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## Piperazinium Chlorocuprates(I)

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## **Piperazinium Chlorocuprates(I).**

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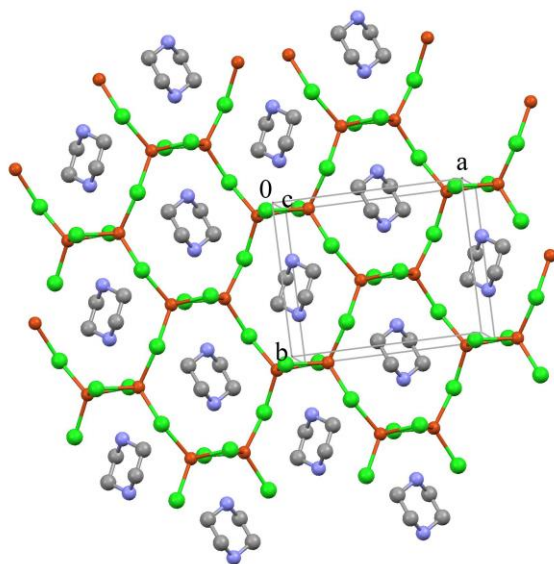
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Index Abstract:

Piperazinium Chlorocuprates(I).

Jacob E. Kuperstock, Amanda N. Ley and Robert D. Pike\*

The synthesis and network structures of four piperazinium hydrochlorides with copper(I) chloride are presented.



## Piperazinium Chlorocuprates(I).

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### Abstract

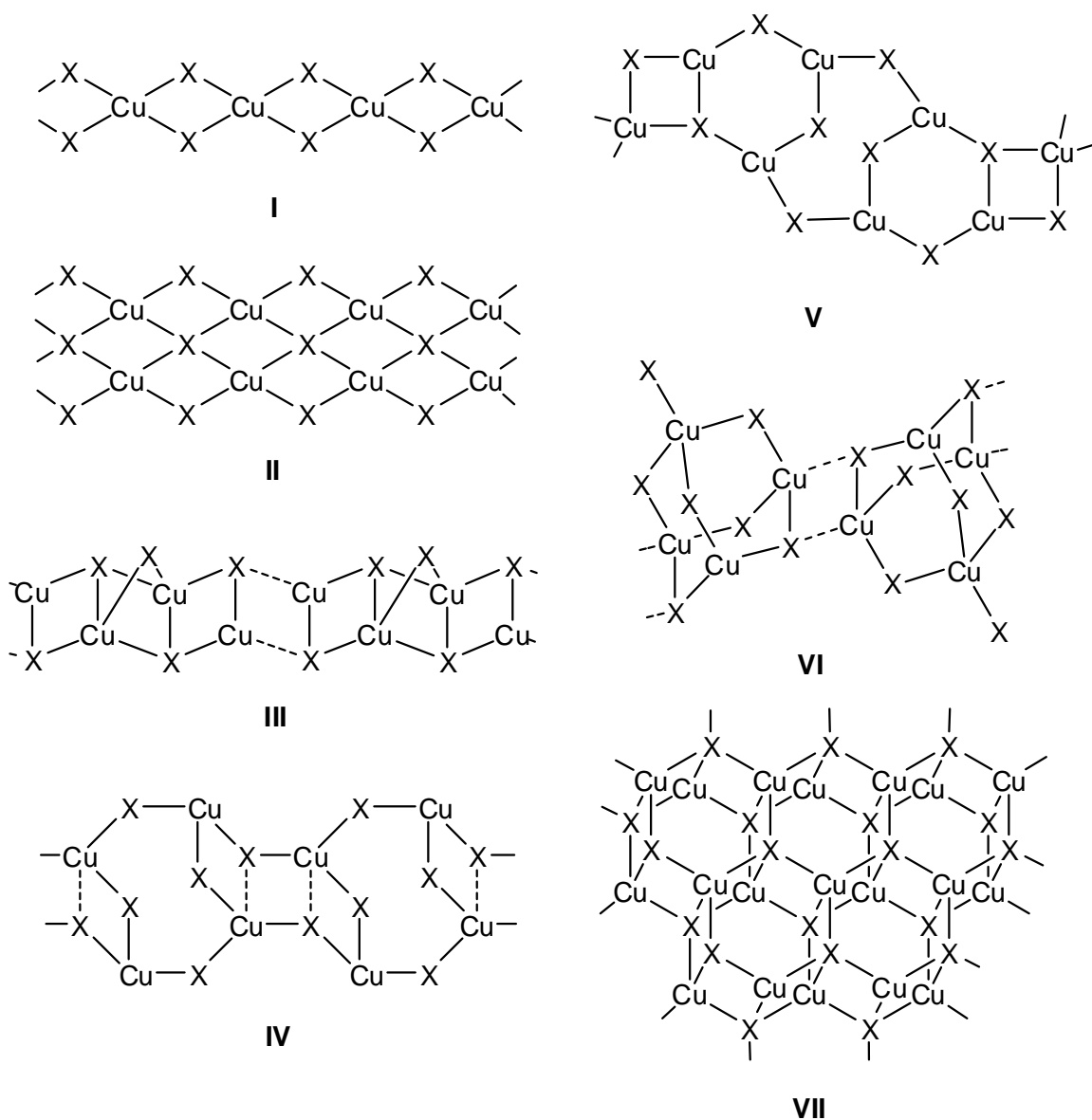
The formation from aqueous solution of networks containing piperazinium hydrochlorides with copper(I) chloride is described. Four new X-ray crystal structures are reported: (H<sub>2</sub>Pip)[Cu<sub>2</sub>Cl<sub>4</sub>] (two isomeric phases: **1A** and **1B**), (H<sub>2</sub>MePip)[Cu<sub>3</sub>Cl<sub>5</sub>] (**2**), and (H<sub>2</sub>Me<sub>2</sub>Pip)[Cu<sub>4</sub>Cl<sub>6</sub>] (**3**) (Pip = piperazine, MePip = N-methylpiperazine, Me<sub>2</sub>Pip = N,N'-dimethylpiperazine. In **1A** (*P*-1,  $a = 6.3141(2)$ ,  $b = 6.8248(2)$ ,  $c = 6.9067(2)$ ,  $\alpha = 90.707(2)$ ,  $\beta = 110.748(2)$ ,  $\gamma = 110.799(2)$ ,  $V = 256.918(13)$ ,  $Z = 2$ ) corner-sharing Cu<sub>2</sub>Cl<sub>2</sub> rhomboid dimers form infinite chains running parallel to the *a*-axis. In **1B** (*Pbcn*,  $a = 9.9442(6)$ ,  $b = 8.0622(5)$ ,  $c = 13.1301(7)$ ,  $V = 1052.67(11)$ ,  $Z = 8$ ) the Cu<sub>2</sub>Cl<sub>2</sub> dimers are linked by  $\mu$ -Cl into Cu<sub>6</sub>Cl<sub>8</sub> rings which form hexagonally tiled sheets running parallel to the *a,b* plane. In **2** (*P*-1,  $a = 8.0815(7)$ ,  $b = 9.6584(9)$ ,  $c = 9.7900(8)$ ,  $\alpha = 70.231(4)$ ,  $\beta = 77.180(4)$ ,  $\gamma = 70.587(4)$ ,  $V = 673.05(10)$ ,  $Z = 2$ ) alternating Cu<sub>3</sub>Cl<sub>3</sub> and Cu<sub>4</sub>Cl<sub>4</sub> rings are fused to form ribbons that run parallel to the *a*-axis. Copper-copper interactions are present. In **3** (*C2/c*,  $a = 17.4026(6)$ ,  $b = 10.5295(4)$ ,  $c = 11.7501(8)$ ,  $\beta = 131.5490(10)$ ,  $V = 1611.35(14)$ ,  $Z = 8$ ) relatively long Cu $\cdots$ Cl interactions connect Cu<sub>4</sub>Cl<sub>6</sub> "adamantane" units into chains running parallel to the *c*-axis. In all cases the piperazinium ions are independent from the chlorocuprate structures, but they do show N-H $\cdots$ Cl interactions.

