

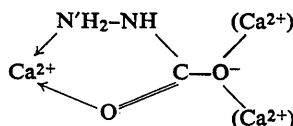
Crystal and Molecular Structure of Anhydrous Calcium Hydrazinecarboxylate

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Calcium hydrazinecarboxylate, $\text{Ca}(\text{N}'\text{H}_2\text{-NH-COO})_2$, forms monoclinic crystals, space group $P2_1/c$. The structure, determined by three-dimensional data, consists of metal-ligand complexes, where calcium exhibits coordination number 7, thus forming a pentagonal bipyramid. The complexes are joined in pairs, with $\text{Ca} \cdots \text{Ca} = 3.7 \text{ \AA}$, by bridging oxygen atoms which form bifurcated bonds with two calcium ions. The bridging oxygen atoms belong to ligands of other pairs, hence a three-dimensional network of complexes results. The two crystallographically independent ligand molecules are practically equal. The bonds and angles in them are compared with bonds and angles of the same ligand in octahedral complexes: the main differences concern the carbon-oxygen bonds of the carboxylic group. The structure



can be assigned to the chelate rings.

Introduction

The compounds of hydrazinecarboxylic acid are interesting for their strict analogy with those of α -aminoacids (Freeman, 1967). They can constitute substitutive examples in cases where well crystallized compounds of α -aminoacids are not obtainable.

The crystal structure of calcium hydrazinecarboxylate monohydrate, $\text{Ca}(\text{N}'\text{H}_2\text{-NH-COO})_2 \cdot \text{H}_2\text{O}$, (Braibanti, Manotti Lanfredi, Pellinghelli & Tiripicchio, 1971) has been determined previously. It presents coordination number 8 around calcium, thus giving rise to distorted pentagonal bipyramid with a centred face. The crystals of the anhydrous compound, $\text{Ca}(\text{N}'\text{H}_2\text{-NH-COO})_2$, which can be obtained by transformation of the hydrated crystals, have now been studied, mainly in an endeavour to find the structural differences between the hydrated and anhydrous forms.

Experimental

Preparation

Crystals of the compound are obtained by evaporation of an aqueous solution of calcium hydroxide and hydrazine treated by carbon dioxide. Prisms of calcium hydrazinecarboxylate monohydrate appear at first, which are fairly stable in the air. By standing in the mother liquor they are transformed into well shaped crystals of anhydrous calcium hydrazinecarboxylate, $\text{Ca}(\text{N}'\text{H}_2\text{-NH-COO})_2$, stable in the air and with many faces.

Crystal data

Compound: Calcium hydrazinecarboxylate
 $\text{Ca}(\text{N}'\text{H}_2\text{-NH-COO})_2$; F.W. 190.18

Crystal class: monoclinic, prismatic

Unit cell (Cu $K\alpha$ radiation, $\lambda = 1.5418 \text{ \AA}$):

$a = 9.590 (15)$, $b = 9.426 (10)$, $c = 9.290 (9) \text{ \AA}$

$\beta = 127.8 (3)^\circ$

$V = 663.2 \text{ \AA}^3$ $Z = 4$; $D_x = 1.904$, $D_m = 1.900 \text{ g.cm}^{-3}$

$\mu(\text{Cu } K\alpha) = 77.74 \text{ cm}^{-1}$.

Space group: $P2_1/c$ [No. 14, C_{2h}^5].

Intensity data

Intensities were recorded photographically on an integrating Weissenberg camera and then measured by a microdensitometer. The crystals were rotated around [100] and [010]. The reflexions of layers $0kl, \dots, 8kl$ and $h0l, \dots, h8l$ were measured (1058 independent reflexions out of 1517 possible).

Calculations

The usual corrections were applied; absorption corrections as for cylindrical specimens ($\mu R_{[100]} = 0.76$; $\mu R_{[010]} = 0.90$) were introduced. Atomic form factors were used following Cromer & Mann (1968).

