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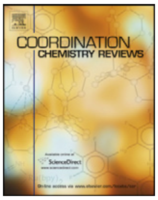

Review

Copper(I) halides: A versatile family in coordination chemistry and crystal engineering

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Contents

Abbreviations: 1,7,13TT18C6, 1,7,3-trithia-18-crown-6; 1,7DT18C6, 1,7-dithia-18-crown-6; A46, 4,6-dibromo-3-chloroanilinium; ahp, 2-amino-3-hydroxypyridinium; [12]aneS_4, 1,4,7,10-tetrathiacyclododecane; ap, 1-allylpyridinium; apl, 3-aminopropanol; apyd, 2-aminopyrimidine; bbol, 2,2′-bis[(4S)-4-benzyl-2-oxazoline]; beap, bis(ethylamidophosphine); bet, bis(ethylenedithio)tetrathiafulvalene; bimpms, bis(6-methyl-2-pyrazylmethyl)sulfide; 2,2′-bipy, 2,2′-bipyridine; bipypz, bis-2,3-(2-pyridyl)pyrazine; biz, benzimidazole; bmpms, bis(6-methyl-2-pyridylmethyl)sulfide; bpb, 1,3-bis[(2,4,6-tri-tert-butylphenyl)phosphanediylmethyl]benzene; bpcae, 1,2-bis(3-yyridylcarbonylamino)ethane; bpds, bis(4-pyridyl)disulfide; bpp, 1,3-bis(4-pyridyl)propane; bpsmb, 1,4-bis(2-pyrimidinesulfanylmethyl)benzene; bpst, 3,4-bis(4-pyridinesulfanylmethyl)thiophene; bta, benzotriazole; *c*-(P_5Ph_5), pentaphenyl-cyclopentaphosphane; cbe, cyanobenzene; cp, cyclopropane; cpi, cyclopentadiene; cpta, 5-(3-cyanophenyl)-tetrazolate; daa, diallylamine; dabco, 1,4-diazabicyclo[2.2.2]octane; dadpm, 4,4-diaminodiphenylmethane; dams$^+$, trans-4-(4-dimethylaminostyryl)-1-methylpyridinium; dapyBr, 3-bromo-2,6-diaminopyridinium; db-24C8, dibenzo-24-crown-8; dcpm, bis(dicyclohexylphosphino)methane; dddtd, 1,12-diphenyl-5,8-dioxa-2,11-dithiadodecane; dimap, 4-(dimethylamino)pyridine; dmasa, trans-4′-(dimethylamino)-4-stilbazole; dmaemamp, 2,6-bis((dimethylaminoethylene(methyl)amino)methyl)phenyl; dmbta, 1,3-N-dimethylbenzotriazolium; dmiz, 3,5-dimethylisoxazole; dmq, 2,3-dimethylquinoxaline; dpam, bis(diphenylarsino)methane; dpey, 3,3′-dipyridylethyne; dpiz, dipyrido[1,2-a:2′,3′-d]imidazole; dpk, di-2-pyridyl ketone; dpmt, 2,5-bis[(diphenylphosphino)methyl]thiophene; dppeSe, 1,2-bis(diphenylselenophosphinyl)ethane; dppm, bis(diphenylphosphino)methane; 1,10DT18C6, 1,10-dithia-18-crown-6; dtpcp, 2,11-dithia[3.3]paracyclophane; eeda, *N*-ethylethylenediammonium; en, ethylenediamine; et, bis(ethylenedithio)tetrathiafulvalene; EtS-4-C_5H_4NEt, ethyl-pyridinium-4-ethylthiol; Et_4tms, tetraethylthiuram monosulfide; fdn, fumarodinitrile; hcc, 1,2,3,6,7,8-hexahydro-cinnolino[5,4,3-*cde*]cinnoline; HDMepyF, N,N′-di(6-methyl-2-pyridyl)formamidine; 4-Hpytz, 3,5-di(4-pyridyl)-1,2,4-triazolate; hmt, 3,5-bis(hydroxymethyl)-1,2,4-triazolate; in, isonicotinato; leof, levofloxacin; lip, α-lipoic acid; mbd, 2-methylbutadiene; $Me_6$12Se3, 3,3,7,7,11,11-hexamethyl-1,5,9-triselenacyclododecane; mcn, methacrylonitrile; meda, *N*-methylethylenediammonium; mnt, 1,2-dicyano-1,2-ethylenedithiolato; moep, meso-octaethylporphyrinogen tetraanion; mpmpms, 2-(6-methylpyridyl)methyl(2-pyridyl)methylsulfide; mptmsa, 2-(6-Methyl)pyridyl)trimethylsilylamido; mstbim, 1,3,5-tris(benzimidazol-1-ylmethyl)-2,4,6-trimethylbenzene; mtea, methyltriethylammonium; *m*-tolyl$_3$P, tri-*m*-tolylphosphine; mtta, 5-methyl-tetrazolate; mxda, *m*-xylylenediammonium; nbe, nitrobenzene; ody, octa-1,7-dien-4-yne; paraquat, 4,4′-dimethyl-4,4′-dipyridyl; PhCN, benzonitrile; psmq, 8-(4-pyridylsulfanylmethyl)quinoline; py, pyridine; pyd, pyrimidine; pyH, pyridinium; pymMe, 4-methylpyrimidine; pyz, pyridazine; pz, pyrazine; qpy, 3,3′:5′,3″:5″,3‴-quaterpyridine; quin, quinoline; quxin, quinoxaline; 4-S-C_5H_4NH, pyridine-4-thiol; 4-S-pyd, pyridine-4-thiol; tea, tetraethylammonium; tetpeb, 1,3,5-triethyl-2,4,6-tris(2-(2-pyridyl)ethyl)benzene; tma, tetramethylammonium; tmcta, tetramethylcyclotetra-arsoxane; tmpa, trimethylphenylammonium; tmtach, *N*,*N*,*N*^{2}-trimethyl-1,3,5-triazacyclohexane; tmtttf, tetrakis(methy1thio)tetrathiafulvalene; tpa, tetrapropylammonium; tpcq, triptycenylquinoxaline; tptmps, tris(plienylthiomethl)phosphane sulfide; tptp, tri-2,3-pyrazino(b,e,h)triptycene; tptpy, 2,4,6-triphenylthiopyrilium; tpypz, tetra-2-pyridylpyrazine; triphos, l,l,l-tris-(diphenylphosphinomethyl)ethane; trz, 1,3,5-triazine; ttt, triallyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione; ttup, 1,4-(1,4,8,11-tetrathiaundecano)phthalazine; tytp, 4-[3-(1H-1,2,4-triazol-1-yl)propyl]-4H-1,2,4-triazole; viph, *o*-vinylphenyl.

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ABSTRACT

The copper(I) halide aggregates represent a versatile family in coordination chemistry and crystal engineering. First discovered a century ago these species have been intensively investigated in the last three decades because of their structural and luminescent uniqueness. This account reviews their research history and frontier (Section 1), synthetic routes (Section 2) and structural diversity (Section 3), and also offers personal perspectives (Section 4) on the growth, property and application of the copper(I) halide aggregates in coordination polymers.

1. Introduction

Copper complexes and clusters have been fascinating chemists for centuries, mostly because of the unique role this species plays in both physical and biological research and application [1]. Particular attention has been paid to the photochemical and photophysical properties of copper(I) complexes in light of the d^{10} electronic configuration which diversifies their luminescent behavior [2–4]. Among several systems, copper(I) halide aggregates represent a prominent and well-investigated family which currently lies at the forefront of both coordination chemistry and crystal engineering. Generally, the copper(I) halide aggregates, whose formula is $Cu_xX_yL_z$ (where X = Cl, Br or I; L = N, S or P based organic ligand, if available), could exist as discrete compounds or as CuX-based building blocks (aka. “connectors” in view of crystal engineering) embedded in coordination polymers. In the following text, some significant milestones and important reviews in the research realm of copper halides will be highlighted.

The investigation into copper(I) halide aggregates probably dates back to a hundred years ago [1], when the technique of X-ray diffraction crystallography was not yet invented and introduced into chemical research. However, in the 1970s, the first and so far most prominent member in the copper(I) halide family, $Cu_4I_4py_4$, still captured the attentions of chemists, when Hardt and Pierre claimed to discover the significant luminescent property of the $Cu_4I_4py_4$ cluster which they termed “luminescence thermochromism” [5]. The pioneering studies by Hardt and co-workers also pointed out that there existed at least three different complexes with the empirical formula of $CuIL_z$ ($z = 1$, 2 or 3), which were regulated by reaction stoichiometry [6]. The structural configuration of the $Cu_4I_4py_4$ cluster was also suggested, but most of the evidence was indirect spectroscopic characterization, until in 1976 the first crystallographic evidence for the $Cu_4I_4py_4$ tetramer unambiguously revealed its tetrahedral cubane-like configuration [7].

Early work on copper(I) halide aggregates, especially the luminescent thermochromism phenomenon, elicited the interest of Ford et al., who continuously embarked on a careful and extensive research project focused on the luminescent properties of $Cu_4I_4py_4$ and its derivatives, both experimentally [8] and theoretically [9]. Thus, this review does not intend to consider the photoluminescent properties of discrete copper(I) halide aggregates, which were discussed in other detailed reviews by Ford et al. [2,8]. This account mainly concerns itself with the general synthetic methods for targeting copper(I) halide aggregates and their structural diversity, especially for those incorporated in coordination polymers as building blocks.

Coordination polymers (also known as metal–organic framework) are a class of newly developed solid-state materials with infinite extended structures constructed from “connectors” (metals) and “linkers” (organic ligands) [10]. In recent years, some amendments have been proposed to complement the synthetic principle of “connectors and linkers”, and one of the most familiar approaches is to introduce inorganic clusters or aggregates as “connectors” in place of single metal ions. It was Champness and co-workers who did the preliminary research and realized that copper halide aggregates could be incorporated in coordination polymers [11]. Moreover, the bridging ligand (connecting the copper halide aggregates) gave rise to more complicated copper(I) halide architectures than did monodentate or bidentate chelating ligands. Thus, the crystal engineering of copper(I) halides extended from only discrete oligomers to one-dimensional (1D) or even two-dimensional (2D) and three-dimensional (3D) architectures. However, the lecture and review by Champness and co-workers only included a few representative examples investigated in their groups, and the structural diversity of copper(I) halides was far from unveiled, which will be the focus of this review to establish a molecular library of copper(I) halides.

Speaking of the structural diversity aspect, a group of Swedish and Australian chemists once composed a review on anionic copper halides (which they termed “halocuprate complexes”) [12]. They considered the crystal engineering of copper halides as a “difficult system”, because the knowledge and understanding of the fundamental aspects of the crystallisation process was insufficient either to permit the control of crystallisation outcomes or to determine the structures of the products. Their review contained a part that summarized the structural variation of known halocuprate complexes (including $Cu^{I}{}_{x}X_y$, $Cu^{II}{}_{x}X_y$ and mixed-valence $Cu^{I/II}{}_{x}X_y$ in which $x < y$), all of which were anionic aggregates, and thus these will be excluded from this review in order not to overlap.

The survey of the documented copper(I) halide aggregates structures is performed mostly based on the last version of the Cambridge Structural Database (CSD) and the authors’ knowledge. This review will cite representative structures of copper(I) halides, especially those involved in coordination polymers, and discuss their general synthetic routes (Section 2) and structural diversity (Section 3). Also, research perspectives on the growth, property and application of copper(I) halide aggregates in coordination polymers will be given in the concluding remarks (Section 4). The authors will not be able to mention all published structures; in this regard they are sorry for any crucial oversights.

2. General synthetic routes for targeting copper(I) halide aggregates

2.1. Direct Cu^IX (X = Cl, Br, I) sources routes: challenges and solutions

The use of copper(I) halide salts to engineer Cu^IX (X = Cl, Br, I) aggregates is a reliable approach but would encounter two inherent challenges. First, the instability of copper(I) halides (especially for CuBr and CuCl) would make the dissolution of the metal salts accompany the oxidation of copper(I) to copper(II) in the presence of dioxygen from the air, and might lead to the eventual reaction products of mixed-valence copper(I/II) halides or even copper(II) halide complexes [13a]. Second, the poor solubility of copper(I) halide salts in most common organic solvents (only sparingly soluble in dichloromethane [13b] and tetrahydrofuran [13c]; moderately soluble in acetonitrile and propionitrile [13d]) makes it difficult to adopt the widely used conventional solution and layering diffusion methods for making crystals.

In order to avoid the oxidation of the copper(I) halides caused by dioxygen from the air, all solvents should be purified prior to being used, by freshly distillation, degassing and drying. In addition, all procedures had better be performed in a glovebox or standard Schlenk line, vacuum line technique as well as syringe techniques under an atmosphere of nitrogen or argon. Alternatively, a synthetic approach tackling the difficulty of oxidation (copper(I) to copper(II)) was developed in our early work: the reaction involving copper(I) halide salts was carried out in the presence of reductive agents such as triphenylphosphine, bis(diphenylphosphino)methane or bis(diphenylphosphino)ethane to stabilize the +1 oxidating state of copper. This approach also partially increased the solubility of the reactants [13e–i].

As to the second challenge of solubility, an effective approach is to use the corresponding saturated alkali metal halide aqueous solution to dissolve the copper(I) halide salts instead of pure water solution (e.g. saturated KI aqueous solution for CuI salt) [14]. This approach was widely adopted in our group [13a,15,16] and proved to be very effective. It worked not only because the solubility of CuI increased dramatically in saturated KI aqueous solution due to the principle of “like dissolves like”, but for the excess iodide ions allowed the formation of Cu^IX aggregates. For example, in an early study, Holt et al. obtained three CuI crown ether based crystal structures – a discrete compound, namely $[Cu_4I_6][Cu_8I_{13}]K_7$(12-crown-4)$_6$, containing two anionic copper(I) iodide clusters, and two 1D coordination polymers, namely $[Cu_4I_6]K_2$(15-crown-5)$_2$ and $[Cu_3I_4]$K(dibenzo-24-crown-8) – from the traditional solution reaction of CuI and different crown ethers in the presence of aqueous KI [14a].

