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Review

Crystal engineering of Cu-containing metal–organic coordination polymers under hydrothermal conditions

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Contents

Abstract

This account reviews Cu-containing polymeric coordination compounds synthesized under hydrothermal conditions. The rapid growth of hydrothermal synthesis of new coordination polymers is largely accredited to the developments in crystal engineering via functional network design. Both projected and unexpected framework structures have been obtained through oxidation, reduction, substitution, chemical rearrangement and regular hydrothermal reactions. New methods and reaction pathways play crucial roles in the formation of novel structures and topology under hydrothermal conditions. This review covers copper iodine-containing metal–organic coordination polymers, copper pyridylcarboxylate-containing metal–organic coordination polymers, and metastable coordination polymers with active copper open metal (OM) sites.

Keywords: Crystal engineering; Inclusion compounds; Mixed valent copper iodine-containing coordination polymers; Hydrothermal synthesis; Oxidation and reduction reactions; Chemical rearrangement reactions

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1. Introduction

In the last decade, rapid developments in the crystal engineering of metal–organic coordination polymers have produced many novel materials with various structural features and properties [1–8]. The synthetic strategies used to prepare these coordination polymers were mostly conventional solution methods in organic solvents. Synthesis under hydrothermal reaction conditions was not investigated as extensively, despite being very complicated. However, hydrothermal conditions were responsible for the formation of crystalline minerals in nature and crystal growth for the

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preparation of many important solids such as zeolites, electronically conducting solids, ceramics and magnetic materials [9]. Hydrothermal synthesis under pressure and at low temperatures (100–200 °C) proved to be an effective method. A variety of synthetic pathways were tested and completed successfully including oxidation, reduction and substitution reactions designed for preparing metal–organic coordination polymers [10]. These new methods and reaction pathways played crucial roles in the formation of new crystal structures and topology under hydrothermal conditions.

The diversity in the structures and topology of new metal–organic coordination polymers was attributed to the selection of metal centers and organic building blocks as well as reaction pathways. Metal centers play a key role in the molecular recognition process in extended materials and biological systems. The considerable amount of interest in copper atoms was mainly due to their attractive magnetic properties [11], mixed-valance oxidation-state pairs, photoluminescence [12], novel structural features [1–8] and biological relevance involving the binuclear "Cu_A" site in cytochrome oxidases and related model compounds [13]. It had been shown that copper ions and pyridylcarboxylate ligands form versatile metal–organic frameworks. Herein, copper atoms displayed mixed octahedral and square pyramidal geometry [14a], square pyramidal coordination two-dimensional (2D) net in an interpenetrating 2D/three-dimensional (3D) structure [14b], a square planar motif [14c], and trigonal bipyramidal centers in a mixed-bonding 3D network [14d]. Copper oxidation states included +1 [10c], +2 [15a,15b], mixed-valence states [10a,11,15c,15d], and/or Cu–Cu bonds [10a,11,12,15d]. These Cu-containing polymeric coordination compounds (primarily synthesized in our laboratory) included (1) copper iodine-containing metal–organic coordination polymers, (2) copper pyridylcarboxylate-containing metal–organic coordination polymers, and (3) metastable coordination polymers with active copper open metal (OM) sites.

2. Iodine copper-containing coordination polymers

Iodine-containing compounds have been an attractive research area in metallophthalocyanines, diphthalocyanines and organic compounds due to their high conductivity and oxidizing properties [16]. However, iodine has not been used in the synthesis of metal–organic coordination polymers until recently [10,17]. The interest in iodine-containing metal–organic coordination polymer research has been three-fold: the impact of donor–acceptor charge transfer interactions in extended coordination frameworks [10c,17a], the metallic appearance of the resulting solids which suggests a potential for conducting framework polymers (single crystals or through intercalation) [10a,10b,17b], and the inclusion effects of solid-state iodine on new open-framework coordination polymers [10b,10c].

2.1. Iodine inclusion coordination polymers

Among the reported iodine inclusion coordination polymers, the inclusion of polyiodide in the large channel framework structure of $[Cu_2(IN)_3]$ (IN: isonicotinato) displayed a remarkable nano-size-channel framework with fused-polyiodide rings (Figs. 1 and 2): $\{[Cu_2(IN)_3]I_5^- \cdot \frac{2}{3}I_2 \cdot H_2O\}$ (**1**) [10b]. This was the first polyiodide inclusion metal–organic coordination polymer synthesized in this field.

$[Cu_2(IN)_3]I_5^- \cdot \frac{2}{3}I_2 \cdot H_2O$ (**1**) consisted of a three-dimensional (3D) large channel metal–organic framework with polyiodide rings formed from fused polyiodide clusters. The polyiodide has an I_5^- unit that is constructed by one I^- and two I_2 units. The metal–organic framework was comprised of two independent Cu atoms and three isonicotinato ligands. Copper atom 1 had a square pyramidal geometry coordinated by two pyridyl groups of two IN units and three oxygen atoms from the three bridging carboxylate groups of the IN units. Copper atom 2 was in a distorted square planar site surrounded by a pyridyl group of one IN ligand and three oxygen atoms from three bridging carboxylate groups of IN units. The two independent copper atoms were bridged by three tridenate isonicotinato ligands bidentate using carboxylate groups. This mixed square planar and square pyramidal binuclear unit, $[Cu_2(IN)_3]$, propagated to form an unusual nano-size channel metal–organic framework polymer (Fig. 2). The $[Cu_2(IN)_3]_6$ fragment displayed a spiral galaxy-shaped open-channel structure along the (1 1 1) direction (Fig. 2). This channel had a diameter of about 1.15 nm, comparable to that of carbon nano hollow tubes (1.2 ± 0.1 nm) [18]. The association of $[Cu_2(IN)_3]_6$ fragments formed triangular and rhombohedral units. These large channel units in the structure extended in three directions.

Another polyiodide inclusion complex obtained was an unexpected nicotinate zwitterion with two-dimensional (2D) herringbone networks sandwiched with polyiodide species [19].

The compound $[Cu(IN)_2]I_2$ (**2**) [14c] also utilized isonicotinato ligands in an open-framework with a 2D structure. This compound consisted of nearly perfect square planar copper centers coordinated by two pyridyl groups on two IN units and two bidenate carboxylate groups on the isonicotinato-ligand monodentate using one of the oxygen atoms. This square planar copper unit connected adjacent copper atoms to form square-grids. The square-grid propagated to form an unusual eclipsed 2D coordination polymer with an open-channel structure. Iodine molecules were included in the open-channels of the 2D structure (Fig. 3). The copper–copper separations in the square-grid channel were 8.849 Å × 8.771 Å. The small separation between adjacent 2D layers (3.629 Å) indicated weak aryl–aryl interactions. Each iodine molecule had weak electrostatic attractions to oxygen O(2) atoms in the neighboring layers (2.947 Å). The distance between adjacent iodine molecules was 5.795 Å

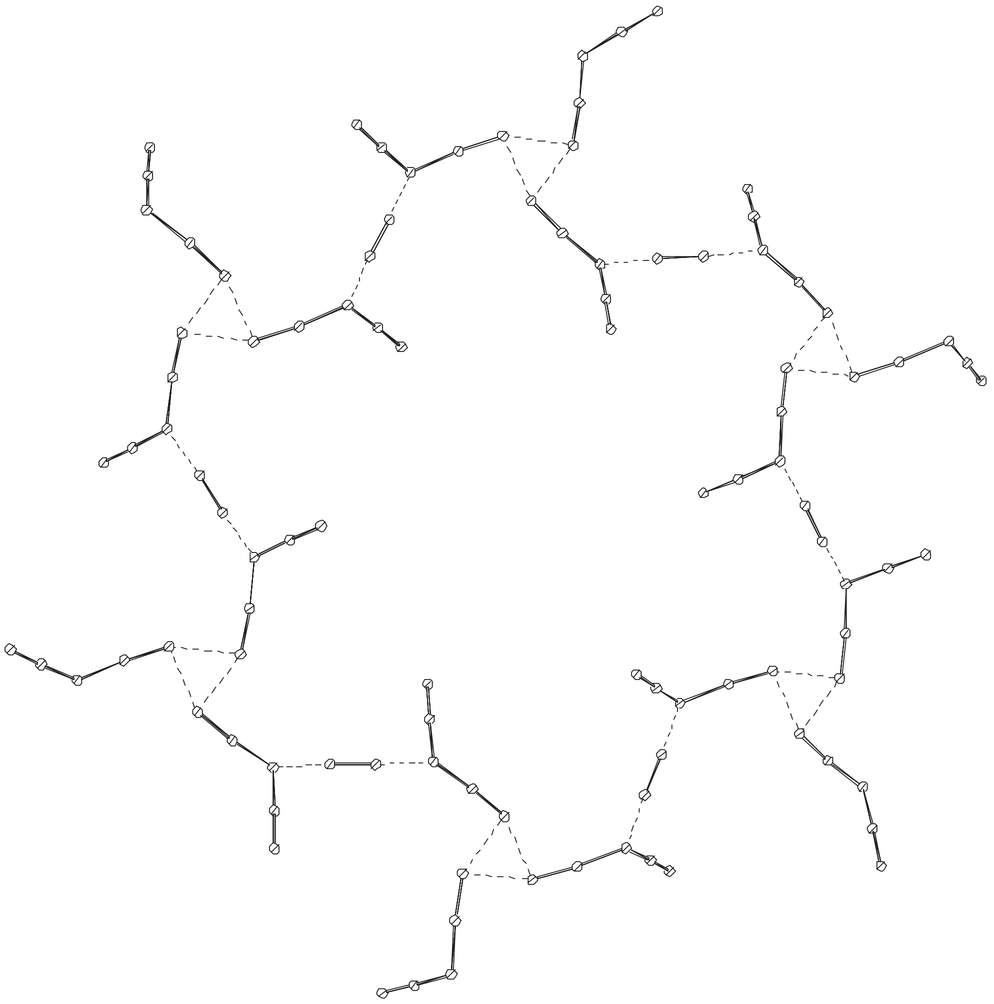

Fig. 1. View of a polyiodide ring in complex **1**.

along each open-channel. Complex **2** is clearly stabilized by both aryl–aryl and iodine–oxygen weak interactions.

The iodine molecules in **2** were removed by evacuating the crystals, causing a color change from black-red to transparent blue. The blue crystals were then subjected to X-ray powder diffraction analysis against the simulation of the iodine-removed single crystal structure of **2**. The two X-ray patterns match very well except for the appearance of a large peak at lower angle, confirms that the composition of the blue crystals were [Cu(IN)$_2$] (**3**). This was also confirmed by a comparison of the single crystal structure simulation of **2** with the iodine-removed single crystal structure's simulated powder pattern. The highest peak at the lower angle was clearly caused by the disappearance of iodine molecules from the structure.

Note that [Cu(IN)$_2$] (**3**), which resulted from the as-synthesized **2** after the removal of iodine, had an eclipsed open-channel 2D structure (Fig. 4) that was only stabilized by weak aryl–aryl interactions between the adjacent layers, after the removal of iodine–oxygen interactions. Amazingly, this eclipsed layer open-channel 2D structure was stable up to 300 °C. Although many stable 3D open-framework and staggered 2D polymers have been characterized, the eclipsed open-channel 2D layers with removable solid-state iodine had never been previously observed. The formation of a stable eclipsed 2D layered open-channel structure with removable iodine molecules revealed interesting interactions between the solid-state iodine and open-framework polymers. Further research to uncover the relationships between solid-state iodine (iodine molecule or polyiodide species) and open-framework polymers now appeared attractive.

