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Engineering of non-interpenetrating 3-D and 2-D networks and guest adsorption based on 4,4′-di(3-methyl)pyridyl sulfide copper(II) complexes

Xun-Cheng Su, Shourong Zhu,* Hua-Kuan Lin, Xue-Bing Leng and Yun-Ti Chen

Department of Chemistry, Nankai University, Tianjin 300071, P.R. China.
E-mail: szhu@nankai.edu.cn

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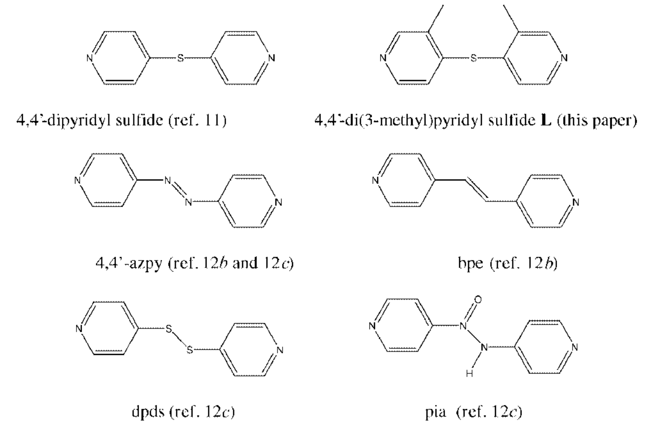
Two new coordination compounds, [Cu(**L**)$_2$SO$_4$]·0.5H$_2$O·0.5CH$_2$Cl$_2$ (**1**) and [Cu(**L**)$_2$(SCN)$_2$]·3CHCl$_3$ (**2**), were synthesized and structurally characterized. The molecular architectures of the 4,4′-di(3-methyl)pyridyl sulfide (**L**) coordination polymer networks are anion dependent. The molecular architecture of **1** is a 3-D non-interpenetrating network, SO_4^{2-} serving as a bridging ligand to connect two copper ions resulting in a rhombic box with a volume of 793 Å^3. While **2** is a 2-D planar network with SCN$^-$ acting as a mono-coordinating ligand. Guest adsorption experiments show that **1** prefers to selectively adsorb 4-chlorophenol rather than nitrobenzene and benzophenone and DMF. In contrast, **2** does not adsorb any of the above guest species.

Introduction

The crystal engineering of metal ion induced self-assembly based on covalent interactions or hydrogen bonding is an expanding field of research.[1–3] Over the past few years, several types of spacing ligands have been employed as building elements and a large number of 1-, 2- and 3-D coordination polymers have been reported.[3,4–6] Of the bidentate spacer ligands, those containing two 4-pyridyl donor units represent an important class, which can afford variable lengths and linear or non-linear geometries.[7–9] The design of polymeric metal complexes with three-dimensional nets is, however, not well-developed and the reported 3-D coordination polymers generated from bipyridine and its derivatives are mostly interpenetrating networks.[9,10] The above networks are usually centered on metal ions such as Zn(II), Cd(II), Cu(I) and Ag(I), which tend to have tetrahedral geometries. In contrast, for Cu(II), Ni(II) and Co(II), the 3-D coordination complexes are much fewer, as the structures for these metal complexes are usually in square and/or octahedral geometries (for the latter, the axial sites are usually occupied by solvent or a non-bridging donor group) and the generated networks can only extend along one or two directions. Recently, an attractive concept in designing coordination crystals with large pores has been the formation of an interpenetrated network. However, interpenetrating networks have large drawbacks in that more condensed structures have either very small pores or no pores at all. This decreases the potential uses in functional materials. Non-interpenetrating coordination polymers with well-defined large pores are therefore particularly desired. It is known that some transition metal ions such as Cu(II) tend to bond bipyridine more tightly than its counter anions such as nitrate, sulfate and acetate. Therefore, if the molar ratio of metal, ligand, counter anion and solvent is reliably modulated, the resulting structure could be predictable. In addition, it is worthy of note that in order to obtain a 3-D network formed by covalent bonds rather than hydrogen bonding, the copper(II) ion should be at least six-coordinated so as to have three directions in which to extend.

In contrast to other types of bipyridines[11, 12] (Scheme 1), 4,4′-dipyridyl sulfide and 4,4′-di(3-methyl)pyridyl sulfide (**L**) remain largely unexplored as bridging ligands[11] and the coordination polymer of 4,4′-di(3-methyl)pyridyl sulfide (**L**) has not yet been observed. Here we chose CuSO$_4$, Cu(NO$_3$)$_2$–KSCN and 4,4′-di(3-methyl)pyridyl sulfide (**L**) as building elements with the aim of exploring: (i) whether the organic and inorganic bridging ligands could cooperate together and self-assemble into 3-D coordination polymers; (ii) the anion contribution to the supramolecular architectures in the self-assembly process. The results show that in the self-assembly process, sulfate ion acts as a bridging ligand, which connects each two 2-D plane formed by copper(II) ion with 4,4′-di(3-methyl)pyridyl sulfide, and a 3-D rhombohedral **1** was formed as a result. The 3-D network is composed of a 793 Å^3 rhombic box, and remains stable up to 220 °C. In contrast, SCN$^-$ only mono-coordinated to the copper ion and the self-assembled aggregate, **2**, was a 2-D network. Guest adsorption experiments revealed that in a mixture of water–methanol the coordination polymer **1** could selectively adsorb 4-chlorophenol rather than other aromatic molecules such as nitrobenzene, benzophenone and toluene, and non-aromatic guests such as methanol and DMF; under the same conditions however, **2** does not adsorb any of the above guest molecules.



