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SYNTHESIS AND STRUCTURAL DETERMINATION OF AZIDOTETRAKIS-(3-ETHYL-4-METHYLPYRIDINE)COPPER(II) PERCHLORATE AND DI-μ(1,1)-AZIDO-[DIAZIDOTETRAKIS(3-ETHYL-4-METHYLPYRIDINE)]DICOPPER(II), [Cu(β-collidine)$_4$(N$_3$)](ClO$_4$) AND [Cu(β-collidine)$_2$(N$_3$)$_2$]$_2$

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Abstract—The preparation and structural characterizations of two new copper(II) azido complexes of 3-ethyl-4-methylpyridine (β-collidine), namely azido tetrakis(β-collidine) copper(II) perchlorate (**1**) and di-μ(1,1)-azido-[diazido-tetrakis(β-collidine)]dicopper(II) (**2**) are described. The spectral results suggest an ionic perchlorate and terminal azido group in complex **1** and different asymmetric azides in **2**. The structure of **1** consists of isolated [Cu(β-collidine)$_4$(N$_3$)]$^+$ cations and ClO$_4$$^-$ anions. The copper atom in the cation is in a tetragonal pyramidal environment with four collidine ligands occupying the basal sites [Cu—N = 2.033(4) Å] and a terminal azido ligand at the apical position with a Cu—N distance of 2.141(6) Å. The centrosymmetric binuclear molecule **2** features monodentate collidine ligands, di-μ(1,1)-azido-bridged Cu$_2$N$_2$ rings, terminal azido ligands and distorted square pyramidal copper(II) coordination geometry.

It has been shown that complexes of the stoichiometry Cu^{II}L(N$_3$)$_2$, where L is a mono-substituted pyridine or quinoline ligand, exist in varying degrees of oligomerization and a wide variety of structural configurations, depending principally on the coordination property and steric bulk of the ligand L.[1] Among these configurations, the five-coordinated dimers[2,3] or polymers[4,5] with distorted square pyramidal geometry or a trigonal bipyramidal environment, as well as six-coordinated octahedra,[6] are common. It now appears that a similar pattern emergies from the study of the class of complexes Cu^{II}L$_2$(N$_3$)$_2$, where L is pyridine or substituted pyridine ligands. For example, structural determinations have shown that [Cu(pyridine)$_2$(N$_3$)$_2$]$_n$ exists in two different forms containing six-coordinate copper centres but different coordination modes of azido ligands.[7,8] While [Cu(4-picoline)$_2$(N$_3$)$_2$]$_n$ features oligomeric edge-sharing chains of polyhedra, containing six- and five-coordinate copper(II) centres[9] and the 1:2 complex of 3-picoline displays two crystallographically independent six-coordinate copper octahedra and contains μ(1,3) and μ(1,1) bridging azido ligands,[10] the corresponding complex of 2,4,6-

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trimethylpyridine (s-collidine) is mono-nuclear and contains square planar four-coordinate copper atoms.[11] Further work has led to the isolation of a new 1 : 2 complex of copper(II) azide with 3-ethyl-4-methylpyridine, also known as β-collidine. In the present study we report the synthesis and structural characterization of this new complex, along with $[Cu(\beta\text{-collidine})_4(N_3)](ClO_4)$, elucidated by X-ray crystallographic and spectroscopic methods.

EXPERIMENTAL

The organic ligand was purchased from Aldrich and the other chemicals were of analytical grade quality.

Preparation of $[Cu(\beta\text{-collidine})_4(N_3)](ClO_4)$ (**1**)

Copper(II) perchlorate hexahydrate (0.74 g, 2 mmol) and β-collidine (1.21 g, 10 mmol) were mixed together in *ca* 40 cm^3 acetone, followed by dropwise addition of an aqueous solution (10 cm^3) of NaN_3 (0.08 g, 1.2 mmol). The final mixture was allowed to stand over several days to produce black crystals with a tint of blue colour. Found : C, 55.5 ; H, 6.7 ; N, 14.0 ; Cu, 9.0. Calc. : C, 57.7 ; H, 6.4 ; N, 14.2 ; Cu, 9.2%.

