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Synthesis, structures of novel zinc and copper compounds based on pyridazino[3,2-*c*]1,2,4-triazole derivatives

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ABSTRACT

Ligands 6-phenyl-3-(4'-pyridinyl) pyridazino[3,2-c]1,2,4-triazole (L^1), 6-phenyl-3-(3'-pyridinyl) pyridazino[3,2-c]1,2,4-triazole (L^2) and 3,6-diphenyl pyridazino[3,2-c]1,2,4-triazole (L^3) have been designed and synthesized. Reactions of these ligands with Cu^{II}, Cu^I and Zn^{II}, five new metal–organic coordination complexes were obtained. X-ray diffraction analyses show that complexes **1**, **3** and **4** are mononuclear structure, **5** is trinuclear complex, while **2** possess 1D chain structure. Complexes **1**, **3**, **4** and **5** were further assembled into infinite 1D structure by weak interactions, while **2** possesses noticeable weak interaction between two Cu^{II} atoms bridged by iodine [Cu^{II}...Cu^I = 2.6616(13) Å] and was extended into 2D sheet by $\pi \cdots \pi$ stacking interaction abilities of the pyridazine or triazole N donors.

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1. Introduction

Over the past decades, the rational design and synthesis of metal-organic supramolecular architectures are interesting and important in producing new functional materials with desired magnetic, catalytic, electric and fluorescent properties as well as potential applications in ion exchange and gas storage [1–3]. Preparing new promising materials by reaction of organic ligands (as building blocks) with different metal ions (or metal clusters) is one of the challenges in this area. The skillful selections of organic ligands and metal ions are pivotal role for designing reasonable complexes [4].

In general, the coordination conformation of metal complexes containing flexible ligands was less predictable due to the possible occurrence of molecular isomerism involving the adoption of different ligand conformations [5–8]. Therefore, to further extend the attractive research, we prepared three new rigid ligands, 6-phenyl-3-(4'-pyridinyl) pyridazino[3,2-c]1,2,4-triazole (L^1), 6-phenyl-3-(3'-pyridinyl) pyridazino[3,2-c]1,2,4-triazole (L^2) and 3,6-diphenyl pyridazino[3,2-c]1,2,4-triazole (L^3), anticipating that the rigidity of ligand may introduce additional structural constraint in controlling the assembly of metal-organic complexes. We also hope to reveal some structural factors of the ligands for dominating the self-assembly, and the result may provide new information of the spacer effect that such ligands exert on their coordination preferences. In this context, three new ligands have also been proven to

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be a series of promising organic connectors in crystal engineering of coordination complex due to the existence of reliable pyridyl groups as well as triazole ring with rich coordination modes. Herein, we report five new coordination complexes with the three ligands, which display different crystal structures. $[Cu(L^1)(ClO_4)Cl](1), \{[Cu(L^2)I]\}_n$ (2), $[Cu(L^3)(CH_3OH)_2(ClO_4)_2]$ (3), $[Zn(L^3)Cl_2]$ (4), $[Cu_3(L^3)Cl_6]$ (5). Complexes 1, 3 and 4 are mononuclear structure, 5 is trinuclear complex, while 2 possess 1D chain structure and noticeable weak interaction between Cu^1 and Cu^1 [2.6616(13)Å]. A systematic investigation of the role of ligand conformation has also been carried out based on this series of complexes (Chart 1).

2. Experimental

2.1. Materials and general methods

Solvents and starting materials for synthesis were purchased commercially and used as received. 3-Phenyl-6-chloropyridazine and L^3 were prepared according to reported procedures [9]. IR spectra were measured on a Brucker Equinox 55 FT-IR spectrometer with KBr Pellets in the range of 4000–400 cm⁻¹. Elemental analyses were performed on a Thermo Flash EA-1112 analyzer.

2.2. Preparation of ligands

2.2.1. Synthesis of **L¹** {6-phenyl-3-(4'-pyridinyl) pyridazino[3,2c]1,2,4-triazole}

3-Phenyl-6-chloropyridazine (0.6 g, 0.003 mol) was dissolved in 1-butanol (15 mL), and isoniazide (0.42 g, 0.003 mol) was added to





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the above solution. The resulting solution was heated to refluxing for 12 h, and then cooled to room temperature, filtered. A yellow residue was obtained. The pure yellow product of L^1 was separated



Chart 2.

by column chromatography on silica gel $(EtOH/CH_2Cl_2)$. Yield: 48.3% (Chart 2).

