

# Self-Assembly of Three Cd<sup>II</sup>- and Cu<sup>II</sup>-Containing Coordination Polymers from 4,4'-Dipyridyl Disulfide

Junhua Luo,<sup>[a]</sup> Maochun Hong,<sup>\*[a]</sup> Ruihu Wang,<sup>[a]</sup> Daqiang Yuan,<sup>[a]</sup> Rong Cao,<sup>[a]</sup> Lei Han,<sup>[a]</sup> Yanqing Xu,<sup>[a]</sup> and Zhengzhong Lin<sup>[a]</sup>

**Keywords:** Cadmium / Coordination polymers / Copper / Fluorescence / Magnetic properties / N ligands

Three new organic/inorganic coordination polymers,  $[\{\text{Cu}(\text{4-DPDS})_2(\text{H}_2\text{O})\} \cdot 2\text{NO}_3 \cdot 3\text{H}_2\text{O}]_n$  (**1**),  $[\{\text{Cu}(\text{4-DPDS})_2(\text{SO}_4)\} \cdot 1.5\text{H}_2\text{O} \cdot \text{CH}_3\text{OH}]_n$  (**2**), and  $[\text{Cd}(\text{4-DPDS})_2\text{Cl}_2]_n$  (**3**), have been synthesized by using the flexible ligand 4,4'-dipyridyl disulfide (4-DPDS). Complex **1** crystallized in the *Ibca* space group:  $a = 10.5275(6)$ ,  $b = 20.2670(1)$ ,  $c = 27.235(1)$  Å,  $V = 5811.5(6)$  Å<sup>3</sup>,  $Z = 16$ . Complex **2** crystallized in the *Pnna* space group:  $a = 10.547(2)$ ,  $b = 14.201(2)$ ,  $c = 19.667(3)$  Å,  $V = 2945.8(8)$  Å<sup>3</sup>,  $Z = 8$ . Complex **3** crystallized in the *P2<sub>1</sub>/c* space group:  $a = 7.6146(3)$ ,  $b = 18.2606(8)$ ,  $c = 9.3203(2)$  Å,  $\beta =$

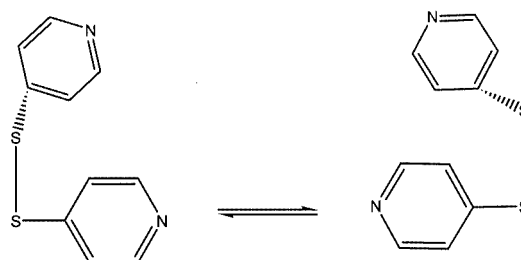
100.26(1)°,  $V = 1275.24(8)$  Å<sup>3</sup>,  $Z = 4$ . The three coordination polymers display a variety of structural architectures, ranging from double-stranded chains (**1**) to two-dimensional channels (**2**) and two-dimensional, puckered, grid-like arrays (**3**). Magnetic characterizations show that complex **1** exhibits antiferromagnetic interactions while **2** is ferromagnetic. Solid-state fluorescence results reveal that **3** exhibits fluorescence emissions at 418 and 575 nm ( $\lambda_{\text{ex}} = 314$  nm). (© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2003)

## Introduction

Self-assembly of organic ligands and inorganic metal ions is one of the most efficient and widely used approaches for the construction of supramolecular architectures. Owing to their potential as new functional solid materials, interest in self-assembled coordination polymers with interesting physical properties has grown rapidly.<sup>[1,2]</sup> An extensive amount of literature exists on networks crystallized from different dipyridyl ligands. A variety of architectures have been obtained over the past few years using the most simple of these ligands, i.e., 4,4'-bipyridyl.<sup>[3,4]</sup> The use of longer bis(pyridyl) spacers has afforded very interesting structural motifs, such as double helices,<sup>[5]</sup> multiple sheets,<sup>[6]</sup> interpenetrated ladders,<sup>[7]</sup> interpenetrated diamondoid nets,<sup>[8]</sup> and other noteworthy species.<sup>[9]</sup> Many of the architectures reported to date, however, are based upon rigid, linear, linker ligands, with only recent efforts being focused on the use of ligands showing conformational flexibility.<sup>[5,6,10,11]</sup> In addition, the design of coordination polymers from flexible ligands is highly influenced by factors such as the nature of coordination of the metal ion, the structural characteristics of the polydentate organic ligand, the metal:ligand ratio, and the possible influences of the counteranion and solvent. Thus, there is still a long way to go to rationalize the design of compounds with well-defined structures and useful func-

tions by developing new architectures of coordination polymers using flexible spacers ligands.

In this report, we focus on 4,4'-dipyridyl disulfide (4-DPDS), in which the two pyridyl rings are bridged by the –S–S– group. Two enantiomeric conformers exist<sup>[12]</sup> (Scheme 1) with idealized dihedral angles (C–S–S–C) of 90° and the compound may assume a twisted conformation because of the flexible –S–S– group. Additionally, the bridging S atom has coordinating ability, which may lead to unique network structures because of its bonding ability to soft metal ions.<sup>[13]</sup> Several coordination polymers have been reported recently from the reaction of 4-DPDS with CuI,<sup>[14]</sup> M(hfac)<sub>2</sub> (M = Cu, Mn; hfac = 1,1,1,5,5,5-hexafluoroacetylacetone),<sup>[15]</sup> Cd(NO<sub>3</sub>)<sub>2</sub>,<sup>[16]</sup> platinum(II) subunits,<sup>[17]</sup> and various silver salts.<sup>[18]</sup> In this report, we describe the syntheses, structures, and properties of three new Cd<sup>II</sup>- and Cu<sup>II</sup>-containing coordination polymers,  $[\{\text{Cu}(\text{4-DPDS})_2(\text{H}_2\text{O})\} \cdot 2\text{NO}_3 \cdot 3\text{H}_2\text{O}]_n$  (**1**),  $[\{\text{Cu}(\text{4-DPDS})_2(\text{SO}_4)\} \cdot 1.5\text{H}_2\text{O} \cdot \text{CH}_3\text{OH}]_n$  (**2**), and  $[\text{Cd}(\text{4-DPDS})_2\text{Cl}_2]_n$  (**3**).



Scheme 1. The two enantiomeric conformers of 4-DPDS

<sup>[a]</sup> State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian, 350002, China  
Fax: (internat.) + 86-591/371-4946  
E-mail: hmc@ms.fjirsm.ac.cn

## Results and Discussion

## Crystal Structures

The energy-dispersive X-ray analyses confirm the presence of copper atoms in **1** and **2**, and cadmium atoms in **3**. On the basis of the results of single-crystal X-ray diffraction and elemental analyses, compounds **1**, **2**, and **3** are characterized as having the formulas  $[\{\text{Cu}(\text{4-DPDS})_2(\text{H}_2\text{O})\} \cdot 2\text{NO}_3 \cdot 3\text{H}_2\text{O}]_n$ ,  $[\{\text{Cu}(\text{4-DPDS})_2(\text{SO}_4)\} \cdot 1.5\text{H}_2\text{O} \cdot \text{CH}_3\text{OH}]_n$ , and  $[\text{Cd}(\text{4-DPDS})_2\text{Cl}_2]_n$ , respectively.

 $[\{\text{Cu}(\text{DPDS})_2(\text{H}_2\text{O})\} \cdot 2\text{NO}_3 \cdot 3\text{H}_2\text{O}]_n$  (**1**)

Figure 1 shows the ORTEP drawing of the copper center of **1**, with a numbering scheme, where the metal sites are in the crystallographic inversion center. The copper atom has a distorted square-pyramidal environment, which is surrounded by four nitrogen atoms from four 4-DPDS ligands in the base plane, and one oxygen atom from a water molecule occupying the axial position. The Cu–N(4-DPDS) bond lengths are 2.032(1) and 2.061(1) Å, and the Cu–O(water) distance is 2.305(1) Å. The *trans* N–Cu–N bond angles are 167.29(6) and 176.9(6)°, and the *cis* N–Cu–N and O–Cu–N bond angles range from 88.5(3) to 96.4(3)°, indicating the distorted square-pyramidal coordination environment of Cu center.

