Construction and Characterization of Organic-Inorganic Hybridized Molecules with Infinite 2D Grid Network and 1D Zigzag Chain Structures

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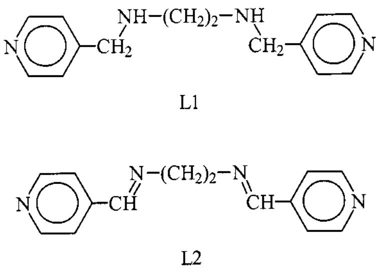
Two coordination polymers with a 2D grid network structure of $[Cu(L1)]NO_3 \cdot H_2O$ (**1**) and $[Cu(L1\text{-}2H)](AcOH)_2 \cdot (C_2H_5)_2O \cdot 4H_2O$ (**2**) were obtained by reaction of the flexible tetradentate ligand 1,2-bis(4′-pyridylmethylamino)ethane (L1) with one mol of $[Cu(CH_3CN)_4]NO_3$ or $Cu(OAc)_2 \cdot H_2O$. The syntheses of a new bridging ligand 1,2-bis(4′-pyridylmethyleneamino)ethane (L2) and its copper(I) complexes are described. When L2 reacts with $[Cu(CH_3CN)_4] \cdot ClO_4$ or $[Cu(CH_3CN)_4] \cdot NO_3$, two interesting complexes with an infinite zigzag chain-like structure $[Cu(L2)(CH_3CN)]NO_3$ (**3**) and $[Cu(L2)(CH_3CN)]ClO_4$ (**4**), involving the coordination of an acetonitrile molecule, were obtained. These coordination complexes were characterized by X-ray crystallography. The results showed that the rigidity of the ligand and the different chemical valence of the transition metal ions have a large effect on the construction of supramolecular frameworks.

Introduction

The metal-ion-directed generation of molecular entities currently provides a very efficient method for the construction of coordination frameworks. Recently, many efforts have been devoted to the investigation of the crystal engineering of one (1D), two (2D) and three-dimensional (3D) coordination polymers.[1,2] However, flexible bridging ligands have not often been employed to construct coordination polymers with transition metal ions, perhaps due to the difficulties in predicting the resulting network structures.[3,4] Previous work has demonstrated that the flexible tetradentate ligand 1,2-bis(4′-pyridylmethylamino)ethane (L1) gives 1D or 2D frameworks depending on the counter anions.[5] In the silver(I) complexes, the structure of $[Ag(L1)]NO_3$ is an infinite 1D hinged cationic chain, while in the case of the complex with a perchlorate anion, $[Ag(L1)]ClO_4 \cdot CH_3CN$ is an infinite 2D cationic network. It is clear that the counter anions play an important role in the construction of these supramolecular complexes.[5] We describe here the reaction of the flexible tetradentate ligand L1 with $[Cu(CH_3CN)_4]NO_3$ and $Cu(OAc)_2 \cdot H_2O$ with the aim of obtaining different network structures by changing the chemical valence of the metal ions.

The generation of supramolecular frameworks is influenced by factors such as the solvent system, templates, counterions, ligand geometry and sometimes the ratio between the metal salt and the ligand.[6−13] In order to add rigidity to L1, we synthesized a new tetradentate ligand 1,2-bis(4′-pyridylmethyleneamino)ethane (L2) (Scheme 1) to detect the influence of the rigidity of the ligand on the supramolecular construction progress.



Scheme 1

We report here the assembly of an infinite 2D cationic grid $[CuL1]^+$, an infinite neutral grid network $[Cu(L1\text{-}2H)](AcOH) \cdot (C_2H_5)_2O \cdot 4H_2O$ and two polymeric copper(I) complexes with infinite zigzag chain-like structures $[Cu(L2)(CH_3CN)]NO_3$ and $[Cu(L2)(CH_3CN)]ClO_4$.

Results and Discussion

Synthesis and Reactivity

In principle, supramolecular networks can be obtained by the concurrent action of both extended coordination and hydrogen bonds. We chose to react the flexible tetradentate ligand 1,2-bis(4′-pyridylmethylamino)ethane (L1) with Cu^I and Cu^{II} salts to construct networks by the formation of coordination bonds. The ligand 1,2-bis(4′-pyridylmethyleneamino)ethane (L2) is a di-Schiff base and an analogue of L1. The difference between the L1 and L2 ligands is that L2 is more rigid.

