Four Copper(II) Pyrazolido Complexes Derived from Reactions of 3{5}-Substituted Pyrazoles with CuF_2 or $Cu(OH)_2$

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Supplementary Information

Table S1 Selected bond lengths and angles for $[\{Cu(\mu\text{-}pz^{Py})(pz^{Py})\}_2]\cdot\frac{1}{2}H_2O\cdot 2CHCl_3$ (**1**$\cdot\frac{1}{2}H_2O\cdot 2CHCl_3$).

Table S2 Metric parameters for the hydrogen bond interactions in $[\{Cu(\mu\text{-}pz^{Py})(pz^{Py})\}_2]\cdot\frac{1}{2}H_2O\cdot 2CHCl_3$ (**1**$\cdot\frac{1}{2}H_2O\cdot 2CHCl_3$).

Table S3 Selected bond lengths and angles for $[\{Cu(\mu\text{-}pz^{Ph})_2\}_4]\cdot\frac{1}{2}C_5H_{12}$ (**2**$\cdot\frac{1}{2}C_5H_{12}$).

Fig S1 Variable temperature magnetic susceptibility data for a bulk sample of **2**

Fig S2 *X*-band EPR spectra of powder samples of **1** and **3** at 115 K.

Table S4 Selected bond lengths and angles for $[\{Cu(\mu\text{-}pz^{Ph})_2\}_4]\cdot\frac{1}{2}C_5H_{12}$ $[Cu_4F_2(\mu_4\text{-}F)(\mu\text{-}Pz^{PhF})_5(HPz^{PhF})_4]\cdot\frac{3}{4}CH_2Cl_2\cdot\text{-}\frac{1}{4}HPz^{PhF}$ (**3**$\cdot\frac{3}{4}CH_2Cl_2\cdot\frac{1}{4}Hpz^{PhF}$).

Table S5 Metric parameters for the hydrogen bond interactions in $[Cu_4F_2(\mu_4\text{-}F)(\mu\text{-}Pz^{PhF})_5(HPz^{PhF})_4]\cdot\frac{3}{4}CH_2Cl_2\cdot\text{-}\frac{1}{4}HPz^{PhF}$ (**3**$\cdot\frac{3}{4}CH_2Cl_2\cdot\frac{1}{4}Hpz^{PhF}$).

Table S6 Selected bond lengths and angles (Å, °) for $[Cu(pz^{PhF})_2(Hpz^{PhF})_2]$ (**4**).

Table S7 Metric parameters for the hydrogen bond interactions in $[Cu(pz^{PhF})_2(Hpz^{PhF})_2]$ (**4**).

Fig S3 View of the complex molecule in **4**, showing the atom numbering scheme employed.

Table S1 Selected bond lengths (Å) and angles (°) for $[\{Cu(\mu\text{-}pz^{Py})(pz^{Py})\}_2]\cdot\frac{1}{2}H_2O\cdot 2CHCl_3$ (**1**$\cdot\frac{1}{2}H_2O\cdot 2CHCl_3$).

