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Coordination preference of hexa(2-pyridyl)benzene with copper(II) directed by hydrogen bonding

Hyunchul Kwon^a and Eunsung Lee^{*ab}

The study of the coordination chemistry of hexa(2-pyridyl)benzene (2-HPB) ligand with copper(II) ions is presented. 2-HPB ligand featuring six pyridine moieties can bind to a metal center in a number of different ways. Herein, we discuss dicopper(II) complexes of 2-HPB that vary in coordination geometry. Thus, the four complexes obtained (1, 2, 3, and 4) adopt two different conformations "(A,B)(C,D)-*trans*" (in 1 and 4) and "(A,B)(D,E)-*trans*" (in 2 and 3). The structure of the complex strongly depends on the solvent used (water, ethanol, and dimethylformamide (DMF)). In an aqueous solution, the formation of complexes 1 and 2 can be controlled by the choice of crystallization conditions. All products were characterized by X-ray diffraction. The coordination preference of 2-HPB is evaluated in the context of hydrogen bonding in the solid state.

Introduction

The development of new architectural motifs in coordination chemistry of multimetallic systems is of rising interest for most chemists due to potential applications of such structures in supramolecular engineering.¹⁻⁴ Up to date, multidentate ligands with 4-, 5- and 6- coordination sites were extensively developed for the synthesis of novel metal-organic architectures.⁵⁻⁹ The coordination preferences of the predesigned ligand, along with hydrogen bonding and interactions between aromatic substituents is the key to control the formation of the desired architectures during the self-assembly process.¹⁰⁻¹⁶ Hexaarylbenzene (HAB) system is one of the niche field of ligand design. Considering the unique non-planar, propeller-shaped topology of hexaarylbenzene derivatives, radially extended six aromatic rings offer a chance to develop a new coordination building block.^{17, 18} Several ligands based on HAB system were synthesized and applied in multimetallic complexes,¹⁹⁻²⁶ supramolecular materials^{18, 27} and metal-organic frameworks (MOFs)²⁸. In addition, in the context of ligand design, pyridine derivatives have been widely used as ligands due to their ability to coordinate to different metals in various binding modes.²⁹⁻⁴⁰

With this in mind, we envisioned the rigid, highly symmetrical hexa(2-pyridyl)benzene (**2-HPB**) molecule as a fascinating structural motif. The combination of six pyridine sites with different transition metal cations is expected to provide a variety of coordination geometries, offering new directions for developing novel supramolecular systems. Previously, our group reported the static and dynamic coordination behaviour of **2-HPB** at various concentration of copper(I) cation in acetonitrile solution.⁴¹ However, the coordination chemistry of copper(I) and **2-HPB** in protic media has not been studied so far. Under these conditions, copper(II) is the stable oxidation state of copper and the corresponding complexes exhibit Jahn-Teller distortion. Therefore, we decided to explore structure and properties of **2-HPB** copper(II) complexes in protic media.^{42,43}

In this publication, we focus on the coordination preferences of **2-HPB** in protic solvents. A study of complex formation with different metals as well as dynamic behaviour of the resulting complexes in aprotic solvents are reported elsewhere.⁴¹

In **Scheme 1**, we suggest four possible coordination geometries of dinuclear **2-HPB** complexes. To describe the binding mode of the ligand, we use the following notation:

^{a.} Department of Chemistry, Pohang University of Science and Technology, 77 Cheongam-Ro, 37673, Pohang, Republic of Korea.

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^b Center for Self-assembly and complexity, Institute for Basic Science (IBS), 77 Cheongam-Ro, 37673, Pohang, Republic of Korea.

^c Division of Advanced Materials Science, Pohang University of Science and Technology, 77 Cheongam-Ro, 37673, Pohang, Republic of Korea.

⁺ Footnotes relating to the title and/or authors should appear here

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Scheme 1. Anticipated coordination geometries of the M₂(2-HPB) species.

