Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Bis(2,2′-bipyridine)nitratocopper(II) nitrate

Katayoun Marjani,[a] Sian C. Davies,[b]* Marcus C. Durrant,[c] David L. Hughes,[b] Nejat Khodamorad[a] and Assadolah Samodi[a]

[a]Faculty of Chemistry, Teacher Training University, 49 Mofateh Avenue, 15614 Tehran, Iran, [b]Department of Biological Chemistry, John Innes Centre, Norwich Research Park, Colney, Norwich NR4 7UH, England, and [c]Computational Biology Group, John Innes Centre, Norwich Research Park, Colney, Norwich NR4 7UH, England

Correspondence e-mail: sianc.davies@bbsrc.ac.uk

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.012 Å
R factor = 0.049
wR factor = 0.092
Data-to-parameter ratio = 8.5

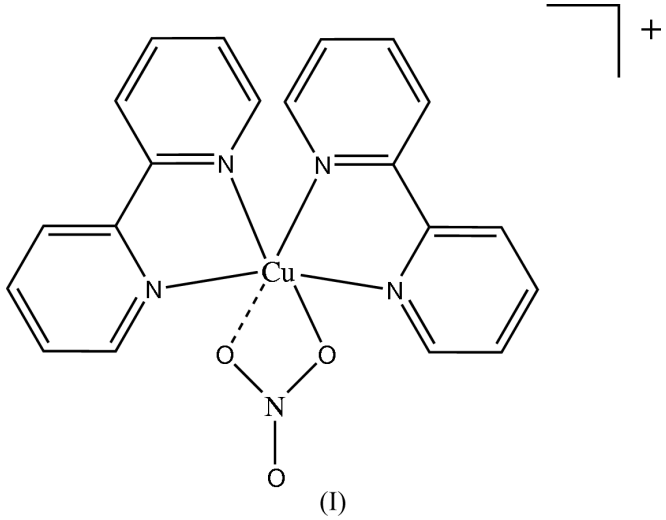
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 16 August 2004
Accepted 22 November 2004
Online 4 December 2004

The title complex, $[Cu(C_{10}H_8N_2)_2(NO_3)]NO_3$, is the first reported unsolvated $[Cu(bipy)_2(NO_3)]NO_3$ structure (bipy is 2,2′-bipyridine). The Cu^{II} atom of the $[Cu(bipy)_2(NO_3)]^+$ complex is six-coordinated, forming a distorted octahedral geometry; bond lengths to the N atoms of the pyridine rings and one of the O atoms of the chelating NO_3 ligand lie in the range 1.975 (5)–2.139 (6) Å, with the second O atom from the NO_3 ligand less tightly coordinated at a distance of 2.520 (6) Å. The geometry of the $CuN_2N'_2OO'$ chromophore more closely resembles that of $[Cu(bipy)_2(NO_2)]^+$ complexes than previously reported $[Cu(bipy)_2(NO_3)]^+$ structures.

Comment

The Cu atom of the title complex, (I), is distorted octahedrally coordinated and is ligated by the four bipyridine N atoms and a chelating NO_3 group, for which one of the O-atom donors lies further from the Cu atom due to Jahn–Teller distortions (Fig. 1).



(I)

The Cu atom has a (4 + 1′ + 1*) stereochemistry (Hathaway, 1973) with pseudo-C_2 symmetry bisecting the NO_3 ligand and passing between the bipyridine ligands. The atoms of the vectors N111···N221 and N121···O31 lie 3.965 (7) and 4.009 (8) Å apart, respectively, and are designated as forming the equatorial plane, with elongation of the N211···O32 distance to 4.512 (8) Å (designated as the axial atoms). The corresponding *X*—Cu—*Y* angles are also distorted from the ideal octahedral value of 180°, with N111—Cu—N221 = 176.2 (3)°, N121—Cu—O31 = 150.0 (2)° and N211—Cu—O32 = 154.4 (2)°. The distortions in the coordination geometry

agree with observations reported (Walsh *et al.*, 1981) for pseudo-Jahn–Teller structures, *i.e.* as one Cu—O bond lengthens, the other shortens, the Cu—N bond *trans* to each O atom lengthens or shortens, respectively, while the second Cu—N bond within the same bipyridine ligand also lengthens or shortens correspondingly but by a smaller amount.

The Cu—N bond lengths to the N atoms in the equatorial plane lie in the range 1.975 (5)–2.013 (6) Å, with the elongated axial Cu—N211 bond length being 2.106 (6) Å (see Table 1); the equatorial Cu—O31 bond length is not unusual, being 2.138 (6) Å (Orpen *et al.*, 1989). The axial NO_3 atom O32 lies 2.520 (6) Å from the Cu atom and constitutes the major distortion from regular octahedral coordination. There are no unusual bond dimensions within either the bipyridine ligands or the chelating NO_3 ligand, where N—O bond lengths lie within the range 1.198 (7)–1.257 (7) Å. Within the nitrate anion, bond lengths lie in the range 1.194 (7)–1.235 (7) Å, as usual for this group.

