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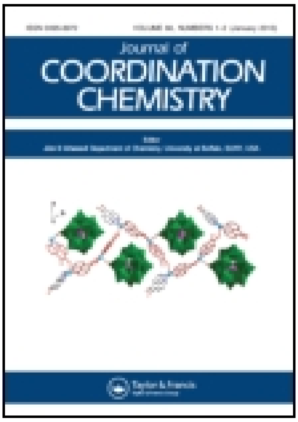

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Synthesis, crystal structures, and magnetic properties of two supramolecular coordination complexes constructed by sulfonate groups

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Synthesis, crystal structures, and magnetic properties of two supramolecular coordination complexes constructed by sulfonate groups

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Two supramolecular coordination complexes, [Cu(hps)(H_2O)] (**1**) (hps = 4-hydroxypyridone-3-sulfonic acid) and [Cu(phen)(SO_4)(H_2O)$_2$] (**2**) (phen = 1,10-phenanthroline), have been synthesized and characterized structurally as well as magnetically. The two complexes both exhibit supramolecular networks originating from interactions such as hydrogen bonding, π–π interactions and C–H$\cdots$O contacts. The magnetic properties of **1** and **2** have been investigated from 1.8 to 300 K. Results indicate that **1** and **2** show antiferromagnetic interactions between Cu(II) centers.

Keywords: Supramolecular network; Copper; Crystal structure; Magnetism

1. Introduction

Supramolecular chemistry has become one of the more topical areas of research [1]. Weak bonding interactions between entities, such as hydrogen bonding and π–π stacking, are important supramolecular forces and can govern the process of molecular recognition and self-assembly [2]. Much work has been studied with metal phosphonates (RPO_3^{2-}) due to their potential applications in ion exchange, catalysis, adsorption, sensors, optical activity, and non-linear optics [3]. Similar to RPO_3^{2-}, sulfonates (RSO_3^-) have been less studied [4], owing to the perception that sulfonate is a poor ligand [5]. Recently, with the development of supramolecular chemistry and crystal engineering, it has been found that sulfonate (RSO_3^-) is a perfect self-assembly unit with potential applications in many fields such as non-linear optics, catalysis, and liquid crystal materials [6]. So far, although some new sulfonic acid complexes have been reported, research on design, synthesis, structure and properties of metal sulfonates is less than expected. Crystal structures and properties of complexes with pyridine sulfonic acid ligands are less reported. 4-Hydroxypyridine-3-sulfonic acid forms complexes of Co^{2+}, Zn^{2+} and Ag^+, [M($C_5H_4NO_4S$)$_2$(H_2O)$_2$] (M = Co,

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Zn), and $[Ag_2(C_5H_4NO_4S)_2]_n{\cdot}2nH_2O$, with the same coordination system [7]. However, Cu(II) complex with 4-hydroxypyridine-3-sulfonic acid has not been reported. Isostructual $[M(C_7H_8NO_3S)_2(H_2O)_4]$ (M = Cu, Co, Zn) and Ag complexes $[Ag(PES)(H_2O)]_n$ and [Ag (PES)(melamine)] have been reported containing 4-pyridine-ethanesulfonic acid [8]. Cu(II) complex containing the second ligand has not been reported while introduction of a second ligand may modify the coordination behavior of RSO_3^- [5,9]. We chose 4-hydroxypyridine-3-sulfonic acid with Cu(II) and 4-pyridine-ethanesulfonic acid, phen and Cu(II), to prepare and characterize new Cu(II) sulfonates.

Herein, we report the synthesis, crystal structures, and magnetic properties of two new supramolecular coordination complexes, $[Cu(hps)(H_2O)]$ (**1**) (hps = 4-hydroxypyridone-3-sulfonic acid) and $[Cu(phen)(SO_4)(H_2O)_2]$ (**2**) (phen = 1,10-phenanthroline).

