis.

As reported by Bohle and Stasko,[4] compound **14** crystallises in the monoclinic space group *C*2/*c*. The asymmetric unit consists of one disordered [Cu(**L**)] unit and one terpyridine (tpy) molecule. The Cu(II) ion lies on a two-fold rotation axis that runs through the centre of the tpy group (Cu1−N37···C40). The Cu−N bond to the **L** ligand lies just off of this axis and the ligand is 50:50 disordered. In this compound, the Cu atom lies on a single site, unlike the preceding 13 compounds.

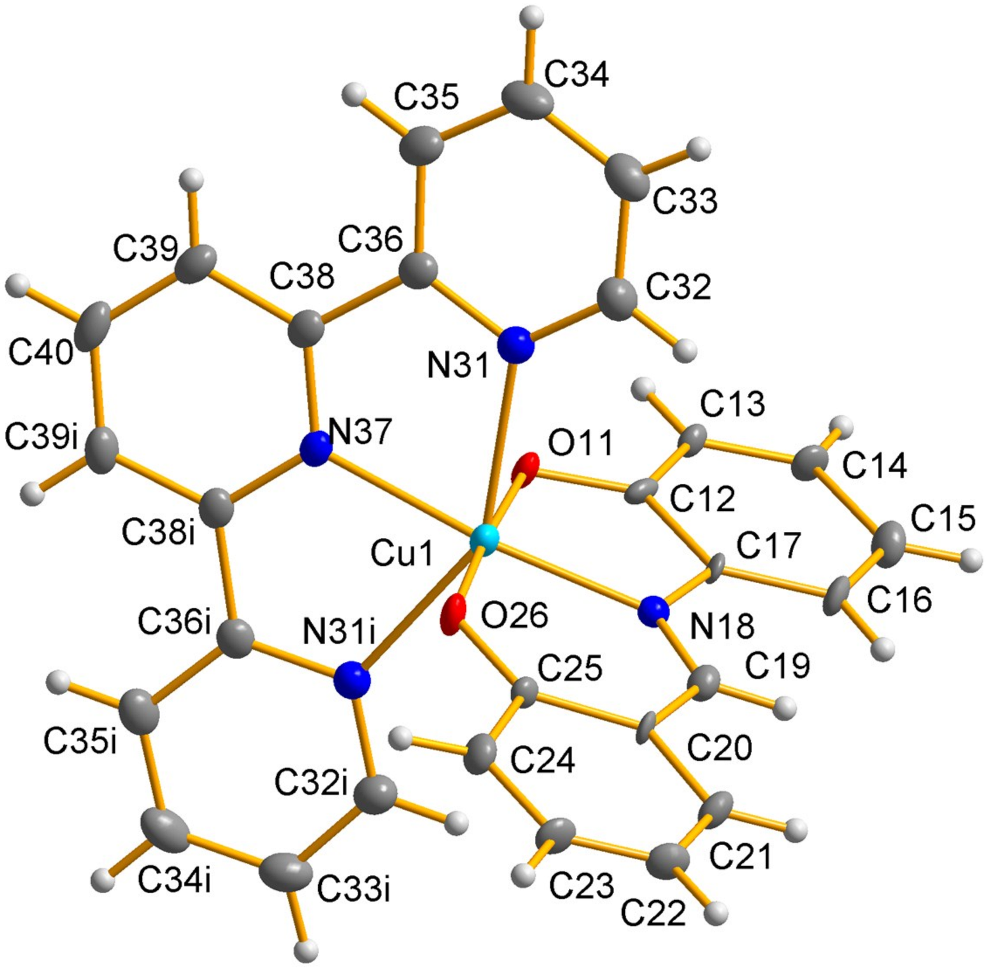


Figure S23 Asymmetric unit and selected symmetry equivalents of **14**. Thermal ellipsoids are at the 50% probability level. One of the disordered **L** components and hydrogen atom labels are omitted for clarity. Symmetry operators: *i*) 1−*x*, *y*, 1½ −*z*.

