

## $\pi$ – $\pi$ Stacking and ferromagnetic coupling mechanism on a binuclear Cu(II) complex†

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The ferromagnetic couplings were observed in an unpublished crystal that consists of binuclear copper(II) complexes, namely,  $[\text{Cu}_2(\mu_{1,3}\text{-SCN})_2(\text{PhenOH})(\text{OCH}_3)_2(\text{HOCH}_3)_2]$  (PhenOH = 2-hydroxy-1,10-phenanthroline), and in the binuclear complex Cu(II) ion assumes a distorted octahedral geometry and thiocyanate anion functions as a  $\mu_{1,3}\text{-SCN}^-$  equatorial–axial (EA) bridging ligand. The analysis for the crystal structure indicates that there are three types of magnetic coupling pathways, in which two pathways involve  $\pi$ – $\pi$  stacking between the adjacent complexes and the third one is the  $\mu_{1,3}\text{-SCN}^-$  bridged pathway. The fitting for the data of the variable-temperature magnetic susceptibilities shows that there is a ferromagnetic coupling between adjacent Cu(II) ions with  $J = 50.02 \text{ cm}^{-1}$ . Theoretical calculations reveal that the two types of  $\pi$ – $\pi$  stacking resulted in ferromagnetic couplings with  $J = 4.16 \text{ cm}^{-1}$  and  $J = 2.75 \text{ cm}^{-1}$ , respectively, and the bridged thiocyanate anions pathway led to a weaker ferromagnetic interaction with  $J = 0.88 \text{ cm}^{-1}$ . The theoretical calculations also indicate that the ferromagnetic coupling sign from the two types of  $\pi$ – $\pi$  stacking does not accord with McConnell I spin-polarization mechanism. The analysis for the Wiberg bond indexes that originate from the  $\pi$ – $\pi$  stacking atoms indicates that the Wiberg bond indexes are relevant to the associated magnetic coupling magnitude and the Wiberg bond index is one of the key factors that dominates the associated magnetic coupling magnitude.

### Introduction

For a long time, the field of molecular magnetism has attracted considerable attention, and major advances have been made in both their description and their application as new molecular-based materials.<sup>1–3</sup> In the area of magneto-structural correlations it is very important to obtain the basic information about magnetic coupling signs, magnitudes and mechanism. In order to obtain this information many fitting models or fitting formulas have been developed and practised, for binuclear,<sup>4</sup> trinuclear,<sup>5–8</sup> tetranuclear<sup>9–15</sup> and one-dimensional systems.<sup>16–21</sup> At the same time, theoretical calculations also have been successfully developed and practised on binuclear<sup>22–31</sup> and trinuclear models<sup>31–33</sup> in order

to reveal the factors that may dominate the magnetic coupling properties. Mostly, fittings and calculations deal with systems where the coupling metallic ions are connected by bridging ligands, namely, the magnetic interactions are through bond exchange. In the materials science area, the  $\pi$ – $\pi$  stacking interaction belongs to one of the intermolecular forces and it has been playing a pivotal role. For example, the  $\pi$ – $\pi$  stacking interaction resulted in a silver complex displaying a highly electrical conducting behaviour,<sup>34</sup> and it also led to a change in the fluorescent emission intensity for some compounds.<sup>35</sup> In the area of magnetic coupling interactions,  $\pi$ – $\pi$  stacking interaction also plays an important role. For example, some authors attributed the strong ferromagnetic order to  $\pi$ – $\pi$  stacking interaction,<sup>36</sup> and other authors found the  $\pi$ – $\pi$  stacking interaction led to a strong antiferromagnetic interaction between spin-carriers.<sup>37–39</sup> In a word, the  $\pi$ – $\pi$  stacking interaction should be one of the key factors that dominant magnetic coupling properties, but the papers with fitting and theoretical calculations for the magnetic coupling of  $\pi$ – $\pi$  stacking systems are very scarce and mostly, these papers only deal with radicals or complexes with radicals as ligands to our knowledge.<sup>37–42</sup> And in the area although the magnetic coupling signs of some compounds have been explained by using McConnell I spin-polarization mechanism and McConnell II charge transfer mechanism,<sup>43–44</sup> there are still a few questionable points to be resolved, and in addition, the factors that dominate the magnetic coupling mechanism have not been

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mentioned by them. Therefore, it is very interesting and important to design and synthesize complexes dealing with  $\pi$ - $\pi$  stacking and study their magnetic coupling mechanism.

2-Hydroxy-1,10-phenanthroline is one of the ideal ligands that possesses both a strong chelated coordination group and a larger conjugation plane which may be useful to form complexes with strong  $\pi$ - $\pi$  stacking and relevant magnetic coupling pathways, but up to now there are few papers<sup>34,45–49</sup> that deal with this compound as a ligand and there is no paper that correlates magnetism with its  $\pi$ - $\pi$  stacking. For the interests of the magnetic coupling mechanism of the  $\pi$ - $\pi$  stacking system, we synthesized the title Cu(II) complex with 2-hydroxy-1,10-phenanthroline as ligand, and in this paper we report its synthesis and magnetic coupling mechanism of the  $\pi$ - $\pi$  stacking and the bridged pathways, which both involve the experimental and theoretical calculations.

## Experimental section

**Materials.** 2-Hydroxy-1,10-phenanthroline was synthesized by the reaction of 2-chloro-1,10-phenanthroline and NaOH. H<sub>2</sub>O solution and all other chemicals are analytical grade and used without further purification.

