Hydrothermal synthesis of copper complexes of 4′-pyridyl terpyridine: From discrete monomer to zigzag chain polymer

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Abstract

Seven copper complexes $[Cu(L1)I_2]$ (**1**), $[Cu_2(L1)_2I_2]_2[Cu_2(\mu\text{-}I)_2I_2]$ (**2**), $[Cu(L2)I_2]$ (**3**), $[Cu_2(L2)(\mu\text{-}I)I(PPh_3)]$ (**4**), $[Cu_4(L2)_2(\mu\text{-}I)_2I_2]$ (**5**), $\{[Cu(L2)I]_2[Cu_2(\mu\text{-}I)_2I_2]\}_n$ (**6**) and $[Cu_2(L2)(\mu\text{-}I)_2]_n$ (**7**) have been prepared by reactions of ligands: 4′-(2-pyridyl)-2,2′:6′,2″-terpyridine (**L1**) and 4′-(3-pyridyl)-2,2′:6′,2″-terpyridine (**L2**) with CuI in hydrothermal conditions, respectively. By alternating the oxidations states of the metal centers, increasing stoichiometric metal/ligand ratio and introducing a second ligand, the compounds, were successfully developed from mononuclear (**1** and **3**) to multinuclear (**2**, **4** and **5**) and polymers (**6** and **7**). The synthesis of these compounds may provide an approach for the construction of coordination compounds of 4′-pyridyl terpyridine with different nuclearity.
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Keywords: Terpyridine; Hydrothermal reaction; Copper mixed-valent complex; Copper iodide; Coordination polymer
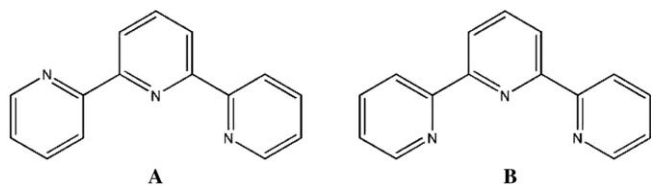
1. Introduction

The design of complex molecular architectures is an important goal for synthetic chemistry as it provides the opportunity to control or encode the properties of a material at the molecular level [1]. Chemists have great interest in the design, synthesis and exploring the properties of coordination polymers. 2,2′:6′,2″-Terpyridine (terpy) and its derivatives have been intensively explored because of their versatility as building blocks for supramolecular assembles and polymers [2,3] and the interesting electronic, photonic, magnetic, reactive and structural properties shown by the transition metal complexes of these ligands [4]. In the last decades, special attention has been drawn to the 4′-functionalized terpyridine ligands, since the appended substituents may be utilized not only to tailor the electronic properties of the ligand and its metal complexes, but also to incorporate new functionalities through

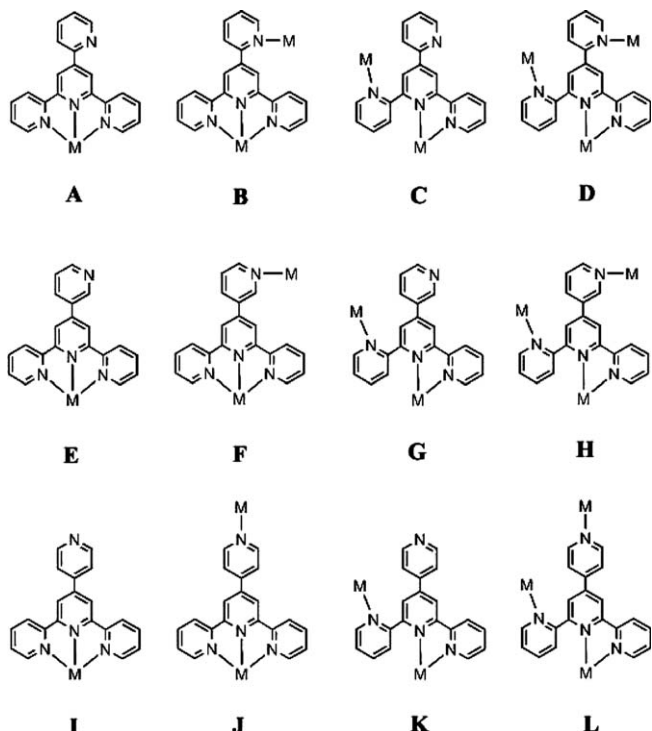further derivative reactions, as well as to introduce terpyridine complexes into polymers [5].

For 4′-functionalized terpyridines, the pyridyl-substituted 4′-pyridyl terpyridines (pyterpy) have been essentially ignored and scarcely reported [6,7]. As an oligopyridine ligand with multi-domain, 4′-pyridyl terpyridine is a potentially bridging ligand, incorporating a tridentate 2,2′:6′,2″-terpyridine functionality and an isolated monodentate pyridyl group. When the terpyridine is bonded to a metal, it isomerizes to a *cis*-configuration (Scheme 1, left), though preferably to *cis–cis*-configuration (Scheme 1, right). At the same time, the different N-donor pyridyl attached to the C(4′) position of a 2,2′:6′,2″-terpyridine ligand may result in different coordination modes (Scheme 2). Constable [7] has reported that the 4′-pyridyl substituent is very weakly electron withdrawing when placed in the C(4′) position of a 2,2′:6′,2″-terpyridine ligand and the extended conjugation make pyterpy a better π-acceptor ligand than terpyridine, such that it stabilizes the lower oxidation states. The pyterpy may be used in the assembly of coordination compounds because of their diverse coordination modes and bridging ability.

