

## Supplementary Information

# **Structural and magnetic properties of the {Cr(pybd)<sub>3</sub>[Cu(cyclen)]<sub>2</sub>}(BF<sub>4</sub>)<sub>4</sub> heteronuclear complex**

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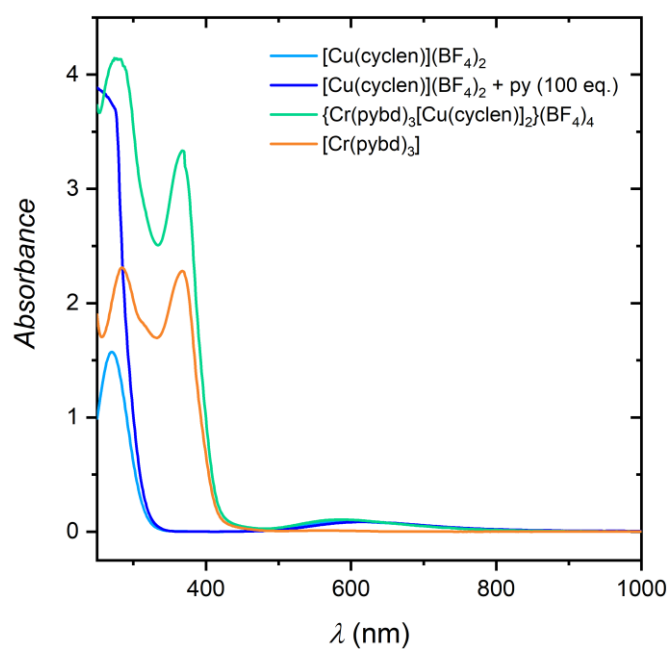
## S.1 Synthetic strategies for precursors.

**General remarks.** All the chemicals employed were used as such without further purification. Compound Hpybd was synthesized according to [1] using anhydrous THF (AcroSeal, ThermoFisher Sci.) and standard Schlenk techniques. The NaOMe used to synthesize Hpybd was prepared by reacting Na with dry MeOH (AcroSeal, ThermoFisher Sci.) under N<sub>2</sub>. All the manipulations requiring an inert atmosphere were performed by using the standard Schlenk technique and N<sub>2</sub> as the inert gas. The glassware employed during these operations was dried in vacuum ( $10^{-2}/10^{-3}$  mbar) with a heat gun.

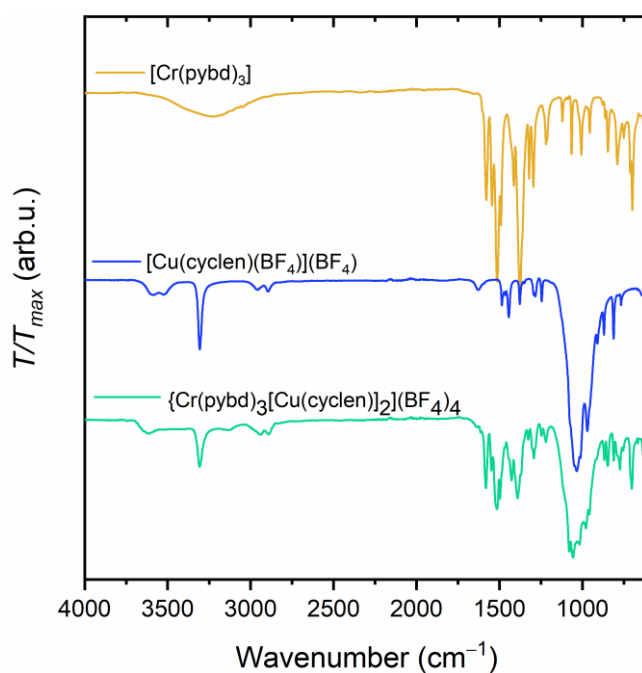
**Synthesis of [Cr(pybd)<sub>3</sub>][2].** CrCl<sub>3</sub>·6H<sub>2</sub>O (1 g, 3.75 mmol) was dissolved in 100 mL of deionized water. Urea (4.5 eq.) and Hpybd (3.5 eq.) were added to the solution, and the temperature increased to 90 °C. The brownish reaction mixture was left to stir for two days and then cooled to room temperature. The light-brown solid was collected and extracted with CHCl<sub>3</sub> (2 x 50 mL), and the solution evaporated to dryness in vacuum. The obtained solid was dissolved in a minimum amount of CH<sub>2</sub>Cl<sub>2</sub>, filtered, and crystallized by keeping the solution at -25 °C for three days. Red crystalline blocks separated from the solution, and they were collected by filtration and washed with cold acetone and CH<sub>2</sub>Cl<sub>2</sub>. The procedure was repeated three times, and 1.25 g of [Cr(pybd)<sub>3</sub>] were obtained. Yield: 62%. Elemental analysis calculated for CrC<sub>27</sub>H<sub>24</sub>N<sub>3</sub>O<sub>6</sub> (found): C 60.22 (60.28), H 4.49 (4.53), N 7.80 (7.73). ESI-MS (positive-ion): m/z = 539.17 [M + H<sup>+</sup>], 561.08 [M + Na<sup>+</sup>]. UV-Vis: λ<sub>max</sub> (|ε| = 10<sup>6</sup> cm<sup>2</sup> mol<sup>-1</sup>) = 284 nm (925), 367 nm (912), 557 (45). FT-IR (ν, cm<sup>-1</sup>) = 3222(b), 1581(s), 1544(m), 1516(vs), 1493(s), 1413(m), 1377(vs), 1322(m), 1295(m), 1217(w), 1121(vw), 1064(w), 1007(w), 956 (vw), 846 (w), 792(m), 752(vw), 700(s), 618(m).

