

# Synthesis, structures and magnetic properties of dissymmetrical Schiff-base copper(II) complexes: $[(\text{Cu}_2\text{L})_2(\text{H}_2\text{O})_4] \cdot (\text{CuL})_2 \cdot 4\text{H}_2\text{O}$ and $[\text{Cu}_2\text{L}(\text{dca})]_n$



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## ABSTRACT

Two new dissymmetrical Schiff-base copper(II) complexes,  $[(\text{Cu}_2\text{L})_2(\text{H}_2\text{O})_4] \cdot (\text{CuL})_2 \cdot 4\text{H}_2\text{O}$  (**1**) and  $[\text{Cu}_2\text{L}(\text{dca})]_n$  (**2**) ( $\text{H}_3\text{L} = 1$ -(2-hydroxybenzamido)-2-(2-hydroxy-3-methoxybenzylideneamino)ethane), have been synthesized and characterized by IR, elemental analysis, X-ray crystal diffraction and magnetic properties. Single-crystal structural analysis shows that complex **1** contains a tetranuclear  $[\text{Cu}_4\text{L}_2(\text{H}_2\text{O})_4]^{2+}$  cation, two  $[\text{CuL}]^-$  anions and four uncoordinated water molecules. Complex **2** is an infinite two-dimensional network structure in which the tetranuclear  $[\text{Cu}_4\text{L}_2]$  cations are interlinked by dicyanamide ( $\text{dca}^-$ ) bridges in the end-to-end ( $\mu_{1,5}$ ) fashion. The magnetic properties of two complexes have been determined in the temperature range of 2.7–300 K.

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The rational design and synthesis of novel polynuclear complexes and coordination polymers are currently attracting intense attention, not only for their intriguing structural motifs but also for their potential applications and fascinating physical properties [1–7]. The design and synthesis novel polydentate ligands with chelating groups have been proved to be one of the most efficient approaches to synthesizing such complexes. Thus, alkoxyl, phenol and carboxyl groups have been utilized as common bridging groups [8–10]. Schiff bases as good polydentate ligands have been widely used to synthesize homo/hetero polynuclear complexes [11]. Recently, the dissymmetrical Schiff-base ligands containing amido and phenol groups have been widely investigated for the construction of polynuclear complexes, some of which exhibit interesting SMM properties [12–18]. Matsumoto and co-workers reported a series of heterometal cyclic tetranuclear complexes with the bridging ligands  $\text{H}_3\text{L}$  ( $\text{H}_3\text{L} = 1$ -(2-hydroxybenzamido)-2-(2-hydroxy-3-methoxybenzylideneamino)ethane) [12–16]. Based on this background, and in continuation of our previous work on polynuclear complexes [19,20], we report the synthesis and the structure of two new coordination complexes  $[(\text{Cu}_2\text{L})_2(\text{H}_2\text{O})_4] \cdot (\text{CuL})_2 \cdot 4\text{H}_2\text{O}$  (**1**) and  $[\text{Cu}_2\text{L}(\text{dca})]_n$  (**2**), and their magnetic properties are also investigated.

Complex **1** was synthesized by the reaction of  $\text{H}_3\text{L}$ ,  $\text{Et}_3\text{N}$  and  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  in a mole ratio of 1:3:2 [21]. Complex **2** was analogously synthesized by the reaction of  $\text{H}_3\text{L}$ ,  $\text{NaOH}$ ,  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{NaN}(\text{CN})_2$  in a mole ratio of 1:2:2:1 [21]. Single-crystal X-ray analyses

