Supplementary Information

Reversible switching of the Electronic Ground State in a pentacoordinated Copper(II) Complex

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1. Experimental Section

1.1. Synthesis of the ligand (L):

H₂Pyeat(L): 2-Aminoterephthalic acid (0.906 g, 5 mmol) was dissolved in 25 mL of methanol in a round bottom flask. Then acetyl pyridine (0.605 g, 5 mmol) was added into the flask. The resulting light yellowish mixture was refluxed for 2 hours. After ca. 30 minutes of heating, the mixture turned deep yellow. After two hours the yellow reaction mixture was cooled to room temperature and the solution was evaporated to dryness under vacuum. The yellow solid obtained was purified by column chromatography (1:4 MeOH:CH₂Cl₂). Yield: 1.06 g (70 %). Found: C, 63.34; H, 4.30; N, 9.83(%); C₁₅H₁₂N₂O₄ requies C, 63.38; H, 4.25; N, 9.85(%). λ_{max} (CH₃OH)/nm 238(ε/dm³mol⁻¹cm⁻¹ 1183), 360(996), 364(1010), 367(1000), 371(975). $\delta_{\rm H}NMR$ (300 MHz, DMSO-*d*₆, Me₄Si) 7.78 (1H, d, CH), 7.39 (s, 1H, CH), 7.02 (1H, d, CH), 2.083 (3H, s, CH₃). *m/z* (M⁺,%) 310 (M + 3H⁺+Na⁺, 30), 328 (M-2H⁺ + 2Na⁺, 55).

1.2 Synthesis of complex 1:

[Cu₂(μ -Cl)₂(HPyeat)₂]: CuCl₂.2H₂O (170 mg, 1 mmol) was added to 20 mL of methanol in a round bottom flask. A methanolic solution of the ligand H₂Pyeat (0.284 mg, 1 mmol) was added dropwise into the copper chloride solution. The mixture was stirred for 2 hours and filtered. The filtrate was left to evaporate slowly. Green needles single crystals suitable for single crystal X-ray diffraction studies were obtained after one week. Yield: 0.28 g (60%). Found: C, 47.16; H, 2.91; N, 7.37(%). C₃₀H₂₂Cl₂Cu₂N₄O₈ requires C, 47.13; H, 2.90; N, 7.33(%). λ_{max} (CH₃OH)/nm 305 (ε/dm³mol⁻¹cm⁻¹ 60), 338 (40).

2. Physical measurements

The Fourier Transform Infrared spectra (4000-400 cm⁻¹) of the ligand H₂Pyeat and of complex 1 were recorded on a Perkin-Elmer RX-I FT-IR spectrophotometer in solid KBr matrix. The electronic spectra of the ligand and of the complex were recorded at room temperature on a Perkin-Elmer λ 40 UV/Vis spectrometer in methanol medium. Elemental analyses (C, H, and N) were carried out with a Perkin-Elmer 2400 II elemental analyzer. The¹H NMR spectrum of the ligand was recorded on a Bruker 300 MHz FT-NMR spectrometer using trimethylsilane as internal standard in DMSO- d_6 . The positive ion ESI-MS for the ligand H₂Pyeat was performed in a QTOF micro mass spectrometer. The magnetic susceptibility measurements were carried out in the temperature range 2-300 K with an applied magnetic field of 0.1 T on a polycrystalline sample of compound 1 (m = 8.06 mg) with a Quantum Design MPMS-XL-5 SQUID susceptometer. The isothermal magnetizations were performed on the same sample at 2 K with magnetic fields up to 5 T. The susceptibility data were corrected for the sample holder previously measured using the same conditions and for the diamagnetic contribution of the salt as deduced by using Pascal's constant tables ($\chi_{dia} = -405.34 \times 10^{-6}$ emu mol⁻¹).¹ The magnetic measurements in solution where performed in the same conditions on ca. 70 µL of a green DMF solution sealed in a quartz tube containing 1 mg of compound 1 (ca. 20 mM). EPR spectra were recorded from 0 to 1 T in the temperature range 77-298 K with an X-band (9.15 GHz) Varian E-9 spectrometer. The EPR parameters reported in the text were obtained by simulating the spectra with the computer program BrukerWinEPR SimFonia.² The emission spectra of the ligand and of the complex were recorded at room temperature on an F-4600FL spectrophotometer in methanol medium.

