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Author's Review

Structural Characteristics of ACuCl₃ Salts*

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The coordination geometries and the electronic structures found in trichlorocuprates(II) are reviewed. Trichlorocuprates occur in two types: dimers and chains. The crystal chemistry of both types is discussed. A simple electrostatic argument, charge compensation, allows the prediction of the overall structure. Interest in the former class is focused on the different ways of dimer stacking, and on low-dimensional physics in the latter.

INTRODUCTION

Copper(II) halides exhibit a wide variety of coordination geometries and characteristic crystal structure types. These were reviewed by Smith in 1976[1], but recent work in our laboratory[2–5] as well as in other laboratories[6–8] have extended the stereochemical range and structural complexity of the salts known. The interest in copper(II) halides range from bioinorganic areas[9] through catalysis[10] and thermochromism[11] to solid state physics[12]. In the latter area, we have been able to take advantage of the plethora of geometries to map out magneto-structural correlation surfaces and design crystal systems which are realizations of important low-dimensional magnetic models[12]. There is also considerable interest in the cooperative Jahn-Teller effects exhibited by these systems.[13]

In this paper we will (a) review briefly copper(II) halide stereochemistry, (b) review the crystal chemistry of $ACuCl_3$ salts, and (c) discuss some of the factors which influence the type of structure assumed.

GEOMETRIC STRUCTURE OF COPPER(II) HALIDE COMPLEXES

The copper(II) ion is a d^9 system. In octahedral or tetrahedral geometry, it is subject to a Jahn-Teller distortion. Thus, these high symmetry configurations are never observed. What is seen, however, is a wide range of stereochemistry from simple distortions of these two basic geometries to highly irregular coordination spheres. The presence of this large variety of coordination geometries is an indication of the fact that the potential surface is relatively flat for Cu(II) complexes. In this section we will examine some of the geometries found in copper halide complexes.

Octahedral Distortions. — The Jahn-Teller theorem predicts that an octahedral d^9 system should distort along one of the symmetry coordinates to produce a species of lower symmetry[14]. For Cu^{2+} complexes of octahedral

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* Dedicated to Professor D. Grdenić on occasion of his 65th birthday.

parentage, the degenerate E_g level distorts to give a species of D_{4h} symmetry. A priori, the distortion can be either an elongation or a compression along the z-axis leading either to a species with four short and two long copper-ligand distances (4 + 2 coordination) or to one with two short and four long distances (2 + 4 coordination). The latter is rarely observed, except when the Cu^{2+} ion is doped into a diamagnetic host lattice[15]. Just as the sign of the distortion is not dictated by the Jahn-Teller theorem, neither is the magnitude of the distortion. Both rather depend upon the details of the shape of the potential surface. Thus, the D_{4h} elogation can range from a very small amount, e. g., distorted octahedron, to the limiting situation where the axial ligands are completely dissociated, yielding a square-planar complex (Table I).

TABLE I

Coordination Geometries in Copper(II) Complexes

	Compressed Octahedron	Octahedron	Elongated Octahedron (tetragonal)	Square Planar
Coordination number	2 + 4	6	4 + 2	4
Point group	D_{4h}	O_h	D_{4h}	D_{4h}
Orbital with single electron	d_{z^2}	$d_{x^2y^2}$ d_{z^2}	$d_{x^2-y^2}$	$d_{x^2-y^2}$
Ground state symmetry	$^2A_{1g}$	^2E_g	$^2B_{1g}$	$^2B_{1g}$
$g_{\parallel}$	2.0	isotripic	$2.0\,(1—4\lambda/\Delta_1)$	$2.0\,(1—4\lambda/\Delta_1)$
$g_{\perp}$	$2.0\,(1—3/\Delta)$	$g > 2$	$2.0\,(1—\lambda/\Delta_2)$	$2.0\,(1—\lambda/\Delta_2)$