Preparation of $[Cu(\beta\text{-collidine})_2(N_3)_2]_2$ (**2**)

To a mixture of copper(II) acetate dihydrate (0.45 g, 2 mmol) dissolved in *ca* 2 cm^3 water and β-collidine (0.60 g, 5 mmol) in *ca* 40 cm^3 acetone was added an aqueous solution (10 cm^3) of NaN_3 (0.26 g, 4 mmol) dropwise. The mixture was allowed to stand over several days until dark green crystals of the complex separated. Alternatively, copper(II) nitrate trihydrate was mixed with the organic ligand in acetone in the above molar ratio followed by addition of an aqueous solution of NaN_3 (0.38 g, 6 mmol). The brown mixture was filtered off and the filtrate allowed to stand over several days to produce green crystals of the complex. Crystals suitable for X-ray measurements were prepared according to the former procedure. Found : C, 49.6 ; H, 5.8 ; N, 29.0 ; Cu, 16.0. Calc. : C, 49.3 ; H, 5.7 ; N, 28.7 ; Cu, 16.3%.

Procedures and instruments used for other physical measurements are as described previously.[11]

X-ray crystallography

A modified STOE four-circle diffractometer was used for single-crystal X-ray measurements. Orientation matrix and lattice parameters were obtained by least-squares refinement of the diffraction data from 52 (compound **1**) and 49 (compound **2**) reflections in the 2θ range 8–19°. Data were collected at 300(1) K using graphite crystal-monochromatized Mo-K_α radiation ($\lambda = 0.71069$ Å) and the ω-scan technique. The intensities were corrected for Lorentz and polarization effects, and for absorption.[12] For compound **2** an intensity decay correction was also included in the data reduction procedure (intensity of three standard reflections dropped to 72% during X-ray exposure). Crystallographic data are given in Table 1.

The structures were solved by Patterson superposition methods and subsequent Fourier analyses. Anisotropic displacement parameters were applied to the non-hydrogen atoms in full-matrix least-squares refinements. The hydrogen atoms were included in the final refinement cycles on calculated positions. The programs DIFABS,[12] SHELX-76,[13] SHELXS-86,[14] PLATON[15] and THE X-RAY SYSTEM[16] were used for computations. Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated.[17] Selected bond distances and bond angles are given in Table 2. Positional parameters, anisotropic displacement parameters, hydrogen atom coordinates, a full list of bond lengths and angles, and observed and calculated structure factors have been deposited with the Editor as supplementary material.

RESULTS AND DISCUSSION

The reactions between copper(II) ions and β-collidine in acetone in the presence of sodium azide afforded a cationic tetrakis-amine complex (**1**) or a 1 : 2 complex (**2**), depending upon the ratio of amine relative to azide ion. Similar reactions with other di-substituted pyridines, however, resulted in copper(II) azide complexes of different stoichiometries. For instance, 3,4-dimethylpyridine was reported[1] to produce a polymeric 1 : 1 copper(II) azide complex, whereas 3,5-dimethylpyridine yielded a dimeric compound, $[Cu(3,5\text{-lutidine})_2(N_3)(NO_3)]_2$.[18] Complex **1** is soluble in ethanol, acetone, DMF and DMSO, and behaves as a 1 : 1 electrolyte in acetone with a molar conductivity value of 125 $\Omega^{-1}cm^2mol^{-1}$.[19] The 1 : 2 complex is insoluble in many polar and non-polar solvents, but is soluble in DMF and DMSO, giving rise to non-conducting solutions.

The principle structural features of complex **1** are illustrated in Figs 1 and 2. The structure of the tetragonal crystals of this complex consists of isolated $[Cu(\beta\text{-collidine})_4(N_3)]^+$ cations and isolated ClO_4^- counteranions. Cl(1) is located on special position 4a ; Cu(1), as well as N(11), N(12) and

