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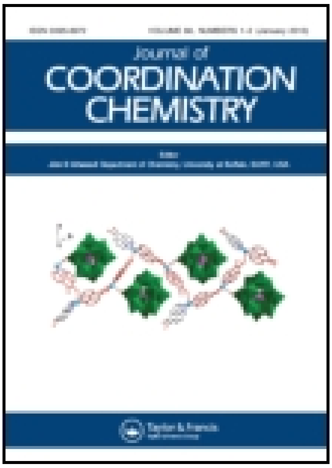

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Synthesis, crystal structures, and magnetic properties of two Cu (II)-complexes based on in situ generated 5-NO_2-2-hydroxyisophthalic acid

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Synthesis, crystal structures, and magnetic properties of two Cu (II)-complexes based on *in situ* generated 5-NO_2-2-hydroxyisophthalic acid

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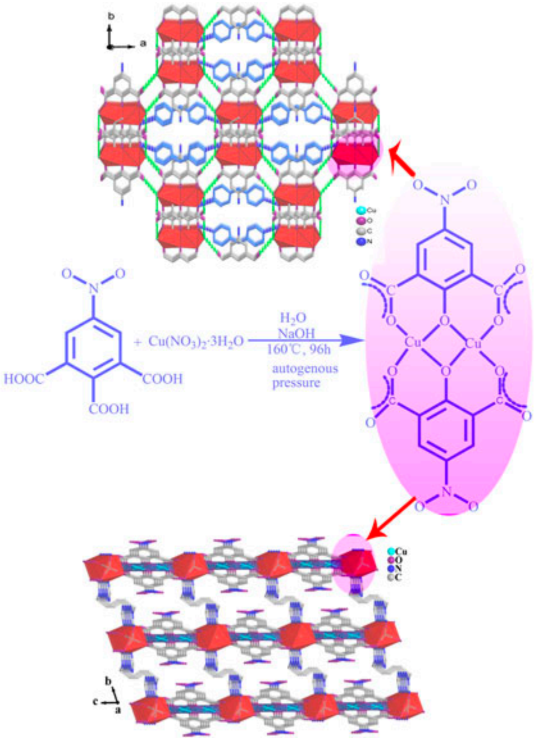

Two new Cu(II)-complexes, $\{[Cu_2(O_2N\text{-}ipO)_2(H_2O)_2]\cdot(H_2dpa)\}_n$ (**1**) and $[Cu_3(O_2N\text{-}ipO)_2(btb)]_n$ (**2**), based on *in situ* generated 5-NO_2-2-hydroxyisophthalic acid were synthesized and characterized. Furthermore, solid-state properties such as thermal stabilities and magnetic properties of the complexes were also discussed.

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Two Cu(II)-complexes, $\{[Cu_2(O_2N\text{-}ipO)_2(H_2O)_2]\cdot(H_2dpa)\}_n$ (**1**) and $[Cu_3(O_2N\text{-}ipO)_2(btb)]_n$ (**2**) (O_2N-ipO = deprotonated 5-NO_2-2-hydroxylisophthalic acid, H_2dpa = protonated dipyridin-4-ylamine and btb = 1,3-bis(1,2,4-triazol-l-yl)butane), were synthesized from an *in situ* generated 5-NO_2-2-hydroxylisophthalic acid and characterized by elemental analysis, FT-IR, single-crystal X-ray diffraction, PXRD, and TGA techniques. Complex **1** exhibits a 3-D alternate supramolecular network extended by the binuclear $[Cu_2(O_2N\text{-}ipO)_2]^{2-}$ unit via intermolecular hydrogen bond interactions. Complex **2** features a 3-D pillar-layered network with a $(4^4 \times 6^{10} \times 8)$ $(4^4 \times 6^2)$-**fsc** topology. Solid-state properties such as thermal stabilities and magnetic properties of the complexes were also investigated.

