metal-organic compounds

New structures in the bipyridine–copper(II) nitrate–methanol system: [(bpy)$_2$Cu(NO$_3$)]NO$_3$·CH$_3$OH and [(bpy)$_2$Cu(NO$_3$)]NO$_3$

Peter Y. Zavalij,* Benjamin L. Burton and Wayne E. Jones Jr

Department of Chemistry and Institute for Materials Research, State University of New York at Binghamton, Binghamton, NY 13902-6016, USA
Correspondence e-mail: zavalij@binghamton.edu
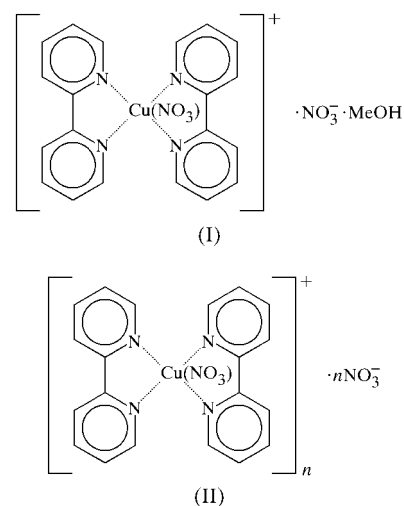
Reaction of 2,2′-bipyridine (bpy) and copper(II) nitrate in methanol results in two complexes, namely light-blue bis(2,2′-bipyridine)nitratocopper(II) nitrate methanol solvate, [Cu(NO$_3$)(C$_{10}$H$_8$N$_2$)$_2$]NO$_3$·CH$_3$OH, (I), which is unstable in air, and the product of its decomposition, *catena*-poly[[[bis(2,2′-bipyridine)copper(II)]-μ-nitrato-*O*:*O*′] nitrate], {[Cu(NO$_3$)(C$_{10}$H$_8$N$_2$)$_2$]NO$_3$}$_n$, (II). The crystal structures of both compounds were determined from one crystal at room temperature. Later, the structure of (I) was redetermined at low temperature. In (I) and (II), the Cu atom is coordinated by two bpy and one or two nitrate ions, respectively. The second nitrate ion in (I), along with the methanol solvent molecule, is found in the outer coordination sphere, not bonded to Cu. The nitrate in (I) is chelating, while in (II), it bridges (bpy)$_2$Cu complexes, forming a one-dimensional chain structure. The Cu cation in (II) lies on a twofold axis and the uncoordinated NO$_3^-$ ion is located close to a twofold axis and is therefore disordered. Compound (I) converts into (II) upon loss of solvent.

Comment

Copper–bipyridine complexes have been proposed as catalysts for the hydrolysis of phosphate triesters, such as those found in toxic nerve agents (Morrow & Trogler, 1989). Although a great deal of research has been carried out on the reaction mechanism (Beaudry *et al.*, 1994), a complete structure of the copper–bipyridine complex has not yet been reported. Noack & Gordon (1968) have proposed that the active catalytic structure contains water coordinated (inner sphere) to the central Cu atom, while Catalan *et al.* (1995) obtained a copper–bipyridine complex with water in the outer coordination sphere. We report here, the single-crystal X-ray structures of two new copper–bipyridine complexes, namely bis(2,2′-bipyridine)nitratocopper(II) nitrate methanol sol-

vate, (I), and *catena*-poly[[[bis(2,2′-bipyridine)copper(II)]-μ-nitrato-*O*:*O*′] nitrate], (II).

(I)

(II)

The reaction of bipyridine (bpy) with copper(II) nitrate in a 1:1 ratio in methanol (see *Experimental*) results in a blue crystalline material. Two types of solid products can be identified under an optical microscope, *viz.* stable intense-blue crystals and light-blue crystalline blocks which are unstable in air. The latter crystals have some clearly visible faces, while the former crystals are effectively shapeless. The crystal structure determination of the intense-blue crystals yields the 1:1 complex [(bpy)Cu(NO$_3$)$_2$] previously studied at 193 K (Tadsanaprasittipol *et al.*, 1998).

