

Dichlorobis(glycoxyamine-O)- copper(II)

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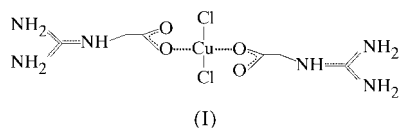
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The title compound, $[\text{CuCl}_2(\text{C}_3\text{H}_7\text{N}_3\text{O}_2)_2]$, is a new copper(II) complex with glycoxyamine [(diaminomethyleneamino)acetic acid], the first complex ever reported with this organic molecule. It is composed of discrete centrosymmetric coordinated Cu^{II} monomers, the Cu atoms being located at inversion centers. Each metal ion is square-planar coordinated by two Cl atoms and two glycoxyamine O atoms. The coordinating glycoxyamine molecule exists as a zwitterion, the H atom from the carboxyl group being transferred to the guanidinium group. A three-dimensional network of hydrogen bonds links the monomers and stabilizes the structure.

Comment

Our recent work has been dedicated to the study of molecular-based magnets in order to understand the magnetic interactions observed between inorganic spin carriers bridged by organic molecules and develop structure–function relationships enabling the design of new magnetic materials. We have focused especially on the magnetic interaction in copper(II) complexes of amino acids (and substituted amino acids). Copper ions are often grouped in dinuclear complexes or even bridged in such a way as to form infinite chains, which results in interesting magnetic behaviour. In these complexes, the copper ions are linked by different types of chemical paths, allowing evaluation of superexchange interactions transmitted over long distances *via* molecular bridges. We report here the synthesis and structure of a new copper(II) complex with glycoxyamine (guanidineacetic acid), (I), the first complex



ever reported with this organic molecule. Glycoxyamine exists in living organisms and is one of the intermediate compounds in the synthesis of creatine *in vivo*. It contains a guanidinium group that has been widely studied by theoretical (Williams & Gready, 1989) and experimental techniques (Kozak *et al.*, 1987) due to the aromatic character of the delocalized

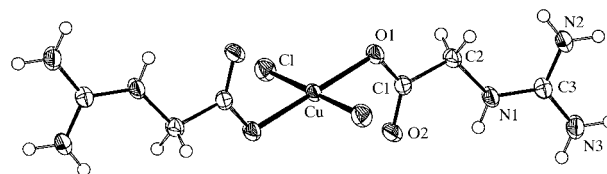


Figure 1

ORTEP (Johnson, 1976) plot of the title compound. Displacement ellipsoids are drawn at the 50% probability level.

π -bonding and its ability to establish intermolecular hydrogen bonds. Glycoxyamine has been used as a food supplement for men and animals. An inspection of the Cambridge Structural Database (release April 2000; Allen & Kennard, 1993) shows that only three structures containing this molecule have been reported, namely that of crystalline glycoxyamine (Guha, 1973; Berthou *et al.*, 1976) and those of the Cl and Br halides (Majumdar *et al.*, 1977; Roy *et al.*, 1967).

The title compound (Fig. 1) is composed of discrete coordinated Cu^{II} monomers which are centrosymmetric, the copper ions being located at inversion centers in the unit cell. The copper ion is square-planar coordinated by two chloride ions and two glycoxyamine O atoms. Both bond distances lie within the range of reported average values (Orpen *et al.*, 1989). The angle Cl–Cu–O1 is close to 90° . Although the Cu...O2 distance [2.782 (2) Å] is significantly shorter than the usual non-bonding contact distance between Cu and O, which may indicate a weak interaction between these atoms, this interaction does not appear to have much influence on the geometry of the other coordination interactions with Cu.

The glycoxyamine molecule exists as a zwitterion, the H atom from the carboxyl group being transferred to the guanidinium group. Pure glycoxyamine has also been found to exist in a zwitterionic form (Guha, 1973; Berthou *et al.*, 1976), but a protonated molecule has also been found in the presence of a stronger acid (Roy *et al.*, 1967; Majumdar *et al.*, 1977). The difference between the two C–O bond lengths [1.278 (2) and 1.226 (2) Å] may be attributed to the fact that only one of the O atoms is coordinated to the copper ion. The guanidinium group is planar, with the sum of the valence angles around C3 equal to $359.99 (19)^\circ$. The C3–N distances are very similar and their average value [1.322 (3) Å] is close to the value expected for the delocalized C=N bond in guanidinium

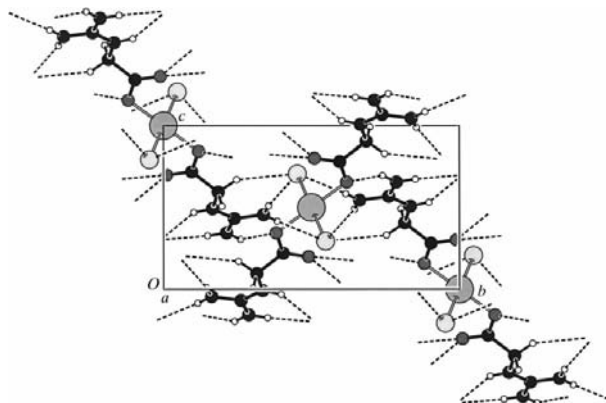


Figure 2

Packing of the molecules projected along *a*. The dashed lines represent hydrogen bonds.

Table 1
Selected geometric parameters (Å, °).

