Acta Crystallographica Section C
**Crystal Structure Communications**
ISSN 0108-2701

# Di-$\mu$-chloro-1:2$\kappa^2$*Cl*;3:4$\kappa^2$*Cl*-hexachloro-1$\kappa^3$*Cl*,4$\kappa^3$*Cl*-tetra-$\mu$-dimethylglycine-2:3$\kappa^8$*O*:*O*′-tetracopper(II)

**M. Ramos Silva,[a]* A. Matos Beja,[a] J. A. Paixão[a] and J. Martin-Gil[b]**

[a]CEMDRX, Departamento de Física, Faculdade de Ciências e Tecnologia, Universidade de Coimbra, P-3004-516 Coimbra, Portugal, and [b]ETSII, Tecnologias del Medio Ambiente, Universidad de Valladolid, SP-47011 Valladolid, Spain
Correspondence e-mail: manuela@pollux.fis.uc.pt

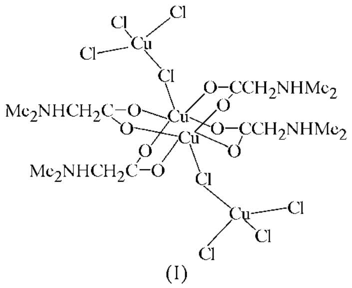
Received 26 May 2005
Accepted 6 July 2005
Online 23 July 2005

The title compound, [$Cu_4Cl_8(C_4H_9NO_2)_4$], crystallizes in the centrosymmetric space group *P*2$_1$/*c* with a unit cell containing two tetranuclear copper(II) complexes sited on crystallographic inversion centres. The coordination geometry around the central Cu atoms is square pyramidal, with four O atoms in the basal plane and a Cl atom in the apical position. The lateral $CuCl_4$ groups are flattened tetrahedral. The bridging dimethylglycine molecules are present in the dipolar zwitterionic form. The tetranuclear copper complexes exist as isolated entities since only intramolecular hydrogen bonds are found.

## Comment

The title compound, (I), was synthesized within a project focused on the study of the magnetic properties of Cu$^{II}$ compounds, in particular dimers and polymeric chains where the transition metal ions are bridged by organic diamagnetic ligands. Polynuclear Cu$^{II}$ complexes are one of the most prominent families of compounds in modern chemistry, since a correlation between the magnetic properties and the molecular structure has been found in some cases. The most extensively studied have been hydroxo-bridged dinuclear compounds, with Hodson & Hatfield (Crawford *et al.*, 1976) establishing a correlation between the exchange coupling constant and the Cu—O—Cu angle. The situation for compounds with higher nuclearity is not so clear, but is increasingly more interesting since their intermediate position between the simplest dinuclear species and bulk materials may generate unexpected magnetic behaviour. Systems with intermediate nuclearity are also important in biology, where trinuclear and tetranuclear arrays of Cu atoms have been found in the active sites of enzymes (Haltia *et al.*, 2003; Chen *et al.*, 2004).

Compound (I) crystallizes in the centrosymmetric space group *P*2$_1$/*c* with a unit cell containing two tetranuclear Cu$^{II}$ complexes. The molecular structure consists of a crystallographic centrosymmetric binuclear copper complex bridged by four dimethylglycine molecules and strongly coordinated to two [$CuCl_4$]$^{2-}$ ions (Fig. 1). The latter orient themselves so as to have the four Cu and four Cl atoms (Cu1, Cu2, Cl1, Cl3 and their centrosymmetric counterparts) almost coplanar [mean deviation = 0.0467 (4) Å].



(I)

The bridged Cu$^{II}$ ions are a short distance from each other [2.7303 (8) Å]. The Cl1—Cu1—Cu1$^{i}$ angle is 164.13 (2)°, Cl1—Cu2—Cl3 is 142.88 (3)° and Cu1—Cl1—Cu2 is 93.45 (3)° [symmetry code: (i) $1 - x, -y, -z$]. According to the procedure described by Addison *et al.* (1984), the shape of the polyhedron around Cu1 can be considered square-based pyramidal, since the $\tau$ value [$\tau$= ($\theta_1 - \theta_2$)/60°, where $\theta_1$ and $\theta_2$ are the largest angle values in the coordination sphere] is 0.04. The deviation of Cu1 from the least-squares plane of the base of the pyramid is 0.250 (1) Å towards the apical Cl atom. The angle between the plane that contains the Cu$^{II}$ ions and the least-squares plane of the base of the pyramid is 85.75 (4)°.