Scheme 1 Bipyridine bridging ligands.

Experimental

Reagents

The chemicals and solvents used in the synthesis of complexes were of reagent grade and were used without further purification. For the synthesis of ligands the reagents were purified according to the literature methods.[13] The ligand 4,4′-di(3-methyl)pyridyl sulfide (**L**) was prepared according to the previously reported procedure.[14]

Measurements

The Fourier-transform IR spectra were taken on FT-IR 170SX(Nicolet) and Bio-Rad FTS 135 spectrometers, and elemental analyses were recorded on a Perkin-Elmer 240C analyzer. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were performed at a scan rate of 20 °C min^{-1} using a Netzsch TG 209 analyzer under an N_2 atmosphere.

Syntheses

Synthesis of [Cu(L)$_2$SO$_4$]·0.5H$_2$O·0.5CH$_2$Cl$_2$ (1). A solution of $CuSO_4·5H_2O$ (0.18 g, 0.7 mmol) in water (10 mL) and ethanol (4 mL) was layered onto a solution of 4,4′-di-(3-methyl)pyridyl sulfide (**L**) (0.30 g, 1.4 mmol) in CH_2Cl_2 (5 mL). The solutions were left for three weeks at room temperature, and bright blue crystals were obtained in 62% yield. Elemental analysis: calc. for $C_{24.5}H_{26}ClCuN_4O_{4.5}S_3$: C, 45.72; H, 4.07; N, 8.70%. Found: C, 45.32; H, 3.95; N, 8.44%. IR (KBr, diffuse reflectance, cm^{-1}): 3407, 3089, 2480, 1593, 1193, 1102, 1080, 1065, 1001, 836, 708, 612.

Synthesis of [Cu(L)$_2$(SCN)$_2$]·3CHCl$_3$ (2). A solution of $Cu(NO_3)_2·3H_2O$ (0.17 g, 0.7 mmol) in water (10 mL) and ethanol (4 mL) was layered onto a solution of 4,4′-di-(3-methyl)pyridyl sulfide (**L**) (0.30 g, 1.4 mmol) in $CHCl_3$ (5 mL), and then a solution of KSCN (0.194 g, 2 mmol) in 5 mL water was slowly added to the above mixtures. The resulting solutions were left for two days at room temperature, and bright green crystals were gradually formed in ≈70% yield. Elemental analysis: calc. for $C_{29}H_{27}Cl_9CuN_6S_4$: C, 35.88; H, 2.78; N, 8.66%. Found: C, 36.04; H, 2.58; N, 8.74%. IR (KBr pellet, cm^{-1}): 2060, 1593, 1473, 1190, 1073, 838, 707.

X-Ray crystallography

Crystals of **1** and **2** suitable for single-crystal X-ray analysis with sizes 0.15 × 0.25 × 0.30 mm and 0.35 × 0.20 × 0.20 mm, respectively, were selected. Structural analyses for **1** and **2** were performed on a Siemens SMART CCD diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) and the structures were solved by direct methods using the SHELXL-97 package.[15] The crystallographic data are summarized in Table 1, and selected bond distances and angles are given in Table 2.

CCDC reference numbers 168662 and 168663.

See http://www.rsc.org/suppdata/dt/b1/b104515f/ for crystallographic data in CIF or other electronic format.

Guest-adsorption experiment

A few milligrams of dry fine powder of **1** or **2** was immersed in a solution of guest molecules (0.01 M) in water–methanol (3 : 1, v/v) for 24 h at room temperature, and then filtered and dried. For the resulting solid, the FT-IR spectrum was examined and elemental analysis was carried out.

Results and discussion

The choice of building elements was based on the following: first, the pyridines, which are separated by a flexible angle (C–S–C ≈ 103°), could not coordinate to the same metal center simultaneously. Second, SO_4^{2-} and SCN^- can act as bridging ligands so as to connect two copper ions through coordinative interactions.[16] Consequently, if such components play their appropriate roles efficiently in the self-assembly process, the supramolecular architecture formed would be a 3-D or 2-D network that can be dependent on the coordination property of the counter anion.

Table 1 Crystallographic data for **1** and **2**

	1	**2**
Formula	$C_{24.5}H_{26}ClCuN_4O_{4.5}S_3$	$C_{29}H_{27}Cl_9CuN_6S_4$
FW	643.66	970.40
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$	$P2(1)/n$
T/K	298(2)	298(2)
a/Å	18.698(2)	12.588(3)
b/Å	14.3969(18)	18.717(5)
c/Å	12.9711(16)	18.227(5)
β/°	121.106(2)	92.980(5)
V/Å^3	2989.7(6)	4288.6(19)
Z	4	4
ρ_{calc}/g cm^{-3}	1.430	1.503
μ/mm^{-1}	1.067	1.292
Goodness-of-fit on F^2	1.098	1.006
Final $R1$	0.0415 [$I > 2\sigma(I)$] 0.0477, all data	0.0712 [$I > 2\sigma(I)$] 0.1906, all data
$wR2$	0.1256 [$I > 2\sigma(I)$] 0.1319, all data	0.1435 [$I > 2\sigma(I)$] 0.1767, all data

$w = 1/[s^2(F_o^2) + (0.0807P)^2 + 3.7342P]$ where $P = (F_o^2 + 2F_c^2)/3$.

