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Synthesis and Structural Determination of Di-μ(1,1)-azido-bis[azido(2-benzoylpyridine)] dicopper(II) and *Catena*-di-μ(1,3)-azido[di-μ(1,1)-azido-bis(ethyl nicotinate)dicopper(II)] *

THOMAS C. W. MAK
Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong

and MOHAMED A. S. GOHER
Department of Chemistry, Faculty of Science, Alexandria University, Alexandria, Egypt

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Abstract

Two 1:1 mixed ligand complexes of copper(II) azide with substituted pyridines, namely di-μ(1,1)-azido-bis[azido(2-benzoylpyridine)] dicopper(II) (**1**) and *catena*-di-μ(1,3)-azido-[di-μ(1,1)-azido-bis(ethyl nicotinate)dicopper(II)] (**2**), have been synthesized and characterized by X-ray crystallography. Crystal data: **1**, $C_{24}H_{18}N_{14}Cu_2O_2$, space group $P\bar{1}$, $a = 7.471(2)$, $b = 10.477(3)$, $c = 9.389(3)$ Å, $\alpha = 100.77(2)$, $\beta = 109.83(2)$, $\gamma = 82.21(2)^\circ$, $Z = 1$, and $R_F = 0.036$ for 2035 observed Mo Kα data; **2**, $C_8H_9N_7CuO_2$, sapce group $P2_1/c$, $a = 9.961(2)$, $b = 5.306(1)$, $c = 22.621(4)$ Å, $\beta = 96.81(2)^\circ$, $Z = 4$, and $R_F = 0.044$ for 869 observed Mo Kα data. In the centrosymmetric binuclear molecule **1**, the Cu(II) atom has distorted square pyramidal coordination geometry involving a bidentate 2-Bzpy ligand, with each μ(1,1) bridging N atom serving simultaneously as a basal ligand to one metal atom and as a distal axial ligand to the other. The polymeric complex **2** features monodentate Et-nic ligands, centrosymmetric di-μ(1,1) azido bridged Cu_2N_2 rings, distorted square pyramidal Cu(II) coordination geometry, and di-μ(1,3) azido bridges which link the centrosymmetric binuclear $Cu_2(\text{Et-nic})_2(N_3)_2$ moieties into infinite chains parallel to the *b* axis.

Introduction

Recently we described the synthesis and X-ray structural characterization of a polymeric 3:2 complex of copper(II) azide with 2-benzoylpyridine (hereafter abbreviated as 2-Bzpy) which features an end-on triply bridging azido ligand [1]. We now report our investigation of the corresponding 1:1 complex (**1**), along with a 1:1 complex (**2**) of copper(II) azide with ethyl nicotinate (abbreviated as Et-nic). While 2-Bzpy generally functions as a bidentate *N,O*-chelating ligand, Et-nic is incapable of exhibiting such coordination behavior, and we anticipated that a comparative study of their mixed ligand complexes with copper(II) azide might yield interesting results. The present work constitutes part of our continuing study of metal pseudohalides containing substituted pyridine ligands [1–4]; further impetus is derived from the recent surge of interest in the structural features of azide binding to biological metals [5].

Experimental

Procedures and instruments used are as described in ref. 2.

Preparation of [Cu(2-Bzpy)(N₃)₂]₂ (1)

$Cu(NO_3)_2\cdot3H_2O$ (1.45 g, 6 mmol) dissolved in 20 ml ethanol and 2-benzoylpyridine (0.732 g, 4 mmol) in 30 ml ethanol were mixed together, followed by the addition of NaN_3 (0.8 g, *ca.* 12 mmol) in 10 ml water. The mixture was stirred for about 30 min and the precipitate filtered off and dried. The black powder was dissolved in a minimum of hot formamide and allowed to stand over several days. Complex **1** was isolated as black well-formed crystals. *Anal.* Found (calc.). Cu: 19.03(19.20); C: 44.23(43.58); H: 3.00(2.74); N: 30.00(29.63)%.

