Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters for non*-H *atoms with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{4}{3}[(B_{11} + B_{22} + B_{33})a^2 + (B_{12} + B_{13} + B_{23})a^2\cos\alpha].$$

	x	y	z	B_{eq}(Å^2)
Ni	5000	10000	5000	2·51
S	6368 (1)	8333 (1)	5202 (1)	3·62
O	3015 (3)	10740 (2)	809 (2)	4·79
N(1)	5283 (3)	8258 (2)	3101 (3)	3·29
N(2)	4747 (2)	9453 (2)	3424 (2)	3·00
N(3)	6738 (3)	6565 (3)	3677 (3)	4·77
C(1)	6087 (3)	7698 (3)	3884 (3)	3·08
C(2)	4067 (3)	10103 (3)	2597 (3)	3·56
C(3)	3771 (3)	9755 (3)	1428 (3)	3·53
C(4)	3970 (3)	8763 (3)	753 (3)	3·94
C(5)	3300 (4)	9117 (4)	−334 (3)	4·68
C(6)	2753 (4)	10314 (4)	−252 (4)	5·11

Table 2. *Bond distances* (Å) *and bond angles* (°) *with e.s.d.'s in parentheses*

Ni—N(2)	1·922 (2)	C(3)—O—C(6)	106·5 (3)
S—C(1)	1·724 (3)	N(2)—N(1)—C(1)	111·6 (3)
O—C(3)	1·386 (4)	Ni—N(2)—N(1)	121·0 (2)
O—C(6)	1·357 (5)	Ni—N(2)—C(2)	125·1 (2)
N(1)—N(2)	1·395 (3)	N(1)—N(2)—C(2)	113·9 (2)
N(1)—C(1)	1·310 (4)	S—C(1)—N(1)	123·7 (3)
N(2)—C(2)	1·289 (4)	S—C(1)—N(3)	116·8 (3)
N(3)—C(1)	1·342 (5)	N(1)—C(1)—N(3)	119·6 (3)
C(2)—C(3)	1·439 (4)	N(2)—C(2)—C(3)	129·2 (3)
C(3)—C(4)	1·340 (5)	O—C(3)—C(2)	110·7 (3)
C(4)—C(5)	1·429 (5)	O—C(3)—C(4)	109·1 (3)
C(5)—C(6)	1·341 (6)	C(2)—C(3)—C(4)	140·1 (3)
		C(3)—C(4)—C(5)	107·4 (3)
		C(4)—C(5)—C(6)	106·0 (3)

trans planar with respect to the two S and two N atoms. A similar coordination is found in bis(thiosemicarbazidato)nickel(II) (Cavalca, Nardelli & Fava, 1962). The furan ring plane is at an angle of 3 (1)° to the coordination plane.

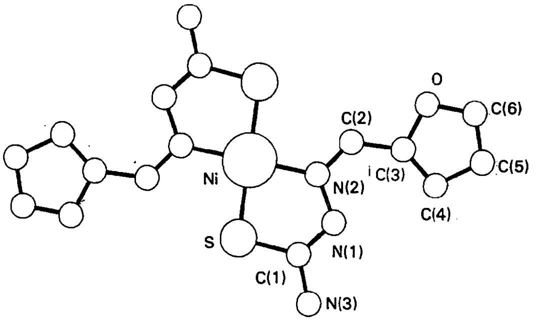

Fig. 1. A perspective view of the molecule.

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The Structures of 1-Methylpyridinium Aqua-di-μ-chloro-trichlorodicuprate(II) and 4-Aminopyridinium Aqua-di-μ-chloro-trichlorodicuprate(II) Hydrate

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Abstract. $C_6H_8N^+.[Cu_2Cl_5(H_2O)]^-$, $M_r = 416{\cdot}50$, monoclinic, $P2_1/n$; at $T \sim 293$ K: $a = 12{\cdot}051$ (3), $b = 7{\cdot}493$ (2), $c = 15{\cdot}211$ (4) Å, $\beta = 108{\cdot}35$ (2)°, $V = 1303{\cdot}5$ (5) Å^3, $Z = 4$, $D_x = 2{\cdot}12$ g cm^{-3}, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71069$ Å, $\mu = 42{\cdot}83$ cm^{-1}, $F(000) = 815{\cdot}85$. Least-squares refinement of 1877 independent observed [$|F| > 3\sigma(F)$] reflections gave $R = 0{\cdot}038$, $wR = 0{\cdot}045$. The structure consists of parallel stacks (parallel to the b axis) of $[Cu_2Cl_5(H_2O)]^-$ planar bibridged dinuclear oligomers separated by parallel stacks of 1-methylpyridinium cations. Adjacent oligomers in the stack are related by centers of inversion.

