Supporting Information

Spin Frustrated Pyrazolato Triangular Cu^{II} Complex. Structure and Magnetic Properties, an Overview.

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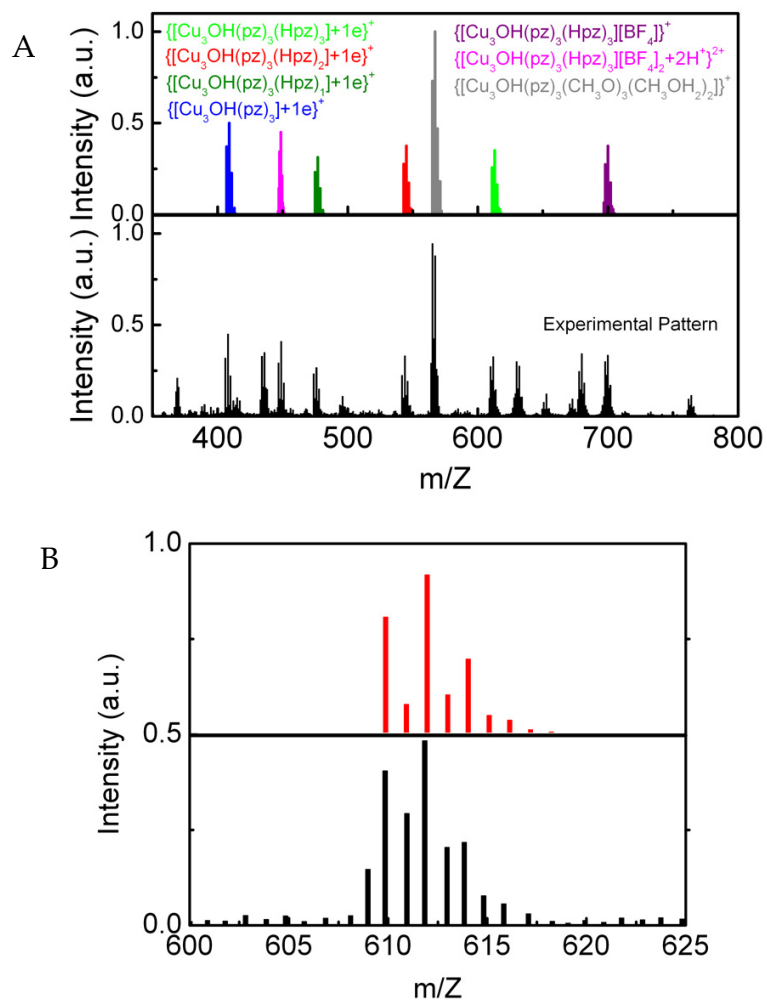# 1. Electrospray-Mass Spectrometry 1−Cu₃

Figure S1. **A**. Electrospray-Mass Spectrum of **1−Cu₃** in the positive mode with the different simulated fragments patterns. **B**. Experimental (red) and simulated (black) pattern of the fragment $\{[Cu_3(\mu_3-OH)(pz)_3(Hpz)_3]+1e^-\}^+$ (m/Z = 613).
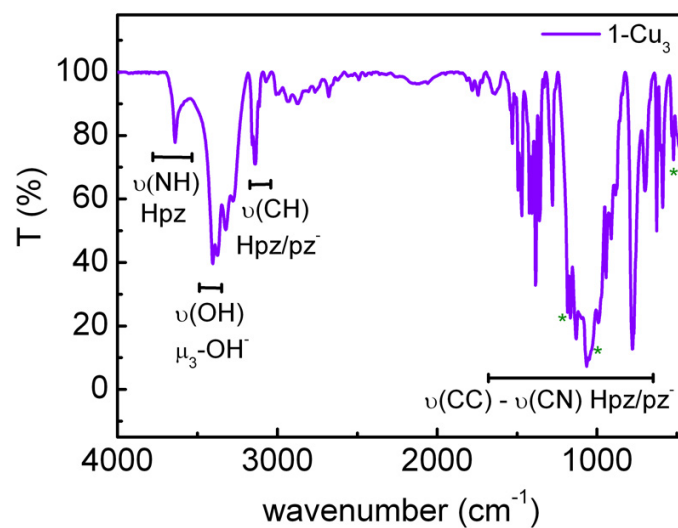
2. FTIR spectra of 1–Cu₃

