Chapter

Structural Diversity in Substituted Pyridinium Halocuprates(II)

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Abstract

The flexible coordination sphere of the Jahn-Teller active Cu(II) ion provides access to a full spectrum of coordination geometries from 4-coordinate (tetrahedral or square planar) to 6-coordinate elongated octahedral. This is further enhanced in anionic halide complexes by the ability of the halide ligand to bridge between Cu(II) centers to generate extended oligomeric or polymeric complexes. Coordination geometry and extended structure of the anionic complex is very sensitive to the nature of the organic counterion. This is especially true for planar substituted pyridinium cations in which minor changes in the nature or position of the substituted group can generate completely different halocuprate(II) structures. Early work focused on reducing ligand-ligand repulsion through strong hydrogen bonding with the organic cation in order to manipulate the Cu(II) coordination sphere. However, many unique structures have been found in which quaternary pyridinium cations were employed-including the remarkable thermochromic compound (1,2,6-trimethylpyridinium)$_2$C uCl$_4$- in which strong hydrogen bonding is absent. More recently aminopyridinium cations, which further increase structural diversity not only through the possibility of having mono- or di-protonated cations but also the ability of monoprotonated cations to coordinate to the Cu(II) center through the amino group, have been investigated.

Keywords: substituted pyridinium compounds, structural chemistry, copper(II) complexes, Jahn-Teller effect

1. Introduction

The d^9 Cu^{2+} ion is, perhaps, the best known example of a Jahn-Teller active ion with an extremely flexible coordination sphere—to the extent that it has been referred to as "a chameleon of coordination chemistry" [1]. To summarize standard arguments [2]: in octahedral coordination the degenerate electronic ground state of d^9 Cu^{2+} is further stabilized by distortion (typically by elongation of one octahedral axis) to yield a non-degenerate electronic ground state (**Figure 1**). (In tetrahedral coordination a flattening distortion toward the square planar limit serves a similar purpose).

The elongated octahedral geometry can be described as 4 + 2 coordinate with four short coordinate covalent bonds (typical Cu-Cl bond lengths in the 2.2–2.4 Å range) and two longer semicoordinate bonds (typical Cu⋯Cl bond lengths ranging from 2.7

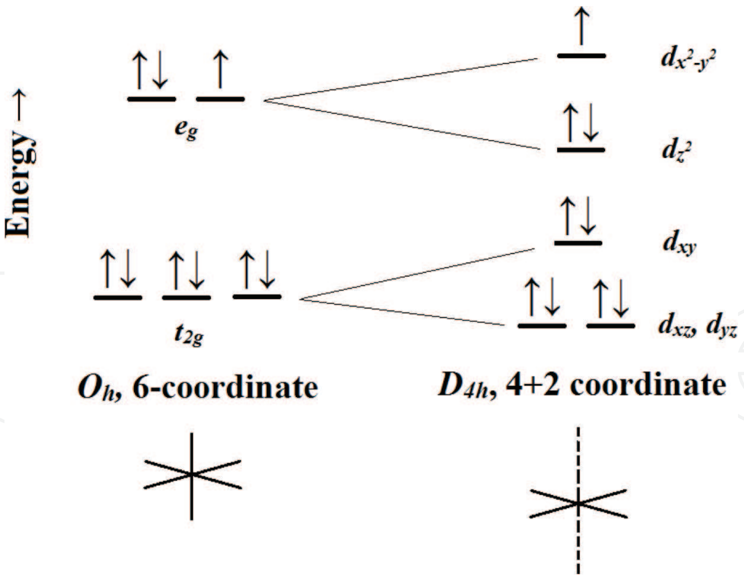


Figure 1.
Schematic diagram of the d-orbital splitting of an octahedral $CuCl_6^{4-}$ *complex undergoing an elongated axis Jahn-Teller distortion.*

to well over 3 Å). The two semicoordinate bonds can be of different lengths leading to 4 + 1 + 1′ coordination. Further elongation of the longer bond eventually leads (conceptually) to removal of that ligand and results in 4 + 1 coordination. In some situations the semicoordinate bond of a 4 + 1 complex is short enough (Cu-Cl distance of 2.6 Å or less) to become a coordinate bond and yielding a five coordinate geometry that is usually found somewhere on the continuum between trigonal bipyramidal and square pyramidal due to a second order Jahn-Teller distortion [3]. Removal of the other semicoordinate ligand yields a 4-coordinate complex that is usually found in a flattened tetrahedral geometry with *trans* Cl-Cu-Cl angles between 130 and 140°. However, these angles are found with a range of values, including 180° in the square planar limit. Square planar $CuCl_4^{2-}$ complexes are rare, and square planar $CuBr_4^{2-}$ complexes are almost completely unknown—a fact attributed to the stronger ligand-ligand repulsion between the larger bromide ions. Thus a wide range of coordination numbers and geometries is available to a copper(II) complex, as depicted in **Figure 2**.

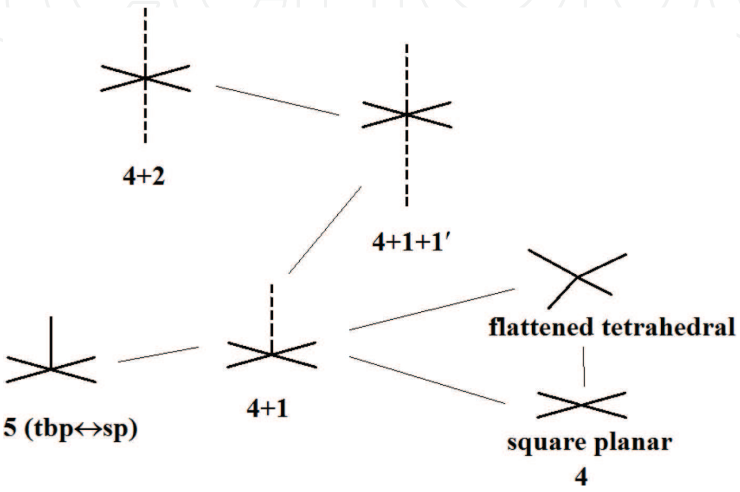
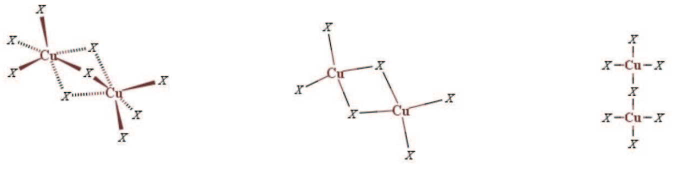


Figure 2.
Coordination numbers and geometries available to a Cu^{2+} *complex.*



face-sharing, tribridged edge-sharing, bibridged corner-sharing, monobridged

Figure 3.
Bridging modes available to halocuprate(II) complexes.

