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Introduction

In the last two decades, coordination supramolecular chemistry has seen great development because of the potential applications in catalysis,¹ small molecule capture or separation,² photoluminescence³ and imaging,⁴ biology,⁵ electronics⁶ etc. In the exploration of novel materials with demanded function, the self-assembly process of supramolecular coordination complexes becomes crucial.⁷ The concept of molecular building blocks (MBBs) made the complicated self-assembly process become a two-step arrangement.⁸ The first step is to build up MBBs with covalent bonds or strong coordination bonds,⁹ and the second step is to assemble MBBs via weak coordination bonds and molecular interactions, such as hydrogen bonds, $\pi \cdots \pi$ stacking, hydrophobic or hydrophilic, and van der Waals interactions.¹⁰ Consequently, the design and construction of MBBs is the foundation of supramolecular architecture.

In this paper, we designed a flexible multidentate ligand H₆L that was embedded with a pair of hydrazides with ten potential coordination atoms. It is well-known that the coordination of hydrazide ligands and metal ions always leads to chelated coordination rings, which are stable in solution.¹¹

Delicate modulated assembly of a new kind of trinuclear copper(II) motif governed by N-containing agents†

Shu-Ting Wu,*ab Hong-Liang Tang,^a Shu-Mei Lu,^a Qiao-Yan Ye,^a Xi-He Huang,^{ab} Chang-Cang Huang,^a Xiao-Lin Hu^a and Shou-Tian Zheng^a

A new kind of trinuclear copper(II) motif [Cu₃L] was prepared in situ by adopting a multidentate ligand, $N^{\prime 2}$, $N^{\prime 2'}$ -bis(2-hydroxybenzoyl)biphenyl-2,2'-dicarbohydrazide (H₆L), in the presence of a series N-containing agents. Featuring five different assembly styles, [Cu₃L(DMF)_{2.5}(hmta)]-3H₂O (1), [Cu₃L(DMA)(H₂O)(Hmor)] (2), [Cu₃L(py)₂]-DMF (3), [Cu₃L(DMF)(H₂O)]-2DMF (4), and [Cu₃L(DMA)(H₂O)]-0.5DMA (5) (hmta = hexamethylenetetramine, Hmor = morphiline, py = pyridine) were obtained. In these assemblies, the [Cu₃L] units are connected with each other into one-dimensional chains via bridging of N-containing agents or via sharing an oxygen atom of L⁶⁻ to fuse together. Furthermore, the connecting styles are found to be governed by the character of the N-containing agents used, which is discussed in detail. Thermal gravimetric analysis and magnetic measurement of some complexes were performed.

> Hydrazide-based coordination compounds have shown fascinating properties in magnetism,¹² molecular recognition,¹³ biological sensing,¹⁴ etc. As we mentioned above, H₆L, which is armed with a pair of hydrazides that are spaced by a biphenyl group (Scheme 1), might be a good candidate to build up stable coordination motifs, and further assemble into supramolecular networks. Five $copper(\pi)$ coordination polymers that were constructed from L⁶⁻ were yielded by employing different N-containing agents. Based on the analysis and discussion of the syntheses and structural features, the modulation of N-containing agents on the assembly process was presented and discussed.

Experiment section

Reagents and instruments

Materials used for synthesis were of reagent grade and used without further purification. ¹H NMR (DMSO-d₆) was carried out on a BRUKER AVANCE III 400 nuclear magnetic resonance spectrometer. IR spectra were recorded in the range of 4000-400 cm⁻¹ on a Perkin-Elmer FT-IR spectrum 2000 spectrometer using the KBr pellet technique. X-ray powder



Scheme 1 The structure of H₆L

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^a College of Chemistry, Fuzhou University, Fuzhou, 350116, PR China. E-mail: shutingwu@fzu.edu.cn

^b State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, PR China [†] Electronic supplementary information (ESI) available: Characterization of H₆L, XRPD patterns and bond length lists of complexes 1-5. CCDC 983128, 983130, and 1005328-1005330. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4ce00898g

diffraction (XRPD) measurements were performed on a Rigaku D/max-3c with Cu K_{α} radiation (λ = 1.5406 Å) in the angular range of 2θ = 5–50° at 293 K. Elemental analyses were performed using a Vario MICRO, CHNOS Elemental Analyzer. The instrument for thermal gravimetric measurements was a Netzsch STA 449C Jupiter. Magnetic susceptibility data were collected over the temperature range of 2–300 K in a magnetic field of 1000 Oe on a MPMS (SQUID)-XL magnetometer. The fluorescence spectrum for H₆L was recorded on an Edinburgh Instrument FL/FS-920 fluorescent spectrometer.

