

Electronic Supplementary Information

Asymmetric heterometal string complexes: Stereochemical control of the unique isomer of (4,0)[CuCuPd(npa)₄Cl][PF₆] and (4,0)[CuCuPt(npa)₄Cl][PF₆]

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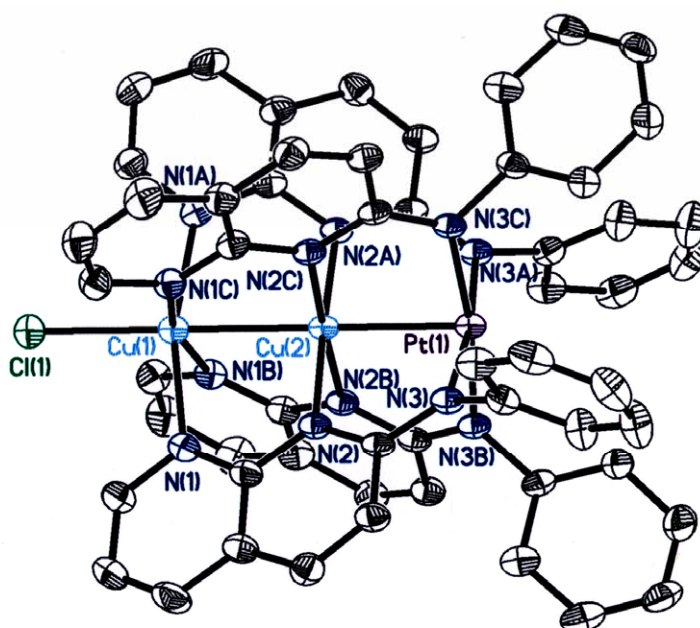


Fig. S1 ORTEP view of the molecular structure of the cation [CuCuPt(npa)₄Cl]⁺ in **2** (30% probability). Hydrogen atoms have been omitted for clarity. Selected bond distances (averaged): Cu(1)-Cl 2.404(5), Cu(1)-Cu(2) 2.486(3), Cu(2)-Pt 2.4357(19), Cu(1)-N 2.089(7), Cu(2)-N 2.007(6), Pt-N 2.029(6) Å.

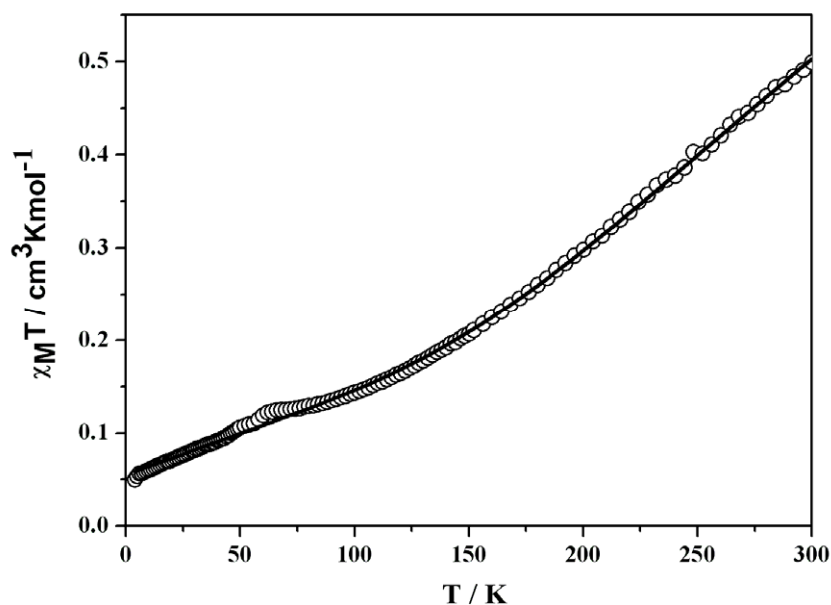


Fig. S2 Plot of $\chi_M T$ versus T for **2**. The solid line represents the best theoretical fit.

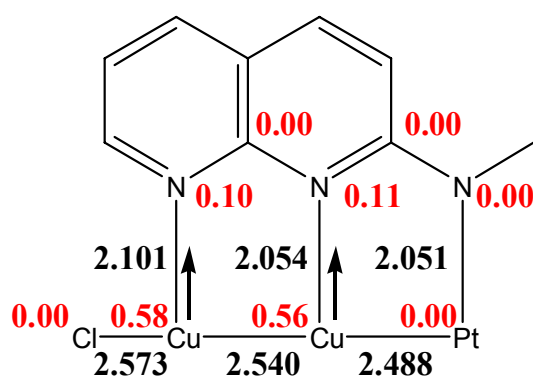


Fig S3 Selected computed bond distances (Å) (black) and atomic spin densities (red) for **2**.

