

Methanol[1-(methoxymethanimidoyl)-2-(pyridin-2-ylmethyl)guanidine]bis-(perchlorato)copper(II)

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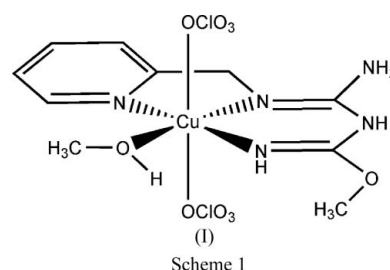
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The title complex, $[\text{Cu}(\text{ClO}_4)_2(\text{C}_9\text{H}_{13}\text{N}_5\text{O})(\text{CH}_3\text{OH})]$, was synthesized from a methanolysis reaction of *N*-(methylpyridin-2-yl)cyanoguanidine (L^3) and copper(II) perchlorate hexahydrate in a 1:1 molar ratio. The Cu^{II} ion is six-coordinated by an N_3O_3 donor set which confers a highly distorted and asymmetric octahedral geometry. Three N-donor atoms from the chelating 1-(methoxymethanimidoyl)-2-(pyridin-2-ylmethyl)guanidine (L^{3m}) ligand and one O atom from the methanol molecule define the equatorial plane, with two perchlorate O atoms in the apical sites, one of which has a long $\text{Cu}-\text{O}$ bond of 2.9074 (19) Å. The dihedral angle between the five- and six-membered chelate rings is 8.21 (8)°. Two molecules are associated into a dimeric unit by intermolecular $\text{N}-\text{H}\cdots\text{O}(\text{perchlorate})$ hydrogen bonds. Additionally, the weakly coordinated perchlorate anions also link adjacent $[\text{Cu}(\text{ClO}_4)_2(L^{3m})(\text{CH}_3\text{OH})]$ dimers by hydrogen-bonding interactions, resulting in a two-dimensional layer in the (100) plane. Further $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds link the two-dimensional layers along [100] to generate a three-dimensional network.

Comment

Amidino-*O*-alkylureas (aOau) are a series of guanidine derivatives which have important roles in supramolecular architectures and bioinorganic systems because of their versatile hydrogen-bonding potential (Hubberstey *et al.*, 2000). Several copper(II) complexes containing *N*-donor aOau ligands with various extended structures have been reported. For example, Suksangpanya and co-workers have reported the synthesis of two-dimensional rhombic (4,4) grids using copper(II) halides of two bidentate (*N*-alkylamidino-*O*-alkylurea) ligands (Suksangpanya *et al.*, 2003). Also, copper(II) halide complexes containing tridentate (Suksangpanya *et al.*, 2004) and tetra-

dentate (Suksangpanya *et al.*, 2002) aOau derivatives have been intensively investigated by single-crystal X-ray diffraction. Crystallographic data indicate that their different extended hydrogen-bonding interactions depend partially on the substituents on the aOau ligand defining the hydrogen-bond donors and acceptors. Recently, we have investigated the DNA binding and nuclease behaviors (Chaveerach *et al.*, 2010) and the interactions with cytosine nucleobase (Meenongwa *et al.*, 2011) of copper(II) complexes containing amidino-*O*-methylurea (L^{1m}) and *N*-(methylphenyl)-amidino-*O*-methylurea (L^{2m}). Herein, we present the structure of the title compound, (I), a copper(II) bis(perchlorate) complex of



1-(methoxymethanimidoyl)-2-(pyridin-2-ylmethyl)guanidine (L^{3m}) (Scheme 1), which was prepared using a procedure similar to that reported previously (Suksangpanya *et al.*, 2004) but using copper(II) perchlorate hexahydrate instead of a copper(II) halide.

