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Synthesis and Spectroscopic and Structural Investigation on Tetrakis(*N*-(2-ammonioethyl)piperazinium) Di-μ-chloro-dodecachlorotricuprate(II) Bis(tetrachlorocuprate(II)), $(C_6H_{18}N_3)_4Cu_5Cl_{22}$

L. Antolini,[1a] G. Marcotrigiano,[1b] L. Menabue,[1a] and G. C. Pellacani*[1a]

Contribution from the Consiglio Nazionale delle Ricerche, Rome, Italy, Istituto di Chimica Generale e Inorganica, University of Modena, 41000 Modena, Italy, and Istituto di Chimica, Facoltà di Medicina-Veterinaria, University of Bari, 70126 Bari, Italy.

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Abstract: A red compound of the type $[N(2amet)pipzH_3]_4Cu_5Cl_{22}$ ($N(2amet)pipzH_3$ = *N*-(2-ammonioethyl)piperazinium cation) was prepared and investigated by means of X-ray structural analysis, magnetic moment, and electronic and infrared spectroscopy. The substance crystallizes with four formula units in space group *Ibam* of the orthorhombic system in a cell of dimensions $a = 16.697$ (5) Å, $b = 14.479$ (3) Å, $c = 23.757$ (7) Å, and $V = 5743.4$ Å^3 at 21 °C. X-ray diffraction data were collected with a Philips PW 1100 automatic four-circle diffractometer, using Mo Kα radiation. The structure was solved by direct methods; least-squares refinement of structural parameters led to a conventional R factor of 0.032 for 1246 independent reflections [$I > 3.0\sigma(I)$]. The unit cell contains a $Cu_3Cl_{14}^{8-}$ anion found for the first time, two unequally flattened $CuCl_4^{2-}$ tetrahedra, and $[N(2amet)pipzH_3]^{3+}$ trications, which are hydrogen bonded to anions. The central Cu atom of the centrosymmetric $Cu_3Cl_{14}^{8-}$ ion has a tetragonally elongated octahedral six coordination, while the terminal Cu atoms have a distorted square-pyramidal pentacoordination; the coordination polyhedra share their axial Cl atoms. The contribution of hydrogen bonding to coordination geometry about the copper atoms is discussed. Its magnetic moment and electronic and infrared spectra are also interpreted on the basis of the known crystal structure.

Introduction

The chlorocuprates(II) are rather interesting, showing a great variety of coordination numbers and geometries. The most common and familiar are the trichloro-, tetrachloro-, pentachloro-, and hexachlorocuprates(II).[2] A remarkable variety of cations serve as counterions in chlorocuprates(II), ranging from simple alkali metal cations to highly complex organic, inorganic, and even organometallic species. A combination of size and hydrogen-bonding effects of counterions is of fundamental importance in determining the coordination geometry of the chlorocuprate(II) anion.

By using a triprotonated counterion, the *N*-(2-ammonioethyl)piperazinium (hereafter abbreviated as $N(2amet)pipzH_3$), for the first time a regular square-pyramidal $CuCl_5^{3-}$ ion was isolated.[3] With the same cation we have also obtained a red, anhydrous compound of formula $[N(2amet)pipzH_3]_4Cu_5Cl_{22}$, which is the only known chlorocuprate(II) with this anion stoichiometry.

Previous reported compounds with unusual stoichiometries, although more simple than that of our compound, are $Cs_3Cu_2Cl_7{\cdot}2H_2O$, which contains discrete binuclear $[Cu_2Cl_7(H_2O)_2]^{3-}$ anions,[4,5] $(Me_3NH)_3Cu_2Cl_7$ having two types of copper(II)-containing anion, a $[CuCl_3^-]_n$ chain and a $[CuCl_4]^{2-}$ tetrahedron,[6a] and $[(CH_3)_3NH]Cu_2Cl_5$ containing discrete bridged $[Cu_4Cl_{10}]^{2-}$ tetramer anions.[6b]

The X-ray analysis was performed on our compound, since there are various chemically reasonable arrangements of 5 Cu^{2+} and 22 Cl^- ions indistinguishible among themselves spectroscopically.

Experimental Section

Preparation of Tetrakis(*N*-(2-ammonioethyl)piperazinium) Di-μ-chloro-dodecachlorotricuprate(II) Bis(tetrachlorocuprate(II)) [N(2amet)pipzH$_3$]$_4$Cu$_5$Cl$_{22}$. The complex was prepared by adding concentrated hydrogen chloride to a blue solution containing $CuCl_2{\cdot}2H_2O$ and *N*-(2-aminoethyl)piperazine in a 1:1 stoichiometric ratio and boiling the solution until a limpid green solution was obtained. From the boiling solution red crystals only separated after a few minutes, while, by cooling the solution, yellow-green crystals, corresponding to the $[N(2amet)pipzH_3]CuCl_5{\cdot}H_2O$ complex,[3] also precipitated. Anal. Calcd for $C_{24}H_{54}Cu_5N_{12}Cl_{22}$: C, 17.91; H, 3.38; Cu, 19.75; N, 10.45; Cl, 48.50. Found: C, 17.89; H, 3.40; Cu, 19.91; N, 10.44; Cl, 48.65.

Physical Measurements. The electronic spectrum of the solid compound was recorded as a mull transmission spectrum with a Shimadzu MPS 50L spectrophotometer. The infrared spectrum, as solid or Nujol mull on KBr pellets (4000–250 cm^{-1}) or on polythene (500–60 cm^{-1}) as supports, was recorded with a Perkin-Elmer 180 spectrophotometer. The room-temperature magnetic moment was measured with the Gouy method by using $Nien_3S_2O_3$ as calibrant and correcting for diamagnetism with the appropriate Pascal constant.