The coordination geometry about the Cu atom in (I) is intermediate between reported (Chemical Database Service, Council for the Central Laboratory of the Research Councils, Daresbury Laboratory) $[Cu(bipy)_2(NO_2)]^+$ structures, *e.g.* $[Cu(bipy)_2(NO_2)]NO_3$ [(II) (Proctor & Stephens, 1969) and (III) (Simmons *et al.*, 1983, 1987)], $[Cu(bipy)_2(NO_2)]BF_4$ [(IV); Walsh *et al.*, 1981], and the four reported $[Cu(bipy)_2(NO_3)]NO_3$ structures $[Cu(bipy)_2(NO_3)]NO_3\cdot H_2O$ [(V) (Nakai, 1980), (VI) (Fereday *et al.*, 1981), (VII) (Catalan *et al.*, 1995)] and $[Cu(bipy)_2(NO_3)]NO_3\cdot HDCI\cdot H_2O$ [(VIII); Prasad *et al.*, 1999; HDCI is 4,5-dicyanoimidazole] (see Table 2). Coordination by the second O atom in (I) at 2.520 (6) Å is tighter than in the reported solvated $[Cu(bipy)_2(NO_3)]^+$ complexes, but is looser than in the $[Cu(bipy)_2(NO_2)]^+$ complexes at room temperature. However, angles about the Cu atom in (I) more closely resemble those in the NO_2-ligated structures than the NO_3-ligated structures, leading to a geometry closer to those in the unsolvated structures.

The crystal packing of the complex in (I) is also similar to that found in the three NO_2-ligated structures, with the cations forming corrugated planes seen edge-on when viewed along the crystallographic *c* axis (Fig. 2). The anions in (I) lie at the apices of the ridges in the cationic 'planes' and form correspondingly corrugated intercationic planes; the anions overlap the ligated NO_3 groups to form chains parallel to the crystallographic *c* axis. This arrangement is as found in the crystal packing of (II), (III) and (IV), where the $[BF_4]^-$ anion in (IV) occupies the same relative position as that of the $[NO_3]^-$ anions in (II) and (III). The inclusion of solvent water in the four previously reported $[Cu(bipy)_2(NO_3)]^+$ structures introduces hydrogen bonding between the anion and solvent molecules and the packing arrangements in these crystal structures differ from those of the NO_2-ligated complexes. Structures (V), (VI) and (VIII) consist of alternating flat cationic and anionic planes. The ligated NO_3 groups in (V) and (VI) lie within the anionic planes, with the water molecules lying within the cationic planes. In (VIII), the HDCI and water molecules all lie within the anionic planes. The packing arrangement in (VII) is different in that the cations form a

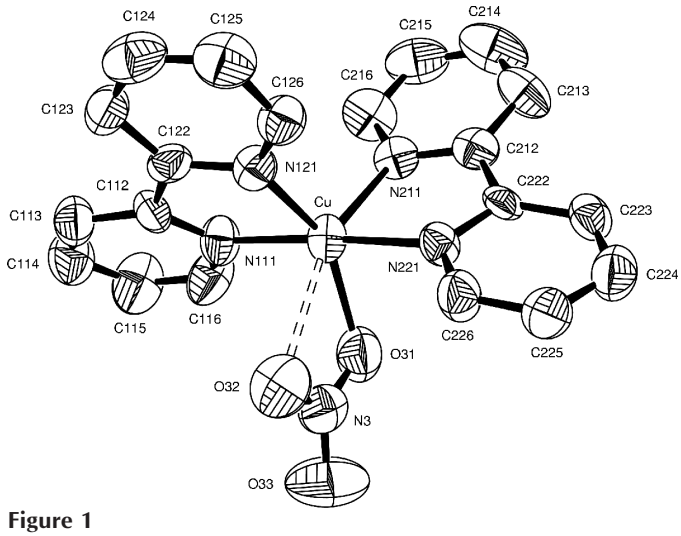


Figure 1
A view of the cation of (I). Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity.

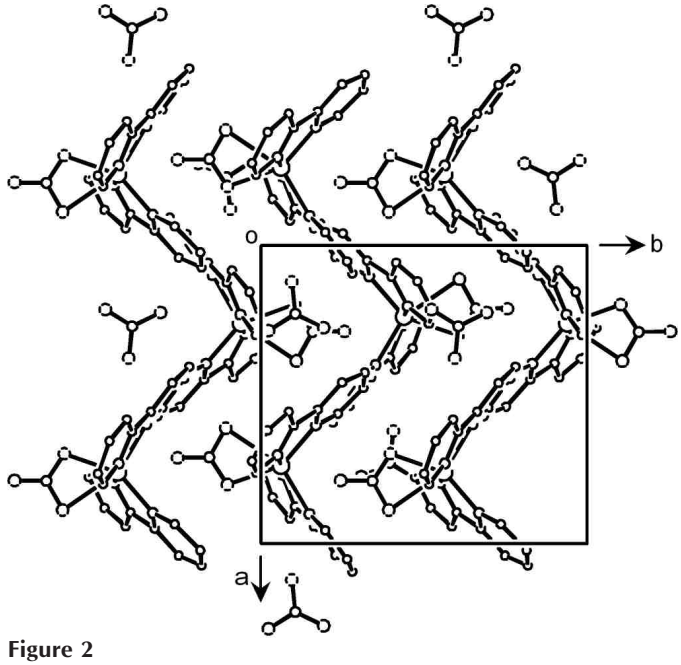


Figure 2
Packing diagram of (I), viewed along the crystallographic *c* axis. Atoms are represented by arbitrary spheres. H atoms have been omitted.

three-dimensional framework, with the anions and water molecules lying in planes within this framework.

These results indicate the sensitivity of the Cu coordination geometry in $[Cu(bipy)_2(NO_3)]^+$ structures to factors such as the identity of the anion and the presence of solvent in the crystal structure. The above examples of $[Cu(bipy)(NO_2)]^+$ coordination complexes crystallize in space group No. 14, $P2_1/n$, with similar unit cells and crystal packing. Hydrogen bonding in the solvated $[Cu(bipy)_2(NO_3)]^+$ structures, however, leads to different molecular arrangements; most crystallize in space group $P\overline{1}$, with different unit cells but similar packing arrangements.