Each copper center is bridged by four 4-DPDS ligands to form a double-stranded chain (Figure 2). As in other double-stranded chain complexes,<sup>[20,21]</sup> two copper atoms

and two 4-DPDS ligands in **1** form a metallacycle in which the non-bonded distance between the two copper atoms is ca. 10.528 Å. The two pyridyl rings of the 4-DPDS ligand are almost perpendicular, with a dihedral angle of 98.6°. The dimensions of the distorted square cavity are ca.  $5 \times 5$  Å. The molecular box in **1** is twisted to make the enclosed cavity a small one, resulting from the flexibility of 4-DPDS and the pentacoordinate geometry of the Cu<sup>II</sup> ion, and no solvent molecules are clathrated in the cavities.

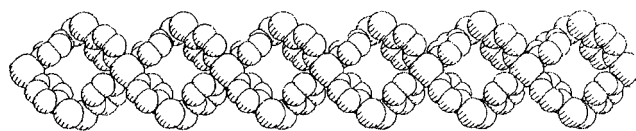


Figure 2. Space-filling representation of the double-stranded chain in **1**

It is interesting to note that in **1** the copper(II) ion has a pentacoordinate geometry and the water molecule occupies the axial position, and that all the axially coordinated water molecules are directed in the same direction. Two such chains lie reversibly and are linked into a ladder structure through hydrogen bonds between the axially coordinated water molecules and lattice water molecules (O1...O1W<sup>#1</sup>, 2.770 Å; O1...O1W<sup>#2</sup>, 2.770 Å; O1W...O1W<sup>#3</sup>, 2.785 Å; O1W...O2W<sup>#4</sup>, 2.769 Å; symmetry codes #1:  $-x, -y, 1-z$ ; #2:  $x, y-1/2, 1-z$ ; #3:  $1/2-x, y, 1-z$ ; #4:  $1/2+x,$

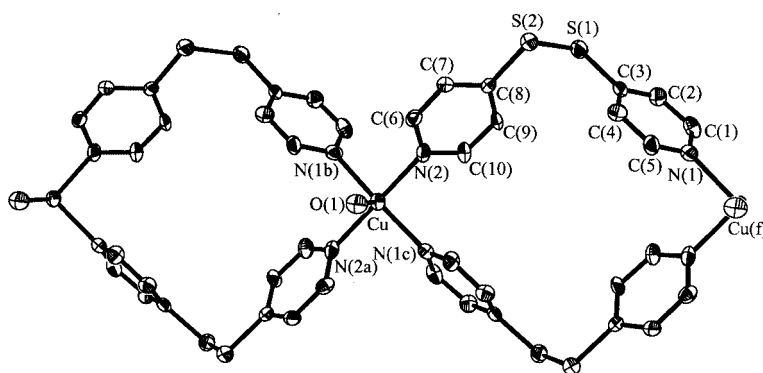


Figure 1. Drawing of the Cu<sup>II</sup> ion coordination environment in **1**, and the atom numbering scheme

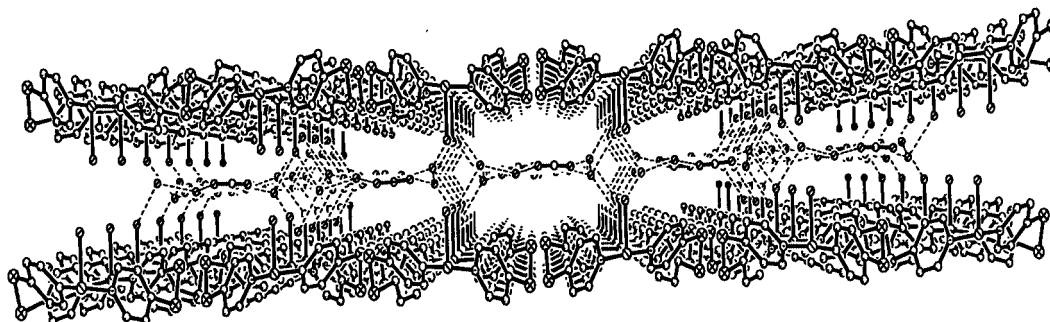


Figure 3. View of the double layer formed by hydrogen bond-mediated linking of the double-stranded chains in **1**

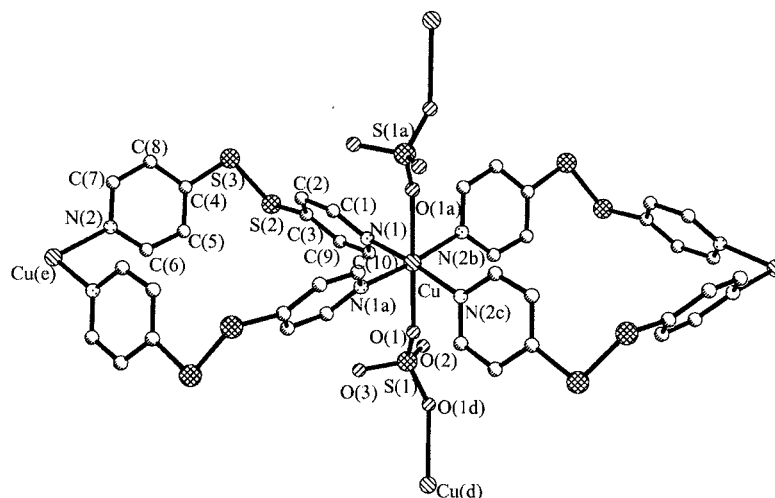


Figure 4. Drawing of the coordination environment of the Cu<sup>II</sup> ion in **2**, and the atom numbering scheme

$x, y, 1 - z$ ) and, furthermore, the ladders are linked into a bilayer through hydrogen bonds between free NO<sub>3</sub><sup>−</sup> anions and the lattice water molecules (O1W...O5<sup>#1</sup>, 2.720 Å; O2W...O4<sup>#2</sup>, 2.893 Å; O2W...O4<sup>#3</sup>, 2.893 Å; symmetry codes #1:  $1/2 + x, y, 1 - z$ ; #2:  $x - 1/2, 1/2 - y, 1 - z$ ; #3:  $-x - 3/2, -y, z - 1/2$ ), as depicted in Figure 3.

#### [{Cu(DPDS)<sub>2</sub>(SO<sub>4</sub>)}·1.5H<sub>2</sub>O·CH<sub>3</sub>OH]<sub>n</sub> (**2**)

Single-crystal X-ray crystallographic analysis of **2** revealed a two-dimensional assembly of Cu<sup>II</sup> ions, wherein each Cu<sup>II</sup> center is bonded to four different molecules of 4,4'-dipyridinedisulfide and two sulfate anions in a six-coordinate manner (Figure 4). Four nitrogen atoms from four 4-DPDS ligands coordinate to the copper(II) center in the base plane, and two oxygen atoms from two sulfate anions are located in the axial positions of the distorted octahedral geometry of the copper(II) center. The Cu–N(4-DPDS) bond lengths are 2.037(8) and 2.040(7) Å, which are similar to those of **1** and the 1D helical compound [4-DPDS·Cu(hfac)<sub>2</sub>]<sup>[15]</sup>. The *cis* N–Cu–N and O–Cu–N bond angles vary from 84.5(2) to 91.1(4)°, and the *trans* O(SO<sub>4</sub><sup>2−</sup>)–Cu–O(SO<sub>4</sub><sup>2−</sup>) bond angle is 179.4(1)°.

Each copper ion is bridged by four 4-DPDS ligands to form a double-stranded chain. The sulfate anions take part in coordination and connect the double-stranded chains into a 2D sheet, as shown in Figure 5(a). The axial Cu–O(SO<sub>4</sub><sup>2−</sup>) distance is 2.459(5) Å, which is similar to that found in other copper sulfate complexes,<sup>[22]</sup> and it is longer than the Cu–O(aqu) distance in **1**. The Cu...Cu separation through the sulfate anion is 7.118 Å, which is much shorter than the Cu...Cu separation through the bridge ligand 4-DPDS, which has a distance of 10.547 Å. Viewed along the *b* axis [Figure 5(b)], there are many one-dimensional channels in the 2D structure that are formed by the metallacycles [Cu<sub>2</sub>(4-DPDS)<sub>2</sub>]<sup>2+</sup> linked by the sulfate anions, and these 1D channels are connected through the copper(II) centers to form the ultimate 2D sheets of **2**.

