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Synthesis and Characterization of Copper(I) Complexes of 4-Methylquinoline, and X-ray Crystal Structure of a Discrete, Centrosymmetric $[Cu_2Cl_2(4\text{-methylquinoline})_3]_2$ Complex with a Cu_4Cl_4 Core of 'Step' Geometry

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Abstract

Copper(I) complexes of the general formula $(CuX)_nL_m$, where L = 4-methylquinoline, $n = 1$, $m = 1$ for X = Cl, Br, I, SCN and N_3, $n = 1$, $m = 2$ for X = NO_3 and ClO_4, and $n = 2$, $m = 3$ for X = Cl and Br were prepared and characterized. Excepting the perchlorate complex all other complexes are colored and exhibit strong CT bands in the visible region. The infrared spectral data suggest the presence of bridging halide and pseudohalide, monodentate nitrate, and bidentate perchlorate groups in the respective complexes. The structure of the 2:3 chloro complex was determined by X-ray crystallography. The crystals are triclinic, space group $P\bar{1}$, with $a = 10.587(1)$, $b = 11.321(3)$, $c = 11.329(3)$ Å, $\alpha = 85.17(2)$, $\beta = 89.67(2)$, $\gamma = 80.88(2)°$ and $Z = 1$. The structure was refined to $R_F = 0.053$ for 3174 observed Mo Kα diffractometer data. The discrete $[Cu_2Cl_2(4\text{-methylquinoline})_3]_2$ molecule is centrosymmetric with a short Cu(1)...Cu(2′) contact of 2.777(1) Å, and has the 'step' structure well known for $Cu_4X_4L_4$ species; however, the copper atoms at the periphery of the 'step' are coordinated by a pair of nitrogen ligands.

Introduction

Adducts of copper(I) halides with unidentate nitrogen bases have recently been widely studied structurally. Among the 1:1:1 copper–halide–base complexes, the tetrameric cluster with cubane stereochemistry is quite common, as exemplified by $[CuIL]_4$ (L = pyridine [1], piperidine [2], morpholine [3] and diethylnicotinamide [4]) and $[CuBrL]_4$ (L = 2-methylpyridine [5]). With regard to the 'step' structure of the Cu_4X_4 core which is adopted by various adducts with phosphine or arsine bases [6–8], no nitrogen base analogue has been reported; instead a series of polymeric complexes are found for which the step might be considered to form the repeating unit. This polymeric structure, known as the ribbon or stair polymer, is exemplified by $[CuX]_\infty$ adducts with pyridine [9], isonicotinic acid [10], methyl cyanide [11, 12], benzonitrile [13] and azomethane [14].

Recently we reported the crystal structures of copper(I) chloride adducts of isonicotinic acid $[CuClL]_\infty$ [10] and nicotinic acid $[CuClL_2]_\infty$ [15]. In the latter complex the $(CuCl)_\infty$ chain takes the place of the Cu_2Cl_2 stair or ribbon in the former, the copper atoms being four-coordinate in both cases.

Further work led to the isolation of, among other adducts, a new 2:3 complex of copper(I) chloride with 4-methylquinoline (hereafter abbreviated as 4-MeQ). As this stoichiometry is uniquely exemplified by $[Cu_4I_4(2\text{-methylpyridine})_6]$ [16], we have carried out an X-ray structure determination of the title complex. The synthesis and characterization of other related copper(I) complexes are also described.

Experimental

Preparation of the Complexes

CuXL complexes (X = Cl, Br, I, SCN or N_3)

4-methylquinoline (5 mmol) was added to a boiled ethanolic solution of $Cu(NO)_3)_2\cdot 3H_2O$ (5 mmol, 50 ml), followed by the addition of excess L-(+-ascorbic acid (vitamin C). The boiled mixture was stirred while an aqueous solution of KX (X = Br, I, SCN or N_3) was added dropwisely, and finally allowed to stand over several hours to produce the crystalline product. Acetone was used for the preparation of the azide complex.

The chloro complex was prepared as yellow needles by the above procedure except that $CuCl_2\cdot 2H_2O$ was used instead of the nitrate salt.

