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Structural, magnetic and theoretical calculations of a ferromagnetically coupled tetranuclear copper(II) square complex†

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ABSTRACT: Condensation of 3-hydroxysalicylaldehyde with 2,4,6-trimethyl-1,3-phenylenediamine gives the ligand *N,N'*-bis(3-hydroxysalicylidene)-2,4,6-trimethyl-*m*-phenylenediamine (H_4L). The dinuclear zinc(II) complex $[Zn(H_2L)]_2$ (**1**) and the tetranuclear copper(II) square complex $[Cu(H_2L)]_4(THF)$ (**2**) were synthesized and structurally characterized by single crystal X-ray diffraction. In **1**, the Zn^{II} ions are bridged by two H_2L molecules and they adopt a tetrahedral geometry. The coordination geometry of the copper atoms in **2** is either square planar or square pyramidal, each metal atom being bound to the NO donor sets of two Schiff base ligands and, in one case, to an extra THF molecule. The arrangement of the tetranuclear complexes in the crystal lattice results in the formation of square channels. Variable temperature magnetic measurements on **2** evidence significant long-range ferromagnetic interactions between the four Cu^{II} centres leading to an $S = 2$ ground state with $J_1 = +5.81$, $J_2 = +2.36$, $J_3 = +1.73$ and $J_4 = +2.37$ cm^{-1} . DFT calculations have been carried out in order to corroborate the experimental fitting and ascertain the origin of this ferromagnetic behaviour.

Introduction

The design and synthesis of polynuclear coordination compounds and in particular copper compounds have always interested inorganic chemists working in the field of magnetochemistry.¹ These compounds can act as models for the multimetal active sites of metalloproteins² and as precursors for high-nuclearity clusters for the preparation of useful magnetic materials.³ The predominant factor in such systems is the control of the magnetic exchange interaction J between magnetic centres; the sign and the amplitude of J are sensitive to small structural variations in the bridge linking the metal centres. The most common interaction through extended bridges is antiferromagnetic, because of the overlapping of the magnetic orbitals.⁴ However, ferromagnetic coupling can be observed when the magnetic orbitals have extensive spatial overlap, but are orthogonal⁵ or when the overlapping of the magnetic orbitals is weak. The origin of the interaction can be explained by delocalisation and/or polarisation phenomena. In the latter case, the McConnell spin polarization mechanism⁶ describes how an unpaired electron on one atom polarizes the electron on the adjacent atom through the bridging ligand. DFT calculations⁷ are often used to explain and predict the nature and the strength of these different behaviours.

In the course of our studies of magnetic interactions in heteropolymetallic 3d-5f and homopolynuclear 5f Schiff base complexes,^{8,9} we prepared the new bicompartamental hexadentate ligand N,N' -bis(3-hydroxysalicylidene)-2,4,6-trimethyl-*m*-phenylenediamine, H_4L (Scheme 1), with the aim to obtain bis-dinuclear $[M(3d)-U]_2$ compounds. Our step-by-step approach consists in synthesizing first the mononuclear $M(3d)$ complex and then the heterodinuclear $M(3d)-U$ compound. The reaction of $Zn(acac)_2$ with H_4L led to the formation of the expected bis-mononuclear complex $[Zn(H_2L)]_2 \cdot 3THF$ (**1**·3THF); see Figure 1. On the other hand, the same reaction with the corresponding copper salt did not afford the bis-copper

complex but led to the formation of a tetranuclear square complex $[\{\text{Cu}(\text{H}_2\text{L})\}_4(\text{THF})]\cdot 4\text{THF}$ (**2**·4THF); see **Figure 2**. Investigation of the magnetic properties of **2**·4THF revealed the presence of long range intramolecular ferromagnetic interactions between copper atoms. Several examples of ferromagnetically coupled tetranuclear copper(II) complexes have been reported so far, most often with a Cu_4O_4 cubane-like structure, or built from two Cu_2 subunits.^{3,4,10} Moreover, ferromagnetic interaction was also reported for dinuclear copper(II) entities chelated by Schiff base ligands similar to the one used in this work.¹¹

Experimental

General Information

The ^1H NMR spectra were recorded on a Bruker DPX 200 instrument and referenced internally using the residual protio solvent resonances relative to tetramethylsilane (δ 0). Magnetic susceptibilities were measured on a MPMS5 magnetometer (Quantum Design). The powdered and dried samples of the compounds were introduced in capsules before the introduction in the magnetometer. The calibration was made at 298 K by using a palladium reference supplied by Quantum Design. The independence of the susceptibility value with regard to the applied field was checked at room temperature. The $\chi_{\text{M}}T$ data were collected over the 2–300 K range at magnetic fields of 1 and 10 KOe and were corrected for diamagnetism. Elemental analyses were performed by Analytische Laboratorien at Lindlar (Germany).

Synthesis

The Schiff base ligand *N,N'*-bis(3-hydroxysalicylidene)-2,4,6-trimethyl-*m*-phenylenediamine (H_4L) was synthesized by condensation of 2 equivalents of 3-hydroxy-salicylaldehyde with

2,4,6-trimethyl-*m*-phenylenediamine in methanol. ^1H NMR (THF- d_8 , 23 °C): δ = 1.98 (s, 3 H, CH₃), 2.12 (s, 6 H, CH₃), 6.73 (t, 2 H, J = 7.8 Hz, aromatic H), 6.85 (d, 2H, J = 8.0 Hz, aromatic H), 6.89 (d, 2 H, J = 8.0 Hz, aromatic H), 7.00 (s, 1 H, aromatic H), 7.97 (s, 2 H, OH), 8.37 (s, 2 H, CH=N) and 13.06 (s, 2 H, OH). The acac compounds Cu(acac)₂ and Zn(acac)₂ (Aldrich) were used without purification.

[Zn(H₂L)]₂·3THF (1·3THF). H₄L (200 mg, 0.51 mmol) was mixed in a 1:1 ratio with Zn(acac)₂ (144 mg, 0.51 mmol) in THF, which led to the formation of a yellow powder at room temperature. Recrystallization at 80 °C afforded yellow crystals of [Zn(H₂L)]₂·3THF (85 mg, 37% yield). ^1H NMR (THF- d_8 , 23 °C): δ = 1.97 (s, 3 H, CH₃), 2.09 (s, 6 H, CH₃), 6.53 (d, 2H, J = 8.2 Hz, aromatic H), 6.59 (t, 2 H, J = 8.0 Hz, aromatic H), 6.86 (d, 2 H, J = 8.1 Hz, aromatic H), 6.95 (s, 1 H, aromatic H), 7.95 (s, 2 H, OH) and 8.06 (s, 2 H, CH=N). The elemental analyses are in agreement with the unsolvated [Zn(H₂L)]₂ complex. Anal. calcd. for C₄₆H₄₀N₄O₈Zn₂: C, 60.8; H, 4.4; N, 6.2. Found: C, 58.9; H, 4.8; N, 6.0.