λ: Spin-orbit coupling parameter

Δ: $E\,(E_g) — E\,(A_{1g})$

Δ_1: $E\,(B_{2g}) — E\,(B_{1g})$

Δ_2: $E\,(E_g) — E\,(B_{1g})$

The presence of the 4 + 2 geometry leads to the concept of semi-coordination, that is, based on many structural and spectroscopic properties, the existence of a copper-ligand interaction which is distinctly weaker than the primary copper-ligand interactions. We have found a convenient operational definition for semi-coordination to be based on ligand-ligand contacts, rather than on some arbitrary copper-ligand distance. Thus, for a given ligand, if all the intracomplex ligand-ligand distances are greater than the sum of the van der Waals radii, the ligand is said to be semi-coordinated. This will be useful in describing some of the five coordinate complexes frequently encountered.

Tetrahedral Distortions. — For $Cu(II)X_4^{2-}$ species, the coordination geometries range from nearly tetrahedral geometry with a small D_{2d} distortion superimposed, to a completely planar D_{4h} species. The extent of the D_{2d} distortion is conveniently characterized by the twist angle, τ, between normals of the two CuX_2 planes, which ranges from 0° (square-planar) to 90° (tetrahedral). (Alternatively, the *trans* L—Cu—L angle, Θ, can be identified, which varies from 180° to 109°, respectively.)

Five Coordinate Species. — It is here that the complexity of the coordination geometry of copper(II) complexes is fully revealed. In Figure 1, we have two »idealized members« depicted: a trigonal bipyramidal species (a) and a square pyramidal species (b). Not all A_3CuX_5 salts however contain five-coordinate coppers. One Cu-ligand distance may be so long that this ligand does not even qualify for semi-coordination (c). Realizations of each of these end members exists: the square pyramidal $CuCl_5^{3-}$ ion in $(C_6H_{15}N_3H_3)CuCl_5 \cdot 2H_2O$,[6] the trigonal bipyramidal $CuCl_5^{3-}$ ion in $Co(NH_3)_6CuCl_5$,[25] and the $CuCl_4^{2-}$, Cl^- pair in $[(CH_3)_2NH_2]_3\,[CuCl_4]Cl$.[26]

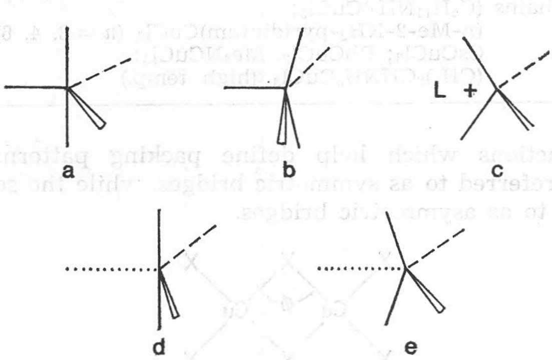

Figure 1. Coordination geometries of Cu^{2+} in the presence of 5 ligands: a) trigonal bipyramidal, b) square pyramidal, c) distorted tetrahedron and separate ligand, d) intermediate between a and b, e) intermediate between a and c.

Also in Figure 1, we have two 4 + 1 coordinate species identified, that is, two species with four primary copper-ligand interactions and one semi-coordinated ligand. The first, labeled (d), is intermediate between the square pyramidal and the trigonal bipyramidal species and is characterized by one linear *trans* L—Cu—L angle, and one bent *trans L—Cu—L* angle. The fifth ligand is at a distance greater than those found in either (a) or (b) and such that it satisfies the criterion for semi-coordination. The bent L—Cu—L bond angle typically varies between 135° and 165°. An example of such a species is found in $CuCl_2 \cdot 2DMSO$[32]. Finally, in (e) a situation intermediate between a trigonal bipyramidal species and a separated CuX_4, X pair is depicted. This can be visualized as being derived from the trigonal bipyramidal species by moving one equatorial ligand away from the copper(II) ion and bending the two axial ligands out towards this ligand. Two different examples of this type are found in $[(CH_3)_2CHNH_3]_2CuCl_4$[17]. Of course, all possible combinations of these distortions may be found in actual species.