2. Experimental

2.1. *Materials and instruments*

All reagents were obtained commercially and used without purification. Elemental analyses were performed on a Perkin-Elmer 240C elemental analyzer. Infrared (IR) spectra were recorded as KBr disks with a Perkin-Elmer 16 PC FT-IR spectrophotometer. Powder X-ray diffraction analysis was performed on a Rigaku D/max 2500 X-ray diffractometer. Magnetic susceptibility data were obtained on polycrystalline samples using a Quantum Design MPMS-XL7 SQUID magnetometer. Data were recorded in 1000 Oe field while warming the samples from 1.8 to 300 K. Diamagnetic corrections were made for both the sample holder and the compound estimated from Pascal's constants [10].

2.2. *Synthesis*

2.2.1. Synthesis of $[Cu(hps)(H_2O)]$ (1). A mixture of $Cu(NO_3)_2{\cdot}3H_2O$ (0.1 mmol, 0.0242 g) and 4-hydroxypyridone-3-sulfonic acid (0.2 mmol, 0.0350 g) was added to 2 mL CH_3OH/H_2O (1 : 1), and the solution was stirred for 10 min in air. The pH of the solution was adjusted to 4.0 using 0.2 M NaOH with stirring for another 10 min. Then the mixture was placed in a Teflon-lined autoclave and heated at 130 °C for 144 h. Upon cooling to room temperature, green crystals of **1** suitable for single crystal X-ray diffraction analyses were obtained with a yield of 40% (based on Cu). Anal. Calcd for **1** ($C_5H_5CuNO_5S$) (%): C, 23.58; H, 1.98; N, 5.50; S, 12.59. Found (%): C, 23.57; H, 1.99; N, 5.51; S, 12.58. IR (KBr, cm^{-1}): 3319(s), 3107(m), 1609(s), 1483(s), 1442(s), 1355(s), 1263(s), 1184(s), 1166 (s), 1107(m), 1064(m), 900(s), 834(s), 747(w), 634(m), 593(m), 556(s), and 526(m).

2.2.2. Synthesis of $[Cu(phen)(SO_4)(H_2O)_2]$ (2). A mixture of $Cu(NO_3)_2{\cdot}3H_2O$ (0.1 mmol, 0.0242 g), 4-pyridineethanesulfonic acid (0.2 mmol, 0.0374 g), and 1,10-phen (0.1 mmol, 0.0198 g) was added to 3 mL CH_3OH/H_2O (1 : 2), and the solution was stirred for 10 min in air. Then the mixture was placed in a Teflon-lined autoclave and heated at 130 °C for 72 h. Upon cooling to room temperature, green crystals of **2** were obtained which were suitable for crystal X-ray diffraction analyses with a yield of 60% (based on

Cu). Anal. Calcd for $C_5H_5CuNO_5S$ (%): C, 38.35; H, 3.22; N, 7.45; S, 8.53. Found (%): C, 38.34; H, 3.23; N, 7.44; S, 8.52. IR (KBr, cm^{-1}): 3431(s), 3049(w), 1627(w), 1606(w), 1584(m), 1515(m), 1423(s), 1347(m), 1107(s), 852(s), 720(s), and 617(s).

2.3. *X-ray crystal structure determinations*

All diffraction data were collected on a Bruker Apex CCD area-detector diffractometer with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Absorption corrections were applied using multiscan program SADABS [11]. The structures were solved by direct methods and refined with a full-matrix least-squares technique using SHELXTL [12]. All non-hydrogen atoms were refined with anisotropic displacement parameters. The crystal data and structure refinement results for these compounds are listed in Supplementary material. Selected bond lengths and angles are listed in table S2. Hydrogen bonds for **1** and **2** are listed in table S3.

3. Results and discussion

3.1. *Structural description*

3.1.1. [Cu(hps)(H_2O)] (1). Single-crystal X-ray diffraction analysis of **1** reveals that it crystallizes in the orthorhombic space group *Pbca*. Cu adopts a distorted NO_4 square-pyramidal coordination environment with two sulfonate oxygens (1.9863(16) Å, 2.2860(16) Å), one hydroxy oxygen (1.9384(17) Å), one water (1.9862(17) Å), and one pyridine nitrogen (1.9900(20) Å) (figure 1(a)). This coordination system is different from that in the literature [7]. O2 is displaced above the N1O1O4O1W plane by *ca.* 2.3344 Å.