Cu—O1	1.9449 (13)	N1—C2	1.447 (3)
Cu—Cl	2.2696 (8)	C3—N2	1.320 (3)
O1—C1	1.278 (2)	O2—C1	1.226 (2)
N3—C3	1.328 (3)	C1—C2	1.509 (3)
N1—C3	1.319 (3)		
O1—Cu—Cl	88.76 (5)	N2—C3—N3	119.43 (19)
N1—C3—N2	121.10 (19)	O2—C1—O1	125.01 (19)
N1—C3—N3	119.46 (19)		
C2—N1—C3—N2	−3.1 (3)	O2—C1—C2—N1	−16.2 (3)
C2—N1—C3—N3	178.04 (19)	O1—C1—C2—N1	163.49 (17)
C3—N1—C2—C1	−153.06 (19)		

compounds (1.328 Å; Allen *et al.*, 1987). The Csp^3 —N bond length between atoms N1 and C2 [1.447 (3) Å] is also similar to that found in pure glycoyamine [1.455 (3) Å].

The geometry of the glycoyamine molecule can be defined in terms of two planes, one containing the carboxylic acid group (O1, O2, C1, C2), the other the amine group (N1, N2, N3, C3), the angle between these least-squares planes being 25.52 (12)°. This angle is much larger than that found in pure glycoyamine (3.99°; Berthou *et al.*, 1976), but equal within error to that found in the protonated molecule (22.6°; Roy *et al.*, 1967).

A three-dimensional network of hydrogen bonds links the monomers and stabilizes the structure (Fig. 2). The guanidyl N2 atom donates its H atoms to each of the Cl atoms of a neighbouring complex. The H atom bonded to N1 is oriented towards the carboxy O2 atom of a third monomer. N3 establishes an intermolecular hydrogen bond to a neighbouring O1 atom, and has its other H atom shared in a bifurcated bond to neighbouring O2 and Cl atoms, the latter bond being somewhat long [3.512 (2) Å].

The shortest Cu···Cu distance is 7.047 (4) Å which excludes the possibility of a direct magnetic interaction between the transition metal atoms. We are currently trying to synthesize new coordination compounds of glycoyamine and Cu^{II} in an attempt to obtain dimers or polymeric chains with the metal ions chelated *via* the carboxy bonds in which low-dimensional magnetic interactions might be observed.

Experimental

Crystals were prepared by adding guanidineacetic acid (99.9%, Aldrich) to an aqueous solution of hydrated CuCl₂ (98% purity, Aldrich) in stoichiometric proportions. Slow evaporation afforded the title compound in polycrystalline form. Good quality blue single crystals were obtained by recrystallization from acetone. A few of these were tested using photographic methods and the best specimen was chosen for data collection.

Crystal data

[CuCl ₂ (C ₃ H ₇ N ₃ O ₂) ₂]	$D_x = 1.868 \text{ Mg m}^{-3}$
$M_r = 368.67$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 25 reflections
$a = 7.047 (4) \text{ \AA}$	$\theta = 9.74\text{--}15.54^\circ$
$b = 12.9533 (13) \text{ \AA}$	$\mu = 2.094 \text{ mm}^{-1}$
$c = 7.297 (2) \text{ \AA}$	$T = 293 (2) \text{ K}$
$\beta = 100.250 (16)^\circ$	Plate, translucent intense blue
$V = 655.5 (4) \text{ \AA}^3$	$0.28 \times 0.27 \times 0.12 \text{ mm}$
$Z = 2$	

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

$D\text{---}H\cdots A$	$D\text{---}H$	$H\cdots A$	$D\cdots A$	$D\text{---}H\cdots A$
N3—H3A···O2 ⁱ	0.86	2.27	3.001 (2)	143
N3—H3A···Cl ⁱ	0.86	2.88	3.512 (2)	132
N3—H3B···O1 ⁱⁱ	0.86	2.18	2.974 (2)	153
N1—H1···O2 ⁱ	0.86	2.13	2.911 (2)	151
N2—H2A···Cl ⁱⁱⁱ	0.86	2.51	3.341 (2)	162
N2—H2B···Cl ⁱⁱⁱ	0.86	2.46	3.295 (2)	163

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

Data collection

CAD-4 diffractometer	$R_{\text{int}} = 0.011$
Profile data from ω - 2θ scans	$\theta_{\text{max}} = 25.07^\circ$
Absorption correction: ψ scan (North <i>et al.</i> , 1968)	$h = 0 \rightarrow 8$
$T_{\text{min}} = 0.619, T_{\text{max}} = 0.778$	$k = 0 \rightarrow 15$
1259 measured reflections	$l = -8 \rightarrow 8$
1162 independent reflections	3 standard reflections
1047 reflections with $I > 2\sigma(I)$	frequency: 180 min
	intensity decay: 6.1%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0348P)^2 + 0.3768P]$
$R[F^2 > 2\sigma(F^2)] = 0.022$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.060$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.087$	$\Delta\rho_{\text{max}} = 0.36 \text{ e \AA}^{-3}$
1162 reflections	$\Delta\rho_{\text{min}} = -0.40 \text{ e \AA}^{-3}$
88 parameters	
H-atom parameters constrained	

Examination of the crystal structure with *PLATON* (Spek, 1995) showed that there are no solvent-accessible voids in the crystal lattice.

Data collection: *CAD-4 Software* (Enraf-Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *HELENA* (Spek, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1108). Services for accessing these data are described at the back of the journal.

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