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Metal Pseudohalide Complexes.* Part VIII. Preparation and Structural Determination of a Polymeric 1:1 Complex of Copper(II) Azide with 3-Picoline, *Catena*-di-μ-azido-[di-μ-azido-bis(3-picoline)-dicopper(II)]

MOHAMED A. S. GOHER

Department of Chemistry, Faculty of Science, Alexandria University, Alexandria, Egypt

and THOMAS C. W. MAK

Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong

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A 1:1 complex of copper(II) azide with 3-picoline has been synthesized and shown to be polymeric by X-ray crystallography. The compound crystallizes in space group C2/c, with a = *23.120(9),* b = *13.751(4),* c = *6.663(2) Å,* β = *100.43(2)°, and Z = 8. The structure has been refined to* $R_F = 0.063$ *for 979 observed MoK*α *diffractometer data. Two azido ligands lying on a crystallographic diad bridge a pair of copper atoms to form a planar* Cu_2N_2 *ring. The rings are linked alternately by pairs of a third type of azido ligands which asymmetrically bridge copper atoms related by the* c *glide, giving rise to a composite column structure. The coordination geometry about the copper atom is distorted trigonal bipyramidal, with the 3-picoline ligand occupying one of the axial positions. Infrared and electronic spectral data are also presented and discussed.*

Introduction

X-Ray analysis of the polymeric complexes $Cu(NH_3)_2(N_3)_2$ [1] and $Cu(py)_2(N_3)_2$ [2] have revealed distorted octahedral coordination about each copper atom with four short (1.98–2.05 Å) and two long (2.50–2.76 Å) metal–ligand bonds. The two azido groups in each complex are in different structural environments: one functions as a terminal ligand whereas the other coordinates at both ends to three different copper centers. We recently established, as part of a continuing study of substituted pyridine complexes of metal pseudohalides, that crystalline $Cu(2\text{-aminopyridine})(N_3)_2(H_2O)$ comprises centrosymmetric dimeric molecules containing both terminal and $\mu(1)$-bridging azido ligands, with the copper atom in a distorted square pyramidal coordination [3]. Among other products obtained from the reaction of copper(II) azide with 3-picoline (hereafter abbreviated as 3-pic) in different media we have isolated a new 1:1 anhydrous crystalline complex whose structure elucidation by X-ray and spectroscopic methods is presented in this report.

TABLE I. Azide and Metal–Ligand Vibrational Modes in Polymeric $Cu(3\text{-pic})(N_3)_2$.

Frequency (cm^{-1})	Assignment
2100vs,sh 2070vs 2020vs	$\nu_{as}N_3$
1340m 1330m 1285s	ν_sN_3
615w 603wm 580m	δN_3
372ms 365ms	$\nu Cu{-}N_3$
240vs	$\nu Cu{-}N(3\text{-pic})$

s = strong, m = medium, w = weak, v = very, sh = shoulder.

Experimental

Preparation of the Complex

An ethanolic solution of 3-picoline (from BDH) (0.93 g, 10 mmol) was added to $Cu(NO_3)_2 \cdot 3H_2O$ (2.41 g, 10 mmol) dissolved in 30 ml ethanol. Upon dropwise addition of an aqueous solution of NaN_3 (1.0 g, 15.5 mmol, in 5 ml water) with thorough

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*Part VII is ref. [3].

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TABLE II. Data Collection and Processing Parameters.

Molecular formula	$C_6H_7N_7Cu$
Molecular weight	240.78
Cell constants	$a = 23.120(9)$ Å $\beta = 100.43(2)°$
	$b = 13.751(4)$ $V = 2083(1)$ Å^3
	$c = 6.663(2)$ $Z = 8$
Density (Calcd.)	1.536 g cm^{-3}
Space Group	$C2/c$
μ(MoKα)	20.75 cm^{-1}
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, k, ±l; $2\theta_{max} = 45°$
Unique data measured	1369
Observed data with $\|F\| > 3\sigma(\|F\|)$, n	979
Number of variables, p	133
$R_F = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$	0.063
Weighting scheme	$w = [\sigma^2(\|F_o\|) + 0.0008\|F_o\|^2]^{-1}$
$R_{wF} = [\Sigma w(\|F_o\| - \|F_c\|)^2/\Sigma w\|F_o\|^2]^{1/2}$	0.081
$S = [\Sigma w(\|F_o\| - \|F_c\|)^2/(n - p)]^{1/2}$	1.63

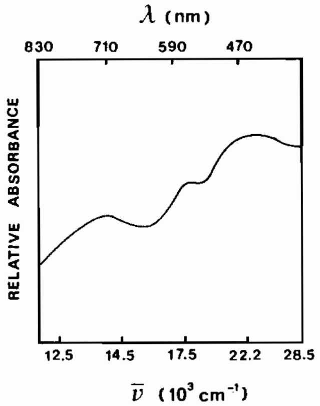

Fig. 1. Reflectance spectrum of solid $Cu(3\text{-pic})(N_3)_2$.

shaking after each addition, a deep green solution was obtained. This mixture was allowed to stand overnight to produce the complex as black needles together with a dark brown powder.

