# The Effect of HCl on the Copper(II) Chloride/Pyridine/Water System: Synthesis, Properties and Crystal Structure of $[(pyH)_2CuCl_4]$ and $[(pyH)_2Cu_3Cl_8(H_2O)_2]_n$

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Bis(pyridinium) tetrachlorocuprate monomer **1** and bis(pyridinium) octachlorodiaquatricuprate polymer **2** were synthesized and their crystal structures were determined. Both complexes contain pyridinium cations with bifurcated H-bridges. These H-bridges stabilize the monomeric structure of the tetrachlorocuprate anion together with the steric demand of the relatively large pyridinium ions in the crystal lattice of **1**. Conversely, at the lower pyridinium ion:copper(II) ratio of **2**, the bifurcated hydrogen bonds reduce the electron density on the chloride ions in such a way that the electron repulsion decreases and coordination spheres with more ligand interactions develop. Obviously, water may be a successful competitor for ligand sites in **2** as well. The octahedral and square-pyramidal structural units condense into polymeric chains which are stabilized by the interchain hydrogen bond networks of the water molecules. The structure motif of SP-5-[*OC-6-SP-5-SP-5*]-OC-6 (–$CuCl_5$-$[CuCl_4(OH_2)_2]$-$CuCl_5$-$CuCl_5]$-$CuCl_4(OH_2)_2$-) were observed in **2**, and the two neighboring square-pyramidal units were found to be localized in a *transoid* position. The IR and ESR spectroscopical characterization of complexes was also performed.

## Introduction

Due to their structural variety, modes of coordination and application in chemical and material sciences[1−4] a great deal of attention has been paid to the study of copper(II) halide complexes. The plasticity of the coordination sphere of the copper cations and the bridge-forming ability of the halide anions can lead to a variety of crystalline architectures with different coordination numbers, geometries and nuclearities.[2] The copper(II) ion in these complexes exhibits normal coordination as well as semi-coordination. In the latter case, the bond lengths are 0.3−1.0 Å longer. The coordination numbers may vary from four to six (with typically distorted geometries). The building species form chains of edge-sharing monomers with halide bridges between the neighboring copper(II) ions. The coordination spheres of the copper atoms in these chains are frequently supplemented with other ligands.

Pyridinium salts of chlorocuprate anions are of special interest both from a theoretical and a practical point of view. This is attributed to the fact that protonation of the pyridine ring decreases its coordination ability, and hydrogen-bond-forming properties of the N−H hydrogen atom introduces additional structure-building possibilities, hence pyridinium cations are capable of stabilizing $MX_4^{2-}$ layer-type structures.[3]

Although the structure and properties of several chlorocuprate(II) compounds of substituted pyridine bases have been documented,[4] no X-ray crystal structure of unsubstituted pyridinium chlorocuprate(II) compounds has yet been reported. In this paper the synthesis, properties and crystal structures of monomeric bis(pyridinium) tetrachlorocuprate(II) (**1**) and polymeric bis(pyridinium) octachlorodiaquatricuprate(II) dihydrate (**2**) are reported.

## Results and Discussion

### Synthesis of Pyridinium Chlorocuprates

The protonation of pyridine ligand led to the formation of complexes **1** and **2**. The key to the formation of these two compounds in the $CuCl_2/C_5H_5N/HCl/H_2O$ system in the presence of excess hydrochloric acid lies in the distribution of the pyridinium cations between chlorocuprate anions. One of the chlorocuprate compounds may contain one copper(II) ion, while the other may have three copper(II) ions. Thus, formation of equimolar amounts of **1** and **2** is possible due to the 1:1 pyridine:copper molar ratio in the polymeric $[CuCl_2(py)]_n$ starting material. Decreasing the amount of HCl in the reaction leads to an increase in the

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amount of **2** formed and to a decrease in the amount of **1**. The increased yield of **2** can be attributed to an incomplete release of pyridine from the $[CuCl_2(py)]_n$ polymer, since the neutral pyridine ligand may form other compounds with $CuCl_2$.[5,9] This way, the molar ratio of pyridinium ion:copper(II) can be lower than 1:1 and formation of the 2:3 pyridinium complex **2** becomes possible. Consequently, complex **1**, which has a pyH:Cu(II) stoichiometry of 2:1, can form in only a small amount.