[CuI(C$_5$H$_3$NI$_2$) $\cdot$ $\frac{1}{2}$I$_2$] (**4**) is another iodine inclusion complex [10c] in which active iodine atoms replaced carboxylate groups in the structure. The copper atom displayed a distorted tetrahedral geometry. Each I(1) atom bridged to three copper atoms. The copper atom and I(1) atom bridge extended along the a axis to form a zigzag ladder network (Fig. 5). The I(1) atom on the ladder was connected to an iodine molecule (I(4)–I(4), 2.717(1) Å) by a strong long-range interaction (I(1) $\cdots$ I(4), 3.485 Å) that was shorter than long-range interactions found in (Hpy)$_2$I$_3$I$_7$ (3.545 Å) [20] but longer than those recently reported by Pennington group

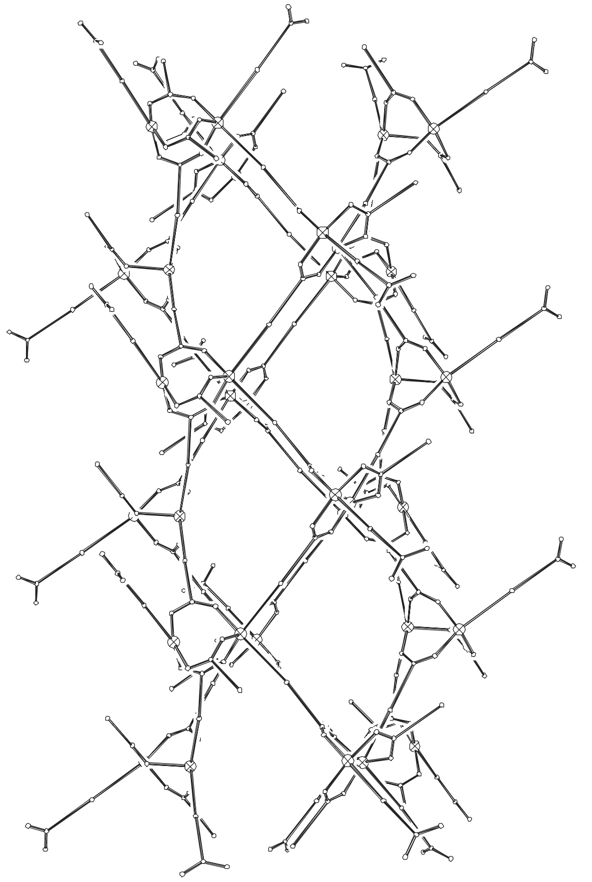

Fig. 2. View of the open-channel network in complex **1**. Isonicotinato units are represented by lines for clarity.

(3.367(1)–3.436(1) Å) [17a]. This extended ladder network with iodine molecular-handles on both sides formed 2D layers. The layers were in turn connected by mutually significant I · · · I contacts (I(1) · · · I(3), 3.697 Å), which were at the shorter end of the reported range (3.643(3)–3.824(3) Å) [21]. The result of these long-range I · · · I interactions was a 3D network structure. The inclusion of iodine molecules in this metal–organic network indicated long-range interactions between inclusion molecules and network structures necessary for constructing metal–organic polymers.

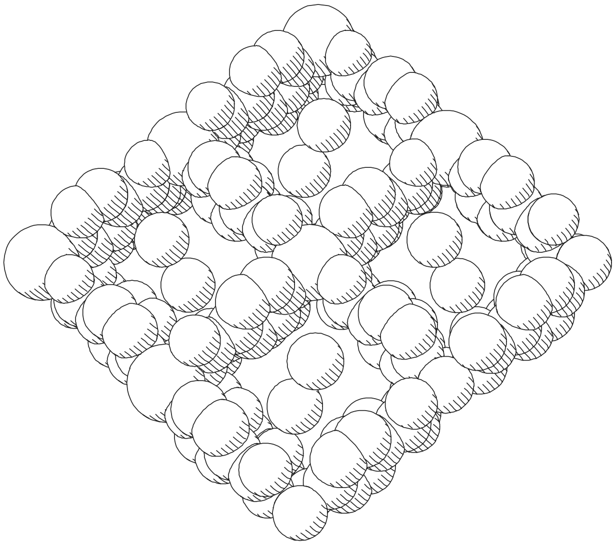

Fig. 3. A space-filling view down to [1 0 0] direction of a section of the eclipsed 2D layers including I_2 molecules in complex **2**.

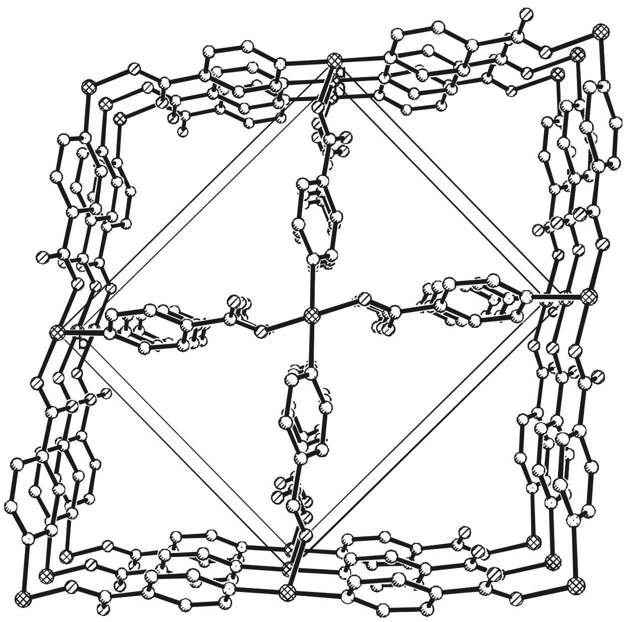

Fig. 4. View of a section of the eclipsed 2D open-channel with unit cell outline in complex **3**.

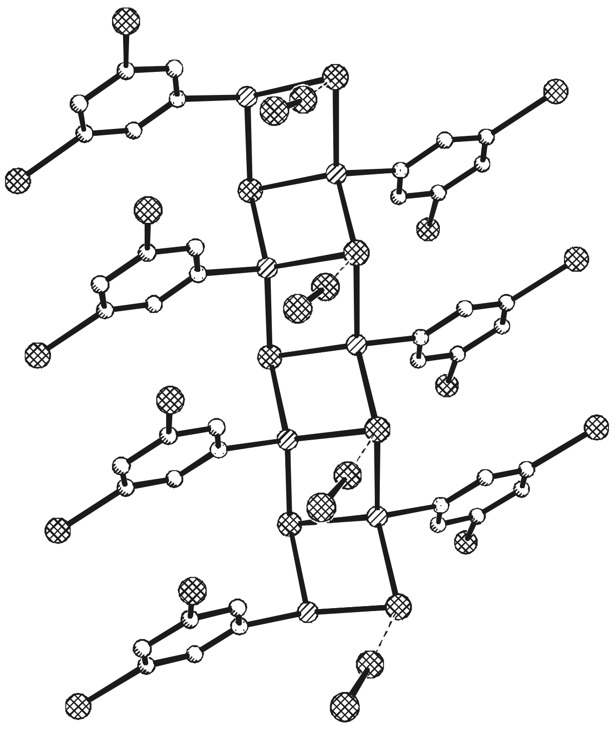

Fig. 5. The ladder network in complex **4**.

2.2. Synthesis of mixed-valent Cu(I)–Cu(II) iodine coordination polymers via oxidation reaction route

Due to the dominance of reduction mechanisms in hydrothermal conditions, the synthesis of coordination polymers through oxidation reaction mechanisms was largely absent. $[(Cu_2I)(IN)_2]$ (IN: isonicotinato) (**5**), with a new mixed-valence $(Cu_2I)^{2+}$ unit, was the first deliberately prepared coordination polymer produced from the oxidation of CuI under hydrothermal conditions [10a].

The $[(Cu_2I)(IN)_2]$ (**5**) complex was initially obtained by reacting CuI with isonicotinic acid in the mole ratio of 2:1, mixed with O_2-treated water under hydrothermal conditions at 140 °C for 3 days. The subsequent reactions successfully employed iodine as the oxidizer. Compound **5** consisted of four crystallographically distinct Cu atoms. The four independent copper atoms were paired: Cu(1)–Cu(2), 2.4496(8) Å; Cu(3)–Cu(4), 2.4371(7) Å. These distances were comparable to Cu–Cu distances found in previous structures [11,22], and shorter than those in metallic copper (2.56 Å) [23]. One of the copper pairs was 90° from the other pair in orientation (Fig. 6). An independent iodine atom bridged each pair of copper atoms. Each Cu atom was also coordinated by a nitrogen atom from an IN and two oxygen atoms from each of the other two IN units (Fig. 6). In other words, each Cu pair bridged by iodine was coordinated by four oxygen atoms from two trans-IN units and two nitrogen atoms from the other two IN ligands. This arrangement produced a unique $(Cu_2I)^{2+}$ unit with mixed Cu(I)–Cu(II) formulation (Fig. 6). These linkages propagated into a 2D open-frame network (Fig. 7). Note that all bridging iodine atoms were on the same side of the layered open-framework (Fig. 7). Adjacent iodine atoms have separations of 10.057 Å × 10.074 Å × 9.991 Å × 9.983 Å. The large cavities do not have any inclusion guest species, however, because they were occupied by iodine atoms of the adjacent layer through face-to-face mutual insertion without direct contact. This arrangement resulted in weak back-to-back interactions between adjacent double layers.

The face-to-face mutual insertion structure was also observed in [(IN)ZnI(INH)] (INH: protonated isonicotinato ligand) (**6**) [24], where the tetrahedral zinc mutual-face-insertion double-layer framework structure was built via both covalent and double-hydrogen bonding interactions (Fig. 8).

Iodine demonstrated to be a successful oxidizer in the preparation of complex **1**, $\{[Cu_2(IN)_3]I_5{}^- \cdot \frac{2}{3}I_2 \cdot H_2O\}$ [10b]. Here, I_2 acted as an oxidizer as well as iodine source. The half-cell potential [25] of iodine in acidic aqueous solution is +0.615 V, and copper is +0.153 V:

$$I_2\,(aq) + 2e \rightleftharpoons 2I^-$$

$$Cu^{2+} + e \rightleftharpoons Cu^+$$

Cu(I) may also undergo disproportionation (auto-oxidation reaction):

$$Cu^{2+}\underline{0.153\,V}\,Cu^{+}\underline{0.521\,V}\,Cu$$

Once the reaction initiated, the formation of the $(Cu_2(IN)_3)^+$ unit along with polyiodide shifted the equilibrium of the following reaction to the right side:

$$IN + CuI + I_2 \rightarrow [(Cu_2(IN)_3](I_5{}^-)$$

Another Cu(I)/Cu(II) mixed-valent coordination polymer $[(Cu_2I)(IN)_2]$ (**7**) [26] was produced via oxidation by raising the reaction temperature to 170 °C, based on the preparation of complex **5**. While the formula $[(Cu_2I)(IN)_2]$ of both

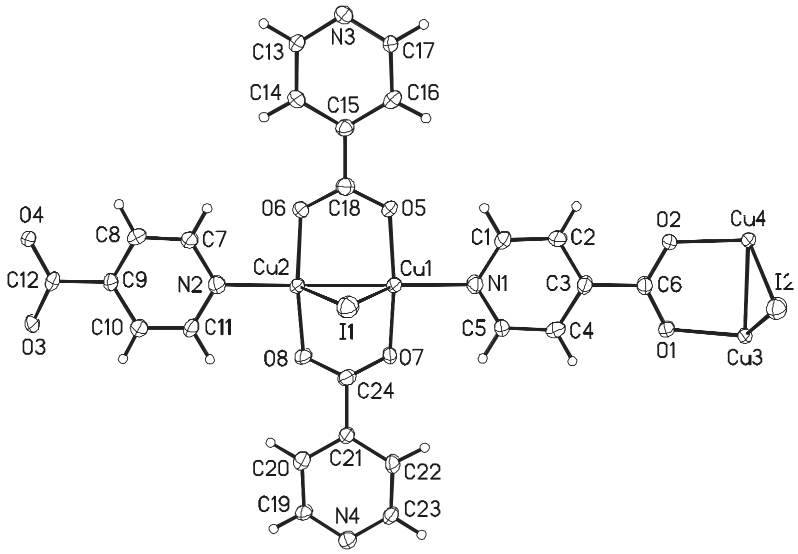

Fig. 6. View of the asymmetric unit showing the atom numbering scheme in complex **5**. Thermal ellipsoids are 60% equiprobability envelopes, with hydrogen as spheres of arbitrary diameter.

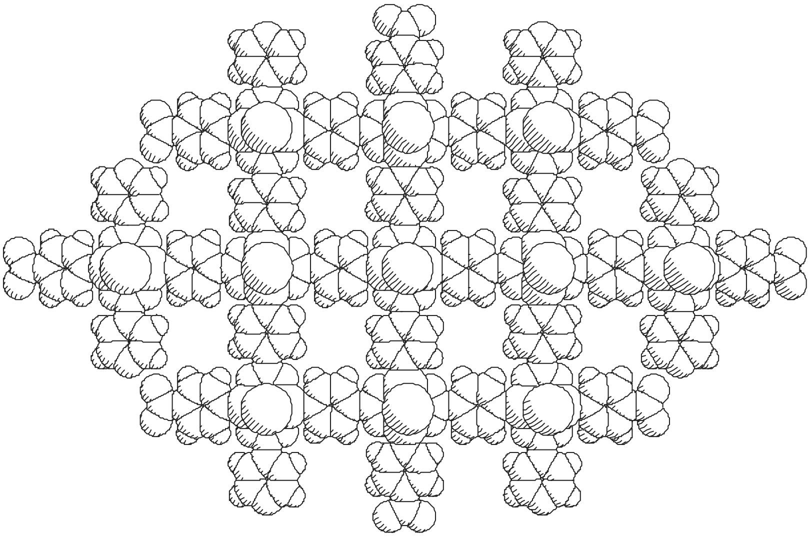

Fig. 7. Space-filling view of the open-framework of a single layer with iodine atoms shown as large spheres in complex **5**.