- (1) The six pyridine rings are labelled A, B, C, D, E, and F in the clockwise order. The ring A is always defined as the pyridine ring coordinated to the metal center. The nitrogen atom in this ring is pointing upside from the plane defined by the central benzene ring. In the name of the complex, rings coordinated to the metal center are listed in the alphabetical order.
- (2) If more than one nitrogen atom coordinates one metal atom, the rings binding with the same metal center are written together in parenthesis. For example, the complex with "(A,B)(C,D)-" coordination mode has two metal centers, each one coordinated by two pyridines.
- (3) For bimetallic species, "cis" indicates that two metal atoms are on the same side of the benzene ring (both pointing upside), while "trans" indicates that the two centers are located on the opposite sides (one pointing up and the other down).

Herein, we report four "trans" bimetallic complexes of 2-HPB and copper(II) ions. As shown in Scheme 2, three dicopper complexes (1, 2 and 3) and a coordination polymer (4) with different coordination modes were synthesized and characterized including single crystal X-ray analysis.

Experimental

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Synthesis of hexa(2-pyridyl)benzene (2-HPB). Under N₂ atmosphere, 2-phenylpyridine (0.16 g, 1.0 mmol), $[(\eta^6 C_6H_6$ RuCl₂]₂ (0.025 g, 0.050 mmol), triphenylphosphine (0.053 g, 0.20 mmol), and potassium carbonate (1.66 g, 12.0 mmol)

were added into a flask containing 5 mL of N-methyl-2pyrrolidone (NMP). The resulting solution was heated to 140 °C while stirring. At this temperature, 2-bromopyridine (1.58 g, 10.0 mmol) was added dropwise by means of a syringe pump over 24 h, and stirring was continued for 24 h at the same temperature. In order to remove NMP, water was added and the mixture was extracted with chloroform several times. Combined organic extracts were dried over anhydrous sodium sulfate and volatiles were removed in vacuo. The residue was purified by column chromatography on silica gel (eluting acetone : methanol : $Et_3N = 20$: 2: 1). Further purification was achieved by recrystallization from THF, providing the target product as a white solid. Hexa(2-pyridyl)benzene (0.077 g, 14.2% yield). ¹H NMR (500 MHz, CD₃CN): δ 8.06 (ddd, J = 5.0, 1.8, 1.0 Hz, 6H), 7.25 (td, J = 7.8, 1.8 Hz, 6H), 6.94 (d, J = 7.8, 6H), 6.84 (ddd, J = 7.2, 4.8, 1.0 Hz, 6H) ppm. ¹³C NMR (125 MHz, CD3CN) δ 158.2, 147.8, 140.2, 134.3, 126.7, 120.7 ppm. HR-MS : [M + H] (m/z) = 541.2139; calcd. value for $C_{36}H_{25}N_6 =$ 541.2141.

Synthesis of (A,B)(C,D)-trans-Cu₂Cl₄(H₂O)₂(2-HPB) • 5.5H₂O (1.0.75H₂O). ⁺ Hexa(2-pyridyl)benzene (27.0 mg. 0.05 mmol, 1 equiv) and CuCl₂·2H₂O (17.1 mg, 0.10 mmol, 2.0 equiv) were dissolved in 1 mL water at 85 °C. The solution was kept at this temperature for 2 h and then was cooled to room temperature. After several days, blue hexagonal crystals formed. The solution was decanted and the crystals were washed with water immediately and dried under vacuum at room temperature. The product was isolated as blue hexagonal crystals (34 mg, 70.9% yield). Crystals of 1 formed during the synthesis were suitable for XRD. Anal. Calcd for (C₃₆H₂₈Cl₄Cu₂N₆O₂·4.75H₂O)·0.75H₂O : C, 45.77; H, 4.16; N, 8.90%. Found: C, 45.72; H, 4.00; N. 8.97%.

Synthesis of (A,B)(D,E)-trans-Cu₂Cl₄(H₂O)₂(2-HPB)·5.5H₂O (2). Hexa(2-pyridyl)benzene (20 mg, 0.38 mmol, 1 equiv) and CuCl₂·2H₂O (17.1 mg, 0.10 mmol, 2.0 equiv) were dissolved in 1 mL water at 85 °C. At the same temperature in the oven, the solvent evaporated slowly until the solvent volume is reduced to the guarter (around 0.25 mL). The solution then cooled down to room temperature. Greenish block crystals formed immediately. After 10 min, the solution was decanted and the crystals were washed with water and THF, dried under vacuum at room temperature. The product was isolated as a light green

