Copper-Organic Coordination Polymers with Porous Structures

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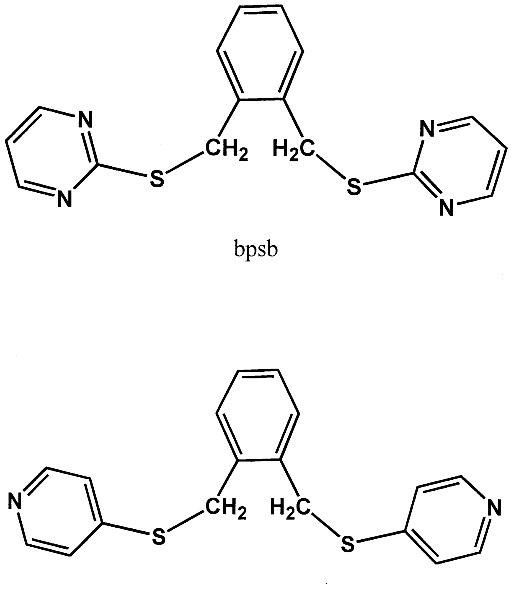
Three copper coordination polymers containing organosulfur ligands ($\{[\mathrm{Cu^I_2(bpsb)_3(ClO_4)}](\mathrm{ClO_4})\}_n$ (**1**), $\{[\mathrm{Cu^I_2(bpsb)_3Cl}](\mathrm{ClO_4})\}_n$ (**2**), and $\{[\mathrm{Cu^{II}(bpb)_2Br}](\mathrm{ClO_4})\cdot 3\mathrm{dmf}\cdot\mathrm{MeCN}\}_n$ (**3**) (bpsb = 1,2-bis[(2-pyrimidinyl)sulfanylmethyl]benzene, bpb = 1,2-bis[(4-pyridyl)sulfanylmethyl]benzene, dmf = *N*, *N*-dimethylformamide)) were synthesized and characterized by X-ray structural analysis. Complexes **1** and **2** have similar structures. In both, each bpsb molecule exhibits an exo-bidentate coordination fashion and bridges 3-coordinated copper(I) and 4-coordinated copper(I) through pyrimidinyl rings. Thus, six copper(I) centers, three 3-coordinated and three 4-coordinated located at two different planes alternatively, are linked by six bpsb molecules forming a crown-like nanocavity; such nanocavities make up a 2-D lamellar structure. In complex **3**, each copper(II) center adopts a distorted square pyramidal coordination mode; each bpb molecule acts as an exo-bidentate ligand through coordinating to copper(II) atoms in two different directions to form a square unit with solvent molecule guests. Such square units share copper atoms and generate a single-stranded infinite 1-D chain structure.

Supramolecular syntheses by employing coordination covalent chemistry and the principle of self-assembly have resulted in numerous metal-ligand networks with fascinating structural topologies, in which selective and spontaneous assemblies rely principally on complexation of multidentate ligands with steric and interactive information and two or more metal ions.[1–3] Therefore, the design of ligands and the selection of metal ions are crucial to the construction of a specific supramolecular architecture, particularly one-, two- and three-dimensional extended network framework types owing to their potential application to separation and catalysis. This problem has been demonstrated by many architecturally highly sophisticated polynuclear complexes, such as molecular grids, racks, bricks, rings, boxes, honeycombs and helicates.[4–10] For instance, rigid ligands, such as pyrazine, 4,4-bipyridine and 1,4-benzenedicarboxylate, result in the formation of molecular racks and grids.[6–8] While flexible ligands, such as bipyridine groups with a longer spacer or 2,2′:6′,2″-terpyridine and its derivates with conformational freedom, might result in the formation of helicates or networks.[9–10] On the other hand, a great deal of the structural information available from coordination chemistry has demonstrated the importance of choosing metal ions for supramolecular self-assembly. For example, the copper(I) and silver(I) ions as extremely soft acids benefit coordination to soft bases, such as S and unsaturated N-containing ligands, and produce an interesting array of complexes with labile coordination modes, such as linear, trigonal, tetrahedral, pentagonal, square-pyramidal and even octahedral fashions; however, Fe(III), Cu(II), and Ln(III) (Ln = Lanthanoid) etc. as hard acids favor coordination to hard bases, such as O, N and P, and give rise to a great deal of coordination polymers with high coordination numbers of over four.[11]

