

# A Two-dimensional Supramolecular Network Built through Unique $\pi$ - $\pi$ Stacking: Synthesis and Characterization of $[\text{Cu}(\text{phen})_2(\mu\text{-IDA})\text{Cu}(\text{phen})\cdot(\text{NO}_3)](\text{NO}_3)\cdot 4(\text{H}_2\text{O})$

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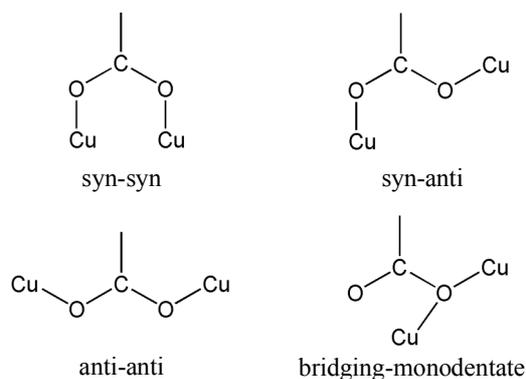
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A novel supramolecular network containing binuclear copper unit  $[\text{Cu}(\text{phen})_2(\mu\text{-IDA})\text{Cu}(\text{phen})\cdot(\text{NO}_3)](\text{NO}_3)\cdot 4(\text{H}_2\text{O})$  (**1**) was synthesized through the self-assembly of iminodiacetic acid ( $\text{H}_2\text{IDA}$ ) and 1,10-phenanthroline (phen) in the condition of pH = 6. It has been characterized by the infrared (IR) spectroscopy, elemental analysis, single crystal X-ray diffraction, and thermogravimetric analysis (TGA). **1** shows a 2-D supramolecular structure assembled through strong and unique  $\pi$ - $\pi$  packing interactions. Density functional theory (DFT) calculations show that theoretical optimized structures can well reproduce the experimental structure. The TGA and powder X-ray diffraction (PXRD) curves indicate that the complex **1** can maintain the structural integrity even at the loss of free water molecules. The magnetic property is also reported in this paper.

**Key Words:** Supramolecular network, Crystal structure,  $\pi$ - $\pi$  Interaction, Quantum chemical calculation, Magnetism

## Introduction

Nowadays, one of the most appealing properties for the binuclear transition metal complexes is the possible appearance of magnetic exchange interactions between the metal ions.<sup>1</sup> Among the binuclear complexes, multi-atomic ligands (carboxylate and dicarboxylate anions) have become the subject of many investigations on their ability to act as numerous bridging coordination modes (Scheme 1).<sup>2</sup> Besides, it is also found that their magnetic properties depend on the metal-metal distances, bond angles between bridging atoms, dihedral angles between planes including metal centers, bond distances and coordination environments around the metal centers. Among considerable complexes, the carboxylate ligands have shown this ability of facilitating the transfer of magnetic interactions.<sup>2,3</sup> However, when the coordination ligand is related to the iminodiacetic acid ( $\text{H}_2\text{IDA}$ ), what would take place in their structural and magnetic properties? Up to now, these have not been investigated extensively.<sup>4</sup>



Scheme 1

On the other hand,  $\text{H}_2\text{IDA}$  shows diverse chelating modes to contribute to their various structures, due to it is a flexible tridentate ligand. As a rule, such ternary coordinated compounds are typical bioinorganic models for the mono- and binuclear copper proteins. In this context, the Cu(II) complex serves as a metal centre, while the tridentate  $\text{H}_2\text{IDA}$  ligand or  $\text{H}_2\text{IDA}$  derivative acts as a protein-like moiety, and the aromatic  $\alpha, \alpha'$ -diimines donors, such as 2,2'-bipyridine (bpy) and 1,10-phenanthroline (phen), play a role of substrate or inhibitor. Moreover, phen has the extended  $\pi$ -systems and it has been successfully employed in modeling the complexes to mimic the non-covalent interactions in the biological processes, e.g. the minor groove binding of  $[\text{Cu}(\text{phen})_2]^{2+}$  ions<sup>5a</sup> or the visible light induced nuclease activity of a  $[\text{Cu}(\text{phen})]^{2+}$  complex with 2-(methylthio)ethylsalicyldimine.<sup>5b</sup>