[{Cu(H₂L)}₄(THF)]·4THF (2·4THF). H₄L (300 mg, 0.77 mmol) was mixed in a 1:1 ratio with Cu(acac)₂ (201 mg, 0.77 mmol) in THF, which led to the formation of a dark brown powder at room temperature. Recrystallization at 80 °C afforded dark brown crystals of [{Cu(H₂L)(THF)}₄·4THF (220 mg, 57% yield). The elemental analyses are in agreement with the [{Cu(H₂L)(THF)}₄·2THF complex; Anal. calcd. for C₁₀₄H₁₀₄N₈O₁₉Cu₄ : C, 61.7; H, 5.1; N, 5.5. Found: C, 61.5; H, 5.0; N, 5.4.

Crystallography

The data were collected at 100(2) K on a Nonius Kappa-CCD area detector diffractometer¹² using graphite-monochromated Mo K α radiation (λ = 0.71073 Å). The crystals were introduced in glass capillaries with a protecting “Paratone-N” oil (Hampton Research) coating. The unit cell parameters were determined from 10 frames, and they were then refined

on all data. The data (φ scans with 2° steps) were processed with HKL2000.¹³ Absorption effects were corrected empirically with the program DELABS in PLATON.¹⁴ The structures were solved by direct methods with SHELXS-97 and subsequent Fourier-difference synthesis and refined by full-matrix least-squares on F^2 with SHELXL-97.¹⁵ All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms bound to oxygen atoms were found on a Fourier-difference map and all the others were introduced at calculated positions (except for the disordered THF molecule in **1·3THF**). All were treated as riding atoms with an isotropic displacement parameter equal to 1.2 times that of the parent atom (1.5 for CH_3). In **1·3THF**, one THF molecule is disordered over two symmetry-related positions sharing two carbon atoms, which have been refined with occupancy parameters of 0.5 and some restraints on displacement parameters. In **2·4THF**, one carbon atom in two THF molecules is disordered over two positions which have been refined with occupancy parameters constrained to sum to unity and restraints on bond lengths; restraints on displacement parameters were applied for the atoms of the THF molecules.

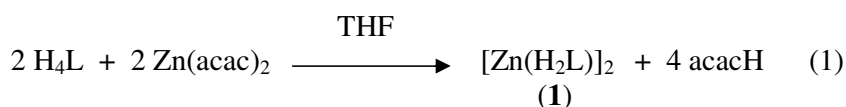
Crystal data and structure refinement details are given in **Table 1**. The molecular plots were drawn with ORTEP-3¹⁶ and VESTA.¹⁷

Computational Details. All theoretical calculations were carried out at the density functional theory (DFT) level using the hybrid B3LYP exchange-correlation functional,¹⁸ as implemented in the Gaussian 09 program.¹⁹ A quadratic convergence method was employed in the self-consistent-field process.²⁰ The triple- ζ quality basis set proposed by Ahlrichs et al. has been used for all atoms.²¹ Calculations were performed on complexes built from experimental geometries as well as on model complexes. The electronic configurations used as starting points were created using the Jaguar 7.9 software.²²

Results and discussion

Syntheses and characterization

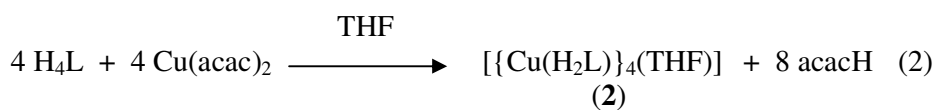
Treatment of H₄L with 1 mol equivalent of Zn(acac)₂ (acac = MeCOCHCOMe) in refluxing THF afforded yellow crystals of the dinuclear compound [Zn(H₂L)]₂·3THF (**1**·3THF) in 37% yield, according to eq 1.



The centrosymmetric compound **1**·3THF, with half a complex molecule and 1.5 THF solvent molecule in the asymmetric unit, is shown in [Figure 1](#), and selected bond lengths and angles are given in [Table 2](#). The two zinc atoms are doubly bridged by the two diimino-*m*-phenylene groups of each ligand and the distance between the metal centres is 7.183(3) Å. The coordination geometry around the zinc atoms can be described as distorted tetrahedral, with angles around the metal atom spanning the range 96.6(3)–127.7(3)° and with a dihedral angle between the two ZnNO planes of the ZnN₂O₂ core of 79.6(2)°. Such a geometry is similar to that encountered in the corresponding dinuclear cobalt complex [Co₂(sal-*m*-phen)₂] (H₂sal-*m*-phen = *N,N'*-bis(salicylidene)-*m*-phenylenediamine)²³ with a dihedral angle of 84.2(1)° but it differs from those in the dinuclear copper complexes [Cu₂(sal-*m*-phen)₂]²⁴ and [Cu₂(L')₂] (H₂L' = *N,N'*-bis(2-hydroxy-3-methoxybenzylidene)-*m*-phenylenediamine),²⁵ with dihedral angles of 43.6 and 51.5(1)°, respectively, for which the geometry is intermediate between cis-planar and tetrahedral. The mean values of the Zn–O and Zn–N bond lengths of 1.921(9) and 2.016(2) Å, respectively, are slightly longer, by ca. 0.3 Å, than in the corresponding copper complexes,^{24, 25} in agreement with the increase in the ionic radius when

passing from copper to zinc with a coordination number of 4.²⁶ Both planar salicylidene-iminato fragments form dihedral angles of $80.2(3)^\circ$ with the bridging phenylene rings to which they are attached. The two central phenylene rings in the molecule correspond to an interplanar separation of 3.35 \AA , but the large offset between the centroids (3.08 \AA) precludes the presence of a π -stacking interaction. Atoms O1 and O4 are both protonated, which results in the formation of intra- and intermolecular bifurcated hydrogen bonds with the neighbouring phenoxide and THF solvent oxygen atoms (Table 3). The intermolecular hydrogen bonds between atoms O1 and O2 from neighbouring molecules result in the formation of chains directed along the *c* axis.