In more recent years, hydro(solvo)thermal methods, typically carried out in sealed teflon reactors (or in sealed glass tubes or ampoules [17,18]) in the temperature range of 100–200 °C under autogenous pressure (generally 10–30 atm), have been used for the synthesis of novel copper(I) halide complexes [13a–b,15,16,19–22]. The exploitation of the hydrothermal techniques is facile for preparing copper(I) halide compounds because the extreme reactive conditions bring the lower viscosity and higher rate of solvent extraction (which would minimize the problems associated with the different solubilities of the reactants) and, most importantly, would facilitate the crystal growth processes. This procedure is relatively more effective in copper(I) halide systems rather than other ones. The handling of the samples should also be carried out under an inert atmosphere in hydro(solvo)thermal methods as those in traditional methods [17]. For instance, in the preparation of two templated copper(I) chloride networks, namely [pyridinium]$_3Cu_3Cl_6$ and $\{[H_3NMe]_6Cl\}[H_3NMe]_2Cu_9Cl_{16}$, the reactants of CuCl, organic ligands and corresponding solvents were placed in a thick walled fused silica tube by using a Schlenk line. Then, the mixture was frozen with liquid N_2 and sealed such that the fused silica vessel was filled to 25% volume. The reaction mixture was heated to 100 °C for a long time and then cooled to low temperature to give a high yield of products [23].

2.2. *In situ generated Cu^IX (X = Cl, Br, I) sources routes: involving in situ hydro(solvo)thermal reactions*

Recently, some *in situ* generated Cu^IX sources routes have been developed as new approaches to synthesize copper(I) halide based complexes. In these approaches, the Cu^IX aggregates originated from various sources other than the specific Cu^IX salts. The Cu^IX is generated *in situ* because the formation of the Cu^IX and the coordination of the organic ligands to the copper(I) ions were simultaneous (in one-pot reactions). These routes include halide substitution, copper oxidation and copper reduction routes, in many cases accompanying *in situ* hydro(solvo)thermal reactions [24], such as organic ligand halogenation, desulfurization, alkylation and cycloaddition.

2.2.1. *Halide substitution routes*

This type of reaction usually uses relatively stable and soluble cuprous salts instead of copper(I) halides to react with alkali metal halides or ammonium halides to afford Cu^IX. Crystals of $[Cu_3X_3(dpmt)_2]$ (X = I, Br, Cl) were prepared from the reaction of a mixture of $[Cu(MeCN)_4]PF_6$, dpmt, KX (X = I, Br) or NaCl in dry N_2 atmosphere by using standard Schlenk and vacuum line techniques. In this reaction, the Cu^IX was generated *in situ* from $[Cu(MeCN)_4]PF_6$ by replacing the hexafluorophosphate group with halide ions [25]. Similar substitution processes were observed in the synthesis of $Cu_3X_2(dppm)_3{}^+$ (X = I, Br, Cl) [26] and $Cu_8Cl[Se_2P(OR)_2]_6(PF_6)$ (R = Et, Pr, ^{i}Pr) [27].

2.2.2. *Copper oxidation routes*

Employing zerovalent metals in the synthesis of corresponding coordination compounds has proven to be a general route, which was also utilized in the copper oxidation routes for preparing copper(I) halide compounds. The spontaneous ionization of copper powder in solution in the presence of various oxidizing agents has received much attention. The reaction of Cu powder, $CuBr_2/CuCl_2$, 1,4-(1,4,8,11-tetrathiaundecano)phthalazine (ttup) in CH_3CN and $CHCl_3$ under a nitrogen atmosphere afforded crystals of $[CuBr(ttup)]_n/[Cu_{1.5}Cl_{1.5}(ttup)]_n$ in ideal yield [28]. In these reactions, copper(II) salts are powerful oxidizing agents in nitrile containing solutions.

The copper oxidation route was extended by Vassilyeva et al. Their treatment of zerovalent copper with ammonium halides in the presence of the crown ether and rubidium halides or cesium halides in solution afforded various crystalline products with structures constructed from anionic halogenocuprates(I) moieties and cationic [Rb(18-crown-6)]$^+$/[Cs(18-crown-6)]$^+$ moieties [29]. It is reasonable to suppose a mechanism whereby the oxidation of copper and complex formation was conditioned by the presence of certain proton-donating agents and dioxygen from the air *via* Eq. (1) (see below) in which copper oxidation occurred under a two-step process of $Cu^0 \rightarrow Cu^+ \rightarrow Cu^{2+}$. The forming Cu^{2+} ion and remaining Cu^0 powder underwent an autocatalytic reaction *via* Eq. (2) (see below) in which the reverse reaction also occurred. It is known that copper(I) ion normally disproportionates in water. However, in the presence of MeCN, K_1 changes from 10^{-6} mol dm^{-3} in water to about 10^{10} mol dm^{-3} in MeCN/water. Moreover, the stability of the halogenocuprate(I) crystalline product further favors the rightward progress of the chemical equilibrium.

$$Cu^0 + 2H^+ + \tfrac{1}{2}O_2 \rightarrow Cu^{2+} + H_2O \qquad (1)$$

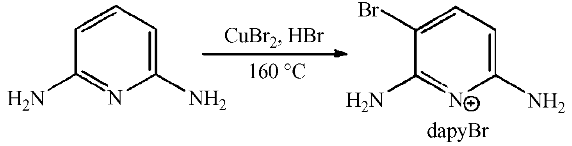
$$Cu^{2+} + Cu^0 \overset{K_1}{\rightleftarrows} 2Cu^+ \qquad (2)$$

Generally, in hydro(solvo)thermal conditions where the reduction mechanisms dominate, the synthesis of copper halide complexes through oxidation reaction mechanisms was largely absent. Lu first prepared and described a series of mixed-valent copper(I/II) iodide coordination polymers produced from the oxidation of CuI under hydrothermal conditions [30]. The first complex $[Cu_2I(in)_2]_n$, was obtained by reacting CuI with the ligand in oxygen-treated water under hydrothermal conditions at 140 °C. Interestingly, when the temperature was raised to 170 °C, a similar reaction yielded a new complex with the same formula, namely $[Cu_2I(in)_2]_n$, but with a different structure. The oxidizer dioxygen could also be replaced with iodine to afford another new complex, $\{[Cu_2(IN)_3]I_5^-{\cdot}1.5I_2{\cdot}H_2O\}_n$. The possible reaction mechanism was discussed in Lu's review [30].

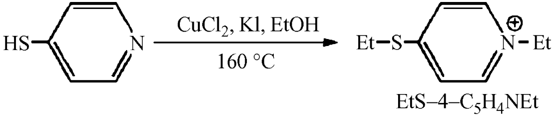
2.2.3. Copper reduction routes

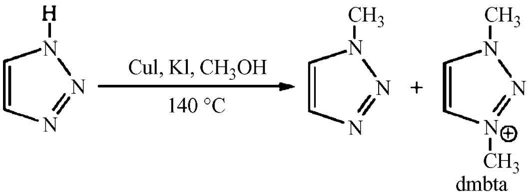
The reduction of cupric salts has proven to be the most promising approach for *in situ* generation of Cu^IX sources. Compared with traditional synthetic methods, hydro(solvo)thermal techniques have more advantages for the *in situ* reduction of copper(II) to copper(I), which has been widely demonstrated in many reports [24]. The presence of pyridine-like ligands (such as bipyridine, terpyridine and pyridylpyrazine [31]) or amine/ammonium analogues ligands (such as 1,4-diazabicyclo[2.2.2]octane, ethylenediamine and *N*-methylethylenediammonium/*N*-ethylethylenediammonium [32]), as proton-acceptors could promote the reduction of the copper(II) and the subsequent formation of Cu^IX aggregates. In these copper reduction routes, several cooperative *in situ* hydro(solvo)thermal reactions occurred:

Halogenation

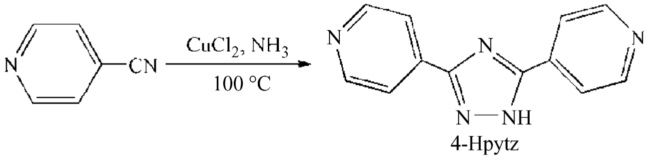


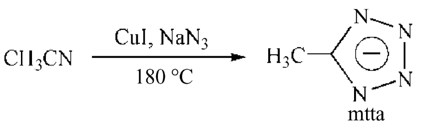
Desulfurization/alkylation





Cycloaddition





Halogenation: Because of strong basicity, the nitrogen atom in the N-containing heteroaromatic ring of the ligand would encounter the competing reactions of coordination and protonation, and therefore halogenation of the organic species accompanying copper reduction is very likely to happen in the presence of halogen excess agents at high temperatures (120–180 °C). For example, crystals of $CuBr_4(dapyBr)_3$ were prepared by adding $CuBr_2$ to the HBr solution of 2,6-diaminopyridine. The activated carbon atom in the pyridine ring of the ligand underwent bromination during the synthesis process in which the reduction of copper(II) to copper(I) was also accomplished [33]. Halogenation of the substituted heteroaromatic cation (such as 3-chloroanilinium) was frequently observed by Willett et al., providing sufficient evidence for this process [34]. Lu et al. rationalized the di-iodonation process of the pyridine-dicarboxylate ligand in which both carboxylate groups were substituted by iodine nucleophiles. They provided a control experiment to show that only single iodine-substitution was observed in the absence the copper(II) salts [35].

Desulfurization/alkylation: There are several more complicated *in situ* hydro(solvo)thermal reactions accompanying the copper reduction routes. Representative work by Yao and co-workers demonstrated a simultaneous redox, alkylation and desulfurization reaction under solvothermal conditions affording a luminescent copper(I) chain polymer $[(Cu_3I_4)(EtS\text{-}4\text{-}C_5H_4NEt)]_n$, and byproducts of $Cu_6Cl_6(4\text{-}S\text{-}C_5H_4NH)_4$ and K_2SO_4 [36a]. This process was targeted *via* the copper reduction route in which the $(Cu_3I_4^-)_n$ chain aggregate was *in situ* generated from $CuCl_2$ and KI undergoing both copper reduction and halide substitution. Based on the isolation of the byproducts and the existence of the iodine in the filtrate, they speculated that the desulfurization process was followed by the oxidation of S^{2-} to S^{6+}/I^- to I_2 and the reduction of Cu^{2+} to Cu^+. Moreover, during the process, the direct alkylation reagent, EtI (derived from the EtOH solvent), interacted with the pyridine-4-thiol to give the intermediate $(EtS\text{-}4\text{-}C_5H_4NEt)I$. This *in situ* copper reduction and ligand desulfurization reaction was further utilized by Yao and co-workers to obtain a novel luminescent three-dimensional (3D) diamondoid $Cu_{10}Cl_{10}$ cluster based coordination polymer $[Cu_{10}Cl_{10}(4\text{-}S\text{-}C_5H_4NH)_4]_n$, with the byproduct of $CuSO_4{\cdot}5H_2O$ [36b]. However, the copper(II) source is not absolutely necessary for the N-alkylation of the organic ligand under hydro(solvo)thermal conditions. We illustrated a similar *in situ* alkylation process, in which the benzotriazole ligand also underwent alkylation regardless of the introduction of CuI (not copper(II) salt) to afford a novel benzotriazolium-templated Cu_nI_n cluster based 3D coordination polymer, namely $\{(Cu_{10}I_{10})(Cu_6I_6)[(Cu(bta)_2]^-{}_3{\cdot}(dmbta)^+{}_4{\cdot}(I^-){\cdot}x(I_2)\}_n$ $(x \approx 1.5)$ [37].

Cycloaddition: Another interesting accompanying reaction in the process of copper reduction and copper(I) halide aggregate formation is *in situ* cycloaddition. For example, a mixture of $CuCl_2$, 4-cyanopyridine, and aqueous ammonia gave crystals of $[Cu_6Cl_3(4\text{-}pytz)_3]_n$ under hydro(solvo)thermal conditions. Chen et al. suggested that the triazolate was derived from the coupling of nitriles and ammonia, which might be assisted by the copper(II) oxidant [38]. Other cycloaddition examples, such as $(CuCl)_2(dmiz)$ [39a] and $[(CuCl)_2(dpiz)]_n$ [39b], were also documented. Also noted, the copper reduction route is not absolutely necessary for the *in situ* cycloaddition. Our recent work showed that the *in situ* formation of tetrazolate could be facilitated in the presence of CuI (not copper(II) salt) as metal catalyst to fabricate a series of unusual cationic CuI aggregates based coordination polymers, namely $[Cu_4I_2(cpta)_2]_n$, $[Cu_6I_2(mtta)_6(CuCN)_2]_n$ and $[Cu_{10}I_4(mtta)_6]_n$ [40].

3. Structural diversity of copper(I) halide aggregates

3.1. General rationales for the structural diversity of copper(I) halide aggregates

Although halides were considered to be the simplest of common ligands, the structural diversity of the chemically simple copper halide coordination systems was far away from comprehensively unveiled: a more fundamental understanding and control of the crystallization process and crystal structure is the prerequisite [12]. The authors state in the following text, three crucial, but not comprehensive, factors that are responsible for the structural variation of copper(I) halide aggregates.

Inner-core variability: This variability arises from the labile coordination numbers and geometries of both copper(I) and halide ions. Copper(I) possesses the coordination numbers of two, three and four, which are related to the typical coordination geometries of linear, trigonal and tetrahedral modes, respectively. Moreover, the redox equilibria between copper(I), mixed copper(I/II) and copper(II) usually occur even in hydro(solvo)thermal conditions where the reduction mechanism dominates [31e]. The coordination configuration of copper(II) ranges from four-connected planar mode to higher coordinating modes such as five-connected pyramid and six-connected octahedron, etc., which complicates the coordination chemistry of copper. Herein, the structural diversity of mixed copper(I/II) and copper(II) halides will be excluded from this review. On the other hand, the strongly coordinating nature of the halide anions, which could act as terminal or μ_2 to μ_8 bridging groups when connected to copper(I) (according to the survey in CSD), contributes significantly to the inner-core variability. Upon combining these two factors, it was no wonder that the simple binary system of copper(I) halides shows such rich structural diversity.

