Two new high-nuclearity copper(II) chloride oligomers with herringbone stacking patterns synthesized by in situ templation[1]

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Abstract: The use of trichloroiminophosphoranes $Cl_3P{=}NR$ to control the concurrent release of the templating cation $[RNH_3]^+$ and chloride ligand via in situ P—N and P—Cl bond cleavage produced two new copper(II) chloride oligomers. The nature of the organic substituent R was a factor in determining the chain lengths. For *n*-propyltrichloroiminophosphorane, the hexanuclear cluster $[n\text{-}PrNH_3]_2[Cu_6Cl_{14}]$ (**1**) was obtained, while *p*-tolyltrichloroiminophosphorane generated the tetranuclear copper chloride salt $[4\text{-}CH_3C_6H_4NH_3][2\text{-}Cl\text{-}4\text{-}CH_3C_6H_3NH_3][Cu_4Cl_{10}]$ (**2**). In both structures a two-dimensional framework displaying a herringbone arrangement is created by Cu—Cl secondary bonding interactions. The direct addition of the $[n\text{-}PrNH_3]^+$ cation to a $CuCl_2{\cdot}2H_2O$ solution under the same reaction conditions produced $[n\text{-}PrNH_3]_2[CuCl_4]$.

Key words: copper halides, templation, oligomers, two-dimensional frameworks.

Résumé : L'utilisation de trichloroiminophosphoranes $Cl_3P{=}NR$ pour contrôler la libération simultanée du cation $[RNH_3]^+$ servant de gabarit et le ligand chlorure par le biais d'un clivage in situ de liaisons P—N et P—Cl conduit à la formation de deux nouveaux oligomères du chlorure de cuivre(II). La nature du substituant organique R est un facteur dans la détermination des longueurs des chaînes. Avec le *n*-propyltrichloroiminophosphorane, il y a formation de l'agrégat hexanucléaire $[n\text{-}PrNH_3]_2[Cu_6Cl_{14}]$ (**1**) alors que le *p*-tolyltrichloroiminophosphorane génère la formation du chlorure de cuivre tétranucléaire $[4\text{-}CH_3C_6H_4NH_3][2\text{-}Cl\text{-}4\text{-}CH_3C_6H_3NH_3][Cu_4Cl_{10}]$ (**2**). Dans les deux structures, il y a création d'un squelette bidimensionnel comportant un arrangement en chevrons formé par des interactions de liaisons secondaires Cu—Cl. L'addition directe du cation $[n\text{-}PrNH_3]^+$ à une solution de $CuCl_2{\cdot}2H_2O$ dans les mêmes conditions réactionnelles conduit à la formation de $[n\text{-}PrNH_3]_2[CuCl_4]$.

Mots clés : halogénures de cuivre, gabarit, oligomères, squelettes bidimensionnels.

[Traduit par la Rédaction]

Introduction

The use of templating reagents is a common technique in the synthesis of inorganic materials (1, 2). This method employs a cation, e.g., alkylammonium $[RNH_3]^+$, to provide charge balance and to regulate the structural arrangement of anionic frameworks through forces such as hydrogen bonding or van der Waals repulsion (3). The traditional procedure for the synthesis of oligomeric copper(II) halide frameworks involves mixing the copper(II) halide with an appropriate organic cation in a concentrated hydrohalic acid solution (4–6). Willett and co-workers (7–9) have used this approach to produce many copper halide oligomers with fascinating structural features and interesting physical properties. Much of their work has focused on the characterization of quasi-planar bibridged Cu_nX_{2n+2} systems (n = 2–7, 10) (10–16). The "softness" of the copper coordination sphere and the nonstereospecific bridging capability of the halide ions allow the formation of secondary bonding interactions (SBIs) between the oligomers, which give rise to various stacking patterns (17).

Recently, some new open-framework zinc phosphates were prepared under solvothermal conditions by using P—N bond cleavage in hexamethylphosphoramide $OP(NMe_2)_3$ to control the simultaneous release of an organic amine and phosphoric acid (18). As part of our investigations of novel inorganic materials, we are particularly interested in the in situ templation synthesis of new copper(II) halide frameworks. In addition to generating new functional compounds, this indirect templation method may contribute to an understanding of the mechanism of network formation. For example, we have shown that the tris(alkylamido)phosphate $OP[N(H)\text{-}t\text{-}Bu]_3$ functions both as an indirect source of the templating $[t\text{-}BuNH_3]^+$ cation and as a proton acceptor in the

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Dedicated to Dr Arthur Carty for his outstanding contributions to Canadian science.