**Preparation of [Cu<sub>2</sub>( $\mu_{1,3}$ -SCN)<sub>2</sub>(PhenOH)(OCH<sub>3</sub>)<sub>2</sub>(HOCH<sub>3</sub>)<sub>2</sub>].** 5 ml methanol solution of NaSCN (0.0405 g, 0.50 mmol) was added into 20 ml methanol solution of containing Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.1853 g, 0.50 mmol) and 2-hydroxy-1,10-phenanthroline (0.1070 g, 0.50 mmol), and the mixed solution was stirred for a few minutes. The green single crystals were obtained after the filtrate was allowed to stand and slowly evaporate at room temperature for about two weeks. IR (cm<sup>-1</sup>): 3132(s), 2114(s), 1623(w), 1560(m), 1458(s), 1391(s), 1024(m). Elemental anal. Calcd. for C<sub>15</sub>H<sub>15</sub>CuN<sub>3</sub>O<sub>3</sub>S: (fw 380.90) C, 47.30; H, 3.97; N, 11.03; Cu, 16.68. Found: C, 47.59; H, 4.31; N, 11.37; Cu, 17.25%.

**Physical measurements.** Infrared spectra were recorded with a Bruker Tensor 27 infrared spectrometer in the 4000–500 cm<sup>-1</sup> region using KBr disks. C, H and N elemental analyses were carried out on a Perkin-Elmer 240 instrument. Variable-temperature magnetic susceptibilities of microcrystalline powder sample were measured in a magnetic field 1 K Oe in the temperature range 2–300 K on a SQUID magnetometer. The data were corrected for the magnetization of the sample holder and for the diamagnetic contributions of the complex which were estimated from Pascal's constants.

**Computational details.** The magnetic interactions between Cu(II) ions were studied on the basis of density functional theory (DFT) coupling with the broken-symmetry approach (BS).<sup>50–52</sup> The exchange coupling constants  $J$  have been evaluated by calculating the energy difference between the high-spin state ( $E_{HS}$ ) and the broken symmetry state ( $E_{BS}$ ). Assuming the spin Hamiltonian is defined as:

$$\hat{H} = -2\hat{J}\hat{S}_1 \cdot \hat{S}_2 \quad (1)$$

If the spin projected approach is used, the equation proposed by Noodleman<sup>50–52</sup> to extract the  $J$  value for a binuclear transition-metal complex is thus:

$$J = \frac{E_{BS} - E_{HS}}{4S_1S_2} \quad (2)$$

To obtain exchange coupling constants  $J$ , Orca 2.8.0 calculations<sup>53</sup> were performed with the popular spin-unrestricted hybrid functional B3LYP proposed by Becke<sup>54–55</sup> and Lee *et al.*,<sup>56</sup> which can provide  $J$  values in agreement with the experimental data for transition metal complexes.<sup>57</sup> Tri- $\zeta$  with one polarization function def2-TZVP<sup>58–59</sup> basis set proposed by Ahlrichs and co-workers for all atoms was used in our calculations. Strong convergence criteria was used in order to ensure that the results are well converged with respect to technical parameters (the system energy was set to be smaller than 10<sup>-7</sup> hartrees).

The  $\pi$ - $\pi$  stacking magnitude was studied based on the calculations of the natural bond orbital (NBO) method, which was developed by Weinhold and is now widely used for analyzing chemical bonds in non-covalent compounds.<sup>60–62</sup> This method is quite robust toward changing the basis set and it is easy to connect traditional bonding concepts with the results of the NBO analysis. In this paper NBO analysis deals with its Wiberg index<sup>63</sup> and the Wiberg index is used to evaluate the associated  $\pi$ - $\pi$  stacking magnitude. The calculations of this section were performed in Gaussian 03 program package<sup>64</sup> at the B3LYP level with LANL2DZ basis set of relativistic effective core potential for Cu cation and the 6-31++G\*\* basis set for other non-metallic atoms.

**X-ray crystallographic analysis of the complex.** A blue single crystal of dimensions 0.32 × 0.18 × 0.16 mm was selected and subsequently glued to the tip of a glass fiber. The determination of the crystal structure at 25 °C was carried out on an X-ray diffractometer (Bruker Smart-1000 CCD) using graphite monochromated Mo-K $\alpha$  radiation ( $\lambda$  = 0.71073 Å). Corrections for  $L_p$  factors were applied and all non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in calculated positions and refined as riding. The programs for structure solution and refinement were SHELXS-97 and SHELXL-97, respectively. The crystal belongs to monoclinic, space group  $P2_1/n$  with  $a$  = 6.9794(15) Å,  $b$  = 22.703(5) Å,  $c$  = 10.259(2) Å,  $\beta$  = 105.843(3)°,  $V$  = 1563.8(6) Å<sup>3</sup>,  $Z$  = 4,  $D_c$  = 1.618 g cm<sup>-3</sup>,  $F(000)$  = 780,  $\theta$  range 1.79–27.00°, index ranges  $-8 \leq h \leq 8$ ,  $-29 \leq k \leq 16$ ,  $-13 \leq l \leq 13$ . A total of 9027 reflections were collected and 3389 were independent ( $R_{int}$  = 0.035), of which 2547 observed reflections with  $I > 2\sigma(I)$  were used in the succeeding refinement. The final refinement including hydrogen atoms converged to  $R$  = 0.0535,  $wR$  = 0.1317,  $(\Delta\rho)_{max}$  = 0.988 e Å<sup>-3</sup>,  $(\Delta\rho)_{min}$  = -0.386 e Å<sup>-3</sup>.

The deposition number of the crystal at the CCDC is 782938.

