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{4-[(Carbamimidoylhydrazono)-methyl-κ^2N^1,N^4]-5-hydroxymethyl-2-methylpyridinium-3-olate-κO}-(methanol-κO)copper(II) dinitrate

Vukadin M. Leovac,[a] Ljiljana S. Vojinović-Ješić,[a] Valerija I. Češljević,[a] Sladjana B. Novaković[b]* and Goran A. Bogdanović[b]

[a]Department of Chemistry, Faculty of Sciences, University of Novi Sad, Trg Dositeja Obradovića 3, 21000 Novi Sad, Serbia, and [b]'Vinča' Institute of Nuclear Sciences, Laboratory of Theoretical Physics and Condensed Matter Physics, PO Box 522, 11001 Belgrade, Serbia
Correspondence e-mail: snovak@vinca.rs

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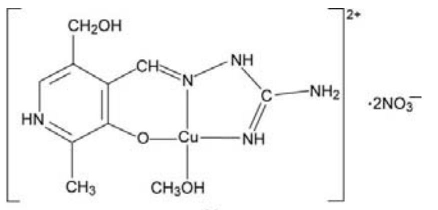
The title compound, $[Cu(C_9H_{13}N_5O_2)(CH_4O)](NO_3)_2$, consists of square-planar cationic complex units where the Cu^{II} centre is coordinated by an *N*,*N*′,*O*-tridentate pyridoxal–aminoguanidine Schiff base adduct and a methanol molecule. The tridentate ligand is a zwitterion exhibiting an almost planar conformation. The dihedral angles between the mean planes of the pyridoxal ring and the six- and five-membered chelate rings are all less than 2.0°. The charge on the complex cation is neutralized by two nitrate counter-ions. Extensive N—H⋯O and C—H⋯O hydrogen bonding connects these ionic species and leads to the formation of layers. The pyridoxal hydroxy groups are the only fragments that deviate significantly from the flat layer structure; these groups are involved in O—H⋯O hydrogen bonding, connecting the layers into a three-dimensional crystal structure.

Comment

Aminoguanidine is a well known inhibitor of the formation of advanced glycation end products and is considered to be promising for the treatment of diabetic complications (Taguchi *et al.*, 1999). The Schiff base of pyridoxal and aminoguanidine (PL–AG) appeared to be more effective than aminoguanidine in preventing nephropathy in diabetic mice. Although the inhibition of glycation by both drugs was similar, unlike the aminoguanidine, the administration of PL–AG did not decrease the amount of the hepatic content of pyridoxal phosphate. The antioxidant activity of the pyridoxal adduct was also far superior (Chen *et al.*, 2003). In view of the importance of PL–AG and copper(II) as a biometal, it was of interest to determine the structure of their complex. Our previous work (Leovac *et al.*, 2007) was concerned with the crystal and molecular structures of the square-pyramidal complex of formula $[CuCl_2(PL–AG)]$. We report here the crystal structure of (I), the complex of Cu^{II} with the same ligand, which consists of the complex $[Cu(PL–AG)(MeOH)]^{2+}$ cation and two nitrate anions.



(I)

In (I), Cu^{II} is in a square-planar coordination environment formed by the *N*,*N*′,*O*-tridentate pyridoxal–aminoguanidine Schiff base adduct and the molecule of methanol (Fig. 1). As in the previous examples of piridoxal Schiff bases (Belicchi Ferrari *et al.*, 1994, 1995; Poleti *et al.* 2003; Leovac *et al.*, 2007), the ligand takes the form of a zwitterion as the H atom from the phenol O atom shifts to the pyridyl N atom. As a result, the Cu1—O1 bond distance, where the oxygen donor from the Schiff base is negatively charged, is considerably shorter than the Cu1—O3 bond with the neutral methanol ligand (Table 1). On the other hand, the bonds with the two nitrogen donors, *viz.* Cu1—N1 and Cu1—N3, have more similar lengths [1.934 (3) and 1.947 (3) Å, respectively], which was not the case with the corresponding bonds in the previously reported complex $[CuCl_2(PL–AG)]$ [1.930 (2) and 1.984 (3) Å]. By coordination to the metal atom, the tridentate ligand forms six- and five-membered chelate rings. The whole Schiff base displays a high degree of planarity owing to the evident electron delocalization. The r.m.s. deviations of the fitted atoms in the three rings [the pyridoxal ring (*A*) and the six- (*B*) and five-membered (*C*) chelate rings] do not exceed 0.01 Å, while the dihedral angles between the mean planes *A* and *B*, *A* and *C*, and *B* and *C* are 1.8 (2), 2.0 (2) and 0.7 (1)°,