4-Hydroxypyridone-3-sulfonic acid adopts η^4, μ^3 coordination to link three Cu ions. Each Cu is bridged to another Cu via 4-hydroxypyridone-3-sulfonic acid to form a 1-D chain along the *c*-axis (figure 1(b)). In the chain, the dihedral angle beween adjacent pyridyl rings of 4-hydroxypyridone-3-sulfonic acid ligands is 10.230°. The sulfonate oxygens from each chain further coordinate to Cu centers in the neighboring chain, forming a 2-D layer (figure 1(c)). There are hydrogen bonds, π–π stacking, and C–H···O contacts in the layers, which contribute to the stability (figure S1 in Supplementary material). The face-to-face distance of pyridyl rings parallel to each other in neighboring chains is *ca.* 3.62 Å, indicating significant π–π interaction. The sulfonate groups are excellent hydrogen bond acceptors; there are many C–H···O contacts involving the aromatic C–H groups and sulfonate. The C···O distances and the C–H···O angles are 2.892(3), 2.987(3) Å and 105(2)°, 113(2)°, respectively. There are also many C–H···O contacts involving aromatic C–H groups and waters. The C···O_W distances and the C–H···O_W angles are 2.908(3) Å and 120(2)°, respectively. Water is also H-bonded to oxygens of sulfonate ($O_W \cdots O = 2.699(2)$ Å, O_W–H···O = 163(3)°). Distances of adjacent Cu centers are 7.5742(15) and 4.2425(8) Å, respectively.

The layers are held together through hydrogen bonds and C–H···O contacts (figure 1 (d)). Water is H-bonded to oxygen of hydroxy ($O_W \cdots O = 2.723(2)$ Å, O_W–H···O = 164 (3)°). The sulfonates are excellent hydrogen bond acceptors so that there are many

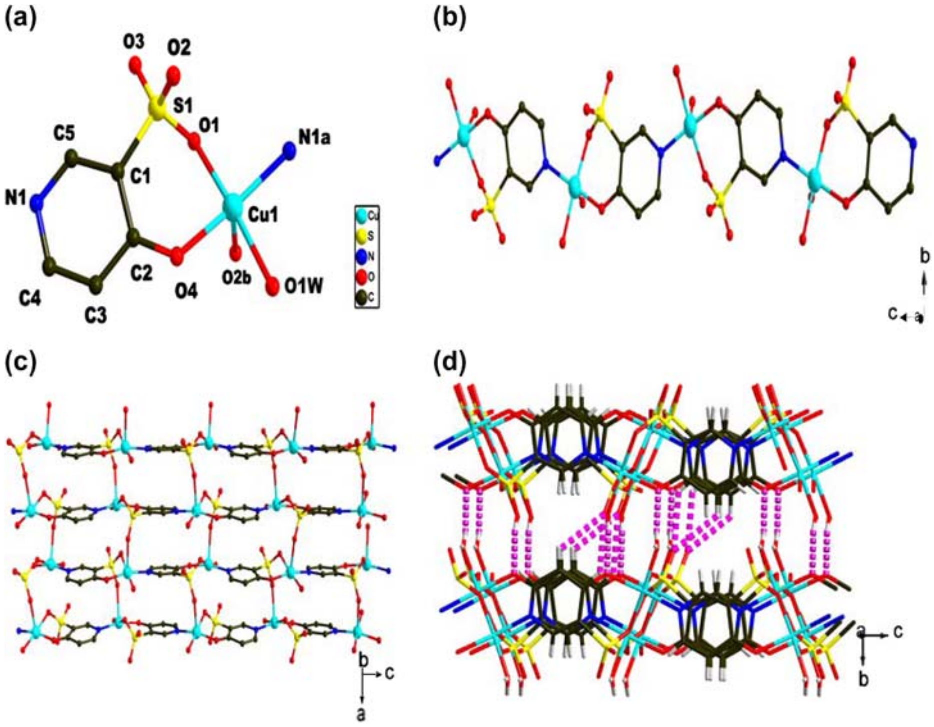

Figure 1. (a) Coordination environment of Cu^{2+} in **1**. Hydrogens are omitted for clarity. (b) The 1-D chain constructed by 4-OH-3-pySO_3 ligands along the *c* direction in **1**. (c) Perspective view of the 2-D layered network of **1** by linkage of 4-OH-3-pySO_3 ligands. (d) 3-D network constructed by hydrogen bonds and C–H···O contacts between layers in **1**.

