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(2,2′-Biquinoline-κ^2N,N')bis(nitrato-κ^2O,O')copper(II)

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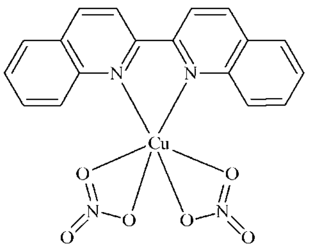
In the title monomer, $[Cu(NO_3)_2(C_{18}H_{12}N_2)]$, the six-coordinated Cu^{II} atom lies on a twofold axis which bisects one of the ligands (a chelating biquinoline) and duplicates the remaining ligand, a chelating nitrate. The latter binds in a very asymmetric way, consistent with a Jahn–Teller distortion in the coordination polyhedron which, due to the triple chelation, is extremely distorted and difficult to describe in terms of any regular model.

Comment

Hydrothermal synthesis refers to a chemical reaction taking place in a sealed heated solution above ambient pressure. The mechanisms involved are not yet fully understood, but the process is often able to generate unique products; see, for instance, Feng & Xu (2001), Moghimi *et al.* (2003) and Walton (2002). Efficient methods for optimizing the yield of crystalline material have also been developed; for a successful application, see, for instance, Contreras *et al.* (2007). However, the exact outcome of such syntheses still seems to be a matter of 'green fingers' and is often prone to serendipity. The *Experimental* section gives details of the fortuitous generation of the title complex, $[Cu(NO_3)_2(C_{18}H_{12}N_2)]$, (I).



(I)

Compound (I) is a monomer built up around a twofold axis passing through the metal centre. The symmetry axis also halves a chelating biquinoline (biq) group which binds through its two N atoms, thus rendering only half of the ligand (and of the whole polyhedron) independent. The remaining four coordinating atoms are provided by one independent nitrate (nit) group and its symmetry-related image, acting also as a chelate (Fig. 1).

A very similar, though nonsymmetric, disposition has been found in a closely related analogue published recently, $[Cu(NO_3)_2(C_{18}H_{10}N_4)]\cdot CH_3CN$, (II) (Fitchett & Steel, 2007), where the role of the biq group is fulfilled by 2,2′-bi-1,5-naphthyridine, an ambivergent ligand differing from the present biq in that the C5—H5 and C5^i—H5^i groups (Fig. 1) are replaced by N atoms, which are potentially active either in coordination or as hydrogen-bonding acceptors. Fig. 2 shows a superposition diagram where the differences and similarities between both molecules can be clearly appreciated.

Both structures show four shorter and two much longer bonds (Table 1), suggesting a Jahn–Teller distortion in a

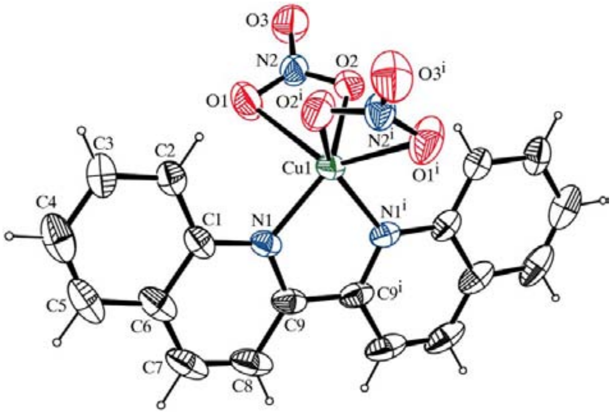


Figure 1
A molecular view of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are represented as small spheres of arbitrary radii. [Symmetry code: (i) $-x + 1, y, -z + \frac{3}{2}$.]

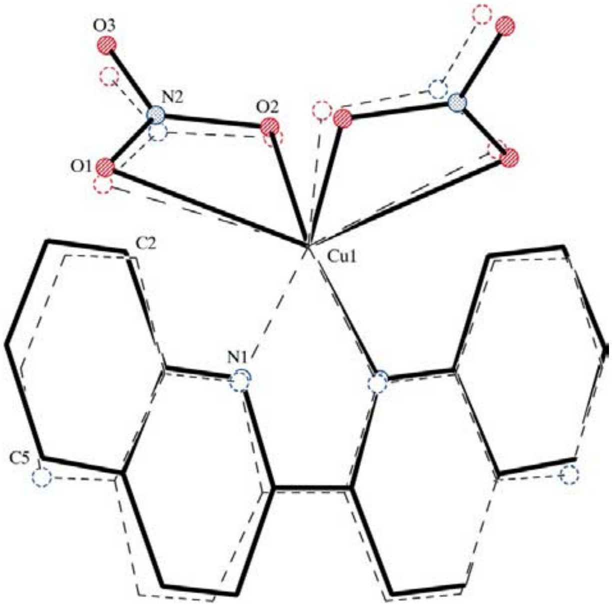


Figure 2
Schematic comparison of (I) (solid lines) and (II) (dashed lines).