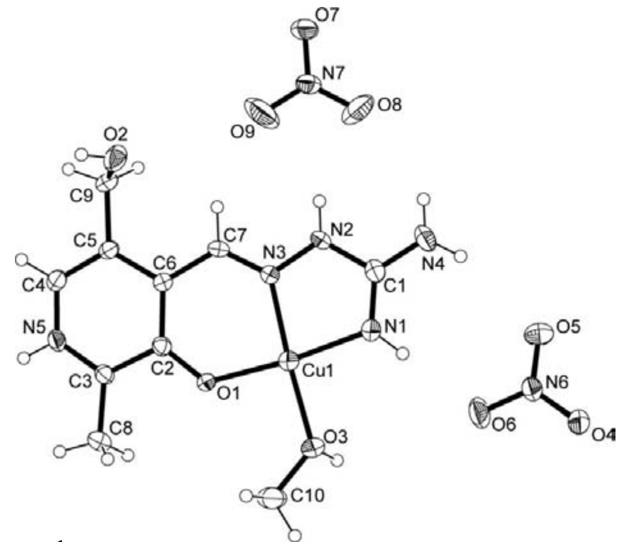


Figure 1
A view of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 40% probability level.

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respectively. This is considerably less than in the case of the [CuCl$_2$(PL–AG)] complex, where the dihedral angles between the five-membered chelate ring and rings *A* and *B* reached 8.3 (2) and 8.9 (2)°, respectively. In addition, the previously observed bending of the O1—Cu1—N1 angle to 165.7 (2)° is less significant in the present compound [174.03 (11)°], probably because the smaller O atom replaces the more voluminous chlorides in the Cu^{II} coordination environment.

Owing to the presence of two uncoordinated nitrate anions and the considerable hydrogen-donor capacity of the tridentate ligand, the crystal structure is stabilized by a very extensive hydrogen-bonding network. The planar complex unit forms hydrogen bonds with both nitrate anions and engages all their oxygen acceptors to assemble into wide ribbons, as shown in Fig. 2. The nitrate unit N7/O7–O9 is located in the middle of the ribbons, forming five N—H···O and three C—H···O hydrogen bonds with three complex units. The other nitrate ion, N6/O4–O6, is positioned on the lateral sides of ribbons, forming seven hydrogen bonds (four N—H···O, two C—H···O and one O—H···O) and interconnecting the four complex cations. The interactions formed by N6/O4–O6 are, however, somewhat stronger than those formed by the other nitrate group, which could be related to the findings that the N—O bond distances in the N6/O4–O6 group are somewhat longer than those in N7/O7–O9 (Table 1). The elongation is particularly pronounced for N6—O4 [1.250 (4) Å], whose O atom serves as the acceptor of a short N5—H5···O4^{iv} hydrogen bond (H5···O4^{iv} = 1.91 Å; symmetry code as in Table 2), and also for N6—O6 [1.242 (4) Å], where the O atom is simultaneously involved in two interactions with H···O6 less than 2.12 Å. The O atom from the shortest interaction [N7—O7 = 1.209 (4) Å] is, on the other hand, engaged in two weak interactions where H···O7 is greater than 2.46 Å. The ribbons of molecules further interact *via* a single C10—H10*B*···O4^{vi} contact, which engages bordering nitrate and methanol methyl groups to form layers (Fig. 2). The layers coincide with the (202) crystallographic plane. Although NO$_3^-$ as free anions can take any orientation, the extensive hydrogen bonding leads to a coplanar arrangement of cations and anions. The separation between the layers is approximately 3.2 Å. The OH group of the pyridoxal unit is the only fragment that deviates significantly from this overall planarity [the dihedral angle between the mean coordination plane and the plane of the pyridoxal C9/O2/H12 group is 77.3 (1)°]. This group is, however, suitably oriented toward the neighboring layer to serve as an acceptor in a very strong O3—H13···O2^{ii} hydrogen bond with the methanol hydroxy group and also as a donor in a second hydrogen bond to a nitrate anion, *viz.* O2—H12···O6^{i} (Table 2). There is no other connection between the planar two-dimensional formations.