C–H···O contacts involving aromatic C–H groups and sulfonate. The C···O distances and the C–H···O angles are 3.111(3) Å, 3.184(3) Å and 131(2)°, 124(2)°, respectively.

3.1.2. [Cu(phen)(SO_4)(H_2O)$_2$] (2).

X-ray structural analysis reveals that **2** crystallizes in the monoclinic space group *C2/c*. Cu has a distorted N_2O_4 octahedral environment constructed by two nitrogens from a phen (2.010(3) Å), two oxygens from two SO_4^{2-} (2.462 (2) Å) and two coordinated waters (1.969(2) Å) (figure 2(a)). O1 is displaced above the N1N1CO3O3D plane by *ca.* 2.4556 Å. The pyridine ring disappeared and sulfonate changed to $SO_4{}^{2-}$ after reaction, which has never been reported and may be due to the complicated reaction under hydrothermal conditions.

The SO_4^{2-} is η^2, μ^2 linking two Cu. Each Cu is bridged to another Cu via SO_4^{2-} to form a 1-D chain along the *c*-axis (figure 2(b)). Adjacent chains form 2-D layers through hydrogen bonds between SO_4^{2-} groups and waters ($O_W \cdots O = 2.609(3)$ Å, 2.663(3) Å, O_W–H···O = 170(4)°, 171°) (figure 2(c)). The C–H···O contacts (C···O = 3.069(4)–3.460(5) Å, C–H···O = 113–154°) interlink adjacent layers to form a 3-D network.

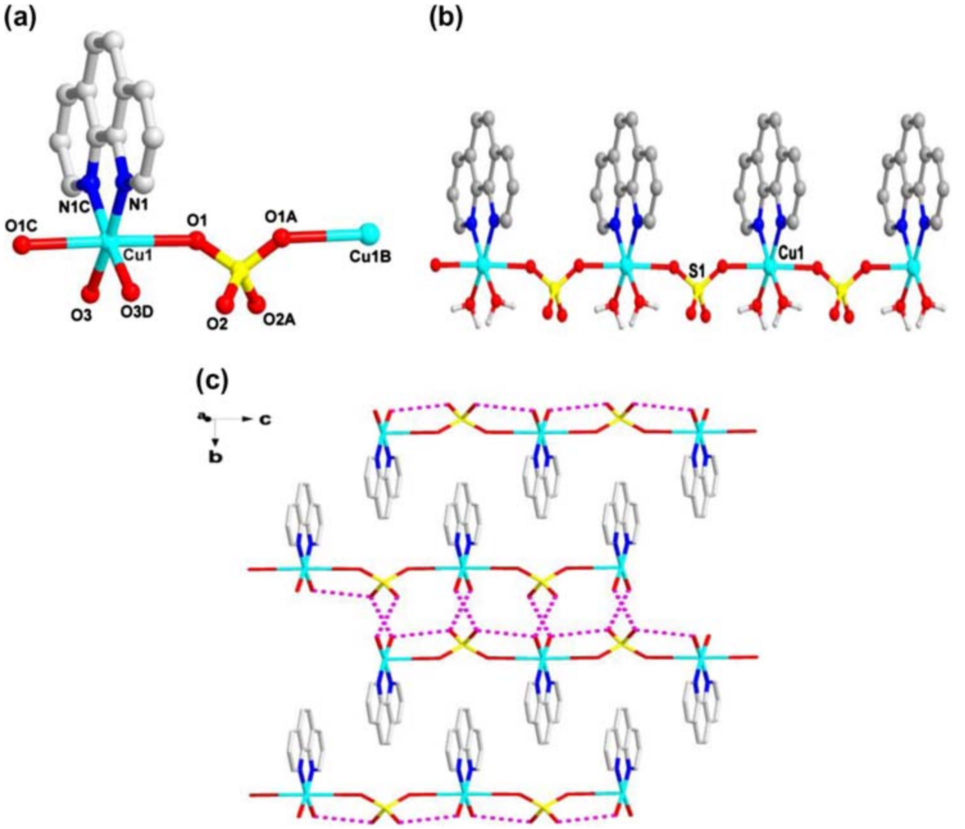

Figure 2. (a) Coordination and linkage modes of Cu^{2+} and ligands in **2**. Hydrogens are omitted for clarity. (b) The 1-D chain linked by SO_4^{2-}. (c) Perspective view of the 2-D layered network of **2** by hydrogen bonds.