The unstable light-blue crystals were covered several times with a thin layer of epoxy prior to carrying out the experiment. Indexing of diffraction peaks yielded two related, but still different, lattices. One lattice, (I), was indexed in a triclinic cell, whereas the other set, (II), was indexed in a monoclinic *C*-centered cell. The monoclinic cell can be reduced to a primitive unit cell with dimensions $a = 7.165$ (1), $b = 10.847$ (2), $c = 14.633$ (3) Å, $\alpha = 110.127$ (4), $\beta = 101.846$ (4) and $\gamma = 96.109$ (4)°, which resemble the cell dimensions of the (I) component. The crystal structures of both the triclinic and monoclinic components were determined and resulted in 2:1 complexes with compositions (bpy)$_2$Cu(NO$_3$)$_2$·CH$_3$OH, (I), and (bpy)$_2$Cu(NO$_3$)$_2$, (II). Essentially, the two crystal structures were determined from one crystal. Interestingly, compound (I) decomposes at some point during the diffraction experiment as a result of evolution of methanol from the crystal. This was in contrast to compound (II), which was stable to the completion of the experiment. Epoxy encapsulation did not prevent decomposition of the crystal, which was stable for about two hours. In multiple experiments, it was noticed that the decomposition of (I) due to the loss of solvent (1–2 h) leads to the formation of compound (II). The diffraction peaks of the resulting 'crystals' were broad and the quality of the diffraction pattern was therefore not suitable for structure refinement. The pattern was, however, good enough for the unit-cell determination.

The crystal structure of (I) was redetermined at low temperature from a single crystal and is described here. Data

obtained from the room-temperature experiment were not suitable for publication due to the crystal decomposition. Despite this, the structure was solved and does not differ significantly from the low-temperature structure except in the orientational disorder of the uncoordinated nitrate ion.

The structure of (II) was determined from the double crystal, which contained the two molecules, (I) and (II). An individual single crystal of (II) suitable for diffraction analysis was not found after numerous attempts. This could mean that (II) only forms from (I) upon the loss of solvent.

Complex (I), with a 2:1 bpy-to-Cu ratio, consists of a $[(bpy)_2Cu(NO_3)]^+$ cation, two nitrate ions and a methanol solvent molecule (Fig. 1). The Cu atom in (I) is coordinated by two bpy molecules and one chelating nitrate (N5) anion. The uncoordinated nitrate ion forms a strong hydrogen bond with the hydroxy group and two weak hydrogen bonds with the methyl group of the solvent (Table 2). The pyridine rings in both the N1/N2 and N3/N4 bpy molecules are tilted around the C—C bond by 9.83 (8) and 3.98 (7)°, respectively. The Cu atom and one pair of N atoms from different bpy molecules almost form a straight line, with an N1—Cu1—N4 angle of 176.01 (5)°. In contrast, the Cu atom and the other pair of N atoms are not linear, with an N2—Cu1—N3 angle of 126.64 (5)°. This indicates that the bpy molecules are tilted from each other around the C3—N1—Cu—N4—C18 line by about 60°.

The configuration of the complex $[(bpy)_2Cu(NO_3)]^+$ cation is quite similar to that in $[(bpy)_2Cu(NO_3)]NO_3·H_2O$ reported by Catalan *et al.* (1995). However, the stacking differs substantially, most likely due to the stronger and more branched hydrogen-bond network of water *versus* methanol.

Complex (II) differs from (I) by the absence of the methanol solvent molecule and consists of a $[(bpy)_2Cu(NO_3)]^+$ cation and an NO_3^- anion (Fig. 2). However, the coordinated nitrate ion is not chelating, but instead bridges the $(bpy)_2Cu$ complex ions, forming a one-dimensional chain. The Cu

coordination polyhedron can be described as a strongly distorted octahedron consisting of four N atoms, with Cu—N distances of less than 2 Å, and two weakly bonded O atoms from the bridging nitrate group in apical positions (Table 3 and Fig. 2). This distorted octahedron agrees well with the Cu1 atomic displacement ellipsoid elongated in the direction of the weakly bonded O atoms. This is probably due to disorder of the Cu atom lying slightly off the twofold axis. Both the $(bpy)_2Cu$ and NO_3^- ions are situated on twofold axes, which pass through the center of the bpy molecules and the Cu atom in the complex, and along the N11—O11 bond of the bridging nitrate ion. The two bpy molecules, denoted A and B in Fig. 2, are tilted around a twofold axis by 46.66 (6)° from one another. The two pyridine rings are tilted from one another by 3.5 (2)° in bpy A and by 10.8 (2)° in bpy B. The isolated NO_3 ion is situated near the twofold axis and is therefore disordered.