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Table 1. Crystal data and structure refinement for **1**, **2**, and **3**.

	1	**2**	**3**
Empirical formula	$C_6H_{20}Cl_{14}Cu_6N_2$	$C_{14}H_{19}Cl_{11}Cu_4N_2$	$C_7H_9Cl_2N$
fw (g)	997.78	859.42	178.05
T (K)	298(2)	298(2)	298(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a (Å)	9.3454(19)	13.031(3)	5.2178(10)
b (Å)	6.0319(12)	6.1151(12)	8.6191(17)
c (Å)	24.159(5)	17.191(3)	18.111(4)
β (°)	97.79(3)	95.66(3)	97.40(3)
V (Å^3)	1349.3(5)	1363.1(5)	807.7(3)
Z	2	2	4
D_{calcd} (g cm^{-3})	2.456	2.094	1.464
μ (mm^{-1})	6.032	4.165	0.724
F(000)	964	840	368
θmin–θmax (°)	3.78–27.50	3.14–25.02	2.62–25.03
Reflections collected	4644	8189	1667
Independent reflections	3075	2362	1154
R(int)	0.0331	0.0537	0.0426
Goodness-of-fit on F^2	1.033	1.101	1.067
Final R indices [$I > 2\sigma(I)$]; R_1, wR_2	0.0393, 0.0804	0.0521, 0.1460	0.0673, 0.1676
R indices (all data); R_1, wR_2	0.0656, 0.0907	0.0654, 0.1568	0.0815, 0.1786
Largest diff. peak and hole (e Å^{-3})	0.732, –0.638	0.786, –0.890	0.521, –0.556

production of a novel copper chloride structural motif that is different from the network synthesized by the direct addition of [t-BuNH$_3$]Cl (19). In the current work we have investigated the use of trichloroiminophosphoranes $Cl_3P{=}NR$ (R = n-Pr, p-tolyl) as an in situ source of both the organic ammonium cation and the Cl^- ligand in the formation of novel copper halide frameworks. We report here the formation and X-ray structures of two high-nuclearity copper chloride oligomers [n-PrNH$_3$]$_2$[Cu$_6$Cl$_{14}$] (**1**) and [4-CH$_3$C$_6$H$_4$NH$_3$][2-Cl-4-CH$_3$C$_6$H$_3$NH$_3$][Cu$_4$Cl$_{10}$] (**2**), both of which exhibit a herringbone structure. For the quasi-planar bibridged Cu_nX_{2n+2} oligomers, this stacking pattern has only been reported in the pentanuclear cluster [Cu$_5$Cl$_{10}$(n-C$_3$H$_7$OH)$_2$] (20). For comparison, the direct addition of [n-PrNH$_3$]$^+$ to a $CuCl_2{\cdot}2H_2O$ solution under the same reaction conditions produced the known copper chloride complex [n-PrNH$_3$]$_2$[CuCl$_4$] (21). The structure of [2-Cl-4-CH$_3$C$_6$H$_3$NH$_3$]$^+$Cl$^-$ (**3**), a by-product of the reaction involving Cl$_3$P=N-p-tolyl, is also reported.

Experimental section

Reagents and general procedures

n-Propyltrichloroiminophosphorane and 4-tolyltrichloroiminophosphorane were prepared according to the literature procedure (22). Tetrachloroethane was dried over CaH_2 and fractionally distilled. Copper chloride dihydrate, phosphorus pentachloride, and chlorobenzene were used as received.

Synthesis of 1

A mixture of copper chloride dihydrate (0.170 g, 1.00 mmol), n-propyltrichloroiminophosphorane (0.194 g, 1.00 mmol), water (0.054 g, 3.00 mmol), and 10 mL toluene were placed in a sealed 23 mL Teflon vessel and heated at 90 °C for 12 h. The reaction vessel was allowed to cool to 23 °C, and yellow crystals of **1** (0.020 g, 12%) were isolated from the yellow precipitate manually.