[22] revealed that complex **1** consists of a tetranuclear  $[\text{Cu}_4\text{L}_2(\text{H}_2\text{O})_4]^{2+}$  cation, two  $[\text{CuL}]^-$  anions and four uncoordinated water molecules. A perspective view of the tetranuclear unit of complex **1** is shown in Fig. 1. In the entity, the four copper ions have two kinds of coordination environments: distorted square planar and octahedral geometry. The Cu1 and Cu1#1 ions are in a distorted square planar with  $\text{CuN}_2\text{O}_2$  surroundings. They are coordinated by two oxygen atoms and two nitrogen atoms from ligand  $\text{L}^{3-}$ . The Cu2 and Cu2#1 ions can be considered as a distorted octahedral geometry. Two oxygen atoms from water, a phenoxo atom from the ligand  $\text{L}^{3-}$  and an amido oxygen atom from another ligand  $\text{L}^{3-}$  build the basal plane, whereas the apical positions are occupied by a phenoxo atom and a methoxy atom from ligand  $\text{L}^{3-}$ . In  $[\text{CuL}]^-$  unit, the Cu3 atom also in a distorted square planar geometry. The Cu–N distances are distributed in the range 1.907(5)–1.925(6) Å, and the Cu–O distances are in the range 1.885(5)–2.378(5) Å, which are similar to the values reported in the literature [12–16]. The Cu–Cu distance through the phenol bridge is 3.163(1) Å. The Cu–Cu distance between  $[\text{Cu}_4\text{L}_2(\text{H}_2\text{O})_4]^{2+}$  cation and  $[\text{CuL}]^-$  anion is 4.622(1) Å.

Complex **2** has an infinite two-dimensional network structure. The asymmetry unit of complex **2** contains a binuclear  $[\text{Cu}_2\text{L}]^+$  cation and a dicyanamide anion. In the binuclear unit, Cu1 ion is a square planar coordination geometry with the  $\text{N}_2\text{O}_2$  donor atoms of the ligand  $\text{L}^{3-}$ . The Cu2 ion is a distorted octahedral coordination geometry. It is coordinated by a phenoxo atom from the ligand  $\text{L}^{3-}$ , two nitrogen atoms from two dicyanamide ligands and an amido oxygen atom from another ligand  $\text{L}^{3-}$ . The axial positions are filled with a phenoxo atom and a methoxy atom from ligand  $\text{L}^{3-}$ . The Cu–O bond lengths range from 1.884(3) to 2.406(3) Å, and Cu–N bond lengths range from 1.906(3) to 1.988(4) Å. They are comparable with the range found in the literature [12–16]. The

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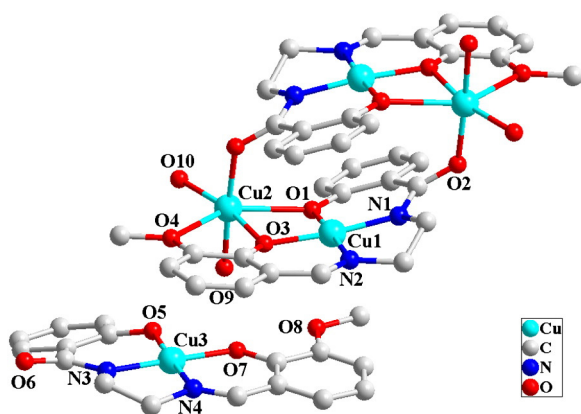


Fig. 1. Molecular structures of the discrete tetranuclear unit and mononuclear component of **1**. Symmetry codes for **1**: #1  $-x + 1, -y + 1, -z + 1$ . Hydrogen atoms and water molecule are omitted for clarity.

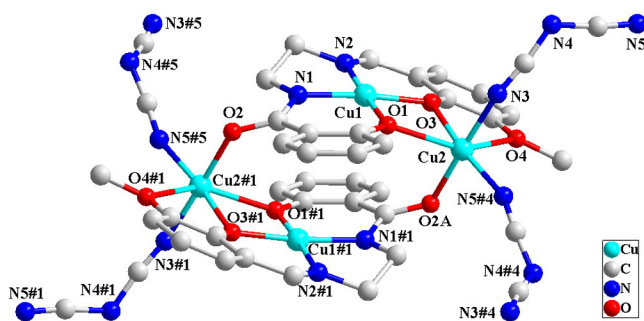


Fig. 2. Tetranuclear unit of the complex **2**. Symmetry codes for **1**: #1  $-x + 1, -y + 1, -z + 2$ . #4  $-x + 1.5, y - 0.5, -z + 1.5$ . #5  $x - 0.5, -y + 1.5, z + 0.5$ . Hydrogen atoms are omitted for clarity.

value of Cu1–Cu2 separation is 3.135(8) Å, which is slightly smaller than complex **1**.

From Fig. 2, we can find that the adjacent binuclear units are bridged together by an amido oxygen atom of ligand  $L^{3-}$  coordinates to Cu1 ions to form a tetranuclear structure. These tetranuclear units are linked by coordinative bonds between dicyanamide nitrogen atoms and Cu ions to form a novel 2D coordination polymer, as illustrated in Fig. 3.