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TABLE I. Analytical Data

Complex	Color	Analysis: Found (calculated) (%)				
		Cu	C	H	N	X
Cu(4-MeQ)Cl	yellow needles	26.00 (26.22)	49.76 (49.59)	3.74 (3.74)	5.88 (5.78)	14.43 (14.66)
Cu(4-MeQ)Br	yellow needles	22.34 (22.16)	42.12 (41.91)	3.32 (3.16)	5.00 (4.89)	27.67 (27.88)
Cu(4-MeQ)I	pale yellow needles	18.78 (19.04)	36.20 (36.00)	2.60 (2.72)	4.42 (4.20)	38.52 (38.04)
Cu(4-MeQ)NCS	pale yellow powder	23.40 (24.00)	45.09 (45.33)	3.21 (3.40)	10.30 (10.58)	
Cu(4-MeQ)N_3	orange–red sheets	25.23 (25.54)	48.07 (48.29)	3.82 (3.62)	22.21 (22.52)	
Cu_2(4-MeQ)$_3Cl_2$	red crystals	20.45 (20.24)	57.00 (57.42)	4.63 (4.34)	6.42 (6.69)	11.12 (11.31)
Cu_2(4-MeQ)$_3Br_2$	red–orange crystals	17.45 (17.73)	50.23 (50.30)	3.96 (3.80)	5.62 (5.86)	22.12 (22.31)
Cu(4-MeQ)$_2NO_3$	yellow crystals	15.52 (15.42)	58.38 (58.32)	4.32 (4.40)	10.40 (10.20)	
Cu(4-MeQ)$_2ClO_4$	white crystals	14.32 (14.13)	53.22 (53.45)	4.22 (4.04)	6.08 (6.23)	

$CuXL_2$ complexes ($X = NO_3$ or ClO_4)

The 1:2 copper(I) nitrate complex was prepared by adding the ligand (10 mmol, 30 ml acetone) to $Cu(NO_3)_2 \cdot 3H_2O$ (5 mmol, 30 ml acetone). The resulting mixture was boiled to one-half its original volume, and standing over several hours produced yellow crystals of the complex.

The perchlorate complex was prepared by adding an aqueous solution of $KClO_4$ to a mixture of $Cu(NO_3)_2 \cdot 3H_2O$ and the ligand (1:2 molar ratio) dissolved in acetone, followed by boiling and standing over several hours.

$Cu_2X_2L_3$ complexes (X = Cl or Br)

The chloro complex was prepared by mixing $CuCl_2 \cdot 2H_2O$ and the ligand (1:3 molar ratio) dissolved in acetone. To this mixture an excess amount of L-(+)-ascorbic acid was added with continuous stirring, and the final mixture boiled and filtered. The filtrate was allowed to stand over several hours to deposit suitable crystals of the complex.

The bromide analogue was prepared according to the method given for the 1:1 complexes except that a Cu/L molar ratio of 1:3 was used.

Elemental analysis results of the isolated complexes are given in Table I.

Spectral Data

The electronic spectral data of the complexes measured as solids mulled in nujol and the infrared absorption bands of the counter ions are collected in Table II. The experimental procedures and instruments used are as described previously [17].

X-ray Structure Analysis

A suitable single crystal of $[Cu_2Cl_2(\text{4-methylquinoline}_3]_2$ was centered on a Nicolet R3m four-circle diffractometer. Unit cell determination and intensity data collection and processing followed established procedures in our laboratory [18]. Pertinent crystal data and processing information are summarized in Table III.

Space group $P\bar{1}$ was favored by intensity statistics and later confirmed by structure analysis. Structure solution was achieved by Patterson and Fourier methods. All thirty-seven non-hydrogen atoms were refined anisotropically. The 18 aromatic H atoms are geometrically generated (C——H bond fixed at 0.96 Å), assigned isotropic thermal parameters, and allowed to ride on their respective parent C atoms in the final least-squares cycles, which coverged to the R_F and R_G indices given in Table III.

All computations were performed on a Data General Corporation Nova 3/22 minicomputer with SHELXTL program package [19]. Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated.

The final atomic parameters are listed in Table IV, atom labelling being shown in Fig. 1. Bond distances, bond angles and torsion angles are tabulated in Table V. Hydrogen coordinates are listed in Table VI.