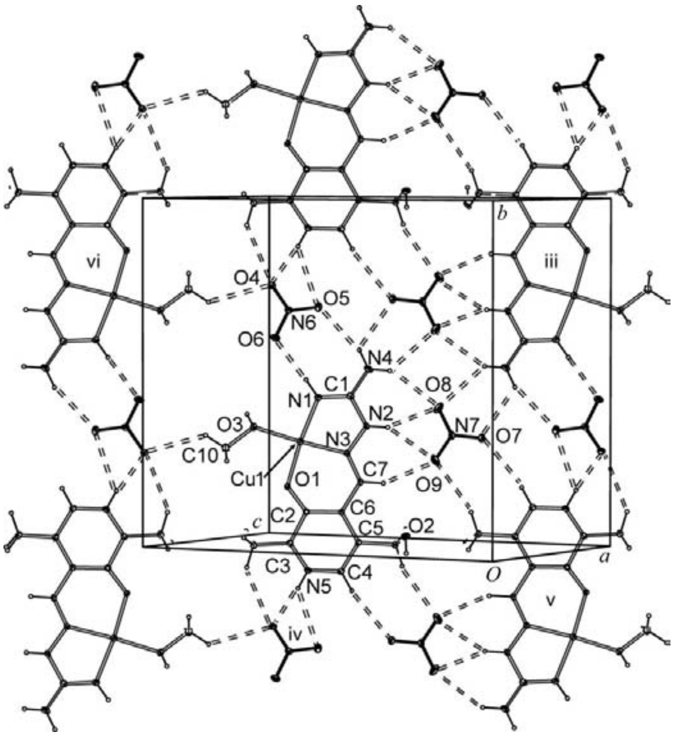

Figure 2
A segment of the crystal packing, showing the ribbon of (I) connected to the neighboring ribbon *via* a single C—H···O interaction. [Symmetry codes: (iii) $-x + 2, -y + 1, -z + 1$; (iv) $x, y - 1, z$; (v) $-x + 2, -y, -z + 1$; (vi) $-x + 1, -y + 1, -z + 2$.]

Experimental

The title complex was synthesized by the reaction of warm equimolar methanol solutions of Cu(NO$_3$)$_2$·H$_2$O and the Schiff base PL–AG·HNO$_3$·HCl obtained by condensation of ethanol solutions of AG·HNO$_3$ and PL·HCl. After 24 h, green monocrystals of the complex were vacuum filtered and washed with methanol and diethyl ether (yield 0.17 g, 77%; m.p. > 623 K).

Crystal data

[Cu(C$_9$H$_{13}$N$_5$O$_2$)(CH$_4$O)](NO$_3$)$_2$
M_r = 442.85
Monoclinic, $P2_1/c$
a = 8.113 (2) Å
b = 13.852 (2) Å
c = 14.9846 (3) Å
β = 103.013 (2)°
V = 1640.8 (5) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 1.40 mm^{-1}
T = 293 K
0.32 × 0.18 × 0.15 mm

Data collection

Oxford Xcalibur S CCD diffractometer
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2008)
T_{min} = 0.622, T_{max} = 0.801
20236 measured reflections
3586 independent reflections
2632 reflections with $I > 2\sigma(I)$
R_{int} = 0.022

