

Bis[*N*-(6-amino-3,4-dihydro-3-methyl-5-nitroso-4-oxopyrimidin-2-yl)glycylglycinato]triacquacalcium: coordination polymer chains linked by hydrogen bonds

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Received 26 February 2001

Accepted 9 March 2001

In the title compound, [Ca(C₉H₁₁N₆O₅)₂(H₂O)₃], the Ca atom lies on a twofold rotation axis in *C2/c* and the three water molecules are all disordered, each over two sites having equal occupancy. The anion acts as a bridging ligand between pairs of Ca sites on the same twofold axis, thus forming a one-dimensional coordination polymer, with the chains lying along the twofold axes. These chains are linked by multiple O—H···O and N—H···O hydrogen bonds into a single three-dimensional framework.

Comment

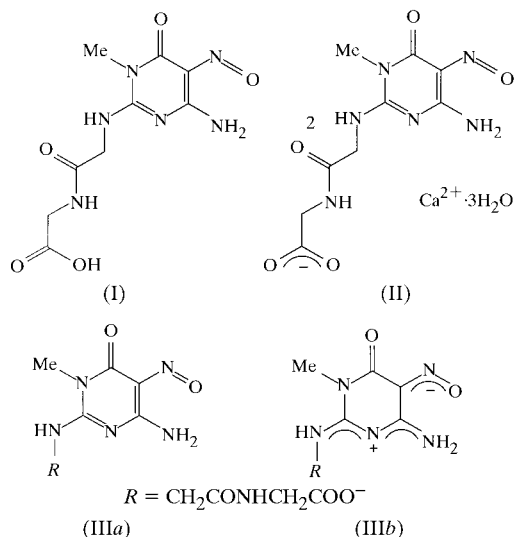
The potassium salt of the pyrimidylglycylglycine (I), *LH*, crystallizes as a monohydrate, K⁺*L*[−]·H₂O, in which the cations and anions form a three-dimensional coordination polymer network, where the water molecules play no significant structural role (Low, Arranz *et al.*, 2001). By contrast, in the calcium salt, which crystallizes as the trihydrate Ca²⁺(*L*[−])₂·3H₂O (II), the cations and anions form a one-dimensional coordination polymer; the individual strands of this polymer are connected into a single three-dimensional framework by means of a series of hydrogen bonds, dominated by those formed by the water molecules.

Compound (II) crystallizes in space group *C2/c* with *Z'* = ½; the Ca atom lies on a twofold rotation axis, selected for convenience to be that along (½, *y*, ¼), with the anion in a

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general position. There are three water molecules coordinated to the calcium, each disordered over two sites with equal occupancy (Fig. 1). The water molecules can only adopt one of the two possible arrangements about the Ca atom through geometry considerations, in order to avoid unacceptably short O···O distances between water molecules bound to the same Ca atom [O1···O2ⁱ 1.802 (7) Å and O3···O2ⁱ 1.289 (6) Å; symmetry code: (i) 1 − *x*, *y*, ½ − *z*].



The Ca atom is also coordinated by four O atoms, two carboxylic acid and two amidic, each from a different anionic ligand (Table 1 and Fig. 2), and the resulting CaO₄ unit can be described as a slight distortion of square planar towards tetrahedral. Overall, the coordination geometry at calcium, including the three water molecules, is distorted pentagonal bipyramidal (Fig. 3). The Ca—O distances involving water span those involving the anionic ligands (Table 1); the carboxylate distance Ca—O23 is, unexpectedly, longer than the amidic distance Ca—O21. This coordination behaviour of the anion *L*[−] towards calcium may be contrasted with its behaviour towards potassium where, in addition to all three of the O atoms in the glycylglycinate side chain, the nitrosyl O5 atom also acts as one of the ligating atoms (Low, Arranz *et al.*,