The initial product was obtained as a purple solid (Scheme 2) with a *d-d* transition at $\lambda_{\text{max}} = 583.0$ nm. The

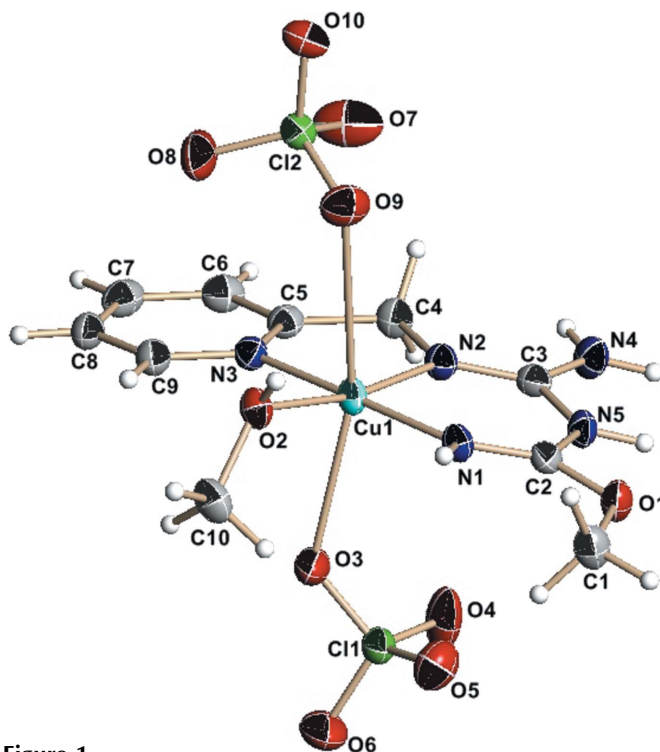
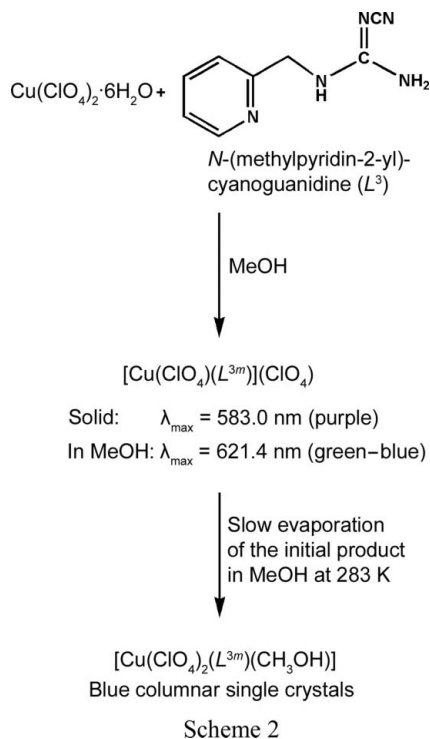


Figure 1
The molecular structure of complex (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

metal-organic compounds

elemental analysis was in agreement with the formula $[\text{Cu}(\text{ClO}_4)(L^{3m})](\text{ClO}_4)$. In the presence of methanol, the product solution turned green–blue in color and displayed an electronic absorption at $\lambda_{\text{max}} = 621.4 \text{ nm}$. This result could mirror the change in the coordination geometry at the Cu^{II} center between solid and solution phases of this complex. Suitable single crystals of the title complex, (I), were obtained by slow evaporation from a methanol solution of the initial product.



The molecular structure of (I) is shown in Fig. 1. This complex crystallizes in the triclinic space group $P\bar{1}$ with one

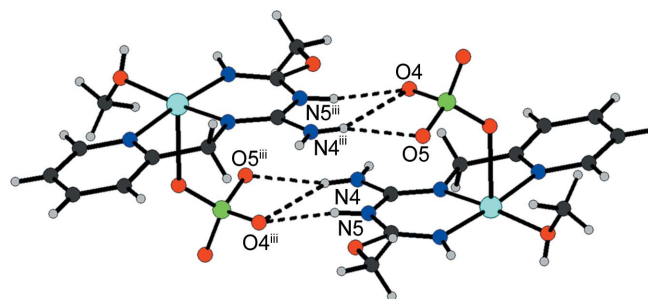


Figure 2
A view of dimer formation in (I), showing the $\text{N}-\text{H} \cdots \text{O}$ hydrogen bonds (dashed lines). Weakly coordinated perchlorate ions have been omitted for clarity. [Symmetry code: (iii) $-x + 1, -y + 1, -z + 2$.]