3.2. *Spectroscopic characterization*

IR spectra of **1** and **2** were measured as KBr pellets from 4000 to 400 cm^{-1}. In IR spectra of **1** (figure S2 in Supplementary material), peaks at 1609, 1483, and 1355 cm^{-1} can be assigned to vibrations of C–N and C–C of pyridine, which are lower energy than in 4-hydroxypyridone-3-sulfonic acid (1637, 1501, and 1370 cm^{-1}), indicating coordination of N of pyridine [13–15]. Characteristic vibrations of $\nu_{as}SO_3^-$ in **1** are 1263 and 1184 cm^{-1}, whereas the $\nu_s(SO_3^-)$ is at 1010 cm^{-1}, both different from that in 4-hydroxypyridone-3-sulfonic acid ($\nu_{as}(SO_3^-)$ at 1255, 1176 cm^{-1} and ν_s (SO_3^-) at 1018 cm^{-1}), due to coordination of SO_3^- with Cu(II). The peak at 1107 cm^{-1} may be assigned to C–O vibration (1117 cm^{-1} in 4-hydroxypyridone-3-sulfonic acid), owing to coordination of hydroxy group. IR spectra of **1** exhibit strong absorption at 3319 cm^{-1} because of the existence of water in **1**. The IR attribution of **1** is consistent with the structural determination.

IR spectra of **2** (figure S3 in Supplementary material) show no strong peaks at 1634 or 1458 cm^{-1}, indicating that there may be no pyridine ring in **2** [13–15]. The peak at

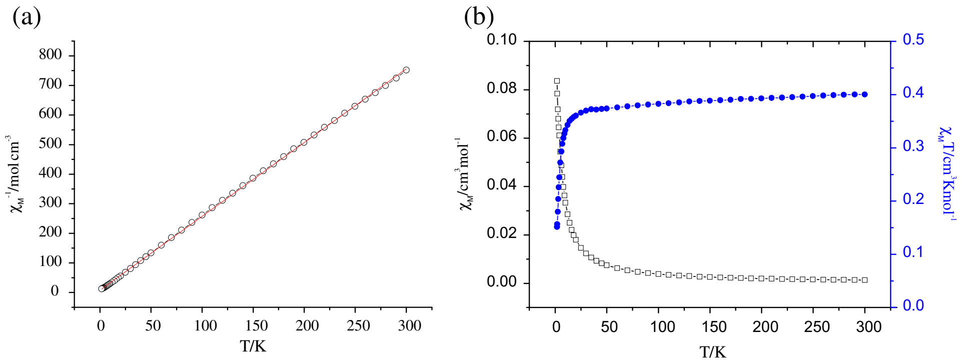

Figure 3. Plots of $\chi_M{}^{-1}$, χ_M, and $\chi_M T$ *vs.* T for **1**.

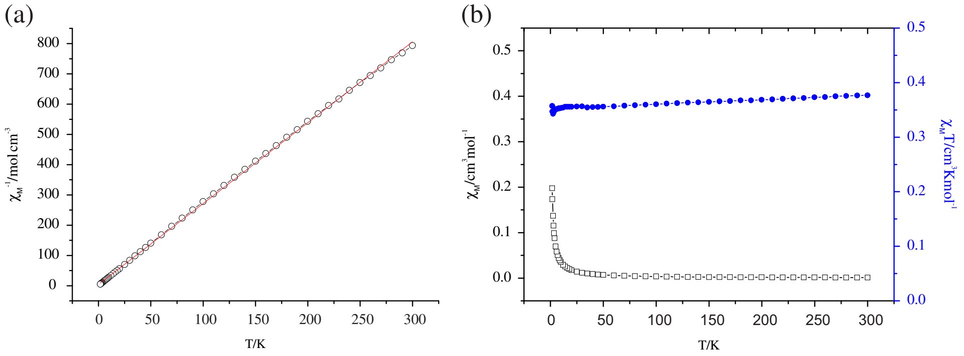

Figure 4. Plots of $\chi_M{}^{-1}$, χ_M, and $\chi_M T$ *vs.* T for **2**.