Key Words: cuprate, piperazinium, polymer, polyanion, network

Shortened Title: Piperazinium Chlorocuprates(I).

## Introduction

Transition metals readily form metallates through coordination of anionic ligands. Univalent Group 10 metals in particular are known to produce a wide range of oligomeric or polymeric polyhalides,  $[M_nX_{n+y}]^{y-}$  ( $X = \text{Cl, Br, I}$ ) and polysulfides,  $[M_{2n}S_{n+y}]^{2y-}$ . Herein, we focus on halocuprate(I) anions,  $[\text{Cu}_n\text{X}_{n+y}]^{y-}$ , of which a large number are known, the majority forming simple corner-sharing chains, **I**.<sup>1</sup> In other cases, further catenation is observed, producing polymeric species such as **II** – **VII**.<sup>2-7</sup> A few more unusual halocuprate arrangements have also been reported as well.<sup>8</sup> Structures **I** – **III** are based solely on rhomboidal  $\text{Cu}_2\text{X}_2$  units, which can share corners or edges, while the more complex structures **VI** – **VII** incorporate cyclic  $\text{Cu}_3\text{X}_3$  and  $\text{Cu}_4\text{X}_4$  units in addition to the ubiquitous  $\text{Cu}_2\text{X}_2$ . Terminal halides, such as seen in **VI**, are not common. The formation of 2D halocuprate networks is very rare with only three cases reported. Two of these are represented by structure **VII**, which consists of linked pairs of (6,3) hexagonal  $\text{CuI}$  sheets. All copper and iodide ions are 4-coordinate, forming edge-sharing  $(\text{Cu}_2\text{I}_2)_3$  propeller units having acute ( $<70^\circ$ )  $\text{Cu-I-Cu}$  angles. The remaining 2D halocuprate is a truncated version of **VII** in which  $(\text{Cu}_2\text{Br}_2)_3$  propeller units are linked by infinite  $\text{CuBr}$  chains; acute  $\text{Cu-Br-Cu}$  angles are again present. No 3D halocuprates are known.



