Synthesis and Characterization of a 3:2 Complex of Copper(II) Azide with 2-Benzoylpyridine: a Polymeric Structure Containing an End-on Triply Bridging Azido Ligand*

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Abstract

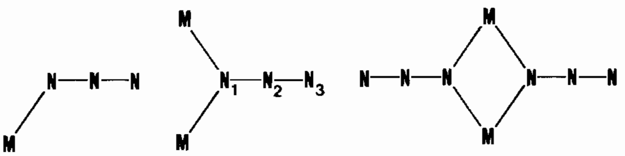
A 3:2 complex of copper(II) azide with 2-benzoylpyridine was synthesized and shown by X-ray crystallography to be polymeric. The compound crystallizes in space group *Pbca*, with $a = 14.803(3)$, $b = 11.282(2)$, $c = 39.31(1)$ Å, and $Z = 8$. The structure was refined to $R_F = 0.079$ for 2736 observed MoKα diffractometer data. The bidentate organic ligands each coordinate to a Cu(II) atom to form a chelate ring, and all six independent azido groups serve to bridge neighboring metal centers [at Cu–N bond distances of 1.975(9)–2.386(9) Å] in the μ(1,1) mode, yielding infinite composite chains which pack laterally to constitute a polymeric crystal structure. The bridging N atom of one azido group forms an additional long bond of 2.627(9) Å with a third Cu(II) atom, thereby furnishing a rare example of pyramidal μ(1,1,1), end-on tridentate, azide coordination.

Introduction

Copper(II) ions are known to form coordination compounds with a wide variety of stereochemistries [1]. The array of structural types are further enriched in copper(II) azide-nitrogen base adducts, owing to the variable manner of azide ligand binding [2], giving rise to the terminal, end-on bridging, and end-to-end bridging modes illustrated in Fig. 1.

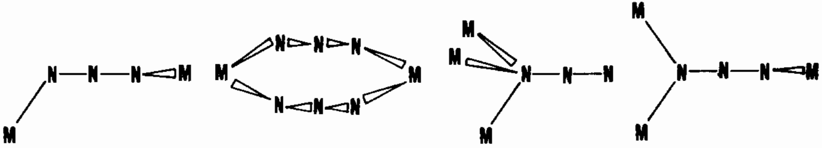
The copper(II) ion is in a tetragonally-distorted octahedral coordination environment in the polymeric complexes $Cu(NH_3)_2(N_3)_2$ [3] and $Cu(py)_2(N_3)_2$ [4], and adopts a distorted square pyramidal

(i) Planar systems



terminal [3–6] μ(1,1) [7] di-μ(1,1) [5–6, 8–11]

(ii) Generally non-planar systems



$\mu(1,3)^a$ [12] di-$\mu(1,3)^b$ [13–17] μ(1,1,1) [18] $\mu(1,1,3)^a$ [5–6, 18]

[a] May adopt a planar configuration. [b] May adopt a planar structure or a chair form with only the azido groups co-planar.

Fig. 1. Coordination modes of azido ligands in metal complexes.

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*Metal Pseudohalide Complexes Part IX. Part VIII is ref. 11.

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TABLE I. Infrared Spectral Data for the Polymeric $Cu_3(2\text{-}Bzpy)_2(N_3)_6$ Complex and Free 2-Benzoylpyridine.

2-Bzpy	Complex	Assignments[a]	References
	2085vs	ν_{as} N_3	[25]
	2060sh		
	2035vs		
1663s	1652s	$\nu C{=}O$	[21, 22]
1580ms	1595s	Pyridine ring	[20]
1560m	1580wm		
995s	1025s		
610ms	645m		
	1328s	ν_s N_3	[25]
	1290s		
	605w	δ N_3	[25]
	587w		
	395s	ν $Cu{-}N_3$	[6, 11]
	382s		
	372s		

[a] Guided by comparison with the IR spectrum of $Cu(2\text{-}Bzpy)_2Cl_2$; w = weak, m = medium, s = strong, v = very, sh = shoulder.

coordination geometry in the $[Cu((CH_2)_6N_4)_2(N_3)_6]^{2-}$ anion [5]. Recently we isolated and characterized the structures of the dimeric $[Cu(2\text{-}ampy)(N_3)_2(H_2O)]_2$ [6] and polymeric $Cu(3\text{-}pic)(N_3)_2$ [11] complexes. The dimer is structurally similar to $[Cu((CH_2)_6N_4)_2(N_3)_6]^{2-}$, whereas the polymer possesses distorted trigonal bipyramidal coordination polyhedra about the copper(II) ions; both complexes contain $\mu(1,1)$ bridging azido groups. Further work led to the synthesis of a new 3:2 complex of copper(II) azide with 2-benzoylpyridine (hereafter abbreviated as 2-Bzpy). The unusual composition of this complex and general interest in the structural features of azide coordination [19] provide the incentive for the present investigation.