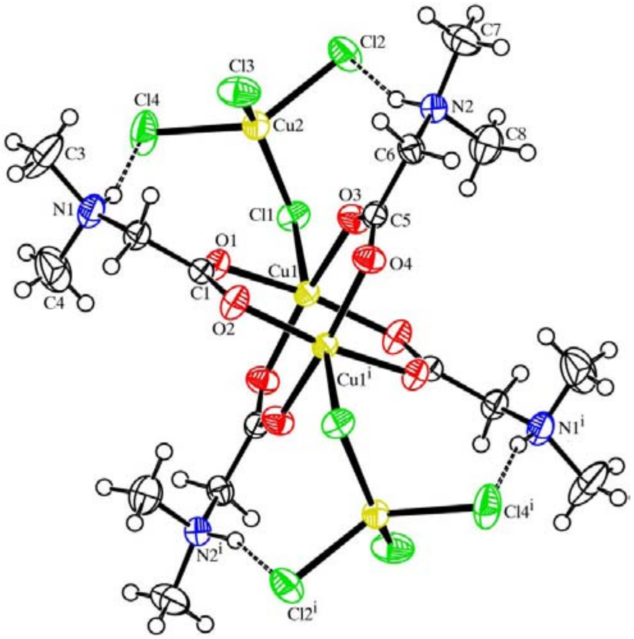


**Figure 1**
A view of the title compound, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Intramolecular hydrogen bonds are shown as dashed lines. [Symmetry code: (i) $1 - x, -y, -z$.]

The distances between Cu1 and the basal O atoms range from 1.9608 (18) to 1.9830 (17) Å, the apical Cl atom being 2.4625 (9) Å from Cu1; Cu2 is coordinated by four Cl atoms in a flattened tetrahedral geometry. The *trans* Cl—Cu2—Cl angles are opened to 136.30 (4) and 142.88 (3)°, which favours a yellow–green colour according to Willett & Zanchini (1990), while the other four range between 96.12 (3) and 97.48 (4)°. The Cu2—Cl distances vary in the range 2.2416 (9)–2.2925 (7) Å. This distortion has been observed in many $[CuCl_4]^{2-}$ salts, and in some of them thermochromic properties are observed and explained by the deformation of $[CuCl_4]^{2-}$ as a function of temperature.

The neutral dimethylglycine molecules are present in the dipolar zwitterionic form. Inspection of the C—O distances in the carboxylate groups [between 1.246 (3) and 1.253 (3) Å] shows that these are deprotonated. The carboxylate groups in (I) are twisted by 13.4 (3) and 16.4 (4)° around the C1—C2 and C5—C6 bonds, respectively. The main skeletons C1—C2—N1—C3 and C5—C6—N2—C8 deviate from planarity, as shown by the corresponding torsion angles of −160.2 (3) and 173.1 (2)°, respectively. The difference in the former angles might be explained by the closer proximity of Cu2 and Cl3 to N1 than to N2.

A few compounds where dimethylglycine coordinates to or bridges metal ions can be found in the Cambridge Structural Database (Version 5.25, November 2004 update; Allen, 2002). Structures have been described in which this substituted amino acid coordinates to the metal ion through the N and one of the O atoms or just by one of the carboxylate O atoms. Platinum (Gravenhorst *et al.*, 1999), copper (Cameron *et al.*, 1973), chromium (Darensbourg *et al.*, 1997), tungsten (Darensbourg *et al.*, 1994) and cobalt (Kojima *et al.*, 1994) complexes are examples of the former, while the latter is found in tin (Khoo *et al.*, 1994) and iron (Ramos Silva *et al.*, 2003) coordination compounds. The bridging properties of dimethylglycine have been observed in an oxo-centred trinuclear iron compound (Ramos Silva *et al.*, 2003) and again in the title compound. When in bridging mode, the carboxylate group is less rotated around C5—C6 than when in the *N*,*O*-coordination conformation, as perceived by the reported average torsion angles for N1—C2—C1—O1 and N1—C2—C1—O2 of 11 (5) and 171 (5)°, respectively, for the bridging conformation, and 27 (4) and 157 (2)°, respectively, for the *N*,*O*-coordination conformation. The simple *O*-coordination conformation presents the smallest degree of rotation, with average torsion angles of 5(3) and 174 (5)°, respectively.