Outer-shell cooperativity: Normally, copper(I) halide aggregates would not occur exclusively in crystals. In the $Cu_xX_yL_z$ (where X = Cl, Br or I; L = N, S or P based organic ligand) system, the coordinating organic components would influence the structures of the copper(I) halide aggregates. This effect further complicates the structural chemistry of copper(I) halide system by turning it into a ternary system, and it was also very important for targeting copper(I) halide based coordination polymers. In crystal engineering, various (even diverse) copper(I) halide aggregates are connected *via* bridging organic ligands to construct infinite coordination architectures. For expatiation, the classical discrete copper(I) halide aggregates only included rhomboid dimer, cubane tetramer and stepped cubane tetramer [1,2,8]. In the early investigation of copper(I) halide based coordination polymers, a richly diverse structural chemistry, such as extended polymeric chains (including split stair, zigzag, helical, staircase, rack and columnar ones), was observed [11,41]. However, the complexity of these examples is little compared to that of those newly attached to this molecular library. For example, an early review stated that neutral 2D copper(I) halide aggregates were not yet documented [11]. Later, such 2D layer-like aggregates were presented by our and other groups [42,43]. It is also noteworthy that the charge, size and shape of the organic components should be taken into account for their cooperative influence on the structures of the copper(I) halide aggregates. A representative example is a colossal cationic $(Cu_{24}I_{10})^{14+}$ cluster sustained by spherical anionic polyoxometalate-based framework [44]. The above named examples will be discussed in detail later in this section.

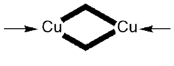
Kinetic tunability: The above two factors could be regarded as thermodynamic considerations, while there exist kinetic influences (especially for the crystallization process) that could not be neglected. It is believed that the formation of the copper halide aggregates involves kinetically fast associative/dissociative equilibria (which leads to the various outcomes for one reaction) and slow crystallization process (which suggests the crystallized species might not be those predominant in the solution in regard to their various solubilities) [12]. Although the final structures of the copper(I) halide aggregates in crystals could hardly be predicted, it has reached the understanding that by careful consideration of the above two processes, the diversity of the copper(I) halide aggregates could be controlled to some degree. The easiest approach to tune the associative/dissociative equilibria was reactant stoichiometry variation, which was demonstrated in early work of targeting $Cu_2I_2py_4$ and (two types of) $Cu_4I_4py_4$ clusters [1,2,8]. In solution, all three derivatives with the structures of rhomboid dimer ($Cu_2I_2py_4$), cubane tetramer ($Cu_4I_4py_4$) and stepped cubane tetramer ($Cu_4I_4py_4$) could exist. A ratio of Cu:I:py = 1:1:1 yielded the major crystalline products of the cubane tetramer along with minor stepped cubane tetramer crystals. However, with the Cu:I:py ratio of 1:1:2, the most common structure was the rhomboid dimer ($Cu_2I_2py_4$). The stoichiometry affected the solution equilibria between three aggregates, making the dominant product seize more opportunities for crystallization. The second process, namely crystallization, could also be tuned; the best example is the utilization of hydro(solvo)thermal techniques. Hydro(solvo)thermal conditions that created high-temperature and high-pressure environments would facilitate the crystallization process, and thus those aggregates with poor solubility would have the chance to be dissolved and crystallized. This might explain why hydro(solvo)thermal reactions usually yielded different resultants from those synthesized via traditional methods (but the thermodynamic stability of the products under hydro(solvo)thermal conditions should also be considered to provide a comprehensive rationale).

3.2. Molecular library of copper(I) halide aggregates: an interpretive but not comprehensive summary

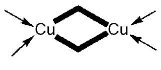
This section cites representative structures of copper(I) halide aggregates, especially for those involved in coordination polymers. The structures were categorized according to the dimensionality and electrostatic charges of the copper(I) halide aggregates (not the resulting coordination polymers). All figures were reproduced by using the original crystallographic data (CIF files) of the complexes. Tables 1–6 summarized the basic information and cross-reference of the cited structures.

3.2.1. Zero-dimensional aggregates

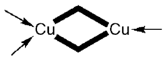
3.2.1.1. Neutral rhomboid dimer and cubane tetramer: the most common types of building blocks. The basic synthon for all copper(I) halides was the rhombohedra with copper and halide atoms at alternate corners, which could be connected or fused by sharing corners or edges to form aggregates with higher nuclearity, such as cubanes, etc. Some common aggregates, including rhomboid (a–c), cubane (d), stepped cubane (e) and open cubane (f), were illustrated as follows. In all charts (not regenerated from the CIF files) showing copper halide synthons (labelled alphabetically), the halide atoms placed at the corners of the rhombohedra were omitted for clarity. The attached arrows showed the possible coordinating modes of these aggregates.



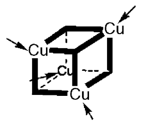
a



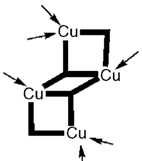
b



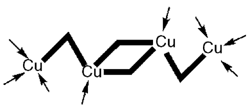
c



d



e



f

The neutral Cu_2X_2 rhomboid dimer (a–c) and Cu_4X_4 cubane tetramer (d) were ususally considered as candidates of secondary building units (SBUs) for constructing higher dimensional coordination polymers because of the existance of the vacant metal coordination sites (shown by the arrows in the above charts). Many crystallographically characterized compounds containing these simple CuX-SBUs are listed in Table 1 [45–49], some of which will be discussed in the following text.

Table 1
Representative common neutral 0D CuX aggregates (Cu_2X_2 and Cu_4X_4) and relating compounds (Sections 3.2.1.1 and 3.2.1.2).

Synthon	Ligand	Compound	Dimensionality	CN(X)	CN(Cu)	Reference
Rhombohedra Cu_2X_2	bmpms	$[Cu_4(bmpms)_2I_4]$	0	2	4	[45a]
	mpmpms	$[Cu_4(mpmpms)_2I_4]$	0	2	3, 4	[45a]
	beap	$[Cu_2I_2(beap)_2]$	0	2	4	[45b]
	1,2-bpsmb	$[Cu_2(1,2\text{-}bpsmb)_2I_2 \cdot CH_3CN]_n$	1	2	4	[16]
	1,3-bpsmb	$[Cu(1,3\text{-}bpsmb)X]_n$ (X = I, Br)	1	2	4	[16]
	1,4-oxathiane	$[Cu_4(1,4\text{-}oxathiane)_4Br_4]_n$	1	2	4	[45c]
	4,4′-bipyridine	$[Cu(4,4'\text{-}bipyridine)X]_n$ (X = Cl, Br, I)	2	2	4	[45d,e]
	bpcae	$[(Cu_2I_2)(bpcae)_2 \cdot (CHCl_3)_3]_n$	2	2	4	[45f]
	qpy	$[qpy \cdot (Cu_2I_2)]_n \cdot 2n(CH_3CN) \cdot H_2O$	2	2	4	[45g]
	qpy	$[qpy \cdot (Cu_2I_2)]_n \cdot 2n(G)$ (G = nbe and cbe)	3	2	4	[45g]
	bpst	$[Cu_2I_2(bpst)_2 \cdot xG]_n$ (G = toluene, $CHCl_3$ CH_2Cl_2)	1, 2	2	4	[49]
	pymMe	$[(CuBr)_3(pymMe)_3]_n$	3	2	4	[45h]
Cubane Cu_4X_4	dadpm	$[(Cu_4I_4)(MeCN)_2(dadpm)]_2 \cdot 2MeCN$	0	3	4	[46a]
	beap	$[Cu_4I_4(beap)_2]$	0	3	4	[45b]
	bpb	$[Cu_4CI_4(bpb)_2] \cdot 3EtOH$	0	3	4	[46b]
	ttt	$[Cu_4Br_4(ttt)_2]_n$	1	2	3	[46c]
	bpds	$[(CuI)2(bpds)]_n$	1	3	4	[13d]
	bpcae	$[Cu_4I_4(bpcae)_2]_n$	2	3	4	[45f]
	dddtd	$[Cu_4I_4(dddtd)_2]_n$	2	3	4	[46d]
	bpp	$[Cu_4I_4(bpp)_2]_n$	3	3	4	[13b]
	$Me_6$12Se3	$[Cu_4I_4(\mu\text{-}Me_6 12Se3)]_n$	3	3	4	[46e]
	hmt	$[(Cu_4I_4)Cu_4(hmt)_4]_n$	3	3	2, 4	[46f]
Step cubane Cu_4X_4	dppm or dpam	$[Cu_4Br_4(L)_2(MeCN)_2]$ (L = dppm, dpam)	0	2, 3	4	[47a]
	dcpm	$[(CuI)_4(dcpm)_2]$	0	2, 4	4	[47b]
	c-(P_5Ph_5)	$[Cu_4Cl_4\{c\text{-}(P_5Ph_5)\}_2]$	0	2, 4	4	[13c]
	quin	$[Cu_4I_4(quin)_4]$	0	2, 3	3, 4	[14b]
	hcc	$[Cu_4I_4(hcc)(CH_3CN)_2]_n$	1	2, 3	4	[47c]
	dmq	$[(dmq)Cu_2Br_2]_n$	1	2, 3	3, 4	[34a]
	tmcta	$[Cu_4I_4(tmcta)_2]_n$	2	2, 3	4	[47d]
Open cubane Cu_4X_4	[12]aneS_4	$[Cu_4Br_4([12]aneS_4)_2]_n$	2	2	4	[48]

Note: CN(X), coordination number of halides; CN(Cu), coordination number of copper(I).

In this category, the most documented 2D coordination polymers featured a (4,4) or (6,3) topology network. The complexes $[Cu_2I_2(bpcae)_2 \cdot (CHCl_3)_3]_n$ (**1**) and $[Cu_4I_4(bpcae)_2]_n$ (**2**) were comprised of Cu_2I_2 rhomboid or Cu_4I_4 cubane aggregates, respectively. Their whole structures exhibited (4,4) topology with obvious distinctions: **1** showed non-interpenetrated layer with elliptical cavities that were occupied by guest molecules, while **2** formed doubly interpenetrated layers with a parallel fashion. Both types of CuI-SBUs (Cu_2I_2 and Cu_4I_4) acted as four-coordinated nodes in the (4,4) network with different square (b) and tetrahedral (d) geometry, respectively, and hence the layer of **2** was more corrugated than that of **1** [45f]. The complexes of $[Cu_2X_2(4,4'\text{-}bipyridine)_2]_n$

Table 2
Representative unusual neutral 0D CuX aggregates and relating compounds (Section 3.2.1.3).

Synthon	Ligand	Compound	Dimensionality	CN(X)	CN(Cu)	Reference
Cu_3X_3	dcpm	$[Cu_3I_3(dcpm)_2]$	0	2, 3	3, 4	[47b]
	dpmt	$[Cu_3X_3(dpmt)_2]$ (X = I, Br, Cl)	0	2, 3	3, 4	[25]
	$[Co\{S_2CN(CH_2)_4\}_3]$	$\{[Co\{S_2CN(CH_2)_4\}_3] \cdot Cu_3Br_3 \cdot MeCN\}_n$	1	2	3, 4	[50]
	ttup	$[Cu_{1.5}(ttup)Cl_{1.5}]_n$	1	2	3, 4	[28]
Cu_4X_4	2,2′-bipyridyl	$Cu_4Cl_4(2,2'\text{-}bipyridyl)_2$	0	2	2, 4	[31b]
	mnt	$\{(NBu^n{}_4)_2[M(mnt)_2Cu_4I_4]\}_n$ (M = Ni, Pd, Pt)	1	2	3, 4	[51a]
	tptmps	$[(tptmps)_2Cu_4I_4]$	0	2	4	[51b]
	dppeSe	$[Cu_4I_4\{dppeSe\}_2]_n$	2	2, 3	4	[51c]
Cu_5X_5	Et_4tms	$[Cu_5(Et_4tms)_2I_5] \cdot EtOH \cdot MeCN$	0	2, 4	4	[52a,b]
Cu_6X_6	m-tolyl$_3$P	$[Cu_6I_6(m\text{-}tolyl_3P)_4(CH_3CN)_2]$	0	2, 3, 4	4	[53a]
	tetpeb	$[Cu_6X_6(tetpeb)_2]_n$ (X = I, Br, Cl)	2	3	4	[53b]
	ttt	$[Cu_6Br_6(ttt)_2]_n$	2	3	4	[46c]
	dimap	$[Cu_6I_6(dimap)]$	0	2, 3	3, 4	[53c]
	bimpms	$[Cu_6I_6(bimpms)_2]_n$	1	2, 3	4	[53d]
	$[Co(S_2CNBu^n{}_2)_3]$	$\{2[Co(S_2CNBu^n{}_2)_3] \cdot 5CuI\}_n$	1	2, 3, 4	4	[50]
	$P(OPh)_3$, trz	$[(Cu_6Cl_6(P(OPh)_3)_6(trz)_2]$	0	2	4	[53e]
	triphos	$[(triphos)CoP_3]_2Cu_6Br_6$	0	2	4	[53f]
	daa	$[Cu_6Cl_6\{daa\}]$	0	2, 3	3, 4	[53g]
	cyclo-(CH_3AsO)	$[Cu_6Br_6(C_6H_5CN)_4\{cyclo\text{-}(CH_3AsO)_4\}]_n$	1	2, 3	3, 4	[17a]
	bta, dmbta	$\{(Cu_{10}I_{10})(Cu_6I_6)[(Cu(bta)_2]^-{}_3 \cdot (dmbta)^+{}_4 \cdot (I^-) \cdot x(I_2)\}_n$	3	2, 3, 4	2, 4	[37]
Cu_8X_8	tptp	$[Cu_4(tptp)(MeCN)I_4]_n \cdot 2nMeCN$	1	2, 3, 4	4	[54]
	dabco	$[(CuI)_7(dabco)_{2.5}]_n$	3	3, 4	3, 4	[32a]
$Cu_{10}X_{10}$	bta, dmbta	$\{(Cu_{10}I_{10})(Cu_6I_6)[(Cu(bta)_2]^-{}_3 \cdot (dmbta)^+{}_4 \cdot (I^-) \cdot x(I_2)\}_n$	3	2, 3, 4	2, 4	[37]
$Cu_{12}X_{12}$	hcc	$\{Cu_{12}I_{12}[Cu(CH_3CN)]_3(hcc)_6\}_n \cdot nCu_3I_6 \cdot nCH_3CN$	3	2, 3, 4	4	[47c]

Table 3
Representative anionic CuX aggregates and relating compounds (Section 3.2.1.4).