The structure was solved by Fourier and Patterson methods and then refined by differential syntheses, with anisotropic thermal parameters. At the end of the refinement no changes in the positional parameters and small changes in the thermal parameters were observed. However, due to the experimental errors affecting the data and to the method of refinement which was followed, no certain physical meaning can be given to the thermal parameters and no assessment can be made of their accuracy. The hydrogen atoms have been localized in the difference synthesis but not refined. The conventional agreement factor for observed reflexions was without H contribution: $R = 7.7\%$, with H contribu-

tion: R 7.5%. The results of the structure determination are reported in Tables 1–5. The observed and calculated structure factors can be obtained from the authors on request.

Table 1. Fractional atomic coordinates $\times 10^4$ (with *e.s.d.*'s)

	<i>x</i>	<i>y</i>	<i>z</i>
Ca	2021 (2)	4732 (1)	5183 (2)
O(1·1)	4006 (13)	6589 (4)	6201 (11)
C(2·1)	4637 (11)	7262 (5)	7634 (11)
N(3·1)	4353 (13)	6791 (4)	8825 (13)
N(4·1)	3010 (14)	5787 (5)	8196 (13)
O(5·1)	5586 (13)	8379 (5)	8107 (12)
O(1·2)	0603 (12)	2773 (5)	3116 (11)
C(2·2)	0721 (12)	2534 (5)	1882 (11)
N(3·2)	1268 (14)	3609 (4)	1330 (13)
N(4·2)	2131 (14)	4814 (4)	2468 (14)
O(5·2)	0306 (9)	1377 (3)	1005 (9)
H(7·1)	4573	7444	9917
H(8·1)	1830	6166	7830
H(9·1)	3673	5053	9135
H(7·2)	1479	3320	0420
H(8·2)	3357	4380	3275
H(9·2)	1930	5694	1714

Table 2. Thermal parameters (\AA^2)

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ca	1.190	0.874	1.119	0.002	0.716	-0.016
O(1·1)	2.737	2.142	1.959	-0.920	1.617	-0.599
C(2·1)	2.038	1.958	1.903	-0.054	1.199	-0.175

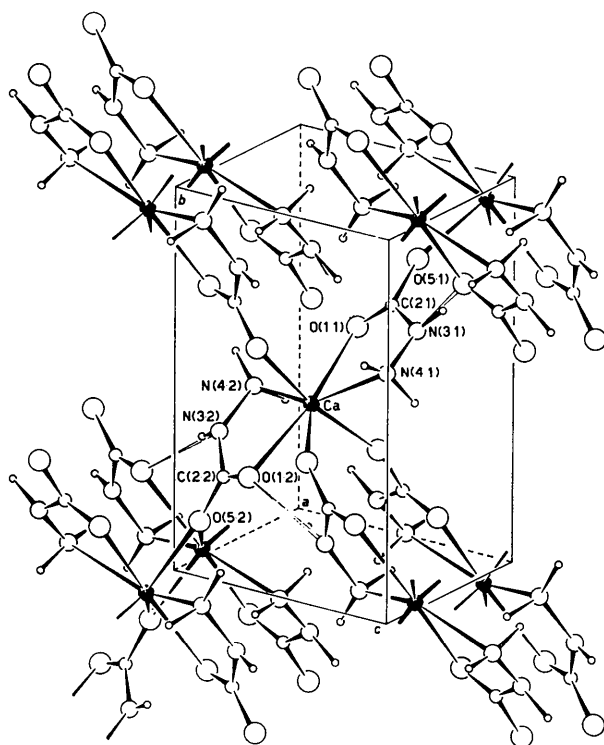


Fig. 1. Clinographic projection of the structure of calcium-hydrazinecarboxylate. In dimer at $0, \frac{1}{2}, \frac{1}{2}$ only one Ca is represented to avoid overlapping.