## Experimental

### Synthesis.

*Piperazinium tetrachlorodicuprate(I)* (**IA**) A 20 mL aqueous solution containing  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (0.852 g, 5.00 mmol) and  $\text{NH}_2\text{OH} \cdot \text{HCl}$  (0.348 g, 10.0 mmol) was warmed to about 70 °C in an open vessel. A 15 mL aqueous solution of piperazine ( $\text{C}_4\text{H}_{10}\text{N}_2$ , 0.431 g, 5.00 mmol) was added in drop-wise fashion. The blue-green color slowly discharged. The colorless solution was allowed to slowly cool first in a 40 °C water bath and then at room temperature, resulting in

the formation of crystals, which were collected by filtration and washed with 95% ethanol and then diethyl ether (0.604 g, 68.0%).

*Piperazinium tetrachlorodicuprate(I) (1B)* was prepared under similar conditions to those used for **1A**, except that 10.0 mmol piperazine was used. (0.238 g, 26.8%)

*N-Methylpiperazinium pentachlorotricuprate(I) (2)* was prepared under similar conditions to those used for **1A**, except that N-methylpiperazine was used ( $C_5H_{12}N_2$ , 0.278 g, 35.5%).

*N,N'-Dimethylpiperazinium hexachlorotetracuprate(I) (3)* was prepared under similar conditions to those used for **1A**, except that N,N'-dimethylpiperazine was used ( $C_6H_{14}N_2$ , 0.332 g, 45.5%).

#### *X-ray crystallography.*

Crystals were grown from the aqueous reaction mixtures as described above. Crystals were mounted on glass fibers. All measurements were made using graphite-monochromated Cu  $K\alpha$  radiation on a Bruker-AXS three-circle diffractometer, equipped with a SMART Apex II CCD detector. Initial space group determination was based on a matrix consisting of 120 frames. The data were reduced using SAINT+,<sup>9</sup> and empirical absorption correction applied using SADABS.<sup>10</sup>

Structures were solved using direct methods. Least-squares refinement for all structures was carried out on  $F^2$ . The non-hydrogen atoms were refined anisotropically. Hydrogen atoms in **1A** and **1B** were located in the Fourier difference map and then allowed to refine isotropically; hydrogen atoms in **2** and **3** were placed in calculated positions attached to adjacent carbon and nitrogen atoms and allowed to refine isotropically as riding models. Structure solution, refinement and the calculation of derived results were performed using the SHELXTL package of computer programs.<sup>11</sup> Packing diagrams were produced using Mercury.<sup>12</sup> Details of the X-ray

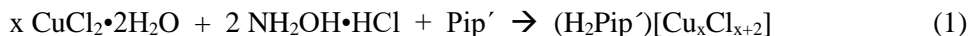
experiments and crystal data are summarized in Table 1. Selected bond lengths and bond angles are given in Table 2 and hydrogen-bonds are listed in Table 3.

## Results and Discussion

### *Synthesis*

The various chlorocuprates described herein (except for **1B**) were prepared from aqueous reaction mixtures using 1:2:1 ratios of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O} : \text{NH}_2\text{OH} \cdot \text{HCl} : \text{Pip}'$  ( $\text{Pip}' = \text{Pip}, \text{MePip}$  or  $\text{Me}_2\text{Pip}$ ). Addition of  $\text{Pip}'$  to a hot solution of copper(II) chloride and hydroxylamine hydrochloride (the reducing agent) caused the blue-green Cu(II) color to discharge, resulting in colorless solutions which crystallized upon cooling. Structural determination of the various crystals revealed an interesting variety of polyanions.

The 1:2:1  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O} : \text{NH}_2\text{OH} \cdot \text{HCl} : \text{Pip}'$  ratio used could be expected to produce  $(\text{H}_2\text{Pip}')[\text{CuCl}_3]$ , as suggested by equation (1),  $x = 1$ . However, in no case was the simple trichlorocuprate(I) anion realized. Instead, a variety of higher chlorocuprates(I) was found, corresponding to a functionally variable Cu: $\text{Pip}'$  ratio. The following product formulas were found:  $(\text{H}_2\text{Pip}')[\text{Cu}_2\text{Cl}_4]$  (**1A**, Cu: $\text{Pip}' = 2:1$ ),  $(\text{H}_2\text{MePip}')[\text{Cu}_3\text{Cl}_5]$  (**2**, Cu: $\text{MePip}' = 3:1$ ), and  $(\text{H}_2\text{Me}_2\text{Pip}')[\text{Cu}_4\text{Cl}_6]$  (**3**, Cu: $\text{Me}_2\text{Pip}' = 4:1$ ). In all cases an excess of copper over  $\text{Pip}'$  was noted in the product, despite the use of 1:1 reactant ratio. Therefore, an experiment was carried out using 1:2:2  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O} : \text{NH}_2\text{OH} \cdot \text{HCl} : \text{Pip}$  in order to increase the Pip loading. Interestingly, instead of altering the Cu: $\text{Pip}$  ratio, the result was formation of a product, **1B**, which was isomeric to **1A**. All of the products described herein are somewhat air-sensitive, decomposing to green Cu(II) materials over the course of several weeks when stored in air at reduced temperature.