Complex (I) is the first reported unsolvated $[Cu(bipy)_2(NO_3)]NO_3$ structure and, although the coordination

geometry may be considered to be similar to that in the structure $[Cu(bipy)_2(NO_3)]NO_3{\cdot}HDCI{\cdot}H_2O$ (Prasad *et al.*, 1999), it more closely resembles the $[Cu(bipy)_2(NO_2)]^+$ structures, both in coordination geometry about the Cu atom and in having a similar packing arrangement in the same space group, *viz.* $P2_1/n$.

Experimental

The preparation of the title compound was carried out under a dinitrogen atmosphere. To a stirred solution of $[Cu(NO_3)(SC_5H_4NH)_2]$ (0.26 g, 0.74 mmol), prepared according to the literature procedure of Davies *et al.* (1997), in MeOH (25 ml) was added bipyridine (bipy; 0.13 g, 1.20 mmol). The mixture was stirred for 20 h and then boiled under reflux for 1 h, giving a green solution. This was allowed to cool and was then filtered. The filtrate was concentrated to *ca* 4 ml *in vacuo*, giving a blue solid. This was filtered off, washed with diethyl ether and dried *in vacuo* as $[Cu(bipy)_2(NO_3)]NO_3$ (yield 0.21 g, 80%). IR: 1600 (*sh*), 1580 (*m*), 1470 (*m*), 1320 (*m*), 1110 (*m*), 830 (*w*), 770 (*s*), 730 (*m*), 630 (*w*), 415 (*w*), 290 (*w*) cm^{-1}. Recrystallization of (I) by slow diffusion of diethyl ether into a methanol solution gave turquoise-coloured crystals.

Table 1
Selected geometric parameters (Å, °).

Cu—N111	1.975 (5)	Cu—N221	1.993 (5)
Cu—N121	2.013 (6)	Cu—O31	2.138 (6)
Cu—N211	2.106 (6)	Cu—O32	2.520 (6)
N111—Cu—N121	80.8 (3)	N211—Cu—O31	101.2 (2)
N111—Cu—N211	102.8 (3)	N221—Cu—O31	87.2 (2)
N111—Cu—N221	176.2 (3)	N111—Cu—O32	83.6 (2)
N121—Cu—N211	108.8 (2)	N121—Cu—O32	96.7 (2)
N221—Cu—N121	99.9 (2)	N211—Cu—O32	154.4 (2)
N221—Cu—N211	80.5 (2)	N221—Cu—O32	92.6 (2)
N111—Cu—O31	90.4 (2)	O31—Cu—O32	53.57 (19)
N121—Cu—O31	150.0 (2)		

Crystal data

$[Cu(C_{10}H_8N_2)_2(NO_3)]NO_3$
M_r = 499.93
Monoclinic, $P2_1/n$
a = 11.3309 (13) Å
b = 12.2714 (14) Å
c = 15.0877 (15) Å
β = 98.281 (8)°
V = 2076.0 (4) Å^3
Z = 4
D_x = 1.600 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 24 reflections
θ = 10–11°
μ = 1.11 mm^{-1}
T = 293 (2) K
Prism, blue–green **Or turquoise?**
0.29 × 0.21 × 0.18 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω/θ scans
Absorption correction: ψ scan (*EMPABS*; Sheldrick *et al.*, 1977)
T_{min} = 0.751, T_{max} = 0.820
3287 measured reflections
2546 independent reflections
1128 reflections with $I > 2\sigma(I)$
R_{int} = 0.028
θ_{max} = 23.0°
$h = -11 \rightarrow 11$
$k = -1 \rightarrow 12$
$l = -1 \rightarrow 15$
3 standard reflections
frequency: 167 min
intensity decay: 2.0%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.092
S = 0.97
2546 reflections
298 parameters
H-atom parameters constrained
$w = \sigma^{-2}(F_o^2)$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.27 e Å^{-3}
$\Delta\rho_{min}$ = −0.28 e Å^{-3}

Table 2
Comparison of bond dimensions (Å,°) for (I) and related structures.