Experimental

Experimental procedures and instruments employed are as described in ref. 6.

Preparation of the Complex

$Cu(NO_3)_2 \cdot 3H_2O$ (1.2 g, 5 mmol) dissolved in 30 ml ethanol was mixed with 0.91 g (5 mmol, in 10 ml ethanol) of 2-benzoylpyridine (from BDH). To this mixture, 0.55 g (~8 mmol) NaN_3 dissolved in a minimum quantity of distilled water was added. Upon allowing the final, deep-green mixture to stand overnight the complex was separated as black needles together with a dark brown powder.

Elemental analysis results (%, with calculated values in parentheses) for the crystalline needles (elongated along *b*) of empirical formula $C_{24}H_{18}N_{20}O_2Cu_3$: C 35.20(35.63); H 2.41(2.24); N 34.20 (34.61); Cu 23.92(23.55).

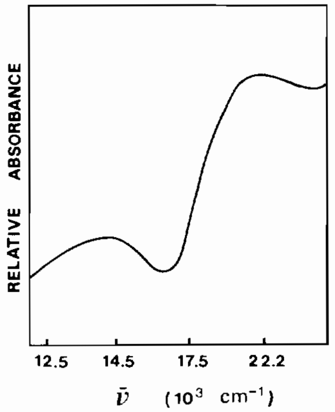

Fig. 2. Reflectance spectrum of solid $Cu_3(2\text{-}Bzpy)_2(N_3)_6$.

Infrared Spectrum

The shift of the vibrational bands originating from the pyridine ring to higher frequencies in the spectrum of the complex (Table I) is consistent with N-coordination of 2-Bzpy [20]. The carbonyl stretching band is expected to shift to lower frequencies when oxygen is coordinated to a metal, and to slightly higher frequencies in the case of only N-coordination [21, 22]. In fact, the lowering of $\nu C{=}O$ by 30–70 cm^{-1} has been taken as good evidence of simultaneous N,O-coordination [23]. Accordingly, the very small decrease of $\nu C{=}O$ in the spectrum (Table I) indicates a weak oxygen–copper interaction [21] in the complex.

The observed splitting of $\nu_{as}N_3$ into at least three bands is indicative of the presence of different azido groups. Similar splitting has been observed in $Cu(NH_3)_2(N_3)_2$ [3] and $Zn(NH_3)_2(N_3)_2$ [24], both known to contain different azido ligands. The asymmetric nature of the azido groups is indicated from the appearance of medium to strong bands in the region 1350–1290 cm^{-1}, associated with the symmetrical stretching vibrational mode [25].

Electronic Spectrum

The spectrum of the solid complex exhibits a d–d absorption band around 14,286 cm^{-1} (Fig. 2). In fact, the position of this band is intermediate between that found for the dimer $[Cu(2\text{-}ampy)(N_3)_2(H_2O)]_2$ (14,490 cm^{-1}, square pyramidal metal coordination) [6] and that of polymeric $Cu(3\text{-}pic)(N_3)_2$ (13,888 cm^{-1}, distorted trigonal bipyramidal metal coordination) [11]. Recently it has been pointed out [26] that the connection between copper(II) stereochemistry and the solid state electronic spectrum is not always straightforward. Indeed, the spectrum of an equimolar mixture of $Cu(3\text{-}pic)(N_3)_2$, $Cu(3\text{-}pic)_2(N_3)_2$ (distorted octahedral Cu(II),

TABLE II. Data Collection and Processing Parameters.