The aim of this work is to carry out a systematic investigation on the structural characterization of the binuclear IDA-Cu(II)-Phen complex by using experimental and theoretical methods. And the result shows that the distinct coordination mode of the primary ligand IDA<sup>2-</sup> leads to the diverse distributing manner of phen ligands along with the unique  $\pi$ - $\pi$  packing modes of the units. The structural investigations on the above compounds were also expanded on the supramolecular aromatic ring  $\pi$ - $\pi$  interactions of the complexes with pyridyl-type ligands.<sup>6</sup> The IR spectrum, thermal stability, and magnetic-structural relationship of the title complex were studied too.

## Experimental

**General.** All analytical reagents were purchased from commercial sources and used without further purification. C, H, and N microanalyses were carried out with a Perkin-Elmer 240 elemental analyzer. The IR spectrum was recorded on

KBr discs on a Bruker Vector 22 spectrophotometer in the 4000 - 400  $\text{cm}^{-1}$  region. Thermogravimetric analysis (TGA) was performed on a simultaneous SDT 2960 thermal analyzer under flowing  $\text{N}_2$  with a heating rate of 10  $^\circ\text{C}/\text{min}$  between ambient temperature and 720  $^\circ\text{C}$ . Powder X-ray diffraction patterns (PXRD) were recorded on a RigakuD/max-RA rotating anode X-ray diffractometer with graphite monochromatic  $\text{Cu K}\alpha$  ( $\lambda = 1.542 \text{ \AA}$ ) radiation at room temperature. Magnetic susceptibility data on the powder-sample were collected over the temperature range of 1.8 - 300 K by using a Quantum Design MPMS7 superconducting quantum interference device magnetometer.

**Synthesis of the complex 1.** Iminodiacetic acid (0.0133 g, 0.2 mmol), 1,10-phenanthroline (0.0396 g, 0.2 mmol), and  $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.1182 g, 0.4 mmol) were dissolved in the solution of  $\text{H}_2\text{O}:\text{CH}_3\text{OH}$  (1:1). The mixture was stirred for an hour. Then, an aqueous sodium hydroxide solution was added dropwise with stirring to neutralize at pH 6. Afterwards, the mixture was filtered. The filtrate was kept for several days at ambient temperature and ultimately blue crystals were formed. They were filtered and washed thoroughly with ether and further dried in the vacuum (yield: 32% based on  $\text{H}_2\text{IDA}$ ). Anal. Calcd for  $\text{C}_{40}\text{H}_{37}\text{Cu}_2\text{N}_9\text{O}_{14}$ : C, 48.29; H, 3.75; N, 12.67. Found: C, 48.12%; H, 3.84 %; N, 12.45%.

**Crystal structure determination and refinement.** Single crystal of approximate dimensions for the complex **1** was selected for structural determinations on a Bruker SMART APEX CCD diffractometer with the graphite monochromatized  $\text{Mo K}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at room temperature using the  $\omega$ -scan technique. Lorentz polarization and absorption corrections were applied. The structure was solved by the direct methods and refined with the full-matrix least-squares technique using the *SHELXS-97* and *SHELXL97* programs.<sup>7</sup> Anisotropic thermal parameters were assigned to all non-hydrogen atoms. Analytical expressions of neutral atom scattering factors were employed, and anomalous dispersion corrections were incorporated. The crystallographic data and selected bond lengths of the complex **1** are listed in Tables 1 and 2.

More details on the crystallographic data for the structure reported in this paper have been deposited with CCDC (Deposition No. CCDC-702868). These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> or from CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, email: deposit@ccdc.cam.ac.uk.

