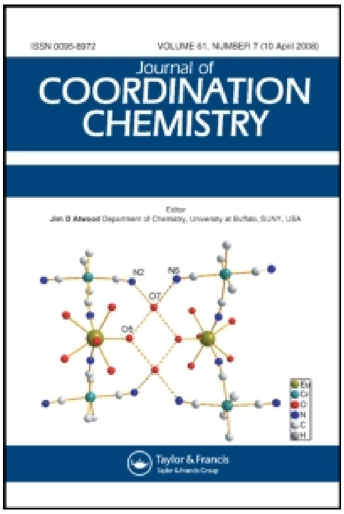

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STRUCTURAL AND SPECTROSCOPIC INVESTIGATION OF DI-ü-(1,1)-AZIDO-DI(*O,O'*-NITRATO)*TETRAKIS*(3-ACETYLPYRIDINE) DICOPPER(II)

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STRUCTURAL AND SPECTROSCOPIC INVESTIGATION OF DI-μ-(1,1)-AZIDO-DI(*O,O'*-NITRATO)*TETRAKIS*(3-ACETYLPYRIDINE) DICOPPER(II)

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A mixed-ligand, 1:2 complex for copper(II) azide with 3-acetylpyridine, namely, di-μ(1,1)-azido-di-(*O,O'*-nitrato)*tetrakis*(3-acetylpyridine)dicopper(II), has been synthesized and characterized by spectroscopic and X-ray crystallographic methods. Spectroscopic results suggest bidentate chelate nitrato groups and a μ(1,1) bridging azido ligand. The dimeric molecule, which possesses a crystallographic inversion centre, contains two μ(1,1) bridging azido ligands. Each copper(II) atom in the cyclic Cu_2N_2 ring is further coordinated by two oxygen atoms from a bidentate, chelating nitrato group [Cu-O = 2.022(8) and 2.571(9)Å] and two nitrogen atoms [Cu-N = 1.995(7) and 2.014(8)Å] from the 3-acetylpyridine molecules. The coordination environment of the copper atom may be described as a very distorted tetragonal bipyramid with a nitrogen atom of an azide group and one oxygen atom of a nitrato group occupying the apical sites. The azido ligands are almost linear [N-N-N angle = 175.9(10)°] and asymmetric (N_α-N_β = 1.235(12) and N_β-N_γ = 1.127(13)Å].

KEYWORDS: copper(II), azide, nitrate, 3-acetylpyridine, X-ray structure

INTRODUCTION

Monopyridyl ketones are potentially bidentate or ambidentate ligands, which may show interesting coordination properties towards metal ions in the border region between class (a) and class (b) acceptors,[1] such as cobalt(II) and nickel(II). On the other hand, the nitrato ligand, NO_3^-, has often been found to behave as a monodentate or a bidentate chelate ligand[2-10] and seldom shows the μ-(*O,O'*) bridging mode in its copper(II) complexes.[11-13] The azido ligand, N_3^-, is also a versatile bridging ligand that can bind two copper atoms in either an end-on (μ-1,1)[14-20] or end-to-end (μ-1,3) mode.[21-24]

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Recently we have shown that copper(II) nitrate trihydrate interacts with 3-picoline in ethanol in the presence of sodium azide to produce a dinuclear copper(II) complex, $[Cu_2(N_3)_2(NO_3)_2(3\text{-picoline})_4(H_2O)]$ with different ligating nitrato groups,[25] whereas similar reactions in acetone with 3,5-dimethylpyridine instead of 3-picoline yielded the complex $[Cu(N_3)(NO_3)(3,5\text{-dimethylpyridine})_2]_2$ which contains only μ-(*O,O′*) nitrato groups.[26] Further work led to the isolation of the title complex whose structure elucidation by spectroscopic and X-ray crystallographic methods is presented in this report. The present work constitutes part of our continuing study of metal pseudohalide complexes containing substituted pyridine ligands.[27,28]

EXPERIMENTAL

Preparation of Complex 1

Copper(II) nitrate trihydrate (0.48 g, 2 mmol) and 3-acetylpyridine (0.73 g, 6 mmol) were mixed together in about 40 cm^3 of acetone. To this mixture, NaN_3 (0.20 g, 3 mmol) dissolved in 5 cm^3 of water was added dropwise. The solution was shaken thoroughly after each addition until its colour became green. This mixture was filtered and the filtrate allowed to stand for several days in an open conical flask until dark green crystals separated. Anal.: calc. (found) for $C_{28}H_{28}Cu_2N_{12}O_{10}$: C, 41.0 (41.1); H, 3.4 (3.3); N, 20.5 (20.4); Cu, 15.5 (15.5)%. The experimental procedures and instruments used for the spectroscopic and other measurements are as described previously.[28]

