

## Aqua(2,2'-bipyridyl)chloronitrato-copper(II)

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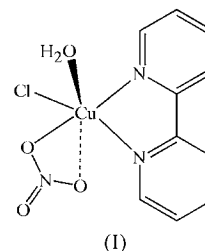
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In a new hydrogen-bonded three-dimensional complex,  $[\text{CuCl}(\text{NO}_3)(\text{C}_{10}\text{H}_8\text{N}_2)(\text{H}_2\text{O})]$ , the Cu atom has an elongated tetragonal octahedral environment, with two 2,2'-bipyridyl N atoms, one nitrate O atom and one Cl atom forming the equatorial plane, and a second O atom of the nitrate anion and a water molecule in the axial positions. The complex molecules are linked to form a three-dimensional supramolecular array by hydrogen-bonding interactions both between the water O atom and nitrate O atoms, and between the water O atom and the Cl atom of a neighboring molecule.

### Comment

In the past decade, the design and synthesis of metal-organic compounds based on the principles of crystal engineering have made rapid progress (Li *et al.*, 2006). Furthermore, the rational design and construction of specific architectures are beneficial for preparing functional materials. Self-assembly of metal compounds by hydrogen bonds into one-, two- and three-dimensional supramolecular architectures connects with biological chemistry, materials chemistry (such as organic films and magnetic materials) and supramolecular chemistry (Chen *et al.*, 2001). Hydrogen bonds play vital roles in highly efficient and specific biological reactions, and are essential for molecular recognition and self-organization of molecules in supramolecular chemistry. Copper complexes have been studied extensively in recent years. Their flexibility, facility of preparation and capacity for stabilizing unusual oxidation states can explain their successful performance in mimicking peculiar geometries around the metal, leading to very interesting spectroscopic properties and varied reactivities (Hathaway, 1987). Moreover, copper complexes have been used extensively as catalysts for a wide variety of reactions, including olefin polymerization (Killian *et al.*, 1996) and oxygen activation (Jung *et al.*, 1996). The stereochemistry of a series of mono(chelate) copper(II) complexes containing an

oxoanion and a halide is currently of interest to us. With the flexible di-2-pyridylamine (dpym) ligand, the complexes  $[\text{CuCl}(\text{NO}_3)(\text{dpym})]\cdot 0.5\text{H}_2\text{O}$  (Mathews & Manohar, 1991),  $[\text{CuCl}(\text{O}_2\text{CCH}_3)(\text{dpym})]$  (Ugozzoli *et al.*, 1997) and  $[\text{CuCl}(\text{O}_2\text{CCH}_2\text{CH}_3)(\text{dpym})]\cdot \text{H}_2\text{O}$  (Youngme *et al.*, 1999) have been found so far. The former involves a polymeric structure bridged by a chloride ion, while the latter two compounds exhibit monomeric units. In the present paper, we report the crystal structure of the less flexible 2,2'-bipyridyl (bpy) complex  $[\text{CuCl}(\text{NO}_3)(\text{bpy})(\text{H}_2\text{O})]$ , (I), in which a three-dimensional supramolecular array is formed by hydrogen-bonding interactions. Structural comparison with related complexes has been made and the spectroscopic properties of the complexes are discussed.



The structure of (I) is made up of discrete  $[\text{CuCl}(\text{NO}_3)(\text{bpy})(\text{H}_2\text{O})]$  units. The Cu atom is six-coordinated in a distorted octahedral arrangement (Table 1), with two N atoms of the bpy ligand, one O atom of the nitrate anion (atom O2) and a chloride anion forming the equatorial plane, while a second nitrate O atom  $[\text{Cu1}-\text{O3} = 2.6262(16) \text{ \AA}]$  and a water O atom occupy the tetragonal positions, thus giving an elongated octahedral geometry with tetragonality ( $T = \text{mean in-plane distance/mean out-of-plane distance}$ ) of 0.84. The tetragonal octahedral arrangement is typical and expected for  $\text{Cu}^{\text{II}}$  in view of the Jahn-Teller effect (Jahn & Teller, 1937). However, the title compound is further distorted with regard to the coordination of atom O3 from the nitrate ligand, which occupies the off-axis tetragonal position with an axial  $\text{O1}-\text{Cu1}-\text{O3}$  angle much less than  $180^\circ$  [ $144.17(1)^\circ$ ], leading to semicoordination to the  $\text{Cu}^{\text{II}}$  ion. The equatorial plane shows a

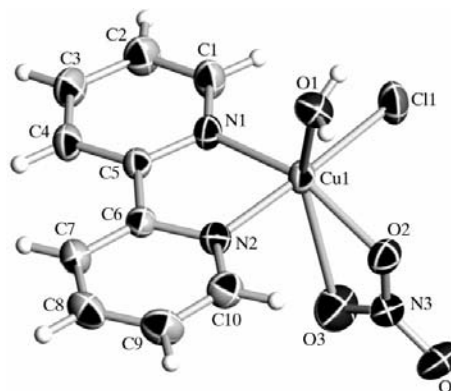


Figure 1

The molecular structure of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme.

slight tetrahedral twist, as is evident from the dihedral angle of  $10.0(1)^\circ$  at which the N1/Cu1/N2 and Cl1/Cu1/O2 planes cross. The local molecular geometry of (I) is best described as elongated octahedral with a long off-axis axial bond giving a  $(4+1+1')$  structure. The equatorial Cu—Cl distance is normal, in agreement with a previous report (Hathaway, 1987).