Compound **15**, as described by Sousa *et al.*,[5] crystallises in the triclinic space group $P\bar{1}$. The asymmetric unit consists of one [Cu(**L**)] unit and one phenanthroline molecule. The phenanthroline chelates the Cu(II) ion, taking the remaining site in the $d_{x^2-y^2}$ and one in the d_{z^2}. A major difference from the previous report is that we have found that the [Cu(**L**)] unit is disordered (63:37), whereas this was previously reported as ordered. From the previous report, three methanol molecules are present, but are so heavily disordered that they could not be successfully located and refined. Analysis with the solvent mask routine in Olex^{2}[6] showed a void in the compound of 295 Å^3 centred at ½,0,0 containing 121 electrons, equivalent to 3.3 MeOH per [Cu(**L**)(phen)] complex and close to the reported value.

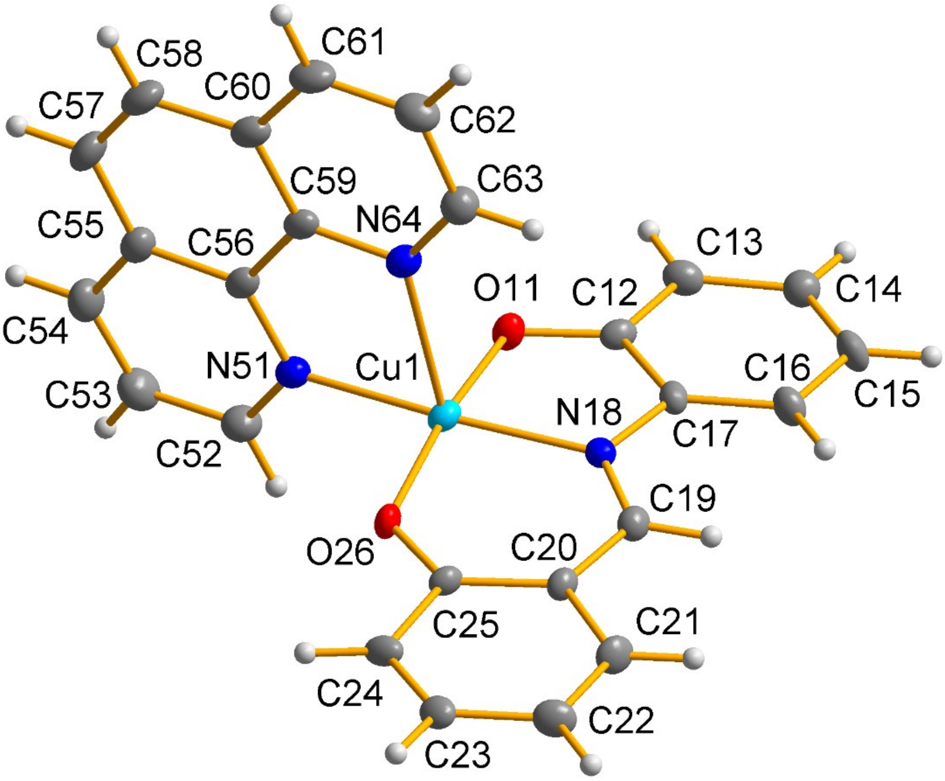


Figure S24 Asymmetric unit of compound **13**. Thermal ellipsoids are at 50 % probability. The minor component of the disordered [Cu(**L**)] groups and hydrogen atom labels are omitted for clarity.