#### [Cd(DPDS)<sub>2</sub>Cl<sub>2</sub>]<sub>n</sub> (**3**)

The crystallographic analysis reveals that each cadmium(II) ion in **3** is coordinated by four nitrogen atoms from four 4-DPDS ligands and two chloride ions in a slightly distorted octahedral geometry (Figure 6). The four nitrogen atoms form the equatorial plane with the Cd center located in the plane, with the deviation of the Cd ion from the mean plane of [N(1b)N(1c)N(2a)] being 0.008(2) Å, and two Cl<sup>−</sup> ions occupy the axial positions with a Cl–Cd–Cl(c) angle of just 180°.

Each 4-DPDS ligand acts as a single bridge to link two cadmium(II) ions through its two pyridine nitrogen atoms, and each cadmium(II) ion connects four 4-DPDS ligands to form an infinite two-dimensional structure with (4,4) topology, as shown in Figure 7. The cadmium(II) atoms, all of which are equivalent, serve as nodes and the ligands (L = 4-DPDS) as rods. Thus, the network is based upon squares (CdL)<sub>4</sub> formed by four 4-DPDS ligands and four quadruply connected cadmium(II) ions, forming 44-membered metallacyclic rings. Each of the four (CdL)<sub>4</sub> grids are joined together through sharing the cadmium apices to give the final two-dimensional layer structure consisting of puckered rhombus grids with dimensions of 12.265 × 12.265 Å based on the Cd...Cd distances. The most intriguing feature of the structure is that the basic grid is puckered (Figure 8), which is a different arrangement from that observed in previous grid-like structure in which the basic grids are usually coplanar or quasi-coplanar.<sup>[23]</sup> The puckered shape of the basic grid in **3** is understandable because the 4-DPDS unit may assume a twisted conformation because of the flexible –S–S– bridging group, which generates the non-linear grid sides and the puckered grids. The C–S–S angles of the 4-DPDS ligand are 105.1(2) and 106.3(2)°, the C–S–S–C torsion angle is 95.1°, and the two pyridine rings in each 4-DPDS ligand are almost perpendicular to one another with a dihedral angle of 81.9°. These data clearly depict the non-linear configuration of 4-DPDS in **3**. We note that the ulti-

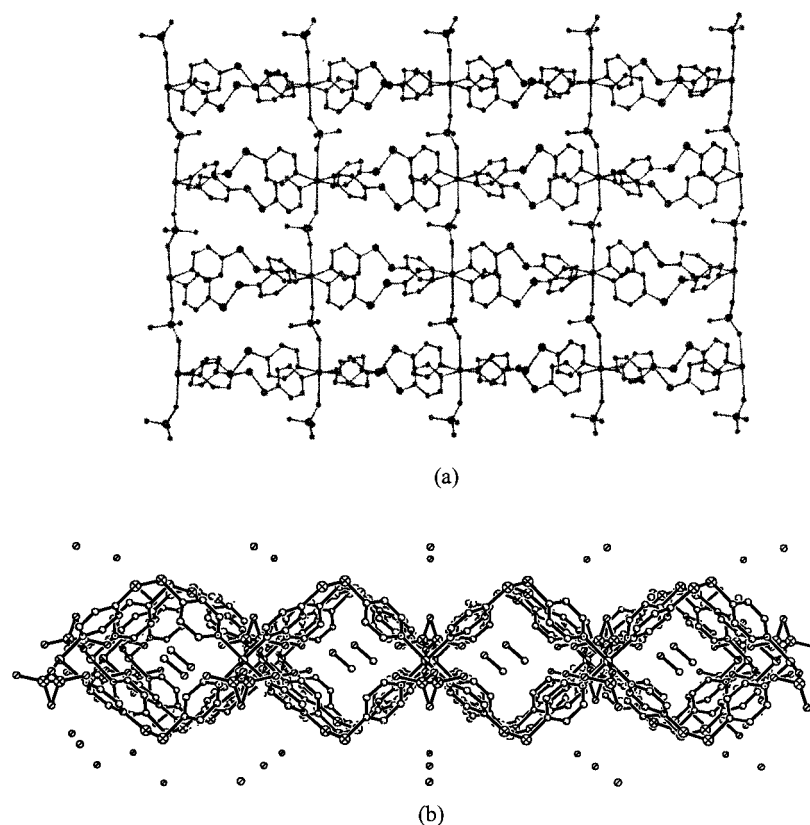


Figure 5. View of the 2D layer of **2** (a) along *a* axis and (b) along *b* axis

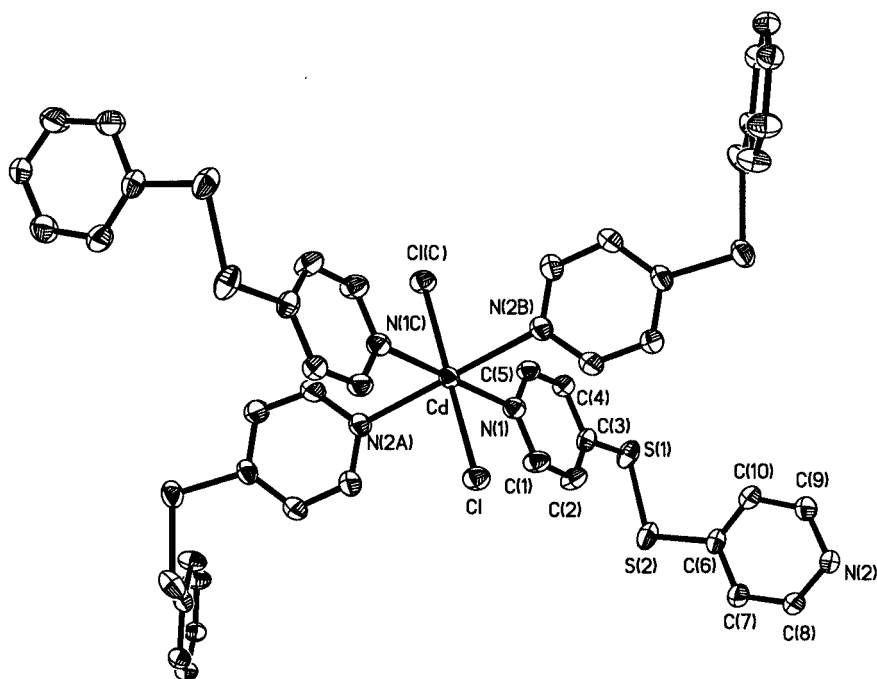
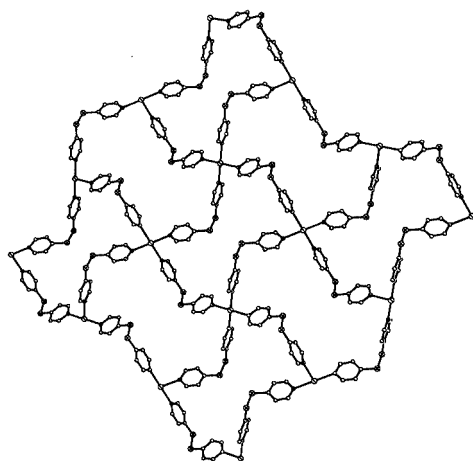


Figure 6. Drawing of the coordination environment of the Cd<sup>II</sup> ion in **3**, and the atom numbering scheme

mate structure of the 2D layer is wave-like with a tightly puckered structure lacking any guest molecules.