Contrary to the dinuclear zinc compound **1** and the previously reported copper^{24,25} and cobalt²³ congeners, dark brown crystals of the tetranuclear compound $[\{\text{Cu}(\text{H}_2\text{L})\}_4(\text{THF})]\cdot 4\text{THF}$ (**2**·4THF) were isolated in 57% yield from reaction of H_4L with 1 mol equivalent of $\text{Cu}(\text{acac})_2$ in refluxing THF, according to eq 2. Such a difference is difficult to explain, resulting either from the ionic radii of the 3d metal atoms, the substitution at the meta position of the salicylaldimine rings, or by the reaction conditions (reflux in the present case).



Complex **2**, represented in Figures 2 and 3, is a tetranuclear square complex devoid of any true symmetry element. However, if the coordinated THF molecule is disregarded, a pseudo four-fold rotation axis bisecting the lines joining the opposite copper atoms is present, together with four orthogonal pseudo two-fold rotation axes, two of them containing opposite copper atoms and the two others containing the centroids of opposite bridging aromatic rings. The complex thus presents an approximate D_4 point symmetry group, with the four ligands

arranged in helical fashion around the copper atoms square; the molecule is consequently chiral, with both right and left forms being present in the crystal since the space group is centrosymmetric. Three of the four copper atoms have a distorted square planar geometry, being bound to two salicylaldiminato moieties from two adjacent Schiff base ligands and the fourth copper atom has a square pyramidal geometry, with the additional oxygen atom of a THF molecule, O1, in the apical position. The dihedral angles between the two halves of the CuN_2O_2 core are $28.1(3)$, $28.5(2)$, $21.0(2)$ and $25.1(2)^\circ$ for Cu1–Cu4, respectively, the copper atoms being localized at $0.189(3)$, $0.118(3)$, $0.121(3)$ and $0.018(3)$ Å from the mean N_2O_2 plane (rms deviations 0.29 , 0.33 , 0.23 and 0.31 Å). The mean values of the Cu–O(Schiff base) and Cu–N bond lengths of $1.896(8)$ and $1.998(6)$ Å, respectively, are in the range of those measured in the dinuclear copper counterparts.^{24,25} The cyclic architecture of the whole assembly can be seen as an open cage with the bis-salicylideneiminato/copper fragments defining the four sides and the central phenylene rings of the ligands defining the vertices, with a methyl substituent pointing inwards. The dihedral angles between the two arms of the ligands, which form two adjacent faces of the cage, are not far from right angles [mean value $81(3)^\circ$]. The bridging phenylene rings form pairs of dihedral angles with the adjacent CuNO planes with mean values of 75.8 , 77.7 , 72.0 and 82.3° when going from Cu1 to Cu4, respectively. The mean value of the intramolecular Cu...Cu distances between adjacent cations is $6.97(12)$ Å. The volume of the inner cavity can be estimated from the distances between two opposite copper atoms, $10.0433(13)$ and $9.6471(12)$ Å, and the distance between the more distant carbon atoms of the two salicylaldimino fragments in the third direction, ca. 10.9 Å. The resulting cavity size, about 1000 Å³, accommodates two THF solvent molecules (Figure 2). Moreover, as in the dinuclear zinc compound, atoms O1 and O4 of the four ligands are protonated, which results in intramolecular hydrogen bonds with the neighbouring phenoxide oxygen atoms (Table 3). The shortest intermolecular Cu...Cu separations,

Cu3...Cu1' and Cu2...Cu4'' of 6.5435(12) and 6.1202(12) Å, respectively, are associated with the presence of slight intermolecular contacts between neighbouring molecules, Cu3...O1A' 2.569(5) and Cu2...O1D'' 2.800(5) Å, these oxygen atoms being in axial positions (symmetry codes: ' = $x - 0.5, 1.5 - y, z - 0.5$; '' = $0.5 - x, 0.5 + y, 1.5 - z$). Each complex is thus connected to four of its neighbours to generate a two-dimensional assembly parallel to (1 0 $\bar{1}$). Within the packing, the cyclic complexes are aligned so as to form channels parallel to the *a* axis, which are occupied by THF molecules (Figure 4). No intermolecular hydrogen bonding occurs, all the hydrogens of the free hydroxyl groups being bound to the neighbouring coordinated oxygen atom on each catechol moiety in the same molecule.

Magnetic properties

The temperature dependence of the $\chi_{\text{M}}T$ product for **2** in the 2–300 K temperature range is shown in Figure 5. At room temperature, $\chi_{\text{M}}T$ is equal to 1.65 cm³ mol⁻¹ K, a value close to that expected for four magnetically isolated spins (1.5 cm³ mol⁻¹ K with $g = 2$). Upon cooling, the value of $\chi_{\text{M}}T$ increases, attaining 3 cm³ mol⁻¹ K at 2 K. This behaviour is typical of a ferromagnetically coupled complex; the observed $\chi_{\text{M}}T$ maximum value is close to the ordinary one for a ground state of $S = 2$ (3.06 cm³ mol⁻¹ K with $g = 2.02$).

The appropriate Hamiltonian for an isolated cyclic tetranuclear compound can be written as in Equation (3), in which $S_1 = S_2 = S_3 = S_4 = 1/2$.

$$\hat{H} = -J_1 S_1 S_2 - J_2 S_2 S_3 - J_3 S_3 S_4 - J_4 S_4 S_1 \quad (3)$$

The magnetic susceptibility has been computed by using the procedure developed by Borrás-Almenar and co-workers (MAGPACK program).²⁷ The best fitting parameters obtained from the $\chi_{\text{M}}T = f(T)$ curve are $J_1 = +5.81$, $J_2 = +2.36$, $J_3 = +2.37$, $J_4 = +1.73$ cm⁻¹, $g = 2.02$ and TIP

= $246 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ (see figure 5). The fit considering only one J value was not satisfactory.

The magnetization data for **2**, at $T = 2 \text{ K}$, are shown in Figure 6 as an M versus H plot, M being the molar magnetization per four copper ions and H the applied magnetic field. As expected, the isothermal curve is well matched by the Brillouin function for an isolated $S = 2$ spin state with $g = 2.02$.

The origin of the ferromagnetism in **2** could not be attributed to copper–copper intermolecular interaction because of the long Cu...O intermolecular distances. Besides, as the unpaired electron of the copper(II) ion is more delocalised towards the four equatorial bonds, it is clear that the spin density on the axial oxygen atom of the adjacent molecule should be very small. Consequently, the ferromagnetic coupling measured in **2** is operating in an intramolecular way through the meta-phenylenediamine bridge.