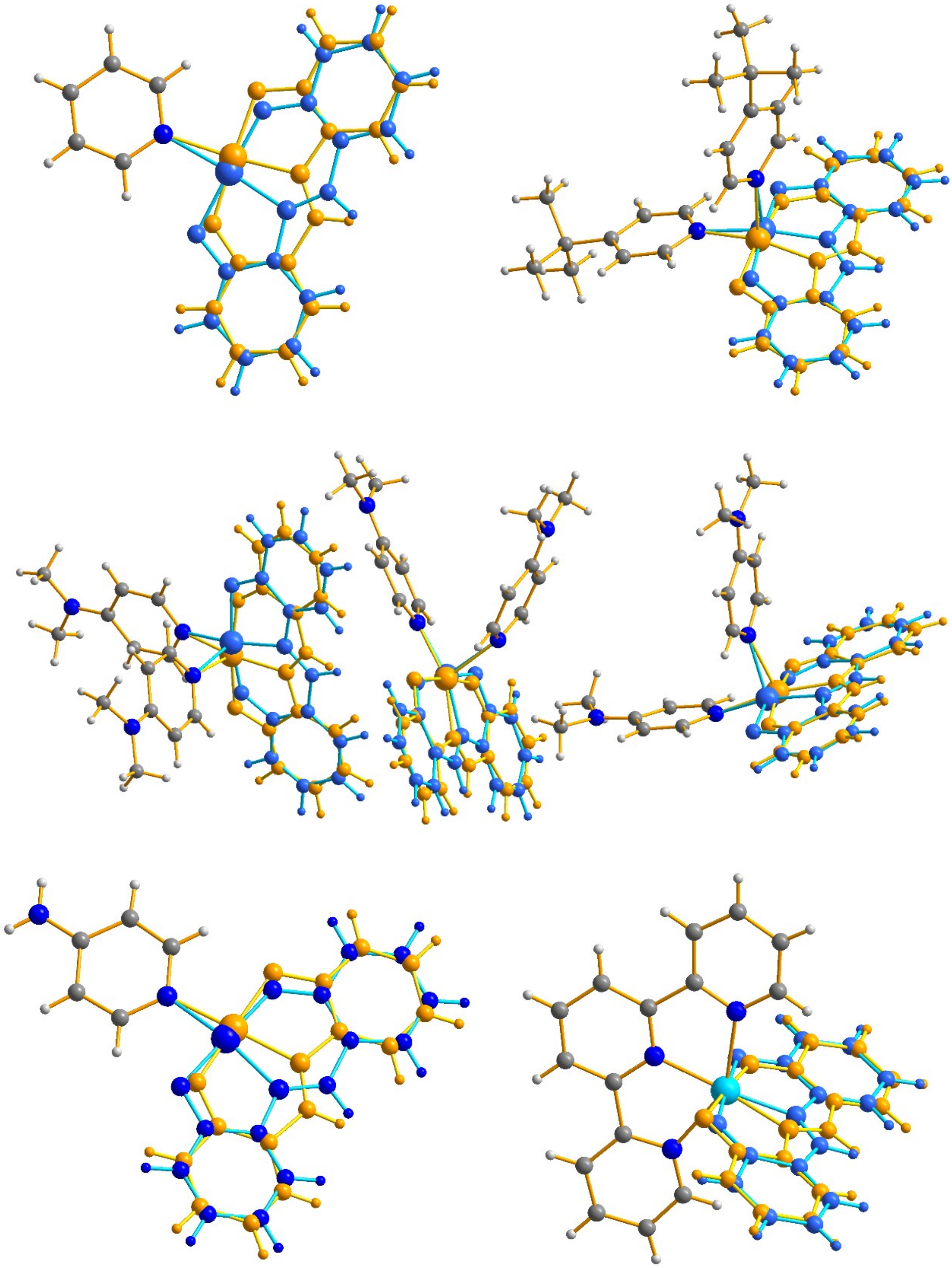


Figure S25 Selected examples of positional disorder in [Cu(**L**)(**M**)] units in this work (major component in blue, minor in orange). Top left: [Cu(**L**)(py)] (**2**); top right: [Cu(**L**)(4-tbpy)$_2$] (**5**); centre: the three [Cu(**L**)(4-dmap)$_2$] units in **9**; bottom left: 0.4 Å resolution structure of [Cu(**L**)(4-ampy)] (**7**) showing 96:4 ratio; bottom right: [Cu(**L**)(tpy)] (**14**), the only complex where the ligand is split, but not the Cu(II) ion.

Structural parameters

Table S2 Selected coordination sphere bond lengths (Å) for the major component.

