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Preparation and Structural Characterization of Di-μ-azido-bis[azido(2-aminopyridine)-aquo]dicopper(II), $[Cu(2\text{-}ampy)(N_3)_2(H_2O)]_2$

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*Di-μ-azido-bis[azido(2-aminopyridine)aquo]dicopper(II), $[Cu(2\text{-}ampy)(N_3)_2(H_2O)]_2$, was synthesized and characterized by X-ray crystallography. The crystals are triclinic, space group $P\bar{1}$, with $a = 7.142(1)$, $b = 7.812(1)$, $c = 9.727(1)$ Å, $\alpha = 96.52(1)$, $\beta = 92.52(1)$, $\gamma = 113.47(1)^\circ$, and $Z = 1$. The structure was refined to $R_F = 0.030$ for 1960 observed MoKα diffractometer data. The dimeric molecule, which possesses a crystallographic inversion center, contains both terminal and $\mu(1)$-bridging azido groups. Each copper(II) atom is further coordinated by a 2-aminopyridine ligand (*via* its ring N atom) and a water molecule to give a distorted square pyramid, with the metal atom raised by 0.17 Å above the N_4 basal plane [Cu–N (ring) = 2.001(2), Cu–N (azide) = 1.962(3)–2.018(2) Å] towards the apical aquo ligand [Cu–O = 2.371(2) Å]. Each water molecule forms an intramolecular O···H–N (amine) acceptor hydrogen bond, and is linked by two O–H···N (terminal azide) intermolecular donor hydrogen bonds to adjacent dimeric complexes to yield a layer structure parallel to (001). Infrared and electronic spectral data are presented and discussed.*

Introduction

The factors influencing the mode of bridging in binuclear $M_2(N_3)_2$ systems, that is, whether the azide groups function as one-end bridges forming a four-membered ring or as end-to-end bridges forming an eitht-membered ring, are not fully understood [1]. For instance, X-ray structural determinations have shown that while di-μ(1,3)-azido bridging of the latter type exists in $Cd(py)_2(N_3)_2$ [2], the two azide groups are crystallographically distinct with different structural environments in $Cu(py)_2(N_3)_2$ [3]. In the copper(II) complex, one azide ligand is monocoordinate whereas the other coordinates asymmetrically to three different metal centers.

As the copper(II) ion forms coordination compounds of a rich variety of stereochemistries [4, 5], it would seem that the reaction of α-substituted pyridines, rather than pyridine itself, with copper(II) azide might lead to a modification of the bonding mode of the bridging azide ligand in the resulting complexes. During the course of our investigation of metal azide complexes containing various substituted pyridine ligands [6, 7], we isolated a 1:1 complex of copper(II) azide with 2-aminopyridine (hereafter abbreviated as 2-ampy) which crystallizes with an additional water molecule. We determined its structure by spectroscopic and X-ray methods, in order to elucidate the details of molecular and coordination geometry and to appraise the steric effect of the organic ligand on the mode of the azide bridging.

Experimental

Preparation of $[Cu(2\text{-}ampy)(N_3)_2(H_2O)]_2$, 1

To $CuSO_4 \cdot 5H_2O$ (2 mmol) in 30 ml of water was added 2-ampy (from BDH, 4 mmol) dissolved in boiled ethanol (10 ml). Upon slow addition of NaN_3 (4 mmol) dissolved in a minimum of distilled water, a greenish-brown colloidal precipitate was formed immediately. The mixture was then stirred for 30 min. Well-formed black crystals of *1*, together with a greenish powder*, were isolated by allowing the final mixture to stand for several weeks.

Elemental Analysis and Spectral Measurements

Micro-analyses of C, H, and N were performed on a Perkin-Elmer 240 Elemental Analyser. Copper was determined by titration against disodium EDTA after decomposition of the complex by boiling with mixtures of concentrated HNO_3 and HCl and evaporation several times. Elemental analysis results (%) for the crystalline product of empirical formula $C_5H_8N_8OCu$ were as follows, with calculated values in parentheses: C 23.85(23.13); H 3.17(3.10); N 43.20(43.14); Cu 24.73(24.45).