The structure of the title complex is found to be different from that of the closely related dpyam complex  $[\text{CuCl}(\text{NO}_3)(\text{dpyam})] \cdot 0.5\text{H}_2\text{O}$  (Mathews & Manohar, 1991). This compound consists of polymeric  $[\text{CuCl}(\text{NO}_3)(\text{dpyam})]_n$  zigzag chains with monodentate nitrate and bridging chloride ligands and involves a distorted square-based pyramidal geometry. The copper environment in (I) is also different from those of the related dpyam complexes with monovalent acetate and propionate oxoanions, *viz.*  $[\text{CuCl}(\text{O}_2\text{CCH}_3)(\text{dpyam})]$  (Ugozzoli, *et al.*, 1997) and  $[\text{CuCl}(\text{O}_2\text{CCH}_2\text{CH}_3)(\text{dpyam})] \cdot \text{H}_2\text{O}$  (Youngme *et al.*, 1999), which comprise mononuclear units with bidentate acetate or propionate ligands and, in the latter, an uncoordinated water molecule, giving a distorted square-based pyramidal geometry. The most similarity to compound (I) is found in the square-pyramidal complex  $[\text{Cu}(\text{NCS})(\text{O}_2\text{CCH}_3)(\text{dpyam})(\text{H}_2\text{O})]$  (Youngme *et al.*, 2006), containing a pseudohalide, a coordinated water molecule and a monodentate acetate ligand. The second O atom of the acetate anion coordinates to the  $\text{Cu}^{\text{II}}$  ion in a similar fashion to that of the nitrate in compound (I), but with a very long Cu—O distance  $[3.064(1) \text{ \AA}]$ . These observations

indicate that both the chelate function of the bpy and dpyam ligands, and the coordination nature of oxoanions, are responsible for the structure of this complex system. This implies that the more flexible dpyam ligand results in a greater variety of geometries and structures (Amournjarusiri & Hathaway, 1991).

The electronic reflectance spectrum of (I) involves a single broad peak at  $13\,850 \text{ cm}^{-1}$ , corresponding to an elongated tetragonal octahedral geometry with off-axial-direction coordination from the normal to the N1/N2/O2/Cl1 plane (Procter *et al.*, 1972). The electronic spectrum of (I) is similar to those found in complexes with similar  $\text{Cu}^{\text{II}}$  environments, *viz.*  $[\text{Cu}(\text{O}_2\text{CCH}_3)_2(\text{dpyam})] \cdot 2\text{H}_2\text{O}$  ( $13\,510 \text{ cm}^{-1}$ ),  $[\text{Cu}(\text{NO}_2)(\text{O}_2\text{CCH}_3)(\text{dpyam})] \cdot \text{H}_2\text{O}$  ( $13\,880 \text{ cm}^{-1}$ ),  $[\text{Cu}(\text{NO}_2)_2(\text{dpyam})]$  ( $13\,890 \text{ cm}^{-1}$ ),  $[\text{Cu}(\text{NO}_3)_2(\text{dpyam})] \cdot 2\text{H}_2\text{O}$  ( $13\,580 \text{ cm}^{-1}$ ) (Youngme *et al.*, 2002) and  $[\text{Cu}(\text{NCS})(\text{O}_2\text{CCH}_3)(\text{dpyam})(\text{H}_2\text{O})]$  ( $15\,980 \text{ cm}^{-1}$ ) (Youngme *et al.*, 2006). The symmetric and antisymmetric NO stretchings appear as strong bands at  $1310$  and  $1384 \text{ cm}^{-1}$ , respectively, consistent with the asymmetric bidentate nitrate group (Lewis *et al.*, 1972). The complex molecules are linked to form a three-dimensional supramolecular array by hydrogen-bonding interactions between the water molecule and the coordinated nitrate O atoms and Cl atom of neighboring molecules (Table 2 and Fig. 2).

## Experimental

The title complex was prepared by adding a warm solution containing  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (0.241 g, 1.0 mmol) in water (5 ml) to a warm solution of 2,2'-bipyridine (0.156 g, 1.0 mmol) in ethanol (20 ml), followed by the addition of solid NaCl (0.029 g, 0.5 mmol). The resulting blue solution was evaporated slowly at room temperature. After several days, blue-green crystals were formed. The crystals were filtered off, washed with mother liquor and air-dried.