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The polymeric complexes [Cu(L1)]$NO_3 \cdot H_2O$ (**1**), [Cu(L1-2H)](AcOH)$_2 \cdot (C_2H_5)_2O \cdot 4H_2O$ (**2**), [Cu(L2)(CH_3CN)]NO_3 (**3**) and [Cu(L2)(CH_3CN)]ClO_4 (**4**) were readily obtained by the reaction of Cu^I or Cu^{II} salts with the ligands L1 and L2 in a molar ratio of 1:1 under mild conditions (see Exp. Section). The elemental C, H and N analysis and X-ray crystal structure analysis confirmed the chemical formulation of these complexes. The complexes **1**, **3** and **4** are stable in the solid state, but not very stable in solution. Crystals of **2** rapidly lose solvent molecules when they are isolated from the reaction mixture.

Crystal Structure Description

The structures of complexes **1**, **2**, **3** and **4** were determined by X-ray crystallography. The crystal and data collection parameters are summarized in Table 1 and selected bond lengths and angles are listed in Table 2.

As shown in Figure 1a, each copper(I) atom in the complex **1** is coordinated by two N atoms of an ethylenediamine unit of one L1, and two N atoms of a pyridyl unit from two other L1 ligands. The coordination geometry of the copper(I) atom is distorted tetrahedral with coordination angles (N−Cu−N) ranging between 85.4(2) to 124.0(3)° and an average Cu−N bond length of 2.082(6) Å (Table 2).

Table 2. Selected bond distances [Å] and angles [deg] for **1**,**2** and **3**

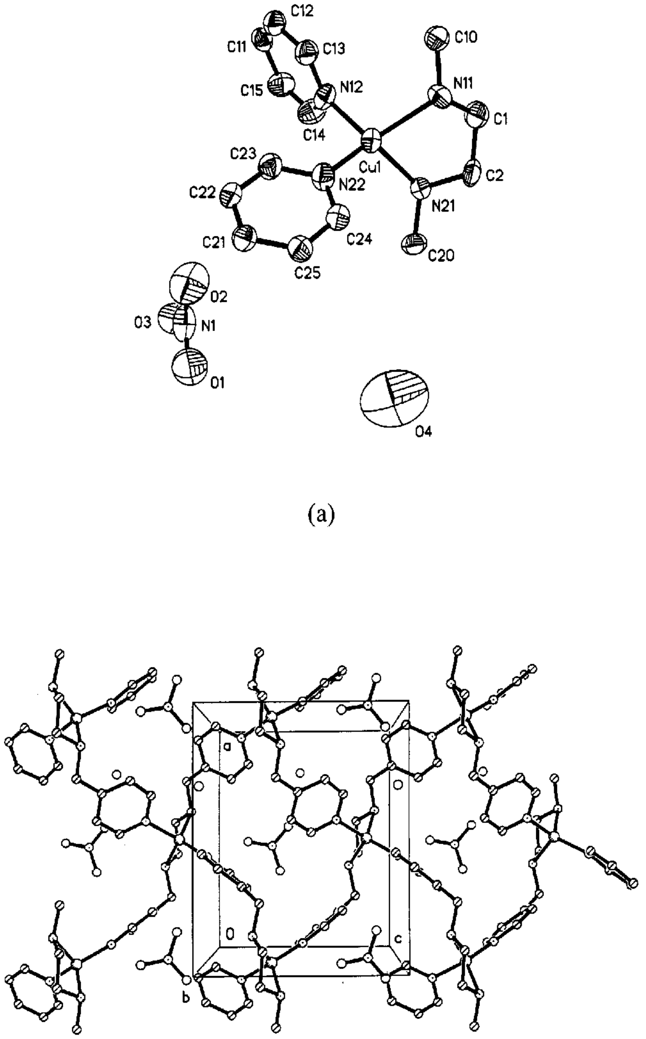
[Cu(L1)]$NO_3 \cdot H_2O$ **1**			
Cu(1)−N(11)	2.125(6)	Cu(1)−N(21)	2.122(6)
Cu(1)−N(12)	2.069(6)	Cu(1)−N(22)	2.014(7)
(Cu−N)av		2.082(6)	
N(11)−Cu(1)−N(12)	109.7(2)	N(11)−Cu(1)−N(21)	85.4(2)
N(11)−Cu(1)−N(22)	124.0(3)	N(12)−Cu(1)−N(21)	114.8(3)
N(12)−Cu(1)−N(22)	105.8(3)	N(21)−Cu(1)−N(22)	116.6(3)
[Cu(L1-2H)](AcOH)$_2 \cdot (C_2H_5)_2O \cdot 4H_2O$ **2**			
Cu(1)−N(1)	2.032(4)	Cu(1)−N(2)	2.008(4)
(Cu−N)av		2.020(4)	
N(1)−Cu(1)−N(1)[a]	84.2(2)	N(1)−Cu(1)−N(2)	178.4(2)
N(1)−Cu(1)−N(2)[a]	94.1 (2)	N(2)−Cu(1)−N(2)[a]	87.5(2)
[Cu(L2)(CH_3CN)]NO_3 **3**			
Cu(1)−N(11)	2.109(3)	Cu(1)−N(12)[b]	2.051(3)
Cu(1)−N(21)	2.044(3)	Cu(1)−N(31)	1.936(3)
(Cu−N)av		2.035(3)	
N(11)−Cu(1)−N(21)	85.0(1)	N(11)−Cu(1)−N(31)	119.5(1)
N(11)−Cu(1)−N(12)[b]	101.0(1)	N(21)−Cu(1)−N(31)	126.2(1)
N(12)[b]−Cu(1)−N(21)	115.6(1)	N(12)[b]−Cu(1)−N(31)	106.1(1)