Molecular structure of [Cu(L)$_2$SO$_4$]·0.5H$_2$O·0.5CH$_2$Cl$_2$ (1)

An aqueous ethanol solution of copper sulfate was layered over a dichloromethane solution of 4,4′-di(3-methyl)pyridyl sulfide (**L**), and bright blue crystals [Cu(**L**)$_2$SO$_4$]·0.5H$_2$O·0.5CH$_2$Cl$_2$ ($C_{24.5}H_{26}ClCuN_4O_{4.5}S_3$) were formed in three weeks (62% yield). Elemental analysis of the compound gave satisfactory results. Single-crystal X-ray analysis revealed a unique, three-dimensional polynuclear assembly of Cu(II) ions, wherein each Cu(II) center is bonded to four different molecules of 4,4′-di-(3-methyl)pyridyl sulfide and two sulfates in a six-coordinate manner (Fig. 1). The sulfate actually takes part in coordination and connects each square-planar sheet through coordinative interactions. Notably, in the non-interpenetrating network, each ligand has an extended geometry in which the C–S–C (in **L**) and O–S–O (in sulfate) has inclination angles 103.2 and 109.8°, respectively. There are two types of square sheets in **1**: one is formed from four Cu(II) and four 4,4′-di(3-methyl)-pyridine (type A); the other is formed from four Cu(II), two 4,4′-di(3-methyl)pyridines and two sulfates (type B). In type A, four Cu(II) centers are separated by 4,4′-di(3-methyl)pyridyl sulfide to give a large square arrangement, where each metal ion adopts an octahedral geometry and is bound equatorially to 4,4′-di(3-methyl)pyridyl sulfide ligands and axially to two sulfate ligands. Four copper(II) ions and four 4,4′-di(3-methyl)-pyridines form a 40-membered ring with a Cu···Cu edge length of 10.892 Å. Four of the 4,4′-di(3-methyl)pyridines and two sulfates in the complex all act as bridging ligands, where two **L** are responsible for extending these squares along the crystallographic *a*-axis. The other two **L** extend the structure into the crystallographic *b*-axis. Thus, a two-dimensional square-planar sheet is formed. While sulfates extend the structure into the *c*-axis, thus the structure is composed of boxes (structurally the same as in Fig. 3(b) except that its axial ligand is SO_4^{2-} rather than SCN^-). In type B, two sulfates and two 4,4′-di(3-methyl)pyridyl sulfides form a 28-membered ring and the Cu···Cu distance is 6.846 Å along the *c*-axis (Fig. 2). Unlike other coordination polymers, the sulfate anion possesses a −2 charge and the framework is therefore neutral. More importantly, there is no water molecule coordinated to the metal center. The volume of the rhombohedral ‘box’ is *ca.* 793 Å^3 (calculated from Cu···Cu distances and angles of the rhombic box). On average, each box is filled (occupancy) with 0.5 dichloromethane and 0.5 water molecules that can be easily removed. The box is large enough (40-membered ring in *x*–*y*

Table 2 Selected bond distances (Å) and angles (°) for **1** and **2**

Complex **1**			
Cu(1)–N(1)	2.047(2)	Cu(1)–N(1)#1	2.047(2)
Cu(1)–N(2)#3	2.061(2)	Cu(1)–N(2)#2	2.061(2)
Cu(1)–O(1)#1	2.427(2)	Cu(1)–O(1)	2.427(2)
S(1)–O(1)#4	1.453(2)	S(1)–O(1)	1.453(2)
S(1)–O(2)#4	1.458(4)	S(1)–O(2)	1.458(4)
N(2)–Cu(1)#5	2.061(2)		
N(1)#1–Cu(1)–N(2)#2	90.46(9)	N(1)–Cu(1)–N(1)#1	180.00(18)
N(1)#1–Cu(1)–N(2)#3	89.54(9)	N(1)–Cu(1)–N(2)#2	89.54(9)
N(1)–Cu(1)–O(1)	88.35(9)	N(1)–Cu(1)–N(2)#3	90.46(9)
N(2)#2–Cu(1)–O(1)	90.47(9)	N(2)#2–Cu(1)–N(2)#3	180.00(8)
N(1)–Cu(1)–O(1)#1	91.65(9)	N(1)#1–Cu(1)–O(1)	91.65(9)
N(2)#2–Cu(1)–O(1)#1	89.53(9)	N(2)#3–Cu(1)–O(1)	89.53(9)
O(1)–Cu(1)–O(1)#1	180.00(9)	N(1)#1–Cu(1)–O(1)#1	88.35(9)
O(1)–S(1)–O(2)	108.0(2)	N(2)#3–Cu(1)–O(1)#1	90.47(9)
O(1)–S(1)–O(2)#4	108.4(2)	O(1)–S(1)–O(1)#4	109.8(2)
O(2)–S(1)–O(2)#4	114.2(5)	O(1)#4–S(1)–O(2)	108.4(2)
C(3)–S(2)–C(7)	103.24(13)	O(1)#4–S(1)–O(2)#4	108.0(2)
C(5)–N(1)–C(1)	117.4(2)	S(1)–O(1)–Cu(1)	171.23(15)
Complex **2**			
Cu(1)–N(6)	1.969(7)	Cu(1)–N(5)	1.971(7)
Cu(1)–N(3)	2.070(5)	Cu(1)–N(4)#1	2.084(5)
Cu(1)–N(1)	2.438(6)	N(1)–C(5)	1.336(8)
N(2)–C(9)	1.307(9)	N(4)–Cu(1)#2	2.084(5)
N(6)–Cu(1)–N(5)	178.7(2)	N(6)–Cu(1)–N(3)	90.0(2)
N(5)–Cu(1)–N(3)	90.8(2)	N(6)–Cu(1)–N(4)#1	89.4(2)
N(5)–Cu(1)–N(4)#1	89.8(2)	N(3)–Cu(1)–N(4)#1	179.2(2)
N(6)–Cu(1)–N(1)	90.7(2)	N(5)–Cu(1)–N(1)	90.3(2)
N(3)–Cu(1)–N(1)	92.8(2)	N(4)#1–Cu(1)–N(1)	87.82(19)
C(5)–N(1)–C(1)	117.1(6)	C(5)–N(1)–Cu(1)	122.9(5)
C(17)–N(3)–Cu(1)	121.6(5)	C(13)–N(3)–Cu(1)	122.2(4)
C(22)–N(4)–C(21)	117.2(6)	C(22)–N(4)–Cu(1)#2	121.1(5)
C(21)–N(4)–Cu(1)#2	121.7(5)	C(24)–N(5)–Cu(1)	160.7(6)
C(3)–S(1)–C(7)	102.9(3)	C(19)–S(2)–C(15)	103.4(3)