## Results and discussion

**Crystal structure of [Cu<sub>2</sub>( $\mu_{1,3}$ -SCN)<sub>2</sub>(PhenOH)(OCH<sub>3</sub>)<sub>2</sub>(HOCH<sub>3</sub>)<sub>2</sub>].** Fig. 1 shows the coordination diagram with the atom numbering scheme. The coordination bonds lengths range from 1.942(3) Å to 3.0581(15) Å and the associated angles change from 82.47(12)° to 173.68(8)°, and it indicates that the Cu(II) ion assumes a distorted six-coordinated CuN<sub>3</sub>O<sub>2</sub>S octahedral geometry. The non-hydrogen atoms of 2-hydroxy-1,10-phenanthroline ligand define an approximate plane within 0.0207 Å with a maximum deviation of -0.0385(33) Å for C8 atom. The two thiocyanate anions function as  $\mu_{1,3}$ -SCN<sup>-</sup> equatorial-axial (EA) bridging ligands and link two Cu(II) ions with a

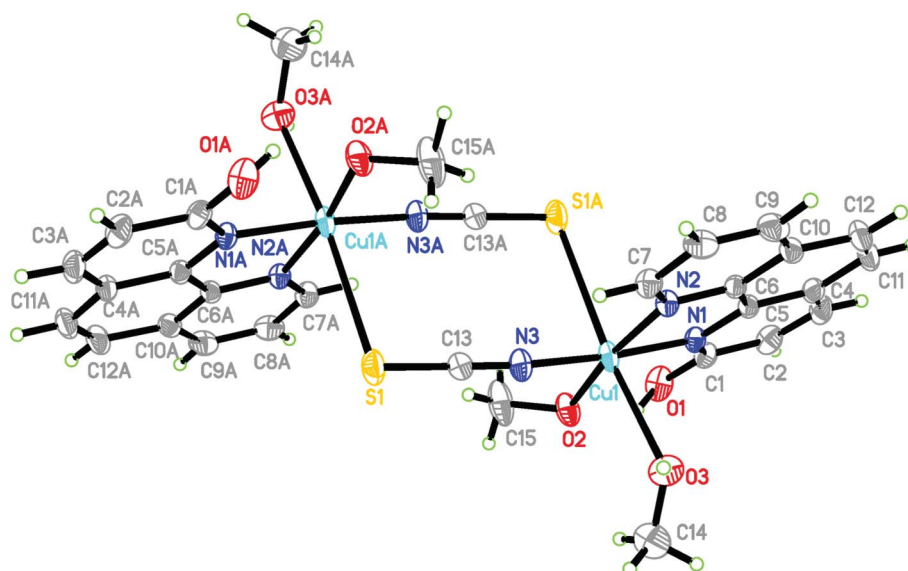


Fig. 1 Coordination diagram of the present complex with the atom numbering scheme.

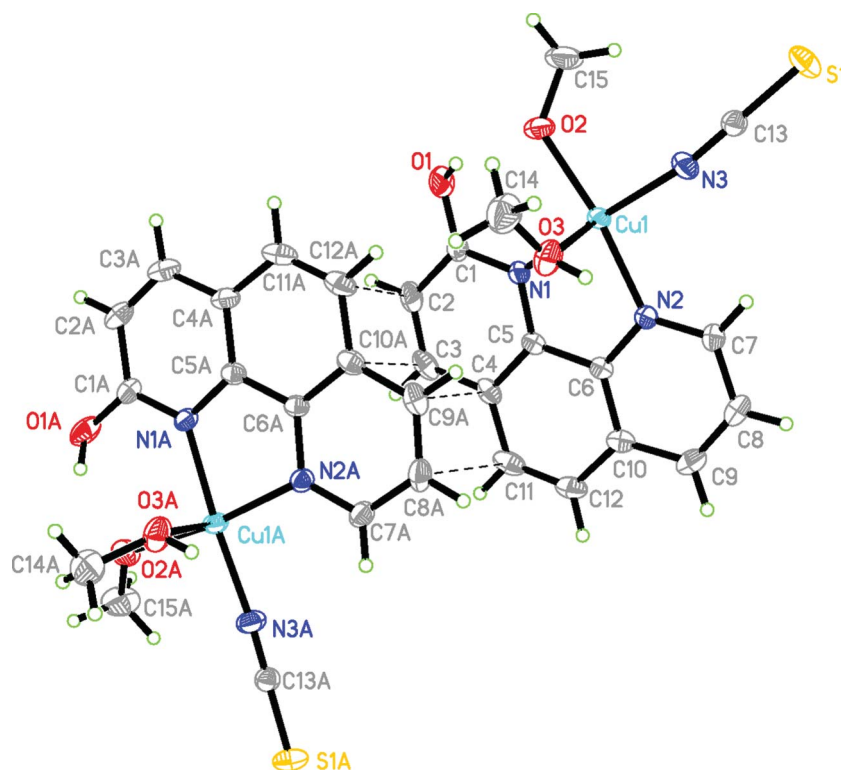


Fig. 2 The  $\pi$ - $\pi$  stacking between the adjacent binuclear complexes with name pi-1.

separation of 5.8706(12) Å and it resulted in the formation of a binuclear unit, but the Cu-S bond length (3.0581(15) Å) is longer than that of other similar  $\mu_{1,3}$ -SCN<sup>-</sup> bridging complexes.<sup>65-67</sup> In addition, there are two types of  $\pi$ - $\pi$  stacking among the adjacent complexes as shown in Fig. 2 with name pi-1 and in Fig. 3 with name pi-2, respectively, and both involve the symmetrically-related 1,10-phenanthroline rings slipped  $\pi$ -stacking with the relevant distances (3.7 Å as a  $\pi$ - $\pi$  stacking maximum limited distance<sup>68</sup>) being O1-C12A, 3.539(5) Å; C1-C12A, 3.285(5) Å; C2-C12A, 3.325(6) Å; C2-C11A, 3.557(6) Å; C2-C10A,