2.1 X-Ray crystallography

Single crystals were mounted on a Xcalibur, Ruby, Gemini X-ray diffractometer, equipped with a CCD area detector and sealed tube enhanced (Mo) X-ray source. Data were collected by means of the ω -scans technique using graphite-monochromated radiation at 296(2) K. Empirical multiscan absorption corrections using equivalent reflections were performed with the scaling algorithm SCALE3 ABSPACK.^{3a} Data collection, data reduction and finalization and cell refinement were carried out through the CrysAlisPro software.^{3b} Structures were solved by means of direct methods using SHELXS-97^{3c} and refined by full-matrix least-squares methods based on F_0^2 with SHELXL-97.^{3d} In the last cycles of refinement, ordered non-hydrogen atoms were refined anisotropically whereas hydrogen atoms were refined isotropically. Hydrogen atoms connected to carbon atoms were included in idealized positions, and a riding model was used for their refinement. There was a disordered water molecule in the structure which was removed using the SOUEEZE routine from PLATON software.^{3e} The molecular graphics and crystallographic illustrations for 1 were prepared using ORTEP, PLATON, Diamond 3.2 and Mercury 2.4 softwares.^{3f} All the relevant crystallographic data and structure refinement parameters for 1 are summarized in Table S1.

3. Results and discussion

3.1 Description of Structure

Single crystal X-ray analysis reveals that complex 1 crystallizes in triclinic space group P-1. An ortep view of the complex and its numbering scheme is shown in Fig. S1. Selected bonding parameters are listed in Table S2. The asymmetric unit contains one monoprotonated Schiff base anionic ligand HPyeat⁻, one chloride anion and one copper(II) atom. The complex contains two

equivalent Cu1 atoms which are surrounded by two chloride anions (Cl1 and Cl1ⁱ, i = -x,1-y,1-z) and a tridentate chelating Schiff ligand connected to the metal atom through N1, N2 and O1 atom (or N1ⁱ, N2ⁱ and O1ⁱ for Cu1ⁱ, Fig.**S1**). The copper atoms adopt a distorted trigonalbipyramidal environment (τ =0.65)⁴ with Cl1i and N1 occupying the axial positions and O1, Cl1 and N2 the equatorial ones. Note that the equatorial Cu-Cl bond length (2.6032(7) Å) is much longer than the axial one (2.2526(6) Å). The Cu-N and Cu-O bond lengths are all in the range 1.958-2.003 Å (Table **S2**). The two chloride atoms act as μ_2 bridging ligands each connecting an equatorial positions with and axial one (eq-ax) forming a Cu₂Cl₂ centro-symmetric dinuclear unit with two identical Cu-Cl-Cu bond angles of 90.06(2)° and a Cu-··Cu distance of 3.444 (Å), larger than sum of the van der Waals radii of two copper atoms(2.80 Å).



Fig.**S1**. Ortep view of complex with numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Symmetry code: -x, 1-y, 1-z

The packing of complex **1** shows an extensive hydrogen bonding network resulting in three different chains of dimers which propagate in three nearly perpendicular directions (Fig. **S2**). The free carboxylate group (O4C8O3) forms a H-bond of the type O4-H4…O2 (Table **S3**) with the free oxygen atom (O2) of the coordinated carboxylate group (O1C1O2) of a neighboring dimer giving rise to a chain of the type $C(9)R^2_2(26)$, after Etter's graph-set notation.⁵ O2 atom also interacts with the H10A of the methyl group of the Hpyeat⁻ ligand of a neighboring dimer (Table **S3**). This methyl group forms a second H-bond with the O3 atom of a non coordinated carboxylate group of a neighboring dimer (Table **S3**). Both H-bond networks propagate in almost perpendicular directions. These chains may be designated by Etter's graph-set notation⁵ as $C(10)R^2_2(16)$ and $C(9)R^2_2(26)$.



Fig. S2. H-bonds networks in the structure of 1.

In addition, two further inter-dimer hydrogen interactions are formed between the H atoms attached to the aromatic C13 and C15 carbon atoms (H13A and H15A, respectively) and the Cl1 atom and a third one between the H atom of C12 (H12A) and the oxygen atom O2 (Fig. **S3** and Table **S3**).



