

Bis[bis(methoxycarbimido)aminato]-
copper(II) 1-methylpyrrolidin-2-one
disolvate

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Received 1 October 2009

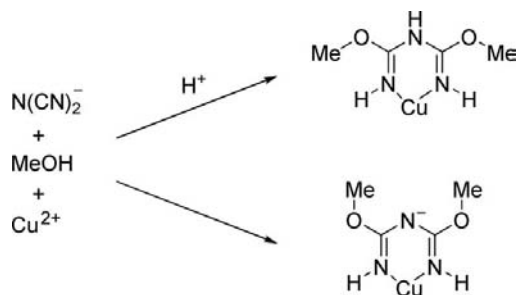
Accepted 13 November 2009

Online 25 November 2009

The title compound, $[\text{Cu}(\text{C}_4\text{H}_8\text{N}_3\text{O}_2)_2] \cdot 2\text{C}_5\text{H}_9\text{NO}$, consists of a neutral copper complex, in which the Cu^{II} centre coordinates to two bis(methoxycarbimido)aminato ligands, solvated by two molecules of 1-methylpyrrolidin-2-one. The complex is planar and centrosymmetric, with the Cu^{II} centre occupying a crystallographic inversion centre and adopting approximately square-planar geometry. $\text{N}-\text{H} \cdots \text{O}$ hydrogen-bonding interactions exist between the amine NH groups of the ligands and the O atoms of the 1-methylpyrrolidin-2-one molecules. The associated units pack to form sheets.

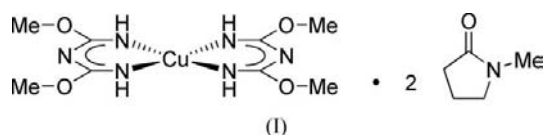
Comment

A number of copper(II) complexes of the bis(methoxycarbimido)amine ligand, $\text{HN}[\text{C}(\text{NH})\text{OCH}_3]_2$ (HL), have previously been prepared by reacting Cu^{II} salts with sodium dicyanamide in methanolic solutions. The ligand is generated *in situ* by nucleophilic addition of the methanol to the dicyanamide anion and, depending on the reaction conditions, may occur in either the protonated or deprotonated form, *i.e.* as HL or L^- (Atkinson *et al.*, 2002) (see scheme).



Neutral HL ligands are found in $[\text{Cu}\{\text{HN}[\text{C}(\text{NH})\text{OCH}_3]_2\}_2] \cdot (\text{ClO}_4)_2 \cdot 2\text{X}$ [$\text{X} = \text{CH}_3\text{OH}$ (Liu *et al.*, 2007) and H_2O (Zheng *et al.*, 2008)] and $[\text{Cu}\{\text{HN}[\text{C}(\text{NH})\text{OCH}_3]_2\}_2] \cdot \text{Br}_2 \cdot 2\text{C}_2\text{H}_5\text{N}_3\text{O}_2 \cdot 2\text{CH}_3\text{OH} \cdot 0.8\text{CH}_3\text{CN}$ ($\text{C}_2\text{H}_5\text{N}_3\text{O}_2 =$ biuret; Bishop *et al.*, 2000). The anion, L^- , occurs in the neutral monomeric complex $[\text{Cu}\{\text{N}[\text{C}(\text{NH})\text{OCH}_3]_2\}_2]$ (Kožíšek *et al.*, 1990; Boča *et al.*, 1996;

Tong *et al.*, 2003) and in the dimer $[\text{Cu}(\mu\text{-OCH}_3)\{\text{N}[\text{C}(\text{NH})\text{OCH}_3]_2\}_2]_2$, in which two $\text{Cu}(\text{L})_2$ units are linked *via* methoxide bridges (Zhao *et al.*, 2006). On heating the neutral monomeric complex with NH_4PF_6 in a $\text{CH}_3\text{OH}/\text{CH}_3\text{CN}$ mixture, $[\text{Cu}\{\text{N}[\text{C}(\text{NH})\text{OCH}_3]_2\}_2]\{\text{HN}[\text{C}(\text{NH})\text{OCH}_3]_2\}\text{PF}_6 \cdot \text{CH}_3\text{CN}$, in which both neutral and anionic ligand species occur, is generated (Atkinson *et al.*, 2002). Recently, attempts to explain the different conformations adopted by the neutral and anionic forms of the ligand in terms of their geometries and electronic structures have been made using *ab initio* molecular orbital (MO) calculations (Majek *et al.*, 2004; Brudíková & Breza, 2004).



