Supplemental Material for:

Importance of Halogen···Halogen Contacts for the Structural and Magnetic Properties of CuX$_2$(pyrazine-*N*,*N*′-dioxide)(H$_2$O)$_2$ (*X* = Cl & Br)

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TITLE RUNNING HEAD: Structure and Properties of CuX$_2$(pyzO)(H$_2$O)$_2$
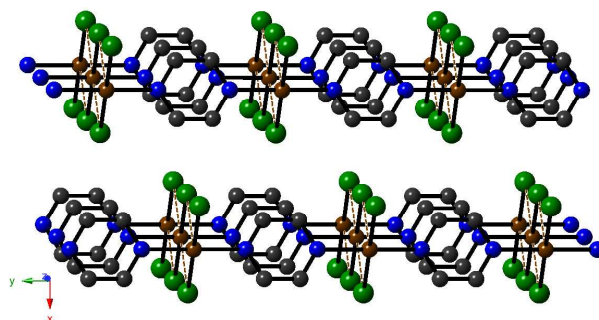
Supplemental Material

Figure S1. Packing diagram of **4**. Dashed lines indicate Cu-Br interactions. Hydrogen atoms omitted for clarity. Compound **3** is isostructural.
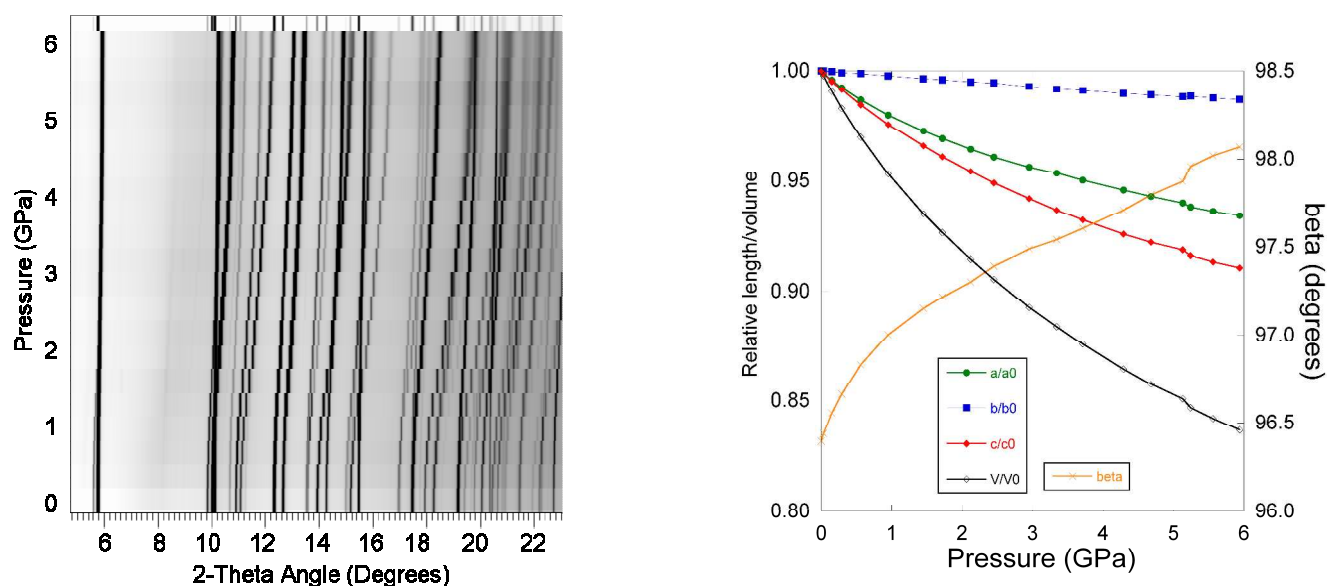