Fig. S3. H-bonds and π - π stacking inter-dimer interactions between the pyridine rings along the 111 direction in **1**.

Moreover π - π stacking, lp- π and a unusual CO···CO non covalent interaction are also involved in stabilizing the crystal packing. Thus, there is an almost perfectly eclipsed π - π stacking involving the pyridine rings of two dimers with a antiparallel disposition of the pyridine rings since there is an inversion center located between both rings (Fig.**S3**). The short interplanar distance (3.662 Å) evidences that this interaction is quite strong,⁶ whereas the almost eclipsed conformation is confirmed by the short offset of the centroids of both rings (0.691 Å). Additionally, there is a double lp- π interaction⁷ formed between the free oxygen atom of the coordinated carboxylate group (O2) and the aromatic ring of the terepthalic acid units of a neighboring dimer with an oxygen-centroid distance of 3.265 Å. Finally, there is an unusual antiparallel C-O···C-O interaction formed between two carboxylic acid moieties with a torsion angle, $\tau = 0.0^{\circ}$, indicating the planar anti-parallel arrangement of the two CO groups. The distance between $O^{\delta} \cdots C^{\delta^+}$ is D1 = D2 = 3.20 Å and the angle between O^{...}C=O moieties is $\alpha \mathbf{1} = \alpha \mathbf{2} = \alpha \mathbf{3}$ = $\alpha \mathbf{4} = 90^{\circ}$ (Scheme S1).



Scheme **S1**. Three types of idealized intermolecular CO…CO interactions: (a) Perpendicular Motif; (b) Anti-Parallel Motif; (c) Sheared Parallel Motif.

4. Magnetic Properties

The thermal variation of the molar magnetic susceptibility per Cu(II) dimer times the temperature ($\chi_m T$) for compound **1** shows a room temperature value of ca. 0.85 emu K mol⁻¹, which is the expected value for two isolated Cu(II) ions (S = 1/2) with g \approx 2.13. When the temperature is lowered, $\chi_m T$ remains constant down to ca. 100 K and below this temperature it shows a progressive increase to reach a value close to 1.1 emu K mol⁻¹ at 2 K (Fig. S4). This behavior clearly indicates that compound **1** presents predominant ferromagnetic Cu-Cu interactions in the dimer.

Since compound 1 presents a Cu(II) dimer with a double chorido bridge, we can use the simple S = 1/2 Bleaney-Bowers dimer model to fit the magnetic data.⁸ This model reproduces

very satisfactorily the experimental data in the whole temperature range with g = 2.075 and J = 10.9 cm⁻¹ (solid line in Fig. S4, the spin Hamiltonian considered was $H = -JS_1S_2$).



Fig. S4. Thermal variation of the $\chi_m T$ product per Cu(II) dimer for compound 1. Solid line represents the best fit to the S = 1/2 dimer model (see text).



Fig. S5 Isothermal magnetization at 2 K of compound 1. Solid is the best fit to a S = 1 Brillouin function. Dashed line is the behavior of two S = 1/2 brillouin functions with g = 2.075.

The isothermal magnetization at 2 K confirms the ferromagnetic nature of the coupling and thus, it can be well reproduced with a Brillouin functions for S = 1 and g = 2.0 (solid line, Fig. **S5**) but cannot be well reproduced with the sum of two S = 1/2 Brillouin functions with g = 2.075. In fact, the sum of two independent Brillouin functions gives lower values than the experimental ones except at high fields probably due to weak antiferromagnetic interdimer interactions (through the H-bonds and π - π interactions) and/or a zero field splitting of the resultant S = 1 ground spin state.