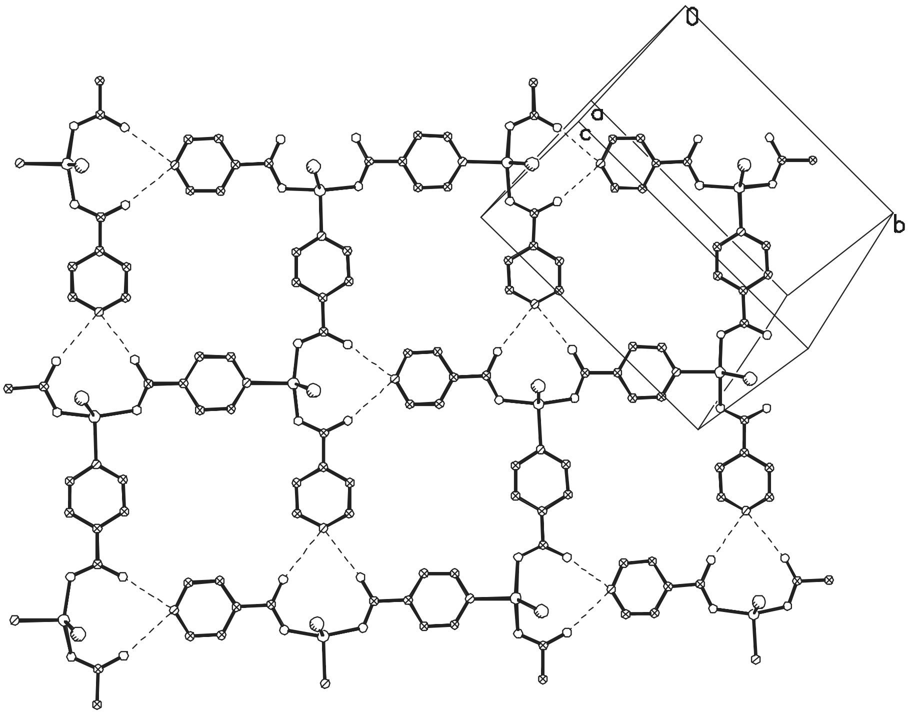

Fig. 8. View of the 2D open-framework in complex **6**.

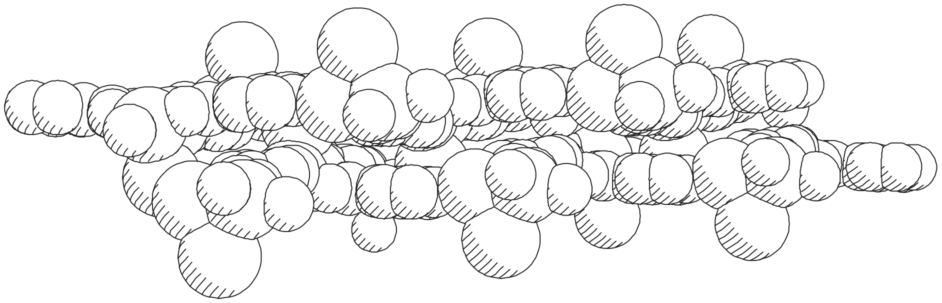

Fig. 9. The interdigitation packing structure in complex **7**. The large balls sticking out of the layers are iodine atoms.

complexes were identical, the structure of complex **7** differed from that of compound **5**. Complex **7** had an interdigitated packing structure with the same $(Cu_2I)^{2+}$ unit, mixed Cu(I)–Cu(II) formulation and Cu–Cu bonds in the structure (Fig. 9).

Recent examples of Cu(I)–Cu(II) mixed-valent complexes synthesized under hydrothermal conditions showed a reduction reaction route from Cu(II) to Cu(I) [2b,15c].

2.3. *Synthesis of Cu(I) iodine coordination polymers via reduction reaction route*

It was accepted that Cu(II) ions could be reduced to Cu(I) by 4,4′-bipyridine (BPY) or 2,2′-dipyridylamine (DPA) under hydrothermal conditions, as demonstrated by two early examples [5b]. Fascinating structures and reaction chemistry could be achieved through the reduction of copper valence states. Hydrothermal processes were considered necessary for these reductions. Complex **4** $[CuI(C_5H_3NI_2)\cdot\frac{1}{2}I_2]$ was produced via a simultaneous reduction of copper(II) to copper(I), and substitution of carboxylato groups by iodo-nucleophiles in a self-assembly chemical process under hydrothermal conditions.

Note the interesting reaction chemistry. This complex was the first coordination polymer constructed through this process. Cu^{2+} ions were likely reduced to Cu^{+} by pyridinedicarboxylate (PDC), while the carboxylate groups on PDC were replaced by iodine nucleophiles:

$$2Cu^{2+} + 2C_5H_3N(COOH)_2 + 5I_2 \\ \rightarrow 2\left[CuI(C_5H_3NI_2)\cdot\tfrac{1}{2}I_2\right] + 4CO_2 + 2I^- + 4H^+$$

Although the precise mechanisms behind redox reactions under hydrothermal conditions were unknown, reactions were conducted in the absence of copper ions in this case under the same reaction conditions as complex **4**. While the reaction of PDC with iodine in molar ratio of 1:1 did not yield crystals of the expected product from 3-day reactions, a 7-day reaction under the same conditions resulted in uniform colorless crystals of a single iodine-substituted complex: IC_5H_3NCOOH. The balanced reaction can be written:

$$C_5H_3N(COOH)_2 + I_2 \rightarrow IC_5H_3NCOOH + CO_2 + HI$$

where iodine was reduced to iodide by pyridinecarboxylate. This result implied that copper ions were necessary for the simultaneous double-substitution, as well as the formation of complex **4** under the given conditions. The catalytic properties of copper ions in redox and substitution reactions were very attractive. This was also the first example of carboxylates being responsible for the reduction of Cu(II) under hydrothermal conditions.

3. Pyridylcarboxylate copper-containing coordination polymers

The functions of metal–organic coordination polymers depended on the metal centers and organic building blocks, as well as their framework structures. A slight variation in the structure may have changed functional features. For example, the nicotinate ligand, a well-known building unit, yielded acentric coordination frameworks such as $[Zn(NA)_2]$ (NA = nicotinate) [27]. Crystallized in a chiral space group, it displayed interesting optical properties. Zinc atoms occupied highly distorted octahedral sites [27]. Another structure with the same formula ($[Zn(NA)_2]$) consisted of distorted tetrahedral zinc metal centers which crystallized in a rare chiral space group Fdd2 [28]. The two $[Zn(NA)_2]$ complexes were only distinguished by the coordination bonding modes of the nicotinate ligands, which defined different coordination geometries.

It had been shown that pyridylcarboxylate ligands tended to bind metal centers with both pyridyl and carboxylate groups to form extended networks, wherein carboxylate groups balance the metal charges. The following sections illustrate the structures and chemistry involved with copper atoms and pyridylcarboxylates under hydrothermal conditions.

3.1. *Open-framework polymers built from copper metal centers and pyridylcarboxylate ligands*

While the utilization of mononuclear copper metal centers and mixed valent copper pairs for building coordination polymers has been documented, the binuclear copper(II) pairs with square pyramidal geometry construction motifs were still particularly attractive. One such example was $[Cu(NA)_2]$ (**8**). The structure of complex **8** consisted of distorted square pyramidal copper centers coordinated by two independent nicotinato ligands (Fig. 10). One nicotinato ligand was tridentate while the other was bidentate to copper metal centers. Every two copper atoms were bridged by two carboxylato groups of the tridentate nicotinato ligands through O(2) and O(4) atoms to form a binuclear copper(II) unit: $Cu_2(NA)_4$. The O(4) atom was at the apical site while two pyridyl groups and the other two oxygen atoms were at the equatorial positions (Fig. 10). The formation of the binuclear units created eight-member rings (Fig. 10), which were linked by nicotinato ligands to form large 24-member rings (Fig. 11). There were four eight-member rings on each 24-member ring, such that two eight-member rings at *trans*-position to each other were also perpendicular to the other two eight-member rings. There were four 24-member rings connected to each eight-member ring via covalent bonding with the binuclear copper centers, such that two 24-member rings were perpendicular to the other two 24-member rings (Fig. 12). The propagation of 24-member rings and eight-member rings extended in three directions to form a 3D framework structure. The isostructural cadmium

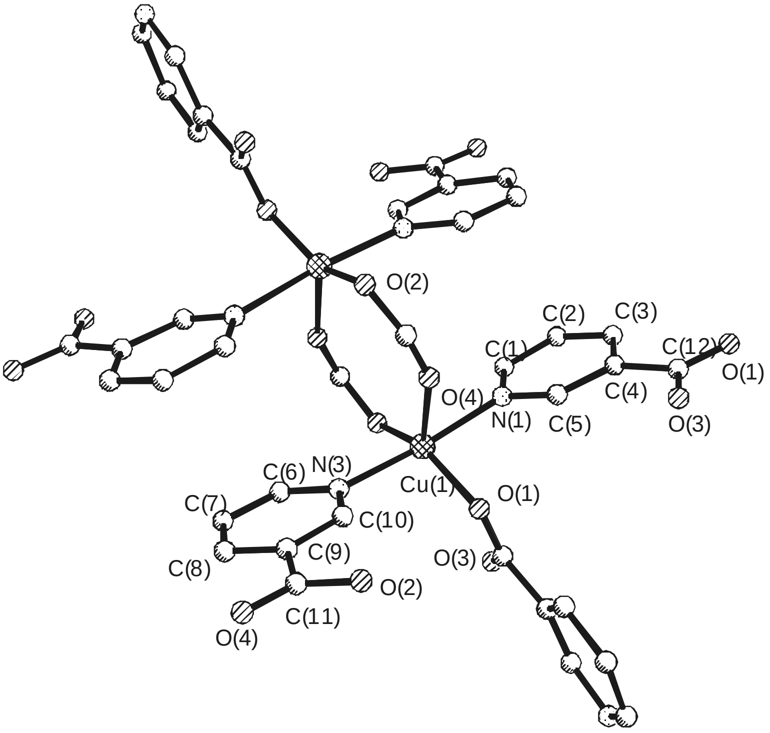

Fig. 10. View of the binuclear copper(II) square pyramidal coordination with atom numbering scheme in complex **8**.

analog of this complex, a rare example of square pyramidal cadmium ($Cd(NA)_2$), had also been prepared [29].

The first one-dimensional (1D) double-helical chain (Fig. 13) coordination polymer, $[(H_2O)Cu(BPDC)]$ (BPDC: 2,2′-biphenyldicarboxylate) (**9**), based upon the binuclear square pyramidal copper(II)-pair motifs, was recently synthesized under hydrothermal conditions and characterized by single crystal X-ray diffraction technique [30].