Sharing mode	Synthon	Compound	Dimensionality	CN(X)	CN(Cu)	Reference
Single sharing mode						
Conner sharing of 3S	$Cu_2Br_5^{3-}$	$(tma)_3 \cdot Cu_2Br_5$	0	1, 2	3	[55a]
	$Cu_3I_6^{3-}$	$\{Cu_{12}I_{12}[Cu(CH_3CN)]_3(hcc)_6\}_n \cdot nCu_3I_6 \cdot nCH_3CN$	3	1, 2	3	[47c]
	$Cu_4I_6^{2-}$	$[Cu_4I_6][Cu_8I_{13}]K_7(12c4)_6$	0	2	3	[14a]
	$Cu_6Br_{10}^{4-}$	$(tmpa)_4 \cdot Cu_6Br_{10}$	0	1, 2	3	[55b]
Edge sharing of 3S	$Cu_2I_4^{2-}$	$\{CuI_3 \cdot [Cu_3(mstbim)_2]\}_2(Cu_2I_4)$	0	1, 2	3	[55c]
Edge sharing of 4S	$Cu_2Br_4^{2-}$	$(bet)_2Cu_2Br_4$	0	1, 2	4	[56a]
	$Cu_2Br_4^{2-}$	$[(bet)Cu_2Br_4]_n$	1	1, 2	4	[56a]
	$Cu_2Br_6^{4-}$	$(mxda)_2Cu_2Br_6$	0	1, 2	4	[56b]
	$Cu_3I_4^{-}$	$(AsPh_3Me)[Cu_3(AsPh_3)_3I_4]$	0	2, 3	4	[56c]
	$Cu_3I_4^{-}$	$[K(Cu_3I_4)(1,7,13TT18C6)]_n \cdot nCH_3CN$	3	2, 3	4	[17b]
	$Cu_6I_8^{2-}$	$[K(Cu_3I_4)(1,7DT18C6)]_n$	1	2, 4	4	[17c]
	$Cu_6I_{11}^{5-}$	$(tea)_6[Cu_6I_{11}]I$	0	1, 3, 4	4	[56d]
	$Cu_7I_{10}^{3-}$	$[Rb(18c6)][Rb(18c6)(MeCN)_3]_2[\{Rb(18c6)\}_6Cu_4I_7][Cu_7I_{10}]_2$	0	2, 3, 4	4	[29a]
	$Cu_8I_{13}^{5-}$	$[Cu_4I_6][Cu_8I_{13}]K_7(12c4)_6$	0	2, 8	4	[14a]
	$Cu_{36}I_{56}^{20-}$	$(pyH)_{24}([Cu_{36}I_{56}]I_4)$	0	2, 3	4	[56e]
Face sharing of 4S	$Cu_2I_3^{-}$	$[PPh_3Me][(PPh_3)_2Cu_2I_3]$	0	2	4	[56f]
	$Cu_5I_7^{2-}$	$(tpa)_2[Cu_5I_7]$	0	2, 5	4	[56g]
Multiple sharing mode						
Corner sharing of 3S, corner sharing between 3S and 4S	$Cu_3Br_5^{2-}$ and $Cu_4Br_5^{-}$	$[(tpypz)_3Cu_{10}Br_{10}]_n$	2	1, 2	3, 4	[31c]
Edge sharing of 4S and edge sharing between 3S and 4S	$Cu_3I_6^{3-}$	$[Co(Cp)_2]_3Cu_3I_6$	0	1, 2, 3	3, 4	[57a]
	$Cu_4I_7^{3-}$	$[Rb(18c6)][Rb(18c6)(MeCN)_3]_2[\{Rb(18c6)\}_6Cu_4I_7][Cu_7I_{10}]_2$	0	1, 3	4	[29a]
	$Cu_4I_8^{4-}$	$[Co(Cp)_2]_4Cu_4I_8$	0	1, 2	3, 4	[57a]
	$Cu_4I_8^{4-}$	$\{[Cu(2,2\text{-dipyridyl})_2]_2\ Cu_4I_8\}$	0	1, 2, 3	3, 4	[57b]
Edge sharing of 4S and corner sharing between2S and 4S	$Cu_6Br_9^{3-}$	$(mtea)_3[Cu_6Br_9]$	0	2, 4	2, 4	[57c]
Face sharing of 4S and edge sharing between 3S and 4S	$Cu_3I_6^{3-}$	$[tmpa]_3[Cu_3I_6]$	0	1, 2, 3	3, 4	[57d]
Face sharing of 4S and edge sharing of 4S	$Cu_{13}I_{14}^{-}$	$[\{Cs(18c6)\}_6Cu_4I_7][Cs_3(18c6)_3][Cu_7I_{10}][Cu_{13}I_{14}]I_2$	0	2, 3, 7	4	[29b]
Edge sharing of 4S, edge sharing of 3S as well as between 3S and 4S	$Cu_8I_{10}^{2-}$	$[Cs_2(18c6)_3][Cu_8I_{10}(MeCN)_2]$	0	2, 3	3, 4	[29b]
Edge sharing of 4S, edge sharing between 3S and 4S, and conner sharing of 3S as well as between 3S and 4S	$Cu_5I_6^{-}$	$[Cs(18c6)_2][Cu_5I_6(MeCN)_2]$	0	2, 3	3, 4	[29b]
	$Cu_6I_{10}^{4-}$	$[Cu_3(apl)_4]_2[Cu_6I_{10}] \cdot DMF$	0	1, 2, 3	3, 4	[57e]

Note: 2S, Linear synthon; 3S, triangular synthon; 4S, tetrahedral synthon.

Table 4
Representative cationic CuX aggregates and relating compounds (Section 3.2.1.5).

Synthon	Ligand	Compound	Dimensionality	CN(X)	CN(Cu)	Reference
Cu_3X^{2+}	dppm, $S_2P(OEt)_2$	$[Cu_3(dppm)_3Cl)S_2P(OEt)_2](PF_6)$	0	3	4	[58a]
$Cu_3X_2{}^{+}$	dppm	$Cu_3(dppm)_3Br_2ClO_4\cdot 2THF$ and $Cu_3(dppm)_3I_2I\cdot 2CH_2Cl_2\cdot CH_3OH$	0	3	4	[26]
$Cu_4X_2{}^{2+}$	cpta	$[Cu_4I_2(cpta)_2]_n$	3	3	4	[40]
$Cu_5X_3{}^{2+}$	dmaemamp	$Cu_5X_3(dmaemamp)_2$	0	2, 3	3, 4	[58b]
$Cu_5X_4{}^{+}$	viph	$[Mg(THF)_6][Cu_5(viph)_2Br_4]_2\cdot THF$	0	2	2, 3	[58c]
Cu_6X^{5+}	dppm, $S_2P(O\mathit{i}Pr)_2$	$[Cu_6(dppm)_2Cl\{S_2P(O\mathit{i}Pr)_2\}_4](BF_4)$	0	4	3, 4	[58a]
$Cu_6X_2{}^{4+}$	mptmsa	$Cu_6X_2(mptmsa)_2\cdot Et_2O$	0	2	2, 3	[58d]
$Cu_6X_2{}^{4+}$	mtta	$[Cu_6I_2(mtta)_6(Cu_2CN)_2]_n$	3	4	3, 4	[40]
$Cu_6X_3{}^{3+}$	4-pytz	$[Cu_6Cl_3(4\text{-}pytz)_3]_n$	3	3, 4	3, 4	[38]
$Cu_6Cl_4{}^{2+}$	tmtach	$[Cu_6Cl_4(tmtach)_4](BF_4)\cdot CH_2Cl_2$	0	2, 3	3, 4	[58e]
Cu_8X^{7+}	$Se_2P(OR)_2$ (R = Et, Pr, *i*Pr)	$Cu_8Cl[Se_2P(OR)_2]_6(PF_6)$ (R = Et, Pr, *i*Pr)	0	8	4	[27]
$Cu_{10}X_4{}^{6+}$	mtta	$[Cu_{10}I_4(mtta)_6]_n$	3	2, 6	4	[40]
$Cu_{13}Cl_6{}^{7+}$	PMe_2	$[Cu(PMe_3)_4]_2[Cu_{13}Cl_6(PMe_2)_9]$	0	1	2, 3	[58f]
$Cu_{14}Cl_2{}^{12+}$	PPh, PMe_3	$Cu_{14}(PPh)_6Cl_2(PMe_3)_8$	0	1	2, 3, 4	[58f]
$Cu_{24}X_{10}{}^{14+}$	typt	$\{[Cu_{24}I_{10}(typt)_{12}][PMo^{V}{}_2Mo^{VI}{}_{10}O_{40}]_3(NH_4)\}_n$	3	4, 6	4	[44]

Table 5
Representative 1D CuX aggregates and relating compounds (Section 3.2.2).

1D Synthon	Ligand	Compound	Dimensionality	CN(X)	CN(Cu)	Reference
Single chain	pyz	$[CuCl(pyz)]_n$	1	2	4	[19]
	pyd	$[CuCl(pyd)]_n$	2	2	4	[18]
	apyd	$[CuBr(apyd)]_n$	2	2	4	[59a]
	dtpcp	$[CuI(dtpcp)]_n\cdot nMeCN$	2	2	4	[59b]
	cyclo-$(MeAsO)_4$	$[Cu_3X_3\{cyclo\text{-}(MeAsO)_4\}_2]_n$ (X = Br, Cl)	3	2	4	[59c]
Double chain	quxin	$[(CuI)_2(quxin)]_n$	2	3	4	[41]
	bbol	$Cu_2I_2(bbol)_n$	1	3	4	[60a]
	psmq	$[Cu_3I_3(psmq)(CH_3CN)]_n$	2	3	4	[60b]
	mcn	$[CuBr(mcn)]_n$	1	2, 3	4	[60c]
	dpiz	$[(CuCl)_2(dpiz)]_n$	1	2, 3	3, 4	[39b]
	meda or eeda	$[CuI_2(L)]_n$ (L = meda, eeda)	1	2	4	[32b]
Looped chain	$[CpMo(CO)_2]$	$[[CpMo(CO)_2]_2(\eta^2\text{-}Sb_2)(CuI)]_n$	1	2, 3	5	[61]
	dmasa	$[CuI(dmasa)]_n$	1	2, 3	3, 4	[53c]
	et	$\{[Cu_4Br_6et](et)_2\}_n$	1	2	3, 4	[56a]
	bipypz	$[Cu_3Cl_3(bipypz)]_n$	2	2, 3	3, 4	[20]
Helical chain	bpp	$[Cu_2Br_2(bpp)]_n$	2	2	3	[21]
	tmtttf	$[(Cu_2Br_2)(tmtttf)]_n$	2	2	4	[62a]
	dpey	$[CuBr(dpey)]_n$	3	2	4	[62b]
	hcc	$[Cu_2Br_2(hcc)CH_2Cl_2]_n$ and $[Cu_2Br_2(hcc)]_n$	3	2	4	[47c]
		$[Cu_2I_3]_n\cdot n(tptpy)$	1	2, 3	4	[62c]
	$[Cs(1,10DT18C6)_2]$	$[Cs\{Cu_5I_6(1,10DT18C6)_2\}]_n$	3	2, 3	2, 4	[22]
Ribbon	pyz	$[(CuX)_2(pyz)]_n$ (X = Cl, Br)	2	3	4	[19]
	2,2′-bipy	$[Cu_3I_3(2,2'\text{-}bipy)]_n$	1	3, 4	4	[31d]
	2,2′-bipy	$[Cu_4I_4(2,2'\text{-}bipy)]_n$	1	3, 4	4	[31d]
	dpiz	$[(CuBr)_3(dpiz)]_n$	1	3	3, 4	[39b]
	biz	$[(CuI)_2(biz)]_n$	1	3, 4	4	[15]
	$[Cu_2(OH)_2(2,2'\text{-}bipy)_2]$	$\{[Cu_2(OH)_2(2,2'\text{-}bipy)_2][Cu_4Br_6]\}_n$	2	2, 4	4	[57b]
Column	trz	$[Cu_3X_3(trz)]_n$ (X = Br or I):	3	3	4	[42]
	trz	$[Cu_2Br_2(trz)]_n$	3	3	4	[42]
Unusual		$[Cu_4I_6]_n\cdot nK_2(15C5)_2$	1	2, 3	4	[14a]
		$[Cu_3I_4]_n\cdot nK(db\text{-}24C8)$	1	2, 3, 4	3, 4	[14a]
	$EtS\text{-}4\text{-}C_5H_4NEt$	$[(Cu_3I_4)(EtS\text{-}4\text{-}C_5H_4NEt)]_n$	1	2, 3	4	[36a]
	$[Rb(1,10DT18C6)_2]$	$[Rb\{Cu_4I_5(1,10DT18C6)_2\}]_n$	2	2, 3	3, 4	[22]
	dmiz	$[(CuCl)_2(dmiz)]_n$	1	3, 4	4	[39a]
	NEt_3	$[Cu_4I_4(NEt_3)_3]_n$	1	3, 4	4	[63a]
		$[Cu_3Br_7]_n\cdot 2nH_2quinine\cdot nH_2O$	1	1, 2	4	[63b]
		$[Cu_5Cl_9]_n\cdot 2nH_2quinine$	1	1, 2	3, 4	[63b]
	$[Cu^{II}{}_4(OH)_4(1,10\text{-}phen)_4]$	$\{[Cu_8Br_{12}]_n[Cu^{II}{}_4(OH)_4(1,10\text{-}phen)_4]\}_n$	1	1, 2, 3	3, 4	[63c]
		$[Cu_3X_6]_n\cdot 3nHpy$ (X = Br, Cl)	1	1, 2	3, 4	[63d]
		$[Cu_9Cl_{16}]_n\cdot n\{[H_3NMe]_6Cl\cdot[H_3NMe]_2\}$	1	1, 2, 3	3, 4	[23]
		$[Cu_2Br_3]_n\cdot n\{Cu(H\text{-}Leof)_2\cdot 2H_2O\}$	1	2, 3	3, 4	[63e]
	$[Cu(2,2'\text{-}bipy)_2]$	$\{[CuCl_2][Cu(2,2'\text{-}bipy)_2]\}_n$	1	2	2, 4	[63f]
	$[(moep)(cp)_2MnCl]$	$\{[Cu_9Cl_{11}]_{0.5}[(moep)(cp)_2MnCl]\}_n$	1	2, 3	2, 4	[63g]
		$[Cu_4Cl_6]_n\cdot n(paraquat)$	1	2, 3	2, 3, 4	[63h]
	ap	$[Cu_2Cl_3(ap)]_n$	1	1, 2, 3	3, 4	[63i]
	pz	$[Cu_3Cl_2CNpz]_n$	3	3	3, 4	[63j]

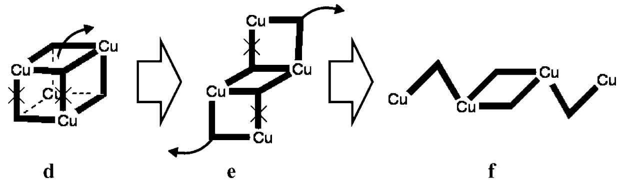
Table 6
Representative 2D and 3D CuX aggregates and relating compounds (Section 3.2.3).