4.1 Magneto-Structural Correlations

The sign and magnitude of the coupling constant, *J*, for penta-coordinated $Cu(\mu_2-X)_2Cu$ dimers depend mainly on the Cu-X-Cu bridging angle *a*, the Cu-X distance, the relative positions of the X bridges, the nature of the terminal ligands and the distortions of the coordination geometry. Square pyramidal and trigonalbipyramid geometries are the most usual ones, including all the possible intermediate geometries. Three different types of doubly bridged square pyramidal (SQP) geometries have been observed (Scheme **S2**): (i) SQP-**I**, when two SQP share two basal positions with co-planar basal planes,(ii) SQP-**II**, when two SQP share an axial and a basal position with parallel basal planes and (iii) SQP-**III**, as in (ii), but with perpendicular basal planes. The trigonalbipyramidal geometrical types TBP-**I** and TBP-**II** are less common but can also be found (Scheme **S2**). In TBP-**I** the bridges occupy an axial and an equatorial position (ax-eq dimer) whereas in TBP-**II** both bridges are located in equatorial positions. (eq-eq dimer). SQP-**I** compounds usually show anti-ferromagnetic behavior with *J* values in the range -30 to -100 cm⁻¹,⁹ but in presence of N as terminal atoms, ferromagnetic behavior is observed (J = +40cm⁻¹).¹⁰SQP-**II** shows small coupling constants that may be ferro- or antiferromagnetic (- $10 < J < +10 \text{ cm}^{-1}$).¹¹ The only SQP-III complex known so far presents ferromagnetic coupling ($J = +43 \text{ cm}^{-1}$).¹² (There are ca. 300 penta-coordinated Cu complexes with double Cl bridges and it is very difficult to check all of them). The TBP-I compounds usually show anti-ferromagnetic interactions^{13c-f} although there are some examples with ferromagnetic coupling^{13a-b} (in agreement with the close relationship between TBP-I and SQP-II, see below). TBP-II compounds often show ferromagnetic couplings.^{13a,13g-h} Note that TBP-I and SQP-II geometries are very close since both are eq-ax dimers and can be inter converted by a simple angular deformation of the other ligands (Scheme S2). From the electronic point of view, all the SQP dimers exhibit a predominantly d_{x^2,y^2} ground state, whereas TBP dimers exhibit a predominantly d_{z^2} ground state. The reported complex 1 is a very rare example of the TBP-I type with ferromagnetic coupling and with the unpaired spin located predominantly in the d_{z^2} orbital. This fact is probably due to the presence of important distortions in the TBP geometry of complex 1.





The ferromagnetic coupling (J= +10.9 cm⁻¹) observed in compound **1** is not surprising since the two Cu(II) ions present a distorted trigonalbipyramidal geometry ($\tau = 0.65$)⁴ with the chlorido bridges connecting an axial with an equatorial position and with a Cu-Cl-Cu bond angle (90.06(2)°) very close to orthogonality (Fig. **S1**, Table **S2**). This situation leads to a negligible orbital overlap and, therefore, to a ferromagnetic coupling since the antiferromagnetic contribution of the coupling is cancelled.¹⁴Although the longer equatorial Cu-Cl distance (2.6032(7) Å) is quite large, a weak ferromagnetic coupling is expected from the magnetostructural correlations (Table **S4**). Additionally, the π - π stacking interaction must be taken into account. The DFT calculations show that the magnetic orbitals are also delocalized on the pyridine ring and, therefore, the π - π interaction between the pyridine rings is expected to generate an inter-dimer anti-ferromagnetic interaction,¹⁵ in agreement with the isothermal magnetization measurements (Fig. **S5**).

Hatfield and co-workers^{13a, 16} have proposed magneto-structural correlations between *J* and the α/R ratio in Cu(μ -X)₂Cu complexes, where R (in Å) is the longer axial Cu-X distance in a SQP(or longer equatorial Cu-X distance in a TBP) and α (in °) is the Cu-X-Cu angle. They observed that when the α/R ratio is within the range 32.6-34.8 ° Å⁻¹, the exchange interaction is ferromagnetic whereas when this ratio is out of this range, the coupling is antiferromagnetic. Although this correlation does not consider the possible deviations in the geometry around the Cu(II) ions, we can observe that in compound **1** this ratio (34.6 ° Å⁻¹) lies in the range where ferromagnetic interactions are expected, in agreement with the experimental data. However, in some complexes anti-ferromagnetic behavior was also observed with α/R ratios lying in the range 32.6-34.8 ° Å⁻¹. The overall anti-ferromagnetic behavior of such complexes is due to other factors as the additional ligands and/or the distortions of the geometry. In these cases it becomes very difficult to explain satisfactorily the sign and magnitude of the *J* values since they may depend on both α and *R* and not only on their ratio.