Up to now, only a few porous metal–organic polymers were reported to have cell volume changes, ranging from ∼2.5% [31], ∼3% [32], to 5% [33] upon inclusion, respectively. Compound $\{[Cu(IN)_2]\cdot 2H_2O\}$ (**10**) [15b] represented a novel material built from copper centers and pyridylcarboxylate ligands with over 8% volume expansion upon inclusion, and that is thermally stable up to 300 °C. The structure was so stable that the expanded crystal structures were

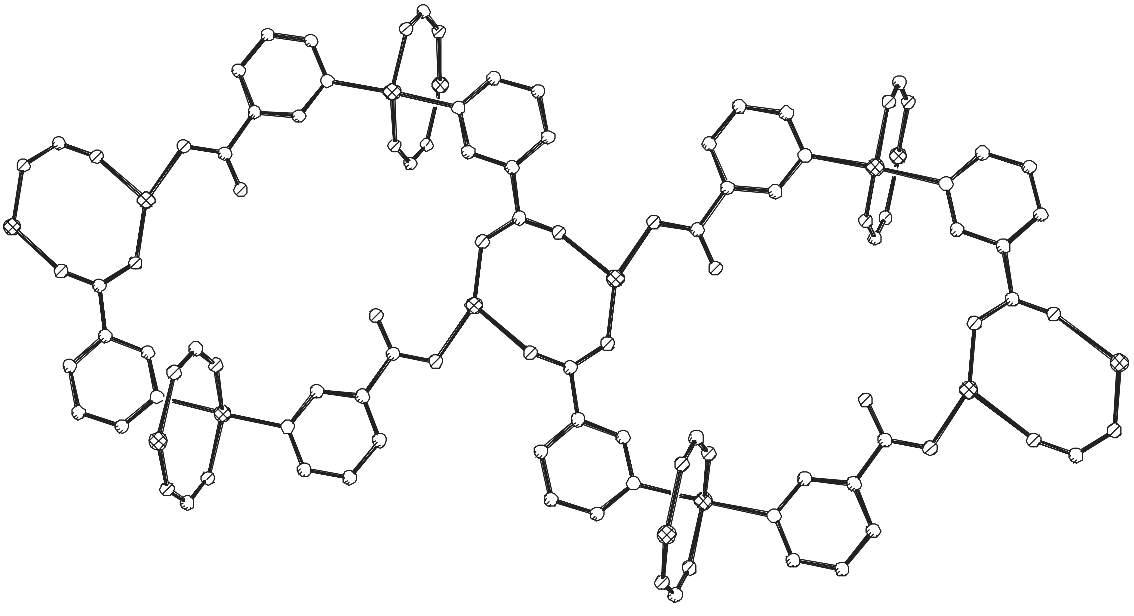

Fig. 11. View of the eight-member rings and 24-member rings in complex **8**.

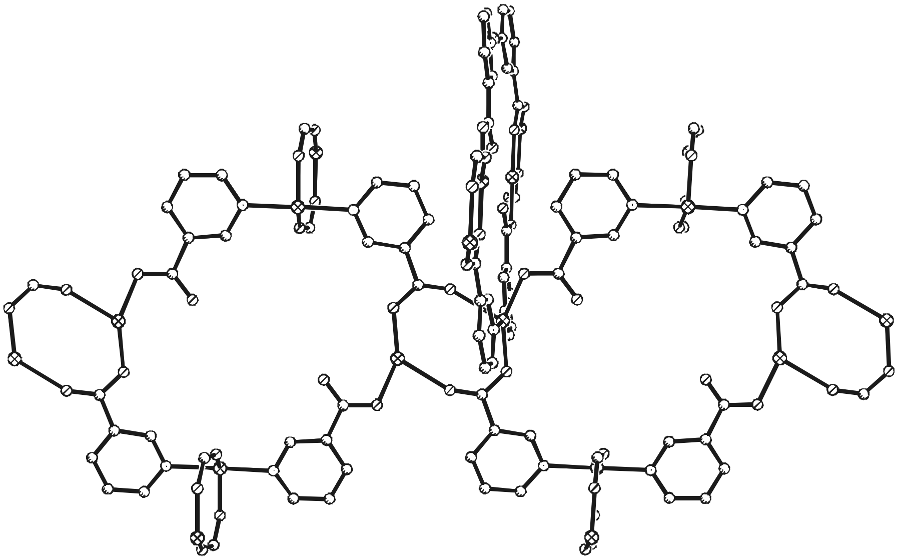

Fig. 12. View of the perpendicular 24-member rings in complex **8**. One parallel 24-member ring is omitted for clarity.

reversible upon removal and binding of guests. The expanded structures were characterized by single crystal X-ray diffraction technique. Due to the presence of functional carboxylate groups in the framework, only the hydrophilic molecules entered into the channels when both alkane and alcohol molecules were present.

Compound $\{[Cu(IN)_2]\cdot 2H_2O\}$ (**10**) had a single-net three-dimensional spiral open-framework with square pyramidal Cu(II) metal centers and IN ligands. The structure of **10** consisted of square pyramidal copper atoms coordinated by two pyridyl groups, and two carboxylate groups of four IN units in a monodentate fashion at the equatorial positions. Another IN moiety occupied the remaining apical site of the square pyramidal geometry using carboxylate monodentate coordination. The square pyramidal copper atoms were linked by five two-connected tridentate IN units such that a novel five-connected 3D network was formed, with spiral open-framework channels running along the a axis (Fig. 14). The channels in the spiral structure of **10** had Cu–Cu separations of 0.8918 × 0.8910 × 0.7903 × 0.8918 nm and were occupied by water molecules. The open-framework was highly stable after the removal of water molecules, such that the open-channel structure of $\{[Cu(IN)_2]$ (**11**) was characterized by single-crystal X-ray diffraction [15b]. By soaking the crystals of **11** in methanol, mixed ethanol–pentane, mixed ethanol-1-propanol and 1-propanol respectively, methanol- and 1-propanol-inclusion complexes were successfully formed. While in the mixed-solvents, the adsorption processes appeared selective, with only ethanol molecules being included in the structure. These three new inclusion polymers were characterized by single crystal X-ray diffraction technique [15b]: $\{[Cu(IN)_2]CH_3OH\}$ (**12**), $\{[Cu(IN)_2]CH_3CH_2OH\}$ (**13**), and $\{[Cu(IN)_2]\cdot \frac{3}{4}CH_3(CH_2)_2OH\}$ (**14**). Surprisingly, these inclusion polymers revealed that the spiral open-framework was not only highly stable in its original dimensions and capable of selective adsorption, but also expandable. The symmetry of the original spiral open-framework structure was maintained in the expanded structures. The volume of the unit cells of **10–14** ranged from 1326.7(2) to 1434.5(2) Å^3. The beta angles changed from 96.920(1)° to 101.559(1)°. The expandability along the spiral open-channel direction was comparable to a tension spring. Note that in the mixtures of alkane and alcohol, only hydrophilic alcohol molecules were found in the channels. Alkane molecules are hydrophobic and could not enter into the structure, even when crystals of **11** were placed in a pentane solution for 48 h. Aromatic molecules were kept from entering into the channels. In the case of mixed ethanol-1-propanol, ethanol molecules took positions in the channels, indicating that the adsorption property of **11** is size-selective.

3.2. Chemical rearrangement reactions of pyridylcarboxylates

Chemical rearrangement reactions of pyridylcarboxylate under hydrothermal conditions showed unique aspects in the synthesis of coordination polymers.

$\{[Cu_2(IN)_4\cdot 3H_2O][Cu_2(IN)_4\cdot 2H_2O]\}\cdot 3H_2O$ (**15**) had an interpenetrating structure with two covalently-bonded open-frameworks with different dimensionality formed from a chemical rearrangement under hydrothermal conditions [14b].

The reaction of $Cu(NO_3)_2\cdot 2.5H_2O$ with nicotinic acid and *trans*-1,2-bis(4-pyridyl)ethylene (BPEn) in the mole ratio of 1:1:1 at 140 °C for 3 days produced dark blue crystals of **15**. The structure of complex **15** consisted of a covalently-bonded three-dimensional open-channel-network and a covalently-bonded two-dimensional open-framework, mutually interpenetrating. The 3D network was comprised

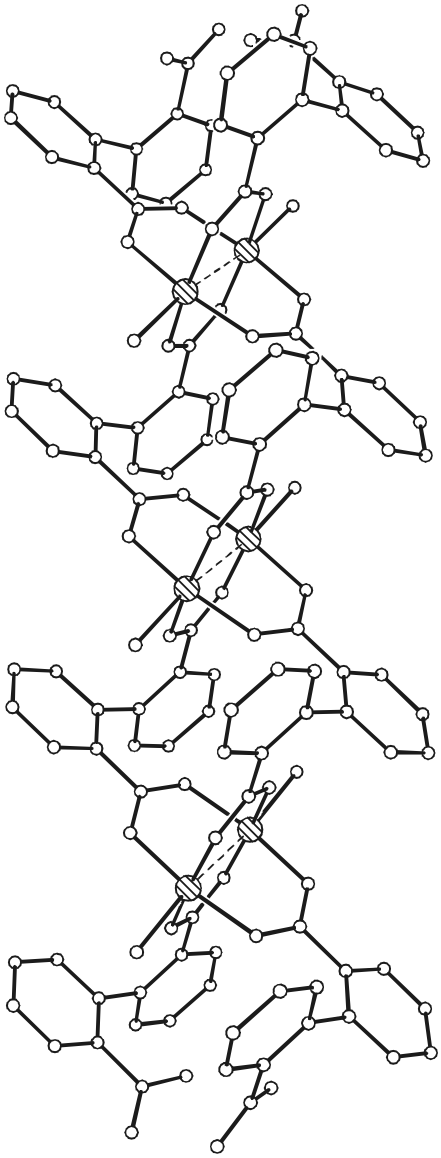

Fig. 13. View of the double-helical chain in complex **9**.

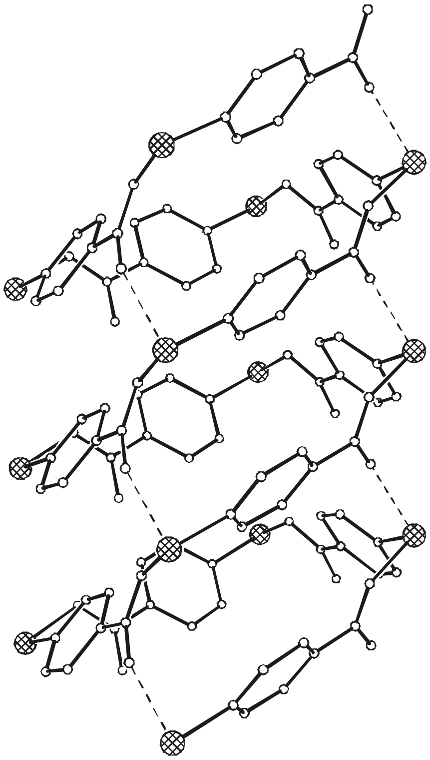

Fig. 14. Side view of the spiral framework in complex 10, with axial Cu–O bonds shown as dashed lines.

of three crystallographically distinct copper atoms. Copper atom 1 was in the square pyramidal position coordinated by two pyridyl groups from two IN units and two carboxylate groups from the other two IN units in a monodentate fashion. A water molecule occupied the remaining site. Copper atoms 2 and 3 were in octahedral sites surrounded by two water molecules occupied the axial positions, two pyridyls and two carboxylates from four IN units occupied the equatorial positions. The mixed square pyramidal and octahedral copper centers were linked by four two-connected tridentate IN units into a single-net 3D open-channel network. The large rectangle in the open-channel network consisted of six copper and six IN units (Fig. 15). Four copper atoms at each corner of the rectangle were separated by 17.776 Å × 8.928 Å. Large rectangular channels in the 3D network extended in two directions, and were perpendicular to each other (Fig. 15). The topology of this 3D network resembled a single net of tetragonal $CdSO_4$ type, as suggested by O'Keeffe and Hyde [34]. The 2D open-framework consisted of two independent copper atoms. Both copper atoms

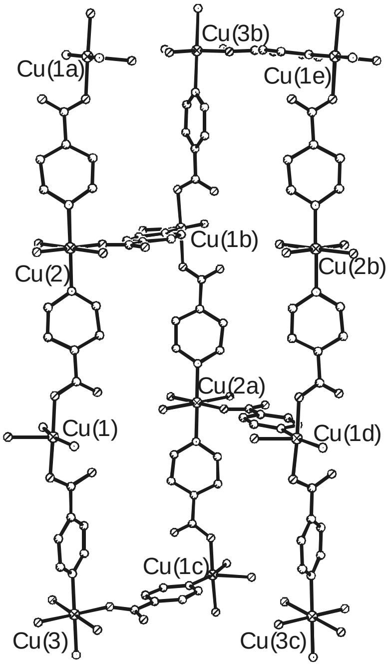

Fig. 15. View of the rectangular open framework in the 3D structure with copper atoms labeled and shown complete coordination in complex **15**.