In order to check the polymer complex, we reproduced some earlier experiments.[5] The reaction of copper(II) chloride and pyridine hydrochloride in a molar ratio of 3:2 in conc. HCl led to the precipitation of **2**, and only a small amount of **1** was formed. If a stoichiometric amount of HCl was used for the reaction only the $[CuCl_2(py)]_n$ polymer was obtained.[5] Further addition of HCl, however, led to the dissolution of the $[CuCl_2(py)]_n$ polymer and the complexes mentioned above could be obtained.

## ESR Spectral Characterization of Pyridinium Chlorocuprate Complexes

The ESR spectra of both compounds were recorded at 77 K and 300 K. No significant effect of the temperature on the signal positions and splittings could be observed.

The tetrachlorocuprate anion in **1** gives a single broad ESR signal at $g = 2.209$. The lack of anisotropy can be explained either by a dynamic Jahn−Teller effect or by strong spin-exchange between centers that are randomly distorted by the static Jahn−Teller interaction. The temperature-independent line-width makes the latter mechanism more likely. The large *g*-factor suggests anionic ligand-to-metal bonds.

Complex **2** has a broad anisotropic ESR signal at $g_{zz} = 2.49$ and $g_{xx} = g_{yy} = 2.126$. The large *g*-factors indicate ionic bonds, the order of *g*-factors reveals a $d_{x^2-y^2}$ ground state for the $3d^9$ electron configuration. This ground state is compatible with square-planar or square-pyramidal coordination. Magnetic interactions between neighboring $Cu^{II}$ centers should be strong, since no hyperfine splitting is observed. Presumably the dipolar interactions dominate over the exchange interactions, since the bonds are not covalent.

## IR Spectroscopic Investigations of 1 and 2

In order to assign the internal vibrations, it was presumed that the proton acts as a complex-forming ligand and the pyridinium ion is a quasi-metallic complex of the pyridine and the hydrogen ion wherein the central pseudo-metallic hydrogen atom can also interact with other atoms. In the IR spectra of both compounds we could identify the IR-active bands of the pyridine ring as well as the stretching vibrations of the N−H bond. The positions of the assigned vibrations were compared with the vibrations of non-complexed free pyridine base and with the vibrations of pyridine-coordinated $MCl_2(py)_2$ complexes.[10]

The values of the coordination-sensitive stretchings of pyridine were found to be up to 640 and 440 $cm^{-1}$, respectively; these values are similar to the values of transition metal complexes.[10] Based on the band shifts, the binding force of the proton in these compounds is very similar to the binding force of copper(II) to the pyridine in $[CuCl_2(py)_2]$. This strong coordination ability of the $H^+$ to the pyridine nitrogen atom may induce the formation of a pyridinium salt instead of an HCl complex of the pyridine-coordinated copper(II) chloride complexes as has been assumed previously.[5] Owing to the similar binding ability of $H^+$ and $Cu^{2+}$ to the pyridine N-atom, however, the formation of N-coordinated Cu-chloro complexes or pyridinium-chlorocuprate complexes depends strongly on the HCl concentration of the $CuCl_2$/pyridine/HCl/$H_2O$ system.

The coordination of the proton to the pyridine N atom generally causes higher band-shifts of the ring-atoms than in the metal complexes. The IR spectra of **1** and **2** are very similar, the position of the C−H out-of plane and in-plane stretchings and ring-stretchings or breathing bands show almost the same frequencies in both spectra. Characteristic bands of the pyridinium ion ($\tilde{\nu} = 1540$, 1327, 1295 and 1250 $cm^{-1}$) can be seen in both spectra, although the degree of degeneracy is lower in **2** due to the more complicated multidendate hydrogen-bonding network structure. Symmetric N−H stretchings are lowered from 3200 $cm^{-1}$ to 2850 $cm^{-1}$ due to the presence of well-defined hydrogen bonds.[11] The OH vibrations in **2** give well-defined bands at $\tilde{\nu} = 3300$ and 3400 $cm^{-1}$.