TABLE II. Electronic and Infrared Spectral Data[a]

Complex	$\tilde{\nu}_{max}$ (MLCT) (kK)	Vibration frequency (cm^{-1}) of the counter ion
Cu(4-MeQ)Cl	26.3s	
Cu(4-MeQ)Br	27.0s	
Cu(4-MeQ)I	28.2s	
Cu(4-MeQ)NCS	27.0s	2005vs, 2060m (νCN), 865, 750m (νCS); 420m (δNCS)
Cu(4-MeQ)N_3	25.0s	2055vs, sp (ν_{as} N_3); 610w, 590w (δ N_3)
Cu_2(4-MeQ)$_3Cl_2$	27.0–22.0vs	
Cu_2(4-MeQ)$_3Br_2$	23.2vs	
Cu(4-MeQ)$_2NO_3$	27.0s	1380vs, br, 1320s (νNO)
Cu(4-MeQ)$_2ClO_4$		1150vs, 1115vs, 1090s (ν_3ClO_4), 945m (ν_1), 645vs, 635vs (ν_4)

[a] kK = 1000 cm^{-1}, s = strong, v = very, m = medium, br = broad, sp = sharp.

TABLE III. Data Collection and Processing Parameters

Molecular formula	[Cu_2Cl_2(4-methylquinoline)$_3$]$_2$, $C_{60}H_{54}N_6Cl_4Cu_4$	
Molecular weight	1255.12	
Cell parameters	a = 10.587(1) Å	α = 85.17(2)°
	b = 11.321(3)	β = 89.67(2)
	c = 11.329(3)	γ = 80.88(2)
	V = 1335.9(5) Å^3	Z = 1
Density (expt)	1.542 g cm^{-3} (flotation in aq. KI)	
Density (calc)	1.560 g cm^{-3}	
Space group	$P\bar{1}$	
Radiation	graphite-monochromatized Mo Kα, λ = 0.71069 Å	
Absorption coefficient	18.23 cm^{-1}	
Crystal size	0.36 × 0.36 × 0.06 mm	
Mean μr	0.18	
Transmission factors	0.566 to 0.758	
Scan type and speed	ω–2θ; 2.02–8.37° min^{-1}	
Scan range	1° below Kα_1 to 1° above Kα_2	
Background counting	stationary counts for one-half of scan time at each end of scan	
Collection range	$h, \pm k, \pm l$; $2\theta_{max}$ = 48°	
Unique data measured	3765	
Observed data with $\lvert F_o \rvert > 3\sigma(\lvert F_o \rvert)$, n	3174	
Number of variables, p	334	
$R_F = \Sigma \lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert / \Sigma \lvert F_o \rvert$	0.053	
Weighting scheme	$w = [\sigma^2(F_o) + 0.001 \lvert F_o\rvert^2]^{-1}$	
$R_G = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2 / \Sigma w \lvert F_o\rvert^2]^{1/2}$	0.071	
$S = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/(n - p)]^{1/2}$	1.619	
Residual extrema in final difference map	+0.97 to −0.58 e Å^{-3}	

Discussion

With the exception of the 1:2 perchlorate complex, all the other copper(I) adducts of 4-methylquinoline are colored and stable against air oxidation. However, this stability is dependent upon the identity of the counter ion as well as the number of ligand molecule(s) per copper atom in the complex. Solutions of the copper(I) halide and pseudohalide adducts are non-conducting in nitrobenzene and acetone. The 1:2 nitrate and perchlorate complexes behave as 1:1 electrolytes, giving rise to molar conductivity values of 31–35 and 140–145 Ω^{-1} cm^2 mol^{-1} in these two solvents, respectively [20, 21].

The electronic spectra (Table II) of these copper(I) adducts exhibit a very strong band in the visible region, undoubtedly due to charge transfer transitions [22] from Cu(I) d^{10} to an empty π^* orbital on

TABLE IV. Atomic Coordinates ($\times 10^5$ for Cu; $\times 10^4$ for other atoms) and Thermal Parameters[a] ($Å^2 \times 10^4$ for Cu and Cl; 10^3 for other atoms) for $[Cu_2Cl_2(4\text{-methylquinoline})_3]_2$