It was found that (I) easily loses a solvent molecule upon exposure to air and converts to (II). The complex $[(bpy)_2Cu(NO_3)]^+$ cations in (I) are stacked on top of each other along the a axis in such a way that atom O3 of the coordinated nitrate anion forms a contact of 3.737 (2) Å with the Cu atom from the next complex (Fig. 3a). During the conversion, one Cu—O bond breaks and a new Cu—O bond forms to the Cu atom of the next complex cation. Thus, in (II), the chelating nitrate group becomes bridging and links the cationic complexes into a one-dimensional chain along the c axis, as shown in Fig. 3(b). Both Cu—O bonds are weak and have equal lengths of 2.696 (4) Å. Therefore, the Cu···Cu distance along the chain is 0.5 Å shorter in (II) (Cu1···Cu1^{iv} in Table 3) then in (I) (Cu1···Cu1^i in Table 1). This structural reorganization also causes changes in the $(bpy)_2Cu$ configuration. The two bpy molecules move to equatorial positions to make space for the second apical nitrate ion. Thus, the
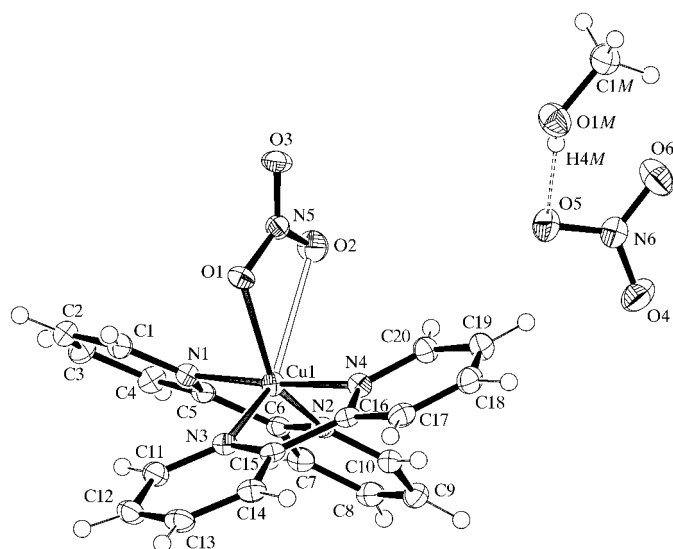

Figure 1
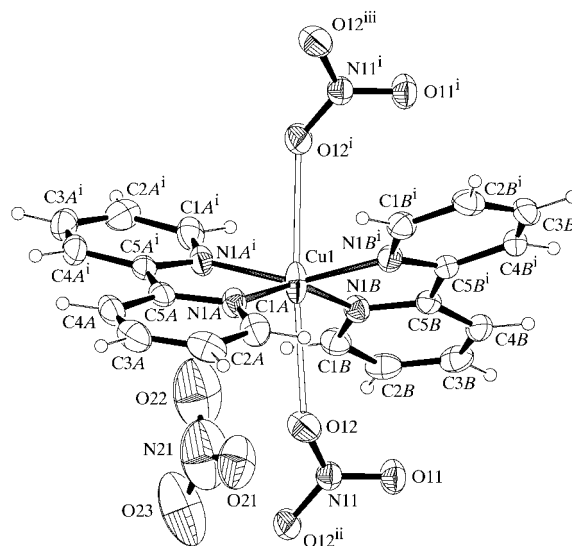Displacement-ellipsoid plot of (I) at the 50% probability level.

Figure 2
Displacement-ellipsoid plot of (II) at the 30% probability level. Disorder of the uncoordinated nitrate ion is not shown. [Symmetry codes: (i) $1 - x$, y, $\frac{1}{2} - z$; (ii) $1 - x$, y, $\frac{3}{2} - z$; (iii) x, y, $z - 1$.]
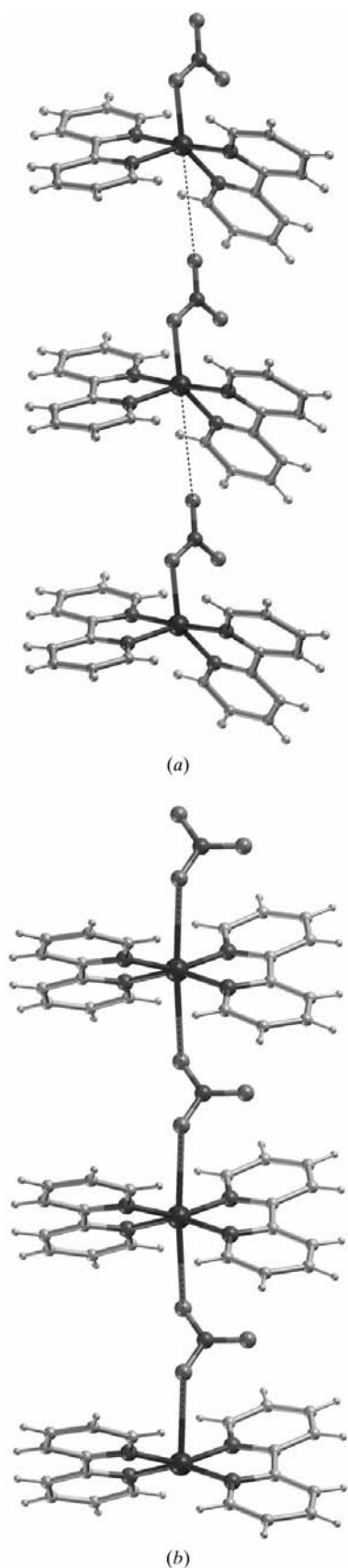
(a)