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Scheme 1. The different configurations of terpyridine.
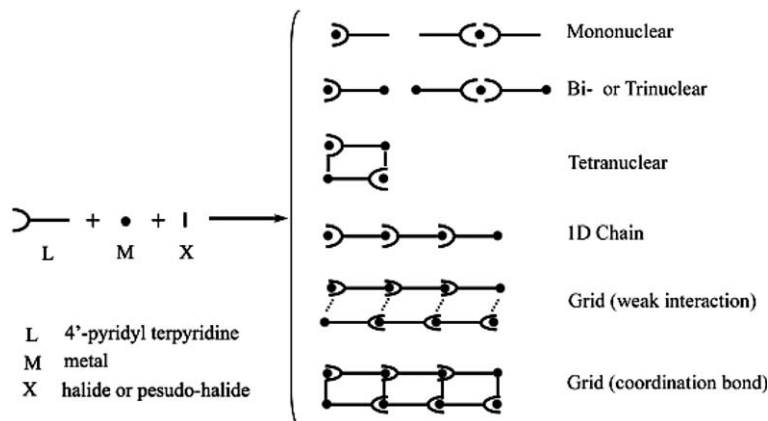

Scheme 2. Coordination modes of pyterpys.

ences of the metal ions can lead to different fantastic polynuclear complexes such as molecular helicates, grids, rings and boxes [8–10]. Sauvage [11] have reported that the coordination preferences of copper in different oxidation states, e.g. four-coordinate copper(I), five- or six-coordinate copper(II), may be used to drive supramolecular systems. On the other hand, copper(I) halide were commonly selected as the metal source due to their ability to form neutral arrays [12], and the strong coordination nature of the halide anion which can bridge two or more copper centers and can be connected to form coordination polymers using diverse bridging ligands. It is reasonable to predict that the copper compounds based on pyterpy and an appropriate linkers, such as halide and pseudo-halide X (Cl, Br, I, SCN or CN), can be developed from monomers to polymers as shown in Scheme 3.

On the basis of our pervious work [13,14], we report the hydrothermal preparation of several compounds of 4′-(2-pyridyl)-2,2′:6′,2″-terpyridine (**L1**) and 4′-(3-pyridyl)-2,2′:6′,2″-terpyridine (**L2**) with copper(I) iodide. By changing the reaction conditions (temperature, stoichiometry, additives), the valence of copper varied form bivalence to mixed-valence and monovalence, the compounds developed from mononuclear to multinuclear and polymers. The result shows that it is an effective way to achieve coordination polymers of pyterpy by controlling the oxidation states of metal centers and selecting appropriate linkers.

2. Experimental

2.1. General

All chemicals and reagents are commercially available and were used as received without further purification. The ligand **L1** and **L2** were synthesized by a modified literature method [26,42]. FT-IR spectra (KBr pellets) were recorded on a Nicolet Avatar 360 FTIR spectrometer in the range 4000–400 cm^{-1} region. Elemental analyses of C, H, and N were determined with a Perkin–Elmer 2400 C elemental analyzer.

Our studies were induced by the interest in the development of different polynuclear complexes of the 4′-pyridyl terpyridine, in which the discrete complex entities are further assembled into larger entities or arrays of defined architectures. Self-assembly processes controlled by the multidentate ligands and the coordinated geometry preferences

Scheme 3. Topologies of some pyterpy compounds.

2.2. Preparation of ligands and complexes

2.2.1. 4′-(2-Pyridyl)-2,2′:6′,2″-terpyridine (L1)

A solution of 2-acetylpyridine (3.64 g, 0.03 mol), and pyridine-3-carboxaldehyde (1.61 g, 0.015 mol) was stirred in basic aqueous ethanolic solution for 15 h at room temperature. After this period either a white solid or an orange gum was precipitated. The reaction of the solid or gum with an excess of ammonium acetate in ethanol resulted in the formation of the desired ligand pyterpy **L1** in 25% yield as a yellow crystalline solid. m.p. 232 °C. *Anal.* Calc. for $C_{20}H_{14}N_4$: C, 77.40; H, 4.55; N, 18.05. Found: C, 77.42; H, 4.53; N, 18.02%. IR (cm^{-1}, KBr): 1581s, 1548m, 1467m, 1393m, 993m, 780m.

2.2.2. 4′-(3-Pyridyl)-2,2′:6′,2″-terpyridine (L2)

It was prepared analogously to **L1** by replacing 2-acetylpyridine with 3-acetylpyridine in the same mole ratio. As a result, yellow crystalline solid was obtained in 35% yield. m.p. 232 °C. *Anal.* Calc. for $C_{20}H_{14}N_4$: C, 77.40; H, 4.55; N, 18.05. Found: C, 77.42; H, 4.53; N, 18.02%. IR (cm^{-1}, KBr): 1581s, 1548m, 1467m, 1393m, 993m, 780m.

2.2.3. [Cu(L1)I₂] (1)

The mixture of CuI (0.0190 g, 0.1 mmol), ligand **L1** (0.0155 g, 0.05 mmol), saturated KI solution (3 ml) and water (6 ml) were placed and sealed in a 10 ml Teflon-lined stainless steel reactor and heated to 140 °C for 72 h, then cooled down to room temperature at a rate of 2 °C/ 20 min. Black bar single crystals suitable for X-ray diffraction were obtained in ca. 60% yield. *Anal.* Calc. for

$C_{20}H_{14}CuI_2N_4$: C, 38.27; H, 2.25; N, 8.93. Found: C, 38.11; H, 2.15; N, 8.98%.

2.2.4. [Cu₂(L1)₂I₂][Cu(μ-I)I] (2)

The mixture of CuI (0.0380 g, 0.2 mmol), ligand **L1** (0.0155 g, 0.05 mmol), saturated KI solution (2.5 ml), 4,4′-bipyridyl (0.0192 g, 0.1 mmol) and water (8 ml) were placed and sealed in a 10 ml Teflon-lined stainless steel reactor and heated to 180 °C for 72 h, then cooled down to room temperature at a rate of 5 °C/1 h. Red block single crystals suitable for X-ray diffraction were obtained in ca. 40% yield. *Anal.* Calc. for $C_{40}H_{28}Cu_3I_4N_8$: C, 47.97; H, 2.82; N, 11.19. Found: C, 47.70; H, 3.07; N, 10.87%.

2.2.5. [Cu(L2)I₂] (3)

The mixture of CuI (0.0190 g, 0.1 mmol), ligand **L2** (0.0155 g, 0.05 mmol), saturated KI solution (3 ml) and water (6 ml) were placed and sealed in a 10 ml Teflon-lined stainless steel reactor and heated to 140 °C for 72 h, then cooled down to room temperature at a rate of 2 °C/ 20 min. Black bar single crystals suitable for X-ray diffraction were obtained in ca. 40% yield. *Anal.* Calc. for $C_{20}H_{14}CuI_2N_4$: C, 38.27; H, 2.25; N, 8.93. Found: C, 38.11; H, 2.15; N, 8.98%.

