Supporting Information

Antisymmetric Spin Exchange in a $\mu$-1,2-Peroxodicopper(II) Complex with an Orthogonal Cu–O–O–Cu Arrangement and $S = 1$ Spin Ground State Characterized by THz-EPR

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### 1.1. Materials and General Methods

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1 Experimental Section

1.1 Materials and General Methods

All reactions, if not stated otherwise, were carried out using standard Schlenk techniques under argon atmosphere, or in a glovebox (MBRAUN LabMaster) under an atmosphere of dinitrogen with less than 0.1 ppm of O₂ and H₂O. Solvents were dried according to standard procedures and degassed by at least three freeze-pump-thaw cycles prior to use and were stored over molecular sieves (3 Å). All chemicals were purchased from commercial sources, prepared according to literature protocols, or the synthetic procedure is described below. 5-(Chloroethyl)-3-(chloromethyl) pyrazole hydrochloride was synthesized according to Figure S1, with slight modifications of the reported method.1 and 1,4-Di(isopropyl)-1,4,7-triazacyclononane ([3-TACN])² and [Cu(MeCN)]₄ClO₄ were synthesized following the reported procedures. Resonance Raman spectra of complex 2 (λex = 633 nm) were recorded with a HORIBA Scientific LabRAM HR 800 (400-1100 nm) spectrometer with an open-electrode CCD detector and a confocal pinhole with user-controlled variable aperture in combination with a free space optical microscope. UV/vis experiments in solution were recorded in quartz cuvettes on an AGILENT Cary 60 or on an AGILENT Cary 8454, which were equipped with an UNISOKU cryostat (CoolSpek) for low temperature measurements connected with a magnetic stirrer, or using a Praying Mantis sampling kit for solid samples. All UV-vis samples and stock solutions were prepared in a glovebox and transferred out of the glovebox prior to the measurement. For the addition of reagents, Hamilton syringes of an appropriate volume were used. ¹H and ¹³C(¹H) NMR spectra were recorded on Bruker Avance 300 and 500 spectrometers. Chemical shifts (δ) are given in ppm relative to residual solvent signals of MeCN-d₃.

Important note: HClO₄ and perchlorate salts are potentially explosive and should be handled with proper precautions.

1.2 SQUID Magnetometry

For temperature dependent susceptibility measurements, a QUANTUM DESIGN MPMS XL-5 SQUID magnetometer with a 5 T magnet was used. The powdered sample was contained in a gel bucket and fixed in a non-magnetic sample holder. Each raw data file for the measured magnetic moment was corrected for the diamagnetic contribution of the sample holder and the gel bucket. The molar susceptibility data were corrected for the diamagnetic contribution. Magnetic properties of the sample were simulated with the software julX_2s.⁴

1.3 Frequency-domain Fourier-transform (FD-FT) THz-EPR

FD-FTTHz-EPR data of complexes 2 and B were acquired at the THz-EPR experiment of the electron-storage ring BESSY II. The setup is described in detail in the literature.⁵ Low-a mode linearly polarized coherent synchrotron radiation (CSR)⁷ or unpolarized radiation emitted by the Hg arc lamp of a FTIR spectrometer (Bruker IFS 125) were used as broad-band (≈ 3–50 cm⁻¹ and >12 cm⁻¹, respectively) excitation sources. It was transmitted via an evacuated transmission line through the FTIR spectrometer and focused on the sample contained in the variable temperature insert of a 10 T superconducting magnet (Oxford Spectromag). Spectra were recorded in Voigt geometry, in the case of CSR, with its magnetic field component B₁ perpendicular to the static magnetic field B₀. The transmitted signal was detected by a Si bolometer detector (IR labs) and Fourier-transformed to yield frequency-domain EPR spectra. The experimental resolution was 1 cm⁻¹, the temperature 5 K. Samples were prepared by homogenizing in a mortar the polycrystalline sample material (CSR: 44 mg 2, 62 mg B; Hg arc: 21 mg 2, 17 mg B) with polyethylene (PE) powder (11-65 mg) and pressing it into a pellet. To remove the incident background transmission from the spectrum, referencing was done between spectra recorded at different fields.⁶,⁸ Magnetic-field division spectra (MDS) at two magnetic fields B₁ and B₂ are presented as relative transmittance T, experimentally obtained from the measured spectral intensities I as Texp = I₁/I₂, and calculated from the simulated absorbance spectra A as Tsim = 10⁻⁵A₁⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻~-~-~

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2 Synthesis

Figure S1. Synthetic Route for HL$^{1,2}$·7 HClO$_4$.

2.1 3-(β-Hydroxyethyl)-5-Hydroxymethylpyrazole Hydrochloride (II)
A solution of 1,6-dihydroxy-2,4-hexadiyne (2.5 g, 22.7 mmol, 1.0 eq.) and H$_2$N-NH$_2$·H$_2$O (3.41 g, 68.11 mmol, 3.0 eq.) in EtOH (130 mL) was heated to 85 °C for 24 hours. The solvent and excess hydrazine were then removed under vacuum by using a cold trap. After drying the yellow oil overnight, ethanolic HCl was added and the product precipitated by adding Et$_2$O, yielding a brown oil or solid (depending on the quality of the educt). The excess solvent was decanted, and the product was dried in vacuum overnight to give II as a brown oil (3.36 g, 18.8 mmol, 83%).

$^1$H-NMR (300 MHz, D$_2$O): $\delta$ [ppm] = 6.24 (s, 1 H, $\text{Py-CH}$), 4.58 (s, 2 H, MeCH$_2$), 3.78 (t, $j$, $\text{Et-CH}_2$), 2.83 (t, $j$, $\text{Et-CH}_2$).

$^{13}$C{$^1$H}-NMR (75 MHz, D$_2$O): $\delta$ [ppm] = 149.1 ($\text{Ar-C}$), 146.1 ($\text{Ar-C}$), 103.3 ($\text{Ar-C}$), 60.3 ($\text{EtOH}$), 55.9 ($\text{MeOH}$), 28.6 ($\text{CH}_2$).

