

## Bis[bis(methoxycarbimido)amine- $\kappa^2N,N'$ ]bis(perchlorato- $\kappa O$ )copper(II) bis[bis(methoxycarbimido)amine- $\kappa^2N,N'$ ]bis(methanol- $\kappa O$ )copper(II) bis(perchlorate) methanol disolvate

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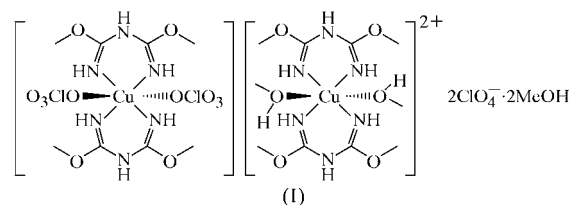
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The title compound,  $[\text{Cu}(\text{ClO}_4)_2(\text{C}_4\text{H}_9\text{N}_3\text{O}_2)_2][\text{Cu}(\text{C}_4\text{H}_9\text{N}_3\text{O}_2)_2(\text{CH}_4\text{O})_2](\text{ClO}_4)_2 \cdot 2\text{CH}_3\text{OH}$ , comprises two independent  $\text{Cu}^{\text{II}}$  species lying on different inversion sites. In the Cu complexes, a distorted octahedral geometry arises (from basic square-planar  $\text{N}_4$  coordination) from the weak coordination of two perchlorate ions (as  $\text{Cu}-\text{O}$ ) in one species and two methanol molecules in the other (also as  $\text{Cu}-\text{O}$ ). Interactions between the O atoms of the perchlorate anions or methanol groups and the imide or amine NH groups afford an extensive intermolecular hydrogen-bonding network.

### Comment

Copper(II) complexes of the bis(methoxycarbimido)amine ligand  $\text{HN}[\text{C}(\text{NH})\text{OCH}_3]_2$  (*L*), though relatively uncommon, are interesting because *L* is usually formed *in situ* from reactions of  $\text{Cu}^{\text{II}}$  salts with sodium dicyanamide (dca) in methanol or mixed solvents (Kozisek *et al.*, 1990; Boca *et al.*, 1996; Bishop *et al.*, 2000; Atkinson *et al.*, 2002; Tong *et al.*, 2003). The formation of *L* involves a nucleophilic addition of the methanol molecule on the dca anion. This reaction is promoted by a coordinative activation of the  $\text{C}\beta$  site of the non-linear dca anion. Under activation, it is susceptible to bending of the linear pseudohalide (*sp*-hybridized C) *via* N-coordination, which alters the  $\text{C}\beta$  site to *sp*<sup>2</sup>-hybridized, with an unsaturated valency and susceptibility to nucleophilic attack. Ligand *L* when coordinated to  $\text{Cu}^{\text{II}}$  exists in its anionic and/or neutral forms. For example, the neutral complex  $[\text{Cu}\{\text{N}[\text{C}(\text{NH})\text{OCH}_3]_2\}_2]$ , (II), contains two anionic  $\{\text{N}[\text{C}(\text{NH})\text{OCH}_3]_2\}^-$  species (Kozisek *et al.*, 1990; Boca *et al.*, 1996; Tong *et al.*, 2003), whereas in  $[\text{Cu}\{\text{HN}[\text{C}(\text{NH})\text{OCH}_3]_2\}_2]$

$(\text{C}_2\text{H}_5\text{N}_3\text{O}_2)_2] \cdot 2\text{C}_2\text{H}_5\text{N}_3\text{O}_2 \cdot 2\text{CH}_3\text{OH} \cdot 0.8\text{CH}_3\text{CN}$  ( $\text{C}_2\text{H}_5\text{N}_3\text{O}_2$  is biuret), (III), the central  $\text{Cu}^{\text{II}}$  atom is coordinated by two neutral  $\text{HN}[\text{C}(\text{NH})\text{OCH}_3]_2$  ligands to form  $[\text{Cu}\{\text{HN}[\text{C}(\text{NH})\text{OCH}_3]_2\}_2]^{2+}$  dications (Bishop *et al.*, 2000). However, a monocationic complex,  $[\text{Cu}\{\text{HN}[\text{C}(\text{NH})\text{OCH}_3]_2\}[\text{N}[\text{C}(\text{NH})\text{OCH}_3]_2]]\text{PF}_6$ , has also been isolated by heating (II) with excess  $\text{NH}_4\text{PF}_6$  in a mixture of  $\text{CH}_3\text{OH}$  and  $\text{CH}_3\text{CN}$  (Atkinson *et al.*, 2002). This consists of a neutral *L* ligand and an anionic  $\{\text{N}[\text{C}(\text{NH})\text{OCH}_3]_2\}^-$  ligand bonded to  $\text{Cu}^{\text{II}}$ . Recently, we have reacted  $\text{Cu}(\text{ClO}_4)_2$  with  $\text{Na}(\text{dca})$  in methanol and isolated a dicationic complex, (I), with methanol solvent molecules,  $[\text{Cu}\{\text{HN}[\text{C}(\text{NH})\text{OCH}_3]_2\}_2](\text{ClO}_4)_2 \cdot 2\text{CH}_3\text{OH}$ ; we report here the crystal structure of (I).