[a] Equivalent atoms generated by 2 −*x*, *y*, *z*. − [b] Equivalent atoms generated by −0.5 + *x*, −0.5 − *y*, *z*.

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

	1	**2**	**3**
Empirical formula	$C_{14}H_{20}CuN_5O_4$	$C_{22}H_{40}CuN_4O_9$	$C_{16}H_{17}CuN_6O_3$
M	385.89	568.13	404.89
Crystal system	Orthorhombic	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	*Cmcm*	$P2_1/a$
a [Å]	10.9975(9)	13.519(2)	9.3258(6)
b [Å]	16.951(2)	12.258(2)	20.632(1)
c [Å]	8.7615(9)	17.975(9)	9.9530(7)
β [°]			113.937(2)
V [$Å^3$]	1633.3(3)	2978(2)	1750.3(2)
Z	4	4	4
D_c [$g \cdot cm^{-3}$]	1.569	1.267	1.536
μ [mm^{-1}]	1.376	0.783	1.277
Crystal habit, color	Orange prism	Blue platelet	Orange platelet
Crystal size [mm]	0.20 × 0.20 × 0.05	0.34 × 0.34 × 0.10	0.35 × 0.30 × 0.10
$2\theta_{max}$ [°]	60	55	55
Index range	$-14 \leq h \leq 14$	$0 \leq h \leq 17$	$-12 \leq h \leq 12$
	$-23 \leq k \leq 23$	$-15 \leq k \leq 8$	$-26 \leq k \leq 26$
	$-12 \leq l \leq 12$	$-23 \leq l \leq 13$	$-12 \leq l \leq 12$
Reflns. Collected	8007	2819	6967
Independent reflns.	2910	1835	3873
R_{int}	0.045	0.059	0.068
Obsd. reflns. [$I > 2\sigma(I)$]	1542	558	2653
Parameters refined	218	111	235
R (obsd. data)	0.0701	0.079	0.0467
wR (obsd. data)	0.1608[a]	0.2375[b]	0.1635[c]
Goodness of fit	1.296	0.983	1.316
Residuals [e $Å^{-3}$]	0.88; −1.44	0.49; −0.84	1.30; −2.67

[a] $\omega = 1/[\sigma^2(F_0)^2 + (0.0500P)^2]$, where $P = (F_0^2 + 2F_c^2)/3$. − [b] $\omega = 1/[\sigma^2(F_0)^2 + (0.1000P)^2]$, where $P = (F_0^2 + 2F_c^2)/3$. − [c] $\omega = 1/[\sigma^2(F_0)^2 + (0.0800P)^2]$, where $P = (F_0^2 + 2F_c^2)/3$.