MS (ESI+): $m/z$ (%) = 143.1 (39) [M+H]$^+$, 125.1 (100) [M-OH]$^+$.

2.2 3-(β-Chloroethyl)-5-Chloromethylpyrazole Hydrochloride (III)
To compound II (3.26 g, 18.3 mmol, 1.0 eq.), thionyl chloride (80 mL) was added slowly at 0 °C. The solution was then heated to 65 °C for one hour, cooled to RT and excess thionyl chloride was removed under vacuum by using a cold trap. The resulting brown oil was dried under vacuum overnight. Addition of EtO and vigorous stirring for 24 h led to the formation of a brown powder. Excess solvent was decanted, the solid dried under vacuum and the product obtained as a beige powder (3.50 g, 16.2 mmol, 89%).

$^1$H-NMR (300 MHz, D$_2$O): $\delta$ [ppm] = 6.57 (s, 1 H, $\text{Py-CH}$), 4.72 (s, 2 H, MeCH$_2$), 3.85 (t, $j$, $\text{EtCH}_2$), 3.20 (t, $j$, $\text{EtCH}_2$).

$^{13}$C{$^1$H}-NMR (75 MHz, D$_2$O): $\delta$ [ppm] = 146.3 ($\text{Ar-C}$), 145.5 ($\text{Ar-C}$), 106.2 ($\text{Ar-C}$), 42.2 ($\text{EtCH}_2$), 34.3 ($\text{MeCH}_2$), 28.4 ($\text{CH}_2$).

MS (ESI+): $m/z$ (%) = 179.0 (100) [M+H]$^+$, 143.0 (31) [M-Cl]$^+$.
2.3 Synthesis of HL_{1,2-7} HClO₄

Compound III (1.16 g, 5.39 mmol, 1.0 eq.), TBABr (643 mg, 1.99 mmol, 0.37 eq.) and Na₂CO₃ (6.46 g, 60.9 mmol, 11.3 eq.) were suspended in MeCN (110 ml) and 1,4-di(iso-propyl)-1,4,7-triazacyclononane (2.5 g, 11.7 mmol, 2.2 eq.) was added via a syringe. The reaction mixture was heated to reflux for 24 h at 100 °C, then cooled to RT and filtered. The residue was washed with MeCN (30-50 ml) and volatiles were removed under vacuum. The resulting brown oil was dissolved in DCM (100 ml) and washed with 1 M NaOH (40 ml). The aqueous phase was extracted with DCM (3 x 80 ml) and the combined organic phases were dried over MgSO₄. Subsequently, the solvent was removed under reduced pressure and the residue dissolved in DME (16 ml). Addition of small amounts of HClO₄ led to the formation of a precipitate, which began to dissolve again after further addition of HClO₄. Then, EtOH/Et₂O (1:1, 100 ml) was added to form a brown viscous mass which was stirred for 1-2 hours. Further washing with EtOH (100 ml) and Et₂O (100 ml) and subsequent drying under vacuum led to the isolation of a beige powder (3.02 g, 2.43 mmol, 45 %).

¹H-NMR (300 MHz, CD₃CN): δ [ppm] = 6.33 (s, 1 H, ArCH), 3.98 (s, 2 H, MeCH₂), 3.86-3.71 (m, 4 H), 3.66-3.57 (m, 4 H), 3.44-3.34 (m, 4 H), 3.26-3.07 (m, 2 H), 3.07-3.00 (m, 2 H), 2.98-2.85 (m, 4 H), 1.60-0.80 (m, 24 H, CH₃). Full assignment of ¹H-NMR signals is difficult due to different protonation states of the ligand.

¹³C(¹H)-NMR (75 MHz, CD₃CN): δ [ppm] = 60.0 (s, 2 CH₃), 48.5 (CH₂), 47.8 (CH₂), 46.9 (CH₃), 45.7 (CH₂), 45.0 (CH₂), 17.5 (CH₂), 17.2 (CH₂), 15.1 (CH₃), 14.9 (CH₃).

MS(ESI⁺): m/z (%) = 633.5 (24) [M-HClO₄ + H⁺], 533 (9) [M+H⁺], 356.3 (34) [M⁺,[TACN]+Cl⁺], 320.3 (21) [M⁺,[TACN]+H⁺], 267.3 (100) [M+2H²⁺].

2.4 Synthesis of [L^{1,2}Cu₂][BPh₄] (1)

HL_{1,2-7} HClO₄ (250 mg, 0.203 mmol, 1.0 eq.) was suspended together with KOtBu (185 mg, 1.65 mmol, 8.15 eq.) in MeOH (2.0 ml). Then a suspension of [Cu(MeCN)₂]+(ClO₄)₃ (133 mg, 0.41 mmol, 2.00 eq.) in MeOH (2.0 ml) was added. The yellow-brown reaction mixture was stirred for 2-4 h and then filtered through a Whatman filter. A solution of NaBPh₄ (104 mg, 0.304 mmol, 1.5 eq.) in MeOH (0.5 ml) was added to the filtrate, forming a beige precipitate which was further stirred for 30 min and then separated by filtration. The residue was dissolved in a minimum of acetone (~0.5 ml) to form a golden brown solution. Subsequent diffusion of Et₂O into the solution over 2-3 days led to the formation of a dark brown oil and a nearly colorless solution. The clear solution was separated and further diffusion of Et₂O provided crystalline material (40 mg, 41 µmol, 20 %) after 1-2 weeks.

¹H-NMR (300 MHz, CD₃CN): δ [ppm] = 1.10-1.15 (m, 6 H, CH₃), 1.18-1.24 (m, 6 H, CH₃), 1.33 (d, J=6.6 Hz, 6 H, CH₃), 2.47-2.96 (m, 28 H, CH₂), 3.05 (sept, J=6.6 Hz, 4 H, CH₃), 3.77 (s, 2 H, CH₂O), 5.72 (s, 1 H, CH₃), 6.81-6.88 (m, 4 H, ArCH), 6.99-7.06 (m, 8 H, ArCH), 7.25-7.32 (m, 8 H, ArCH).