X-ray Crystal Structure Analysis of 1

X-ray measurements were made on a crystal mounted inside a flame-sealed 0.3 mm thin-walled glass capillary under nitrogen atmosphere. Orientation matrix and lattice parameters were obtained on a modified STOE four circle diffractometer by least-squares refinement of the diffraction data from 27 reflections in the 2θ range 8–20°. Intensity data ($\pm h$, $\pm k$, l; 3519 reflections, $2\theta_{max} = 52°$) were collected at 298(1)K using Mo-Kα radiation (λ = 0.71069 Å, graphite monochromator) and the ω-2θ-scan technique. The data were corrected for Lorentz and polarisation effects, and for absorption.[29] Equivalent reflections were averaged [$R_{merge} = 0.037$ on (I)] and those 1594 with $F_o > 3\sigma(F_o)$ were retained for structure analysis. Crystallographic data are given in Table 1.

The structure was solved by the heavy-atom approach. Approximate copper atom coordinates were derived from a Patterson map. The remaining non-hydrogen atoms were located in a weighted F_o Fourier synthesis phased by the copper atom. Several rounds of full-matrix least-squares adjustments of non-hydrogen atom positional and thermal parameters (at first isotropic, then anisotropic) followed. Hydrogen atoms were incorporated at their calculated positions in the later iterations which converged (max. shift:esd = 0.02) at $R = 0.064$ ($R_w = 0.062$). A final difference Fourier synthesis revealed no unusual features (max. 0.76, min. −0.81 e/Å^3; both in the vicinity of the copper atom). Crystallographic calculations were performed using the programs DIFABS,[29] SHELX-76,[30] SHELXS-86,[31] PLATON[32] and XRAY SYSTEM.[33] For all structure-factor calculations, neutral

Table 1 Crystallographic data for $[Cu(N_3)(NO_3)(3\text{-acethylpyridine})_2]_2$, 1.

Molecular formula	$C_{28}H_{28}Cu_2N_{12}O_{10}$
Molecular weight	819.70
Crystal system	Triclinic
Space group	$P\bar{1}$ (No. 2)
a/Å	7.996(3)
b/Å	9.995(3)
c/Å	11.044(4)
α(°)	96.75(3)
β(°)	107.82(3)
γ(°)	95.44(3)
V/Å^3	826.4(5)
Z	1
F(000)	418
μ(MoKα)/mm^{-1}	1.36
D_{calc};D_{obs}/g cm^{-3}	1.647;1.63(2)
Approx. crystal size (mm)	0.35 × 0.25 × 0.08
Data collection limits	$\pm h$, $\pm k$, l; $2\theta < 52°$;
Scan mode and width/(°)	ω-2θ-scan; 1.80
Intensity control refl.; variation	022, -211, -222; <3%
Total no. of refls. recorded	3519
Obs. refls. $(F_o > 3\sigma(F_o))$	1594
Least squares parameters	243
$R = \Sigma\|\|F_o\|-\|F_c\|\| / \Sigma\|F_o\|$	0.064
$R_w = [\Sigma w(\|F_o\|-\|F_c\|)^2/\Sigma w\|F_o\|^2]^{1/2}$	0.062
Weighting scheme	$1.645\sigma^{-2}(F_o)$
Final Δρ(eÅ^{-3})max.; min.	0.76; -0.81

atom scattering factors and their anomalous dispersion corrections were taken from ref. 34. In the least-squares iterations, $\Sigma w\Delta^2$ [$w = 1.645/\sigma^2(|F_o|)$, $\Delta = (|F_o|-|F_c|)$] was minimized. Fractional atomic coordinates are listed in Table 2; selected distances and bond angles are given in Table 3. A view of the solid-state structure of 1, with the atom numbering scheme, is presented in Figure 1.