Keywords: Cu(II) coordination complexes; Crystal structure; *In situ* synthesis; Magnetic properties

1. Introduction

Hydro(solvo)thermal *in situ* ligand synthesis has become a promising approach for the formation of complexes, especially for those which are not accessible from a direct reaction of metal ions and ligands since first proposed by Champness and Schröder in 1997 [1]. A variety of complexes involving *in situ* synthesized ligands via hydro(solvo)thermal methods were documented [2–5], and more than 10 types of hydro(solvo)thermal *in situ* metal–ligand reactions have been found and reviewed by Zhang and Chen [6, 7], respectively. Although hydrothermal and hydroxylation are the two kinds of reactions observed by several authors [8–11], decarboxylation accompanying hydroxylation in the same synthetic system is often difficult, except for being catalyzed by some activated metal ions. One outstanding example was 1,2,3-benzenetricarboxylic acid undergoing an *in situ* decarboxylation to form isophthalate (ip), while hydroxylation of ip also occurred resulting in 2-hydroxyisophthalate (ipO) in the presence of Cu(II) [11]. Both ip and ipO participates in metal coordination, with different N-containing co-ligands to produce a variety of new complexes with diverse structures as well as interesting properties [12].

A nitryl-substituted ligand, 5-NO_2-1,2,3-benzenetricarboxylic acid (5-O_2N-btcH_3), ligated to Ni(II), Mn(II), Zn(II), and Cd(II) with different N-containing co-ligands, generated a series of diverse structures [13–15]. In this work, the tricarboxylate ligands in these complexes varied only in the degree of deprotonation, with no new ligand found in the resultant structures. Additionally, a series of Cu(II) compounds were prepared and formed *in situ* in the reaction of 5-NO_2-1,2,3-benzenetricarboxylic acid [16, 17]. Considering the possibility of an *in situ* transformation of 5-O_2N-btcH_3 and seeking possible structural variations and property changes, we have focused our attention on utilizing 5-O_2N-btcH_3 and N-donor co-ligands as well as different metal ions to generate complexes. Herein, we report the synthesis, crystal structure, and magnetic properties of two new Cu(II)-complexes, $\{[Cu_2(O_2N\text{-}ipO)_2(H_2O)_2]\cdot(H_2dpa)\}_n$ (**1**) and $[Cu_3(O_2N\text{-}ipO)_2(btb)]_n$ (**2**). Interestingly, a new ligand O_2N-ipO, which was formed *in situ* under hydrothermal conditions is incorporated into each of the complexes. Moreover, the thermogravimetric analysis and magnetic properties of the complexes were also discussed.

2. Experimental

2.1. *Materials and general methods*

The ligands 5-NO_2-1,2,3-benzenetricarboxylic acid, dipyridin-4-ylamine, and 1,3-bis (1,2,4-triazol-l-yl) butane were obtained from Alfa Aesar China Co. Ltd and used as received. All other reagents and solvents were commercially available and used as supplied without purification. C, N, and H elemental analyses were performed on a GmbH VariuoEL V3.00 automatic elemental analyzer. Infrared spectra were recorded using KBr pellets on a Thermo Electron NEXUS FT-IR spectrophotometer from 400 to 4000 cm^{-1}. Powder X-ray diffraction patterns were recorded on a Shimadzu XRD-7000 X-ray diffractometer with Cu Kα radiation ($\lambda = 1.5406$ Å). Thermogravimetric analyses were recorded with a NETZSCH STA 449C microanalyzer in air at a heating rate of 10 °C min^{-1}. The magnetic susceptibilities were obtained on crystalline samples using a Quantum Design MPMS SQUID magnetometer under an applied field of 1KOe from 2 to 300 K.

2.2. *Syntheses of 1 and 2*

Single-crystal samples of **1** and **2**, suitable for X-ray analysis were obtained by similar methods as described for **1**.

2.2.1. {[$Cu_2(O_2N$-ipO$)_2(H_2O)_2$]·(H_2dpa)}$_n$ (1).