2.2.2. Synthesis of L^2 {6-phenyl-3-(3'-pyridinyl) pyridazino[3,2-c]1,2,4-triazole}

The pure yellow product of L^2 was obtained in the same way as for L^1 by using nicotinic hydrazide instead of isoniazide. Yield: 57%.

2.3. Synthesis of complexes 1-5

2.3.1. [Cu(L¹)(ClO₄)Cl] (1)

A solution of $CuCl_2 \cdot 2H_2O$ (17 mg, 0.10 mmol) and $Cu(ClO_4)_2 \cdot 6H_2O$ (37 mg, 0.10 mmol) in CH_3OH (8 mL) was added into a solu-

 Table 1

 Crystallographic data and structure refinement summary for complexes 1–5.

tion of L^1 (7 mg, 0.025 mmol) in CHCl₃ (8 mL). The system was left for about 1 month at room temperature, and blue crystals were obtained. Yield: 26.5%. Anal. Calcd for $C_{64}H_{44}CuCl_2N_{20}O_8$: C, 56.70; H, 3.27; N, 20.66%. Found: C, 56.60; H, 3.24; N, 20.69%. IR (cm⁻¹, KBr pellets): 3458*vs*, 3091*s*, 2704*w*, 2471*w*, 1636*vs*, 1558*s*, 1546*vs*, 1471*s*, 1457*vs*, 1336*vs*, 1286*s*, 1266*m*, 1222*m*, 1207*m*, 1163*m*, 1085*vs*, 999*vs*, 942*w*, 839*vs*, 774*vs*, 756*vs*, 744*vs*, 695*vs*, 668*s*, 624*s*, 593*w*.

2.3.2. { $[Cu(\mathbf{L}^2)I]$ }_n (2)

A solution of CuI (19 mg, 0.10 mmol) in CH₃CN (8 mL) was added into a solution of L^2 (6.8 mg, 0.025 mmol) in CHCl₃ (8 mL). The system was left for about 2 months at room temperature, and yellow crystals were obtained. Yield: 19.3%. Anal. Calcd for C₁₆H₁₁CuIN₅: C, 41.44; H, 2.39; N, 15.10%. Found: C, 41.31; H, 2.41; N, 14.96%. IR (cm⁻¹, KBr pellets): 3595s, 3112m, 3049w, 2735s, 2659m, 1615s, 1589m, 1476m, 1356s, 1286m, 1056s, 965m, 900s, 820m, 756m, 723m, 650m.

2.3.3. [Cu(L³)(CH₃OH)₂(ClO₄)₂] (3)

A solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (37 mg, 0.10 mmol) in CH_3OH (8 mL) was added into a solution of L^3 (6.8 mg, 0.025 mmol) in CH_3OH (8 mL). The system was left for about 2 weeks at room temperature, and blue crystals were obtained. Yield: 31%. Anal. Calcd for $C_{70}H_{56}CuCl_2N_{16}O_{10}$: C, 59.39; H, 3.99; N, 15.83%. Found: C, 59.43; H, 3.97; N, 15.79%. IR (cm⁻¹, KBr pellets): 3431s, 3121w, 3071w, 2986w, 1600m, 1554s, 1525m, 1469vs, 1454s, 1394m, 1368m, 1351vs, 1293m, 1095vs, 1011s, 950m, 821m, 769vs, 687vs, 622s, 569m, 485w.