Preparation of Polymeric Cu(Et-nic)(N₃)₂ (2)

An ethanolic solution of ethyl nicotinate (BDH) (1.50 g, 10 mmol) was added to $Cu(NO_3)_2\cdot3H_2O$ (1.45 g, 6 mmol) dissolved in 20 ml ethanol. After dropwise addition of 0.85 g (13 mmol) of NaN_3 dissolved in a minimum of water to the stirred solution, the final mixture was heated and filtered.

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* 'Metal Pseudohalides Complexes, Part XI', part X is ref. 4.

0020-1693/86/$3.50

The filtrate was boiled for about 20 min, cooled, and allowed to stand overnight to produce black needle-like crystals of **2**. *Anal.* Found (calc.). C: 33.00-(32.18); H: 3.00(3.04); N: 32.72(32.82); Cu: 21.62-(21.27)%.

Spectral Data

The infrared spectrum of **1** shows absorption bands (v = very, w = weak, m = medium, s = strong, sh = shoulder, br = broad) at 2058vs, 2040vs ($\nu_{as}N_3$); 1610ms (ν C=O); 1588ms, 1565ms, 1020m, 655wm (pyridine ring); 1332s, 1282m (ν_s N_3); 642s, 610w (δ N_3); 390s, 375s (ν Cu–N_3) cm^{-1}. Free 2-benzoylpyridine exhibits absorption bands at 1663s, 1580ms, 1560m, 995s, and 610ms cm^{-1}; the substantial shifts of the C=O band to lower frequency and the pyridine ring vibrations to higher frequencies upon complexation suggest simultaneous *N,O*-coordination of the ligand. Complex **2** absorbs at 2070sh, 2035vs (ν_{as} N_3); 1345w*, (ν_s N_3); 655wm, 640w, 610w (δ N_3); 365s,br (ν_s Cu–N_3); 270s (ν Cu–N(L)) cm^{-1}.

The electronic spectra of the solid complexes are shown in Fig. 1. The d–d absorption band of **1** appears at 15 625 cm^{-1} with a shoulder at 12 578 cm^{-1}, whereas that of **2** is very strong and broad with a maximum around 12 048 cm^{-1}. The distinct band observed for **2** at 18 018 cm^{-1}, which is generally taken as good evidence for the presence of a binuclear Cu_2N_2 structural unit, is absent in the electronic spectrum of **1**. These results lend further support to the realization that there is no clear correlation between copper(II) stereochemistry and the solid state electronic spectrum [6].

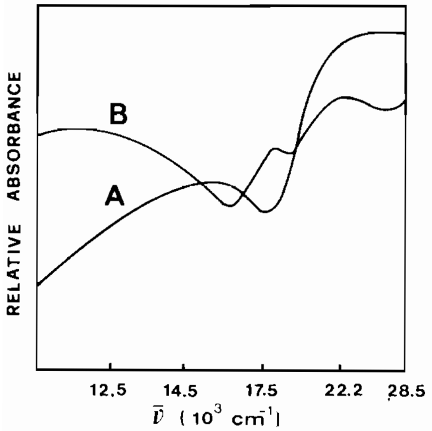

Fig. 1. Reflectance spectrum of solid complexes [Cu(2-Bzpy)(N_3)$_2$]$_2$ (**1**, curve A) and Cu(Et-nic)(N_3)$_2$ (**2**, curve B).

X-ray Structure Determination

Both complexes were handled in the same manner. Data collection on a Nicolet R3m four-circle diffractometer followed established procedures in our laboratory [7], and pertinent unit-cell and data processing parameters are summarized in Table I.

Structure solution was achieved by Patterson and Fourier methods. In the refinement of **1** by blocked-cascade least-squares, all twenty-one non-hydrogen atoms were assigned anisotropic thermal parameters, and the nine aromatic H atoms were geometrically generated (C–H fixed at 0.96 Å), assigned fixed isotropic temperature factors, and allowed to ride on their respective parent C atoms. Complex **2** was similarly refined with inclusion of all aromatic and methyl H atoms, except that its eight C atoms were varied isotropically in view of the unfavorable data-to-parameter ratio.

