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**Key indicators**

Single-crystal X-ray study  
 T = 298 K  
 Mean  $\sigma(\text{N}-\text{C}) = 0.005 \text{ \AA}$   
 R factor = 0.045  
 wR factor = 0.117  
 Data-to-parameter ratio = 13.2

For details of how these key indicators were  
 automatically derived from the article, see  
<http://journals.iucr.org/e>.

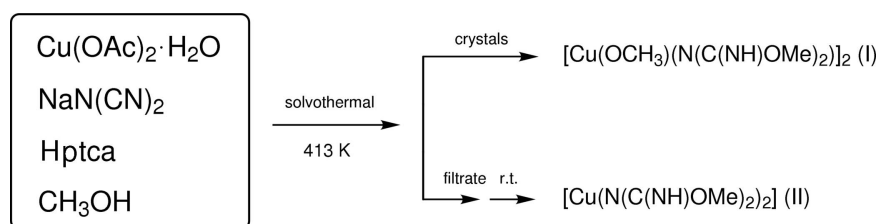
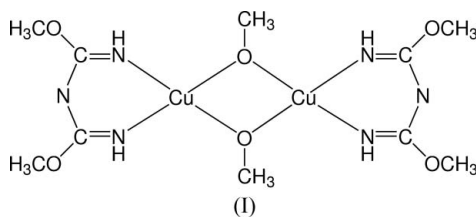
## Di- $\mu$ -methoxo-bis{[bis(methoxycarbimido)-aminato]copper(II)}

In the centrosymmetric dinuclear title complex,  $[\text{Cu}_2(\text{CH}_3\text{O})_2(\text{C}_4\text{H}_8\text{N}_3\text{O}_2)_2]$ , the two  $\text{Cu}^{\text{II}}$  ions are linked by a pair of methoxide bridges, with a non-bonding  $\text{Cu} \cdots \text{Cu}$  distance of 3.048 (1)  $\text{Å}$ . Each  $\text{Cu}^{\text{II}}$  center adopts a  $\text{CuO}_2\text{N}_2$  square-planar geometry, coordinated by the bidentate bis(methoxycarbimido)aminato and two methoxide ligands.

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### Comment

Recently, polymeric coordination architectures based on the dicyanamide (dca) anion and auxiliary organic co-ligands have been explored extensively due to their diverse network structures and interesting magnetic properties (Batten & Murray, 2003). During our attempt to prepare new metal-dca coordination frameworks with the aid of 2-(4-pyridyl)thiazole-4-carboxylic acid (Hptca) under solvothermal conditions in a methanol medium, an unexpected methoxide-bridged dinuclear  $\text{Cu}^{\text{II}}$  complex  $[\text{Cu}(\mu\text{-OCH}_3)(\text{N}(\text{C}(\text{NH})\text{OMe})_2)_2]$  (I) was obtained, followed by the isolation of a monomeric species  $[\text{Cu}(\text{N}(\text{C}(\text{NH})\text{OMe})_2)_2]$  (II) (see scheme). Notably, it is confirmed that the presence of the Hptca ligand in the above synthetic route is not required. In both complexes, the chelating ligand bis(methoxycarbimido)aminato originates from the *in situ* alcoholization of the dca anion. Complex (II) has been reported with crystallographic characterization (Boca *et al.*, 1996), and the crystal structure of (I) is described here.



The molecular structure of (I) is centrosymmetric; the anionic ligand  $[\text{N}(\text{C}(\text{NH})\text{OMe})_2]^-$  is produced from the metal-assisted nucleophilic addition of dca by methanol. As

shown in Fig. 1, each  $\text{Cu}^{\text{II}}$  ion is four-coordinated by the chelating ligand bis(methoxycarbimido)aminato and a pair of methoxide anions in a square-planar geometry. Selected geometric parameters are listed in Table 1. Two methoxide ligands bridge adjacent  $\text{Cu}^{\text{II}}$  centers, generating a dimeric structure with the formation of a perfectly planar  $\text{Cu}_2\text{O}_2$  core. The intramolecular  $\text{Cu}\cdots\text{Cu}$  separation is 3.048 (1) Å and the  $\text{Cu}-\text{O}-\text{Cu}$  bridging angle is 103.6 (1)°. Similar to those in the structure of (II) (Boca *et al.*, 1996), the distances in the bond sequence  $\text{N1}-\text{C1}-\text{N2}-\text{C2}-\text{N3}$  of the chelating ligand in (I) are 1.307 (6), 1.332 (6), 1.327 (6) and 1.301 (6) Å; the similar values also indicate a strongly delocalized  $\pi$ -bonding system. This conjugation also results in a planar configuration of the six-membered  $\text{Cu}-\text{N}-\text{C}-\text{N}-\text{C}-\text{N}$  chelate ring, with a mean deviation of the atoms from this plane of only 0.037 (5) Å; the ring is inclined to the central  $\text{Cu}_2\text{O}_2$  ring with a small dihedral angle of 6.4 (3)°. The whole  $[\text{N}(\text{C}(\text{NH})\text{OMe})_2]^-$  ligand also adopts a planar configuration, as suggested by the  $\text{C3}-\text{O1}-\text{C1}-\text{N1}$  [179.5 (5)°] and  $\text{C4}-\text{O2}-\text{C2}-\text{N3}$  [-177.4 (4)°] torsion angles. Analysis of the crystal packing of (I) indicates that these dinuclear molecules are isolated, with parallel columns stacking along [100]. The shortest intermolecular  $\text{Cu}\cdots\text{O}$  and  $\text{Cu}\cdots\text{N}$  distances are 3.270 (3) and 3.296 (4) Å, respectively; these are arrayed along the two opposite axial sites of each  $\text{Cu}^{\text{II}}$  pseudo-octahedral coordination environment.