¹³C(¹H)-NMR (75 MHz, CD₃CN): δ [ppm] = 19.9 (CH₃), 20.6 (CH₂), 21.6 (CH₃) 26.9 (Et-pCH₃), 50.9 (CH₃), 51.1 (CH₃), 51.3 (CH₃), 51.8 (CH₂), 52.3 (CH₂), 53.2 (CH₂, 55.3 (Me-pCH₃) 58.6 (CH), 58.7 (CH₃), 101.5 (4-Cₖ), 122.7 (αCH), 126.6 (αCH), 136.7 (αCH), 149.3 (Cₖ), 150.1 (Cₖ).

2.5 Synthesis of [L^{1,2}Cu₂(μ-η¹⁻: η¹O₂)](BPh₄) (2)

Complex 1 (30 mg, 31 µmol) was dissolved in acetone (1.0 ml) and Et₂O (1.0 ml) was added. The solution was then transferred in a test tube which was placed in a Schlenk tube containing Et₂O. The Schlenk tube containing the test tube with the solution of 1 was then cooled down to −30 °C and the atmosphere in the Schlenk tube was replaced by dioxygen. Then the solution was left for slow Et₂O diffusion at −26 °C for several weeks, causing the formation of crystalline material (20 mg, 19.8 µmol, 64%) of 2 suitable for X-ray diffraction analysis.

UV/Vis (MeCN, T = −40°C): λ_{max} [nm] (ε[M⁻cm⁻¹]) = 437 (2000), 520 (5500), 617 (sh, 3300).

rR (solution, λ_{exc} = 633 nm): ϕ_{0-0}[cm⁻¹] = 804 (Δ(10O⁺−10O⁻) = 57).

rR (solid, λ_{exc} = 633 nm): ϕ_{0-0}[cm⁻¹] = 807 (Δ(14O⁺−14O⁻) = 50).

EA: Calculated for C₆H₆·HNO₃Cu₂·O₂·H₂O C: 63.08, H: 7.94, N: 10.90; Found: C: 62.87, H: 7.88, N: 10.53. Complex 2 tends to be hygroscopic under aerobic conditions, therefore H₂O was included.
3 Analytical Data

3.1 NMR Spectroscopy

Figure S2. $^1$H-NMR spectrum (300 MHz) of Complex 1 in CD$_3$CN at RT.

Figure S3. $^{13}$C-NMR spectrum (75 MHz) of Complex 1 in CD$_3$CN at RT.
**Figure S4.** $^1$H-$^1$H COSY (300 MHz) spectrum of complex 1 in CD$_3$CN.

**Figure S5.** $^1$H-$^1$H NOESY (300 MHz) spectrum of complex 1 in CD$_3$CN.
Figure S6. $^1$H-$^1$C HMBC (300 / 75 MHz) spectrum of complex 1 in CD$_3$CN.

Figure S7. $^1$H-$^1$C HSQC (300 / 75 MHz) spectrum of complex 1 in CD$_3$CN.
3.2 UV/Vis Spectroscopy

Figure S8. UV/Vis spectrum of complex 1 (black) and formation of complex 2 (purple) after addition of dioxygen in MeCN at –40 °C.

Figure S9. Gradual conversion (left to right) of complex 1 in acetone at room temperature to the corresponding peroxodicopper(II) complex 2 by diffusion of ambient air.
3.3 Resonance Raman Spectroscopy

Figure S10. Resonance RAMAN spectrum of complex 2 in MeCN at room temperature ($\lambda_{ex} = 633$ nm). Isotopically labeled samples were prepared by exposure of complex 1 to $^{18}$O$_2$ instead of $^{16}$O$_2$. The inset shows the difference spectrum between 650 and 900 nm.

3.4 Magnetic Measurements

Figure S11. Open circles represent $\chi_m T$ vs. $T$ data recorded in the temperature range of 2–295 K and at $B_0 = 0.5$ T (left) and iso-field magnetization $M_{mol}$ recorded at 1 T, 3 T, and 5 T vs. $\mu_B/kT$ (right) for crystalline samples of 2. The solid lines represent the best global fit (obtained with juli_2s) for both data sets, including antisymmetric exchange (DM interaction). Parameters obtained: $J = +26.9$ cm$^{-1}$; $d = (0, 0, 33.6)$ cm$^{-1}$; $g = 2.05, 2.05, 2.33$. 

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3.5 FD-FT THz-EPR Spectroscopy

In the following, FD-FT THz-EPR spectra for complexes 2 (Figure S12) and B (Figure S13 and Figure S14) are shown alongside simulations with Eq. 1 in the main text assuming antisymmetric exchange without (Figure S12 and Figure S14) and with (Figure S13) symmetric anisotropic exchange. Differences in the simulated line shapes obtained with these models are outlined in Figure S15.

3.5.1 Complex 2: simulation with antisymmetric exchange and no symmetric anisotropic exchange

Figure S12. (a) Simulated field-dependent spin energy levels for 2 with $B_0$ aligned along the equatorial and axial components of the $d$ vector. Arrows indicate $\Delta M_{S_1} = -1$, $\Delta M_{S_2} = +1$ and $\Delta S_I = -1$ transitions. (b, c) SQUID data points (as in main text Figure 7) and simulated curves for crystalline samples of 2. (d, e) Experimental (as in Figure 7) and simulated FD-FT THz-EPR magnetic-field division spectra for pellets of polycrystalline 2. Branches of $\Delta M_{S_1} = -1$, $\Delta M_{S_2} = +1$ and $\Delta S_I = -1$ transitions are indicated. Simulations in all panels are based on the optimized spin Hamiltonian parameters in Table S1.
3.5.2 Complex B: simulation with antisymmetric exchange and symmetric anisotropic exchange