The tetranuclear copper complexes in (I) exist almost as isolated dimeric entities, further stabilized by intramolecular N—H···Cl bonds between N2 and Cl4 [3.194 (3) Å and 162 (3)°] and N2 and Cl2 [3.188 (3) Å and 153 (3)°]. Among other interactions, there are weak C—H···Cl and C—H···O intermolecular interactions supporting the cohesion of the structure; one of the symmetry-independent organic ligands shares three H atoms with two neighbouring complexes, while the other ligand donates only one H atom to a neighbouring $CuCl_4$ chlorine atom.

## Experimental

Dimethylglycine (5 mmol) was added to hydrated copper chloride (2.5 mmol) in an aqueous solution (50 ml). After a few months at room temperature, small single crystals of the title compound had grown, and these were used for the structure analysis. Surprisingly, after a few weeks, all the crystals had spontaneously dissolved in the solution and during the following few weeks new crystals formed, but this time of a different phase, which is currently under study.

*Crystal data*

$[Cu_4Cl_8(C_4H_9NO_2)_4]$
$M_r$ = 950.25
Monoclinic, $P2_1/c$
$a$ = 9.759 (1) Å
$b$ = 12.861 (1) Å
$c$ = 14.060 (1) Å
$\beta$ = 99.20 (3)°
$V$ = 1741.8 (3) Å$^3$
$Z$ = 2

$D_x$ = 1.812 Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta$ = 9.9–15.9°
$\mu$ = 3.06 mm$^{-1}$
$T$ = 293 (2) K
Block, green
0.49 × 0.46 × 0.39 mm

*Data collection*

Enraf–Nonius CAD-4 diffractometer
Profile data from $\omega/2\theta$ scans
Absorption correction: $\psi$ scan (North *et al.*, 1968)
$T_{min}$ = 0.202, $T_{max}$ = 0.303
3266 measured reflections
3075 independent reflections
2625 reflections with $I > 2\sigma(I)$

$R_{int}$ = 0.030
$\theta_{max}$ = 25.0°
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 15$
$l = -16 \rightarrow 16$
3 standard reflections frequency: 180 min intensity decay: 4.1%

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)]$ = 0.024
$wR(F^2)$ = 0.064
$S$ = 1.09
3075 reflections
191 parameters
H atoms: see below

$w = 1/[\sigma^2(F_o^2) + (0.0325P)^2 + 1.4695P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.48 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.43 e Å$^{-3}$

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

| | | | |
|---|---|---|---|
| Cu1—O4$^{i}$ | 1.9608 (19) | Cu1—Cu1$^{i}$ | 2.7303 (8) |
| Cu1—O2$^{i}$ | 1.9656 (18) | Cu2—Cl4 | 2.2416 (9) |
| Cu1—O3 | 1.9735 (18) | Cu2—Cl3 | 2.2490 (8) |
| Cu1—O1 | 1.9830 (17) | Cu2—Cl2 | 2.2523 (9) |
| Cu1—Cl1 | 2.4625 (9) | Cu2—Cl1 | 2.2925 (7) |
| | | | |
| Cl1—Cu1—Cu1$^{i}$ | 164.13 (2) | Cu2—Cl1—Cu1 | 93.45 (3) |
| Cl4—Cu2—Cl2 | 136.30 (4) | | |
| | | | |
| Cl4—Cu2—Cl1—Cu1 | −105.25 (3) | Cl2—Cu2—Cl1—Cu1 | 116.58 (3) |
| Cl3—Cu2—Cl1—Cu1 | 5.77 (6) | Cu1$^{i}$—Cu1—Cl1—Cu2 | −24.95 (10) |