Synthesis of the ligand and title complexes

2,2'-Biphenyldicarbonyl chloride. A mixture of 2,2-biphenyldicarboxylic acid (1.452 g, 6.0 mmol) and thionyl chloride (10 mL) was refluxed for 9 h, with one drop of DMF (*N*,*N*-dimethylformamide). After reaction, solvent and excess thionyl chloride were removed by rotary evaporation, leaving a colorless solid of 2,2-biphenyldicarbonyl chloride. Yield: 88.37%.

 N^2 , N'^2 '-Bis(2-hydroxybenzoyl)biphenyl-2,2'-dicarbohydrazide (H₆L). A 10 mL DMF solution of 2,2-biphenyldicarbonyl chloride (5.0 mmol) and 10 mL DMF solution of triethylamine (1.4 mL) and salicylhydrazide (13.7 mmol) were mixed within an ice-bath. The mixture was warmed to room temperature and refluxed for 9 h. The solvent was removed with reduced pressure distillation to obtain the crude product as a reddish brown solid. After washing with ethanol for several times, a white product was obtained with 78.54% yield. The product was characterized by ¹H NMR (DMSO- d_6), IR spectroscopy and fluorescence spectroscopy, the data for which are listed in the ESI,† Fig. S1–S3.

 $[Cu_3L(DMF)_{2.5}(hmta)]$ ·3H₂O (1). H₆L (0.0125 mmol, 6.4 mg), Cu(Ac)₂·H₂O (0.0375 mmol, 7.5 mg) and hmta (hexamethylenetetramine, 0.0375 mmol, 5.3 mg) were mixed and dissolved in 5 mL DMF. Blue rhombic plate-like crystals were obtained in five days, in 13.54% yield (on the basis of Cu).

 $[Cu_3L(DMA)(H_2O)(Hmor)]$ (2). H₆L (0.0125 mmol, 6.4 mg) and Cu(Ac)₂·H₂O (0.0375 mmol, 7.5 mg) were mixed and dissolved in 5 mL DMA (*N*,*N*-dimethylacetamide) with one drop of Hmor (morphiline, *ca.* 0.58 mmol). Dark blue blockshaped crystals were obtained in two months, in 18.31% yield (on the basis of Cu). IR (KBr, cm⁻¹): 3245w, 3055w, 2973w, 2932w, 2844w, 1600s, 1562m, 1500s, 1464m, 1400s, 1321m, 1250s, 1186m, 1155m, 1109m, 1092m, 1019m, 873m, 852m, 750s, 700m, 637m, 543w, 462m, 433m.

 $[Cu_3L(py)_2]$ ·DMF (3). H₆L (0.05 mmol, 25.5 mg) and Cu(Ac)₂·H₂O (0.15 mmol, 30.4 mg) were mixed and dissolved in 5 mL DMF with one drop of pyridine. Dark blue column-like crystals were obtained in two weeks, in 56.01% yield (on the basis of Cu). Anal. calcd. (found) for C₄₁H₃₃Cu₃N₇O₇ (%): C, 52.85 (53.14); H, 3.51 (3.51); N, 10.35; (10.58). IR (KBr, cm⁻¹): 3689w, 3060w, 3005w, 2925w, 2107w, 1675s, 1600s, 1500s, 1450m, 1400s, 1324m, 1253m, 1217m, 1153w, 1091w, 1063m, 901m, 848m, 780m, 754s, 641m, 572w, 437w.

 $[Cu_3L(DMF)(H_2O)]$ ·2DMF (4). H_6L (0.025 mmol, 12.8 mg) and $Cu(Ac)_2$ · H_2O (0.075 mmol, 15.0 mg) were mixed and dissolved in a mixed solvent of DMF (3 mL) and acetonitrile (3 mL). Blue columnar crystals were obtained in two weeks, in 37.03% yield (on the basis of Cu). Anal. calcd. (found) for $C_{37}H_{39}Cu_3N_7O_{10}$ (%): C, 47.28 (47.62); H, 4.45 (4.10); N, 8.12; (10.51). IR (KBr, cm⁻¹): 3400w, 3060w, 2928w, 1647s, 1600s, 1564m, 1500s, 1476m, 1406s, 1385s, 1322w, 1230m, 1156m, 1103m, 1048w, 905m, 847m, 756m, 699m, 581w, 545w, 453w.