Atom	x	y	z	U_{eq}
Cu(1)	-1415(7)	16158(6)	22892(7)	482(3)
Cu(2)	9666(7)	1556(7)	-10747(7)	573(3)
Cl(1)	278(1)	1696(1)	166(1)	448(5)
Cl(2)	-124(1)	461(1)	-2847(1)	473(5)
Organic ligand I				
N(1)	931(4)	2458(4)	3343(4)	40(2)
C(1)	1237(6)	1967(5)	4421(5)	48(2)
C(2)	1648(6)	2574(6)	5347(5)	52(2)
C(3)	1710(5)	3769(5)	5175(5)	47(2)
C(4)	1386(5)	4350(5)	4030(5)	43(2)
C(5)	1359(6)	5596(6)	3730(7)	58(3)
C(6)	1027(7)	6117(6)	2638(7)	65(3)
C(7)	721(7)	5429(6)	1759(7)	65(3)
C(8)	704(6)	4220(5)	1994(6)	52(2)
C(9)	1017(5)	3666(5)	3132(5)	38(2)
C(10)	2135(7)	4427(7)	6170(6)	68(3)
Organic ligand II				
N(2)	-1965(4)	2583(4)	2379(4)	44(2)
C(11)	-2444(6)	3275(5)	1420(5)	45(2)
C(12)	-3633(6)	3992(5)	1346(5)	47(2)
C(13)	-4457(6)	4017(5)	2307(6)	50(2)
C(14)	-3989(5)	3266(5)	3357(5)	38(2)
C(15)	-4728(6)	3203(6)	4383(6)	59(2)
C(16)	-4244(7)	2517(7)	5372(6)	66(3)
C(17)	-2992(6)	1857(6)	5368(6)	56(2)
C(18)	-2269(6)	1863(5)	4391(5)	48(2)
C(19)	-2749(5)	2581(5)	3346(5)	40(2)
C(20)	-5756(7)	4773(7)	2259(7)	72(3)
Organic ligand III				
N(3)	2753(4)	-598(4)	-546(4)	42(2)
C(21)	2913(6)	-1118(6)	521(5)	53(2)
C(22)	4091(7)	-1766(6)	951(6)	59(3)
C(23)	5164(7)	-1874(5)	271(6)	56(2)
C(24)	5010(5)	-1288(5)	-904(5)	42(2)
C(25)	6039(7)	-1307(6)	-1711(7)	63(3)
C(26)	5842(7)	-741(7)	-2838(7)	74(3)
C(27)	4643(7)	-150(7)	-3196(6)	66(3)
C(28)	3629(6)	-115(5)	-2440(5)	51(2)
C(29)	3809(5)	-677(5)	-1282(5)	43(2)
C(30)	6424(7)	-2578(7)	707(8)	79(3)

[a] Equivalent isotropic temperature factor U_{eq} defined as 1/3 of the trace of the orthogonalised **U** matrix.

4-MeQ. The λ_{max} value of the MLCT bands decreases in the order I > Br > Cl. Since the excited state has considerable Cu(II) character, we may assume that if the crystal field splitting Δ for copper(I) halides follows the order I < Br < Cl, the most destabilized is the set of t_2 orbitals (the metal d orbitals in a tetrahedral field involved in MLCT) in the case of the chloro complex. The difference in energy, $\Delta\epsilon$, between this t_2 set and the lowest vacant π^* orbital on the ligand is a minimum in the chloride and a maximum in the iodide. This explains the halide ion dependence of the MLCT bands. A similar situation occurs [23] in the bis{(2-phenylazo)pyridine}copper(I) complex [24].

The vibrational frequencies (Table II) for the 1:2 nitrate complex exhibiting two NO stretching bands