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*Shown to be a mixture of high $Cu(N_3)_2$ content by IR spectroscopy.

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Infrared spectra in the region 4000–200 cm^{-1} were recorded on a Unicam SP 2000 spectrophotometer. Solid samples were measured as Nujol mulls and the liquid 2-ampy ligand as a capillary film. Reflectance spectra of solid complexes were measured over the 220–1000 nm range on a Zeiss-Jena VSU-1 instrument with MgO as a standard and diluent.

X-Ray Crystallography

A single crystal of approximate dimensions 0.36 × 0.28 × 0.12 mm was centered on a Nicolet R3m four-circle diffractometer system. Accurate unit-cell dimensions were obtained from least-squares refinement of the 2θ values of 24 strong reflections with non-zero diffraction indices and χ angles within the range 90 (or 270) ±30°. Data collection and reduction were conducted using established procedures [8], and pertinent crystallographic information are summarized in Table I.

Intensity statistics strongly favored space group $P\bar{1}$, and the structure was solved by direct phase determination based on negative quartets [9]. All fifteen non-hydrogen atoms in the asymmetric unit were located from the best E-map. After several cycles of blocked-cascade [10] least-squares refinement, the four aromatic H atoms were geometrically generated (C–H bond fixed at 0.96 Å), assigned isotropic thermal parameters, and allowed to ride on their respective parent C atoms. At $R_F = 0.039$, a difference Fourier map clearly revealed the positions of the remaining amine and water protons. These four H atoms were assigned fixed isotropic temperature factors and included in the final least-squares cycles, which converged to the R_F and R_{wF} indices shown in Table I. The final difference map was essentially flat, with residual extrema lying between 0.54 and −0.71 $e\text{Å}^{-3}$.

TABLE I. Data Collection and Processing Parameters.

Molecular formula	$C_{10}H_{16}N_{16}O_2Cu_2$
Molecular weight	519.44
Cell constants	$a = 7.142(1)$ Å, $\alpha = 96.52(1)°$ $b = 7.812(1)$, $\beta = 92.52(1)$ $c = 9.727(1)$, $\gamma = 113.47(1)$ $V = 492.2(2)$ Å^3, $Z = 1$
D_m (flotation in CCl_4/ $BrCH_2CH_2Br$)	1.77 g cm^{-3}
D_c	1.752 g cm^{-3}
Space group	$P\bar{1}$
Radiation	graphite-monochromatized MoKα, $\lambda = 0.71069$ Å
Absorption coefficient	22.11 cm^{-1}
Mean μr	0.31
Transmission factors	0.530–0.815
Scan type and speed	ω–2θ; 2.02–8.37 deg 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	$h, \pm k, \pm l$; $2\theta_{max} = 55°$
Unique data measured	2121
Observed data with $\|F\| > 3\sigma(\|F\|)$, n	1960
Number of variables, p	148
$R_F = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$	0.030
Weighting scheme	$w = [\sigma^2(F_o) + 0.0002\|F_o\|^2]^{-1}$
$R_{wF} = [\Sigma w(\|F_o\| - \|F_c\|)^2/\Sigma w\|F_o\|^2]^{1/2}$	0.035
$S = [\Sigma w(\|F_o\| - \|F_c\|)^2/(n - p)]^{1/2}$	1.59

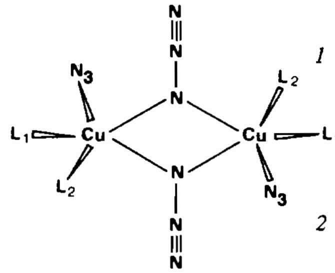
All computations were performed on a Data General Corporation Nova 3/12 minicomputer with the SHELXTL program package [11]. Analytical expressions of neutral atom scattering factors were employed, and anomalous dispersion corrections were incorporated [12].

The final positional and thermal parameters for the non-hydrogen atoms are listed in Table II; atom labelling follows that shown in Fig. 1. Hydrogen coordinates are given in Table III, and bond distances and angles in Table IV. A table of structure factors is available on request from the second author.