Table 2 (cont.)

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
N(3·1)	3.042	2.759	2.252	-0.833	1.864	-0.494
N(4·1)	2.237	1.895	1.962	-0.391	1.383	-0.324
O(5·1)	3.252	2.755	3.243	-1.656	1.897	-1.050
O(1·2)	3.147	1.724	2.354	-0.802	2.144	-0.466
C(2·2)	1.579	1.497	1.335	0.090	0.884	-0.006
N(3·2)	3.347	1.703	2.506	-0.821	2.096	-0.619
N(4·2)	2.997	1.768	2.681	-0.423	1.912	-0.389
O(5·2)	1.811	1.146	1.566	-0.090	1.100	-0.112

In the last cycle for all the atoms the average shift $|\Delta B_{ij}|_{av}$, and the maximum shift, $|\Delta B_{ij}|_{max}$, were

$$|\Delta B_{ij}|_{av} = 0.041$$

$$|\Delta B_{ij}|_{max} = 0.165$$

	<i>B</i>	<i>B</i>
H(7·1)	2.50	H(7·2) 2.30
H(8·1)	2.00	H(8·2) 2.40
H(9·1)	2.00	H(9·2) 2.40

Table 3. Atomic peak heights (e. \AA^{-3}), curvatures (e. \AA^{-5}) and *e.s.d.*'s

	ρ	$-A_{hh}$	$-A_{kk}$	$-A_{ll}$	A_{hk}	A_{hl}	A_{kl}
Ca	obs. 59.4	660	674	658	4	405	-14
	calc. 59.6	656	665	654	3	403	-12
O(1·1)	obs. 13.5	114	122	136	-11	80	-4
	calc. 13.7	113	121	133	-9	78	-3
C(2·1)	obs. 10.9	119	109	117	-4	71	-1
	calc. 11.1	119	109	118	-4	71	-1
N(3·1)	obs. 11.6	118	103	114	-8	77	-11
	calc. 11.8	119	104	113	-6	77	-10
N(4·1)	obs. 11.8	106	121	127	-4	77	-1
	calc. 11.8	106	120	126	-4	77	-1
O(5·1)	obs. 12.2	105	103	118	-9	69	-2
	calc. 12.4	106	103	119	-4	70	-2
O(1·2)	obs. 14.2	142	118	158	-8	104	-3
	calc. 14.4	143	117	154	-6	102	-3
C(2·2)	obs. 11.2	121	104	126	10	76	-12
	calc. 11.3	120	104	125	10	75	-11
N(3·2)	obs. 11.8	109	123	116	6	73	-11
	calc. 11.9	110	121	115	8	71	-10
N(4·2)	obs. 11.8	109	128	119	-1	76	-7
	calc. 11.8	109	126	118	-1	76	-6
O(5·2)	obs. 15.7	149	159	153	1	95	-8
	calc. 15.7	149	158	152	1	94	-8
<i>e.s.d.</i>		0.2	3	3	2	2	2

	ρ		ρ
H(7·1)	obs. 1.2	H(7·2)	obs. 0.9
	calc. 1.4		calc. 0.9
H(8·1)	obs. 0.9	H(8·2)	obs. 1.0
	calc. 1.1		calc. 1.4
H(9·1)	obs. 1.4	H(9·2)	obs. 1.0
	calc. 1.5		calc. 1.3

Discussion

The clinographic projection of the structure (Fig. 1) shows how the coordination polyhedra around calcium are grouped in pairs at the symmetry centres $(0,0,0)$ and $(0, \frac{1}{2}, \frac{1}{2})$. Two calcium atoms of the same pair are 3.71 \AA distant from each other, whereas distances between calcium atoms of adjacent dimers are $\text{Ca} \cdots \text{Ca} = 6.19$ and $\text{Ca} \cdots \text{Ca} = 6.26$ \AA . The connexions within the same dimer are by bridging oxygen atoms forming bifurcated bonds with two calcium ions. The bridging

oxygen atoms, however, belong to adjacent dimers, so that a three-dimensional network of complexes extends throughout the structure.