The focus of this chapter is on copper(II) halide complexes—ergo the bond length and angle examples previously given. Chloride complexes have been more thoroughly investigated than bromide complexes [4]. This may be due to the wide variety of colors exhibited by chloride complexes of differing geometries and coordination numbers: ranging from reds to orange to yellow to greens. The author has found in some situations crystals of three or four different colors growing in the same beaker as identifiably distinct compounds. In contrast, the visible spectra of bromide complexes is dominated by ligand-to-metal charge transfer to give an intensely dark purple color with little variation across compounds [5, 6]. In both cases, however, the chloride and bromide ligands can bridge between copper(II) centers, as shown in **Figure 3**, to increase structural complexity by forming oligomeric or polymeric species.

2. The utility of pyridinium cations

2.1 Anionic halocupreates(II)

Halocuprate(II) complexes, whether isolated monocopper(II) or oligomeric or polymeric, are anionic and in crystalline solids are always accompanied by a cationic species. Earliest studied compounds used highly symmetric alkali metal or ammonium cations [7–10] but a wide variety of conterions have been used, including cationic inorganic or organometallic complexes. A broad array of organic cations, often readily and commercially available, have been most frequently employed [2].

2.2 Structures with organoammonium cations

Organoammonium cations can quickly become bulky with larger groups and higher degrees of substitution which prevents formation of polymeric complexes. Consider, for example, the $(Et)_x(Me)_{4-x}$ series of chlorocuprates with an approximate 1:1 ratio of organic cation to $CuCl_2$. For tetramethylammonium ($x = 0$) a tribridged chain of face sharing $CuCl_6$ octahedra is found in $(Me_4N)CuCl_3$ [11]. For x = 1, in $EtMe_3N)_4Cu_5Cl_{14}$ a linear chain is also found, but with a mix of bi- and tribridging that "stretches" the chain in order to accommodate the bulkier organic cation [12]. For $x = 2$, a $(Cu_4Cl_{11}^{3-})_n$ with even more frequent bibridging is found [13]. Organic cations with $x = 3$ and 4 are so bulky that a continuous chain is no longer possible, and isolated $Cu_3Cl_9^{3-}$ [2, 14] and $Cu_4Cl_{12}^{4-}$ [15] oligomers are found. Primary alkylammonium cations favor formation of layer perovskite A_2CuX_4 (A = monopositive cation and X = Cl, Br) compounds in which layers of corner sharing CuX_6 octahedra are separated by bilayers of organic cations with $-NH_3$ head groups directed toward the inorganic layer to form multiple N-H…X hydrogen bonds [16].

2.3 Structures with anilinium versus structures with pyridinium cations

Substituted planar aromatic cations, i.e. anilinium or pyridinium, provide a wealth of counterion possibilities while avoiding the bulkiness found with organoammonium ions. With a protonated $_{-}NH_3^+$ head group, an anilinium cation can function structurally as a primary ammonium cation. Indeed, (anilinium)$_2$CuCl$_4$ exists as a layer perovskite system [17]. With pyridinium cations, however, the ring nitrogen acts as a single hydrogen bond donor (when protonated) that generally forms a single direct or a bifurcated hydrogen bond to halide(s) on a neighboring complex. The ring nitrogen can also be readily quaternized to examine halocuprate(II) structures in the absence of N-H hydrogen bonding. Pyridinium compounds have been more heavily studied than anilinium compounds: a Cambridge Structural Database (CSD) substructure search [18] on the anilinium core versus the pyridinium core with tetrachlorocuprate(II) complexes yields 24 compounds (14 of which are layer perovskites) and 120 compounds, respectively. This difference might be due to the tendency for anilinium cations to decompose in the presence of Cu(II) (presumably acting as a one-electron oxidation catalyst). In the author's experience, crystal growth under ambient conditions of anilinium chlorocuprate(II) compounds often yields brown or black residues. Indeed, there are no reported structures of ring substituted methyl or dimethylanilinium chlrocuprate(II) compounds in the CSD, whereas there are a handful of chlorozincate(II) compounds (where Zn(II) with a d^{10} configuration does not have access to a + 1 oxidation state) and numerous ring substituted methyl or dimethylpyridinium chlorocuprate(II) compounds.

3. A_2CuX_4 compounds containing isolated CuX_4^{2-} complexes

3.1 General properties

Compounds containing isolated CuX_4^{2-} complexes are readily prepared by slow evaporation of a solution, e.g. hydrohalic acid or alcoholic, containing a stoichiometric amount of organic cation halide and copper(II) halide, and examples are regularly reported. These most commonly contain flattened tetrahedral complexes with *trans* *X*-Cu-*X* angles in the range 130–140°. Strong hydrogen bonding between the organic cation and the halide ions of the inorganic complex is thought to reduce ligand-ligand repulsion and allow for larger *trans* *X*-Cu-*X* angles. Examples of these complexes are more rare, especially those with larger *trans* angles, Crystals containing chloro complexes with the commonly found *trans* angle are yellow/orange in color and become progressively more green in coloras the *trans* angle increases to reach an intensely dark green color at the square planar limit (180°) [19].

3.2 Square planar complexes

A recent example of square planar $CuCl_4^{2-}$ is in the isonicotinamidium (H-INAc) salt where strong bifurcated hydrogen bonds from the protonated ring nitrogen stabilize the *sp* geometry (**Figure 4**). This particular compound is also interesting since there is a companion compound in which neutral isonicotinamide molecules coordinate to the copper(II) center as terminal ligands in di-μ_2-chloro polymeric chains. Exposure of these chains to moist HCl vapor protonates the pyridine and generates the *sp* complex in a reversible process [20]. In some cases green *sp* complexes undergo

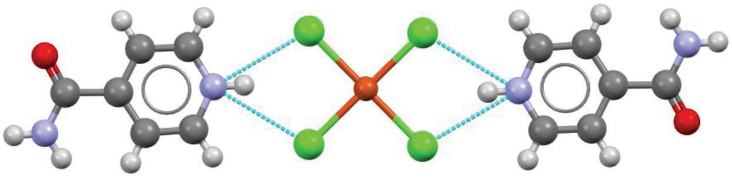


Figure 4.
Ball-and-stick model of the formula unit of bis(isonicotinadium) tetrachlorocuprate(II) showing the strong, bifurcated hydrogen bonds that stabilize the sp geometry.

abrupt (green to yellow) thermochromic phase transitions to *tet* complexes on heating as increased thermal motion weakens the hydrogen bonding that stabilizes the *sp* geometry [19]. While no such transition is reported for the H-INAc salt, it is possible that heating might result in deprotonation of the pyridine before a transition occurs.