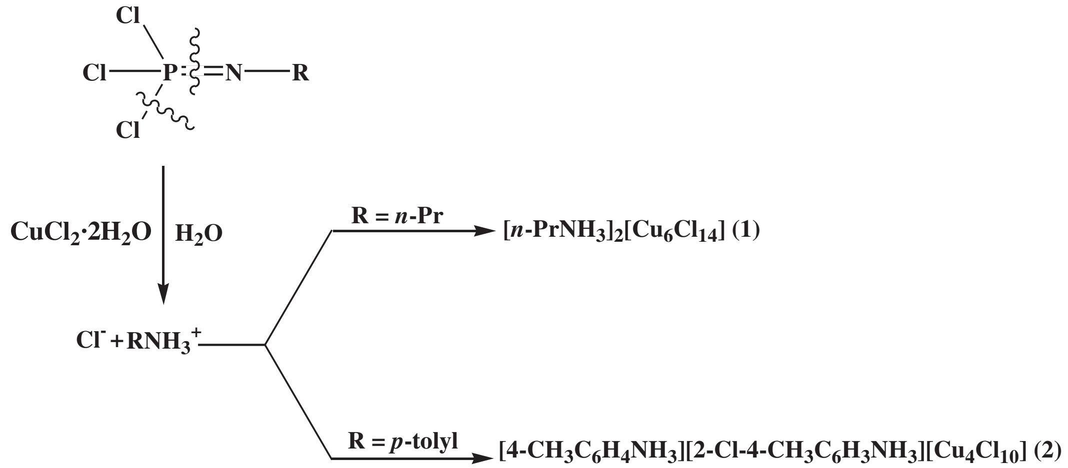
Syntheses of 2 and 3

A mixture of copper chloride dihydrate (0.170 g, 1.00 mmol), p-tolyltrichloroiminophosphorane (0.243 g, 1.00 mmol), water (0.054 g, 3.00 mmol), and 10 mL toluene were placed in a sealed 23 mL Teflon vessel and heated at 90 °C for 12 h. The reaction vessel was allowed to cool to 23 °C. Yellow crystals of **2** (0.040 g, 18%) and a few pale yellow crystals of **3** were separated from the black precipitate manually.

X-ray structural analyses

Suitable crystals of the complexes (**1**, yellow block (0.18 × 0.12 × 0.12 mm^3); **2**, yellow plate (0.20 × 0.04 × 0.04 mm^3); **3**, pale yellow plate (0.24 × 0.08 × 0.08 mm^3)) were selected, coated with oil (Paratone 8277, Exxon), and mounted on glass fibres. The measurements were made on a Nonius KappaCCD diffractometer with graphite-monochromated Mo Kα radiation. Data were collected at 25 °C, using the ω and ϕ scans to a maximum θ value of 27.5°, 25.02°, and 25.03° for **1**, **2**, and **3**, respectively. The data were corrected for Lorentz and polarization effects and for absorption using the multiscan method (23). Since the crystals did not show any sign of decay during data collection, a decay correction was deemed unnecessary. The structures were solved by direct methods SHELXS-97 (24). The C atoms of the n-propyl groups in **1** were disordered over three positions with unequal site occupancy factors in an approximate ratio of 2:1:1; the C3 and C2a atoms were also disordered at the same position in a 1:1 ratio. In **2**, the cations [4-CH$_3$C$_6$H$_4$NH$_3$] and [2-Cl-4-CH$_3$C$_6$H$_3$NH$_3$] were disordered at the same position with equal site occupancy

Scheme 1.



factors. All non-hydrogen atoms were refined anisotropically except the disordered atoms. All the hydrogen atoms were included at geometrically idealized positions. Crystallographic data for **1**, **2**, and **3** are summarized in Table 1. Additional data are available in the Supporting information.[3]