RESULTS AND DISCUSSION

The present study has shown the title complex to be $[Cu(N_3)(NO_3)(3\text{-acetylpyridine})_2]_2$ (Fig. 1) in which the dinuclear molecule is disposed about a crystallographic inversion centre. The azido ligand functions as a μ(1,1) bridge, giving rise to a cyclic Cu_2N_2 unit. The Cu-N(N_3) distances of 1.987(8) and 2.339(8)Å within the Cu_2N_2 ring match corresponding values usually reported for copper(II) azido complexes of related organic ligands containing a dinuclear Cu_2N_2 core.[14–20] The Cu-N(N_3)-Cu angle (Table 3), however, is a little smaller than that reported [103.1(1)°] for the dimeric molecule [Cu)2-aminopyridine) $(N_3)_2$ $(H_2O)]_2$,[16] but greater than that observed [93.6(1)°] in the structure of [Cu(2-Bzpy)$(N_3)_2$] (2-Bzpy = 2-benzoylpyridine).[20] Each copper atom in the Cu_2N_2 unit is further coordinated by two oxygen atoms from a bidentate chelating nitrato group at Cu-O distances of 2.022(8) and 2.571(9)Å, and two nitrogen atoms from the 3-acetylpyridine molecules with Cu-N bond lengths of 1.995(7) and 2.014(8)Å. The latter Cu-N distances are very close to corresponding values found in copper(II) azido complexes of other 3-substituted pyridine ligands, *e.g.*, Cu(3-picoline)$(N_3)_2$

Table 2 Non-hydrogen atom fractional coordinates (× 10^4) and equivalent isotropic thermal parameters (× 10^3) for $[Cu(N_3)(NO_3)(3\text{-acetylpyridine})_2]_2$, 1. ($U_{eq}$ is one third of the trace of the U_{ij} tensor; estimated standard deviations in parantheses).

Atom	*x/a*	*y/b*	*z/c*	U_{eq}(Å^2)
Cu(1)	364(2)	3913(1)	3905(1)	28(1)
N(11)	1823(9)	5453(7)	5226(8)	34(5)
N(12)	3447(11)	5639(8)	5747(8)	38(6)
N(13)	4914(10)	5849(10)	6286(11)	68(8)
N(3)	-641(12)	1865(9)	1900(10)	47(7)
O(3)	-1437(9)	2449(7)	2620(8)	44(5)
O(4)	1003(10)	2234(8)	2205(8)	58(6)
O(5)	-1473(13)	984(9)	958(9)	85(8)
N(1)	1106(9)	2543(7)	5069(8)	26(5)
C(1)	2779(11)	2207(9)	5372(9)	29(6)
C(2)	3349(11)	1291(8)	6187(10)	28(6)
C(3)	2184(12)	723(9)	6773(11)	40(7)
C(4)	473(12)	1049(9)	6438(10)	32(6)
C(5)	11(12)	1960(9)	5621(10)	37(7)
C(6)	5247(13)	964(9)	6506(11)	37(6)
C(7)	5842(14)	16(12)	7423(13)	64(9)
O(1)	6168(9)	1467(8)	5936(9)	59(6)
N(2)	-25(9)	5111(7)	2526(8)	31(5)
C(8)	-1680(11)	5452(9)	1968(9)	29(6)
C(9)	-1978(11)	6342(9)	1078(9)	28(6)
C(10)	-557(12)	6836(10)	712(11)	40(6)
C(11)	1104(13)	6484(10)	1259(10)	39(6)
C(12)	1321(12)	5635(10)	2181(11)	37(6)
C(13)	-3797(13)	6721(10)	574(11)	40(7)
C(14)	-4162(14)	7580(13)	-450(13)	62(8)
O(2)	-4940(9)	6322(8)	1030(9)	60(6)

[Cu-N(L) = 1.999(9)Å],[17] $Cu(3\text{-picoline})_2(N_3)_2$ Cu-N(L) = 2.010(6)Å].[35] The coordination about each copper atom in the dinuclear centrosymmetric complex molecule may be described as a very distorted tetragonal bipyramid with a nitrogen atom of the azido ligand and one oxygen atom of the nitrato group occupying the apical sites (Fig. 1).

In agreement with general aspects already found for coordinated azido groups, both μ(1,1)-bridging azides are almost linear (Table 3). They are, however, asymmetric with the long N-N distances being between the central nitrogen atom and the nitrogen atom bonded to the metal atom. The asymmetry of the two azido groups (Δd), that is the difference between the two N-N distances, is much greater than Δd found in any other copper(II) azido complex containing μ(1,1) azides [range from 0.01 to 0.09 Å].[14–20] The Δd value of 0.11 Å found in the present structure, however, agrees with that reported for $[Cu(N_3)_2]_\infty$ [Δd = 0.12Å], containing the μ(1,1,3)-bridging azido ligand.[36] The Cu...Cu distance of 3.282(2) Å within the Cu_2N_2 unit is intermediate between those reported for $Cu(2\text{-picoline})(N_3)_2$ [3.095(1)Å][37] or $[Cu(N_3)_2]_\infty$ [3.08(1)Å][36] and the value of 3.78(1)Å found for $Cu(N_3)_2L'$ (L' = 2-aminoethylpyridine).[38]