A mixture of $Cu(NO_3)_2·3H_2O$ (0.0495 g, 0.2 mM), O_2N-btcH (0.0255 g, 0.1 mM), dpa (0.0171 g, 0.1 mM), NaOH (1.0 mL, 0.1 M L^{-1}), and H_2O (9 mL) was stirred under air for 15 min and then sealed in a 25 mL Teflon-lined stainless steel vessel. After heating for 96 h at 160 °C, the reaction system was cooled to room temperature and blue needle-like crystals of **1** were collected by filtration, washed with water, and dried in air. Yield: 53%. Anal. Calcd for $C_{26}H_{19}N_5O_{16}Cu_2$: C, 39.80; H, 2.44; N, 8.93%. Found: C, 39.78; H, 2.41; N, 8.94%. IR (KBr pellet, cm^{-1}): 3430(m), 3093 (m), 1607(s), 1563(m), 1448(m), 1344(m), 1096(m), 839(m), 743(m).

2.2.2. [$Cu_3(O_2$ N-ipO$)_2$(btb)]$_n$ (2).

This complex was prepared in a method similar to that of **1** except for dpa replaced by btb (0.0192 g, 0.1 mM). Yield: 38%. Anal. Calcd for $C_{26}H_{19}N_5O_{16}Cu_2$: C, 34.69; H, 1.94; N, 13.48%. Found: C, 34.67; H, 1.96; N, 13.43%. IR (KBr pellet, cm^{-1}): 3445(m), 1606(s), 1564(m), 1479(m), 1354(m), 1135(m), 830(m), 750(m).

2.3. *X-ray crystallography*

Single-crystal X-ray diffraction analysis of **1** and **2** was collected on a Bruker SMART APEX II CCD diffractometer equipped with graphite monochromated MoKα radiation (λ = 0.71073 Å) by using φ/ω scan technique at 296(2) K. The structures were solved by direct methods with SHELXS-97 [18]. A full-matrix least-squares refinement on F^2 was carried out using SHELXL-97 [19]. Absorption corrections were applied by using SADABS [20]. The hydrogens were assigned with common isotropic displacement factors and included in the final refinement by the use of geometrical restraints. Generally, the positions of C/N-bound hydrogens were generated by a riding model on idealized geometries. The hydrogens of coordinated waters were first located in difference Fourier maps and then fixed in the calculated sites as riding. The crystallographic data and selected bond lengths and angles for **1** and **2** are listed in table 1 and tables S1 and S2 see online supplemental material at http://dx.doi.org/10.1080/00958972.2014.927062.

Table 1. Crystal data and structure refinement parameters for **1** and **2**.

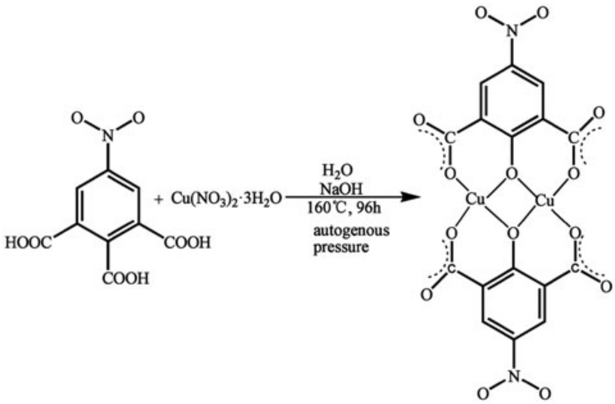
Complex	**1**	**2**
Empirical formula	$C_{26}H_{19}N_5O_{16}Cu_2$	$C_{24}H_{16}N_8O_{14}Cu_3$
Formula weight	784.54	831.07
Temperature (K)	296(2)	296(2)
Crystal system	Monoclinic	Triclinic
Space group	$C2/c$	$P\bar{1}$
a (Å)	14.384(5)	8.3970(7)
b (Å)	22.994(8)	8.5672(7)
c (Å)	8.774(4)	10.0051(8)
α (°)	90.00	71.7540(10)
β (°)	109.803(4)	88.1560(10)
γ (°)	90.00	83.6730(10)
Volume (Å^3)	2730.2(19)	679.40(10)
Z	4	1
ρ_{Calcd} (g cm^3)	1.909	2.031
Absorption coefficient (mm^{-1})	1.654	2.419
F (0 0 0)	1584	415
Data/restraints/parameters	2365/9/233	3244/0/223
Goodness-of-fit on F^2	1.026	1.024
Final R^a indices [$I > 2\sigma(I)$]^a	0.0700, 0.1933	0.0409, 0.1105
R^b indices (all data)	0.0790, 0.2006	0.0429, 0.1123