Symmetry transformations used to generate equivalent atoms: For **1**: #1 $-x, -y, -z$; #2 $-x + 1/2, y - 1/2, -z + 1/2$; #3 $x - 1/2, -y + 1/2, z - 1/2$; #4 $-x, y, -z + 1/2$; #5 $-x + 1/2, y + 1/2, -z + 1/2$. For **2**: #1 $x - 1/2, -y + 1/2, z - 1/2$; #2 $x + 1/2, -y + 1/2, z + 1/2$.

plane and 28-membered ring in the *z*-axis) to accommodate some small neutral molecules. To the best of our knowledge, the coordination polymer is the first 3-D non-interpenetrated architecture bridged by sulfate ion which is remarkably different to that of the 1-D chain polymer, in which sulfate ion is only mono-coordinated to the metal center.[17]

Molecular structure of [Cu(L)$_2$(SCN)$_2$]·3CHCl$_3$ 2

It is known that when KSCN reacts with Cu(NO$_3$)$_2$ a dark coordination polymer of Cu(SCN)$_2$ results. In order to avoid the dark polymer, layering experiments using Cu(NO$_3$)$_2$·3H$_2$O in water and ethanol with **L** in CHCl$_3$ have been employed to yield crystals suitable for X-ray structural study.

Single-crystal X-ray analysis revealed a new, two-dimensional polynuclear assembly of Cu(II) ions as infinite planar arrays wherein each Cu(II) center is bonded to two different molecules of 4,4′-di(3-methyl)pyridyl sulfide and two SCN$^-$ in a six-coordination mode (Fig. 3). Coordination to the Cu(II) center in **2** is provided by four pyridine groups of 4,4′-di(3-methyl)pyridyl sulfide, resulting in an almost square-planar arrangement (the same as that in **1**). The remaining coordinating sites are provided by two SCN$^-$ modifying the coordination geometry to an octahedral environment. As a result there is only a two-dimensional network with no interpenetration. The bent angle of the sulfur atom adopts C–S–C = 103°, which is identical to complex **1** and indicates that the axial ligand has no influence on the ligand structure. The structure of complex **2** is actually the same as that of **1** in ligand–copper(II) two-dimensional (*a* and *b* direction) structure. However, the central symmetry in **1** is totally absent in **2**. In complex **1**, there are actually two different ligands which coordinate to copper(II) at 2.047 and 2.061 Å, respectively and SO$_4^{2-}$ is coordinated to copper axially at 2.427 Å. In **2**, all four ligands are different. All N(py)–Cu distances are longer than those in **1**, and SCN$^-$ coordinates to copper much more strongly than does the pyridine nitrogen atom. The two pyridine groups in **2** should be treated as axially coordinated ligands (2.44 Å). Four copper(II) ions and four 4,4′-di(3-methyl)pyridyl sulfides form a 40-membered ring with an internuclear Cu–Cu distance of around 12.588, 10.803 and 11.342 Å, which is longer than that in **1** due to the weak coordination of the pyridines. These structures show that the strongly coordinating SCN$^-$ ligand leads to significant changes in the structure of the complex, in that two pyridine ligands become axial and coordinate to copper very weakly. From the structure (bond distances) we can see that **2** is less stable than **1**. We can further prove this from TA and DTA curves as shown below.