	1	2	3	4	5
Chemical formula	C ₆₄ H ₄₄ CuCl ₂ N ₂₀ O ₈	C ₁₆ H ₁₁ CuIN ₅	C70H56CuCl2N16O10	C ₃₄ H ₂₄ ZnCl ₂ N ₈	C68H48Cu3Cl6N16
Formula weight	1355.63	463.7	1415.75	680.88	1492.54
Crystal system	Tetragonal	Triclinic	Monoclinic	Triclinic	Triclinic
Space group	P4/n	PĪ	P2(1)/c	PĪ	PĪ
T/K	293(2)	293(2)	293(2)	293(2)	293(2)
a/Å	17.023(2)	9.1024(18)	10.1994(3)	10.256(2)	11.936(2)
b/Å	17.023(2)	9.5071(19)	15.2497(4)	11.027(2)	12.399(3)
c/Å	11.384(2)	10.351(2)	20.3126(5)	13.684(3)	12.949(3)
βl°	90	72.00(3)	100.4940(10)	81.03(3)	65.93(3)
V/Å ³	3298.7(9)	775.1(3)	3106.53(14)	1499.2(5)	1696.4(6)
Z	2	2	2	2	1
D/g cm ⁻³	1.365	1.987	1.514	1.508	1.461
μ/mm^{-1}	0.482	3.406	0.516	1.038	1.222
F(000)	1390	448	1462	696	757
Total/unique/R _{int}	24410/2915/0.0541	7678/3521/0.0389	24877/5778/0.0263	14401/6623/0.0284	16666/7630/0.0306
$R^{\rm a}/wR^{\rm b}$	0.0732/0.2364	0.0382/0.1271	0.0443/0.1125	0.0332/0.0961	0.0631/0.2741

^a $R = \Sigma(||F_0| - |F_c||)/\Sigma|F_0|.$

^b $wR = [\Sigma w(|F_o|^2 - |F_c|^2)^2 / \Sigma w(F_o^2)]^{1/2}.$

Table 2	
Selected bond lengths (Å) and angles (°) for complexes 1	-5

Complex 1 Cl(2)-Cu(1) N(5)-Cu(1)-Cl(2) N(5)#2-Cu(1)-N(5)#3	2.390(3) 98.56(10) 88.73(3)	Cu(1)—N(5)#2 N(5)—Cu(1)—N(5)#2	2.042(3) 162.9(2)
Complex 2 Cu(2)···Cu(2)#2 I(1)-Cu(2)#2 Cu(2)-N(5)#1 N(1)-Cu(2)-N(5)#1 N(5)#1-Cu(2)-I(1)	2.6616(13) 2.7085(13) 2.074(4) 109.51(15) 109.78(12)	I(1)—Cu(2) Cu(2)—N(1) N(1)—Cu(2)—I(1) I(1)—Cu(2)—I(1)#2	2.6115(13) 2.058(4) 110.19(11) 119.99(3)
Complex 3 Cu(1)—N(3) Cu(1)—O(5) N(3)#1—Cu(1)—N(3) O(5)—Cu(1)—O(5) N(3)—Cu(1)—O(5)	1.9958(18) 2.451(2) 180.00(12) 180.00(10) 85.83(7)	Cu(1)-N(8) N(8)#1-Cu(1)-N(8) N(3)#1-Cu(1)-N(8) N(8)-Cu(1)-O(5)	2.0742(18) 180.00(10) 91.02(7) 91.65(5)
Complex 4 Zn(1)–N(1) Zn(1)–Cl(2) N(5)–Zn(1)–Cl(2) N(5)–Zn(1)–N(1) Cl(2)–Zn(1)–Cl(3)	2.0276(17) 2.2366(10) 110.58(5) 104.84(7) 114.67(3)	Zn(1)—N(5) Zn(1)—Cl(3) N(5)—Zn(1)—Cl(3) N(1)—Zn(1)—Cl(3)	2.0674(17) 2.2254(10) 100.78(5) 118.10(6)
Complex 5 Cu(2)-N(5) Cu(2)-Cl(3) Cu(2)-Cl(4) N(2)-Cu(1) Cl(4)-Cu(2)-N(1) Cl(4)-Cu(2)-Cl(3) N(2)-Cu(1)-Cl(4) N(2)#1-Cl(4)	1.991(4) 2.2715(19) 2.5651(15) 1.998(4) 87.81(12) 102.52(7) 88.41(12) 88.41(12)	Cu(2)-N(1) Cu(2)-Cl(5) Cl(4)-Cu(1) Cl(4)-Cu(2)-N(5) Cl(4)-Cu(2)-Cl(5) N(2)#1-Cu(1)-Cl(4) N(2)-Cu(1)-Cl(4)#1	2.046(4) 2.3223(19) 2.2711(15) 99.55(15) 94.08(7) 91.59(12) 91 59(12)

Symmetry code for **1**: #1 - y + 1/2, *x*, *z*; #2 - x + 1/2, -y + 1/2, *z*; #3, -x + 1/2, *z*; for **2**: #1 - x + 1, -y + 2, -z + 1; #2 - x + 1, -y + 2, -z; for **3**: #1 - x + 2, -y + 1, -z; for **5**: #1 - x, -y, -z + 1.