The $\gamma$(NH) band at around 900 $cm^{-1}$ is very sensitive to the presence of hydrogen bonds. There is one band in compound **1** at 905 $cm^{-1}$, and an irregular triplet is present at 875, 900 and 905 $cm^{-1}$ in the spectrum of **2**. This also indicates the presence of characteristic hydrogen bonds. The strength of the hydrogen bonds of **1** and **2** is similar to the strength of the N−H···Br bond in [pyNH]Br.[11]

The bands of the Cu−Cl and Cu−O vibrations fall outside the detection limit of our IR spectrometer (400 $cm^{-1}$). The broad Cu−N bands between 400 and 440 $cm^{-1}$could not be observed in the IR spectra of either compound. The narrow band at 405 $cm^{-1}$ is a characteristic pyridine-ring vibration.[10]

## X-ray Crystal structures of 1 and 2

The structural chemistry of chlorocuprate(II) salts was studied recently.[1−4] In tetrachlorocuprate(II) compounds the Cu−Cl distances vary between 2.205 Å and 2.265 Å and the *trans*-Cl bond angles vary from 104.5 to 180° (i.e. between the limiting values of tetrahedral and square-planar geometry). In **1** (Figure 1 and Table 1) the Cu−Cl(3) bond is slightly shorter [2.233(1) Å] than the Cu−Cl(2) bond [2.251(1) Å, Table 2]. Both chloride ions take part in the network of the hydrogen bonds (Table 2), and form a bifurcated bridge to the cationic proton of the pyridinium ion. The crystal structure of compound **1** is composed of discrete $CuCl_4{}^{2-}$ polyhedra and isolated pyridinium cations. The copper atom sits on a crystallographic twofold axis.

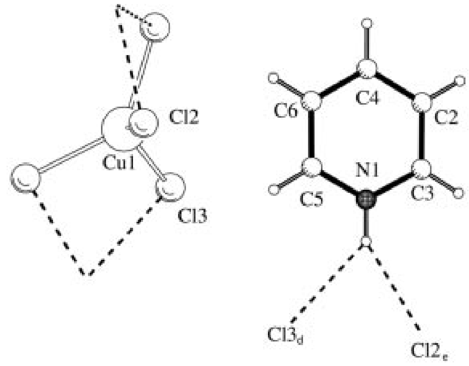

Figure 1. Molecular structure of bis(pyridinium) tetrachlorocuprate(II) (**1**) with atomic numbering and hydrogen-bond contacts indicated in broken lines

Table 2. Coordination geometry and normalized hydrogen bonding data (Å, °) with their esd's for non-hydrogen atoms in (**1**)

| M−X | M−X(Å) | X−M−X | X−M−X(°)[a] |
|---|---|---|---|
| Cu1−Cl3 | 2.2327(6) | $Cl3-Cu1-Cl3_i$ [b] | 101.82(2) |
| | | $Cl2-Cu1-Cl2_i$ | 100.53(2) |
| Cu1−Cl2 | 2.2505(6) | $Cl2-Cu1-Cl3_i$ | 97.83(2) |
| | | Cl2−Cu1−Cl3 | 132.05(2) |
| Donor···H···Acceptor | D−H (Å) | H···A | D-H···A (°) |
| $N(1)\cdots H(1)\cdots Cl(3)_{ii}$ [c] | 1.009 | 2.604 | 133.1 |
| $N(1)\cdots H(1)\cdots Cl(2)_{iii}$ [d] | 1.009 | 2.386 | 141.4 |

[a] Only non-redundant angles are shown. [b] $i = 1 - x, y, 1/2 - z$. [c] $ii = 1 - x, -y, -z$. [d] $iii = x, -y, -1/2 + z$.