Figure S2. FTIR Spectrum of **1–Cu₃** highlighting the bands of the protonated (Hpz) and deprotonated (pz⁻) pyrazolato ligand. The stretching of the μ₃–OH⁻ unit is also observed. The green asterisks show the vibrations associated to the [BF₄]⁻ group.

3. X-Ray Diffraction of 1−Cu3

Table S1. Crystal data and structure refinement for **1−Cu3**.	
Identification code	**1−Cu3**
CCDC	2174487
Empirical formula	$Cu_3C_{18}H_{22}N_{12}OB_2F_8$
Formula weight	786.75
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	16.4768(17)
b/Å	10.4768(4)
c/Å	17.6691(10)
α/°	90
β/°	107.092(9)
γ/°	90
Volume/Å³	2915.4(4)
Z	4
ϱ_{calc}g/cm³	1.793
μ/mm⁻¹	2.257
F(000)	1564.0
Crystal size/mm³	0.15 × 0.08 × 0.07
Radiation	$MoK\alpha$ (λ = 0.71073)
2Θ range for data collection/°	6.196 to 51.998
Index ranges	-20 ≤ h ≤ 17, -12 ≤ k ≤ 12, -21 ≤ l ≤ 21
Reflections collected	23679
Independent reflections	5713 [R_{int} = 0.1041, R_{sigma} = 0.1118]
Data/restraints/parameters	5713/4/413
Goodness-of-fit on F²	1.010
Final R indexes [I>=2σ (I)]	R_1 = 0.0515, wR_2 = 0.0769
Final R indexes [all data]	R_1 = 0.0997, wR_2 = 0.0930
Largest diff. peak/hole / e Å⁻³	0.62/-0.61

Table S2. Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å²×10³) for **1−Cu₃**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	x	y	z	U(eq)
Cu1	1738.7(4)	6996.5(5)	4839.1(3)	15.06(17)
Cu2	2756.7(5)	4387.6(5)	5773.9(4)	16.39(17)
Cu3	2809.3(4)	7117.4(5)	6782.5(3)	15.24(17)
F1	4681(2)	7419(3)	5236.8(17)	32.8(9)
F2	4035(2)	7437(3)	6212.2(16)	29.5(9)
F3	3956(2)	5662(3)	5455.1(16)	24.5(8)
F4	3241(2)	7461(3)	4926.1(17)	27.6(8)
F5	1474(2)	3175(3)	5942.1(18)	29.5(8)
F6	644(2)	3301(3)	6754.6(16)	29.6(9)
F7	27(2)	3187(3)	5435.3(17)	35.3(9)
F8	736(2)	5044(3)	5971.0(19)	37.9(9)
O1	2207(2)	6039(3)	5857.1(18)	13.3(8)
N1	2027(3)	8474(4)	6288(2)	15.8(10)
N2	1606(3)	8424(4)	5496(2)	15.3(10)
N3	1739(3)	5416(4)	4259(2)	15.8(10)
N4	2184(3)	4375(4)	4634(2)	18.8(11)
N5	3395(3)	5608(4)	7310(2)	18.9(11)
N6	3299(3)	4459(4)	6923(2)	17.2(11)
N7	4188(3)	8942(4)	7501(3)	21.9(11)
N8	3511(3)	8321(4)	7612(2)	18.1(11)
N9	1487(3)	8115(4)	3871(2)	18.4(11)
N10	762(3)	8178(4)	3274(3)	23.2(11)
N11	3266(3)	2676(4)	5710(2)	16.6(10)
N12	2836(3)	1578(4)	5732(3)	18.2(11)
C1	1754(4)	9509(4)	6586(3)	20.0(13)
C2	1152(4)	10150(4)	6000(3)	21.3(14)
C3	1084(4)	9435(4)	5320(3)	16.9(12)
C4	1382(4)	5108(5)	3497(3)	21.9(14)
C5	1585(4)	3857(5)	3364(3)	23.4(14)
C6	2088(4)	3446(5)	4090(3)	24.6(15)
C7	3663(4)	3563(5)	7449(3)	22.8(14)
C8	4009(4)	4105(5)	8190(3)	24.6(14)
C9	3823(4)	5392(5)	8073(3)	20.7(13)
C10	4508(4)	9794(5)	8072(3)	28.3(15)
C11	4035(4)	9744(5)	8590(3)	24.1(14)
C12	3423(4)	8822(5)	8280(3)	20.9(14)
C13	2003(4)	8959(5)	3685(3)	23.8(14)
C14	1605(4)	9545(5)	2962(3)	32.1(16)
C15	817(4)	9028(6)	2722(3)	35.9(17)
C16	3986(4)	2332(5)	5585(3)	20.0(13)
C17	4019(4)	1002(5)	5521(3)	24.9(14)
C18	3284(4)	572(5)	5614(3)	27.6(15)
B1	3997(4)	6995(5)	5448(3)	16.8(14)
B2	710(5)	3687(6)	6010(4)	20.6(16)