The asymmetric unit of (I) consists of two halves of the  $[\text{Cu}\{\text{HN}[\text{C}(\text{NH})\text{OCH}_3]_2\}_2]^{2+}$  species, two perchlorate anions and two methanol molecules. The existence of two distinct  $\text{Cu}^{\text{II}}$  systems in the asymmetric unit is uncommon and only two examples (Curtis & Puschmann, 2004; Suksangpanya *et al.*, 2003) were found in the Cambridge Structural Database (Allen, 2002). In (I), the  $\text{Cu}^{\text{II}}$  complexes lie with the Cu centre on different inversion centres and with each  $\text{Cu}^{\text{II}}$  atom coordinated by four N atoms in a basic square-planar geometry, forming two six-membered metallo-rings (Figs. 1 and 2). The  $(\text{H})\text{N}=\text{C}$  bonds are typical double bonds [the average bond length is 1.276 (2) Å], while the average bond length for the  $(\text{H})\text{N}-\text{C}$  bonds is 1.365 (2) Å, indicating a weak delocalized  $\pi$ -bonding system. The average  $\text{Cu}-\text{N}$  bond length of 1.970 (2) Å (Table 1) is slightly longer than in (II) [1.948 (1) Å] but close to the corresponding length in (III) [1.965 (3) Å].

In one complex, two perchlorate ions bind weakly to Cu, forming a distorted octahedral  $[\text{Cu}\{\text{HN}[\text{C}(\text{NH})\text{OCH}_3]_2\}_2]$

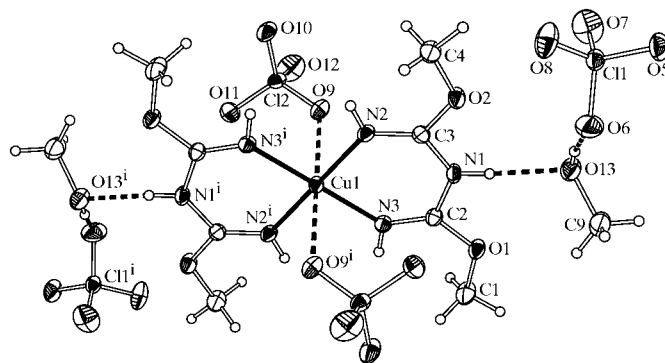
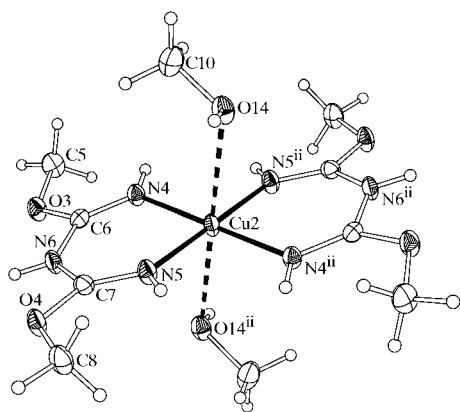


Figure 1

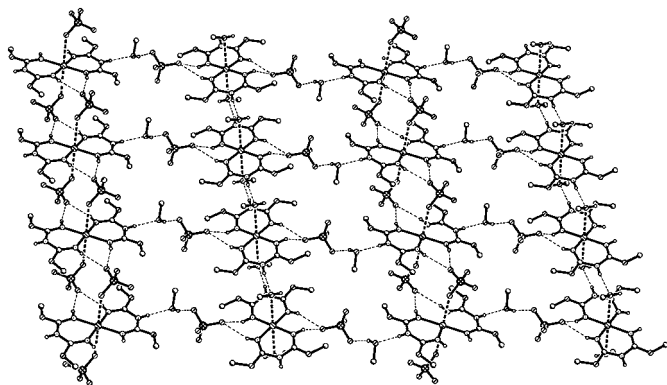
A view of the perchlorate-coordinated species in (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii. The dashed lines represent  $\text{Cu}\cdots\text{O}$  bonds. [Symmetry code: (i)  $-x + 1, -y + 1, -z + 1$ .]