A noteworthy feature of the planar assembly is the presence of SCN$^-$ instead of NO$_3^-$. The crystal structure further showed that the nitrate was actually not included in the coordination polymer **2** and was entirely exchanged by SCN$^-$ instead. IR spectra showed that there was no absorption of NO$_3^-$ around 1384 cm^{-1} in **2**, while IR absorption around 2060 cm^{-1} could be ascribed to SCN$^-$, indicating that SCN$^-$ was mono-coordinated to the metal ion.[18]

From the above X-ray analysis results, we see that both **1** and **2** form non-interpenetrating structures which are significantly different from those of bipyridine derivatives that have interpenetrating structures[12*b*] or smaller microchannels.[12*c*] The structures of **1** and **2** are also distinguished from those of Co(SCN)$_2$ and CoCl$_2$ with 4,4′-dipyridyl sulfide,[11] in which the former is a double-stranded chain structure and the latter a two-layer interwoven sheet structure. In addition, **1** differs from **2** in that **1** is a 3-D while **2** is a 2-D network, and we can ascribe the different coordination structures of **1** and **2** to the counter anion

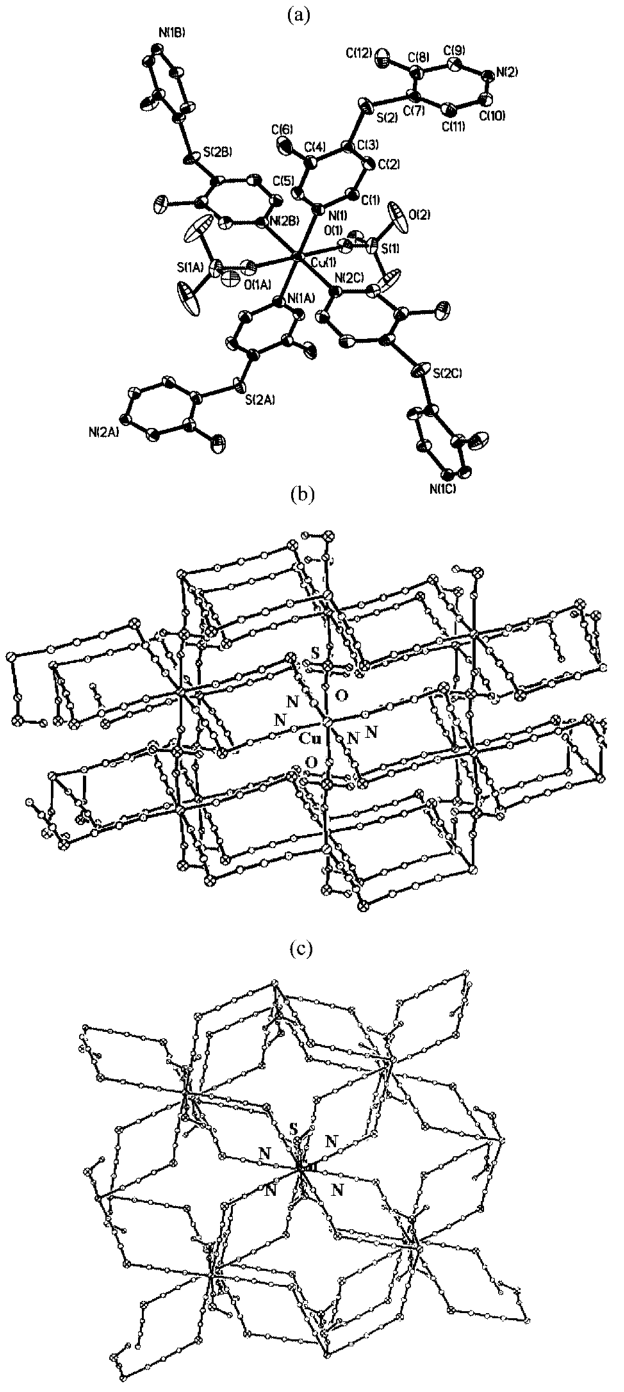


Fig. 1 (a) A view of the copper(II) coordination environment in **1**. (b) A view of **1** along the *b*-axis that illustrates the each two-dimensional square connected by sulfate. (c) A view of **1** along the *c*-axis that illustrates the planar arrangement formed by copper with 4,4-di-(3-methyl)pyridyl sulfide. For clarity the disordered water and dichloromethane are omitted and the pyridyl group was placed by its ring baricenter.

control in the self-assembly, SO_4^{2-} acting as a bridge connecting two metal centers and SCN^- being a mono-coordinating ligand. Therefore, we might conclude that in the self-assembly process of organic ligand and metal ion, not only does the metal ion play a crucial role in determining the structure of the supramolecular aggregate, but the counter anion also plays a key role.

Thermogravimetric analysis (TGA)

In Fig. 4, it is seen that the coordination polymer **1** is very stable, it does not decompose upon exposure to the atmosphere. The TGA trace displays a gradual weight loss of 10.6% (calculated 8.0%) from 40–140 °C, which corresponds to the weight of 0.5 water and 0.5 CH_2Cl_2, and the complex remains stable up to 220 °C. When the temperature exceeds 240 °C the complex then slowly decomposes with loss of ligand and sulfate ion to yield the metal oxide. In contrast **2** is stable up to only 140 °C. As the temperature is gradually increased, coordination polymer **2** decomposes with the evaporation of ligand **L** and decomposition of SCN^-. From Fig. 5 it can be seen that the two decomposition processes may take place simultaneously.