 $[Cu_3L(DMA)(H_2O)]$ ·0.5DMA (5). The preparation of 5 was similar to that of 4, but 5 mL DMA that was dissolved with piperazine hexahydrate (0.025 mmol, 4.9 mg) was used as the solvent instead of the mixed solvent. Blue square plate-like crystals were obtained in two weeks, in 55.74% yield (on the basis of Cu). Anal. calcd. (found) for C₆₈H₅₉Cu₆N₁₁O₁₇ (%): C, 48.30 (48.47); H, 4.10 (3.73); N, 9.56; (9.15). IR (KBr, cm⁻¹): 3369w, 3069w, 1603s, 1511s, 1480s, 1397s, 1379s, 1303m, 1227s, 1157m, 1103m, 1046m, 906s, 847s, 750s, 695m, 670m, 595m, 464m, 443m.

X-ray crystallography. Diffraction data for complex 1 were collected on an Agilent technologies SuperNova Micro Focus diffractometer. Diffraction data for complexes 2 and 3 were collected on a RIGAKU/SATURN 724 CCD diffractometer. Data for complexes 4 and 5 were collected on a Rigaku R-AXIS RAPID diffractometer. All diffractometers were operated using graphite-monochromatized Mo K_{α} radiation ($\lambda = 0.71073$ Å) in the ω scan mode. Absorption coefficients were applied using a multi-scan technique. All the structures were solved by the direct method of SHELXS-97 and refined by full-matrix leastsquares techniques using the SHELX-97 program.¹⁵ Nonhydrogen atoms were refined anisotropically. Hydrogen atoms of organic molecules were generated geometrically and refined by a riding mode. The SQUEEZE subroutine of the PLATON software suite¹⁶ was applied for the data of complexes 2 and 5 to avoid diffraction interference. The resulting new HKL files were used for further refinement. A summary of crystallographic data and structure determination for 1-5 is provided in Table 1.

Results and discussion

Crystal structures and discussion

[Cu₃L(DMF)_{2.5}(hmta)]·3H₂O (1). Complex 1 crystallizes in the monoclinic system, space group C2/c, featuring a 1D infinite structure which forms a 2D supramolecular bilayer structure by hydrogen bonding. The asymmetric unit for 1 contains three crystallographically unique Cu^{II} ions, one L⁶⁻, one hmta, two and a half DMF molecules, and three lattice water molecules. Three kinds of distinct coordination geometries around Cu^{II} are observed (Fig. 1a). Cu1 adopts a distorted octahedral geometry. The equatorial plane is completed by three atoms from L⁶⁻ (O1, N1, O3) and one N atom from hmta. Axial positions of the octahedron are occupied by two O atoms from DMF molecules, adopting elongated bond lengths (2.6367(83) and 2.5011(57) Å), which could be attributed to the Jahn-Teller effect. Cu2 displays a compressed tetrahedral geometry, with two pairs of N and O atoms from L^{6-} (O2, O5, N2, O3). The geometry around

Table 1 Crystal data and structure refinement parameters for complexes 1-5

Complex	1	2^a	3	4	5^a
Formula	C _{41.5} H _{51.5} Cu ₃ N _{10.5} O _{11.5}	C36H36Cu3N6O9	C41H33Cu3N7O7	C37H39Cu3N7O10	C ₆₈ H ₆₃ Cu ₆ N ₁₁ O ₁₇
$M_{ m r}$	1072.05	887.33	926.36	932.37	1683.50
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
a/Å	41.720(3)	25.985(5)	14.760(3)	9.6951(19)	22.533(4)
b/Å	8.6534(5)	13.713(3)	14.694(3)	21.832(4)	23.066(5)
c/Å	28.881(2)	24.798(5)	18.395(4)	19.246(4)	14.201(3)
$\alpha / ^{\circ}$	90	90	90	90	90
β/°	120.329(5)	112.39(3)	98.88(3)	97.76(3)	90
y/°	90	90	90	90	90
$V/Å^3$	8999.6(10)	8170(3)	3941.7(14)	4036.4(14)	7381(3)
T/K	113(2)	113(2)	293(2)	293(2)	293(2)
Space group	C2/c	C2/c	$P2_1/c$	$P2_1/c$	Pba2
Z	8	8	4	4	4
R _{int}	0.0602	0.0808	0.0499	0.1194	0.0801
Reflections collected	28465	27 620	36 450	37 325	68 0 8 6
GOF on F^2	1.050	1.136	0.922	0.959	0.850
$R_1[I > 2\sigma(I)]^b$	0.0634	0.0746	0.0421	0.0720	0.0535
wR_2 (all data) ^c	0.1486	0.1692	0.1233	0.1626	0.1312
Flack parameter					0.374(14)