Table S3. Anisotropic Displacement Parameters (Å²×10³) for **1−Cu₃**. The Anisotropic displacement factor exponent takes the form: -2π²[h²a*²U₁₁+2hka*b*U₁₂+…].

Atom	U₁₁	U₂₂	U₃₃	U₂₃	U₁₃	U₁₂
Cu1	20.1(4)	11.7(3)	13.2(3)	1.1(3)	4.5(3)	0.1(3)
Cu2	21.4(4)	11.9(3)	15.9(3)	0.6(3)	5.6(3)	2.9(3)
Cu3	17.9(4)	13.3(3)	13.7(3)	0.0(3)	3.4(3)	-0.8(3)
F1	25(2)	48(2)	30.5(18)	-9.2(16)	14.9(18)	-11.3(17)
F2	40(2)	34.2(18)	18.6(16)	-10.7(14)	14.8(18)	-12.4(17)
F3	24(2)	23.4(17)	24.0(17)	-3.3(14)	4.5(16)	2.1(15)
F4	25(2)	25.2(17)	30.8(18)	7.7(15)	4.6(17)	3.5(16)
F5	24(2)	16.8(16)	53(2)	1.2(15)	19.9(19)	4.3(15)
F6	40(2)	26.0(17)	24.0(17)	-0.3(14)	12.0(18)	-9.6(17)
F7	31(2)	37(2)	31.5(18)	-11.1(16)	0.3(18)	-1.7(18)
F8	37(3)	36(2)	44(2)	-0.8(17)	17(2)	-2.0(18)
O1	14(2)	13.0(18)	13.9(18)	-0.5(15)	5.3(18)	-4.1(16)
N1	19(3)	14(2)	14(2)	-3.4(19)	4(2)	-3(2)
N2	16(3)	11(2)	18(2)	0.4(19)	4(2)	-1(2)
N3	18(3)	13(2)	17(2)	-3.0(19)	5(2)	-1(2)
N4	22(3)	16(2)	18(2)	4(2)	5(2)	2(2)
N5	19(3)	21(2)	15(2)	2(2)	3(2)	1(2)
N6	25(3)	9(2)	18(2)	0.7(19)	7(2)	2(2)
N7	24(3)	26(3)	19(3)	-6(2)	10(2)	-3(2)
N8	14(3)	20(2)	19(2)	2(2)	2(2)	-2(2)
N9	21(3)	19(2)	15(2)	3(2)	6(2)	2(2)
N10	17(3)	29(3)	21(3)	13(2)	3(3)	1(2)
N11	19(3)	10(2)	23(2)	-0.2(19)	10(2)	-5(2)
N12	15(3)	13(2)	28(3)	3(2)	10(3)	-3(2)
C1	31(4)	13(3)	18(3)	-6(2)	10(3)	-4(3)
C2	25(4)	5(3)	36(3)	-2(2)	12(3)	3(2)
C3	20(3)	11(3)	21(3)	3(2)	7(3)	1(2)
C4	26(4)	22(3)	16(3)	-1(2)	3(3)	3(3)
C5	33(4)	22(3)	12(3)	-6(2)	3(3)	-2(3)
C6	39(4)	13(3)	22(3)	-7(2)	9(3)	3(3)
C7	32(4)	17(3)	22(3)	1(2)	12(3)	5(3)
C8	24(4)	29(3)	19(3)	8(3)	2(3)	5(3)
C9	18(4)	28(3)	16(3)	-4(2)	4(3)	1(3)
C10	30(4)	29(3)	22(3)	-10(3)	2(3)	-12(3)
C11	22(4)	26(3)	21(3)	-7(3)	1(3)	0(3)
C12	28(4)	31(3)	6(3)	0(2)	8(3)	4(3)
C13	18(4)	25(3)	28(3)	7(3)	6(3)	-3(3)
C14	25(4)	37(4)	35(4)	25(3)	10(3)	2(3)
C15	28(4)	50(4)	28(3)	26(3)	6(3)	10(3)
C16	13(3)	22(3)	24(3)	0(2)	3(3)	3(3)
C17	30(4)	16(3)	29(3)	-4(3)	11(3)	10(3)
C18	39(4)	12(3)	32(3)	0(3)	10(3)	5(3)
B1	18(4)	14(3)	21(3)	2(3)	9(3)	2(3)
B2	26(5)	15(3)	22(4)	2(3)	9(4)	-3(3)