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Cu—Cl distances within the oligomer average 2·265 (20) (terminal) and 2·316 (27) Å (bridging) and Cu—O = 1·992 (3) Å with the bridging Cu—Cl—Cu angles averaging 94·7 (9)°. The stacking leads to formation of long semi-coordinate bonds between adjacent dimeric units, giving each Cu^{II} ion a 4+1+1 coordination. $C_5H_7N_2^+.[Cu_2Cl_5(H_2O)]^-.H_2O$, $M_r = 435·50$, monoclinic, $P2_1/n$; at $T \sim 295$ K: $a = 3·740$ (1), $b = 11·948$ (3), $c = 15·355$ (4) Å, $\beta = 93·76$ (2)°, $V = 684·7$ (3) $Å^3$, $Z = 2$, $D_x = 2·11$ g cm^{-3}, Mo $K\alpha$ radiation, $\lambda = 0·71069$ Å, $\mu = 42·88$ cm^{-1}, $F(000) = 427·92$. Least-squares refinement with 726 independent observed $[|F| > 3\sigma(F)]$ reflections gave $R = 0·043$, $wR = 0·049$. The structure consists of $[Cu_2Cl_5(H_2O)]^-$ and $(NH_2C_5H_4NH.H_2O)^+$ cations. The cations and anions stack in a similar manner to the 1-methylpyridinium salt except that the stacking is parallel to the *a* axis and the cations and anions are disordered so as to impose a crystallographic center of inversion upon each. The $[Cu_2Cl_5(H_2O)]$ geometry is nearly identical to that in the 1-methylpyridinium structure. The water molecule in the cation is hydrogen bonded to the pyridinium proton. Hydrogen bonding between the two water molecules, and between the amino group and the halides, provides stability to the crystal structure.

Introduction. Copper(II) halide structures have been of interest in our laboratory for several reasons, including the elucidation of magneto–structural correlations (Willett, 1985; Willett, Grigereit, Halverson & Scott, 1987), structural phase transitions (Bloomquist & Willett, 1982) including dynamic Jahn–Teller effects (Willett, Bond, Haije, Soonieus & Maaskant, 1987), and redox chemistry (Willett, 1987; Place & Willett, 1987). The copper(II) coordination sphere is very flexible, forming both normal and semi-coordinate bonds, and the halide ions impose few steric constraints, leading to a plethora of coordination geometries (Smith, 1976). When this is combined with the ability of the halide ion to form bridges between copper(II) ions, a truly diverse array of structural systems becomes accessible, the stability of which is largely determined by the steric and bonding capabilities of the counterions. Thus, in addition to the monomeric compounds, many types of oligomeric and polymeric species exist, which frequently aggregate through the formation of semi-coordinate bonds. The structural characteristics of $ACuCl_3$ salts (A = monopositive cation) (Willett & Geiser, 1984) and $[Cu_nX_{2n+2}]^{2-}$ ($X = Cl^-$ or Br^-) (Geiser, Willett, Lindbeck & Emerson, 1986) have recently been reviewed. In this paper, we report the structures of two new species of stoichiometry $ACu_2Cl_5(H_2O)$ which were prepared as part of our search for new magnetic and structural systems.

Experimental.