Elemental analysis of the crystalline product of empirical formula $C_6H_7N_7Cu$; % with calculated values in parentheses: C 29.27 (29.95); H 2.75 (2.93); N 40.52 (40.73); Cu 26.53 (26.39).

Spectral Data

The infrared absorption bands are listed in Table I and the electronic spectrum of the solid complex is shown in Fig. 1. The experimental procedures used in making the spectral measurements have been noted previously [3].

X-Ray Crystallography

A single crystal of approximate dimensions 0.05 × 0.05 × 0.20 mm (elongated about c) was centered on a Nicolet R3m computer-controlled diffractometer system. Data collection using graphite-monochromatized MoKα radiation ($\lambda = 0.71069$ Å) followed established procedures in our laboratory [4], and pertinent crystal data and processing information are summarized in Table II.

Space group $C2/c$ was favored by intensity statistics and later confirmed by structure analysis. Structure solution was achieved by direct phasing based on negative quartets [5], and all 17 non-hydrogen atoms were located from a subsequent difference Fourier map. After several cycles of blocked-cascade [6] anisotropic 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. The orientation of the methyl group was deduced from the next difference map, and the methyl H atoms were also treated using a riding model in the final least-squares cycles, which converged to the R_F and R_{wF} indices given in Table II. The final difference map was essentially flat, with residual extrema lying between 0.76 and −0.48 eÅ^{-3}.

All computations were performed on a Data General Corporation Nova 3/12 minicomputer with the SHELXTL program package [7]. Analytical expressions of neutral atom scattering factors were employed, and anomalous dispersion corrections were incorporated [8].

TABLE III. 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_{11}/U	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cu	6619(6)	6371(10)	35205(21)	274(8)	377(9)	357(8)	8(9)	−23(5)	−10(9)
N(1)	0	−298(11)	2500	34(9)	33(9)	52(10)	0	−7(8)	0
N(2)	0	−1167(14)	2500	51(11)	45(12)	41(10)	0	10(8)	0
N(3)	0	−1986(14)	2500	125(19)	47(13)	110(17)	0	−5(14)	0
N(4)	0	1502(11)	2500	30(9)	26(9)	67(11)	0	−1(8)	0
N(5)	0	2398(18)	2500	36(11)	126(20)	123(18)	0	11(12)	0
N(6)	0	3319(15)	2500	66(15)	51(14)	359(41)	0	13(20)	0
N(7)	1100(4)	−293(7)	5535(14)	25(6)	50(7)	37(6)	15(5)	0(5)	5(5)
N(8)	1608(4)	−450(7)	5642(13)	31(7)	48(7)	31(6)	3(5)	1(5)	1(6)
N(9)	2089(5)	−634(10)	5783(17)	33(7)	101(10)	73(8)	6(8)	9(6)	15(8)
N(10)	1230(4)	1729(7)	4281(14)	35(6)	37(6)	39(6)	0(5)	1(5)	−7(5)
C(1)	1292(5)	2400(9)	2899(21)	33(7)	47(9)	61(9)	−15(8)	9(7)	−10(7)
C(2)	1631(6)	3244(10)	3326(23)	42(8)	49(9)	89(12)	−6(9)	31(8)	−3(7)
C(3)	1941(6)	3321(11)	5353(23)	46(9)	63(10)	90(12)	−42(9)	−2(8)	−14(8)
C(4)	1885(6)	2652(11)	6739(23)	53(9)	56(10)	65(10)	−10(8)	−5(8)	−14(8)
C(5)	1529(5)	1854(11)	6183(19)	44(8)	73(10)	42(8)	−13(8)	−6(7)	0(8)
C(6)	1650(8)	3996(11)	1696(28)	100(14)	67(12)	111(15)	4(11)	47(12)	−19(11)
H(1)	1091	2301	1523	64					
H(3)	2197	3867	5730	96					
H(4)	2090	2723	8119	97					
H(5)	1495	1372	7197	69					
H(6*a*)	1711	4470	2812	120					
H(6*b*)	1283	4147	758	120					
H(6*c*)	1980	4026	958	120					

[a] Exponents of anisotropic and isotropic (assigned values for H atoms) temperature factors take the forms: $-2\pi^2 \Sigma_i \Sigma_j U_{ij} h_i h_j a_i^* \cdot a_j^*$ and $-8\pi^2 U \sin^2\theta/\lambda^2$, respectively.