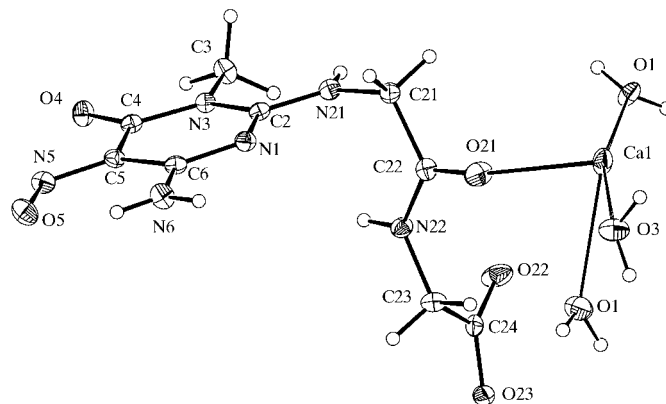


Figure 1

The asymmetric unit of compound (II) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

2001). The mean value of the Ca—O distances is 2.420 (4) Å; if the outlier value for the rather weakly bound O1 is omitted, the mean value of the other six Ca—O distances is 2.377 (4) Å; the mean value of the K—O distances in the analogous $K^+L^-\cdot H_2O$ salt is 2.731 (2) Å (Low, Arranz *et al.*, 2001). The difference between the mean Ca—O and K—O distances, *ca* 0.31 Å if Ca is regarded as seven-coordinate or *ca* 0.35 Å if it is regarded as six-coordinate, precisely reflect the differences between the corresponding ionic radii, as tabulated by Shannon & Prewitt (1970): K^+ (six-coordinate) 1.38, Ca^{2+} (seven-coordinate) 1.07 and Ca^{2+} (six-coordinate) 1.00 Å.

The supramolecular structure can be most readily analysed and described using the substructure approach (Gregson *et al.*, 2000). Each anion acts as a bridging ligand between adjacent Ca centres on a given twofold axis, thus generating a chain of 14-membered rings, fused in a spiro fashion at the Ca atom (Fig. 2). Four of these chains run through each unit cell, along the lines $(\frac{1}{2}, y, \frac{1}{4})$, $(\frac{1}{2}, y, \frac{3}{4})$, $(1, y, \frac{1}{4})$ and $(1, y, \frac{3}{4})$, and each chain is linked to four neighbouring chains by means of O—H...O hydrogen bonds in which the coordinated water molecules act as donors (Table 2). It is necessary to emphasize at this point, in respect of the disorder of the water sites, that although the site occupancies are fully correlated at each individual Ca centre, as described earlier, there are no such constraints on the water-site occupancies at neighbouring Ca sites along a chain, or on those at Ca sites in different chains.

The water O1 atom at (x, y, z) acts as hydrogen-bond donor, *via* H1AW, forming a rather long weak hydrogen bond, to O22 at $(1-x, y, \frac{1}{2}-z)$, which is part of the same [010] chain; similarly O3 at (x, y, z) acts as donor, *via* H3AW, to O22 at $(1-x, 1+y, \frac{1}{2}-z)$, also part of the same chain. The other four O—H...O hydrogen bonds all serve to link adjacent chains. The water O2 atom at (x, y, z) is a component of the chain along $(\frac{1}{2}, y, \frac{1}{4})$; O2 acts as hydrogen-bond donor, *via* H2AW, to O22 at $(\frac{3}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z)$, which is a component of