3.3 Polymorphism and supramolecular interactions

Polymorphic crystalline forms of these systems can be obtained and studied with different polymorphs possible upon crystallization from different solvents or using different methods. An example occurs with 2,6-dimethylpyridinium in which a monoclinic structure (*C2*/c) is obtained from acidic aqueous solution [21] and an orthorhombic (P*bcn*) polymorph is obtained from ethanol [22]. Supramolecular interactions were examined in both polymorphs, which illustrates a common application of A_2CuX_4 systems. Since they are readily prepared, it is convenient to use them to study supramolecular interactions with variations in pyridinium ring substitution, e.g. a recent study of halogen bonding in (chloromethyl)pyridinium salts [23].

3.4 Catalytic ring substitution

Willett et al. provided a classic series of papers detailing Cu(II) as a catalytically active species in serendipitous ring substitution reactions of pyridines. For example, recrystallization of 2-amino, 3-methylpyridine with $CuBr_2$ in a slightly acidic solution yielded partial bromination of the pyridine to give (2-amino, 5-bromo, 3-methylpyridinium)(2-amino, 3-methylpyridinium) tetrabromocuprate(II) [24]. Likewise, recrystallization of 2,6-diaminopyridine with $CuCl_2{\cdot}2H_2O$ in slightly acidic solution yields (2,6-diamino, 3,5-dichlropyridinium) tetrachlorocuprate(II) [25] (the bromo analog more recently reported [26]).

3.5 Structural complexity

A_2CuX_4 systems can also provide examples of structural complexity, e.g. through complex packing arrangements or symmetrically inequivalent CuX_4^{2-} complexes with different degrees of flattening. Well known older examples, the incommensurate phase of $[(CH_3)_4N]CuCl_4$ [27] and the thermochromic compound $[CH_3CH_2NH_3]_2CuCl_4$ (which contains three distinctly different $CuCl_4^{2-}$ complexes with one unit cell axis length ~ 45 Å) [28], do not contain pyridinium cations but there are more recent examples that do. The compound [bis(pyridinium-3-ylmethyl) ammonium]$_4(CuCl_4)_5Cl_2$ contains four distinct $CuCl_4^{2-}$ complexes with *trans* Cl-Cu-Cl angles ranging from 128 to 155° [29]. The high symmetry compound (1,3,4-trimethylpyridinium)$_2CuCl_4$ crystallizes in orthorhombic *Fdd*2 with complex anions found between layers of organic cations. The diamond glide symmetry generates a four organic cation layer repeat sequence and leads to a ~ 35 Å *b*-axis length. The corresponding bromide compound is in lower symmetry monoclinic $P2_1/c$ with symmetrically inequivalent organic cations that are segregated into separate layers, as another form of structural complexity [30].

This *Fdd*2 structure is found across a range of (1,3,4-trimethylpyridinium)$_2M$Cl$_4$ compounds (*M* = Co, Ni, Zn [31–33]) but larger metal ions (Mn, Cd [34, 35]) crystallize in monoclinic *C*2/*c*. A CSD search shows that *C*2/*c* is the second most commonly reported space group for pyridinium A_2CuCl$_4$ compounds (~40 structures) and slightly exceeds the number of compounds reported in the most commonly reported space group for all compounds, monoclinic $P2_1/c$. (The most commonly reported space group from pyridinium A_2CuCl$_4$ structures is triclinic $P\bar{1}$ with ~60 structures.) Since in the *C*2/*c* structure both organic cations are symmetrically equivalent, this suggests a strategy in pursuing structurally complex compounds by mixing different organic cations to give $A'A$CuCl$_4$ structures. A few examples are known, such as the 2-amino-3-methylpyridinium example cited above in which organic cations are similar, or the (dimethylammonium)(3,5-dimethylpyridinium)CuCl$_4$ structure [36] where the organic cations are quite different. A systematic study could be conducted by redissolving existing stocks of A_2CuCl$_4$ compounds in a 1:1 molar ratio and recrystallizing.

4. Quasi-planar oligomers

4.1 Overview

Halocuprate(II) complexes can form linear multicopper complexes through edge sharing of neighboring CuX_4 complexes. At the simplest level this is a dicopper(II) complex which, with a monopositive organic cation, has the typical formulation A_2Cu$_2X_6$ for a 1:1 organic cation:Cu(II) stoichiometry More copper rich stoichiometries are needed for longer $\mathrm{Cu}_nX_{2n+2}{}^{2-}$ oligomers. Crystallization of a particular type of oligomer is not predictable, unlike the 2:1 stoichiometry A_2CuX_4 compounds which are readily formed. Thus it is common when exploring the halocuprate(II) structural landscape to prepare solutions of different stoichiometries, e.g. 2:1, 1:1, and 1:2. The stoichiometry of the crystals obtained from solution is not necessarily the same as starting stoichiometry. These compounds require crystallographic analysis to establish their identities as dissolution destroys the compounds.

4.2 Stacking of quasiplanar oligomers

With bulky organic cations the oligomers are isolated and are formed from edge-sharing CuX_4 flattened tetrahedra. For planar or less bulky cations, the oligomers are now quasi planar, formed from edge sharing of CuX_4 square planes, and are no longer isolated with halide ions from one oligomer form semicoordinate bonds with Cu(II) centers on neighboring oligomers to aggregate into stacks [4]. Neighboring oligomers are offset from each other by a half-integral multiple of a CuX_4 edge length with the pattern simply communicated by a bracketed pair. For example, 2[1/2,1/2] indicates that neighboring dicopper oligomers are offset from one another by ½ an edge length parallel to the long axis of the oligomer and ½ an edge length perpendicular (the 2 in front of the bracket identifies these as dicopper(II) complexes). These stacking