3.450(5) Å; C3-C10A, 3.429(5) Å; C3-C9A, 3.668(6) Å; C3-C6A, 3.578(5) Å; C4-C10A, 3.675(5) Å; C4-C9A, 3.354(5) Å; C4-C8A, 3.538(5) Å; C5-C9A, 3.410(5) Å; C11-C8A, 3.470(6) Å; Cu-Cu1A, 9.0448(15) Å (symmetry code:  $1/2 + X, 1/2 - Y, 1/2 + Z$ ) for pi-1 and C1-C7A, 3.436(5) Å; C1-C8A, 3.525(5) Å; C2-C7A, 3.582(5) Å; C2-C8A, 3.426(6) Å; C2-C9A, 3.488(6) Å; C3-C8A, 3.632(6) Å; C3-C9A, 3.376(6) Å; O1-C7A, 3.495(5) Å; Cu-Cu1A, 6.9794(15) Å (symmetry code:  $1 + X, Y, Z$ ) for pi-2. The  $\pi$ - $\pi$  stackings led to the formation of a three-dimensional supramolecular structure.

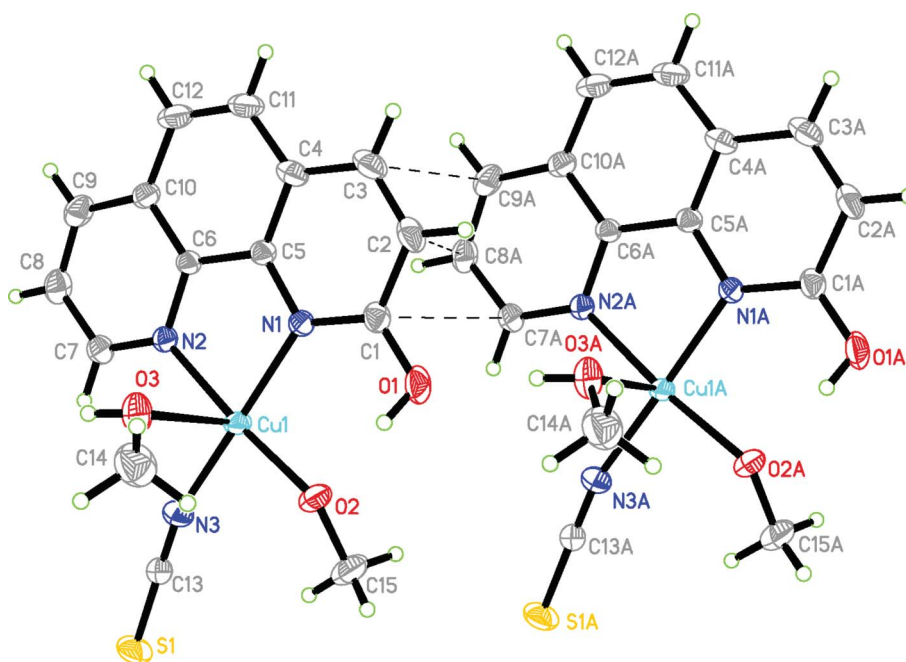


Fig. 3 The  $\pi$ - $\pi$  stacking between the adjacent binuclear complexes with name pi-2.

## Magnetic studies

**Fitting results for experimental data.** The experimental data of variable-temperature (2–300 K) magnetic susceptibilities are shown in Fig. 4, where  $\chi_M$  is the molar magnetic susceptibility per binuclear Cu(II) unit,  $\mu_{\text{eff}}$  is the magnetic moment per binuclear Cu(II) ions. Fig. 4 displays that the  $\chi_M$  value increases with decreasing temperature, reaching a maximum at 2.00 K. The  $\mu_{\text{eff}}$  value at 300 K is 2.40 B.M., which is a little smaller than isolated binuclear Cu(II) ions (2.45 B.M. for  $g_{\text{av}} = 2$ ) at room temperature, and the  $\mu_{\text{eff}}$  value increases slowly with temperature decrease until about 12 K, and then the  $\mu_{\text{eff}}$  value increases sharply with temperature drop and reaches 2.98 B.M. at 2.00 K. The Bleaney–Bowers eqn (4)<sup>69</sup> for exchange coupled binuclear Cu(II), which was obtained based on isotropic Hamiltonian as presented as in eqn (3), was used to fit the experimental data, in which TIP ( $1.2 \times$

$10^{-6}$ ) is the temperature-independent paramagnetism. The eqn (4) gave a good fitting for the experimental data as shown

$$\hat{H} = -2J\hat{S}_{\text{Cu1}}\hat{S}_{\text{Cu2}} \quad (3)$$

$$\chi_M = \frac{2Ng^2\beta^2}{\kappa(T - \theta)} [3 + \exp(-2J/\kappa T)]^{-1} + \text{TIP} \quad (4)$$