(b)

Figure 3
Chains of [bpy₂Cu(NO₃)]⁺ complexes in (*a*) (I) and (*b*) (II). Cu1···O3 contacts between different complexes in (I) are shown as dashed lines (Accelrys, 2001).

bpy$_{center}$—Cu—bpy$_{center}$ angle is 151.19 (5)° in (I) and linear in (II). In both compounds, the bpy molecules are tilted towards each other due to the steric interaction between the C—H groups next to the coordinated N atoms.

Experimental

Reagent grade $Cu(NO_3)_2 \cdot 2.5H_2O$ and 2,2′-bipyridine (bpy) were purchased from commercial sources (Aldrich Chemical Company Inc.) and used without further purification. Reagent grade methanol was purchased from a commercial source (EM Science) and used without purification. The complexes were prepared based on the literature procedure of Morrow & Trogler (1989). A 50 ml solution of methanol containing stoichiometric ratios of $Cu(NO_3)_2 \cdot 2.5H_2O$ and bpy (1:2 ratio) was purged with a blanket of N_2 and heated at reflux for approximately 12 h under constant mixing. After reflux was complete, the reaction solution was rotary evaporated to reduce the volume by half. The remaining solution was left to crystallize. Results of the elemental analyses of compounds (I) and (II), theoretical: C 48.0, H 3.2, N 16.8%; found: C 47.6, H 3.1, N 16.6%. Key IR peaks: 778, 1384, 3075 cm^{-1}. The approximately 0.044 M solution remaining after rotary evaporation was wrapped in aluminium foil to reduce exposure to light and left to crystallize at room temperature. After 3 d at room temperature, crystals of sufficient size for X-ray diffraction experiments were obtained. Crystals were harvested directly from the reaction vessel immediately prior to conducting the diffraction experiments.

Compound (I)

Crystal data

[Cu(NO₃)(C₁₀H₈N₂)₂]NO₃·CH₄O	$Z = 2$
$M_r = 531.97$	$D_x = 1.578$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 7.6862$ (6) Å	Cell parameters from 6220
$b = 11.8902$ (9) Å	reflections
$c = 13.3644$ (11) Å	$\theta = 2.7$–31.1°
$\alpha = 109.492$ (3)°	$\mu = 1.03$ mm^{-1}
$\beta = 92.902$ (4)°	$T = 100$ (2) K
$\gamma = 101.347$ (4)°	Prism, blue
$V = 1119.9$ (2) Å^3	$0.45 \times 0.38 \times 0.34$ mm

Data collection

Bruker SMART CCD diffractometer	5643 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.030$
Absorption correction: multi-scan	$\theta_{max} = 30.5°$
(*SADABS*; Sheldrick, 1996)	$h = -10 \rightarrow 10$
$T_{min} = 0.634$, $T_{max} = 0.704$	$k = -16 \rightarrow 16$
22 064 measured reflections	$l = -18 \rightarrow 19$
6676 independent reflections	Intensity decay: -0.8%

Table 1
Selected geometric parameters (Å, °) for (I).

Cu1—N1	1.970 (1)	Cu1—O1	2.157 (1)
Cu1—N4	1.987 (1)	Cu1—O2	2.665 (1)
Cu1—N2	2.018 (1)	Cu1···Cu1^i	7.6862 (6)
Cu1—N3	2.098 (1)	Cu1···Cu1^{ii}	7.5234 (6)
N1—C5—C6—N2	−7.04 (18)	N3—C15—C16—N4	−3.58 (19)
C4—C5—C6—C7	−9.5 (2)	C14—C15—C16—C17	−4.1 (2)

Symmetry codes: (i) $1 + x, y, z$; (ii) $1 - x, 2 - y, 2 - z$.