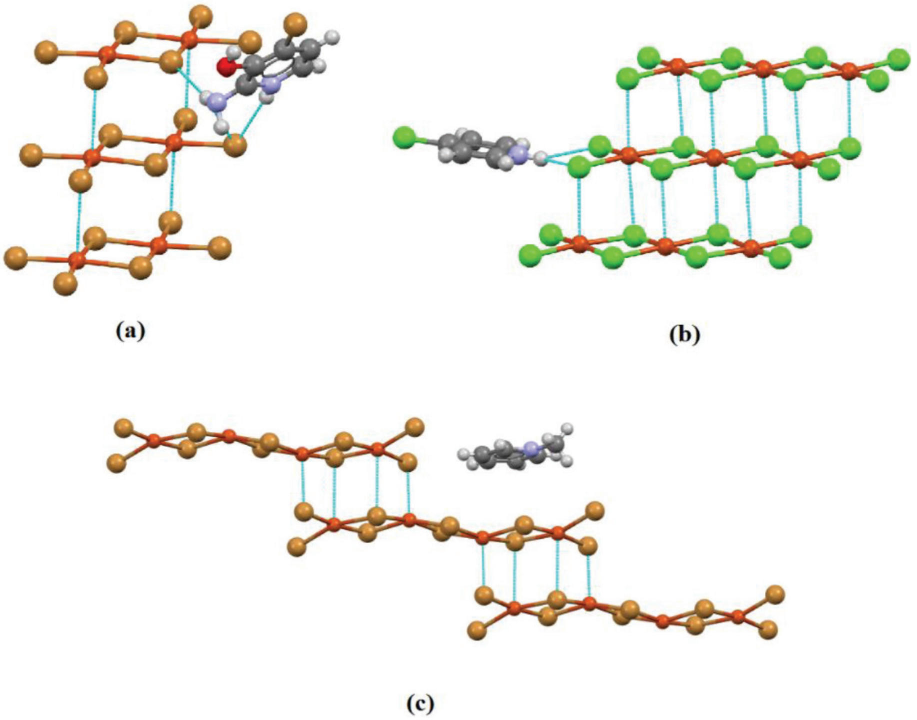


Figure 5.
(a) 2[1/2,1/2] stacking in (2-amino-4-bromo-3-hydroxopyridinium)$_2Cu_2Br_6\cdot 2H_2O$ (water molecules omitted for clarity) [38], (b) 3[1/2,1/2] stacking in (4-chloropyridinium)$_2Cu_3Cl_8$ [39], and (c) 4[5/2,1/2] stacking in (1-methylpyridinium)$_2Cu_4Br_{10}$ [40].

patterns vary by compound, and can become more complicated with different oligomers in the stack having different stacking environments [37]. A selection of different oligomer structures with associated stacking patterns are shown in **Figure 5**.

4.3 Pyridinium cation interactions in oligomer stacking

While many different kinds of cations generate oligomer stacks, distinctions can be observed for pyridinium cations. Where hydrogen bonding is present, the oligomer is often terminated with a bifurcated hydrogen bond which mimics the bibridged structure within the oligomer, as shown in **Figure 6**.

Oligomer stacks can often be visualized as sections of a layer from the CuX_2 parent structure. This is particularly true for situations where hydrogen bonding is not possible and the structures can be described as CuX_2 layers in which organic cation pairs replace $(Cu_nX_2n_{-2})^{2+}$ fragments, as illustrated in **Figure 7** for (1-methylpyridiniuim)$_2Cu_4Br_{10}$ [40]. In this case the shape of the organic cation may have more to do with templating the inorganic structure rather than directed intermolecular interactions.

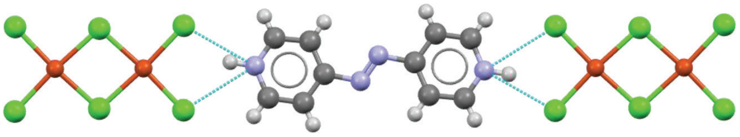


Figure 6.
Hydrogen bonding scheme in (4,4′-diazenediyldipyridinium) Cu_2Cl_6 [41].

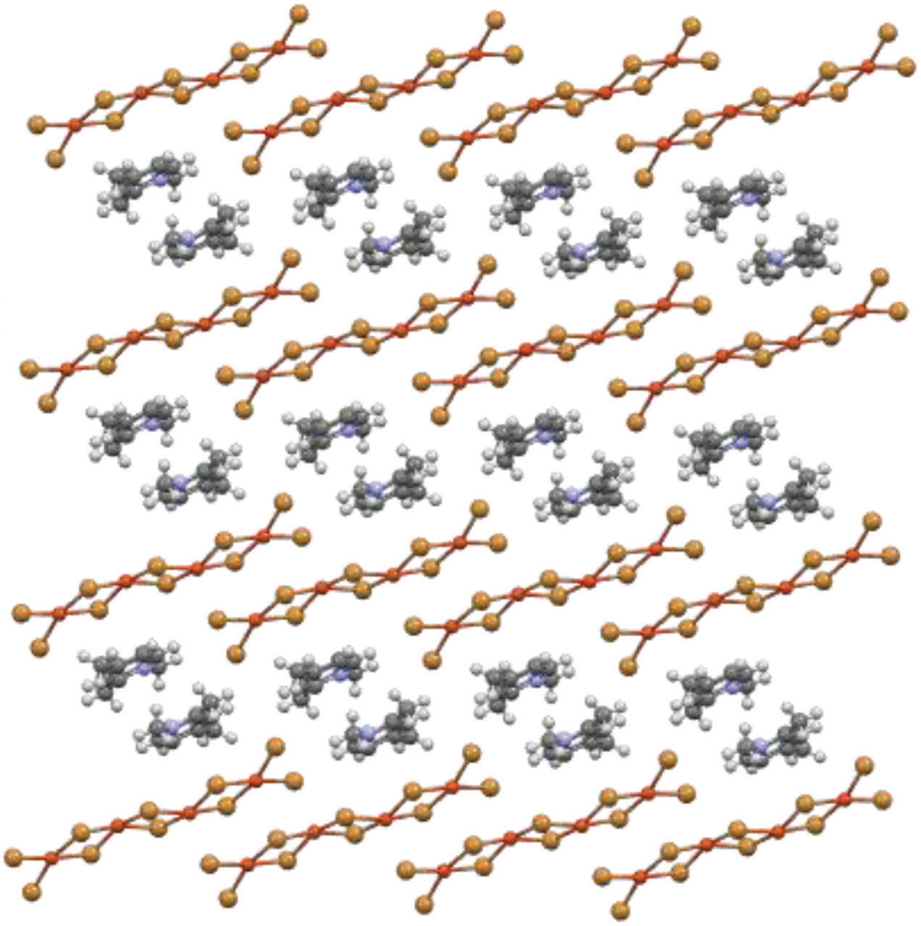


Figure 7.
Layer structure of (1-methylpyridinium)$_2Cu_4Br_{10}$.

4.4 High-nuclearity oligomers

Oligomers containing more than four Cu(II) centers are rare. Only one example of a $Cu_5X_{12}{}^{2-}$ oligomer is known (in 2-chloro-1-methylpyridinium)$_2Cu_5Br_{10}$ [40]) in which oligomers are still found in isolated stacks (the neutral pentacopper oligomer $Cu_5Cl_{10}(n\text{-}CH_3CH_2CH_2OH)_2$ has long been known [42]). 1,2 dimethylpyridinium crystallizes with a hexacopper oligomer ($Cu_6Cl_{14}{}^{2-}$) and a heptacopper oligomer ($Cu_7Br_{16}{}^{2-}$) [43]. For these longer oligomers the stacks are no longer isolated, but overlap one another to form layers with the organic cations sandwiched between layers, as illustrated in **Figure 8**.