**Figure S13.** (a) Simulated field-dependent spin energy levels for B with $B_0$ aligned along the x, y and z components of the d vector. Solid and dashed arrows indicate $\Delta M_S$ and $\Delta S_t$ transitions, respectively. (b, c) SQUID data points and simulated curves (TIP = 92 $\times$ 10$^{-6}$ cm$^3$ mol$^{-1}$) for crystalline samples of B: (b) $\chi_T$ vs. $T$ recorded at $B_0 = 0.5$ T and (c) iso-field magnetization $M_{mol}$ recorded at 1 T, 3 T, and 5 T vs. $\mu_B B_0/kT$. (d, e) Experimental and simulated FD-FT THz-EPR magnetic-field division spectra for pellets of polycrystalline B recorded at $T = 5$ K acquired using (d) low-α mode synchrotron radiation and (e) an Hg arc lamp. They were calculated by division of a transmission spectrum recorded at (d) $B_0 + 3$ T or (e) $B_0 + 0.5$ T by a corresponding one measured at $B_0$ (see SI section 1.3). Thus, maxima correspond to stronger absorption at $B_0$, minima to increased absorption at the higher field. Branches of $\Delta M_S$ = -1, $\Delta M_S$ = +1 and $\Delta S_t$ = -1 transitions are indicated, as well as $\Delta M_S$ = +2, -1 and +1 peak positions in the 0.5/0 T simulations in (e). Simulations in all panels are based on the optimized spin Hamiltonian parameters in main text Table 2.
3.5.3 Complex B: simulation with antisymmetric exchange and no symmetric anisotropic exchange

Figure S14. (a) Simulated field-dependent spin energy levels for B with \( B_0 \) aligned along the equatorial and axial components of the \( d \) vector. Arrows indicate \( \Delta M_S = -1, \Delta M_S = +1 \) and \( \Delta S = -1 \) transitions. (b, c) SQUID data points (as in Figure S13) and simulated curves (TIP = 109 \( \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1} \)) for crystalline samples of B. (d, e) Experimental (as in Figure S13) and simulated FD-FT THz-EPR magnetic-field division spectra for pellets of polycrystalline B. Branches of \( \Delta M_S = -1, \Delta M_S = +1 \) and \( \Delta S = -1 \) transitions are indicated. Simulations in all panels are based on the optimized spin Hamiltonian parameters in Table S1.
Figure S15. The effect of symmetric anisotropic exchange in complexes B (a) and 2 (b) is demonstrated by simulations of the intra-triplet transitions in the experimental FD-FT THz-EPR spectra (black) at magnetic fields >6 T, comparing the simulations with $\hat{H}_{\text{ani}}$ (top, Table 2) and those without $\hat{H}_{\text{ani}}$ (bottom, Table S1). Simulated spectra are shown on vertically expanded scales, 3x in (a) (compare Figures 7e, S12e) and 2x in (b) (compare Figure S13e, S14e) for better comparability to the experimental spectra. The field-dependent discrepancies of the relative signal intensities in all our simulations are thought to arise from ordering effects in the samples at high magnetic fields. As indicated on top, the splitting of the $\Delta M_S = -1$ transitions in the experimental spectra is reproduced only in the presence of symmetric anisotropic contributions, while the $\Delta M_S = -1$ signal is unsplit in their absence. (Reasons for the remaining mismatch of peak positions, particularly for complex B, are discussed below.) As a consequence, also the relative heights of the $\Delta M_S = -1$ and +1 peaks are much better reproduced in the presence of $\hat{H}_{\text{ani}}$.

Table S1. Optimized Spin Hamiltonian Parameters for Complexes 2 and B from Global Simulations of the FD-FT THz-EPR and Magnetometry Data Including only the Terms $\hat{H}_{\text{HDvV}}, \hat{H}_{\text{DM}}$ and $\hat{H}_{\text{Zeeman}}$ but without Considering $\hat{H}_{\text{ani}}$ (Compare Eq. 1 in the main text).$^a$

|     | 2      | B      |
|-----|--------|--------|
| $g_{\perp\perp}$ | 2.20   | 2.07$^b$ |
| $g_{\parallel\parallel}$ | 2.08   | 2.16$^b$ |
| $g_{\perp\parallel}$ | 2.09   | 2.07$^b$ |
| $g_{\parallel\parallel}$ | 2.27   | 2.16$^b$ |
| $J_{\text{iso}}$ / cm$^{-1}$ | 25.3   | 76.1   |
| $d_\epsilon$ / cm$^{-1}$ | 34.5   | 45.7   |

$^a$ For the Euler angles describing the orientations of the $g$ tensors relative to the $d$ frame see Figure S16. $^b$ $g$ tensors $g_1$ and $g_2$ of Cu1 and Cu2, respectively, were constrained to be identical.
**Figure S16.** Orientations of the coordinate frames of the DM pseudovector $\mathbf{d}$ (central) and the $g$ tensors ($g_1$ on Cu1, $g_2$ on Cu2) in complexes (a) 2 and (b) B employed in the global simulations of FD-FT THz-EPR and magnetometry data. The top row depicts the entire structures, omitting hydrogen atoms, solvent molecules and counter ions for clarity; the bottom row provides a view of only the Cu centers with their first coordination spheres along the $d_z$ axis. The relative orientations of the $g$ tensors with respect to the $d$ frame can be described by rotations by the Euler angles $[\alpha, \beta, \gamma]$ as $[-47, 93, 24]^\circ$ for $g_1$ and $[-17, 196, -55]^\circ$ for $g_2$ of 2, and $[0, -1, -33]^\circ$ for $g_1$ and $[0, 181, -33]^\circ$ for $g_2$ of B. Color scheme: atoms: Cu gold, O red, N blue, C grey; axes: x red, y green, z blue.