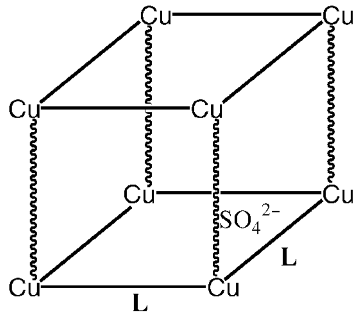


Fig. 2 Schematic representation of the rhombohedral unit in the non-interpenetrating three-dimensional network formed by **L** [4,4-di-(3-methyl)pyridyl sulfide] with copper sulfate.

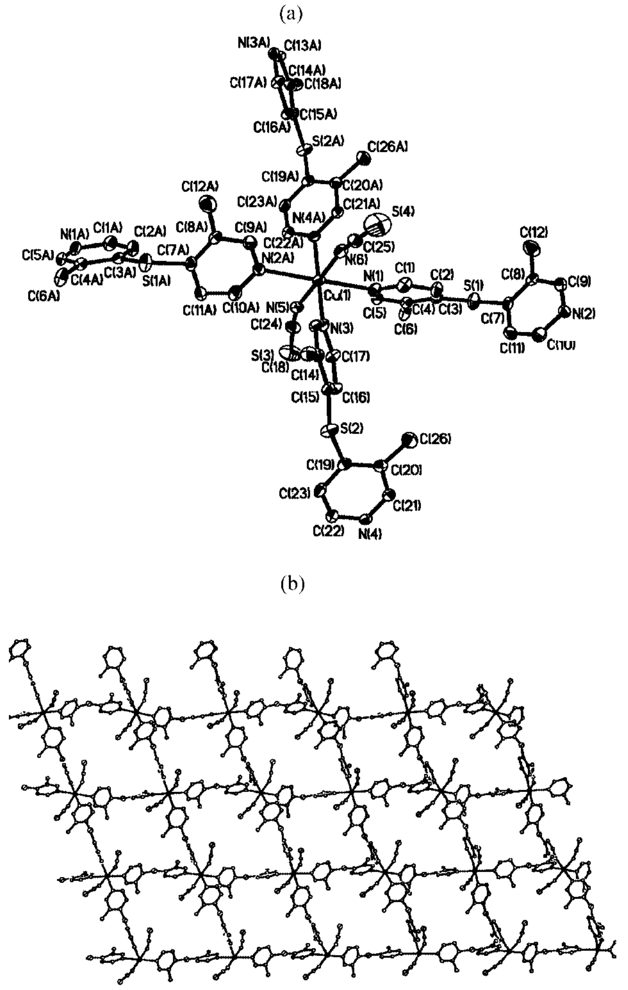


Fig. 3 (a) A view of the copper(II) coordination environment in **2**. (b) A view of the 2-D network in **2**.

Comparison of Fig. 4 and 5 shows that the 3-D coordination polymer **1**, formed by **L** and copper sulfate, is much more stable than the 2-D coordination polymer **2**, formed from **L**, copper ion and SCN^-. Bridging the 2-D complex polymer to give a 3-D complex polymer will increase its thermal stability, as observed in organic polymers. The thermal analysis is in good agreement with the X-ray structure.

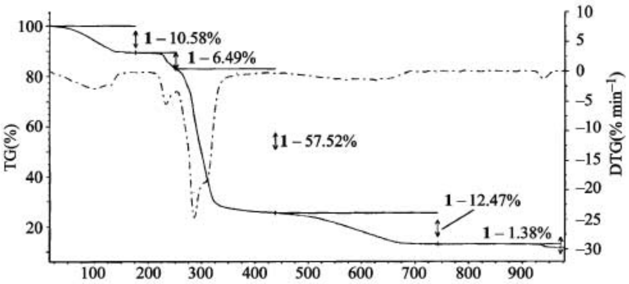


Fig. 4 Overlay of TG and DTG traces of the 3-D coordination polymer **1**. The sample was heated at 20 °C min^{-1} in a nitrogen atmosphere from 20 °C.

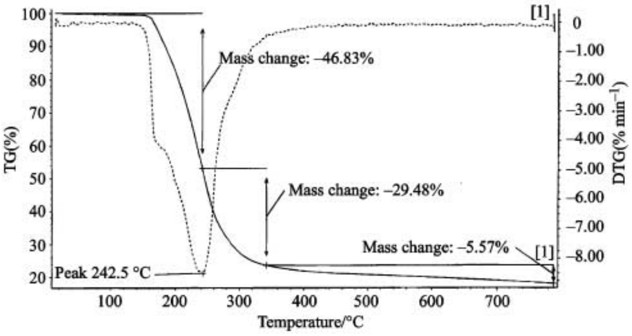


Fig. 5 Overlay of TG and DTG traces of the 2-D coordination polymer **2**. The sample was heated at 20 °C min^{-1} in a nitrogen atmosphere from 20 °C.