2.2.6. [Cu₂(L2)(μ-I)I(PPh₃)] (4)

The mixture of CuI (0.0190 g, 0.1 mmol), ligand **L2** (0.0155 g, 0.05 mmol), saturated KI solution (2.5 ml), triphenylphosphine (PPh₃) (0.0262 g, 0.1 mmol) and water (6 ml) were placed and sealed in a 10 ml Teflon-lined stainless steel reactor and heated to 180 °C for 72 h, then cooled down to room temperature at a rate of 5 °C/1 h. Red block

Table 1
Crystal data and structure refinement parameters for complexes **1–7**

Parameter	1	2	3	4	5	6	7
Formula	$C_{20}H_{14}CuI_2N_4$	$C_{40}H_{28}Cu_3I_4N_8$	$C_{20}H_{14}CuI_2N_4$	$C_{38}H_{29}Cu_2I_2N_4P$	$C_{20}H_{14}Cu_2I_2N_4$	$C_{20}H_{14}Cu_2I_3N_4$	$C_{20}H_{14}Cu_2I_2N_4$
M_r	627.69	1318.92	627.69	953.50	691.23	818.13	691.23
T (K)	295(2)	295(2)	295(2)	295(2)	295(2)	295(2)	295(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	triclinic	triclinic	orthorhombic	monoclinic	monoclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$Pca2_1$	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a (Å)	8.4785(5)	9.888(2)	19.136(1)	14.081(3)	9.3094(6)	7.7388(15)	9.5014(19)
b (Å)	9.4286(6)	11.090(2)	14.9546(8)	14.931(3)	16.6148(11)	9.5312(19)	9.992(2)
c (Å)	12.5448(8)	19.121(4)	13.7467(7)	18.061(4)	13.6598(9)	16.777(3)	11.427(2)
α (°)	82.771(1)	90.62(3)	90	90	90	90.02(3)	69.52(3)
β (°)	85.006(1)	99.06(3)	90	108.98(3)	101.5710(10)	100.42(3)	81.39(3)
γ (°)	87.183(1)	93.28(3)	90	90	90	111.17(3)	89.00(3)
V (Å^3)	990.4(1)	2066.7(7)	3934.0(4)	3590.7(12)	2069.9(2)	1132.0(4)	1004.1(3)
Z	2	2	8	4	4	2	2
D_{calc} (g cm^{-3})	2.105	2.119	2.120	1.764	2.218	2.400	2.286
μ (mm^{-1})	4.232	4.557	4.262	2.981	5.051	5.984	5.206
Reflections collected	8587	10874	23912	30175	12799	8211	7345
Unique reflections	4427	7168	6808	8170	4691	3958	3525
R_{int}	0.016	0.0184	0.041	0.0340	0.0237	0.0191	0.0168
Goodness-of-fit on F^2	1.10	1.012	1.031	1.059	1.051	1.062	1.033
R_1,[a] wR_2[b] [$I > 2\sigma(I)$]	0.030, 0.075	0.0424, 0.0967	0.0409, 0.0886	0.0359, 0.0793	0.0312, 0.0669	0.0326, 0.0661	0.0565, 0.1345
R_1,[a] wR_2[b] (all data)	0.035, 0.087	0.0599, 0.1070	0.0511, 0.0958	0.0551, 0.0928	0.0399, 0.0702	0.0390, 0.0708	0.0655, 0.1420

[a] $R_1 = \sum ||F_o| - |F_c||/\sum |F_o|$.
[b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$.

single crystals suitable for X-ray diffraction were obtained in ca. 50% yield. *Anal*. Calc. for $C_{38}H_{29}Cu_2I_2N_4P$: C, 47.86; H, 3.07; N, 5.88. Found: C, 46.70; H, 3.01; N, 5.67%.

2.2.7. [Cu$_4$(**L2**)$_2$(μ-I)$_2$I$_2$] (**5**)

The mixture of CuI (0.0380 g, 0.2 mmol), ligand **L2** (0.0155 g, 0.05 mmol), copper powder (0.0128 g, 0.2 mmol), saturated KI solution (2.5 ml), acetonitrile (2 ml) and water (6 ml) were placed and sealed in a 15 ml Teflon-lined stainless steel reactor and heated to 140 °C for 72 h, then cooled down to room temperature at a rate of 5 °C/1 h. Brown bar single crystals suitable for X-ray diffraction were obtained in ca. 45% yield. *Anal*. Calc. for $C_{20}H_{14}Cu_2I_2N_4$: C, 34.75; H, 2.04; N, 8.11. Found: C, 34.70; H, 2.01; N, 8.06%.

2.2.8. {[Cu(**L2**)I]$_2$[Cu$_2$(μ-I)$_2$I$_2$]}$_n$ (**6**)

The mixture of CuI (0.0380 g, 0.2 mmol), ligand **L2** (0.0155 g, 0.05 mmol), saturated KI solution (2.5 ml), acetonitrile (2 ml) and water (6 ml) were placed and sealed in a 15 ml Teflon-lined stainless steel reactor and heated to 140 °C for 72 h, then cooled down to room temperature at a rate of 5 °C/1 h. Brown bar single crystals suitable for X-ray diffraction was obtained in ca. 25% yield. *Anal*. Calc. for $C_{20}H_{14}Cu_2I_3N_4$: C, 29.36; H, 1.72; N, 6.85. Found: C, 29.30; H, 1.70; N, 6.80%.

2.2.9. [Cu$_2$(**L2**)(μ-I)$_2$]$_n$ (**7**)

The mixture of CuI (0.0190 g, 0.1 mmol), ligand **L2** (0.0155 g, 0.05 mmol), saturated KI solution (2 ml), bis(diphenylphosphanyl)methane (dppm) (0.0192 g) and water (10 ml) were placed and sealed in a 15 ml Teflon-lined stainless steel reactor and heated to 180 °C for 72 h, then cooled down to room temperature at a rate of 5 °C/1 h. Rufous block single crystals suitable for X-ray diffraction were obtained in ca. 50% yield. *Anal*. Calc. for $C_{20}H_{14}Cu_2I_2N_4$: C, 34.75; H, 2.04; N, 8.11. Found: C, 34.70; H, 2.01; N, 8.15%.