The Cl−Cu−Cl bond angles in **1** vary between 97.83(2) and 132.05(2)° showing a geometry intermediate between square planar and tetrahedral coordination. The 0.695 packing coefficient of **1** indicates close packing. The mean plane of the chloride anions lies perpendicular to the *b* crystallographic axis, and the pyridinium ions lie almost perpendicular to the Cu−Cl(2) vector. These data together with the crystal packing (Figure 2) show the basic forces directing crystal growth. Packing appears as separate columns of cations and anions. The cations are oriented so as to minimize electrostatic repulsion between identical charges and simultaneously maximize attraction between opposite ones. The steric demand of the pyridinium cations neighbouring to each tetrachlorocuprate(II) anion, their hydrogen bonds and the shielding as a joint effect isolates the tetrachlorocuprate anions in the monomeric form. Since the nearest non-covalent Cu−Cu and the shortest Cl···Cl distances are both longer than the sum of the respective van der Waals radii, there is no visible interaction between the tetrachlorocuprate(II) anions.

The structure of **2** shows a very distinct pattern (Figure 3). The tetrachlorocuprate anions polymerize with the formation of a condensed Cl-bridged chain-structure by complementing the coordination sphere with water. The building block of the crystal may be described as an endless concatenation of edge-sharing five-coordinate square-pyramidal ($MX_4Y$ type *SP*) and hexacoordinate octahedral ($MX_4Y_2$ type *OC*) metal centers. The *SP*-[*OC*-*SP*-*SP*]-*OC* sequence is repeated throughout the crystallographic trans-

Table 1. Crystal data and details of the structure determination for **1** and **2**

| | **1** | **2** |
|---|---|---|
| Empirical formula | $(C_5H_5NH)_2[CuCl_4]$ | $(C_5H_5NH)_2[Cu_3Cl_8(H_2O)_2]$ |
| Molecular weight | 365.57 | 670.47 |
| Crystal system | Monoclinic | Monoclinic |
| Space group | *C*2/*c* (No.15) | *P*2$_1$/*c* (No. 14) |
| *a* [Å] | 7.980(1) | 7.889(1) |
| *b* [Å] | 13.818(1) | 14.145(1) |
| *c* [Å] | 13.523(1) | 9.914(1) |
| β [°] | 94.81(1) | 99.20(1) |
| *V* [Å$^3$] | 1485.9(2) | 1092.1(2) |
| Z | 4 | 2 |
| *D*(calc) [Mg/m$^3$] | 1.634 | 2.039 |
| μ (Mo-$K_\alpha$) [mm$^{-1}$] | 2.2 | 3.9 |
| Crystal Size [mm] | 0.25 × 0.30 × 0.40 | 0.15 × 0.25 × 0.50 |
| Temperature (K) | 295 | 295 |
| Radiation λ [Å, Mo-$K_\alpha$] | 0.7107 | 0.7107 |
| Θ min.-max. [°] | 3.0, 35.0 | 2.5, 34.9 |
| Data set *h*, *k*, *l* (min, max) | −12→12; −22→22; −21→21 | −12→12; −22→8; 0→15 |
| Total, Unique data, $R_{(int)}$ | 6900, 3254, 0.023 | 5143, 4769, 0.025 |
| Observed data [$I > 2.0\sigma(I)$] | 1725 | 3033 |
| $N_{ref}$, $N_{par}$ | 3254, 84 | 4769, 116 |
| $R_1$, $wR2$, $S$ | 0.0385, 0.1018, 0.93 | 0.0562, 0.1439, 0.94 |
| Max. and av. shift/error | 0.01, 0.00 | 0.01, 0.00 |
| Min. and max. resid. dens. [e/Å$^3$] | −0.47, 0.71 | −1.95, 1.85 |

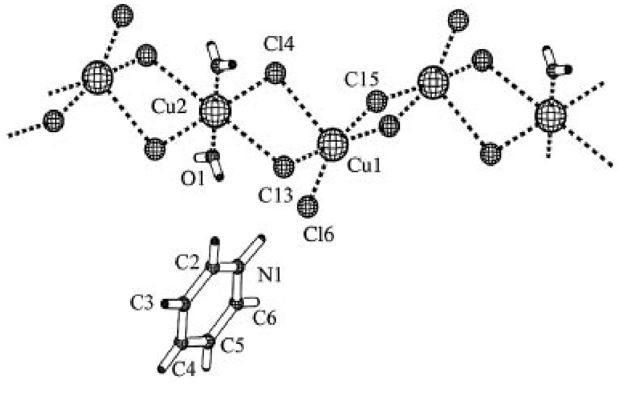

Figure 2. Packing motif in bis(pyridinium) tetrachlorocuprate(II) (**1**); hydrogen bonds are shown by broken lines