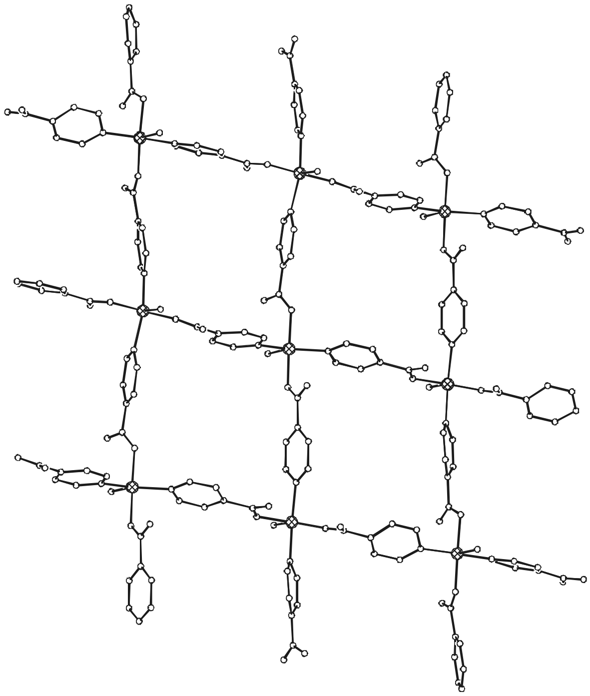

Fig. 16. View of a representative section of the 2D lattice in complex **15**. Note that all Cu atoms have square pyramidal coordination.

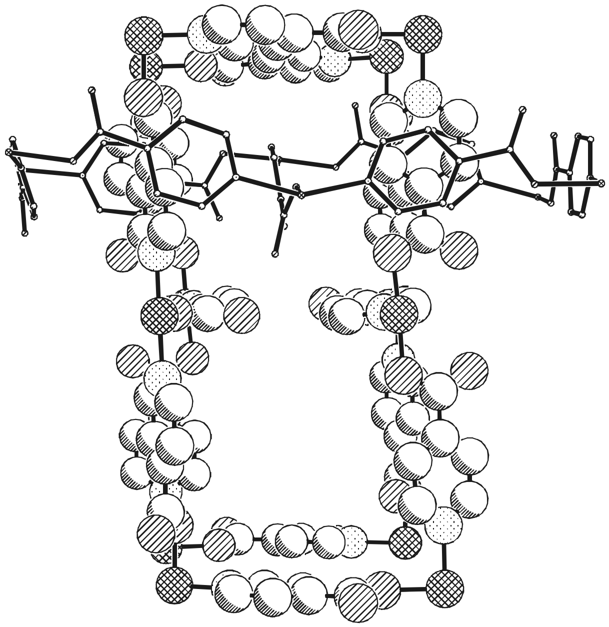

Fig. 17. Interlocked units in the interpenetrating structure of complex **15**. Only two of the 2D square grids are shown for clarity.

4 and 5 were in square pyramidal positions, and each copper atom was coordinated by two carboxylate groups from two IN units and two pyridyl groups from the other two IN units in a monodentate fashion. A water molecule occupied the remaining apical site. The square pyramidal copper atoms were linked into a two-dimensional square grid network by four two-connected tridentate IN units (Fig. 16). The Cu–Cu lengths in a square grid were 8.871 Å × 8.862 Å. The 3D and 2D open-frameworks interpenetrated to form an unprecedented mixed 2D–3D structure, such that each 3D closed-circuit displaying a “table-frame” shape interlocked with four square grids of a 2D sheet (Fig. 17), with each rectangular open-channel in the 3D network interpenetrating with two 2D sheets. In spite of the interpenetrating networks in complex **15**, a dozen of water molecules were included in each unit cell.

The reaction was conducted via a self-assembly process under mild hydrothermal conditions. The interpenetrating structure in complex **15** was stabilized due to unexpected chemical rearrangement of the ligand. While the reaction is repeatable, all attempts made to produce compound **15** using isonicotinate instead of nicotinate as a starting material failed. The hydrolysis of *trans*-1,2-bis(4-pyridyl)ethylene might have produced IN groups. However, the chemical rearrangement from nicotinate to isonicotinate was also observed in the case of [(NABr)Cu(IN)] (**16**) (Fig. 18), in which isolated cavities were found within the 3D open-framework [35]. *trans*-1,2-bis(4-Pyridyl)ethylene was present as a necessary component in reactions of both complexes **15** and **16**.

While both unpredictable structures and rational designs were achieved, as those demonstrated above, open-framework coordination polymers constructed via chemical rearrangement of pyridinecarboxylate to oxalate had never been previously observed. $\{[(H_2O)_2(oxa)Zn_2(IN)_2]\cdot 2(H_2O)\}$ (oxa $= C_2O_4^{2-}$) (**17**) was an isonicotinato and oxalato mixed-ligand guest-inclusion open-framework coordination polymer synthesized from a chemical rearrangement of pyridinecarboxylate to oxalate in a self-assembly chemical process under hydrothermal conditions [36].

The reaction of $Zn(NO_3)_2\cdot 6H_2O$ with isonicotinic acid and iodine in the mole ratio of 2:2:1 under hydrothermal conditions at 120 °C for four days produced the pale yellow crystals of complex **17**. The structure of complex **17** consisted of one crystallographically distinct zinc atom surrounded by a bidentate oxalato group, a terminal water molecule, a pyridyl group of the IN unit, and a bidentate carboxylato-group of the IN unit. The zinc metal centers were linked by both a tetradentate oxalato-ligand and a tridentate isonicotinato-ligand to form a large open-framework unit wherein water molecules resided (Fig. 19). The propagation of the open-framework unit afforded an extended non-interpenetrating 2D open-framework with included water molecules (Fig. 19).

Note that the chemical rearrangements in these reactions were unique. A third of the building ligands in the structure of compound **17** were the oxalates formed from the chemical rearrangements of the starting isonicotinate ligands. Although the carboxylate groups of pyridinecarboxylates could have been released or replaced under hydrothermal conditions [10c], the formation of oxalate from carboxylate groups under hydrothermal conditions was intriguing. Pressure un-

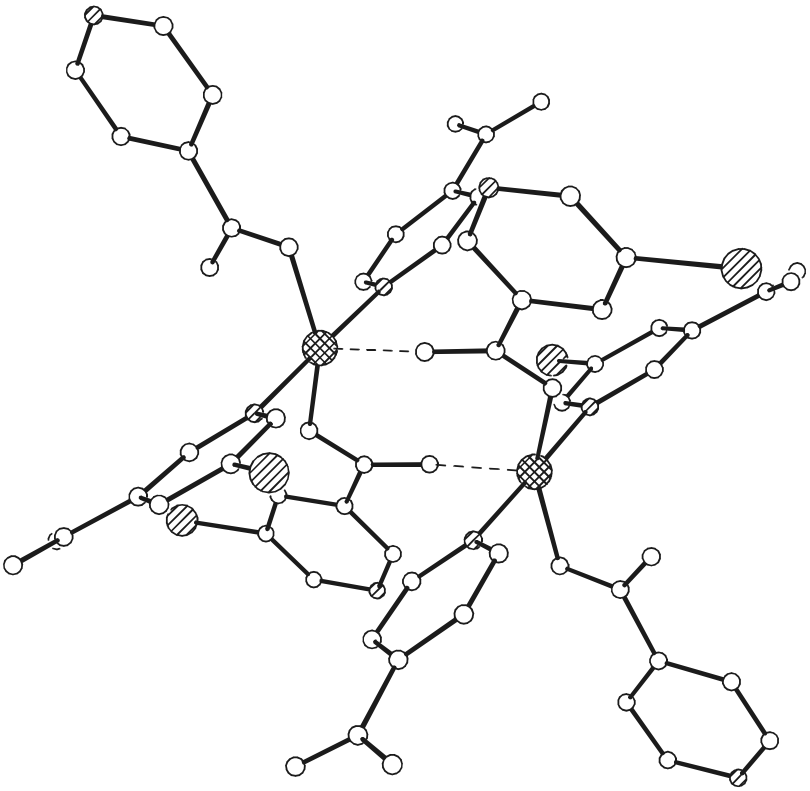

Fig. 18. View of the coordination sphere about copper in complex **16**.

der hydrothermal conditions was a necessary factor in the rearrangement. This unique chemical rearrangement reaction was repeatable with similar yield under the given conditions, and subsequent reactions to synthesize compound **17** by using mixed oxalate and isonicotinate ligands had a much higher yield [36].

3.3. Reactions using extended structure of oxide as a copper-ion source

The important function of catalysis may be attributed to the metal centers in a framework structure. Metal centers were obtained from a variety of sources to provide metal

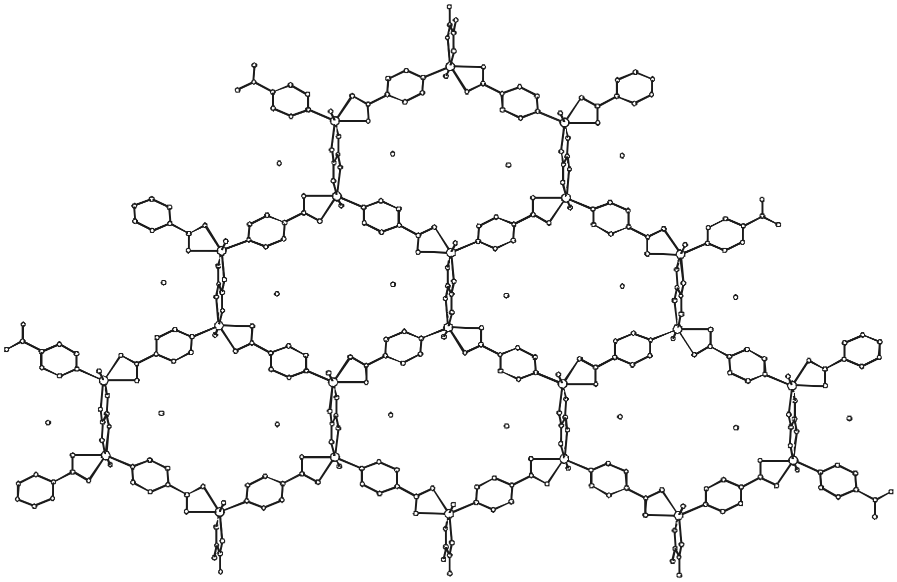

Fig. 19. View showing several rings forming a single layer with water molecules as guests in compound **17**.

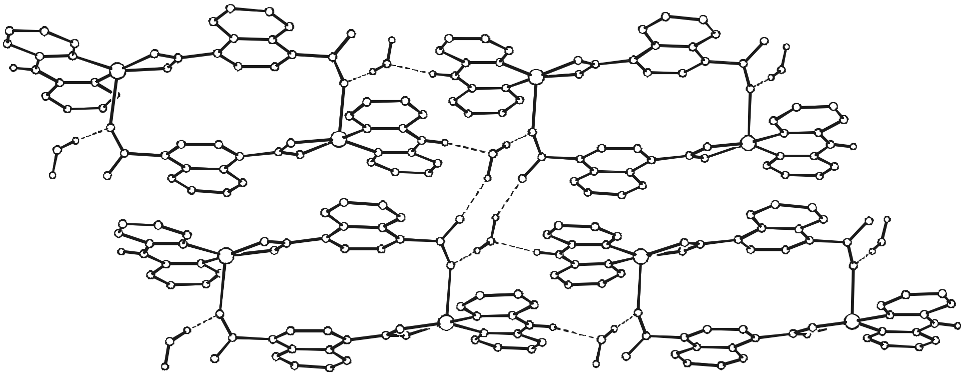

Fig. 20. View of a section of one two-dimensional sheet showing the triple-hydrogen-bonding between dimers in compound **18**.

ions for the self-assembly of coordination compounds. Metal sources included metal halides, metal nitrates, metal carbonates and other inorganic salts. In recent studies, we noticed that the final structures differed greatly depending on the source of the metal ions. For example, $\{[Cu_2(IN)_3]I_5^- \cdot \frac{2}{3}I_2 \cdot H_2O\}$ (**1**) [10b] was obtained by reacting CuI with isonicotinic acid and iodine in the mole ratio of 1:2:1 under hydrothermal conditions at 140 °C for 3 days, while $[Cu(IN)_2]I_2$ (**2**) [14c] was obtained by reacting $Cu(NO_3)_2{\cdot}2.5H_2O$ with isonicotinic acid and iodine in the same mole ratio and reaction temperature as that of complex **1**. The only difference between the two reactions was the inorganic salt. Complex **1** had a three-dimensional nano-size channel structure with polyiodide rings inclusion, whereas complex **2** displayed a two-dimensional open-channel structure with removable iodine molecules. To investigate the effects of varied metal ion sources on the coordination structures, we used starting materials with extended solid-state structures. Three new coordination polymers were synthesized using tenorite, a mineral with extended structure, as a starting material. The first was 1,4-naphthalenedicarboxylate (NDC) bridged coordination dimer linked by a triple-hydrogen-bonding water molecule into a 2D network (Fig. 20), $[(DPA)Cu(NDC)]{\cdot}H_2O$ (DPA: 2,2′-dipyridylamine) (**18**) [37]. The second was a hydrogen-bonded complex metal cation and complex metal anion network (Fig. 21), $\{[Cu(DPA)_2][Cu(PDC)_2]\}$ (PDC: 2,5-pyridinedicarboxylate) (**19**) [37]. The third was $\{[Cu(DPA)_2]_2(NDC)\}$ (**20**) [38], which consisted of two metal cations and an organic anion linked by hydrogen bonds to create an extended network in which Cu(II) was reduced to Cu(I) under hydrothermal conditions. The tenorite had a distorted PdO or PtS structure in which the O–Cu–O angles were 84.5 and 95.5°, giving copper(II) four coplanar bonds with Cu–O distance of 1.96 Å [39]. The next closest neighbors were two oxygen atoms at 2.78 Å. The planar copper open metal sites in tenorite might have attracted nucleophiles during the reactions, facilitating the