Collection and Processing of the X-ray Diffraction Data. The crystal selected for X-ray analysis, sealed on a glass fiber, was directly mounted, in a random orientation, on a Philips PW 1100 automated four-circle diffractometer

All the measurements were carried out at room temperature, by using graphite-monochromated Mo Kα radiation.

Details specific to the X-ray diffraction data collection and processing are reported in Table I.

A survey of the complete data set revealed the systematic absences hkl for $h + k + l = 2n + 1$, $0kl$ for $k = 2n + 1$, and $h0l$ for $h = 2n + 1$. Possible space groups are the noncentrosymmetric orthorhombic space group *Iba*2 (C_{2v}^{21}, no. 45) and the centrosymmetric orthorhombic space group *Ibam* (D_{2h}^{26}, no. 72). The latter was chosen as the correct space group on the basis of distribution of peaks in the Patterson function,[8] and because the statistics on E factors clearly indicated a centric space group. It is confirmed by the successful refinement.

All data were corrected for Lorentz and polarization effects, but not for absorption in view of the small crystal size and absorption coefficient. Of the 2014 independent nonzero reflections 1246, for which $I > 3.0\sigma(I)$, were noted as observed and used in the structure analysis.

Solution and Refinement of the Structure. Scattering factors for Cu^{2+} and Cl^- ions, including real and imaginary terms of anomalous dispersion, and for N, C, and H atoms were taken from published tables.[9]

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(1) (a) University of Modena. (b) University of Bari.

(2) Smith, D. W. *Coord. Chem. Rev.* **1976**, *21*, 93, and references cited therein.

(3) Antolini, L.; Marcotrigiano, G.; Menabue, L.; Pellacani, G. C. *J. Am. Chem. Soc.* **1980**, *102*, 1303.

(4) Wells, H. L.; Dupee, L. C. *Z. Anorg. Chem.* **1894**, *5*, 300.

(5) Vogt, W.; Haas, H. *Acta Crystallogr., Sect. B* **1971**, *27*, 1528.

(6) (a) Clay, R. M.; Murray-Rust, P.; Murray-Rust, J. *J. Chem. Soc., Dalton Trans.* **1973**, 595. (b) Caputo, R. E.; Vukosavovic, M. J.; Willett, R. D. *Acta Crystallogr., Sect. B* **1976**, *32*, 2516.

(7) "User Manual for PW 1100 Philips"; Eindhoven, The Netherlands.

(8) Buerger, M. J. "Vector Space"; Wiley: New York, 1959.

(9) "International Tables for X-ray Crystallography", Vol. IV; Kynoch Press: Birmingham, England, 1974; pp 99–101, 149–150.

0002-7863/80/1502-5506$01.00/0

Table I. Summary of Crystal Data Collection[a] for $(N(2amet)pipzH_3)_4Cu_5Cl_{22}$

diffractometer	Philips PW 1100
radiation	graphite-monochromated Mo Kα (λ = 0.710 69 Å)
temp, °C	21 ± 2
crystal system	orthorhombic
space group	*Ibam* (D_{2h}^{26}, No. 72)
a, Å	16.697 (5)
b, Å	14.479 (3)
c, Å	23.757 (7)
V, Å^3	5743.4
Z	4
mol wt	1626.61
ρ(calcd), g/cm^3	1.881
ρ(obsd), g/cm^3	1.90 (by flotation in CCl_4-CH_3I mixture)
reflections measd	$+h$, $+k$, $+l$
scan type	coupled θ(crystal)-2θ(counter)
2θ range, deg	6.0-46.0
scan speed	3.0°/min in 2θ
scan width, deg	1.2
background time	10 s at beginning and end of 2θ scan
standards	2 every 120 reflections (no significant changes)
collected reflections	4730, yielding 2014 nonzero independent data
obsd reflections	1246 with $I > 3.0\sigma(I)$ [$\sigma(I)$ = (peak counts + total background counts)$^{1/2}$]
crystal size, mm	~0.23 × 0.15 × 0.08
absorption coefficient, cm^{-1}	29.4
absorption correction	not applied

[a] The unit cell parameters and their estimated standard deviations were obtained from least-squares refinement of the setting angles of 25 strong high-angle reflections, by using the standard control program of the PW 1100 system[7] for a randomly oriented crystal.

The function minimized during least-squares refinements was $\sum w(|F_o| - |F_c|)^2$; discrepancy indices used below are $R = (\sum ||F_o| - |F_c||)/\sum |F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^1/_2$, where w is the weighting factor.

All calculations were performed on the CDC Cyber 76 computer of the Centro di Calcolo Interuniversitario dell'Italia Nord-Orientale at Bologna, by using the programs detailed in ref 10.

An approximate absolute scale factor and an overall thermal parameter were obtained from a Wilson plot.

After failure of all our attempts to interpret the Patterson function, initial parameters for the Cu and the Cl atoms were obtained from an E map calculated from 250 $E(hkl)$'s > 1.58, whose signs were determined by the MULTAN direct-method program. All the N and C atoms were easily located in a subsequent Fourier-difference map. The starting set of parameters gave $R = 0.124$ and $R_w = 0.135$ ($w = 1.0$). Block-diagonal least-squares refinement of atomic positional and isotropic thermal parameters, using unit weights, led to convergence at $R = 0.059$ and $R_w = 0.066$. At this stage all hydrogen bonding atoms were located in a Fourier-difference map computed with reflections having $\sin \theta/\lambda < 0.40$, because over this value the contribution of H atoms to the structure factor was negligible. Final full-matrix least-squares refinement of positional and anisotropic thermal parameters for nonhydrogen atoms and of positional parameters only for hydrogen atoms, to which an isotropic temperature factor 1.0 Å^2 greater than the bonded atom was assigned, led to convergence at $R = 0.032$ and $R_w = 0.032$.