(ClO<sub>4</sub>)<sub>2</sub> species. The Cu—O bond length [2.7010 (17) Å] is longer than in [Cu(L')(ClO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O [2.543 (3) Å; L' is 3-(4,6-diamino-1,3,5-triazin-2-yl)-1,3,5,8,12-pentaazacyclotetradecane] and [Cu(HL)(ClO<sub>4</sub>)<sub>2</sub>](ClO<sub>4</sub>)·H<sub>2</sub>O [2.590 (4) Å] (Comba *et al.*, 2002). In the other complex, the two methanol molecules are coordinated to atom Cu2 to form [Cu{HN[C(NH)OCH<sub>3</sub>]<sub>2</sub>]<sub>2</sub>(CH<sub>3</sub>OH)<sub>2</sub>]<sup>2+</sup> octahedral species. The Cu2—O distance [2.7192 (18) Å] is much longer than those found in [Cu(L'')<sub>2</sub>(CH<sub>3</sub>OH)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub> [2.298 (4) Å; L'' is 1-(2-pyridyl)benzotriazole; Richardson & Steel, 2003] and [Cu(L''')<sub>2</sub>(CH<sub>3</sub>OH)<sub>2</sub>](SiF<sub>6</sub>)<sub>2</sub> [2.481 (5) Å; L''' is di-2-pyridylamine; Casellas *et al.*, 2005].

The crystal structure of (I) is stabilized by extensive N—H···O and O—H···O hydrogen-bonding interactions (Table 2). The O atoms of the coordinated perchlorate anions in the [Cu{HN[C(NH)OCH<sub>3</sub>]<sub>2</sub>]<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub>] species interact with the imide groups of neighbouring species to afford intermolecular N—H···O hydrogen-bonding interactions, thereby forming one-dimensional chains along the *a*-axis direction.



**Figure 2**  
A view of the methanol-coordinated species in (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii. The dashed lines represent Cu···O bonds. [Symmetry code: (ii)  $-x, -y + 3, -z + 2$ .]



**Figure 3**  
The layer structure of (I) parallel to (012̄). The dashed lines indicate N—H···O and O—H···O interactions.

The [Cu{HN[C(NH)OCH<sub>3</sub>]<sub>2</sub>]<sub>2</sub>(CH<sub>3</sub>OH)<sub>2</sub>]<sup>2+</sup> complexes are also linked *via* intermolecular interactions between the O atoms of coordinated methanol molecules and amine groups to form another one-dimensional chain. Between the two chains are sandwiched free perchlorate anions and methanol solvent molecules. In addition, the O atoms from the free perchlorate ions and methanol solvent molecules interact with the imide and amine groups of adjacent species of the two chains to afford a two-dimensional network along the (012̄) plane (Fig. 3). Furthermore, the O atoms of the coordinated perchlorate anions interact with the coordinated methanol molecules of adjacent layers to afford hydrogen bonds [O14···O11<sup>iv</sup> and O14···O12<sup>iv</sup>; symmetry code: (iv)  $-x, -y + 2, -z + 1$ ], thus forming a three-dimensional structure.

### Experimental

To a solution of Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (370 mg, 1.0 mmol) in methanol (15 ml) was added a solution containing sodium dicyanamide (100 mg, 1.12 mmol) in methanol (10 ml). The mixture was stirred for 2 h at 323 K to form a green solution. Slow diffusion of diethyl ether into the filtrate gave rise to purple crystals of (I) (yield 48%). Analysis found: C 20.23, H 4.38, N 14.15%; calculated for C<sub>20</sub>H<sub>52</sub>Cl<sub>4</sub>Cu<sub>2</sub>N<sub>12</sub>O<sub>28</sub>: C 20.40, H 4.45, N 14.27%. IR (KBr,  $\nu$ , cm<sup>-1</sup>): 3008 (w), 2942 (w), 2920 (w), 1633 (m), 1558 (m), 1465 (m), 1427 (m).