The S–S bond length, the C–S–S–C torsion angles, and the dihedral angles of the two pyridyl rings in 4-DPDS

in the three complexes **1**, **2**, and **3** are listed in Table 1. The S–S bond lengths are all ca. 2 Å, the C–S–S–C torsion angles are ca. 90° and the dihedral angles of the two pyridyl rings all show slight deviation from 90°. From these values

Figure 7. View of the 2D sheets of **3**

we see that the 4-DPDS ligand maintains its characteristic conformation despite the differences in the coordination schemes, but some notable differences exist between them. For the same metal ions, the M...M distances through the single 4-DPDS bridge are longer than those through the double 4-DPDS bridge (e.g., the Cd...Cd distance is 12.265 Å in **3**, but only 11.1 Å in the 1D structure [Cd(4-DPDS)<sub>2</sub>(H<sub>2</sub>O)]·2NO<sub>3</sub>·2EtOH·2H<sub>2</sub>O,<sup>[16]</sup> and the Cu...Cu separation is 11.26 Å in the single-helical chain complex [4-DPDS·Cu(hfac)<sub>2</sub>],<sup>[15]</sup> while it is 10.528 Å in the double-stranded chain compound **1** and 10.547 Å in **2**). The most interesting differences in the present complexes are that the torsion angles of M–(4-DPDS)–M change from 15.1° in **1**

and 15.0° in **2** to 37.9° in **3**, which we ascribed to the different coordination schemes of 4-DPDS. The 4-DPDS units in **1** and **2** link the metal ions to form double-stranded chains, but the 4-DPDS ligands in **3** connect the metal ions into a 2D grid-like sheet; the 4-DPDS ligand is more constrained in the double-stranded chains and more twisted in the 2D sheet because of steric factors.

### Electronic Spectra

The reflectance spectra of the complexes in the solid state were recorded in the range 200–1100 nm. The visible reflectance spectra for **1** contain bands at  $13.8 \cdot 10^3 \text{ cm}^{-1}$  with a shoulder  $9.72 \cdot 10^3 \text{ cm}^{-1}$ , characteristic of a copper(II)  $d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}$  transition<sup>[24]</sup> via ( $^2B_1 \rightarrow ^2E$ ) in a tetragonal ligand field, in which the copper(II) atom has a distorted square-based pyramidal coordination environment. The absorption of **2** at  $14.97 \cdot 10^3 \text{ cm}^{-1}$  without a shoulder is assigned to copper(II)  $d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}$  transitions<sup>[25]</sup> via ( $^2B_{1g} \rightarrow ^2E_g$ ) in a square-planar geometry (or elongated octahedron, due to the bridging sulfate anions), with the unpaired electron mainly located in the  $d_{x^2-y^2}$  orbital. The d–d transition energy of complex **1** is lower than that of **2**, which is consistent with the crystal field splitting energy of the tetragonal ligand field when compared with that of the square planar ligand field in cases when there are similar or the same ligand field strengths of the donor ligands. The information obtained from the electronic spectra about the coordination configurations of the copper(II) ions in the two complexes is in agreement with that given by the structural data.

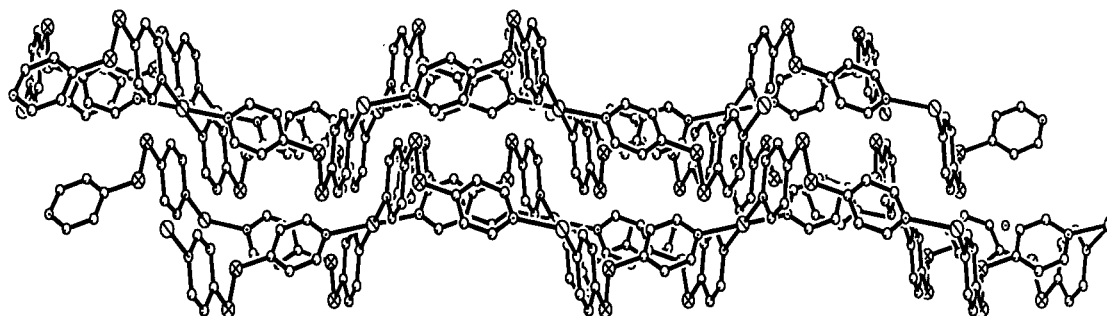
Figure 8. The tightly packed structure of **3**; only two layers are shown for clarity

Table 1. S–S bond lengths [Å] and C–S–S–C torsion angles [°], the dihedral angles of the two pyridyl rings [°] in the 4-DPDS ligands, and the M–[4-DPDS]–M torsion angles [°], for **1**, **2**, and **3**

Complexes	S–S distance (Å)	C–S–S–C torsion angle (°)	M...M separation through 4-DPDS (Å)	Dihedral angle of the two pyridyl rings (°)	M–(4-DPDS)–M torsion angle (°)
<b>1</b>	2.027(5)	89.8	10.528 (Cu...Cu)	98.6	15.1
<b>2</b>	2.033(5)	88.4	10.547 (Cu...Cu)	83.5	15.0
<b>3</b>	2.022(3)	95.1	12.265 (Cd...Cd)	81.9	37.9



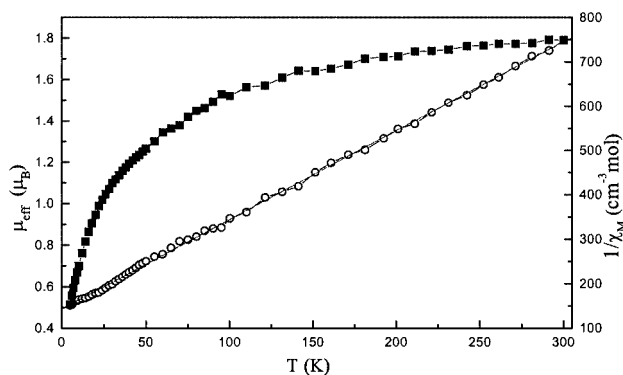


Figure 9. The plots for **1** of the effective magnetic moment  $\mu_{\text{eff}}$  vs.  $T$  and  $1/\chi_M$  vs.  $T$ .

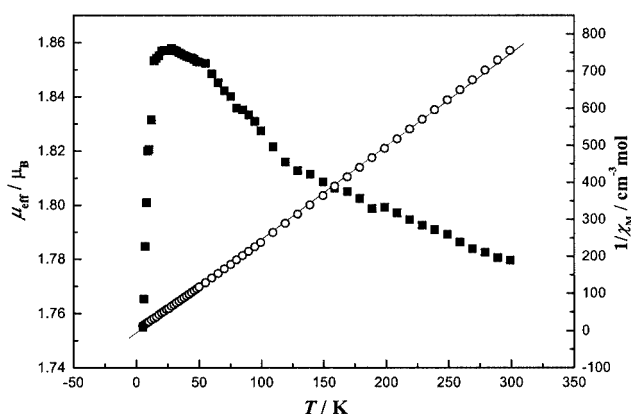


Figure 10. The plots for **2** of the effective magnetic moment  $\mu_{\text{eff}}$  vs.  $T$  and  $1/\chi_M$  vs.  $T$ .

## Magnetic Properties

Temperature-dependent magnetic susceptibility measurements for **1** and **2** were performed on the polycrystalline samples. The temperature dependence of  $1/\chi_M$  and  $\mu_{\text{eff}}$  [ $\chi_M$  being magnetic susceptibility for one  $\text{Cu}^{\text{II}}$  ion, and  $\mu_{\text{eff}} = (8\chi_M T)^{1/2}$ ] are shown in Figures 9 and 10, respectively. The value of  $\mu_{\text{eff}}$  for **1** is  $1.79 \mu_B$  at room temperature, which is slightly larger than the spin-only value for an uncoupled  $\text{Cu}^{\text{II}}$  ion ( $g = 2.0$ ,  $\mu_{\text{eff}} = 1.73 \mu_B$ ). As the temperature decreases, the value of  $\mu_{\text{eff}}$  decreases continuously and reaches  $0.52 \mu_B$  at 4 K, which indicates the occurrence of an antiferromagnetic interaction between the  $\text{Cu}^{\text{II}}$  ions in the double-stranded chain of **1**. A nonlinear fit of  $\chi_M = C/(T - \Theta)$  to the data reveals a Curie–Weiss behavior, with the Weiss constant  $\Theta = -2.27$  K. Taking into account the one-dimensional character of **1**, the magnetic susceptibility data were simulated by the Bonner–Fisher model<sup>[26]</sup> using the following polynomial expression:

$$\chi_M^J = \frac{N\beta^2 g^2 S(S+1)}{3kT} \frac{1+u}{1-u} \quad \left( u = \coth \left[ \frac{JS(S+1)}{kT} \right] - \left[ \frac{kT}{JS(S+1)} \right] \right) \quad (1)$$

In this expression,  $\chi = |J|/kT$  ( $2J$  is the singlet–triplet splitting energy or the exchange integral in the spin Hamiltonian  $H = -2J\mathbf{S}_1\mathbf{S}_2$ ) and other symbols have their usual meanings. A satisfactory least-squares fitting of the observed data at 4–300 K led to  $g = 2.13$  and  $J/k = -2.5$  K. The small negative coupling constant implies the existence of a weak antiferromagnetic interaction between the copper(II) centers in the chain of **1**.