Table 1. Selected Crystal Data and Refinement Details.						
1		2	3	4		
Empirical formula C ₃₆ H	_{37.5} Cl ₄ Cu ₂ N ₆ O _{6.75}	$C_{36}H_{39}Cl_4Cu_2N_6O_{7.5}$	$C_{38}H_{32}Cl_4Cu_2N_6O_2$	$C_{39}H_{31}Cl_4Cu_2N_7O_1$		
Formula weight 931.2	10	944.61	873.57	441.29		
Temperature/K 100		100	100	100		
Crystal system Tricli	nic	Triclinic	Triclinic	Monoclinic		
Space group P-1		P-1	P-1	C2/c		
a/Å 12.50	09(3)	9.081(5)	9.263(3)	8.9606(5)		
b/Å 13.68	89(3)	10.926(5)	11.838(4)	20.9052(13)		

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c / Å	14.613(3)	12.055(7)	17.404(5)	20.0946(10)
α/°	94.72(3)	113.957(18)	85.270(12)	90
β/°	115.28(3)	111.576(17)	89.651(12)	91.240(2)
γ/°	114.86(3)	91.514(16)	86.120(12)	90
Volume/Å3	1945.6(9)	994.5(9)	1897.7(11)	3763.2(4)
Z	2	1	2	8
Radiation	synchrotron (λ = 0.63000)	ΜοΚα (λ = 0.71073)	ΜοΚα (λ = 0.71073)	ΜοΚα (λ = 0.71073)
R1 [I>=2δ (I)]	0.0644	0.0580	0.0726	0.0372



block-shaped crystals (16.3 mg, 47.0% yield. Crystals of **2** formed during the synthesis were suitable for XRD. Anal. Calcd for $C_{36}H_{28}Cl_4Cu_2N_6O_2$ *5.5 H_2O : C, 45.77; H, 4.16; N, 8.90%. Found: C, 45.39; H, 4.00; N. 9.56%.

Synthesis of (A,B)(D,E)-trans-Cu₂Cl₄(MeOH)₂(2-HPB) •0.6H₂O (3 • 0.6H₂O). The solutions of hexa(2-pyridyl)benzene (10.0 mg. 0.019 mmol, 1 equiv) and of CuCl₂ • 2H₂O (10.0 mg, 0.058 mmol, 3.0 equiv), in 1 mL methanol each, were mixed and the mixture was heated up to 85 °C. Light green rod-shaped crystals formed immediately. The reaction mixture was kept at elevated temperature for 10 minutes and then cooled down to room temperature. The methanol solution was decanted, the crystals were washed with cold methanol and dried under vacuum. The product was isolated as green rod-shaped crystals (10.4 mg, 63.2% yield). Crystals of **3** formed during the synthesis were suitable for XRD. Anal. Calcd for C₃₈H₃₂Cl₄Cu₂N₆O₂ • 0.6H₂O : C, 51.61; H, 3.78; N, 9.50%. Found: C, 51.25; H, 3.60; N, 9.42%.

Synthesisof[(A,B)(C,D)-trans-Cu₂Cl₄(2-HPB) • DMF]_n• 0.5(DMF)_n • 0.5(H₂O)_n $([4]_n • 0.5(DMF)_n • 0.5(H_2O)_n)$.*Hexa(2-pyridyl)benzene(13.5mg,0.025mmol,1equiv)andCuCl₂ • 2H₂O(12.5mg,0.075mmol,3.0equiv)were placed in a4mL vial and dissolved in 4mL of DMF. The vial was placed inan oven at 85°C for 24h. After this time, the green solutionwas decanted and dark green crystals were washed with THF

and dried under high vacuum. The product was isolated as dark green crystals (13.1 mg, 62.2% yield). Crystals of **4** formed during the synthesis were suitable for XRD. Anal. calcd for $C_{39}H_{31}Cl_4Cu_2N_7O\cdot 0.5(C_3H_7O)\cdot 0.5H_2O$: C, 52.41; H, 3.85; N, 11.32%. Found: 52.19; H, 3.44; N, 11.50%.