5. **DFT calculations**

The coupling constant, *J*, has been determined with two independent DFT calculations carried out for the highest spin state and for the broken symmetry state. The hybrid functional¹⁷ has been used as implemented in Gaussian98.¹⁸ The basis used in all the calculations is the triple- ζ basis-set proposed by Ahlrichs et al.¹⁹ for transition metals and the double- ζ basis set proposed by the same authors for the other atoms.²⁰ The obtained *J* values are deduced from the energy difference $E_{HS}-E_{BS} = -(2S_1S_2+S_2)J$, where E_{HS} and E_{BS} are the energies of high spin and broken symmetry states respectively, S_1 and S_2 being the spin of the two metal involved (here $S_1 = S_2 = 1/2$). We assume that the energy of the broken symmetry state is a good approximation of low spin state energy, following Ruiz et al.²¹ The orbitals shown here as magnetic orbitals are the so-called Unoccupied Magnetic Spin Orbitals (UMSOs).^{22,23} The calculated *J* value is +12.7 cm⁻¹, in reasonable agreement with experimental value of +10.9 cm⁻¹, giving reliability to the DFT calculations and the level of theory.

As expected, the two magnetic orbitals for **1** have an important contribution on the two metal atoms which is essentially directed towards the four short metal-ligand bonds (Fig. **S8**). These orbitals are also delocalized on the surrounding ligands. The interaction between the metal and the ligand is antibonding in nature, as expected from simple molecular orbital theory arguments. As already discussed before, the geometry of one copper atom (the two copper atoms of the dimer being related by inversion) in intermediate between SQP and TBP. From simple crystal field theory, it is expected that the unpaired electron will be localized in a d_{z^2} orbital for TBP

symmetry and in a $d_{x^2-y^2}$ orbital for SQP geometry. The actual geometry observed between for the two copper atoms is indeed intermediate between a d_{z^2} and a $d_{x^2-y^2}$ orbital. On one hand, the orbital at copper Cu1 can be described as a first approximation as a d_{z^2} one, having its main axis along the almost liner N1-Cu1-Cl1ⁱ sequence (N1-Cu1-Cl1ⁱ = 176.83(5)°). In that way of describing the orbital, the equatorial "donut" part is strongly flattened along Cu1-Cl1 direction. On the other hand, the orbital at copper Cu1 can be described as a first approximation as a distorted $d_{x^2-y^2}$ one, having its four lobes directed towards the four short copper ligand distances Cu1-N1, Cu1-N2, Cu1-O1 and Cu1-Cl1ⁱ. In a first approximation, the geometry of this dichlorido-bridged Cu(II) dimer can be described as TBP-I or as SQP-II (both with parallel basal planes), justifying the relatively weak value for the interaction.²³



Fig. S8. Two views of the unoccupied magnetic spin orbitals (UMSOs) for 1.

6. Theoretical study of non covalent interactions

The energies were computed at the BP86-D3/def2-TZVPD level of theory using the crystallographic coordinates within the program TURBOMOLE version 6.4.²⁴ The interaction energies were calculated with correction for the basis set superposition error (BSSE) by using the Boys-Bernardi counterpoise technique.²⁵ For the calculations we have used the BP86 functional with the latest available correction for dispersion (D3). The "atoms-in-molecules" (AIM)²⁶ analysis was performed at the BP86/def2-TZVP level of theory. The calculation of AIM properties was done using the AIM2000 program.²⁷

The energetic and geometric features of the non-covalent interactions observed in the solid state structure have been analyzed in order to evaluate the different forces that govern the crystal packing. Our study is focused on the different interactions that have a strong influence on the crystal packing and the solid state architecture. Moreover, we have analyzed the role of the methyl group of the Hpyeat ignad in several complexes, since its participation in hydrogen bonding interactions influence the geometric features of some arrangements observed in the solid-state structure.

Firstly, we have analyzed the π - π stacking interaction between the pyridine rings of the ligand. The crystal fragment used to evaluate the stacking interaction is shown in Fig. **S9**. The π - π distance between both pyridine moieties is 3.662 Å and, interestingly, the stacking presents an almost perfect face-to-face disposition with a centro-symmetric disposition (see above). This eclipsed disposition of the aromatic ring is probably due to the effect of its coordination to cooper atoms and the establishment of additional interactions.