**Quantum chemical calculation.** All the calculations have been performed with the Gaussian 03<sup>8</sup> software package on a Pentium IV computer using the default convergence criteria. Density functional theory (DFT) calculations were all self-consistent Kohn-Sham calculations that employed the hybrid B3LYP density functional (Becke's three parameter nonlocal exchange functional along with the Lee-Yang-Parr correlation functional).<sup>9</sup> "Double- $\xi$ " quality basis set LANL-2DZ, which uses Dunning D95V basis set on first row atoms and Los Alamos ECP plus DZ on Na-Bi, was employed as the basis set. This has been proved to be useful and satisfactory for the metal complexes.<sup>10</sup> Geometry optimization was performed using the Bery gradient optimization method. The

**Table 1.** Crystal data and structure refinement for the title complex

Empirical formula	$\text{C}_{40}\text{H}_{37}\text{Cu}_2\text{N}_9\text{O}_{14}$
Formula weight	994.87
Crystal system	Monoclinic
Space group	P 21/c
$a$ , $\text{\AA}$	12.491(2)
$b$ , $\text{\AA}$	15.288(3)
$c$ , $\text{\AA}$	21.499(4)
$\alpha$ , deg	90.00
$\beta$ , deg	95.326(4)
$\gamma$ , deg	90.00
$V$ , $\text{\AA}^3$	4087.6(12)
$Z$	4
$\mu$ , $\text{mm}^{-1}$	1.123
Reflections collected	21545
Unique reflections	8015
Obs. reflections [ $I > 2\sigma(I)$ ]	5093
$R_{\text{int}}$	0.0578
$R_1$ [ $I > 2\sigma(I)$ ]	0.0554
$wR_2$ [ $I > 2\sigma(I)$ ]	0.1245
Goodness-of-fit	1.059

$$R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

$$wR_2 = \left\{ \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]} \right\}^{1/2}$$

**Table 2.** Selected molecular structure parameters for the title complex.

Parameter	Experimental	Calculated	Error <sup>a</sup>
Bond lengths ( $\text{\AA}$ )			
Cu1-O1	2.326(3)	2.484	0.158
Cu1-O3	1.930(3)	1.962	0.032
Cu1-O6	2.580(3)	2.416	-0.164
Cu1-N1	2.017(3)	2.104	0.087
Cu1-N2	1.999(3)	2.026	0.027
Cu1-N7	2.029(3)	2.073	0.044
Cu2-O1	2.042(3)	2.067	0.025
Cu2-O2	2.673(3)	2.627	-0.046
Cu2-N3	2.002(3)	2.037	0.035
Cu2-N4	2.151(3)	2.261	0.110
Cu2-N5	2.038(3)	2.120	0.072
Cu2-N6	1.998(3)	2.018	0.020
Bond angles (deg)			
O1-Cu1-N7	78.04(12)	76.586	-1.454
O3-Cu1-N1	173.88(12)	170.301	-3.579
O3-Cu1-N7	84.34(12)	84.897	0.557
N1-Cu1-N2	82.04(12)	81.322	-0.718
N1-Cu1-N7	101.69(13)	104.403	2.713
N2-Cu1-O3	91.85(12)	90.284	-1.566
O1-Cu2-N3	91.35(12)	91.378	0.028
O1-Cu2-N5	151.32(13)	153.512	2.192
O1-Cu2-N4	99.49(12)	103.106	3.616
O1-Cu2-N6	90.92(12)	92.028	1.108
N3-Cu2-N4	80.44(13)	79.015	-1.425
N3-Cu2-N5	95.86(13)	94.666	-1.194
N3-Cu2-N6	177.59(14)	175.772	-1.818
N4-Cu2-N6	99.99(13)	102.632	2.642
N5-Cu2-N6	81.75(13)	81.208	-0.542

<sup>a</sup>Error = Calculated value - Experimental value.

related binuclear skeleton  $[\text{Cu}(\text{phen})_2(\mu\text{-IDA})\text{Cu}(\text{phen})\cdot(\text{NO}_3)]^+$  (**1**) with the experimental geometry was used to calculate and evaluate the electronic structure.