lation along the *c* axis. The *OC-SP* link occurs through the edge sharing of the axial ligands of both the *SP* and the *OC* polyhedra. Consequently, edge-sharing occurs between the connected *SP-SP* polyhedra through the equatorial positions. The coordination geometry of the two independent $Cu^{II}$ ions forming the asymmetric unit is different not only in their ligating relationships but also in the water that coordinates solely to the hexacoordinate $Cu^{II}$. Pentacoordinate Cu(1) binds only to chlorides. This latter polyhedron has approximately equal and ideal equatorial distances ranging from 2.267(1) Å to 2.313(1) Å, while the axial distance is longer [2.675(1) Å], due to a Jahn−Teller effect. The shape of the coordination polyhedron is intermediate but relatively close to a square-pyramid conformation (τ descriptor[12] is 0.20). The value of 85.2% of the Berry pseudorotation from the trigonal bipyramid form to the *SP* one is also in agreement with this conclusion. The pyridinium cation behaves as if it would replace a missing sixth coordination site opposite the true ligand, the axial Cl(4) chloride ion. The SP-coordinated polyhedron is capped from this second axial ligand position (see Figure 3). The other metal [Cu(2)] has an apparently more regular coordination. Symmetry dependence makes the polyhedron more symmetric on the one hand, and distorted from the coordination distances on the other (Table 3). The long axial distance occupied by Cl(3) [2.874(1) Å] is the longest observed here, while the water has a rather short equatorial distance. The other equatorial distance pair [2.279(1) Å] maintained by the Cl(4) is in agreement with the expected value of approx. 2.3 Å. The alternating Cu(1)···Cu(1)···Cu(2)···Cu(1) metal centers are displaced by 3.597(1) Å−3.411(1) Å−3.597(1) Å from each other. The polymeric chains running in the *c* direction at $x = 0$ and $x = 1/2$ are crosslinked by hydrogen bonds (Table 3, Figure 4). Both edge-sharing anions of the hexacoordinate metal are involved in four acceptor interactions, while the pentacoordinated one assumes five acceptor interactions, four of which are common to the hexacoordinated one. One of the three chloride anions [Cl(5)] does not take part in any hydrogen bonds as it is shielded in the central edge-sharing between the two neighboring *SP* polyhedra. Three of these six H-bridges are of the weaker C−H···Cl type. Interestingly, these three bridges also serve as cross-links between the two *ortho*- and the *para*-positioned hydrogen atoms of the pyridinium cations. Analogously to **1** the cationic proton of the pyridinium ion appears in the bifurcated hydrogen bridge.

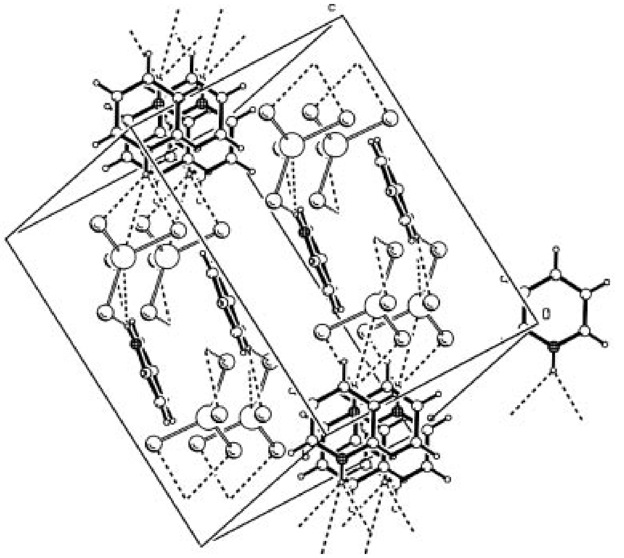

Figure 3. Crystal structure of bis(pyridinium) octachlorodiaquatricuprate(II) (**2**); only the atoms forming the asymmetric unit are numbered; polymeric contacts are shown by broken lines