DFT calculations

In an effort to get complementary information on compound **2**, and in order to confirm the magneto-structural correlation mentioned above, we have performed DFT calculations following the Broken-Symmetry (BS) approach from the model crystal structure depicted in Figure 7, in which the four different chemical environments of the copper centres have been considered. This local asymmetry, therefore, leads to six different J values: four corresponding to the square sides and two to the diagonals. These values could, in turn, be calculated from eight different BS spin states, namely, one quintuplet (+ + + +), four triplets (− + + +, + − + +, + + − +, and + + + −), and three singlets (− − + +, + − − +, and − + − +). From the equations issued from these spin states we got the following J values, in cm^{-1} : sides, $J_1 = +5.5$, $J_2 = +6.3$, $J_3 = +7.2$, $J_4 = +4.2$, and diagonals, $J_5 = -0.008$, $J_6 = +0.003$, which are in agreement with the experimental values found for this complex. From these values, it is

clear that the diagonal contribution is almost negligible and could be omitted from the magnetic coupling pathway scheme, the main contribution being the coupling along the square sides, which gives a small ferromagnetic behaviour. Furthermore, these lateral J values are all very similar, independently of the 4 or 4 + 1 copper coordination. Thus, the axially coordinated neutral ligand has a limited influence on the basal magnetic orbital, as expected. That all these Cu–Cu magnetic interactions are ferromagnetic in nature have been ascertained by taking just one side of the square (that corresponding to the J_1 pathway, see [Figure 7](#)), leading to a dinuclear model structure ($\mathbf{2}_{\text{intra}}$), see [Figure 8](#) (left), in which all the remaining terminal valences coming from the broken bonds have been replaced by hydrogen atoms and the copper coordination set to 4 in both centres. The remaining geometrical parameters have been kept as they appear in the crystal structure. From this building block we have then calculated a J_{intra} value of $+6.5 \text{ cm}^{-1}$, in agreement with the original value calculated for $\mathbf{2}$ ($+5.5 \text{ cm}^{-1}$). Thus, the magnetic coupling between the copper centres is ferromagnetic in nature and there is a very small effect of the axially coordinated ligands on the J magnitude. In addition, in order to evaluate the intermolecular magnetic exchange, we have also calculated an approximate magnetic coupling constant (J_{inter}) between two Cu_4 units by considering just two copper centres at the square vertices, leading to a model ($\mathbf{2}_{\text{inter}}$) consisting of a copper dimer ([Figure 8, right](#)). In this case, the calculated magnetic exchange constant is only $+0.04 \text{ cm}^{-1}$, and so, should have a very small impact on the global ferromagnetic behaviour, as expected. Therefore, from a magnetic point of view, we can consider the magnetic contribution as coming from isolated squares formed by tetracoordinated copper(II) cations.

The spin density map constructed for the tetranuclear unit ([Figure 9, left](#)) indicates a possible source of the ferromagnetic behaviour: a polarization spin mechanism²⁸ operating between the copper centres through the aromatic ligands ([Figure 9, right](#)). This mechanism is

based on an alternation of the spin density sign from the bonded ligand atoms, which suffer a direct exchange mechanism, through the π -cloud of aromatic bridges (Table 4). As expected, the main spin density lies on the copper ions, as they are the magnetic centres. Moreover, the spin density on the metal-bonded oxygen atoms in the THF and *o*-hydroxyphenol ligands completing the 4 + 1 copper coordination sphere is nearly zero, thus corroborating the weak influence that these axially positioned ligands could exert on the main basal magnetic pathways. Some representative spin density values are collected in Table 4.

In the original crystal structure, the copper atoms are displaced from the neighbouring trimethylbenzene planes, as indicated by the values of the corresponding Cu–N–C–C torsion angles, which differ by about 5 to 20° from the ideal value of 90°. In the case of a spin polarization mechanism, the value of this angle would be somewhat irrelevant. In order to corroborate this point, we have additionally prepared a new model compound (**2_{model}**) consisting also of a dinuclear compound derived from an edge of the square (as **2_{intra}**), but with idealized ligands, angles and distances as shown in Figure 10. From this model, we have symmetrically varied the torsion angle from 90 to 60° by 15° steps for both metallic moieties, obtaining a set of calculated *J* parameters with very similar values despite the high angular variation introduced: +2.9, +2.7 and +1.5 cm⁻¹, respectively. These results point out that the nature of the magnetic coupling between the metallic centres is clearly ferromagnetic, and that the mechanism of the magnetic exchange pathway corresponds well to a spin polarization mechanism. These conclusions corroborate with those reported for dinuclear copper compounds with the same *m*-phenylene bridge.^{11a,11b} Moreover, as proposed by G. Aromi and coworkers,^{11b} the strength of the magnetic coupling seems to be related to the electronic properties of the ligand and in particular to the sum of the absolute values of the atomic spin population on the atoms of the *m*-N- Φ -N moiety.

Conclusion

The Schiff base ligand *N,N'*-bis(3-hydroxysalicylidene)-2,4,6-trimethyl-*m*-phenylenediamine (H_4L) is efficient to stabilize either the dinuclear zinc(II) complex $[Zn(H_2L)]_2$ (**1**) or the tetranuclear copper(II) complex $[Cu(H_2L)]_4(THF)$ (**2**). In the latter compound, the single crystal X-ray diffraction study shows an unusual cyclic geometry with each copper atom bounded to the NO donor sets of two Schiff base ligands, the arrangement of the neighbouring tetranuclear units in the crystal lattice resulting in the formation of square channels. The magnetic study on **2** revealed ferromagnetic interactions between the four Cu^{II} centres leading to an $S = 2$ ground state with $J_1 = +5.81$, $J_2 = +2.36$, $J_3 = +1.73$ and $J_4 = +2.37 \text{ cm}^{-1}$. DFT calculations have been carried out, which corroborate the experimental results and ascertain the origin of this ferromagnetic behaviour. Moreover, detailed analysis of the DFT calculation point out that the mechanism of the magnetic exchange pathway is in agreement with a spin polarization mechanism. Eventually, modifications of this ligand could permit to increase the strength of the coupling exchange and/or the dimensionality of these materials through the formation of bridges between the isolated tetranuclear species so as to afford new metal–organic frameworks.

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Table 1. Crystal data and structure refinement details.