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classical octahedral Cu environment. Although in both cases the bond distances are normal for six-coordinate copper complexes [Cambridge Structural Database, Version 5.28; Allen (2002)], the chelating character of the three ligands involved induces highly distorted coordination polyhedra. Table 1 shows the departure of '*trans*' angles in (I) from their expected regular values of 180°.

These facts make the polyhedra difficult to describe by any regular model, and in this regard both compounds are quite suitable for testing the vectorial bond-valence model (VBVM) proposed by Harvey *et al.* (2006), a novel approach tending towards a simpler description of multidentate binding in which the action of each ligand is replaced by a single interaction vector, or VBV, derived from the individual bond valences of the coordinating atoms.

For the present kind of three-ligand coordination geometry, the VBVM would predict a planar array of the three VBV vectors and a nil resultant of their vectorial sum. These requirements are quite satisfactorily fulfilled in both structures. The first condition (a planar array of vectors) applies in a strict sense in (I) due to the intrinsic twofold symmetry around copper, and is well within experimental error in (II), where the calculated angles between bond-valence vectors differ from 360° by less than 0.005°. The second condition is also very satisfactorily complied with in both cases, with a resultant bond-valence vector of 0.02 valence units (v.u.) for (I) and 0.08 v.u. for (II). In both cases, a twofold interaction symmetry is evidenced [real in (I) and pseudo in (II)].

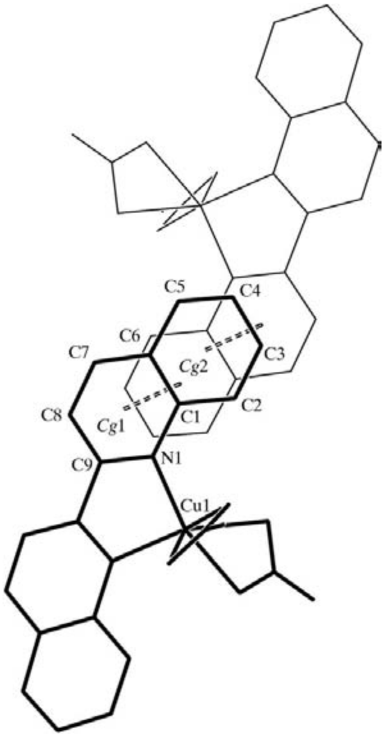

Figure 3
Overlapping view of two neighbouring molecules. Double-dashed lines represent π–π bonds relating centrosymmetrically related units and *Cg* labels denote the ring centroids.

The ligands of (I) look normal, without unprecedented features. Both are planar within experimental error [maximum deviations from the least-squares planes are 0.07 (1) Å for C3/C3^{i} in biq and 0.02 (1) Å for N2 in nit; symmetry code: (i) $1 - x$, y, $-z + \frac{3}{2}$]. The biq unit is in fact made up of two lateral hemiplanes (maximum deviation of 0.02 Å for C3/C3*A*), rotated with respect to each other by 3.1 (1)° around the central C9—C9^{i} axis; the coordination planes make dihedral angles with each other of 60.5 (1) (biq–nit) and 83.4 (1)° (nit–nit). N—O distances in the nit group are compatible with double bonds at O2 and O3, and a single bond at O1 (Table 1).

In the absence of strong hydrogen bonds, there are a number of second-order interactions in the structure of (I) which play definite roles (in spite of their intrinsic weakness), both in the molecular geometry and in the packing disposition. Full details are presented in Tables 2 and 3, and Fig. 4 shows their contribution to the molecular shape. Single broken lines indicate the intramolecular C—H$\cdots$O bond connecting a biq aromatic H atom with nit atom O2 (first entry in Table 2), pulling the ligand towards the cation and partially contributing to the large asymmetry in the coordination of the anion.

As far as the packing is concerned, the (weak) intermolecular interactions are of two different types. Firstly, π–π bonds link the lateral wings of the biq groups (Fig. 3 and Table 3), thus giving rise to simple π-connected chains of monomers evolving along [101]. Secondly, a couple of nonclassical C—H$\cdots$O hydrogen bonds (second and third entries in Table 2) link these chains together into a weakly connected three-dimensional network (Fig. 4).

As expected from their molecular similarities, almost all of these types of interactions in (I) are also present in (II), though with different strengths and structural consequences. For example, the two intramolecular hydrogen bonds are equivalent by symmetry in (I), but are independent and