	(II)	(III)	(IV)	(I)	(V)	(VI)	(VII) Molecule 1/2	(VIII)
Cu—N	1.980 (11)	1.980 (3)	1.990 (5)	1.975 (5)	1.984 (5)	1.986 (5)	1.974 (3)/1.969 (3)	1.980 (4)
Cu—N_O	2.065 (10)	2.074 (4)	2.052 (5)	2.013 (6)	2.022 (5)	2.023 (5)	2.021 (3)/2.036 (3)	2.032 (3)
Cu—N*	2.006 (10)	1.988 (3)	2.004 (5)	1.993 (5)	1.982 (5)	1.973 (5)	1.978 (3)/1.981 (3)	2.008 (4)
Cu—N_O*	2.100 (9)	2.085 (4)	2.142 (5)	2.106 (6)	2.045 (5)	2.051 (5)	2.109 (3)/2.097 (3)	2.185 (3)
Cu—O	2.238 (10)	2.230 (5)	2.117 (6)	2.138 (6)	2.299 (7)	2.301 (5)	2.116[a]/2.184 (3)	2.078 (3)
Cu—O*	2.329 (10)	2.320 (5)	2.462 (6)	2.520 (6)	2.818 (7)	2.832 (5)	2.822 (4)/2.717 (3)	2.639 (4)
O—Cu—N_O	157.8 (4)	157.7 (2)	164.1 (1)	150.0 (2)	127.8 (3)	127.5 (2)	143.77 (13)/135.28 (12)	161.5 (1)
O*—Cu—N_O*	151.1 (4)	151.3 (2)	149.2 (1)	154.4 (2)	139.5 (4)	139.2 (1)	138.11 (12)/144.49 (11)	141.8[a,b]
N—Cu—N*	179.6 (4)	179.7 (2)	178.6 (1)	176.2 (3)	170.9 (3)	170.7 (1)	177.05 (14)/177.46 (13)	176.7 (1)
O—Cu—O*	52.5 (4)	52.8 (2)	52.7 (2)	53.6 (2)	47.7 (4)	47.7 (1)	48.25 (11)/50.66 (10)	53.0[a,b]
O—Cu—N_O*	99.2 (4)	99.3 (2)	97.3 (2)	101.2 (2)	92.1 (3)	91.8 (2)	90.64 (12)/94.69 (11)	90.8 (1)
O*—Cu—N_O	105.6 (4)	105.4 (1)	111.9 (2)	96.7 (2)	80.3 (4)	80.0 (1)	96.10 (12)/85.13 (11)	109.5[a,b]
N_O—Cu—N_O*	103.0 (4)	102.8 (1)	98.5 (2)	108.8 (2)	140.2 (3)	140.7 (1)	125.52 (13)/130.01 (13)	107.5 (1)
O—Cu—N	93.5 (4)	93.7 (2)	94.1 (2)	90.4 (2)	86.7 (3)	86.3 (2)	88.86 (13)/89.74 (12)	92.5 (1)
O—Cu—N*	86.8 (4)	86.5 (2)	87.2 (2)	87.2 (2)	85.5 (3)	85.5 (2)	89.88 (13)/88.00 (12)	88.1 (1)
O*—Cu—N	89.1 (4)	89.3 (1)	89.5 (2)	83.6 (2)	81.8 (4)	81.6(1)[b]	86.56 (13)/88.14 (12)	90.6[a,b]
O*—Cu—N*	91.2 (4)	90.7 (2)	90.9 (2)	92.6 (2)	89.5 (4)	89.6(1)[b]	90.62 (14)/89.53 (12)	87.3[a,b]
N—Cu—N_O	81.1 (4)	80.0 (2)	80.8 (2)	80.8 (3)	81.1 (3)	81.5 (2)	81.60 (14)/81.40 (13)	81.1 (1)
N—Cu—N_O*	99.4 (4)	100.6 (1)	101.0 (2)	102.8 (3)	103.6 (3)	103.7 (2)	102.55 (13)/100.72 (13)	104.2 (1)
N*—Cu—N_O	98.7 (4)	99.8 (2)	97.8 (2)	99.9 (2)	100.0 (3)	100.0 (2)	97.88 (14)/99.40 (13)	97.4 (1)
N*—Cu—N_O*	80.3 (4)	79.6 (2)	79.4 (2)	80.5 (2)	81.4 (3)	81.0 (2)	80.13 (13)/80.63 (13)	79.0 (1)

Notes: (*a*) s.u. values not reported; (*b*) value was not reported and was calculated using *GEOM* (Owen, 1981); N_O denotes N *trans* to an O atom; * denotes the loosely coordinated axial O atom, the axial N atom *trans* to it and the second (equatorial) N atom within the same bipyridine ligand.

H atoms were geometrically constrained to ride on the parent atoms (C—H = 0.93 Å), with $U_{iso}(H) = 1.2U_{eq}$(parent atom).

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1992); cell refinement: *CAD*-4 *EXPRESS*; data reduction: *CAD*-4 processing program (Hursthouse, 1976); program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP* (Johnson, 1971) and *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

KM thanks FOCTTU, Tehran, for financial support.

References

Catalan, K. J., Jackson, S., Zubkowski, J. D., Perry, D. L., Valente, E. J., Feliu, L. A. & Polanco, A. (1995). *Polyhedron*, **14**, 2165–2171.

Davies, S. C., Durrant, M. C., Hughes, D. L., Leidenberger, K., Stapper, C. & Richards, R. L. (1997). *J. Chem. Soc. Dalton Trans.* pp. 2409–2418.

Enraf–Nonius (1992). *CAD*-4 *EXPRESS*. Enraf–Nonius, Delft, The Netherlands.

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

Fereday, R. J., Hodgson, P., Tyagi, S. & Hathaway, B. J. (1981). *J. Chem. Soc. Dalton Trans.* pp. 2070–2077.

Hathaway, B. J. (1973). *Struct. Bonding* (*Berlin*), **14**, 49–67.

Hursthouse, M. B. (1976). *CAD*-4 processing program. Queen Mary College, London.

Johnson, C. K. (1971). *ORTEP*II. Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee, USA.

Nakai, H. (1980). *Bull. Chem. Soc. Jpn*, **53**, 1321–1326.

Orpen, A. G., Brammer, L., Allen, F. H., Kennard, O., Watson, D. G. & Taylor, R. (1989). *J. Chem. Soc. Dalton Trans.* pp. S1–83.

Owen, J. D. (1981). *GEOM*. Rothamsted Experimental Station, Harpenden, Herts, England.

Prasad, B. L. V., Sato, H., Enoki, T., Cohen, S. & Radhakrishnan, T. P. (1999). *J. Chem. Soc. Dalton Trans.* pp. 25–29.

Proctor, I. M. & Stephens, F. S. (1969). *J. Chem. Soc. A*, pp. 1248–1256.

Sheldrick, G. M., Orpen, A. G., Reichert, B. E. & Raithby, P. R. (1977). *EMPABS*. 4th European Crystallographic Meeting, Oxford, Abstracts, p. 147.

Sheldrick, G. M. (1985). *SHELXS*86. University of Göttingen, Germany.

Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.