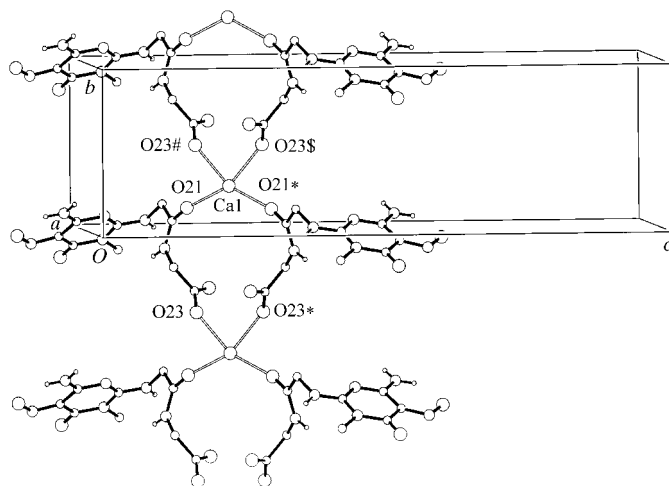


Figure 2 Part of the crystal structure of (II) showing the formation of the one of the [010] chains formed by the cations and anions. For the sake of clarity, H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*), hash (#) or dollar sign (\$) are at the symmetry positions $(1-x, y, \frac{1}{2}-z)$, $(x, 1+y, z)$, and $(1-x, 1+y, \frac{1}{2}-z)$, respectively.

the chain along $(1, y, \frac{1}{4})$, and it also acts as hydrogen-bond donor, *via* H2BW, to O5 at $(x, -y, \frac{1}{2}+z)$, which is a component of the chain along $(\frac{1}{2}, y, \frac{3}{4})$. Propagation by the space group of these two interchain O—H...O hydrogen bonds, both formed by the water O2 atom, would of itself be sufficient to link all of the chains into a single framework. There are, however, several more hydrogen bonds which further reinforce the links between the chains. The water O3 atom at (x, y, z) acts as donor, *via* H3BW, to O22 at $(-\frac{1}{2}+x, \frac{1}{2}+y, z)$, which is a

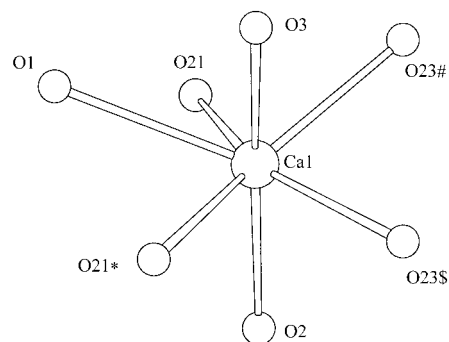


Figure 3 Part of the crystal structure of (II) showing the coordination at calcium. Atoms marked with an asterisk (*), hash (#) or dollar sign (\$) are at the symmetry positions $(1-x, y, \frac{1}{2}-z)$, $(x, 1+y, z)$, and $(1-x, 1+y, \frac{1}{2}-z)$, respectively. Only one set of positions for O1, O2 and O3 is shown (see text).

component of the chain along $(0, y, \frac{1}{4})$, and the water O1 atom at (x, y, z) acts as donor, *via* H1BW, and in a rather weak hydrogen bond, to O5 at $(1-x, -y, -z)$, a component of the chain along $(\frac{1}{2}, y, -\frac{1}{4})$. Thus, by means of these four O—H...O hydrogen bonds, the reference chain along $(\frac{1}{2}, y, \frac{1}{4})$ is directly linked to those along $(\frac{1}{2}, y, -\frac{1}{4})$ and $(\frac{1}{2}, y, \frac{3}{4})$, and to those along $(1, y, \frac{1}{4})$ and $(0, y, \frac{1}{4})$. Three hydrogen bonds with N—H donors provide further links (Table 2); N21 at (x, y, z) in the chain along $(\frac{1}{2}, y, \frac{1}{4})$ acts as donor to O23 at $(\frac{1}{2}+x, \frac{1}{2}+y, z)$ in the chain along $(1, y, \frac{1}{4})$, while N6 at (x, y, z) acts as donor, *via* H6A, to O4 at $(-\frac{1}{2}+x, \frac{1}{2}+y, z)$ in the chain along $(0, y, \frac{1}{4})$, and finally, N22 at (x, y, z) forms a rather weaker hydrogen bond to N5 at $(\frac{3}{2}-x, -\frac{1}{2}-y, -z)$, a component of the chain along $(1, y, -\frac{1}{4})$. Each $Ca(H_2O)_3$ unit along each chain gives rise to a similar set of hydrogen bonds, hence tying all the metal–anion chains into a single bundle.