(a)

(b)

Figure 1. (a) Crystal structure of [Cu(L1)]NO_3 **1** with the ellipsoids drawn at the 50% probability level; (b) infinite grid structure of [Cu^I(L1)]NO_3 **1**

Complex **1** forms an infinite 2D grid network connected by Cu−N coordination bonds (Figure 1b) in which each L1 ligand has an almost linear conformation with a dihedral angle of 82.5° between the two terminal pyridyl rings of the L1 ligand.1

Complex **1** has one water molecule in the crystal in addition to the nitrate anion, as confirmed by thermogravimetric analysis: the TGA data of complex **1** showed an initial weight loss of 4.9% (calcd. 4.7%) centered at 80 °C, representing the loss of uncoordinated water molecule. The nitrate anions and water molecules are located at the vacancy between the two adjacent cationic layers through two N−H···O and three C−H···O hydrogen bonds as tabulated in Table 3. In the previously reported analog [Cu(L1)]ClO_4, there is only one C−H···O hydrogen bond between the ClO_4^- and pyridyl ring of the adjacent ligand.[5] In addition to these hydrogen bonds, there are T-type edge-to-face π-π interactions between pyridine rings which are similar to those of the perchlorate analog, as discussed previously.[5,14]

Table 3. Hydrogen bonds data for complexes **1**, **2** and **3**

D−H···A	Distance of D···A (Å)	Angle of D−H−A (°)
	[Cu(L1)]NO_3·H_2O **1**	
N(11)−H···O(3)[a]	3.107(7)	151.8
N(21)−H···O(2)[b]	3.322(10)	164.6
C(2)−H···O(4)[c]	3.35(2)	148.0
C(10)−H···O(4)[d]	3.393(19)	148.5
C(22)−H···O(1)[e]	3.472(11)	164.1
	[Cu(L1-2H)](AcOH)$_2$·(C_2H_5)$_2$O·4H_2O **2**	
C(5)−H···O(1)	3.164(8)	129.8
C(32)−H···O(4)	2.77(3)	111.9
	[Cu(L2)(CH_3CN)]NO_3 **3**	
C(12)−H(6)···N(31)	3.428(6)	168.6
C(14)−H(8)···O(41)[f]	3.502(6)	161.1
C(22)−H(11)···O(43)[g]	3.455(7)	156.9
C(25)−H(14)···N(31)	3.396(6)	143.4

[a] Equivalent atoms generated by $1.5 - x, -y, -0.5 + z$. − [b] Equivalent atoms generated by $0.5 + x, 0.5 - y, 1 - z$. − [c] Equivalent atoms generated by $1 + x, y, z$. − [d] Equivalent atoms generated by $1.5 - x, -y, 0.5 + z$. − [e] Equivalent atoms generated by $0.5 + x, -0.5 - y, -z$. − [f] Equivalent atoms generated by $-0.5 + x, -0.5 - y, 1 + z$. − [g] Equivalent atoms generated by $2.5 - x, 0.5 + y, -z$.

In contrast to the tetrahedral geometry of Cu^I, four-coordinate Cu^{II} complexes are usually square planar. After several attempts at reactions between the L1 and Cu^{II} salts with various anions, we finally succeeded in obtaining single crystals of a complex of Cu(OAc)$_2$ with L1, i.e. [Cu(L1-2H)](AcOH)$_2$·(C_2H_5)$_2$O·4H_2O (**2**). The structure around the Cu^{II} atom is shown in Figure 2a, along with the atom numbering scheme. The atoms Cu(1), N(1), N(2), C(1), C(2) and C(3) are all at special positions in the crystallographic mirror plane. The ethylenediamine moiety is deprotonated since all its' atoms are completely coplanar. The existence of acetic acid rather than an acetate anion was confirmed by IR spectroscopy. Each Cu^{II} atom is coordinated by four N atoms from three L1 ligands with a square-planar coordination geometry. The bond lengths of Cu(1)−N(1) and Cu(1)−N(2) are 2.032(4) and 2.008(4) Å, respectively. Each L1 ligand coordinates to three Cu^{II} atoms. Such a coordination mode means that complex **2** forms an infinite 2D network (Figure 2b). It is obvious that the 2D sheet of **2** is different from that of complex **1**, even though they are both grids. First, the sheet of **2** is completely planar and each grid is a square (see Figure 1b and Figure S1 in the Supporting Information) while that of **1** has a corrugated and wavy network structure. In addition, the ligand forms a "V" shape to match the coordination geometry of **2**, while in the case of **1** L1 has an almost linear