	Molecule A (X = A)	Molecule B (X = B)
Cu(1X)–N(3X)	1.975(3)	1.969(3)
Cu(1X)–N(9X)	2.130(3)	2.100(3)
Cu(1X)–N(15X)	1.991(3)	1.992(3)
Cu(1X)–N(25X)	1.945(3)	1.964(3)
Cu(1X)–N(31X)	2.174(3)	2.222(3)
Cu(2X)–N(4X)	1.990(3)	1.972(3)
Cu(2X)–N(14X)	1.948(3)	1.962(3)
Cu(2X)–N(20X)	2.090(3)	2.100(3)
Cu(2X)–N(36X)	1.936(3)	1.953(3)
Cu(2X)–N(42X)	2.196(3)	2.257(3)
Cu(1X)…Cu(2X)	3.7318(7)	3.8931(7)
N(3X)–Cu(1X)–N(9X)	78.62(13)	79.61(13)
N(3X)–Cu(1X)–N(15X)	94.76(13)	95.23(13)
N(3X)–Cu(1X)–N(25X)	168.54(14)	170.43(14)
N(3X)–Cu(1X)–N(31X)	96.32(13)	97.84(12)
N(9X)–Cu(1X)–N(15X)	142.28(13)	151.78(12)
N(9X)–Cu(1X)–N(25X)	91.20(13)	91.89(14)
N(9X)–Cu(1X)–N(31X)	95.98(13)	98.00(12)
N(15X)–Cu(1X)–N(25X)	96.53(13)	94.34(13)
N(15X)–Cu(1X)–N(31X)	121.72(13)	110.21(12)
N(25X)–Cu(1X)–N(31X)	79.38(13)	78.86(12)
N(4X)–Cu(2X)–N(14X)	94.27(13)	95.48(13)
N(4X)–Cu(2X)–N(20X)	142.56(12)	155.06(13)
N(4X)–Cu(2X)–N(36X)	95.60(13)	93.79(13)
N(4X)–Cu(2X)–N(42X)	113.65(12)	112.74(12)
N(14X)–Cu(2X)–N(20X)	79.53(13)	79.98(13)
N(14X)–Cu(2X)–N(36X)	169.81(13)	170.21(14)
N(14X)–Cu(2X)–N(42X)	94.51(12)	101.31(13)
N(20X)–Cu(2X)–N(36X)	94.08(13)	90.28(14)
N(20X)–Cu(2X)–N(42X)	103.67(12)	92.18(12)
N(36X)–Cu(2X)–N(42X)	79.18(12)	77.89(13)

Table S2 Metric parameters for the hydrogen bond interactions in $[\{Cu(\mu\text{-}pz^{Py})(pz^{Py})\}_2]\cdot\frac{1}{2}H_2O\cdot 2CHCl_3$ (**1**$\cdot\frac{1}{2}H_2O\cdot 2CHCl_3$) (Å, °).

	D–H	H...A	D...A	D–H...A
C(47)–H(47)…O(63)	1.00	2.21	3.159(6)	158.8
C(59)–H(59)…N(37B)	1.00	2.20	3.182(7)	166.7
O(63)–H(63B)…N(37A)	0.846(10)	1.996(13)	2.823(4)	166(4)
O(63)–H(63A)…N(26B)	0.847(10)	2.03(2)	2.824(4)	155(5)

Table S3 Selected bond lengths (Å) and angles (°) for [{Cu(μ-pz^{Ph})$_2$}$_4$]·½C$_5$H$_{12}$ (**2**·½C$_5$H$_{12}$). The suffixes A, B, and C refer to different disordered sites for the same N atoms. For clarity only the range exhibited by the nine different angles formed by the disordered atoms N(5A, 5B, 5C)–Cu(1)–N(83A, 83B, 83C) is given.