Figure S2. Left: X-ray powder diffraction data as a function of pressure for **4**. No phase transitions are observed for pressures up to 6 GPa. The final scan (top of figure) was taken after the sample was returned to ambient pressure at the conclusion of the experiment. Right: Unit cell parameters as a function of pressure.
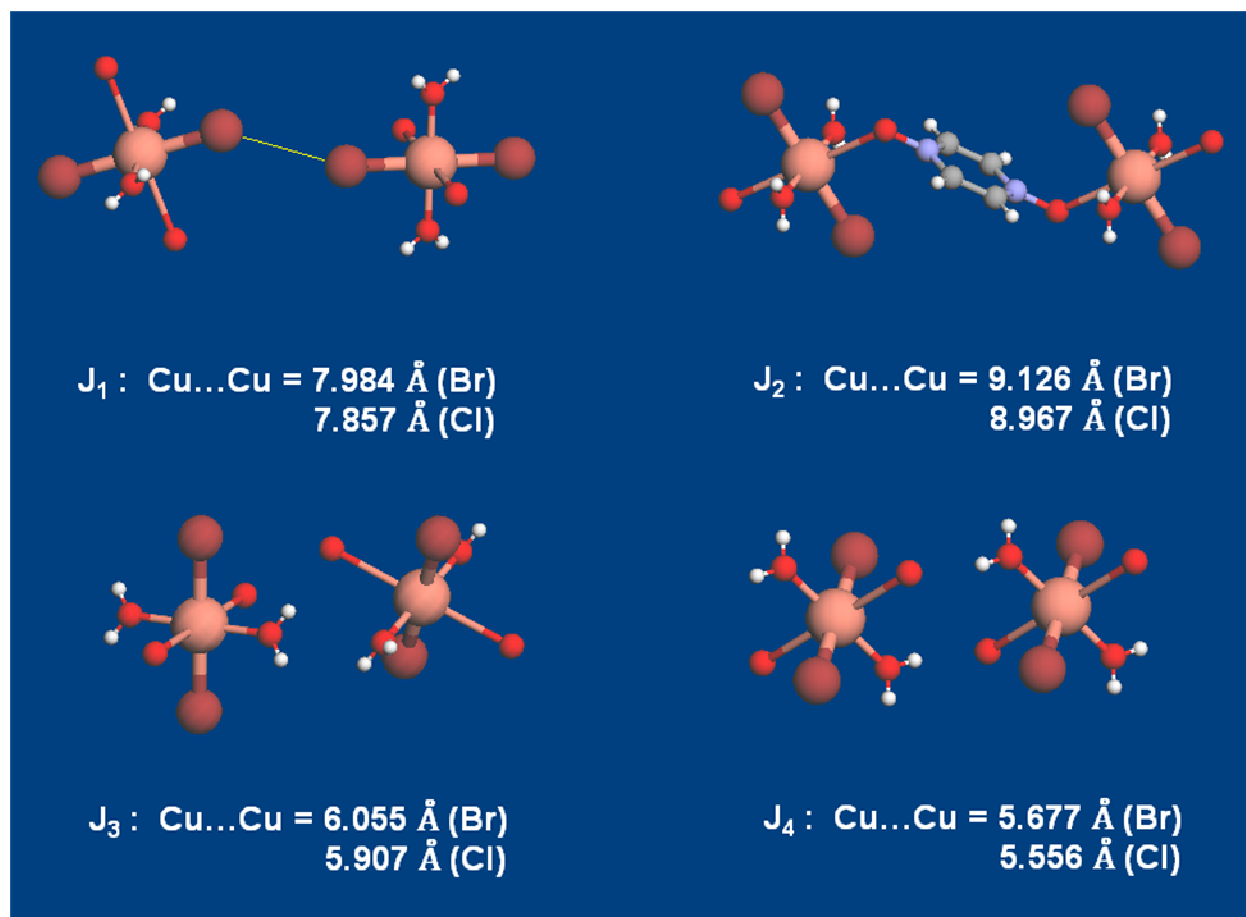
Figure S3. Four spin exchange paths $J_1 - J_4$ considered for $CuX_2(pyzO)(H_2O)_2$ (X = Cl & Br)

FM: Br (0, 0), Cl (0, 0)

AF1: Br (-32.4, -22.4), Cl (-8.2, -5.4)

AF2: Br (-31.6, -21.8), Cl (-7.7, -5.1)

AF3: Br (-0.5, 0.3), Cl (-0.3, -0.2)