This refinement was performed with Cruickshank's weighting method $w = (10.9 - 0.03|F_o| + 0.00004|F_o|^2)^{-1}$ to remove an F_o and $\sin \theta/\lambda$ dependence in the quantity $w(|F_o| - |F_c|)^2$, previously observed either with $w = 1/\sigma^2(F)$ or with unit weights.

In the final least-squares cycle the shifts in all parameters were less than 0.3 of an esd. The "goodness of fit", defined as $[\sum w(|F_o| - |F_c|)^2/(N_o - N_v)^{1/2}]$, where $N_o = 1246$ is the number of reflections and $N_v = 209$ is the number of parameters varied, was 2.24.

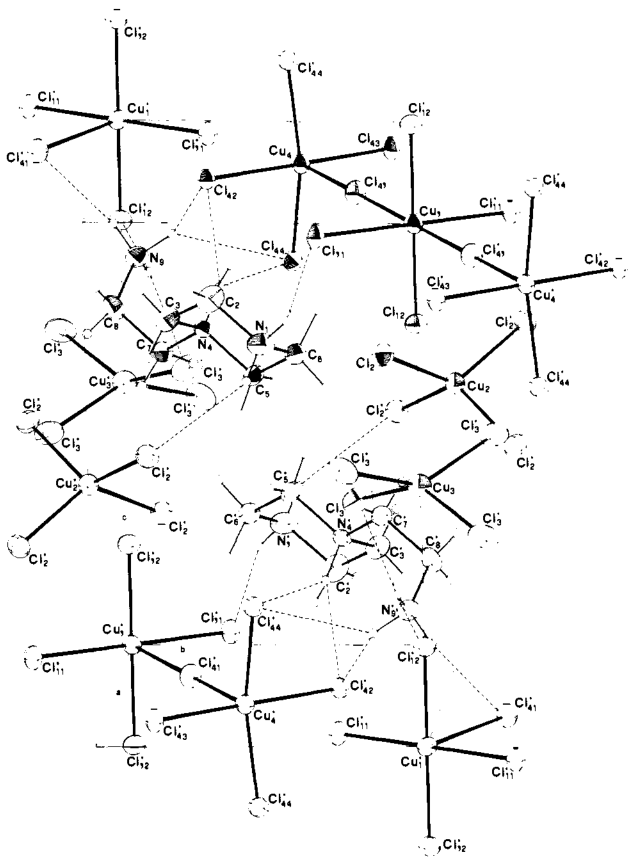

Figure 1. ORTEP drawing of a little more than one-eighth of the unit cell of $(N(2amet)pipzH_3)_4Cu_5Cl_{22}$ showing the labeling scheme and thermal motion ellipsoids (40%) for nonhydrogen atoms. The spheres corresponding to the hydrogen atoms are on an arbitrary scale. Hydrogen bonds are shown as dashed lines. The atoms arising from symmetry transformations (19) of reference coordinates are marked with an asterisk.

A final difference electron density map was featureless, with no peaks greater than 0.45 e Å^{-3}. Correction for secondary extinction was not deemed necessary. The final structural parameters appear in Table II. A list of $10|F_o|$ and $10|F_c|$ is available.[11]

Analyses. C, H, and N were analyzed by using a Carlo Erba elemental analyzer. The chlorine was directly determined in an aqueous solution of the title compound with the Volhard method. The copper was determined titrimetrically with EDTA.

Results and Discussion

Description of the Structure. A drawing of the structure, showing the labeling scheme, is given in Figure 1; interatomic distances and bond angles are listed in Table III. A list of bond angles involving hydrogen atoms is available.[11]

The structure consists of discrete $Cu_3Cl_{14}^{8-}$ anions, of two crystallographically independent $CuCl_4^{2-}$ units, and of $[N(2amet)pipzH_3]^{3+}$ cations, which are hydrogen bonded to the anions.

$Cu_3Cl_{14}^{8-}$ Anion. The centrosymmetric $Cu_3Cl_{14}^{8-}$ anion, found for the first time, is made up of two crystallographically independent Cu atoms and six independent Cl atoms, all but one [Cl(44)] lying in special positions. The structure may be described as a linear chain of three Cu atoms with two μ-chloro bridges; terminal Cu atoms have distorted square-pyramidal five coordination, while the central Cu atom, which lies on a $2/m$ symmetry site, has tetragonally elongated octahedral six coordination. Bridging Cl atoms occupy the shared axial positions of coordination polyhedra; half-equatorial Cl atoms lie from their constrained positions on the mirror plane at $z = {}^1/_2$, while the other six equatorial Cl atoms deviate by only small amounts from the perpendicular plane through the μ-chloro-bridged copper chain

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(10) Programs used in the structure determination include MULTAN by Main, Woolfson, and Germain [*Acta Crystallogr., Sect. A* **1971**, *27*, 368] for automatic solution of crystal structures; MIQUAD by A. Immirzi [*Ric. Sci* **1967**, *37*, 743] for least-squares refinements; FFSYNT by A. Immirzi [*J. Appl. Crystallogr.* **1973**, *6*, 246] for Fourier syntheses; and Johnson's ORTEP plotting program.

(11) See paragraph at end of paper regarding supplementary material.