**Synthesis of [Cu(cyclen)BF<sub>4</sub>](BF<sub>4</sub>).** Cyclen (0.86 g, 5.00 mmol) and Cu(BF<sub>4</sub>)<sub>2</sub>·xH<sub>2</sub>O (1.68 g, 7.00 mmol) were added to 50 mL of MeOH and stirred overnight at room temperature. The solution turned deep blue. Then, the solvent was removed under reduced pressure, and the blue solid residue dissolved in 75 mL acetone. The obtained solution was filtered, added to 25 mL of toluene, and left to evaporate. After 24 h, a crystalline product was collected by filtration, washed with toluene/acetone 1:1 (3 x 10 mL) and pentane, and dried on air (0.88 g). Yield: 43%. Elemental analysis calculated for CuC<sub>8</sub>N<sub>4</sub>H<sub>20</sub>B<sub>2</sub>F<sub>8</sub> (found): C 23.47 (23.46), H 4.92 (4.93), N 13.68 (13.68). FT-IR (ν, cm<sup>-1</sup>) = 3591(w), 3516(w), 3306(s), 2961(vw), 2899(vw), 1629(vw), 1486(w), 1444(w), 1377(w), 1283(w), 1246(w), 1037(vs, b), 1017(vw, b), 972(s), 924(vw), 871(m), 813(m), 767(vw). UV-Vis: λ<sub>max</sub> (|ε| = 10<sup>6</sup> cm<sup>2</sup> mol<sup>-1</sup>) = 271 nm (629), 601 nm (35).