2-Chloro-1-methylpyridinium also crystallizes with a $Cu_7Br_{16}{}^{2-}$ oligomer in a structure that is almost identical to that of 1,2-dimethylpyridinium. The chloro and methyl groups are disordered, indicating no directed intermolecular interaction with the oligomer and templating of the oligomer on the cation shape may be more important [40].

The longest reported oligomer is found in (3,5-dibromopyridinium)$Cu_{10}Br_{22}$. The authors rationalize formation of the decacopper(II) oligiomer in terms of halogen bonding contacts with the organic cation [44]. This laboratory has obtained also a $Cu_{10}Br_{22}{}^{2-}$ for 2,6-dimethylpyridinium shown in **Figure 9** [45]. In spite of similarity in shape of the cation and similar unit cell parameters, the two structures are not superimposable. Longer oligomers are certainly possible, but these high copper(II) stoichiometries are rarely investigated so that further discoveries are likely to be serendipitous.

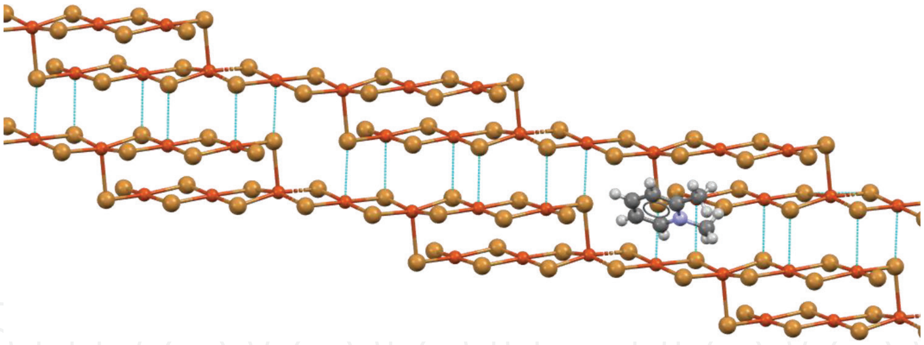


Figure 8.
Overlapping of oligomer stacks to form a layer with one organic cation shown for the compound (1,2-dimethylpyridinium)$_2Cu_7Br_{16}$.

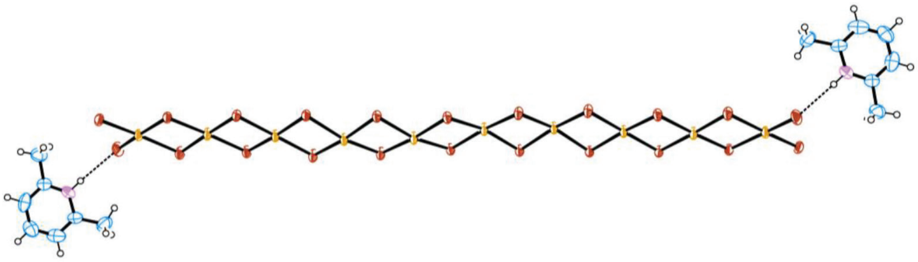


Figure 9.
Thermal ellipsoid plot (at the 50% level) of the formula unit of (2,6-dimethylpyridinium)$_2Cu_{10}Br_{22}$ *at 295 K. H-atoms are drawn as circles of arbitrary radii.*

4.5 Asymmetrically bridged dicopper(II) oligomers

An exception to the symmetrically bridged oligomers discussed above are situations where two CuX_4 square planes stack offset from each other to form long semicoordinate bonds between halide ligands of one complex and the Cu(II) center of the other. This leads to two asymmetric bridges with one short Cu-X bond and one long Cu···X bond, as shown in **Figure 10**. Stacks of CuX_4 square planes are not known, but such stacking would lend itself to formation of linear chain structures—which are known.

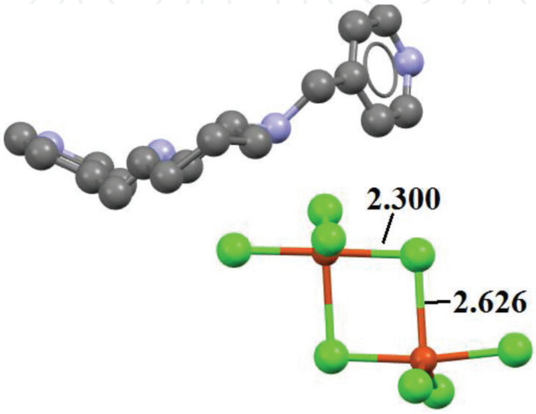


Figure 10.
Asymmetric dicopper(II) oligomer in 4,4′-((cyclohexane-1,2-diylbis(ammoniumdiyl))bis(methylene)) bis(pyridin-1-ium $Cu_2Cl_8{\cdot}H_2O$ *[46]. Hydrogen atoms and water molecule are omitted for clarity. Bond distances in the dimer bridge are shown in units of Å.*

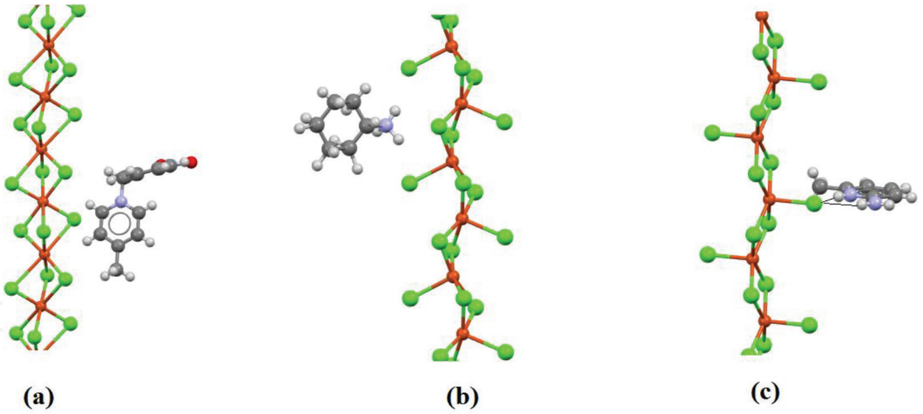


Figure 11.
(a) The tribridged chain in 1-(4′-nitrobenzyl)-4-methylpyridinium $CuCl_3$*, (b) the bibridged chain in cyclohexylammonium* $CuCl_3$ *showing the ammonium head group in postion to hydrogen bond to canted apical chloride ligands, and (c) the bibridged chain in 2-amino-6-methylpyridinium* $CuCl_3$ *showing hydrogen bonds from the pyridine and amino N atoms that stabilize the apical chloride ligand as non-bridging.*