$^aR = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$; $^bwR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

3. Results and discussion

3.1. *Synthesis chemistry and* in situ *generated 5-NO$_2$-2-hydroxyisophthalic acid*

Hydro(solvo)thermal *in situ* metal–ligand reactions have attracted interest due to many advantages over conventional synthetic routes in coordination chemistry and organic synthetic chemistry [16, 17, 21]. Our attempt was to explore the effects of Cu(II), N-donor co-ligands and systematic pH on the *in situ* reaction of 5-NO$_2$-1,2,3-benzenetricarboxylic acid (O$_2$N-btcH$_3$). The synthetic strategy for Cu(II)-O$_2$N-btcH$_3$ system is depicted in scheme 1, which shows that the *in situ* reactions can occur with O$_2$N-btcH$_3$ and Cu(II) under similar reactions. Previous studies indicated that other transition metal ions (such as Zn^{II}, Cd^{II}, Mn^{II}, Ni^{II}, etc.) could not support the *in situ* reaction at suitable basic condition



Scheme 1. Generation of the subunit [$Cu_2(O_2N\text{-}ipO)_2$] from *in situ* reactions involving 5-NO$_2$-1,2,3-benzenetricarboxylic acid (O$_2$N-btcH$_3$).

under hydrothermal system [13–15]. In this work, basic conditions and Cu(II) have a critical impact on the decarboxylation and hydroxylation procedure of the starting O_2N-btcH_3 under hydrothermal system which resulted in formation of 5-NO_2-2-hydroxylisophthalic acid.

3.2. *Structural analysis*

3.2.1. Structure of $\{[Cu_2(O_2N\text{-ipO})_2(H_2O)_2]\cdot(H_2dpa)\}_n$ (1). Single-crystal X-ray diffraction analysis reveals that the asymmetric unit of **1** contains one crystallographically independent Cu(II) with square pyramidal geometry, two halves of O_2N-ipO, one coordinated water and half H_2dpa [figure 1(a)]. The Cu–O bond distances range from 1.894(5) to 2.234(7) Å. These values are similar to those reported for similar complexes containing Cu–O motifs [22]. Cu1 and Cu1A ions are bridged by μ_4-N_2O-ipO anions (μ_4: η^1, η^2, η^1) to generate the $[Cu_2\,(O_2N\text{-ipO})_2]^{2-}$ building block with a Cu_2O_2 core (Cu1···Cu2 2.962(2) Å). For balancing the electric charge, the free dpa was protonated and generated H_2dpa, which might provide sites for the formation of hydrogen bonds. In **1**, the adjacent $[Cu_2(O_2N\text{-ipO})_2]^{2-}$ building blocks were extended by strong hydrogen bond interactions (O9–H···O2, 2.771 Å, 159.87°) to give a 1-D zigzag supramolecular chain structure along the *c* axis [figure 1(b)]. Moreover, these supramolecular chains are bridged by oxygens from carboxyl groups (O7) and coordinated water (O9–H···O7, 2.771 Å, 152.77°) from the neighboring chains, which resulted in the final 3-D supramolecular networks [figure 1(c)]. The protonated dpa molecules play a complementary role for stabilizing and strengthening the overall structure of **1** by strong hydrogen bond interactions (N3–H···O1, 2.821 Å, 169.85°) [figure 1(d)].