Because metal thiolato complexes are well known to adopt various nuclearity and great structural complexity, previous interests in our laboratory have concentrated on using some simple ligands with mixed phosphine or nitrogen and thiolato donor atoms for supramolecular synthesis. As a result, some supramolecular polymers with linear chain or 3-D network structures have been obtained.[12–14] Recently, we have designed a series of multidentate ligands containing pyrimidinyl or pyridyl rings by using simple ligands with sulfur and nitrogen atoms from earlier work, such as 2,4,6-tris[(4-pyridyl)methylsulfanyl]-1,3,5-triazine (tpst), 1,2-bis[(2-pyrimidinyl)methylsulfanyl]benzene (bpsb) and 1,2-bis[(4-pyridyl)methylsulfanyl]benzene (bpb), and obtained several unique structural motifs in supramolecular chemistry.[15,16] Considering the basic requirement for supramolecular synthesis, that the coordination possibility of ligands should match the steroelectronic preferences and coordination geometry of the metal ions, we expected to prepare some coordination polymers containing a nanometer-sized cavity by using designed bridging ligands, bpsb, in which a spatial effect of coordination sites prevent it from forming high coordination-number complexes and bpb in which a longer bis(4-pyridyl) spacer can produce bigger holes in the ring by bridging metal ions at larger distances [17–18] (Scheme 1), and suitable metal ions.

In this paper, we describe the syntheses and the structural characterization of two 2-D lamellar coordination polymers containing crown-like nanocavities, $\{[\mathrm{Cu^I_2(bpsb)_3(ClO_4)}](\mathrm{ClO_4})\}_n$ (**1**), $\{[\mathrm{Cu^I_2(bpsb)_3Cl}](\mathrm{ClO_4})\}_n$ (**2**), and one single-stranded 1-D chain complex containing square rings with solvent molecule guests, $\{[\mathrm{Cu^{II}(bpb)_2Br}](\mathrm{ClO_4})\cdot 3\mathrm{dmf}\cdot\mathrm{MeCN}\}_n$ (**3**).



bpsb

bpb

Scheme 1.

Experimental

General Procedures and Measurements. All of the reagents were commercially available and used as purchased without further purification. Sodium pyrimidine-2-thiolate and sodium pyridine-4-thiolate were obtained through the reaction of 2-mercaptopyrimidine and 4-mercaptopyrimidine with $NaOCH_3$ in MeOH, respectively. The ligands bpsb and bpb were prepared in situ from the reaction of 1,2-bis(bromomethyl)benzene and sodium pyrimidine-4-thiolate or sodium pyridine-4-thiolate, respectively, in methanol. $[Cu(CH_3CN)_4]ClO_4$ was prepared according to literature methods.[19] The IR spectra as a KBr disk were recorded on a Magna 750 FT-IR spectrophotometer. Elemental analysis (C, H, N) was determined on an Elementar Vario ELIII elemental analyzer.