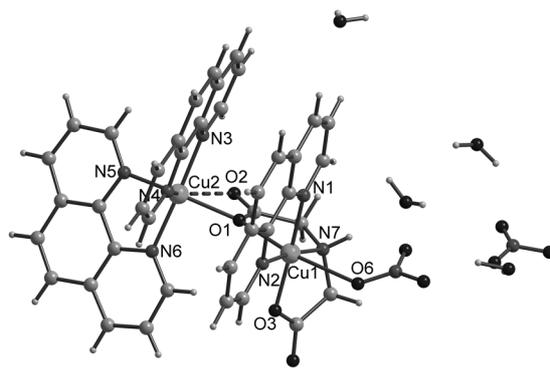
## Results and Discussion

**Crystal structure.** A single-crystal X-ray diffraction study reveals that **1** adopts a binuclear copper structure. There are two crystallographically unique Cu(II) centers assuming similar coordination geometries (4+2 type) in the asymmetric unit, as illustrated in Figure 1. The Cu1 center exhibits a slightly distorted octahedral geometry where the angles of the coordinated N and O atoms subtended at the center Cu1 atom vary from  $78.04(12)$  to  $173.88(12)^\circ$ . As can be seen from Figure 1, two nitrogen atoms (N1, N2) from one phen, N7 and one carboxylate oxygen atom (O3) from  $\text{IDA}^{2-}$  occupy the equatorial positions (The Cu1 atom deviates from the square plane by  $-0.0537 \text{ \AA}$ ); O1 from  $\text{IDA}^{2-}$  and one nitrate oxygen atom (O6) occupy the axial sites of the Cu1 ion. At first glance, Cu2 should take a slightly distorted square-pyramidal coordination sphere, which is coordinated by four nitrogen atoms of two phen and one carboxylate oxygen atom. However, the distance is  $2.673 \text{ \AA}$  between Cu2 and O2 of the carboxylate, suggests a nonnegligible interaction between them and the O1C37O2 carboxylate can be described as a semi-chelating coordination mode.<sup>11</sup> Hence, the Cu2 atom may be also described as in an octahedral coordination environment.

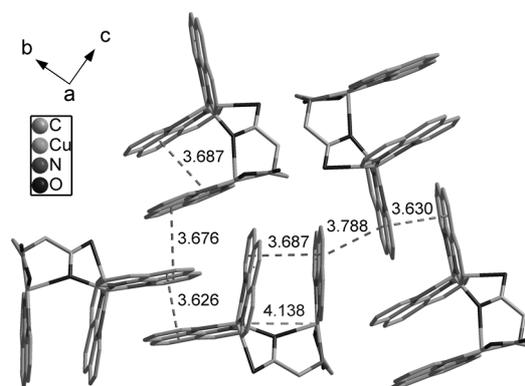
In **1**,  $\text{IDA}^{2-}$  serves as a bridging ligand linking two different moieties, viz.  $[\text{Cu}(\text{phen})_2]^{2+}$  and  $[\text{Cu}(\text{phen})]^{2+}$ , via a carboxylate group. The bridging coordination modes establish a kind of physical bridge between the bicopper centers, imposing the separation of  $4.138 \text{ \AA}$  for the title complex. Least-squares planarity analysis shows that pair of phen skeletons in the asymmetric unit of **1** are almost parallel to each other (dihedral angle is  $7.8^\circ$ ), as shown in Figure 2. There are  $\pi$ - $\pi$  stacking interactions between their aromatic rings and the shortest Cg...Cg' distance of  $3.687 \text{ \AA}$ , where Cg and Cg' are the centroids of the pyridine ring (C19-C23/N4) and the benzene ring (C4-C7/C11/C12), respectively. Usually, a normal range for such interactions is  $3.3 - 3.8 \text{ \AA}$ .<sup>12</sup>