Results

Synthesis. 2-HPB was synthesized by dropwise addition of 2bromopyridine to the mixture of 2-phenylpyridine, [$(\eta^6 - C_6H_6)RuCl_2]_2$, PPh₃, and K₂CO₃ (base) in *N*-methyl-2-pyrrolidone (NMP) solvent. The active complex that was formed from [$(\eta^6 - C_6H_6)RuCl_2]_2$ and PPh₃ (supporting ligand) catalyses oxidative addition of 2-bromopyridine⁴⁴ and the successive crosscoupling reaction of phenyl C-H bond directed by pyridine group

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Figure 1. Molecular structures of (A,B)(C,D)-trans-Cu₂Cl₄(H₂O)₂(2-HPB) 1 (a) and (A,B)(D,E)-trans-Cu₂Cl₄(H₂O)₂(2-HPB) 2 (b). Ellipsoids are shown at the 25% probability level for 1 and 2. Hydrogen atoms and lattice water molecules are omitted for clarity.



Figure 2. Molecular structures of complex 1 (a), complex 2 (b) $^{\circ}$, a linear chain of 1 (c) and 2 (d) formed due to hydrogen bonding.

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Figure 3. Molecular structures of complex 1 (a) and 2 (b) with lattice water molecules displayed. Hydrogen bonds between donor and acceptor atoms are marked as dotted lines.

to afford **2-HPB**. The ¹H and ¹³C NMR spectra are in accordance with the structure (Figure S2 and S3). The copper(II) complexes 1, 2, 3, and 4 were prepared by combining the ligand with copper(II) chloride in different solvents, as described in the experimental section. The complexes 1 and 2 were formed in the aqueous solution of 2-HPB in presence of two equivalents of CuCl₂ · 2H₂O. Because of solubility issue, the solution was prepared at 85 °C and then cooled to room temperature. After several days, hexagonal blue crystals (1) were formed. On the other hand, when the solvent was evaporated, greenish block-shaped crystals (2) were formed within minutes at the edge of the vaporization site. Under an optical microscope, these crystals displayed a different colour and morphology compared to the crystals of 1 (Figure S11). By this method, a mixture of 1 and 2 obtained, determined by PXRD (Figure S1 (b)). Isolation of 2 as a sole product was achieved when the solution concentrated by evaporation at 85 °C for several hours. Upon cooling to room temperature, greenish block-shaped crystals (2) formed within minutes.

Complex **3** was obtained from a methanol solution of **2**-HPB and 3 equivalents of $CuCl_2 \cdot 2H_2O$ at 85 °C. The greenish rod-shaped crystals were formed immediately, over less than a minute. When the crystals dried out completely, their color changed to blue. The complex **4** was obtained from a DMF solution of **2**-HPB and 2 equivalents of $CuCl_2 \cdot 2H_2O$ at 85 °C after 1 day as dark green crystals. All compounds were air stable and could be stored at 25 °C without any indication of decomposition.

TGA and PXRD study

check the thermal stability of the compound, То thermogravimetric analysis (TGA) was performed with 1, 2, 3, and 4 within the 25 °C to 800 °C temperature range (Figure S5). The TGA measurements for 1, 2, 3, and 4 exhibit two distinct weight loss steps. In 1 and 2, the first weight loss between 30° C and 100 °C assigned to the lattice and coordinated water molecules. Then, a continual weight loss occurs between 310° C and 560 °C, which is attributed to the decomposition of the 2-HPB ligands and halide anions. In 3, the first weight loss between 90 °C and 100 °C assigned to coordinated methanol molecules. Then, a similar weight loss pattern was observed between 310 °C and 580 °C, indicating decomposition of the 2-HPB ligands and halide anions. In 4, a sharp weight loss occurred around 200 °C which corresponds to the loss of lattice DMF molecules. Then, the weight loss between 310 °C and 580 °C was observed as an indication of ligand decomposition.

Powder X-ray diffraction (PXRD) was carried out at room temperature (**Figure S1**). All of the major peaks of PXRD patterns of as-synthesized **1**, **2**, **3**, and **4** were well matched with those simulated from crystal data, securing the bulk purity of each product in the solid state (**Figure S1** (b)).