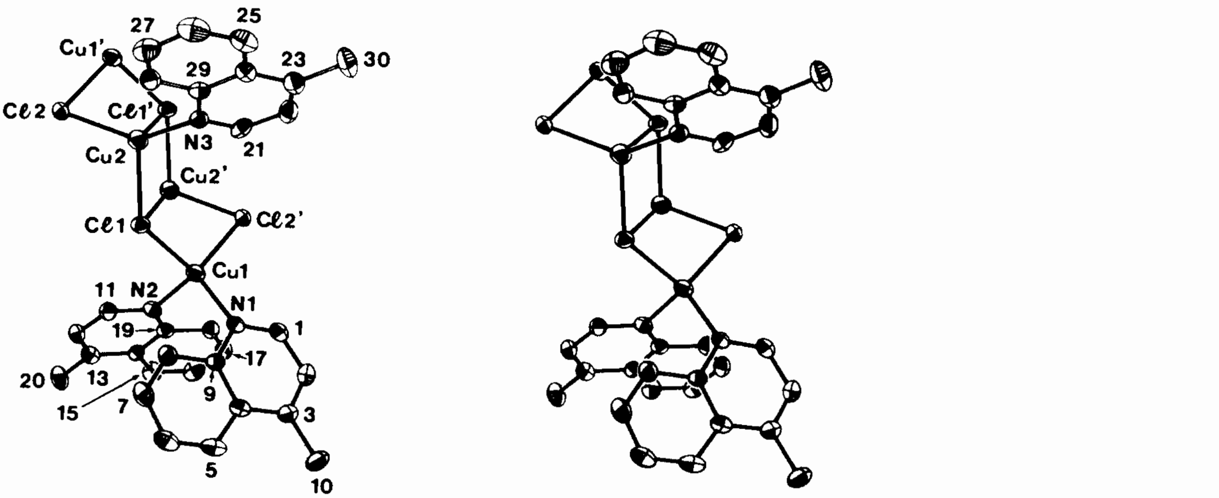

Fig. 1. Structure and atom labelling of the centrosymmetric $[Cu_2Cl_2(4\text{-methylquinoline})_3]_2$ molecule. The primed atoms are related to the unprimed ones by the inversion centre at (0, 0, 0), and three organic ligands have been omitted for clarity.

TABLE V. Bond Lengths (Å) and Bond Angles (°)[a] in $[Cu_2Cl_2(4\text{-methylquinoline})_3]_2$