molecule of $[\text{Cu}(\text{ClO}_4)_2(L^{3m})(\text{CH}_3\text{OH})]$ in the asymmetric unit. The Cu^{II} cation is coordinated in an equatorial plane by three N donor atoms (N1, N2 and N3) from the chelating L^{3m} ligand and by atom O2 from the methanol molecule (as a result of crystal growth from that solvent), while atoms O3 and O9 from mutually *trans* perchlorate anions are located at the two apical sites. The $\text{Cu}-\text{N}$ bond distances range from 1.9315 (17) to 1.9711 (17) Å and the $\text{Cu1}-\text{O2}$ bond distance is 2.0132 (16) Å, while perchlorate atom O3 lies at a distance of 2.4935 (17) Å from the Cu^{II} center. The remaining axial site at Cu1 is occupied by atom O9 from another perchlorate anion. Although the $\text{Cu1}-\text{O9}$ distance of 2.9074 (19) Å is quite long (Dobrzyńska *et al.*, 2010; Husain *et al.*, 2011) compared with the average $\text{Cu}-\text{O}(\text{perchlorate})$ bond of 2.495 Å calculated from 91 examples of a perchlorate ion terminally coordinated to copper (Orpen *et al.*, 1989), the role of O9 in completing the coordination around the Cu^{II} center results in the overall geometry being a distorted octahedron. The $\text{N1}-\text{Cu1}-\text{N3}$ and $\text{N2}-\text{Cu1}-\text{O2}$ angles are approximately linear (Table 1). Atom Cu1 is displaced by 0.0531 (2) Å from the mean plane