Table II. Positional and Thermal Parameters and Their Estimated Standard Deviations[a]

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu(1)	0.5	0.5	0.5	2.12 (8)	1.98 (8)	1.85 (7)	0.70 (7)	0.0	0.0
Cu(2)	0.0	0.5	0.25	2.14 (8)	1.97 (8)	2.25 (8)	0.0	0.0	0.0
Cu(3)	0.5	0.5	0.25	1.69 (7)	2.98 (9)	2.64 (8)	0.0	0.0	0.0
Cu(4)	0.207 78 (8)	0.297 77 (9)	0.5	1.96 (5)	1.80 (5)	1.94 (5)	0.40 (5)	0.0	0.0
Cl(11)	0.5640 (2)	0.3580 (2)	0.5	1.9 (1)	1.8 (1)	3.0 (1)	0.3 (1)	0.0	0.0
Cl(12)	0.5	0.5	0.4044 (1)	2.1 (1)	2.6 (1)	1.9 (1)	−0.3 (1)	0.0	0.0
Cl(2)	0.0832 (1)	0.4010 (1)	0.2932 (1)	2.5 (1)	2.6 (1)	2.6 (1)	0.5 (1)	−0.1 (1)	0.3 (1)
Cl(3)	0.4096 (1)	0.3952 (2)	0.2188 (1)	2.7 (1)	4.7 (1)	3.2 (1)	−1.4 (1)	−0.7 (1)	0.9 (1)
Cl(41)	0.3469 (2)	0.3953 (2)	0.5	2.0 (1)	2.3 (1)	3.0 (1)	−0.2 (1)	0.0	0.0
Cl(42)	0.2878 (1)	0.1635 (2)	0.5	1.7 (1)	1.7 (1)	2.2 (1)	0.3 (1)	0.0	0.0
Cl(43)	0.1286 (2)	0.4262 (2)	0.5	2.5 (1)	1.8 (1)	2.9 (1)	0.8 (1)	0.0	0.0
Cl(44)	0.1929 (1)	0.2798 (1)	0.4042 (1)	2.4 (1)	2.2 (1)	1.9 (1)	0.4 (1)	−0.1 (1)	0.1 (1)
N(1)	0.4912 (4)	0.2637 (4)	0.3822 (2)	2.9 (3)	3.9 (3)	2.4 (3)	−1.4 (3)	0.2 (3)	−0.3 (3)
C(2)	0.4693 (4)	0.1873 (6)	0.4211 (4)	2.1 (3)	3.8 (4)	3.6 (4)	−0.1 (3)	−0.7 (3)	0.8 (3)
C(3)	0.4183 (4)	0.1152 (5)	0.3910 (3)	2.1 (4)	3.1 (4)	2.8 (4)	0.1 (3)	−0.2 (3)	0.6 (3)
N(4)	0.3438 (3)	0.1601 (4)	0.3676 (2)	1.8 (3)	1.7 (2)	1.5 (2)	−0.1 (2)	0.1 (2)	−0.2 (2)
C(5)	0.3670 (4)	0.2372 (5)	0.3283 (3)	3.2 (3)	2.1 (3)	2.1 (3)	−0.7 (3)	0.1 (3)	0.3 (3)
C(6)	0.4170 (5)	0.3072 (5)	0.3586 (3)	3.3 (4)	2.2 (3)	2.1 (3)	−1.0 (3)	0.0 (3)	−0.2 (3)
C(7)	0.2910 (4)	0.0927 (5)	0.3358 (3)	2.4 (3)	2.0 (3)	2.0 (3)	−0.9 (3)	0.1 (3)	−0.3 (3)
C(8)	0.2567 (5)	0.0162 (5)	0.3712 (3)	2.2 (3)	2.2 (4)	3.3 (3)	−0.3 (3)	0.5 (3)	−0.9 (3)
N(9)	0.1877 (3)	0.0447 (4)	0.4060 (3)	2.5 (3)	2.6 (3)	2.6 (3)	−0.8 (2)	0.9 (2)	−0.1 (3)

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
H(11)	0.507 (6)	0.305 (6)	0.408 (4)	3.9[b]	H(61)	0.387 (5)	0.339 (6)	0.395 (4)	3.6
H(12)	0.518 (5)	0.243 (6)	0.352 (3)	3.9	H(62)	0.440 (5)	0.354 (6)	0.331 (4)	3.6
H(21)	0.438 (5)	0.215 (6)	0.448 (4)	3.8	H(71)	0.252 (6)	0.133 (6)	0.317 (3)	3.3
H(22)	0.513 (6)	0.159 (6)	0.438 (3)	3.8	H(72)	0.322 (5)	0.063 (6)	0.309 (3)	3.3
H(31)	0.400 (5)	0.073 (6)	0.415 (4)	3.6	H(81)	0.286 (5)	−0.008 (6)	0.396 (3)	3.3
H(32)	0.445 (5)	0.088 (6)	0.359 (4)	3.6	H(82)	0.243 (5)	−0.026 (6)	0.343 (3)	3.3
H(41)	0.310 (5)	0.183 (5)	0.402 (4)	2.6	H(91)	0.146 (5)	0.057 (6)	0.384 (4)	3.5
H(51)	0.320 (5)	0.264 (6)	0.316 (3)	3.4	H(92)	0.203 (5)	0.101 (6)	0.431 (4)	3.5
H(52)	0.392 (5)	0.218 (6)	0.296 (3)	3.4	H(93)	0.177 (5)	0.009 (7)	0.436 (3)	3.5

[a] The form of the anisotropic thermal parameter is $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$. [b] The fixed isotropic temperature factor assigned to hydrogen atoms is 1.0 Å^2 greater than the last isotropic temperature factor of the bonded atom.