1107 cm^{-1} can be assigned to vibration of SO_4^{2-}, different from that in 4-pyridineethanesulfonic acid (ν_{as} (SO_3^-) at 1253, 1159 cm^{-1}, and ν_s (SO_3^-) at 1026 cm^{-1}). The adsorptions of phen (1419, 850, and 738 cm^{-1}) shift to 1423, 852, and 720 cm^{-1}, respectively, due to its coordination with Cu(II) [16]. IR spectra of **2** exhibit strong absorption at 3431 cm^{-1} from water in **2**.

3.3. *Magnetism*

The magnetic susceptibility data of **1** and **2** were collected from 1.8 to 300 K, figures 3 and 4. The $\chi_M T$ value is 0.400 cm^3 K mol^{-1} at 300 K for **1**, larger than the spin only value of 0.375 cm^3 K mol^{-1} (g = 2.0) expected for a total spin S = 1/2 [10,17], owing to mixing of angular momentum from excited states via spin-orbit coupling [14,18]. The $\chi_M T$ decreases continuously with decreasing temperature and reaches a minimum of 0.151 cm^3 K mol^{-1} near 1.8 K. The $1/\chi_M$ *versus* T plot obeys the Curie–Weiss law with a Weiss constant of $\theta = -4.91$ K and a Curie constant C of 0.404 cm^3 K mol^{-1}. The negative θ value is indicative of dominant antiferromagnetic interactions between Cu^{2+} centers [13,19]. The $\chi_M T$ value is 0.377 cm^3 K mol^{-1} at 300 K for **2**, which is close to the spin only value of 0.375 cm^3 K mol^{-1} (g = 2.0) expected for a total spin S = 1/2. The $\chi_M T$ decreases slightly with decreasing temperature and at low temperature it increases slightly, which may be because the sample is not pure. The $1/\chi_M$ *versus* T plot obeys the Curie–Weiss law with a Weiss constant $\theta = -1.56$ K and a Curie constant C of $0.374\ \mathrm{cm^3\,K\,mol^{-1}}$. The negative θ value is indicative of antiferromagnetic interactions between copper centers.

The layer structure of **1** contains 1-D chains linked by 4-hydroxypyridone-3-sulfonic acid ligands. The Cu···Cu distance of 7.5742(15) Å through the chain is so long that exchange couplings would be extremely weak. The neighboring chains are bridged by sulfonate from each chain. The Cu···Cu distance of neighboring chains is 4.2425(8) Å, shorter than that of 7.5742(15) Å. Considering these, the antiferromagnetic interactions observed in **1** could be mainly attributed to the exchange couplings through sulfonate linking neighboring chains. The structure of **2** contains 1-D chains linked by SO_4^{2-} and adjacent chains form 2-D layers through hydrogen bonds between SO_4^{2-} and water. The antiferromagnetic interactions observed in **2** could be mainly attributed to exchange couplings through SO_4^{2-} linking neighboring Cu(II) centers.

4. Conclusion

Two supramolecular coordination complexes constructed by sulfonate [Cu(hps)(H_2O)] (**1**) and [Cu(phen)(SO_4)(H_2O)$_2$] (**2**) have been synthesized and magnetically characterized. Both exhibit supramolecular networks originating from interactions such as hydrogen bonding, π–π interactions, and C–H···O contacts. Magnetic studies reveal that **1** and **2** show antiferromagnetic interactions between Cu(II) centers.

Supplementary material

Supplementary data to this article can be found online. Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary material, CCDC Nos. 827357 and 817163 for **1** and **2**. Copies of this information may be obtained free of charge on application from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336033, E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.

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