Results and discussion

The products obtained from the solvothermal reactions of trichloroiminophosphoranes $Cl_3P{=}NR$ with $CuCl_2{\cdot}2H_2O$ in toluene at 90 °C exhibit distinctly different structural motifs depending on the identity of the R group (Scheme 1). In the case of R = *n*-Pr, the hexanuclear copper chloride chain $[Cu_6Cl_{14}]^{2-}$ is isolated as the $[n\text{-}PrNH_3]^+$ salt, whereas for the aryl subsituent (R = *p*-tolyl), the tetranuclear $[Cu_4Cl_{10}]^{2-}$ fragment is obtained in conjunction with the $[4\text{-}CH_3C_6H_4NH_3]^+$ and $[2\text{-}Cl\text{-}4\text{-}CH_3C_6H_3NH_3]^+$ cations. The chloride ions in these syntheses are generated by in situ hydrolysis of the P—Cl bonds in $Cl_3P{=}NR$, which is achieved by the addition of a stoichiometric amount of water to the reaction mixture. Concomitantly, the in situ generated organoammonium cations $[RNH_3]^+$ exhibit an indirect templation function in the generation of these anionic copper halide frameworks. The formation of bibridged Cu_nX_{2n+2} oligomers in previous reports is viewed to involve fragments cut from infinite CuX_2 chains by charge-compensating cations acting as "molecular scissors" (10, 12). The weak interaction between the Cl^- ion and the cation results in the termination of the CuX_2 chains. This is a common modification in the formation of copper halide oligomers. In the new synthesis described herein the copper chloride oligomers are built up by replacement of the aqua ligands in the $CuCl_2{\cdot}2H_2O$ monomer (25) by the stronger chloride ligands provided by the hydrolysis of $Cl_3P{=}NR$. The formation of the new cation $[2\text{-}Cl\text{-}4\text{-}CH_3C_6H_3ClNH_3]^+$ in the synthesis of **2** presumably occurs by the chlorination of the $[4\text{-}CH_3C_6H_4NH_3]^+$ cation during the solvothermal process. The chloride salt $[2\text{-}Cl\text{-}4\text{-}CH_3C_6H_3NH_3]^+Cl^-$ (**3**) was also isolated from the reaction products and characterized by X-ray crystallography (vide infra). A similar observation has been reported for the bromination of the 3-chloroanilinium cation by $CuBr_2$ in HBr solution to give the 6-bromo-3-chloroanilinium cation (26).

The direct reaction of $[n\text{-}PrNH_3]Cl$ and $CuCl_2{\cdot}2H_2O$ under the solvothermal conditions employed for the synthesis of **1** generated the known mononuclear anion $[CuCl_4]^-$ (21) as the $[n\text{-}PrNH_3]^+$ salt, demonstrating the structure-directing effect of the indirect templation method, as previously reported for the generation of a novel anionic copper halide framework by in situ templation employing $[t\text{-}BuNH_3]^+$, which is provided by the amidophosphate reagent $OP(NH\text{-}t\text{-}Bu)_3]$ (19). Interestingly, the outcome of the indirect templation method is sensitive to reaction conditions, notably the polarity of the solvent. When the reaction of $Cl_3P{=}N\text{-}n\text{-}Pr$ with $CuCl_2{\cdot}2H_2O$ takes place in ethanol at 90 °C, the final product is $[n\text{-}PrNH_3]_2[CuCl_4]$. This difference may be attributable to the faster rate of hydrolysis of $Cl_3P{=}N\text{-}n\text{-}Pr$ in the more polar solvent ethanol compared with that in toluene. The rapid cleavage of P—Cl and P—N bonds apparently results in a templation effect similar to that observed for the direct addition of Cl^- and $[n\text{-}PrNH_3]^+$ (in the form of the salt $[n\text{-}PrNH_3]Cl$).

Complexes **1** and **2** were identified by single-crystal X-ray analyses (Tables 2 and 3). As illustrated in Fig. 1, compound **1** contains an anionic hexanuclear copper chloride oligomer with a different stacking pattern from that found in $[C_7H_{10}N]_2[Cu_6Cl_{14}]$ (11). In **1**, the $[Cu_6Cl_{14}]^{2-}$ dianion connects to four neighbours of adjacent stacks via two long Cu—Cl bonds (Cl2—Cu2c = 2.6266(12) Å) and two Cu—Cl secondary bonding interactions (Cl2—Cu1d = 2.8080(13) Å), which extend the structure to a 2D herringbone motif. By contrast, the stacks of oligomers in

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[3] Supplementary data for this article are available on the journal Web site (http://canjchem.nrc.ca) or may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0R6, Canada. DUD 4081. For more information on obtaining material refer to http://cisti-icist.nrc-cnrc.gc.ca/irm/unpub_e.shtml. CCDC 277576 (**1**), 277577 (**2**), and 277578 (**3**) contain the crystallographic data for this manuscript. These data can be obtained, free of charge, via www.ccdc.cam.ac.uk/conts/retrieving.html (Or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax +44 1223 336033; or deposit@ccdc.cam.ac.uk).

Table 2. Selected bond lengths (Å) and bond angles (°) for **1**.