Cu(1)–N(5A, 5B, 5C)	1.909(17), 2.080(13), 1.97(2)	Cu(3)–N(28)	1.973(2)
Cu(1)–N(16)	1.990(2)	Cu(3)–N(39)	1.965(2)
Cu(1)–N(72)	1.988(2)	Cu(3)–N(49)	1.983(2)
Cu(1)–N(83A, 83B, 83C)	2.040(16), 2.006(12), 1.886(14)	Cu(3)–N(60)	1.994(2)
Cu(2)–N(6A, 6B, 6C)	2.058(17), 1.888(15), 1.96(3)	Cu(4)–N(50)	1.953(2)
Cu(2)–N(17)	1.977(2)	Cu(4)–N(61)	1.984(2)
Cu(2)–N(27)	1.993(2)	Cu(4)–N(71)	2.004(2)
Cu(2)–N(38)	1.987(2)	Cu(4)–N(82A, 82B, 82C)	2.033(17), 1.827(10), 2.030(15)
Cu(1)…Cu(2)	3.2881(6)	Cu(3)…Cu(4)	3.2771(7)
Cu(2)…Cu(3)	3.2839(7)	Cu(1)…Cu(4)	3.3342(7)
N(5A, 5B, 5C)–Cu(1)–N(16)	92.5(8), 90.2(5), 96.0(4)	N(28)–Cu(3)–N(39)	87.71(9)
N(5A, 5B, 5C)–Cu(1)–N(72)	100.1(8), 99.9(8), 94.2(4)	N(28)–Cu(3)–N(49)	101.58(9)
N(5A, 5B, 5C)–Cu(1)–N(83A, 83B, 83C)	153.2(6)-162.5(6)	N(28)–Cu(3)–N(60)	142.78(9)
N(16)–Cu(1)–N(72)	146.58(9)	N(39)–Cu(3)–N(49)	154.97(9)
N(16)–Cu(1)–N(83A, 83B, 83C)	88.7(7), 95.5(3), 89.0(7)	N(39)–Cu(3)–N(60)	91.40(9)
N(72)–Cu(1)–N(83A, 83B, 83C)	92.6(7), 84.3(3), 93.1(7)	N(49)–Cu(3)–N(60)	94.73(9)
N(6A, 6B, 6C)–Cu(2)–N(17)	88.0(6), 87.3(4), 90.6(6)	N(50)–Cu(4)–N(61)	87.83(9)
N(6A, 6B, 6C)–Cu(2)–N(27)	90.7(8), 94.2(4), 88.4(7)	N(50)–Cu(4)–N(71)	92.62(9)
N(6A, 6B, 6C)–Cu(2)–N(38)	157.2(5), 152.1(3), 156.0(6)	N(50)–Cu(4)–N(82A, 82B, 82C)	155.3(6), 152.7(4), 159.5(4)
N(17)–Cu(2)–N(27)	148.55(9)	N(61)–Cu(4)–N(71)	143.43(9)
N(17)–Cu(2)–N(38)	100.76(9)	N(61)–Cu(4)–N(82A, 82B, 82C)	98.6(8), 103.3(4), 95.5(5)
N(27)–Cu(2)–N(38)	92.44(9)	N(71)–Cu(4)–N(82A, 82B, 82C)	96.0(6), 92.8(3), 96.5(4)

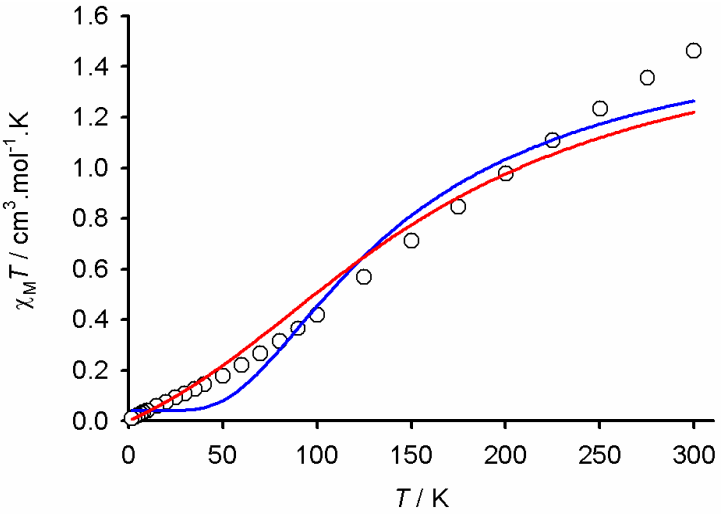

Fig S1 Variable temperature magnetic susceptibility data for a dried bulk sample of **2** (○). The blue line shows the best fit of these data (line) to a Hamiltonian describing a square of S = ½ copper(II) centres (equation 2 in the main paper). The fitted parameters are J = –89(3) cm^{-1}, g = 2.2 (fixed) and the paramagnetic impurity ρ = 10.0(3) %. The red line is the best fit of the data to a Hamiltonian describing an antiferromagnetic chain of copper(II) spins, which gives J = –71(3) cm^{-1} and g = 2.2 (fixed). See the main paper for more details.