Synthon	ligand	Compound	Dimensionality	CN(X)	CN(Cu)	Reference
2D (6,3) net	CO	$[CuCl(CO)]_n$	2	3	4	[64a]
	mbd	$[Cu_2Cl_2(mbd)]_n$	2	3	4	[64b]
	fdn	$[Cu_2Cl_2(fdn)]_n$	3	3	4	[64c]
	trz	$[Cu_2I_2(trz)]_n$	3	3	4	[42]
	bpsmb	$\{[Cu_6I_5(bpsmb)_3](BF_4)\cdot H_2O\}_n$	3	2, 3	4	[43]
	A46	$[Cu_2Br_4(A46)_2]_n$	2	2	4	[34b]
	$C_{10}H_{10}Co$	$[(Cu_{12}I_{16})\cdot(Cu_6I_{11})\cdot(C_{10}H_{10}Co)_9]_n$	2	3, 4, 5	4	[64d]
2D (4,4) net	lip	$[Cu_3(lip)_2Cl_3]_n$	2	2, 4	4	[65]
2D $(4,8^2)$ net	ody	$[Cu_3Cl_3(ody)_2]_n$	2	2, 3	3, 4	[66]
2D (4,6,8)(6,6,8)	pyz	$[(CuI)_2(pyz)]_n$	2	3	4	[67]
2D others	$dams^+$	$\{[Cu_5I_6](dams^+)\}_n$	2	4	4	[68]
	ahp	$[Cu_3Br_4(ahp)]_n$	2	2, 3, 4	4	[34c]
3D diamond	PhCN	$[(CuI)_2(PhCN)]_n$	3	3, 4	4	[69]
	4-S-pyd	$[Cu_{10}Cl_{10}(4\text{-}S\text{-}pyd)_4]_n$	3	2, 4	4	[36b]
		$\{Cu_7Cl_{11}[Cu(en)_2]_2\}_n$	3	2, 3	4	[32c]

(X = Cl, Br, I) (**3**–**5**) featured a series of unusual mutual interpenetrating (6,3) sheets, in which the binuclear Cu_2I_2 units played the role of three-connected nodes (c). The linear 4,4′-bipyridine ligands connected these nodes to complete the hexagonal rings in the (6,3) nets, which further constructed the triple interlocking 3D framework [45d,e].

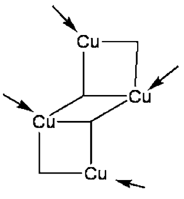
Some regular 3D coordination polymers could be constructed from the rigid tetrahedral Cu_4I_4 building units (d). The complex $[Cu_4I_4(\mu\text{-}Me_612Se3)]_n$ (**6**) existed as a common doubly interpenetrated 3D diamondoid architecture, which contained the four-connected Cu_4I_4 cubane tetramers [46e]. The complex of $[Cu_4I_4(bpp)_2]_n$ (**7**) showed a rare chiral triple-interpenetrated quartz net with the vertex symbol of $6^4.8^2$. In this quartz net, the four-connected tetrahedral Cu_4I_4 nodes were connected by the ditopic bpp linkers to form helical subchain motifs with six-fold screw axes along the *c*-axis direction, which were interwoven to generate pseudo-hexagonal channels [13b]. More recently, semi-regular nets constructed from the tetrahedral Cu_4I_4-SBUs were also reported, including an unprecedented (3,4)-connected jph-type framework, namely $[(Cu_4I_4)Cu_4(hmt)_4]_n$ (**8**), in which the Cu_4I_4-SBUs connected alternating left- and right-handed helices. In this network, the Cu_4I_4-SBUs served as tetrahedral four-connected nodes while the hmt ligands acted as triangular three-connected nodes [46f].

Some unusual structural features were observed in CuX-SBUs based coordination polymers. For example, a 2D coordination polytube $[(Cu_2I_2qpy)\cdot 2(CH_3CN)\cdot H_2O]_n$ (**9**) described by Fujita et al., composed of four-connected Cu_2I_2 aggregates (b) and conformationally helicated qpy ligand, was shown to possess the affinity for guest inclusion. Upon templation with different aromatic guest molecules such as nitrobenzene (nbe) and cyanobenzene (cbe), two 3D polytubes, namely $[(Cu_2I_2qpy)\cdot 2(nbe)]_n$ (**10**) and $[(Cu_2I_2qpy)\cdot 2(cbe)]_n$ (**11**), were obtained. The different inclusion molecules drastically influenced the overall structures. However, the Cu_2I_2 aggregate retained the four-connected planar configuration, showing the rigidity and stability of this type in constructing coordination polymers [45 g]. This feature was also indicated by a pair of reported topological isomers, namely $[Cu_4I_4(bpds)_2]_n$ (**12** and **13**), which were triggered by the solvent-induced ligand conformational variation. The tetrahedral Cu_4I_4 cubane aggregates (d) stayed stable and were linked to give either necklace or tubular coodination polymers [13d]. Our recent work further confirmed the ability and enriched the diversity of the Cu_2I_2 rhomboid aggregate in illustrating supramolecular isomerism based on a series of solvent-dependent Cu_2I_2 based pseudo-polymorphs, namely $[Cu_2I_2(bpst)_2\cdot xG]_n$ (**14**–**16**) (G = none, toluene, $CHCl_3$ or CH_2Cl_2), with various structures ranging from 1D double chains, 1D ribbon to 2D layer [49].



3.2.1.2. Neutral stepped cubane and open cubane tetramers: their deforming structural relationship. The Cu_4X_4 stepped cubane (e) [13c,14b,34a,47] and open cubane (f) [48] tetramers were less common than, but both derived from, the normal cubane tetramer (d). The stepped cubane (e) could be envisioned as the deformation of the normal cubane (d) by breaking two *trans*-Cu–X bonds located in the same face of the cubane tetramer and bending the free rhombohedra to fulfill the chair conformation. The cleavage of the two Cu–X bonds created two more coordinating vacancies for the tetrahedral copper(I) ions in the stepped cubane tetramer, warranting this Cu_4X_4 aggregate to act as six-connected SBUs in constructing coordination polymers. The open cubane (f) was further derived from the stepped cubane (e) by breaking two more Cu–X bonds in the terminal rhombohedra to release two pairs of Cu–X–Cu linkages. This configuration was rarely documented [48]: the Cu_4X_4 aggregate contained two terminal tetrahedral copper(I) ions with three vacant coordinating sites, and the whole aggregate could be viewed as an eight-connected SBU.

The above mentioned deformed Cu_4I_4 cubane tetramers were crystallograpically documented in some structures of coordination polymers. The 1D ribbon structure, namely $[Cu_4I_4(hcc)(CH_3CN)_2]_n$ (**17**), was isolated with tetradentate fused pyridazine ligands (hcc) bridging Cu_4I_4 stepped cubane tetramers (e) constituted of three fused Cu_2I_2 rhombohedra. The tetramer was connected with four pyridazine-N atoms from two hcc ligands and two terminal acetonitrile ligands to complete the six-connected configuration [47c]. The structure of $[Cu_4Br_4([12]aneS_4)_2]_n$ (**18**) revealed a 2D network containing the rare fragment of Cu_4Br_4 open cubane tetramer (f). The triple coordination requirements of the terminal copper atoms of Cu_4Br_4 open cubane moiety were satisfied by three sulfur donors from one macrocycle, and the remaining free sites of the central copper atoms were completed by the fourth sulfur atom of another macrocycle, giving a whole polymeric structure with (4,4) topology [48].



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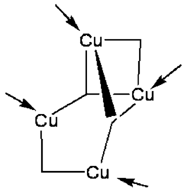

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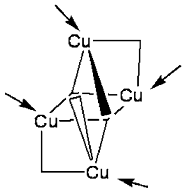

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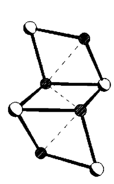

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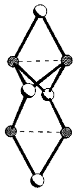

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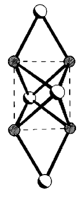

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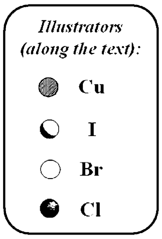
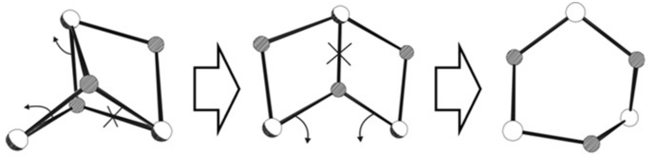


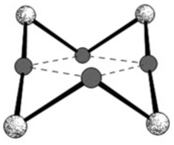
There were further deforming structural documentations about the stepped cubane tetramers (e, g, h). In **17**, the Cu_4X_4 stepped cubane tetramer (e) displayed a parallelogram with four copper(I) atoms. As shown in the above figure, the two copper(I) atoms with the same configuration (connected with two or three bridging iodide atoms) were placed at the diagonal of the parallelogram [47c]. In contrast, in the complex of $[Cu_4I_4(quin)_4]$ (**19**), a distorted form of Cu_4X_4 stepped cubane tetramer (g) was observed, which contained a similar bridging parallelogram, but with the same-configuration copper(I) atoms (connected with two or three bridging iodide atoms) located at the same short sides (top side with three-connected copper(I); down side with two-connected one) of the parallelogram. [14b] Both of the above tetramers contained μ_2- and μ_3-bridging iodide ligands. Another distorted Cu_4X_4 stepped cubane tetramer (h) was observed in $[Cu_4Cl_4\{c\text{-}(P_5Ph_5)\}_2]$ (**20**). In this tetramer, the four copper(I) atoms, arranged in a rectangular array with sound Cu···Cu contacts, were all three-connected and bounded by μ_2- or μ_4-bridging iodide atoms. The dicapping crown-like c-(P_5Ph_5) ligand was responsible for the shape-bounding of this unusual deformed tetramer [13c]. A related deformed tetramer (h) was observed in the complex of $[Cu_4I_4(dcpm)_2]$ (**21**) [47b]. Herein (**17**, **19**, **20**) and in the text below, the actual configuration of the copper(I) halide aggregates were reproduced by using the original crystallographic data (CIF files) of the complexes. The illustrators in the inserted box of the above figure showed the representative atoms of Cu, I, Br and Cl, respectively, in the following figures along the text.

3.2.1.3. Unusual neutral Cu_nX_n (n = 3–12) aggregates: from low to high nuclearity. Compared with the above named relatively common neutral aggregates such as Cu_2X_2 dimer and Cu_4X_4 tetramers, coordination architectures constructed by discrete high-nuclear Cu_nX_n clusters (n > 4) were less documented. In this section some unusual neutral Cu_nX_n aggregates (n = 3–12) were discussed in light of their nuclearity (from low to high) and structural relationship. Listed in Table 2 [50–54] were some of the crystallographically characterized compounds containing these unusual Cu_nX_n aggregates.



22 **23 – 25** **26, 27**

Cu_3X_3: The above three illustrated Cu_3X_3 aggregates were structurally related. In a discrete compound $[(Cu_3I_3(dcpm)_2]$ (**22**), there existed a Cu_3I_3 distorted octahedron, in which the three copper(I) atoms were arranged in trigonal-planar array bounded by two dicapping μ_3- and one μ_2-bridging iodide atoms [47b]. One type of deformed Cu_3X_3 aggregate, which was found in a series of discrete compounds $[Cu_3X_3(dpmt)_2]$ (X = I, Br, Cl) (**23**–**25**), could be envisioned as a "three-runged ladder" structure by breaking one Cu–X bond and repositing the two associated Cu–X bonds in the distorted Cu_3X_3 octahedron in **22** [25]. Similarly, by simply breaking the middle Cu–X bond and repositing the two associated Cu–X bonds in the Cu_3X_3 "three-runged ladder" in **23**–**25**, another deformation of the Cu_3X_3 aggregates was generated, which exhibited a six-membered cyclic Cu_3X_3 array (with alternating copper and halogen atoms) with a quasi-boat conformation. This type of Cu_3X_3 aggregate was presented in two reported 1D coordination polymers, namely, $\{Cu_3Br_3[Co\{S_2CN(CH_2)_4\}_3]\cdot MeCN\}_n$ (**26**) [50] and $[Cu_3Cl_3(ttup)_2]_n$ (**27**) [28]. The diverse supporters with suitable bridging length and spatial arrangement were presumably responsible for the very divergent conformation of the trinuclear Cu_3X_3 units.