Compound	$\mathrm{Cu{-}O_{salicyl}}$	$\mathrm{Cu{-}O_{phenol}}$	$\mathrm{Cu{-}N_{imine}}$	$\mathrm{Cu{-}}\mathbf{M}_{\mathrm{planar}}$	$\mathrm{Cu{-}}\mathbf{M}_{\mathrm{axial}}$	[Cu(**L**)] disorder
2	1.899(14)	1.922(13)	1.949(8)	2.017(6)	−	50:50
3	1.914(4)	1.946(3)	1.976(4)	2.043(4)	2.310(12)	−
	1.920(4)	1.943(4)	1.996(5)	2.051(4)	2.287(6)	−
4	1.873(15)	1.928(10)	1.941(7)	1.977(5)	−	57:43
5	1.906(6)	1.957(7)	1.973(5)	2.063(4)	2.280(4)	65:35
	1.923(7)	1.947(8)	1.973(5)	2.060(4)	2.297(4)	65:35
6	1.900(6)	1.938(6)	1.935(5)	2.034(4)	−	70:30
7	1.898(2)	1.947(2)	1.960(3)	2.001(3)	−	96:4
8	1.951(5)	1.946(5)	1.967(4)	2.019(3)	2.284(3)	70:30
9	1.913(7)	1.968(7)	1.973(6)	2.083(4)	2.229(4)	55:45
	1.925(10)	1.957(8)	1.992(7)	1.995(6)	2.327(6)	66:34
	1.919(6)	1.960(4)	1.990(4)	1.981(3)	2.251(4)	70:30
10	1.876(11)	1.929(10)	1.955(8)	2.023(7)	[2.367(11)][a]	58:42
11	1.890(4)	1.923(3)	1.952(3)	2.008(2)	−	80:20
12	1.899(5)	1.958(5)	1.946(5)	2.016(4)	−	78:22
	1.894(6)	1.965(4)	1.949(4)	1.997(4)	−	85:15
13	1.931(2)	1.952(2)	1.966(2)	2.017(2)	[2.292(2)][b]	94:6
14	1.851(7)	2.079(6)	1.996(3)	2.080(2)	2.331(14)	50:50
15	1.844(8)	1.996(7)	1.964(3)	2.034(2)	2.283(2)	63:37

a) The axial ligand is from dimerisation to another [Cu(**L**)(4-cnpy)] complex; *b*) The axial ligand is water.