2.3. Crystallography

Suitable crystals of the compounds were mounted with glue at the end of a glass fiber, respectively. Diffraction data were collected at 295(2) K with a Bruker-AXS SMART CCD area detector diffractometer using ω rotation scans width of 0.3° and Mo Kα radiation ($\lambda = 0.71073$ Å). The crystal parameters and experimental details of the data collection are summarized in Table 1. The data collections covered the full spheres of the reciprocal space of the complexes. Empirical absorption corrections were carried out utilizing SADABS routine. The structures were solved by the direct method and refined by full-matrix least-squares refinements based on F^2. All non-hydrogen atoms were refined with anisotropic thermal parameters, and all hydrogen atoms were included in calculated positions and refined with isotropic thermal parameters riding on those of the parent atoms. Structure

Table 2
Selected bond lengths (Å) and bond angles (°) for **1**–**7**[a]

Complex 1			
Cu(1)–I(1)	2.5850(5)	I(1)–Cu(1)–N(3)	99.19(8)
Cu(1)–I(2)	2.8323(5)	I(2)–Cu(1)–N(1)	95.53(9)
Cu(1)–N(1)	2.062(3)	I(2)–Cu(1)–N(2)	96.98(8)
Cu(1)–N(2)	1.955(3)	I(2)–Cu(1)–N(3)	98.35(8)
Cu(1)–N(3)	2.061(3)	N(1)–Cu(1)–N(2)	79.0(1)
I(1)–Cu(1)–I(2)	100.36(2)	N(1)–Cu(1)–N(3)	155.1(1)
I(1)–Cu(1)–N(1)	98.57(8)	N(2)–Cu(1)–N(3)	78.8(1)
I(1)–Cu(1)–N(2)	162.65(9)		
Complex 2			
I1–Cu3	2.4888(14)	N1–Cu1–N2	75.51(18)
I2–Cu3	2.5733(14)	N2–Cu1–N3	74.93(17)
I2–Cu3#1	2.5960(13)	N1–Cu1–N3	150.44(17)
Cu3–Cu3#1	2.636(2)	N5–Cu1–N6	79.57(19)
N1–Cu1	2.296(5)	N6–Cu1–N7	79.08(19)
N2–Cu1	2.036(4)	N5–Cu1–N7	158.03(19)
N3–Cu1	2.332(5)	N2–Cu1–N5	98.13(18)
N5–Cu1	2.063(5)	N2–Cu1–N7	103.84(18)
N6–Cu1–	1.939(5)	N2–Cu1–N6	165.51(19)
N7–Cu1	2.060(5)	N1–Cu1–N7	97.10(18)
N4–Cu2	2.057(6)	N1–Cu1–N5	88.54(18)
I3–Cu2	2.4990(14)	N3–Cu1–N5	95.33(19)
I4–Cu2	2.5057(14)	N3–Cu1–N7	90.17(18)
I1–Cu3–I2	120.31(5)	N3–Cu1–N6	90.96(18)
I1–Cu3–I2#1	120.98(5)	N1–Cu1–N6	118.52(18)
I2–Cu3–I2#1	118.68(5)	N3–Cu2–I4	119.52(16)
Cu3–I2–Cu3#1	61.32(5)	N4–Cu2–I4	110.42(16)
I1–Cu3–Cu3#1	178.27(7)	I3–Cu2–I4	130.06(5)
Complex 3			
Cu1–N1	2.053(5)	N1–Cu1–N2	79.2(2)
Cu1–N2	1.953(5)	N2–Cu1–N3	79.2(2)
Cu1–N3	2.065(6)	N1–Cu1–N3	157.2(2)
Cu1–I1	2.560(1)	I1–Cu1–I2	104.57(4)
Cu1–I2	2.862(1)	N5–Cu2–N6	78.8(3)
Cu2–N5	2.047(6)	N6–Cu2–N7	78.9(2)
Cu2–N6	1.951(6)	N5–Cu2–N7	157.4(3)
Cu2–N7	2.036(6)	I3–Cu2–I4	110.77(4)
Cu2–I3	2.572(1)		
Cu2–I4	2.806(1)		
Complex 4			
I1–Cu2	2.6137(8)	I1–Cu1–N1	98.92(8)
I1–Cu1	2.6617(8)	I1–Cu1–N2	117.72(7)
I2–Cu2	2.4870(7)	N1–Cu1–N2	77.11(10)
Cu1–N1	2.062(3)	N1–Cu1–Cu2	91.28(8)
Cu1–P1	2.2106(10)	N2–Cu1–Cu2	59.39(7)
Cu1–N2	2.231(3)	N2–Cu2–N3	74.26(10)
Cu1–Cu2	2.6791(9)	N3–Cu2–I2	133.18(8)
Cu2–N3	2.041(3)	N3–Cu2–I1	105.98(8)
Cu2–N2	2.464(3)	N3–Cu2–Cu1	84.48(8)
P1–Cu1–N1	125.96(9)	Cu1–I1–Cu2	61.03(3)
P1–Cu1–N	111.75(7)	I1–Cu2–I2	118.74(2)
P1–Cu1–I1	118.81(4)		
P1–Cu1–Cu2	140.49(3)		
Complex 5			
Cu1–N1	2.046(3)	N1–Cu1–N2	77.17(10)
Cu1–N2	2.241(2)	N1–Cu1–I1	119.34(8)
Cu2–N3	1.990(3)	N2–Cu1–I1	105.21(7)
Cu2–N4#1	1.979(3)	N1–Cu1–I2	105.87(8)
I1–Cu1	2.5036(6)	N2–Cu1–I2	118.78(7)
I2–Cu1	2.6515(5)	I1–Cu1–I2	122.351(18)
I2–Cu2	2.6102(5)	N3–Cu2–I2	108.11(8)

(continued on next page)

Table 2 (*continued*)

Complex 5			
Cu2–Cu1	2.6626(7)	N4#1–Cu2–I2	118.97(8)
		N4#1–Cu2–N3	131.40(11)
		Cu2–I2–Cu1	60.794(15)
Complex 6			
Cu1–N1	2.024(4)	N1–Cu1–N2	79.10(16)
Cu1–N2	1.949(4)	N2–Cu1–N3	79.39(16)
Cu1–N3	2.027(4)	N3–Cu1–N1	158.39(16)
Cu1–N4#1	2.124(4)	N2–Cu1–N4#1	124.06(16)
Cu1–I1	2.6365(10)	N2–Cu1–I1	131.95(12)
Cu2–I2	2.5833(14)	N4#1–Cu1–I1	103.92(11)
Cu2–I3	2.4856(10)	I2–Cu2–I3	119.86(4)
Cu2–I2#2	2.5799(13)	I2–Cu2–I2#2	120.16(4)
Cu2–I2#2	2.5799(13)	I3–Cu2–I2#2	119.97(4)
Cu2–Cu2#2	2.5752(15)		
Complex 7			
N1–Cu1	2.404(9)	N1–Cu1–N2	71.4(3)
N2–Cu1	2.121(7)	N2–Cu1–N3	74.9(3)
N3–Cu1	2.252(8)	N3–Cu1–N1	144.5(3)
N4#1–Cu2	2.025(7)	N2–Cu1–I1	142.6(2)
I1–Cu1	2.6307(16)	N2–Cu1–I2	107.6(2)
I2–Cu1	2.781(2)	I1–Cu1–I2	109.69(6)
I1–Cu2	2.5281(17)	I1–Cu2–I2	120.96(7)
I2–Cu2	2.5576(18)	N4#1–Cu2–I1	116.5(2)
Cu1–Cu2	2.754(3)	N4#1–Cu2–I2	110.0(2)