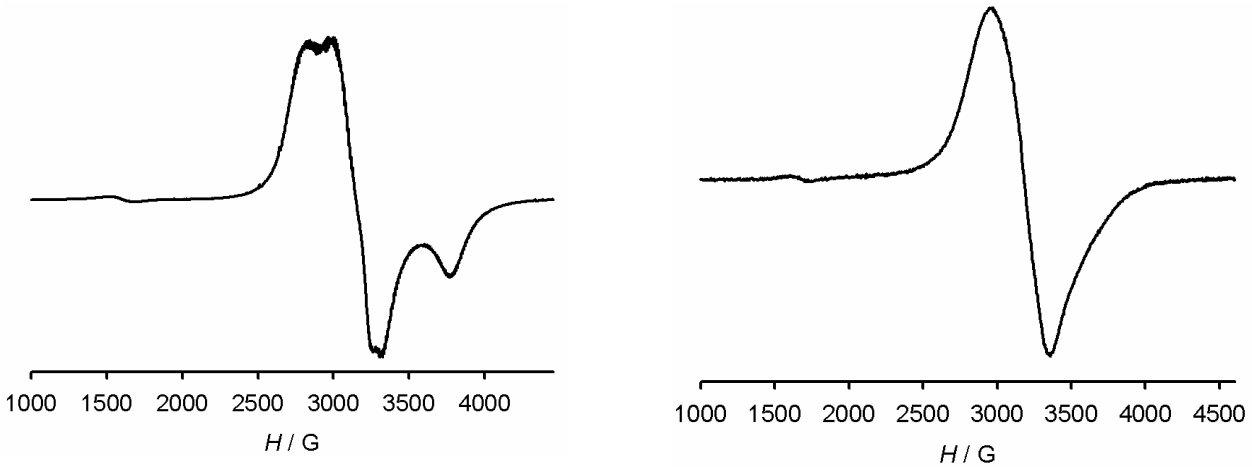

Fig S2 *X*-band EPR spectra of powder samples of **1** (left) and **3** (right) at 115 K. The *W*-band EPR spectrum of **1** is shown in the main paper.

Table S4 Selected bond lengths (Å) and angles (°) for $[Cu_4F_2(\mu_4\text{-}F)(\mu\text{-}Pz^{PhF})_5(HPz^{PhF})_4]\cdot¾CH_2Cl_2\cdot¼HPz^{PhF}$ (**3**·¾CH_2Cl_2·¼Hpz^{PhF}). The suffixes C and D refer to different disordered sites for N atoms located in molecules A and B respectively.