5. $ACuX_3$ linear chains

The $CsNiCl_3$ structure consisting of chains of face-sharing $NiCl_6$ octahedra separated by monopositive cations is the parent structure for $ACuX_3$ linear chains. In the parent structure each Ni(II) ion is linked to its neighbor by three symmetric bridges. However, due to the axial Jahn-Teller distortion of the $CuCl_6$ octahedron, in $ACuX_3$ chains each Cu(II) is linked to its neighbor by two asymmetric bridges and only one symmetric bridge. In the absence of hydrogen bonding interactions from the counterion, in the case of Cs, $(CH_3)_4N^+$, or the quaternary4-methyl-1-(4′-nitrobenzyl)-4-methylpyridinium (shown in **Figure 11a** [47]) cations, the tribridged chain is observed. Hydrogen bonding from the cation to the halides of the chain provides charge compensation to the halides that permits lengthening of the Jahn-Teller elongated Cu-Cl bond. For strong enough hydrogen bonding the semicoordinate bond is broken and the chain is converted into a symmetrically bibridged chain of $CuCl_5$ square pyramids. This is illustrated by the (cyclohexylammonium)$CuCl_3$ structure where hydrogen bonding from the ammonium head group leads to elongation of the Jahn-Teller axial bond to a distance of 3.48 Å (as compared to elongated distances of 2.76 and 2.96 Å in the chain shown in 11(a)). At this distance the chloride ligand is, at best, weakly interacting with the neighboring Cu(II) center and a nascent $CuCl_5$ square pyramid has formed with two symmetric bridges now connecting Cu(II) centers with the apical Cu-Cl bond still canted at an acute angle relative to the chain axis (see **Figure 11b** [48]). In 2-amino-6-methylpyridinium $CuCl_3$ both the pyridine nitrogen and amino group serve as hydrogen bond donors forming multiple hydrogen bonds to the apical chloride and providing sufficient charge compensation that the apical Cu-Cl bond is perpendicular to the chain axis and no longer involved in bridging (see **Figure 11c** [49]).

6. Quaternary pyridinium cations

6.1 Overview

While hydrogen bonding has traditionally been seen as a means to control halocuprate(II) geometry, quaternary pyridinium cations provide a means of examining the effect of a lack of N-H hydrogen bonding on structure. Common methods used (in this laboratory) for preparation of quaternary pyridinium cations are (1) reaction of a substituted pyridine with an excess of iodomethane, then anion exchange with an excess of the appropriate silver halide in H_2O or (2) direct combination of condensed chloro- or bromomethane (in excess) with chilled substituted pyridine in a pressure vessel that is then sealed and allowed to warm to room temperature for 24 hr. Examples of structures containing quaternary pyridinium cations have been mentioned in passing already. Here two particularly interesting systems are discussed.

6.2 "Knobby" chains in (1,4-dimethylpyridinium)$_4$Cu$_5$Cl$_{14}$

The quaternary 1,4-dimethylpyridinium cation might be expected to crystallize with a tribridged $(CuCl_3)_n$ chain due to the lack of hydrogen bonding—just as the quaternary cation example cited in the previous section and as is, notably, the case for (1,4-dimethylyrdinium) $PbBr_3$ [50]. Instead it templates a highly unusual $(Cu_5Cl_{14})_n$ "knobby" chains in which $CuCl_4$ flattened tetrahedral "knobs" edge-share so as to bridge adjacent Cu(II) ions in the central chain [12]. The chain structure is distinctive since it exhibits the three major coordination numbers of Cu(II). Besides the flattened tetrahedral "knobs" on the outside of the chain, the central Cu(II) ion of the Cu_5Cl_{14} repeat unit has the elongated octahedral 4 + 2 coordination. This bibridges on either side to 5-coordinated Cu(II) complexes with the intermediate *sqp*/*tbp* geometry. These 5-coordinate complexes then bibridge to 5-coordinate complexes on neighboring Cu_5Cl_{14} units to complete the chain (**Figure 12**). With the lack of directed intermolecular interactions, the inorganic structure must template on the cation shape, although it is difficult to discern specifically the driving force behind formation of the structure. The knobs on the chain are found between stacks of organic cations with bridging chlorides close to the pyridinium N atoms as the most prominent point of interaction. There has been no reported attempt to prepare the bromide analog.

6.3 *sp* to *tet* phase transitions in (1,2,6-trimethylpyridinium)$_2$CuX_4

The second interesting case is the (1,2,6-trimethylpyridinium)$_2$CuX_4 system [51]. Both the chloride and the bromide salts contain square planar CuX_4^{2-} in a low temperature phase (below 60°C for the chloride and below −48°C for the bromide). Both compounds undergo a solid-solid phase transition on heating to a high temperature phase in which CuX_4^{2-} is flattened tetrahedral, resulting in a thermochromic transition for the chloride salt (from dark green to yellow). As previously described, these

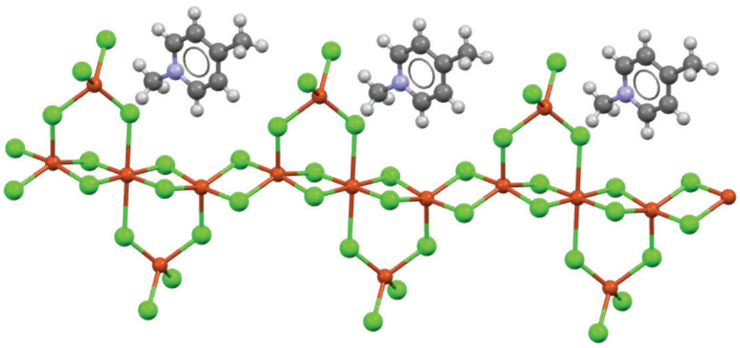


Figure 12.
A section of the "knobby" chains found for (1,4-dimethylpyridinium)Cu_5Cl_{15}.

sp to *tet* transitions are thought to occur due to a weakening of hydrogen bonding. Furthermore *sp* $CuBr_4^{2-}$ is not expected, even with strong hydrogen bonding, due to the greater ligand-ligand repulsion of the larger bromide. So the occurrence of *sp* complexes and *sp* to *tet* transitions in systems without strong hydrogen bonding is highly unusual, if not unprecedented. (It is also worth mentioning that the transitions go from higher symmetry (monoclinic *C*2/m) to lower symmetry (triclinic $P\bar{\mathbf{1}}$), which is also quite unusual.)