1-*Methylpyridinium* $[Cu_2Cl_5(H_2O)]$

Single crystals of $[C_5H_5NCH_3][Cu_2Cl_5(H_2O)]$ were obtained by mixing equimolar quantities of 1-methylpyridinium chloride and copper(II) chloride dihydrate in concentrated HCl solution. The 1-methylpyridinium chloride was synthesized using the method of Carpio, King, Lindstrom, Nardi & Hussey (1979), *i.e.* ~ 25 ml of chloromethane were liquefied in a dry-ice–ethanol bath and added to 32 ml of chilled pyridine in a 130 ml Parr bomb, the bomb sealed, allowed to warm to room temperature, and product removed after ~ 2·5 days. A red block-shaped single crystal, size 0·25 × 0·29 × 0·33 mm, was glued to the end of a glass fiber and mounted on a Syntex $P2_1$ automated four-circle diffractometer which has been upgraded to Nicolet *R*3*m* specifications. Preliminary cell parameters were determined using an autoindexing procedure and a least-squares refinement of the angular settings of ten centered reflections identified from a rotation photograph (Campana, Shepherd & Litchman, 1980). More accurate cell parameters were obtained from 25 well centered reflections in the range $35 < 2\theta < 37°$. With Mo $K\alpha$ radiation and a graphite monochromator, 2609 reflection intensities were measured $\{[(\sin\theta)/\lambda]_{max} = 0·595$ $Å^{-1}$, $2 \le 2\theta \le 50°$, $0 \le h \le 14$, $0 \le k \le 8$, $-17 \le l \le 17\}$ with ω scans (scan speed: min. = 3·91, max. = 29·3° min^{-1}; scan range = 1°). Four reflections rejected because of unsymmetrical backgrounds, one reflection rejected because of an asymmetric peak shape, and one reflection rejected as off-center to give 2603 reflections. Three check reflections were monitored every 93 reflections during the data collection, variations within counting statistics. Lp, crystal decay, and numerical absorption (Sheldrick, 1986) ($T_{max} = 0·418$, $T_{min} = 0·317$) corrections were applied. Equivalent reflections were averaged ($R_{merge} = 0·029$), 2281 independent reflections with 1877 observed $[|F| > 3\sigma(F)]$. Systematic absences ($h0l$, $h+l$ odd; $0k0$, k odd) unambiguously identify the space group as $P2_1/n$. The *SHELXTL* package of programs provided by Nicolet (Sheldrick, 1986) was used for structure solution and refinement. The positions of the two Cu atoms were identified from the electron density map calculated after direct methods. The structure was refined using a blocked cascade least-squares method. All other atom positions, including the H atoms, were identified from subsequent electron density difference maps and placed in the refinement. The anion was refined in the initial stages as a $Cu_2Cl_6^{2-}$ dimer without coordinated water. An abnormally large thermal parameter of one of the Cl ions and the presence of only one, instead of two, monopositive counterions per oligomer dictated that a lighter neutral ligand must be coordinated at that site. Since the crystals were grown from aqueous solution, a water molecule was the most logical choice for ligand. Anisotropic thermal parameters were refined for all non-H atoms with common isotropic thermal parameters for the groups of ring, methyl and aqua H atoms. Bond lengths for the ring and methyl H atoms were constrained to 0·96 Å while a common bond length was refined for the hydrate H atoms. The distance between the hydrate H atoms was constrained to 1·63 times their common O—H bond distance while the other H atoms were constrained to idealized geometries. Final refinement of the structure with 146 least-squares parameters gave $R = 0{\cdot}038$, $wR = 0{\cdot}045$ (0·047 for both for all data) with the goodness of fit equal to 1·401. The function minimized during least-squares calculations was $\sum w(F_o - F_c)^2$ with $w = [\sigma^2(F) + g|F|^2]^{-1}$ and g refined to the value 0·00039. The final least-squares cycle gave $|\Delta/\sigma(\text{mean})| = 0{\cdot}004$ and $|\Delta/\sigma(\text{max.})| = 0{\cdot}020$. The excursions in the final electron density difference map were between 0·67 e Å^{-3}, near Cu(1), and −0·70 e Å^{-3}. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). Fig. 1. contains a view of a formula unit with the labels of the atoms. Table 1 contains a list of non-H-atom positions and interatomic distances and angles are listed in Table 2.*

Table 1. *Atomic coordinates* (× 10^4) *and equivalent isotropic thermal parameters* (Å^2 × 10^3) *for* $[C_5H_5NCH_3][Cu_2Cl_5(H_2O)]$

The equivalent isotropic U is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Cu(1)	4 (1)	1586 (1)	6062 (1)	25 (1)
Cu(2)	48 (1)	3389 (1)	4017 (1)	25 (1)
Cl(1)	−1194 (1)	1571 (1)	4503 (1)	27 (1)
Cl(2)	1213 (1)	3380 (1)	5536 (1)	26 (1)
Cl(3)	−1105 (1)	−491 (1)	6457 (1)	29 (1)
Cl(4)	1229 (1)	5335 (2)	3603 (1)	30 (1)
Cl(5)	1237 (1)	1874 (2)	7540 (1)	34 (1)
O	−1147 (3)	3783 (5)	2787 (2)	32 (1)
N	−583 (3)	2352 (5)	9404 (2)	30 (1)
C(1)	−1154 (4)	2056 (7)	10015 (3)	42 (2)
C(2)	−575 (5)	2192 (8)	10946 (4)	55 (2)
C(3)	579 (5)	2660 (8)	11243 (4)	55 (2)
C(4)	1150 (4)	2946 (7)	10614 (4)	48 (2)
C(5)	557 (4)	2785 (7)	9683 (3)	41 (2)
C(6)	−1234 (4)	2212 (8)	8405 (3)	48 (2)

Table 2. *Interatomic distances* (Å) *and angles* (°) *for* $[C_5H_5NCH_3][Cu_2Cl_5(H_2O)]$

