Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

catena-Poly[[[aquachloridocopper(II)]-μ-*N*-(6-amino-3-methyl-5-nitroso-4-oxo-3,4-dihydropyrimidin-2-yl)glycinato] monohydrate] redetermined at 120 K: a highly polarized ligand within coordination polymer chains linked by hydrogen bonds

Justo Cobo,[a] Rafael López,[a] Paloma Arranz[a] and Christopher Glidewell[b]*

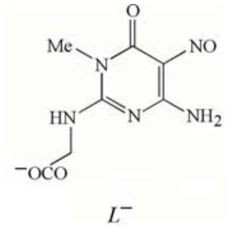
[a]Departamento de Química Inorgánica y Orgánica, Universidad de Jaén, 23071 Jaén, Spain, and [b]School of Chemistry, University of St Andrews, Fife KY16 9ST, Scotland
Correspondence e-mail: cg@st-andrews.ac.uk

Received 5 May 2009
Accepted 13 May 2009
Online 27 May 2009

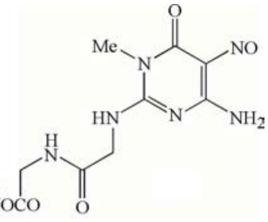
In the title compound, $\{[Cu(C_7H_8N_5O_4)Cl(H_2O)]\cdot H_2O\}_n$, the bond lengths in the *N*-pyrimidinylglycinate unit provide evidence for a strongly polarized electronic structure. This ligand is coordinated to three Cu^{II} centres, resulting in the formation of a coordination polymer in the form of a chain containing two types of centrosymmetric ring. These chains are linked by an extensive series of hydrogen bonds, including O—H···O, N—H···O, O—H···Cl and N—H···Cl types, into a continuous three-dimensional structure.

Comment

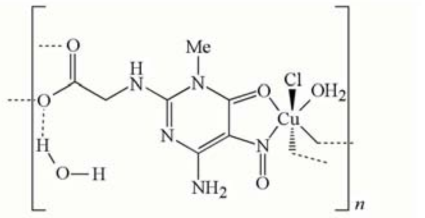
The structure of the title compound, (I), was reported some years ago, determined using diffraction data collected at ambient temperature (Moreno *et al.*, 1999). This determination was reported essentially as proof of constitution, with no discussion either of the geometry of the organic ligand or of the hydrogen bonding: indeed, the noncoordinated water component was not mentioned anywhere in this report. Since the publication of this mixed-ligand structure, the geometries of amino-acid-substituted pyrimidinones of the type present in compound (I) have been extensively analysed (Low *et al.*, 2000; Low, Moreno Sánchez *et al.*, 2001), as these systems consistently exhibit some highly unusual geometric features. Similarly, since the report of Moreno *et al.* (1999), the structures have been reported for a substantial number of complexes and salts formed by the same organic ligand with a variety of metal ions, and these encompass a very wide range of architectures. Accordingly, we have now taken the opportunity to redetermine the structure of (I) (Fig. 1) using diffraction data collected at 120 K, and here we (*a*) discuss the geometry of the organic ligand in (I), (*b*) re-evaluate the copper geometry and compare the coordination polymer formed in (I) with those formed by the same organic ligand with a wide variety of other metal ions, and (*c*) discuss the hydrogen-bonding system which links the coordination polymer chains in (I).



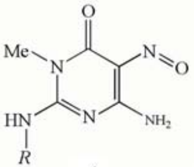
L⁻



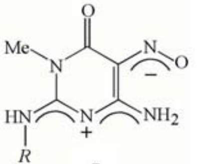
L′⁻



(I)



A



B

The bond distances within the *N*-pyrimidinylglycinate unit (Table 1) show a number of unusual values. The C4—C5 and C5—C6 distances, which represent formally single and double bonds, respectively, differ only slightly; the four C—N distances between N2 and N6 span only a narrow range, and the shortest of these distances corresponds to the formal single bond C6—N6 rather than to the formal double bond N1═C2; and the distances C5—N5 and N5—O5 differ by only *ca* 0.08 Å, whereas in simple unperturbed C-nitroso compounds, this difference generally exceeds 0.20 Å (Talberg, 1977;