The coordination number of calcium is 7 and the polyhedron can be described as a slightly deformed pentagonal bipyramid (Fig. 2). Either oxygen or nitrogen atoms enter the coordination sphere of the

metal. The bonds between calcium and nitrogen, $\text{Ca-N}(4\cdot1)=2\cdot543$ and $\text{Ca-N}(4\cdot2)=2\cdot589$ Å, resemble very closely the corresponding distances in the hydrated compound. The bonds between calcium and surrounding oxygen atoms range from 2.224 to 2.433 Å, with average $\text{Ca-O}_{\text{av}}=2\cdot35$ Å, against an average in the hydrated compound $\text{Ca-O}_{\text{av}}=2\cdot44$ Å, and a range

Table 4. Main bond distances and angles

		x	$\frac{1}{2}-y$	$\frac{1}{2}+z$		
		x	$\frac{3}{2}-y$	$\frac{1}{2}+z$		
		$-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$		
	iv	x	$\frac{1}{2}-y$	$-\frac{1}{2}+z$		
	v	$1-x$	$-\frac{1}{2}+y$	$\frac{3}{2}-z$		
Ca—O(1·1)	2·318 (10) Å	O(1·1)—Ca—N(4·1)		66·2 (4)°		
Ca—N(4·1)	2·543 (13)	Ca—O(1·1)—C(2·1)		124·0 (9)		
O(1·1)—C(2·1)	1·246 (11)	O(1·1)—C(2·1)—N(3·1)		119·5 (8)		
C(2·1)—N(3·1)	1·366 (16)	C(2·1)—N(3·1)—N(4·1)		118·0 (9)		
N(3·1)—N(4·1)	1·404 (16)	N(3·1)—N(4·1)—Ca		110·4 (9)		
C(2·1)—O(5·1)	1·280 (12)	O(1·1)—C(2·1)—O(5·1)		124·2 (11)		
N(4·1)—O(1·1)	2·663 (19)	O(5·1)—C(2·1)—N(3·1)		116·3 (8)		
Ca—O(1·2)	2·396 (8) Å	O(1·2)—Ca—N(4·2)		65·5 (3)°		
Ca—N(4·2)	2·589 (15)	Ca—O(1·2)—C(2·2)		123·5 (7)		
O(1·2)—C(2·2)	1·240 (15)	O(1·2)—C(2·2)—N(3·2)		118·8 (6)		
C(2·2)—N(3·2)	1·376 (14)	C(2·2)—N(3·2)—N(4·2)		119·5 (10)		
N(3·2)—N(4·2)	1·421 (10)	N(3·2)—N(4·2)—Ca		110·3 (8)		
C(2·2)—O(5·2)	1·270 (8)	O(1·2)—C(2·2)—O(5·2)		125·4 (9)		
N(4·2)—O(1·2)	2·700 (16)	O(5·2)—C(2·2)—N(3·2)		115·7 (9)		
Ca—O(5·2')	2·433 (12) Å	O(1·1)—Ca—N(4·2)		82·0 (3)°		
Ca—O(5·2'')	2·362 (9)	O(1·2)—Ca—O(5·2')		76·1 (3)		
Ca—O(5·1 ^v)	2·224 (11)	O(5·2')—Ca—N(4·1)		72·0 (3)		
		O(5·2'')—Ca—O(5·1 ^v)		167·2 (3)		
		O(5·2'')—Ca—O(1·1)		89·9 (3)		
		O(5·2'')—Ca—N(4·2)		96·7 (3)		
		O(5·2'')—Ca—O(1·2)		102·8 (3)		
		O(5·2'')—Ca—O(5·2')		78·6 (3)		
		O(5·2'')—Ca—N(4·1)		82·2 (3)		
		O(5·1 ^v)—Ca—O(1·1)		85·0 (3)		
		O(5·1 ^v)—Ca—N(4·2)		94·1 (4)		
		O(5·1 ^v)—Ca—O(1·2)		87·7 (3)		
		O(5·1 ^v)—Ca—O(5·2')		97·4 (4)		
		O(5·1 ^v)—Ca—N(4·1)		85·0 (4)		