(i) Bonding in the central part of the molecule					
Cu(1)–Cl(1)	2.440(2)	Cu(1)–Cl(2′)	2.355(1)	Cu(2)–Cl(2)	2.295(2)
Cu(2)–Cl(1)	2.355(2)	Cu(2)–Cl(1′)	2.772(2)	Cu(1)–N(1)	2.043(5)
Cu(1)–N(2)	2.070(4)	Cu(2)–N(3)	2.019(4)	Cu(1)...Cu(2′)	2.777(1)
Cu(2)...Cu(2′)	3.205(2)				
Cl(1)–Cu(1)–N(1)	118.7(1)	Cl(1)–Cu(1)–N(2)	103.1(1)	N(1)–Cu(1)–N(2)	103.9(2)
Cl(1)–Cu(1)–Cl(2′)	103.0(1)	N(1)–Cu(1)–Cl(2′)	111.0(1)	N(2)–Cu(1)–Cl(2′)	117.5(1)
Cl(1)–Cu(2)–Cl(2)	111.6(1)	Cl(1)–Cu(2)–N(3)	107.2(1)	Cl(2)–Cu(2)–N(3)	135.1(2)
Cl(1)–Cu(2)–Cl(1′)	103.1(1)	Cl(2)–Cu(2)–Cl(1′)	95.1(1)	N(3)–Cu(2)–Cl(1′)	97.3(1)
Cu(1)–Cl(1)–Cu(2)	130.9(1)	Cu(1)–Cl(1)–Cu(2′)	64.0(1)	Cu(2)–Cl(1)–Cu(2′)	76.9(1)
Cu(2)–Cl(2)–Cu(1′)	73.3(1)	Cu(1)–N(1)–C(1)	118.8(4)	Cu(1)–N(1)–C(9)	122.0(3)
Cu(1)–N(2)–C(11)	118.4(4)	Cu(1)–N(2)–C(19)	125.7(3)	Cu(2)–N(3)–C(21)	118.3(4)
Cu(2)–N(3)–C(29)	123.9(4)				
I		**II**		**III**	
(ii) Organic ligands					
N(1)–C(1)	1.319(7)	N(2)–C(11)	1.338(7)	N(3)–C(21)	1.299(7)
N(1)–C(9)	1.386(7)	N(2)–C(19)	1.370(7)	N(3)–C(29)	1.388(7)
C(1)–C(2)	1.409(9)	C(11)–C(12)	1.384(8)	C(21)–C(22)	1.410(9)
C(2)–C(3)	1.362(9)	C(12)–C(13)	1.390(9)	C(22)–C(23)	1.365(10)
C(3)–C(4)	1.422(8)	C(13)–C(14)	1.444(8)	C(23)–C(24)	1.434(9)
C(3)–C(10)	1.510(10)	C(13)–C(20)	1.500(9)	C(23)–C(30)	1.504(10)
C(4)–C(5)	1.419(8)	C(14)–C(15)	1.401(8)	C(24)–C(25)	1.417(9)
C(4)–C(9)	1.421(8)	C(14)–C(19)	1.415(7)	C(24)–C(29)	1.398(8)
C(5)–C(6)	1.348(10)	C(15)–C(16)	1.362(9)	C(25)–C(26)	1.381(11)
C(6)–C(7)	1.386(11)	C(16)–C(17)	1.416(9)	C(26)–C(27)	1.384(10)
C(7)–C(8)	1.375(9)	C(17)–C(18)	1.342(9)	C(27)–C(28)	1.367(10)
C(8)–C(9)	1.403(8)	C(18)–C(19)	1.427(8)	C(28)–C(29)	1.409(10)
C(1)–N(1)–C(9)	116.3(5)	C(11)–N(2)–C(19)	115.9(5)	C(21)–N(3)–C(29)	117.6(5)
N(1)–C(1)–C(2)	124.9(5)	N(2)–C(11)–C(12)	125.3(5)	N(3)–C(21)–C(22)	123.3(6)
C(1)–C(2)–C(3)	120.1(5)	C(11)–C(12)–C(13)	120.6(5)	C(21)–C(22)–C(23)	121.8(6)
C(2)–C(3)–C(4)	117.5(6)	C(12)–C(13)–C(14)	116.0(5)	C(22)–C(23)–C(24)	115.6(6)
C(2)–C(3)–C(10)	120.3(6)	C(12)–C(13)–C(20)	122.2(5)	C(22)–C(23)–C(30)	122.6(6)
C(4)–C(3)–C(10)	122.2(6)	C(14)–C(13)–C(20)	121.9(5)	C(24)–C(23)–C(30)	121.8(6)
C(3)–C(4)–C(5)	124.0(6)	C(13)–C(14)–C(15)	121.7(5)	C(23)–C(24)–C(25)	122.2(5)
C(3)–C(4)–C(9)	119.0(5)	C(13)–C(14)–C(19)	118.9(5)	C(23)–C(24)–C(29)	119.7(5)
C(5)–C(4)–C(9)	117.0(5)	C(15)–C(14)–C(19)	119.4(5)	C(25)–C(24)–C(29)	118.1(5)
C(4)–C(5)–C(6)	122.2(7)	C(14)–C(15)–C(16)	120.3(6)	C(24)–C(25)–C(26)	120.2(6)
C(5)–C(6)–C(7)	120.1(6)	C(15)–C(16)–C(17)	120.2(6)	C(25)–C(26)–C(27)	120.7(7)
C(6)–C(7)–C(8)	120.8(6)	C(16)–C(17)–C(18)	121.3(6)	C(26)–C(27)–C(28)	120.6(6)
C(7)–C(8)–C(9)	119.9(6)	C(17)–C(18)–C(19)	119.7(5)	C(27)–C(28)–C(29)	119.7(6)
N(1)–C(9)–C(4)	122.2(2)	N(2)–C(19)–C(14)	123.2(5)	N(3)–C(29)–C(24)	122.0(5)
N(1)–C(9)–C(8)	117.9(5)	N(2)–C(19)–C(18)	117.6(5)	N(3)–C(29)–C(28)	117.3(5)
C(4)–C(9)–C(8)	119.9(5)	C(14)–C(19)–C(18)	119.1(5)	C(24)–C(29)–C(28)	120.7(5)

[a] The primed atoms are generated by the symmetry transformation $(-x, -y, -z)$.

suggest a monodentate nitrate group, whereas those of the perchlorate analogue are consistent with a bidentate perchlorate group [25]. Accordingly the copper atoms may attain three- and four-coordination, respectively. The 1:1 thiocyanate adduct shows two CN and two CS stretching bands, which are suggestive of a μ(N, S) thiocyanate ligand [26]. The 1:1 azide complex on the other hand shows a very sharp band at 2055 cm^{-1}, which is very similar to that reported for $[(PPh_3)_2CuN_3]_2$ having μ(1, 3) azido bridging [27]. The existence of this type of bridging azide in the 1:1 complex of 4-MeQ is supported by the disappearance of the stretching azide frequencies in the region 1350–1280 cm^{-1}. Accordingly, both com-

TABLE VI. Hydrogen Atomic Coordinates ($\times 10^4$) and Thermal Parameters[a] ($Å^2 \times 10^3$)