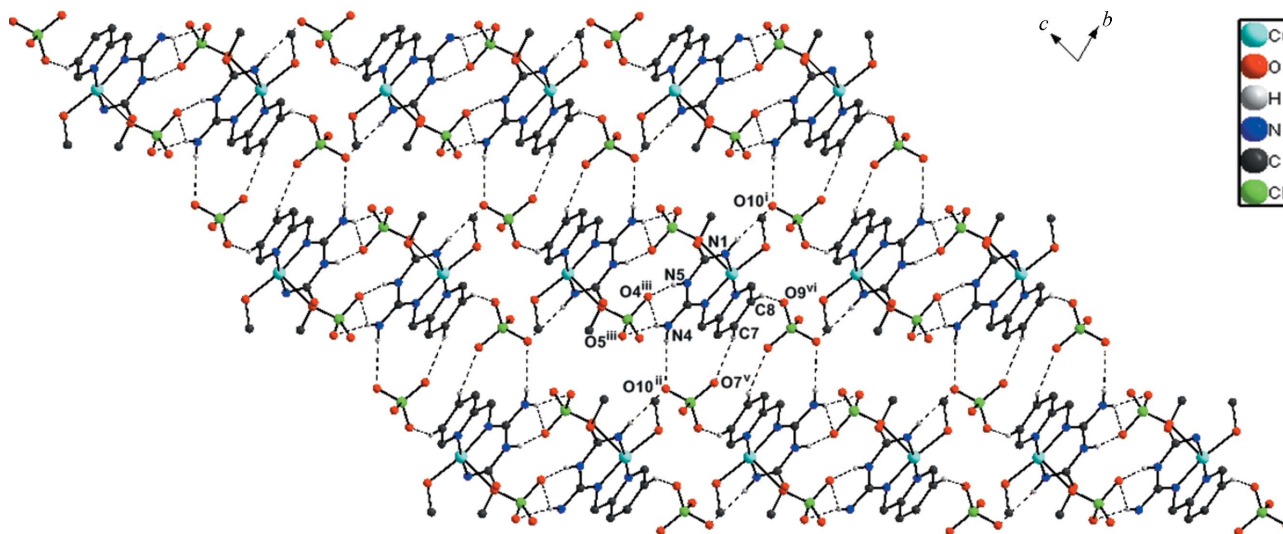


Figure 3
A view of the crystal packing of (I) in the (100) plane, showing how the hydrogen bonds (dashed lines) involving perchlorate counter-ions form a two-dimensional layer. All H atoms not involved in the depicted interactions and hydrogen bonds within the dimer and the two-dimensional layer have been omitted for clarity. [Symmetry codes: (i) $-x + 1, -y + 2, -z + 1$; (ii) $-x + 1, -y + 1, -z + 1$; (v) $-x, -y + 1, -z + 1$; (vi) $x - 1, y, z$.]

through the equatorial donor atoms in the direction of the O3 axial donor, with a dihedral angle of 8.21 (8)° between the least-squares mean planes of the five-membered CuN₂C₂ and six-membered CuN₃C₂ chelate rings.

Two [Cu(ClO₄)₂(L^{3m})(CH₃OH)] molecules form a dimeric unit (Fig. 2) *via* N—H...O hydrogen bonds (Table 2, entries 3, 4 and 5). The weakly coordinated perchlorate anion plays a major role in constructing an extensive network *via* N—H...O (Table 2, entries 1 and 2), O—H...O (Table 2, entry 6) and C—H...O (Table 2, entry 7) hydrogen bonds to form a two-dimensional layer in the (100) plane (Fig. 3). Further C—H...O hydrogen bonds (Table 2, entries 8 and 9) along [100] link the two-dimensional layers to generate a three-dimensional network. Although the title complex contains aromatic moieties, these are not observed to participate in π - π stacking interactions.

A comparison between (I) and the previously reported copper(II) complex containing the same L^{3m} ligand but with halide anions instead of perchlorate anions, [CuX₂(L^{3m})] (X = Cl or Br; Suksangpanya *et al.*, 2004), is also possible: both complexes show differences in geometry and chromophore. The [CuX₂(L^{3m})] complex displays a slightly distorted square-pyramidal geometry with a CuN₃X₂ chromophore, while a CuN₃O₃ chromophore with a highly-distorted octahedral geometry is observed in (I). This difference may arise from the fact that perchlorate anions are more sterically demanding than halide anions, but the fact that perchlorate is a poorly coordinating ligand may also be significant. As a result, the remaining free basal position is coordinated by a methanol molecule from the recrystallization solvent.

In summary, we have determined the crystal structure of [Cu(ClO₄)₂(L^{3m})(CH₃OH)], (I). This is controlled not only by the high potential for hydrogen-bond formation exhibited by the L^{3m} ligand, resulting in a three-dimensional packing motif, but also by the size, geometry and weak coordination of the perchlorate anion.

Experimental

The *N*-(methylpyridin-2-yl)cyanoguanidine precursor (L³) was prepared as described previously (Rose & Swain, 1956; Shapiro *et al.*, 1961). The copper(II) complex was prepared by mixing a 1:1 molar ratio of the *N*-(methylpyridin-2-yl)cyanoguanidine precursor (0.1760 g, 1 mmol) and copper(II) perchlorate hexahydrate (0.3705 g, 1 mmol, Sigma-Aldrich, 98%) in methanol (50 ml). The reaction was refluxed for 24 h. The resulting green-blue mixture was then cooled to ambient temperature and filtered to remove excess solids. The solvent was removed *in vacuo* to give a deep-purple solid (yield 0.4448 g, 94.8%; m.p. 492.5–495 K). Selected IR data (KBr pellet, ν , cm⁻¹): 3390 (*m*, N—H), 1686 (*s*, C=N), 1571 (*m*, NH₂), 1547 (*m*, C=C), 1346 (*m*, C—O), 1144 (*s*, ClO₄), 1088 (*s*, ClO₄). Diffuse reflectance (λ_{\max} , nm): 583.0. Visible (2 mM in MeOH, λ_{\max} , nm): 621.4. Analysis calculated for [Cu(ClO₄)(L^{3m})(ClO₄), (C₉H₁₃Cl₂CuN₅O₉): C 23.00, H 2.77, N 14.91%; found: C 23.13, H 2.76, N 15.04%. ESI+ MS (*m/z*): 371 [Cu(ClO₄)(L^{3m}) + H]²⁺, 271 [Cu(L^{3m})]²⁺.