The value of  $\mu_{\text{eff}}$  for **2** is  $1.78 \mu_B$  at room temperature, which is slightly larger than the spin-only value for an uncoupled  $\text{Cu}^{\text{II}}$  ion ( $g = 2.0$ ,  $\mu_{\text{eff}} = 1.73 \mu_B$ ). As the temperature decreases, the value of  $\mu_{\text{eff}}$  increases gradually to  $1.86 \mu_B$  at 24 K, and then sharply decreases to  $1.76 \mu_B$  at 4 K, which implies the presence of ferromagnetic interactions between  $\text{Cu}^{\text{II}}$  ions in the 2D sheets of **2**. The nonlinear fit of  $\chi_M = C/(T - \Theta)$  to the data reveals a Curie–Weiss behavior, with the Weiss constant  $\Theta = 2.58$  K. According to the structural data, the polymer may exhibit two types of  $\text{Cu}^{\text{II}}-\text{Cu}^{\text{II}}$  magnetic exchange interactions: type one is through a long double bridge, via 4-DPDS between copper centers in the double-stranded chain  $[\text{Cu}(4\text{-DPDS})_2]_n^{2n+}$ , which is considered as the intrachain interaction; and type two is through a short bridge, via the sulfate groups between the adjacent chains, which is treated as the interchain interaction. The  $\chi_M$  data are well interpreted based on the following expression:

A satisfactory least-squares fitting of the observed data at 4–300 K led to  $g = 2.10$ ,  $J/k = -2.3$  K,  $zJ'/k = 4.2$  K. The value of  $J$  may be assigned to type one and that of  $zJ'$  to type two. The small negative  $J$  and small positive  $zJ'/k$  imply the existence of a weak intrachain antiferromagnetic interaction and a weak interchain ferromagnetic interaction. The interchain ferromagnetic interaction is stronger than the intrachain antiferromagnetic interaction, and **2** shows a overall weak ferromagnetic interaction between the copper(II) ions.

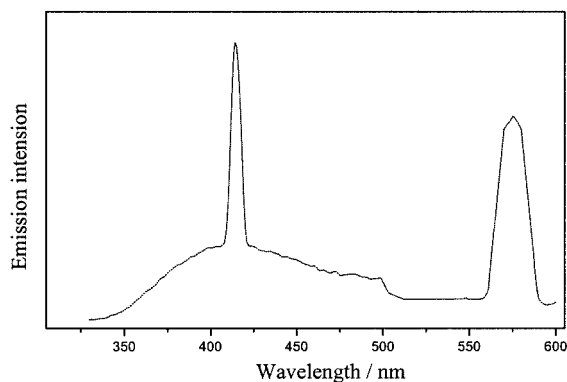
$$\chi_M^{J+J'} = \frac{\chi_M^J}{1 - (2zJ' \times \chi_M^J / Ng^2 \beta^2)} \quad (2)$$

$$(\chi_M^J = \frac{N\beta^2 g^2 S(S+1)}{3kT} \frac{1+u}{1-u}; \quad u = \coth \left[ \frac{JS(S+1)}{kT} \right] - \left[ \frac{kT}{JS(S+1)} \right])$$

The ESR spectra of **1** and **2** have been obtained at room temperature and 77 K, respectively; these spectra are almost the same. For **1** and **2**, both spectra exhibit the typical pattern, with the  $d_{x^2-y^2}$  ground state [ $g(2.36) > g_{\perp}(2.03) > 2.00$  for **1**;  $g(2.14) > g_{\perp}(2.06) > 2.00$  for **2**], indicating the occupation of the unpaired  $d$  electron in the  $d_{x^2-y^2}$  state.

## Fluorescence Characterization

The diffuse reflectance UV/Vis spectra for 4-DPDS and the as-synthesized polymer of **3** (Figure 11) show different absorption features. There are two bands for the 4-DPDS ligand, with the longer- (332 nm) and shorter-wavelength (220 nm) absorptions corresponding to the intraligand  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  transitions, respectively. In comparison with the two bands for 4-DPDS, the shorter-wavelength

Figure 11. Solid-state emission spectra of **3** at room temperature

band for polymer **3** has the same energy, whereas the longer-wavelength band shifts to higher energy at 282 nm. This hypsochromic shift must be related to the coordination of Cd<sup>2+</sup> to the 4-DPDS ligand, and it may arise from the same  $n \rightarrow \pi^*$  transitions. We note that the absorption intensity of **3** is markedly higher than that of the ligand. We attribute this increase in absorption intensity to the involvement of charge-transfer transitions from the N atoms of the ligands to the Cd<sup>2+</sup> centers. The emission spectra of **3** show a broad emission band centered at 418 nm and a middle-intensity emission band occurring at 575 nm ( $\lambda_{\text{ex}} = 314$  nm). The former may be assigned to the interligand transfer,<sup>[27]</sup> because the same emission appears also for the

ligand 4-DPDS, and the latter may be due to the ligand-to-metal charge-transfer (LMCT) transition.<sup>[28]</sup>

### Thermogravimetric Analysis

Thermogravimetric analysis (TGA) were performed to investigate the thermal stability of compounds **1–3**. All samples were heated under an N<sub>2</sub> atmosphere at a rate of 10 °C/min to 700 °C. The results show that **1** is stable up to 264 °C, although the first weight loss of 7.54% (calculated: 7.71), which corresponds to the loss of three lattice water molecules, occurred over the temperature range 65–128 °C. Complex **2** first lost one and a half water molecules and one CH<sub>3</sub>OH molecule (obsd.: 8.68%; calcd.: 8.95%) and then gradually decomposed when the temperature reached 285 °C. Complex **3** is stable up to 302 °C, and above this temperature it decomposes.

### Conclusions

Through the diffusion method, using different solvent systems, we acquired three coordination polymers (**1**, **2**, and **3**) derived from the flexible ligand 4-DPDS. The flexible ligand shows different coordination modes in the three complexes. In **1** and **2**, the 4-DPDS unit bridges the metal ions into double-stranded chains, but the 4-DPDS unit in **3** bridges the metal ions into a puckered (4,4) net sheet. The significant role of the anion is manifested in the dimension-

Table 2. Crystallographic data for the compounds **1**, **2**, and **3**

	<b>1</b>	<b>2</b>	<b>3</b>
Molecular formula	C <sub>10</sub> H <sub>12</sub> Cu <sub>0.5</sub> N <sub>3</sub> O <sub>5</sub> S <sub>2</sub>	C <sub>10.5</sub> H <sub>11.5</sub> Cu <sub>0.5</sub> N <sub>2</sub> O <sub>3.25</sub> S <sub>2.5</sub>	C <sub>10</sub> H <sub>8</sub> Cd <sub>0.5</sub> ClN <sub>2</sub> S <sub>2</sub>
Molecular mass	350.12	329.64	311.95
<i>T</i> [K]	293(2)	293(2)	293(2)
Wavelength [Å]	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Orthorhombic	Monoclinic
Space group	<i>Ibca</i>	<i>Pnna</i>	<i>P2<sub>1</sub>/c</i>
<i>a</i> [Å]	10.5275(6)	10.547(2)	7.6146(3)
<i>b</i> [Å]	20.270(1)	14.201(2)	18.2606(8)
<i>c</i> [Å]	27.235(1)	19.667(3)	9.3203(2)
$\alpha$ [°]	90	90	90
$\beta$ [°]	90	90	100.26(1)
$\gamma$ [°]	90	90	90
<i>V</i> [Å <sup>3</sup> ]	5811.5(6)	2945.8(8)	1275.24(8)
<i>Z</i>	16	8	4
<i>D</i> <sub>calcd.</sub> [Mg·m <sup>-3</sup> ]	1.601	1.487	1.625
Absorption coefficient [mm <sup>-1</sup> ]	1.101	1.139	1.409
<i>F</i> (000)	2872	1352	620
Crystal size [mm]	0.20 × 0.28 × 0.18	0.21 × 0.28 × 0.23	0.35 × 0.28 × 0.25
$\theta$ range for data collection [°]	1.50–25.00	1.77–25.00	2.23–25.05
Index ranges	10 ≤ <i>h</i> ≤ 10 −19 ≤ <i>k</i> ≤ 17 −20 ≤ <i>l</i> ≤ 26	−10 ≤ <i>h</i> ≤ 10 −13 ≤ <i>k</i> ≤ 13 −18 ≤ <i>l</i> ≤ 18	−9 ≤ <i>h</i> ≤ 9 −18 ≤ <i>k</i> ≤ 21 −11 ≤ <i>l</i> ≤ 5
Reflections collected	5746	9421	4067
Independent reflections	1356 ( <i>R</i> <sub>int</sub> = 0.047)	1380 ( <i>R</i> <sub>int</sub> = 0.0415)	2235 ( <i>R</i> <sub>int</sub> = 0.0306)
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>	Full-matrix least-squares on <i>F</i> <sup>2</sup>	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Parameters	219	197	142
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.102	1.194	1.202
<i>R</i> <sub>1</sub> indices [ <i>I</i> > 2σ( <i>I</i> )]	0.0527	0.0543	0.0532
<i>wR</i> <sub>2</sub> indices (all data)	0.1300	0.1478	0.1066