All computations were performed on a Data General Nova 3/12 minicomputer with the SHELXTL program package [8]. Analytic expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated [9].

The final atomic parameters are listed in Table II; atom labelling schemes follow those shown in Figs. 2 and 3 for complexes **1** and **2**, respectively. Bond distances and angles are tabulated in Table III. Hydrogen coordinates are listed in Table IV.

Discussion

As illustrated in Fig. 2, the dimeric molecule **1** processes crystallographic $\bar{1}$ symmetry and contains both terminal (N5 to N7) and μ(1,1)-bridging (N2 to N4) azido groups. Each metal center is further chelated by a 2-Bzpy ligand, giving rise to a square pyramidal coordination with the N2 atom serving simultaneously as a basal ligand to Cu and as a distal axial ligand to Cu′ [Cu–N2 = 1.984(3) and N2–Cu′ = 2.424(3) Å]. The chelate ring deviates only slightly from planarity [N(1)–C(5)–C(6)–O = 4.2(5)°], and the relative orientation of the two rings in the 2-Bzpy ligand is described by the C(5)–C(6)–C(7)–C(8) torsion angle of 50.2(5)°. Conforming to the general characteristics of coordinated azides [1, 10], both azido groups are nearly linear and noticeably asymmetric, the shorter N–N bonds being more remote from the metal atoms. The measured values in Table III indicate that the asymmetry is greater in the case of μ(1,1) bridging.

The centrosymmetric binuclear structure of **1** resembles that of di-μ(1,1)-azido-bis[azido(2-aminopyridine)aqua]dicopper(II) (**3**) [2], but also differs from it in several subtle aspects. Although complex **3** also exhibits tetragonal pyramidal coordination about each copper(II) atom, the μ(1,1)-bridging N

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*Ethyl nicotinate exhibits strong absorption in the range 1360–1280 cm^{-1} which obscures the ν_s N_3 mode.

TABLE I. Data Collection and Processing Parameters

Compound	**1**	**2**
Molecular formula	$[Cu(2\text{-}Bzpy)(N_3)_2]_2$, $C_{24}H_{18}N_{14}Cu_2O_2$	$Cu(Et\text{-}nic)(N_3)_2$, $C_8H_9N_7CuO_2$
Molecular weight	661.58	298.74
Cell constants		
a (Å)	7.471(2)	9.961(2)
b (Å)	10.477(3)	5.306(1)
c (Å)	9.389(3)	22.621(4)
α (°)	100.77(2)	–
β (°)	109.83(2)	96.81(2)
γ (°)	82.21(2)	–
V (Å^3)	676.9(3)	1187.2(3)
Z	1	4
Density (exp.)	1.65 g cm^{-3} (flotation in CCl_4/ $BrCH_2CH_2Br$)	1.66 g cm^{-3} (flotation in CCl_4/ $BrCH_2CH_2Br$)
Density (calc)	1.623 g cm^{-3}	1.671 g cm^{-3}
Space group	$P\bar{1}$	$P2_1/c$
Radiation	graphite-monochromatized MoKα, λ = 0.71069 Å	
Absorption coefficient	16.25 cm^{-1}	18.49 cm^{-1}
Crystal size	0.28 × 0.24 × 0.14 mm	0.12 × 0.08 × 0.04 mm
Mean μr	0.12	0.06
Transmission factors	0.711–0.896	0.817–0.900
Scan type and speed	ω–2θ; 2.02–8.37 deg min^{-1}	
Scan range	1° below $K\alpha_1$ to 1° above $K\alpha_2$	
Background counting	stationary counts for one-half of scan time at each end of scan	
Collection range	$h, \pm k, \pm l$; $2\theta_{max} = 50°$	$h, k, \pm l$; $2\theta_{max} = 40°$
Unique data measured	2195	1095
Observed data with $\lvert F_o\rvert > 3\sigma(\lvert F_o\rvert)$, n	2035	869
Number of variables, p	190	126
$R_F = \Sigma \lVert F_o\rvert - \lvert F_c\rVert / \Sigma \lvert F_o\rvert$	0.036	0.044
Weighting scheme	$w = [\sigma^2(F_o) + 0.0005\lvert F_o\rvert^2]^{-1}$	
$R_{wF^2} = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2 / \Sigma w \lvert F_o\rvert^2]^{1/2}$	0.045	0.046
$S = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/(n - p)]^{1/2}$	1.461	1.274
Residual extrema in final difference map	+0.67 to −0.28 eÅ^{-3}	+0.39 to −0.39 eÅ^3