Table III. Interatomic Distances (Å) and Bond Angles (deg) for $(\mathrm{N(2amet)pipzH_3})_4\mathrm{Cu_5Cl_{22}}$

A. Within $\mathrm{Cu_3Cl_{14}}^{8-}$ Anion							
Cu(1)–Cl(11)	2.318 (3)	Cu(4)–Cl(43)	2.281 (3)	Cl(11)···Cl(41)	3.665 (5)	Cl(42)···Cl(43)	4.641 (5)
Cu(1)–Cl(12)	2.270 (3)	Cu(4)–Cl(44)	2.304 (2)	Cl(12)···Cl(41)	3.739 (5)	Cl(42)···Cl(44)	3.245 (5)
Cu(1)–Cl(41)	2.971 (3)	Cu(1)···Cu(4)	5.690 (1)	Cl(41)···Cl(42)	3.499 (4)	Cl(43)···Cl(44)	3.290 (4)
Cu(4)–Cl(41)	2.719 (3)	Cl(11)···Cl(12)	3.244 (4)	Cl(41)···Cl(43)	3.672 (5)	Cl(44)···Cl(44)^a	4.551 (5)
Cu(4)–Cl(42)	2.359 (3)			Cl(41)···Cl(44)	3.820 (5)		
Cl(11)–Cu(1)–Cl(12)	90.0	Cl(12)–Cu(1)–Cl(41)	90.0	Cl(41)–Cu(4)–Cl(44)	98.68 (4)		
Cl(11)–Cu(1)–Cl(11)^b	180.0	Cl(41)–Cu(1)–Cl(41)^b	180.0	Cl(42)–Cu(4)–Cl(43)	179.10 (6)		
Cl(12)–Cu(1)–Cl(12)^a	180.0	Cu(1)–Cl(41)–Cu(4)	179.38 (2)	Cl(42)–Cu(4)–Cl(44)	88.17 (4)		
Cl(11)–Cu(1)–Cl(41)	86.81 (3)	Cl(41)–Cu(4)–Cl(42)	86.80 (6)	Cl(43)–Cu(4)–Cl(44)	91.69 (4)		
Cl(11)–Cu(1)–Cl(41)^b	93.19 (3)	Cl(41)–Cu(4)–Cl(43)	94.09 (6)	Cl(44)–Cu(4)–Cl(44)^a	162.02 (6)		
B. Within $\mathrm{CuCl_4}^{2-}$ Anions							
Cu(2)–Cl(2)	2.245 (2)	Cl(2)···Cl(2)^d	3.455 (4)	Cu(3)–Cl(3)	2.266 (2)	Cl(3)···Cl(3)^c	3.378 (4)
Cl(2)···Cl(2)^c	3.525 (4)	Cl(2)···Cl(2)^e	3.993 (4)	Cl(3)···Cl(3)^f	3.364 (4)	Cl(3)···Cl(3)^g	4.282 (4)
Cl(2)–Cu(2)–Cl(2)^c	103.47 (5)	Cl(2)–Cu(2)–Cl(2)^e	125.64 (5)	Cl(3)–Cu(3)–Cl(3)^c	96.44 (5)		
Cl(2)–Cu(2)–Cl(2)^d	100.62 (5)	Cl(3)–Cu(3)–Cl(3)^f	95.87 (5)	Cl(3)–Cu(3)–Cl(3)^g	141.82 (5)		
C. Between Anions							
Cu(4)···Cl(11)^h	3.293 (3)	Cu(4)···Cl(11)–Cu(1)^h	160.69 (2)				
Cu(3)···Cl(12)	3.669 (3)	Cu(1)–Cl(12)···Cu(3)	180.0				
Cl(41)–Cu(4)···Cl(11)^h	168.08 (5)						
D. Within $(\mathrm{N(2amet)pipzH_3})^{3+}$ Cation							
N(1)–C(2)	1.50 (1)	C(7)–C(8)	1.50 (1)	C(3)–H(32)	0.96 (10)	C(7)–H(72)	0.92 (10)
N(1)–C(6)	1.50 (1)	C(8)–N(9)	1.48 (1)	N(4)–H(41)	1.04 (10)	C(8)–H(81)	0.85 (10)
C(2)–C(3)	1.51 (1)	N(1)–H(11)	0.89 (11)	C(5)–H(51)	0.93 (10)	C(8)–H(82)	0.93 (10)
C(3)–N(4)	1.51 (1)	N(1)–H(12)	0.89 (10)	C(5)–H(52)	0.91 (10)	N(9)–H(91)	0.89 (11)
N(4)–C(5)	1.51 (1)	C(2)–H(21)	0.92 (10)	C(6)–H(61)	1.09 (10)	N(9)–H(92)	1.03 (10)
N(4)–C(7)	1.52 (1)	C(2)–H(22)	0.91 (11)	C(6)–H(62)	1.02 (10)	N(9)–H(93)	0.89 (10)
C(5)–C(6)	1.50 (1)	C(3)–H(31)	0.90 (10)	C(7)–H(71)	0.98 (10)		
N(1)–C(2)–C(3)	110.8 (3)	C(2)–N(1)–C(6)	110.1 (3)	C(3)–N(4)–C(7)	112.7 (3)	C(5)–N(4)–C(7)	108.4 (3)
N(1)–C(6)–C(5)	110.8 (3)	C(3)–N(4)–C(5)	109.6 (3)	N(4)–C(5)–C(6)	110.2 (3)	C(7)–C(8)–N(9)	113.9 (3)
C(2)–C(3)–N(4)	110.2 (3)			N(4)–C(7)–C(8)	114.6 (3)		

Superscripts refer to the following transformations of the coordinates. [a] $x, y, 1-z$. [b] $1-x, 1-y, 1-z$. [c] $x, 1-y, \frac{1}{2}-z$. [d] $-x, y, \frac{1}{2}-z$. [e] $-x, 1-y, z$. [f] $1-x, y, \frac{1}{2}-z$. [g] $1-x, 1-y, z$. [h] $x-\frac{1}{2}, \frac{1}{2}-y, z$.