**Discussion of remaining deviations between experimental and simulated spectra after inclusion of symmetric anisotropic exchange $\tilde{H}_{ani}$:**

Our simulations demonstrate that symmetric anisotropic exchange is the origin of the orientationally dependent $\Delta M_{Sz} = -1$ splitting. However for 2, upon inclusion of the $\tilde{H}_{ani}$ term, discrepancies are still observed in the positions of the $\Delta M_{Sz} = -1$ lines and the very small Zeeman shift of the $\Delta S_t = -1$ transition is still overestimated. One reason may be a deviation of the actual $d$ vector orientation from that in ideal $C_2$ symmetry, which however cannot be determined from our data on polycrystalline samples. This is also true for a rotation of the $J_{ani}$ relative to the $d$ frame. Concerning B, it is noted that in $C_2$ symmetry only the $y$ components of the $J_{ani}$ tensor and the $d$ vector are required to be aligned, coinciding with the $C_2$ axis, but computations indicate for model systems that rotations of $J_{ani}$ around the $d_y$ axis are small. Further deviations possibly arise from ordering effects in both samples at high magnetic fields, apparent from deviating line intensities and widths in all fits.
3.6 Uncoupled and Coupled Representations of the 2-Spin System: Effect of Exchange Coupling Terms

To illustrate the contributions of the four spin states in the uncoupled representations \(|M_{S,1},M_{S,2}>\) to the total spin states in the coupled representation \(|S_{0},M_{S}>\) depending on the various types of exchange interaction considered, we have calculated the respective eigenvectors upon diagonalizing the spin Hamiltonians, employing the optimized coupling parameters of complex 2 (Table 2). The situations in Tables S3 and S5 correspond to the simulations shown in Figures 7 and S12, respectively, for complex 2 (and Figures S13 and S14, respectively, for complex B). From Tables S2 and S3, it is seen that inclusion of the DM term adds an imaginary part to the contribution from \(|M_{S,1},M_{S,2}> = |+1/2,-1/2>\) to \(|S_{0},M_{S}> = |1,0>\) and \(|0,0>\) (the linear combinations of \(|M_{S,1},M_{S,2}> = |+1/2,-1/2>\) and \(|-1/2,+1/2>\)) and \(|-1/2,-1/2>\). This kind of mixing of the states is how the DM interaction engenders non-zero transition probabilities from the \(S_{z} = 1\) ground state manifold to the \(S_{z} = 0\) excited state. From Tables S4 and S5, it is furthermore seen that the symmetric anisotropic exchange term lifts the degeneracy of the \(|S_{0},M_{S}> = |1,1>\) and \(|1,-1>\) and \(|1,+1>\) states, as portrayed in the respective spin state energy schemes (Figures 7a, S13a). It is noted that in the presence of symmetric anisotropic exchange, \(M_{S,3} = -1\) and \(+1\) strictly speaking do not represent good quantum numbers for these states, since in this case they are linear combinations of \(|M_{S,1},M_{S,2}> = |+1/2,+1/2>\) and \(|-1/2,-1/2>\). However, for the sake of a coherent nomenclature and understandability, we are using this notation throughout the manuscript regardless of the model considered.

It is noted that the relative eigenvalues of the triplet state sublevels (i.e. the relative energies of \(|S_{0},M_{S}> = |1,0>\), \(|1,-1>\) and \(|1,+1>\) can be parametrized by the axial and rhombic parameters \(D_{t}\) and \(E_{t}\) of an effective ZFS term. In an external magnetic field, the effective spin Hamiltonian for the total spin \(S_{z} = 1\) state is

\[
\hat{H}_{t} = \hat{H}_{ZFS} + \hat{H}_{Zeeman,t} = D_{t} \left[ \hat{S}_{t,x} \hat{S}_{t,y} - \frac{1}{3} \hat{S}_{t,z}(\hat{S}_{t,z} + 1) \right] + E_{t} \left( \hat{S}_{t,x}^2 - \hat{S}_{t,y}^2 \right) + \mu_{B} B_0 g \hat{S}_{t} \tag{Eq. S1}
\]

**Table S2.** Spin Hamiltonian Energies \(E\) of the Coupled Total Spin States \(|S_{0},M_{S}>\) and the Corresponding Eigenvectors of the Uncoupled Representations \(|M_{S,1},M_{S,2}>\) for HDvV Exchange only.

| \(|S_{0},M_{S}>\) | \(|1,0>\) | \(|1,-1>\) | \(|1,+1>\) | \(|0,0>\) |
|----------------|----------|----------|----------|----------|
| \(|+1/2,+1/2>\) | -12.7 | -12.7 | -12.7 | 38.2 |
| \(|+1/2,-1/2>\) | 0 | 0 | 1 | 0 |
| \(|-1/2,+1/2>\) | 0 | 0 | 0 | 0.71 |
| \(|-1/2,-1/2>\) | 0 | 1 | 0 | 0 |

**Table S3.** Spin Hamiltonian Energies \(E\) of the Coupled Total Spin States \(|S_{0},M_{S}>\) and the Corresponding Eigenvectors of the Uncoupled Representations \(|M_{S,1},M_{S,2}>\) with HDvV and DM Exchange.

| \(|S_{0},M_{S}>\) | \(|1,0>\) | \(|1,-1>\) | \(|1,+1>\) | \(|0,0>\) |
|----------------|----------|----------|----------|----------|
| \(|+1/2,+1/2>\) | 0 | 0 | 1 | 0 |
| \(|+1/2,-1/2>\) | -17.0 | -12.7 | -12.7 | 43.5 |
| \(|-1/2,+1/2>\) | -0.60 + 0.37i | 0 | 0 | 0.60 - 0.37i |
| \(|-1/2,-1/2>\) | 0 | 1 | 0 | 0 |

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Table S4. Spin Hamiltonian Energies $E$ of the Coupled Total Spin States $|S_tM_S,t\rangle$ and the Corresponding Eigenvectors of the Uncoupled Representations $|M_{S,1},M_{S,2}\rangle$ with HDvV and Symmetric Anisotropic exchange.

| $|S_tM_S,t\rangle$ | $|1,0\rangle$ | $|1,-1\rangle$ | $|1,+1\rangle$ | $|0,0\rangle$ |
|----------------|----------------|----------------|----------------|----------------|
| $E / \text{cm}^{-1}$ | -13.4 | -13.6 | -11.2 | 38.2 |
| $|+1/2,+1/2\rangle$ | 0 | -0.71 | 0.71 | 0 |
| $|+1/2,-1/2\rangle$ | 0.71 | 0 | 0 | 0.71 |
| $|-1/2,+1/2\rangle$ | 0.71 | 0 | 0 | -0.71 |
| $|-1/2,-1/2\rangle$ | 0 | 0.71 | 0.71 | 0 |