	1·3THF	2·4THF
Empirical formula	C ₅₈ H ₆₄ N ₄ O ₁₁ Zn ₂	C ₁₁₂ H ₁₂₀ Cu ₄ N ₈ O ₂₁
<i>M</i> _r /g mol ⁻¹	1123.88	2168.32
Crystal system	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> /Å	12.235(3)	13.2695(8)
<i>b</i> /Å	16.9476(18)	26.7073(11)
<i>c</i> /Å	13.042(3)	29.3020(17)
<i>β</i> /°	103.294(9)	99.835(3)
<i>V</i> /Å ³	2631.8(9)	10231.8(10)
<i>Z</i>	2	4
<i>ρ</i> _{calcd.} /g cm ⁻³	1.418	1.408
<i>μ</i> (Mo-K _α)/mm ⁻¹	0.977	0.896
<i>F</i> (000)	1176	4528
Reflections collected	16859	60892
Independent reflections	4594	18131
Observed reflections	2167	11073
[<i>I</i> > 2σ(<i>I</i>)]		
<i>R</i> _{int}	0.116	0.113
Parameters refined	355	1338
<i>R</i> ₁	0.094	0.081
<i>wR</i> ₂	0.220	0.225
<i>S</i>	1.010	1.021
Δ <i>ρ</i> _{min} /e Å ⁻³	-0.50	-0.70
Δ <i>ρ</i> _{max} /e Å ⁻³	0.76	1.08

Table 2. Selected bond lengths (Å) and angles (°) in compounds **1**·3THF and **2**·4THF.

1 ·3THF	Zn–O2	1.930(6)	O2–Zn–N1	96.7(3)
	Zn–O3'	1.912(6)	N1–Zn–N2'	111.1(3)
	Zn–N1	2.018(8)	N2'–Zn–O3'	96.6(3)
	Zn–N2'	2.014(7)	O3'–Zn–O2	108.2(3)
	Zn···Zn'	7.183(3)	O2–Zn–N2'	127.7(3)
			N1–Zn–O3'	118.3(3)
Symmetry code: ' = 1 – x, 1 – y, 1 – z				
2 ·4THF	Cu1–O2A	1.904(5)	N1A–Cu1–O2A	91.6(2)
	Cu1–O3D	1.905(5)	O2A–Cu1–N2D	90.0(2)
	Cu1–N1A	2.002(6)	N2D–Cu1–O3D	90.6(2)
	Cu1–N2D	1.991(6)	O3D–Cu1–N1A	90.6(2)
	Cu1–O1	2.405(6)	N1A–Cu1–N2D	152.5(2)
	Cu1···Cu2	7.1706(12)	O2A–Cu1–O3D	174.1(2)
	Cu2–O2B	1.881(5)	N1B–Cu2–O2B	92.1(2)
	Cu2–O3A	1.892(4)	O2B–Cu2–N2A	91.5(2)
	Cu2–N1B	2.008(6)	N2A–Cu2–O3A	92.0(2)
	Cu2–N2A	2.003(6)	O3A–Cu2–N1B	90.1(2)
	Cu2···Cu3	6.8691(11)	N1B–Cu2–N2A	154.3(2)
			O2B–Cu2–O3A	167.1(2)
	Cu3–O2C	1.894(5)	N1C–Cu3–O2C	91.8(2)
	Cu3–O3B	1.903(5)	O2C–Cu3–N2B	89.3(2)
	Cu3–N1C	1.999(6)	N2B–Cu3–O3B	91.4(2)
	Cu3–N2B	1.996(6)	O3B–Cu3–N1C	89.8(2)
	Cu3···Cu4	6.9683(12)	N1C–Cu3–N2B	159.9(2)
			O2C–Cu3–O3B	173.5(2)
	Cu4–O2D	1.891(5)	N1D–Cu4–O2D	92.7(2)
	Cu4–O3C	1.896(5)	O2D–Cu4–N2C	89.6(2)
	Cu4–N1D	1.997(6)	N2C–Cu4–O3C	92.6(2)
	Cu4–N2C	1.987(6)	O3C–Cu4–N1D	90.8(2)
	Cu4···Cu1	6.8876(12)	N1D–Cu4–N2C	161.3(2)
			O2D–Cu4–O3C	162.5(2)

Table 3. Hydrogen bonding geometry (Å, °) in compounds **1**·3THF and **2**·4THF.

D-H...A	D-H	H...A	D...A	D-H...A
1 ·3THF				
O1-H1...O2	0.94	2.13	2.680(8)	116
O1-H1...O2'	0.94	2.12	2.751(9)	123
O4-H4...O3	0.98	2.26	2.658(9)	103
O4-H4...O6	0.98	2.08	2.81(2)	130
Symmetry code: ' = 1 - x, 1 - y, -z				
2 ·4THF				
O1A-H1A...O2A	0.86	2.19	2.624(6)	111
O4A-H4A...O3A	0.91	2.09	2.625(7)	116
O1B-H1B...O2B	0.90	2.07	2.624(7)	119
O4B-H4B...O3B	0.88	2.12	2.631(7)	116
O1C-H1C...O2C	0.91	2.08	2.641(7)	119
O4C-H4C...O3C	0.92	2.10	2.660(7)	118
O1D-H1D...O2D	0.98	2.07	2.627(7)	114
O4D-H4D...O3D	0.91	1.99	2.620(7)	125

Table 4. Spin density values (in e^-) on selected atoms for the calculated model of complex **2**.

Atoms ^a	Ground (quintuplet) state
Cu1/Cu2/Cu3/Cu4	+0.6240/+0.5848/+0.6118/+0.5829
N1/N2/N3/N4 ^b	+0.0841/+0.0952/+0.0884/+0.0963
O1/O2/O3/O4 ^b	+0.0936/+0.0944/+0.0922/+0.0951
O _{THF}	+ 0.0010
O _{hydroxyphenol}	+0.0003
N–C–C–C–N ^c	+0.0823/–0.0074/+0.0150/–0.0027/+0.0925

^a Indexes 1, 2, 3 and 4 refer to the Cu1, Cu2, Cu3 and Cu4 atoms, respectively. ^b Mean values between each pair of N (imino) and O (phenoxo) atoms bonded to each copper ion. ^c Alternating spin density values along the N–C–C–C–N pathway connecting the Cu1 and Cu2 centres.

Captions to Scheme and Figures

Scheme 1. The Schiff base H₄L under study.

Figure 1. View of the complex $[(Zn(H_2L))_2]$ (**1**). The carbon-bound hydrogen atoms are omitted. The displacement ellipsoids are drawn at the 50% probability level. Symmetry code: $' = 1 - x, 1 - y, 1 - z$.

Figure 2. View of the complex $[\{Cu(H_2L)\}_4(THF)] \cdot 4THF$ (**2·4THF**). The solvent molecules, methyl substituents and carbon-bound hydrogen atoms are omitted. The displacement ellipsoids are drawn at the 10% probability level.