Discussion

Molecular Structure and Crystal Packing

Dimeric molecules of *1*, which has crystallographically imposed $\bar{1}$ symmetry, contain both terminal and μ(1)-bridging azido groups (Fig. 1). Each metal centre is further coordinated by a 2-ampy ligand *via* its ring N(1) atom and a water molecule. The stereochemistry about each Cu(II) atom is best described as a distorted square pyramid, with the water molecule at its apex and the metal atom raised by 0.17 Å above the N_4 basal plane. Atoms N(4), N(5), and N(6) all lie within 0.22 Å of the central Cu_2N_2 ring. In conformity to the general trend for coordinated azides [1], both azido ligands in *1* are very nearly linear and asymmetric, the shorter N–N bonds being more remote from the metal atoms. Comparison of their measured dimensions (Table IV) show that the asymmetry is greater in the case of μ(1)-bridging.



1 $L_1 = H_2O$, L_2 = 2-ampy

2 $L_1 = (CH_2)_6N_4$, $L_2 = N_3^-$

In most aspects *1* is strucutally similar to the di-μ-azidotetraazidobis(hexamethylenetetramine)dicopper(II) anion (*2*) of $2/m$ molecular symmetry [13], which has its two-fold axis passing through

TABLE II. Atomic Coordinates ($\times 10^5$ for Cu; $\times 10^4$ for other atoms) and Anisotropic Temperature Factors[a] ($Å^2 \times 10^4$ for Cu; $\times 10^3$ for other atoms).

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cu	8223(4)	36780(4)	41138(3)	383(2)	320(2)	196(1)	−35(1)	−36(1)	218(1)
C(1)	−22(4)	2589(3)	1028(2)	39(1)	28(1)	24(1)	−1(1)	0(1)	19(1)
C(2)	−1263(4)	1469(4)	−173(3)	45(1)	41(1)	23(1)	−2(1)	−4(1)	24(1)
C(3)	−2781(4)	−235(4)	−69(3)	40(1)	44(2)	37(1)	−13(1)	−11(1)	20(1)
C(4)	−3100(4)	−846(4)	1222(3)	40(1)	36(1)	51(2)	−1(1)	1(1)	6(1)
C(5)	−1879(4)	323(4)	2357(3)	46(2)	40(1)	34(1)	7(1)	7(1)	14(1)
N(1)	−367(3)	2035(3)	2288(2)	36(1)	29(1)	22(1)	−1(1)	−1(1)	16(1)
N(2)	1510(4)	4270(3)	956(2)	59(2)	40(1)	28(1)	5(1)	−1(1)	7(1)
N(3)	1074(3)	5020(3)	6057(2)	53(1)	54(1)	24(1)	−11(1)	−11(1)	39(1)
N(4)	2219(3)	5176(3)	7052(2)	43(1)	40(1)	25(1)	−1(1)	1(1)	27(1)
N(5)	3297(4)	5342(4)	8001(3)	69(2)	81(2)	36(1)	−4(1)	−13(1)	49(2)
N(6)	2643(4)	2484(3)	4648(2)	52(1)	41(1)	41(1)	−11(1)	−16(1)	31(1)
N(7)	2577(4)	1012(3)	4140(2)	54(1)	43(1)	31(1)	0(1)	−7(1)	31(1)
N(8)	2579(6)	−408(5)	3705(4)	145(3)	67(2)	75(2)	−27(2)	−38(2)	78(2)
O	3610(3)	6345(2)	3570(2)	38(1)	31(1)	45(1)	−5(1)	−8(1)	15(1)

[a]The exponent takes the form: $-2\pi^2\Sigma_i\Sigma_j U_{ij}h_ih_j a_i^* \cdot a_j^*$.