AF4: Br (-32.3, -22.3), Cl (-8.0, -5.3)

$$E_{FM} = (-4J_1 - 4J_2 - 8J_3 - 4J_4)N^2/4$$

$$E_{AF1} = (+4J_1 + 4J_2 - 8J_3 - 4J_4)N^2/4$$

$$E_{AF2} = (+4J_1 - 4J_2 + 8J_3 - 4J_4)N^2/4$$

$$E_{AF3} = (-4J_1 + 4J_2 + 8J_3 - 4J_4)N^2/4$$

$$E_{AF4} = (+4J_1 + 4J_4)N^2/4$$

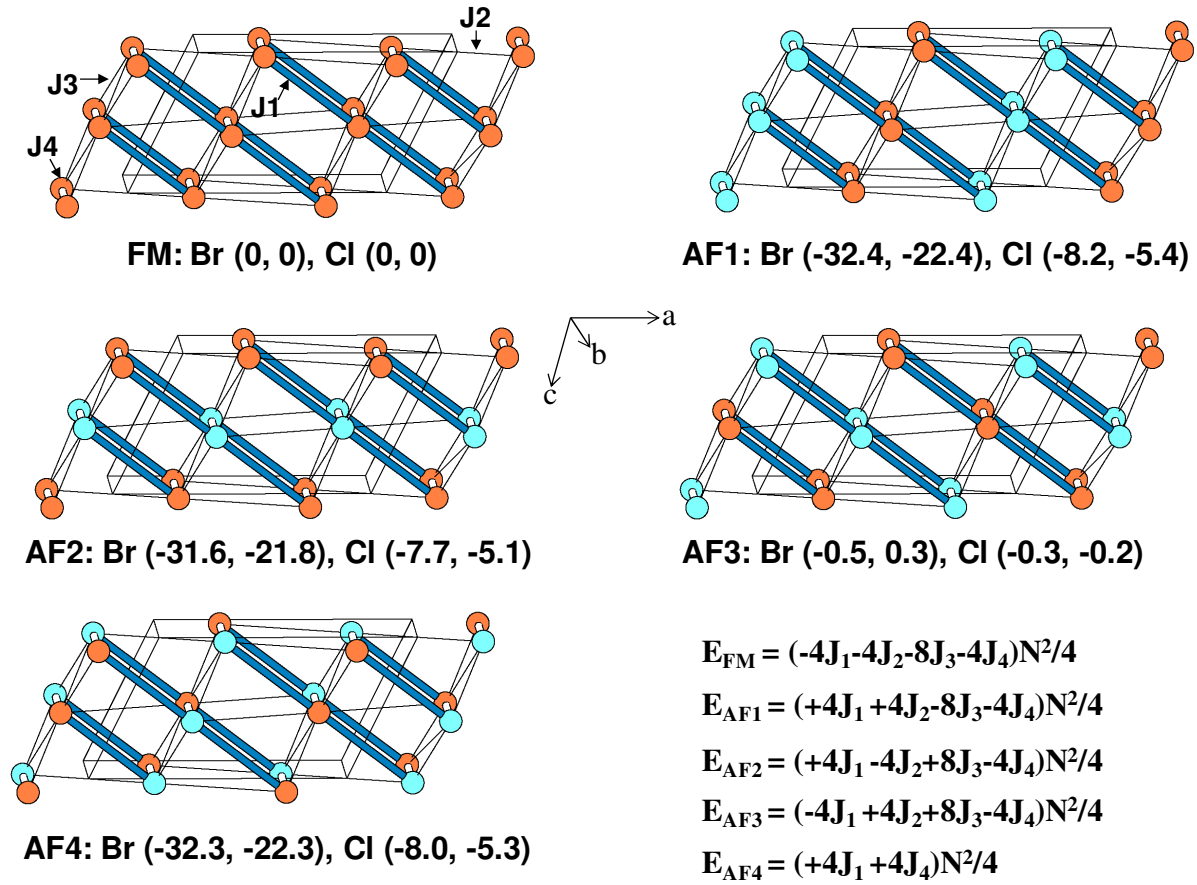**Figure S4**. Five ordered spin states used to extract the values of $J_1 - J_4$ of $CuX_2(pyzO)(H_2O)_2$ (X = Cl & Br), where the up-spin and down-spin Cu^{2+} sites are indicated by brown and cyan circles, respectively. The numbers in each parenthesis (from left to right) refer to the relative energies (in meV per 4 formula units) obtained from the GGA+U calculations with U = 4 and 6 eV, respectively. The total spin exchange energies (per 4 formula units) of the five ordered spin states, expressed in terms of $J_1 - J_4$, are also given.
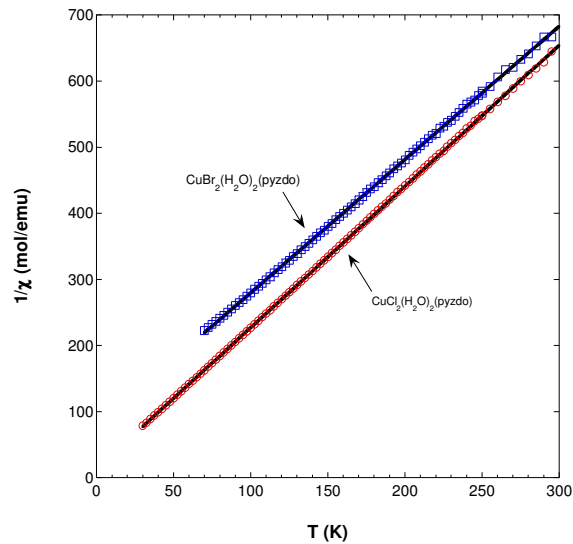
Figure S5. Theoretical fits of the reciprocal magnetic susceptibility, $1/\chi$, for **1** (red circles) and **2** (blue squares) with a Curie-Weiss law.
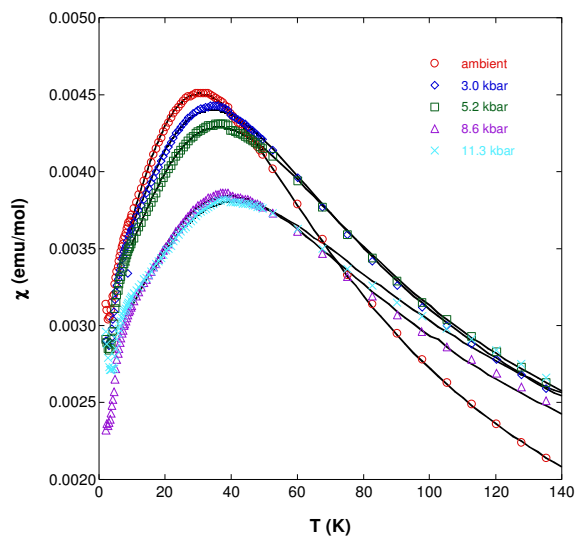