The dielectric role of both ligand types (pyridinium and water molecules) in insulating the octahedral and square-pyramidal copper coordination centers is such that they effectively and simultaneously shield and compensate for opposite charges. Since the hydrogen bond network removes the charges of the chloride ions, the anion may relax back towards the square-planar geometry favored by crystal-field effects.[10] Other factors may have an influence on the size and nature of the distortions of the octahedral units of the $CuX_4Y_2$ octahedra, for instance the Jahn−Teller distortion and the difference between the donor strength of the axial water ligands and the equatorial chloro-bridges may be the main reasons for the tetragonal distortion of the OC-6 units in **2**.[13,14] The 0.732 packing coefficient of **2** indicates fairly close packing in the crystal.

## Conclusions

Based on the results of the chemical analysis, the IR, the Raman and the ESR spectroscopic studies and the single crystal investigations, the structure of water-soluble compounds formed in the $CuCl_2$/pyridine/HCl/$H_2O$ system has been determined. The two compounds, namely bis(pyridinium) tetrachlorocuprate monomer **1** and bis(pyridinium) octachlorodiaquatricuprate polymer **2** are formed in an obviously pH-dependent manner. The effect of steric and electronic supplements in building the structural units can be

Table 3. Coordination geometry and normalized hydrogen-bonding data (Å, °) with their esd's for non-hydrogen atoms in (**2**) a) coordination geometry (Å, °)

| M−X | M−X/Y (Å) | X−M−Y | X−M−Y (°)[a] |
|---|---|---|---|
| | | Cl3−Cu1−Cl4 | 88.98(3) |
| | | Cl3−Cu1−Cl5 | 91.29(3) |
| Cu1−Cl3 | 2.2672(8) | Cl3−Cu1−Cl6 | 91.46(3) |
| Cu1−Cl4 | 2.6748(9) | Cl3−Cu1−$Cl5_i$ [b] | 172.84(4) |
| Cu1−Cl5 | 2.3128(9) | Cl4−Cu1−Cl5 | 98.77(3) |
| Cu1−Cl6 | 2.2934(8) | Cl4−Cu1−Cl6 | 100.35(3) |
| Cu1−$Cl5_i$ | 2.2937(9) | Cl4−Cu1−$Cl5_i$ | 97.33(3) |
| | | Cl5−Cu1−Cl6 | 160.72(3) |
| | | Cl5−Cu1−$Cl5_i$ | 84.45(3) |
| | | $Cl5_i$−Cu1−Cl6 | 90.71(3) |
| | | Cl3−Cu2−Cl4 | 84.00(3) |
| | | Cl3−Cu2−O1 | 93.76(7) |
| | | Cl3−Cu2−$Cl4_{ii}$ [c] | 96.00(3) |
| Cu2−Cl3 | 2.8735(8) | Cl3−Cu2−$O1_{ii}$ | 86.24(7) |
| Cu2−Cl4 | 2.2788(8) | $Cl3_{ii}$−Cu2−Cl4 | 96.00(3) |
| Cu2−O1 | 1.978(2) | Cl4−Cu2−O1 | 88.87(6) |
| | | Cl4−Cu2−$O1_{ii}$ | 91.13(6) |

| Donor···H···Acceptor | D-H (Å) | H···A | D-H···A (°) |
|---|---|---|---|
| N(1)···H(1N)···Cl(3) | 1.009 | 2.399 | 134.8 |
| N(1)···H(1N)···Cl(6) | 1.009 | 2.495 | 140.6 |
| O(1)···H(1O)···$Cl(6)_{iii}$ [d] | 0.980 | 2.717 | 109.4 |
| C(2)···H(2)···$Cl(3)_{iv}$ [e] | 1.083 | 2.644 | 134.5 |
| C(4)···H(4)···$Cl(4)_{v}$ [f] | 1.083 | 2.640 | 145.5 |
| C(6)···H(6)···$Cl(4)_{vi}$ [g] | 1.083 | 2.631 | 154.5 |

[a] Only non-redundant and symmetry-unconstrained angles are shown. Constrained angles (such as Cl3−Cu2−$Cl3_{ii}$ = 180, Cl4−Cu2−$Cl4_{ii}$ = 180 and O1−Cu2−$O1_{ii}$ = 180) are not given explicitly. [b] $i = -x, 1 - y, -z$. [c] $ii = -x, 1 - y, 1 - z$. [d] $iii = x, 1/2 - y, 1/2 + z$. [e] $iv = 1 - x, 1 - y, 1 - z$. [f] $v = 1 + x, 1/2 - y, 1/2 + z$. [g] $vi = -x, -1/2 + y, 1/2 - z$.