Cu(1)—Cl(1)	2·355 (1)	N—C(1)	1·338 (7)
Cu(1)—Cl(2)	2·303 (2)	N—C(5)	1·344 (6)
Cu(1)—Cl(3)	2·253 (2)	N—C(6)	1·477 (5)
Cu(1)—Cl(5)	2·281 (1)	C(1)—C(2)	1·371 (7)
Cu(1)···Cl(4*A*)	2·875 (2)	C(2)—C(3)	1·366 (8)
Cu(2)—Cl(1)	2·311 (2)	C(3)—C(4)	1·360 (9)
Cu(2)—Cl(2)	2·294 (1)	C(4)—C(5)	1·375 (7)
Cu(2)—Cl(4)	2·261 (2)		
Cu(2)—O	1·992 (3)		
Cu(2)···Cl(3*A*)	2·727 (2)		

Cl(1)—Cu(1)—Cl(2)	84·7 (1)	Cl(4)—Cu(2)—O	88·5 (1)
Cl(1)—Cu(1)—Cl(3)	92·2 (1)	Cl(1)—Cu(2)···Cl(3*A*)	91·1 (1)
Cl(2)—Cu(1)—Cl(3)	171·6 (1)	Cl(2)—Cu(2)···Cl(3*A*)	94·3 (1)
Cl(1)—Cu(1)—Cl(5)	174·1 (1)	Cl(4)—Cu(2)···Cl(3*A*)	93·0 (1)
Cl(2)—Cu(1)—Cl(5)	90·0 (1)	O—Cu(2)···Cl(3*A*)	97·4 (1)
Cl(3)—Cu(1)—Cl(5)	93·4 (1)	Cu(1)—Cl(1)—Cu(2)	93·8 (1)
Cl(1)—Cu(1)···Cl(4*A*)	89·7 (1)	Cu(1)—Cl(2)—Cu(2)	95·6 (1)
Cl(2)—Cu(1)···Cl(4*A*)	90·7 (1)	Cu(1)—Cl(3)···Cu(2*A*)	96·5 (1)
Cl(3)—Cu(1)···Cl(4*A*)	97·1 (1)	Cu(2)—Cl(4)···Cu(1*A*)	93·6 (1)
Cl(5)—Cu(1)···Cl(4*A*)	87·8 (1)	C(1)—N—C(5)	121·2 (4)
Cl(1)—Cu(2)—Cl(2)	85·9 (1)	C(1)—N—C(6)	118·7 (4)
Cl(1)—Cu(2)—Cl(4)	175·7 (1)	C(5)—N—C(6)	120·1 (4)
Cl(2)—Cu(2)—Cl(4)	92·5 (1)	N—C(1)—C(2)	120·0 (5)
Cl(1)—Cu(2)—O	92·2 (1)	C(1)—C(2)—C(3)	119·6 (6)
Cl(2)—Cu(2)—O	168·1 (1)	C(2)—C(3)—C(4)	119·7 (5)
		C(3)—C(4)—C(5)	119·8 (5)
		N—C(5)—C(4)	119·7 (5)

4-*Aminopyridinium* $[Cu_2Cl_5(H_2O)]$ *hydrate*

Single crystals of the 4-aminopyridinium salt were grown by evaporation of a dilute HCl solution containing a 2:1 ratio of the pyridine base and $CuCl_2.2H_2O$. Red-orange needle crystals were obtained which appeared pleochroic (red–yellow) when viewed under the polarizing microscope. A crystal with dimensions 0·54 × 0·12 × 0·08 mm was selected and mounted on a Nicolet *R*3*m*/*E* diffractometer system. Cell constants from 25 reflections in the range $31 \leq 2\theta \leq 35°$. Intensities of 1091 reflections were measured $\{[\sin\theta)/\lambda]_{\max} = 0{\cdot}539$ Å^{-1}, $2\theta \leq 45°$, $0 \leq h \leq 4$, $0 \leq k \leq 12$, $-15 \leq l \leq 15\}$ with ω scans (scan range = 1·0°; scan speed: min. = 3·91, max. = 29·3° min^{-1}). Twenty-eight of these reflections were rejected because of unsymmetrical background intensities and fifteen were omitted from the final refinement because of obvious presence of intensity in the scan due to twinning. Two check reflections were measured every 96 reflections during the data collection, variations within counting statistics. Lp, crystal decay, and numerical absorption (Sheldrick, 1984) ($T_{\min} = 0{\cdot}230$, $T_{\max} = 0{\cdot}659$) corrections were applied. Intensities of equivalent reflections were averaged ($R_{\text{merge}} = 0{\cdot}043$), 862 independent reflections, 726 observed $[|F| > 3\sigma(F)]$. Systematic absences ($h0l$, $h+l$ odd; $0k0$, k odd) unambiguously identify the space group as $P2_1/n$. The structure solution was attained *via* direct methods