in Fig. 4, and the relevant fitting parameters are  $g = 1.90$ ,  $J = 50.02 \text{ cm}^{-1}$ ,  $\theta = 0.39219 \text{ K} = 0.27 \text{ cm}^{-1}$  and agreement factor  $R = 2.0 \times 10^{-4}$  [ $R = \Sigma(\chi_{\text{obsd}} - \chi_{\text{calcd}})^2 / (\chi_{\text{obsd}})^2$ ]. The value of  $J = 50.02 \text{ cm}^{-1}$  indicates that there is a medium ferromagnetic interaction between adjacent Cu(II) ions. To further support the ferromagnetic coupling nature provided by the temperature dependence of the magnetization, the field dependence of the magnetization for the complex was measured in a field 0–50 K Oe at 2 K. The experimental value of  $M$  for the title compound was compared with those calculated by the Brillouin function corresponding to an  $S = 2/2$  spin state with  $g = 1.90$  as shown in Fig. 5, which displays that the plot of  $M$  vs.  $H$  approached the Brillouin curve based on  $S = 2/2$ . This behavior confirms that the ground state of  $S = 2/2$  results from the ferromagnetic interaction of the binuclear Cu(II) ions. Generally, the magnetic coupling magnitude of binuclear Cu(II) complexes with  $\mu_{1,3}$ -SCN<sup>-</sup> as bridging ligand is relevant to the Cu–S bond length and bridging mode.<sup>65–67</sup> Because the present  $\mu_{1,3}$ -SCN<sup>-</sup> assumes equatorial–axial (EA) bridging mode and the Cu–S bond length is larger than 3 Å, the relevant magnetic coupling magnitude should be very weak.<sup>65–67</sup> Therefore it is reasonable to doubt whether the obtained magnetic coupling magnitude  $J = 50.02 \text{ cm}^{-1}$  is from the  $\mu_{1,3}$ -SCN<sup>-</sup> bridged pathway. In addition, how much magnetic coupling magnitude does arise from the two types of  $\pi$ - $\pi$  stacking? In order to understanding the complicated magnetic coupling mechanism theoretical calculations were performed.

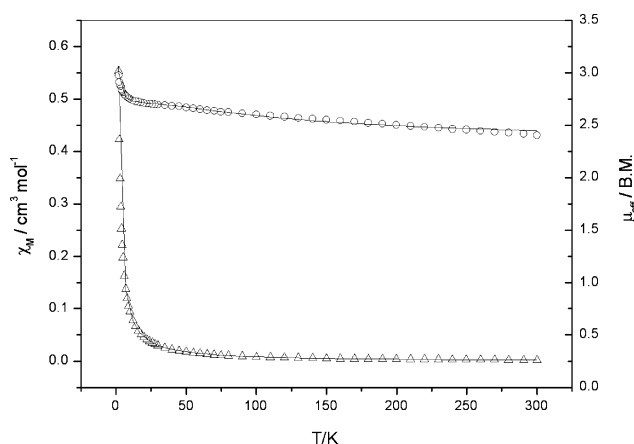


Fig. 4 Plots of  $\chi_M$  (the open triangle for the experimental data and the curve for the fitting values) and  $\mu_{\text{eff}}$  (the open circle for the experimental data and the curve for the fitting value) versus  $T$  for the present complex.



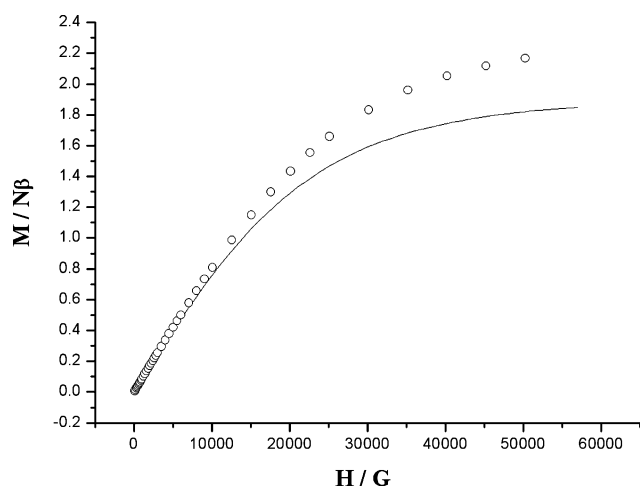


Fig. 5 Plot of  $M$  versus  $H$  (open circle) and the Brillouin curve for two independent Cu(II) ions.

**Theoretical study on magnetic interaction.** Density function calculations were based on model 1, model 2 and model 3 as shown in Fig. 6, Fig. 7 and Fig. 8, respectively, and which stand for the two types of the  $\pi$ - $\pi$  stacking pi-1 and pi-2 as mentioned above and the  $\mu_{1,3}$ -SCN<sup>-</sup> bridged binuclear Cu(II) complex, respectively. The calculations were constrained by the data of the bond lengths, the associated angles and the relevant locations of the adjacent  $\pi$ - $\pi$  stacking complexes which are from the X-ray structure of the present crystal. According to eqn (2), the calculations gave  $J = 4.16 \text{ cm}^{-1}$  for model 1  $\pi$ - $\pi$  stacking binuclear Cu(II) complex,  $J = 2.75 \text{ cm}^{-1}$  for model 2  $\pi$ - $\pi$  stacking binuclear Cu(II) complex and  $J = 0.88 \text{ cm}^{-1}$  for the  $\mu_{1,3}$ -SCN<sup>-</sup> bridged binuclear Cu(II) complex, respectively, namely, all the three types of exchange pathway function ferromagnetic interaction, but the magnetic coupling magnitude from the  $\mu_{1,3}$ -SCN<sup>-</sup> bridge pathway is smaller