2.3.4. $[Zn(L^3)Cl_2]$ (4)

Colorless crystals of **4** suitable for X-ray analysis were obtained by the similar method described for **3**, except for using $ZnCl_2 \cdot 2H_2O$ instead of $Cu(ClO_4)_2 \cdot 6H_2O$. Yield: ~27.8%. Anal. Calcd for $C_{34}H_{24}ZnCl_2N_8$: C, 59.98; H, 3.55; N, 16.46%. Found: C, 60.02; H, 3.53; N, 16.51%. IR (cm⁻¹, KBr pellets): 3606s, 3265m, 3001m, 2765w, 2224m, 1976m, 1653s, 1526s, 1456m, 1309m, 1228w, 1156vs, 1087s, 964m, 867m, 777m, 654s.

2.3.5. $[Cu_3(L^3)Cl_6]$ (5)

Blue crystals of **5** suitable for X-ray analysis were obtained by the similar method described for **3**, except for using CuCl₂·2H₂O instead of Cu(ClO₄)₂·6H₂O. Yield: 33%. Anal. Calcd for C₆₈H₄₈Cu₃Cl₆N₁₆: C, 54.72; H, 3.24; N, 15.01%. Found: C, 54.79; H, 3.26; N, 15.06%. IR (cm⁻¹, KBr pellets): 3442s, 3079m, 1698w, 1533s, 1474vs, 1454s, 1360s, 1297s, 1178m, 1126m, 1074m, 1008m, 826m, 772vs, 691vs, 635m, 565m, 486w, 434w.

2.4. X-ray crystallography

Single-crystal X-ray diffraction measurements for complexes 1-5 were carried out on a R-AXIS SPIDER diffractometer equipped with a graphite crystal monochromator situated in the incident beam for data collection at 293(2) K. The determinations of unit cell parameters and data collections were performed with MoK α radiation (λ = 0.71073 Å) and unit cell dimensions were obtained with least-squares refinements. The program SAINT [10] was used for integration of the diffraction profiles. All structures were solved by direct methods using the SHELXS program of the SHELXTL package and refined with SHELXL [11]. Metal atoms in each complex were located from the E-maps and other non-hydrogen atoms were located in successive difference Fourier syntheses and refined with anisotropic thermal parameters on F^2 . Hydrogen atoms of carbon were included in calculated positions and refined with fixed thermal parameters riding on their parent atoms. The hydrogen atoms of part of water were located from Fourier difference maps with suitable restraint, and those of the remaining part could not be located in the difference map. Crystallographic data and experimental details for structural analyses are summarized in Table 1.

CCDC reference numbers 690056 (for 1), 684730 (for 2), 683208 (for 3), 684729 (for 4), 684731 (for 5). For crystallographic data in





Fig. 2. (a) Coordination environment of Cu¹ center in **2**, view of (b) the 1D polymeric chain in **2**, and (c) the 2D sheet through the adjacent chains $\pi \cdots \pi$ stacking interactions (H atoms omitted for clarity).

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3. Results and discussion

3.1. Synthesis and general characterization

All ligands were prepared as yellow powder by the reaction of 3-phenyl-6-chloropyridazine with different hydrazines. The infrared spectra of ligands exhibit characteristic absorptions of C=N bond on the triazole ring at about 1410 cm⁻¹, whereas the corresponding C=N bond absorption of complexes **1–5** appear at about 1450–1500 cm⁻¹ due to coordinate. In infrared spectra of **1–5**, the stretching vibration of the CH bond on the pyridazine ring appears in the region of 3400–3650 cm⁻¹ as strong sharp bands compared with 3100–3300 cm⁻¹ of the free ligands due to coordinate. In the IR spectra of **1** and **3**, there are characteristic bands of the CIO₄⁻ anions at 930–1080 cm⁻¹.