Bond lengths (Å)			
Cu(3)—Cl(6)	2.2631(13)	Cu(2)—Cl(4)	2.2674(13)
Cu(3)—Cl(7)	2.2674(13)	Cu(2)—Cl(3)	2.2807(12)
Cu(3)—Cl(7a)	2.2809(12)	Cu(2)—Cl(6)	2.2933(12)
Cu(3)—Cl(5)	2.2880(12)	Cu(2)—Cl(5)	2.3070(13)
Cu(1)—Cl(1)	2.2581(14)	Cu(2)—Cl(2b)	2.6266(12)
Cu(1)—Cl(2)	2.2723(12)	Cl(2)—Cu(2c)	2.6266(12)
Cu(1)—Cl(4)	2.3116(12)	Cl(7)—Cu(3a)	2.2809(12)
Cu(1)—Cl(3)	2.3381(13)	Cl(2)—Cu(1d)	2.8080(13)
Bond angles (°)			
Cl(6)-Cu(3)-Cl(7)	179.47(5)	Cl(3)-Cu(2)-Cl(6)	170.30(4)
Cl(6)-Cu(3)-Cl(7a)	92.72(4)	Cl(4)-Cu(2)-Cl(5)	167.35(4)
Cl(7)-Cu(3)-Cl(7a)	87.28(4)	Cl(3)-Cu(2)-Cl(5)	93.16(4)
Cl(6)-Cu(3)-Cl(5)	86.73(4)	Cl(6)-Cu(2)-Cl(5)	85.58(4)
Cl(7)-Cu(3)-Cl(5)	93.29(4)	Cl(4)-Cu(2)-Cl(2b)	95.25(4)
Cl(7a)-Cu(3)-Cl(5)	177.93(5)	Cl(3)-Cu(2)-Cl(2b)	97.72(4)
Cl(1)-Cu(1)-Cl(2)	96.52(5)	Cl(6)-Cu(2)-Cl(2b)	91.98(4)
Cl(1)-Cu(1)-Cl(4)	88.95(4)	Cl(5)-Cu(2)-Cl(2b)	97.30(4)
Cl(2)-Cu(1)-Cl(4)	170.83(4)	Cu(3)-Cl(6)-Cu(2)	94.07(5)
Cl(1)-Cu(1)-Cl(3)	172.53(5)	Cu(3)-Cl(5)-Cu(2)	93.04(4)
Cl(2)-Cu(1)-Cl(3)	89.69(4)	Cu(2)-Cl(4)-Cu(1)	94.51(5)
Cl(4)-Cu(1)-Cl(3)	84.37(4)	Cu(2)-Cl(3)-Cu(1)	93.45(4)
Cl(4)-Cu(2)-Cl(3)	86.71(4)	Cu(1)-Cl(2)-Cu(2c)	97.54(4)
Cl(4)-Cu(2)-Cl(6)	92.42(4)	Cu(3)-Cl(7)-Cu(3a)	92.72(4)

Note: Symmetry transformations used to generate equivalent atoms: $a = -x - 1, -y + 1, -z$; $b = x, y - 1, z$; $c = x, y + 1, z$; $d = -1 - x, 1/2 + y, 1/2 - z$.

Table 3. Selected bond lengths (Å) and bond angles (°) for **2**.

Bond lengths (Å)			
Cu(2)—Cl(3)	2.2743(18)	Cu(1)—Cl(2)	2.2589(17)
Cu(2)—Cl(5)	2.2846(18)	Cu(1)—Cl(4)	2.3143(18)
Cu(2)—Cl(4)	2.2897(16)	Cu(1)—Cl(3)	2.3187(17)
Cu(2)—Cl(5a)	2.2975(16)	Cl(5)—Cu(2a)	2.2975(16)
Cu(2)—Cl(2b)	2.6764(17)	Cl(2)—Cu(2c)	2.6764(17)
Cu(1)—Cl(1)	2.237(2)	Cl(2)—Cu(1d)	3.0724(18)
Bond angles (°)			
Cl(3)-Cu(2)-Cl(5)	170.35(7)	Cl(1)-Cu(1)-Cl(2)	95.53(8)
Cl(3)-Cu(2)-Cl(4)	85.68(6)	Cl(2)-Cu(1)-Cl(4)	92.10(7)
Cl(5)-Cu(2)-Cl(4)	93.02(6)	Cl(1)-Cu(1)-Cl(3)	89.37(7)
Cl(3)-Cu(2)-Cl(5a)	92.79(6)	Cl(2)-Cu(1)-Cl(3)	169.85(7)
Cl(5)-Cu(2)-Cl(5a)	86.87(6)	Cl(4)-Cu(1)-Cl(3)	84.11(6)
Cl(4)-Cu(2)-Cl(5a)	170.29(6)	Cu(2)-Cl(5)-Cu(2a)	93.13(6)
Cl(3)-Cu(2)-Cl(2b)	94.48(7)	Cu(2)-Cl(4)-Cu(1)	94.41(6)
Cl(5)-Cu(2)-Cl(2b)	95.18(6)	Cu(2)-Cl(3)-Cu(1)	94.70(6)
Cl(4)-Cu(2)-Cl(2b)	97.97(6)	Cu(1)-Cl(2)-Cu(2c)	99.70(6)
Cl(5a)-Cu(2)-Cl(2b)	91.71(6)		