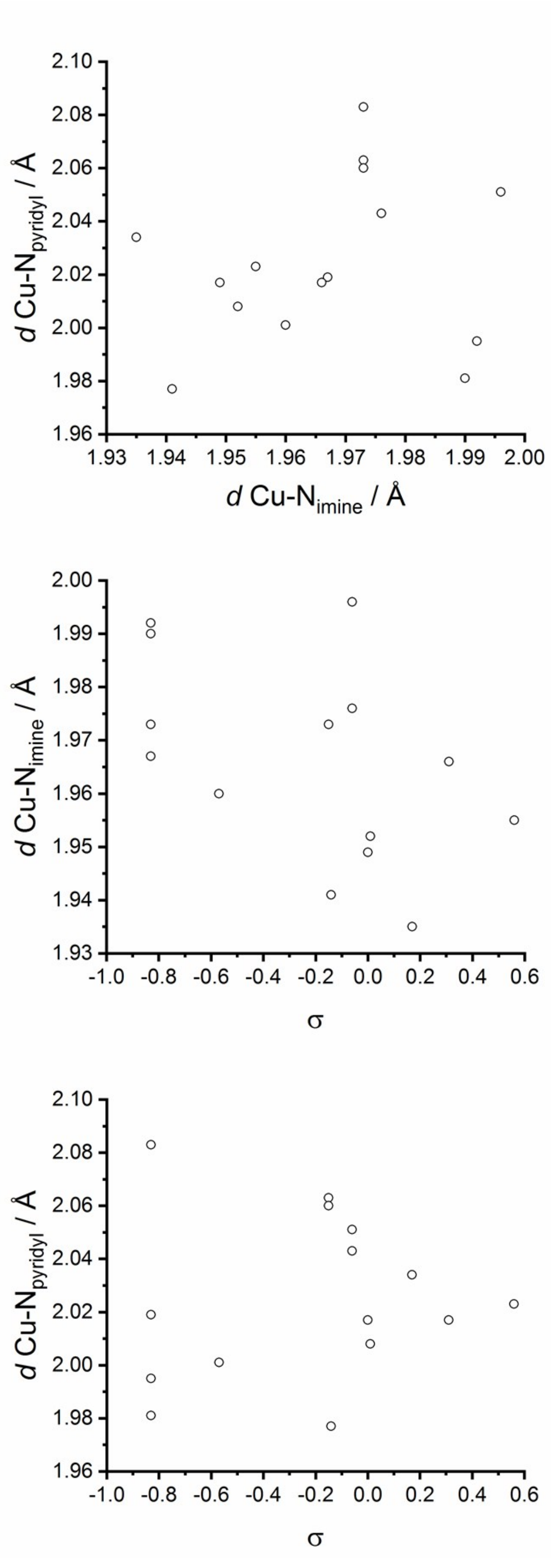


Figure S26 Top: plot of *d* Cu−N$_{(imine)}$ vs *d* Cu−N$_{(pyridyl)}$; middle: plot of *d* Cu−N$_{(imine)}$ vs Hammett parameter; bottom: plot of *d* Cu−N$_{(pyridyl)}$ vs Hammett parameter. In all three plots, no clear correlation is observed.

Table S3 Geometric distortion parameters of the Cu(II) coordination spheres (major component only). τ_4 and τ_4' are geometric distortion parameters for 4-coordinate complexes and τ_5 is for five-coordinate complexes.

The parameters are derived as:

$$\tau_4 = \frac{360° - (\alpha + \beta)}{360° - 2\theta}$$

so that for square planar, $\tau_4 = 0$; for saw-horse, $\tau_4 = 0.425$ and for tetrahedral, $\tau_4 = 1$.[7]

$$\tau_4' = \frac{\beta - \alpha}{360° - \theta} + \frac{180° - \beta}{180° - \theta}$$

so that for square planar, $\tau_4' = 0$; for saw-horse, $\tau_4' = 0.240$ and for tetrahedral, $\tau_4' = 1$.[8]

$$\tau_5 = \frac{\beta - \alpha}{60°}$$

so that for square-based pyramidal, $\tau_5 = 0$ and for trigonal bipyramidal, $\tau_5 = 1$.[9]

where α and β are the largest angles between ligands and $\alpha < \beta$.

Compound	α / °	β / °	τ_4	τ_4'	τ_5	$d_{\max}$ / Å [a]
2	169.6	173.6	0.119	0.107		0.180(12)
3	162.49	173.19			0.178	0.287(4)
	164.3	172.05			0.129	0.268(4)
4	172.3	173.9	0.098	0.093		0.267(13)
5	164.3	168.0			0.062	0.169(4)
	168.5	165.3			0.053	0.167(4)
6	171.9	174.2	0.099	0.091		0.153(6)
7	167.67	174.54	0.126	0.105		0.205(3)
8	163.3	170.05			0.113	0.159(6)
9	96.85	102.3			0.041	0.136(7)
	95.1	109.5			0.237	0.250(6)
	97.71	100.47			0.028	0.151(5)
10	170.6	178.1			0.125	0.145(10)
11	174.47	178.15	0.052	0.041		0.078(2)
12	170.6	173.5	0.113	0.104		0.147(5)
	171.0	173.3	0.111	0.104		0.150(6)
13	166.98	175.43			0.141	0.168(2)
15	168.2	168.87			0.011	0.267(7)