3.2. Description of the crystal structure

3.2.1. $[Cu(L^1)(ClO_4)Cl]$ complex (1)

The single crystal X-ray analysis revealed that complex **1** crystallizes in the tetragonal space group *P*4/*n* and the selected bond distances and angles were listed in Table 2, the Cu^{II} center is five-coordinated with square-pyramidal configuration, with four N atoms from four distinct L¹ ligands [Cu—N = 2.042(3) Å] defining the basal plane, and the Cl atom occupying the axial position [Cu—Cl = 2.390(3) Å] (see Fig. 1a). The angle of Cl(2)—Cu(1) —N(5) is 98.56(10)° while N(5)—Cu(1)—N(5) angles are 88.73(3)° and 162.9(2)°, respectively. Four N(5) atoms coordinated to Cu^{II} center are coplanar with a square arrangement [length of side, N(5)—N(5) = 2.856 Å]. The Cl atom and the Cu^{II} center lie on the axis of the square. All atoms of L¹ ligand are nearly planar and the dihedral angles between the two distinct ligands are 66.7°, 78°, 113.3°, respectively. It is worth noting that Complex **1** consist of a [Cu(L¹)₄Cl]⁺ cation and a ClO₄⁻ in mononuclear basic unit. In



Fig. 3. (a) Coordination environment of Cu^{II} center in **3**, (b) the 1D polymeric layer through the O(5)–H(5)···O(2) and C(8)–H(8A)···O(2) weak interactions (H atoms omitted for clarity).

general, the effect of anions on the frameworks of complexes can be explained as their differences in sizes and coordination ability [12]. In this complex, the Cl⁻ anion is both counteranion and donor, coordinate to Cu^{II} center due to its relatively strong coordination ability than that of ClO_4^- [13], while the ClO_4^- anion is used as counteranion and weakly bridge two adjacent **1** molecules to assemble into an infinite 1D supramolecular chain by the C(2)-H(2A)···O(4) [the distance of O(4)···H(2A) is 2.468 Å] weak interactions (Fig. 1b). It is interesting to note that although every **L**¹ ligand has a few reasonable coordination sites, only N from pyridine bond to the Cu^{II} center, which may be attributed to steric hindrance of the substituents.

3.2.2. { $[Cu(L^2)I]$ }_n complex (2)

Complex **2** crystallizes in triclinic space group $P\bar{1}$ and the selected bond distances and angles were listed in Table 2. The X-ray diffraction analysis shows that **2** has a 1D chain structure and all the Cu¹ centers and **L**² are equivalent. Each Cu¹ center coordinates to two bridging iodine atoms [Cu—I lengths are 2.7085(13) Å and 2.6115(13) Å, respectively] and one N atom of pyridine from one **L**² ligand and one N atom of triazole from another **L**² ligand (Fig. 2a). The Cu(2)—N(5) bond distance is 2.074(4) Å, whereas the Cu(2)—N(1) bond distance is 2.058(4) Å. The bond angles [N(1)—Cu(2)—N(5) = 109.51(15)°, N(5)—Cu(2)—I(1) = 109.78(12)°, N(1)—Cu(2)—I(1) = 110.19(11)° and I(1)—Cu(2)—I(1) = 119.99(3)°] indicate a nearly regular tetrahedral coordination environment

around each Cu¹ center. It should be pointed out that the intramolecular Cu¹...Cu¹ distance [Cu¹...Cu¹ = 2.6616(13) Å] found in the complex is shorter than the sum of the van der Waals' radii of copper (2.8 Å) [14], indicating there exists Cu¹...Cu¹ weak interaction.

In **2**, each L^2 ligand bridges two adjacent Cu¹ centers in bidentate coordination fashion, adjacent Cu¹ centers and L^2 ligands generate a 1D chain containing two types of metallacyclic rings (A and B) with different sizes. In A ring, two L^2 jointly coordinate to two Cu¹ centers by using one pyridyl N atom and one triazole N atom of each ligand to form a 14-membered unit. The centrosymmetric unit is constructed in which a pair of ligand-bridged Cu¹...Cu¹ distance is 7.805 Å. In B ring, two Cu¹ centers are linked by two bridging I atoms to form the parallelogram. All L^2 ligands are almost parallel to each other in the complex. Besides, these 1D chains were further extended into 2D supramolecular sheet by inter-sheet $\pi \dots \pi$ stacking interactions between the phenyl ring and pyridazino ring from adjacent chains (Fig. 2c). The centroid-centroid separation is 3.238 Å.