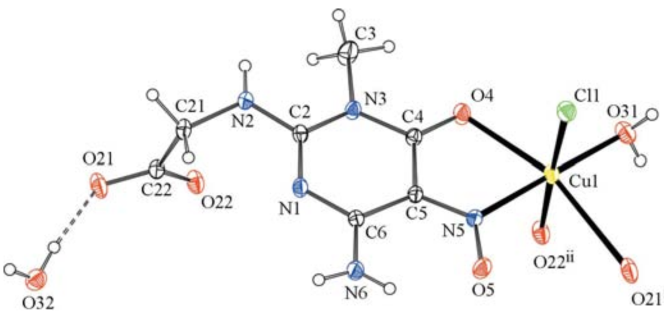


Figure 1
The asymmetric unit of compound (I), showing the atom-labelling scheme and the coordination of the Cu^{II} centre, but with the long contact to O5 omitted. Displacement ellipsoids are shown at the 30% probability level. [Symmetry codes: (i) $x, y, 1 + z$; (ii) $1 - x, 1 - y, 1 - z$.]

doi:10.1107/S0108270109018149

Schlemper *et al.*, 1986). Taken together, these observations indicate that the polarized, charge-separated form *B* (see scheme) is a more appropriate representation of the electronic structure than the classically localized form *A*.

The Cu^{II} centre in the title compound (I) shows the usual (4+2) distorted octahedral coordination, augmented by a rather long contact to nitroso atom O5 (Table 1), which itself may be associated with the polarized electronic structure which leads to an enhanced negative charge at atom O5. This contact could be interpreted as one component of a very asymmetric η^2-coordination of the nitroso group; such coordination contrasts with the corresponding coordination in the potassium complex $[K(L)(H_2O)]$ (Low, Moreno Sánchez *et al.*, 2001), where the K$\cdots$N and K$\cdots$O distances are 3.016 (2) and 3.132 (2) Å, respectively, indicating almost ideally symmetric η^2-coordination. The coordination polyhedron of the Cu centre at (x, y, z) consists of a chloride ion and a water molecule, the atoms O4, N5 and O5 from the *N*-pyrimidinylglycinate anion at (x, y, z) and carboxylate atoms O21 and O22 from the *N*-pyrimidinylglycinate anions at (x, y, $1 + z$) and ($1 - x$, $1 - y$, $1 - z$), respectively. The axial sites in the elongated pseudo-octahedron are occupied by ketonic atom O4 and carboxylate atom O21 at (x, y, $1 + z$). However, it seems unwise to invoke the Jahn–Teller effect as an explanation for the geometry at the Cu centre. With such a disparate group of ligating atoms, even ignoring the long contact to the nitroso O atom but including both neutral and anionic O atoms as well as three anionic ligands in a *mer* arrangement, it is implausible that any selection of metal–ligand distances could give rise to a degenerate electronic configuration at Cu.

The *N*-pyrimidinylglycinate anion at (x, y, z) thus coordinates to three Cu^{II} centres, *viz.* those at (x, y, z), (x, y, $-1 + z$) and ($1 - x$, $1 - y$, $1 - z$). Propagation by translation and inversion of these ligating interactions generates a one-dimensional coordination polymer in the form of a chain of centrosymmetric edge-fused rings running parallel to the [001] direction, in which eight-membered rings centred at ($\frac{1}{2}$, $\frac{1}{2}$, n), where n represents an integer, alternate with 18-membered rings centred at ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2} + n$), where n represents an integer (Fig. 2).