Molecular formula	$Cu_3(2\text{-}Bzpy)_2(N_3)_6$, $C_{24}H_{18}N_{20}O_2Cu_3$
Molecular weight	809.17
Cell constants	$a = 14.803(3)$, $b = 11.282(2)$, $c = 39.31(1)$ Å, $V = 6565(2)$ Å^3, $Z = 8$
Density (Calcd.)	1.637 g cm^{-3}
Space Group	*Pbca* (No. 61)
Radiation	graphite-monochromatized MoKα, λ = 0.71069 Å
Absorption coefficient	19.88 cm^{-1}
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, k, l; $2\theta_{max} = 45°$
Unique data measured	4192
Observed data with $\lvert F_o \rvert > 3\sigma(\lvert F_o \rvert)$, n	2736
Number of variables, p	293
$R_F = \Sigma \lVert F_o \rvert - \lvert F_c \rVert / \Sigma \lvert F_o \rvert$	0.079
Weighting scheme	$w = [\sigma^2(F_o) + 0.0010 \lvert F_o \rvert^2]^{-1}$
$R_{wF} = [\Sigma w(\lvert F_o \rvert - \lvert F_c \rvert)^2 / \Sigma w \lvert F_o \rvert^2]^{1/2}$	0.078
$S = [\Sigma w(\lvert F_o \rvert - \lvert F_c \rvert)^2 / (n - p)]^{1/2}$	1.337
Residual extrema	0.74 to −0.67 eÅ^{-3}

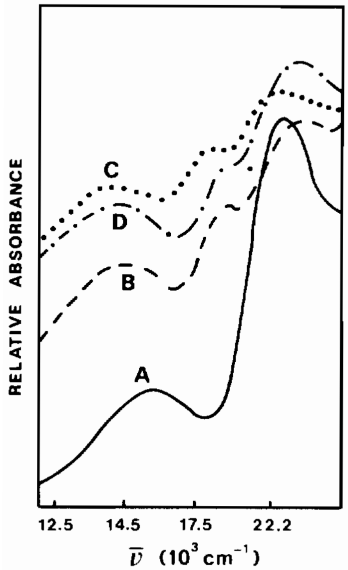

Fig. 3. Electronic spectra of some azido Cu(II) complexes. The labels A, B, C and D refer to $Cu(3\text{-pic})_2(N_3)_2$, $[Cu(2\text{-ampy})(N_3)_2(H_2O)]_2$, $Cu(3\text{-pic})(N_3)_2$ and an equimolar mixture of all three complexes, respectively.

d–d band around 15,400 cm^{-1}) and $[Cu(2\text{-ampy})(N_3)_2(H_2O)]_2$ shows a d–d band around 14,285 cm^{-1} (Fig. 3).

X-Ray Structure Analysis

A single crystal of dimensions *ca.* 0.12 × 0.30 × 0.08 mm was centered on a Nicolet R3m four-circle diffractometer. Unit-cell determination and intensity data collection and processing followed established procedures in our laboratory [27], and pertinent information are summarized in Table II.

Direct phase determination using negative quartets [28] yielded the positions of the three Cu atoms in the asymmetric unit, and the other forty-six non-hydrogen atoms were located from successive difference Fourier maps. In order to maintain a reasonable data-to-parameter ratio, the phenyl rings were refined as rigid groups (hexagons of side 1.395 Å), and other C atoms treated isotropically. Anisotropic thermal parameters were applied to the Cu, N and O atoms in blocked-cascade least-squares [29]. refinement, but N(9) became non-positive definite and was therefore held isotropic. All eighteen aromatic H atoms were geometrically generated (C–H bond fixed at 0.96 Å), assigned fixed isotropic thermal parameters, and allowed to ride on their respective parent C atoms in the final least-squares cycles, which converged to the R_F and R_{wF} indices given in Table II.

All computations were performed on a Data General Corporation Nova 3/12 minicomputer with the SHELXTL program package [30]. Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorportated [31].

The final positional parameters are listed in Table III; atom labelling follows that shown in Fig. 4. Selected bond distances, bond angles, and torsion angles are tabulated in Table IV. Thermal para-

TABLE III. Atomic Coordinates (×10^5 for Cu; ×10^4 for Other Atoms) for Polymeric $Cu_3(2\text{-Bzpy})_2(N_3)_6$.