Simmons, C. J., Clearfield, A., Fitzgerald, W., Tyagi, S. & Hathaway, B. (1983). *J. Chem. Soc. Chem. Commun.* pp. 189–190.

Simmons, C. J., Hathaway, B. J., Amornjarusiri, K., Santarsiero, B. D. & Clearfield, A. (1987). *J. Am. Chem. Soc.* **109**, 1947–1958.

Walsh, A., Walsh, B., Murphy, B. & Hathaway, B. J. (1981). *Acta Cryst.* B**37**, 1512–1520.

supporting information

Acta Cryst. (2005). E**61**, m11–m14 [https://doi.org/10.1107/S1600536804030788]

Bis(2,2′-bipyridine)nitratocopper(II) nitrate

Katayoun Marjani, Sian C. Davies, Marcus C. Durrant, David L. Hughes, Nejat Khodamorad and Assadolah Samodi

Bis(2,2′-bipyridine)nitratocopper(II) nitrate

Crystal data

$[Cu(C_{10}H_8N_2)_2(NO_3)]NO_3$
$M_r = 499.93$
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
$a = 11.3309$ (13) Å
$b = 12.2714$ (14) Å
$c = 15.0877$ (15) Å
$\beta = 98.281$ (8)°
$V = 2076.0$ (4) Å^3
$Z = 4$
$F(000) = 1020$
$D_x = 1.600$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å
Cell parameters from 24 reflections
$\theta = 10$–11°
$\mu = 1.11$ mm^{-1}
$T = 293$ K
Prism, blue green
0.29 × 0.21 × 0.18 mm

Data collection

Enraf-Nonius CAD-4 diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
scintillation counter; ω/θ scans
Absorption correction: ψ scan (EMPABS; Sheldrick et al., 1977)
$T_{min} = 0.751$, $T_{max} = 0.820$
3287 measured reflections
2546 independent reflections
1128 reflections with $I > 2\sigma(I)$
$R_{int} = 0.028$
$\theta_{max} = 23.0°$, $\theta_{min} = 1.5°$
$h = -11 \rightarrow 11$
$k = -1 \rightarrow 12$
$l = -1 \rightarrow 15$
3 standard reflections every 167 min
intensity decay: 2.0%

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.092$
$S = 0.97$
2546 reflections
298 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = \sigma^2(F_o^2)$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.27$ e Å^{-3}
$\Delta\rho_{min} = -0.28$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.
3287 reflections were collected to θ_{max} of 23° (h_{max}, k_{max}, l_{max} of 12, 13, 16), with 2887 unique reflections and 1172 observed. Those greater than 22°, however, were found to be too unreliable and were not used in the final refinement, leaving 2546 unique reflections and 1128 observed. H atoms were geometrically constrained to ride on the parent atoms, with isotropic displacement parameters set to be $1.2U_{eq}$ of the parent atom. Data were corrected for Lorentz-polarization effects, decay of the intensities (Hursthouse, 1976), absorption (Sheldrick *et al.*, 1977) and negative intensities (French *et al.*, 1978) before structure solution and refinement.
French, *S.* & Wilson, K. (1978). Acta Cryst. A34, 517–525.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cu	0.23885 (8)	0.43850 (8)	0.12480 (6)	0.0508 (3)
N111	0.2036 (5)	0.4497 (5)	0.2489 (4)	0.0543 (16)
C112	0.1041 (6)	0.3999 (6)	0.2653 (5)	0.046 (2)
C113	0.0581 (6)	0.4147 (7)	0.3445 (5)	0.063 (2)
H113	−0.0127	0.3814	0.3541	0.076*
C114	0.1197 (8)	0.4796 (7)	0.4076 (6)	0.074 (3)
H114	0.0904	0.4914	0.4613	0.089*
C115	0.2234 (8)	0.5277 (7)	0.3939 (6)	0.087 (3)
H115	0.2676	0.5685	0.4390	0.104*
C116	0.2619 (7)	0.5149 (7)	0.3120 (6)	0.076 (3)
H116	0.3295	0.5521	0.3002	0.091*
N121	0.1031 (5)	0.3316 (5)	0.1175 (4)	0.0471 (17)
C122	0.0503 (6)	0.3258 (6)	0.1924 (5)	0.048 (2)
C123	−0.0407 (6)	0.2512 (6)	0.2003 (6)	0.057 (2)
H123	−0.0776	0.2486	0.2514	0.069*
C124	−0.0733 (7)	0.1822 (7)	0.1301 (7)	0.073 (3)
H124	−0.1322	0.1306	0.1347	0.087*
C125	−0.0226 (7)	0.1861 (7)	0.0535 (6)	0.070 (3)
H125	−0.0454	0.1390	0.0059	0.084*
C126	0.0649 (6)	0.2647 (6)	0.0509 (5)	0.053 (2)
H126	0.0990	0.2707	−0.0014	0.064*
N211	0.4007 (5)	0.3514 (5)	0.1403 (4)	0.0487 (16)
C212	0.4419 (6)	0.3379 (6)	0.0608 (6)	0.051 (2)
C213	0.5386 (7)	0.2717 (7)	0.0557 (6)	0.071 (3)
H213	0.5665	0.2623	0.0012	0.085*
C214	0.5936 (8)	0.2200 (7)	0.1300 (8)	0.092 (4)
H214	0.6582	0.1743	0.1264	0.111*
C215	0.5530 (9)	0.2359 (7)	0.2105 (7)	0.085 (3)
H215	0.5904	0.2019	0.2621	0.101*