Note: Symmetry transformations used to generate equivalent atoms: $a = -x - 4, -y - 3, -z - 2$; $b = x, y + 1, z$; $c = x, y - 1, z$; $d = -4 - x, -1/2 + y, -3/2 - z$.

$[C_7H_{10}N]_2[Cu_6Cl_{14}]$ are interlocked to give a layer pattern parallel to the *ab* plane. Each copper centre in **1** is coordinated to four chloride ligands. All the copper ions protrude from the ligand plane, displaying a square pyramidal distortion. The central Cu3 atom shows the smallest distortion with a dihedral angle of 2.0° between the Cl7-Cu3-Cl5 and Cl7a-Cu3-Cl6 planes. The most significant deviation from the square plane is observed at the Cu2 center with a dihedral angle of 16.3° between the Cl5-Cu2-Cl3 and Cl6-Cu2-Cl4 planes. The terminal Cu1 atom has a dihedral angle of 8.0° between the Cl4-Cu1-Cl1 and Cl3-Cu1-Cl2 planes. The terminal copper(II)—chloride bond lengths are 2.2581(14) (Cu1—Cl1) and 2.2723(12) Å (Cu1—Cl2), whereas the bridging copper(II)—chloride bond lengths are 2.3381(13) Å

Fig. 1. Molecular structure and atomic numbering scheme for **1**. Thermal ellipsoids are shown at the 70% level.

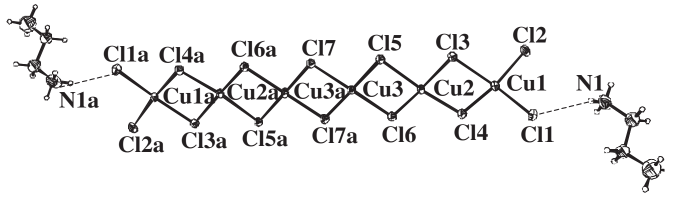
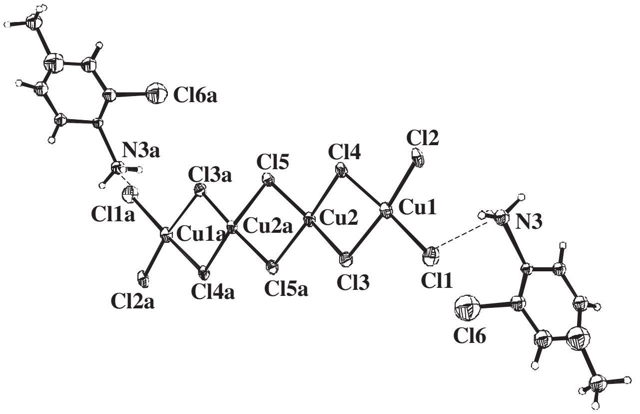


Fig. 2. Molecular structure and atomic numbering scheme for **2**. Thermal ellipsoids are shown at the 50% level.