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Cu(1)	21692(11)	58396(14)	12368(4)	2-Bzpy I			
Cu(2)	30045(11)	35028(14)	15953(4)	C(9)	3542(8)	4208(10)	3276(4)
Cu(3)	15839(11)	29827(14)	9383(4)	C(10)	2995(8)	3328(10)	3417(4)
Azide I				C(11)	2620(8)	2457(10)	3209(4)
N(1)	3083(8)	4646(10)	1085(3)	C(12)	2792(8)	2465(10)	2860(4)
N(2)	3424(9)	4606(10)	815(4)	2-Bzpy II			
N(3)	3717(9)	4562(13)	538(3)	O(2)	296(7)	1856(10)	981(2)
Azide II				N(20)	1091(8)	2957(10)	455(3)
N(4)	2302(7)	4991(8)	1673(2)	C(13)	1458(9)	3590(12)	211(3)
N(5)	1928(17)	5220(15)	1927(5)	C(14)	1067(10)	3703(13)	−102(4)
N(6)	1447(18)	5404(14)	2148(5)	C(15)	285(10)	3119(13)	−160(4)
Azide III				C(16)	−96(11)	2438(13)	86(4)
N(7)	3681(7)	2059(9)	1432(3)	C(17)	314(8)	2373(11)	403(3)
N(8)	4397(10)	1961(14)	1452(6)	C(18)	−51(8)	1717(11)	692(3)
N(9)	5163(10)	1821(19)	1438(9)	C(19)	−870(6)	971(10)	662(2)
Azide IV				C(20)	−962(6)	130(10)	405(2)
N(10)	2597(7)	1881(10)	830(3)	C(21)	−1727(6)	−591(10)	393(2)
N(11)	2849(8)	1660(10)	540(4)	C(22)	−2401(6)	−469(10)	638(2)
N(12)	3101(9)	1443(13)	274(4)	C(23)	−2310(6)	373(10)	896(2)
Azide V				C(24)	−1544(6)	1093(10)	908(2)
N(13)	1879(7)	2683(9)	1432(3)	Geometrically generated hydrogen atoms			
N(14)	1254(10)	2632(11)	1625(4)	H(1)	4719	4790	1417
N(15)	673(9)	2540(14)	1818(3)	H(2)	6133	5203	1674
Azide VI				H(3)	6390	4429	2203
N(16)	1028(10)	4557(12)	1028(3)	H(4)	5198	3769	2548
N(17)	289(12)	4709(14)	939(4)	H(8)	4090	4822	2831
N(18)	−446(13)	4838(18)	861(4)	H(9)	3800	4808	3420
2-Bzpy I				H(10)	2876	3323	3658
O(1)	2817(7)	2952(11)	2164(3)	H(11)	2243	1851	3306
N(19)	4124(8)	4123(11)	1829(3)	H(12)	2534	1865	2717
C(1)	4811(9)	4588(12)	1652(3)	H(13)	2021	3984	255
C(2)	5671(11)	4792(16)	1798(4)	H(14)	1347	4174	−277
C(3)	5788(12)	4416(14)	2113(4)	H(15)	−13	3194	−376
C(4)	5107(11)	3967(14)	2313(4)	H(16)	−645	2009	43
C(5)	4238(9)	3848(12)	2159(3)	H(20)	−498	46	236
C(6)	3430(10)	3339(12)	2334(4)	H(21)	−1790	−1170	215
C(7)	3339(8)	3345(10)	2720(4)	H(22)	−2928	−964	630
C(8)	3713(8)	4217(10)	2928(4)	H(23)	−2773	457	1065
				H(24)	−1481	1673	1085

TABLE IV. Selected Bond Distances (Å), Bond Angles (deg) and Torsion Angles (deg).

(i) Coordination polyhedra (standard deviations *ca.* 0.009 Å and 0.4°)