Figure S6. Magnetic susceptibility of **4** as a function of pressure. The solid lines represent theoretical fits to the data as described in the text.
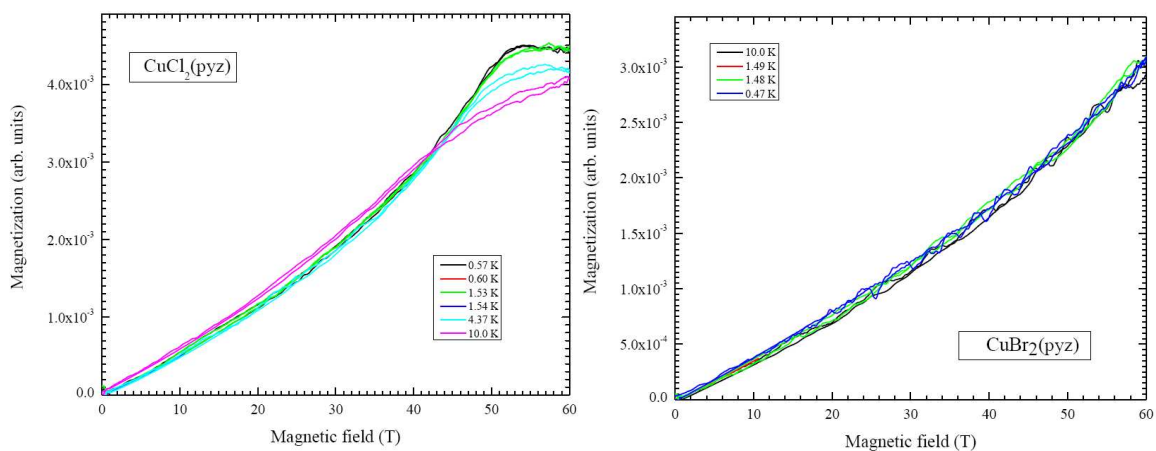
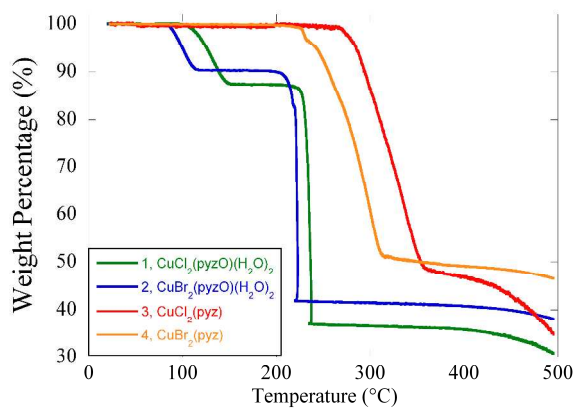**Figure S7.** Magnetization of **3** and **4** as a function of magnetic field.