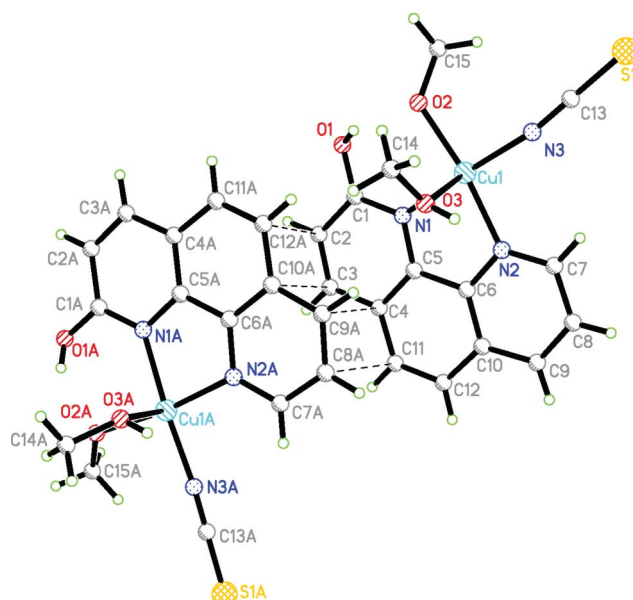


Fig. 6 Model 1 that stands for the  $\pi$ - $\pi$  stacking system of the pi-1.

than those of both Model 1 and Model 2. It means that the ferromagnetic coupling information from the experimental fitting is closely related to the  $\pi$ - $\pi$  stacking, and maybe it should be attributed to the three types of magnetic coupling pathway and especially to the two types of  $\pi$ - $\pi$  stacking pathway.

On magnetic coupling the sign of the  $\pi$ - $\pi$  stacking McConnell I spin-polarization mechanism<sup>43</sup> has been used to explain the ferromagnetic interaction of  $[\text{Mn}(\text{Cp}^*)_2]^+[\text{Ni}(\text{dmit})_2]^-$  complex successfully,<sup>70</sup> and McConnell I spin-polarization mechanism considers that a global ferromagnetic coupling arises from the interaction between spin densities of opposite sign being predominant, whereas an anti-ferromagnetic coupling results from dominant

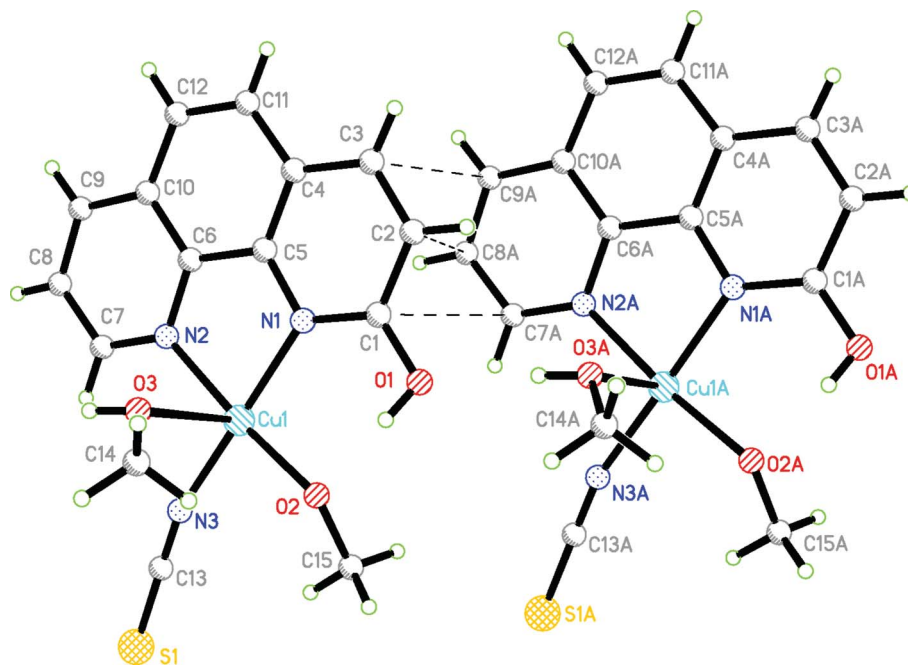
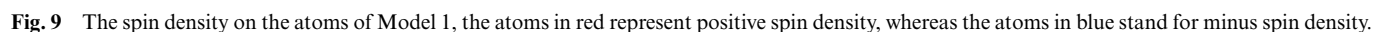


Fig. 7 Model 2 that stands for the  $\pi$ - $\pi$  stacking system of the pi-2.



atoms (C1...C12A, C3...C10A, C4...C9A and O1...C12A) that display different spin density interaction, and the number of the same spin density interaction is larger than that of the different spin density interaction, and mostly, neither the shortest distance nor the largest spin density are found on the pairs of atoms with the different spin density. Obviously, the McConnell I spin-polarization mechanism is unable to explain the ferromagnetic coupling mechanism of Model 1.

Table 2 and Fig. 10 reveal the spin density population of the ground state of Model 2 and just as Model 1 the spin delocalization also occurs in Model 2 from the Cu(II) ions to the associated coordinated atoms, and at the same time there also exists spin polarization in Model 2. In the  $\pi$ - $\pi$  stacking system the pair number of the atoms with the same spin density interaction (C1...C7A, C2...C8A, C3...C9A, and O1...C7A) equals the

**Table 1** Calculated atomic spin population of the ground state for Model 1

C1	-0.00681	C1A	-0.006689
C2	0.00249	C2A	0.002376
C3	-0.003921	C3A	-0.003907
C4	0.002431	C4A	0.002242
C5	-0.001172	C5A	-0.001414
C6	-0.001738	C6A	-0.001315
C7	-0.007608	C7A	-0.007359
C8	0.004726	C8A	0.00458
C9	-0.005186	C9A	-0.005034
C10	0.002905	C10A	0.00283
C11	0.001132	C11A	0.001184
C12	0.000005	C12A	0.000146
C13	-0.001371	C13A	-0.001121
C14	-0.000384	C14A	-0.000358
C15	-0.001433	C15A	-0.001821
Cu1	0.571658	Cu1A	0.568504
N1	0.066488	N1A	0.066873
N2	0.064794	N2A	0.063362
N3	0.077308	N3A	0.075954
O1	-0.001225	O1A	-0.001219
O2	0.207243	O2A	0.213215
O3	0.000365	O3A	0.000349
S1	0.005713	S1A	0.004913