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0637P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.036$	$+ 0.0117P]$
$wR(F^2) = 0.100$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.07$	$(\Delta/\sigma)_{max} = 0.001$
6676 reflections	$\Delta\rho_{max} = 0.76$ e Å^{-3}
398 parameters	$\Delta\rho_{min} = -0.22$ e Å^{-3}
H-atom parameters constrained	

Table 2
Hydrogen-bonding geometry (Å, °) for (I).

$D—H\cdots A$	$D—H$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
$O1M—H4M\cdots O5$	0.74 (3)	2.15 (3)	2.882 (2)	170 (3)
$C1M—H3M\cdots O4^i$	0.95 (2)	2.90 (2)	3.431 (3)	116 (2)
$C1M—H1M\cdots O6$	0.94 (1)	2.65 (2)	3.261 (3)	123 (2)

Symmetry code: (i) $1 + x, y, z$.

Compound (II)

Crystal data

$[Cu(NO_3)(C_{10}H_8N_2)_2]NO_3$	$D_x = 1.619$ Mg m^{-3}
$M_r = 499.93$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 2067
$a = 12.347$ (3) Å	reflections
$b = 26.540$ (6) Å	$\theta = 3.0–23.3°$
$c = 7.1648$ (16) Å	$\mu = 1.12$ mm^{-1}
$\beta = 119.129$ (4)°	$T = 295$ (2) K
$V = 2051.0$ (8) Å^3	Prism, light blue
$Z = 4$	$0.38 \times 0.30 \times 0.20$ mm

Data collection

Bruker SMART CCD	1063 reflections with $I > 2\sigma(I)$
diffractometer	$R_{int} = 0.100$
ω scans	$\theta_{max} = 24.2°$
Absorption correction: multi-scan	$h = -14 \rightarrow 14$
(*SADABS*; Sheldrick, 1996)	$k = -30 \rightarrow 30$
$T_{min} = 0.623$, $T_{max} = 0.800$	$l = -8 \rightarrow 8$
7462 measured reflections	Intensity decay: 0.2%
1645 independent reflections	

Table 3
Selected geometric parameters (Å, °) for (II).

$Cu1—N1B^i$	1.977 (4)	$Cu1—O12^{ii}$	2.696 (4)
$Cu1—N1B$	1.977 (4)	$Cu1—O12^{iii}$	2.696 (4)
$Cu1—N1A^i$	1.984 (4)	$Cu1\cdots Cu1^{iv}$	7.1648 (16)
$Cu1—N1A$	1.984 (4)	$Cu1\cdots Cu1^v$	7.637 (2)
$N1B—C5B—C5B^i—N1B^i$	11.8 (8)	$N1A—C5A—C5A^i—N1A^i$	5.5 (8)
$C4B—C5B—C5B^i—C4B^i$	11.5 (11)	$C4A—C5A—C5A^i—C4A^i$	3.5 (10)

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

Refinement

Refinement on F^2	H atoms: see below
$R[F^2 > 2\sigma(F^2)] = 0.059$	$w = 1/[\sigma^2(F_o^2) + (0.0673P)^2]$
$wR(F^2) = 0.139$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{max} < 0.001$
1645 reflections	$\Delta\rho_{max} = 0.42$ e Å^{-3}
163 parameters	$\Delta\rho_{min} = -0.26$ e Å^{-3}

The H atoms in (I) were refined with C—H distances restrained to be the same. The average C—H distance refined to 0.92 (1) Å for bpy and 0.94 (1) Å for methanol molecules. The H atoms in (II) were allowed for as riding, with C—H distances of 0.93 Å. U_{iso} values were refined independently for all H atoms in (I) and were assigned as $1.2U_{eq}$ of the attached C atom in (II).

For compounds (I) and (II), data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997) and *Materials Studio* (Accelrys, 2001); software used to prepare material for publication: *SHELXL*97.

References

Accelrys (2001). *Materials Studio*. Accelrys Inc., San Diego, CA, USA.
Beaudry, W. T., Wagner, G. W. & Ward, J. R. (1994). *J. Mol. Catal.* **93**, 221–231.
Bruker (1999). *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Catalan, K. J., Jackson, S. & Zubkowski, J. D. (1995). *Polyhedron*, **14**, 2165–2171.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565–565.
Morrow, J. R. & Trogler, W. C. (1989). *Inorg. Chem.* **28**, 2330–2333.
Noack, M. & Gordon, G. (1968). *J. Chem. Phys.* **48**, 2689–2699.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.
Tadsanaprasittipol, A., Kraatz, H.-B. & Enright, G. D. (1998). *Inorg. Chim. Acta*, **278**, 143–149.