Table S5. Spin Hamiltonian Energies $E$ of the Coupled Total Spin States $|S_tM_S,t\rangle$ and the Corresponding Eigenvectors of the Uncoupled Representations $|M_{S,1},M_{S,2}\rangle$ with HDvV, DM and Symmetric Anisotropic Exchange.

| $|S_tM_S,t\rangle$ | $|1,0\rangle$ | $|1,-1\rangle$ | $|1,+1\rangle$ | $|0,0\rangle$ |
|----------------|----------------|----------------|----------------|----------------|
| $E / \text{cm}^{-1}$ | -17.6 | -13.6 | -11.2 | 42.4 |
| $|+1/2,+1/2\rangle$ | 0 | -0.71 | 0.71 | 0 |
| $|+1/2,-1/2\rangle$ | -0.71 | 0 | 0 | 0.71 |
| $|-1/2,+1/2\rangle$ | -0.61 - 0.37i | 0 | 0 | -0.61 - 0.37i |
| $|-1/2,-1/2\rangle$ | 0 | 0.71 | 0.71 | 0 |
3.7  X-Ray Crystallography

Crystal data and details of the data collections are given in Table S6, selected bond lengths angles in Table S7. Molecular structures are shown in Figure S17 & Figure S18. X-ray data were collected on a STOE IPDS II diffractometer (graphite monochromated Mo-Kα radiation, λ = 0.71073 Å) by use of ω scans at −140 °C. The structures were solved with SHELXT and refined on F² using all reflections with SHELXL.14,15 Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and assigned to an isotropic displacement parameter of 1.5/1.2 Ueq(C). Face-indexed absorption corrections were performed numerically with the program X-RED.16 CCDC 2155127-2155128 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

Table S6. Crystal data and refinement details for 1 and 2.

| compound | 1 (jg17) | 2 (jg24) |
|----------|----------|----------|
| empirical formula | C₅₄H₇₉BCu₂N₈ | C₆₂H₉₀BCu₂N₄O₄ |
| moiety formula | C₃₀H₅₉Cu₂N₈⁺, C₂₄H₂₀B⁻ | C₃₀H₅₉Cu₂N₈O₂⁺, C₂₄H₂₀B⁻, 2(C₆H₁₀O) |
| formula weight | 978.14 | 1158.38 |
| crystal size [mm³] | 0.32 x 0.11 x 0.07 | 0.50 x 0.48 x 0.43 |
| crystal system | orthorhombic | monoclinic |
| space group | Pca2₁ (No. 29) | P2₁/n (No. 14) |
| a [Å] | 31.3337(7) | 12.4116(3) |
| b [Å] | 17.3506(5) | 26.3561(4) |
| c [Å] | 18.5568(5) | 19.3892(4) |
| β [°] | 90 | 102.930(2) |
| V [Å³] | 10088.6(5) | 6181.8(2) |
| Z | 8 | 4 |
| ρ [g·cm⁻³] | 1.288 | 1.245 |
| F(000) | 4176 | 2488 |
| μ [mm⁻¹] | 0.888 | 0.739 |
| Tmin / Tmax | 0.4962 / 0.7615 | 0.7140 / 0.8746 |
| θ-range [°] | 1.174 - 25.767 | 1.326 - 26.858 |
| hkl-range | ±38, -19 to 21, ±22 | ±15, ±33, ±24 |
| measured refl. | 61627 | 85935 |
| unique refl. [Rint] | 18998 [0.1099] | 13123 [0.0544] |
| observed refl. (I > 2σ(I)) | 12175 | 10606 |
| data / restr. / param. | 18998 / 1 / 1187 | 13123 / 0 / 706 |
| goodness-of-fit (F²) | 1.024 | 1.120 |
| R1, wR2 (I > 2σ(I)) | 0.0650 / 0.1306 | 0.0689 / 0.1976 |
| R1, wR2 (all data) | 0.1225 / 0.1540 | 0.0833 / 0.2086 |
| res. el. dens. [e·Å⁻³] | -0.442 / 1.166 | -0.630 / 2.037 |
Table S7. Selected distances [Å] and angles [°].

|                  | 1°                                    | 2                  |
|------------------|---------------------------------------|--------------------|
| Cu–N             | 1.890(7) - 2.306(8)                   | 1.932(4) - 2.278(4) |
| Cu–O             | -                                     | 1.884(3) / 1.897(3) |
| O–O              | -                                     | 1.452(4)           |
| Cu···Cu          | 4.0597(16) / 4.0807(13)               | 3.6964(7)          |
| Cu–N–N–Cu        | 43.0(10) / 52.6(10)                   | 29.5(5)            |
| Cu–O–O–Cu        | -                                     | 86.5(2)            |
| Cu–O–O–O         | -                                     | 109.0(2) / 112.5(2) |