### Crystal data

$[\text{CuCl}(\text{NO}_3)(\text{C}_{10}\text{H}_8\text{N}_2)(\text{H}_2\text{O})]$   
 $M_r = 335.20$   
 Monoclinic,  $P2_1/n$   
 $a = 10.8944(3) \text{ \AA}$   
 $b = 10.6760(3) \text{ \AA}$   
 $c = 11.0496(3) \text{ \AA}$   
 $\beta = 106.860(1)^\circ$   
 $V = 1229.92(6) \text{ \AA}^3$

$Z = 4$   
 $D_x = 1.810 \text{ Mg m}^{-3}$   
 Mo  $K\alpha$  radiation  
 $\mu = 2.01 \text{ mm}^{-1}$   
 $T = 273(2) \text{ K}$   
 Rhombus, blue-green  
 $0.43 \times 0.35 \times 0.28 \text{ mm}$

### Data collection

Siemens SMART CCD area-detector diffractometer  
 $\omega$  scans  
 Absorption correction: multi-scan (SADABS; Sheldrick, 2000a)  
 $T_{\min} = 0.441$ ,  $T_{\max} = 0.576$

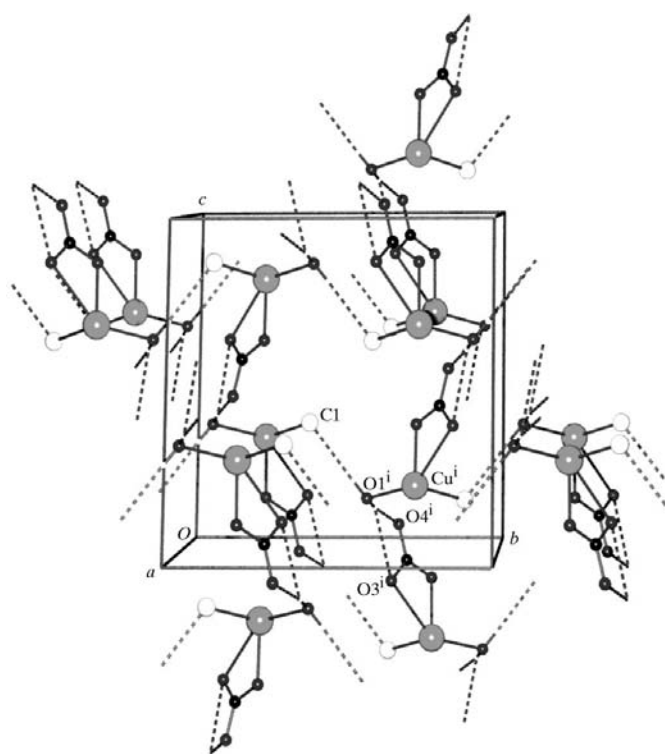
7471 measured reflections  
 2718 independent reflections  
 2466 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.016$   
 $\theta_{\max} = 27.1^\circ$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.024$   
 $wR(F^2) = 0.066$   
 $S = 1.09$   
 2718 reflections  
 180 parameters

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0371P)^2 + 0.3286P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.30 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -0.63 \text{ e \AA}^{-3}$



**Figure 2**

The packing of (I), with hydrogen bonds shown as dashed lines, showing the two-dimensional structure along the  $a$  axis. The bpy ligand has been omitted for clarity. [Symmetry code: (i)  $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$ .]

**Table 1**

Selected geometric parameters (Å, °).

Cu1—N2	2.0110 (14)	Cu1—Cl1	2.2581 (5)
Cu1—N1	2.0161 (14)	Cu1—O1	2.3040 (13)
Cu1—O2	2.0296 (13)		
N2—Cu1—N1	81.03 (6)	O2—Cu1—Cl1	91.49 (4)
N2—Cu1—O2	91.60 (6)	N2—Cu1—O1	86.15 (5)
N1—Cu1—O2	158.17 (6)	N1—Cu1—O1	108.23 (5)
N2—Cu1—Cl1	176.88 (4)	O2—Cu1—O1	91.60 (5)
N1—Cu1—Cl1	95.91 (4)	Cl1—Cu1—O1	94.22 (4)

**Table 2**

Hydrogen-bond geometry (Å, °).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
O1—H11···O3 <sup>i</sup>	0.82 (2)	2.54 (2)	3.165 (2)	134 (2)
O1—H11···O4 <sup>i</sup>	0.82 (2)	2.13 (2)	2.941 (2)	171 (2)
O1—H12···Cl1 <sup>ii</sup>	0.84 (2)	2.36 (2)	3.1918 (15)	173 (2)
Cl1—H1···Cl1	0.93	2.68	3.265 (2)	122
C10—H10···O2	0.93	2.57	3.064 (2)	114

Symmetry codes: (i)  $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$ ; (ii)  $-x + \frac{5}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$ .

H atoms in the bpy ligand were placed in idealized positions and constrained to ride on their parent atoms, with C—H distances of 0.93 Å and  $U_{\text{iso}}(\text{H})$  values of  $1.2U_{\text{eq}}(\text{C})$ . H atoms bonded to the water O atom were visible in a difference map and were refined with a DFIX (*SHELXTL*; Sheldrick, 2000b) restraint of O—H = 0.85 (1) Å and with  $U_{\text{iso}}(\text{H})$  values refined freely.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2000b); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV3035). Services for accessing these data are described at the back of the journal.

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