Table 1. Crystallographic data and processing parameters

Compound	**1**	**2**
Molecular formula	$C_{32}H_{44}ClO_4CuN_7$	$C_{16}H_{22}CuN_8$
Molecular weight	689.74	389.95
Crystal system	Tetragonal	Triclinic
a (Å)	14.830(4)	8.205(4)
b (Å)		8.654(4)
c (Å)	15.882(6)	13.168(6)
α (°)		96.32(3)
β (°)		92.36(3)
γ (°)		92.74(3)
V (Å^3)	3493(2)	927.3(8)
Space group	$P4/ncc$ (No. 130)	P-1 (No. 2)
Z	4	2
$F(000)$	1452	406
μ(Mo-K_α) (mm^{-1})	0.75	1.19
D_{calc}/D_{obs} (Mgm^{-3})	1.312/1.31(2)	1.397/1.40(2)
Approx. crystal size (mm)	0.65 × 0.55 × 0.35	0.35 × 0.35 × 0.08
Data collection limits	h, k, l; $2\theta < 55°$	$\pm h$, $\pm k$, l; $2\theta < 53°$
Scan mode	ω-scan, $\Delta\omega = 1.50°$	ω-scan, $\Delta\omega = 1.50°$
$F_o > 3\sigma(F_o)$	990	1987
Least squares parameters	109	244
R	0.061	0.054
R_w	0.060	0.053
Weighting scheme	$4.502\sigma^{-2}(F_o)$	$1.599\sigma^{-2}(F_o)$
Residual extrema in final difference map (e Å^{-3})	+0.56/−0.32	+0.61/−0.79

Table 2. Selected bond distances (Å) and bond angles (°)

[Cu(β-collidine)$_4$(N$_3$)](ClO$_4$) (**1**)			
Cu(1)—N(1)	2.033(4)	Cu(1)—N(11)	2.141(6)
N(11)—N(12)	1.161(9)	N(12)—N(13)	1.148(10)
N(1)—C(1)	1.343(8)	N(1)—C(5)	1.339(8)
Cl(1)—O(1)	1.366(12)		
N(1)—Cu(1)—N(11)	96.8(1)	N(1)—Cu(1)—N(1a)	89.2(2)
N(1)—Cu(1)—N(1b)	166.5(2)	Cu(1)—N(11)—N(12)	180.0
N(11)—N(12)—N(13)	180.0		
[Cu(β-collidine)$_2$(N$_3$)$_2$]$_2$ (**2**)			
Cu(1)···Cu(1′)	3.445(2)	Cu(1)—N(1)	2.005(5)
Cu(1)—N(2)	2.010(5)	Cu(1)—N(11)	1.996(5)
Cu(1)—N(21)	1.989(5)	Cu(1)—N(11′)	2.585(5)
N(11)—N(12)	1.184(8)	N(12)—N(13)	1.179(9)
N(21)—N(22)	1.189(8)	N(22)—N(23)	1.161(8)
N(1)—Cu(1)—N(2)	171.5(2)	N(1)—Cu(1)—N(11)	92.1(2)
N(1)—Cu(1)—N(21)	90.1(2)	N(1)—Cu(1)—N(11′)	92.7(2)
N(2)—Cu(1)—N(11)	90.5(2)	N(2)—Cu(1)—N(21)	88.2(2)
N(2)—Cu(1)—N(11′)	95.7(2)	N(11)—Cu(1)—N(21)	173.7(2)
N(11)—Cu(1)—N(11′)	83.3(2)	N(21)—Cu(1)—N(11′)	90.7(2)
Cu(1)—N(11)—N(12)	124.6(4)	Cu(1)—N(11)—Cu(1′)	96.7(2)
N(12)—N(11)—Cu(1′)	118.1(4)	N(11)—N(12)—N(13)	178.2(6)
Cu(1)—N(21)—N(22)	121.7(5)	N(21)—N(22)—N(23)	176.9(7)

Symmetry code: (a) $y, 1/2-x, z$; (b) $1/2-x, 1/2-y, z$; (d) $1/2-y, x, z$; (′) $-x, -y, 1-z$.

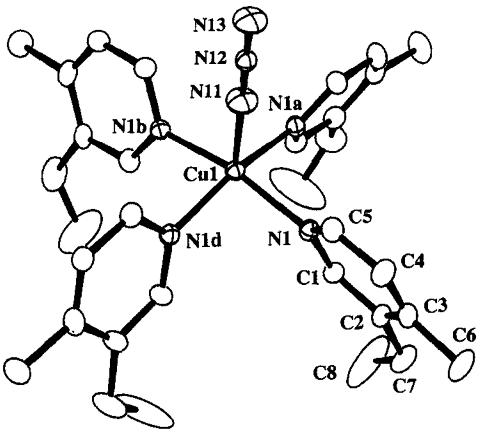

Fig. 1. The molecular geometry and atom numbering scheme of the $[\mathrm{Cu}(\beta\text{-collidine})_4(\mathrm{N}_3)]^+$ cation.