Table IV. Selected Least-Squares Planes and Atomic Deviations (Å) Therefrom[a]

atom	dev	atom	dev
1. Equation:[b] $-0.5228x + 0.8524y = 1.8065$			
Cl(44)	−0.037	Cl(41)	0.044
Cu(4)	0.055	Cl(12)	0.0
Cl(44)[c]	−0.037	Cu(1)	0.0
2. Equation: $0.8204x + 0.5718y = 5.1261$			
Cl(42)	0.170	Cl(44)[c]	−0.167
Cl(44)	−0.167	Cu(4)*	0.186
Cl(43)	0.165		
3. Equation: $-0.7505x + 0.1705y + 0.6385z = 0.9693$			
C(2)	−0.004	C(6)	0.004
C(3)	0.004	N(1)*	−0.677
C(5)	−0.004	N(4)*	0.694

[a] Atoms not used in calculating the plane are marked with an asterisk. [b] x, y, z are fractional crystal coordinates. [c] Symmetry transformation: x, y, $1 - z$.

Table V. Hydrogen-Bonding Distances (Å) and Angles (deg) with Their Esd's

atoms	Cl···N	Cl···H	∠Cl···H–N
N(1)–H(11)···Cl(11)	3.343 (7)	2.52 (11)	156 (5)
N(1)–H(12)···Cl(2)[a]	3.539 (8)	2.74 (10)	149 (4)
N(4)–H(41)···Cl(42)	3.281 (6)	2.38 (10)	144 (4)
N(4)–H(41)···Cl(44)	3.180 (6)	2.41 (9)	131 (4)
N(9)–H(91)···Cl(12)[b]	3.200 (7)	2.63 (11)	123 (1)
N(9)–H(91)···Cl(3)[c]	3.492 (7)	2.69 (11)	149 (3)
N(9)–H(92)···Cl(42)	3.276 (8)	2.35 (10)	148 (4)
N(9)–H(92)···Cl(44)	3.405 (8)	2.68 (10)	127 (5)
N(9)–H(93)···Cl(41)[d]	3.162 (8)	2.28 (10)	169 (6)

Superscripts refer to the following transformations of the coordinates. [a] $^1/_2 + x$, $^1/_2 - y$, z. [b] $x - {}^1/_2$, $^1/_2 - y$, z. [c] $^1/_2 - x$, $^1/_2 - y$, $^1/_2 - z$. [d] $^1/_2 - x$, $y - {}^1/_2$, z.

Table VI. Ideal and Observed Dihedral Angles (deg) for for $CuCl_5$ Polyhedra

complex	shape[a] determining δ' angles (e_3, e_1, e_2)	δ angles (a_2, a_5, and remaining angles)
ideal trigonal bipyramid[b]	53.1 53.1, 53.1	101.5, 101.5, 101.5, 101.5, 101.5, 101.5
$[N(2amet)pipzH_3]_4$-Cu_5Cl_{22}[c]	16.4 70.2, 70.2	82.5, 81.9, 112.3, 112.3, 114.9, 114.9
$[N(2amet)pipzH_3]$-$CuCl_5 \cdot 2H_2O$[d]	0.1 74.0, 77.9	74.9, 77.2, 116.9, 119.1, 120.0, 122.1
ideal tetragonal pyramid[b]	0.0 75.7, 75.7	75.7, 75.7, 119.8, 119.8, 119.8

[a] e_n and a_n refer to pairs of adjacent triangular faces which form equatorial or axial edges, respectively. [b] The ratio Cu–Cl_{eq} to Cu–Cl_{ax} bond lengths for the idealized models is set at unity and a Cl_a–Cu–Cl_e (basal) angle of 102° is assumed for C_{4v} model. [c] This work. [d] Reference 3.

(see Table IV). The anion possesses crystallographically imposed C_{2h} symmetry and only approximate D_{4h} symmetry.

The arrangement of chlorines about the Cu atoms is not too dissimilar to that found in $[(CH_3)_3CHNH_3]_2CuCl_4$,[12a] which can be visualized as being built up of trimeric units packed together to form infinite ribbons.

Axial and equatorial bond distances of the octahedrally coordinated Cu atom may be compared with the "short" and the "long" Cu–Cl distances previously found in compounds of the type $(RNH_3)_2CuCl_4$, which contain planar $CuCl_4^{2-}$ ions linked by essentially linear Cu–Cl–Cu bridges, to form infinite layers or ribbons.[2,12b] Our values of 2.270 (3) and 2.318 (3) Å for the two independent Cu–Cl_{eq} bond distances are only slightly below and above the observed range of mean short Cu–Cl distances, which run from 2.274 to 2.316 Å. The longer of our Cu–Cl_{eq} distances might be related to the one we have assumed as a strong nonbonding interaction (3.293 (3) Å) between Cl(11) and the Cu(4) atom from an adjacent $Cu_3Cl_{14}^{8-}$ unit. Previously found mean values for long Cu–Cl distances fall in a rather wide range, whose limits are 2.793 (5) Å in $(NH_4)_2CuCl_4$[13] and 3.257 (4) Å in $[Pt(NH_3)_4]CuCl_4$;[14] our unique Cu–Cl_{ax} bond distance of 2.971 (3) Å is very close to the values 2.975 (5) Å found in $(EtNH_3)_2CuCl_4$[15] and 2.946 (4) Å found in $(NH_3C_3H_6NH_3)$-$CuCl_4$.[12b] There is some doubt that Cl atoms as far away as 3 Å are definitely bonded to the copper;[2] our assumption is rather poorly based on the strong lengthening (0.149 Å) of the axial Cu–Cl bond of the square-pyramidal $CuCl_5$ moiety with respect to the value found in a nearly idealized C_{4v} geometry,[3] and also based on the rather high symmetry (D_{4h}) of the whole $Cu_3Cl_{14}^{8-}$ ion.