Table 5. Bond distances and angles involving hydrogen atoms

Asymmetric units: see Table 4.			
N(3·1)—H(7·1)	1·091 Å	H(7·1)—N(3·1)—C(2·1)	123·3°
N(4·1)—H(8·1)	1·026	H(7·1)—N(3·1)—N(4·1)	111·8
N(4·1)—H(9·1)	0·982	H(8·1)—N(4·1)—H(9·1)	121·4
		H(8·1)—N(4·1)—N(3·1)	116·6
		H(9·1)—N(4·1)—N(3·1)	100·2
		H(8·1)—N(4·1)—Ca	100·4
		H(9·1)—N(4·1)—Ca	107·7
N(3·2)—H(7·2)	1·020 Å	H(7·2)—N(3·2)—C(2·2)	116·3°
N(4·2)—H(8·2)	1·015	H(7·2)—N(3·2)—N(4·2)	120·6
N(4·2)—H(9·2)	1·025	H(8·2)—N(4·2)—H(9·2)	118·6
		H(8·2)—N(4·2)—N(3·2)	96·3
		H(9·2)—N(4·2)—N(3·2)	111·0
		H(8·2)—N(4·2)—Ca	89·4
		H(9·2)—N(4·2)—Ca	125·9
Hydrogen bonds			
N(3·1)—O(1·1'')	2·866 (15) Å	H(7·1)—N(3·1)—O(1·1'')	14·3°
N(3·2)—O(1·2 ^{1v})	2·947 (16)	N(3·1)—H(7·1)—O(1·1'')	157·3
		H(7·2)—N(3·2)—O(1·2 ^{1v})	21·8
		N(3·2)—H(7·2)—O(1·2 ^{1v})	147·5

from 2.37 to 2.50 Å. The significantly shorter bonds in the anhydrous compound are one of the causes of its thermodynamic stability with respect to the hydrated compound.

Among the calcium–oxygen bonds, Ca–O(5.1) = 2.224 Å is much shorter than the two bonds radiating

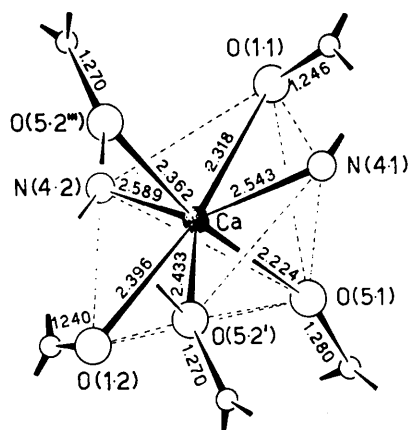


Fig. 2. Coordination polyhedron around calcium.

from O(5.2), Ca–O(5.2) = 2.362 and Ca–O(5.2) = 2.433 Å in which O(5.2) is shared between two calcium atoms; therefore, all Ca–O(5.2) bonds are consistent with the equivalence of C(2.1)–O(5.1) = 1.280 and C(2.2)–O(5.2) = 1.270 Å and with the pronounced single bond character of C(2.2)–O(5.2) with respect to C(2.2)–O(1.2). On the other hand, Ca–O(1.2) bonds are significantly different from one another, Ca–O(1.1) = 2.318 and Ca–O(1.2) = 2.396 Å, notwithstanding the equivalence of C(2.1)–O(1.1) = 1.246 and C(2.2)–O(1.1) = 1.240 Å. The more or less pronounced ionic character of the carboxylic oxygen atoms is emphasized also by comparison with the calcium–nitrogen bonds. The latter, which can be considered as ion-dipole interactions, are significantly longer than the bonds between calcium and oxygen.