CRYSTAL CHEMISTRY OF $ACuCl_3$ SALTS

For purposes of this paper, the structures of $ACuCl_3$ salts will be classified as dimeric or chain-like (Table II), depending upon the nature of the bridging between the copper ions. Primary bridges, involving only short Cu—Cl bonds, are used to define the principle structural units. Secondary bridges, involving one short Cu—Cl bond and one long (semi-coordinate) Cu—Cl bond, provide

TABLE II

$ACuCl_3$ Structures

Type	Compound	Reference
I. $Cu_2Cl_6^{2-}$ dimers		
A. Isolated	$\Phi_4AsCuCl_3$; Φ_4PCuCl_3	16, 17
B. Planar	$KCuCl_3$; NH_4CuCl_3; (melamineH_2)Cu_2Cl_6	18, 19
C. Bifolded	$(CH_3)_2NH_2CuCl_3$; $(CH_3)_2CHNH_3CuCl_3$; (low temperature)	20, 5
	(paraquatH_2)Cu_2Cl_6; ($\Phi C_2H_4NH_2CH_3$)$CuCl_3$	21, 22
II. Chains		
A. Bibridged chains	($C_6H_{11}NH_3$)$CuCl_3$;	2
	(n-Me-2-NH_2-pyridinium)$CuCl_3$ ($n = 3, 4, 6$)	4
B. Tribridged	$CsCuCl_3$; $RbCuCl_3$, Me_4NCuCl_3;	23, 13, 24
	$(CH_3)_2CHNH_3CuCl_3$ (high temp.)	5

additional interactions which help define packing patterns. The primary bridges are also referred to as symmetric bridges, while the secondary bridges may be referred to as asymmetric bridges.

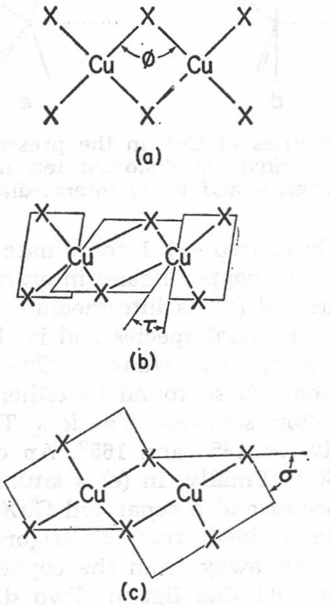

Figure 2. Angles in Cu_2X_6 dimers: a) bridging angle, Φ, b) twist angle, τ, c) bifold angle, σ.

Dimeric Structures. — The basic symmetric bibridged building block of many $ACuCl_3$ systems is the symmetric bibridged $Cu_2Cl_6^{2-}$ dimer. This comes in one of three basic geometrical configurations as illustrated in Figure 2; a planar dimer, Figure 2a; a twisted dimer, Figure 2b; and a bifolded dimer, Figure 2c. The planar dimers and bifolded dimers form stacks in such a manner that each Cu(II) ion expands its coordination to 4 + 2 and 4 + 1, respectively.

The Cu—Cl distance within the dimer are generally around 2.3 Å, with the bridging Cu—Cl distance systematically longer than the terminal distance, and the terminal Cu—Cl distances shorter in the twisted dimers than in the other types.

The twisted $Cu_2Cl_6^{2-}$ dimers occur in systems with large, bulky non-hydrogen bonding counterions such as Φ_4As^+ [16] or Φ_4P^+ [17] and, possibly, $(but)_4N^+$ [28]. The twist gives the Cu(II) ions a coordination geometry intermediate between square planar and tetrahedral. The dihedral angle between the bridging Cu_2Cl_2 plane and the terminal $CuCl_2$ plane, τ, is approximately 50°. This twist is associated with the electrostatic repulsions between the chloride ions, which can be relieved by allowing the coordination sphere to distort towards a tetrahedral geometry.