alities of the phases isolated, as well as the detailed coordination geometries about the copper(II) center in **1** and **2**. The configuration of the Cu<sup>II</sup> atoms is a square-based pyramid in **1** and an elongated-octahedron in **2**. The anions in **1** are non-coordinated, but the anions in **2** act as bridges between the double-stranded chains and link the double-stranded chains into a 2D channel-type sheet. The UV-Vis reflectance spectra and ESR spectra are consistent with the crystal structures. Magnetic characterizations of **1** and **2** show that complex **1** exhibits antiferromagnetic interactions while **2** is ferromagnetic. Complex **3** displays an emission band at 575 nm that is due to ligand-to-metal charge transfer.

## Experimental Section

**General:** Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O, CuSO<sub>4</sub>·5H<sub>2</sub>O, and CdCl<sub>2</sub>·2.5H<sub>2</sub>O were purchased commercially and used without further purification. 4,4'-Dipyridyl disulfide was purchased from Fluka. Elemental analyses of C, H, and N were determined on a Perkin–Elmer 240C analyzer. IR spectra were measured as KBr pellets on a Nicolet Magna 750 FT-IR spectrometer in the range 200–4000 cm<sup>−1</sup>. Thermogravimetric analyses were performed on a NETSCH STA-449C thermoanalyzer under N<sub>2</sub> (over a 26–750 °C range) at a heating rate of 10°/min. Electronic reflectance spectra were recorded on a Lambda 35 spectrometer. ESR spectra were recorded on powdered samples at an X-band frequency of ca. 9.77 GHz at room temperature or liquid nitrogen temperature (77 K) using a Bruker ER420 automatic spectrometer. Variable-temperature magnetic susceptibilities were determined in the temperature range 5–300 K on a Quantum Design MPMS SQUID magnetometer at 10 T. Corrections were applied for diamagnetism calculated from Pascal constants. Effective magnetic moments were calculated by the equation  $\mu_{\text{eff}} = 2.828(\chi_{\text{M}}T)^{1/2}$ , where  $\chi_{\text{M}}$  is the magnetic susceptibility per formula unit. Fluorescence characterization was performed on an Edinburgh F900 analytical instrument in Fuzhou University.

**[{Cu(4-DPDS)<sub>2</sub>(H<sub>2</sub>O)}·2NO<sub>3</sub>·3H<sub>2</sub>O]<sub>n</sub> (**1**):** A solution of Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (0.12 g, 0.5 mmol) in a methanol/water mixture (5:1, 5 mL) was slowly added to a solution of 4,4'-dipyridyl disulfide (0.22 g, 1 mmol) in dichloromethane (4 mL). After 4 days, blue crystals (0.25 g, 72% yield based on copper nitrate) grew at the bottom of the test tube. C<sub>20</sub>H<sub>24</sub>CuN<sub>6</sub>O<sub>10</sub>S<sub>4</sub> (700.24): calcd. C 34.27, H 3.43, N 12.00; found C, 34.36, H 3.46, N 12.07%. IR (KBr):  $\tilde{\nu}$  = 3408 cm<sup>−1</sup> (br), 1589 (s), 1543 (m), 1477 (m), 1414 (s), 1385 (s), 1308 (w), 1213 (m), 1099 (m), 1057 (m), 798 (s), 715 (s), 499 (s) cm<sup>−1</sup>.

**[{Cu(4-DPDS)<sub>2</sub>(SO<sub>4</sub>)}·1.5H<sub>2</sub>O·CH<sub>3</sub>OH]<sub>n</sub> (**2**):** A solution of CuSO<sub>4</sub>·5H<sub>2</sub>O (0.125 g, 0.5 mmol) in a methanol/water mixture (5:1, 5 mL) was allowed to diffuse slowly into a solution of 4,4'-dipyridyl disulfide (0.22 g, 1 mmol) in chloroform (5 mL). Immediately, a blue precipitate formed at the interface of the two layers. Blue single crystals (0.21 g, 64% base on the copper sulfate) were formed after 3 days. C<sub>21</sub>H<sub>23</sub>CuN<sub>4</sub>O<sub>6.5</sub>S<sub>5</sub> (659.28): calcd. C 38.22, H 3.49, N 8.49; found C, 38.31, H 3.52, N 8.57%. IR (KBr):  $\tilde{\nu}$  = 3412 (br), 1596 (s), 1548 (m), 1481 (s), 1417 (s), 1245 (w), 1218 (m), 1071 (m), 1035 (m), 815 (s), 802 (s), 713 (s), 494 (s) cm<sup>−1</sup>.

**[Cd(4-DPDS)<sub>2</sub>Cl<sub>2</sub>]<sub>n</sub> (**3**):** A colorless solution of CdCl<sub>2</sub>·2.5H<sub>2</sub>O (0.114 g, 0.5 mmol) in methanol/water (5:1, 5 mL) was carefully

layered onto a solution of 4,4'-dipyridyl disulfide (0.22 g, 1 mmol) in acetonitrile (5 mL). Diffusion between the two phases over a period of 5 days produced light-yellow crystals (0.26 g, 84% yield based on cadmium chloride). C<sub>20</sub>H<sub>16</sub>CdN<sub>4</sub>Cl<sub>2</sub>S<sub>4</sub> (623.9): calcd. C 38.47, H 2.56, N 8.98; found C, 38.52, H 2.59, N 9.05%. IR (KBr):  $\tilde{\nu}$  = 1585 (s), 1543 (m), 1479 (s), 1414 (s), 1321 (w), 1223 (m), 1063 (m), 1009 (m), 820 (s), 808 (s), 708 (s), 496 (s) cm<sup>−1</sup>.

**X-ray Crystallography:** Suitable single crystals of **1**, **2**, and **3** were selected for X-ray diffraction studies. The unit cell parameters and intensities were collected at 299 K on a Siemens SMART CCD diffractometer with graphite-monochromated Mo-*K*<sub>α</sub> ( $\lambda$  = 0.71073 Å) radiation. Measurements were made by using the  $\omega$  scan mode in the range 1.50° <  $\theta$  < 20° for **1**, 1.77° <  $\theta$  < 20° for **2**, and 2.23° <  $\theta$  < 25.05° for **3**. The structures were solved by direct methods and refined on *F*<sup>2</sup> by full-matrix least-squares procedures using SHELXTL software.<sup>[19]</sup> All non-hydrogen atoms were anisotropically refined. All H atoms were located theoretically and not refined. A summary of the crystallographic data of **1**, **2**, and **3** are presented in Table 2, and the selected bond lengths and bond angles are in Table 3.