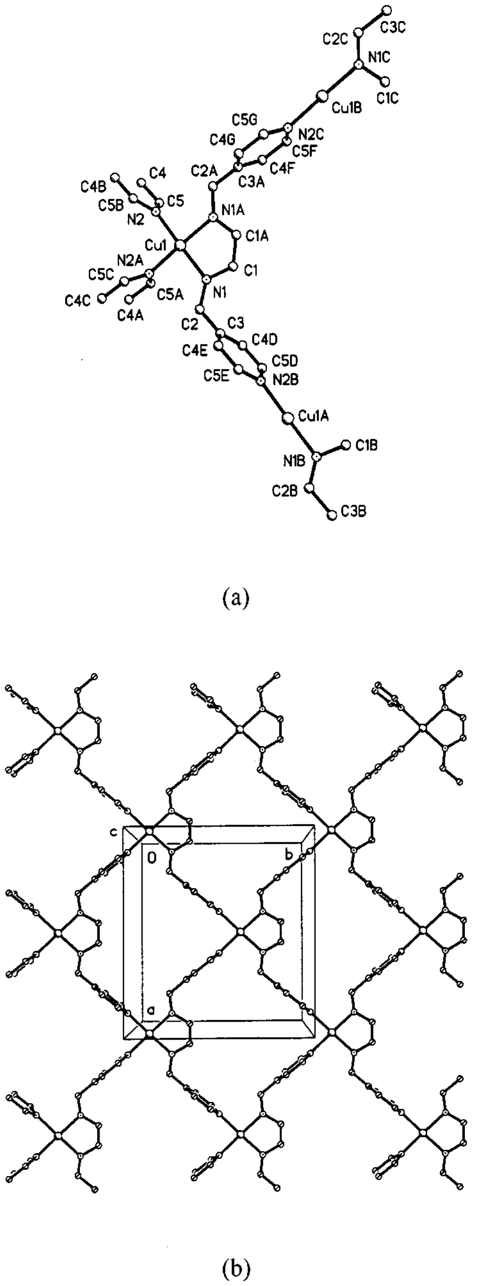


Figure 2. (a) Crystal structure of the cationic moiety of [Cu(L1-2H)](AcOH)$_2$·(C$_2$H$_5$)$_2$O·4H$_2$O **2** with atom numbering scheme; (b) infinite 2D grid network of [Cu(L1-2H)](AcOH)$_2$·(C$_2$H$_5$)$_2$O·4H$_2$O **2**

conformation. The Cu−Cu separation in the square of **2** is 9.12 Å. There are open channels in **2** since the two adjacent sheets are parallel to each other (see Figure S2 in the Supporting Information). The channels are occupied by distorted acetic acid, diethyl ether and water molecules (see Figures S1 and S2 in the Supporting Information). The Cu−Cu distance between two adjacent sheets is 9.40 Å. There are two C(5)−H···O(1) and C(32)−H···O(4) hydrogen bonds (Table 3). Complex **2** rapidly loses diethyl ether in the air; however, the presence of water and acetic acid can be confirmed by thermogravimetric analysis. The TGA data of **2** showed a loss of water and acetic acid centered at 110 and 180 °C, respectively.

We obtained two unexpected infinite zigzag chains **3** and **4** by using a readily prepared ligand L2. The very similar cell parameters of complexes **3** and **4** indicate that they are isomorphous and isostructural. Therefore, only the structure of **3** is described here. The repeat unit of the crystal structure of **3** is illustrated in Figure 3a. Each Cu^{I} atom is coordinated by two N atoms of the ethylenediimine unit of one L2, a pyridine group of the other L2 and one acetonitrile molecule. The coordination environment of the copper(I) atom is a distorted tetrahedron. The average Cu−N distance of 2.035(3) Å is similar to those (2.02−2.07 Å) of four-coordinate copper(I) complexes,[15] and is shorter than that of complex **1** [2.082(6) Å]. The Cu(1)−N(31) (MeCN) distance of 1.936(3) Å is in the range of reported four-coordinate copper(I) complexes with acetonitrile ligands [1.86−2.26 Å].[16−18] The Cu−Cu separation of 7.54 Å is much longer than that in Cu metal (2.56 Å), and implies no Cu^{I}−Cu^{I} interactions in the crystal. The dihedral angle between the two terminal pyridine units of the L2 ligand is 8.6° which is different from that of **1** (82.5°). It has been reported that a di-Schiff base ligand obtained from pyridine-2-carbaldehyde and ethane-1,2-diamine, when reacted with silver(I) complexes, forms a dinuclear double-stranded helical complex.[19]

It is interesting to note that one pyridine unit of the L2 ligand remains uncoordinated, with one acetonitrile molecule coordinating to the Cu^{I} atom instead. This phenomenon is unusual in tetradentate bridging ligands since the coordination ability of acetonitrile is weaker than that of the pyridine unit. Such a coordination mode gives an extended polynuclear Cu^{I} cation with a zigzag chain-like structure as illustrated in Figure 3 (b and c). It is noteworthy that each Cu^{I} atom in **3** is coordinated by three N atoms from two L2 ligands and, in turn, each L2 ligand connects two Cu^{I} atoms, while in the case of **1**, **2** and other complexes with the L1 ligand, each metal ion is coordinated by four N atoms from three L1 ligand and each L1 ligand connects three metal ions. The nitrate counter ions are located between the two chains by formation of two C−H···O hydrogen bonds between the oxygen atom and pyridyl C−H group (Table 3).