a) maximum deviation from CuN_2O_2 mean square plane

Hammett plot for pyridyls

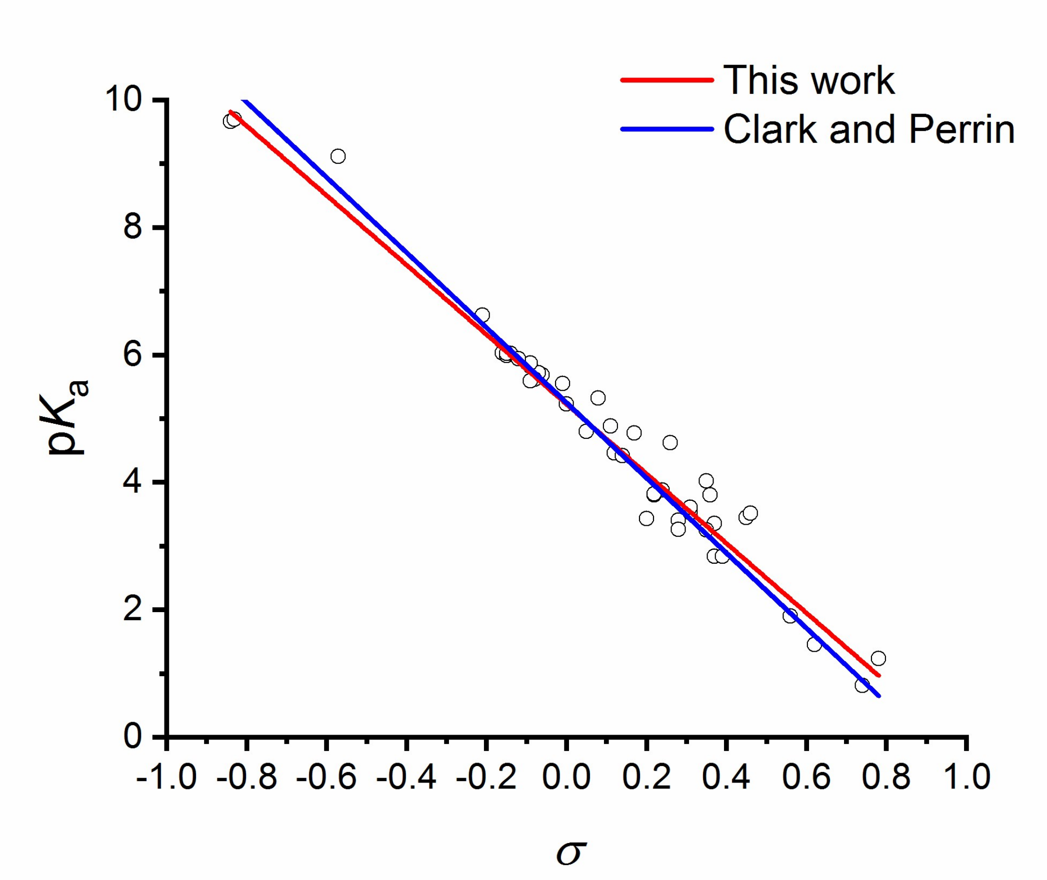


Figure S27 plot of pK_a vs Hammett parameter, σ, for known pyridyl ligands from literature. Equation of line is 5.23 – 5.46(14)σ. where the intercept is fixed at the pK_a value for pyridine (pK_a^0 = 5.23). R^2 = 0.9952.

Thus, pK_a of a pyridyl is:

$$pK_a = pK_a^0 - \rho\sum\sigma$$

$$pK_a = 5.23 - 5.46\sum\sigma$$

Table S4 Hammett parameters (σ)[10–12] and experimental pK_a values[12–15] for substituted pyridyls with calculated pK_a values from the Hammett equation from this work and by Clark and Perrin.[16]

	σ	pK_a	This work	Clark and Perrin
H	0	5.23	5.23	5.25
3−Cl	+0.37	2.84	3.21	3.07
3−I	+0.35	4.02	3.32	3.19
3−CH_2CH_3	−0.07	5.70	5.61	5.66
3−$C(CH_3)_3$	−0.09	5.82	5.72	5.78
3−NO_2	+0.74	0.81	1.19	0.88
3−OCH_3	+0.11	4.88	4.63	4.60