*Piperazinium tetrachlorodicuprate(I) chain isomer (1A)*



Significant structural diversity was observed in the various chlorocuprate(I) polyanions prepared in the course of this study. The simplest of these networks was found for **1A**, which crystallizes in the triclinic space group  $P\bar{1}$ ; a packing diagram is shown in Figure 1. Compound **1A** is formed from a single independent copper atom and two chlorine atoms. The structure contains copper-sharing chains of rhomboid  $\text{Cu}_2\text{Cl}_2$  dimers. The two  $\text{Cu}\cdots\text{Cu}$  distances across the dimer units measure 3.1620(7) and 3.1671(7) Å, *i.e.* significantly larger than the van der Waals sum of two copper atoms (2.8 Å). The  $(\text{Cu}_2\text{Cl}_2)_n$  chains propagate parallel to the crystallographic  $a$ -axis. Formation of such chains is a very common phenomenon in halocuprate chemistry.<sup>1</sup> As is the case with all of the networks reported herein, the dications (in this case  $\text{H}_2\text{Pip}^{2+}$ ) are independent of the polyanions, except for the existence of  $\text{N}\cdots\text{H}\cdots\text{Cl}$  hydrogen-bonding. The  $\text{H}_2\text{Pip}^{2+}$  units are only half crystallographically independent, being centered about an inversion center. Hydrogen-bonding  $\text{N}(1)\cdots\text{H}\cdots\text{Cl}(2)$  involves all Pip nitrogen atoms and half of the chlorides.

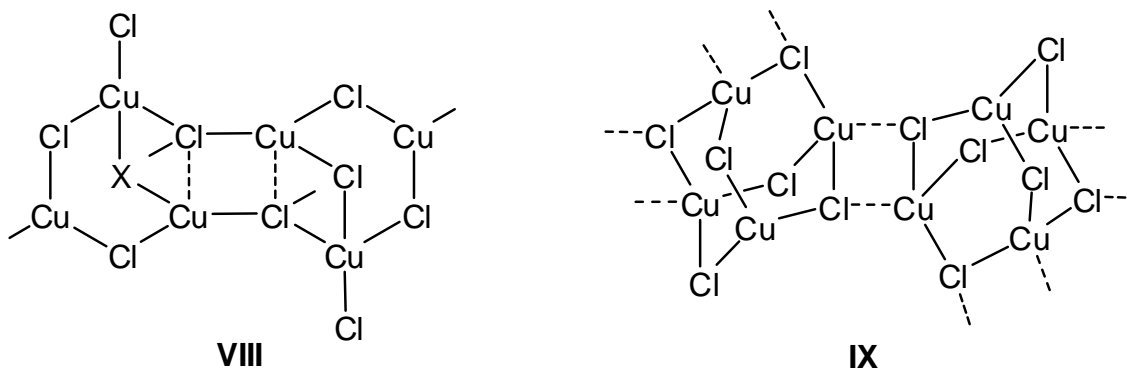
*Piperazinium tetrachlorodicuprate(I) sheet isomer (1B)*

As described above, the use of additional Pip in the standard reaction did not alter the product formula, but instead produced an isomer of **1A**. This isomer, **1B**, crystallizes in the orthorhombic space group  $Pbcn$ . The chlorocuprate network in **1B** forms an unusual honeycomb 2D sheet network, see Figure 2. The single independent copper center, Cu1, is linked by bridging atom Cl2 to form zigzag chains running parallel to the  $b$ -axis. Additionally, Cl1 knits the chains together parallel to the  $a$ -axis by forming  $\text{Cu}_2\text{Cl}_2$  dimers. The resulting sheets contain hexagonal  $\text{Cu}_6\text{Cl}_8$  units and are oriented parallel to the  $a,b$ -plane. The dimer  $\text{Cu1}\cdots\text{Cl1}\cdots\text{Cu1}'$  angle is typically acute at  $77.53(4)^\circ$ , however the in-plane  $\text{Cu1}\cdots\text{Cl2}\cdots\text{Cu1}'$  angle is almost twice as large at  $149.03(6)^\circ$ . The dimers in **1B** have slightly more acute angles at Cl than do those in **1A**. This effect is reflected in a slightly shorter  $\text{Cu}\cdots\text{Cu}$  distance of 2.9645(16) Å. The half-independent  $\text{H}_2\text{Pip}^{2+}$  ions lie between the chlorocuprate sheets and are aligned with the centers of the

vacancies in the sheets, as is evident in the roughly *c*-axis projection, Figure 4. Three interactions, two between N1 and Cl1 and one between N1 and Cl2, are sufficiently short to suggest hydrogen-bonding.