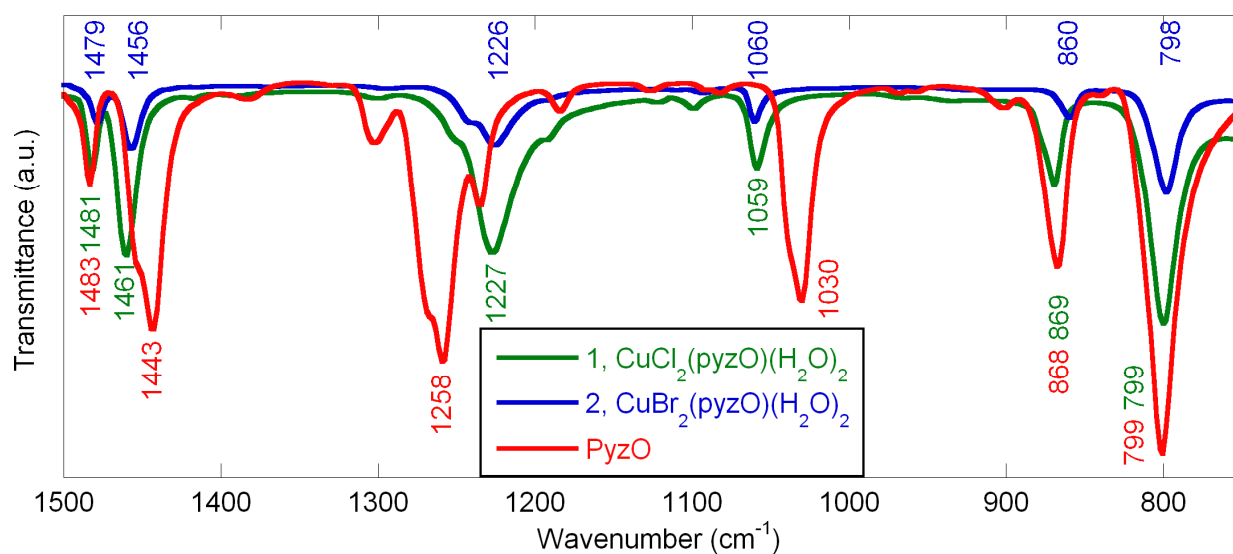**Figure S8.** Thermogravimetric analysis of compounds **1-4**.

Figure S9. Infrared spectra of compounds **1** and **2**, as compared to the non-coordinated pyzO ligand.

Table S1. Parameters from third-order Birch-Murnaghan equations of state fit to lattice volumes using the EOS-FIT v5.2 program by R. J. Angel.

	P-range / GPa	No. data	V_0 / Å^3	K_0 / GPa	K'	R_u / %	R_w /%
2	0-3.3	11	968(3)	16.0(16)	8.0(15)	0.75	0.89
4	0-3.7	13	329.9(6)	16.5(11)	8.4(11)	0.26	0.23

Table S2. Spin exchanges $J_1 - J_4$ (in k_BK) of $CuX_2(PyzO)(H_2O)_2$ (X = Cl, Br) obtained from GGA+U calculations with $U = 4$ and 6 eV.

	X = Br		X = Cl	
	U = 4 eV	U = 6 eV	U = 4 eV	U = 6 eV
J_1	-184	-127	-47	-31
J_2	-3.7	-2.5	-0.5	-0.4
J_3	0.4	0.4	1.0	0.7
J_4	-1.5	-1.0	-0.6	-0.4