3−Br	+0.39	2.84	3.10	2.95
3−CH$_3$	−0.06	5.68	5.56	5.60
3−CH(CH$_3$)$_2$	−0.07	5.72	5.61	5.66
3−C=O−NH$_2$	+0.28	3.40	3.70	3.60
3−CN	+0.62	1.45	1.84	1.59
3−NH−C=O−CH$_3$	+0.12	4.46	4.57	4.54
3−C=O−OCH$_2$CH$_3$	+0.37	3.35	3.21	3.07
3−NH$_2$	−0.16	6.03	6.10	6.19
3−NH−C=O−(C$_6$H$_5$)	+0.22	3.80	4.03	3.95
3−CHO	+0.36	3.80	3.26	3.13
3−SCH$_3$	+0.14	4.42	4.47	4.42
3−(C$_6$H$_5$)	+0.05	4.80	4.96	4.96
3−NHSO$_2$CH$_3$	+0.20	3.43	4.14	4.07
3−NH(CH$_3$)(C=OCH$_3$)	+0.31	3.52	3.54	3.42
4−Cl	+0.24	3.88	3.92	3.83
4−I	+0.35	3.25	3.32	3.19
4−CH$_2$CH$_3$	−0.15	6.02	6.05	6.14
4−C(CH$_3$)$_3$	−0.15	5.99	6.05	6.14
4−NO$_2$	+0.78	1.23	0.97	0.65
4−OCH$_3$	−0.21	6.62	6.38	6.49
4−Br	+0.22	3.82	4.03	3.95
4−CH$_3$	−0.14	6.02	5.99	6.08
4−CH(CH$_3$)$_2$	−0.15	6.02	6.05	6.14
4−C=O−NH$_2$	+0.31	3.61	3.54	3.42
4−CN	+0.56	1.90	2.17	1.95
4−NH−C=O−CH$_3$	−0.09	5.87	5.72	5.78
4−C=O−OCH$_2$CH$_3$	+0.45	3.45	2.77	2.60
4−NH$_2$	−0.57	9.11	8.34	8.61
4−NH−C=O−(C$_6$H$_5$)	+0.08	5.32	4.79	4.78
4−NHMe	−0.84	9.66	9.82	10.21
4−SCH$_3$	−0.12	5.94	5.89	5.96
4−(C$_6$H$_5$)	−0.01	5.55	5.28	5.31
4−CH=CH$_2$	−0.08	5.62	5.67	5.72
4−CH$_2$(C$_6$H$_5$)	−0.09	5.59	5.72	5.78
4−N(CH$_3$)$_2$	−0.83	9.70	9.76	10.15
4−NH(CH$_3$)(C=OCH$_3$)	+0.26	4.62	3.81	3.72
4−C=O−OCH$_3$	+0.28	3.26	3.70	3.60
4−C=O−CH$_3$	+0.46	3.51	2.72	2.54
4−(2−pyridyl)	+0.17	4.77	4.30	4.25

Notes on Hammett parameters and approximations

Where possible, experimentally measured Hammett and pK_a values for the pyridyl ligands and their substituents have used from the literature (see table above). For pyrazine and imidazole, accepted approximations were used to account for heterocyclic rings and 5-membered rings.[11]

Prediction of Hammett parameters (σ) and pK_a for pyridyls

- *4,4'-dithiodipyridine (4,4'-dtdp)*

$-4-\mathrm{SCH_3}$ σ = 0.00
$-4-\mathrm{S(C_6H_4)}$ σ = +0.13
$\Delta\sigma$ = +0.13
$-4-\mathrm{SSCH_3}$ σ = +0.13
Transmission effect of −S− = × 0.41

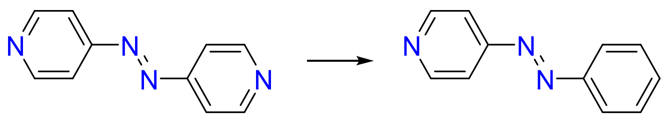
+0.13 + (0.41 × 0.13) = +0.18
Inductive correction for py−SR = −0.10
σ ≈ +0.08
pK_a (this work) = **4.79**
pK_a (Clark and Perrin, 1964) = 4.78
pK_a (experimental)[17] = **4.80**