**Table 2** Calculated atomic spin population of the ground state for Model 2

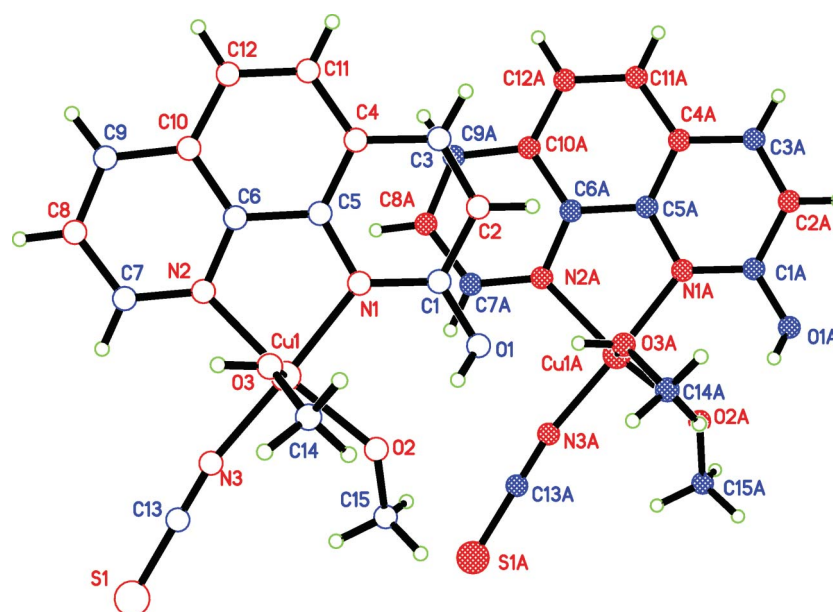
C1	-0.006642	C1A	-0.007092
C2	0.002278	C2A	0.002645
C3	-0.004043	C3A	-0.004449
C4	0.001956	C4A	0.002167
C5	-0.001357	C5A	-0.001002
C6	-0.001782	C6A	-0.001927
C7	-0.007099	C7A	-0.007488
C8	0.00444	C8A	0.004334
C9	-0.005233	C9A	-0.005175
C10	0.002805	C10A	0.002533
C11	0.001442	C11A	0.001394
C12	0.000021	C12A	0.000218
C13	-0.001735	C13A	-0.001363
C14	-0.000434	C14A	-0.000387
C15	-0.001757	C15A	-0.001848
Cu1	0.569424	Cu1A	0.557894
N1	0.064516	N1A	0.061547
N2	0.061885	N2A	0.059766
N3	0.078321	N3A	0.077906
O1	-0.001249	O1A	-0.001366
O2	0.21369	O2A	0.22798
O3	0.000407	O3A	0.000343
S1	0.006505	S1A	0.007341

pair number of the atoms with the different spin density interaction (C1...C8A, C2...C7A, C2...C9A and C3...C8A), and the spin densities on the atoms with the different spin density interaction are not clearly larger than that of the same spin density interaction, and the distances between the pair's atoms with the different spin density interaction are not clearly smaller than that of the same spin density interaction. Therefore, the ferromagnetic coupling reality is hard to explain in terms of McConnell I spin-polarization mechanism in the present situation. Obviously it is a challenge how to explain the present magnetic coupling phenomena.

Table 3 and Fig. 11 reveal the spin density population of the ground state of Model 3 and both Table 3 and Fig. 11 imply that just as Model 1 and Model 2 there is spin delocalization and

spin polarization in Model 3. Because the thiocyanate anions act in an equatorial-axial (EA) bridging mode, namely, its N atom and its S atom coordinate to different d orbitals of the Cu(II) ions, respectively, it is certain that there is orthogonality of the magnetic orbitals,<sup>71–73</sup> and the magnetic interaction between the bridged binuclear Cu(II) unit must be ferromagnetic coupling. In addition, because the Cu–S bond length is so long (3.0581(15) Å) and the spin density on the  $d_{z^2}$  orbital of the each Cu(II) ions is only 0.00336, the magnetic coupling magnitude of the bridged binuclear Cu(II) unit must be very weak.

Generally, it is accepted that the magnetic coupling magnitude of  $\pi$ – $\pi$  stacking is related to associated spin density and distance of associated  $\pi$ – $\pi$  stacking atoms, and the larger the spin density



**Fig. 10** The spin density on the atoms of Model 2, and atoms in red represent positive spin density, whereas the atoms in blue stand for minus spin density.

**Table 3** Calculated atomic spin population of the ground state for Model 3

C1	-0.006829	C1A	-0.006833
C2	0.002261	C2A	0.002262
C3	-0.00369	C3A	-0.003684
C4	0.002432	C4A	0.002475
C5	-0.001414	C5A	-0.001442
C6	-0.000749	C6A	-0.000717
C7	-0.007399	C7A	-0.007386
C8	0.004782	C8A	0.004773
C9	-0.005296	C9A	-0.005297
C10	0.002885	C10A	0.002911
C11	0.001092	C11A	0.001074
C12	0.000265	C12A	0.000218
C13	-0.002581	C13A	-0.002577
C14	-0.00049	C14A	-0.00049
C15	-0.00134	C15A	-0.001337
Cu1	0.60316	Cu1A	0.603172
N1	0.065895	N1A	0.065884
N2	0.064594	N2A	0.064591
N3	0.068382	N3A	0.068378
O1	-0.001119	O1A	-0.001118
O2	0.19212	O2A	0.192121
O3	0.000257	O3A	0.000257
S1	0.001047	S1A	0.001046