3.2.2. Structure of $[Cu_3(O_2N\text{-ipO})_2(btb)]_n$ (2). Different from **1**, **2** features a 3-D pillar-layered framework with (4,6)-connected $(4^4 \times 6^{10} \times 8)(4^4 \times 6^2)$-**fsc** topology. The fundamental unit of **2** is composed of one six-coordinate Cu^{II}, two symmetry-related four-coordinate Cu^{II} ions, two O_2N-ipO anions and one btb. As shown in figure 2(a), the Cu1 shows a distorted octahedral coordination geometry $[CuN_2O_4]$, which is completed by four carboxylate oxygens from four $O_2N\text{-ipO}^{3-}$ anions and two nitrogens from two btb ligands. Similar with **1**, symmetrical Cu2 and Cu2A ions are bridged by μ_4-N_2O-ipO anions (μ_4: η^1, η^2, η^1) to generate the $[Cu_2(O_2N\text{-ipO})_2]^{2-}$ building block with a Cu_2O_2 core (Cu1···Cu2 2.950(6) Å). The Cu–O distances are 1.862(2)–2.409(2) Å and the Cu–N distance is 1.972(2) Å, which are close to those reported for similar complexes containing Cu–O/N motifs [23]. The alternating binuclear $[Cu_2(O_2N\text{-ipO})_2]$ units and mononuclear $[[CuN_2O_4]$ bridged by the carboxylate oxygens give a 2-D layer structure in the *ac* plane [figure 2(b)]. Additionally, adjacent 2-D layers are pillared by btb ligands to generate a 3-D pillar-layered framework [figure 2(c)]. From topology, if binuclear $[Cu_2(O_2N\text{-ipO})_2]$ is considered as a 4-connected node, the Cu1 ions are 6-connected nodes and bridging btb molecules are regarded as linear linkers. Hence, the structure of **2** can be best regarded as a 2-nodal (4,6)-connected **fsc** topology with a point symbol of $(4^4 \times 6^{10} \times 8)(4^4 \times 6^2)$ [figure 2(d)].

3.3. *PXRD and thermogravimetric analysis*

In order to confirm the phase purity of the bulk materials, X-ray powder diffraction (PXRD) was used to confirm the phase purity of bulk **1** and **2** at room temperature (figures S1 and