## S.2 UV-Vis and FT-IR Characterization

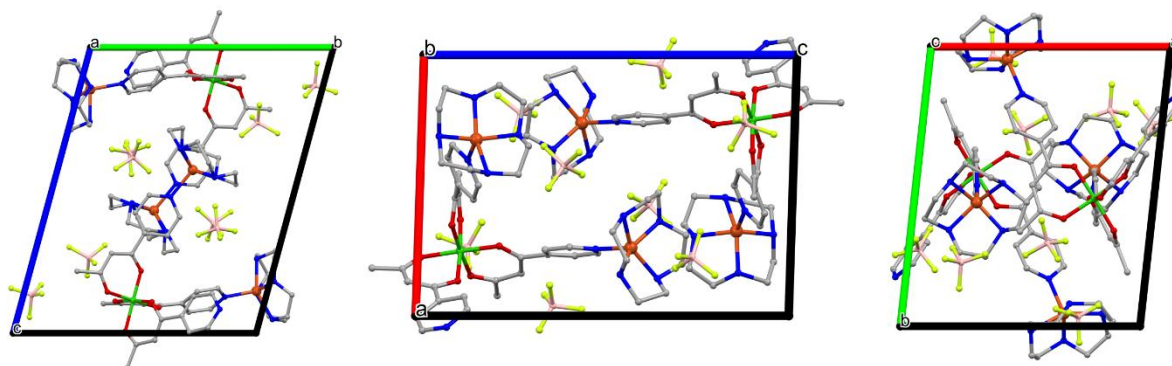


**Figure S1.** UV-Vis absorption spectra of equimolar solutions (0.25 mM) of all the investigated complexes.

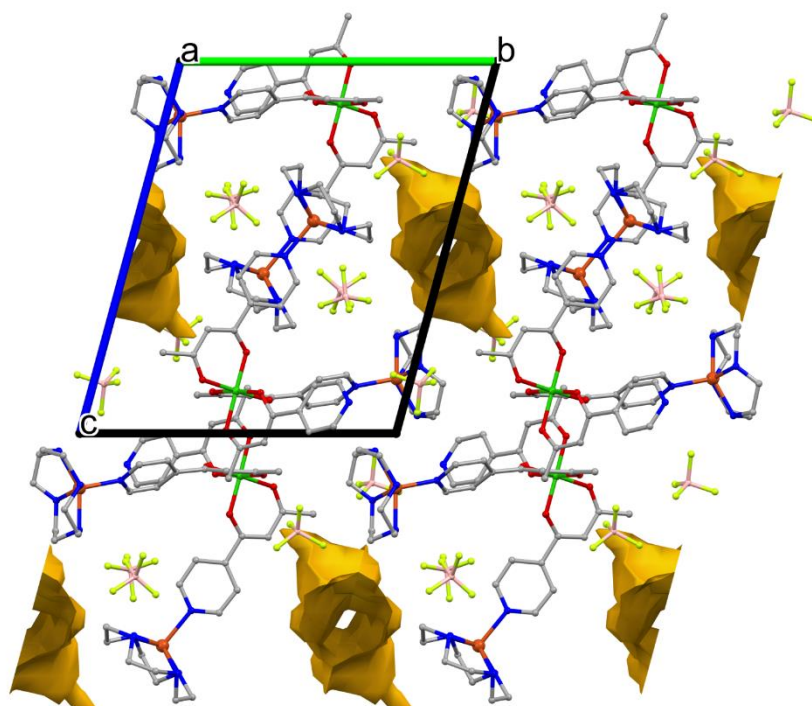


**Figure S2.** FT-IR spectra collected on  $[\text{Cr}(\text{pybd})_3]$ ,  $[\text{Cu}(\text{cyclen})\text{BF}_4](\text{BF}_4)$ , and  $\{\text{Cr}(\text{pybd})_3[\text{Cu}(\text{cyclen})_2]\}(\text{BF}_4)_4$  powder samples.