^a Symmetry codes: (#1) −*x*, −*y* + 2, −*z* − 1 for **2**; (#1) −*x* + 1, −*y* + 1, −*z* + 2 for **5**; (#1) *x* − 1, *y* − 1, *z* (#2) −*x* + 3, −*y*, −*z* for **6**; (#1) *x*, *y* + 1, *z* − 1 for **7**.

solutions, refinements and graphics were performed with the SHELXL-97 [43] package. Selected bond lengths and angles are given in Table 2.

3. Results

3.1. Structure of [Cu(**L1**)I₂] (**1**)

There is only one copper(II) metal center in the crystal structure of complex 1 (Fig. 1). The copper(II) atom displayed a distorted square pyramidal geometry and was coordinated by a tridentate terpyridine, in a *cis–cis*-configuration, and two independent iodine atoms to form a monomer. In the monomer, one iodine atom was in the apical site while the terpyridine and the other one iodine atom were at the equatorial positions. The distances of Cu–I varied from 2.5850(5) to 2.8323(5) Å and Cu–N from 1.955(3) to 2.062(3) Å, respectively; the angles around the distorted pyramidal copper atom vary from 78.8(1)° to 162.65(9)° (Table 1), which are all similar to the reported
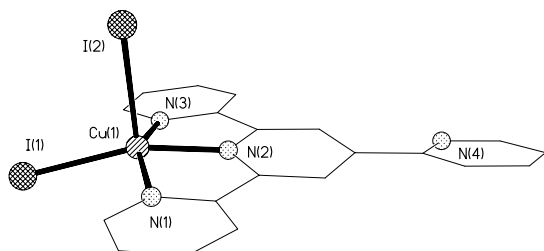

Fig. 1. View of complex **1**, a Cu^{II} mononuclear structure (Hydrogen atoms are omitted for clarity.).

values [24]. The terpyridine of **L1** are approximately planar (interannular torsion angles: 4.2°, 8.7°), the pendent pyridyl has rotated slightly and formed a dihedral angle with the central pyridyl ring of 12.5°.

3.2. Structure of [Cu₂(**L1**)₂I₂][Cu(μ-I)I] (**2**)

Complex **2** is mixed-valent. The asymmetric unit of **2** contains three crystallographically independent metal centers in the crystal structure (Fig. 2). The bivalence Cu(1) atom has a distorted octahedron geometry and was chelated by two ligands to form a CuN₆ polyhedron. The equatorial positions of the octahedron are occupied by three N atoms from a terpyridine and a N atom of the central pyridyl ring from another terpyridine. The remaining two apical positions are occupied by the terpyridine side pyridyls. As a result of the ligand geometry constraint and the Jahn-Teller effect of Cu²⁺ ion [27,28], the Cu–N distances vary from 1.939(5) to 2.332(5) Å and the angels around Cu(1) vary from 74.93(17)° to 165.51(19)°.

The monovalence Cu(2) has a slightly distorted trigonal planar geometry and was coordinated by two independent iodine atoms and the pendant pyridyl ring of pyterpy. The Cu–I distances were 2.4990(14) and 2.5057(14) Å; the Cu–N distance was 2.057(6) Å, comparable with the distances in other complexes in this work. The angles around Cu(2) vary from 110.42(16)° to 130.06(5)°, deviated from the idea value 120°.

Interestingly, the positive charge of the mixed-valence species is balanced by a counteranion [Cu₂I₄]²⁻, in which two Cu(I) ions are symmetrically bridged by two I⁻ ions and coordinated by two I⁻ ions, leading to a dimer of triangularly coordinated Cu(I) with the three angles of 120.31(5)°, 120.98(5)° and 118.68(5)°, respectively. The two symmetric copper atoms have a shorter distance of 2.636(2) Å, which is comparable with the distances of the analogues reported [21,29–33], indicating a strong interaction between them.

3.3. Structure of [Cu(**L2**)I₂]₂ (**3**)

X-ray diffraction proved that complex **3** is a racemic twin with Flack parameter refined to be 0.49(3) and two
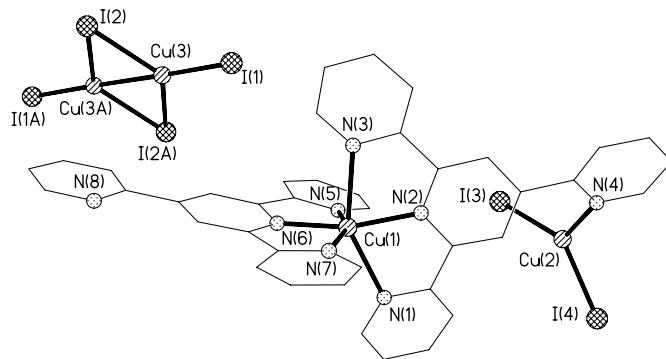

Fig. 2. View of complex **2**, containing Cu^I dinuclear and Cu^I–Cu^{II} dinuclear fragments (Hydrogen atoms are omitted for clarity.). Symmetry codes: (A) −*x*, −*y* + 2, −*z* − 1.
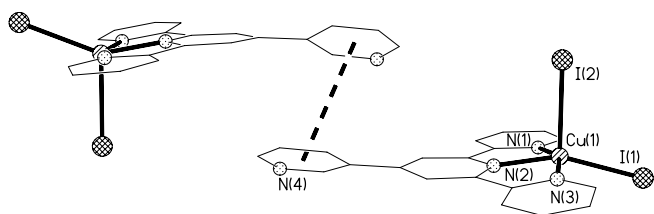
Fig. 3. View of complex **3**, a twin Cu^{II} mononuclear structure (Hydrogen atoms are omitted for clarity.).