Table 3. Selected bond lengths [Å] and angles [°] for **1**, **2**, and **3**

Complex <b>1</b> <sup>[a]</sup>			
Cu–N(2)	2.032(1)	Cu–N(1b)	2.061(1)
Cu–O(1)	2.305(1)	S(1)–S(2)	2.027(5)
S(1)–C(3)	1.792(2)	S(2)–C(8)	1.754(2)
N(2)–Cu–N(1b)	88.5(4)	N(2)–Cu–N(1c)	91.8(4)
N(2)–Cu–O(1)	88.5(3)	N(1b)–Cu–O(1)	96.4(3)
C(3)–S(1)–S(2)	105.2(4)	C(8)–S(2)–S(1)	104.9(4)
Complex <b>2</b> <sup>[b]</sup>			
Cu–N(1)	2.037(8)	Cu–N(2b)	2.040(7)
Cu–O(1)	2.459(5)	S(2)–S(3)	2.033(5)
S(2)–C(3)	1.785(9)	S(3)–C(4)	1.775(9)
O(6)–C(11)	1.45(9)		
N(1a)–Cu–N(1)	91.4(4)	N(1)–Cu–N(2b)	89.2(3)
N(2b)–Cu–N(2c)	91.3(4)	O(1)–Cu–O(1a)	179.4(1)
O(1)–Cu–N(1a)	87.7(1)	O(1)–Cu–N(2b)	84.5(2)
C(3)–S(2)–S(3)	105.0(4)	C(4)–S(3)–S(2)	105.0(4)
Complex <b>3</b> <sup>[c]</sup>			
Cd–N(2a)	2.410(5)	Cd–N(1)	2.418(5)
Cd–Cl	2.571(2)	S(1)–S(2)	2.022(3)
S(1)–C(3)	1.780(6)	S(2)–C(6)	1.775(6)
N(2A)–Cd–N(1)	96.20(2)	N(2a)–Cd–Cl	90.06(3)
N(2B)–Cd–N(1)	83.80(2)	N(2b)–Cd–Cl	89.94(3)
N(1)–Cd–Cl(c)	90.81(1)	N(1)–Cd–Cl	89.19(2)
C(6)–S(2)–S(1)	106.3(2)	C(3)–S(1)–S(2)	105.1(2)

<sup>[a]</sup> Symmetry codes: (a)  $-x, -y - 1/2, z$ ; (b)  $x + 1, y, z$ ; (c)  $-x - 1, -y - 1/2, z$ . <sup>[b]</sup> Symmetry codes: (a)  $x, -y + 1/2, -z + 1/2$ ; (b)  $x - 1, y, z$ ; (c)  $x - 1, -y + 1/2, -z + 1/2$ . <sup>[c]</sup> Symmetry codes: (a)  $-x + 1, y + 1/2, -z + 1/2$ ; (b)  $x - 1, -y + 1/2, z - 1/2$ ; (c)  $-x, -y + 1, -z$ .

CCDC-192657 (**1**), -192656 (**2**), and -192655 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at [www.ccdc.cam.ac.uk/contents/retrieving.html](http://www.ccdc.cam.ac.uk/contents/retrieving.html) [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-0333; E-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)].



## Acknowledgments

We thank NNSFC, the Natural Foundation of Fujian Province, and the key project of CAS for financial support.