Solid-State Structures of 1 and 2. Figure 1 shows the molecular structures of 1 and 2. The complex 1 adopts (A,B)(C,D)-trans (or



 $\label{eq:Figure 4.} Figure 4. Molecular structure of the (A,B)(C,D)-trans-Cu_2Cl_4(MeOH)_2(2-HPB) 3. Ellipsoids are shown at the 25\% probability level. Hydrogen atoms are omitted for clarity.$

(A,B)(E,F)-*trans*, considering the chirality of the complex) coordination geometry where **2-HPB** serves as a bis-bidentate ligand for two copper(II) centers. The remaining two pyridine rings are not involved in the coordination. The two copper centers exhibit a distorted square pyramidal geometry and are located on the opposite sides of the benzene ring. Each copper atom binds with two pyridine sites of the ligand (bite angle :

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85.31(19)° for ∠N1-Cu1- N2 and 86.54(19)° for ∠N3-Cu2-N4), one water molecule and two chlorides. The lengths of Cu2-Cl4 and Cu1-Cl3 bonds are 2.264(3) Å and 2.308(2) Å respectively. The axial bonds Cu2-Cl2 and Cu1-Cl1 are longer (2.5128(17) Å and 2.5196(19) Å respectively) due to the Jahn-Teller effect of axial elongation on d⁹ copper(II) ion. The distance between the copper(II) atoms in the complex is 7.229 Å.

In complex **2**, the ligand adopts (A,B)(D,E)-trans conformation coordinating the two copper(II) atoms. The two non-coordinating pyridines (rings C and F) are in the para position with respect to each other. The two copper(II) centers exhibit a distorted square pyramidal geometry in complete analogy to complex **1**. Each copper atom binds with two pyridine sites of the ligand (bite angle : $85.29(15)^{\circ}$ for $\angle N1$ -Cu1-N2), one water molecule and two chlorides. The length of Cu1-Cl2 bond is 2.283(2) Å while the length of Cu1-Cl1 bond is 2.423(17) Å due to the Jahn-Teller effect. In addition, the water molecules in **2** serve as hydrogen bond donors for nitrogen atoms in rings C and F with the distance of 2.799(6) Å (For O1···N3).

Figure 2 shows the alignment of complexes 1 and 2 in the solid state. In complex 1, the water ligand attached to the copper(II) atom forms hydrogen bonds with non-coordinating pyridine nitrogen and chlorine atoms of the neighbouring molecule. The lengths of hydrogen bonds formed in 1 are 2.753 Å and 2.892 Å for $O \cdots N$ and 3.421 Å and 3.136 Å for $O \cdots CI$. The molecules of the complex assemble to a 1D linear chain due to the presence of pairs of $O \cdots N$ and $O \cdots CI$ hydrogen bonds linking the monomers to each other. The distance between the planes defined by the central arene rings of the monomers is 7.383 Å in the chain.

In complex 2, water molecules coordinated to the copper(II) centers form intermolecular hydrogen bonds between each other with the distance of 2.797 Å (For O1···O1). The complex molecules are linked side to side by these intermolecular hydrogen bonds and form a 1D linear chain. The distance between the planes defined by the central arene in the monomers is 8.336 Å, which is longer than the corresponding interval in the linear chain of 1. In addition, in 1 and 2 the water molecules and chlorides coordinated to the copper atoms engage in hydrogen bonding with lattice water molecules forming 2D hydrogen bond networks (Figure 3). In case of complex 1, the chlorides and the water molecules form a 2D sheet located between two 2-HPB units. The 2D sheet consists of four chlorides, two water molecules and six lattice water molecules. The distance between donor and acceptor atoms is 2.644 Å to 2.905 Å for O···O and 3.032 Å to 3.421 Å for O···Cl. On the other hand, in complex 2 three lattice water molecules are sandwiched by the two 2-HPB to form a 2D hydrogen bond network. The distance between donor and acceptor atoms is 2.630 Å to 2.771 Å for O···O and 3.182 Å to 3.277 Å for O····Cl. Additional information about distances and angles in the networks is given in Table S1.