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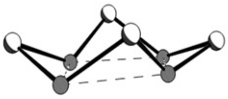

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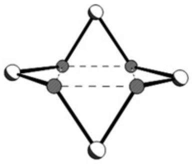

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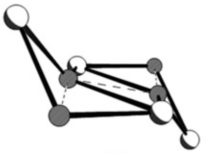

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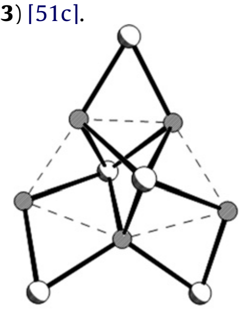
Cu_4X_4: The eight-membered ring was considered to be another isomeric form of the Cu_4X_4 cubane-series aggregates discussed above. There were five complexes, namely $[Cu_4Cl_4(2,2'\text{-bipyridyl})_2]$ (**28**) [31b], $\{(NBu^n{}_4)_2[M(mnt)_2Cu_4I_4]\}_n$ (M = Ni, Pd, Pt) (**29**–**31**) [51a], and $[Cu_4I_4(tptmps)_2]$ (**32**) [51b], that contained this type of Cu_4X_4-ring aggregate. As shown in the figures, aggregates **28**, **29**–**31** and **32** consisted of perfectly planar Cu_4 parallelograms. The differences lay in the positions of the iodide atoms related to the Cu_4 planes. In **28**, the four μ_2-Cl ions were evenly distributed with two adjacent ones upwards while the other two downwards to the plane. In **29**–**31**, instead, all the four μ_2-I ions were located above the plane, featuring a crown-like shape. Interestingly, in **32**, two μ_2-I ions and the Cu_4 parallelogram formed a six-membered planar plane, where the other two μ_2-I ions lay up and down respectively. No obvious Cu···Cu bonding exists in these complexes, because the short Cu···Cu distances were mainly determined by the spatial arrangement and bridging length of the ligands and the electronic properties of the bridging anions. Another form of the Cu_4X_4 aggregates should be highlighted, which featured a rare stepped zig-zag oligomer-SBU where both μ_2- and μ_3-bridging iodide atoms were located. This Cu_4I_4 aggregate could be regarded as the fusion of three Cu_2I_2 rhomboid dimmers. It was confirmed in the structure of a 2D (4,4)-net coordination polymer, namely $[Cu_4I_4(dppeSe)_2]_n$ (**33**) [51c].



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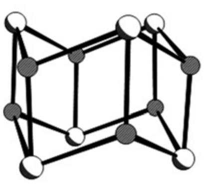
Cu_5X_5: There was only one example of Cu_5X_5 aggregate hitherto documented in the literature, namely, $\{[Cu_5I_5(Et_4tms)_2]\cdot EtOH\cdot MeCN\}$ (**34**) [52]. The structure of this aggregate might be described as a distorted pentagonal bipyramid, in which the five copper(I) ions formed the distorted five-membered basal plane while two μ_4-bridging iodide ions occupied the apical positions. Additionally, three other μ_2-bridging iodide ions and two Et_4tms ligands were unevenly fused to the distorted pentagonal bipyramid to support this configuration.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Cu_6X_6: The structures of the Cu_6X_6 aggregates varied from cages, rings to ladder-like oligomers. A prestigious member of the Cu_6X_6 cage-like aggregates was first found in a 2D coordination polymer in 2002, namely $[Cu_6Br_6(ttt)_2]_n$ (**35**). This prism-like Cu_6Br_6 aggregate was similar to the double six-membered rings (D6R, hexagonal prisms) found in zeolites: the two face-to-face six-membered Cu_3I_3 chair-rings were alternatingly arranged, and were connected by six pairs of perpendicular alternating Cu–I bonds [46c]. Later, in 2005, similar typs of Cu_6X_6 cage-like aggregates were documented in another series of 2D structures, namely $[Cu_6X_6(tetpeb)_2]_n$ (X = I, Br, Cl) (**36**–**38**) [53b]. Another member of the Cu_6X_6 cage-like aggregates, the unprecedented bicapped adamantoid cage-like Cu_6I_6 cluster, was reported in 2004, which was then involved in a discrete compound $[Cu_6I_6(m\text{-}tolyl_3P)_4(CH_3CN)_2]$ (**39**). The Cu_4I_6 "adamantane" was composed of four six-membered Cu_3I_3 chair-rings, while the other two copper(I) ions were positionally disordered, occupying four Cu_3I_3 faces and acting as capping atoms [53a]. Most recently, in 2008, our group reported a unique 3D coordination polymer, namely, $\{(Cu_{10}I_{10})(Cu_6I_6)[(Cu(bta)_2]^-{}_3\cdot(dmbta)^+{}_4\cdot(I^-)\cdot x(I_2)\}_n$ $(x\approx 1.5)$ (**40**), which contained this similar type of bicapped adamantoid Cu_6I_6 cluster. Compared with the previous documentation, the Cu_4I_6 "adamantane" was slightly distorted. It was the first time that such unusual neutral high-nuclear Cu_nX_n aggregates, Cu_6I_6 and $Cu_{10}I_{10}$ (which will be discussed later), acted as SBUs for constructing cluster-based coordination polymers [37].


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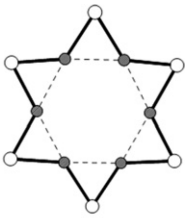
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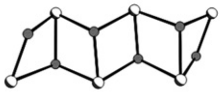
The Cu_6X_6 ring-like aggregates were very rare and have never been observed in coordination polymers. The discrete complex $[(Cu_6Cl_6(P(OPh)_3)_6(trz)_2]$ (**41**) revealed a 12-membered puckered oblate spheroid Cu_6Cl_6 core, which was templated by the μ_3-triazine ligands and bounded peripherally by the bulky terminal triphenyl phosphite ligands [53e]. Another interesting example of the Cu_6X_6 ring-like aggregates was found in a discrete complex, namely $\{Cu_6Br_6[(triphos)CoP_3]_2\}$ (**42**), which exhibited a unique Cu_6Br_6 hexagram structure where the six copper(I) ions defined the inner hexagon while the six bromide ions occupied the outer hexagon [53f]. The formation of these macrocycles for the copper(I) halide aggregates was configurationally unfavored, apparently requiring the direction of templating agents or capping ligands to occupy the central positions of the macrocycles.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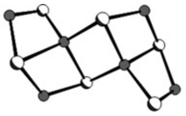
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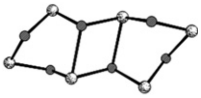
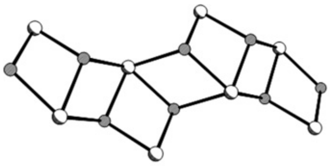

46, 47

The Cu_6X_6 ladder-like oligomers were not regular and might have randomly appeared. A common Cu_6X_6 step-like hexamer, which could be considered as derived from the Cu_6X_6 D6R hexagonal prism (in **35**–**38**) by breaking two parallel Cu–X bonds of the D6R, was observed in a discrete complex $[Cu_6I_6(dimap)]$ (**43**) [53c], and a 1D ribbon-like coordination polymer $[Cu_6I_6(bimpms)_2]_n$ (**44**) [53d]. Additionally, a non-linear Cu_6X_6 ladder-like aggregate was involved in a 1D double-stranded chain-like coordination polymer, namely, $\{2[Co(S_2CNBu^n{}_2)_3]\cdot 5CuI\}_n$ (**45**) [50], while the Cu_6X_6 mixed ring/ladder (6-4-6-membered ring) aggregate was included in the structure of oligomeric $[Cu_6Cl_6\{daa\}]$ (**46**) [53g] and polymeric (1D) $\{Cu_6Br_6(C_6H_5CN)_4[cyclo\text{-}(CH_3AsO)_4]\}_n$ (**47**) [17a].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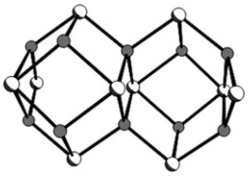
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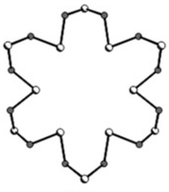
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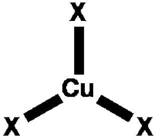
Cu_8X_8, *$Cu_{10}X_{10}$* and *$Cu_{12}X_{12}$*: Neutral Cu_nX_n aggregates with nuclear numbers higher than eight were considered to be extremely large SBUs. The structure of a 2D undulating layered coordination polymer, $\{[Cu_8I_8(tptp)_2(MeCN)_2]\cdot 2MeCN\}_n$ (**48**), contained the Cu_8I_8 ladder-like oligomer substructure. This Cu_8I_8 ladder was not linear—it could be viewed as the zig-zag fusion of three Cu_4I_4 stepped cubanes by sharing the terminal Cu_2I_2 dimers [54]. Another Cu_8I_8 aggregate was simply constructed by linking two reverse Cu_4I_4 cubane tetramers via a pair of parallel alternating Cu–I bonds. This Cu_8I_8 cluster, along with the previous shown D6R Cu_6I_6 cluster (in **35**–**38**), builded up a pair of 3D isomeric coordination polymers, namely $[(Cu_8I_8)(Cu_6I_6)(dabco)_5]_n$ (**49a**–**b**) [32a]. In a unique 3D coordination polymer recently reported by our group, namely, $\{(Cu_{10}I_{10})(Cu_6I_6)[(Cu(bta)_2]^-{}_3\cdot(dmbta)^+{}_4\cdot(I^-)\cdot x(I_2)\}_n$ $(x\approx 1.5)$ (**40′**), two types of high-nuclear CuI-SBUs were found—the previous mentioned bicapped adamantoid Cu_6I_6 cluster and the unprecedented "S-shaped-double-bowl" $Cu_{10}I_{10}$ cluster. This $Cu_{10}I_{10}$ S-shaped double bowl could be described as the splitting of a distorted rhombic dodecahedron by adding an inverse center in one face of the dodecahedron [37]. The highest nuclearity for neutral Cu_nX_n aggregates was presented in a 3D coordination polymer, $\{Cu_{12}I_{12}[Cu(CH_3CN)]_3(hcc)_6\cdot Cu_3I_6\cdot CH_3CN\}_n$ (**50**). These inorganic

crown-ether-like $Cu_{12}I_{12}$ rings stacked face to face with each other to form hexagonal tubes (inner diameter *ca.* 4.1 Å), which were further extended via tetradentate fused pyridazine ligands (hcc) to complete the 3D framework. Surprisingly, the configurationally unfavored 24-membered rings were not directly bonded by any template agent; instead, discrete anionic $Cu_3I_6^{3-}$ aggregates and acetonitrile solvent molecules were involved in the tubes. The strong rigidity and planarity of the fused pyridazine ligand might by responsible for the uniqueness of this crown-ether-like $Cu_{12}I_{12}$ aggregate [47c].

3.2.1.4. Anionic Cu_xX_y ($x < y$) aggregates: isolated "halocuprate complexes". The investigation of the anionic copper(I) halide aggregates was a historic topic termed as "halocuprate complexes" in crystal engineering during 1980s to 1990s. As mentioned in the Introduction, the structural diversity of such anionic aggregates was reviewed by Arnby et al. [12], and hence related aggregates and complexes will not be discussed in detail herein. Moreover, most of the anionic copper(I) halide aggregates existed as isolated compounds, rather than serving as SBUs in coordination polymers, which also contradicted the main point of this review to comment on CuX-based coordination polymers.

Linear Synthon (2S)

i



Triangular Synthon (3S)

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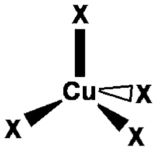
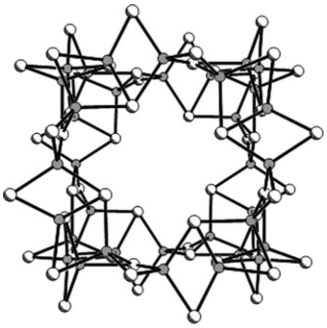


Tetrahedral Synthon (4S)

k

Still, we note that nearly all the anionic copper halide aggregates were derived from the corner/edge/face sharing modes of three simple anionic synthons, namely, linear CuX_2^- anion (i), planar triangular CuX_3^{2-} anion (j) and tetrahedral CuX_4^{3-} anion (k). The largest anionic copper(I) halide aggregate by far was the colossal $Cu_{36}I_{56}^{20-}$ macrocycle which was found in the complex $[(Cu_{36}I_{56})I_4(pyH)_{24}]$ (**51**) [56e]. Table 3 [55–57] cites some of the crystallographically characterized compounds containing anionic copper(I) halide aggregates derived from the three simple synthons.



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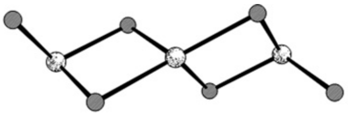
3.2.1.5. Cationic Cu_xX_y ($x > y$) aggregates: the most unusual types of building blocks. Compared with the extensively investigated neutral and anionic species, the formation and structures of cationic copper(I) halide aggregates remained unexplored. Only a few cationic Cu_xX_y ($x > y$) clusters were reported, which were mostly isolated by anionic organic ligands containing P, S, Se or As donors. Examples that showed the cationic Cu_xX_y ($x > y$) aggregates serving as SBUs in coordination polymers were sporadic. Herein the authors wished to briefly discuss those involved in coordination polymers, because the number of the examples was too limited to demonstrate general structural features. Table 4 [58] listed some representative cationic copper(I) halide aggregates (including isolated ones).



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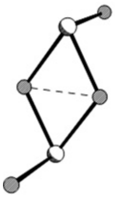

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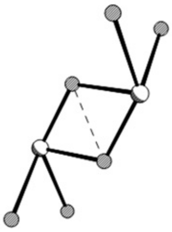

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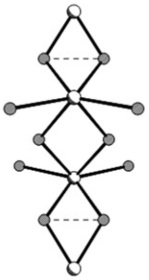

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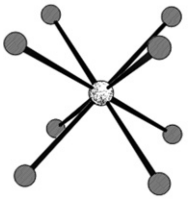
There were two representative examples for illustrating simple cationic CuX-SBU-based coordination polymers. In a systematic investigation on copper(I) triazolates-related complexes shown by Chen et al., one of the targeted complexes, namely $[Cu_6Cl_3(4\text{-}pytz)_3]_n$ (**52**)—a 3D coordination polymer, involved the cationic $Cu_6Cl_3^{3+}$ cluster with unusual μ_3- and μ_4-Cl bridging modes. The $Cu_6Cl_3^{3+}$ aggregate could be viewed as a Cl-vertex-sharing rhomboid fusion terminated by two copper(I) ions, which was stabilized by the coordination of the deprotonated anionic pytz ligands to yield the neutral 3D coordination polymer [38]. Another example was reported by our group recently, in which a series of unprecedented cation copper(I) iodide aggregates, $Cu_4I_2^{2+}$, $Cu_6I_2^{4+}$ and $Cu_{10}I_4^{6+}$ were trapped in the *in situ* formation of anionic-tetrazolate-based coordination polymers, namely $[Cu_4I_2(cpta)_2]_n$ (**53**), $[Cu_6I_2(mtta)_6(Cu_2CN)_2]_n$ (**54**) and $[Cu_{10}I_4(mtta)_6]_n$ (**55**), respectively. These series of cationic aggregates were also derived from the simple neutral Cu_2I_2 rhombohedra via sharing iodide ions and terminating copper(I) ions, and the versatile iodide anions, with μ_3-, μ_4- or μ_6-bridging modes, were responsible for the formation of such unusual aggregates [40].