Suitable single crystals of (I) were obtained as blue columns from a methanol solution of the initial product by slow evaporation at 283 K over a period of one week.

Table 1

Selected geometric parameters (Å, °).

Cu1—N1	1.9315 (17)	Cu1—O2	2.0132 (16)
Cu1—N2	1.9319 (17)	Cu1—O3	2.4935 (17)
Cu1—N3	1.9711 (17)	Cu1—O9	2.9074 (19)
N1—Cu1—N2	92.08 (7)	N3—Cu1—O2	93.13 (7)
N1—Cu1—N3	174.89 (7)	N1—Cu1—O3	91.34 (7)
N2—Cu1—N3	83.78 (7)	N2—Cu1—O3	98.56 (7)
N1—Cu1—O2	91.42 (7)	N3—Cu1—O3	86.34 (6)
N2—Cu1—O2	170.60 (7)	O2—Cu1—O3	90.08 (6)

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>
N1—H1...O10 ⁱ	0.88	2.26	3.129 (3)	167
N4—H4A...O10 ⁱⁱ	0.88	2.25	2.932 (3)	134
N4—H4B...O4 ⁱⁱⁱ	0.88	2.59	3.328 (3)	143
N4—H4B...O5 ⁱⁱⁱ	0.88	2.11	2.950 (3)	159
N5—H5...O4 ⁱⁱⁱ	0.88	2.03	2.889 (3)	167
O2—H11...O9 ^j	0.75 (3)	2.18 (3)	2.919 (3)	176
C4—H4C...O6 ^{iv}	0.99	2.37	3.316 (3)	159
C7—H7...O7 ^v	0.95	2.58	3.413 (4)	146
C8—H8...O9 ^{vi}	0.95	2.59	3.461 (3)	152

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

Crystal data

[Cu(ClO ₄) ₂ (C ₉ H ₁₃ N ₅ O)(CH ₄ O)]	$\gamma = 86.176$ (4)°
$M_r = 501.73$	$V = 905.9$ (4) Å ³
Triclinic, $P\bar{1}$	$Z = 2$
$a = 8.034$ (2) Å	Mo $K\alpha$ radiation
$b = 9.804$ (3) Å	$\mu = 1.56$ mm ⁻¹
$c = 12.093$ (3) Å	$T = 150$ K
$\alpha = 74.720$ (4)°	$0.30 \times 0.15 \times 0.10$ mm
$\beta = 80.455$ (4)°	

Data collection

Bruker SMART APEX CCD area-detector diffractometer	8026 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	4119 independent reflections
$T_{\min} = 0.656, T_{\max} = 0.746$	3857 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.014$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.031$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.081$	$\Delta\rho_{\max} = 0.47$ e Å ⁻³
$S = 1.07$	$\Delta\rho_{\min} = -0.27$ e Å ⁻³
4119 reflections	
259 parameters	

H atoms bonded to C and N were positioned geometrically and refined using a riding model, with N—H = 0.88 Å and C—H = 0.98, 0.99 or 0.95 Å for methyl, methylene and aromatic H atoms, respectively, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$ and $1.5U_{\text{eq}}(\text{methyl C})$. The H atom bonded to the methanol O atom was located in a difference Fourier map and refined freely.

Data collection: SMART (Bruker, 2001); cell refinement: SAINT (Bruker, 2000); data reduction: SAINT and SHELXTL (Sheldrick, 2008); program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick,

2008); molecular graphics: *SHELXTL*; software used to prepare material for publication: *pubCIF* (Westrip, 2010).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FN3103). Services for accessing these data are described at the back of the journal.

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