Fig. 4. View of Complex **4**, a Cu^{I} dinuclear structure (Hydrogen atoms are omitted for clarity.).

independent copper metal centers in the crystal structure have shown +2 oxidation states (Fig. 3). The copper(II) atoms have shown the same configurations as complex **1** and formed a pair of monomers: Cu(L)I$_2$. The distances of Cu–I vary from 2.560(1) to 2.862(1) Å and Cu–N from 1.951(6) to 2.065(6) Å; the angles around the distorted pyramidal copper atom vary from 78.8(3)° to 157.4(3)° (Table 1), similar to those in complex **1** and the reported values [24].

The terpyridines are also approximately planar (interannular torsion angles: 3.2°, 5.6°; 4.2°, 7.6°), but the pendent pyridyl has rotated and formed a dihedral angle with the central pyridyl ring of 29.3° and 29.9°, respectively. Weak intermolecular face-to-face π–π stacking is found within the two pendant pyridyls (centroid–centriod distance 3.820 Å), which may resulted in the formation of the dimeric structure. The dimers aggregate into a pair of layers supported by π–π stacking with intra- and interlayer hydrogen bonds. In the pair of layers, the underlayer has shown a network of C–H···I and C–H···N hydrogen bonds, while the layer over it has shown pairs of hydrogen bonded parallel zigzag chains. This is quite different from the hydrogen bonding of **1** and the complex [Cd(L)(H$_2$O)(NO$_3$)$_2$] [L = 4′-(4-pyridyl)-2,2′:6′,2″-terpyridine] [6]. The pairs of layers are packed in a parallel manner and extended to a three-dimensional structure.

3.4. Structure of [Cu$_2$(L2)(μ-I)I(PPh$_3$)] (4)

The asymmetric unit of **4** contains two crystallographically independent copper(I) metal centers in the crystal structure (Fig. 4). Both of the copper atoms have shown distorted tetrahedron geometry. The two side rings and the pendent ring of ligand **L2** have twisted to form three interplanar angles with the central ring: 21.2°, 33.1° and 35.6°, respectively. Therefore, the terpyridine of **L2** has shown a *cis*-configuration, acting as two bidentate ligands coordinated to the copper atoms. Cu(1) is coordinated by N(1), N(2), I(1) and P(1) at the four apical positions, while Cu(2) is coordinated by N(2), N(3), I(1) and I(2). Here, the N(2) and I(1) act as two double bridging between the two copper metal centers. The two copper(I) atoms have a distance of 2.6791(9) Å indicating a strong Cu^{I}–Cu^{I} interaction, which is comparable with Cu^{I}–Cu^{I} distance found previously [25,26]. To be noticeable, the Cu(2) and N(2) distance of 2.464(3) Å is longer than normal Cu(I)–N dis-

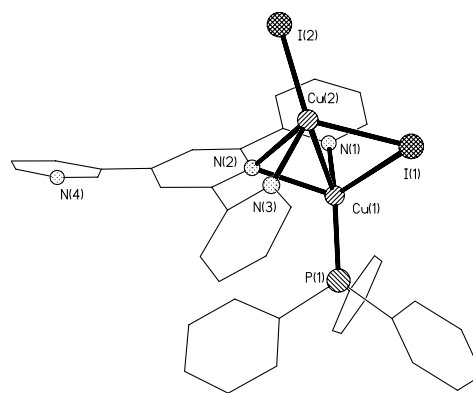tances. The fact that the sum of the angles around Cu(2), I(1)–Cu(2)–I(2), I(1)–Cu(2)–N(3) and I(2)–Cu(2)–N(3) of 357.9°, close to 360°, and the Cu(2) atom rising from the I(1)–I(2)–N(3) basal plane by 0.1933 Å, indicates Cu(2), I(1), I(2), N(3) in an approximately coplanar. Thus, there may have no or only a weak interaction between Cu(2) and N(2). If the interaction between Cu(2) and N(2) could be ignored, the coordination geometry of Cu(2) were more like the trigonal planar than the tetrahedron geometry. The angles around Cu(1) from 77.11(10)° to 125.96(9)° deviate from the ideal value 109.5°. These may be attributed to the geometric constraints imposed by the twisting of ligand **L2**.

3.5. Structure of [Cu$_4$(L2)$_2$(μ-I)$_2$I$_2$] (5)

The asymmetric unit of **5** contains two crystallographically independent copper(I) metal centers in the crystal structure (Fig. 5). The Cu(1) and Cu(2) have a distorted tetrahedron and a slightly distorted trigonal planar geometry, respectively. The terpyridine of **L2** has shown a *cis*-configuration and acts as a bidentate and a monodentate ligand coordinated to the copper(I) atoms, respectively. Cu(1) is coordinated by the bidentate part and two independent
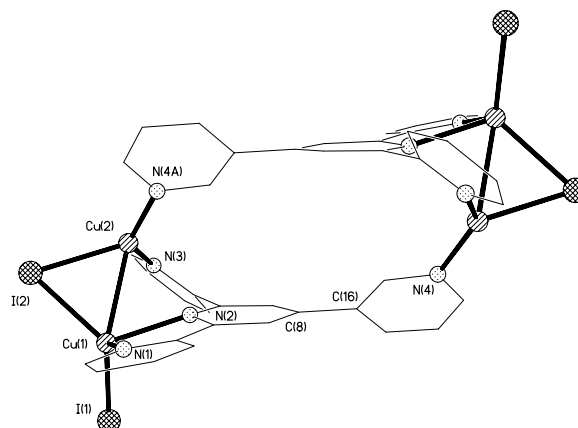

Fig. 5. View of complex **5**, a tetranuclear Cu^{I} structure (Hydrogen atoms are omitted for clarity.). Symmetry codes: (A) −x + 1, −y + 1, −z + 2.

iodine atoms: I(1) and I(2); Cu(2) is coordinated by the monodentate part with the pendent pyridyl group of another pyterpy and I(2). I(2) doubly bridges the two copper(I) metal centers. The two monovalent copper(I) atoms have a distance of 2.6626(7) Å and is comparable with that in **4**, indicating a strong Cu^I–Cu^I interaction. The Cu–N distances vary from 1.979(3) to 2.241(2) Å and Cu–I distances from 2.5036(6) to 2.6515(5) Å. The angles around Cu(1) of 77.17(10)–122.351(18)° and the angels around Cu(2) of 108.11(8)–131.40(11)° have deviated from the ideal value 109.5° and 120°, respectively. These may be attributed to the differences of coordination geometry and the geometric constraints imposed by the twisting of ligand **L2**.