*N-Methylpiperazinium pentachlorotricuprate(I) (2)*

The unsymmetrical *N*-methylpiperazinium cation forms a 3:1 Cu:H<sub>2</sub>MePip complex. The product, which is shown in Figures 5 and 6, crystallizes in the space group *P*-1. The H<sub>2</sub>MePip<sup>2+</sup> unit is fully independent, as are the three copper and five chlorine atoms. The pentachlorotricuprate(I) units incorporate 3-coordinate Cu1 and Cu2 and 4-coordinate Cu3. The latter coordinates an unusual terminal chloride, Cl5. The Cu2 atom shows a slight tendency toward 4-coordination. It features three normal length Cu–Cl bonds: Cu2–Cl2 = 2.2510(10), Cu2–Cl1' = 2.2928(10), and Cu2–Cl4' = 2.3527(10) Å. However, the resulting Cl–Cu–Cl angles add up to a total of about 354.5°. In addition, there is a pair of long Cu2⋯Cl4 interactions (not shown in Figures 5 and 6, shown dashed in **VIII**) measuring 2.9562(11) Å. Weak interactions between copper atoms are present. The Cu1⋯Cu2 distance of 2.7109(8) Å and the Cu1⋯Cu3 distance of 2.8751(8) Å are both close to the van der Waals radius sum. The overall structure of the chlorocuprate network is a novel ribbon structure, **VIII**, propagating parallel to the crystallographic *a*-axis and which is closely related to known halocuprate networks **IV**, **V**, and **VI**. The methyl-bearing nitrogen atom, N1, shows a single hydrogen-bonding interaction to Cl5. The NH<sub>2</sub> nitrogen atom, N2, shows potential hydrogen-bonding interactions to Cl3, Cl4 and Cl5. However, as was the case for **1B**, only two of these interactions are formally allowable, given the presence of only two hydrogen atoms at this site.



*N,N'*-Dimethylpiperazinium hexachlorotetracuprate(I) (**3**)

The dimethylpiperazinium chlorocuprate network crystallizes in monoclinic space group  $C2/c$ . The chlorocuprate anions (see Figures 7 and 8) consist of tetrahedral adamantane-like  $\text{Cu}_4\text{Cl}_6^{2-}$  units that weakly link together to form ribbons running parallel to the crystallographic  $c$ -axis. Two independent copper atoms are present: 3-coordinate Cu1 and roughly 3-coordinate Cu2. The latter shows three regular Cu–Cl bonds: Cu2–Cl3 = 2.2645(5), Cu2–Cl1' = 2.3052(5), and Cu2–Cl4 = 2.3242(5). However, the Cl–Cu–Cl angles total to only about  $355.8^\circ$ . An additional pair of long Cu2 $\cdots$ Cl3 interactions measuring 2.7623(6) Å link the  $\text{Cu}_4\text{Cl}_6^{2-}$  units together to form a ribbon running parallel to the  $c$ -axis (see Figure 8). An even longer pair of Cu1 $\cdots$ Cl1 interactions measuring 3.0568(5) Å (slightly under the van der Waals sum of 3.15 Å) further links the ribbons in a direction between the  $a$ - and  $b$ -axes to form a 2D sheet network (see **IX**). All of the chloride atoms form simple bridges between copper centers, except Cl3, which (taking into account the long Cu2 $\cdots$ Cl3 bond) is triply bridging and in T-shaped geometry. All Cu–Cl–Cu bond angles within the polyhedra are in the range of  $77.152(18)$  to  $89.10(3)^\circ$ . The  $\text{Cu}_4\text{X}_6^{2-}$  unit is widely recognized in Cu(I) halide networks,<sup>8a,13</sup> but linking of these units into ribbons has only a single precedent.<sup>6c</sup> The two hydrogen-bonding interactions in **3** involve the proton attached to N1 and the chlorocuprate Cl1 and Cl3 atoms.

## Conclusions

Four new piperazinium salt structures were added the known catalog of halocuprate coordination modes. Network **1B** is a very rare example of a chlorocuprate forming a 2D sheet structure and networks **2** and **3** are relatively unusual examples of chlorocuprate ribbons formed from linking of polyhedra.