Preparation of $\{[Cu^I_2(bpsb)_3(ClO_4)](ClO_4)\}_n$ (1): A solution of 1,2-bis(bromomethyl)benzene (0.13 g, 0.5 mmol) and sodium pyrimidine-2-thiolate (0.11 g, 1 mmol) in MeOH (30 mL) was heated to 50 °C for 6 h with vigorous stirring. After cooling, a CH_3CN (10 mL) solution of $AgClO_4$ (0.22 g, 1 mmol) was added to remove any Br^-. The mixture was stirred for 30 min and then filtered. To the filtrate was added dropwise a CH_3CN (10 mL) solution of $[Cu(CH_3CN)_4]ClO_4$ (0.18 g, 0.5 mmol), and the reaction mixture was stirred for 1 h to give a yellow solution, which was filtered. Yellow crystalline complex **1** was obtained by keeping the resulting solution in the air for one week. Yields: 0.17 g (0.13 mmol, 78.14%). Calcd for $C_{48}H_{42}Cl_2Cu_2N_{12}O_8S_6$: C, 44.13; H 3.22; N, 12.87; S, 14.71%. Found: C, 43.97; H, 3.16; N, 12.73; S, 14.49%. IR (KBr pellet) 3115 (vw), 3068 (vw), 2938 (vs), 1574 (s), 1551 (vs), 1491 (w), 1446 (w), 1429 (w), 1381 (vs), 1252 (w), 1217 (m), 1181 (vs), 1088 (vs), 945 (w), 847 (w), 796 (m), 762 (m), 706 (m), 687 (w), 648 (w), 623 (m), 602 (w), 563 (w), 474 (w), 463 (w), 449 (m) cm^{-1}.

Preparation of $\{[Cu^I_2(bpsb)_3Cl](ClO_4)\}_n$ (2): A solution of 1,2-bis(bromomethyl)benzene (0.13 g, 0.5 mmol) and sodium pyrimidine-2-thiolate (0.11 g, 1 mmol) in dmf (20 mL) was heated to 50 °C for 6 h with vigorous stirring. After cooling, a CH_3CN (10 mL) solution of $AgClO_4$ (0.22 g, 1 mmol) was added to remove any Br^-. The mixture was stirred for 30 min and then filtered. To the filtrate was added dropwise a CH_3CN (10 mL) solution of CuCl (0.05 g, 0.5 mmol); the reaction mixture was stirred for 0.5 h at 50 °C and then filtered. Yellow crystalline complex **2** was obtained by slow diffusion of diethyl ether into the resulting solution for two weeks. Yields: 0.11 g (0.09 mmol, 52.38%). Calcd for $C_{48}H_{42}Cl_2Cu_2N_{12}O_4S_6$: C, 48.40; H, 3.38; N, 13.53; S, 15.47%. Found: C, 48.27; H, 3.26; N, 13.32; S, 15.42%. IR (KBr pellet): 3109 (vw), 3074 (vw), 3024 (w), 2960 (vw), 1566 (vs), 1549 (vs), 1491 (w), 1450 (vw), 1429 (vw), 1385 (vs), 1254 (w), 1186 (s), 1099 (s), 1088 (s), 985 (w), 951 (w), 847 (w), 812 (m), 795 (w), 773 (w), 766 (s), 748 (m), 706 (w), 648 (w), 638 (w), 623 (m), 602 (w), 565 (w), 465 (w), 449 (w) cm^{-1}.

Preparation of $\{[Cu^{II}(bpb)_2Br](ClO_4)\cdot 3dmf\cdot MeCN\}_n$ (3): A solution of 1,2-bis(bromomethyl)benzene (0.13 g, 0.5 mmol) and sodium pyridine-4-thiolate (0.12 g, 1 mmol) in dmf (15 mL) was heated to 50 °C for 6 h with vigorous stirring. After cooling, a pale-yellow solution was filtered. Then, a solution of $Cu(ClO_4)_2\cdot 6H_2O$ (0.14 g, 0.5 mmol) in CH_3CN (10 mL) was added and the reaction mixture was stirred for 1 h to give a blue solution. A dark-blue crystalline complex **3** was obtained by diffusion of diethyl ether into the resulting solution after two days. Yields: 0.18 g (0.16 mmol, 62.07%). Calcd for $C_{47}H_{56}BrClCuN_8O_7S_4$: C, 48.95; H 4.86; N, 9.72; S, 11.11%. Found: C, 48.17; H, 4.47; N, 9.56; S, 10.93%. IR (KBr pellet) 3070 (w), 3043 (vw), 3012 (vw), 2470 (vw), 1597 (vs), 1537 (w), 1489 (m), 1452 (w), 1427 (S), 1331 (w), 1225 (m), 1149 (m), 1120 (s), 1080 (s), 1016 (w), 827 (m), 723 (m), 631 (m), 503 (m) cm^{-1}.