Fig. S9. Left: Crystal fragment used to evaluate the π - π stacking interaction between the pyridine rings. Additional H-bonding interactions are indicated by dashed lines (distances in Å). Theoretical model used to evaluate the π - π stacking interaction in the absence of the other interactions and the cooper atoms.

The computed interaction energy is unexpectedly large (-36.6 kcal/mol), probably due to the additional interactions (dashed lines in Fig. **S9**), mostly C-H···O(Cl) H-bonds between the aromatic hydrogen atoms of the pyridine ring and the methyl group. We have computed the same complex shown at the left side of Figure **S9**, replacing the methyl group by a hydrogen atom, and the interaction energy (denoted as ΔE_{H} , see Fig. **S9**) is reduced to -31.8 kcal/mol, indicating that the energy of each C-H···O H-bond involving the methyl group is approximately 2.4 kcal/mol. In order to know the effects of the other hydrogen bonds and the coordination of the pyridine ring to the cooper atoms, we have computed the interaction energy of a model where the cooper atoms with their corresponding ligands have been removed. The interaction energy is reduced to -8.2 kcal/mol in the absence of Cu(II) metal centers, which confirms the strong influence of the Lewis acidic cooper atoms on the π -binding ability of the pyridine rings. This result is in agreement with the magnetic calculations presented above, which show a significant orbital delocalization on the pyridine rings, indicating the critical role played by the π - π staking interaction in the magnetic behavior of complex **1**.

Secondly, our study was devoted to a very interesting and unusual binding mode observed for the carboxylic groups of the ligand. A C-O···C-O stacking interaction is observed between two carboxylic moieties. A similar interaction has been described for the carbonyl group, where three possible configurations for carbonyl-carbonyl interactions have been proposed. These configurations are anti-parallel, perpendicular and sheared parallel.²⁸ In compound **1**, we observe an antiparallel arrangement of the C-OH bonds of the carboxylic groups, which have a partial double bond character. Fig. **S10** shows the crystal fragment used to evaluate this interaction that causes the formation of an infinite ladder. It can be observed that the C-O···C-O distance is very short (3.20 Å) and there is also a weak hydrogen bond between the methyl group and one oxygen atom of the carboxylic group. The interaction energies are indicated in Fig. **S10**, where ΔE_{H} represents the interaction energy obtained replacing the methyl group by a hydrogen atom. We can conclude that the binding energy of the C-O···C-O interaction is ca. -6.7 kcal/mol and that each weak C-H···O=C hydrogen bond contributes in ca.1.0 kcal/mol.

Another relevant contact that has been analyzed is the lp- π interaction, which is established between the carboxlylate group and the terephthalic ring of the ligand. Fig. **S11** shows this interaction and the crystal fragment used to evaluate it. As can be observed, a double lp- π interaction is established between the C=O and the aryl ring that is π -acidic due to the presence of two electron withdrawing carboxylic/carboxylate groups and the coordination of the carboxylate group to the Cu(II) ion. In this supramolecular complex a weak hydrogen bond between the methyl group and the C=O is also established (dashed lines in Fig. **S11**).



Fig. **S10**. Theoretical model used to analyze the CO stacking interaction.



Fig. **S11**. Theoretical model used to compute the lp- π interaction

The distance from the carboxylic oxygen atom (O2) to the terephthalic ring centroid is 3.26 Å. The interaction energy of the complex is -17.3 kcal/mol, which is reduced to -13.3 kcal/mol when the methyl group is replaced by a hydrogen atom. Thus the contribution of each hydrogen bond interaction is ca. -2.0 kcal/mol. The lp- π interaction is favored due to the presence of the copper atom coordinated to one of the carboxylic groups that causes the aromatic ring be more electron deficient. We have computed the double lp- π complex in the absence of copper atoms in order to evaluate this effect, and the interaction energy (see Fig. **S11** right) is further reduced to -10.2 kcal/mol, thus confirming that the presence of the copper atoms strengthens this interaction.