The bond distances (Table 1) within the heterocyclic ring show evidence of a marked polarization of the electronic structure of this ring, as noted in previous studies (Low *et al.*, 2000; Low, Moreno Sánchez *et al.*, 2001; Low, Arranz *et al.*, 2001). In particular, the C2—N1 bond is the longest of the C—N bonds in the sequence N2—C2—N1—C6—N6, although it is the only such bond which is represented as a double bond in the conventional representation (IIIa); bonds C4—C5 and C5—C6, respectively single and double bonds in form (IIIa), do not differ significantly in length, and the difference between the nitroso C5—N5 and N5—O5 distances is far smaller than expected from (IIIa) (Low *et al.*, 2000). All of these observations point to the importance of the polarized form (IIIb), confirmed by the behaviour of O5 as a hydrogen-bond acceptor.

In the glycyglycinate side chain, the two C—O distances in the carboxylate group are very similar, and the amidic C—O distance is identical, within experimental uncertainty, to the amidic distance C4—O4. The conformation of the side chain (Table 1), which shows some unexpected torsion angles, is probably largely determined by a combination of the requirements of O21 and O23 in coordinating to different Ca sites, and the extensive hydrogen bonding involving both donor and acceptor sites in the side chain.

Experimental

Crystals of compound (II) were obtained adventitiously during preparation of the potassium salt derived from the ligand HL, (I) (Low, Arranz *et al.*, 2001).

Crystal data

[Ca(C ₉ H ₁₁ N ₆ O ₅) ₂ (H ₂ O) ₃]	$D_x = 1.708 \text{ Mg m}^{-3}$
$M_r = 660.60$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 2553 reflections
$a = 12.7815 (7) \text{ \AA}$	$\theta = 1.6\text{--}26.3^\circ$
$b = 7.7010 (7) \text{ \AA}$	$\mu = 0.34 \text{ mm}^{-1}$
$c = 26.271 (2) \text{ \AA}$	$T = 150 (2) \text{ K}$
$\beta = 96.418 (5)^\circ$	Plate, colourless
$V = 2569.7 (4) \text{ \AA}^3$	$0.15 \times 0.08 \times 0.01 \text{ mm}$
$Z = 4$	

Data collection

KappaCCD diffractometer	1641 reflections with $I > 2\sigma(I)$
φ scans, and ω scans with κ offsets	$R_{\text{int}} = 0.090$
Absorption correction: multi-scan (SORTAV; Blessing, 1995, 1997)	$\theta_{\text{max}} = 26.3^\circ$
$T_{\text{min}} = 0.951$, $T_{\text{max}} = 0.997$	$h = -15 \rightarrow 15$
17 345 measured reflections	$k = -9 \rightarrow 9$
2553 independent reflections	$l = -32 \rightarrow 32$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0683P)^2 + 1.8308P]$
$R[F^2 > 2\sigma(F^2)] = 0.049$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.135$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.00$	$\Delta\rho_{\text{max}} = 0.32 \text{ e \AA}^{-3}$
2553 reflections	$\Delta\rho_{\text{min}} = -0.36 \text{ e \AA}^{-3}$
214 parameters	
H-atom parameters constrained	

Compound (II) crystallized in the monoclinic system. Space groups Cc and $C2/c$ were permitted by the systematic absences; $C2/c$ was chosen and confirmed by the successful structure analysis. H atoms were treated as riding atoms, with C—H distances of 0.98 (CH₂) or 0.99 Å (CH₃) and an N—H distance of 0.88 Å. Water molecules were initially handled *via* DFIX, with an O—H distance of 0.87 (3) Å, and after this refinement had fully converged, the H atoms were treated as riding atoms using AFIX.

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2001); software used to prepare material for publication: *SHELXL97* (Sheldrick, 1997) *PRPKAPPA* (Ferguson, 1999).