The coordination geometry about the terminal Cu atom may be compared to that in $[N(2amet)pipzH_3]CuCl_5 \cdot 2H_2O$,[3] which contains discrete $CuCl_5^{3-}$ ions having strictly square-pyramidal geometry. As reported above, the bridging of the apical Cl atom determines a strong lengthening of the axial Cu–Cl bond from 2.570 (2) to 2.719 (3) Å, while the mean equatorial Cu–Cl bond distance of 2.312 Å is not significantly different from the previous value of 2.318 Å. It may be noted that the longer Cu–Cl_{eq} bond distance (2.359 (3) Å) is associated with the Cl atom engaged in the strongest hydrogen bonding, the shortest (2.281 (3) Å) being associated with the only Cl atom not involved in hydrogen bonding (see Table V). Another relevant feature of the $CuCl_5$ moiety is a strong deviation from previously found planarity of the four equatorial Cl atoms (see Table IV). As a consequence, there is a relevant distortion of the square-pyramidal geometry toward the trigonal-bipyramidal coordination, as clearly shown by means of a detailed analysis of the geometry, as suggested by Muetterties and Guggenberger.[16] The results are reported in Table VI.

$CuCl_4^{2-}$ Anions. The unit cell contains two crystallographically independent tetrahedral $CuCl_4^{2-}$ anions, which possess, from constrained positions of the Cu atoms, imposed D_2 symmetry and nearly idealized D_{2d} symmetry. Their extent of distortion from T_d symmetry may be properly quantified by means of the θ angle, the averaged value of the two Cl–Cu–Cl angles greater than 109.5°,[17] which in our case are unique because of crystallographic symmetry requirements. Presently found values of 125.64 (5) and 141.82 (5)°, respectively, of the θ angle indicate a rather strongly different flattening for the two $CuCl_4^{2-}$ tetrahedra. Because all the Cl atoms of both anions are engaged in only very weak and not significantly different hydrogen bonds (see Table V), the large difference in degree of distortion may be attributed to crystal packing forces only; two symmetry-related Cl(12) atoms lie on the c axis, 3.669 (3) Å apart from the Cu atom of the flattest tetrahedron. Previous X-ray studies[2,18,19] of $CuCl_4^{2-}$ ions yielded θ angles ranging from 129.2° for Cs_2CuCl_4[17] to 180.0° of the square-planar limit as in $(PhC_2H_4NH_2CH_3)_2CuCl_4$ (low-temperature form);[20] in our case it may be outlined that, while the θ value of the flattest $CuCl_4^{2-}$ tetrahedron fall in the usually found range, the second independent $CuCl_4^{2-}$ anion is the least flattened of the already reported $CuCl_4^{2-}$ tetrahedra having D_{2d} symmetry. Tetragonal distortion of this $CuCl_4^{2-}$ moiety, for which no short interion contacts other than very weak Cl···H interactions were found, may be interpreted as due to the Jahn–Teller effect, rather

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(12) (a) Anderson, D. L.; Willett, R. D. *Inorg. Chim. Acta* **1974**, *8*, 167. (b) Phelps, D. W.; Losee, D. B.; Hatfield, W. E.; Hodgson, D. J. *Inorg. Chem.* **1976**, *15*, 3174.

(13) Willett, R. D. *J. Chem. Phys.* **1964**, *41*, 2243.

(14) Morosin, B.; Fallon, P.; Valentine, J. S. *Acta Crystallogr., Sect. B* **1975**, *31*, 2200.

(15) Steadman, J. P.; Willett, R. D. *Inorg. Chim. Acta* **1970**, *4*, 367.

(16) Muetterties, E. L.; Guggenberger, L. J. *J. Am. Chem. Soc.* **1974**, *96*, 1748.

(17) McGinnety, J. A. *J. Am. Chem. Soc.* **1972**, *94*, 8406.

(18) Harlow, R. L.; Wells, W. J.; Watt, G. W.; Simonsen, S. H. *Inorg. Chem.* **1975**, *14*, 1768, and references cited therein.

(19) Battaglia, L. P.; Bonamartini Corradi, A.; Marcotrigiano, G.; Menabue, L.; Pellacani, G. C. *Inorg. Chem.* **1979**, *18*, 148.

(20) Harlow, R. L.; Wells, W. J.; Watt, G. W.; Simonsen, S. H. *Inorg. Chem.* **1974**, *13*, 2106.

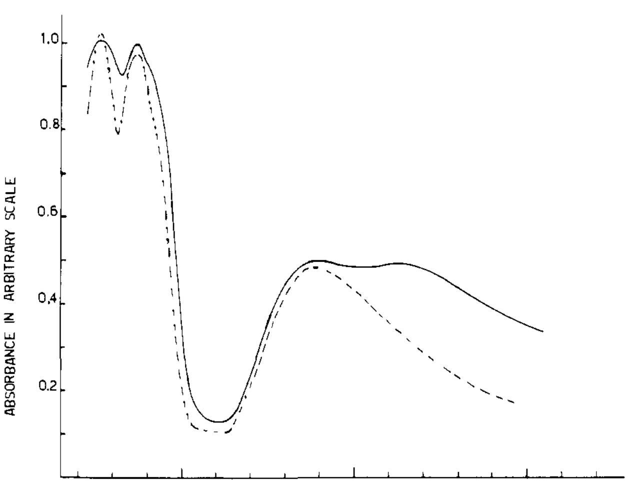

Figure 2. Electronic spectra of $(N(2amet)pipzH_3)_4Cu_5Cl_{22}$ (—) and $(N(2amet)pipzH_3)CuCl_5{\cdot}2H_2O$[3] (---) complexes.

than to crystal packing forces. The unique Cu–Cl bond distances of 2.245 (2) and 2.266 (2) Å, respectively, for the two independent $CuCl_4^{2-}$ ions agree with previously found values, which range from 2.209 to 2.271 Å,[2] but are significantly different. Such a difference agrees with the predicted correlation[2] between the Cu–Cl bond length and the flattening angle θ, with the greatest angular distortion related to longest Cu–Cl distance, and vice versa.