Finally, we have used the Bader's theory of "atoms in molecules"(AIM), which provides an unambiguous definition of chemical bonding, to further describe the noncovalent interactions presented above, specially for the unusual C-O···C-O bond and the face-to-face stacking interaction. The AIM theory has been successfully used to characterize and understand a great variety of interactions including the ones studied herein. Fig. **S12** shows the distribution of critical points (CPs) and bond paths computed for both complexes.



Fig. **S12**. AIM analysis of the non covalent interactions observed in the solid state geometry in **1**. Bond, ring and cage critical points are represented by red, yellow and green spheres, respectively. The bond paths connecting bond critical points are also represented.

First, in the π - π stacking model (top of Fig. **S12**), the interaction is characterized by the presence of four bond CPs and four ring critical points symmetrically distributed. The bond CPs inter-connect four carbon atoms of each ring. The interaction is further characterized by the presence of a cage CP, which is common in face-to-face stacking interactions. The different hydrogen bonding interactions (represented by the letters **a**-**c**) are characterized by the presence of a bond CP that connects the hydrogen atom with the O/Cl atom. These interactions

corresponds to the dashed lines indicates in Fig. **S9**. Second, in the CO stacking interaction (bottom of Fig. **S12**), the distribution of critical points shows two bond CPs connecting the carbon and the oxygen atoms, as a consequence a ring CP is generated that also characterizes this interaction. This result confirms the existence of the anti-paralell CO···CO interaction involving the carboxylic groups. The values of the Laplacian at the bond CPs are in all cases positive, as is common in closed shell interactions.

7. Fluorescence study

The fluorescence properties of the carboxylate based Schiff base ligand (H₂Pyeat) and its Cu(II) complex (**1**) were studied at room temperature (298 K) in methanol medium (Fig. **S13**). The H₂pyeat ligand displays an emission spectrum at 440 nm whereas complex **1** shows a very weak fluorescence. Since upon excitation at 365 nm, the free ligand emission shows an intense peak at ca. 440 nm we can conclude that the emission observed in the ligand is due to the intra ligand proton-transfer fluorescence or that the copper ions quench the fluorescence emission of the ligand. As the blue fluorescence shown by the ligand in methanol becomes colorless upon addition of non coordinating sodium cations, we can conclude that the emission is due to the intra ligand proton transfer rather.



Fig. **S13**. Fluorescence emission spectrum of the H_2 pyeat ligand and of complex **1**.

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empirical formula	$C_{30}H_{22}Cl_2Cu_2N_4O_8$
formula weight	764.52
crystal system	Triclinic
space group	P-1
temperature	296(2)
a (Å)	8.9063(6)
b (Å)	9.0860(5)
c (Å)	11.3268(6)
α(°)	92.966(4)
$\beta(°)$	93.718(5)
$\gamma(^{\circ})$	114.679(6)
$V(Å^3)$	827.98(9)
Ζ	1
$d_{\rm calc} ({\rm g}{\rm cm}^{-3})$	1.533
$\mu(mm^{-1})$	1.499
<i>F</i> (000)	386
crystal size (mm ³)	0.56 x 0.5 x 0.2
θ range (deg)	5.21-37.52
measured reflections	15329
independent reflections	8315
<i>R</i> (int)	0.0398
goodness-of-fit on F^2	1.016
final <i>R</i> indices[$I > 2\sigma(I)$]	$R1 = 0.0645, wR^2 = 0.1636$
<i>R</i> indices (all data)	$RI = 0.1130, wR^2 = 0.1862$
ρ_{\min} and $\rho_{\max}(e.\text{\AA}^{-3})$	-0.747 and 0.797
CCDC No	881999

Table S1. Crystallographic Data and Structure Refinement for 1

Atoms	distance	Atoms	angle
Cu1-Cl1	2.6032(7)	Cl1-Cu1-O1	101.64(5)
Cu1-O1	1.9576(15)	Cl1-Cu1-N1	88.81(5)
Cu1-N1	1.9744(15)	Cl1-Cu1-N2	119.07(5)
Cu1-N2	2.003(2)	Cl1-Cu1-Cl1 ⁱ	89.94(2)
Cu1-Cl1 ⁱ	2.2525(6)	O1-Cu1-N1	88.61(7)
		O1-Cu1-N2	137.56(7)
		Cl1 ⁱ -Cu1-O1	94.49(5)
		N1-Cu1-N2	81.20(7)
		Cl1 ⁱ -Cu1-N1	176.83(5)
		Cl1 ⁱ -Cu1-N2	96.88(6)
		Cu1-Cl1-Cu1 ⁱ	90.06(2)