The quaternary ammonium cations in the low temperature structures form zipper-like ribbons with *sp* $CuCl_4^{2-}$ complexes between the ribbons, as shown in **Figure 13**, that act to template the *sp* geometry. Crystallographic mirror planes are perpendicular to this layer and bisect both the organic cation and the $CuCl_4^{2-}$ complex. The three dimensional structure is built up by stacking these layers so that organic cations of one layer sit above or below $CuCl_4^{2-}$ complexes in another so that the complexes are truly isolated. The structural transformation that occurs on heating disrupts this ribbon structure and results in two symmetrically inequivalent organic cations with aromatic planes tilted with respect to each other.

The 1,2,3-trimethylpyridinium cation has a similar shape as 1,2,6-trimethylpyridinium, and also crystallizes as zipper-like ribbons with chlorocuprate(II) complexes between the ribbons to from layers. However the complexes formed are not isolated $CuCl_4^{2-}$ but asymmetrically bridged $[CuCl_3(H_2O)]_2$ dicopper complexes [52]. **Figure 14** illustrates the similar layer structure, right down to similar symmetry: monoclinic *C*2/m. As before, the mirror plane is perpendicular to the layer and bisects the organic cation. In this case, however, the N-atom lies off the mirror plane resulting in two-fold positional disorder that is not present in the 1,2,6-trimethylpyridinium analog. Does positional disorder stabilize a different structure?

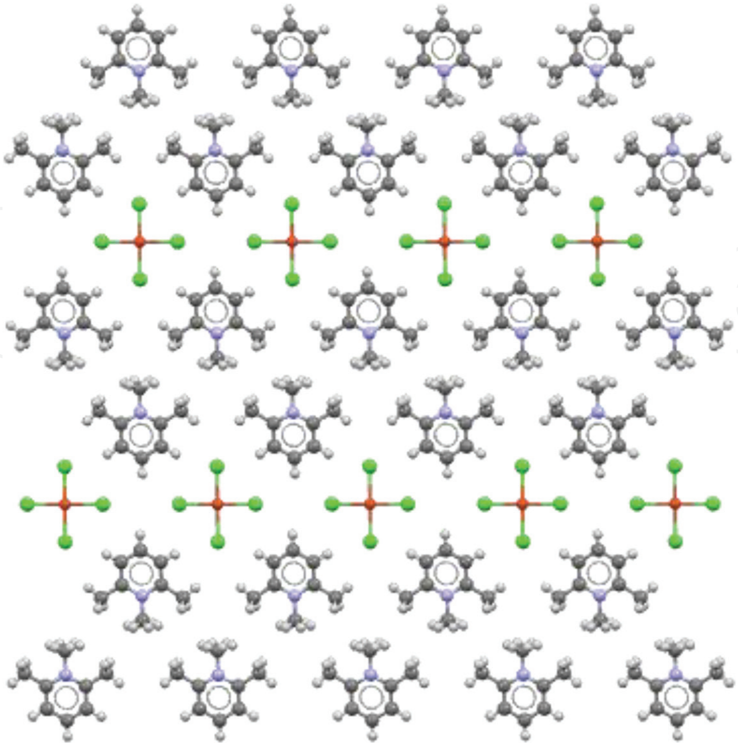


Figure 13.
Layer structure of (1,2,6-trimethylpyridinium)$_2$*CuCl*$_4$ *showing the zipper-like ribbons of organic cations with methyl groups directed toward the center of the ribbon and with isolated sp* $CuCl_4^{2-}$ *between the ribbons. Mirror plane symmetry is perpendicular to the layer and bisects the organic cations and* $CuCl_4^{2-}$ *complexes.*

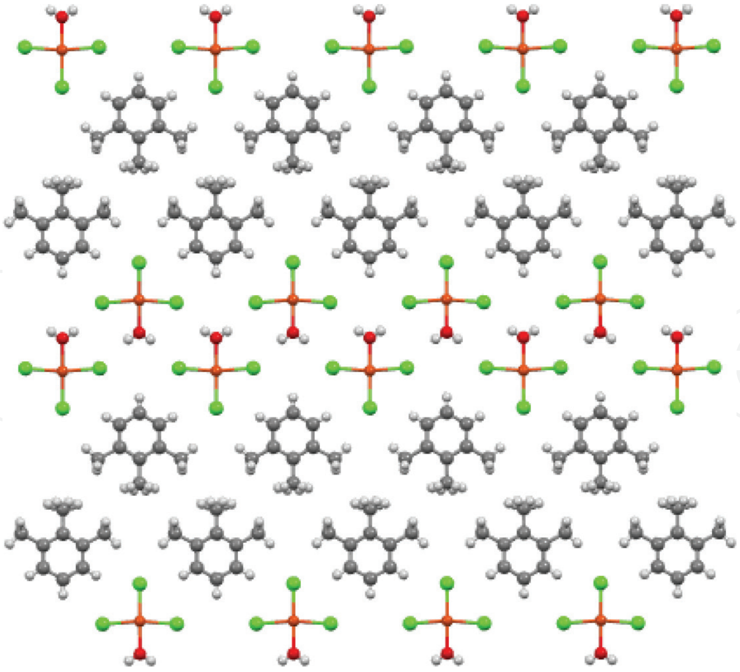


Figure 14.
Layer structure in (1,2,3-trimethylpyridinium) $CuCl_3(H_2O)$ *showing the zipper-like ribbons of organic cations separating inorganic complexes. Another layer stacks with offset inorganic complexes to form asymmetrically bridged dimers. Mirror plane symmetry is perpendicular to the layer and bisects the organic cations and the inorganic complex to produce two-fold positional disorder of the organic cation.*

That is a difficult question to answer. Nevertheless, the *sp* CuX_4 complex appears to be inaccessible with the 1,2,3-trimethylpyridinium cation. While (1,2,3-trimethylpyridinium)$_2$$CuBr_4$ is known, it is a conventional flattened tetrahedral complex that is isostructural to (1,2,3-trimethylpyridinium)$_2$$CoCl_4$ (both in monoclinic $C2/c$). Preliminary work from this laboratory indicates that mixed crystals of (1,2,6-trimethylpyridinium)$_x$(1,2,3-trimethylpyridinium)$_{2-x}$$CuCl_4$ do contain *sp* complexes in a situation where positional disorder is reduced [53]. In any case, these two examples indicate how minor changes in cation can produce major differences in halocuprate(II) structure. It would be interesting to study structures produced by the shape-similar 2,3,4- and 3,4,5-trimethylpyridinium cations which would now also introduce N-H hydrogen bonding interactions. Since these pyridines are not commercially available, a collaboration with a synthetic organic chemist is underway to prepare them.