Cu(1)–N(1)	2.000	Cu(1)–N(4)	1.975	Cu(1)–N(16)	2.370
Cu(1)–N(7)[a]	2.016	Cu(1)–N(10)[a]	2.014	Cu(1)–N(13)[a]	2.627
N(1)–Cu(1)–N(4)	82.2	N(1)–Cu(1)–N(16)	94.3	N(1)–Cu(1)–N(7)[a]	174.4
N(4)–Cu(1)–N(7)[a]	93.6	N(16)–Cu(1)–N(7)[a]	95.9	N(1)–Cu(1)–N(10)[a]	92.3
N(4)–Cu(1)–N(10)[a]	162.9	N(16)–Cu(1)–N(10)[a]	101.7	N(7)[a]–Cu(1)–N(10)[a]	90.7
N(1)–Cu(1)–N(13)[a]	104.9	N(4)–Cu(1)–N(13)[a]	94.4	N(16)–Cu(1)–N(13)[a]	165.1
N(7)[a]–Cu(1)–N(13)[a]	71.5	N(10)[a]–Cu(1)–N(13)[a]	71.2		
Cu(2)–N(1)	2.386	Cu(2)–N(4)	1.999	Cu(2)–N(7)	2.018
Cu(2)–N(13)	2.010	Cu(2)–O(1)	2.336	Cu(2)–N(19)	2.020
N(1)–Cu(2)–N(4)	72.6	N(1)–Cu(2)–N(7)	98.3	N(4)–Cu(2)–N(7)	170.3

(continued overleaf)

TABLE IV. *(continued)*

N(1)–Cu(2)–N(13)	91.2	N(4)–Cu(2)–N(13)	90.2	N(7)–Cu(2)–N(13)	86.5
N(1)–Cu(2)–O(1)	162.4	N(4)–Cu(2)–O(1)	90.8	N(7)–Cu(2)–O(1)	98.6
N(13)–Cu(2)–O(1)	94.8	N(1)–Cu(2)–N(19)	98.9	N(4)–Cu(2)–N(19)	93.8
N(7)–Cu(2)–N(19)	91.0	N(13)–Cu(2)–N(19)	169.9	O(1)–Cu(2)–N(19)	75.8
Cu(3)–N(10)	1.995	Cu(3)–N(13)	2.017	Cu(3)–N(16)	1.989
Cu(3)–O(2)	2.296	Cu(3)–N(20)	2.037		
N(10)–Cu(3)–N(13)	86.5	N(10)–Cu(3)–N(16)	154.9	N(13)–Cu(3)–N(16)	94.0
N(10)–Cu(3)–O(2)	107.1	N(13)–Cu(3)–O(2)	91.0	N(16)–Cu(3)–O(2)	97.9
N(10)–Cu(3)–N(20)	93.4	N(13)–Cu(3)–N(20)	166.7	N(16)–Cu(3)–N(20)	91.7
O(2)–Cu(3)–N(20)	76.3				
(ii) Azido ligands (standard deviations *ca.* 0.02 A for N–N, 1.5° for N–N–N, 0.4° for Cu–N–Cu, and 1.0° for Cu–N–N)					
N(1)–N(2)	1.18	N(4)–N(5)	1.17	N(7)–N(8)	1.07
N(2)–N(3)	1.17	N(5)–N(6)	1.11	N(8)–N(9)	1.15
N(10)–N(11)	1.23	N(13)–N(14)	1.20	N(16)–N(17)	1.16
N(11)–N(12)	1.14	N(14)–N(15)	1.16	N(17)–N(18)	1.14
N(1)–N(2)–N(3)	176.3	N(4)–N(5)–N(6)	171.3	N(7)–N(8)–N(9)	172.9
N(10)–N(11)–N(12)	178.3	N(13)–N(14)–N(15)	176.7	N(16)–N(17)–N(18)	177.7
Cu(1)–N(1)–Cu(2)	94.6	Cu(1)–N(1)–N(2)	125.7	Cu(2)–N(1)–N(2)	139.4
Cu(1)–N(4)–Cu(2)	109.0	Cu(1)–N(4)–N(5)	126.0	Cu(2)–N(4)–N(5)	124.2
Cu(2)–N(7)–Cu(1)[b]	111.2	Cu(2)–N(7)–N(8)	123.5	Cu(1)[b]–N(7)–N(8)	125.2
Cu(3)–N(10)–Cu(1)[b]	108.8	Cu(3)–N(10)–N(11)	123.7	Cu(1)[b]–N(10)–N(11)	124.6
Cu(1)–N(16)–Cu(3)	108.1	Cu(1)–N(16)–N(17)	133.3	Cu(3)–N(16)–N(17)	117.9
Cu(2)–N(13)–Cu(3)	114.2	Cu(2)–N(13)–N(14)	117.5	Cu(3)–N(13)–N(14)	116.6
Cu(2)–N(13)–Cu(1)[b]	90.7	Cu(1)[b]–N(13)–N(14)	124.1	Cu(3)–N(13)–Cu(1)[b]	88.1
(iii) Chelate rings (standard deviations *ca.* 0.02 A and 1.2°)					
O(1)–C(6)	1.21	C(6)–C(5)	1.49	C(5)–N(19)	1.35
O(2)–C(18)	1.26	C(18)–C(17)	1.46	C(17)–N(20)	1.34
Cu(2)–O(1)–C(6)	110.0	O(1)–C(6)–C(5)	119.3	C(6)–C(5)–N(19)	115.4
Cu(3)–O(2)–C(18)	110.1	O(2)–C(18)–C(17)	119.3	C(18)–C(17)–N(20)	116.6
Cu(2)–N(19)–C(5)	117.5	Cu(2)–N(19)–C(1)	121.6	C(1)–N(19)–C(5)	119.7
Cu(3)–N(20)–C(17)	117.1	Cu(3)–N(20)–C(13)	121.8	C(13)–N(20)–C(17)	120.7
(iv) Torsion angles (standard deviation *ca.* 0.9° for X–Cu–Y–Z, 1.4° for Cu–X–Y–Z, and 1.7° for others)					
Cu(2)–O(1)–C(6)–C(5)	−11.6	Cu(3)–O(2)–C(18)–C(17)	−7.8		
O(1)–C(6)–C(5)–N(19)	16.9	O(2)–C(18)–C(17)–N(20)	9.7		
C(6)–C(5)–N(19)–Cu(2)	−12.6	C(18)–C(17)–N(20)–Cu(3)	−6.0		
C(5)–N(19)–Cu(2)–O(1)	5.3	C(17)–N(20)–Cu(3)–O(2)	1.5		
N(19)–Cu(2)–O(1)–C(6)	3.8	N(20)–Cu(3)–O(2)–C(18)	3.5		
C(4)–C(5)–C(6)–C(7)	24.6	C(16)–C(17)–C(18)–C(19)	5.1		
C(5)–C(6)–C(7)–C(8)	30.4	C(17)–C(18)–C(19)–C(20)	50.3		