From the present and previous studies it was found that both metal ions and organic ligands have a great influence on the construction of supramolecular frameworks. The reactions between the flexible ligand L1 and Ag^{I}, Cu^{I}, Cu^{II} salts with different anions are summarized schematically in Figure 4. It has been reported that different 2D networks can be prepared by reactions of 2,1,3-benzothiadiazoles with copper(I) perchlorate and nitrate due to the different coordination ability of perchlorate and nitrate ions.[20] However, in the case of our copper(I) complexes, the same frameworks were obtained from L1 and Cu(CH$_3$CN)$_4$ClO$_4$ and Cu(CH$_3$CN)$_4$NO$_3$. This implies that there is no obvious influence of the anions on the formation of networks

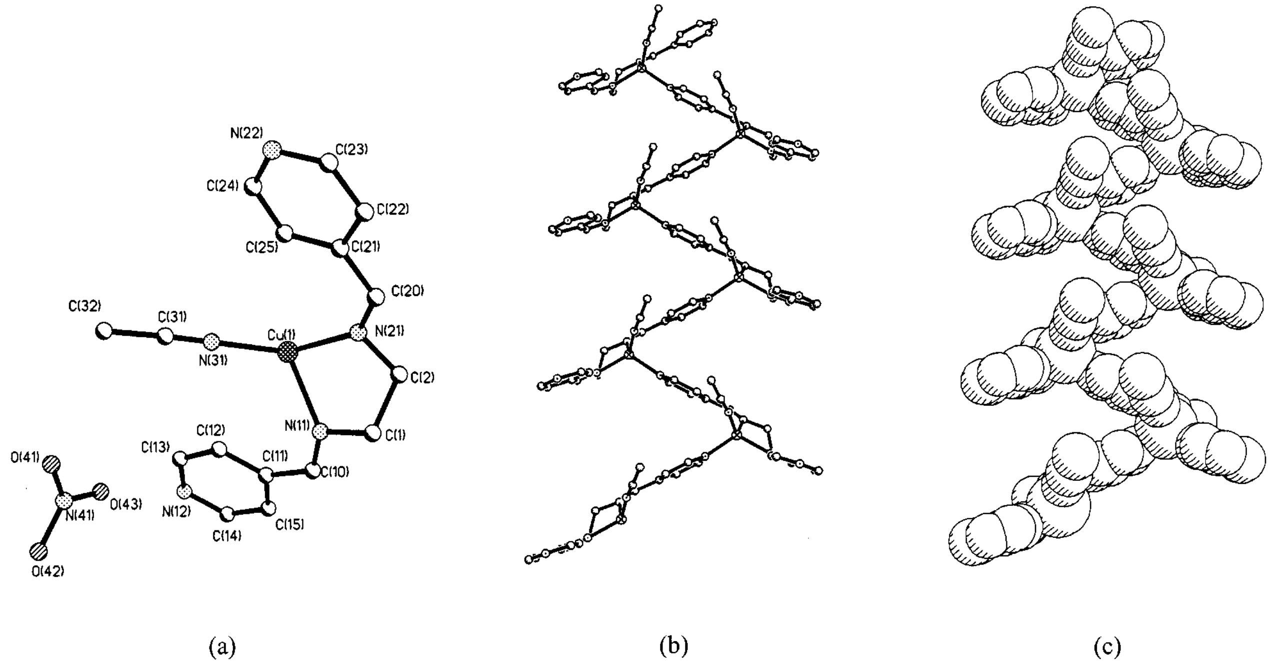


Figure 3. (a) Crystal structure of [Cu(L2)(CH_3CN)]NO_3 **3** with atom numbering scheme; (b) part of the single helical structure of **3**; (c) space-filling representation of **3**