TABLE II. Atomic Coordinates (×10^5 for Cu; ×10^4 for other atoms) and Thermal Parameters[a] (Å^2 × 10^4 for Cu; ×10^3 for other atoms)

Atom	x	y	z	U_{eq} or U
$[Cu(2\text{-}Bzpy)(N_3)_2]_2$ (**1**)				
Cu	22982(5)	49905(3)	52598(4)	319(2)*
O	1964(4)	4178(3)	3091(3)	52(1)*
N(1)	4339(4)	3476(2)	5580(3)	32(1)*
C(1)	5586(5)	3217(3)	6907(4)	40(1)*
C(2)	6913(5)	2152(4)	7011(4)	47(1)*
C(3)	6965(5)	1340(4)	5701(4)	48(1)*
C(4)	5680(5)	1607(3)	4306(4)	42(1)*
C(5)	4373(4)	2669(3)	4275(4)	33(1)*
C(6)	2928(4)	3090(3)	2874(4)	32(1)*
C(7)	2667(4)	2330(3)	1325(4)	37(1)*
C(8)	2448(6)	1004(4)	1028(4)	53(2)*
C(9)	2146(6)	329(4)	−444(5)	64(2)*
C(10)	2056(6)	984(5)	−1610(4)	62(2)*
C(11)	2264(6)	2292(5)	−1330(4)	64(2)*
C(12)	2560(5)	2978(4)	142(4)	48(1)*
N(2)	99(4)	6284(3)	4603(3)	39(1)*
N(3)	−47(4)	7371(3)	5279(3)	38(1)*
N(4)	−279(5)	8400(3)	5894(4)	61(2)*
N(5)	3397(4)	5885(3)	7310(4)	51(1)*
N(6)	2724(4)	6124(3)	8305(3)	48(1)*
N(7)	2129(6)	6357(6)	9310(4)	100(2)*
Polymeric $Cu(Et\text{-}nic)(N_3)_2$ (**2**)				
Cu	6008(9)	34315(17)	5606(4)	353(4)*
O(1)	5109(6)	5646(11)	2110(2)	62(2)*
O(2)	6705(5)	2759(11)	1984(2)	53(2)*
N(1)	2471(6)	2180(11)	808(3)	33(2)*
C(1)	3316(7)	3269(16)	1239(3)	37(2)
C(2)	4634(7)	2422(14)	1390(3)	34(2)
C(3)	5061(8)	367(15)	1095(3)	43(2)
C(4)	4202(8)	−770(15)	646(3)	42(2)
C(5)	2904(8)	208(16)	513(3)	44(2)
C(6)	5490(9)	3807(17)	1866(3)	42(2)

(continued overleaf)