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Table S4. Bond Lengths for **1−Cu₃**.					
Cu1	F4	2.482(3)	N3	N4	1.371(5)
Cu1	O1	2.005(3)	N3	C4	1.341(6)
Cu1	N2	1.945(4)	N4	C6	1.344(6)
Cu1	N3	1.948(4)	N5	N6	1.371(5)
Cu1	N9	2.013(4)	N5	C9	1.344(6)
Cu2	F3	2.580(3)	N6	C7	1.333(6)
Cu2	F5	2.556(3)	N7	N8	1.354(6)
Cu2	O1	1.978(3)	N7	C10	1.334(6)
Cu2	N4	1.957(4)	N8	C12	1.339(5)
Cu2	N6	1.965(4)	N9	N10	1.342(6)
Cu2	N11	1.997(4)	N9	C13	1.333(6)
Cu3	F2	2.531(3)	N10	C15	1.344(6)
Cu3	O1	1.995(3)	N11	N12	1.358(5)
Cu3	N1	1.945(4)	N11	C16	1.319(6)
Cu3	N5	1.943(4)	N12	C18	1.338(6)
Cu3	N8	2.019(4)	C1	C2	1.380(7)
F1	B1	1.362(7)	C2	C3	1.391(6)
F2	B1	1.412(6)	C4	C5	1.390(7)
F3	B1	1.398(6)	C5	C6	1.375(7)
F4	B1	1.401(7)	C7	C8	1.386(7)
F5	B2	1.407(7)	C8	C9	1.384(7)
F6	B2	1.410(6)	C10	C11	1.367(7)
F7	B2	1.379(7)	C11	C12	1.388(7)
F8	B2	1.425(6)	C13	C14	1.396(7)
N1	N2	1.369(5)	C14	C15	1.355(8)
N1	C1	1.338(6)	C16	C17	1.401(7)
N2	C3	1.342(6)	C17	C18	1.347(8)

Table S5. Bond Angles for **1−Cu₃**.