The magnetic susceptibility of complexes **1** and **2** has been measured in the range of 2.7–300 K. For complex **1** (Fig. 4), the  $\chi_M T$

value at 300 K is 2.23 cm<sup>3</sup> mol<sup>-1</sup> K, which is slightly lower than the spin-only value (2.25 cm<sup>3</sup> mol<sup>-1</sup> K) for six uncoupled copper(II) ( $S = 1/2$  with  $g = 2.0$ ) systems. Upon cooling the  $\chi_M T$  values decrease regularly, approaching a minimum around 5 K with  $\chi_M T = 0.861$  cm<sup>3</sup> mol<sup>-1</sup> K. At lower temperatures, the  $\chi_M T$  curve increases until a value equal to 0.989 cm<sup>3</sup> mol<sup>-1</sup> K at 2.7 K. For complex **2** (Fig. 5), the  $\chi_M T$  value at 300 K is 0.735 cm<sup>3</sup> mol<sup>-1</sup> K, which is slightly lower than the spin-only value (0.75 cm<sup>3</sup> mol<sup>-1</sup> K) for two uncoupled copper(II) ( $S = 1/2$  with  $g = 2.0$ ) systems. When the temperature is lowered, the  $\chi_M T$  values decrease regularly, and reach a minimum value of 0.019 cm<sup>3</sup> mol<sup>-1</sup> K at 2.7 K, which possibly is due to the anti-ferromagnetic interaction between the tetranuclear units.

From a magnetic viewpoint, we take complex **1** as an isolated binuclear copper complex and a free copper ion. The magnetic analysis was carried out by using the theoretical expression of the magnetic susceptibility deduced from the spin Hamiltonian  $\hat{H} = -2J\hat{S}_{Cu1}\hat{S}_{Cu2}$ . The expression of the magnetic susceptibility for a Cu(II)–Cu(II) binuclear unit is

$$\chi_M = \frac{2Ng^2\beta^2}{KT} \left[ \frac{1}{3 + \exp(-2J/KT)} \right] + N_{\alpha}, N_{\alpha} = 120 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}.$$

Take into account the presence of free copper ion. Thus the expression of the magnetic susceptibility for complex **1** becomes

$$\chi'_M = \chi_M + \frac{Ng_{Cu}^2\beta^2}{3KT} S(S+1).$$

The molecular field approximation ( $zj'$ ) to deal with magnetic exchange interactions between binuclear units and free copper ion gives the expression

$$\chi''_M = \frac{\chi'_M}{1 - 2zj'_M / Ng^2\beta^2}$$

where  $J$  is the exchange integral between two copper ions in the binuclear moiety and  $N_{\alpha}$  is the temperature-independent paramagnetism. The best-fit parameters are  $J = -25.07$  cm<sup>-1</sup>,  $g_{Cu} = 2.02$ , and  $zj' = 0.92$  cm<sup>-1</sup>. The agreement factor  $R = \sum(\chi_{\text{obsd}} - \chi_{\text{calcd}})^2 / \sum\chi_{\text{obsd}}^2$  is  $3022 \times 10^{-4}$  and is satisfactory as seen in Fig. 4. The negative  $J$  value suggests that the interactions between Cu(II) ions are antiferromagnetic.  $zj' > 0$ , indicating that the interactions between trinuclear units and copper ions are ferromagnetic, which is also consistent with the  $\chi_M T$  value increasing as temperature is lowered from 9 to 2.7 K.