Atom	*x*	*y*	*z*	*U*
H(1)	1175	1132	4588	57
H(2)	1885	2145	6100	62
H(5)	1586	6084	4324	70
H(6)	1002	6966	2470	79
H(7)	519	5801	975	78
H(8)	478	3755	1380	62
H(11)	-1920	3276	725	54
H(12)	-3891	4477	626	57
H(15)	-5580	3646	4390	71
H(16)	-4755	2480	6074	79
H(17)	-2652	1396	6079	67
H(18)	-1433	1387	4395	58
H(21)	2192	-1057	1043	63
H(22)	4139	-2143	1744	71
H(25)	6875	-1715	-1474	75
H(26)	6545	-759	-3379	89
H(27)	4523	240	-3983	79
H(28)	2798	290	-2697	61

[a] The exponent of the isotropic temperature factor *U* takes the form $-8\pi^2 U \sin^2 \theta/\lambda^2$.

plexes have the same type of bridging pseudohalide groups assuming dimeric or polymeric structures for these 1:1 adducts.

In the far infrared spectra (400–200 cm^{-1}) of the 1:1 and 2:3 copper(I) chloride adducts of 4-MeQ no bands could be attributed to terminal ν(Cu——Cl). This result suggests the presence of bridging chlorides in such complexes. For the 1:1 copper(I) halide adducts we may assume tetrameric structures corresponding to that of [Cu_4I_4(quin)$_4$] which forms a variation of the chair structure with copper atoms grouped into two close pairs (Cu···Cu = 2.558 Å) [28]. The bridging nature of the halide atom in the 2:3 adducts is supported by crystal structure analysis of the chloride complex.

The present study has established the title complex as [Cu_2Cl_2(4-methylquinoline)$_3$]$_2$ (Figs. 1 and 2), the second example of a metal–halide–base complex of 2:2:3 stoichiometry to be structurally characterized for a nitrogen–base system. This tetranuclear complex is disposed about a crystallographic inversion center, with a Cu_4Cl_4 core which conforms not to the cubane type structure commonly observed in tetranuclear [(CuXL)$_4$] species such as [Cu_4I_4(2-Mepy)$_4$] [16], but rather to the 'step' (also referred to as 'chair') structure which is uniquely exemplified by [Cu_2I_2(2-Mepy)$_3$]$_2$ [16] for a nitrogen–base ligand. Accordingly the present complex differs from dinuclear complexes of the same stoichiometry previously established in the systems [Cu_2Cl_2-(PPh_3)$_3$] [29] and [Cu_2Cl_2(PPh_3)$_2$·C_6H_6] [30], in which two copper atoms are held by two chloride bridges. In adducts of copper(I) halides with phosphine or arsine ligands where the occurrence of the 'step' structure has been previously established, it has been found that as the size of the ligand increases, the 'cubane' core undergoes increasingly large distortions and eventually opens up to the 'step' form. With very bulky ligands the latter form apparently tends to dissociate further into smaller units, as observed for the 1:1 complex of tricyclophosphine with copper(I) chloride which exists as a halide-bridged dimer [31]. In the present complex the different properties of nitrogen bases as compared to phosphorus or arsenic bases become apparent, with coordination of not one but two 4-methylquinoline ligands at the peripheral metal positions which thereby become four- rather than three-coordinate. The central copper atom is also four-coordinate while the halide bridges, as usually found in this type of structure, are in two- and three-coordinate environments.

In many aspects the structure of the present complex is similar to that of the previously reported (CuCl)$_4$(DPM)$_2$·$xC_2H_4Cl_2$ complex, (DPM = bis(diphenylphosphino)methane), which is also centrosymmetric with the 'step' structure for its Cu_4Cl_4 core

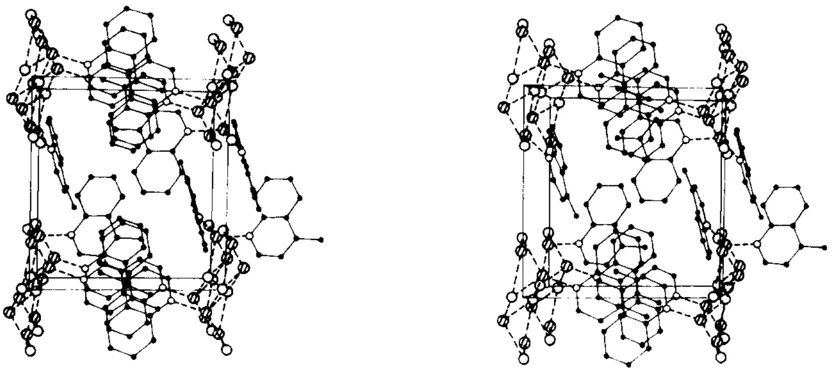

Fig. 2. Stereoview of the molecular packing. The origin of the unit cell lies at the upper left corner, with *a* pointing from left to right, *b* towards the reader, and *c* downwards. The molecules (shown only in part) are located at the corners of the unit cell.