Table S2. Bond Distances (Å) and Angles (°) in 1

Symmetry Code: (i)-x, 1-y, 1-z

 Table S3. Hydrogen bonding parameters in 1

Atoms	D-H(Å)	H A(Å)	D-H A(Å)	< D-H A (°)	Symmetry
O4-H4 O2	0.8200	1.7700	2.574(2)	167.00	1+x,1+y, z
C10-H10A O2	0.9600	2.5900	3.403(3)	143.00	-x, 1-y, -z
C10-H10B O3	0.960(2)	2.603(2)	3.510(3)	157.5(2)	
C12-H12A O2	0.930(2)	2.661(2)	3.552(3)	160.6(2)	
C13-H13ACl1	0.9300	2.7900	3.590(3)	144.00	1-x,1-y,1-z
C15-H15ACl1	0.9300	2.7500	3.310(3)	119.00	-x,1-y,1-z

Compound ^a	Cu-Cu (Å)	R (Å) ^b	ac	$\alpha/R(^{\circ}.\text{\AA}^{-1})^{d}$	$J (\mathrm{cm}^{-1})^{\mathrm{e}}$	Geometry ^f	Refs.
$[Cu(Et_3en)Cl_2]_2$	3.703	2.728	94.84	34.75(Y)	+0.05	TBP-I	13a
$[Cu(ampy)Cl_3]_2$		2.330	94.90	40.73(N)	+21.0	TBP-I	13b
$[Co(en)_3]_2[CuCl_8]Cl_2$	3.722	2.703	95.20	35.22(Y)	-7.30	TBP-I	13c
[Cu(dmtcp)Cl ₂] ₂	3.570	2.543	95.34	37.49(Y)	-19.40	TBP-I	13d
[Cu(guaH)Cl ₃] ₂	3.575	2.447	97.90	40.01(Y)	-41.3	TBP-I	13e
[Cu(4-Metz)(DMF)Cl ₂] ₂	3.721	2.724	95.30	34.99(Y)	-1.80	TBP-I	13f
[Cu(btaH) ₂ Cl ₂] ₂ .H ₂ O	3.520	2.694	89.30	33.77(Y)	+0.90	TBP-II	13g
$[Cu_2Cl_3(bmdz)_5]Cl.4H_2O$	3.386	2.424	89.10	33.90(Y)	+2.80	TBP-II	13a
[CuLCl] ₂	3.424	2.444	89.23	36.51(N)	+0.76	TBP-II	13h
[Cu(Hpyeat)(Cl)] ₂	3.445	2.603	90.06	34.6 (Y)	+10.9	TBP-I	This work

Table S4. Structural and Magnetic Properties of some $Cu(\mu-Cl)_2Cu$ dimers

^{*a*}Abbreviations: Et₃en, *N*,*N*,*N*-triethylenediamine; ampy, 3-aminopyridinium; en, ethylenediamine; dmtcp, 3,5-dimethyl-1-thiocarboxamide pyrazole; guaH, guaninium; 4-Metz, 4-methylthiazole; DMF, *N*,*N*-dimethylformamide; btaH, benzotriazole; bmdz, benzimidazole; HL, 2-methyl-6-[(pyridine-2-ylmethylene) amino]phenol; H₂pyeat, 2-(1-(pyridine-2-yl)ethylideneamino)benzene-1,4-dioic acid.^b*R* = longest Cu-Cl bond length in the bridge. ^c α = Cu-Cl-Cu bond angle in the bridge. ^dY or N: obeys or not the correlation between *J* and α/R .^eThehamiltonian is written as H = -*J*S₁S₂.^fTBP-I = trigonalbipyramid sharing eq-ax atoms; TBP-II = trigonalbipyramid sharing eq-eq atoms.



Fig.S14 X-band EPR spectra of **1** dissolved in: (a) DMSO; (b) DMF and (c) CH_3CN . Diphenylpicrylhydrazyl (dpph) is the standard field marker (g = 2.0036).