## Experimental

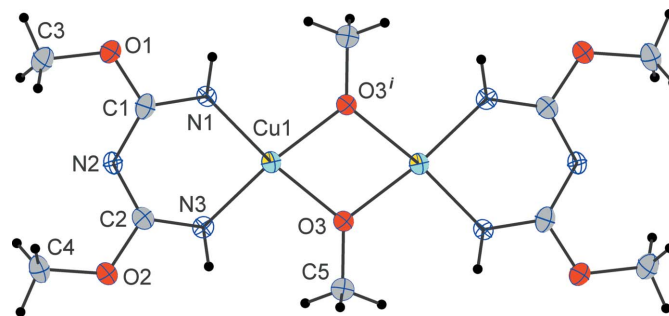
A mixture of  $\text{Cu}(\text{OAc})_2\cdot\text{H}_2\text{O}$  (10.0 mg, 0.05 mmol), sodium dicyanamide (4.5 mg, 0.05 mmol), Hptca (10.3 mg, 0.05 mmol), and methanol (10 ml) was sealed in a Teflon-lined stainless steel vessel (20 ml), which was heated to 413 K for 72 h and then cooled to room temperature at the rate of 5 K  $\text{h}^{-1}$ . Purple needle-like crystals of (I) were collected by filtration in 48% yield (5.4 mg, based on sodium dicyanamide). Analysis calculated for  $\text{C}_{10}\text{H}_{22}\text{Cu}_2\text{N}_6\text{O}_6$ : C 26.73, H 4.93, N 18.70%; found: C 26.58, H 5.30, N 18.65%. The filtrate was allowed to stand at room temperature and deep-red block-shaped crystals of (II) were obtained after several days in 40% yield (1.6 mg, based on sodium dicyanamide).

### Crystal data

$[\text{Cu}_2(\text{C}_4\text{H}_8\text{N}_3\text{O}_2)_2(\text{CH}_3\text{O})_2]$	$V = 421.3 (2) \text{ \AA}^3$
$M_r = 449.42$	$Z = 1$
Triclinic, $P\bar{1}$	$D_x = 1.771 \text{ Mg m}^{-3}$
$a = 3.8897 (11) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 7.621 (2) \text{ \AA}$	$\mu = 2.56 \text{ mm}^{-1}$
$c = 14.520 (4) \text{ \AA}$	$T = 298 (2) \text{ K}$
$\alpha = 99.309 (3)^\circ$	Needle, purple
$\beta = 92.020 (3)^\circ$	$0.22 \times 0.08 \times 0.06 \text{ mm}$
$\gamma = 96.588 (4)^\circ$	

### Data collection

Bruker APEX-II CCD area-detector diffractometer	2281 measured reflections
$\varphi$ and $\omega$ scans	1480 independent reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	1134 reflections with $I > 2\sigma(I)$
$T_{\text{min}} = 0.614$ , $T_{\text{max}} = 0.861$	$R_{\text{int}} = 0.026$
	$\theta_{\text{max}} = 25.0^\circ$



**Figure 1**

The molecular structure of the title complex, showing the atom labeling and 30% probability displacement ellipsoids (symmetry code: 1 -  $x$ , 2 -  $y$ , 2 -  $z$ ).

### Refinement

Refinement on $F^2$	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.045$	$w = 1/[\sigma^2(F_o^2) + (0.0689P)^2]$
$wR(F^2) = 0.117$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.02$	$(\Delta/\sigma)_{\text{max}} < 0.001$
1480 reflections	$\Delta\rho_{\text{max}} = 0.56 \text{ e \AA}^{-3}$
112 parameters	$\Delta\rho_{\text{min}} = -0.59 \text{ e \AA}^{-3}$

**Table 1**

Selected geometric parameters (Å, °).

$\text{Cu1}-\text{N1}$	1.920 (4)	$\text{Cu1}-\text{O3}$	1.939 (3)
$\text{Cu1}-\text{N3}$	1.924 (4)	$\text{Cu1}-\text{O3}^i$	1.938 (3)
$\text{N1}-\text{Cu1}-\text{N3}$	89.17 (16)	$\text{N1}-\text{Cu1}-\text{O3}$	173.41 (15)
$\text{N1}-\text{Cu1}-\text{O3}^i$	97.28 (14)	$\text{N3}-\text{Cu1}-\text{O3}$	97.14 (14)
$\text{N3}-\text{Cu1}-\text{O3}^i$	173.44 (14)	$\text{O3}^i-\text{Cu1}-\text{O3}$	76.37 (14)

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

All H atoms were located in difference Fourier maps and refined as riding ( $\text{C}-\text{H} = 0.96 \text{ \AA}$  and  $\text{N}-\text{H} = 0.86 \text{ \AA}$ ), with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$  and  $1.2U_{\text{eq}}(\text{N})$ . The methyl group of the methoxide ligand was rotated to fit the electron density.

Data collection: APEX2 (Bruker, 2003); cell refinement: APEX2 and SAINT (Bruker, 2001); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Bruker, 2001); software used to prepare material for publication: SHELXTL.

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