and the shorter the distance will lead to a stronger magnetic coupling magnitude. In addition, for a long time the Wiberg bond index<sup>63,74</sup> has been used to evaluate the number of covalent bonds, or evaluate the strength of covalent bonds. In  $\pi$ - $\pi$  stacking systems if the distance of a pair of atoms is within 3.7 Å, we assume that there is a special  $\pi$ - $\pi$  stacking bond for this pair of atoms and its bond strength should be evaluated by the Wiberg bond index. In this way we try to evaluate the bond strengths of the present  $\pi$ - $\pi$  stacking system with the Wiberg bond index and accordingly correlate magnetic coupling magnitude with bond strength. Table 4 and Table 5 display the Wiberg bond indexes and the spin density of the associated  $\pi$ - $\pi$  stacking atoms for Model 1 and Model 2, respectively. From both tables it can be seen that the sum of the spin density of the atoms for Model 2 is a little larger than that of Model 1, but the sum of the Wiberg bond indexes of Model 1 is nearly three times the sum of the Wiberg bond indexes of Model 2. Now we correlate the magnetic coupling magnitude with the associated Wiberg bond indexes for Model 1 and Model 2, and we assume that the larger Wiberg bond indexes of Model 1 resulted in

**Table 4** Wiberg bond indexes and the spin density for Model 1

Model 1	Wiberg bond index	Spin-density (absolute value)
C1...C12A	0.0020	0.00681 + 0.000146
C2...C12A	0.0020	0.00249 + 0.000146
C2...C11A	0.0005	0.00249 + 0.001184
C2...C10A	0.0007	0.00249 + 0.00283
C3...C10A	0.0009	0.003921 + 0.00283
C3...C9A	0.0004	0.003921 + 0.005034
C3...C6A	0.0010	0.003921 + 0.001315
C4...C9A	0.0017	0.002431 + 0.005034
C4...C10A	0.0007	0.002431 + 0.00283
C4...C8A	0.0008	0.002431 + 0.00458
C5...C9A	0.0019	0.001172 + 0.005034
C11...C8A	0.0015	0.001132 + 0.00458
O1...C12A	0.0023	0.001225 + 0.000146
sum	0.0164	0.072554

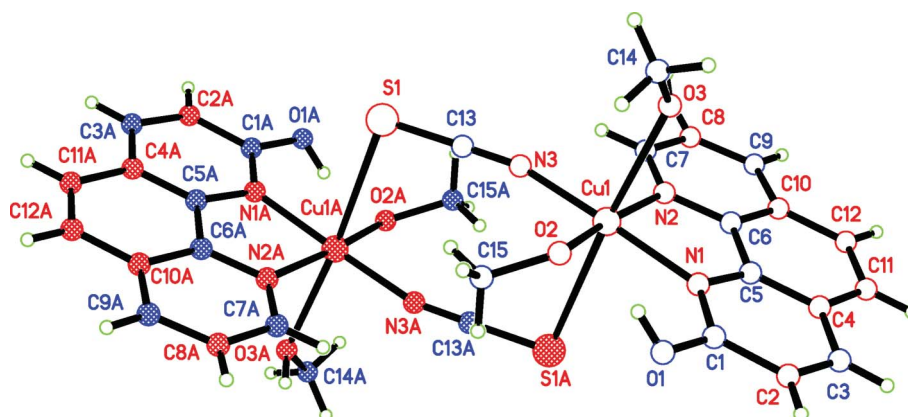
**Table 5** Wiberg bond indexes and the spin density for Model 2

Model 2	Wiberg bond index	Spin-density (absolute value)
C2...C7A	0.0005	0.007099 + 0.002645
C1...C7A	0.0012	0.007099 + 0.007092
O1...C7A	0.0007	0.007099 + 0.001366
C3...C8A	0.0005	0.00444 + 0.004449
C2...C8A	0.0006	0.00444 + 0.002645
C1...C8A	0.0007	0.00444 + 0.007092
C3...C9A	0.0012	0.005233 + 0.004449
C2...C9A	0.0006	0.005233 + 0.002645
sum	0.0060	0.077466

its larger magnetic coupling magnitude as compared with Model 2. It seems that the Wiberg bond index is one of the key factors that govern the magnetic coupling magnitude. Of course, more examples should be investigated in order to confirm that it is a general law and it does apply to other examples.

## Conclusions

A new binuclear Cu(II) complex with 2-hydroxy-1,10-phenanthroline and thiocyanate anion as ligands has been synthesized and its crystal structure displays that there are three types of magnetic coupling pathways. The experimental fitting for its variable-temperature magnetic susceptibility data with binuclear Cu(II) formula reveals that there is a medium



**Fig. 11** The spin density on the atoms of Model 3, and atoms in red represent positive spin density, whereas the atoms in blue stand for minus spin density.



ferromagnetic coupling magnitude between adjacent Cu(II) ions. The theoretical calculations further reveal that all three types of magnetic exchange pathways exhibit ferromagnetic couplings and the magnetic coupling magnitude from the two types of  $\pi$ - $\pi$  stacking pathways is larger than that of the  $\mu_{1,3}$ -SCN<sup>-</sup> bridged pathway. The magnetic coupling sign of the both  $\pi$ - $\pi$  stacking pathways is not explained with McConnell I spin-polarization mechanism. The magnetic coupling magnitude of both the  $\pi$ - $\pi$  stacking pathways seems relevant with the Wiberg bond indexes of the  $\pi$ - $\pi$  stacking system and this is the first suggestion that correlates magnetic coupling magnitude with their relevant Wiberg bond indexes.

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