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

Cu–N(1)	2.020(10)	Cu–N(4)	1.960(9)
Cu–N(7)	1.993(9)	Cu–N(10)	1.999(9)
Cu–N(7)^a	2.436(10)	N(1)–N(2)	1.19(2)
N(2)–N(3)	1.13(3)	N(4)–N(5)	1.23(3)
N(5)–N(6)	1.27(3)	N(7)–N(8)	1.19(1)
N(8)–N(9)	1.13(2)	N(10)–C(1)	1.33(2)
N(10)–C(5)	1.34(2)	C(1)–C(2)	1.40(2)
C(2)–C(3)	1.41(2)	C(2)–C(6)	1.51(2)
C(3)–C(4)	1.33(2)	C(4)–C(5)	1.38(2)
N(1)–Cu–N(4)	76.9(5)	N(1)–Cu–N(7)	94.5(4)
N(1)–Cu–N(10)	170.5(4)	N(1)–Cu–N(7)^a	90.2(2)
N(4)–Cu–N(7)	153.2(3)	N(4)–Cu–N(10)	93.9(4)
N(4)–Cu–N(7)^a	104.4(2)	N(7)–Cu–N(10)	94.7(4)
N(7)–Cu–N(7)^a	101.0(3)	N(10)–Cu–N(7)^a	90.1(4)
Cu–N(1)–N(2)	129.5(3)	Cu–N(4)–N(5)	127.4(4)
Cu–N(7)–N(8)	122.3(8)	Cu–N(7)^a–N(8)^a	118.0(7)
Cu–N(1)–Cu^b	100.9(7)	Cu–N(4)–Cu^b	105.3(7)
Cu–N(7)^a–Cu^a	116.1(5)	N(7)–N(8)–N(9)	177.2(13)
Cu–N(10)–C(1)	119.7(8)	Cu–N(10)–C(5)	122.6(9)
C(1)–N(10)–C(5)	117.6(11)	N(10)–C(1)–C(2)	124.2(12)
C(1)–C(2)–C(3)	115.1(13)	C(1)–C(2)–C(6)	120.7(13)
C(3)–C(2)–C(6)	124.2(13)	C(2)–C(3)–C(4)	121.1(13)
C(3)–C(4)–C(5)	119.5(13)	N(10)–C(5)–C(4)	122.4(13)

Symmetry transformations: ^{a}x, −y, −: + z; ^{b}−x, y, ½ − z.

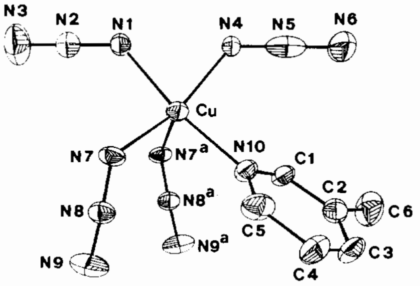

Fig. 2. A perspective view of the coordination geometry about the Cu(II) atom. Thermal ellipsoids are drawn at the 35% probability level, and hydrogen atoms have been omitted for clarity.

The final positional and thermal parameters are listed in Table III. Atom labelling in the asymmetric unit are shown in Fig. 2, and bond distances and angles in Table IV. A table of structure factors has been deposited with the Editor.

Discussion

Infrared Spectrum

The band assignments in Table I are facilitated by comparison of the spectrum with those of the free ligand and of the related $Cu(3\text{-pic})_2(SCN)_2$ complex. The strong split band with at least three peaks between 2100 cm^{-1} and 2020 cm^{-1} can be attributed to asymmetric azide stretching [9, 10]. This splitting of $\nu_{as}N_3$ is very similar to that reported [11] for tetrahedral $Zn(NH_3)_2(N_3)_2$, which contains four asymmetric and crystallographically different azido groups. The stretching band at approximately 1300 cm^{-1} also provides strong evidence for the asymmetric nature of the azido ligands.

Electronic Spectrum

The solid complex has its *d–d* band lying at 13,888 cm^{-1}, accompanied by a distinct absorption band at 18,018 cm^{-1}. The present *d–d* value falls in the range of those usually found for five-coordinate copper(II) complexes [12, 13]. The whole spectrum (Fig. 1) in fact closely resembles that reported (see Fig. 3 of ref. 3) for discrete dimeric $[Cu(2\text{-ampy})(N_3)_2(H_2O)]_2$ which features square pyramidal metal coordination, except that corresponding bands in the latter are shifted to higher energies at 14,490 cm^{-1} and 18,860 cm^{-1}, respectively. Further work is needed to ascertain whether these two spectral curves may be used to differentiate between trigonal bipyramidal and square pyramidal coordination geometries in copper(II) azide complexes.