C216	0.4556 (7)	0.3029 (7)	0.2139 (6)	0.072 (3)
H216	0.4281	0.3143	0.2683	0.087*
N221	0.2685 (5)	0.4364 (5)	−0.0022 (3)	0.0437 (14)
C222	0.3758 (6)	0.3955 (5)	−0.0144 (5)	0.0402 (18)
C223	0.4158 (6)	0.4111 (6)	−0.0968 (5)	0.052 (2)
H223	0.4903	0.3853	−0.1058	0.062*
C224	0.3446 (8)	0.4647 (7)	−0.1649 (5)	0.067 (2)
H224	0.3713	0.4768	−0.2195	0.080*
C225	0.2346 (8)	0.4997 (6)	−0.1510 (5)	0.067 (2)
H225	0.1842	0.5340	−0.1968	0.081*
C226	0.1994 (6)	0.4840 (6)	−0.0696 (5)	0.058 (2)
H226	0.1240	0.5076	−0.0608	0.069*
N3	0.2103 (7)	0.6582 (7)	0.1169 (4)	0.063 (2)
O31	0.3019 (5)	0.6029 (5)	0.1307 (4)	0.0780 (19)
O32	0.1127 (5)	0.6081 (5)	0.1012 (4)	0.090 (2)
O33	0.2120 (6)	0.7558 (5)	0.1158 (5)	0.124 (3)
N4	0.7290 (7)	0.3951 (7)	0.3817 (5)	0.068 (2)
O41	0.7854 (5)	0.4768 (5)	0.3685 (4)	0.0811 (19)
O42	0.6221 (5)	0.4057 (5)	0.3877 (4)	0.091 (2)
O43	0.7756 (6)	0.3078 (5)	0.3912 (5)	0.126 (3)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu	0.0470 (5)	0.0616 (6)	0.0451 (5)	−0.0043 (6)	0.0114 (4)	−0.0019 (6)
N111	0.056 (4)	0.070 (5)	0.037 (4)	−0.006 (4)	0.011 (3)	−0.006 (4)
C112	0.043 (5)	0.049 (5)	0.050 (5)	0.008 (4)	0.015 (4)	−0.007 (4)
C113	0.054 (5)	0.073 (7)	0.066 (6)	0.008 (5)	0.021 (5)	0.009 (5)
C114	0.082 (7)	0.084 (7)	0.057 (6)	0.001 (6)	0.017 (5)	−0.004 (5)
C115	0.102 (8)	0.103 (8)	0.057 (7)	−0.034 (6)	0.013 (5)	−0.024 (5)
C116	0.085 (6)	0.084 (7)	0.060 (7)	−0.028 (5)	0.011 (5)	−0.001 (6)
N121	0.042 (4)	0.051 (4)	0.048 (4)	−0.002 (3)	0.005 (3)	0.003 (4)
C122	0.040 (5)	0.042 (5)	0.061 (6)	0.006 (4)	0.006 (4)	0.016 (5)
C123	0.048 (5)	0.061 (6)	0.065 (6)	0.000 (5)	0.015 (5)	0.018 (5)
C124	0.064 (6)	0.056 (6)	0.093 (8)	−0.018 (5)	−0.005 (6)	0.001 (6)
C125	0.066 (6)	0.066 (7)	0.075 (7)	−0.010 (5)	−0.001 (5)	−0.010 (6)
C126	0.048 (5)	0.056 (6)	0.056 (6)	−0.008 (5)	0.006 (4)	−0.001 (5)
N211	0.040 (4)	0.051 (4)	0.052 (4)	−0.004 (3)	−0.004 (4)	0.000 (4)
C212	0.038 (5)	0.046 (5)	0.067 (6)	−0.009 (4)	0.003 (4)	−0.008 (5)
C213	0.051 (6)	0.073 (7)	0.087 (7)	0.020 (5)	0.000 (5)	−0.017 (6)
C214	0.054 (6)	0.085 (8)	0.129 (10)	0.027 (5)	−0.020 (7)	−0.024 (8)
C215	0.081 (8)	0.067 (7)	0.097 (9)	0.007 (6)	−0.019 (6)	0.017 (6)
C216	0.067 (6)	0.081 (7)	0.063 (7)	0.005 (5)	−0.013 (5)	−0.005 (5)
N221	0.049 (4)	0.050 (4)	0.031 (4)	0.006 (4)	0.005 (3)	−0.005 (3)
C222	0.052 (5)	0.029 (4)	0.041 (5)	0.006 (4)	0.009 (4)	−0.011 (4)
C223	0.053 (5)	0.051 (6)	0.052 (5)	−0.006 (4)	0.014 (4)	−0.016 (5)
C224	0.085 (6)	0.067 (7)	0.053 (6)	−0.017 (5)	0.025 (5)	−0.008 (5)
C225	0.089 (7)	0.064 (6)	0.051 (6)	0.011 (5)	0.016 (5)	0.005 (4)

C226	0.065 (5)	0.068 (6)	0.042 (5)	0.011 (4)	0.011 (5)	0.009 (5)
N3	0.090 (7)	0.061 (6)	0.040 (4)	−0.004 (5)	0.008 (5)	−0.003 (5)
O31	0.067 (4)	0.094 (5)	0.077 (4)	0.014 (4)	0.024 (3)	0.015 (4)
O32	0.082 (4)	0.097 (5)	0.089 (5)	−0.014 (4)	0.005 (4)	0.000 (4)
O33	0.166 (7)	0.054 (4)	0.143 (6)	−0.007 (5)	−0.013 (5)	−0.012 (5)
N4	0.087 (7)	0.063 (6)	0.055 (5)	−0.006 (6)	0.012 (5)	0.007 (5)
O41	0.081 (5)	0.068 (4)	0.097 (5)	0.001 (3)	0.021 (4)	0.012 (4)
O42	0.078 (4)	0.096 (5)	0.103 (5)	−0.013 (4)	0.031 (4)	0.000 (4)
O43	0.132 (6)	0.048 (4)	0.198 (8)	0.027 (4)	0.026 (5)	0.032 (5)