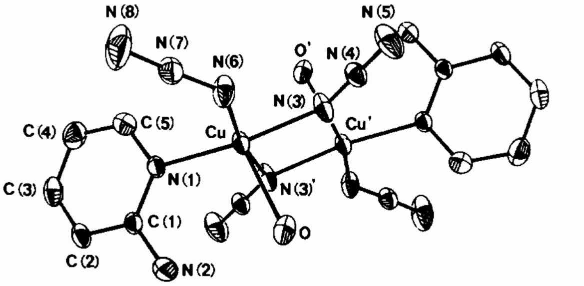


Fig. 1. A perspective view of the $[Cu(2\text{-ampy})(N_3)_2(H_2O)]_2$ molecule showing the atom labelling. Thermal ellipsoids are drawn at the 40% probability level, and hydrogen atoms have been omitted for clarity.

TABLE III. Hydrogen Coordinates ($\times 10^3$) and Assigned Isotropic Thermal Parameters[a] ($Å^2 \times 10^3$).

Atom	x	y	z	U
H(2)	−104	191	−106	60
H(3)	−364	−101	−88	60
H(4)	−415	−206	131	60
H(5)	−210	−97	325	60
H(N2*a*)	249(4)	485(4)	171(2)	70
H(N2*b*)	201(5)	440(5)	9(2)	70
H(O*a*)	328(4)	737(3)	375(3)	60
H(O*b*)	484(3)	662(4)	407(3)	60

[a]Form of isotropic temperature factor: $\exp(-8\pi^2 U \sin^2\theta/\lambda^2)$.

the $\mu(1)$-bridging azides. Despite the differences in charge and sub-units in these two dimeric Cu(II) complexes, there is remarkably good agreement between corresponding bond distances and bond angles in the azido groups and the central Cu_2N_2 ring. The relevant dimensions reported for *2*: Cu–N (bridging) = 2.018(1) Å, Cu–N (terminal) = 1.979(2) Å, Cu–N–Cu′ = 103.7(1)°, N–N = 1.201(3) and 1.141(4) Å for bridging azide, N–N = 1.118.8(2) and 1.150(2) Å for terminal azide, and Cu–N–N = 128.2(1)° for terminal azide may be compared with those of *1* listed in Table IV.

All C and N atoms of the organic ligand are coplanar (within experimental error) and most of the measured dimensions closely match those reported for uncomplexed 2-ampy [14]. A notable difference is that the bond configuration about N(2) in *1* is distinctly pyramidal, and the NH_2 group makes a dihedral angle of 33° with the pyridine ring, as opposed to an angle of 15° for the sp^2-hydbridized amino group in 2-ampy. This is mainly caused by the formation of an intramolecular hydrogen bond [N(2)–H···O = 2.852(6) Å], and the geometrical requirement is such that the N(1)–C(1)–C(2) angle is enlarged relative to the corresponding angle in free 2-ampy, so that the Cu–O bond leans away from the organic ligand.

The water molecule plays a unique role in dictating the structure of the present complex. Besides serving as a ligand and forming an acceptor intramolecular hydrogen bond with the amino group, it is further involved in intermolecular donor hydrogen bonding [O–H···N(8)″ = 2.901(7), O–H···N(6)‴ = 2.878(6) Å] with different terminal azido groups of two adjacent dimeric complexes. In the crystal structure (Fig. 2) the dimeric molecules are thus linked by O–H···N hydrogen bonds to form layers parallel to (001), with only weak van der Waals interaction between the stacked layers. Full utilization of the lone pairs and protons of the water molecule in coordinate and hydrogen bonding also accounts for the fact that the Cu–O bond of 2.371-

TABLE IV. Bond Distances (Å) and Angles (deg).