The interplanar angles of the two side rings with the central ring of them were 9.7° and 42.1°, respectively. At the same time, there was a rotation about the interannular bond C(8)-C(16), given place to a dihedral angle of 46.0° between the planes of the pendent 4′-pyridyl group and the central pyridyl ring. This rotation is significant larger than those of the complexes in this work and the approximate magnitude 39.5° [6], 40.64° [34]. Furthermore, this twisting of the aromatic rings resulted in the formation of a tetranuclear grid-like dimer. The central pyridyl ring and the pendent pyridyl ring of another ligand have a centroid–centroid distance of 4.586 Å in the dimer, indicating aryl–aryl interaction is absent.

3.6. Structure of {[Cu(**L2**)I]₂[Cu₂(μ-I)₂I₂]}ₙ (**6**)

The asymmetric unit of **6** contains two crystallographically independent metal centers in the crystal structure (Fig. 6). The bivalent Cu(1) atom is five-coordinated and its distorted square pyramidal sites include three nitrogen
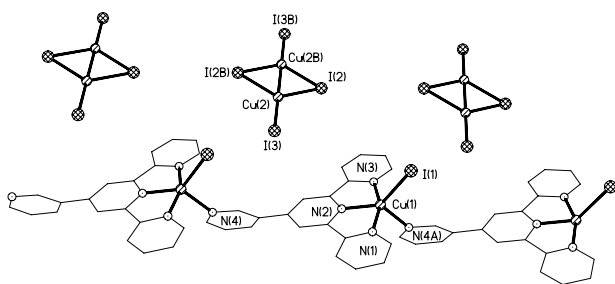
atoms from the terpyridine of **L2** and a nitrogen atom from the pendent pyridyl group of another pyterpy at the equatorial positions. The remaining apical position is occupied by an independent iodine atom. As a result, a cation unit $[Cu(L)I]^+$ was formed. The Cu–I has a distance of 2.6365(10) Å and the Cu–N distances vary from 1.949(4) to 2.124(4) Å. The angles around Cu(1) from 79.10(16)° to 158.39(16°) are comparable with those in the Cu^{II} monomers **1** and **3**. The counteranion $[Cu_2I_4]^{2-}$ is similar to that in complex **2** with different angles and distance between both Cu^I atoms. The Cu–Cu distance of 2.5752(15) Å is shorter than those in **2**, **4** and **5**, indicating a stronger interaction.

The ligand **L2** bridges the bivalent copper atoms, propagated to afford an infinite one-dimensional zigzag chain (Fig. 7) with the counterions $[Cu_2I_4]^{2-}$ along it. The two closest zigzag chains, in an approximate inversion pattern, supported by weak aryl-aryl stacking interactions (centroid distance 3.978 Å) and weak C–H⋯I hydrogen bonds (H⋯I = 3.058 Å, 3.158 Å), resulting in the formation of a 2D grid-like motif. The grids were connected by the $[Cu_2I_4]^{2-}$ units with C–H⋯I hydrogen bonds propagated to form a three-dimensional network.

3.7. Structure of [Cu₂(**L2**)(μ-I)₂]ₙ (**7**)

The structure of **7** consists of two crystallographically independent copper(I) atoms (Fig. 7). The Cu(1) has a distorted square pyramidal geometry and is coordinated by a terpyridine part of **L2** and I(1) at the equatorial position, the apical position is occupied by I(2). The Cu–N bond lengths vary from 2.121(7) to 2.404(9) Å and the angles around the metal center range from 71.4(3)° to 144.5(3)°. Compared with the above complexes, the differences of bond lengths and angels may be due to the unusual five-coordinated copper(I) geometry. The two iodine atoms also act as two double bridging atoms between the two copper atoms forming a Cu_2I_2 connector as reported [35,36]. The Cu–Cu distance of the Cu_2I_2 connector is 2.754(3) Å, which is comparable with those in the above complexes, indicating a strong interaction.

Cu(2) bears a distorted trigonal planar geometry and is coordinated by two iodine atoms and a pendent pyridyl group of another terpyridine ligand. The Cu–I bond lengths from 2.5281(17) to 2.781(2) Å are comparable with those in the above complexes and other previously reported I-bridged copper(I) complexes [12,26,35].

Fig. 6. View of the Cu^{II} zigzag chain polymer and Cu^I counterions $[Cu_2I_4]^{2-}$ in complex **6** (Hydrogen atoms are omitted for clarity.). Symmetry codes: (A) $x - 1$, $y - 1$, z; (B) $-x + 3$, $-y$, $-z$.
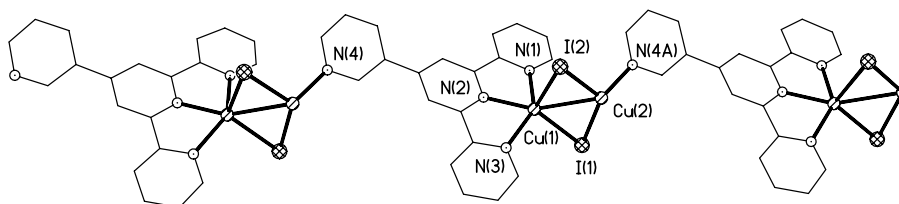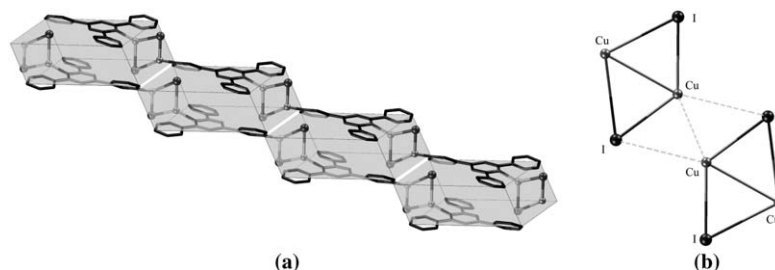

Fig. 7. View of the Cu^I zigzag chain of complex **7** (Hydrogen atoms are omitted for clarity.) Symmetry codes: (A) x, $y + 1$, $z - 1$.

Fig. 8. View of the Cu_4I_4 moiety and a section of 2D grid formed by weak interactions (Hydrogen atoms are omitted for clarity.).