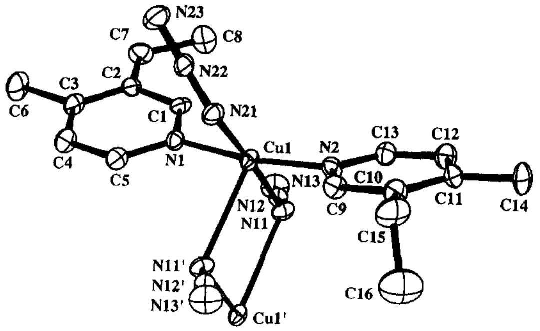

Fig. 3. The molecular geometry and atom numbering scheme of $[\mathrm{Cu}(\beta\text{-collidine})_2(\mathrm{N}_3)_2]_2$ (**2**).

N(13) of the mono-coordinated azide group, are located on special position 4c. In addition, the asymmetric unit contains only one O(1) of the perchlorate anion and one molecule of the β-collidine ligand; the other three O(1) atoms of the perchlorate anion and collidine molecules are generated by space group symmetry. The coordination polyhedron of the copper centre is therefore an exact tetragonal pyramid, with N(1) of β-collidine ligands at basal sites [Cu(1)—N(1) = 2.033(4) Å] and N(11) of the azido group occupying the apical site [Cu(1)—N(11) = 2.141(6) Å]. The unusual Cu(1)—N(11)—N(12) and N(11)—N(12)—N(13) bond angles of 180° are also a consequence of space group restriction.

The structure of complex **1** is very similar to the corresponding azido-tetrakis(β-collidine)copper(II) nitrate complex, which crystallizes in triclinic space group $P\bar{1}$ and contains the isolated cations $[\mathrm{Cu}(\beta\text{-collidine})_4(\mathrm{N}_3)]^+$, having a distorted tetragonal pyramidal copper(II) coordination geometry.[11] In this latter complex, the Cu—N(coll) distances range from 2.018(7) to 2.041(7) Å and the Cu—N(azide, at apical position) bond is a little longer [2.193(7) Å] than the corresponding value in the present structure. Both complexes, however, possess a slightly asymmetric terminal azido ligand; the values given for the nitrate complex are N_α—N_β = 1.169(11) and N_β—N_γ = 1.150(14) Å, the shortest N—N bonds being more remote from the metal atoms as found in other metal azido complexes containing terminal azido ligands.[20,21]

As illustrated in Figs 3 and 4, the dimeric molecule **2** possesses crystallographic $\bar{1}$ symmetry and contains both terminal [N(21)-N(23)] and μ(1,1) bridging [N(11)-N(13)] azido groups. Each copper centre is further coordinated by two β-collidine molecules via their N(1) and N(2) atoms. The stereochemistry about each copper atom is best described as a distorted square pyramid with the nitrogen atom of the bridging azido group at its apex, with a Cu—N(11) distance of 1.996(5) Å. Conforming to the general characteristics of coordinated azides,[22,23] both azido groups are nearly linear. The measured values for N—N bonds in Table 2 indicate that the terminal azide is asymmetric, whereas the μ(1,1) bridging is nearly symmetric (Δd, the difference between two N—N distances, is 0.004 Å). This result is the reverse of

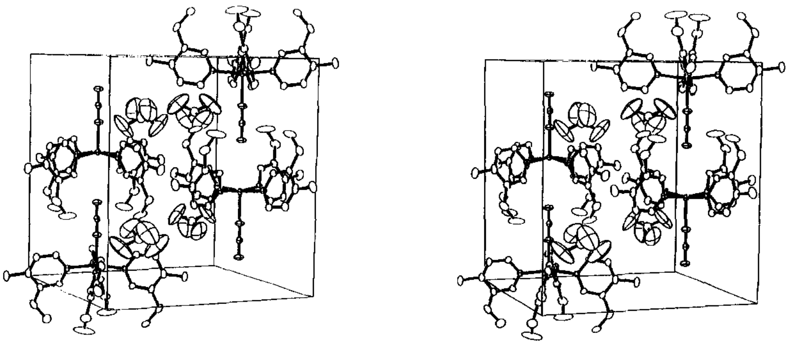

Fig. 2. Unit cell plot of $[\mathrm{Cu}(\beta\text{-collidine})_4(\mathrm{N}_3)](\mathrm{ClO}_4)$ (**1**), viewed along the a-axis of the unit cell.