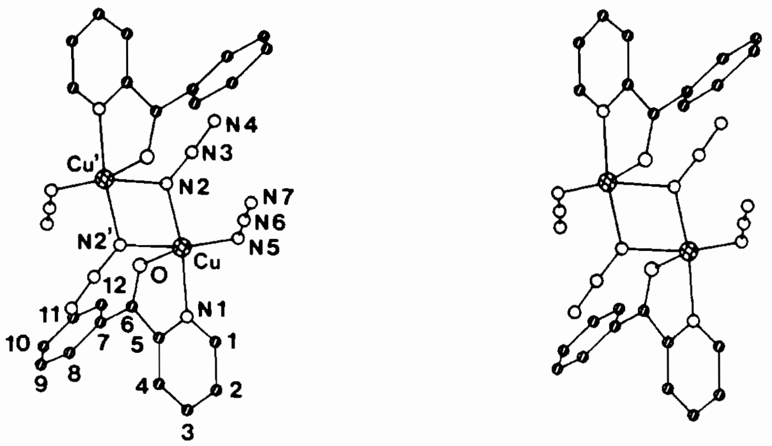

Fig. 2. A stereoview of the centrosymmetric $[Cu(2\text{-}Bzpy)(N_3)_2]_2$ dimeric molecule in **1**, showing the atom labelling.

TABLE II. *(continued)*

Atom	x	y	z	U_{eq} or U
C(7)	7590(9)	3808(18)	2478(4)	64(3)
C(8)	8309(12)	5993(22)	2304(5)	104(4)
N(2)	−1151(6)	4750(12)	168(2)	36(2)*
N(3)	−2182(8)	5005(12)	390(3)	37(3)*
N(4)	−3177(7)	5236(16)	592(3)	74(3)*
N(5)	736(7)	6723(14)	1205(3)	41(3)*
N(6)	242(6)	8647(11)	1064(2)	37(2)*
N(7)	−288(7)	10599(14)	921(4)	60(3)*

[a] Asterisks indicate equivalent isotropic temperature factor U_{eq} defined as 1/3 of the trace of the orthogonalised **U** matrix. The exponent of the isotropic temperature factor takes the form $-8\pi^2 U \sin^2\theta/\lambda^2$.

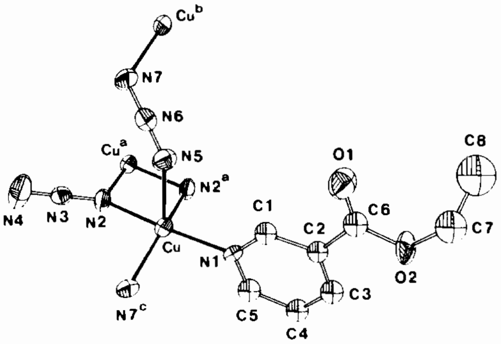

Fig. 3. A perspective view of the coordination geometry about the Cu(II) ion in polymeric $Cu(Et\text{-}nic)(N_3)_2$ (**2**), showing the atom labelling scheme. Thermal ellipsoids are drawn at the 45% probability level. Symmetry transformations are given at the end of Table IV.

TABLE III. Bond Lengths (Å) and Bond Angles (deg)

$[Cu(2\text{-}Bzpy)(N_3)_2]_2$ (**1**)

Cu–O	1.999(3)	Cu–N(1)	2.036(2)
Cu–N(2)	1.984(3)	Cu–N(5)	1.928(3)
Cu–N(2)′	2.424(3)	N(2)–N(3)	1.206(4)
N(3)–N(4)	1.145(4)	N(5)–N(6)	1.177(5)
N(6)–N(7)	1.148(6)	N(1)–C(1)	1.328(4)
C(1)–C(2)	1.383(5)	C(2)–C(3)	1.368(5)
C(3)–C(4)	1.388(5)	C(4)–C(5)	1.375(4)
C(5)–N(1)	1.358(4)	C(5)–C(6)	1.487(4)
C(6)–C(7)	1.485(4)	C(7)–C(8)	1.386(5)
C(8)–C(9)	1.388(6)	C(9)–C(10)	1.376(7)
C(10)–C(11)	1.366(7)	C(11)–C(12)	1.393(5)
C(12)–C(7)	1.382(6)		
Cu–N(2)–Cu′	96.3(1)	Cu–N(2)–N(3)	124.6(2)
N(2)–N(3)–N(4)	176.7(3)	Cu–N(5)–N(6)	128.0(3)
N(5)–N(6)–N(7)	177.7(4)	N(2)–Cu–N(5)	96.9(1)
N(1)–Cu–N(2)	170.1(1)	N(1)–Cu–N(2)′	92.7(1)
N(1)–Cu–N(5)	93.0(1)	N(5)–Cu–N(2)′	105.6(1)