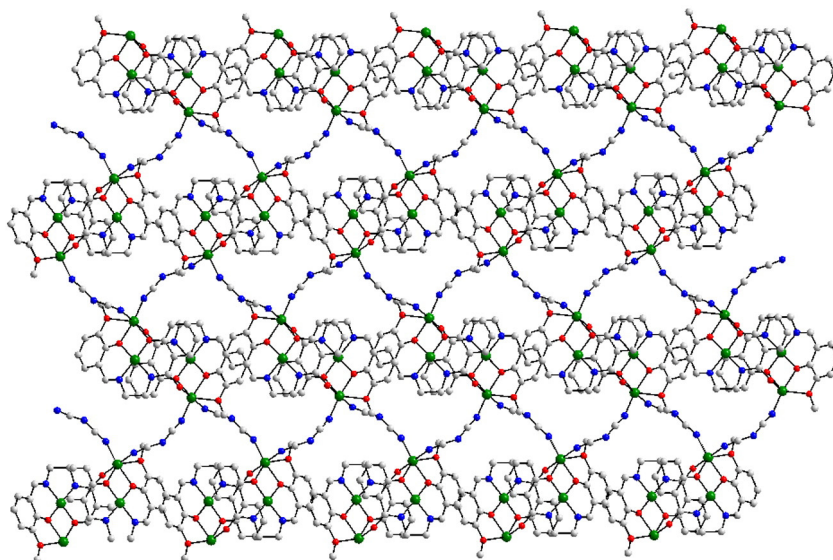


Fig. 3. Perspective view of the 2D coordination polymer **2**.

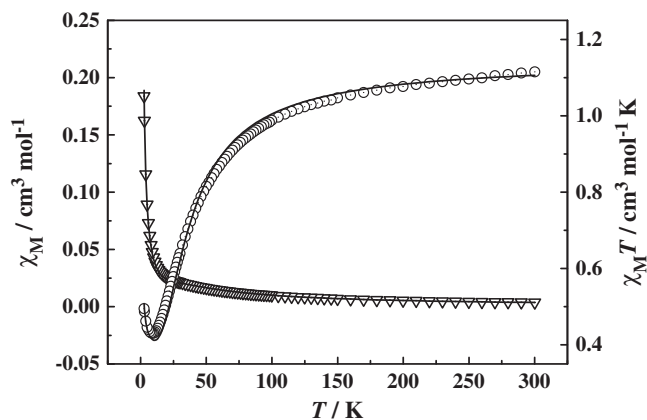


Fig. 4.  $\chi_M T$  versus  $T$  plots for complex 1.

For complex 2, no formula to reproduce the magnetic susceptibility of such a complex system is available in literatures. As a preliminary treatment, we take this system as an isolated binuclear complex.

The magnetic analysis was carried out by using the theoretical expression of the magnetic susceptibility deduced from the spin Hamiltonian  $\hat{H} = -2J\hat{S}_{\text{Cu1}}\hat{S}_{\text{Cu2}}$ . The expression of the magnetic susceptibility for a Cu(II)–Cu(II) binuclear unit is

$$\chi_M = \frac{2Ng^2\beta^2}{KT} \left[ \frac{1}{3 + \exp(-2J/KT)} \right] + N_\alpha. N_\alpha = 120 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}.$$

The molecular field approximation ( $zj'$ ) to deal with magnetic exchange interactions between binuclear units gives the expression

$$\chi_M' = \frac{\chi_M}{1 - (2zj'/Ng^2\beta^2)\chi_M}.$$

In order to overcome the paramagnetic impurities, we introduce  $\rho$  to take into account the presence of such impurities. Thus, the expression of the magnetic susceptibility for this system becomes

$$\chi_M' = \chi_M(1 - \rho) + \frac{Ng^2\beta^2}{3KT} \sum S_i(S_i + 1)\rho.$$

where  $J$  is the exchange integral between two copper ions in the binuclear moiety and  $N_\alpha$  is the temperature-independent paramagnetism. The best-fit parameters are  $J = -19.91 \text{ cm}^{-1}$ ,  $g_{\text{Cu}} = 2.11$ ,  $\rho = 5.3 \times 10^{-3}$ , and  $zj' = -4.56 \text{ cm}^{-1}$ . The agreement factor  $R = \Sigma(\chi_{\text{obsd}} - \chi_{\text{calcd}})^2 / \Sigma\chi_{\text{obsd}}^2$  is  $7.01 \times 10^{-4}$  and is satisfactory as seen

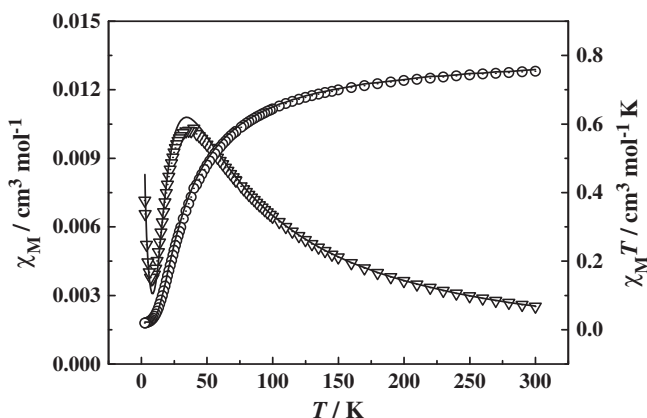


Fig. 5.  $\chi_M T$  versus  $T$  plots for complex 2.

in Fig. 5. The negative  $J$  and  $zj'$  values suggest that the interactions between Cu(II) ions and between binuclear systems are all antiferromagnetic.