Atom	Atom	Atom	Angle (°)		Atom	Atom	Atom	Angle (°)
O1	Cu1	F4	85.92(12)		N3	N4	Cu2	121.3(3)
O1	Cu1	N9	169.14(17)		C6	N4	Cu2	131.4(4)
N2	Cu1	F4	95.57(15)		C6	N4	N3	107.2(4)
N2	Cu1	O1	86.03(15)		N6	N5	Cu3	120.5(3)
N2	Cu1	N3	170.27(17)		C9	N5	Cu3	131.2(3)
N2	Cu1	N9	91.58(16)		C9	N5	N6	107.6(4)
N3	Cu1	F4	92.57(15)		N5	N6	Cu2	120.0(3)
N3	Cu1	O1	89.24(15)		C7	N6	Cu2	132.0(3)
N3	Cu1	N9	94.61(16)		C7	N6	N5	107.9(4)
N9	Cu1	F4	83.78(15)		C10	N7	N8	111.9(4)
F5	Cu2	F3	174.02(10)		N7	N8	Cu3	121.0(3)
O1	Cu2	F3	87.72(11)		C12	N8	Cu3	134.2(4)
O1	Cu2	F5	90.80(12)		C12	N8	N7	104.3(4)
O1	Cu2	N11	177.04(15)		N10	N9	Cu1	127.6(3)
N4	Cu2	F3	86.97(14)		C13	N9	Cu1	127.5(4)
N4	Cu2	F5	87.22(15)		C13	N9	N10	104.9(4)
N4	Cu2	O1	89.40(16)		N9	N10	C15	111.7(5)
N4	Cu2	N6	177.55(18)		N12	N11	Cu2	121.9(3)
N4	Cu2	N11	91.12(17)		C16	N11	Cu2	132.0(3)
N6	Cu2	F3	93.53(14)		C16	N11	N12	106.0(4)
N6	Cu2	F5	92.22(15)		C18	N12	N11	110.3(5)
N6	Cu2	O1	88.22(15)		N1	C1	C2	110.5(4)
N6	Cu2	N11	91.21(17)		C1	C2	C3	104.1(4)
N11	Cu2	F3	95.21(14)		N2	C3	C2	110.0(5)
N11	Cu2	F5	86.32(14)		N3	C4	C5	109.9(5)
O1	Cu3	F2	90.67(12)		C6	C5	C4	104.3(5)
O1	Cu3	N8	171.50(15)		N4	C6	C5	110.6(5)
N1	Cu3	F2	103.06(14)		N6	C7	C8	110.2(5)
N1	Cu3	O1	86.65(15)		C9	C8	C7	104.3(5)
N1	Cu3	N8	91.84(17)		N5	C9	C8	110.0(5)
N5	Cu3	F2	87.52(15)		N7	C10	C11	107.6(5)
N5	Cu3	O1	89.41(16)		C10	C11	C12	104.8(5)
N5	Cu3	N1	168.74(18)		N8	C12	C11	111.4(5)
N5	Cu3	N8	93.57(17)		N9	C13	C14	110.9(5)
N8	Cu3	F2	81.52(14)		C15	C14	C13	105.0(5)
B1	F2	Cu3	121.4(3)		N10	C15	C14	107.5(5)
B1	F3	Cu2	124.1(3)		N11	C16	C17	110.1(5)
B1	F4	Cu1	130.5(3)		C18	C17	C16	105.4(5)
B2	F5	Cu2	127.7(3)		N12	C18	C17	108.2(5)
Cu2	O1	Cu1	115.77(15)		F1	B1	F2	110.3(5)
Cu2	O1	Cu3	115.33(18)		F1	B1	F3	112.0(5)
Cu3	O1	Cu1	114.79(15)		F1	B1	F4	110.7(4)
N2	N1	Cu3	120.1(3)		F3	B1	F2	107.9(4)
C1	N1	Cu3	132.1(4)		F3	B1	F4	108.5(5)
C1	N1	N2	107.8(4)		F4	B1	F2	107.2(4)
N1	N2	Cu1	121.9(3)		F5	B2	F6	106.6(5)
C3	N2	Cu1	130.2(4)		F5	B2	F8	109.6(5)
C3	N2	N1	107.7(4)		F6	B2	F8	110.1(4)
N4	N3	Cu1	120.3(3)		F7	B2	F5	110.5(4)
C4	N3	Cu1	131.6(4)		F7	B2	F6	108.0(5)
C4	N3	N4	108.0(4)		F7	B2	F8	111.9(5)