The centrosymmetric, planar $Cu_2Cl_6^{2-}$ dimers, as found in $KCuCl_3$ and NH_4CuCl_3 [18], are really just short segments out of the infinite bibridged chain found in the $CuCl_2$ structure. Examples where trimeric, tetrameric, and pentameric segments exist are also known.[29–31] The dimers are locked into the planar configurations by the way they stack (Figure 3), which again is a segment of the stacked chain structure found in $CuCl_2$. Each dimer is »displaced« with respect to its neighbors so that each copper(II) ion forms two semi-coordinate interactions with its neighbors at distances of 2.8—3.1 Å. This stacking is represented schematically in Figure 4a and is referred to as the double chain structure since both copper ions are involved in bridge (semi-coordinate bond) formation between dimers. It leads to a characteristic short repeat distance of 3.9—4.1 Å. The interaction between the counterions and the dimers is essentially electrostatic in nature, the K^+ or NH_4^+ ion having nine nearest chloride neighbors. The NH_4^+ ion is almost certainly dynamically disordered, reducing the effectiveness of any hydrogen bonding.

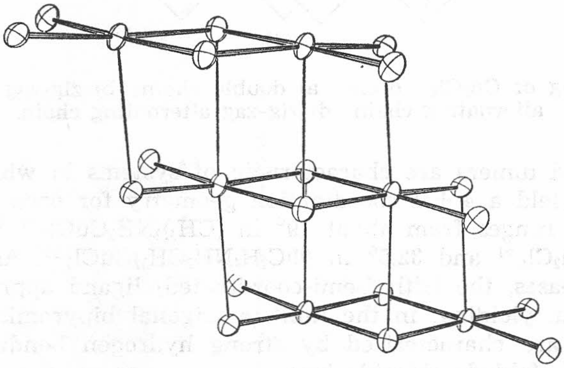

Figure 3. The crystal structure of $KCuCl_3$, data after reference 18a.

An interesting variation of this structure is found in $(melamine\ H_2)Cu_2Cl_6$ [19]. The dimers are no longer centrosymmetric, and one half of the dimer shows significant distortion from planarity. The packing of the dimers is again such that each copper has a 4 + 2 coordination geometry. However, as shown schematically in Figure 4b, the stacking of the dimers is different with the displacement direction perpendicular to the long dimer axis alternating down the chain.

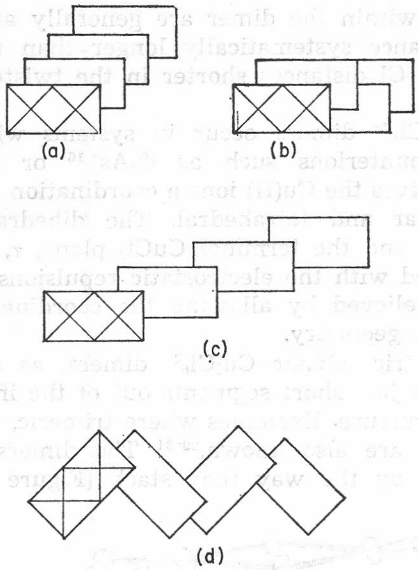

Figure 4. Stacking of $Cu_2Cl_6^{2-}$ dimer a) double chain, b) zig-zag double chain, c) alternating chain, d) zig-zag alternating chain.

The bifolded dimers are characteristic of systems in which the stacking of the dimers yield a 4 + 1 coordination geometry for each copper ion. The bifold angle, σ, ranges from about 19° in $(CH_3)_2NH_2CuCl_3$ [20] to nearly 32° in (paraquat H_2) Cu_2Cl_6 [21] and 32.5° in $(\Phi C_2H_4NH_2CH_3)CuCl_3$ [22]. As the folding of the dimer increases, the fifth (semi-coordinated) ligand approaches closer to the copper atom, yielding, in the limit, a trigonal bipyramidal coordination. The structures are characterized by strong hydrogen bonding between the counterions and »folded« chloride ions.