The structure of the title complex 1 differs from that of $[CU_2(N_3)_2(NO_3)_2(3\text{-picoline})_4(H_2O)]$, 2, and $[Cu(N_3)(NO_3)(3,5\text{-dimethylpyridine})_2]_2$, 3, although 2 and 3 feature six-coordinate copper(II) stereochemistry, μ(1,1)-bridging azido ligands and dinuclear Cu_2N_2 units.[24,25] In complex 2, which lacks the inversion centre that relates the Cu polyhedra in 1, the nitrato groups function differently; one group acts

Table 3 Interatomic distances (Å) and angles (deg.) for $[Cu(N_3)(NO_3)(3\text{-acetylpyridine})_2]_2$, 1, with estimated standard deviations in parantheses.

Cu(1)...Cu(1′)	3.283(2)	Cu(1)-O(3)	2.022(8)
Cu(1)-O(4)	2.571(9)	Cu(1)-N(1)	1.995(7)
Cu(1)-N(2)	2.014(8)	Cu(1)-N(11)	1.987(8)
Cu(1)-N(11′)	2.339(8)	O(1)-C(6)	1.217(13)
O(2)-C(13)	1.229(14)	O(3)-N(3)	1.284(13)
O(4)-N(3)	1.260(13)	O(5)-N(3)	1.245(14)
N(11)-N(12)	1.235(12)	N(12)-N(13)	1.127(13)
O(3)-Cu(1)-O(4)	54.5(3)	O(3)-Cu(1)-N(1)	89.5(3)
O(3)-Cu(1)-N(2)	88.5(3)	O(3)-Cu(1)-N(11)	171.4(3)
O(3)-Cu(1)-N(11′)	89.9(3)	O(4)-Cu(1)-N(1)	85.1(3)
O(4)-Cu(1)-N(2)	83.3(3)	O(4)-Cu(1)-N(11)	133.9(3)
O(4)-Cu(1)-N(11′)	144.4(3)	N(1)-Cu(1)-N(2)	167.0(3)
N(1)-Cu(1)-N(11)	92.8(3)	N(1)-Cu(1)-N(11′)	94.4(3)
N(2)-Cu(1)-N(11)	91.1(3)	N(2)-Cu(1)-N(11′)	98.4(3)
N(11)-Cu(1)-N(11′)	81.6(3)	Cu(1)-O(3)-N(3)	107.2(6)
Cu(1)-O(4)-N(3)	81.8(6)	O(3)-N(3)-O(4)	116.3(9)
O(3)-N(3)-O(5)	120.9(10)	O(4)-N(3)-O(5)	122.8(11)
Cu(1)-N(11)-N(12)	128.0(7)	N(12)-N(11)-Cu(1')	128.2(7)
Cu(1)-N(11)-Cu(1′)	98.4(3)	N(11)-N(12)-N(13)	175.9(10)
C(2)-C(6)-0(1)	117.2(9)	O(1)-C(6)-C(7)	123.4(10)
C(9)-C(13)-O(2)	119.3(9)	O(2)-C(13)-C(14)	121.9(10)

symmetry code: (′) $-x$, $1-y$, z.

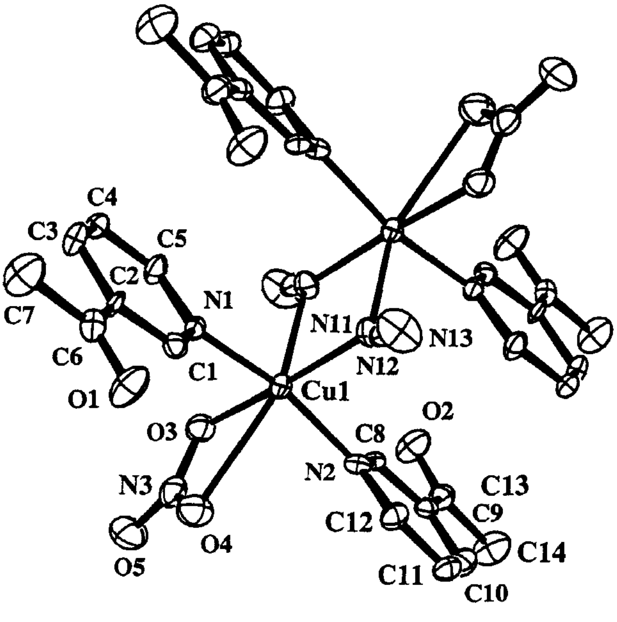

Figure 1 ORTEP diagram showing the atom numbering scheme and solid state conformation of $[Cu(N_3)(NO_3)(3\text{-acetylpyridine})_2]_2$, 1; unlabelled atoms are related to the labelled atoms by a crystallographic centre of symmetry. Hydrogen atoms are omitted for clarity.