#### Crystal data

[Cu(ClO<sub>4</sub>)<sub>2</sub>(C<sub>4</sub>H<sub>9</sub>N<sub>3</sub>O<sub>2</sub>)<sub>2</sub>]-  
[Cu(C<sub>4</sub>H<sub>9</sub>N<sub>3</sub>O<sub>2</sub>)<sub>2</sub>(CH<sub>4</sub>O)<sub>2</sub>]-  
(ClO<sub>4</sub>)<sub>2</sub>·2CH<sub>4</sub>O  
*M<sub>r</sub>* = 1177.64  
Triclinic, P1̄  
*a* = 7.444 (2) Å  
*b* = 10.067 (2) Å  
*c* = 15.330 (3) Å  
 $\alpha$  = 85.06 (3)°  
 $\beta$  = 89.91 (3)°  
 $\gamma$  = 80.20 (3)°  
*V* = 1127.7 (5) Å<sup>3</sup>  
*Z* = 1  
*D<sub>x</sub>* = 1.734 Mg m<sup>-3</sup>  
Mo K $\alpha$  radiation  
 $\mu$  = 1.28 mm<sup>-1</sup>  
*T* = 153 (2) K  
Block, purple  
0.32 × 0.30 × 0.26 mm

#### Data collection

Rigaku Mercury diffractometer  
 $\omega$  scans  
Absorption correction: multi-scan  
(Jacobson, 1998)  
*T*<sub>min</sub> = 0.684, *T*<sub>max</sub> = 0.731  
10868 measured reflections  
4082 independent reflections  
3857 reflections with *I* > 2 $\sigma$ (*I*)  
*R*<sub>int</sub> = 0.017  
 $\theta$ <sub>max</sub> = 25.3°

#### Refinement

Refinement on *F*<sup>2</sup>  
*R*[*F*<sup>2</sup> > 2 $\sigma$ (*F*<sup>2</sup>)] = 0.027  
*wR*(*F*<sup>2</sup>) = 0.076  
*S* = 1.01  
4082 reflections  
339 parameters  
H atoms treated by a mixture of independent and constrained refinement  
 $w = 1/[\sigma^2(F_o^2) + (0.0482P)^2 + 0.6301P]$   
where  $P = (F_o^2 + 2F_c^2)/3$   
( $\Delta/\sigma$ )<sub>max</sub> = 0.001  
 $\Delta\rho$ <sub>max</sub> = 0.72 e Å<sup>-3</sup>  
 $\Delta\rho$ <sub>min</sub> = -0.37 e Å<sup>-3</sup>

**Table 1**  
Selected geometric parameters (Å, °).

Cu1—N2	1.9708 (17)	Cu2—N4	1.9691 (16)
Cu1—N3	1.9786 (16)	Cu2—N5	1.9609 (17)
Cu1—O9	2.7010 (17)	Cu2—O14	2.7192 (18)
N2—Cu1—N3	88.70 (7)	N4—Cu2—N5	88.51 (7)
N2—Cu1—O9	86.69 (6)	N5—Cu2—O14	92.66 (6)
N3—Cu1—O9	94.68 (6)	N4—Cu2—O14	96.83 (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...O13	0.84 (1)	1.95 (1)	2.774 (2)	168 (2)
N2—H2...O10 <sup>iii</sup>	0.84 (1)	2.25 (1)	3.067 (2)	165 (2)
N3—H3...O10 <sup>v</sup>	0.84 (1)	2.29 (1)	3.102 (2)	163 (2)
N4—H4...O5 <sup>ii</sup>	0.84 (1)	2.23 (1)	3.011 (2)	154 (2)
N5—H5...O5	0.84 (1)	2.50 (2)	3.123 (2)	132 (2)
N5—H5...O12 <sup>iv</sup>	0.84 (1)	2.48 (2)	3.078 (2)	129 (2)
N6—H6...O14 <sup>v</sup>	0.84 (1)	1.98 (1)	2.808 (2)	169 (2)
O13—H13...O6	0.83 (1)	2.02 (1)	2.833 (2)	166 (3)
O14—H14...O11 <sup>iv</sup>	0.83 (1)	2.33 (2)	3.101 (2)	155 (3)
O14—H14...O12 <sup>iv</sup>	0.83 (1)	2.47 (2)	3.196 (3)	146 (3)

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

The methyl H atoms were included in the refinement in the riding-model approximation [ $C-H = 0.98$  Å and  $U_{iso}(H) = 1.5U_{eq}(C)$ ]; the groups were rotated to fit the electron density. The N- and O-bound H atoms were located in difference Fourier maps and were refined with distance restraints [ $N-H = O-H = 0.85$  (1) Å]; their displacement parameters were refined freely.

Data collection: *CrystalClear* (Rigaku/MSC, 2001); cell refinement: *CrystalClear*; data reduction: *CrystalStructure* (Rigaku/MSC, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG3051). Services for accessing these data are described at the back of the journal.

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