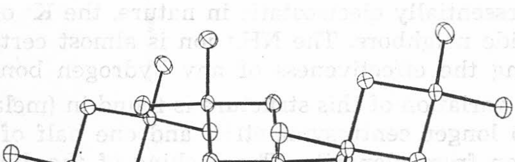

Figure 5. Dimer-chain structure of isopropylammonium copper chloride. Data from reference 5.

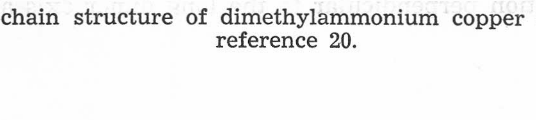

Figure 6. Dimer-chain structure of dimethylammonium copper chloride. Data from reference 20.

The stacking of the dimers, illustrated in Figure 5, is such that there is one pair of asymmetric Cu—Cl—Cu bridges (e. g., bridges composed of one short Cu—Cl distance and one long Cu—Cl distance) between adjacent dimers. This results in a chain-type structure, with alternating symmetric and asymmetric bibridged units. Schematically, this stacking is illustrated in Figure 4c. It can be thought of »displacing« subsequent dimers so that only one copper ion on the adjacent dimer is covered. This leads to a characteristic repeat distance along the chain of 6.0—6.2 Å. The isopropylammonium, paraquat, and N-methyl-phenethylammonium salts crystallize in this manner. An alternative stacking, which leads to the same bifolded arrangement within the dimer, is assumed by $(CH_3)_2NH_2CuCl_3$ [20]. This is shown schematically in Figure 4d and illustrated in Figure 6. It involves a rotation of the dimer by approximately 90° in addition to the translation.

Chain Structures. — Under certain circumstances, determined by the size, shape, and ability of the cation to form hydrogen bonds, the $ACuCl_3$ compounds can form infinite-chain structures. In principle, there are three categories possible, as depicted in Figure 7: Monobridged, four-coordinate (a); bibridged, five-coordinate (b); and tribridged six-coordinate (c). Of these only the second and third, as well as an intermediate have been observed with trihalocuprates. A monobridged chain of tetrahedra has been suggested for the T ≥ 100 °C phase of isopropylammonium copper bromide. The type shown in Figure 7b, a bibridged chain of square pyramidal units, is realized in the salts *n*-methyl-2-amino-pyridinium copper chloride, where $n = 3$, 4, and 6 [4]. The apical chlorides on adjacent complexes are pointing in exactly opposite directions. The organic cation in this case is large and flat, but rigid, with ample opportunities for hydrogen bonding. Using a more flexible cation of similar size, such as cyclohexylammonium[2], the chain forms in a more collapsed shape (Figure 8), halfway between the bibridged, five-coordinate and the tribridged, six-coordinate type. From the criteria mentioned earlier in this article the interaction between the copper ion and an adjacent apical chloride does not qualify as semicoordinated in this case, so that the chain is still considered bibridged, square-pyramidal. The tribridged structures are found with cations such as tetramethylammonium[24], Rb^+ [13,14], and Cs^+ [23],

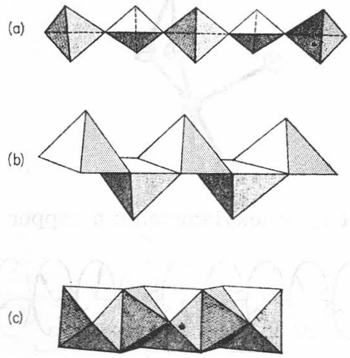

Figure 7. CuX_3^- chains: a) monobridged, four-coordinate, b) bibridged, five-coordinate, c) tribridged, six-coordinate.