This chain of edge-fused rings appears to be a unique motif in metal complexes of the ligand L^-. One-dimensional coordination polymers containing the ligand L^- have been reported previously for the isostructural pair of complexes $[M(L)_2(H_2O)_5]\cdot H_2O$ based on strontium (Glidewell *et al.*, 2002) and barium (Godino Salido *et al.*, 2004), where the metal centres are eight coordinate, and where the polymer takes the form of a simple chain with no ring formation. By contrast, the calcium complex $[Ca(L)_2(H_2O)_4]\cdot 4H_2O$ contains finite aggregates in which the Ca atom is six coordinate (Godino Salido *et al.*, 2004); the manganese complex $[Mn(L)_2(H_2O)_4]\cdot 6H_2O$ similarly forms a finite aggregate (Low, Moreno Sánchez *et al.*, 2001). Two-dimensional coordination polymers in the form of organic–inorganic hybrid sheets are formed in both the sodium and potassium derivatives, *viz.* $[Na_2(L)_2(H_2O)_3]$ and $[K(L)(H_2O)]$, in which the metal ions are, respectively, five- and seven-coordinate, including an unusual η^2-coordination of the nitroso group in L^- to potassium (Low, Moreno Sánchez *et al.*, 2001). The lithium compound $[Li(L)(H_2O)_3]$, on the other hand, forms a finite complex containing tetrahedral Li (Low, Moreno Sánchez *et al.*, 2001). Different from all of these complexes in which the L^- anion acts as a coordinating ligand, are the magnesium (Arranz Mascarós *et al.*, 2000) and zinc complexes (Arranz-Mascarós *et al.*, 1999), *viz.* $[M(H_2O)_6]$-$(L)_2\cdot 2H_2O$, which despite having identical constitutions are not isomorphous: here the anion is not coordinated to the metal centre, but forms simple salts with the hexaaqua cations. However, chains of spiro-fused rings are formed in the calcium (Low, Arranz *et al.*, 2001) and strontium (Godino Salido *et al.*, 2004) complexes of the analogous *N*-pyrimidinylglycylglycinate L'^- anion (see scheme). These Ca and Sr complexes crystallize as a trihydrate and tetrahydrate, respectively, but they are effectively isomorphous and almost isostructural, with the metal centres lying on twofold rotation axes in the space group $C2/c$.

An extensive series of hydrogen bonds encompassing O—H$\cdots$O, N—H$\cdots$O, O—H$\cdots$Cl and N—H$\cdots$Cl types (Table 2) links the coordination polymer chains into a continuous three-dimensional framework of considerable complexity. However, the formation of this framework is readily analysed in terms of just the two N—H$\cdots$Cl hydrogen bonds, which generate a sheet lying parallel to (001) (Fig. 3). The combination of this simple sheet and the chains along [001] is sufficient to generate the three-dimensional structure. The framework is considerably strengthened by the hydrogen bonds formed by the water molecules: the coordinated water molecule acts as a double donor of hydrogen bonds, while the noncoordinated water

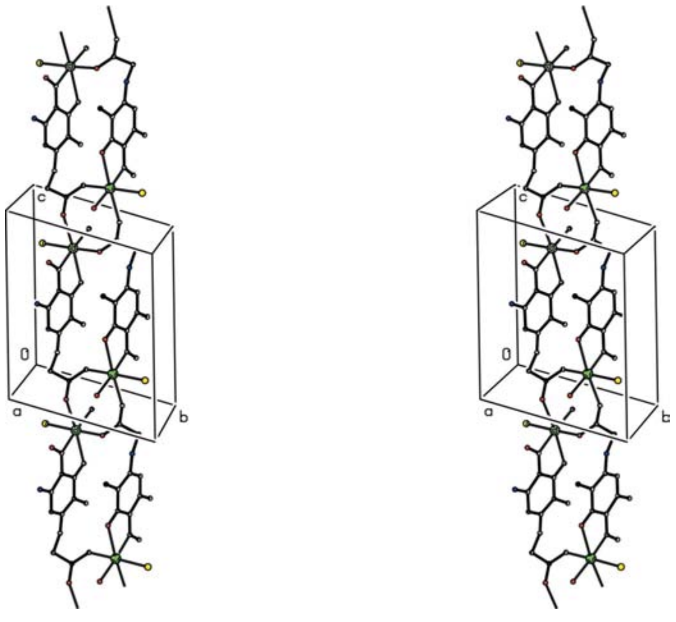


Figure 2
A stereoview of part of the crystal structure of compound (I), showing the formation of a coordination polymer chain parallel to the [001] direction. For the sake of clarity, the noncoordinated water molecule and all H atoms have been omitted, as has the long contact between atoms Cu1 and O5.

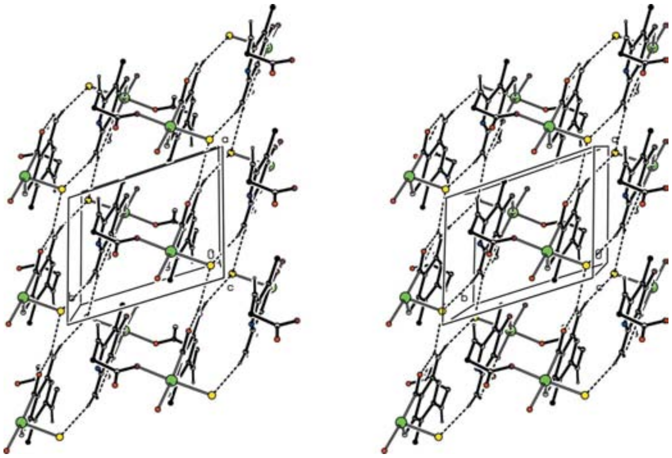


Figure 3
A stereoview of part of the crystal structure of compound (I), showing the formation of a hydrogen-bonded sheet parallel to (001). For the sake of clarity, the noncoordinated water molecule and H atoms bonded to C or O atoms have been omitted, as has the long contact between atoms Cu1 and O5.

molecule acts as both a double donor and a double acceptor of hydrogen bonds.