(continued on facing page)

TABLE III. *(continued)*

O–Cu–N(2)	91.7(1)	O–Cu–N(2)′	91.7(1)
O–Cu–N(5)	161.4(1)	O–Cu–N(1)	79.2(1)
Cu–O–C(6)	117.2(2)	Cu–N(1)–C(1)	126.6(2)
Cu–N(1)–C(5)	114.6(2)	N(1)–C(5)–C(6)	113.1(2)
O–C(6)–C(5)	115.4(3)	N(1)–C(1)–C(2)	122.4(3)
C(1)–C(2)–C(3)	119.1(3)	C(2)–C(3)–C(4)	119.0(3)
C(3)–C(4)–C(5)	119.3(3)	C(4)–C(5)–N(1)	121.3(3)
C(5)–N(1)–C(1)	118.8(3)	C(4)–C(5)–C(6)	125.6(3)
C(5)–C(6)–C(7)	122.3(3)	O–C(6)–C(7)	122.3(3)
C(6)–C(7)–C(12)	118.8(3)	C(6)–C(7)–C(8)	121.7(3)
C(7)–C(8)–C(9)	120.3(4)	C(8)–C(9)–C(10)	119.7(4)
C(9)–C(10)–C(11)	120.5(4)	C(10)–C(11)–C(12)	120.2(4)
C(11)–C(12)–C(7)	119.8(4)	C(12)–C(7)–C(8)	119.5(3)
Polymeric Cu(Et-nic)$(N_3)_2$ (**2**)			
Cu–N(1)	1.995(6)	Cu–N(2)	1.988(6)
Cu–N(5)	2.269(7)	Cu–N(2)^{a}	2.040(6)
Cu–N(7)^{c}	1.969(8)	N(2)–N(3)	1.204(10)
N(3)–N(4)	1.145(11)	N(5)–N(6)	1.161(9)
N(6)–N(7)	1.190(10)	N(1)–C(1)	1.340(9)
C(1)–C(2)	1.391(10)	C(2)–C(3)	1.372(11)
C(3)–C(4)	1.385(10)	C(4)–C(5)	1.393(11)
C(5)–N(1)	1.339(10)	C(2)–C(6)	1.486(11)
O(1)–C(6)	1.204(11)	C(6)–O(2)	1.330(10)
O(2)–C(7)	1.450(10)	C(7)–C(8)	1.442(15)
Cu–N(2)–Cu^{a}	102.8(3)	Cu–N(2)–N(3)	126.8(5)
N(2)–N(3)–N(4)	178.7(8)	Cu–N(5)–N(6)	120.6(5)
N(5)–N(6)–N(7)	178.7(8)	N(6)–N(7)–Cu^{b}	124.8(6)
N(2)–Cu–N(5)	89.9(2)	N(1)–Cu–N(2)	169.5(2)
N(1)–Cu–N(2)^{a}	93.0(2)	N(1)–Cu–N(5)	95.4(2)
N(5)–Cu–N(2)^{a}	98.9(2)	N(1)–Cu–N(7)^{c}	94.6(3)
N(2)–Cu–N(7)^{c}	92.3(3)	N(5)–Cu–N(7)^{c}	108.5(3)
N(2)^{a}–Cu–N(7)^{c}	150.7(3)	Cu–N(1)–C(1)	123.1(5)
Cu–N(1)–C(5)	117.7(5)	C(1)–N(1)–C(5)	119.2(6)
N(1)–C(1)–C(2)	122.2(7)	C(1)–C(2)–C(3)	118.4(7)
C(2)–C(3)–C(4)	120.1(7)	C(3)–C(4)–C(5)	118.2(7)
C(4)–C(5)–N(1)	121.9(7)	C(1)–C(2)–C(6)	117.5(7)
C(3)–C(2)–C(6)	124.1(7)	O(1)–C(6)–C(2)	123.2(7)
O(2)–C(6)–C(2)	111.6(7)	O(1)–C(6)–O(2)	125.1(7)
C(6)–O(2)–C(7)	116.7(6)	O(2)–C(7)–C(8)	111.9(7)