3.2.3. $[Cu(L^3)(CH_3OH)_2(ClO_4)_2]$ complex (3)

Complex **3** crystallizes in the monoclinic space group P2(1)/cand the selected bond distances and angles were listed in Table 2. The X-ray diffraction analysis shows that the mononuclear basic unit (see Fig. 3a) contains one Cu^{II} ion, two coordinated methanol molecules (two solvated methanol molecules), four L³ ligands, and two uncoordinated ClO₄⁻ groups. Thus, the slightly distorted octahedral coordination geometry CuN₄O₂ is formed by two oxygen CI2





Fig. 4. (a) Coordination environment of Zn^{II} center in 4, (b) the 1D polymeric chain through the C(23)–H(23A)···Cl(2) weak interactions (H atoms omitted for clarity).

atoms [Cu–O = 2.451(2) Å] from two independent methanol molecules and four N atoms from four independent L³ ligands [the distances of the Cu-N are 1.9958(18) Å and 2.0742(18) Å, respectively]. The Cu^{II} center is coordinated by the nitrogen atom from triazole of L³ ligand, whereas the nitrogen atoms from pyridazine of L³ ligand do not take part in coordination, probably due to the steric hindrance. The Cu^{II} center is located at an inversion center. The bond angles around the Cu^{II} center are close to the orthogrequirement [the angles of N(3) - Cu(1) - N(8)onal N(3)-Cu(1)-O(5) and N(8)-Cu(1)-O(5) are 91.02(7)°, 85.83(7)° and 91.65(5)°, respectively]. It should be pointed out that all atoms of L³ are nearly planar, and two adjacent L³ planes are nearly perpendicular to each other, whereas two distant L³ planes are almost parallel to each other in **3**. In addition, the ClO_4^- anions weakly bridge two adjacent 3 molecules, and the distances of O...H are 2.603 and 2.262 Å, respectively, the O atoms are well located. Therefore, such molecules were further assembled into an infinite supramolecular layer by the $O(5)-H(5)\cdots O(2)$ and 1D C(8)-H(8A)···O(2) weak interactions between adjacent molecules (Fig. 3b).

а

3.2.4. $[Zn(L^3)Cl_2]$ complex (4)

The X-ray structural analysis reveals that the structure of complex **4** is a mononuclear unit composed of one Zn^{II} ion, two L³ ligands and two chlorine atoms. As shown in Fig. 4a, the Zn^{II} center with a slightly distorted tetrahedral coordination environment is surrounded by two N atoms from two distinct L³ ligands and two Cl atoms. The Zn(1)—N(1), Zn(1)—N(5), Zn(1)—Cl(2), Zn(1)—Cl(3) bond lengths are 2.0276(17) Å, 2.0674(17) Å, 2.2366(10) Å and 2.2254(10) Å, respectively, within the normal range of Zn—N and Zn—Cl lengths in analogous zinc configuration [15]. The angles of N(5)—Zn(1)—Cl(2), N(5)—Zn(1)—Cl(3) are 110.58(5)°, 100.78(5)°, 104.84(7)°, 118.10(6)° and 114.67(3)°,

respectively, confirms a nearly regular tetrahedral environment around the Zn^{II} center. In L^3 ligand, the central triazole is nearly coplanar with the adjacent pyridazine ring with a dihedral angle of 1.5°. Two L^3 ligands are not equivalent in **4**. In one L^3 ligand, two phenyl rings are twisted with respect to the central reference plane (the central trizole and the pyridazine ring), having the dihedral angle of 158.9° and 137.3°, two phenyl rings make a dihedral angle of 56.5°. For another ligand, it is interesting to note that two phenyl rings are almost coplanar with respect to the central reference plane, having the dihedral angle of 25.1° and 2.5°. Two phenyl rings make a dihedral angle of 27.1°.