**Supplementary Material:** Tables of atomic coordinates for each structure are available as supplementary material. CCDC 679163–679166 contain the crystallographic data for this paper. These data can be obtained free of charge by e-mailing [data\\_request@ccdc.cam.ac.uk](mailto:data_request@ccdc.cam.ac.uk) or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ UK; Fax +44(0)1223-336033; [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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Table 1. Crystal and Structure Refinement Data.<sup>a</sup>

	<b>1A</b>	<b>1B</b>	<b>2</b>
CCDC deposit no.	679163	679164	679165
color and habit	colorless needle	colorless blade	colorless blade
size, mm	0.42 × 0.08 × 0.07	0.30 × 0.10 × 0.02	0.33 × 0.11 × 0.03
formula	C <sub>2</sub> H <sub>6</sub> Cl <sub>2</sub> Cu <sub>1</sub> N <sub>1</sub>	C <sub>4</sub> H <sub>12</sub> Cl <sub>4</sub> Cu <sub>2</sub> N <sub>2</sub>	C <sub>5</sub> H <sub>14</sub> Cl <sub>5</sub> Cu <sub>3</sub> N <sub>2</sub>
formula weight	178.52	178.52	470.05
space group	<i>P</i> -1 (#2)	<i>Pbcn</i> (#60)	<i>P</i> -1 (#2)
<i>a</i> , Å	6.3141(2)	9.9442(6)	8.0815(7)
<i>b</i> , Å	6.8248(2)	8.0622(5)	9.6584(9)
<i>c</i> , Å	6.9067(2)	13.1301(7)	9.7900(8)
$\alpha$ , deg	90.707(2)	90	70.231(4)
$\beta$ , deg	110.748(2)	90	77.180(4)
$\gamma$ , deg	110.799(2)	90	70.587(4)
volume, Å <sup>3</sup>	256.918(13)	1052.67(11)	673.05(10)
<i>Z</i>	2	8	2
$\rho_{\text{calc}}$ , g cm <sup>-3</sup>	2.308	2.253	2.319
<i>F</i> <sub>000</sub>	176	704	460
$\mu(\text{Cu K}\alpha)$ , mm <sup>-1</sup>	14.251	13.913	14.387
radiation	CuK $\alpha$	CuK $\alpha$	CuK $\alpha$
	( $\lambda = 1.54178$ Å)	( $\lambda = 1.54178$ Å)	( $\lambda = 1.54178$ Å)
temperature, K	200	200	100
residuals: <sup>a</sup> <i>R</i> ; <i>R</i> <sub>w</sub>	0.0282; 0.0715	0.0394; 0.1145	0.0383; 0.1043
goodness of fit	1.089	1.047	1.059

${}^a\mathbf{R} = R_l = \Sigma|F_o| - |F_c| / \Sigma|F_o|$  for observed data only.  $\mathbf{R}_w = wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$   
for all data.



Table 1. (cont'd)

<b>3</b>	
CCDC deposit no.	679166
color and habit	colorless prism
size, mm	0.18 × 0.07 × 0.06
formula	C <sub>3</sub> H <sub>8</sub> Cl <sub>3</sub> Cu <sub>2</sub> N
formula weight	291.53
space group	C2/c (#15)
<i>a</i> , Å	17.4026(6)
<i>b</i> , Å	10.5295(4)
<i>c</i> , Å	11.7501(8)
$\alpha$ , deg	90
$\beta$ , deg	131.5490(10)
$\gamma$ , deg	90
volume, Å <sup>3</sup>	1611.35(14)
<i>Z</i>	8
$\rho_{\text{calc}}$ , g cm <sup>-3</sup>	2.403
<i>F</i> <sub>000</sub>	1136
$\mu(\text{Cu K}\alpha)$ , mm <sup>-1</sup>	14.948
radiation	CuK $\alpha$ ( $\lambda = 1.54178$ Å)
temperature, K	100
residuals: <sup>a</sup> <i>R</i> ; <i>R</i> <sub>w</sub>	0.0191; 0.0455
goodness of fit	1.105

${}^a\mathbf{R} = R_l = \Sigma|F_o| - |F_c| / \Sigma|F_o|$  for observed data only.  $\mathbf{R}_w = wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$   
for all data.

Table 2. Selected Bond Distances (Å) and Angles (°).

	<b>1A</b>	<b>1B</b>	<b>2</b>	<b>3</b>
Cu–Cl	2.3798(7), 2.3923(7), 2.3466(7), 2.4064(7)	2.3234(12), 2.4103(13), 2.3797(13), 2.4052(13)	2.2265(10), 2.2363(10), 2.2510(10), 2.2929(10), 2.3255(9), 2.3392(10), 2.3528(10), 2.3704(10), 2.3797(10), 2.4195(10), 2.9562(11) <sup>a</sup>	2.2577(6), 2.2645(5), 2.2840(5), 2.3052(5), 2.3242(5), 2.3262(5), 2.7623(6) <sup>a</sup> , 3.0568(5) <sup>a</sup>
Cu··Cu	3.1620(7), 3.1671(7)	2.9645(16)	2.7109(8), 2.8751(8)	2.8616(4), 2.8759(6), 2.8794(4)
Cl–Cu–Cl	96.45(2), 96.99(2), 108.97(3), 116.02(3), 119.47(3), 119.78(3)	101.98(4), 107.30(5), 107.63(5), 109.16(5), 114.43(5), 115.25(4)	85.94(3) <sup>a</sup> , 97.58(3), 99.47(4) <sup>a</sup> , 105.70(4), 106.99(3), 107.44(4), 107.96(4), 108.25(3), 110.72(3) <sup>a</sup> , 110.92(4), 111.20(4), 112.02(4), 124.04(4), 136.73(4), 137.84(4)	88.057(18) <sup>a</sup> , 96.549(18) <sup>a</sup> , 103.228(18) <sup>a</sup> , 107.518(16), 115.401(19), 116.21(2), 117.064(19), 126.187(17), 132.88(2)
Cu–Cl–Cu	83.01(2), 83.55(2)	77.53(4), 149.03(6)	68.97(3) <sup>a</sup> , 69.28(3) <sup>a</sup> , 74.52(3), 78.11(3), 82.31(3), 104.53(4), 111.56(4), 123.52(4)	76.771(17) <sup>a</sup> , 77.152(18), 77.677(18), 79.12(3), 89.10(3), 151.75(2) <sup>a</sup>