Solid-State Structure of 3. The complex **3** is formed in a methanol solution of **2-HPB** and $CuCl_2 \cdot 2H_2O$ (**Figure 4**). The complex adopts the (A,B)(C,D)-*trans* coordination mode, with

coordinated rings A and B pointing up and the ring C (or F) participating in intramolecular hydrogen bonding with the methanol molecule coordinated to copper. Each copper(II) atom exhibits a distorted square pyramidal geometry while binding with two pyridine sites (bite angle : $82.48(19)^{\circ}$ for \angle N2-Cu1-N3 and $81.96(19)^{\circ}$ for \angle N1-Cu2-N4), one methanol molecule and two chlorides. The lengths of the Cu1-Cl1 and Cu2-Cl2 bonds are 2.2758(17) Å and 2.2702(17) Å, respectively. The axial Cu1-Cl3 and Cu2-Cl4 bonds are longer (2.4024(18) Å and 2.4003(17) Å, respectively) due to the Jahn-Teller effect. The hydrogen bonding distance from the coordinated methanol hydroxyl group to the non-coordinating



Figure 5. Molecular structure of [(A,B)(C,D)-trans-Cu₂Cl₄(2-HPB)· DMF]_n [**4**]_n ((a): monomeric unit, (b) polymer). Ellipsoids are shown at the 50% probability level for [**4**]_n. Hydrogen atoms are omitted for clarity.

pyridine varies from 2.776 Å to 2.785 Å (For O2···N5 and O1···N6, respectively). In addition, unlike **1** or **2**, the complex **3** does not form 1D or 2D networks by intermolecular hydrogen bonding and no additional solvent molecule is present in the lattice (Figure S16).

Solid-State Structure of [4]_n. 1D coordination polymer 4 was obtained when dimethylformamide (DMF) was used as a solvent (Figure 5). The monomeric unit in 4 adopts the (A,B)(C,D)-*trans* coordination geometry. The monomers are linked by Cu₂Cl₄ clusters forming a coordination polymer. The copper(II) center in the cluster is in distorted pyramidal environment with two pyridines of the ligand and three chlorides coordinated. The bonding distances are 2.2367(8) Å, 2.296 Å and 2.7509(7) Å (For Cu1-Cl2, Cu1-Cl1 and Cu1-Cl1', respectively.). The long Cu1-Cu1'distance (2.75 Å) is mainly due to the Jahn-Teller effect. The Cu₂Cl₄ cluster is composed of a four membered ring [Cu₂(μ -Cl)₂] core and two chlorides binding to the copper (II) atoms (Figure S13). The distance between the two copper atoms in the cluster is 3.718 Å.

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Discussion

Coordination Isomers, 1 and 2. As mentioned above, the complexes 1 and 2 were obtained from the same solution. This outcome indicates that 1 and 2 are in equilibrium when dissolved. This is further supported by UV-VIS spectroscopy, as the same spectra were obtained for the solution of 1 and 2 (Figure S4). In the solid state, the interaction between monomers in 2 is expected to be much weaker than in 1. Since the number and the types of covalent bonds are the same in both isomers, the difference in stability of the complexes originates from the strength of hydrogen bonds connecting the monomers. In complex 1, there are four hydrogen bonds between the monomers (two O···N and two O···Cl) while only one hydrogen bond $(0 \cdot \cdot \cdot 0)$ connects the monomers in 2. This results in a shorter distance between the monomers in the linear chain of 1 (7.229 Å) as compared to 2 (7.383 Å). Moreover, considering the stability gained from the presence of 2D hydrogen bond networks, 1 is expected to be thermodynamically more stable than 2. Higher stability of 1 is also confirmed by observations made during the synthesis. When the aqueous solution of 2-HPB with CuCl₂·2H₂O stored at room temperature for several days, complex 1 formed as the sole product. However, when the hot and concentrated solution was cooled to the room temperature, the crystals of 2 formed within a minute. This experimental outcome indicates that the formation of 2 is kinetically more favourable while the formation of 1 is thermodynamically more favourable.