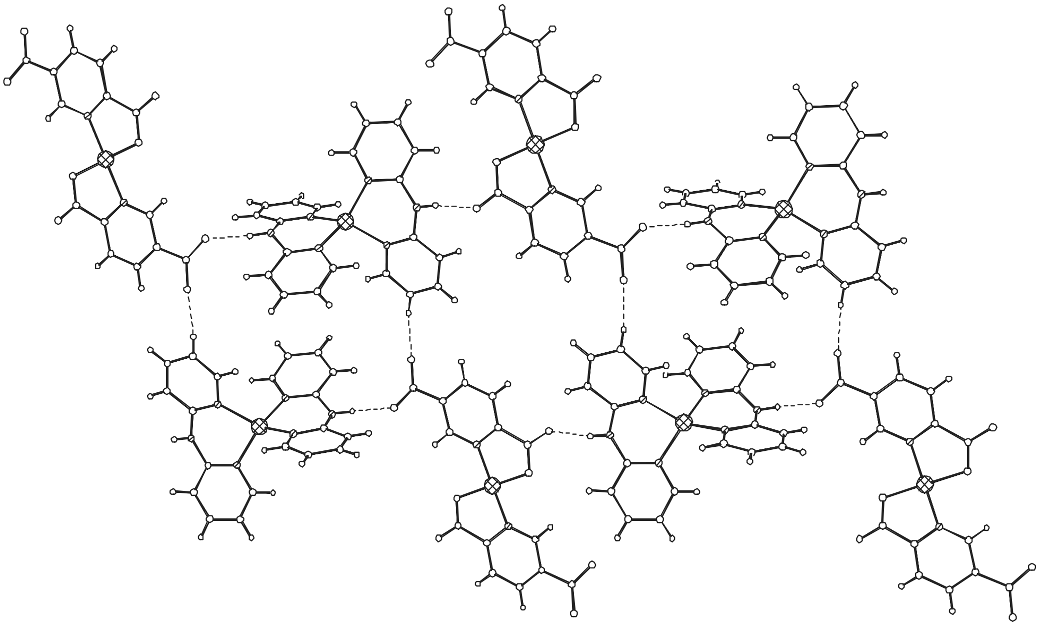

Fig. 21. View of the hydrogen bonding network in compound **19**.

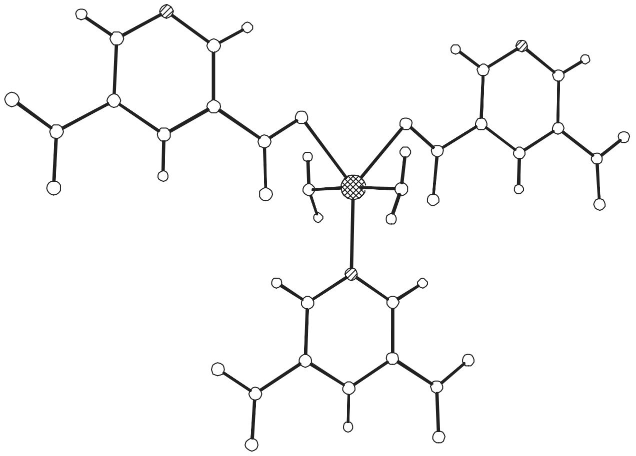

Fig. 22. View of the complete trigonal bipyramidal coordination about Cu atom in complex **21**.

release of copper–metal centers for the formation of new self-assembled complexes.

3.4. Oxidation reactions from Cu(I) to Cu(II)

We observed the oxidation from Cu(I) to Cu(II) without iodine involvement in the final product, again under hydrothermal conditions. For example, $[(H_2O)_2Cu(PDC)]$ (**21**), was a 3D network constructed via both projected covalent and O–H···O hydrogen bonding interactions, in which Cu(II) atom was in a trigonal bipyramidal site (Fig. 22) [14d].

Compound **21** was synthesized through a reaction of CuI with 3,5-pyridinedicarboxylic acid in the mole ratio of 1:1 for 3 days at 140 °C under hydrothermal conditions. The structure of complex **21** consisted of trigonal bipyramidal copper centers coordinated by one pyridyl group and two carboxylate groups of PDC ligands at the equatorial positions, with two water molecules coordinated to the metal center at the axial positions. The network extended along the *a*- and *b*-axes. This extended 2D network consisted of 20-membered large rings (Fig. 23) that were subsequently linked into a three-dimensional structure by inter-layer hydrogen bonds, between the coordination water molecules and the carboxylate oxygen atoms in adjacent layers. The Cu–O bonds at the axial positions were shorter than those at the equatorial positions, as expected, such that the copper atoms were in +2 oxidation state. In this reaction, the Cu(I) probably underwent disproportionation (auto-oxidation reaction) reactions. The formation of complex **21** stabilized copper(II) under the reaction conditions.

By using the same crystal engineering design, the isostructural cobalt complex of compound **21** was also synthesized, $[(H_2O)_2Co(PDC)]$ (**22**) [40].[1]

3.5. Reduction reactions from Cu(II) to Cu(I)

The copper atoms in tenorite could have been released to provide more metal centers for new self-assembled complexes [37]. In the case of $\{[Cu(DPA)_2]_2(NDC)\}$ (**20**) [38], the Cu(II) atoms released from tenorite were reduced to Cu(I), possibly by DPA under hydrothermal conditions. The structure of compound **20** consisted of two independent tetrahedral copper(I) metal centers coordinated by DPA ligands. The two copper(I) centers were linked by NDC anions, via hydrogen bonding, to form a chain (Fig. 24), which was then linked by hydrogen bonds between NDC units.

The known examples of reduction from Cu(II) to Cu(I) by DPA and BPY under hydrothermal conditions had been reported prior to this study [5b].

3.6. Mixed-ligand route for the construction of new structures

The multiple-layer 2D open-framework structures have many potential applications, such as molecular adsorption and separation, because of their attractive features attributed by both 3D and 2D open-frameworks. While various open-framework coordination polymers and interpenetrating architectures had been synthesized, multiple-layer 2D open-frameworks were rarely reported. The multiple-layer here was defined as two-dimensional layer networks with more than two covalently bonded layers. Zaworotko reviewed several bilayer architectures in which the bilayers were formed by partial interdigitation [1a]. One of our research interests has been focusing on open-framework metal–organic polymers constructed by using mixed building blocks. Bidentate organic ligands such as 4,4′-bipyridine and *trans*-1,2-bis(4-pyridyl)ethylene were used extensively as single spacers to link network structures. The isonicotinato (IN) ligand also showed interesting properties [8b,14b]. Copper(II) ions demonstrated a strong tendency to form square pyramidal geometry in open-framework structures when coordinated by isonicotinate ligands in $\{[Cu_2(IN)_4\cdot 3H_2O][Cu_2(IN)_4\cdot 2H_2O]\}\cdot 3H_2O$ (**15**) (Fig. 16), while at the same time forming octahedral geometry as well [14b]. By replacing the water molecules in the apical positions with isonicotinate ligands in Fig. 16, the square pyramidal layered network could have been used to terminate extended networks at the third dimension. Bidentate ligands such as BPEn could have been used to bridge the Cu(II) octahedral centers between square pyramidal terminal layers; thus was a multiple-layer two-dimensional open-framework structure self-assembled. Although this 2D multi-layer network was only one of many possible choices, our initial attempt at self-assembly of a multi-layered two-dimensional structure resulted in dark blue polyhedral crystals that were

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[1] The compound **22** synthesized from our laboratory crystallizes in monoclinic crystal system, space group *C*2/*c* with unit cell dimensions of 9.921(14) Å × 12.006(14) Å × 7.394(10) Å, $\beta = 105.36(19)$; $V = 849.2$ Å^3. Which is similar to the result obtained at different reaction conditions.

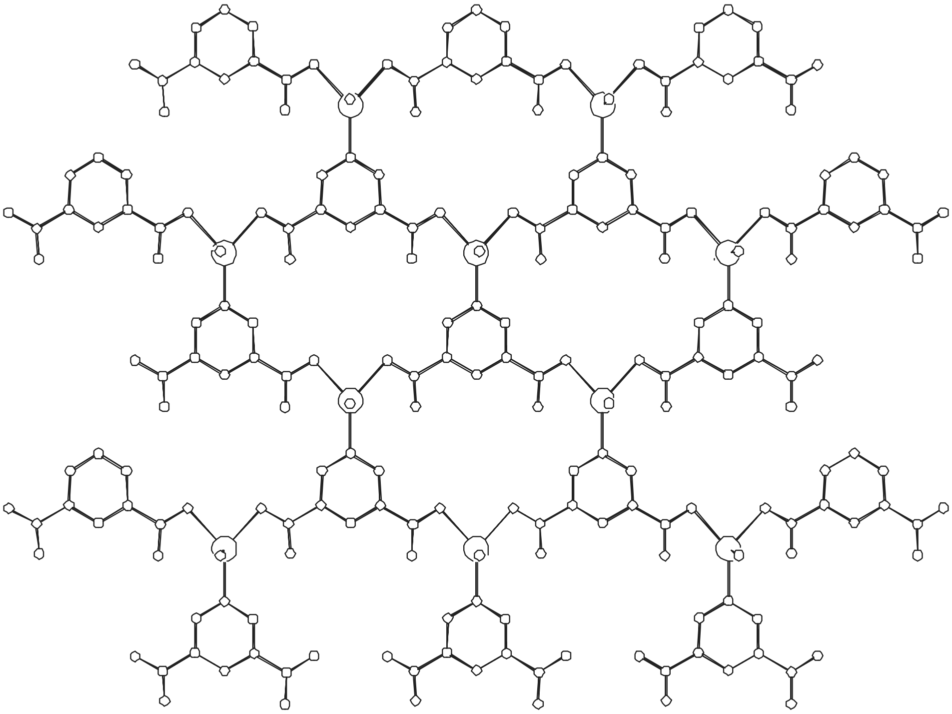


Fig. 23. View of the 2D network in complex **21**.

later revealed, by single crystal X-ray diffraction analysis, to have unprecedented two-dimensional triple-layer open-framework structure stack-interlocked into a 3D polymeric coordination network: $[Cu_3(BPEn)(IN)_6(H_2O)_2]$ (**23**) [14a].

The structure of complex **23** consisted of two independent copper atoms. The first copper atom had square pyramidal geometry, while the second copper atom was in an octahedral site. The octahedral copper metal centers were coordinated by two carboxylate groups of two IN units in a monodentate fashion at the axial positions, with two water molecules and two BPEn spacers at the equatorial sites. Axial IN units utilizing pyridyl groups occupied the apical positions of the square pyramidal copper atoms, while four equatorial positions of the square pyramidal copper atoms were coordinated by two pyridyl groups and two carboxylate groups of four IN ligands. Thus, the octahedral copper centers bridged two square pyramidal copper-centered networks by two-connected tridentate IN units to form a triple-layer open-framework structure. The structure was assembled such that the Cu octahedral centers were close to the centers of adjacent Cu–BPEn–Cu linkages. The triple-layer 2D open-frameworks propagated along the *b*- and *a*-axes, terminating along the *c*-axis (Fig. 25). This novel triple-layer 2D open-framework was then stack-interlocked into a 3D structure. The BPEn linear unit diagonally bridged octahedral copper centers in the middle of the square column (Fig. 26).