In **4**, only N atom from triazole bond to the metal ion, the coordinated mode is same as that of complex **3**. Two Cl atoms in the metal salt are also bound to the zinc ion. In addition, the C(23)—H(23A)···Cl(2) [Cl(2)····H(23A) = 2.896 Å] weak interactions were observed between adjacent molecules. Therefore, such molecules were further assembled into an infinite 1D supramolecular chain by the C(23)—H(23A)···Cl(2) weak interactions between adjacent molecules (Fig. 4b).

3.2.5. $[Cu_3(L^3)Cl_6]$ complex (5)

Complex **5** crystallizes in the triclinic space group $P\bar{1}$ and the selected bond distances and angles were listed in Table 2. The X-ray diffraction analysis shows that **5** which consist of three coppers, six Cl atoms and four L^3 ligands is centrosymmetric with the inversion center being located at the Cu(1) atom. Three Cu^{II} atoms are in one line [Cu(2)–Cu(1)–Cu(2) = 180°] and Cu(1) atom is situated nicely at the middle of two Cu(2) atoms (see Fig. 5a). The nonbonding distance is 3.330 Å between two adjacent copper atoms. The four L^3 ligands are nearly parallel with a Z-shaped, containing two types of coordination modes.

The conformations of the outer two coppers are identical. Each Cu(2) has a distorted square-pyramidal geometry and they are five-coordinate with N2Cl3 donor set. The basal plane, which the



Fig. 5. (a) The trinuclear structure of 5 showing coordination environments of the Cu^{II} ions, (b) the 1D polymeric chain through the C(4)–H(4A)…Cl(5) weak interactions (H atoms omitted for clarity).

mean deviation is *ca.* 0.1019 Å, consists of two N atoms from two distinct L^3 ligands and two Cl atoms. The Cu(2)–N(5), Cu(2)–N(1), Cu(2)—Cl(3), Cu(2)—Cl(5) bond lengths are 1.991(4) Å, 2.046 (4) Å, 2.2715(19) Å and 2.3223(19) Å, respectively. The apical position is occupied by bridging Cl(4) atom with a distance of [2.5651(15) Å]. Cl(4)-Cu(2)-N(1),Cl(4)-Cu(2)-N(5), The angles of Cl(4)—Cu(2)—Cl(3) and Cl(4)—Cu(2)—Cl(5) are 87.81(12)°, 99.55(15)°, 102.52(7)° and 94.08(7)°, respectively. Additionally, Cl(3) and Cl(5) in the metal salt are also bound to the Cu(2) ion, the distances of Cl(4)—Cl(4) and Cl(3)—Cl(5) are both 4.542(8) Å.

The environment of central copper atom is nearly regular square-planar geometry, being coordinated by two N donors from two distinct ligands and two bridging Cl(4) atoms. The distances of Cu—N and Cu—Cl are 1.998(4)Å and 2.2711(15)Å, respectively. The sum (value of 360.0°) of the angles Cl(4)-Cu(1)-N(2)[91.59(12)°, 88.41(12)°, 91.59(12)° and 88.41(12)°] Confirms a planar and nearly orthogonal environment around the Cu(1) center. In addition, the C(4)–H(4A)···Cl(5) [Cl(5)···H(4A) = 2.841 Å] weak interactions were observed between adjacent molecules. Therefore, such molecules were further assembled into an infinite 1D supramolecular chain by the C(4)—H(4A)···Cl(5) weak interactions between adjacent molecules (Fig. 5b).

4. Conclusion

In order to try to know the function of structural constraint in controlling the assembly of metal-organic networks, we design three rigid ligands. We find steric hindrance of the substituents may to influence N atom coordination ability. We obtain complex $[Cu(L^1)(Cl)(ClO_4)]$ (1) and know by analyzing the conformation of 1 that Cl⁻ is both donor and counteranion while the ClO₄⁻ is counteranion and weakly bridge two adjacent 1 molecules to assemble into an infinite 1D supramolecular chain. Furthermore, in 2, it should be pointed out that the intramolecular Cu^I...Cu^I distance $[Cu^{I} \cdots Cu^{I} = 2.6616(13) \text{ Å}]$ is shorter than the sum of the van der Waal's radii of copper (2.8 Å), indicating there exists $Cu^{I} \cdots Cu^{I}$ weak interaction. 3 and 4 are mononuclear structure, 5 is trinuclear complex.

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