Furthermore, another more interesting phenomenon is observed for the title complex, as shown in Figure 3. The units of  $[\text{Cu}(\text{phen})_2]^{2+}$  are interleaved antiparallely with the center-to-center inter-rings separations of  $3.626 - 3.788 \text{ \AA}$ , and the smallest distance from an atom in one aromatic moiety to the mean plane of another stacking moiety is *ca.*  $3.332 \text{ \AA}$ , indicating significant  $\pi$ - $\pi$  packing interactions between them. Progression of the stacking interactions through the phen ligands of neighbouring binuclear units yields a 2-D infinite supramolecular structure in the *bc* plane. In comparison with the simplex  $\pi$ - $\pi$  interaction mode of the complexes with pyridyl-type ligands,<sup>6</sup> the multifarious intermolecular  $\pi$ - $\pi$  interactions between the aromatic rings in the title complex are very unique; this is resulted in the distinct bridging mode of the  $\text{IDA}^{2-}$  ligand. They are the primary factor controlling the self-assembly of the 2-D supramolecular network.

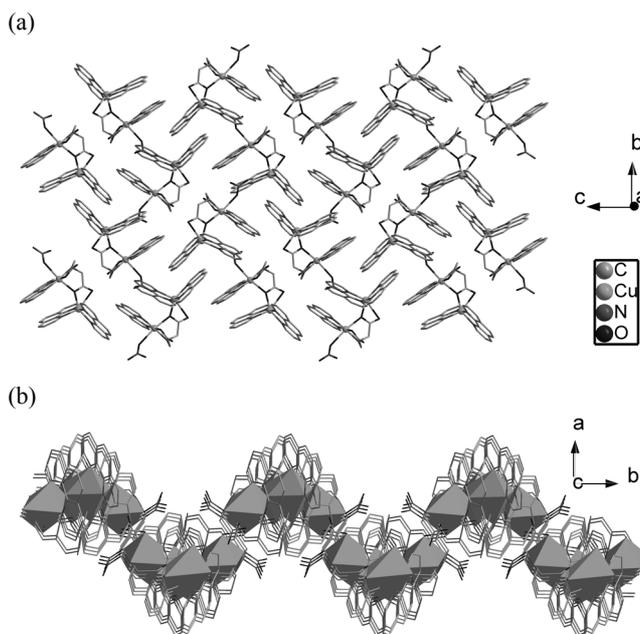
**Optimized geometry.** The title complex **1** was optimized at



**Figure 1.** Molecular structure of complex **1** showing the coordination environment of the Cu(II) ions.



**Figure 2.** The multifarious centroid-centroid distances for  $\pi$ - $\pi$  stacking interactions of the aromatic rings in **1**. Hydrogen atoms and anions have been omitted for clarity.



**Figure 3.** (a) Perspective view of the 2-D supramolecular network formed by the  $\pi$ - $\pi$  stacking interaction along the *b* axis. (b) Polyhedral representation of the 2D network along the *c* axis of **1**. Hydrogen atoms and the uncoordinated  $\text{NO}_3^-$  anions have been omitted for clarity.

the B3LYP/LANL2DZ level of theory and the calculated geometric parameters for **1** were described in Table 2 together with the corresponding single-crystal X-ray diffraction data. After careful comparison, several features can be observed as follows. First, on the whole, most of the optimized bond lengths are slightly larger than the experimental values. This is due to the fact that theoretical calculations belong to the isolated molecules in the gas phase at 0 K, whereas the experimental results belong to the molecules in the solid state. The intermolecular interactions in the experiment are not presented in the DFT calculations applied here. Given the solid-state effect considered, they would be rather compatible as a whole. On the other hand, the largest discrepancies in the bond length between theoretical and experimental structures of the complexes **1** is 0.163 Å and 0.161 Å. This indicates that the calculation precision is satisfactory.<sup>13</sup> Additionally, there are slight differences for some bond angles with the largest error of 3.616° for **1**, due to the existence of  $\pi$ - $\pi$  stacking and hydrogen bonds in the experimental complex. In spite of these, the gaseous and solid structure represents a good approximation, that is, the B3LYP/LANL2DZ level is suitable for the binuclear complex studied here.