In this work, the structure of the title compound, $[\text{Cu}\{\text{N}[\text{C}(\text{NH})\text{OCH}_3]_2\}_2] \cdot 2\text{C}_5\text{H}_9\text{NO}$ ($\text{C}_5\text{H}_9\text{NO} =$ 1-methylpyrrolidin-2-one), (I), a solvate of the neutral complex $[\text{Cu}\{\text{N}[\text{C}(\text{NH})\text{OCH}_3]_2\}_2]$, is reported. The starting materials for the synthesis were copper(I) dicyanamide, $\text{CuN}(\text{CN})_2$, 1-methylpyrrolidin-2-one and methanol. Cu^+ is oxidized to Cu^{2+} during the reaction. It has previously been reported that oxidation of the Cu^+ in $\text{CuN}(\text{CN})_2$ occurs in aqueous ammonia/hydrazine, accompanied by partial hydration of dicyanamide to cyanourea, $\text{H}_2\text{N}-\text{CO}-\text{NH}-\text{CN}$, to generate the layered cop-

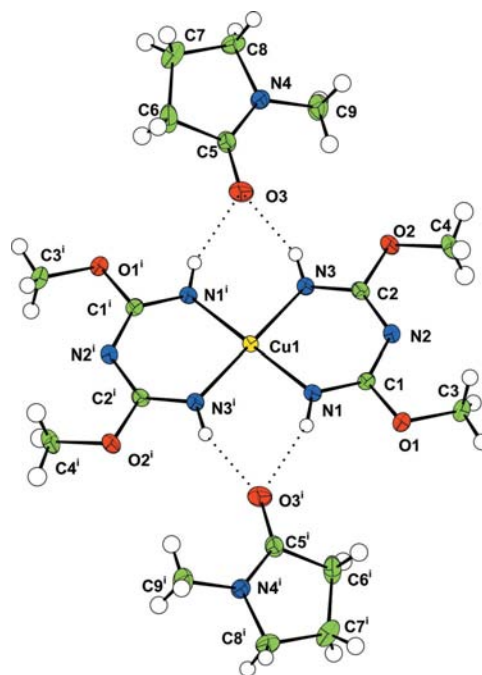
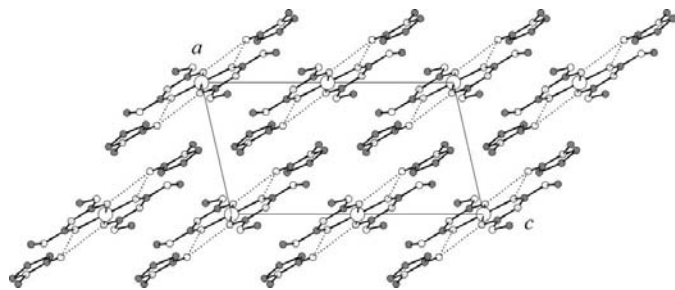


Figure 1
The title compound, consisting of a square-planar Cu^{II} complex and 1-methylpyrrolidin-2-one. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radius. The dashed lines represent $\text{N}-\text{H} \cdots \text{O}$ interactions. [Symmetry code: (i) $-x, -y + 1, -z + 1$.]


Figure 2

View along the *b* axis, showing the stacking of the Cu^{II} complex and associated solvent molecules. The dashed lines represent N–H...O hydrogen bonds. Key: large white spheres are Cu, small white spheres are O, small light-grey spheres are N and small dark-grey spheres are C atoms.

per(II) hydroxide, Cu₂(OH)₃[H₂NC(O)NCN]·2H₂O (Chippindale *et al.*, 2009).

In the title compound, copper(II) is coordinated to two {N[C(NH)OCH₃]₂}₂ ligands to form a neutral complex containing two six-membered metallocycles (Fig. 1). The Cu^{II} ion lies on an inversion centre, at special position 2*a*, coordinated by four N atoms in an approximately square-planar array. The bond lengths and angles within the complex are similar to those observed previously in [Cu{N[C(NH)OCH₃]₂}₂] (Boča *et al.*, 1996). The (H)N–C bonds (N1–C1 and N3–C2) and N2–C bonds (N2–C1 and N2–C2) have average lengths of 1.302 (1) and 1.335 (1) Å, respectively (Table 1). These values, together with the planarity of the metallocycle, indicate a highly delocalized π-bonding system. The conformations adopted by the methyl groups at C3 and C4, which point away from N1 and N3 with torsion angles N1–C1–O1–C3 and N3–C2–O2–C4 of 178.7 (1) and 178.2 (1)°, respectively, agree with those predicted previously for the anionic form of the ligand from MO calculations (Majek *et al.*, 2004; Brudíková & Breza, 2004) and database mining (Atkinson *et al.*, 2002).