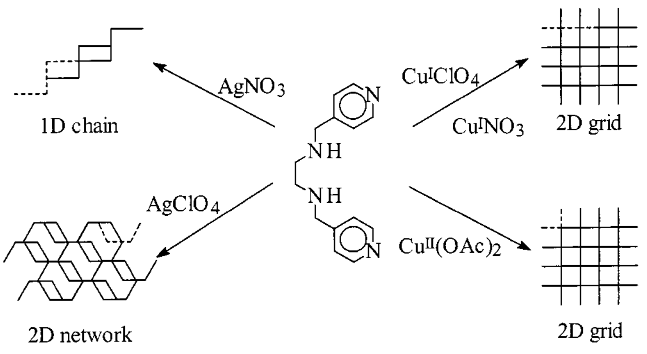


Figure 4. Schematic drawing for reactions between the L1 and Ag^I, Cu^I and Cu^{II} salts; the dashed line refers to one of the L1 ligands

in the Cu^I−L1 system; in the case of silver(I) complexes with the same L1 ligand, 1D and 2D arrays were formed by self-assembly of L1 with silver(I) nitrate and perchlorate, respectively.[5] These results imply that the assembly process is also influenced by the nature of the metal ions. The different structures of complexes **1** and **2** were considered to be caused by the different geometric needs of Cu^I and Cu^{II} ions.

Properties

Powdered samples of the Cu^{II} complex of L1 (**2**) showed photoluminescence with an emission maximum at 430 nm upon excitation at 310 nm. However, no photoluminescence was observed for the Cu^I complex **1**. Powdered **3**, with the di-Schiff base ligand, also showed photoluminescence, with an emission maximum at 391 nm upon excitation at 291 nm. These results indicate that the luminescent properties of the synthesized complexes depend on the nature of the organic ligand and the oxidation state of the metal ions.

The magnetic properties of complex **2** were studied by susceptibility measurements. The effective moment of complex **2** is 1.98 μ_B ($\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}) at 300 K and 1.73 μ_B at 75 K, which is the same as the spin-only value of 1.73 μ_B expected for isolated Cu^{II} ($S = 1/2$). The slight smooth decrease of μ_{eff} with T shows that a very weak antiferromagnetic exchange is operative due to the large intermetallic distance, as revealed by the X-ray crystal structure.

Conclusion

We have shown that the ligand L1 reacts with [Cu(CH_3CN)$_4$]NO_3 and Cu(OAc)$_2$·H_2O to afford two coordination networks. The two grids of complexes **1** and **2** are slightly different, the ligand in the structure of **1** is linear, whilst in **2** it is in a "V" shape. This is due to the different coordination requirement of the metal ions, which in turn is due to the different ionic radii. These results indicate that even if the same ligand is used, the assembly process may be different due to the different valence of te metal ions. To the best of our knowledge, examples of this are very rare.

The ligand L2 is similar to L1 except for the rigidity: when they react with [Cu(CH_3CN)$_4$]NO_3, the resulting supramolecular frameworks are very different. One product is an infinite chain structure and the other is a 2D grid network. In addition, complexes of **1** and **2** are stabilized by T-type edge-to-face π-π interactions, whereas no such interactions were observed in the structure of **3**. This suggests that the rigidity of a ligand may have a significant effect on the construction of complexes.

These results imply that the coordination geometry of the ligand and the coordination requirement of the transition metal ion are the primary factors in the construction of supramolecular structures.

Experimental Section

General Methods: All commercially available chemicals were of reagent grade and used as received without further purification. Acetonitrile and ethanol were dried and purified by distillation before use. L1 and $[Cu(CH_3CN)_4]NO_3$ were prepared according to literature methods.[5,21] Samples for C, H and N analyses were dried in vacuum and the analyses were made on a Perkin−Elmer 240C elemental analyzer at the analysis center of Nanjing University. ^1H NMR spectroscopy was performed on a Bruker AM-500 NMR spectrometer, using TMS ($SiMe_4$) as an internal reference at room temperature. Thermogravimetric and differential analyses were taken on a simultaneous SDT 2960 thermal analyzer under N_2 with a heating rate of 10 °C/min. Luminescence spectra were recorded on an Hitachi 850 fluorescence spectrophotometer at room temperature (25 °C). Magnetic measurements on powdered samples were carried out using a CHAN-2000 Faraday magnetometer in the $75 \approx 300$ K temperature range. The apparatus was calibrated with $[Ni(en)_3]S_2O_3$ (en = ethylenediamine). Diamagnetic corrections were made using Pascal's constants.