Crystal Structure Determination. Single crystals of complexes **1**–**3** with approximate dimensions (0.10×0.14×0.16 mm for **1**, 0.65×0.60×0.60 mm for **2**, and 0.43×0.38×0.25 mm for **3**) were used for data collections on a Siemens Smart CCD diffractometer with graphite-monochromated Mo-$K\alpha$ radiation (λ = 0.71073 Å) at 298 K. Empirical absorption corrections were applied by using the SADABS program for the Siemens area detector. The structures were solved by direct methods and all calculations were performed with the SHELXL PC program. The coordinates of the heavy atoms were obtained from an E-map; successive difference Fourier syntheses gave all of the coordinates of the non-hydrogen atoms. The positions of H atoms were generated geometrically (C–H bond fixed at 0.96 Å), assigned isotropic thermal parameters, and allowed to ride on their parent carbon atoms before the final cycle of refinement. The structure was refined by full-matrix least-squares minimization of $\Sigma(F_o-F_c)^2$ with anisotropic thermal parameters for all atoms, except the H atoms. Table 1 gives the crystal data and structure determination summary for **1**–**3** and Table 2–4 list the selected bond lengths and angles for **1**–**3**. Crystallographic data (excluding structure factors) for the three structures have been deposited in the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 160678, 160679 and 160680. Copies of the data can be obtained free of charge by applying to CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: (+44) 1223-336-033; Email: deposit @ccdc.cam.ac.uk). The details of structures have been deposited as Document No. 75017 at Office of the Editor of Bull. Chem. Soc. Jpn.

Results and Discussion

Syntheses: In our previous work, the self-assembly reactions of bpsb and bpb ligands with the Ag(I) species resulted in

Table 1. Crystallographic Data for the Three Crystal Structures

Compound	$\{[\mathrm{Cu^I_2(bpsb)_3(ClO_4)}](\mathrm{ClO_4})\}_n$	$\{[\mathrm{Cu^I_2(bpsb)_3Cl}](\mathrm{ClO_4})\}_n$	$\{[\mathrm{Cu^{II}(bpb)_2Br}](\mathrm{ClO_4})\cdot 3\mathrm{dmf}\cdot \mathrm{MeCN}\}_n$
Formula	$C_{48}H_{42}Cl_2Cu_2N_{12}O_8S_6$	$C_{48}H_{42}Cl_2Cu_2N_{12}O_4S_6$	$C_{47}H_{56}BrClCuN_8O_7S_4$
Fw	1305.27	1241.28	1152.14
Crystal size(mm)	0.10 × 0.14 × 0.16	0.65 × 0.60 × 0.60	0.43 × 0.38 × 0.25
Crystal system	Trigonal	Hexagonal	Triclinic
Space group	$P3_1c$	$P6_3$	$P\bar{1}$
a/Å	14.31(2)	14.292(2)	10.6173(6)
b/Å	14.31(2)	14.292(2)	11.8589(6)
c/Å	15.56(5)	14.769(3)	23.9307(1)
α/°			92.956(1)
β/°			100.620(1)
γ/°	120	120	108.193(1)
V/Å^3	2760(11)	2612.7(8)	2802.9(3)
Z	2	2	2
ρ_{calcd}/g cm^{-3}	1.571	1.578	1.365
μ/mm^{-1}	1.158	1.213	1.352
T/K	293(2)	293(2)	293(2)
λ(Mo $K\alpha$)/Å	0.71073	0.71073	0.71073
Reflections collected	13559	13572	15381
Unique reflections	3023	2549	9854
Observed reflections ($F > 4.0\sigma(F)$)	1940	2299	4308
parameters	235	223	592
S on F^2	1.070	1.041	1.020
R_1	0.0680	0.0335	0.0676
R_{w}	0.1259	0.0403	0.1192
$\Delta\rho_{\mathrm{min}}$ and $\Delta\rho_{\mathrm{max}}$ [e/Å^3]	0.484 and −0.784	0.344 and −0.581	1.037 and −1.004