- [1] [1a] B. Moulton, M. J. Zaworotko, *Chem. Rev.* **2001**, *101*, 1629–1658. [1b] K. Kim, *Chem. Soc. Rev.* **2002**, *31*, 96–107. [1c] O. R. Evans, W. Lin, *Acc. Chem. Res.* **2002**, *35*, 511–522. [1d] B. F. Abrahams, B. F. Hoskins, R. Robson, *J. Am. Chem. Soc.* **1991**, *113*, 3606–3607. [1e] M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. O'Keeffe, O. M. Yaghi, *Acc. Chem. Res.* **2001**, *34*, 319–330. [1f] W. B. Lin, L. Ma, O. R. Evans, *Chem. Commun.* **2000**, 2263–2264. [1g] Q. Wang, X. Wu, W. Zhang, T. Sheng, P. Lin, J. Li, *Inorg. Chem.* **1999**, *38*, 2223–2226. [1h] M. Hong, Y. Zhao, W. Su, R. Cao, Z. Zhou, A. S. C. Chan, *Angew. Chem. Int. Ed.* **2000**, *39*, 2468–2470. [1i] M. Hong, Y. Zhao, W. Su, R. Cao, M. Fujita, Z. Zhou, A. S. C. Chan, *J. Am. Chem. Soc.* **2000**, *122*, 4819–4820. [1j] O. M. Yaghi, G. Li, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 207–209. [1k] O. M. Yaghi, H. Li, C. Davis, D. Richardson, T. L. Groy, *Acc. Chem. Res.* **1998**, *31*, 474–484.
- [2] [2a] M. P. Byrm, C. J. Curits, Y. Hsiou, S. I. Khan, P. A. Sawin, A. Terzis, C. E. Strouse, *Comprehensive Supramolecular Chemistry*, Vol. 6, *Solid State Supramolecular Chemistry: Crystal Engineering* (Eds.: D. D. MacNicol, F. Toda, R. Bishop), Elsevier, Oxford, UK, **1996**. [2b] M. Eddaoudi, H. Li, O. M. Yaghi, *J. Am. Chem. Soc.* **2000**, *122*, 1391–1397. [2c] O. Kahn, *Acc. Chem. Res.* **2000**, *33*, 647–657 and references therein. [2d] X. H. Bu, W. Chen, S. L. Lu, R. H. Zhang, D. Z. Liao, M. Shionoya, F. Brisse, J. Ribas, *Angew. Chem. Int. Ed.* **2001**, *40*, 3201–3203.
- [3] [3a] P. Losier, M. J. Zaworotko, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2779–2782. [3b] M. Fujita, Y. J. Kwon, S. Washizu, K. Ogura, *J. Am. Chem. Soc.* **1994**, *116*, 1151–1152. [3c] R. W. Gable, B. F. Hoskins, R. Robson, *J. Chem. Soc., Chem. Commun.* **1990**, 1677–1678. [3d] M. L. Tong, H. J. Chen, X. M. Chen, *Inorg. Chem.* **2000**, *39*, 2235–2238. [3e] O. M. Yaghi, H. Li, *J. Am. Chem. Soc.* **1995**, *117*, 10401–10402. [3f] L. R. MacGillivray, S. Subramanian, M. J. Zaworotko, *J. Chem. Soc., Chem. Commun.* **1994**, 1325–1326. [3g] L. Carlucci, G. Ciani, D. M. Proserpio, A. Sironi, *J. Chem. Soc., Chem. Commun.* **1994**, 2755–2756. [3h] C. V. K. Sharma, G. A. Broker, J. G. Huddleston, J. W. Baldwin, R. D. Metzger, R. F. Rogers, *J. Am. Chem. Soc.* **1999**, *121*, 1137–1144.
- [4] [4a] M. Fujita, D. Oguro, M. Miyazawa, H. Oka, K. Yamaguchi, K. Ogura, *Nature* **1995**, *378*, 469–471. [4b] A. J. Blake, N. R. Champness, P. Hubberstey, W. S. Li, M. A. Wilthersby, M. Schröder, *Coord. Chem. Rev.* **1999**, *183*, 117–138. [4c] S. Leiniger, B. Olenyuk, P. J. Stang, *Chem. Rev.* **2000**, *100*, 853–908. [4d] M. L. Tong, B. H. Ye, J. W. Cai, X. M. Chen, S. W. Ng, *Inorg. Chem.* **1998**, *37*, 2645–2650. [4e] K. Briadha, C. Seward, M. J. Zaworotko, *Angew. Chem. Int. Ed.* **1999**, *38*, 492–495.
- [5] [5a] L. Carlucci, G. Ciani, D. W. v. Gudenberg, D. M. Proserpio, *Inorg. Chem.* **1997**, *36*, 3812–3813.
- [6] [6a] T. Hennigar, D. C. MacQuarrie, P. Loiser, R. D. Rogers, M. J. Zaworotko, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 972–973. [6b] L. Carlucci, G. Ciani, D. M. Proserpio, S. Rizzato, *Chem. Commun.* **2000**, 1319–1320.
- [7] [7a] A. J. Blake, N. R. Champness, A. Khlobystov, D. A. Lemenovskii, W.-S. Li, M. Schröder, *Chem. Commun.* **1997**, 2027–2028. [7b] M. Fujita, O. Sasaki, K.-y. Watanabe, K. Ougra, K. Yamaguchi, *New J. Chem.* **1998**, *22*, 189–192. [7c] L. Carlucci, G. Ciani, D. M. Proserpio, *J. Chem. Soc., Dalton Trans.* **1999**, 1799–1804.
- [8] [8a] A. J. Blake, N. R. Champness, S. S. M. Chung, W.-S. Li, M. Schröder, *Chem. Commun.* **1997**, 1005–1006. [8b] M. A. Wilthersby, A. J. Blake, N. R. Champness, P. A. Cooke, P. Hubberstey, A. L. Realf, S. J. Teat, M. Schröder, *J. Chem. Soc., Dalton Trans.* **2000**, 3261–3268. [8c] C. He, B.-G. Zhang, C. Duan, J. Li, Q.-J. Meng, *Eur. J. Inorg. Chem.* **2000**, 2549–2554.
- [8d] S. R. Batten, J. C. Jeffery, M. D. Ward, *Inorg. Chim. Acta* **1999**, *292*, 231–237.
- [9] [9a] L. Carlucci, G. Ciani, M. Moret, D. M. Proserpio, S. Rizzato, *Angew. Chem. Int. Ed.* **2000**, *39*, 1506–1507. [9b] L. Carlucci, G. Ciani, D. M. Proserpio, *Chem. Commun.* **1999**, 449–450. [9c] M. J. Plater, M. R. St. J. Foreman, T. Gelbrich, M. B. Hursthouse, *Cryst. Eng.* **2001**, *4*, 319–328.
- [10] [10a] M. B. Zaman, M. D. Smith, H.-C. z. Loye, *Chem. Commun.* **2001**, 2256–2257. [10b] B. Moulton, E. B. Rather, M. J. Zaworotko, *Cryst. Eng.* **2001**, *4*, 309–317. [10c] M. Du, X.-H. Bu, Y.-M. Guo, H. Liu, S. R. Batten, J. Ribas, T. C. W. Mak, *Inorg. Chem.* **2002**, *41*, 4904–4908. [10d] M.-L. Tong, Y.-M. Wu, J. Ru, X.-M. Chen, H.-C. Chang, S. Kitagawa, *Inorg. Chem.* **2002**, *41*, 4846–4848. [10e] Z.-Y. Fu, X.-T. Wu, J.-C. Dai, S.-M. Hu, W.-X. Du, *New J. Chem.* **2002**, *26*, 978–980. [10f] M. J. Plater, M. R. St. J. Foreman, T. Gelbrich, M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.* **2000**, 1995–2000.
- [11] [11a] M. J. Plater, M. R. St. J. Foreman, T. Gelbrich, S. J. Coles, M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.* **2000**, 3065–3073. [11b] M. Fujita, Y. J. Kwon, M. Miyazawa, K. Ogura, *J. Chem. Soc., Chem. Commun.* **1994**, 1977–1978. [11c] M. Fujita, Y. J. Kwon, O. Sasaki, K. Yamaguchi, K. Ogura, *J. Am. Chem. Soc.* **1995**, *117*, 7287–7288. [11d] X.-C. Su, S.-R. Zhu, H.-K. Lin, X.-B. Leng, Y.-T. Chen, *J. Chem. Soc., Dalton Trans.* **2001**, 3163–3168.
- [12] [12a] H. Kessler, W. Rundel, *Chem. Ber.* **1968**, *101*, 3350–3359. [12b] R. R. Fraser, G. Boussard, J. K. Saunder, J. B. Lambert, C. E. Mixan, *J. Am. Chem. Soc.* **1971**, *93*, 3822–3823. [12c] H. Kessler, A. Rleker, W. Rundel, *J. Chem. Soc., Chem. Commun.* **1968**, 475–476. [12d] F. Seel, W. Gombler, R. Bunde, *Justus Liebigs Ann. Chem.* **1970**, *735*, 1–7.
- [13] M. Hong, W. Su, R. Cao, M. Fujita, J. Lu, *Chem. Eur. J.* **2000**, *3*, 427–431.
- [14] A. J. Blake, N. R. Brooks, N. R. Champness, M. Crew, A. Deveson, D. Fenske, D. H. Gregory, L. R. Hanton, P. Hubberstey, M. Schröder, *Chem. Commun.* **2001**, 1432–1433.
- [15] R. Horikoshi, T. Mochida, H. Moriyama, *Inorg. Chem.* **2001**, *40*, 2430–2433.
- [16] M. Kondo, M. Shimamura, S. Noro, Y. Kimura, K. Uemura, S. Kitagawa, *J. Solid State Chem.* **2000**, *152*, 113–119.
- [17] F. M. Tabellion, S. R. Seidel, A. M. Arif, P. J. Stang, *J. Am. Chem. Soc.* **2001**, *123*, 7740–7741.
- [18] R. Horikoshi, T. Mochida, N. Maki, S. Yamada, H. Moriyama, *J. Chem. Soc., Dalton Trans.* **2002**, 28–33.
- [19] G. M. Sheldrick, SHELXTL NT Version 5.1. *Program for Solution, Refinement of Crystal Structures*, University of Göttingen, Göttingen, Germany, **1997**.
- [20] [20a] M. L. Hernández, M. G. Barandika, M. K. Urtiaga, R. Cortés, L. Lezama, M. I. Arriortua, T. Rojo, *J. Chem. Soc., Dalton Trans.* **1999**, 1401–1406. [20b] M. J. Plater, M. R. St. J. Foreman, J. M. S. Snakle, *Cryst. Eng.* **2001**, *4*, 293–308.
- [21] [21a] O. S. Jung, S. H. Park, D. C. Kim, K. M. Kim, *Inorg. Chem.* **1998**, *37*, 610–611. [21b] M. T. Bujaci, X. Wang, S. Li, C. Zheng, *Inorg. Chim. Acta* **2002**, *333*, 152–154.
- [22] [22a] D. Hargman, R. P. Hammond, R. Haushalter, J. Zubieta, *Chem. Mater.* **1998**, *10*, 2091–2100. [22b] X.-M. Chen, T. C. W. Mak, *Struct. Chem.* **1992**, *3*, 369–374.
- [23] [23a] K. Biradha, M. Fujita, *J. Chem. Soc., Dalton Trans.* **2000**, 3805–3811. [23b] K. Biradha, M. Fujita, *Chem. Commun.* **2001**, 15–16. [23c] K. Biradha, Y. Hongo, M. Fujita, *Angew. Chem. Int. Ed.* **2000**, *39*, 3843–3845.
- [24] M. Melnik, *Coord. Chem. Rev.* **1981**, *36*, 287–301.
- [25] L. Araya, J. Vargas, J. Costamagna, *Trans. Met. Chem.* **1986**, *11*, 321–326.
- [26] J. C. Bonner, M. E. Fisher, *Phys. Rev.* **1964**, *A135*, 640–658.
- [27] [27a] N. W. Alcock, P. R. Barker, J. M. Haider, M. J. Hannon, C. L. Painting, Z. Pikramenou, E. A. Plummer, K. Rissanen, P. Saarenketo, *J. Chem. Soc., Dalton Trans.* **2000**, 1447–1462. [27b] K.-Y. Ho, W.-Y. Yu, K.-K. Cheung, C.-M. Che, *J. Chem. Soc., Dalton Trans.* **1999**, 1581–1586.

<sup>[28]</sup> <sup>[28a]</sup> A. Meijerink, G. Blasse, M. Glasbeek, *J. Phys. Condense. Matter* **1990**, 2, 6303–6313. <sup>[28b]</sup> R. Bertoncello, M. Bettinelli, M. Casarin, A. Gulino, E. Tondello, A. Vittadini, *Inorg. Chem.* **1992**, 31, 1558–1565. <sup>[28c]</sup> J. Tao, M. L. Tong, J. X. Shi, X. M. Chen, S. W. Ng, *Chem. Commun.* **2000**, 2043–2044. <sup>[28d]</sup> Z. Y. Fu, X. T. Wu, J. C. Dai, L. M. Wu, C. C. Cui, S. M. Hu, *Chem.*

*Commun.* **2001**, 1856–1857. <sup>[28e]</sup> W. Chen, J.-Y. Wang, C. Chen, Q. Yi, H.-M. Yuan, J.-S. Chen, S.-N. Wang, *Inorg. Chem.* **2003**, 42, 944–946.

Received March 19, 2003

Early View Article

Published Online August 14, 2003