The Effect of Hydrogen Bonding in the Coordination Mode. All

four complexes adopt trans coordination geometry. The synthesis of the complex with cis coordination mode could not be achieved, presumably because of steric issues. The complex 1 adopts (A,B)(C,D)-trans coordination mode while complex 2 adopts (A,B)(D,E)-trans coordination mode. This difference originates from the hydrogen bonding between pyridine nitrogen and coordinated water molecule in the complex. In 1, the coordinated water molecules form intermolecular hydrogen bonds with adjacent pyridines in the linear chain. In 2, the coordinated water molecules form hydrogen bonds with the pyridines in an intramolecular manner. We assume that the intramolecular hydrogen bonding between coordinated water molecules and pyridines in the ligand directs (A,B)(D,E)trans conformation while the intermolecular hydrogen (A,B)(C,D)-trans the two directs bonding between conformation. This assumption is confirmed indirectly by the synthesis of complex 3. In this case, methanol was used as a solvent providing complex 3 in which a methanol molecule serves as a ligand for the copper(II) center. The presence of methanol methyl group prevents intermolecular hydrogen bonding due to steric factors. Additionally, in case of methanol only one proton is available for this type of bonding. Indeed, the complex 3 adopts (A,B)(D,E)-trans coordination mode with intramolecular hydrogen bonding between the coordinated methanol molecule and the pyridine nitrogen in the ligand.

The effect of intramolecular hydrogen bonding can be correlated to the O-Cu-N angle in the complex (oxygen from

coordinated methanol or water molecule and nitrogen from the pyridyl group on the cis position with respect to the oxygen). An intramolecular interaction between the hydroxyl group and the pyridine nitrogen would narrow down this angle by constraining the Cu-O bond. In complex 3, the corresponding angles are 82.02° (O2-Cu1-N2) and 82.55° (O1-Cu2-N1), while the angle in 2 is 85.24° (O1-Cu1-N2) and the angles in 1 are 89.57° (O2-Cu1-N2) and 90.2° (O1-Cu2-N4). Complex 3 exhibits the narrowest O-Cu-N angle since the hydroxyl group interact with one pyridine nitrogen exclusively to form an intramolecular hydrogen bond. On the other hand, the water molecule in 2 forms both inter- and intramolecular hydrogen bonds. That additional intermolecular interaction with another hydroxyl group releases the constraint originating from the intramolecular hydrogen bonding with the nitrogen atom (Figure 2 (b)). In addition, in 1 there are no constraint imposed on the angle since the water molecule forms hydrogen bonds only in an intermolecular manner.

In protic solvents, the binuclear complexes 1, 2 and 3 incorporating coordinated solvent molecules are obtained, thus preventing the formation of polymeric materials. In contrast, in DMF solution no solvent incorporation takes place and a polymeric complex 4 is formed instead. The monomers in 4 adopt (A,B)(C,D)-trans coordination mode presumably because it results in a short distance between the monomers and allows for dense packing of the coordination polymer chains.

Conclusion

Four novel dicopper(II) complexes with hexa(2pyridyl)benzene (2-HPB) ligand were prepared and characterized by single crystal X-ray diffraction. These complexes contain two equivalents of copper(II) chloride per 2-HPB ligand and exhibit solvent-dependent coordination geometry.

In an aqueous solution, complexes with (A,B)(C,D)-trans conformation (1) and (A,B)(D,E)-trans conformation (2) were formed. The ratio of the two species can be influenced by varying the crystallization conditions. The water molecules coordinated to the copper(II) centers in 1 and 2 participate in an inter- or intramolecular hydrogen bonding with free pyridine sites, respectively. The (A,B)(D,E)-trans complex 3 was formed in a methanol solution. In this case, the coordinated methanol molecule forms a hydrogen bond with a pyridine site in an intramolecular manner. In a DMF solution, no solvent molecules were incorporated in the complex and a polymeric chain 4 was obtained. In 4, each monomer adopts (A,B)(C,D)trans conformation and the monomers share Cu₂Cl₄ clusters with [Cu₂(μ -Cl)₂] cores forming a coordination polymer.

We hope that this work will inspire new synthetic strategies for the construction of multimetallic complexes and supramolecular materials utilizing unique features of hexaarylbenzene derivatives.

Conflicts of interest

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There are no conflicts to declare

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Notes

[‡] We named the complexes **1** and **4** with the prefix of "(A,B)(C,D)-" for a convenience however, these complexes are racemic mixtures of "(A,B)(C,D)-" and "(A,B)(E,F)-".

§ In **Figure 2** (b), the hydrogen atoms in the coordinated water molecules are not fitted in the range of the intermolecular hydrogen bonding. This is due to the symmetry of the complex **2** and we believe one hydrogen atom should be in the dotted line of O1…O1'.

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