7. Systems with 3-aminopyridines

Aminopyridines of various types have been prominent in the preparation of halocuprate(II) compounds, with some examples cited already. 3-Aminopyridines, in contrast to 2- or 4-aminooyridines, are capable of protonating both the pyridine and amino N-atoms. Typically the pyridine N-atom protonates first, and if a monoprotonated cation is desired care must be taken to crystallize compounds from solutions that are weakly acidic to avoid diprotonation. At the same time, the monoprotonated cation is capable of coordinating Cu(II) through the amino N-atom—which enables even further structural diversity. Willett et al. reported the earliest compounds with 3-aminopyridine and copper(II) halides. The 3-ammoniumpyridinium cation is found in CuX_4 layer perovskite structures for both the chloride and bromide by virtue

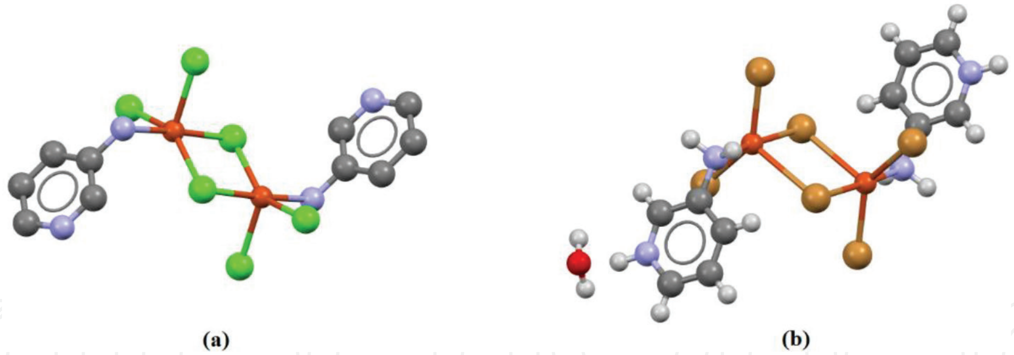


Figure 15.
(a) The symmetrically bridged [$CuCl_3$(3-aminopyridinium]$_2$ dicopper complex and, (b) the asymmetrically bridged [$CuBr_3$(3-aminopyridinium)]$_2$ dicopper(II) complex as a monohydrate.

of the $–NH_3$ head group [54]. Other reported compounds have coordinated 3-aminopyridinium ligands: a symmetrically and asymmetrically bridged dicopper(II) complex for the chloride and the bromide (as a monohydrate in the latter case), respectively, as shown in **Figure 15** [55].

A structure for (3-aminopyridinium)$_2CuCl_4$ has been reported as a typical compound containing flattened tetrahedral $CuCl_4^{2-}$. This reported structure, however, is almost identical to that of (2-aminopyridinium)$_2CuCl_4$, in both unit cell constants and atom positions, and is, in all likelihood, misreported [56]. In order to check this structure, this laboratory undertook crystal growth from acidic aqueous solution and managed to obtain crystals of (3-aminopyridinium)$_2CuCl_4$ by means that can only be described as serendipitous. These crystals gave completely different unit cell constants than the, likely, misreported structure.

In an effort to rationally synthesize crystals of this compound, crystals were grown from various organic solvents (1-proponal, acetonitrile, and tetrahydrofuran) by a thermal gradient technique in sealed, screwcap test tubes placed in a heater block with wells maintained at 40°C. Green crystals of (3-ammoniumpyridinium)$CuCl_4$ were loaded into individual test tubes containing each organic solvent and crystal growth commenced. Another portion of these green crystals were ground together with a stoichiometric amount of 3-aminopyridine and a red-orange solid obtained. Portions of this solid were similarly loaded for crystal growth.

Two new compounds (**Figure 16**) have been obtained in crystal growth from 1-proponal: (1) green crystals of an asymmetrically bridged dicopper complex isomeric to the symmetrically bridged dimer reported by Willett el al.; and (2) red

Figure 16.
Thermal ellipsoid plots of (a) the asymmetrically bridged dicopper(II) complex [$CuCl_3$(3-aminopyridine]$_2$ and (b) the formula unit of (3-aminopyridinium) [$CuCl_4$(3-aminopyridinium)].

crystals of a monocopper complex with a coordinated 3-aminopyridinium ligand and a 3-aminopyridinium lattice cation. The latter compound, [3-aminopyridinium][(3-aminopyridinium)tetrachlorocuprate(II)], is identical in formulation to (3-aminopyridinium)$_2$CuCl$_4$ but with one organic cation moved to the inner coordination sphere. (Crystal growth from acetonitrile yields the known compounds (3-ammoniumpyridinium)CuCl$_4$ and (3-aminopyridinium)$_2$CuCl$_4$) [57]. So far five different compounds have been obtained from the 3-aminopyridine:CuCl$_2$ system just by varying crystal growth conditions. Studies are underway to investigate compounds of the corresponding bromides and of substituted 3-aminopyridines such as 3-amino-2-methylpyridine.

8. Conclusion

The use of pyridinium cations as counterions for halocuprate(II) complexes has provided a wealth of unusual structures due, in part, to the thin profile of the cation, the variety of possible substituent groups, and the easy ability to form a quaternary cation. Previous work has relied heavily on pyridines that are commercially available, but future advances may greatly benefit from targeted pursuit of synthetically prepared pyridines. Mixed cation structures, particularly of A_2CuX_4 systems, have been rarely studied and offer the potential for discovery of new compounds with structural complexity. Different crystallization conditions and solvents have been used in the past to prepare different polymorphs, but now find use in preparation of diverse 3-aminopyridinium halocuprate(II) compounds. While pyridinium halocuprate(II) compounds have been widely studied and dispayed an amazing range of structural diversity, recent discoveries show that they still have the capacity to surprise.

Notes

Structure graphics software used

Ball-and-stick diagrams were plotted using *Mercury 4.0* [58]. Thermal ellipsoid plots were drawn using *ORTEP-3 for Windows* [59].

Crystal data for (2,6-dimethylpyridinium)$_2$Cu$_{10}$Br$_{22}$

Triclinic, $P\bar{1}$, 295 K, a = 9.4862(5) Å, b = 10.0507(5) Å, c = 13.0217(5) Å, α = 104.108(3)°, β = 90.442(3)°, γ = 92.708(3)°, V = 1202.5(1) Å^3, Z = 2. Reflections total/observed = 10,393/3691. θ(max) = 35.139°. Number of least squares parameters = 218. R_{ovserved} = 0.0926, wR_{observed} = 0.2117, goodness of fit = 1.001, Δρ(max/min) = 2.181/−2.585 e$^-$/Å^3.

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