Molecule A		Molecule B	
Cu(1A)–F(1A)	2.253(2)	Cu(1B)–F(1B)	2.267(2)
Cu(1A)–F(2A)	1.971(2)	Cu(1B)–F(2B)	1.971(2)
Cu(1A)–N(7A)	1.981(3)	Cu(1B)–N(7B)	1.988(3)
Cu(1A)–N(9A)	1.994(3)	Cu(1B)–N(9B)	1.993(3)
Cu(1A)–N(12A)	2.006(3)	Cu(1B)–N(12B, 12D)	1.825(18), 2.111(15)
Cu(2A)–F(1A)	2.245(2)	Cu(2B)–F(1B)	2.269(2)
Cu(2A)–F(3A)	1.946(2)	Cu(2B)–F(3B)	1.936(2)
Cu(2A)–N(1A)	1.999(3)	Cu(2B)–N(1B)	1.996(3)
Cu(2A)–N(4A)	1.965(3)	Cu(2B)–N(4B)	1.948(3)
Cu(2A)–N(14A, 14C)	2.040(15), 2.003(19)	Cu(2B)–N(14B, 14D)	1.95(2), 2.09(2)
Cu(3A)–F(1A)	2.295(2)	Cu(3B)–F(1B)	2.324(2)
Cu(3A)–N(2A)	1.971(3)	Cu(3B)–N(2B)	1.974(3)
Cu(3A)–N(3A)	1.988(3)	Cu(3B)–N(3B)	1.981(3)
Cu(3A)–N(6A)	1.996(3)	Cu(3B)–N(6B)	1.984(3)
Cu(3A)–N(16A)	2.013(3)	Cu(3B)–N(16B)	2.018(3)
Cu(4A)–F(1A)	2.254(2)	Cu(4B)–F(1B)	2.226(2)
Cu(4A)–N(5A)	1.990(3)	Cu(4B)–N(5B)	1.989(3)
Cu(4A)–N(8A)	2.011(3)	Cu(4B)–N(8B)	2.016(3)
Cu(4A)–N(10A)	1.969(3)	Cu(4B)–N(10B)	1.975(3)
Cu(4A)–N(18A)	2.025(3)	Cu(4B)–N(18B)	2.023(3)
Cu(1A)…Cu(2A)	3.8169(7)	Cu(1B)…Cu(2B)	3.8104(7)
Cu(1A)…Cu(3A)	4.1812(6)	Cu(1B)…Cu(3B)	4.2577(7)
Cu(1A)…Cu(4A)	3.2719(6)	Cu(1B)…Cu(4B)	3.2570(6)
Cu(2A)…Cu(3A)	3.2863(6)	Cu(2B)…Cu(3B)	3.2836(6)
Cu(2A)…Cu(4A)	4.1654(7)	Cu(2B)…Cu(4B)	4.1901(7)
Cu(3A)…Cu(4A)	3.1899(6)	Cu(3B)…Cu(4B)	3.2199(6)
F(1A)–Cu(1A)–F(2A)	84.26(8)	F(1B)–Cu(1B)–F(2B)	82.67(9)
F(1A)–Cu(1A)–N(7A)	88.73(10)	F(1B)–Cu(1B)–N(7B)	87.40(11)
F(1A)–Cu(1A)–N(9A)	96.18(11)	F(1B)–Cu(1B)–N(9B)	97.16(10)
F(1A)–Cu(1A)–N(12A)	107.28(11)	F(1B)–Cu(1B)–N(12B, 12D)	110.9(7), 109.6(5)
F(2A)–Cu(1A)–N(7A)	98.28(10)	F(2B)–Cu(1B)–N(7B)	98.03(11)
F(2A)–Cu(1A)–N(9A)	173.72(11)	F(2B)–Cu(1B)–N(9B)	174.16(12)
F(2A)–Cu(1A)–N(12A)	85.50(11)	F(2B)–Cu(1B)–N(12B, 12D)	85.6(10), 85.4(8)
N(7A)–Cu(1A)–N(9A)	88.00(13)	N(7B)–Cu(1B)–N(9B)	87.79(13)
N(7A)–Cu(1A)–N(12A)	163.87(14)	N(7B)–Cu(1B)–N(12B, 12D)	161.7(7), 163.0(5)
N(9A)–Cu(1A)–N(12A)	88.39(13)	N(9B)–Cu(1B)–N(12B, 12D)	89.0(10), 89.2(8)
F(1A)–Cu(2A)–F(3A)	83.83(9)	F(1B)–Cu(2B)–F(3B)	83.28(9)
F(1A)–Cu(2A)–N(1A)	89.19(11)	F(1B)–Cu(2B)–N(1B)	88.43(11)
F(1A)–Cu(2A)–N(4A)	92.98(10)	F(1B)–Cu(2B)–N(4B)	93.89(11)
F(1A)–Cu(2A)–N(14A, 14C)	116.1(7), 110.7(7)	F(1B)–Cu(2B)–N(14B, 14D)	113.4(6), 117.5(6)
F(3A)–Cu(2A)–N(1A)	96.48(11)	F(3B)–Cu(2B)–N(1B)	96.35(11)
F(3A)–Cu(2A)–N(4A)	172.72(12)	F(3B)–Cu(2B)–N(4B)	172.12(12)
F(3A)–Cu(2A)–N(14A, 14C)	89.3(9), 86.2(9)	F(3B)–Cu(2B)–N(14B, 14D)	81.3(4), 91.9(4)
N(1A)–Cu(2A)–N(4A)	90.00(13)	N(1B)–Cu(2B)–N(4B)	90.91(14)
N(1A)–Cu(2A)–N(14A, 14C)	154.6(7), 160.1(7)	N(1B)–Cu(2B)–N(14B, 14D)	157.4(6), 153.6(6)
N(4A)–Cu(2A)–N(14A, 14C)	86.2(9), 88.8(9)	N(4B)–Cu(2B)–N(14B, 14D)	93.1(4), 82.9(4)
F(1A)–Cu(3A)–N(2A)	85.07(11)	F(1B)–Cu(3B)–N(2B)	84.49(10)
F(1A)–Cu(3A)–N(3A)	92.15(10)	F(1B)–Cu(3B)–N(3B)	93.68(11)
F(1A)–Cu(3A)–N(6A)	106.72(10)	F(1B)–Cu(3B)–N(6B)	104.93(11)
F(1A)–Cu(3A)–N(16A)	94.33(10)	F(1B)–Cu(3B)–N(16B)	93.89(11)
N(2A)–Cu(3A)–N(3A)	89.58(13)	N(2B)–Cu(3B)–N(3B)	90.18(13)
N(2A)–Cu(3A)–N(6A)	89.22(13)	N(2B)–Cu(3B)–N(6B)	89.51(13)
N(2A)–Cu(3A)–N(16A)	179.21(13)	N(2B)–Cu(3B)–N(16B)	178.09(13)
N(3A)–Cu(3A)–N(6A)	160.91(13)	N(3B)–Cu(3B)–N(6B)	161.27(13)