The copper(I) atoms are bridged by ligand **L2** and are propagated to form a zigzag chain. Interestingly, the Cu_2I_2 units of the two approximately parallel zigzag chains were connected by Cu···Cu and Cu···I interactions to construct a Cu_4I_4 motif, a polymeric staircase of CuI (Fig. 8b). The Cu···Cu and Cu···I distances are 3.200(9) and 3.319(9) Å, significant larger than the distances in above complexes and their analogues[37–39], however, compared with the typical values of Cu···Cu distances range 2.53–3.58 Å [40,41], implying weak interactions. The Cu_4I_4 units are combined by weak aryl-aryl staking interactions (centroid distance 4.078 Å) and weak C–H···I hydrogen bonds (H···I distance range 3.228–3.339 Å), resulting in the formation of a two-dimensional grid (Fig. 8a). The grids are arranged in a parallel fashion and connected by weak C–H···I hydrogen bonds to form a three-dimensional network.

4. Discussion

It is understandable that terpyridine prefer to chelate metal ions to form mononuclear compounds. For pyridyl-substituted terpyridine, the variability of the 4′-pyridyls may increase the possibility of forming multinuclear complexes. Tuning up the terpyridine chelate effect and activating the substituted 4′-pyridyls are very important to develop complexes from mononuclear to polymers. To increase the nuclearity of the complexes, the following strategies may be feasible: (1) alternating the oxidations states of the metal centers; (2) increasing stoichiometric metal/ligand ratio; (3) introducing a second ligand. Different oxidation states of metal centers will result in different coordination preferences [11] and coordination molecular architecture can be directly constructed by coordination bonds using metal ions existing in varied coordination geometries to combine with multifunctional ligands into multi-dimensional frameworks [15]. For example, it is easy to form a chelating compound by two terpyridines with a six-coordinate copper(II), but it hard to form the same structure with a four-coordinate copper(I). Therefore, for pyterpy, monovalent copper(I) will provide more possibility for the 4′-pyridyls to participate in the reactions. To increase metal/ligand ratio or introduce a second ligand is also to increase the possibility of developing the compounds with higher nuclearity. At the same time, it will help to prevent the chelation of two different pyterpys with

the terpyridyl sites. In this context, several compounds were successfully developed from mononuclear to polymers as predicted in Scheme 3.

Mononuclear **1** containing **L1** with terpyridine chelating copper(II) center was obtained by the reaction of CuI and **L1** in a 2:1 ratio. When the ratio increases to 4:1 and in the presence of 4,4′-pyridine, a complex $[Cu_2(\mathbf{L1})_2I_2][Cu(\mu\text{-}I)I]$ containing a mixed-valent dinuclear $[Cu_2(\mathbf{L1})_2I_2]$ cation and a monovalent $[Cu(\mu\text{-}I)I]$ anion was obtained. The reduction of Cu(II) to Cu(I) under hydrothermal conditions by the reducing agents, such as 4,4′-bipyridyl or pyridine derivatives, has been reported previously [17–20]. The formation of counterion $[Cu_2(\mu\text{-}I)_2I_2]$ may be attribute to the excessive CuI. Similar $[Cu_2(\mu\text{-}I)_2I_2]$ species have also been found in other coordination compounds [30–32]. The result indicates that the higher CuI/ligand ratio benefit the coordination of pendent pyridyl.

Both **1** and its analogue **3** have shown *cis–cis*-configuration and the copper atoms of them have shown square pyramidal geometries and +2 oxidation states. In each monomer, the pendent 4′-pyridyl was not coordinated to any metal centers. Obviously, the six-coordinate feature of copper(II) determine the chelating preference in the formation of the structures. Changing the oxidations states of copper atoms may give chances to construct different compounds.

Other reducing agents such as PPh_3, copper powder or dppm were employed. Addition of PPh_3 results in a binuclear compound $[Cu_2(\mathbf{L2})I_2PPh_3]$ (**4**). In **4**, the ligand has shown *cis*-configuration and the metal centers have shown +1 oxidation states. Though the 4′-pyridyl was still not coordinated to any metal centers, it seems that the lower oxidation states of copper atoms can drive the ligand forming a different configuration. The compound **4** proved that the additive PPh_3 participating in the reactions will give more variability. The similar strategy using different cations, anions, ligands even some unusual additives to alter the thermodynamic and kinetic factors, had been used to synthesize complexes of 3,5-dimethyl-1,2,5-triazolate [16].

Using a higher metal-to-ligand ratio 4:1, $[Cu_4(\mathbf{L2})_2(\mu\text{-}I)_2I_2]$ (**5**) was obtained in 140 °C by adding reducing agent copper powder. The ligands in it have twisted into a *cis–cis*-configuration and coordinated to four copper(I) metal centers to form a tetranuclear grid-like dimmer (Fig. 5). In contrast, $\{[Cu(\mathbf{L2})I]_2[Cu_2(\mu\text{-}I)_2I_2]\}_n$ (**6**), containing a copper(II) zigzag chain and counterions $[Cu_2(\mu\text{-}I)_2I_2]$ was obtained in absence of reducing agents. $[Cu_2(\mathbf{L2})(\mu\text{-}I)_2]_n$

(**7**), a copper(I) zigzag chain, has been successfully achieved by adding dppm.

Up to now, the copper-pyterpy compounds were successfully driven from simple mononuclear compounds to polymers. By adding some reducing additives, the oxidations states of copper atoms had been controlled successfully. Hydrothermal processes are also considered necessary for these reductions [22]. This may be due to that the higher temperature stabilize the Cu^+ under hydrothermal conditions, though Cu^+ ions are known to disproportionate in water to produce Cu^{2+} and Cu, and such a stabilization may promote the redox and ligand rearrangement process [19,23].

5. Conclusion

In summary, we have successfully designed and synthesized several copper-pyterpy complexes with different nuclearity by one-pot reactions in hydrothermal conditions. By controlling temperature, stoichiometry, reducing agents or solvents, the compounds had been developed from discrete monomers to zigzag polymeric chains. These results proved that it was an effective way to synthesize different copper coordination compounds of pyterpy. In these processes, metal coordination geometry may play an important role in the formations of the complexes. For oftentimes, fascinating structures and reactions can be achieved from the reduction of copper valence states [19,20]. These results had also proved that the halogen may not be good linkers or second ligands, a longer or flexible linker or second ligand will be in favor of the formation of coordination polymers. Although more investigations are needed to understand the intrinsic mechanism, the synthesis of the compounds may provide a new approach for the construction of coordination polymers.

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2006.04.035.

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