^{*a*} The formula and M_r of 2 and 5 in the table are results of excluding the disordered solvent that was removed by the SQUEEZE process. The overall formula for 2 should be $C_{36}H_{42}Cu_3N_6O_{12}$, with M_r 941.33, F(000) 3868. The overall formula for 5 should be $C_{68}H_{64}Cu_6N_{11}O_{17.5}$, with M_r 1692.50, F(000) 3452. ^{*b*} $R_1 = \sum ||F_0| - |F_c|| / \sum |F_0|$. ^{*c*} $wR_2 = [\sum w(F_0^2 - F_c^2)^2 / \sum w(F_0^2)]^{1/2}$.



Fig. 1 (a) Ellipsoid representation of the coordination environment for Cu^{II} ions in complex **1** (ellipsoid probability 50%). Hydrogen atoms and lattice solvent molecules are omitted for clarity. Symmetry code: A = x, 2 - y, 0.5 + z. (b) Side view of the hydrogen bonding bilayer structure for **1** (hydrogen bonds show as blue dashed lines). The green and pink chains represent separate one-dimensional structures. The biphenol groups of L^{6-} fill the void space of the bilayers, which is shown in space filling mode in only one channel for clarity. (c) Representation of the 1D chain in **1**. Hydrogen atoms and solvent molecules (coordinated and lattice) are omitted for clarity.

Cu3 is an axially elongated square-pyramid, with three atoms from L^{6-} (O4, N4 and O6) one N atom from hmta, and one O atom from DMF.

The as-synthesized ligand is completely deprotonated, behaving as an organic host that embeds three Cu^{II} ions, *in situ* generating a $[Cu_3L]$ motif. As shown in Fig. 1c, the $[Cu_3L]$ motifs are linked by hmta into an infinite one-dimensional structure, which means the $[Cu_3L]$ motifs could serve as MBBs for further assembly if the linker hmta is substitutable. There are multiple hydrogen bonds between lattice water

molecules and hmta, DMF, and deprotonated hydroxyl groups of L^{6-} , which direct the supramolecular bilayer structure in the (011) plane. As shown in Fig. 1b, the void space in the bilayer structure is filled by the biphenyl group of L^{6-} .

 $[Cu_3L(DMA)(H_2O)(Hmor)]$ (2). By substituting hmta with Hmor, crystals of 2 were obtained, featuring a distinct onedimensional structure. The asymmetric unit contains three crystallographically unique Cu^{II} ions, one L⁶⁻, one Hmor, one DMA molecule, and one lattice water molecule. A similar $[Cu_3L]$ motif exists in the structure. Major differences are the coordination geometries around Cu1 and Cu3. Both Cu1 and Cu3 adopt similar distorted square-pyramid geometries. As shown in Fig. 2a, the equatorial plane of Cu1 is completed by three atoms from L^{6-} (O1, N1 and O2) and one N atom from Hmor. The axial position is occupied by an O atom from a DMA molecule. Differently, symmetrically related Hmor coordinates to Cu3 at the axial site. The equatorial plane of Cu3 is completed by one water molecule and three atoms from L^{6-} (O5, N4 and O6). The resulting one-dimensional structure shows a waved chain along the *c* axis (Fig. 2c). Coordinated water molecules (O1W) serve as hydrogen bonding donors, affording hydrogen bonds with oxygen atoms (O1S) of DMA molecules and deprotonated hydroxyl groups (O6) of L^{6-} , which leads to a 2D supramolecular layer structure (Fig. 2b).

Compared to the crystal structure of 1, in which linker hmta connects $[Cu_3L]$ motifs by a pair of equatorial coordination bonds, the linker Hmor in 2 displays another kind of connecting style by one equatorial bond and one axial bond. To distinguish both assembly styles, we opt to label the assembly style in 1 as Eq-hmta-Eq and that in 2 as Eq-Hmor-Ax.