**IR spectrum.** As is well known, IR spectrum is not only a basic property of the compound, but also a facile measure to analyze or identify the coordination modes of the complexes. The amino N-H stretching vibration of IDA<sup>2-</sup> appears at 3356 cm<sup>-1</sup>. In the middle range of the IR spectrum, the vibration modes are commonly employed to distinguish the coordination modes of the carboxylate groups.<sup>14</sup> Up to date, there have been several coordination modes of the carboxylate group for the known carboxylate complexes (see Scheme 1). The general correlation between the carboxylate coordination modes and the metal ions can be described according to the difference in the infrared data [ $\Delta\nu(\text{COO}) = \nu_{\text{as}}(\text{COO}) - \nu_{\text{s}}(\text{COO})$ ] of the coordination compounds.<sup>15</sup> In the title complex, the stretching vibrations of  $\nu_{\text{as}}(\text{COO})$  and  $\nu_{\text{s}}(\text{COO})$  occur at 1619, 1548 and 1427, 1375 cm<sup>-1</sup>, respectively. And the two carboxylate groups of the IDA<sup>2-</sup> anion both exhibit the monodentate coordination modes (monodentate and bridging monodentate, respectively) which can also be seen from the separations between  $\nu(\text{CO}_2)$  of 202 cm<sup>-1</sup> (bands at 1630 and 1428 cm<sup>-1</sup>) and 218 cm<sup>-1</sup> (bands at 1602 and 1384 cm<sup>-1</sup>), respectively. In this case, the X-ray diffraction analysis was allowed to assign unambiguously the binding modes of the carboxylate groups.

**Thermal stability.** In order to characterize the title complex more fully in terms of thermal stability, we have studied its thermal behavior by TGA. As shown in Figure 4, the first weight loss of 7.35 % (calcd 7.24%) occurred below 125 °C, corresponding to the removal of four solvated water molecules per formula unit. Subsequently, a plateau region was observed over 210 °C, and then the consecutive decomposition took place in the range of 210-260 °C attributed to the removal of two NO<sub>3</sub><sup>-</sup> anions (obsd 12.28%, calcd 12.46 %). Moreover, the consecutive decomposition in the higher temperature region further suggests the total destruction of the framework by the oxidation of the organic component. As a whole, the TGA curve indicates that the solvated water molecules can be removed after heating and the framework is stable below 210

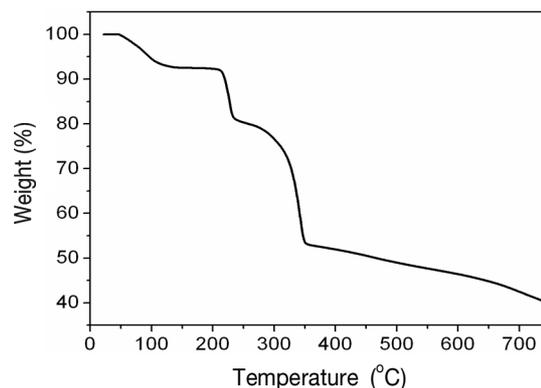


Figure 4. Thermogravimetric analysis curve of the complex **1**.

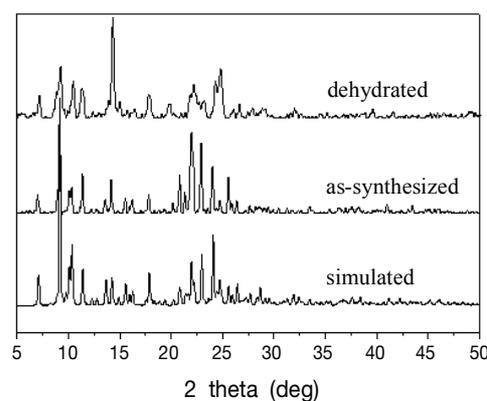
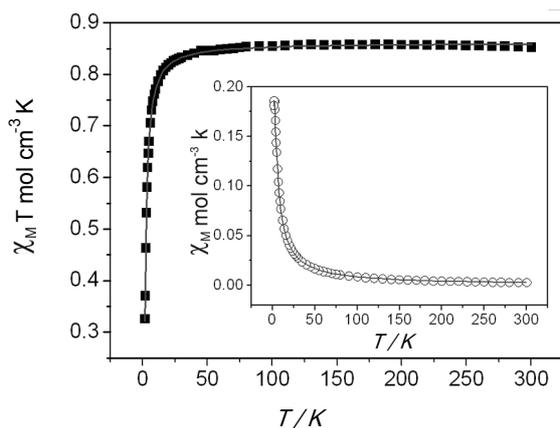


Figure 5. The PXRD patterns for simulated **1** (bottom), as-synthesized **1** (middle), and dehydrated **1** (top).