Table 2. Selected Bond Lengths [Å] and Angles [°] for $\{[\mathrm{Cu^I_2(bpsb)_3(ClO_4)}](\mathrm{ClO_4})\}_n$

Cu(1)–N(1)	2.004(8)	Cu(1)–N(1B)	2.004(8)
Cu(1)–N(1D)	2.004(8)	Cu(2)–O(3)	1.91(2)
Cu(2)–N(4)	2.134(8)	Cu(2)–N(4A)	2.134(8)
Cu(2)–N(4E)	2.134(8)		
N(1)–Cu(1)–N(1B)	119.21(8)	N(1)–Cu(1)–N(1D)	119.21(8)
N(1B)–Cu(1)–N(1D)	119.21(8)	O(3)–Cu(2)–N(4)	110.3(2)
O(3)–Cu(2)–N(4A)	110.3(2)	O(3)–Cu(2)–N(4E)	110.3(2)
N(4A)–Cu(2)–N(4)	108.6(2)	N(4A) –Cu(2)–N(4E)	108.6(2)
N(4)–Cu(2)–N(4E)	108.6(2)		

Symmetry transformations used to generate equivalent atoms: A: $-x+y+1$, $-x+1$, z; B: $-y+1$, $x-y$, z ; D: $-x+y+2$, $-x+1$, z; E: $-y+1$, $x-y-1$, z.

Table 3. Selected Bond Lengths [Å] and Angles [°] for $\{[\mathrm{Cu^I_2(bpsb)_3Cl}](\mathrm{ClO_4})\}_n$

Cu(1)–N(1A)	1.986(3)	Cu(1)–N(1)	1.986(3)
Cu(1)–N(1C)	1.986(3)	Cu(2)–N(4)	2.149(4)
Cu(2)–N(4B)	2.149(4)	Cu(2)–N(4E)	2.149(4)
Cu(2)–Cl(2)	2.294(2)		
N(1A)–Cu(1)–N(1)	119.890(13)	N(1A)–Cu(1)–N(1C)	119.890(13)
N(1)–Cu(1)–N(1C)	119.890(13)	N(4)–Cu(2)–N(4B)	100.58(13)
N(4)–Cu(2)–N(4E)	100.58(13)	N(4B)–Cu(2)–N(4E)	100.58(13)
N(4)–Cu(2)–Cl(2)	117.34(11)	N(4B)–Cu(2)–Cl(2)	117.34(11)
N(4E)–Cu(2)–Cl(2)	117.34(11)		

Symmetry transformations used to generate equivalent atoms: A: $-x+y+2$, $-x$, z; B: $-x+y+2$, $-x+1$, z; C: $-y$, $x-y-2$, z; E: $-y+1$, $x-y-1$, z.

Table 4. Selected Bond Lengths [Å] and Angles [°] for $\{[Cu^{II}(bpb)_2Br](ClO_4)\cdot 3dmf\cdot MeCN\}_n$

Cu(1)–N(2)	2.035(8)	Cu(1)–N(1A)	2.043(9)
Cu(1)–N(3A)	2.043(8)	Cu(1)–N(4)	2.058(8)
Cu(1)–Br(1)	2.723(2)		
N(2)–Cu(1)–N(1A)	89.9(3)	N(2)–Cu(1)–N(3A)	167.3(4)
N(1A)–Cu(1)–N(3A)	88.2(3)	N(2)–Cu(1)–N(4)	90.0(3)
N(1A)–Cu(1)–N(4)	168.1(4)	N(3A)–Cu(1)–N(4)	89.3(3)
N(2)–Cu(1)–Br(1)	94.0(3)	N(1A)–Cu(1)–Br(1)	96.8(3)
N(3A)–Cu(1)–Br(1)	98.6(3)	N(4)–Cu(1)–Br(1)	95.0(3)

Symmetry transformations used to generate equivalent atoms: A: $x+1$, $y+1$, z.