 $[Cu_3L(py)_2]$ ·DMF (3). Complex 3 crystallizes in the monoclinic system, space group $P2_1/c$. The asymmetric unit contains three crystallographically unique Cu^{II} ions, one L⁶⁻, two pyridine molecules and one lattice DMF molecule. A similar $[Cu_3L]$ motif is also observed. In the $[Cu_3L]$ motif, both Cu1 and Cu3 display distorted square-pyramidal geometries, with two pyridine molecules coordinated to Cu1 and Cu3 in the equatorial plane (Fig. 3a). The axial positions of the geometries around Cu1 and Cu3 are occupied by O atoms from symmetrically related L⁶⁻. In this way, the $[Cu_3L]$ motifs are self-assembled in a stepwise fashion into one-dimensional structure (Fig. 3b). Because the axial coordination bonds play a key role in the assembly, we denote this kind of assembly

style as AxAx. The 1D chains pack with each other with embedded lattice DMF molecules occupying the void space.

 $[Cu_3L(DMF)(H_2O)]$ ·2DMF (4). The crystal structure for 4 also features one-dimensional structures constructed from the $[Cu_3L]$ motif, however, with a different assembly style. The asymmetric unit includes one $[Cu_3L]$ motif, three DMF molecules and one water molecule. As shown in Fig. 3c, both Cu1 and Cu3 display distorted square-pyramidal geometries. The axial position of Cu1 is occupied by a water molecule, leaving an equatorial position for an O1A atom from a symmetrically related L⁶⁻. On the other hand, one DMF molecule coordinates to Cu3 equatorially (O1S), leaving the axial position for O6B from another symmetrically related L⁶⁻. Consequently, adjacent $[Cu_3L]$ motifs connect with each other *via* sharing a pair of μ_2 -O atoms into a one-dimensional structure (Fig. 3d). Due to the different coordination environments around Cu1 and Cu3, the assembly style present in 4 could be labelled as EqAx.

 $[Cu_3L(DMA)(H_2O)]$ ·0.5DMA (5). X-ray single crystal diffraction analysis reveals that 5 crystallizes in non-centrosymmetric space group *Pba2*. The asymmetric unit includes two $[Cu_3L]$ motifs, three DMA molecules and two water molecules. The two $[Cu_3L]$ motifs feature similar structures and assembly styles, so only one of them will be described herein. As shown in Fig. 3e, both Cu1 and Cu3 display distorted square-pyramidal geometries, with one water molecule and one DMA molecule coordinated to Cu1 and Cu3 respectively at the axial position. There are μ_2 -O atoms (O6A and O1B) that coordinate to Cu1 and Cu3 in the equatorial plane, leading $[Cu_3L]$ motifs to fuse with each other (Fig. 3f). The assembly style found in complex 5 can be labelled as EqEq.

Synthesis and structural discussion. The bihydrazide ligand H_6L is a multidentate compound which offers up to ten available coordination atoms. Structural analysis of complexes 1-5



Fig. 2 (a) Ellipsoid representation of the coordination environment for Cu^{II} ions in complex 2 (ellipsoid probability 50%). Hydrogen atoms and lattice solvent molecules are omitted for clarity. Symmetry code: B = x, 2 - y, -0.5 + z. (b) Top view of the 2D hydrogen bonding structure for 2. The green and pink waved chains represent separate one-dimensional structures. (c) Representation of the 1D chain in 2. Hydrogen atoms and solvent molecules (coordinated and lattice) are omitted for clarity. The colour scheme is the same as Fig. 1.



Fig. 3 Ellipsoid representations of the coordination environment for Cu^{II} ions (a, c, e) and 1D structures (b, d, f) observed in complex 3–5 respectively (ellipsoid probability 50%). Hydrogen atoms and lattice solvent molecules are omitted for clarity. The colour scheme is the same as Fig. 1. Symmetry code: (a) A = 1 - x, 1 - y, -z, B = 2 - x, 1 - y, 1 - z; (c) A = 1 - x, 1 - y, 1 - z; (e) A = 0.5 - x, -0.5 + y, z, B = 0.5 - x, 0.5 + y, z.