Figure 3. View of the complex $[\{Cu(H_2L)\}_4(THF)] \cdot 4THF$ (**2·4THF**). The carbon-bound hydrogen atoms and two THF molecules are omitted. The displacement ellipsoids are drawn at the 10% probability level.

Figure 4. Crystal packing in $[\{Cu(H_2L)\}_4(THF)] \cdot 4THF$ (**2·4THF**) viewed down the *a* axis. Hydrogen atoms are omitted.

Figure 5. Thermal dependence of $\chi_M T$ for complex $[\{Cu(H_2L)\}_4(THF)]$ (**2**). The solid line was generated from the best fit parameters given in the text. The inset represents the coupling exchange pathways.

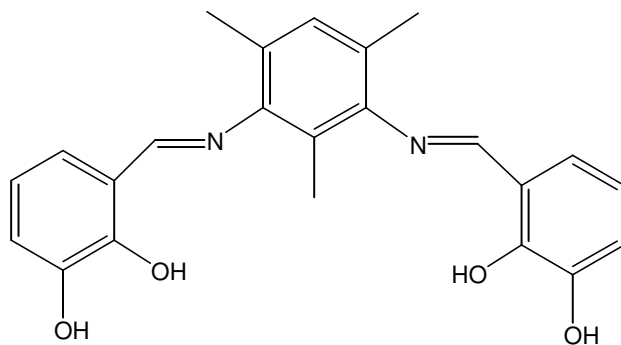
Figure 6. Field dependence of the magnetization for complex $[\{Cu(H_2L)\}_4(THF)]$ (**2**) at 2, 4 and 6 K. The solid lines correspond to the Brillouin functions for the $S = 2$ ground state.

Figure 7. The tetranuclear structure (**2**) considered for the DFT calculations and the corresponding J scheme.

Figure 8. Dinuclear models established for calculating the nature of the magnetic coupling for intra- (left, $\mathbf{2}_{\text{intra}}$), and intermolecular (right, $\mathbf{2}_{\text{inter}}$) magnetic interactions.

Figure 9. Left: Calculated spin densities for the tetranuclear model of complex **2** in the ground (quintuplet) state. The represented isodensity surface corresponds to a cut-off value of $0.0008 \text{ e bohr}^{-3}$. Grey and blue colors correspond to positive and negative values, respectively. Right: Scheme of the polarization mechanism operating between the copper centres showing the spin density relative values.

Figure 10. Dinuclear model ($\mathbf{2}_{\text{model}}$) established for calculating the effect of the Cu–N–C–C torsion angle value on the magnitude of the magnetic coupling.