In summary, two new coordination polymers have been synthesized and characterized structurally and magnetically. Complex 1 contains a tetranuclear  $[\text{Cu}_4\text{L}_2(\text{H}_2\text{O})_4]^{2+}$  cation, two  $[\text{CuL}]^-$  anions and four uncoordinated water molecules. Complex 2 is an infinite two-dimensional network structure in which the tetranuclear  $[\text{Cu}_4\text{L}_2]$  cations are interlinked by dicyanamide ( $\text{dca}^-$ ) bridges in the end-to-end ( $\mu_{1,5}$ ) fashion. Their magnetic properties are also investigated.

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## Appendix A. Supplementary material

CCDC 936260 (1) and 936261 (2) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif), 12 Union Road, Cambridge CB21EZ, UK [Fax: int code +44(1223)336-033; E-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)]. Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.inoche.2013.07.010>.

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- [21] Synthesis of **1**: H<sub>3</sub>L (0.0313 g, 0.1 mmol) and Et<sub>3</sub>N (0.0303 g, 0.3 mmol) were dissolved in 20 mL ethanol with stirring, then CuSO<sub>4</sub>·5H<sub>2</sub>O (0.0499 g, 0.2 mmol) was added. The resultant solution was filtered, the filtrate was left to stand at room temperature. Red crystals of **1** were obtained in two weeks. Yield: 42% based on copper. Anal. calcd for C<sub>68</sub>H<sub>76</sub>N<sub>8</sub>O<sub>24</sub>Cu<sub>6</sub>: C 46.13; H 4.33; N 6.33. Found: C 45.95; H 4.48; N 6.37 %. IR (KBr, cm<sup>-1</sup>): 3380, 2940, 1649, 1600, 1571, 1525, 1449, 1383, 1330, 1290, 1248, 1218, 1150, 1080, 984, 950, 895, 849, 761, 736, 658, 544. Synthesis of **2**: H<sub>3</sub>L (0.0313 g, 0.1 mmol) and NaOH (0.008 g, 0.2 mmol) were dissolved in 30 mL ethanol with stirring, then Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.0741 g, 0.2 mmol) and NaN(CN)<sub>2</sub> (0.0089 g, 0.1 mmol) were added. The resultant solution was filtered, the filtrate was left to stand at room temperature. Blue crystals of **2** were obtained in one month. Yield: 48% based on copper. Anal. calcd for C<sub>19</sub>H<sub>15</sub>N<sub>5</sub>O<sub>4</sub>Cu<sub>2</sub>: C 45.24; H 2.99; N 13.88. Found: C 45.12; H 3.17; N 13.94 %. IR (KBr, cm<sup>-1</sup>): 3425, 2933, 2326, 2265, 2187, 1650, 1597, 1564, 1525, 1469, 1454, 1397, 1378, 1328, 1294, 1247, 1221, 1084, 982, 949, 895, 739, 712, 656, 604, 516.
- [22] Crystallographic data: complex **1**, Formula: C<sub>68</sub>H<sub>76</sub>N<sub>8</sub>O<sub>24</sub>Cu<sub>6</sub>, FW = 1770.61, Monoclinic, P2<sub>1</sub>/c, a = 15.271(3) Å, b = 23.570(4) Å, c = 11.4815(19) Å, β = 110.968(4)° V = 3859.1(11) Å<sup>3</sup>, T = 296(2) K, Z = 2, μ(Mo Kα) = 11.2310(11) Å, c = 17.9001(16) Å, β = 113.052(5)° V = 1945.4(3) Å<sup>3</sup>, T = 296(2) K, Z = 4, μ(Mo Kα) = 2.224 mm<sup>-1</sup>, 9954 Reflections collected, 3626 unique [R(int) = 0.0437]. Final R indices [I > 2σ(I)] was R1 = 0.0427, wR2 = 0.0862.