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

**Table 2**
Hydrogen-bond geometry (Å, °).

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| C6—H6$B$···Cl4$^{ii}$ | 0.97 | 2.63 | 3.529 (3) | 155 |
| C7—H7$C$···O2$^{iii}$ | 0.96 | 2.31 | 3.254 (4) | 167 |
| C2—H2$A$···Cl3$^{iv}$ | 0.97 | 2.69 | 3.625 (3) | 162 |
| C8—H8$C$···Cl4$^{ii}$ | 0.96 | 2.78 | 3.616 (4) | 146 |
| N1—H1···Cl4 | 0.82 (3) | 2.40 (4) | 3.194 (3) | 162 (3) |
| N2—H2···Cl2 | 0.91 (3) | 2.35 (3) | 3.188 (3) | 153 (3) |

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

*Acta Cryst.* (2005). C**61**, m380–m382 Ramos Silva *et al.* • $[Cu_4Cl_8(C_4H_9NO_2)_4]$ **m381**

H atoms were placed in calculated positions. Those not involved in hydrogen bonding were allowed to ride on their parent atoms, with C—H distances in the range 0.96–0.97 Å and with $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}(C)$, while atoms H1 and H2 were refined with isotropic displacement parameters. Examination of the crystal structure with *PLATON* (Spek, 2003) showed that there were no solvent-accessible voids in the crystal lattice.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *PLATON* (Spek, 2003); 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*.

This work was supported by the Fundação para a Ciência e a Tecnologia under project No. POCI/FIS/57876/2004.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BG1009). Services for accessing these data are described at the back of the journal.

## References

Addison, A. W., Rao, T. N., Reedijk, J., van Rijn, J. & Verschoor, G. C. (1984). *J. Chem. Soc. Dalton Trans.* pp. 1349–1356.

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.

Cameron, T. S., Prout, K., Rossotti, F. J. C. & Steele, D. (1973). *J. Chem. Soc. Dalton Trans.* pp. 2626–2629.

Chen, P., Gorelsky, S. I., Ghosh, S. & Solomon, E. I. (2004). *Angew. Chem. Int. Ed.* **43**, 4132–4140.

Crawford, W. H., Richardson, H. W., Wasson, J. R., Hodgson, D. J. & Hatfield, W. E. (1976). *Inorg. Chem.* **15**, 2107–2110.

Darensbourg, D. J., Atnip, E. V., Klausmeyer, K. K. & Reibenspies, J. H. (1994). *Inorg. Chem.* **33**, 5230–5237.

Darensbourg, D. J., Draper, J. D. & Reibenspies, J. H. (1997). *Inorg. Chem.* **36**, 3648–3656.

Enraf–Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.

Gravenhorst, O., Bruhn, C., Herzog, R. & Steinborn, D. (1999). *Z. Anorg. Allg. Chem.* **625**, 1349–1353.

Haltia, T., Brown, K., Tegoni, M., Cambillau, C., Saraste, M., Mattila, K. & Djinovic-Carrego, K. (2003). *Biochem. J.* **1**, 77–78.

Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Khoo, L. E., Goh, N. K., Otieno, M. A., Lucero, R. A., Eng, G., Luo, B. S. & Mak, T. C. W. (1994). *Appl. Organomet. Chem.* **8**, 33–36.

Kojima, M., Saito, R., Nakajima, K., Ouyang, Y. & Fujita, J. (1994). *Bull. Chem. Soc. Jpn*, **67**, 108–112.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Ramos Silva, M., Matos Beja, A., Paixão, J. A. & Martin-Gil, J. (2003). *Z. Kristallogr. New Cryst. Struct.* **218**, 557–560.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

Willett, R. D. & Zanchini, P. (1990). *Inorg. Chem.* **29**, 3027–3030.

**m382** Ramos Silva *et al.* • $[Cu_4Cl_8(C_4H_9NO_2)_4]$ *Acta Cryst.* (2005). C**61**, m380–m382