as a monodentate ligand whereas the other behaves as a bidentate bridge with Cu-O distances of 2.681(9) and 2.668(8)Å. The structure of 3 resembles that of 1, except that the nitrato groups in 3 act as μ(*O,O′*) bridging groups with Cu-O distances of 2.465(3) and 2.568(3)Å. As compared to 2 and 3, the Cu-N(L) distances in 1 match very well the Cu-N(pic) distances [from 1.985(9) to 2.017(9) Å in 2 and Cu-N(lut) [2.003(3) and 2.012(3)Å] in 3, whereas the Cu...Cu distance is larger than 3.087(3) Å in 2[24] or 3.013(2)Å found in 3.[25]

The structures of dimeric complexes 1–3 are different from the linear polymeric copper(II) complex $[Cu_2(N_3)_2(NO_3)_2(Me_3NCH_2CO_2)_2]_n$, 4.[13] The structure of 4 contains two copper atoms in chemically different environments. Cu(1) is *trans*-coordinated by two carboxy oxygens in an elongated octahedral environment. Cu(2) is *trans*-coordinated by two nitrato oxygens and *cis*-coordinated by two carboxy oxygens and two azido nitrogens to adopt another elongated octahedral geometry. Every pair of adjacent copper atoms are simultaneously bridged by μ(1,1) azido, μ(*O,O′*)-nitrato and μ(*O,O*)-carboxy groups of the (trimethylammonio)acetato ligand. The apical positions of both polyhedral are occupied by oxygen atoms of nitrato groups [Cu-O = 2.419(4) and 2.446(3)Å]. The remaining copper-ligand bond lengths are in the range 1.960(4) to 1.997(3)Å. The separation of the two different copper(II) centres in complex 4 [3.436(1) Å] is much longer than in 1, giving rise to an unusually large Cu-N(N_3)-Cu angle of 119.5(2)°.[13]

The IR spectrum of the solid complex shows a very strong band at 2050 cm^{-1} associated with the asymmetric stretch mode of the azide group. The position of this band is not consistent with the $\nu_{as}N_3$ *vs* Δd (Δd = difference between the two N-N bond distances) relationship reported earlier for other azido complexes.[39,40] However, the appearance of a single $gn_{as}N_3$ band agrees well with the crystal structure results which revealed that both azido ligands have the same degree of asymmetry (Δd = 0.11 Å). This great degree of asymmetry is strongly evidenced by the appearance of a very strong band at 1275 cm^{-1} and a medium band at 1360 cm^{-1}. The spectrum exhibits also strong to very strong nitrato vibration bands at 1450, 1290 and 1010 cm^{-1}. The separation of the two highest frequency bands by 160 cm^{-1} suggests the presence of chelating bidentate nitrato ligands.[41] In the far infrared region, we tentatively assigned to the metal-ligand vibrations the following frequencies[41]: 365 and 345 cm^{-1} to ν[Cu-N(N_3)], the bands at 315 and 290 cm^{-1} to ν[Cu-O(NO_3)] and the bands at 268 and 235 cm^{-1} to ν[Cu-N(L)].

The electronic spectrum of 1 measured as a solid mulled in nujol shows a d-d absorption band around 16,400 cm^{-1}, suggesting a six-coordinate *pseudo*-octahedral copper(II) environment.[42,43] A strong absorption band at 25,640 cm^{-1} is due to $N_3 \rightarrow Cu(II)$ charge transfer. Surprisingly, the spectrum does not exhibit any absorption band in the region 17,000-20,000 cm^{-1}, as is frequently observed in copper(II) azido complexes containing a binuclear Cu_2N_2 unit with μ(1,1) bridging azido ligands.[16–20]

SUPPLEMENTARY DATA

Additional material consisting of hydrogen atom coordinates, displacement parameters, observed and calculated structure factors and a complete list of bond distances and bond angles is available from F.A.M.

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