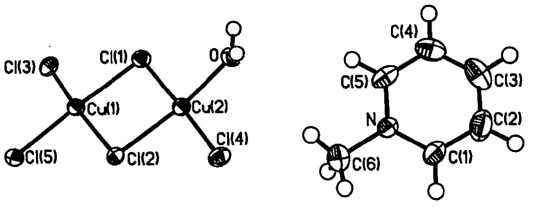

Fig. 1. View of a formula unit of 1-methylpyridinium aqua-di-μ-chloro-trichlorodicuprate(II) with atom labels.

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* Lists of structure factors, anisotropic thermal parameters, and H-atom positions and stereographic unit cell packing diagrams for both crystal structures have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44248 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

(Sheldrick, 1984), which yielded the positions of the Cu and Cl atoms defining an apparent $Cu_2Cl_6^{2-}$ anion located on an inversion center. The structure was refined using the previously described set of programs. The positions of the atoms in the 4-aminopyridinium cation, located about a second center of inversion, were identified from subsequent electron density difference maps. The thermal parameter of one Cl atom was found to be abnormally large. With the assumption of a monopositive charge on the organic cation, charge neutrality dictated a $Cu_2Cl_5(H_2O)$ stoichiometry for the anion. Subsequent electron density difference maps were interpreted in terms of disordered anions and cations, and revealed the presence of an additional (disordered) water molecule associated with the cation. This resulted in the structure of Fig. 2, where one nondisordered structural unit is shown. The refinement then proceeded with the following constraints: site occupancy factors constrained to 0·5 for N(1), C(3), N(4), *W*(1), *W*(2), Cl(3*a*) and associated protons; positional parameters of N(1) and C(3) constrained to be equal; Cu—*W* and Cu*a*—Cl(3*a*) distances constrained loosely to 2·00 and 2·24 Å, respectively; positional parameters of H atoms bonded to C(1), C(2), N(4) and *W*(1) constrained to idealized geometries; positional parameters for H atoms bonded to N(1) and *W*(2) calculated and held fixed during the final cycles of refinement; thermal parameters for H atoms held fixed. Final refinement with 93 least-squares parameters gave $R = 0{\cdot}043$, $wR = 0{\cdot}049$ for the 3σ data set (0·054 and 0·064, respectively, for all data) with the goodness of fit equal to 1·301. The function minimized was $\sum w(F_o - F_c)^2$ with $w = [\sigma^2(F) + gF^2]^{-1}$ and g refined to a value of 0·0007. The last least-squares cycle gave $|\Delta/\sigma(\text{mean})| = 0{\cdot}001$ and $|\Delta/\sigma(\max.)| = 0{\cdot}003$. The excursions in the final difference map were between 0·6 e Å^{-3}, near Cu, and −0·4 e Å^{-3}. Isotropic extinction corrections were included in the least-squares refinement ($g = 1{\cdot}9 \times 10^{-3}$). Non-H-atom positional parameters are given in Table 3 with interatomic distances and angles given in Table 4.*

Discussion. The structures consist of segregated stacks of the planar $[Cu_2Cl_5(H_2O)]^-$ anions and of the respective cations. These are the first examples of a

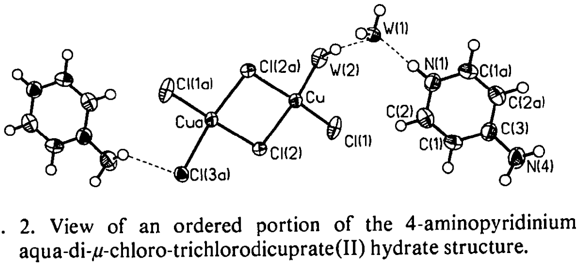

Fig. 2. View of an ordered portion of the 4-aminopyridinium aqua-di-μ-chloro-trichlorodicuprate(II) hydrate structure.