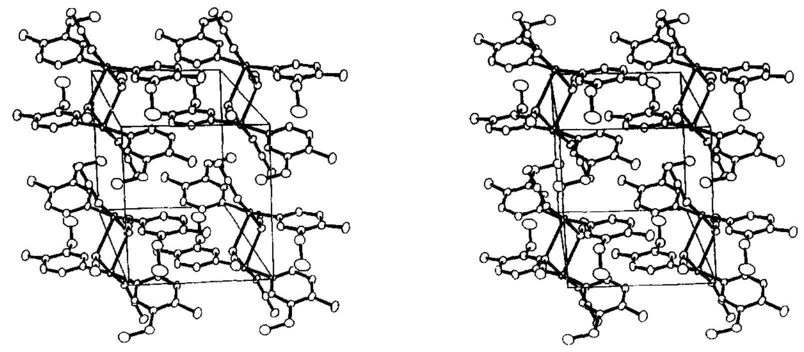

Fig. 4. Unit cell of $[Cu(\beta\text{-collidine})_2(N_3)_2]_2$ (**2**), viewed approximately along the *c*-axis of the unit cell.

that reported previously[24] for $[Cu(3\text{-acetylpyridine})_2(N_3)_2]_2$ (**3**), which is very close to the present structure. In the case of the 3-acetylpyridine complex, the $\mu(1,1)$ bridging azido group is asymmetric [$N_\alpha—N_\beta = 1.201(4)$ and $N_\beta—N_\gamma = 1.156(4)$ Å], whereas the terminal azide is symmetric ($\Delta d = 0.005$ Å). This may be due to the difference between the electron-attracting power of the acetyl group in comparison with the electron-releasing property of the methyl and ethyl substituents. In **3**, the acetyl group attracts the electron density from the nitrogen atom, which in turn attracts the electrons from copper and in turn enhances electron donation from the bridging nitrogen atom to copper. This effect manifests itself in the $Cu—N(\mu\text{-}N_3)$ bond lengths in complex **3** (av. 2.196 Å), which are shorter than the corresponding values in the present complex (av. 2.283 Å).

Complex **2** is structurally similar to di-$\mu(1,1)$ azido-bis-[azido(2-aminopyridine)aqua]dicopper (II) (**4**), of $P\bar{1}$ molecular symmetry, which also displays distorted square pyramidal copper(II).[2] In complex **4**, the $\mu(1,1)$ bridging azido group serves as a basal ligand to both metal centres [Cu—N distances of 2.003(2) and 2.018(2) Å] in the dimeric molecule, and the apical aquo ligand forms an intramolecular acceptor hydrogen bond with the amino group. Both complexes, however, differ in that the terminal and bridging azide ligands are asymmetric [N—N = 1.201(3) and 1.137(3) Å for bridging azide and N—N = 1.180(4) and 1.143(5) Å for terminal azide]. The Cu—N—Cu′ angle in the cyclic Cu_2N_2 ring is greater in **4** [103.1(1)°] than Cu—N(11)—Cu′ in **2** [96.7(2)°].