The mixed-ligand structures were also constructed with other metal centers and ligands, including $\{[(H_2O)_2(oxa)Zn_2(IN)_2]\cdot 2(H_2O)\}$ [36], $[Cu(DPA)CO_3]\cdot 3H_2O$ [41], $[(oxa)M(DPA)]$ (M = Ni, Fe, Co) [42], $[(oxa)Co(BPE)]$ (BPE: 1,2-bis(4-pyridyl)ethane) [42a], $[(H_2O)_2M(BPY)(BPE)_2]\cdot 1.75(BPE)\cdot 0.25(BPY)\cdot 2NO_3\cdot 4.45H_2O$ (M = Zn, Cd; BPY: 4,4′-bipyridine) [43] and $[(H_2O)_2M(BPY)(BPE)_2]\cdot(BPE)_{1.6}\cdot(BPY)_{0.4}\cdot 2NO_3\cdot 4.65H_2O$ (M = Co, Ni) [44].

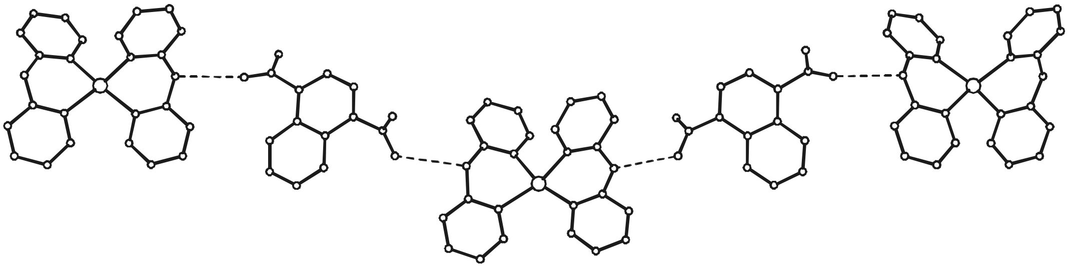


Fig. 24. View of the two copper(I) centers linked by NDC anions via hydrogen bonding to form a chain in complex **20**.

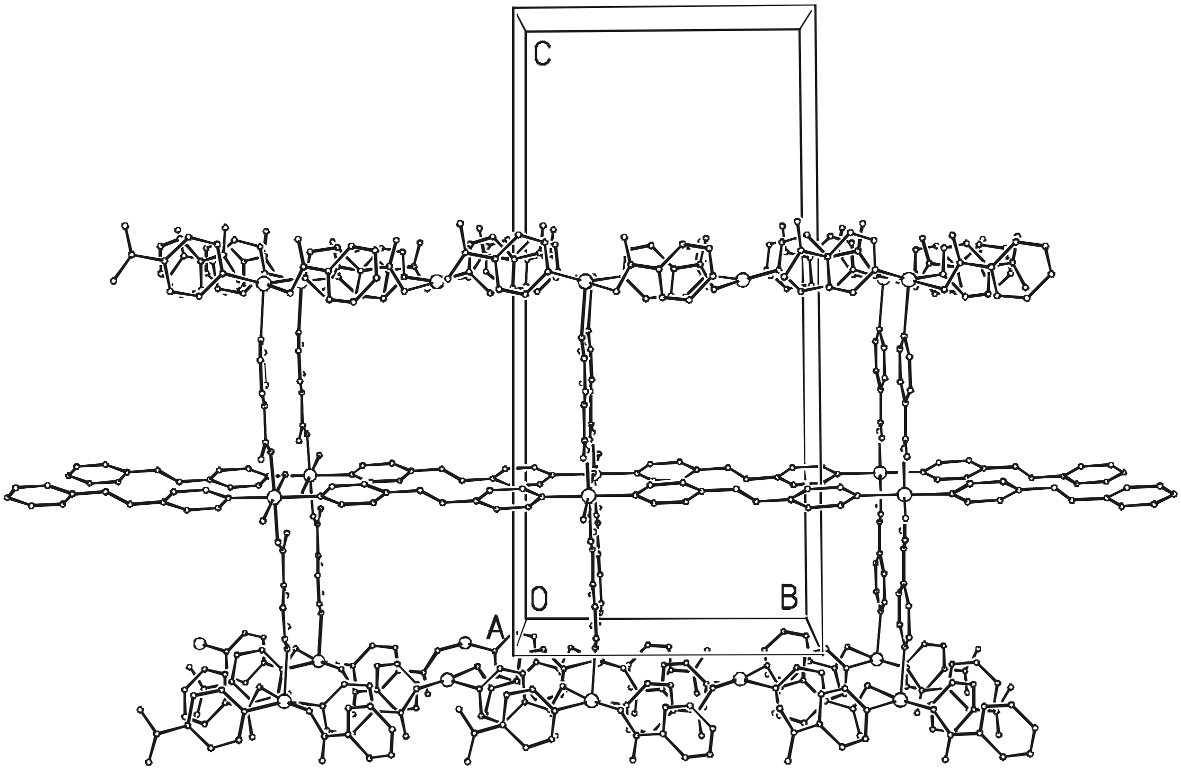


Fig. 25. View of a portion of the triple-layer structure in complex **23**.

4. Metastable coordination polymers with active copper open metal (OM) sites

Functional features of the metal–organic coordination polymers were derived from active transition metal centers such as open metal sites (unsaturated metal centers) [45], as well as organic building blocks with hydrophobic or hydrophilic properties, and the metal–organic open-framework structures with potential in molecular transformation and storage [15b]. While the OM sites played very important roles in molecular recognition in catalysis and biological systems, characterizations of as-synthesized framework polymers with active OM sites by single crystal X-ray structures were rare. Although, a recent paper demonstrated a successful generation of OM sites by thermal removal of the labile coordinating water molecules from the as-synthesized structure of a 3D coordination polymer [45]. The single crystal structures were mostly derived from stable phases that relied on good crystallization of the compound, to yield single crystals of suitable quality for X-ray diffraction. As-synthesized compounds with OM sites, however, were metastable. The isolation of single crystals of such metastable species was difficult to achieve due to their reactive nature and inherent difficulty to stabilization at that stage of crystallization.

$[(BPY)Cu(NO_3)_2]$ (**24**) was an as-synthesized metastable coordination polymer with active OM sites [46]. Using the active OM sites in complex **24** resulted in a new open-framework 3D coordination polymer $[Cu_2(BPY)_4(H_2O)_3](NO_3)_4$ (**25**) [46]. Both crystal structures were characterized by single crystal X-ray diffraction technique.

The previous report of OM sites from framework structures used metal-carboxylate as secondary building unit (SBU), in which the carboxylates were stronger nucleophiles than pyridyl-based functional groups [45]. The electron-withdrawing ability of carboxylates assisted the OM sites of the metal centers to be readily coordinated (coordinatively saturated, including the coordination from labile coordinating water molecules) so that the OM sites on the as-synthesized structures became difficult to maintain. We chose 4,4′-bipyridine (BPY) as building blocks, to isolate as-synthesized coordination polymers with active OM sites. BPY was probably one of the most extensively studied bidentate linear building units in metal–organic polymers research, due to its selective functionality to guest species and larger pore size contributions [4b,43,47]. Its electronic coordination nature was relatively mild, so that the BPY will facilitate the stabilization of the OM sites on the as-synthesized structures. The ideal structural model of this objective had the metal centers adopt a square planar geometry. These metal centers would then have been coordinated by either labile species such as nitrates and linked by BPY to form a 1D structure, or coordinated by BPY and linked perpendicularly by BPY ligands, to result in a 2D network with nitrates as counter anions. One of the key factors in this ideal scheme was to stop the reaction and crystallization at the right stage. The crystals, after isolation, should have been stable enough to allow single crystal X-ray diffraction characterization.

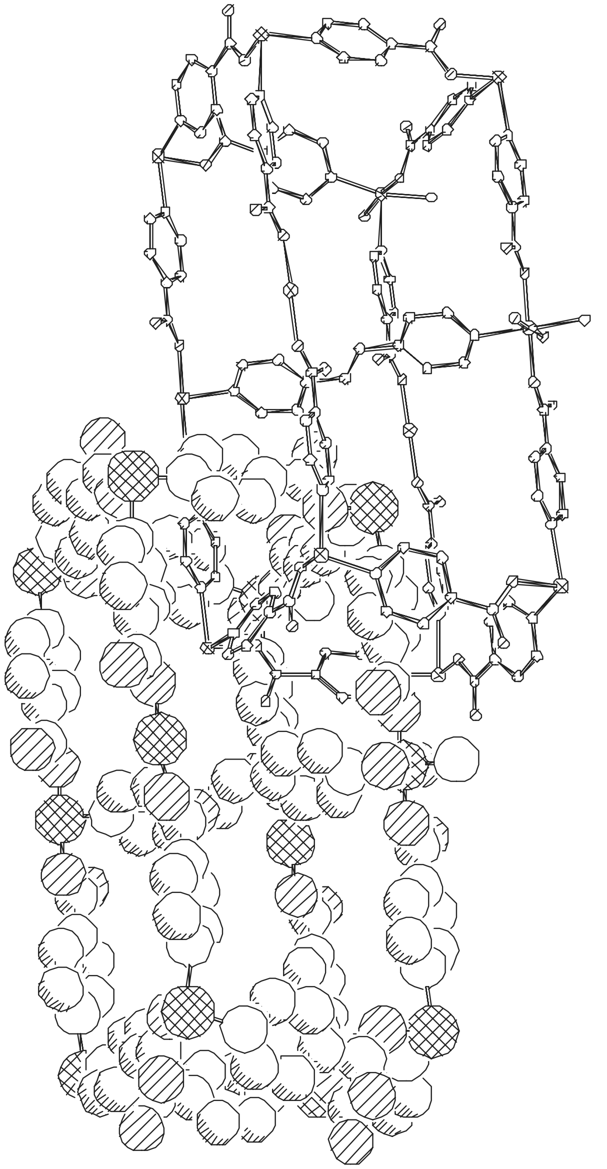
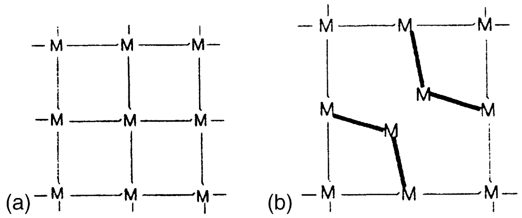


Fig. 26. View of two interlocked square columns in complex **23**.



Scheme 1. View of the square-grid open networks.

The projected target was achieved by the following synthesis: reacting $Cu(NO_3)_2{\cdot}2.5H_2O$ with BPY in a mole ratio of 1:1 or 1:2, in the presence of iodine, under hydrothermal conditions at 120 °C for 3 days. The resulting purple crystals were isolated and dried in air. Subsequent reactions absent of iodine failed to produce compound **24**. The structure of complex **24** consisted of one independent copper atom and a BPY ligand in the asymmetric unit. The copper atom had an ideal square planar environment (with six angles of 89.77(7), 89.78(7), 90.22(7), 90.22(7), 179.6 (1), and 180.0°, respectively), was coordinated by two *trans*-nitrates, and linked by BPY linear ligands to form a 1D metal–organic coordination polymer (Fig. 27). Each Cu(II) metal center had two OM sites *trans* to the square planar motif, in addition to the two replaceable labile nitrate sites. The 1D chains in crystal **24** were packed similarly in orientation to those found in BaU_2O_7, except that the chains in compound **24** did not share any atoms or edges with other chains [39]. In other words, the 1D chains in complex **24** were perpendicular to each other in adjacent layers.

By replacing the labile nitrates with water molecules and using additional BPY ligands at the OM sites in complex **24**, square-grid structures were constructed (see Scheme 1a, a known square-grid network). Since the large M–BPY–M square grid was flexible in terms of bending and twisting features, the central M atom in Scheme 1a could have been replaced by two independent M atoms. One would have been linking the layer above and the other connecting the layer below, to form a very large square-grid network (Scheme 1b). The square-grid in Scheme 1a had “broken” into Scheme 1b to become a complementary square-grid building unit for the larger grid dimensions. The 2D network transformed into a three-dimensional open-framework structure. Although this scheme was only one of many possible structures, the utilization of the active OM sites in compound **24** produced a new guest-inclusion metal–organic open-framework polymer: $\{[Cu(BPY)_2(H_2O)_2][Cu(BPY)_2(H_2O)]\}(NO_3)_4{\cdot}12H_2O$ (**25**).