Table 3. *Atomic positions and equivalent isotropic thermal parameters* (Å^2) *for* $[C_5NH_5NH_2.H_2O][Cu_2Cl_5(H_2O)]$

The equivalent isotropic U is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Cu	0·1921 (2)	0·5382 (1)	0·5992 (1)	0·0330 (3)
Cl(1)	0·6284 (5)	0·4680 (2)	0·6915 (1)	0·0539 (8)
Cl(2)	0·1828 (4)	0·3826 (1)	0·5108 (1)	0·0338 (6)
Cl(3)	0·1255 (12)	0·7060 (3)	0·6725 (3)	0·032 (1)
W(2)	0·296 (3)	0·6830 (8)	0·6576 (8)	0·036 (4)
C(1)	0·112 (2)	0·3950 (6)	0·9828 (5)	0·046 (3)
C(2)	0·078 (2)	0·4706 (7)	0·9171 (5)	0·046 (3)
C(3)	0·039 (2)	0·4232 (6)	1·0656 (5)	0·044 (2)
N(1)	−0·039 (2)	0·5768 (6)	−0·0656 (5)	0·044 (2)
N(4)	0·084 (4)	0·3448 (12)	1·1293 (9)	0·059 (5)
W(1)	−0·130 (3)	0·7247 (7)	0·7924 (6)	0·037 (3)

Table 4. *Interatomic distances* (Å) *and angles* (°) *for* $[C_5NH_5NH_2.H_2O][Cu_2Cl_5(H_2O)]$

Cu—Cl(1)	2·252 (2)	C(1)—C(2)	1·35 (1)
Cu—Cl(2)	2·300 (2)	C(1)—C(3)	1·36 (1)
Cu*a*—Cl(3*a*)	2·321 (4)	C(2*a*)—C(3)	1·37 (1)
Cu—*W*(2)	1·976 (10)	C(3)—N(4)	1·36 (1)
Cu···Cl(1*a*)	2·747 (2)	N(1)—C(1*a*)	1·36 (1)
Cu—Cl(2*a*)	2·326 (2)	N(1)—C(2)	1·37 (1)
Cu···Cl(2*b*)	3·120 (2)		
Cl(1)—Cu—Cl(2)	93·0 (1)	*W*(2)—Cu···Cl(1*a*)	99·7 (3)
Cl(1*a*)—Cu*a*—Cl(3*a*)	96·5 (1)	*W*(2)—Cu—Cl(2*a*)	93·7 (3)
Cl(1)—Cu—*W*(2)	85·8 (3)	Cl(1*a*)—Cu*a*—Cl(2*a*)	93·0 (1)
Cl(1)—Cu···Cl(1*a*)	96·4 (1)	Cu*a*—Cl(2)—Cu	94·9 (1)
Cl(1)—Cu—Cl(2*a*)	170·6 (1)	Cu—Cl(2*a*)—Cu	96·4 (1)
Cl(2)—Cu*a*—Cl(3*a*)	170·5 (1)	C(2)—C(1)—C(3)	121·1 (7)
Cl(2)—Cu—*W*(2)	166·0 (3)	C(3)—C(2)—C(1)	120·4 (5)
Cl(2)—Cu*a*—Cl(1*a*)	94·3 (1)	C(1)—C(3)—N(4)	118·6 (8)
Cl(2)—Cu—Cl(2*a*)	85·1 (1)	C(2)—C(3)—N(4)	121·7 (9)
Cl(3*a*)—Cu*a*···Cl(1)	84·5 (1)	C(1)—C(3)—C(2)	119·7 (7)
Cl(3*a*) Cu*a*—Cl(2*a*)	85·5 (1)	C(1)—N(1)—C(2)	119·7 (7)

Hydrogen-bonding distances (Å)

W(2)···*W*(1)	2·74 (1)	*H*(2*a*)···*W*(1)	1·80
N(1)···*W*(1^{i})	2·81 (1)	H(3)···*W*(1^{i})	1·88
W(2)···Cl(3^{ii})	3·11 (1)	H(2*b*)···Cl(3^{ii})	2·08
W(1)···Cl(1^{iii})	2·92 (1)	H(1a)···Cl(1^{iii})	1·98
W(1)···Cl(3^{iv})	3·24 (1)	H(1b)···Cl(3^{iv})	2·30
N(4)···Cl(2^{v})	3·55 (1)	H(4a)···Cl(2^{v})	2·61
N(4)···Cl(3^{vi})	3·25 (1)	H(4b)···Cl(3^{vi})	2·48

Symmetry code: (i) $x, y, 1+z$; (ii) $1+x, y, z$; (iii) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{3}{2}-z$; (iv) $-1+x, y, z$; (v) $-\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$; (vi) $-x, 1-y, 2-z$

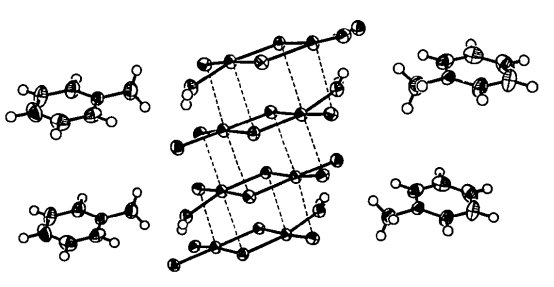

Fig. 3. View of the stacking pattern of copper oligomers in 1-methylpyridinium aqua-di-μ-chloro-trichlorodicuprate(II) showing the short equatorial coordinate bonds and the long axial semi-coordinate bonds.