Formally speaking, the ligands form pentatomic chelate rings, but their structure can be represented by

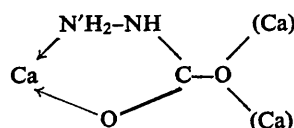


Table 6. Hydrazinecarboxylate anion in various compounds

	Ca(N'H ₂ -NH-COO) ₂	Octahedral complexes*	Ca(N'H ₂ -NH-COO) ₂ ·H ₂ O
	<i>d</i>	<i>d</i>	<i>d</i>
O(1)–C(2)	1.244 (9) Å	†1.224 (6) Å	
O(5)–C(2)	1.273 (7)	†1.293 (6)	1.268 (5) Å
N(3)–C(2)	1.372 (11)	1.381 (7)	1.355 (6)
N(3)–N(4)	1.416 (14)	1.422 (7)	1.425 (6)
	—	—	—
O(1)–C(2)–N(3)	119.05 (48)°	118.97 (49)	118.27 (33)°
C(2)–N(3)–N(4)	118.67 (67)	119.14 (42)	120.00 (46)
O(1)–C(2)–O(5)	124.92 (70)	124.11 (50)	125.53 (41)
O(5)–C(2)–N(3)	116.04 (60)	116.74 (45)	116.06 (44)

* Averages taken from Braibanti, Manotti Lanfredi, Tiripicchio & Pellinghelli (1971).

† O(1) and O(5) interchanged

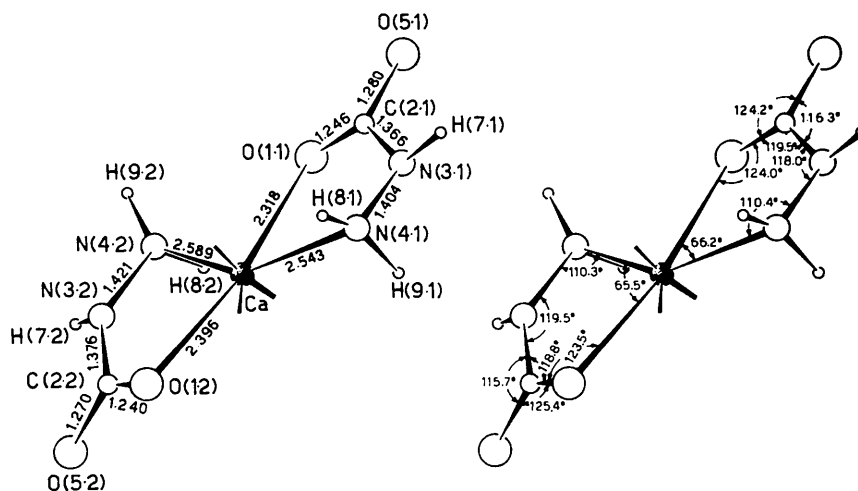


Fig. 3. Bond distances (Å) and angles in chelate rings of calcium hydrazinecarboxylate.

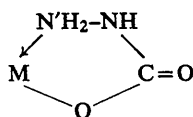
Table 7. Analysis of the planarity of the chelate molecules

Plane	(A) Ring 1						(B) Ring 2					
	0.68286X - 0.56118Y + 0.46772Z = -1.14921						-0.67653X - 0.31375Y + 0.66622Z = -0.10161					
	in				out		in				out	
Atoms	O(1.1)	C(2.1)	N(3.1)	O(5.1)	N(4.1)	Ca	O(1.2)	C(2.2)	N(3.2)	O(5.2)	N(4.2)	Ca
$\Delta \cdot 10^4 (\text{\AA})$	+24	-62	+23	+27	-3172	-2684	-53	+145	-57	-33	+3155	+5489
$\sigma 10^4 (\text{\AA})$	104	100	110	112	110	20	105	105	121	85	130	40
$\Sigma(\Delta/\sigma)^2$	0.55						2.52					