<sup>a</sup>Values associated with long Cu··Cl interactions.

Table 3. Hydrogen-bond Distances (Å) and Angles (°).

Network	D–H···A	D–H dist.	H···A dist.	D···A dist.	D–H···A angle
<b>1A</b>	N1–H2···C11 <sup>a</sup>	0.88(3)	2.48(3)	3.307(2)	158(3)
	N1–H1···C12 <sup>b</sup>	0.86(5)	2.67(4)	3.306(2)	132(3)
	N1–H1···C11 <sup>b</sup>	0.86(5)	2.78(4)	3.361(2)	126(3)
	N1–H1···C12 <sup>c</sup>	0.86(5)	2.87(4)	3.242(2)	108(3)
<b>1B</b>	N1–H2···C12 <sup>d</sup>	0.76(6)	2.98(5)	3.420(4)	120(4)
	N1–H2···C11 <sup>e</sup>	0.76(6)	2.71(5)	3.177(4)	121(4)
	N1–H2···C11 <sup>d</sup>	0.76(6)	2.62(5)	3.171(4)	131(4)
	N1–H1···C12 <sup>f</sup>	0.89(6)	2.33(6)	3.209(4)	170(5)
<b>2</b>	N1–H1···C15 <sup>g</sup>	0.93	2.12	3.045(3)	172.7
	N2–H2C···C14 <sup>h</sup>	0.92	2.31	3.200(3)	163.6
	N2–H2D···C15	0.92	2.38	3.132(3)	138.3
	N2–H2D···C13 <sup>h</sup>	0.92	2.81	3.258(3)	111.1
	N2–H2D···C13	0.92	2.85	3.381(3)	118.3
<b>3</b>	N1–H1···C11 <sup>i</sup>	0.93	2.64	3.2848(17)	127.0
	N1–H1···C13 <sup>j</sup>	0.93	2.64	3.3094(16)	129.2

Symmetry transformations used to generate equivalent atoms: <sup>a</sup> $-x+1, -y+1, -z+1$ ; <sup>b</sup> $x, y+1, z$ ;

<sup>c</sup> $-x+1, -y+1, -z+2$ ; <sup>d</sup> $-x+1, -y+1, -z+1$ ; <sup>e</sup> $x+1, y-1, z$ ; <sup>f</sup> $-x+3/2, y-1/2, z$ ; <sup>g</sup> $-x+1, -y+2, -z+1$ ;

<sup>h</sup> $-x+1, -y+1, -z+1$ ; <sup>i</sup> $-x+1/2, y-1/2, -z+1/2$ ; <sup>j</sup> $-x+1/2, -y+1/2, -z$ .

## Captions for Figures.

Figure 1. Thermal ellipsoid (50%) drawing of **1A**.

Figure 2. Network and packing diagram for **1A**. Hydrogen atoms omitted for clarity.

Figure 3. Thermal ellipsoid (50%) drawing of **1B**.

Figure 4. Network and packing diagram for **1B**. Hydrogen atoms omitted for clarity.

Figure 5. Thermal ellipsoid (50%) drawing of **2**.

Figure 6. Network and packing diagram for **2**. Hydrogen atoms omitted for clarity.

Figure 7. Thermal ellipsoid (50%) drawing of **3**.

Figure 8. Network and packing diagram for **3**. Hydrogen atoms omitted for clarity.

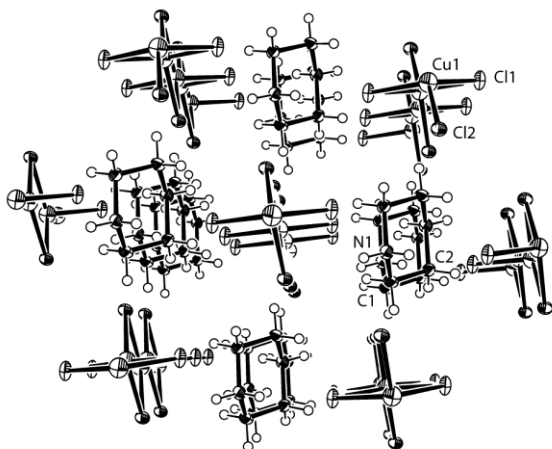
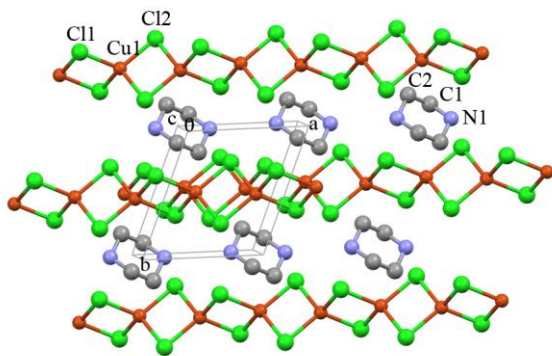
Figure 1. Thermal ellipsoid (50%) drawing of **1A**.Figure 2. Network and packing diagram for **1A**. Hydrogen atoms omitted for clarity.