Regardless of whether simple salts are formed as for Mg and Zn, or finite aggregates as for Li and Ca, or one-dimensional coordination polymers as for Sr and Ba, or two-dimensional coordination polymers as for Na and K, extensive hydrogen bonding links the metal-containing components, the noncoordinated water molecules where these are present and the free anions where these are present into a continuous three-dimensional framework structure in every case. Thus, in all metal derivatives containing the L^- anion, either as a ligand or as a counter-ion, which have so far been structurally characterized the components are linked by hydrogen bonds into three-dimensional systems, regardless of the overall composition of the material and of the nature of the interactions between the metal ion and L^-.

Experimental

The title compound was prepared according to the published method of Moreno *et al.* (1999).

Crystal data

$[Cu(C_7H_8N_5O_4)Cl(H_2O)]\cdot H_2O$
$M_r = 361.21$
Triclinic, $P\overline{1}$
$a = 6.9807$ (5) Å
$b = 9.1462$ (6) Å
$c = 11.2512$ (6) Å
$\alpha = 107.357$ (5)°
$\beta = 105.037$ (5)°
$\gamma = 102.028$ (6)°
$V = 629.54$ (8) Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 1.98$ mm^{-1}
$T = 120$ K
0.41 × 0.25 × 0.22 mm

Data collection

Bruker–Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{min} = 0.601$, $T_{max} = 0.647$
3745 measured reflections
2889 independent reflections
2569 reflections with $I > 2\sigma(I)$
$R_{int} = 0.084$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.080$
$S = 1.04$
2889 reflections
203 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 0.72$ e Å^{-3}
$\Delta\rho_{min} = -0.66$ e Å^{-3}

Table 1
Selected bond lengths (Å).

Cu1—Cl1	2.2813 (6)	N3—C4	1.394 (2)
Cu1—O4	2.3797 (16)	C4—C5	1.453 (3)
Cu1—N5	1.9957 (18)	C5—C6	1.440 (3)
Cu1—O5	2.837 (2)	C6—N1	1.341 (3)
Cu1—O21^{i}	2.7445 (19)	C2—N2	1.333 (3)
Cu1—O22^{ii}	1.9845 (16)	C4—O4	1.223 (3)
Cu1—O31	1.9642 (17)	C5—N5	1.343 (3)
N1—C2	1.323 (3)	N5—O5	1.259 (2)
C2—N3	1.375 (3)	C6—N6	1.310 (3)

Symmetry codes: (i) $x, y, z+1$; (ii) $-x+1, -y+1, -z+1$.

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2···O32^{iii}	0.82 (3)	2.13 (3)	2.829 (3)	144 (3)
N6—H6A···Cl1^{iv}	0.85 (3)	2.58 (4)	3.382 (2)	158 (3)
N6—H6B···Cl1^{v}	0.81 (3)	2.91 (4)	3.466 (2)	128 (3)
N6—H6B···O5	0.81 (3)	2.02 (3)	2.658 (3)	135 (3)
O31—H311···O32^{vi}	0.81 (4)	1.97 (4)	2.779 (3)	177 (4)
O31—H312···O21^{ii}	0.77 (3)	1.89 (4)	2.607 (3)	154 (3)
O32—H321···O21	0.83 (4)	1.97 (4)	2.775 (3)	165 (3)
O32—H322···Cl1^{vii}	0.78 (3)	2.78 (3)	3.358 (2)	133 (2)