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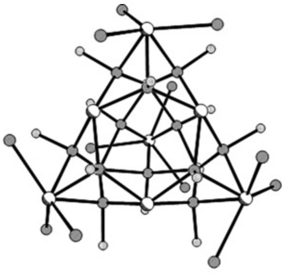

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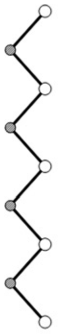
For more sophisticated examples of cationic copper(I) halide aggregates, one could find the documentation of a μ_8-Cl-centered cube-like Cu_8Cl^{7+} cluster, which was bounded in a series of discrete compounds, namely, $\{Cu_8Cl[Se_2P(OR)_2]_6(PF_6)\}$ (**56**–**58**) (R = Et, Pr, ^{i}Pr) [27]. A nanometer-scale $Cu_{24}I_{10}^{14+}$ cage assembled in an intriguing (4,12)-connected 3D coordination polymer, namely, $\{[Cu_{24}I_{10}(typt)_{12}][PMo^V{}_2Mo^{VI}{}_{10}O_{40}]_3(NH_4)\}_n$ should also be highlighted (**59**). A detailed description of this unprecedented aggregate could be found in the original paper by Wang et al. The formation of this colossal cationic motif was shape and charge dependant by the introduction of the anionic ball-shaped Keggin anions [44].

3.2.2. One-dimensional aggregates

The examination of the higher-dimensional (other than zero-dimensional) copper(I) halide aggregates did not attract considerable interest and attention until 1990s when research concerning coordination polymers rapidly expanded. Champness and co-workers firstly realized that neutral 1D and 2D copper(I) halide aggregates could also serve as SBUs in targeting coordination polymers by the introducing proper bridging ligands [11]. Since then, the structural diversity of the 1D copper(I) halide aggregates have been continuously unveiled, including typical motifs of single chains, double chains, looped chains, helical chains, ribbons and columns, etc. Table 5 [59–63] summarized some representative 1D copper(I) halide aggregates, some of which will be shown and discussed later.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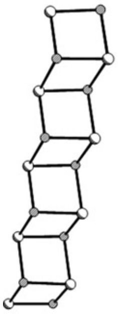
62


63, 64

Single-chain motifs: The common motifs in $(CuX)_n$ aggregates were the zigzag chains, which could be regarded as a ring-opening form of the rhomboid dimer. The zigzag $(CuX)_n$ chain was usually extended by fulfilling the tetrahedral coordination of the copper(I) ions via multidentate bridging ligands to construct a 2D sheet network, such as $[CuCl(pyd)]_n$ (**60**) [18] and $[CuBr(apyd)]_n$ (**61**) [59a]. Different from the zigzag $(CuX)_n$ chains where all copper(I) ions and all halides ions were in straight-line arrangements, the so-called castellated $(CuI)_n$ chain shown in a 3D coordination polymer, namely, $\{[CuI(dtpcp)]MeCN\}_n$ (**62**), was arranged in a way that both the copper(I) ions and the halide ions were positioned with a zigzag fashion [59b]. An uncommon motif found in the complexes of $\{(CuX)_3[cyclo\text{-}(MeAsO)_4]_2\}_n$ (**63**, **64**) (X = Br, Cl) added to the diversity of single $(CuX)_n$ chains. Compared with the regular castellated chain, there were additional Cu–X linkages which separated the valleys which lay in one side of the castellated chain [59c].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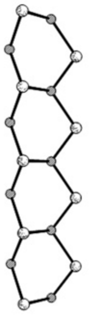
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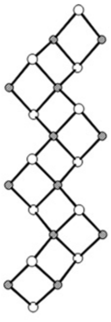
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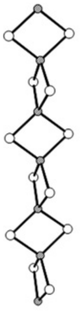
69

Double-chain motifs: The staircase double $(CuX)_n$ chain involved in the 2D $[(CuI)_2(quxin)]_n$ (**65**) [41] and 1D $[(CuI)_2(bbol)]_n$ (**66**) [60a] could be viewed as the linear extension of the Cu_4X_4 stepped cubane, or the linkage of two single zigzag $(CuX)_n$ chains via alternating middle Cu–I rungs. The distinction was made between the two staircase $(CuX)_n$ chains because the bulky bidentate bbol ligands in **66** produced the more corrugated conformation of the stair, compared with the ideal ladder shown in **65**. In the complex of 1D double-chain $[(CuCl)_2(dpiz)]_n$ (**67**), two adjacent zigzag $(CuCl)_n$ chains wriggled in opposite directions to generate six-membered Cu_3Cl_3 chair-ring units via the linkages of *cis* Cu–Cl bonds [39b]. The displaced $(CuBr)_n$ zigzag-stair in the 1D $[CuBr(mcn)]_n$ (**68**) complex could be regarded as the extension of the zigzag-ladder-like Cu_8X_8 oligomer observed in **48** [60c], while two typical castellated single $(CuI)_n$ chains shown in **62** composed the double-chain $(CuI)_n$ castellated ladder with alternating Cu–I bonding rungs shown in the complex of 2D $[(CuI)_3(psmq)(CH_3CN)]_n$ (**69**) [60b].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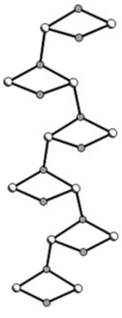
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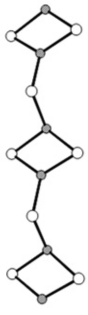
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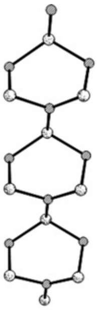
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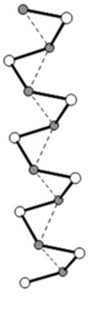
Looped-chain motifs: Looped-chain motifs were supposed to be those 1D copper(I) halide aggregates with four- or six-membered-ring units but without fused Cu–X rungs to implement the "ladders". It could be observed in the 1D complexes of $[CuI_2(L)]_n$ (**70**, **71**) (L = meda or eeda) where the anionic $(CuI_2{}^-)_n$ looped chain was constructed from a line of copper-vertex-sharing rhombohedra [32b]. When the Cu_2X_2 rhombohedra was linked via Cu–X bonds other than the copper-vertex-sharing mode, two related neutral $(CuX)_n$ looped chains were generated in the complexes of 1D $[(CuI)[CpMo(CO)_2]_2(\mu,\eta^2\text{-}Sb_2)]_n$ (**72**) [61] and 1D $[(CuI)(dmasa)]_n$ (**73**) [53c]. The difference between these two $(CuX)_n$ looped chains was obvious: the Cu_2I_2 rhombohedra in the former complex was connected with a *trans* configuration while the latter looped chain showed a 2_1 screw axis with a *cis* offset connecting mode. In complex **74**, namely, $\{[Cu_4Br_6et](et)_2\}_n$, the adjacent Cu_2I_2 dimers were connected by Cu–Br–Cu linkage with a *cis* configuration [56a]. In complex **75**, namely $[Cu_3Cl_3(bipypz)]_n$, the above four-membered rhombohedral "loops" were enlarged to generate six-membered Cu_3Cl_3 chair-like "loops", which were directly connected via Cu–Cl bonds among adjacent loops [20].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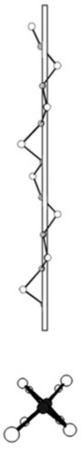
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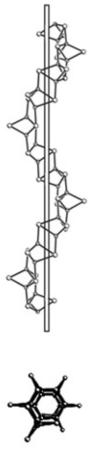
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82

Helical-chain motifs: There were several types of helical $(CuX)_n$ chains reported in coordination polymers, including 2_1, 4_1, 6_1, 3_1 and *meso*-helices. The above figures showed both of the side and top views of these types of helical $(CuX)_n$ chains. Complexes $[(CuBr)_2(bpp)]_n$ (**76**) [21] and $[(CuBr)_2(tmtttf)]_n$ (**77**) [62a] both contained similar 1D inorganic 2_1 helical $(CuBr)_n$ SBUs which were further connected by organic ligands to yield the overall 2D grid network. It was interesting that short $Cu\cdots Cu$ distances (*ca.* 2.84 Å) along the $(CuBr)_n$ chains exsited in the structure of **76**, which warranted the zigzag arrangement of the copper(I) atoms in the $(CuBr)_n$

chains, while such Cu···Cu contacts were not observed in **77**. Unlike the situation in **76** and **77**, the two-folded helix in complex **78**, namely $[(\text{CuBr})(\text{dpey})]_n$, run along two parallel axes instead of 2_1 screw axis forming *meso*-helices [62b]. The examples for the 4_1 helical $(\text{CuBr})_n$ SBUs were involved in a pair of related 3D compounds $[(\text{CuBr})_2(\text{hcc})\text{CH}_2\text{Cl}_2]_n$ (**79**) and $[(\text{CuBr})_2(\text{hcc})]_n$ (**80**). In the former complex $(\text{CuBr})_n$ helices existed with opposite handedness, while in the latter one, a homochiral alignment of the subunits was observed [47c]. The above mentioned helical motifs were based on neutral single-chain $(\text{CuX})_n$ helice, but the more complicated 6_1 and 3_1 helical-chain motifs were based on anionic double-chain copper(I) halide subunits. Complex $[(\text{Cu}_2\text{I}_3)(\text{tptpy})]_n$ (**81**) crystallized in a chiral space group $P6_1$ and was built of the infinite helical-chain $(\text{Cu}_2\text{I}_3{}^-)_n$ anions and the discrete tptp cations. The anionic $(\text{Cu}_2\text{I}_3)_n$ helical-chain coiled around the 6_1 axis was constructed from the previously mentioned CuI_4 tetrahedral synthon (k) of anionic copper(I) halide aggregates via sharing faces and edges of the tetrahedra [62c]. Complex $[(\text{Cu}_5\text{I}_6)\text{Cs}(1{,}10\text{DT18C6})_2]_n$ (**82**) also crystallized in a chiral space group $P3_121$ and contained an infinite $(\text{Cu}_5\text{I}_6{}^-)_n$ helical motif propagated through 3_1 screw. The 3_1 helical chain could be viewed as the tricyclic arrangement of the Cu_4I_4 stepped cubane (e) tetramers linked via I–Cu–I bridges. The neighbouring helical chains were connected by the sandwich-like $[\text{Cs}(1{,}10\text{DT18C6})_2]$ metalloligands to generate a 3D network [22].

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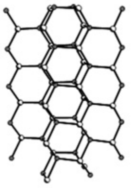

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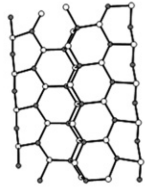

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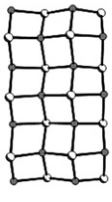

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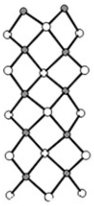

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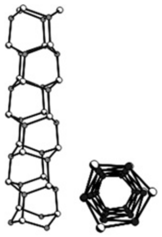


90 – 92

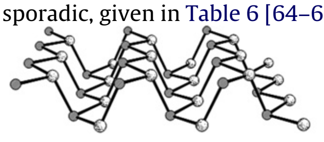
Ribbon and column motifs: The $(\text{CuX})_n$ ribbons were a higher-degree aggregation of the inorganic copper(I) halide components. For examples, ribbons constructed from the combination of 1D zigzag chains and 1D double-stranded ladder chains were found in complexes $[(\text{CuX})_2(\text{pyz})]_n$ (**83**, **84**) (X = Cl, Br) [19], $[(\text{CuI})_3(2{,}2'\text{-bipy})]_n$ (**85**) [31d], $[(\text{CuI})_4(2{,}2'\text{-bipy})]_n$ (**86**) [31d] and $[(\text{CuBr})_3(\text{dpiz})]_n$ (**87**) [39b]. In **83** and **84**, the 1D aggregates contained simple double-chain ladders (shown in **65** and **66**) which were further linked to two simple zigzag chains via Cu–X bonds, forming two adjacent fused 1D ladders with six-membered Cu_3X_3 chair-ring units (like those in **67**) oriented perpendicularly to the central ladders. An extension of the above $(\text{CuX})_n$ substructures was found in **85**, where the attached 1D zigzag chains were located only on one side of the simple ladders, and two simple ladders were placed offset face to face and linked via two sets of Cu–I bonds, forming a range of fused D6R Cu_6I_6 cores (as observed in **35**–**38**) arrayed along the central axis. Likewise, a larger 1D ribbon aggregate was observed in **86**, where two arrays of fused Cu_6I_6 D6R-based motifs could be observed, while the 1D ribbon in **87** could be viewed as adding two zigzag $(\text{CuI})_n$ chains oriented perpendicular to the 1D motifs in **83** and **84**.

There were other types of regular 1D ribbons merely built of the simple Cu_2X_2 rhombohedra. The complex of $[(\text{CuI})_2(\text{biz})]_n$ (**88**) was reported by our group to contain the 1D zigzag quadruple-chain and triple-ladder $(\text{CuI})_n$ ribbon which was sustained by the side-armed benzimidazole ligands [15]. The 2D sheet of the complex of $[(\text{Cu}_4\text{Br}_6)\text{Cu}_2(\text{OH})_2(2{,}2'\text{-bipy})_2]_n$ (**89**) contained 1D $(\text{Cu}_4\text{Br}_6{}^{2-})_n$ ribbons that could be regarded as the corner-joint combination of two anionic $(\text{CuX}_2{}^-)_n$ looped-chain motifs (shown in **70** and **71**) [57b].