Figure 3. Thermal ellipsoid (50%) drawing of **1B**.

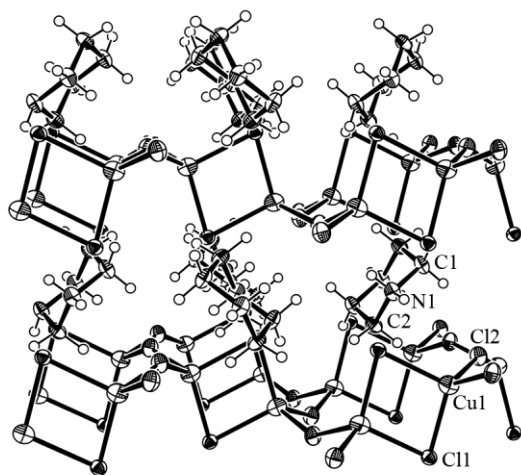


Figure 4. Network and packing diagram for **1B**. Hydrogen atoms omitted for clarity.

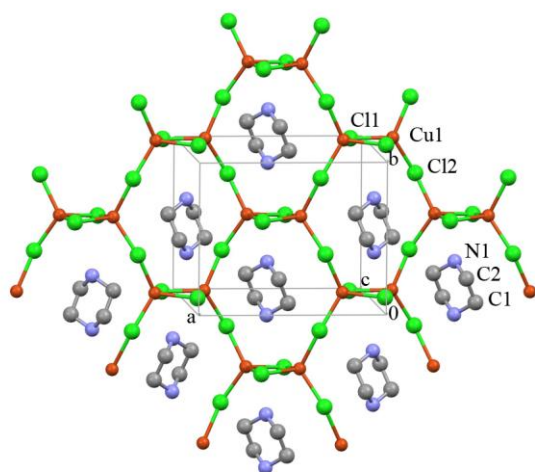


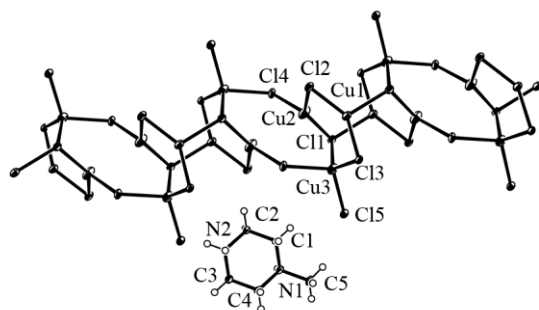
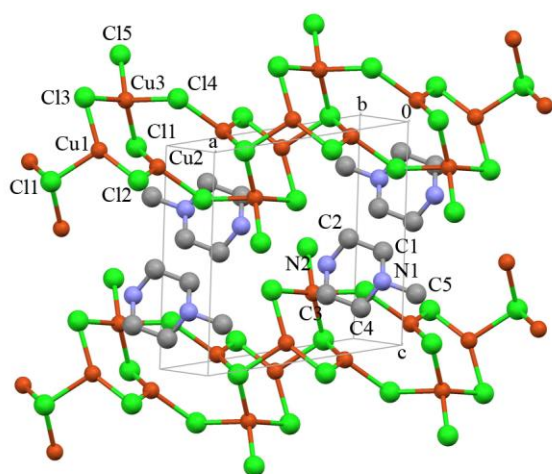
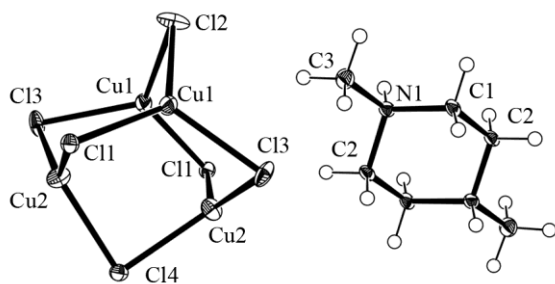
Figure 5. Thermal ellipsoid (50%) drawing of **2**.Figure 6. Network and packing diagram for **2**. Hydrogen atoms omitted for clarity.



Figure 7. Thermal ellipsoid (50%) drawing of **3**.Figure 8. Network and packing diagram for **3**. Hydrogen atoms omitted for clarity.