At elevated temperatures isopropylammonium copper trichloride adopts a tribridged structure[5], and the type is also found in crystals of $[(CH_3)_3NH]_3Cu_2Cl_7$ [35] besides isolated $CuCl_4^{2-}$ complexes. These face-sharing distorted octahedral chains have received interest by solid-state physicists because the 4 + 2 (Jahn-Teller) distortion leads to a modulation of the underlying hexagonal structure. In the cesium salt the direction of the distortion is arranged in a helical

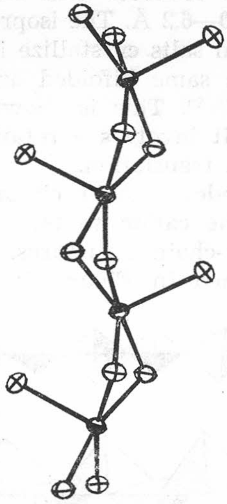

Figure 8. Chain structure of cyclohexylammonium copper chloride. From reference 2.

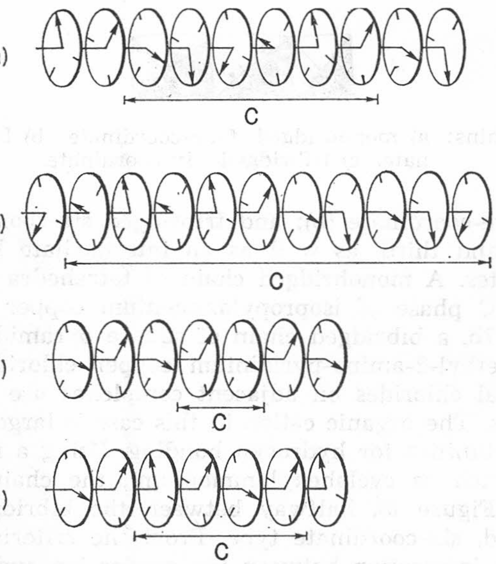

Figure 9. Schematic representation of the direction of the Jahn-Teller distortion in several bibridged chain structures. c denotes the repeat distance along the chain a) $CsCuCl_3$, b) $TMCuCl_3$, c) high-temperature $(CH_3)_2CHNH_3CuCl_3$, d) low-temperature $RbCuCl_3$ (presumed).

fashion and there is a true 6_1 screw axis along the chain at room temperature. The tetramethylammonium salt, however, consists of helical segments extending over five copper sites each. Between such segments the sense of rotation is inverted for the length of one copper-copper distance (Figure 9b). In the trimethylammonium, and the high temperature isopropylammonium compounds no distinct helical pattern exists. Rather the twist handedness between consecutive distortion directions changes with every Cu—Cu translation (Figure 9c.). The alkali compounds, $RbCuCl_3$ and $CsCuCl_3$ (together with some similar Cr^{2+} salts), show phase transitions to structures of higher symmetry at elevated temperatures: at 423K for Cs^+ [35,36], and at 339K for Rb^+ [13,34]. There is evidence for phase changes in the 300—400K range in the $(CH_3)_4N^+$ compound[37]. $RbCuCl_3$ also undergoes a second phase transition at 261—263K[13,34,38]. The low temperature phase is believed[13,34] to consist of segments with alternating handedness, each extending over two Cu—Cu distances (Figure 9d).

STRUCTURAL PRINCIPLES

One helpful guide in seeking to correlate the various structural features observed is the concept of charge compensation. The lattice may be visualized as being built up of single Cu^{2+} cations, Cl^- anions, and alkali metal or organic ammonium (+1)-counterions. Electrostatically, the complete charge separation represented by this description is energetically unfavorable. Structurally, the lattice will react in such a manner as to minimize, or compensate for, this charge separation. Three principle mechanisms appear to be operative: (a) strengthening (shortening) of the primary Cu—Cl bonds leading to some degree of covalency, (b) formation of symmetric (two short Cu—Cl bonds) bridges or asymmetric (one short and one long Cu—Cl bond) bridges, or (c) formation of the strong electrostatic or hydrogen bonding interactions between the halide ions and the counterions.