Geometric parameters (Å, º)

Cu—N111	1.975 (5)	N211—C216	1.333 (8)
Cu—N121	2.013 (6)	N211—C212	1.359 (8)
Cu—N211	2.106 (6)	C212—C213	1.374 (9)
Cu—N221	1.993 (5)	C212—C222	1.450 (9)
Cu—O31	2.138 (6)	C213—C214	1.359 (11)
Cu—O32	2.520 (6)	C213—H213	0.930
N111—C112	1.337 (7)	C214—C215	1.373 (11)
N111—C116	1.342 (8)	C214—H214	0.930
C112—C113	1.383 (9)	C215—C216	1.382 (10)
C112—C122	1.488 (9)	C215—H215	0.930
C113—C114	1.355 (9)	C216—H216	0.930
C113—H113	0.930	N221—C226	1.326 (7)
C114—C115	1.357 (9)	N221—C222	1.352 (7)
C114—H114	0.930	C222—C223	1.397 (9)
C115—C116	1.378 (10)	C223—C224	1.378 (9)
C115—H115	0.930	C223—H223	0.930
C116—H116	0.930	C224—C225	1.362 (9)
N121—C126	1.322 (8)	C224—H224	0.930
N121—C122	1.354 (8)	C225—C226	1.359 (9)
C122—C123	1.396 (9)	C225—H225	0.930
C123—C124	1.365 (9)	C226—H226	0.930
C123—H123	0.930	N3—O33	1.198 (7)
C124—C125	1.363 (10)	N3—O31	1.233 (7)
C124—H124	0.930	N3—O32	1.257 (7)
C125—C126	1.388 (9)	N4—O43	1.194 (7)
C125—H125	0.930	N4—O41	1.220 (7)
C126—H126	0.930	N4—O42	1.235 (7)
N111—Cu—N121	80.8 (3)	N121—C126—C125	124.5 (8)
N111—Cu—N211	102.8 (3)	N121—C126—H126	117.8
N111—Cu—N221	176.2 (3)	C125—C126—H126	117.8
N121—Cu—N211	108.8 (2)	C216—N211—C212	120.1 (7)
N221—Cu—N121	99.9 (2)	C216—N211—Cu	127.9 (6)
N221—Cu—N211	80.5 (2)	C212—N211—Cu	111.7 (5)
N111—Cu—O31	90.4 (2)	N211—C212—C213	120.0 (8)
N121—Cu—O31	150.0 (2)	N211—C212—C222	115.2 (7)

N211—Cu—O31	101.2 (2)	C213—C212—C222	124.8 (8)
N221—Cu—O31	87.2 (2)	C214—C213—C212	120.3 (9)
N111—Cu—O32	83.6 (2)	C214—C213—H213	119.9
N121—Cu—O32	96.7 (2)	C212—C213—H213	119.9
N211—Cu—O32	154.4 (2)	C213—C214—C215	119.5 (9)
N221—Cu—O32	92.6 (2)	C213—C214—H214	120.3
O31—Cu—O32	53.57 (19)	C215—C214—H214	120.3
C112—N111—C116	118.9 (6)	C214—C215—C216	119.2 (9)
C112—N111—Cu	115.8 (5)	C214—C215—H215	120.4
C116—N111—Cu	124.6 (6)	C216—C215—H215	120.4
N111—C112—C113	122.2 (7)	N211—C216—C215	121.0 (8)
N111—C112—C122	114.2 (7)	N211—C216—H216	119.5
C113—C112—C122	123.6 (8)	C215—C216—H216	119.5
C114—C113—C112	117.7 (8)	C226—N221—C222	120.1 (6)
C114—C113—H113	121.2	C226—N221—Cu	124.7 (5)
C112—C113—H113	121.2	C222—N221—Cu	114.5 (4)
C113—C114—C115	121.2 (8)	N221—C222—C223	118.9 (6)
C113—C114—H114	119.4	N221—C222—C212	116.6 (7)
C115—C114—H114	119.4	C223—C222—C212	124.4 (7)
C114—C115—C116	118.7 (8)	C224—C223—C222	119.9 (7)
C114—C115—H115	120.7	C224—C223—H223	120.0
C116—C115—H115	120.7	C222—C223—H223	120.0
N111—C116—C115	121.1 (8)	C225—C224—C223	119.1 (7)
N111—C116—H116	119.4	C225—C224—H224	120.4
C115—C116—H116	119.4	C223—C224—H224	120.4
C126—N121—C122	117.8 (7)	C226—C225—C224	119.2 (8)
C126—N121—Cu	127.6 (5)	C226—C225—H225	120.4
C122—N121—Cu	114.5 (5)	C224—C225—H225	120.4
N121—C122—C123	121.7 (7)	N221—C226—C225	122.6 (7)
N121—C122—C112	113.7 (7)	N221—C226—H226	118.7
C123—C122—C112	124.5 (8)	C225—C226—H226	118.7
C124—C123—C122	117.5 (8)	O33—N3—O31	122.5 (8)
C124—C123—H123	121.3	O33—N3—O32	120.2 (9)
C122—C123—H123	121.3	O31—N3—O32	117.3 (8)
C125—C124—C123	122.4 (9)	N3—O31—Cu	104.1 (5)
C125—C124—H124	118.8	N3—O32—Cu	85.0 (5)
C123—C124—H124	118.8	O43—N4—O41	121.7 (8)
C124—C125—C126	116.0 (8)	O43—N4—O42	120.4 (9)
C124—C125—H125	122.0	O41—N4—O42	117.9 (8)
C126—C125—H125	122.0		

