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

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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.

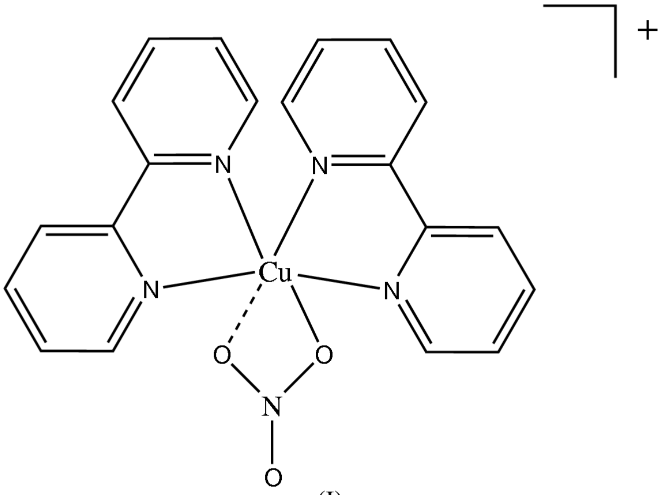
Key indicators

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.

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

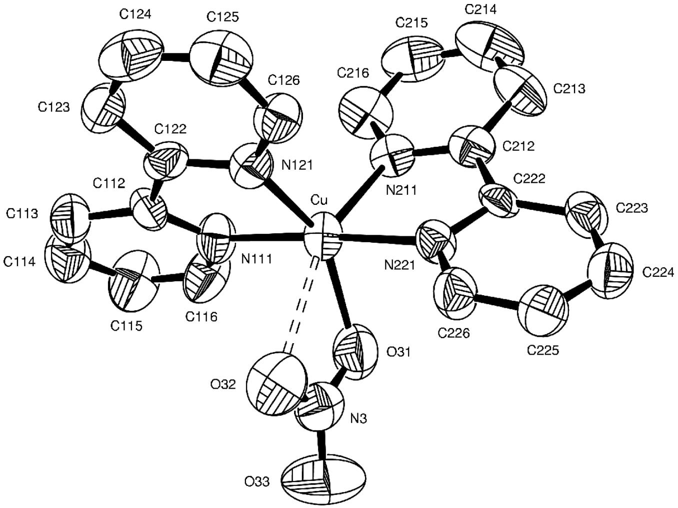


Figure 1
A view of the cation of (I). Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity.

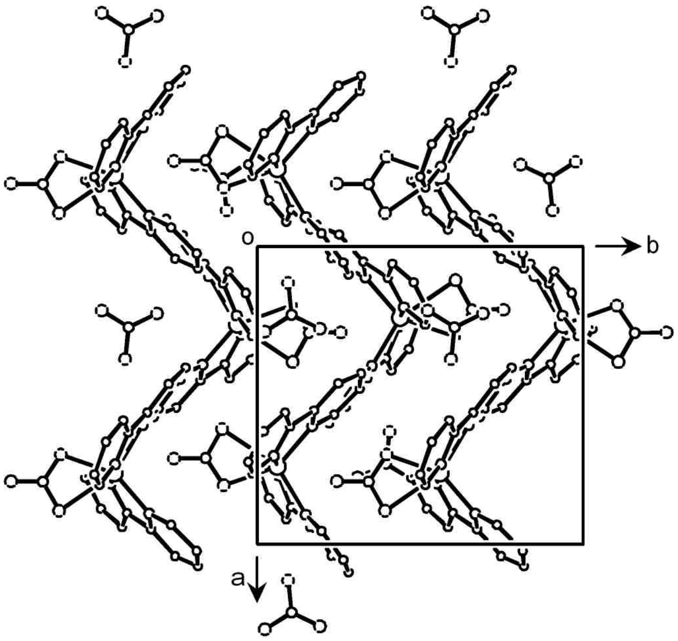


Figure 2
Packing diagram of (I), viewed along the crystallographic *c* axis. Atoms are represented by arbitrary spheres. H atoms have been omitted.

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}

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.

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.

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