Crystal Structure

In accordance with expectation, the 3-picoline ligand is bound to the copper atom. More unusual is the fact that the asymmetric unit (Fig. 2) contains three distinct $\mu(1)$-bridging azido groups: ligands *I* [N(1) to N(3)] and *II* [N(4) to N(6)] lying on the

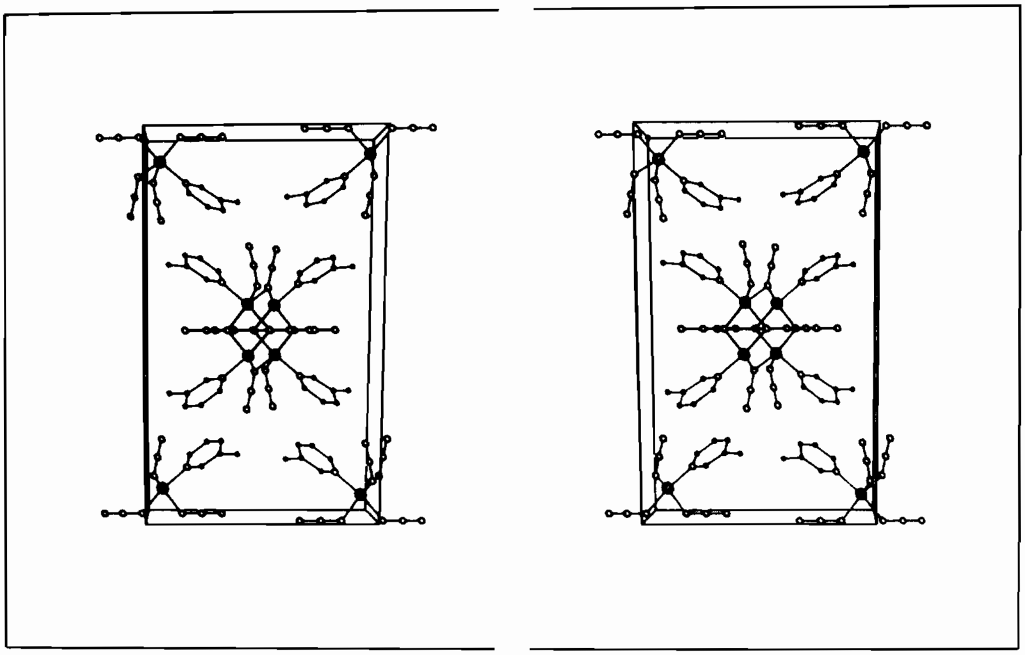

Fig. 3. Stereodrawing of the polymeric structure of crystalline $Cu(3\text{-pic})(N_3)_2$. The composite columns are viewed almost end-on. The origin of the unit cell lies at the upper left corner, with *a* pointing downwards, *b* from left to right, and *c* towards the reader.

same crystallographic diad, and *III* [N(7) to N(9)] occupying a general position. Azides *I* and *II* bridge a pair of Cu atoms related by two-fold rotation, forming a planar Cu_2N_2 ring, whereas *III* asymmetrically links alternate Cu atoms generated by the *c*-glide operation to yield an infinite zigzag chain. The crystal structure is built up from composite columns all aligned parallel to the *c* axis, lateral packing being rendered efficient through juxtaposition of neighbouring columns by *C*-lattice centering (Fig. 3). In view of its polymeric nature, the complex should be formulated as *catena*-di-μ-azido-[di-μ-azido-bis(3-picoline)dicopper(II)].

Coordination of the Cu(II) atom by the 3-picoline and azido ligands may be described as distorted trigonal bipyramidal, with N(1) and N(10) in the axial positions and N(4), N(7) and $N(7)^a$ in the equatorial positions (Fig. 2). The shortest and longest metal–ligand bonds are Cu–N(4) = 1.960(9) Å and Cu–$N(7)^a$ = 2.436(10) Å respectively, while the other three are virtually equal at 1.993(9)–2.020(10) Å (Table IV) and compare well with corresponding distances observed in the discrete dimer $[Cu(2\text{-ampy})(N_3)_2(H_2O)]_2$. Strong bonding of Cu with N(4) is reflected in the significantly longer N–N bonds within azide *II*, as compared to those in *I* and *III* (Table IV). On the other hand, the much weaker interaction between Cu and $N(7)^a$ is consistent with the fact that angle N(4)–Cu–N(7) exceeds the other two angles in the 'equatorial plane' of the CuN_5 kernel by about 50°. To a good approximation the present complex consists of dimeric $[Cu(3\text{-pic})(N_3)_2]_2$ units which are further connected by weaker metal-azide bonds to yield a polymeric structure (Figs. 2 and 3).

In the 3-picoline ligand, the shortest C–C bond occurs between C(3) and C(4), and the molecular skeleton plus the Cu–N(10) bond are exactly planar. The steric bulk of the organic ligand accounts for the fact that the three N(10)–Cu–N(equatorial) angles are all obtuse.

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