Table S4 continued.

N(3A)–Cu(3A)–N(16A)	89.92(12)	N(3B)–Cu(3B)–N(16B)	88.91(13)
N(6A)–Cu(3A)–N(16A)	91.45(12)	N(6B)–Cu(3B)–N(16B)	91.89(13)
F(1A)–Cu(4A)–N(5A)	109.18(10)	F(1B)–Cu(4B)–N(5B)	108.91(11)
F(1A)–Cu(4A)–N(8A)	84.25(10)	F(1B)–Cu(4B)–N(8B)	83.93(10)
F(1A)–Cu(4A)–N(10A)	90.07(11)	F(1B)–Cu(4B)–N(10B)	92.46(11)
F(1A)–Cu(4A)–N(18A)	99.82(11)	F(1B)–Cu(4B)–N(18B)	98.24(11)
N(5A)–Cu(4A)–N(8A)	87.01(13)	N(5B)–Cu(4B)–N(8B)	87.67(13)
N(5A)–Cu(4A)–N(10A)	160.48(13)	N(5B)–Cu(4B)–N(10B)	158.35(13)
N(5A)–Cu(4A)–N(18A)	91.01(12)	N(5B)–Cu(4B)–N(18B)	92.59(13)
N(8A)–Cu(4A)–N(10A)	91.91(13)	N(8B)–Cu(4B)–N(10B)	91.29(13)
N(8A)–Cu(4A)–N(18A)	175.88(13)	N(8B)–Cu(4B)–N(18B)	177.60(14)
N(10A)–Cu(4A)–N(18A)	88.74(13)	N(10B)–Cu(4B)–N(18B)	87.58(13)
Cu(1A)–F(1A)–Cu(2A)	116.13(9)	Cu(1B)–F(1B)–Cu(2B)	114.32(9)
Cu(1A)–F(1A)–Cu(3A)	133.68(9)	Cu(1B)–F(1B)–Cu(3B)	136.11(9)
Cu(1A)–F(1A)–Cu(4A)	93.10(8)	Cu(1B)–F(1B)–Cu(4B)	92.92(8)
Cu(2A)–F(1A)–Cu(3A)	92.76(8)	Cu(2B)–F(1B)–Cu(3B)	91.28(8)
Cu(2A)–F(1A)–Cu(4A)	135.62(9)	Cu(2B)–F(1B)–Cu(4B)	137.55(10)
Cu(3A)–F(1A)–Cu(4A)	89.06(7)	Cu(3B)–F(1B)–Cu(4B)	90.07(8)

Table S5 Metric parameters for the hydrogen bond interactions in $[Cu_4F_2(\mu_4\text{-}F)(\mu\text{-}Pz^{PhF})_5(HPz^{PhF})_4]\cdot¾CH_2Cl_2\cdot¼HPz^{PhF}$ (**3**$\cdot¾CH_2Cl_2\cdot¼Hpz^{PhF}$) (Å, °).