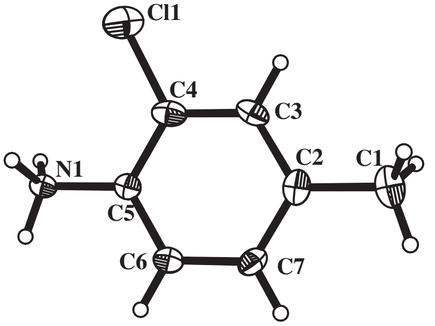
(Cu1—Cl3), 2.3116 Å (Cu1—Cl4), 2.2674(13) Å (Cu2—Cl4), 2.2807(12) Å (Cu2—Cl3), 2.3070(13) Å (Cu2—Cl5), 2.2933(12) Å (Cu2—Cl6), 2.2880(12) Å (Cu3—Cl5), 2.2631(13) Å (Cu3—Cl6), 2.2809 (12) Å (Cu3—Cl7a), and 2.2674(13) Å (Cu3—Cl7), respectively. These values are in agreement with the rule of variations in in-plane bond lengths of bibridged Cu_nX_{2n+2} oligomers, demonstrating a short-long-short··· alternation for the t-b1-b2··· sequence.[4] The bridging Cu-Cl-Cu bond angles range from 94.51° for the terminal fragment to 92.72° for the central units.

The structural characteristics of compound **2** are similar to those of **1** except that the anion is tetranuclear (Fig. 2). The $[Cu_4Cl_{10}]^{2-}$ fragment in $[Me_4N]_2[Cu_4Cl_{10}]$ has the same stacking pattern as that in **2**, but with a different mode of anion–cation interactions. In **2**, the oligomer is linked to four neighbours of adjacent stacks (Cl2—Cu2c = 2.6764(17) Å, Cl2—Cu1d = 3.0724(18) Å), whereas in $[Me_4N]_2[Cu_4Cl_{10}]$ the influence of the cations restricts these interactions to two neighbours (12). The Cu1 atom in **2** displays a small tetrahedral distortion, while the Cu2 atom exhibits a square pyramidal distortion with a dihedral angle of 14.0° between the Cl4-Cu2-Cl5 and Cl3-Cu2-Cl5a planes. The terminal Cl1 and Cl2 ligands coordinate with the Cu1 atom (Cu1—Cl1 = 2.237(2) Å, Cu1—Cl2 = 2.2589(17) Å), whereas the bridging ligands Cl3, Cl4, and Cl5 connect the adjacent copper atoms with a mode (Cu1—Cl3 = 2.3187(17) Å, Cu1—Cl4 = 2.3143(18) Å, Cu2—Cl3 = 2.2743(18) Å, Cu2—Cl4 = 2.2897(16) Å, and Cu2—Cl5 = 2.2846(18) Å). These values are typical and show the short-long-short alternation observed for **1**. The bridging Cu-Cl-Cu bond angles vary from 94.70° to 93.13°.

Table 4. Bond lengths (Å) and bond angles (°) for **3**.

Bond lengths (Å)			
Cl(1)—C(4)	1.719(5)	C(5)—C(3)	1.397(8)
C(7)—C(6)	1.379(7)	C(4)—C(2)	1.394(8)
C(7)—C(5)	1.396(8)	C(3)—C(2)	1.399(8)
C(6)—C(4)	1.387(7)	C(3)—C(1)	1.497(8)
C(6)—N(1)	1.454(7)		
Bond angles (°)			
C(6)-C(7)-C(5)	120.5(5)	C(2)-C(4)-Cl(1)	118.0(4)
C(7)-C(6)-C(4)	119.3(5)	C(6)-C(4)-Cl(1)	121.6(4)
C(7)-C(6)-N(1)	120.6(4)	C(5)-C(3)-C(2)	117.6(5)
C(4)-C(6)-N(1)	120.2(4)	C(5)-C(3)-C(1)	121.8(5)
C(3)-C(5)-C(7)	121.1(5)	C(2)-C(3)-C(1)	120.6(5)
C(2)-C(4)-C(6)	120.4(5)	C(4)-C(2)-C(3)	121.1(5)

Fig. 3. Molecular structure and atomic numbering scheme for the cation in **3**. Thermal ellipsoids are shown at the 50% level.



The X-ray analysis of compound **3** (Table 4) revealed that chlorination occurred in the position ortho to the NH_3^+ group to give the $[2\text{-}Cl\text{-}4\text{-}CH_3C_6H_3NH_3]^+$ cation (Fig. 3). The bond lengths and bond angles in this cation (C—Cl = 1.719(5) Å, C6—N1 = 1.454(7) Å; C2-C4-Cl1 = 118.0(4)°, C6-C4-Cl1 = 121.6(4)°) are similar to those reported for the related anilinium cation, $[3\text{-}Cl\text{-}6\text{-}BrC_6H_3NH_3]^+$ (26).