[7]. In the DPM complex one of the chloride ligands links two copper atoms at distances of 2.270(4) and 2.324(6) Å, whereas the second chloride is involved in two short (2.315(6), and 2.358(6) Å) and one long (2.740(4) Å) Cu——Cl bonds. These values are comparable to those of the corresponding Cu——Cl distances in the present complex (Table V).

In the $[CuXL]_4$ system, structurally defined representatives of the step structure are established only for X = Br or I, whereas with X = Cl the predominant structural type is the tetrameric cubane. The cubane Cu_4Cl_4 core in the complex $[CuCl(PPh_3)]_4$ is characterized by long Cu——Cl distances in the range 2.362(2) to 2.505(2) Å [32], whereas in the present complex they range from 2.295(2) to 2.440(2) Å, if we exclude the long Cu——Cl bond of 2.772(2) Å. As far as the latter bond is concerned, a comparison with the complex $[Cu_2I_2(2\text{-Mepy})_3]_2$ shows that the three-coordinate iodine atom is nearly equidistant from the metal atoms bonded to it, the Cu——I distances varying from 2.661(2) to 2.721(2) Å [16]. On the contrary, in the present complex Cl(1) is involved in two short and one long Cu–Cl bonds, the difference amounting to 0.4 Å. It is not clear whether these differences are due to steric and/or electronic factors.

Fluorescence in the solid state is generally understood to involve (a) ligand centers, (b) metal-ligand charge transfer (MLCT) and/or (c) metal-centered transitions. It has been found that all the solid complexes $[CuIL]_4$ (L = nitrogen donor ligand) show copper–copper distances of less than 2.8 Å, and despite the diversity of ligands represented, all show emission at 550–628 nm attributed to metal–metal interaction [33]. The assignment is supported by the absence of this band in polymeric structures of the same stoichiometry and ligand identity in which Cu...Cu distances are longer. Accordingly, the 2:3 copper(I) chloride complex of 4-methylquinoline, with its Cu...Cu distance of 2.777(1) Å, is expected to demonstrate visible evidence of excitation of types (b) and (c), since both $[CuI(\text{quinoline})]_4$ (Cu...Cu = 2.558(10) Å) and $[Cu_2I_2(\text{quinoline})_4]$ (Cu...Cu = 3.364(5) Å) display room-temperature emission due to MLCT excitation [28]. However, neither the 2:3 chloride nor the bromide analogue display emission at room temperature. It is known that copper(I) complexes of quinaldic acid esters display no visible emission when excited in the UV range [34]. The non-emitting character of these complexes was considered to be effected by the electron-withdrawing ester groups which alter the energy levels of the aromatic ring to make the excitation of greater energy or to make other, radiationless, decay mechanisms more efficient. However, this is not the case in the 2:3 complexes of 4-MeQ with the electron-releasing methyl group. In earlier communications we reported that copper(I) complexes of pyridine ligands, which absorb above 440 nm due to their MLCT, display no emission in the visible region [35, 36]. This conclusion was based on the fact that CuX(isonicotinic acid) (X = Cl, Br or I) exhibiting strong MLCT bands above 460 nm display no emission while those of its methyl or ethyl esters (MLCT bands below 440 nm) do so in the visible range. On the other hand, complexes $CuXL_2$ of these esters exhibiting strong MLCT bands above 470 nm do not fluoresce at room temperature whereas $CuXL_2$ and $CuXL_3$, where L is a pyridine ligand with an electron-releasing group, are room-temperature emitting materials [37]. Thus the nature of the non-emitting character of the 2:3 copper(I) chloride and bromide complexes of 4-MeQ remains unclear and further studies are required.

Supplementary Material

Anisotropic thermal parameters and structure factors are available from the author on request.

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