Scheme 1

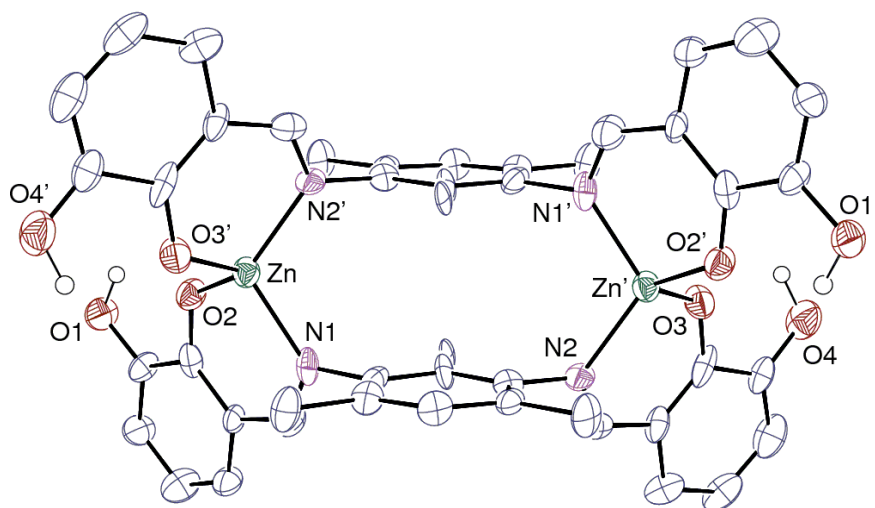


Figure 1

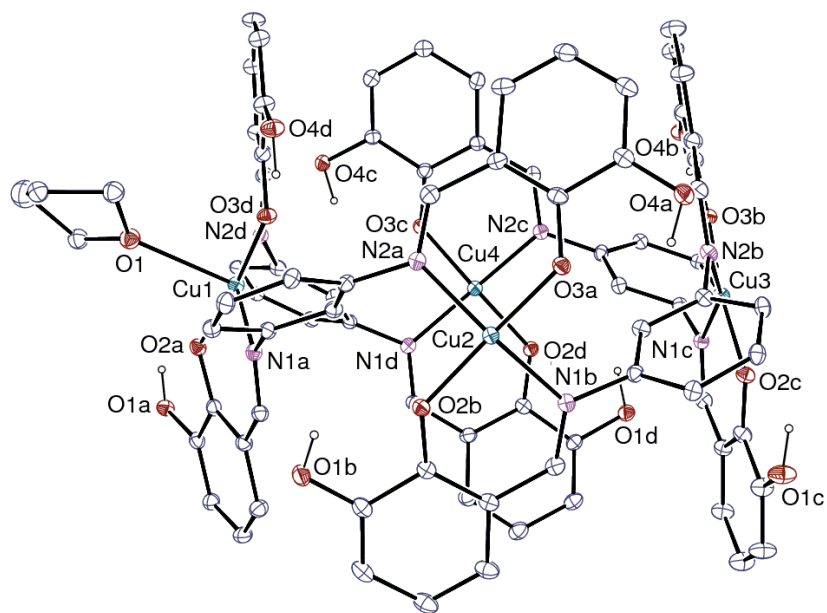


Figure 2

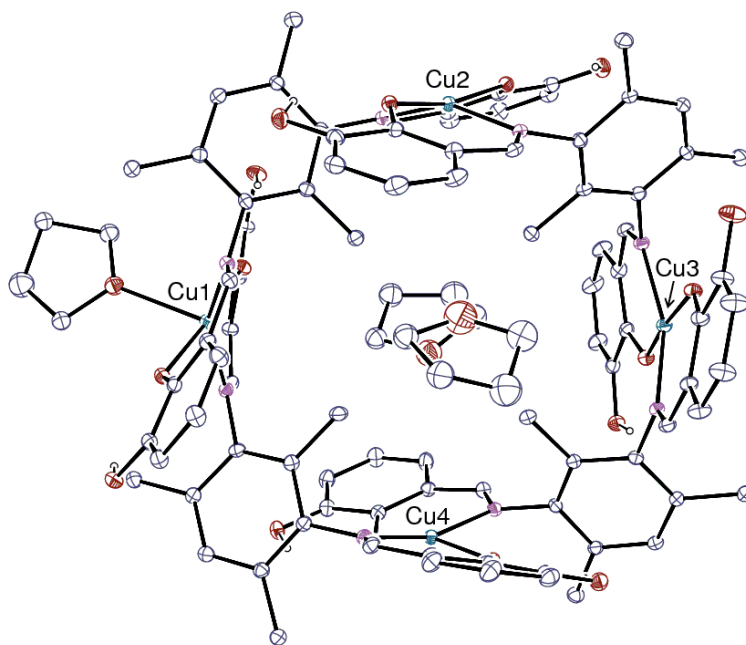


Figure 3

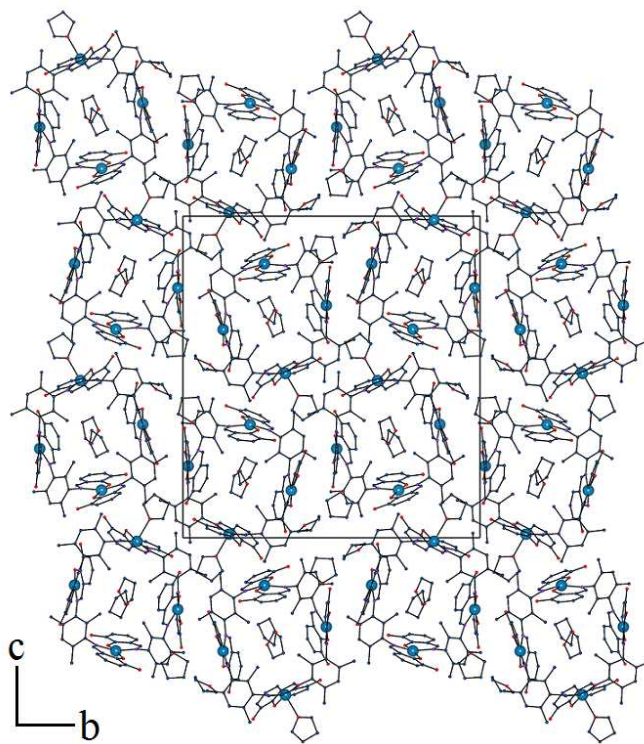


Figure 4

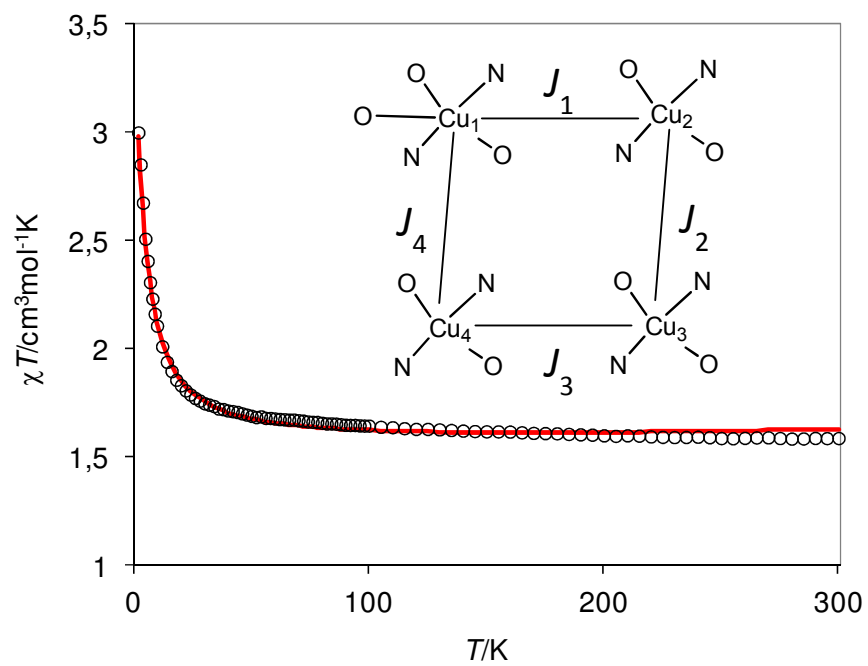


Figure 5

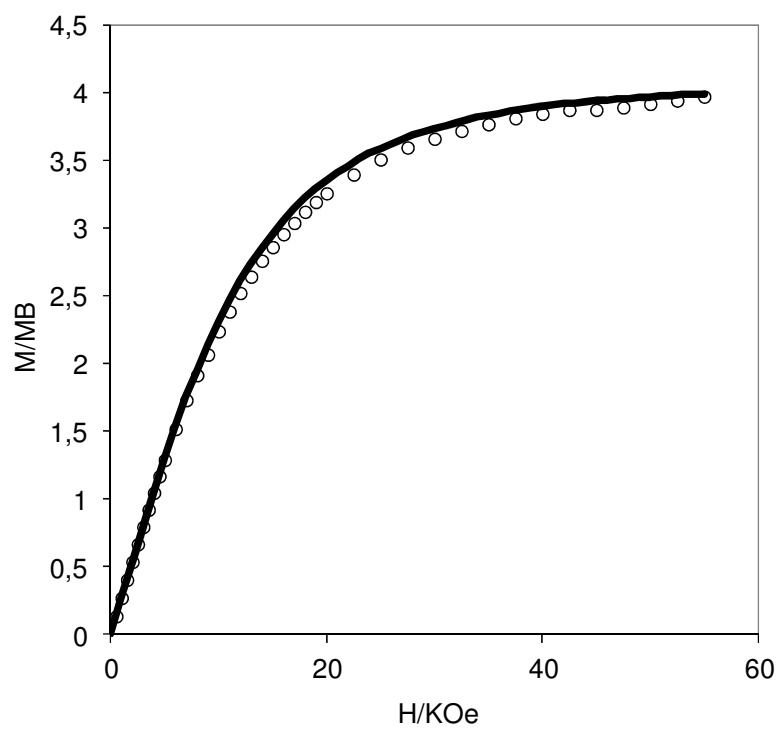


Figure 6

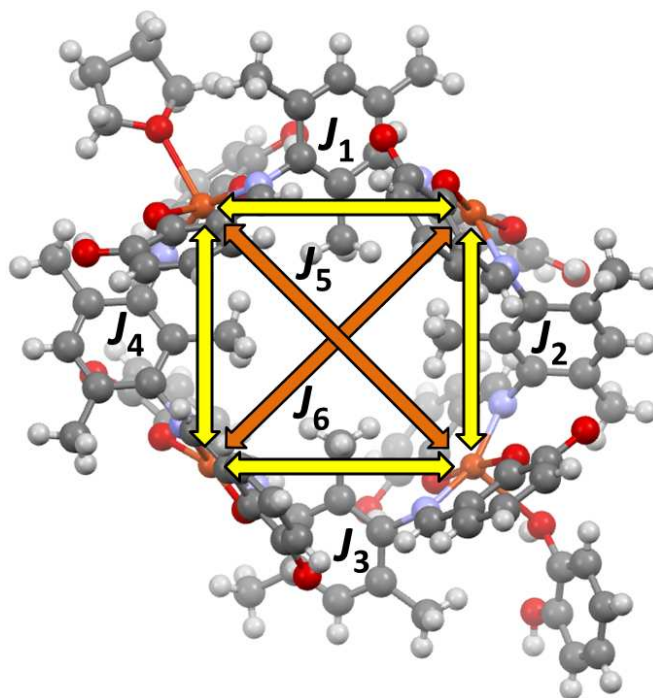