Cu–N(1)	2.001(2)	Cu–N(3)	2.018(2)
Cu–N(6)	1.962(3)	Cu–N(3)′	2.003(3)
Cu–O	2.371(2)	C(1)–N(1)	1.346(3)
C(1)–N(2)	1.345(3)	C(1)–C(2)	1.406(3)
C(2)–C(3)	1.359(3)	C(3)–C(4)	1.390(4)
C(4)–C(5)	1.366(4)	C(5)–N(1)	1.355(3)
N(3)–N(4)	1.201(3)	N(4)–N(5)	1.137(3)
N(6)–N(7)	1.180(4)	N(7)–N(8)	1.143(5)
N(2)–H(N2*a*)	0.93(2)	N(2)–H(N2*b*)	0.93(2)
O–H(O*a*)	0.92(3)	O–H(O*b*)	0.92(2)
N(1)–Cu–N(3)	161.8(1)	N(6)–Cu–N(3)′	169.5(1)
N(1)–Cu–N(3)′	92.0(1)	N(1)–Cu–N(6)	96.9(1)
N(3)–Cu–N(6)	93.1(1)	N(3)–Cu–N(3)′	76.9(1)
O–Cu–N(1)	104.9(1)	O–Cu–N(6)	92.0(1)
O–Cu–N(3)	89.8(1)	O–Cu–N(3)′	91.1(1)
Cu–N(1)–C(1)	125.6(1)	Cu–N(1)–C(5)	115.5(2)
C(1)–N(1)–C(5)	118.1(2)	N(1)–C(1)–N(2)	118.1(2)
C(2)–C(1)–N(2)	120.9(2)	N(1)–C(1)–C(2)	121.0(2)
C(1)–C(2)–C(3)	119.5(2)	C(2)–C(3)–C(4)	119.8(2)
C(3)–C(4)–C(5)	118.1(2)	C(4)–C(5)–N(1)	123.5(3)
Cu–N(3)–Cu′	103.1(1)	Cu–N(3)–N(4)	127.2(2)
N(3)–N(4)–N(5)	179.2(3)	Cu–N(6)–N(7)	126.5(2)
N(6)–N(7)–N(8)	176.5(3)	H(O*a*)–O–H(O*b*)	108(3)
Cu–O–H(O*a*)	108(1)	Cu–O–H(O*b*)	115(2)
C(1)–N(2)–H(N2*a*)	119(2)	C(1)–N(2)–H(N2*b*)	115(2)
H(N2*a*)–N(2)–H(N2*b*)	115(2)		
H(N2*a*)···O	1.98(2)	N(2)–H(N2*a*)···O	156(2)
H(O*a*)···N(8)″	2.00(3)	O–H(O*a*)···N(8)″	168(3)
H(O*b*)···N(6)‴	1.97(2)	O–H(O*b*)···N(6)‴	170(2)

Symmetry transformations: ′ −*x*, 1 − *y*, 1 − *z*; ″ *x*, 1 + *y*, *z*; ‴ 1 − *x*, 1 − *y*, 1 − *z*.

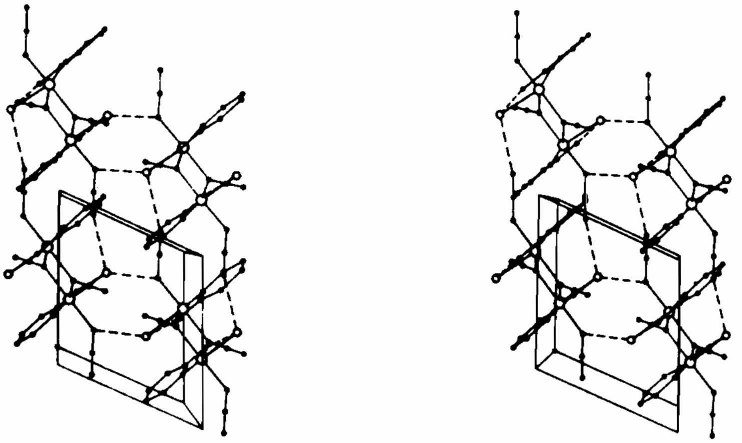


Fig. 2. Stereo drawing of the crystal structure of *1*. Hydrogen bonds are represented by broken lines. The origin of the unit cell lies at the lower left corner, with *a* pointing from left to right at a slant, *b* upwards, and *c* towards the reader.

(2) Å is significantly longer than the corresponding distance of 2.286(2) Å in aquo[N,N′-bis(2′-pyridine-carboxamido)-1,2-benzene]copper(II) [15]. In the latter complex, which possesses a similar square-pyramidal CuN_4O kernel, the water molecule forms two hydrogen bonds [2.825(3) and 2.769(3) Å] with carbonyl O atoms of adjacent chelate molecules, but no use is made of the remaining lone pair.