As illustrated in Fig. 4, the structures of **1** and **2** are both extended into two-dimensional networks by SBIs that give rise to a herringbone motif. The terminal chloride ligand Cl2 in **1** acts as a μ_2 bridge connecting to the copper centres located in the adjacent fragments. The Cu1 and Cu2 atoms adopt a 4+1+1 coordination mode, while the Cu3 atom has a 4+2 coordination geometry, in which the secondary bonding interactions for Cu1, Cu2, and Cu3 are 2.808 and 3.008 Å, 2.627 and 3.213 Å, and 2.981 and 2.960 Å, respectively. In compound **2**, the Cu1 atom adopts a 4+2 coordination mode with SBIs of 3.072 and 3.127 Å. The Cu2 atom has a 4+1+1 coordination mode with SBIs of 2.676 and 3.194 Å. The stacking patterns of **1** and **2** are denoted as 6(3/2, 1/2) and 4(3/2, 1/2), respectively, according to the notation of Willett and co-workers (17). Like most bibridged Cu_nX_{2n+2} oligomers, the charge-compensating cations $[n\text{-}PrNH_3]^+$ in **1** and $[2\text{-}Cl\text{-}4\text{-}CH_3C_6H_3NH_3]^+$ and $[4\text{-}CH_3C_6H_4NH_3]^+$ in **2** form hydrogen bonds with a pair of trans terminal chloride ligands (N—Cl = 3.245 Å for **1** and 3.253 Å for **2**).

In summary, a new synthetic approach involving the simultaneous in situ generation of Cl^- and $[RNH_3]^+$ ions for

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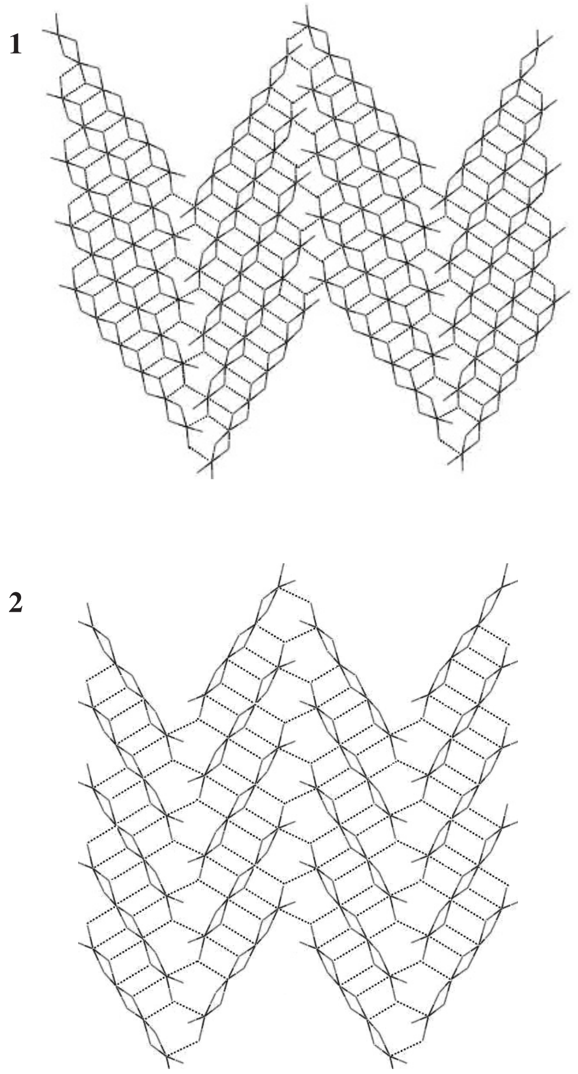
[4] The Ith Cu—Cl bond length is denoted by bI, starting from the terminal atom; b = bridging, t = terminal (27).

Fig. 4. Packing diagrams of compounds **1** and **2**. The Cu—Cl secondary bonding interactions are represented by broken lines.



the production of anionic copper chloride oligomers is introduced in this study. Variation of the R group in the precursors $Cl_3P{=}NR$ creates different lengths of the anionic chains. The structures of both oligomers exhibit a herringbone stacking pattern. These findings provide another example of the generation of new inorganic structural frameworks via *indirect* templation using P-N reagents (18, 19). There is considerable scope for the construction of novel inorganic architectures via variation in reaction conditions in these solvothermal processes, as indicated by the influence of solvent polarity in the current work.

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