several structures,[16] this prompting us to extend our work to other metal ions and hope to obtain some novel structures that are different from those of silver(I) complexes. Unfortunately, the reaction of bpsb with $Cu(ClO_4)_2\cdot 6H_2O$ in dmf/CH_3CN produced an uncharacterized yellow oil, and changing the copper(II) starting materials to copper nitrate or acetate was not helpful for the reactions. After a careful study of the coordination geometry of bpsb, we sensed that the unsatisfactory results may have been caused by a mismatching coordination geometry between bpsb and Cu(II). As is known, Cu(II) favors a square-planar or square-pyramidal coordination geometry, requiring four bpsb molecules to coordinate to Cu(II) owing to the non-chelating coordination mode of bpsb, which would cause a large space hindrance, and thereby render the formation of stable compounds. We thus introduced Cu(I) into the reaction in view of the same d^{10} configurations and similar coordination geometry between Cu(I) and Ag(I). As expected, complex **1**, which possesses a similar structure to its silver analogue,[16a] was isolated from the reaction of bpsb and $[Cu(CH_3CN)]ClO_4$ in good yields. The differences of **1** and **2** may come from the different anions present in the synthetic reactions, similar to the case of the Ag(I) reaction. When bpb was used as a ligand, it was possible for four bpb molecules to coordinate to one Cu(II) center, and complex **3** was isolated in an in situ reaction of bpb with $Cu(ClO_4)_2\cdot 6H_2O$, giving satisfactory yields. However, Br^- is necessary to saturate the square-pyramidal coordination geometry of Cu(II) in this reaction, and the removal of Br^- from the reaction system resulted in a failure to isolate **3**.

Description of Complex 1: The crystal structure of complex **1** is shown in Figs. 1 and 2. Copper(I) atoms in the complex have two different coordination geometry. Cu(1) is coordinated by three nitrogen atoms from different, but symmetry-equivalent, bpsb ligands related by threefold axes passing through the Cu(1) atom. Thus, each Cu(1) atom is in an unusual, but precedent, trigonal geometry of $Cu(N)_3$[20] [Cu(1)–N = 2.004(8) Å, N–Cu(1)–N = 119.21(8)°]. However, the coordination geometry around the Cu(2) atom is a distorted tetrahedral arrangement with an oxygen atom of perchlorate occupying the apical position (Cu–O = 1.912(17) Å) and three nitrogen atoms of different bpsb ligands lying in the basal sites. The Cu(I)–N bond distances for the four-coordinated Cu(I) are 2.134(8) Å, which are longer than 2.004(8) Å for the three-coordinated Cu(I). Each bpsb molecule acts as an exo-bidentate ligand. Two nitrogen atoms from different pyrimidinyl rings coordinate to two crystallographically independent Cu(I) atoms in different directions to form a 2-D lamellar structure with crown-like nanocavities. Therefore, the six copper(I) centers (three 3-coordinated and the three 4-coordinated) located at two different planes, alternatively, are linked by six

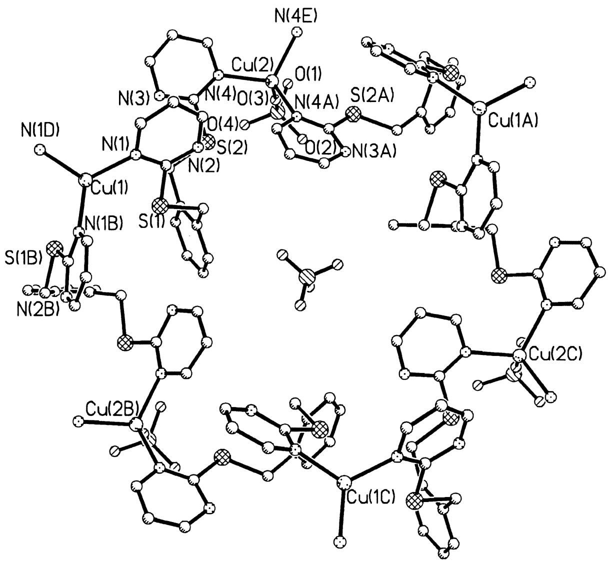


Fig. 1. View of the hexanuclear coppers nanocavity in **1**.