These effects can be seen in the various structures discussed previously. For example, the isolated, planar $Cu_2Cl_6^{2-}$ dimer is electrostatically unbalanced, with only the middle two halide ions having achieved charge compensation. If it remains isolated, as with the large, bulky Φ_4As^+ or Φ_4P^+ cations, the copper(II) ion distorts its coordination sphere towards tetrahedral geometry, so that the terminal Cu—Cl bond distance can shorten. In the double chains (Figure 4a), four long Cu—Cl interactions occur between each pair of dimers. The structure can be stabilized by small cations such as K^+ or NH_4^+ which interact electrostatically with the two nonbridging terminal halides. In the alternating chain of dimer structures (Figures 4c and 4d), only two long Cu—Cl interactions occur between pairs of dimers. However, these do provide charge compensation for two of the four terminal halides. This structure seems to be prefered by small to moderate size organic cations which can form strong hydrogen bonds with the two remaining terminal halides. The isopropylammonium ion is an example of this, where the primary hydrogen bonding contacts of the $—NH_3$ moiety are all with the two remaining terminal halides.

In the bibridged $ACuCl_3$ chains, two of the halides are charge compensated through formation of the symmetric bridges. However, the third halide is in a nonbridging position and, in addition, has a substantially longer Cu—Cl distance due to the square pyramidal geometry. Thus, this structure can be stabilized only with organic cations capable of forming several hydrogen bonds with this apical halide.

In the tribridged $ACuCl_3$ chains, on the contrary, all three halides are involved in Cu—Cl—Cu bridges, one of the symmetrical and two of the asymmetrical type. Thus this structure is characteristic of medium size, diffuse cations with no hydrogen bonding capability, such as Cs^+ or Me_4N^+. An interesting variation of this occurs in $[(CH_3)_3NH]_3Cu_2Cl_7$, which consists of a tribridged $(CuCl_3)_n^{n-}$ chain surrounded by groups of $[(CH_3)_3NH^+]$ and $CuCl_4^{2-}$ ions.

These principles can be applied to understand the nature of structural phase transitions that occur in a few copper halide salts. Thus, the low temperature phase of $[(CH_3)_2CHNH_3]CuCl_3$ is an alternating chain of dimers, with the organic cation strongly hydrogen bonded to dimer. At the phase transition, the organic cation becomes dynamically disordered, effectively breaking the hydrogen bond structure, thus mimicing Me_4N^+. The copper-chloride framework now goes over to the tribridged chain structure so that the charge compensation lost from the hydrogen bonding is regained by the formation of new Cu—Cl—Cu bridges.

CONCLUSIONS

Compounds of the stoichiometry $ACuCl_3$ show a large variety in coordination geometry and overall structure. Three main classes emerge from the abundance: isolated $Cu_2Cl_6^{2-}$ dimers, stacked dimers, and pure chains.

Future research in the first of the above classes will probably aim at a more detailed understanding of the electronic properties of copper dimers, presumably by spectroscopic methods (UV/VIS/NIR, EPR, inelastic neutron scattering, etc.). The second and third area present more of a challenge to the structural chemist; by far not all dimer-stacking possibilities and chain types have been realized to date. Particularly beautiful structures to aim for would be a helical arrangement of dimers in the second category, and a chain of corner-sharing $CuCl_4^{2-}$ tetrahedra (like certain silicates) in the third category. The phase transitions of the tribridged chains will certainly receive continuing interest in the future. The relationship between the structural and the magnetic properties will continue to be examined in great detail.

The factors deciding on the type and the finer details are: cation size, shape, and flexibility, as well as the ability of forming hydrogen bonds. The qualitative charge compensation model helps in predicting the overall structure, given a particular cation, but of course, its classical nature prohibits its use in detail matters.

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SAŽETAK

Strukturne karakteristike $ACuCl_3$ soli

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Dan je pregled koordinacija i elektronskih struktura triklorokuprata(II). Triklorokuprati se javljaju u dva tipa: dimeri i lanci. Diskutira se o kristalokemiji oba tipa. Jednostavan elektrostatski pristup, kompenzacija naboja, dopušta predviđanje cijele strukture. Interes je kod prvog tipa usmjeren na različite načine slaganja dimera, a kod drugoga na fiziku niskih dimenzija.