- *4-(4-Nitrobenzyl)pyridine (4-nbpy)*

$-4-\mathrm{(C_6H_5)}$ σ = −0.01
$-4-\mathrm{(4\text{-}C_6H_5NO_2)}$ σ = +0.23
$\Delta\sigma$ = +0.24
$-4-\mathrm{CH_2(C_6H_5)}$ σ = −0.09
Transmission effect of –CH$_2$− = × 0.41

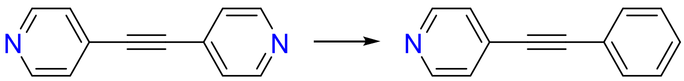
−0.09 + (0.41 × +0.24) = +0.01
σ ≈ +0.01
pK_a (this work) = **5.17**
pK_a (Clark and Perrin, 1964) = 5.21

- *Approximations for 4,4'-azpy and 4,4'-bpac*[15]



4,4'-azpy

pK_a = ((3.10))
σ = +0.39



4,4'-bpac

pK_a = 4.62
σ = +0.16

pK_a for 4,4′-azpy calculated from Hammett parameter for phenyl analogue. pK_a for 4-(phenylethynyl)pyridine from reference 12.

References

1 S. V. F. Beddoe, A. J. Fitzpatrick, J. R. Price, N. Mallo, J. E. Beves, G. G. Morgan, J. A. Kitchen and T. D. Keene, *Cryst. Growth Des.*, 2017, **17**, 6603–6612.
2 M. K. Koley, S. U. Parsekar, N. Duraipandy, M. S. Kiran, B. Varghese, P. T. Manoharan and A. P. Koley, *Inorganica Chim. Acta*, 2018, **478**, 211–221.
3 P. Pfeiffer, T. Hesse, H. Pfitzner, W. Scholl and H. Thielert, *J. Prakt. Chemie*, 1937, **149**, 217–296.
4 D. S. Bohle and D. Stasko, *Acta Crystallogr.*, 2002, E**58**, m340–m341.
5 E. Labisbal, J. A. Garcia-Vazquez, J. Romero, S. Picos, A. Sousa, A. Castiñeiras and C. Maichle-Mössmer, *Polyhedron*, 1995, **14**, 663–670.
6 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339–341.
7 L. Yang, D. R. Powell and R. P. Houser, *Dalton Trans.*, 2007, 955–964.
8 A. Okuniewski, D. Rosiak, J. Chojnacki and B. Becker, *Polyhedron*, 2015, **90**, 47–57.
9 A. W. Addison, T. N. Rao, J. Reedijk, J. van Rijn and G. C. Verschoor, *J. Chem. Soc., Dalton Trans.*, 1984, 1349–1356.
10 C. Hansch, A. Leo and R. W. Taft, *Chem. Rev.*, 1991, **91**, 165–195.
11 D. D. Perrin, B. Dempsey and E. P. Serjeant, *pK a Prediction for Organic Acids and Bases*, Springer Netherlands, Dordrecht, 1981.
12 A. Fischer, W. J. Galloway and J. Vaughan, *J. Chem. Soc.*, 1964, 3591.
13 W. P. Jencks and J. Regenstein, *Handbook of Biochemistry and Molecular Biology, Fourth Edition*, CRC Press, Boca Raton, 4th edn., 2010.
14 A. Rabold, R. Bauer and G. Zundel, *J. Phys. Chem.*, 1995, **99**, 1889–1895.
15 A. R. Katritzky, D. J. Short and A. J. Boulton, *J. Chem. Soc.*, 1960, 1516.
16 J. Clark and D. D. Perrin, *Q. Rev. Chem. Soc.*, 1964, **18**, 295.
17 Í. de S. Moreira, L. T. de S. Parente and D. W. Franco, *Quim. Nova*, 1998, **21**, 545–550.