Symmetry transformations: [a]½ – *x*, ½ + *y*, *z*; [b]½ – *x*, –½ + *y*, *z*.

meters (Table V) and structure factors (Table VI) have been deposited with the Editor.

Discussion

Crystal Structure

The formulation $Cu_3(2\text{-}Bzpy)_2(N_3)_6$ accurately represents the asymmetric unit in the polymeric structure (Fig. 5). The 2-benzoylpyridine ligands each coordinates to a metal atom to form a five-membered chelate ring. As may be seen from the torsion angles given in Table IV, the two puckered chelate rings take up slightly different conformations, and the organic ligand molecules differ mainly in regard to the relative orientation of the phenyl and pyridine rings. All six azido groups serve to bridge

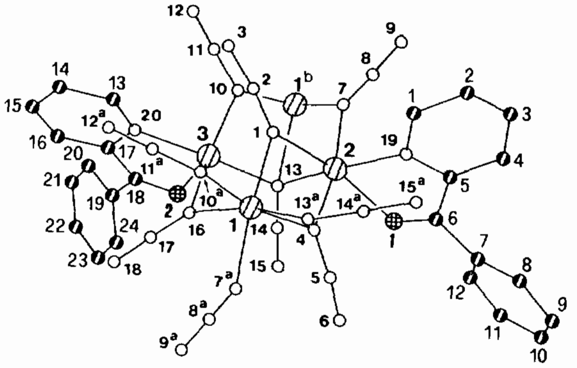

Fig. 4. A perspective view of the coordination geometries about the three Cu(II) ions, showing the atom labelling scheme. Atom types are differentiated by size and shading. Note the distorted tetrahedral bond configuration about N(13) belonging to $\mu(1,1,1)$ azido ligand V. Symmetry transformations are given at the end of Table IV.