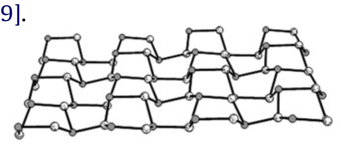
The only $(\text{CuX})_n$ column motif was reported in 3D complexes of $[(\text{CuX})_3(\text{trz})]_n$ (**90**, **91**) (X = Br or I) and $[(\text{CuBr})_2(\text{trz})]_n$ (**92**). The 1D $(\text{CuX})_n$ columnar motif (shown in the figure both its side and top views) could be described as a series of perpendicularly stacked Cu_3X_3 chairs, which were alternately rotated by 60° and linked by Cu–X contacts [42]. A detailed comparison of the three structures (**90**–**92**) could be found in a previous short review [11]. Some irregular 1D copper(I) halide aggregates [63] listed in Table 5 are not discussed in the text.

3.2.3. Two- and three-dimensional aggregates

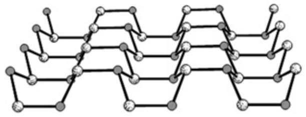
The structures of 2D and 3D copper(I) halide aggregates were sporadic, given in Table 6 [64–69].



93



94



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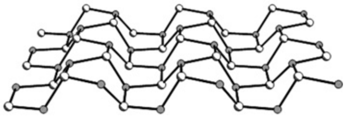
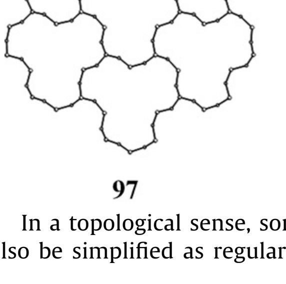
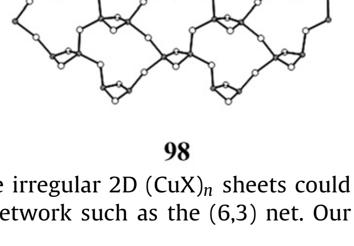


96

Two-dimensional motifs: The above four neutral 2D $(\text{CuX})_n$ undulating layers, which were observed in complexes $[(\text{CuCl})(\text{CO})]_n$ (**93**) [64a], $[(\text{CuCl})_2(\text{mbd})]_n$ (**94**) [64b], $[(\text{CuCl})_2(\text{fdn})]_n$ (**95**) [64c] and $[(\text{CuI})_2(\text{trz})]_n$ (**96**) [42], were all based on fused six-membered Cu_3X_3 ring-subunits and could be topologically simplified to a (6,3) network by denoting copper(I) atoms and iodide ions as three-connected nodes. The two types of typical conformations of the six-membered rings were presented in the Cu_3X_3 ring-subunits, namely, chair conformation in **93** and boat conformation in **94** and **95**. In **93**, the valleys of the undulating sheet were placed by the zigzag fusing seams of the face-to-face "chairs", while in **94** and **95** the valleys were placed by the faces of the "boats". The 2D $(\text{CuCl})_n$ sheet in **94** was a distorted form of the regular 2D boat-sheet in **95** because of the steric hindrance of the supporting organic ligands, which caused a squashing effect to the undulating sheet. In **96**, the Cu_3I_3 rings adopted another conformation other than chair and boat ones: the six-membered rings were two-folded, and were fused via castellated $(\text{CuI})_n$ chains (shown in **62**), other than via zigzag chains in **93**–**95**. The different $(\text{CuX})_n$ layers in **93**–**96** provided considerable evidence to support the contention that the ligands severely influenced the formation of the copper(I) halide substructures.

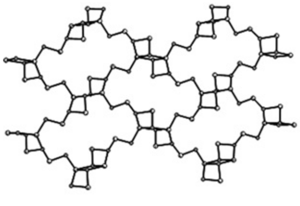


97



98

In a topological sense, some irregular 2D $(\text{CuX})_n$ sheets could also be simplified as regular network such as the (6,3) net. Our group reported a chiral 3D inorganic-organic hybrid coordination polymer, $\{[(Cu_6I_5)(bpsmb)_3](BF_4)\cdot H_2O\}_n$ (**97**), which contained a 2D inorganic $(Cu_6I_5^+)_n$ layer composed of three interwoven 1D $(CuI)_n$ right-handed helices in different directions. When regarding the Cu_3I junction as a three-connected node, this 2D undulating layer could be viewed as a (6,3)-topology net. The formation of this rare chiral 2D $(Cu_6I_5^+)_n$ layer was probably due to the involvement of the highly flexible bpsmb ligand [43]. Additionally, copper(I) atoms exhibiting a tetrahedral coordination mode could also form 2D CuX layers with hexagonal units, as found in $[(Cu_2Br_4)(A46)_2]_n$ (**98**), which contained an unusual 2D $(CuBr_2^-)_n$ layer. The key feature of this layer was represented by two adjacent tetrahedral copper(I) atoms connected via two iodide ions to form two three-connected junctions, thus generating a deforming (6,3) net [34b].



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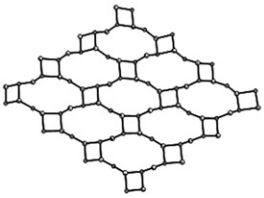
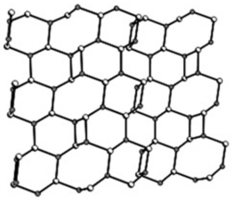


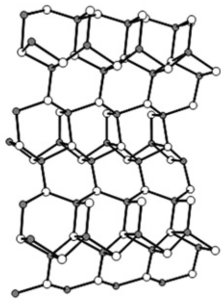
100



101

There were three other topological types of 2D $(CuX)_n$ nets. Complex $[(CuCl)_3(lip)_2]_n$ (**99**) was a 2D sandwich structure with middle $(CuCl)_n$ layer peripherally bound by the lip ligands. The $(CuCl)_n$ layer contained the Cu_4Cl_4 chair-like stepped-cubane building unit, which was linked to four adjacent units via –Cu–Cl– linkages. By denoting the Cu_4Cl_4 chair units as four-connected nodes, the 2D $(CuCl)_n$ layer could be rationalized to a simple (4,4)-topology net [65]. Complex $[(CuCl)_3(ody)_2]_n$ (**100**) exhibited a 2D undulating $(CuCl)_n$ sheet with small quadrilateral Cu_2Cl_2 and dodecagonal Cu_6Cl_6 ring-units, and thus the 2D $(CuCl)_n$ sheet could be topologically regarded as a three-connected (4.8^2) net in light of the fact that both the copper(I) and chloride ions could serve as three-connected nodes [66]. Complex $[(CuI)_2(pyz)]_n$ (**101**) was a 2D wavy coordination polymer featuring a novel $(CuI)_n$ sheet with fused 4-, 6- and 8-membered CuI-rings. Each 4-membered Cu_2I_2 ring was surrounded by two 6-membered Cu_3I_3 rings and two 8-membered Cu_4I_4 rings, and each 6-membered ring was surrounded by one 4-membered, two 6-membered and three 8-membered rings, while each 8-membered ring was surrounded by two 4-membered and six 8-membered rings. This semi-regular 2D sheet was described as a binodal (4,6,8)$(6^2,8)$ net in topology [67].

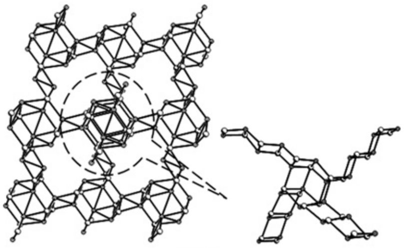
102



103

Finally, two 2D double-layer copper(I) halide motifs were introduced. In the complex of $[(Cu_5I_6)\cdot(dams^+)]_n$ (**102**), a regular 2D double-layer $(Cu_5I_6^-)_n$ sheet (shown in both top and side views) was presented. Each single layer could be viewed as a slightly corrugated hexagonal $(CuI)_n$ chair-(6,3)-sheet (observed in **93**), while viewing from the perpendicular direction there was the typical D6R Cu_6I_6 aggregate (observed in **35**–**38**) fused to six surrounding D6Rs [68]. The irregular 2D sheet involved in the complex of $[(Cu_3Br_4)(ahp)]_n$ (**103**) was an incomplete double-layer motif, in which a puckered 2D hexagonal $(CuBr)_n$ layer was decorated with $(CuBr_2^-)_n$ chains. These one-legged-ladder-like chains lay alternately on the opposite sides of the 2D hexagonal sheets [34c].

104



105

Three-dimensional motifs: Only three examples of 3D copper(I) halide polymeric aggregates were found in the CSD. A novel 3D diamondoid complex, namely $[Cu_{10}Cl_{10}(4\text{-}S\text{-}pyd)_4]_n$ (**104**), contains a decanuclear $Cu_{10}Cl_{10}$ clusters which exhibited a regular array that six copper(I) ions formed an octahedron and the other four were located at the capping sites of the four faces of the octahedron. Each decanuclear $Cu_{10}Cl_{10}$ unit was four-connected to other four units via four μ_4-Cl atoms, resulting in a 3D framework. By simplifying the $Cu_{10}Cl_{10}$ unit into a tetrahedral four-connected node and the bridging Cl ions into a linear two-connected linker, the overall framework could be described as a diamondoid net [36b]. A previously reported compound $[(CuI)_2(PhCN)]_n$ (**105**) could also be described as a diamondoid network. The tetrahedral four-connected node in this diamondoid net was generated by four Cu_8I_8 ladder motifs (shown in the inserted figure), which were all centrosymmetric and extended along the four directions of the tetrahedral node. Each nest-like octanuclear Cu_8I_8 aggregate was linked via the Cu_2I_2 rhombic face to four adjacent units to generate the diamondoid topology [69]. Another double-interpenetrated 3D diamondoid copper chloride framework was found in the complex of $\{(Cu_7Cl_{11})[Cu(en)_2]_2\}_n$ (**106**). The tetrahedral four-connected node was composed of an unusual Cu_4 tetrameric building block which was constructed by four basic anionic $CuCl_4$ tetrahedral synthons (k). The figure for this 3D aggregate was unavailable because of the disorder of the Cu_4 tetrameric unit in the crystal data, but a detailed description and illustration can be found in the original paper [32c].

4. Concluding remarks: perspectives on the growth, property and application of copper(I) halide aggregates in coordination polymers

This review attempts to partially answer the questions encountered in the "difficult system" [12] of copper(I) halide aggregates, and to broaden the scope of this versatile family in coordination chemistry and crystal engineering, especially in the field of coordination polymers. It deals with the preliminary progress achieved—mostly the synthetic (Section 2) and structural (Section 3) aspects of copper(I) halide aggregates. Herewith, the authors wish to share their perspectives on the remaining challenges of the growth, properties and applications of copper(I) halide aggregates in coordination polymers.

Growth: The copper(I) halide aggregates could be readily prepared via various routes (discussed in Section 2), but the difficulty of this system is to visualize and control the crystallization processes, where the aggregates transform from the solution phase to the crystal phase undergoing constitutional or conformational changes [12]. In crystalline state, the growth of the chemically simple copper(I) halide aggregates rely heavily on crystallographic or symmetric constraints, resulting in certain topologically regular architectures. For instance, Champness and co-workers showed a series of different $(CuX)_n$ polymeric framework tuned by triazine ligands could be traced as certain parts of the 3D hexagonal wurtzite structure of copper(I) halides [11].

In this sense, the judicious selection of the organic ligands, taking note of their charges, sizes and shapes, was the key to engineer copper(I) halide architectures (as shown in Section 3.2.1.5). Organometallic components, such as P or As functionalized organometallic ligands (reviewed by Scheer recently) [70], could also be introduced to cope with the construction of copper(I) halide architectures, sometimes yielding spectacular polymers trapping copper(I) halide moieties, such as the intriguing highly symmetrical “inorganic fullerene” nanocluster and its derivatives [71].

However, a precise prediction of the resulting structures is still unavailable. The authors speculate at least two major scientific developments must be achieved before tackling this obstacle: (i) the plentiful empirical results should be summarized to become a database, as accomplished by Long et al. in what they called a “dimensional reduction” database for binary metal–anion solid frameworks [72]; (ii) computational methods such as density functional theory (DFT) should be utilized for the prediction of polymeric copper(I) halide aggregates, especially for those incorporating cuprophilic interactions [73].

Properties: Speaking of the cuprophilic interaction, an important associating property of CuX-based coordination polymers is cluster-based luminescence and thermochromism. Luminescent coordination polymers (also known as luminescent metal–organic frameworks) are currently a hot topic in material science and have been recently reviewed [74]. Since the luminescence aspects of the copper(I) halide aggregates have been extensively investigated both experimentally [8] and theoretically [9], they are suitable candidates for serving as building blocks to construct cluster-based luminescent coordination polymers.

In order to rule out the complications from the luminescence of halide to ligand charge transfer (XLCT) to the cluster centered (CC) emission, a strategy for targeting CuX CC-emissive coordination polymers is to select organic ligands that show no ligand-based or charge transfer emissions. An example could be found in a recent work where a non-aromatic bis-thioether ligand was chosen to combine with Cu_2I_2 or Cu_4I_4 clusters, yielding a 1D loop chain and 2D network coordination polymers. In this study, the structural evidence for the luminescence thermochromism was unambiguously presented [75]. Also highlighted herein was a recently reported photoluminescence switch based on a 3D coordination polymer constructed by Cu_4I_4 clusters linking calixcrowns [76].

Applications: In material science, applications of the copper halide components are relatively rare. A prominent example is a range of self-assembled hybrid inorganic-organic materials containing the 2D double-layer $(Cu_5I_6^-)_n$ sheets (shown as **102**) which exhibited giant second-order nonlinear optical (NLO) responses [68].

In stark contrast, a collateral family of copper(I) halides namely, copper(I) pseudohalides (CuCN and CuSCN), can be used in photovoltaic cells for light absorbers and hole conductors [77]. The coordination chemistry and crystal engineering of the copper(I) pseudohalide aggregates are closely related to those of copper(I) halide aggregates, but have their own unique features, which are currently under our investigation and review.

Acknowledgements

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