Infrared Spectrum

The observed absorption bands in the infrared spectrum of complex *1* are listed in Table V. The

TABLE V. Infrared Spectral Data of $[Cu(2\text{-}ampy)(N_3)_2(H_2O)]_2$.

Frequency[a] (cm^{-1})	Assignments[b]	References
3460vs 3340vs 3240vs	νNH_2 mixed with νH_2O	[16]
2090–2060vs,br	$\nu_{as}N_3$	[3, 17]
1645ms	δNH_2	
1625vs	δH_2O mixed with highest $\nu C–C$	
1350m 1305s 1290s	$\nu_s N_3$	[18]
670m 635m 605wm 585wm	δN_3	[18]
455m	$\nu Cu–O$	[19, 20]
400s 380s	$\nu Cu–N_3$	
290s	$\nu Cu–N(L)$	[21]

[a] s = strong, m = medium, w = weak, br = broad, v = very. [b] Guided by comparison with the IR spectra of free 2-ampy and of $Co(2\text{-}ampy)_2(SCN)_2$.

vibrational modes of the coordinated water molecule are superimposed on those due to the amino group, and this mixing of the νOH and νNH_2 modes accounts for the appearance of very strong bands in the 3500–3200 cm^{-1} region, and of the slight shifts of νNH_2 fequencies in the spectrum of the complex compared to those (3420, 3340, and 3240 cm^{-1}) in the spectrum of free 2-ampy. Other band assignments and relevant references are given in Table V.

Electronic Spectrum

The electronic spectrum of the solid complex exhibits the *d–d* transition band with a maximum around 14,490 cm^{-1} accompanied by a distinct absorption at 18,860 cm^{-1} (Fig. 3). The former value corresponds very closely to that usually found for five-coordinate copper(II) complexes [22, 23]. The electronic spectra of a series of monoamine adducts of bisethylenediamine–copper(II) complexes show an intense band above 17,000 cm^{-1} with a shoulder on the low frequency side, considered by Tomlinson and Hathaway [24] as being consistent with five-coordinate stereochemistry. Kohout *et al.* [25] has reported that the electronic spectra of cyanato–copper(II) complexes derived from some imidazole ligands exhibit *d–d* transitions as an intense band around 14,000–15,000 cm^{-1} accompanied by a high wavenumber shoulder above 17.000 cm^{-1}. They suggested either five-coordinate or rhombic octahedral geometry, in line with those found for a series of mono(diethylenetriamine)copper(II) complexes [26] exhibiting similar spectra. More recently, Hathaway *et al.* [27] reported for the regular trigonal bipyramidal $[Cu\{tris(2\text{-}aminoethyl)amine\}(NH_3)]^{2+}$ cation an electronic spectrum showing also a high frequency shoulder, but as a whole shifted in respect of our case by *ca.* 3000 cm^{-1} to lower energies. The data suggest that Fig. 3 may be of value in the diagnosis of square-pyramidal coordination geometry in Cu(II) complexes.

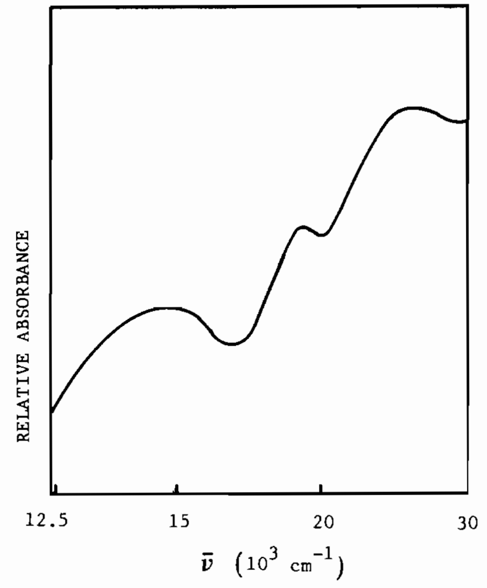


Fig. 3. Reflectance spectrum of solid complex *1*.

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