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.045
$wR(F^2)$ = 0.141
S = 1.06
3586 reflections
251 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.70 e Å^{-3}
$\Delta\rho_{min}$ = −0.73 e Å^{-3}

Almost all H atoms were visible in a difference Fourier map, but those bonded to C and N atoms were placed at geometrically calculated positions and refined using a riding model. C—H distances were fixed at 0.93–0.97 Å, with U_{iso}(H) values equal to 1.2 (phenyl and methylene) or 1.5 (methyl) times U_{eq}(C). N—H distances were fixed at 0.86 Å, with U_{iso}(H) values equal to 1.2U_{eq}(N). The H atoms

Table 1
Selected geometric parameters (Å, °).

Cu1—O1	1.885 (2)	C2—C6	1.419 (4)
Cu1—O3	1.977 (3)	C2—C3	1.440 (5)
Cu1—N1	1.934 (3)	C3—C8	1.483 (5)
Cu1—N3	1.947 (3)	C4—C5	1.366 (5)
O1—C2	1.283 (4)	C5—C6	1.411 (5)
O2—C9	1.428 (5)	C5—C9	1.501 (4)
O3—C10	1.424 (5)	C6—C7	1.442 (5)
N1—C1	1.300 (4)	N6—O4	1.250 (4)
N2—C1	1.376 (4)	N6—O5	1.226 (4)
N3—C7	1.275 (5)	N6—O6	1.242 (4)
N4—C1	1.310 (4)	N7—O7	1.209 (4)
N5—C3	1.317 (4)	N7—O9	1.213 (5)
N5—C4	1.338 (4)	N7—O8	1.228 (4)
N2—N3	1.355 (4)		
N1—Cu1—N3	81.99 (13)	C7—N3—N2	119.5 (3)
N1—Cu1—O3	94.37 (12)	N1—C1—N2	116.1 (3)
O1—Cu1—N3	92.10 (11)	O1—C2—C6	127.3 (3)
O1—Cu1—O3	91.47 (11)	O1—C2—C3	115.7 (3)
O1—Cu1—N1	174.03 (11)	C2—C6—C7	121.5 (3)
O3—Cu1—N3	175.01 (12)	N3—C7—C6	123.0 (3)
N3—N2—C1	116.2 (3)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H12···O6^{i}	0.82	2.09	2.705 (4)	132
O3—H13···O2^{ii}	0.94 (6)	1.85 (6)	2.691 (4)	147 (5)
N1—H1···O6	0.86	2.12	2.978 (4)	175
N2—H2···O8	0.86	2.20	3.004 (5)	155
N2—H2···O9	0.86	2.34	3.103 (6)	149
N4—H4*A*···O5	0.86	2.40	3.229 (5)	162
N4—H4*A*···O7^{iii}	0.86	2.46	2.998 (5)	121
N4—H4*B*···O8	0.86	2.49	3.241 (5)	147
N4—H4*B*···O8^{iii}	0.86	2.51	3.164 (5)	133
N5—H5···O4^{iv}	0.86	1.91	2.750 (4)	167
N5—H5···O5^{iv}	0.86	2.59	3.239 (4)	132
C4—H4···O7^{v}	0.93	2.62	3.534 (5)	167
C7—H7···O9	0.93	2.29	3.149 (7)	152
C8—H8*A*···O4^{iv}	0.96	2.67	3.440 (5)	138
C9—H9*B*···O9^{v}	0.97	2.60	3.546 (6)	164
C10—H10*B*···O4^{vi}	0.96	2.67	3.388 (6)	131

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

bonded to O atoms were both located in the difference map. The refinement of atom H12 yielded an unreasonable O—H distance; it was therefore placed in a geometrically calculated position, with a fixed O—H distance of 0.82 Å and U_{iso}(H) = 1.5U_{eq}(O2). Atom H13 was refined isotropically.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2008); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2008); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *PLATON* (Spek, 2009); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SF3109). Services for accessing these data are described at the back of the journal.

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