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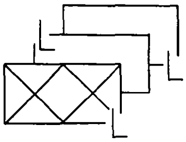
* See deposition footnote.

$Cu_2Cl_5L^-$ anion, although both the dinegative $Cu_2Cl_6^{2-}$ (Willett, Dwiggens, Kruh & Rundle, 1963) and the neutral $Cu_2Cl_4L_2$ (Willett & Rundle, 1964) dimers are known. The symmetrically bibridged anions contain square-planar-coordinated copper(II) ions with the water occupying a terminal position. The dimers aggregate into stacks through the formation of long semi-coordinate Cu—Cl bonds, one approximately 2·7–2·8 Å long and a second 3·0–3·2 Å long, leading to a 4+1+1 coordination geometry. The stacking pattern for the 1-methylpyridinium salt, shown pictorially in (I), would be designated as $2(\frac{1}{2},\frac{1}{2},180)$ in the



(I)

notation previously introduced (Geiser, Willett, Lindbeck & Emerson, 1986) where the 2 denotes a dimer and the $(\frac{1}{2},\frac{1}{2},180)$ indicates that successive dimers are translated $\frac{1}{2}$ of the edge Cl–Cl distance parallel to the Cu–Cu direction and $\frac{1}{2}$ of that distance perpendicular to that direction with a rotation of 180° about the normal to the dimer plane. In the 4-aminopyridinium hydrate salt, the cations and anions are disordered so the length of the chain axis is halved.

The structure of the 1-methylpyridinium salt consists of stacks of $Cu_2Cl_5(H_2O)$ units parallel to the y axis. The dicopper oligomers are canted with respect to the y axis, the normal of the plane formed by the central atoms of the unit [Cu(1), Cu(2), Cl(1) and Cl(2)] forming an angle of 36·1° with the y axis. The stacking axis passes through the inversion centers of the unit cell with the dicopper unit centers lying midway between inversion centers; thus adjacent dicopper oligomers are related by inversion. This results in the water of hydration appearing alternately on opposite ends of adjacent anions. The 1-methylpyridinium cations also occur in parallel stacks with nearest neighbors related by inversion. The plane of the cation is canted 23·5° with respect to the plane of the anion and the normal to the plane forms an angle of 14·5° with respect to the y axis. A view of the stacking geometry is shown in Fig. 3.

The bonding geometry around Cu(1) shows a 4+1+1 coordination, *i.e.* four short bonds, one long semi-coordinate bond, and one even longer semi-coordinate bond. The Cu(1)—Cl bonds in the plane of the anion (equatorial) are all in the range 2·25–2·35 Å in contrast to the semi-coordinate bonds (axial) to the terminal chloride of the adjacent anion, with a distance of 2·875 (2) Å, and to a bridging chloride of the other adjacent anion, with a distance of 3·028 (2) Å. The bonding geometry around Cu(2) shows the same coordination if we classify the Cu—O bond as a short bond with the equatorial Cu—Cl bonds; the axial bond distances are 2·727 (2) and 3·047 (2) Å in this case. The Cu(2) semi-coordinate bonds are to terminal and bridging chloride ions not semi-coordinated to Cu(1). All chloride ions have one semi-coordinate bond to a copper ion except for Cl(5). The short Cu—Cl semi-coordinate bonds are to the terminal Cl(3) and Cl(4) atoms, while the long semi-coordinate bonds are to the two bridging Cl(1) and Cl(2) atoms. The axial Cu—Cl bonds are shown in Fig. 3. The short contact distance (~ 2·4 Å) between Cl(5) and the hydrate H atoms on the adjacent oligomer implies some hydrogen bonding between these two terminal ligands.