$[N(2amet)pipzH_3]^{3+}$ Cation. All structural features of the cation, whose piperazine ring exhibits the expected "chair" conformation, with torsion angles ranging, as absolute value, from 57.1 to 58.9°, are in good agreement with our previous results for the same trication.[3] In particular the previously observed C–N bond lengthening and C–C bond shortening are confirmed; their mean values of 1.501 and 1.506 Å, respectively, are very close to the previously found mean distances of 1.495 and 1.513 Å, respectively.

Hydrogen Bonding. An infinite three-dimensional hydrogen-bonding network, on which crystal packing depends, was found. Hydrogen bonds, summarized in Table V, involve all N-bonded H atoms and all but one Cl atom. The shortest interaction involves the bridging Cl atom, while some hydrogen bonds are very weak, such as those involving the $CuCl_4^{2-}$ tetrahedra. The weakening of interactions is mainly due to formation of bifurcated hydrogen bonds with N–H···Cl angles strongly deviating from 180°.

Although the cation bulk is perhaps a dominant factor, there is no doubt that hydrogen bonding is a decisive contributor to the factors which control the preferred coordination geometry about the copper atoms in chlorocuprates(II).[2] Present results confirm that with not large, bulky cations and with weak hydrogen bonding a moderately flattened tetrahedral geometry of $CuCl_4^{2-}$ ion is the preferred coordination; strongest hydrogen bonds, lowering the charges on the Cl atoms and counteracting the effects of the shortest Cl–Cl distances, allow the formation of polymeric layer of ribbon structures, leading to tetragonal octahedral coordination, or, as in our case, to trinuclear $Cu_3Cl_{14}^{8-}$ ions on which also a pentacoordinate Cu atom is present. From present results it may be argued also that the water molecules of $[N(2amet)pipzH_3]CuCl_5{\cdot}2H_2O$,[3] which are directly involved in hydrogen bonds with Cl atoms and which increase the hydrogen-bonding ability of the trication, play a decisive role in determining the suitable hydrogen-bonded network on which the square-pyramidal $CuCl_5^{3-}$ ion is stabilized.

Magnetic Moment and Electronic and Infrared Spectra. The room-temperature magnetic moment of the compound (μ_{eff} = 1.69 μ_B for copper atom) indicates the presence of weak exchange interaction between Cu ions via Cl bridges.[12b]

The electronic spectrum of the complex shows two band maxima in the near-infrared region at 8890 and 10 990 cm^{-1}, arising from d–d transitions, which may be only explained in view of its known crystal structure. The band at 10 990 cm^{-1}, nearly coincident with the maximum of the $[N(2amet)pipzH_3]CuCl_5{\cdot}2H_2O$ complex, which contains a square-pyramidal $CuCl_5^{3-}$ unit[3] (Figure 2), may be attributed to the two distorted square-pyramidal Cu atoms in the $Cu_3Cl_{14}^{8-}$ anion, but also to the more distorted tetrahedral $CuCl_4^{2-}$ unit, which would produce a band at 10 700 cm^{-1}.[19] The band at 8890 cm^{-1} for shape and position may be associated with the least distorted tetrahedral $CuCl_4^{2-}$ unit.

The absence of a band maximum around 16 000 cm^{-1} characteristic of square-planar tetrachlorocuprates(II)[21] agrees with the structural interpretation of the geometry of the central copper atom of the centrosymmetric $Cu_3Cl_{14}^{8-}$ ion, as elongated tetragonal octahedral, further confirming that the "long" axial Cu–Cl interactions may be considered as bond distances. The band maxima of the elongated tetragonal octahedral chlorocuprate(II), which could appear in the 10 000–14 000-cm^{-1} spectral range,[22] may be masked within the band envelope observed.

However, the apparent inconsistency between the simple electronic spectrum and the complex molecular structure of the complex emphasizes the dangers inherent in attempting to predict molecular structures from electronic spectroscopy.

The infrared spectrum shows evidence of intermolecular and intramolecular hydrogen bonding in our complex of the same extent as those found in the $[N(2amet)pipzH_3]CuCl_5{\cdot}2H_2O$ complex.[3] In fact the positions of their NH motions are very similar (3100–2400 cm^{-1} for undistinguished $\nu(^+NH_3)$, $\nu(^+NH_2)$, and $\nu(^+NH)$ in both complexes; 1580, 1500, and 1360 cm^{-1} in $[N(2amet)pipzH_3]CuCl_5{\cdot}2H_2O$ and 1578–1565, 1495, and 1362 cm^{-1} in $[N(2amet)pipzH_3]_4Cu_5Cl_{22}$ for $\delta(^+NH_3)$, $\delta(^+NH_2)$, and $\delta(^+NH)$, respectively) and similar to those found for other primary, secondary, and tertiary amine hydrohalides involved in strong hydrogen bonds.[19,23-25]

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Supplementary Material Available: Bond angles involving hydrogen atoms and observed and calculated factors (7 pages). Ordering information is given on any current masthead page.

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(21) Hitchman, M. A.; Cassidy, P. J. *Inorg. Chem.* **1979**, *18*, 1745, and references cited therein.

(22) Hitchman, M. A.; Cassidy, P. J. *Inorg. Chem.* **1978**, *17*, 1682, and references cited therein.

(23) Colthup, N. B.; Daly, L. H.; Wiberley, S. E. "Introduction to Infrared and Raman Spectroscopy"; Academic Press: New York, 1975; p 282.

(24) Bellamy, L. J. "The Infrared Spectra of Complex Molecules"; Chapman and Hall: London, 1975; pp 267–291.

(25) Marcotrigiano, G.; Menabue, L.; Pellacani, G. C. *Inorg. Chem.* **1976**, *15*, 2333.