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

All H atoms were located in difference maps. H atoms bonded to C atoms were then treated as riding atoms in geometrically idealized positions, with C—H distances of 0.98 (CH_3) or 0.99 Å (CH_2) and with $U_{iso}(H) = kU_{eq}(C)$, where $k = 1.5$ for the methyl group, which was permitted to rotate but not to tilt, and 1.2 for the other H atoms bonded to C atoms. H atoms bonded to N atoms were initially treated as riding atoms in geometrically idealized positions, with N—H distances of 0.88 Å and $U_{iso}(H) = 1.2U_{eq}(N)$, while the H atoms of the two water molecules were initially permitted to ride at the distances deduced from the difference maps, with $U_{iso}(H) = 1.2U_{eq}(O)$. In the final refinement cycles, the coordinates of H atoms bonded to N and O atoms were freely refined, giving N—H distances in the range 0.81 (3)–0.85 (3) Å, O—H distances in the range 0.77 (3)–0.83 (4) Å and H—O—H angles of 110 (3) and 113 (3)°. None of the residual features in the difference map could plausibly be reconciled with any further chemical entities, but they possibly reflect the relatively poorer quality of the weak data, particularly those beyond $(\sin\theta)/\lambda = 0.60$.

Data collection: *COLLECT* (Hooft, 1999); cell refinement: *DIRAX/LSQ* (Duisenberg *et al.*, 2000); data reduction: *EVALCCD* (Duisenberg *et al.*, 2003); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97* and *PLATON*.

X-ray data were collected at the EPSRC National Crystallography Service, University of Southampton, England; the authors thank the staff of the Service for all their help. The authors thank 'Servicios Técnicos de Investigación of Universidad de Jaén' and the staff for data collection. JC thanks the Consejería de Innovación, Ciencia y Empresa (Junta de Andalucía, Spain) and the Universidad de Jaén for financial support. RL and PA thank the Junta de Andalucía, Spain, for financial support (project reference P06-FQM-01585).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3322). Services for accessing these data are described at the back of the journal.

References

Arranz Mascarós, P., Cobo Domingo, J., Godino Salido, M., Gutiérrez Valero, M. D., López Garzón, R. & Low, J. N. (2000). *Acta Cryst.* C**56**, e4–e5.

Arranz-Mascarós, P., Godino, M. L., López, R., Cuesta, R., Valenzuela-Calahorro, C. & Martín-Ramos, D. (1999). *Acta Cryst.* C**55**, 2049–2051.

Duisenberg, A. J. M., Hooft, R. W. W., Schreurs, A. M. M. & Kroon, J. (2000). *J. Appl. Cryst.* **33**, 893–898.

Duisenberg, A. J. M., Kroon-Batenburg, L. M. J. & Schreurs, A. M. M. (2003). *J. Appl. Cryst.* **36**, 220–229.

Glidewell, C., Low, J. N., Arranz Mascarós, P., Cuesta Martos, R. & Gutiérrez Valero, M. D. (2002). *Acta Cryst.* C**58**, m61–m64.

Godino Salido, M. L., Arranz Mascarós, P., López Garzón, R., Gutiérrez Valero, M. D., Low, J. N., Gallagher, J. F. & Glidewell, C. (2004). *Acta Cryst.* B**60**, 46–64.

Hooft, R. W. W. (1999). *COLLECT*. Nonius BV, Delft, The Netherlands.

Low, J. N., Arranz, P., Cobo, J., Fontecha, M. A., Godino, M. L., López, R., Cannon, D., Quesada, A. & Glidewell, C. (2001). *Acta Cryst.* C**57**, 680–682.

Low, J. N., López, M. D., Arranz Mascarós, P., Cobo Domingo, J., Godino, M. L., López Garzón, R., Gutiérrez, M. D., Melguizo, M., Ferguson, G. & Glidewell, C. (2000). *Acta Cryst.* B**56**, 882–892.

Low, J. N., Moreno Sánchez, J. M., Arranz Mascarós, P., Godino Salido, M. L., López Garzon, R., Cobo Domingo, J. & Glidewell, C. (2001). *Acta Cryst.* B**57**, 317–328.

Moreno, J. M., Arranz-Mascarós, P., López-Garzón, R., Gutiérrez-Valero, M. D., Godino-Salido, M. L. & Cobo-Domingo, J. (1999). *Polyhedron*, **18**, 1635–1640.

Schlemper, E. O., Murmann, R. K. & Hussain, M. S. (1986). *Acta Cryst.* C**42**, 1739–1743.

Sheldrick, G. M. (2003). *SADABS*. Version 2.10. University of Göttingen, Germany.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.

Talberg, H. J. (1977). *Acta Chem. Scand. Ser. A*, **31**, 485–491.