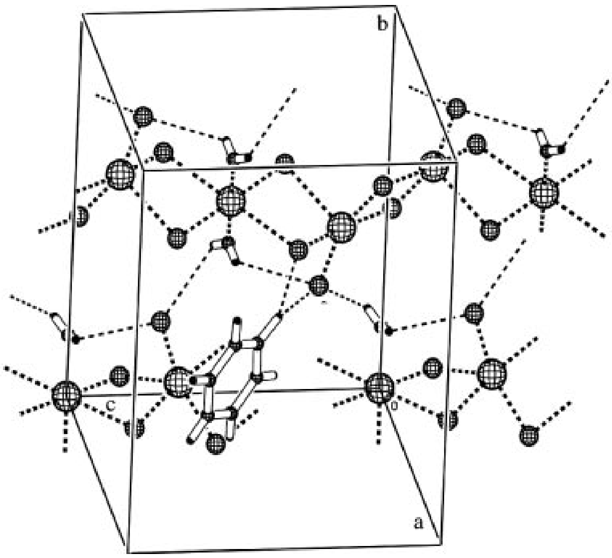

Figure 4. Packing viewed down $c^*$ in bis(pyridinium) octachlorodiaquatricuprate(II) (**2**), with hydrogen bonds indicated by broken lines

rationalized on the basis of their crystal structures. Both complexes contain pyridinium cations in bifurcated H-bridges. As the HCl concentration increases the coordinating ability of the pyridine-nitrogen decreases due to protonation, with a concomitant enhancement of the H-bond formation ability. These H-bridges stabilize the monomeric structure of the tetrachlorocuprate anion together with the steric demand of the relatively large pyridinium ions in the crystal lattice of **1**. Conversely, at the lower pyridinium ion:copper(II) ratio of **2**, the bifurcated hydrogen bonds reduce the electron density on the chloride ions in such a way that the electron repulsion decreases and coordination spheres with more ligand interactions develop. Obviously, water may be a successful competitor for ligand sites in **2** as well. The octahedral and square-pyramidal structural units condense into the polymeric chains, which are stabilized by the interchain hydrogen bond networks of the water molecules. In **2** the two neighboring pyramidal units are localized in the *transoid* positions. To the best of our knowledge the SP-5-[*OC-6-SP-5-SP-5*]-OC-6 -$CuCl_5$-$[CuCl_4(OH_2)_2$-$CuCl_5$-$CuCl_5]$-$CuCl_4(OH_2)_2$- structural motif observed in **2** has not been detected yet.

## Experimental Section

**General:** Analytical grade $CuCl_2{\cdot}2H_2O$, conc. HCl (35% by wt.) and pyridine (99.8%, anhydrous) were purchased from Aldrich. Anhydrous copper(II) chloride (13.5 g, 0.1 mol) obtained by thermal treatment of $CuCl_2{\cdot}2H_2O$ at 150 °C in a dry HCl stream was mixed with equimolar amount of pyridine (0.1 mol, 8 mL) in dry acetone. The blue solution formed was refluxed for 3 h.[5] The gray precipitate formed was filtered off, then dissolved in 500 mL of conc. hydrochloric acid. From the solution obtained nearly equal amounts of compound **1** (green prisms or brownish microcrystals) and compound **2** (yellow plates) crystallized concurrently.

The carbon, hydrogen and nitrogen contents of compounds **1** and **2** were determined with a Fisons CHN 1018S elemental analyser. The chloride content was determined by argentometric microtitration using a chloride-selective electrode, and the copper content was determined by an ICP spectrometer (Atomscan 25, Thermo Jarrel Ash).