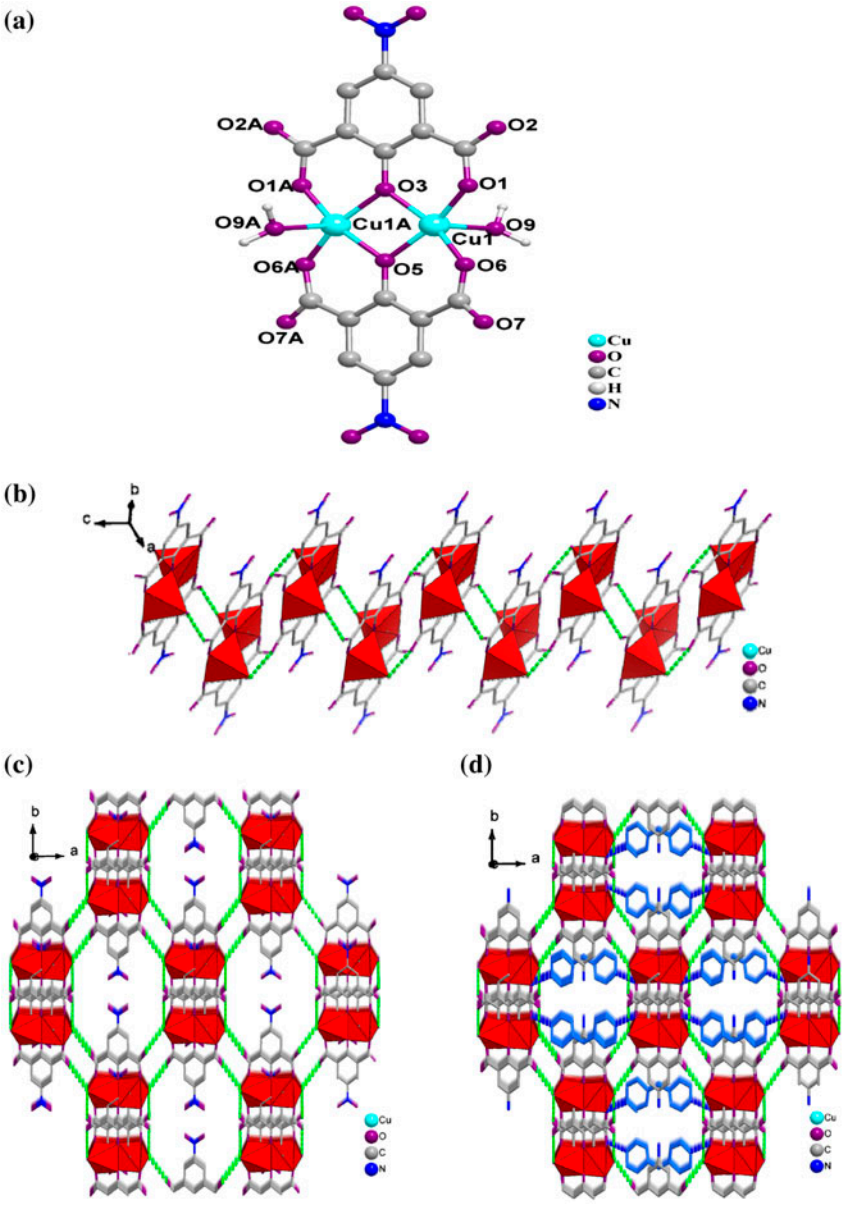


Figure 1. (a) View of the coordination environments of Cu(II) of **1**. The hydrogens of phenyl are omitted for clarity. Symmetry codes: A: $-x$, y, $0.5-z$; (b) the 1-D chain structure via hydrogen bonds of **1**; (c) the 3-D supramoelcular networks. The protonated dpa molecules and hydrogens were omitted here; and (d) the complicated 3-D supramoelcular networks of **1**. The protonated dpa molecules and the hydrogen bonds are highlighted by light blue and green (see http://dx.doi.org/10.1080/00958972.2014.927062 for color version).

S2 in the Supplementary material). Although the experimental patterns show slightly broadened diffraction peaks in comparison to those simulated from the single-crystal data, it can still be regarded that the bulk as-synthesized materials represent the pure phases of **1** and **2**.