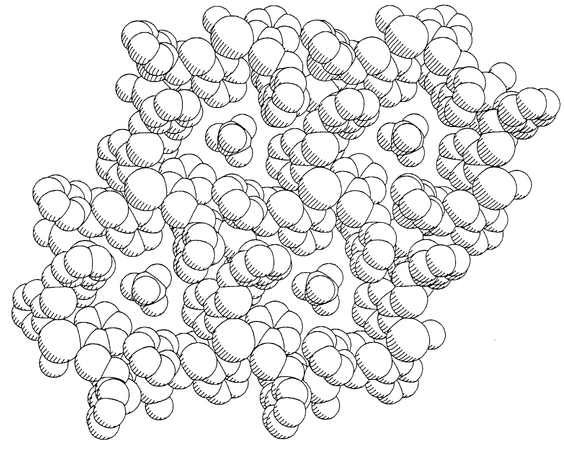


Fig. 2. Space-filling of the lamellar structure in complex **1**, along *ab* plane, coordinated perchlorates were omitted for clarity.

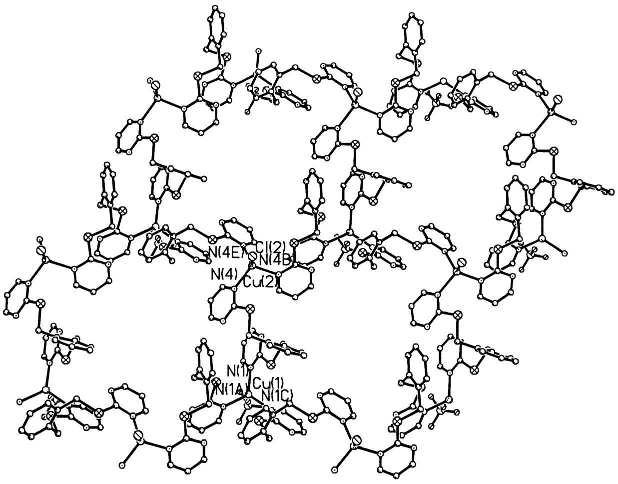


Fig. 3. View of the lamellar structure in **2**, along *ab* plane.

flexible bpsb ligands forming a crown-like $[Cu_6(bpsb)_6]$ unit with dimensions of 20.84×14.45 Å, in which uncoordinated perchlorate is partially encapsulated. The crown-like $[Cu_6(bpsb)_6]$ units generate a 2-D lamellar structure by a symmetry operation, which are quite different from the usual hexanuclear copper(I) units[20–22] and similar to the silver(I) coordination polymer.[16a]

Description of Complex 2: A crystallographic analysis revealed that complexes **2** and **1** have similar structures. Namely, they have an analogous coordination geometry of Cu(I) atoms and the same crown-like lamellar structure. The molecular structure of complex **2** is shown in Fig. 3. Similar to **1**, Cu(I) atoms have two different coordination fashions. The Cu(1) atom is coordinated by three nitrogen atoms from different, but symmetrically related, bpsb molecules forming an unusual, but precedented, 3-coordinated trigonal geometry.[20] (Cu(1)–N = 1.986(3) Å, N–Cu(1)–N = 119.889(13)°). The Cu(2) atom exhibits a distorted tetrahedral geometry with one Cl^- occupying the apical position (Cu(2)–Cl = 2.292(2) Å) and three nitrogen atoms from different bpsb molecules comprising the equatorial plane (Cu(2)–N = 2.149(4) Å, N–Cu(2)–N = 100.58(13)°). In this complex, bpsb molecules act as interconnecting ligands of Cu(I) atoms with different coordination geometry to form a 2-D lamellar structure with crown-like nanocavities. The dimensions of the nanocavities are similar to those of compound **1** and Ag(I) polymer.[16a]