Results of the elemental analysis: **1**: $(C_5H_5NH)_2[CuCl_4]$ (365.57): calcd. C 32.85, H 3.30, N 7.66, Cl 38.79, Cu 17.38; found C 33.49, H 3.35, N 7.68, Cl 41.11, Cu 17.68. **2**: $(C_5H_5NH)_2[Cu_3Cl_8(H_2O)_2]$ (670.47); calcd. C 17.91, H 2.40, N 4.18, Cl 42.30, Cu 28.43; found C 17.98, H 2.41, N 4.18, Cl 42.21, Cu 28.18.

Diffraction-quality single crystals of **1** and **2** were obtained by slow crystallization from the hydrochloric acid solution. For the diffraction measurements the single crystals (**1** and **2**) were placed into glass capillaries. The single-crystal X-ray diffraction data were recorded by means of an Enraf−Nonius CAD4 diffractometer (graphite monochromator; Mo-$K_\alpha$ radiation, $\lambda = 0.71070$ Å) at 295(2) K in the range of $2.95 < \theta < 34.96°$ for **1** and $2.53 < \theta < 34.94°$ for **2** using $\omega/2\theta$ scans. The intensities of three standard reflections were monitored regularly in both cases. In order to establish the final structure models, the initial structures obtained by direct methods were refined by standard procedures (anisotropic full-matrix least-squares refinement on $F^2$ for all non-hydrogen atoms, riding H atoms except the N−H ones which were found in difference electron-density maps).[6] Figures and geometry analyses were done by means of PLATON.[7]

Cell parameters were determined by least-squares of the setting angles of 25 standard reflections (**1**: $8.67 \leq \theta \leq 17.3°$; **2**: $15.34 \leq \theta \leq 16.70°$). In the case of **1**, the intensities of the standard reflections remained constant within experimental error throughout the data collection. A total of 6900 reflections were collected of which 3254 were unique [$R$(int) = 0.0226, $R(\sigma)$ = 0.0415]; the intensities of 1725 reflections were greater than $2\sigma(I)$. Completeness to $2\theta$ = 100%. No absorption correction was applied. Final model yielded $R_1 = 0.0385$ and $wR^2 = 0.0915$ for 1725 [$I > 2\,\sigma(I)$] and $R_1 = 0.0869$ and $wR^2 = 0.1018$ for all 3254 intensity data (goodness-of-fit = 0.925; the maximum and mean shift/esd 0.008 and 0.001). The maximum and minimum residual electron density in the final difference map was 0.706 and −0.474 e·Å$^{-3}$.

In the case of **2** the intensities of the standard reflections indicated a crystal decay of 4% (the data were corrected for decay). A total of 5143 reflections were collected of which 4769 were unique [$R$(int) = 0.0249, $R(\sigma)$ = 0.0370]; the intensities of 3033 reflections were greater than $2\sigma(I)$. Completeness to $2\theta$ = 99.7%. An empirical (psi scan)[8] absorption correction was applied to the data (the minimum and maximum transmission factors were 0.6767 and 1.000). Final model gave $R_1 = 0.056$ and $wR^2 = 0.134$ for 3033 [$I > 2\sigma(I)$] and $R_1 = 0.088$ and $wR2 = 0.144$ for all 4769 intensity data [goodness-of-fit = 0.942; the maximum and mean shift/esd 0.009 and 0.002; extinction coefficient 0.027(2)]. The maximum and minimum residual electron density in the final difference map was 1.851 and −1.954 e·Å$^{-3}$. The crystallographic data and refinement results for **1** and **2** are collected in Table 1.

CCDC-192665 (**1**) and -192666 (**2**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44−1223/336−033; E-mail: deposit@ccdc.cam.ac.uk].

Infrared spectra were recorded by the diffuse reflectance method in KBr. Measurements were carried out between 4000−400 cm$^{-1}$ by means of a Nicolet 170SX FT-IR spectrometer with a resolution of 1 cm$^{-1}$. ESR spectra were recorded by a JEOL JES-FE/3X ESR spectrometer (upgraded for data acquisition with an IBM PC Pentium I), in the X microwave band with 100 kHz field modulation. Manganese(II)-doped magnesium oxide powder was used as a standard for calibration of the $g$-values.

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