X-ray data were collected at the EPSRC X-ray Crystallographic Service, University of Southampton, using a Nonius KappaCCD diffractometer. The authors thank the staff for all their help and advice.

Table 1

Selected geometric parameters (Å, °).

Ca1—O1	2.676 (4)	C4—O4	1.231 (3)
Ca1—O2	2.278 (4)	C5—N5	1.339 (4)
Ca1—O3	2.334 (4)	N5—O5	1.288 (3)
Ca1—O21	2.388 (2)	C6—N6	1.322 (3)
Ca1—O23 ⁱ	2.437 (2)	N21—C21	1.460 (4)
N1—C2	1.341 (3)	C21—C22	1.513 (4)
C2—N3	1.384 (3)	C22—O21	1.232 (3)
N3—C4	1.392 (4)	C22—N22	1.327 (4)
C4—C5	1.455 (4)	N22—C23	1.447 (4)
C5—C6	1.449 (4)	C23—C24	1.526 (4)
C6—N1	1.337 (4)	C24—O22	1.250 (3)
C2—N21	1.324 (4)	C24—O23	1.260 (3)
N3—C3	1.477 (3)		
O21—Ca1—O21 ⁱⁱ	128.61 (11)	O21—Ca1—O1	72.63 (12)
O23 ⁱ —Ca1—O23 ⁱⁱⁱ	77.97 (10)	O21—Ca1—O2	85.89 (12)
O21—Ca1—O23 ⁱ	80.29 (7)	O21—Ca1—O3	110.60 (13)
O21—Ca1—O23 ⁱⁱⁱ	147.44 (7)	O23 ⁱ —Ca1—O1	119.34 (11)
O1—Ca1—O2	113.79 (16)	O23 ⁱ —Ca1—O2	117.14 (12)
O1—Ca1—O3	69.53 (15)	O23 ⁱ —Ca1—O3	71.28 (13)
O2—Ca1—O3	163.04 (16)		
N3—C2—N21—C21	177.1 (2)	C22—N22—C23—C24	−111.7 (3)
C2—N21—C21—C22	80.8 (3)	N22—C23—C24—O22	21.3 (4)
N21—C21—C22—N22	−0.5 (4)	N22—C23—C24—O23	−160.1 (2)
C21—C22—N22—C23	177.5 (3)		

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

Table 2

Hydrogen-bonding geometry (Å, °).

$D\text{---}H\cdots A$	$D\text{---}H$	$H\cdots A$	$D\cdots A$	$D\text{---}H\cdots A$
O1—H1AW \cdots O22 ⁱ	0.90	2.16	3.048 (5)	168
O1—H1BW \cdots O5 ⁱⁱ	0.88	2.32	2.962 (5)	130
O2—H2AW \cdots O22 ⁱⁱⁱ	0.87	1.82	2.667 (4)	166
O2—H2BW \cdots O5 ^{iv}	0.85	1.82	2.655 (5)	164
O3—H3AW \cdots O22 ^v	0.89	1.82	2.692 (5)	166
O3—H3BW \cdots O22 ^{vi}	0.89	1.89	2.744 (5)	162
N6—H6B \cdots O5	0.88	1.94	2.598 (3)	131
N6—H6A \cdots O4 ^{vi}	0.88	1.97	2.761 (3)	149
N21—H21 \cdots O23 ^{vii}	0.88	2.05	2.861 (3)	152
N22—H22A \cdots N5 ^{viii}	0.88	2.34	3.132 (3)	150

Symmetry codes: (i) $1 - x, y, \frac{1}{2} - z$; (ii) $1 - x, -y, -z$; (iii) $\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (iv) $x, -y, \frac{1}{2} + z$; (v) $1 - x, 1 + y, \frac{1}{2} - z$; (vi) $x - \frac{1}{2}, \frac{1}{2} + y, z$; (vii) $\frac{1}{2} + x, \frac{1}{2} + y, z$; (viii) $\frac{3}{2} - x, -\frac{1}{2} - y, -z$.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1048). Services for accessing these data are described at the back of the journal.

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