revealed that deprotonated L⁶⁻ could form ten coordination bonds with three Cu^{II} ions, leading to a [Cu₃L] motif. As shown in Fig. 4, the [Cu₃L] motif in 1-5 shows four active coordination sites for further assembly. Considering the typical elongated Jahn-Teller effect of Cu^{II} coordination geometry, the equatorial coordination bond length of Cu^{II} would be shorter than the axial one (tables of bond lengths for 1-5 are listed in the ESI[†]), the strength of equatorial bond must be stronger than the axial bond. Consequently, the involved N-containing agent, which is available for coordination, is able to play a key role in the assembly of the [Cu₃L] motif. In our study, hmta, Hmor, pyridine, acetonitrile, and piperazine, with diverse coordination abilities and structural features were introduced, directing five kinds of assembly styles. It should be mentioned that although DMF and DMA are also N-containing agents, this paper won't discuss their influence, because their properties are similar, and they are the major solvents in the synthesis of each complex.

First, the N-containing agents act as linkers in the assembly of $[Cu_3L]$ motifs, exhibiting Eq-hmta-Eq (complex 1) and Eq-Hmor-Ax (complex 2) styles. Hmta features an adamantinelike structure, offering four identical tertiary amines for coordination. Those tertiary amines compete to coordinate with Cu^{II} ions at equatorial sites. However, it is difficult for hmta to act as a three-connected or four-connected linker because of the steric effect of the $[Cu_3L]$ motif. In practice, two tertiary amines are observed to coordinate with the $[Cu_3L]$ motif equatorially, resulting in Eq-hmta-Eq style for 1. Whereas Hmor features a chair-shaped conformation, offering a secondary amine and an ether group, which is a less competitive ligand. Perhaps because the Hmor was added greatly in excess, both amine and ether groups of Hmor coordinate with Cu^{II}. The ether group, which has lower reaction activity, coordinates with Cu^{II} on the axial site, while the secondary amine coordinates equatorially. As a result, the assembly style for the $[Cu_3L]$ motif in 2 is Eq-Hmor-Ax.

Second, the N-containing agents act as structure-directing agents, leading to the self-assembly of [Cu₃L] motifs. The [Cu₃L] motifs were self-assembled through a pair of μ_2 -O bridges, showing AxAx, EqAx, and EqEq styles in the structures of 3-5, respectively. The choice of these styles is also related to the coordination ability of the N-containing agents. In the structure of complex 3, pyridine, which is a good candidate to coordinate with Cu^{II}, occupies both equatorial active sites of the [Cu₃L] motif. As a result, the assembly of [Cu₃L] motifs in 3 is AxAx style. When the N-containing agent is acetonitrile or piperazine, complex 4 or 5 is obtained respectively, although their crystal structures do not contain these agents. Further experiments showed that if acetonitrile or piperazine are omitted from the reaction, complex 4 or 5 would not be obtained, which indicates both agents might be structure-directing agents. The coordination abilities of acetonitrile and piperazine are weaker than pyridine. However, the large amount of acetonitrile may provide a good chance for acetonitrile to coordinate with Cu^{II} randomly, which gives rise to the EqAx assembly style for 4. It is worth mentioning that crystals of complex 4 were not easy to reproduce, which might indicate that the EqAx style is an "unstable state" in the assembly process. The EqEq assembly style exists in 5, which might be attributed to the weak coordination ability and small amount of addition of piperazine.

As shown in Fig. 4, the diverse assembly styles of $[Cu_3L]$ motifs give rise to various Cu…Cu distances between two adjacent $[Cu_3L]$ motifs. It is obvious that self-assembly of $[Cu_3L]$ motifs reduces the Cu…Cu distance. The minimum



Fig. 4 The assembly of the $[Cu_3L]$ motif modulated by N-containing agents. On the left, the diagram represents a typical structure of the $[Cu_3L]$ motif with orange arrows indicating the active coordination sites. "Eq site" means potential equatorial assembly style, while "Ax site" means potential axial assembly style. On the right, the differences among complexes 1–5 are highlighted with orange coloured areas which represent linkers (complexes 1 and 2) or joints (complexes 3–5). Green dashed lines and numbers in green represent the Cu…Cu distances. The colour scheme for atoms is the same as Fig. 1.

value of the Cu…Cu distance is 2.996 Å with the EqEq assembly style for complex 5.

Thermal stabilities and magnetism study

Owing to the low yield of complexes 1 and 2, only complexes 3–5 were studied by X-ray powder diffraction (XRPD) to confirm the phase purity (Fig. S4–S6 in ESI†). Further investigation on thermal stabilities and magnetism were carried out for complexes 3 and 5; the two complexes with distinct assembly styles (AxAx for 3, EqEq for 5).