Figure 7

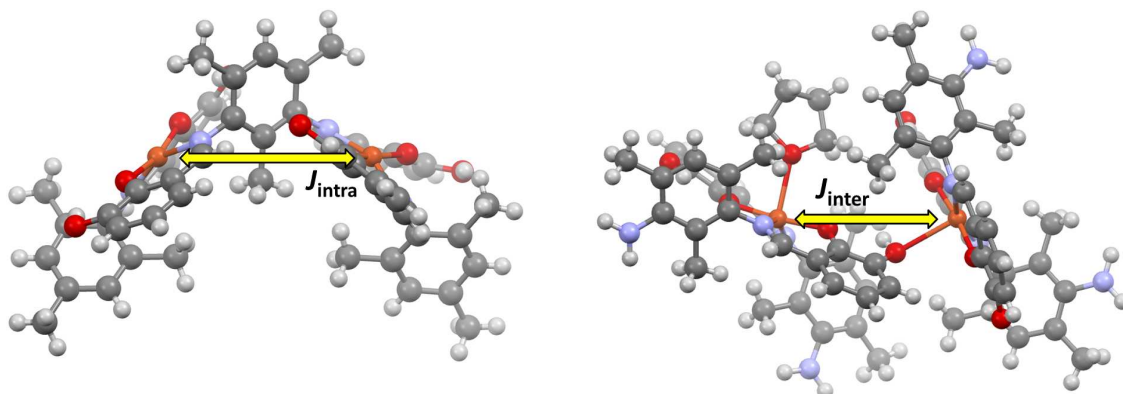


Figure 8

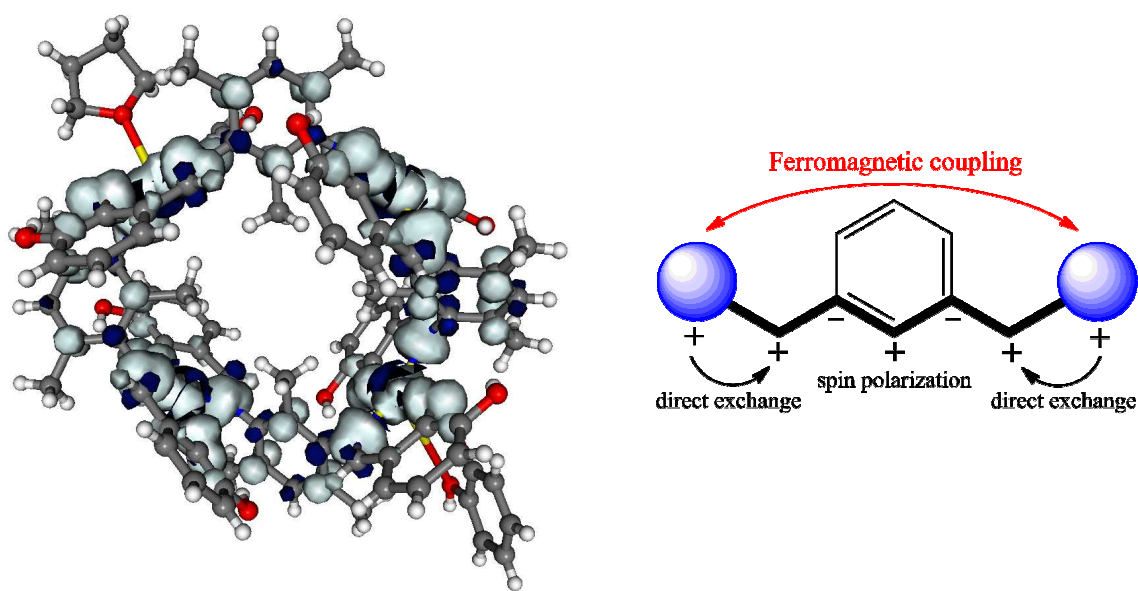


Figure 9

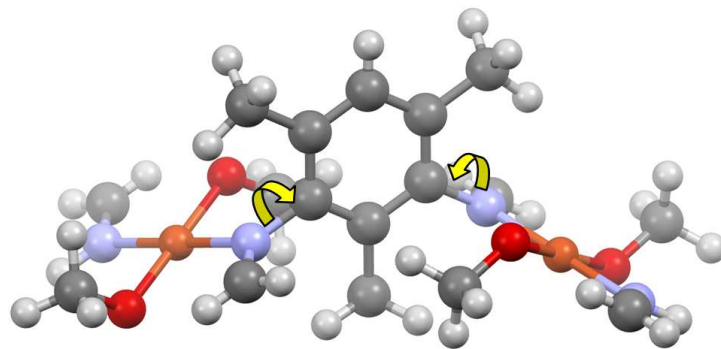
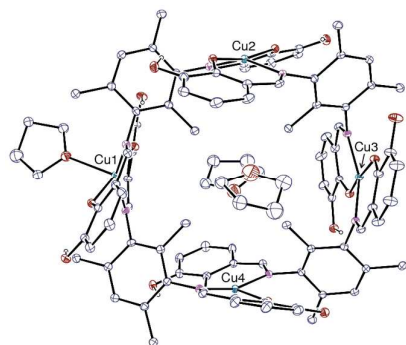


Figure 10



Ferromagnetic interactions in tetranuclear copper(II) square complex $[\{Cu(H_2L)\}_4(THF)]$ with Schiff base ligand L.