Associated with each copper complex are two 1-methylpyrrolidin-2-one molecules held in place by hydrogen-bonding interactions between N1 and N3 of the copper complex and O3 of the pyrrolidinone [average N–O3 distance = 3.014 (2) Å] (Table 2). The associated units pack in flat sheets parallel to the (101) plane and these stack *abab* along the *a* axis (Fig. 2). There are no strong interactions between neighbouring units within or between the sheets.

On gentle heating under an N₂ atmosphere, the single crystal of [Cu{N[C(NH)OCH₃]₂}₂]·2C₅H₉NO loses all solvent and forms polycrystalline [Cu{N[C(NH)OCH₃]₂}₂] (Boča *et al.*, 1996). The packing of the copper complexes in this case reflects the fact that weak hydrogen-bonding interactions are formed between the amine NH groups and the O atoms of methoxy groups in neighbours.

Experimental

Copper(I) dicyanamide (50 mg; Wang *et al.*, 1990) was dissolved in 1-methylpyrrolidin-2-one (6 ml) to form a dark-green solution. A 2 ml portion of this solution was transferred to a small sample vial,

which was sealed inside a larger vial containing methanol (8 ml). No solid appeared after a period of one month. However, vapour diffusion over a period of 18 months led to the growth of a single crystal of [Cu{N[C(NH)OCH₃]₂}₂]·2C₅H₉NO within the inner vial in the form of a dark-pink block of dimensions 0.2 × 0.2 × 5 mm. A fragment of the crystal was used for the diffraction experiment. Attempts have not so far been made to optimize the crystallization conditions. Heating the crystal of the title compound under nitrogen from room temperature to 350 K over 30 min led to the complete loss of 1-methylpyrrolidin-2-one and the formation of violet–red polycrystalline [Cu{N[C(NH)OCH₃]₂}₂] (Boča *et al.*, 1996), as confirmed by powder X-ray diffraction. During the desolvation reaction, bubbles were observed on the surface of the crystal.

Crystal data

[Cu(C ₄ H ₈ N ₃ O ₂) ₂]·2C ₅ H ₉ NO	<i>V</i> = 1193.15 (5) Å ³
<i>M_r</i> = 522.08	<i>Z</i> = 2
Monoclinic, <i>P</i> 2 ₁ / <i>c</i>	Mo <i>K</i> α radiation
<i>a</i> = 7.52863 (18) Å	<i>μ</i> = 0.97 mm ^{−1}
<i>b</i> = 11.5650 (3) Å	<i>T</i> = 150 K
<i>c</i> = 14.0547 (3) Å	0.36 × 0.17 × 0.15 mm
<i>β</i> = 102.833 (2)°	

Data collection

Oxford Diffraction Xcalibur diffractometer	8090 measured reflections
Absorption correction: multi-scan (<i>CrysAlis RED</i> ; Oxford Diffraction, 2006)	3880 independent reflections
<i>T_{min}</i> = 0.82, <i>T_{max}</i> = 0.87	3244 reflections with <i>I</i> > 2σ(<i>I</i>)
	<i>R_{int}</i> = 0.013

Refinement

<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.022	17 restraints
<i>wR</i> (<i>F</i>) = 0.025	Only H-atom coordinates refined
<i>S</i> = 1.04	Δ <i>ρ</i> _{max} = 0.33 e Å ^{−3}
3097 reflections	Δ <i>ρ</i> _{min} = −0.41 e Å ^{−3}
196 parameters	

Table 1

Selected geometric parameters (Å, °).

Cu1–N1	1.9424 (7)	Cu1–N3	1.9427 (7)
N1–Cu1–N3	88.61 (3)	Cu1–N3–C2	126.68 (6)
Cu1–N1–C1	126.76 (6)		

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

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–H11...O3 ⁱ	0.856 (10)	2.201 (10)	3.0168 (14)	159 (1)
N3–H34...O3	0.856 (12)	2.201 (12)	3.0113 (14)	158 (1)

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

All H atoms were located in difference Fourier maps. Their fractional coordinates were refined subject to bond-length restraints [C–H = 0.95 (1) Å and N–H = 0.85 (1) Å], with isotropic displacement parameters fixed at *U*_{iso}(H) = 1.2*U*_{eq}(C,N).

Data collection: *Xcalibur* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006); data reduction:

CrysAlis RED; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *CAMERON* (Watkin *et al.*, 1996); software used to prepare material for publication: *CRYSTALS*.

The authors thank the EPSRC for a grant in support of a single-crystal diffractometer and a studentship for EJB.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG3219). Services for accessing these data are described at the back of the journal.

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