Angle between the planes: 18.25°

X, Y, Z orthogonal coordinates. Matrix $\begin{pmatrix} a & 0 & c \cos \beta \\ 0 & b & 0 \\ 0 & 0 & c \sin \beta \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}$

emphasizing the bridging function of the ligand, rather than by



as generally observed in octahedral complexes of the ligand. These features are clearly shown by the comparison, in Table 6, of the bond angles in octahedral complexes, and in anhydrous and hydrated calcium hydrazinecarboxylates. The carbon-oxygen bonds of both crystallographically independent ligands of the anhydrous calcium compound (see also Fig. 3) can be assigned to two different classes, one with $C-O(1.n)_{av} = 1.243 \text{ \AA}$ and the other with $C-O(5.n) = 1.275 \text{ \AA}$. The latter can be assigned prevailing single bond character, the former prevailing double bond character. They match the carbon-oxygen bonds and angles in octahedral complexes of hydrazinecarboxylic acid if O(1) and O(5) are interchanged. These facts agree with the bridging function of the ligand in the anhydrous calcium compound as underlined by the formulation proposed. All other distances and angles agree very well with those of the octahedral complexes.

The configurations of N(3.1) and N(3.2) are approximately sp^2 as shown by the angles $C(2.1)-N(3.1)-N(4.1) = 118.0^\circ$ and $C(2.2)-N(3.2)-N(4.2) = 119.5^\circ$. The angles formed by H(7.1) which is bound to N(3.1) are not in complete agreement with an sp^2 configuration for N(3.1), while the angles formed by H(7.2), closer to 120° , are more acceptable. The configurations of N(4.1) and N(4.2) should be sp^3 and the angles $N(3.1)-N(4.1)-Ca = 110.4^\circ$ and $N(3.2)-N(4.2)-Ca = 110.3^\circ$ confirm this assignment, while angles involving the hydrogen atoms are rather uncertain.

The comparison with the chelate molecules of the hydrated calcium compound shows that the main differences concern the C-O bonds which in the hydrated compound are all equivalent; they suggest,

therefore, a more pronounced ionic character for the carboxylic group in the hydrated than in the anhydrous compound; even the angle O(1)-C(2)-O(5), again in agreement with the trend to ionic character, is larger in the hydrated than in the anhydrous compound. Another structural characteristic, probably in favour of the higher thermodynamic stability of the anhydrous compound, which differentiates the two calcium compounds from one another, is the relative orientation of the independent ligands in the coordination polyhedron. They tend to be parallel (angle 18.25°), with O(1.1), O(1.2) and N(4.1), N(4.2) in *trans* positions, in the anhydrous compound, while they tend to be orthogonal (angle 73.64°) in the hydrated compound with equal atoms which are neighbours.

The analysis of the planarity of the two rings (Table 7) shows how in each ring the atoms O(1.n), C(2.n), N(3.n), O(5.n) lie in the same plane, whereas Ca and N(4.n) are out of that plane and both on the same side.

The planarity of the group $O-C \begin{matrix} \swarrow O \\ \searrow N \end{matrix}$, and also the deviations of Ca and N(4), confirm a general property of this ligand, that some conjugation exists in the rigid group and that the molecule is flexible at other points.

There are in the structure only two hydrogen bonds, one intra-chain, $N(3.1)-O(1.1') = 2.866 \text{ \AA}$ and one inter-chain, $N(3.2)-O(1.2'') = 2.947 \text{ \AA}$. Other short intermolecular contacts are $N(4.1)-O(5.2') = 2.952 (12)$, $O(1.1)-O(5.1'') = 3.068 (8)$ and $O(1.2)-O(5.2') = 2.977 (16) \text{ \AA}$.

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