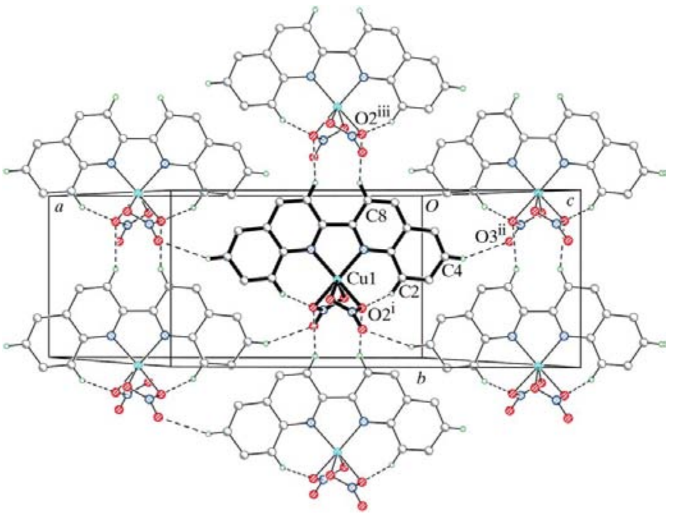

Figure 4
A packing view of (I) down [101], showing the network of weak hydrogen bonds (dashed lines) around the reference molecule (bold solid lines) in the centre of the figure. [Symmetry codes: (i) $1 - x, y, \frac{3}{2} - z$; (ii) $x - \frac{1}{2}, y - \frac{1}{2}, z$; (iii) $1 - x, y - 1, \frac{3}{2} - z$.]

midway in strength in (II), *i.e.* one is shorter and one longer than that in (I), leading to a slightly different deformation of the polyhedron (Fig. 2). On the other hand, π–π contacts between aromatic rings, though also present, are definitely second-order interactions compared with the C—H···N bonds, which are unique to (II) due to the outermost N atoms not being present in (I). These interactions define molecular ribbons which are linked *via* the π–π stacking and this fact, together with the presence of an acetonitrile solvent molecule which is not present in the unsolvated compound (I), define a quite different packing assembly.

Experimental

The title compound was unexpectedly generated in a hydrothermal bath set up for the synthesis of a copper–vanadium hybrid complex. The synthesis also included phosphate, but the principal crystalline component in the multiphase outcome proved to be the title compound, (I), in a good yield of irregular light-brown crystals suitable for single-crystal X-ray diffraction. For the synthesis, a mixture of $Cu(NO_3)_2 \cdot 3H_2O$ (1.375 mmol), V_2O_5 (0.5 mmol), 2,2-biquinoline (1.0 mmol) and H_3PO_4 (5 ml, 7.4 mmol) was sealed in a Teflon-lined acid digestion bomb and heated at 390 K for 3 d under autogenous pressure (pH = 2.5), followed by slow cooling at a rate of 20 K h^{-1} to room temperature.

Crystal data

$[Cu(NO_3)_2(C_{18}H_{12}N_2)]$
$M_r = 443.86$
Monoclinic, $C2/c$
$a = 19.310$ (8) Å
$b = 8.342$ (4) Å
$c = 13.160$ (6) Å
$\beta = 125.084$ (5)°
$V = 1734.7$ (14) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 1.31$ mm^{-1}
$T = 291$ (2) K
0.45 × 0.25 × 0.20 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2001)
$T_{min} = 0.66$, $T_{max} = 0.77$
6551 measured reflections
1914 independent reflections
1125 reflections with $I > 2\sigma(I)$
$R_{int} = 0.061$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.056$
$wR(F^2) = 0.153$
$S = 1.11$
1914 reflections
132 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.35$ e Å^{-3}
$\Delta\rho_{min} = -0.30$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—N1	1.959 (3)	Cu1—O1	2.455 (4)
Cu1—O2	2.002 (4)		
N1—Cu1—O2	144.31 (14)	O1^{i}—Cu1—O1	136.00 (18)

Symmetry code: (i) $-x+1, y, -z+\frac{3}{2}$.

H atoms were placed in calculated positions, with C—H = 0.93 Å, and allowed to ride. They were assigned an isotropic displacement parameter $U_{iso}(H) = 1.2U_{eq}(C)$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2···O2^{i}	0.93	2.32	3.030 (7)	133
C4—H4···O3^{ii}	0.93	2.57	3.440 (8)	155
C8—H8···O2^{iii}	0.93	2.57	3.400 (6)	148

Symmetry codes: (i) $-x+1, y, -z+\frac{3}{2}$; (ii) $x-\frac{1}{2}, y-\frac{1}{2}, z$; (iii) $-x+1, y-1, -z+\frac{3}{2}$.

Table 3
Geometry of π–π contacts (Å, °) for (I).

*Cg*1 is the centroid of the N1/C1/C6–C9 ring and *Cg*2 is the centroid of the C1–C6 ring. CCD is the centroid-to-centroid distance, IPD is the mean interplanar distance and SA is the mean slippage angle [for details, see Janiak (2000)].

Group 1···Group 2	IPD	CCD	SA
*Cg*1···*Cg*2^{iv}	3.363 (3)	3.556	19.362

Symmetry code: (iv) $\frac{1}{2}-x, \frac{1}{2}-y, 1-z$.

Data collection: *SMART-NT* (Bruker, 2001); cell refinement: *SAINT-NT* (Bruker, 2000); data reduction: *SAINT-NT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL-NT* (Sheldrick, 2000), *ORTEPIII* (Burnett & Johnson, 1996) and *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXTL-NT* and *PLATON* (Spek, 2003).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DN3060). Services for accessing these data are described at the back of the journal.

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