In the 4-aminopyridinium salt, the disordered cationic and anionic stacks are parallel to the crystallographic a axis, which is one-half the length of the b axis of the 1-methylpyridinium salt, but in other aspects the stacking pattern is analogous to that in the previously described salt. The a-axis repeat distance (3·740 Å) is considerably shorter than that observed for other $A_2Cu_2Cl_6$, $Cu_2Cl_4L_2$ ($A = K^+$, 4·029 Å; $A = NH_4^+$, 3·84 Å; $L = CH_3CN$, 3·84 Å) (Willett, Dwiggens, Kruh & Rundle, 1963; Willett & Rundle, 1964), $A_2Cu_3Cl_8$ (A = 2-amino-5-methylpyridinium, ~ 3·9 Å) (Grigereit, Ramakrishna, Place, Willett, Pellacani, Manfredini, Menabue, Bonamartini-Corradi & Battaglia, 1987) and $A_2Cu_4Cl_{10}$ (A = 2-amino-4-methylpyridinium, 3·847 Å) (Halverson, Grigereit & Willett, 1987) systems with similar stacking patterns. The hydrogen bonding is complex but logical. The pyridinium–water complex is held together by a strong N—H···O hydrogen bond to $W(1)$. The water molecule on the $[Cu_2Cl_5(H_2O)]$ anion also hydrogen bonds to $W(1)$. At the other end of the pyridinium cation, the amino group forms N—H···Cl hydrogen bonds to Cl(2) and Cl(3a). The N—H···O···H—O linkage has essentially the same extent as the C—N—H···Cl linkage, making the observed disorder possible. This is in contrast to the 1-methylpyridinium salt where no hydrogen bonding exists between cation and anion, resulting in a stack of ordered dimers. Additional hydrogen bonds between water and amino protons and the chloride ions help tie the crystal structure together (Table 4).

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Structure of Chlorotriphenylphosphonium Hexachloromolybdate

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Abstract. $[PCl(C_6H_5)_3]_2[MoCl_6]$, $M_r = 904{\cdot}15$, trigonal rhombohedral, $R\bar{3}$, hexagonal cell $a = 13{\cdot}163\,(2)$, $c = 18{\cdot}876\,(7)$ Å, $V = 2832{\cdot}5\,(5)$ Å^3, $Z = 3$, $D_x = 1{\cdot}58$ Mg m^{-3}, D_m not measured, $\lambda(\text{Mo}\,K\alpha) = 0{\cdot}71069$ Å, $\mu = 10{\cdot}20$ cm^{-1}, $F(000) = 1362$, $T = 292$ K, $R = 0{\cdot}024$ for 1674 observed data with $I \geq 3\sigma(I)$. The complex contains an Mo atom at the centre of a regular octahedron of chloride ions and is the first accurately determined structure of this anion. The chlorophosphonium cations $[PClPh_3]^+$ have the expected tetrahedral symmetry with the P—Cl bonds directed towards opposite faces of the $[MoCl_6]^-$ octahedron.

Introduction. In a continuation of our studies of the reactions of molybdenum complexes with sulfur-containing reagents (Povey & Richards, 1984; Povey, Richards & Shortman, 1986), we have investigated the reactions of S_2Cl_2, widely used in organic chemistry for generating sulfur- and chloride-containing compounds (Kutney & Turnbull, 1982). In inorganic chemistry S_2Cl_2 is often used as a reactive solvent in the synthesis of thiohalide species, such as $NbCl_2S_2$ (Schäfer & Beckman, 1966), $Mo_3Cl_4S_7$ (Ul'ko & Kolesnicheno, 1980), and $ReCl_3S$ (Marcole, Rabenau, Mootz & Wunderlich, 1974). The product of the reaction between $[MoX_2(CO)_2(PPh_3)_2]$ (X = Br or Cl) and S_2Cl_2 does not, however, contain sulfur, but is the yellow complex $[PClPh_3]_2[MoCl_6]$, which has been structurally characterized by X-ray crystallography.

$$[MoBr_2(CO)_2(PPh_3)_2] + 4S_2Cl_2 \xrightarrow[293\ \text{K}]{CH_2Cl_2} [PClPh_3]_2[MoCl_6] + 2CO + 2Br^- + 8S \quad (1)$$

$$[MoCl_2(CO)_2(PPh_3)_2] + 3S_2Cl_2 \xrightarrow[293\ \text{K}]{CH_2Cl_2} [PClPh_3]_2[MoCl_6] + 2CO + 6S \quad (2)$$

Experimental. Accurate unit-cell parameters were measured on a CAD-4 diffractometer using 25 accurately centred reflexions (θ range 19·5–25·7°) from a crystal of dimensions 0·2 × 0·25 × 0·25 mm mounted in a capillary because of instability. A full hemisphere of reciprocal space was measured ($-18 \leq h \leq 18$; $-18 \leq k \leq 18$; $0 \leq l \leq 26$), θ limit = 30°, $\omega/2\theta$ scan, scan speed 4° min^{-1}, with the 600 reflexion monitored

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