Symmetry transformations: ′ $-x, 1-y, 1-z$; ^{a} $-x, 1-y, -z$; ^{b} $x, 1+y, z$; ^{c} $x, -1+y, z$.

atom serves as basal ligand to both metal centers [at Cu–N distances of 2.003(2) and 2.018(2) Å] in the dimeric molecule, and the apical aqua ligand forms an intramolecular acceptor hydrogen bond with the amino group. As compared to **3**, **1** has vastly different Cu–N(bridging) bond lengths, a less diamond-like Cu_2N_2 ring with interior angles closer to 90°, and an unusual pyramidal bond configuration about the $\mu(1,1)$-bridging N2 atom (sum of the three valence angles about N2, Σ_μ, is 330.4°, as opposed to the commonly encountered value of 360°).

The principal structural features of the Cu(Et-nic)$(N_3)_2$ complex **2** are illustrated in Fig. 3. The coordination environment of the Cu(II) atom is distorted square pyramidal, with basal Cu–N bonds in the range 1.969–2.040 Å and a longer apical bond of 2.269 Å to N(5) (Table III). The Et-nic molecule coordinates to the metal through N1. The N2–N4 azido ligand functions in the $\mu(1,1)$ mode through N2, giving rise to a cyclic Cu_2N_2 system located about a crystallographic inversion center. The other N5–N7 azido ligand bridges the metal atoms of neighboring Cu_2N_2 units in an asym-

TABLE IV. Coordinates ($\times 10^4$) and Assigned Isotropic Temperature Factors[a] ($Å^2 \times 10^3$) for Hydrogen Atoms

Atom	x	y	z	U
$[Cu(2\text{-}Bzpy)(N_3)_2]_2$ (1)				
H(1)	5559	3787	7829	48
H(2)	7790	1988	7989	54
H(3)	7868	591	5747	56
H(4)	5706	1066	3366	48
H(8)	2512	551	1845	64
H(9)	2002	−591	−644	74
H(10)	1848	517	−2628	71
H(11)	2200	2745	−2148	74
H(12)	2704	3898	342	58
Polymer $Cu(Et\text{-}nic)(N_3)_2$ (2)				
H(1)	2999	4674	1451	51
H(3)	5956	−289	1201	56
H(4)	4492	−2194	432	55
H(5)	2300	−549	201	59
H(7a)	7063	4291	2788	80
H(7b)	8237	2551	2626	80
H(8a)	8849	5140	2029	129
H(8b)	8896	6498	2662	129
H(8c)	7881	7491	2110	129

[a] The exponent takes the form: $-8\pi^2 U \sin^2\theta/\lambda^2$.

metric $\mu(1,3)$ fashion, resulting in polymeric chains extending in the direction of the b axis (Fig. 4). The two independent azide ions are essentially linear, and the N_α–N_β and N_β–N_γ bond lengths show a much smaller difference in the case of $\mu(1,3)$ bridging (Table III).