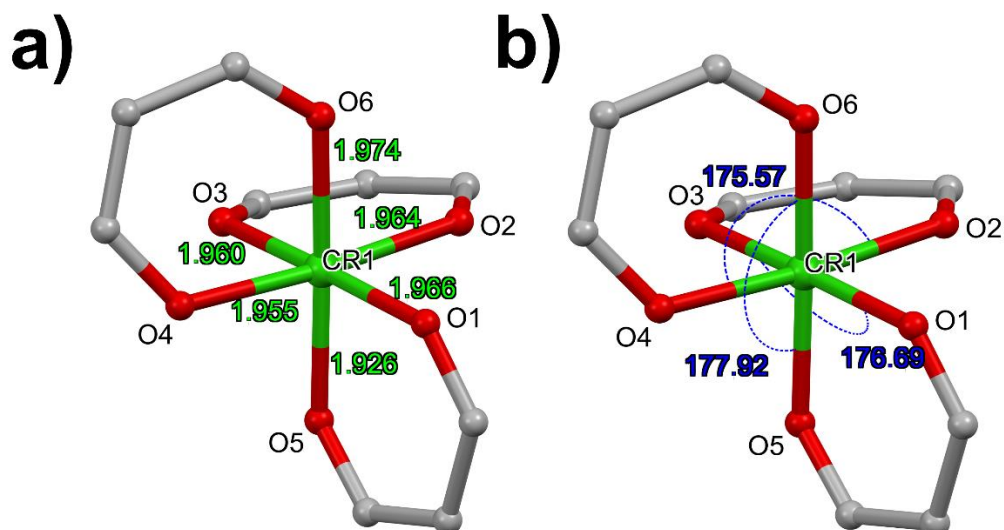
### S.3 Structural Characterization



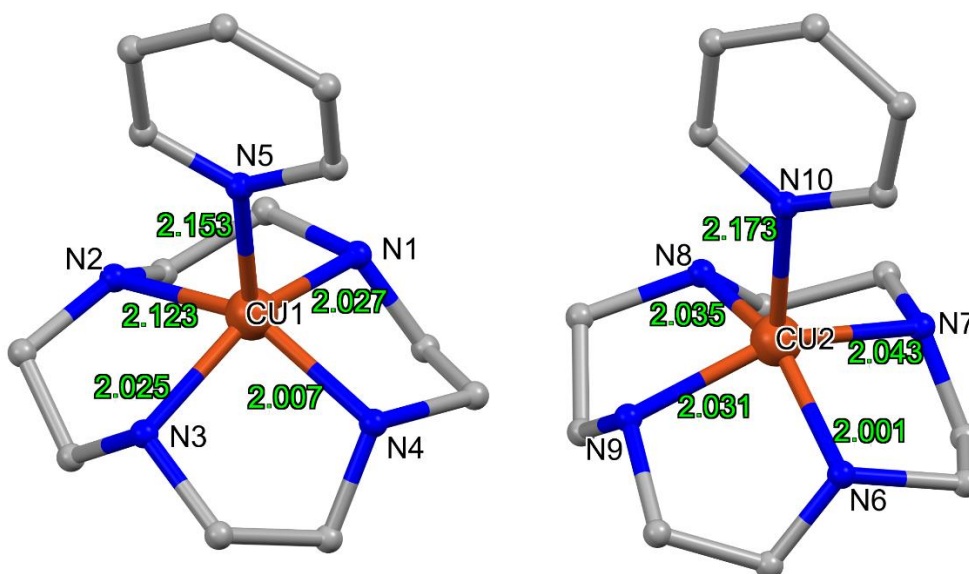
**Figure S3.** From the left to the right, view of the crystal unit cell of  $\{\text{Cr}(\text{dypb})_3[\text{Cu}(\text{cyclen})]\}(\text{BF}_4)_2$  along with the  $a$ ,  $b$ , and  $c$  crystallographic axes. Color code: Cr = green, Cu = copper, B = Pink, C = gray, N = blue, O = red, F = yellow/green. Hydrogens are omitted for clarity.



**Figure S4.** View along the  $c$  axis of a  $2 \times 2 \times 1.5$  cell highlighting the porous nature of crystalline  $\{\text{Cr}(\text{dypb})_3[\text{Cu}(\text{cyclen})]\}(\text{BF}_4)_2$ . The voids (given as solvent accessible surface) are calculated considering a spherical probe of 1.25 Å radius and reported as yellowish surface.

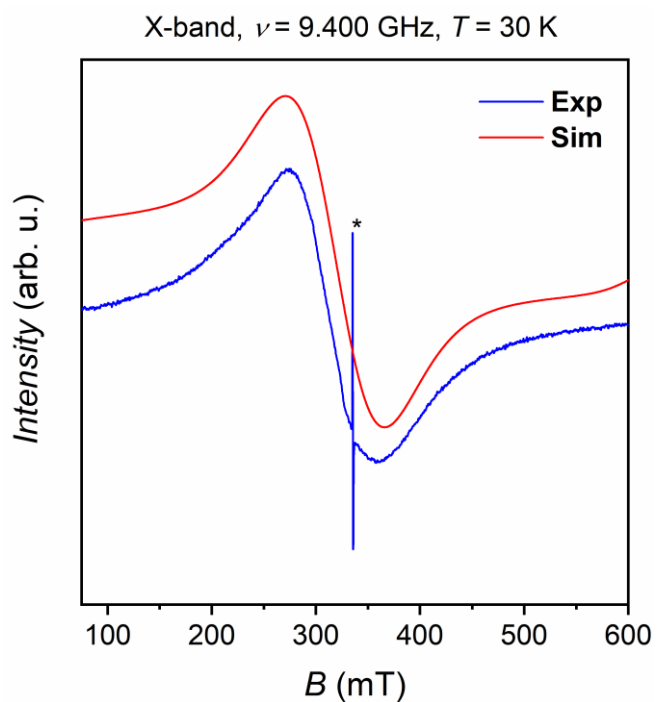


**Figure S5.** a) Generic view of the first coordination sphere of the  $\text{Cr}^3$  ion reporting the six values of Cr–O distances. b) Generic view of the first coordination sphere of the  $\text{Cr}^{3+}$  ion reporting the three values of O–Cr–O angles.



**Figure S6.** Generic view of the two Cu(cyclen) moieties highlighting the square-pyramidal coordination environment of the  $\text{Cu}^{2+}$  ion. The Cu–N distances are reported in green within the figure.

## S.4 Additional X-band EPR Experiments



**Figure S7.** X-band CW EPR spectrum of a  $\{\text{Cr}(\text{dypb})_3[\text{Cu}(\text{cyclen})]\}(\text{BF}_4)_2$  powder sample collected at 30 K. The simulation was performed by using the same Hamiltonian parameters reported in Table 2 of the main text and by fitting the linewidth of the  $\text{Cr}^{\text{III}}$  and  $\text{Cu}^{\text{II}}$  signals. The asterisk corresponds to the radical signal at  $g = 2.004$  used for calibration.