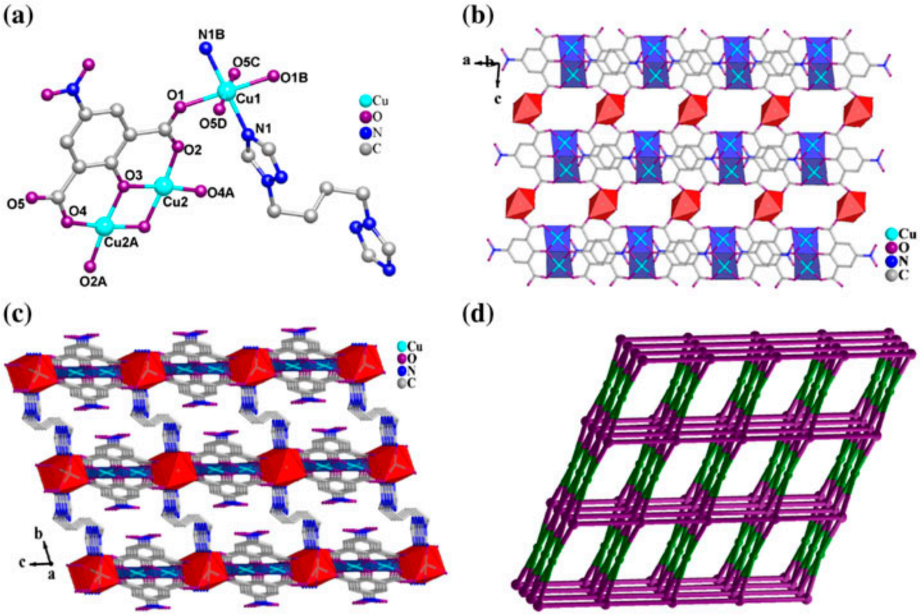


Figure 2. (a) View of the coordination environments of Cu(II) of **2**. The hydrogens of phenyl and methylene are omitted for clarity. Symmetry codes: A: 1 − *x*, −2 − *y*, −*z*; B: 2 − *x*, −2 − *y*, −*z*; C: 1 − *x*, −1 − *y*, −*z*; D: 1 − *x*, 1 − *y*, 1 – *z*; (b) the 2-D layer structure via dinuclear [$Cu_2(O_2N\text{-ipO})_2$] unit and [CuO_4N_2] unit of **2**; (c) the 3-D pillar-layered framework of **2**; and (d) schematic description of the 2-nodal (4,6)-connected **fsc** topology with a point symbol of $(4^4 \times 6^{10} \times 8)(4^4 \times 6^2)$ of **2** (green: binuclear [$Cu_2(O_2N\text{-ipO})_2$] nodes; violet: Cu1 nodes, see http://dx.doi.org/10.1080/00958972.2014.927062 for color version).

Thermogravimetric analysis (TGA) was carried out in air to examine the thermal stabilities of **1** and **2** (figures S3 and S4 in the Supplementary material). For **1**, the first weight loss of 4.55% from 40 to 180 °C is related to the loss of three coordinated waters (Calcd 4.59%). The residue is stable to 200 °C and the remaining residue is CuO (obsd. 21.45%, Calcd 21.37%). For **2**, there are no lattice and coordination waters and thus the composition is stable to 260 °C. After 260 °C, the network of **2** gradually collapses corresponding to the decomposition of organic components, and the remaining residue is CuO (obsd. 28.85%, Calcd 28.88%).

3.4. *Magnetic properties*

The magnetic susceptibilities (χ_M) of **1** and **2** were measured under a magnetic field of 1 KOe from 2 to 300 K. The plots of $\chi_M T$, $1/\chi_M$ *versus* T for **1** and **2** are depicted in figures 3 and 4. The $\chi_M T$ values of **1** and **2** at 300 K are 0.65 and 1.14 cm^3 K M^{-1}, which were slightly smaller than that of two isolated spin-only Cu(II) ions (0.75 cm^3 K M^{-1}, $S = 1/2$) and larger than the spin-only value of 1.13 cm^3 K M^{-1} expected for three $Cu^{II}(S = 1/2)$ ions in the asymmetric unit, respectively. As the temperature was lowered from 300 to 2 K, the $\chi_M T$ of **1** and **2** steadily decreased to 0.45 and 0. 49 cm^3 K M^{-1}, indicating overall antiferromagnetic interactions of **1** and **2**. In **1** and **2**, there is only one magnetic exchange pathway, dihydroxo-bridged binuclear copper(II) unit, which provides small metal–metal distances and results in a good overlap of the magnetic orbitals, inducing anti-ferromagnetic coupling