The di-$\mu(1,3)$ mode of azide bridging has previously been found in the discrete dinuclear complexes $[Cd(py)_2(N_3)_2]$ [11], $[Cu(PPh_3)_2(N_3)_2]$ [12], $[Ni_2(tren)_2(N_3)_2]^{2+}$ where tren = 2,2′,2″-triaminotriethylamine [13], $[Cu_2(Me_5dien)_2(N_3)_2]^{2+}$ [14], $[Cu_2(N_3)_4\subset(\text{macrocyclic ligand})]$ [15], and $[Cu(Me_4en)_2(N_3)_2]$ [16], whereas a single $\mu(1,3)$ azido bridge occurs in the cation in $[Ni_2(Me_4\text{-}cyclam)_2(N_3)_3]I$ [17]. Furthermore, X-ray analysis of $Mn(acac)_2N_3$ has established the presence of single $\mu(1,3)$ azide bridging, which links adjacent metal atoms to form polymeric chains of six-coordinate Mn(III) polyhedra [18]. Complex **2** is, however, novel in that di-$\mu(1,3)$ azido bridging occurs between a pair of Cu_2N_2 units, rather than simply between two metal atoms, and to our knowledge it is the only example featuring the coexistence of di-$\mu(1,1)$ and di-$\mu(1,3)$ azido bridging in the same structure.

It is of interest to compare the 1:1 mixed ligand complexes, **1–4** respectively, of copper(II) azide with the substituted pyridines 2-Bzpy, Et-nic, 2-aminopyridine (monodentate and accompanied by H_2O), and 3-picoline. Common structural features in this series of complexes are five-coordination about the copper atom (distorted square pyramidal in **1–3**, distorted trigonal pyramidal in **4**) and a planar Cu_2N_2 unit (centrosymmetric in **1–3**, two-fold rotation axis through azido ligands in **4**) generated by di-μ-(1,1) azido bridging. The dimeric nature of **1** arises from the fact that the three remaining coordinating sites around each metal atom are taken up by a terminal azide and a chelating bidentate organic ligand. Complex **3** is likewise binuclear, but the structure is further modified by the formation of intramolecular O•••H–N (amine) acceptor and intermolecular O–H•••N (terminal azide) donor hydrogen bonds [2]. The organic ligand is monodentate in **2** and **4** [3], and unsaturation in the copper(II) coordination sphere is satisfied by converting the remaining azide from terminal to $\mu(1,3)$ and $\mu(1,1)$ modes, respectively, thereby resulting in the formation of linear polymeric chains.

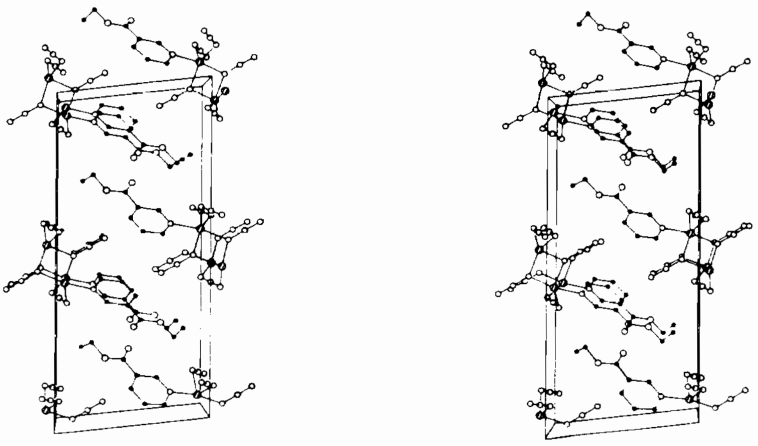

Fig. 4. Stereodrawing showing the crystal packing in polymeric $Cu(Et\text{-}nic)(N_3)_2$ (**2**). The unit-cell origin lies at the upper left corner, with a pointing from left to right, b towards the reader, and c downwards.

It has been known for a long time that complexes of stoichiometry $Cu^{I}LX$ exist in varying degrees of oligomerization and a wide variety of structural configurations, depending principally on the coordinating property and steric bulk of the ligand L [4, 19–21]. It now appears that a similar pattern emerges from our study of the class of complexes $Cu^{II}L(N_3)_2$ where L = substituted pyridine.

Supplementary Material

Structure factors have been deposited with the Editor-in-Chief.

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