	D–H	H...A	D...A	D–H...A
N(11A)–H(11A)…F(3A)	0.88	1.98	2.752(4)	145.5
N(13A, 13C)–H(13A, 13C)…F(2A)[a]	0.88, 0.88	1.81, 1.91	2.66(2), 2.749(19)	162.2, 157.5
N(15A)–H(15A)…F(2A)	0.88	1.93	2.693(4)	143.7
N(17A)–H(17A)…F(3A)	0.88	1.78	2.647(4)	168.9
N(11B, 11D)–H(11B, 11D)…F(3B)[a]	0.88, 0.88	2.05, 1.82	2.787(8), 2.656(9)	141.1, 157.6
N(13B, 13D)–H(13B, 13D)…F(2B)[a]	0.88, 0.88	1.93, 1.90	2.73(2), 2.73(2)	149.2, 157.9
N(15B)–H(15B)…F(2B)	0.88	1.90	2.689(4)	148.7
N(17B)–H(17B)…F(3B)	0.88	1.78	2.644(4)	167.5

[a]This interaction involves a disordered N–H group, and should be interpreted with caution.

Table S6 Selected bond lengths and angles (Å, °) for [Cu(pz^{PhF})$_2$(Hpz^{PhF})$_2$] (**4**).

Cu(1)–N(2)	1.985(4)	Cu(1)–N(26)	1.978(4)
Cu(1)–N(14)	1.952(3)	Cu(1)–N(38)	1.950(3)
N(2)–Cu(1)–N(14)	97.21(14)	N(14)–Cu(1)–N(26)	140.69(16)
N(2)–Cu(1)–N(26)	96.41(14)	N(14)–Cu(1)–N(38)	93.27(13)
N(2)–Cu(1)–N(38)	143.76(16)	N(26)–Cu(1)–N(38)	97.10(13)

Table S7 Metric parameters for the hydrogen bond interactions in [Cu(pz^{PhF})$_2$(Hpz^{PhF})$_2$] (**4**).

	D–H	H...A	D...A	D–H...A
N(3)–H(3)…N(15)	0.88	1.92	2.682(5)	144.2
N(27)–H(27)…N(39)	0.88	1.92	2.669(5)	141.7

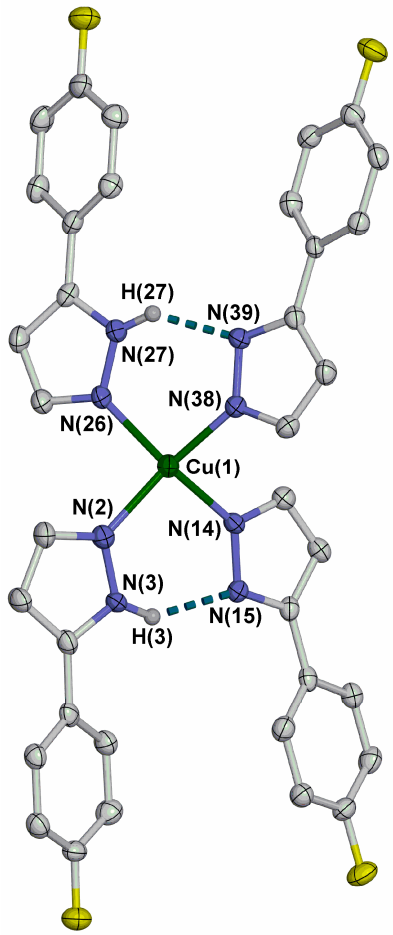

Fig S3 View of the complex molecule in **4**, showing the atom numbering scheme employed. All C-bound H atoms have been omitted for clarity, and thermal ellipsoids are at the 50% probability level. Colour code: C = white, H = grey, Cu = green, N = blue, F = yellow.