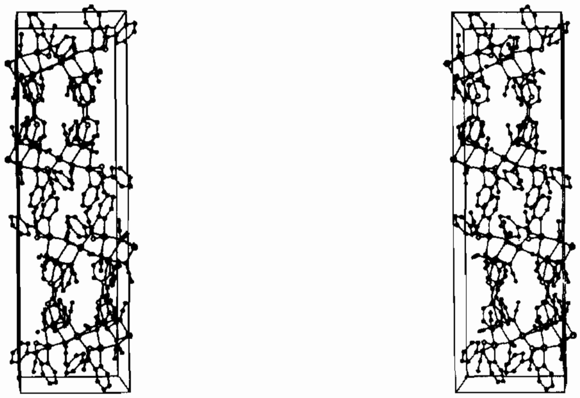

Fig. 5. Stereodrawing showing the crystal packing in polymeric $Cu_3(2\text{-}Bzpy)_2(N_3)_6$. The unit-cell origin lies at the lower left corner, with *a* pointing towards the reader, *b* from left to right, and *c* upwards.

neighboring metal atoms in the end-on mode, and the *b* glide operation generates a composite polymeric chain running in the direction of the *b* axis. The crystal structure is built up from a lateral packing of these polymeric chains, which relate to one another by the other two glide planes in the space group (Fig. 5).

The Cu(1) atom is surrounded by four azido ligands at Cu–N distances of 1.975–2.016 Å, and by two others at 2.370 and 2.627 Å; the coordination geometry may be described as distorted octahedral, with N(16) and N(13)^a occupying the distal axial positions. The Cu(2) atom is likewise six-coordinate, with four short equatorial Cu–N bonds in the range 1.999–2.020 Å and two long axial bonds of 2.336 and 2.386 Å to O(1) and N(1), respectively. The stereochemistry about Cu(3) is a distorted square pyramid with basal Cu–N bonds of 1.989–2.037 Å and an apical bond of 2.296 Å with O(2).

Azido Ligand in the End-on Triply Bridging Mode

The most notable feature in the present structure is the occurrence of the pyramidal $\mu(1,1,1)$ bridging mode by an azido ligand (Fig. 4). Atom N(13) of azide **V** forms strong bonds of 2.010 and 2.017 Å with Cu(2) and Cu(3) respectively, and a much weaker bond of 2.627 Å with Cu(1)^b. To our knowledge this type of end-on tridentate, or end-on triply bridging, azide coordination has been observed only once before in the polymeric structure of $Cu(N_3)_2$ featuring two independent azido groups, in one of which an end nitrogen atom symmetrically bridges two metal atoms [2.003(4) Å X 2] and forms a further long bond of 2.709(7) Å with a third. In the $\mu(1,1)$ mode commonly found in metal azide complexes, the sum of the three valence angles about the bridging N_1 atom, Σ_μ, generally conforms closely to 360° (Fig. 1). In the present $Cu_3(2\text{-}Bzpy)_2(N_3)_6$ complex, the Σ_μ value for N(13) of azide **V** is 348.3° if its weaker coordination to Cu(1)^b is ignored, whereas those for the other five azido groups lie in the range 357.1–359.9°. Similarly in $Cu(N_3)_2$, discounting the long Cu–N bond leads to a Σ_μ value of 352.5° for the $\mu(1,1,1)$ azido ligand, as opposed to 359.6° for the bidentate end of the other $\mu(1,1,3)$ azide. A comparison of these two copper(II) azide complexes suggests that the extent of 'pyramidization' of the tridentate N atom correlates well with the length of the third (long) metal–ligand bond.

A brief survey of known copper(II)–N(azide) bond distances showed that they can be conveniently classified into three categories: strong (1.95–2.15 Å), medium (2.30–2.45 Å) and weak (2.60–2.75 Å). The last type of metal-ligand interaction is certainly non-trivial, as its presence in the $Cu(N_3)_2$ and $Cu_3(2\text{-}Bzpy)_2(N_3)_6$ structures converts the bond configuration about a bridging N atom from trigonal planar $\mu(1,1)$ to distorted tetrahedral $\mu(1,1,1)$. It would seem appropriate to refer to this as a semi-coordinate bond [32], in line with the terminology suggested for long Cu(II)–O covalent interactions in the range 2.5–3.0 Å [33, 34].

The di-$\mu(1,1)$ type of azide bridging (Fig. 1) results in three distinguishable Cu_2N_2 rings in the present structure, namely Cu(1)N(1)Cu(2)N(4), Cu(1)^{b}N(7)-Cu(2)N(13) and Cu(1)^{b}N(10)Cu(3)N(13) (Fig. 4). The sum of the interior angles are 358.4, 359.9 and 354.6°, respectively, and the approximate planarity of these rings is in accord with the general pattern observed for metal azides containing di-$\mu(1,1)$ cyclic systems.

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