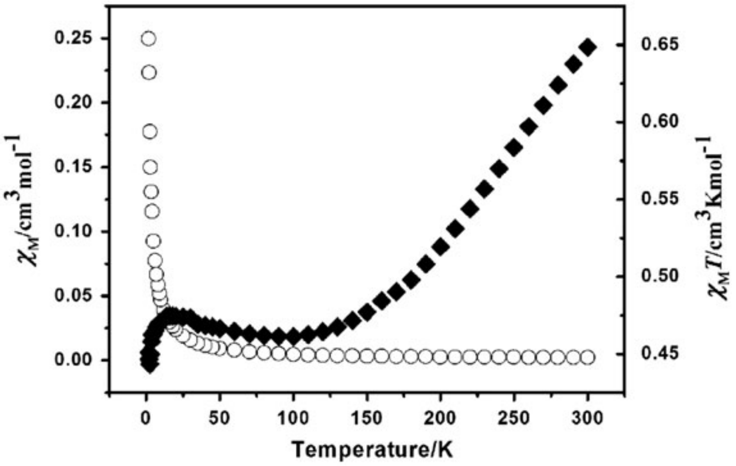


Figure 3. The plot of χ_M and $\chi_M T$ vs. T for **1** at 2–300 K.

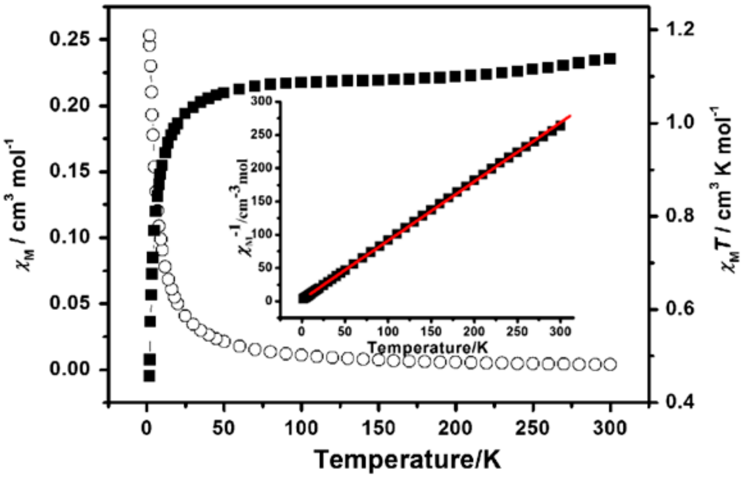


Figure 4. The plot of χ_M and $\chi_M T$ vs. T for **2** at 2–300 K.

as observed in other structurally relevant binuclear Cu(II) hydroxo-bridge compounds [16]. The temperature dependence of the reciprocal susceptibilities ($1/\chi_M$) of **2** obey the Curie–Weiss law [$\chi = C/(T - \theta)$] above 30 K with $\theta = -3.06$ K, $C = 1.12$ cm^3 K M^{-1}. The moderate negative θ value indicates the presence of antiferromagnetic interactions between Cu^{II} cations which is comparable to the conclusion predicted by Hatfield–Hodgson [24]. The antiferromagnetic interactions of **2** might be attributed to the dinuclear units of [$Cu_2(O_2N$-ipO$)_2$]. Although attempting to fit the magnetic susceptibility data of **1** and **2**, we did not obtain satisfactory results employing available formulas for the models.

4. Conclusion

Cu(II)-based coordination complexes containing carboxylates and N-donor coligands could show structural motifs with various topologies as well as useful functional properties. Many Cu(II) compounds based on carboxylates and N-donor coligands have been constructed and exhibit interesting properties [25–32]. In this work, two Cu(II) coordination complexes based on *in situ* generated 5-NO_2-2-hydroxyisophthalic acid were synthesized and characterized. Complexes **1** and **2** exhibit a 3-D supramolecular network and 3-D pillar-layered **fsc-**$(4^4 \times 6^{10} \times 8)(4^4 \times 6^2)$ network, respectively. Compared to reported Cu(II) coordinated compounds based on carboxylates incorporating different N-donor coligands [16, 27], the overall magnetic interactions existing in these compounds were antiferromagnetic due to the different structures. These results not only reveal the generation of new organic ligands that can be metal-directed from *in situ* ligand synthesis, but also modulate magnetic properties via introducing different N-donor coligands.

Supplementary material

CCDC 958688 and 958689 contain the supplementary crystallographic data for **1** and **2**. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif. Selected bond lengths and angles parameters, TGA, powder X-ray patterns can be found in the supporting file.

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