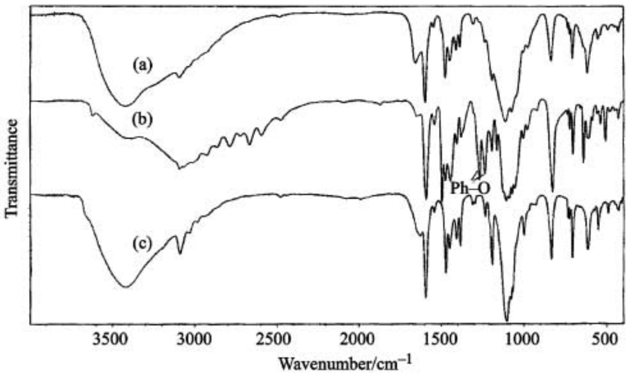


Fig. 6 IR spectra of: (a) The resulting solid of the adduct of **1** with 4-chlorophenol after soaking in DMF; (b) adduct of **1** with 4-chlorophenol; (c) **1**.

Guest-adsorption

To evaluate the framework rigidity of **1**, the absorption of guests was examined by FT-IR spectroscopy and elemental analysis. The experiments were performed by immersing a powder sample of **1** in a methanol–water (1 : 3, v/v) solution of guest. After filtration and drying, a solid containing 4-chlorophenol was obtained (the resulting solid was darker compared to free **1**). The Fourier-transform of the infrared spectrum of the resulting solid showed peak absorption of $\nu_{\mathrm{C-O}}$ at 1270 and 1237 cm^{-1}, corresponding to that of 4-chlorophenol (Fig. 6), which was further confirmed by elemental analysis. Elemental analysis indicated that the coordination polymer **1** included two 4-chlorophenol molecules. Anal. calc. for $(\mathbf{L})_2\mathrm{CuSO_4}\cdot 2\mathrm{G}$ (G: 4-chlorophenol): C, 50.91; H, 4.00; N, 6.60%. Found: C, 51.25; H, 4.08; N, 6.38%. IR (KBr pellet, cm^{-1}): 3386, 3094, 2929, 1591, 1495, 1475, 1445, 1270, 1237, 1108, 1089, 829, 705, 642, 507.

For other aromatic molecules such as nitrobenzene and benzophenone and aromatic free guests such as DMF, there was no characteristic FT-IR absorption for the respective guest in the resulting solid under the same conditions as for 4-chlorophenol. This means that the polymer **1** does not adsorb guests that only contain active hydrogen such as DMF or aromatic groups such as nitrobenzene and benzophenone. Thus it may be concluded that the driving force for absorbing guest is the cooperation of hydrogen bonding and π–π interactions.

Interestingly, the absorption of 4-chlorophenol is reversible. Once the adduct of 4-chlorophenol with **1** was immersed in methanol or DMF for 12 h, the color of the solid changed slowly from brown to light blue, which was that of free **1** as shown in the IR spectra (Fig. 6). This indicates that the structure of complex **1** remains intact after or during guest removal. In our opinion, copper(II) favors nitrogen rather than oxygen, 4-chlorophenol has much a weaker coordination ability compared with pyridine. It cannot act as a bridging ligand either so the adsorbed guest cannot break down the coordination polymer structure in **1** which may be the reason why the adsorption is reversible.

IR spectra show that under the same conditions **2** does not adsorb any of the above mentioned guest molecules.

The comparison of guest adsorption experiments for **1** and **2** might lead to the conclusion that in the methanol–water solution, coordination polymer **1** could adsorb *para*-substituted phenol, while **2** does not. The different adsorbing ability for guest molecules might be ascribed to the different structures of **1** and **2**. As for **1**, it has a rhombohedral 'box' with a volume of about 793 Å^3 that can accommodate guests, pyridines that can interact with guest molecules through π–π stacking and $\mathrm{SO_4}^{2-}$ that has oxygen to interact with guests through hydrogen bonding. The 'box' can also greatly stabilize guests. For **2**, although it also has pyridines that can interact with guest molecules through π–π stacking and a square cavity that can also be filled with guest species,[19] the coordinated SCN^- cannot interact with guest molecules through hydrogen bonding. Therefore, we might conclude that the 3-D 'box' and/or anion in the self-assembled aggregates plays a crucial role in the guest adsorption ability and the existence of C–S–C might decide whether or not the guest can be selectively adsorbed.

Conclusion

In summary, we represent here two novel non-interpenetrating 3-D and 2-D coordination networks of Cu(II) with dipyridyl sulfides, the structures of which are anion dependent. A noteworthy feature of the self-assembled aggregate box is the presence of sulfate on the modules which connect planar sheets, formed by copper and 4,4′-di(3-methyl)pyridyl sulfides, into a three-dimensional network *via* coordinative interaction, resulting in considerably large cavities. Cu^{2+}–SCN^- and 4,4′-di(3-methyl)pyridyl sulfides self-assembled into a non-interpenetrated 2-D network, indicating the important role played by the counter anion in the self-assembly process. In addition, through H-bonding or the 3-D 'box' structure, the counter anion in the coordination polymer may decide whether guest molecules can be adsorbed selectively. It is clear that the cavity possessed by coordination polymer **1** has the potential to selectively include large guest molecules, and we are currently exploring the effects of guest size and anions on controlling the formation of this type of non-interpenetrating structure.

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References

1 (*a*) J.-M. Lehn, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 1304; (*b*) S. R. Batten and R. Robson, *Angew. Chem., Int. Ed.*, 1998, **37**, 1460; (*c*) O. M. Yaghi, H. Li and T. L. Groy, *Inorg. Chem.*, 1997, **36**,

4292; (*d*) M. Fujita, Y. J. Kwon, S. Washizu and K. Ogura, *J. Am. Chem. Soc.*, 1994, **116**, 1151.