Description of Complex 3: A crystallographic analysis of complex **3** indicates that it possesses an infinite 1-D polymeric chain which constitutes basic square units of $[Cu_2(bpb)_2Br_2]^{2+}$. The molecular structure is shown in Figs. 4 and 5. Each Cu(II) center acts as a joint of a square ring and is coordinated by one Br^- atom lying in the apical position and four nitrogen atoms from different, but symmetry-equivalent, bpb ligands occupying the basal sites. Thus, the coordination environment around Cu(II) can best be described as a distorted square-pyramidal form of CuN_4Br. The Cu(II)–N(bpb) and Cu(II)–Br^- bond distances fall in the range of 2.043(8)–2.058(8) Å and 2.732(2) Å, respectively. The Cu(II)–Cu(II) separations are of 5.613(3) Å in length. The bond angles of *cis* N–Cu–N(bpb) are close to a value of 90°. Each bpb molecule exhibiting an exo-bidentate coordination mode bridges two Cu(II) centers with two nitrogen atoms from different pyridyl rings to form a square ring with the size of 8.5 × 8.5 Å, which accommodates one dmf molecule; the other solvent molecules are out of the square ring. Such square rings, constituting two bidentate bpb ligands in which two nitrogen atoms from different pyridyl rings coordinate to two Cu(II) centers in different directions and two Cu(II) centers which are shared by two different square units form an infinite 1-D chain.

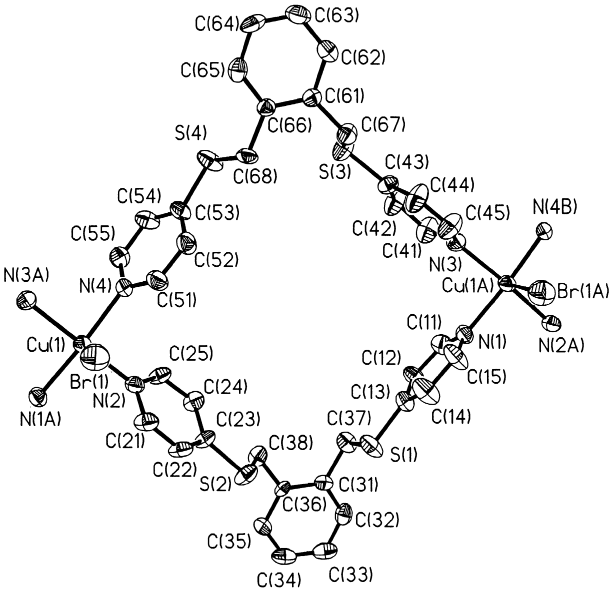


Fig. 4. View of the basic box unit in the polymeric chain of **3** with perchlorates, solvent molecules omitted for clarity.

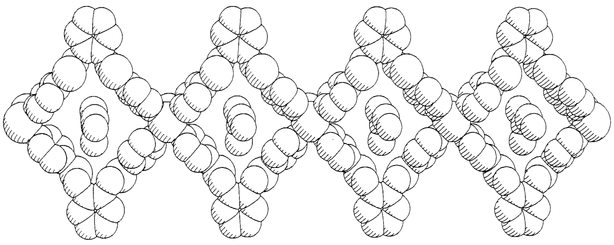


Fig. 5. Space-filling representation of complex **3** with dmf solvent molecules in the cavities.

Conclusion

The self-assembly of two designed non-chelating bridging ligands, bpsb and bpb, with Cu(I) and Cu(II), respectively, in a 1 : 1 metal : ligand ratio yielded two 2-D lamellar polymers containing crown-like nanocavities and a single-stranded infinite 1-D chain polymer containing square rings with solvent molecule guests, respectively. The ligands bpsb and bpb act as exo-bidentate ligands through coordinating to two copper atoms in different directions with two nitrogen atoms from different pyrimidinyl rings or pyridyl rings, respectively. The results of this study illustrate that a spatial effect of coordination atoms, the geometry and rigidity of the ligand, and the coordination form of metal ions play important roles in constructing of supramolecular architecture. This contributes to own ability to predict and control certain structural topologies through the self-assemble of multidentate ligands with suitable metal ions in supramolecular chemistry and coordination chemistry. Further research concerning self-assembly bpsb and bpb ligands with other bridging or terminal ligating moieties and suitable metal ions is now being explored in our laboratory.

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