Complex **25** was obtained by leaving purple crystals of complex **24** in the solution with BPY molecules overnight, so that additional BPY ligands and water molecules replaced labile nitrates and active OM sites in compound **24** to form the polyhedral blue crystals of **25**. Complex

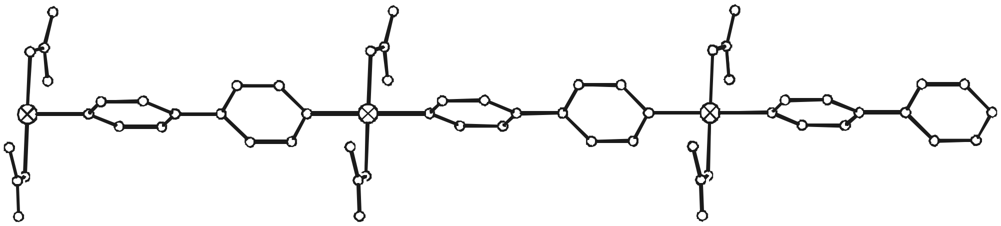


Fig. 27. A Section of one linear polymeric chain in compound **24**.

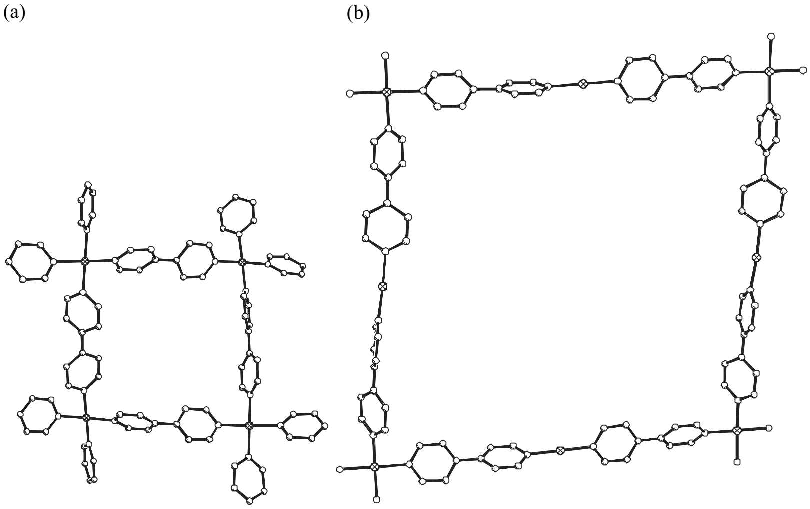


Fig. 28. (a) View of a square-grid with 11.105 Å × 11.137 Å copper atoms separations in complex **25**. (b) View of a square-grid with 22.208 Å × 22.273 Å copper atoms separations in complex **25**.

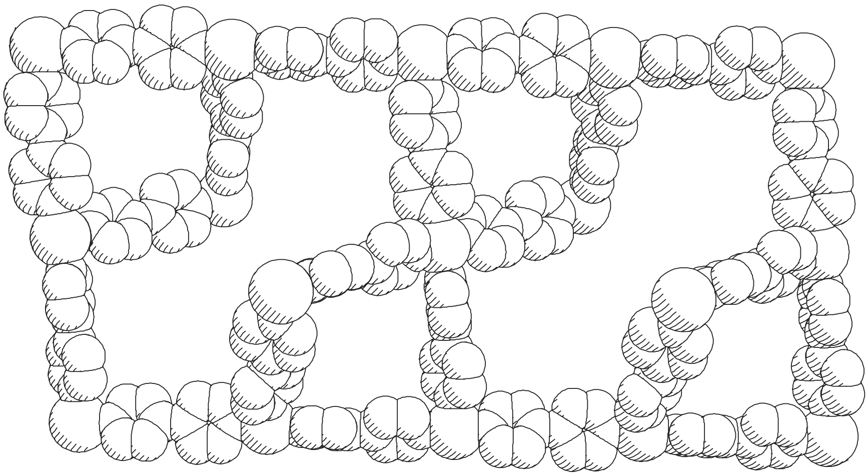


Fig. 29. View of the linkages between the two types of the square-grid networks in complex **25**.

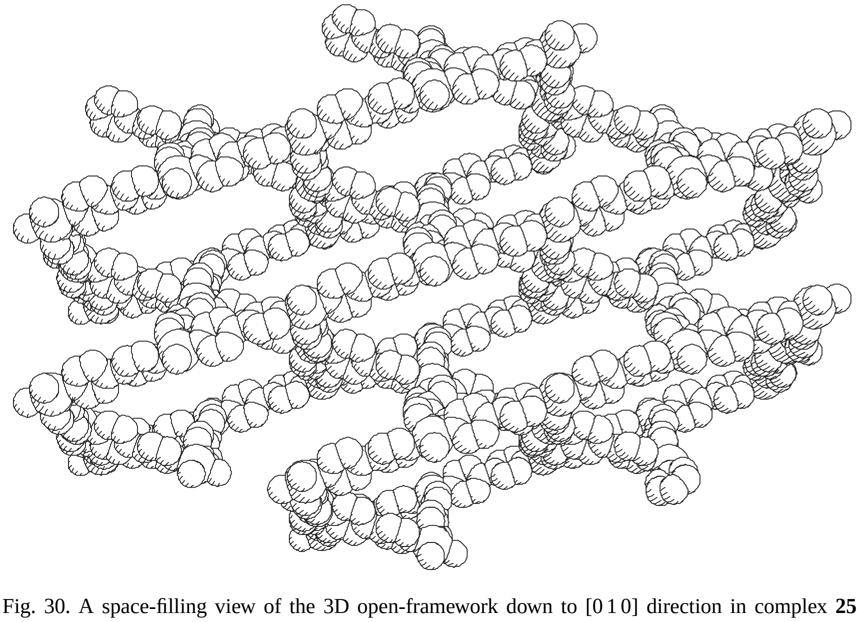


Fig. 30. A space-filling view of the 3D open-framework down to [0 1 0] direction in complex **25**.

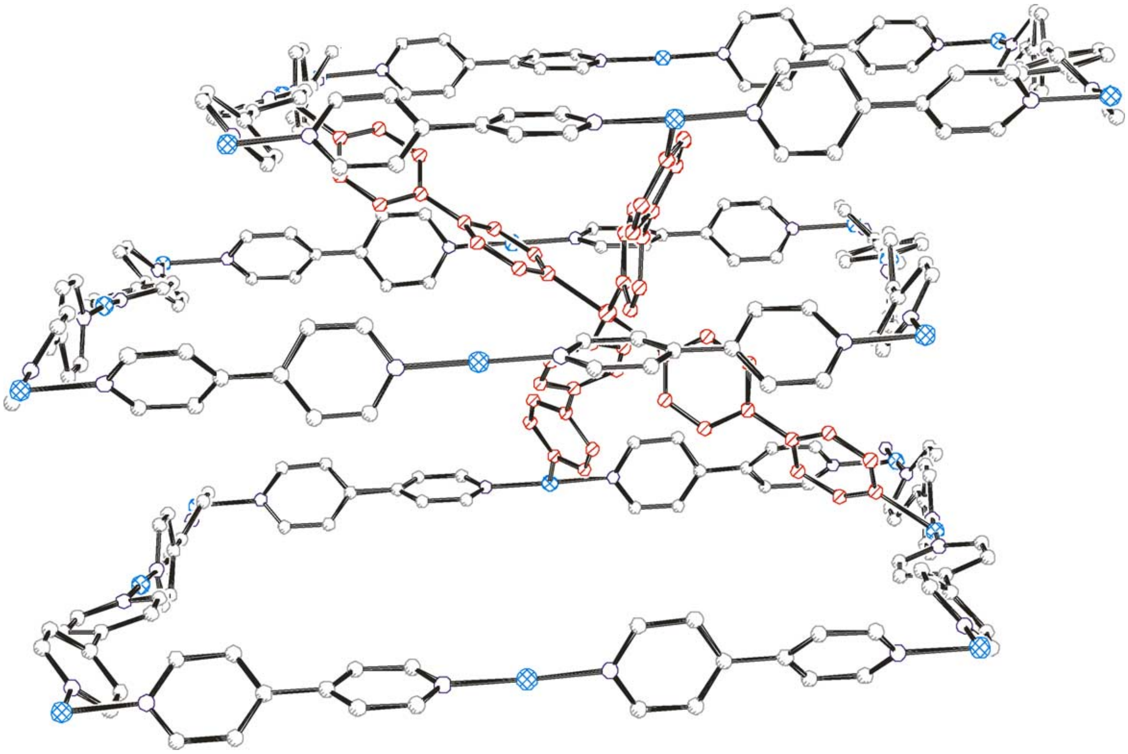


Fig. 31. View of the 3D open-framework linkages in complex **25**. The “bending” part of the square-grid is in red color. The copper atoms are in blue color.

25 was also obtained by reacting $Cu(NO_3)_2 \cdot 2.5H_2O$ with BPY under hydrothermal conditions, resulting in a higher yield. The structure of **25** consisted of two independent copper-centered structural units. Copper atom 1 had an octahedral configuration surrounded by four BPY, at the equatorial positions, and two water molecules at the axial positions. Copper atom 1 had a weak interaction with oxygen atom 2 (<2.5 Å), differentiating it from copper atom 2. Copper atom 2 was in a square pyramidal position coordinated by four BPY, and a water molecule. Both copper atoms 1 and 2 clearly showed Jahn-Teller distortions. Each independent network had two types of square-grids with copper atom separations of 11.105 Å × 11.137 Å (Fig. 28a), and 22.208 Å × 22.273 Å (Fig. 28b). These two types of square-grid linkages were the same as those described in Scheme 1b (Fig. 29). The linkages between the two types of square-grid in each independent network extended into 3D open-frameworks with channels in three directions (Fig. 30). The larger square-grid networks in the two independent networks were parallel to each other, and each 3D network was linked by the complementary square-grid (Fig. 31), leading to a one-fold mutual interpenetration between the large square-grid networks (Fig. 32). The minimal interpenetration of the two 3D networks in complex **25** enabled this open-channel structure to accommodate a large number of water molecules and nitrate anions. Inclusion phenomena in interpenetrating open-frameworks were very attractive, especially in open-channel structures with minimal interpenetrating frameworks [14b,48].

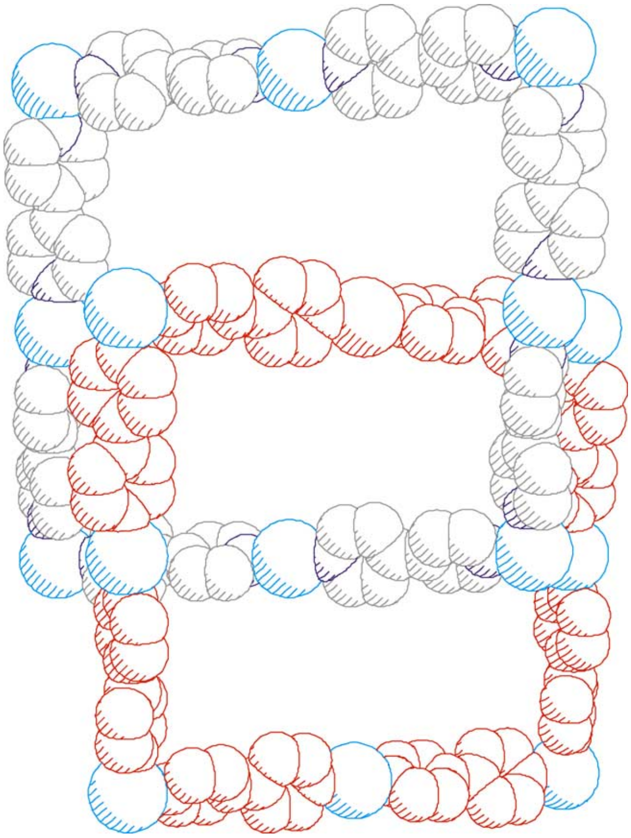


Fig. 32. View of the one-fold interpenetrating network in **25**. The copper atoms are in blue color.

Note that the non-centrosymmetric feature in coordination polymer **24** was maintained in the 3D coordination polymer **25**, implying that the self-assembly process from complex **24** to **25** favored the reactivity of the OM sites.

5. Concluding remarks

Synthesis of functional coordination polymers under hydrothermal conditions has been a rapidly developing research area, stimulated by crystal engineering via functional network designs. Both projected and unexpected framework structures were obtained. While the projected results promoted structural design via crystal engineering, the unexpected but exciting results created by chemical rearrangement reactions indicated that structural control of metal–organic network structures under hydrothermal conditions could be challenging in the long-term. The fundamental foundation of crystal engineering required that all chemical information necessary for designing extended crystal structures aided the development of rational design, and synthesis of new coordination polymers via self-assembly processes. It was therefore expected that prediction and control of crystal structures remained elusive for more complicated coordination networks, but will be continued to be addressed and advanced by the rapid development of crystal engineering for functional coordination polymers [49].

Acknowledgements

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