Synthesis of 1,2-Bis(4′-pyridylmethyleneamino)ethane (L2): 1,2-Ethanediamine (0.53 mL, 7.9 mmol) was dissolved in 30 mL of refluxing absolute methanol and pyridine-4-carbaldehyde (1.41 mL, 15.0 mmol) in 30 mL of absolute methanol was added slowly to give a clear yellowish solution. The mixture was refluxed for 3 h and stirred overnight at ambient temperature. The solvents were removed by evaporation, then 30 mL deionized water was added, and the products were extracted with chloroform (4 × 25 ml). The chloroform solution was evaporated to a syrupy residue under reduced pressure. A powder was obtained by recrystallization of the residue from chloroform and diethyl ether. Washing with diethyl ether and drying in vacuum gave L2 (1.64 g, 92%). − ES-MS: $m/z = 239.1$ $[L2 + H]^+$. − $C_{14}H_{14}N_4$ (238.29): calcd. C 70.56, H 5.92, N 23.51; found C 70.49, H 5.64, N 23.53.

Synthesis of $[Cu(L1)]NO_3{\cdot}H_2O$ (1): All the procedures for synthesis and spectral measurements were carried out under an argon atmosphere. An acetonitrile solution of $Cu(CH_3CN)_4NO_3$ (0.1 mmol) was added dropwise to a solution of L1 (24.2 mg, 0.1 mmol) in acetonitrile (10 mL) at room temperature to give a clear solution. Orange single crystals (22.1 mg, 40%) suitable for X-ray diffraction were obtained by slow diffusion of diethyl ether into the clear filtrate for several days. − ^1H NMR (CD_3CN, 25 °C): $\delta = 2.81$ (s, 4 H), 3.79 (s, 4 H), 7.36 (br, 4 H), 8.60 (br, 4 H). − $C_{14}H_{18}CuN_5O_3$ (367.87): calcd. C 45.71, H 4.93, N 19.04; found C 45.77, H 5.17, N 19.18.

Synthesis of $[Cu(L1\text{-}2H)](AcOH)_2{\cdot}(C_2H_5)_2O{\cdot}4H_2O$ (2): A deionized aqueous solution (1 mL) of $Cu(OAc)_2{\cdot}H_2O$ (19.9 mg, 0.1 mmol) was added dropwise to an ethanol solution (10 mL) of L1 (24.2 mg, 0.1 mmol) at 50 °C and stirred for 20 min. Blue single crystals (45.2 mg, 70%) suitable for X-ray diffraction were obtained by slow diffusion of diethyl ether into the clear filtrate for several days. − $C_{18}H_{28}CuN_4O_6$ (459.99): calcd. C 47.00, H 6.14, N 12.18; found C 47.38, H 6.01, N 11.93. (The diethyl ether and part of water molecules might be lost during the drying process)

Synthesis of $[Cu(L2)(CH_3CN)]NO_3$ (3): The complex was prepared in the same way as complex **1** except that L1 was replaced by L2. Orange single crystals suitable for X-ray diffraction were obtained (25.8 mg, 64%). − $C_{16}H_{17}CuN_6O_3$ (404.89): calcd. C 47.46, H 4.23, N 20.75; found C 47.24, H 4.32, N 20.89.

Synthesis of $[Cu(L2)(CH_3CN)]ClO_4$ (4): The procedure was similar to that of complex **3** except $[Cu(CH_3CN)_4]NO_3$ was changed to $[Cu(CH_3CN)_4]ClO_4$. Orange single crystals were obtained (26.5 mg, 60%). − $C_{16}H_{17}ClCuN_5O_4$ (442.34): calcd. C 43.44, H 3.87, N 15.83; found C 43.65, H 4.19, N 15.76.

X-ray Crystal Structure Analysis for Complexes 1, 2 and 3: The intensity data were collected at −50 °C for **1** and **3** on a Rigaku RAXIS-RAPID Imaging Plate diffractometer. The data collection for **2** was performed on a Rigaku AFC7S automatic four-circle diffractometer at room temperature, using graphite-monochromated Mo-K_α radiation ($\lambda = 0.7107$ Å). The structures were solved by direct methods with SIR92,[22] and expanded using Fourier techniques.[23] All data were refined anisotropically by the full-matrix least-squares method for non-hydrogen atoms. The hydrogen atoms were generated geometrically. All calculations were carried out on SGI workstation using the teXsan crystallographic software package of Molecular Structure Corporation.[24]

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-154337 (**1**), CCDC-154338 (**2**) and CCDC-154339 (**3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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