2 P. J. Hagrman, D. Hagrman and J. Zubieta, *Angew. Chem., Int. Ed.*, 1999, **38**, 2638.

3 (*a*) O. M. Yaghi, H. Li, C. Davis, D. Richardson and T. L. Groy, *Acc. Chem. Res.*, 1998, **31**, 474; (*b*) P. J. Stang and B. Olenyuk, *Acc. Chem. Res.*, 1997, **30**, 502.

4 (*a*) J. Kim, D. Whang, J. I. Lee and K. Kim, *J. Chem. Soc., Chem. Commun.*, 1993, 1400; (*b*) O. M. Yaghi, G. Li and H. Li, *Nature*, 1995, **378**, 703.

5 R. H. Groeneman, L. R. MacGillivray and J. L. Atwood, *Chem. Commun.*, 1998, 2735.

6 (*a*) H. J. Choi and M. P. Suh, *Inorg. Chem.*, 1999, **38**, 6309; (*b*) K. S. Min and M. P. Suh, *J. Am. Chem. Soc.*, 2000, **122**, 6834.

7 (*a*) A. J. Blake, S. J. Hill, P. Hubberstey and W.-S. Li, *J. Chem. Soc., Dalton Trans.*, 1997, 913; (*b*) M. X. Li, G. Y. Xie, Y. D. Gu, J. Chen and P. J. Zheng, *Polyhedron*, 1995, **14**, 1235; (*c*) X.-M. Chen, M.-L. Tong, Y.-J. Luo and Z.-N. Chen, *Aust. J. Chem.*, 1996, **49**, 835; (*d*) L. Carlucci, G. Ciani, D. M. Proserpio and A. Sironi, *J. Chem. Soc., Dalton Trans.*, 1997, 1801; (*e*) J. Li, H. Zeng, J. Chen, Q. Wang and X. Wu, *Chem. Commun.*, 1997, 1213.

8 (*a*) M. Kondao, T. Yoshitomi, K. Seki, H. Matsuzaka and S. Kitagawa, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1725; (*b*) O. M. Yaghi and G. Li, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 207; (*c*) M.-L. Tong, B.-H. Ye, J.-W. Cai, X.-M. Chen and S. W. Ng, *Inorg. Chem.*, 1998, **37**, 2645.

9 (*a*) L. Carlucci, G. Ciani, D. M. Proserpio and A. Sironi, *J. Chem. Soc., Chem. Commun.*, 1994, 2755; (*b*) S. Lopez, M. Kahraman, M. Harmata and S. W. Keller, *Inorg. Chem.*, 1997, **36**, 38; (*c*) O. M. Yaghi and H. Li, *J. Am. Chem. Soc.*, 1995, **117**, 10401; (*d*) K. N. Power, T. L. Hennigar and M. J. Zaworotko, *Chem. Commun.*, 1998, 595; (*e*) M. O'Keeffe, *Nature*, 1998, **392**, 879.

10 (*a*) L. Carlucci, G. Ciani, D. M. Proserpio and A. Sironi, *Chem. Commun.*, 1996, 1393; (*b*) P. C. M. Duncan, D. M. L. Goodgame, S. Menzer and D. J. Williams, *Chem. Commun.*, 1996, 2127; (*c*) M. A. Withersby, A. J. Blake, N. R. Champness, P. Hubberstey, W.-S. Li and M. Schröder, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2327 and references therein.

11 O.-S. Jung, S. H. Park, D. C. Kim and K. M. Kim, *Inorg. Chem.*, 1998, **37**, 610.

12 (*a*) A. J. Blake, N. R. Champness, P. Hubberstey, W.-S. Li, M. A. Withersby and M. Schröder, *Coord. Chem. Rev.*, 1999, **183**, 117; (*b*) M. A. Withersby, A. J. Blake, N. R. Champness, P. A. Cooke, P. Hubberstey, A. L. Realf, S. J. Teat and M. Schröder, *J. Chem. Soc., Dalton Trans.*, 2000, 3261; (*c*) M. Kondo, M. Shimamura, S. Noro, Y. Kimura, K. Uemura and S. Kitagawa, *J. Solid State Chem.*, 2000, **152**, 113.

13 D. D. Perrin, W. L. F. Armarego and D. R. Perrin, *Purification of Laboratory Chemicals*, 4th edn., Pergamon Press, Oxford, England, 1996.

14 L. A. Summers, *J. Heterocycl. Chem.*, 1987, **24**, 533.

15 G. M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, University of Göttingen, Germany, 1997.

16 J. E. Huheey, *Inorganic Chemistry: Principles of Structure and Reactivity*, 3rd edn., Harper & Row, New York, USA, 1983.

17 D. Hagrman, R. P. Hammond, R. C. Haushalter and J. Zubieta, *Chem. Mater.*, 1998, **10**, 2091.

18 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordinated Compounds*, 4th edn., Wiley & Sons, New York, USA, 1986.

19 M. Fuijita, Y. J. Kwon, S. Washizu and K. Ogura, *J. Am. Chem. Soc.*, 1994, **116**, 611.