N121—Cu—N111—C112	−9.4 (5)	N121—Cu—N211—C212	97.2 (5)
N211—Cu—N111—C112	−116.7 (5)	O31—Cu—N211—C212	−85.3 (5)
O31—Cu—N111—C112	141.7 (5)	O32—Cu—N211—C212	−76.2 (7)
O32—Cu—N111—C112	88.5 (5)	C216—N211—C212—C213	1.7 (11)
N121—Cu—N111—C116	−179.7 (6)	Cu—N211—C212—C213	−172.0 (5)
N211—Cu—N111—C116	73.0 (6)	C216—N211—C212—C222	−179.4 (6)
O31—Cu—N111—C116	−28.5 (6)	Cu—N211—C212—C222	6.9 (7)

O32—Cu—N111—C116	−81.8 (6)	N211—C212—C213—C214	−0.3 (12)
C116—N111—C112—C113	1.2 (11)	C222—C212—C213—C214	−179.1 (7)
Cu—N111—C112—C113	−169.7 (6)	C212—C213—C214—C215	−1.1 (14)
C116—N111—C112—C122	−177.3 (6)	C213—C214—C215—C216	1.0 (15)
Cu—N111—C112—C122	11.9 (8)	C212—N211—C216—C215	−1.8 (11)
N111—C112—C113—C114	−2.1 (12)	Cu—N211—C216—C215	170.8 (6)
C122—C112—C113—C114	176.2 (6)	C214—C215—C216—N211	0.4 (13)
C112—C113—C114—C115	−0.5 (12)	N121—Cu—N221—C226	74.6 (6)
C113—C114—C115—C116	3.9 (14)	N211—Cu—N221—C226	−177.8 (6)
C112—N111—C116—C115	2.5 (12)	O31—Cu—N221—C226	−76.0 (6)
Cu—N111—C116—C115	172.4 (7)	O32—Cu—N221—C226	−22.7 (6)
C114—C115—C116—N111	−5.0 (14)	N121—Cu—N221—C222	−114.7 (5)
N111—Cu—N121—C126	−171.7 (6)	N211—Cu—N221—C222	−7.1 (5)
N221—Cu—N121—C126	12.1 (6)	O31—Cu—N221—C222	94.7 (5)
N211—Cu—N121—C126	−71.1 (6)	O32—Cu—N221—C222	148.0 (5)
O31—Cu—N121—C126	113.9 (7)	C226—N221—C222—C223	4.5 (10)
O32—Cu—N121—C126	106.0 (6)	Cu—N221—C222—C223	−166.7 (5)
N111—Cu—N121—C122	5.0 (5)	C226—N221—C222—C212	−175.7 (6)
N221—Cu—N121—C122	−171.2 (5)	Cu—N221—C222—C212	13.1 (8)
N211—Cu—N121—C122	105.5 (5)	N211—C212—C222—N221	−13.4 (9)
O31—Cu—N121—C122	−69.5 (7)	C213—C212—C222—N221	165.5 (7)
O32—Cu—N121—C122	−77.4 (5)	N211—C212—C222—C223	166.4 (6)
C126—N121—C122—C123	0.7 (10)	C213—C212—C222—C223	−14.7 (11)
Cu—N121—C122—C123	−176.2 (5)	N221—C222—C223—C224	−1.9 (10)
C126—N121—C122—C112	176.8 (6)	C212—C222—C223—C224	178.3 (6)
Cu—N121—C122—C112	−0.2 (7)	C222—C223—C224—C225	−1.4 (11)
N111—C112—C122—N121	−7.5 (9)	C223—C224—C225—C226	2.1 (12)
C113—C112—C122—N121	174.0 (7)	C222—N221—C226—C225	−3.9 (11)
N111—C112—C122—C123	168.4 (7)	Cu—N221—C226—C225	166.3 (6)
C113—C112—C122—C123	−10.1 (11)	C224—C225—C226—N221	0.5 (12)
N121—C122—C123—C124	1.3 (10)	O33—N3—O31—Cu	179.6 (7)
C112—C122—C123—C124	−174.3 (7)	O32—N3—O31—Cu	−2.2 (8)
C122—C123—C124—C125	−1.7 (12)	N111—Cu—O31—N3	−80.5 (5)
C123—C124—C125—C126	0.1 (12)	N221—Cu—O31—N3	96.5 (5)
C122—N121—C126—C125	−2.5 (10)	N121—Cu—O31—N3	−8.5 (8)
Cu—N121—C126—C125	174.0 (5)	N211—Cu—O31—N3	176.3 (5)
C124—C125—C126—N121	2.1 (12)	O32—Cu—O31—N3	1.2 (4)
N111—Cu—N211—C216	8.6 (7)	O33—N3—O32—Cu	−180.0 (8)
N221—Cu—N211—C216	−173.3 (6)	O31—N3—O32—Cu	1.8 (7)
N121—Cu—N211—C216	−75.9 (6)	N111—Cu—O32—N3	94.1 (5)
O31—Cu—N211—C216	101.5 (6)	N221—Cu—O32—N3	−85.7 (5)
O32—Cu—N211—C216	110.7 (7)	N121—Cu—O32—N3	174.0 (5)
N111—Cu—N211—C212	−178.3 (5)	N211—Cu—O32—N3	−12.3 (8)
N221—Cu—N211—C212	−0.1 (5)	O31—Cu—O32—N3	−1.1 (4)