Upon heating from room temperature, complex 3 remains stable up to 120 °C. When the temperature goes higher, an obvious weight loss (19.7%) occurs in the range of 120 °C to 310 °C, which is lower than the theoretical value (25.0%) for the sum of DMF (7.9%) and pyridine molecules (17.1%). This might be attributed to the stable coordination bonds of Cu^{II} and nitrogen atoms from pyridine (bond distances 2.014(3) and 2.006(3) Å in Table S7†). There is a slight weight loss in the range of 310 °C (80.3%) to 380 °C (79.1%), followed by a

sharp decline when the temperature becomes higher, which means that the decomposition temperature for 3 is about 380 °C. A similar thermal stability study was also undertaken for complex 5. Upon heating from room temperature, the sample of complex 5 loses weight gradually, with 17.6% mass loss before 280 °C (Fig. 5a), corresponding to the contained solvent molecules (theoretical value 17.7%). In the range of 280 °C to 400 °C, there is a plateau. When the temperature is higher than 400 °C, significant weight loss occurs, indicating that complex 5 might decompose at 400 °C. Comparing the two thermal gravimetric curves, 5 shows better thermal stability than 3, which indicates that the EqEq assembly style for 5 benefits the thermal stability.

Magnetic behaviors of complexes 3 and 5 are depicted in Fig. 5 in the form of $\chi_m T vs. T$ and $\chi_m^{-1} vs. T$. For complex 3, the room temperature value for $\chi_m T$ is 1.29 cm³ mol⁻¹ K, which is slightly higher than that of three non-interacting Cu^{II} with S = 1/2 (1.125 cm³ mol⁻¹ K). Upon cooling, the value of $\chi_m T$ decreases gradually. When the temperature is lower than 100 K, the $\chi_m T$ value decreases significantly, reaching a



Fig. 5 (a) The thermal gravimetric curves for complex 3 (red line) and 5 (black line). (b, c) Temperature dependence curves of $\chi_m T$ (\blacksquare) and χ_m^{-1} (\square) for complex 3 (b) and 5 (c).

minimum value of 0.48 cm³ mol⁻¹ K at 10 K. There is an increase from 10 K to 2 K, with $\chi_m T$ value changing from 0.48 to 0.54 cm³ mol⁻¹ K. The curve of χ_m^{-1} vs. *T* for complex 3 follows the Curie–Weiss law above 46 K, with Curie constant $C = 1.40 \text{ cm}^3 \text{ mol}^{-1}$ K and Weiss constant $\theta = -20.5$ K, which indicates the antiferromagnetic property of complex 3.

The magnetic behavior upon cooling for complex 5 is significantly different from complex 3. The value of $\chi_m T$ at 300 K is 1.12 cm³ mol⁻¹ K, which is close to the theoretical value of three non-interacting Cu^{II} ions with S = 1/2 (1.125 cm³ mol⁻¹ K). The decline slope for the $\chi_m T \sim T$ curve of complex 5 in the range of 300 K to 100 K is larger than that for complex 3. A minimum $\chi_m T$ value (0.38 cm³ mol⁻¹ K) exists at 2 K. The curve of $\chi_m^{-1} vs$. T follows the Curie–Weiss law above 152 K, with C = 3.38 cm³ mol⁻¹ K and $\theta = -623.7$ K, which indicates a strong antiferromagnetic property.

Both complexes feature negative Weiss constants, while the absolute values are greatly different, which could be attributed to the different assembly styles in the crystal structures. As we discussed above, the EqEq style in 5 has the minimum value of the Cu…Cu distance at 2.996 Å, while the values for the AxAx style in 3 are 3.411 and 3.243 Å. This difference might explain the reason for the larger absolute value of the Weiss constant for 5 compared to that for 3.

Conclusions

Five coordination polymers based on a multidentate bihydrazide ligand H_6L and Cu^{II} were synthesized and characterized, which revealed the assembly of a new kind of $[Cu_3L]$ motif. The $[Cu_3L]$ motif shows four active coordination sites, directing the assembly styles by modulation from the coordination ability of involved N-containing agents. Complexes 3 and 5 showed good thermal stabilities and antiferromagnetic property, especially complex 5. Based upon the current study, the $[Cu_3L]$ motif has shown promising ability in the modulated assembly of supramolecular coordination chemistry.

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