The Cu···Cu separation within the Cu_2N_2 ring in copper(II) azide complexes possessing di-$\mu(1,1)$ bridging azido ligands falls in the range between 3.78 Å in $CuL(N_3)_2$ [L = (2-aminoethyl)-pyridine][25] and 3.08 Å in $[Cu(N_3)_2]_n$, which has infinite chains of planar $Cu(N_3)_2$ units.[26] The Cu···Cu distance of 3.445(2) Å within the cyclic Cu_2N_2 ring in the present structure, although in the above range, is a little longer than corresponding values [3.336(2) Å] in the analogous dinuclear complex of 3-acetylpyridine (**3**), but shorter than the value of 3.546(2) Å found in the polymeric structure of $Cu(3\text{-picoline})_2(N_3)_2$.[10]

The IR absorption spectra of complexes **1** and **2** are collected in Table 3. The spectrum of **1** shows only a single very strong band associated with the azide stretching mode, as well as a medium band due to the symmetric stretch mode. These observations are consistent with the crystal structure, which revealed the asymmetric nature of the terminal azido ligand. The spectrum also exhibits a very strong and broad band and a medium band; both are related to the ionic perchlorate anion.[27] The IR spectrum of complex **2**, however, shows only a single very strong absorption band associ-

Table 3. IR spectral data

Frequency (cm^{-1})		
Complex **1**	Complex **2**	Assignments
2068 vs	2043 vs	$\nu_{as}(N_3)$
1342 m	1338 m	$\nu_s(N_3)$
	1284 s	
1097 vs, br		$\nu_3(ClO_4)$
622 m		$\nu_4(ClO_4)$
593 wm	612 wm	$\delta(N_3)$
	590 m	
388 m	364 s	$\nu[Cu—N(N_3)]$
268 ms	260 s	$\nu[Cu—N(L)]$

w = weak, m = medium, s = strong, v = very, br = broad.

ated with the azide asymmetric stretching mode, as well as two bands in the vicinity of the $\nu_s(N_3)$ absorption region. These observations are not consistent with the crystal structure of this complex. In fact, two bands due to $\nu_{as}(N_3)$ and one band due to $\nu_s(N_3)$ are expected, since one of the two azides is symmetric and the ν_s for this is IR-inactive.[27] Similar discrepancies have been observed in the case of $[Cu(pyridine)_2(N_3)_2]_n$.[7] In the far-IR region, we tentatively assigned to the metal–ligand vibrations the following frequencies[27] (cm^{-1}) : 388 m and 364 s for ν[Cu—N(N$_3$)] and 268 ms and 260 s, for ν[Cu—N(L)], for complexes **1** and **2**, respectively.

The electronic spectra of the solid complexes **1** and **2** are given in Fig. 5. Both complexes exhibit the *d–d* absorption band at 16,000 cm^{-1}, along with a shoulder on the high frequency side at 18,000 cm^{-1} for complex **2**. The spectra of penta-amine copper(II) complexes with square-based pyramidal geometry have been found to exhibit an intense absorption *d–d* band in the 17,000–15,000 cm^{-1} range, with a shoulder on the low frequency side around 11,000 cm^{-1}.[28] The spectra of both complexes are consistent with the above CuN_5 format, and suggest tetragonal pyramidal copper(II) environments. Additionally, complex **2** shows a moderate absorption band around 26,000 cm^{-1}. These bands are assigned as $N_3^- \rightarrow Cu^{II}$ LMCT transitions, since the ligands and their copper(II) chloride complex do not absorb in this range.

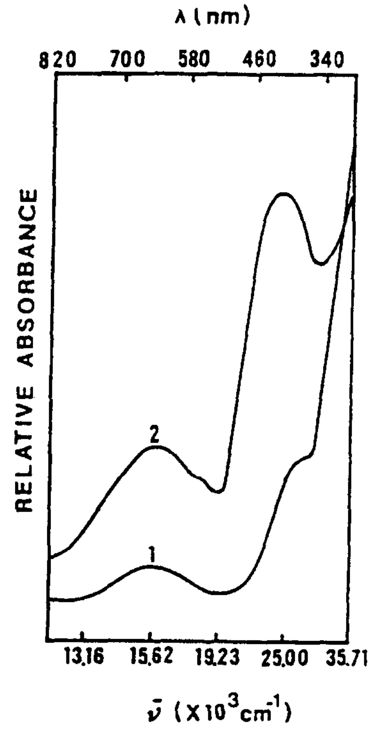

Fig. 5. Reflectance spectra of solid complexes. **1** : $[Cu(\beta\text{-collidine})_4(N_3)](ClO_4)$; **2** : $[Cu(\beta\text{-collidine})_2(N_3)_2]_2$.

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