°C. In order to verify the above speculation, the as-synthesized samples of **1** were calcined at 150 °C for 3 h. The powder XRD patterns of the as-synthesized **1** and the dehydrated samples show no dramatic changes (see Figure 5), which indicates that the title compound can maintain the structural integrity even at the loss of free water molecules. Undoubtedly, the  $\pi$ - $\pi$  interactions play an important role in the stabilization of the supramolecular network of **1**.

**Magnetic property.** The magnetic behavior of the title complex is shown in Figure 6 as the variation of  $\chi_M T$  and  $\chi_M$  (insert) vs  $T$ . The  $\chi_M T$  value at 300 K is 0.85 cm<sup>3</sup> K mol<sup>-1</sup>, which is close to the expected value (0.75 cm<sup>3</sup> K mol<sup>-1</sup>) of two uncorrelated spins of Cu<sup>II</sup> ions ( $S = 1/2$ ,  $g = 2.0$ ). As the temperature decreases, the  $\chi_M T$  decreases continuously to a value of 0.33 cm<sup>3</sup> K mol<sup>-1</sup> at 1.8 K, indicating that there is a dominant intermetallic antiferromagnetic interaction in the complex **1**. On the contrary, as the temperature decreases, the  $\chi_M$  increases monotonously. It changes from 0.00283 cm<sup>3</sup> mol<sup>-1</sup> at 300 K to a maximum of 0.1858 cm<sup>3</sup> mol<sup>-1</sup> at 1.8 K. Thus we can use the Bleaney-Bowers equation<sup>16</sup>  $\chi_M = 2Ng^2\beta^2 / kT \cdot [3 + \exp(-2J/kT)]^{-1}$  for a binuclear compound with a total spin  $S = 1/2$ , and a fit will be obtained by minimizing the function  $R = \sum (\chi_M T_{\text{obs}} - \chi_M T_{\text{obs}})^2 / \sum (\chi_M T_{\text{obs}})^2$ . In the present study, the best fit parameters found are  $J = -1.21$ ,  $g = 2.14$ , and  $R = 4.5 \times 10^{-6}$ , here, the  $J$  value obtained corresponds to a weak antiferromagnetic coupling between the adjacent copper



**Figure 6.** Temperature dependence of  $\chi_M T$  and  $\chi_M$  (insert) established for the complex **1**. The solid curve represents the best fit, as discussed in the text.

(II) ions. From the structure information, it is known that the shortest Cu...Cu distance is 4.138 Å, which is bridged through a oxygen atom of a carboxylate with the angle Cu-O-Cu of 142.54°. The observed antiferromagnetic interaction possibly arises from the magnetic superexchange through the oxygen bridges. The phenomenon we have found for the complex **1** is in good agreement with that found in other similar oxygen bridged binuclear Cu(II) complexes.<sup>17</sup>

### Conclusions

A novel supramolecular complex (**1**) constructed from H<sub>2</sub>IDA and phen has been successfully isolated and structurally characterized. It exhibits a binuclear structure with intra- and inter-molecular  $\pi$ - $\pi$  stacking interactions to form a 2-D supramolecular network. The H<sub>2</sub>IDA ligand exhibits a novel coordination mode compared to the previously reported complexes. Theoretical and experimental studies on the molecular structure are in good agreement. The skeleton of **1** is thermally stable up to 210 °C and keeps intact in the absence of guest water molecules. The magnetic susceptibility data demonstrate that there are antiferromagnetic interactions in the binuclear Cu(II) units of the title complex.

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