*) two crystallographically independent molecules

Figure S17. Plot (50% probability thermal ellipsoids) of the molecular structure of the cationic part of 1 (hydrogen atoms omitted for clarity). Only one of the two crystallographically independent molecules is shown. Selected bond lengths [Å] and angles [°]: Cu1–N1 1.933(8), Cu1–N4 2.055(9), Cu1–N3 2.233(7), Cu1–N5 2.306(8), Cu2–N2 1.921(8), Cu2–N8 2.156(8), Cu2–N7 2.159(8), Cu2–N6 2.195(8), Cu3–N11 1.918(7), Cu3–N14 2.100(9), Cu3–N15 2.209(8), Cu3–N13 2.236(9), Cu4–N12 1.890(7), Cu4–N17 2.072(9), Cu4–N18 2.181(9), Cu4–N16 2.233(9), Cu1···Cu2 4.0807(13), Cu3···Cu4 4.0597(16); N1–Cu1–N4 149.4(4), N1–Cu1–N3 149.4(4), N1–Cu1–N3 149.4(4), N4–Cu1–N3 85.0(3), N1–Cu1–N5 120.9(3), N4–Cu1–N5 85.4(3), N3–Cu1–N5 79.0(3), N2–Cu2–N8 135.4(3), N2–Cu2–N8 140.5(3), N8–Cu2–N7 84.0(3), N2–Cu2–N6 100.4(3), N8–Cu2–N6 83.2(3), N7–Cu2–N6 83.8(3), N11–Cu3–N14 143.5(4), N11–Cu3–N15 126.3(3), N14–Cu3–N15 85.9(3), N11–Cu3–N13 84.6(3), N14–Cu3–N13 83.5(3), N15–Cu3–N13 82.2(3), N12–Cu4–N17 147.8(4), N12–Cu4–N18 125.8(3), N17–Cu4–N18 86.1(4), N12–Cu4–N16 101.0(3), N17–Cu4–N16 85.5(4), N18–Cu4–N16 81.5(3).
Figure S18. Plot (50% probability thermal ellipsoids) of the molecular structure of the cationic part of 2 (hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Cu1–N1 1.932(4), Cu1–N3 2.131(4), Cu1–N5 2.174(4), Cu1–N4 2.187(4), Cu1–O1 1.884(3), Cu1–O2 1.897(3), Cu2–N2 1.980(4), Cu2–N6 2.113(4), Cu2–N7 2.135(4), Cu2–N8 2.278(4), Cu1–Cu2 3.6964(7), O1–O2 1.452(4); O1–Cu1–N1 98.57(13), O1–Cu1–N3 174.73(14), N1–Cu1–N3 80.80(15), O1–Cu2–N2 96.45(13), O2–Cu2–N6 172.73(13), N2–Cu2–N6 90.62(14), O2–Cu2–N7 160.63(15), N6–Cu2–N7 83.61(14), O2–Cu2–N8 92.34(13), N2–Cu2–N8 113.76(14), N6–Cu2–N8 83.21(14), N7–Cu2–N8 83.96(14), O2–O1–Cu1 109.8(2), O1–O2–Cu2 112.5(2)
4 DFT Calculations

Preliminary single point calculations on coordinates obtained by the X-ray diffraction experiments were performed with the ORCA\textsuperscript{17} software (ver. 4.2.1). Since all C-H bonds obtained from the diffraction experiment are too short, only the positions of the hydrogen atoms have been re-optimized (unrestricted broken-symmetry DFT calculations with the bp86 functional, RI approximation, def2-tzvp and def2/j basis sets\textsuperscript{18,19}). Broken-symmetry (BS) unrestricted DFT calculation (B3LYP, RIJCOSX approximation, def2-tzvp and def2-tzvp/j basis sets) revealed that the triplet ground-state is favored. ORCA offers three computations schemes to calculate $J$\textsuperscript{20-24}:

$$J^{(1)} = \frac{E^{(HS)} - E^{(BS)}}{\frac{S^2}{\text{max}}} = +173 \text{ cm}^{-1}$$

$$J^{(2)} = \frac{E^{(HS)} - E^{(BS)}}{S_{\text{max}}(S_{\text{max}}+1)} = +86 \text{ cm}^{-1}$$

$$J^{(3)} = \frac{\langle S^2 \rangle^{(HS)} - \langle S^2 \rangle^{(BS)}}{\langle S^2 \rangle^{(HS)} - \langle S^2 \rangle^{(BS)}} = +171 \text{ cm}^{-1}$$

All determined values were higher than the experimentally obtained value of $J_{\text{iso}} = +25 \text{ cm}^{-1}$, but indeed confirmed the ferromagnetic exchange coupling. Overlap of the magnetic orbitals was derived by broken-symmetry state analysis of the corresponding orbitals 187$\alpha$ and 187$\beta$ (Figure S19), revealing a value of 0.09 for the magnetic overlap integral, confirming the triplet ground state.

**Figure S19.** Magnetic orbital pair 187$\alpha$ (left) and 187$\beta$ (right) of complex 2 for the broken-symmetry state with a contour value of 0.08. (Copper in red, oxygen in green, nitrogen in blue, carbon in grey, hydrogen atoms are omitted for clarity).
DFT Coordinates:

| Atom | X          | Y          | Z          |
|------|------------|------------|------------|
| Cu   | 1.86583122637013 | 0.12810642412944 | 0.02937968063501 |
| Cu   | -1.81850071476946 | -0.16758712358868 | 0.07147571596253 |
| O    | 0.64180704852753 | -0.67005672654943 | -1.15944703118248 |
| O    | -0.52929338991515 | 0.18118104975332 | -1.27548993191816 |
| N    | 0.61830967894849 | 0.69073185062981 | 1.39200190807756 |
| N    | 3.24883458987171 | 0.86241322560678 | 1.47515556083965 |
| N    | 3.38311860074821 | 0.9035623485173 | -1.34202717070175 |
| N    | 3.13034704515634 | -1.63846796268264 | 0.11296872296339 |
| N    | -0.67937988129486 | 0.3458446052437 | 1.6069454338426 |
| N    | -3.43380266033777 | -0.56666714941437 | 1.37354438651555 |
| N    | -2.93433495892385 | -1.36885571770305 | -1.29528147341468 |
| N    | -3.17763875352272 | 1.50635340417589 | -0.6643538783222 |
| C    | 1.08935726359383 | 1.29797190641490 | 2.4950368557780 |
| C    | 2.51486082067578 | 1.75536276513805 | 2.40794545643619 |
| C    | 4.38421678199242 | 1.54841918958291 | 0.82694007382463 |
| C    | 3.68150427431980 | -0.37212871516735 | 2.17129661779735 |
| C    | 4.01986671497205 | 1.99754179127638 | -0.57164590150151 |
| C    | 4.34288310517489 | -0.22046314051933 | -1.56671854115629 |
| C    | 2.76828320438140 | 1.37278405280933 | -2.62573325037196 |
| C    | 3.74056616081065 | -1.57494931162223 | -1.2351304865039 |
| C    | 4.10138794476030 | -1.46255639125558 | 1.20987417737304 |
| C    | 2.29256732723356 | -2.88192843753492 | 0.24849805759229 |
| C    | -1.00764621905380 | 0.74138835040009 | 2.84946205960640 |
| C    | 0.11050647682372 | 1.32753433455202 | 3.46046858974254 |
| C    | 1.58189020013348 | 2.27902966884984 | -2.38247743496999 |
| C    | 3.78444143740992 | 2.04027728106394 | -3.56037911668255 |
| C    | 1.49036104044005 | -2.86328948648423 | 1.54166561069418 |
| C    | 3.1070685588053 | -4.18068045272616 | 0.13859882972445 |
| C    | -3.04010404002747 | -0.71845538097179 | 2.80675517736769 |
| C    | -3.92465537597031 | -1.89329389835405 | 0.90561991633697 |
| C    | -4.48762701289288 | 0.47584058760407 | 1.1928972243837 |
| C    | -4.11451982267382 | -1.9410705300704 | -0.60364967659831 |
| C    | -3.32001506979387 | -0.35131989327291 | -2.32534192984453 |
| Element | X          | Y          | Z          |
|---------|------------|------------|------------|
| C       | -0.2084691012557 | -2.38589726641095 | -1.90574720651534 |
| C       | -3.97713126573343 | 0.88276031472995 | -1.74675867661232 |
| C       | -3.97542794583387 | 1.76104549309862 | 0.5573207617072 |
| C       | -2.42687037042729 | 2.70402588662848 | -1.16149031713721 |
| C       | -2.36719000751591 | 0.50377234687493 | 3.40156348934683 |
| C       | -1.49533598844364 | -3.32970728326120 | -0.85089691405204 |
| C       | -2.64085589274713 | -3.16387036645032 | -3.07404676099200 |
| C       | -1.37947555452878 | 3.19218773573597 | -0.16478451955888 |
| C       | -3.34594929523743 | 3.87599922108845 | -1.52635446941588 |
| H       | 2.55469199364864 | 2.77163814863548 | 1.98579512693925 |
| H       | 3.00450776925367 | 1.79073791033526 | 3.3966658436610 |
| H       | 5.24283723398946 | 0.86596533705349 | 0.80146985913724 |
| H       | 4.71177026001505 | 2.41743543577884 | 1.42036090329308 |
| H       | 2.81715133740761 | -0.70904278935168 | 2.76136526477885 |
| H       | 4.50129079738621 | -0.15464388027369 | 2.88250961788852 |
| H       | 3.29254557415711 | 2.81907314716055 | -0.51133813115066 |
| H       | 4.92297949641747 | 2.39221607070168 | -1.07167485626781 |
| H       | 5.24828693658091 | -0.04929378914906 | -0.97165335591649 |
| H       | 4.67414006470579 | -0.24270839787006 | 2.61485199531324 |
| H       | 2.39051973077811 | 0.44925412874331 | -3.09225072484816 |
| H       | 2.93084299189438 | -1.7968659074694 | -1.94528027347083 |
| H       | 4.52774353352635 | -2.3397205958892 | -1.37410868001946 |
| H       | 5.09027888428206 | -1.24140232213402 | 0.78296075380309 |
| H       | 4.23211369134405 | -2.39584551119187 | 1.77766920350788 |
| H       | 1.58295309436909 | -2.81470667550011 | -0.5897828545969 |
| H       | 0.16686724435805 | 1.73868261418640 | 4.46373605065155 |
| H       | 1.08109445205194 | 2.4784163786904 | -3.34012184733427 |
| H       | 1.88098153612763 | 3.25648141436582 | -1.97516048156900 |
| H       | 0.84563939645465 | 1.80885098548354 | -1.71602789838280 |
| H       | 3.32632473917045 | 2.20978595444222 | -4.54398387049546 |
| H       | 4.68500832300663 | 1.43232990447000 | -3.72424697535770 |
| H       | 4.09850836898830 | 3.02070472128192 | -3.17640475157440 |
| H       | 0.80598251295038 | -3.7224692698982 | 1.55645543377949 |
| H       | 0.89299662784748 | -1.94479387123129 | 1.62382681026019 |
H  2.13446326430921  -2.95190686141714  2.42991844126814
H  2.42939519908669  -5.04329129245144  0.1990827339666
H  3.83278371451580  -4.28170371201810  0.95936036611766
H  3.6506594466095  -4.25873605215116  -0.81220967858585
H -2.35058764134985  -1.57281292686653  2.85869747530801
H -3.94172922083630  -0.97585746802370  3.39481253499646
H -4.86816710714945  -2.16477311543272  1.41723486930102
H -3.16636292750790  -2.62801095973031  1.20123180717793
H -4.94841401990282  0.71874663866788  2.16428521617471
H -5.29062948765907  0.04922532569570  0.57783552950583
H -4.28885610833720  -2.93684980642223  -0.90710653592567
H -5.01287097817485  -1.3860494378767  -0.902495513055
H -3.99350312211225  -0.78693030399224  -3.0841964438870
H -2.37861857784113  -0.06867368961529  -2.8176864576350
H -1.8317968156647  -1.79001487620928  -2.2758357167454
H -4.13969463711245  1.59152671805816  -2.57349255493607
H -4.98165886481584  0.64688725129830  -1.36935465303696
H -4.84787979950456  2.41541941407025  0.36832457327162
H -3.31857535233130  2.2847261429415  1.2635434948644
H -1.89895550658117  2.34017417792161  -2.05634428626019
H -3.00907439301653  1.39353116358960  3.27706550101076
H -2.29394567004036  0.35216408804277  4.4889372857435
H -0.71694528422955  -3.96962992232799  -1.28810071215968
H -2.2729543233099  -3.99864182371004  -0.45158653789470
H -1.04040651401732  -2.76604064281516  -0.02284107649225
H -1.88068746729679  -3.83508277527879  -3.49650550605792
H -2.98266093828742  -2.50872473566180  -3.88543771744898
H -3.48655838885275  -3.79602796526007  -2.76081829418197
H -0.77518036904233  3.97394467959168  -0.6450483620007
H -0.70734819104317  2.38575032159014  0.14712657997819
H -1.83666622802151  3.64725637009633  0.72586641026994
H -2.76035236174347  4.67560179449874  -1.99994850414156
H -3.81476891609997  4.30365896134380  -0.62872808079168
H -4.14380492663301  3.59923822923841  -2.2300598838826
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