Table S6. Hydrogen Atom Coordinates (Å×10⁴) and Isotropic Displacement Parameters (Å²×10³) for 1−Cu₃.				
Atom	x	y	z	U(eq)
H1A	1666(12)	5780(40)	5950(20)	17(14)
H7A	4350(20)	8750(50)	7092(14)	50(20)
H10A	300(14)	7770(40)	3250(30)	40(20)
H12A	2345(11)	1590(50)	5810(20)	30(18)
H1	1944.51	9760.32	7113.38	24
H2	858.41	10889.11	6047.66	26
H3	729.9	9629.67	4818.09	20
H4	1048.33	5651.81	3114.3	26
H5	1418.17	3400.65	2891.84	28
H6	2328.93	2637.76	4190.08	30
H7	3683.21	2699.01	7335.6	27
H8	4300.15	3697.28	8658.59	30
H9	3972.63	6014.42	8464.75	25
H10	4970.78	10325.77	8110.7	34
H11	4106.55	10223.03	9047.81	29
H12	3003.97	8582.04	8508.5	25
H13	2553.2	9133.52	3995.6	29
H14	1831.72	10157.85	2701.11	39
H15	391.73	9225.91	2259.48	43
H16	4409.67	2891.19	5544.29	24
H17	4455.93	518.13	5432.55	30
H18	3116.75	-277.74	5598.45	33

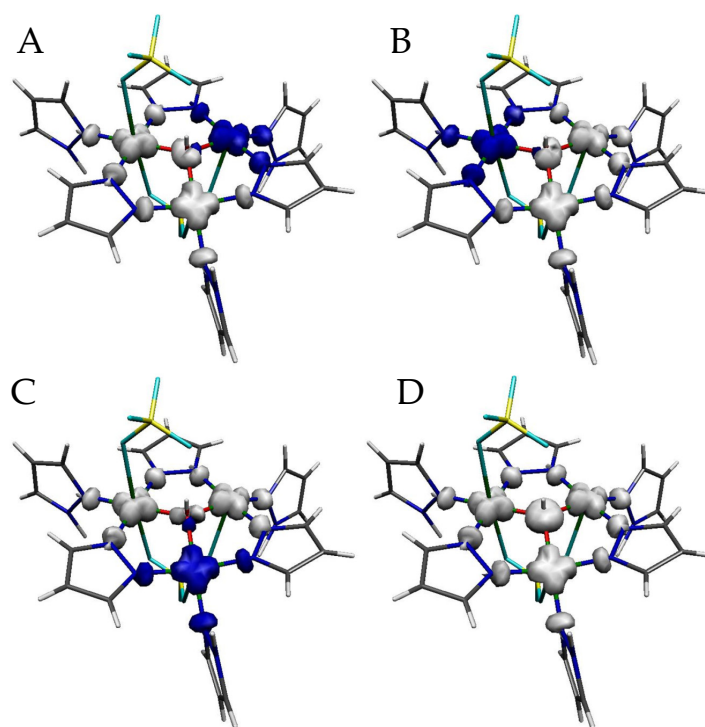**4. Spin density surfaces of 1−Cu₃.**

Figure S3. Spin density surfaces for **1−Cu₃** of the antiferromagnetic configurations (A-C) and the ferromagnetic one (D). Grey colour corresponds to alpha spin density and blue colour to beta spin density