Computational details.

Calculations and geometry optimizations on **1** and **2** had been carried out using the Density Functional Theory (DFT) formalism with the spin unrestricted option, as implemented in the Gaussian03 software, with the B3LYP exchange-correlation functional. All-electron valence double- ζ basis sets (D95V) were used to describe C, N, and H atoms. Los Alamos core potentials were used to model the neon cores of Cl and Cu and the ns , np , and nd cores of heavier metal atoms ($n = 3$ for Pd, $n = 4$ for

Pt). The valence shell of chlorine and all types of metal atoms were described at the double- ζ level (LanL2DZ basis). The antiferromagnetic low-spin state had been characterized and its geometry was optimized using the broken symmetry (BS) approach that was first proposed by Ginsberg,¹ and then developed by Noodleman.² The exchange parameter J between two magnetic centers A and B is defined as follows by Heisenberg-Dirac-van Vleck (HDvV) Hamiltonian:

$$\hat{H}^{\text{HDvV}} = -J\hat{S}_A \cdot \hat{S}_B$$

Since the broken-symmetry solutions were not proper eigenvalues of \hat{S}^2 , but a weighted average of the energies of the pure spin multiplets, an approximate projection technique was employed, as proposed and used by Yamaguchi et al. within the ab initio or the DFT frameworks:³

$$J = 2(E^{\text{BS}} - E^{\text{HS}}) / (\langle S^2 \rangle^{\text{HS}} - \langle S^2 \rangle^{\text{BS}})$$

where $\langle S^2 \rangle^{\text{HS}}$ and $\langle S^2 \rangle^{\text{BS}}$ denote the total spin angular momentum calculated in the high spin and in the broken symmetry solutions, respectively.

X-ray Structure Determinations:

For compound **1**, crystallographic data were collected on a BRUKER SMART APEXCCD area detector using graphite-monochromatized Mo-K α radiation ($\lambda = 0.71073$ Å). Cell parameters were retrieved and refined using the *Bruker SAINT* software on all observed reflections. Data reduction was performed with the *Bruker SAINT* software.⁴ An empirical absorption was based on the symmetry-equivalent reflection and absorption corrections were applied with the SORTAV program.⁵ The structures were solved and refined with *SHELX* programs.⁶ There are some difficulties in the refinement of anion and solvent molecule. The electron density is diffused in

the region of anion and solvent molecule. The anion is refined with constrained geometry, isotropical temperature factor and half occupancy (from balancing the charge and reasonable temperature factors) and the DMF solvent is refined as constrained geometry with fixed temperature factors and half occupancy. This causes the close contact between a fluorine atom (PF_6^-) and the oxygen atom (DMF). It is acceptable due to their half occupancy.

For compound **2**, crystallographic data were collected on a a NONIUS Kappa CCD diffractometer using graphite-monochromatized Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). Cell parameters were retrieved and refined using *DENZO-SMN* software on all observed reflections. Data reduction was performed with the *DENZO-SMN* software.⁷ An empirical absorption was based on the symmetry-equivalent reflection and absorption corrections were applied with the SORTAV program.⁵ The structures were solved and refined with *SHELX* programs.⁶ There are also some difficulties in the refinement of anion and solvent molecule. The anion and solvent molecule are refined by the method, similar to that for compound **1**.

The hydrogen atoms were included in calculated positions and refined using a riding mode.

- 1 A. P. Ginsberg, *J. Am. Chem. Soc.*, 1980, **102**, 111.
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- Noodleman, C. Y. Peng, D. A. Case and J. M. Mouesca, *Coord. Chem. Rev.*, 1995, **144**, 199.
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- 4 SAINT: Computing cell refinement & data reduction, version 6.0; Bruker-axs, Madison, WI, 2000.
- 5 Blessing, R. H. *Acta Crystallogr., Sect. A* 1995, 33.
- 6 Sheldrick, G. M. *SHELXL-97, Program for the Solution of Crystal Structures*, University of Göttingen, Göttingen, Germany, 1997.
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