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Crystal and Molecular Structure of Calcium Hydrazinecarboxylate Monohydrate

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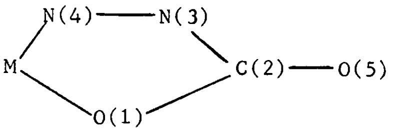
Calcium hydrazinecarboxylate monohydrate, $Ca(NH_2–NH–COO)_2.H_2O$, forms triclinic crystals, space group $P\bar{1}$. The structure has been determined by means of three-dimensional photographic data. The main characteristic of the structure is that the anions both chelate one calcium cation and bridge adjacent calcium cations, thus forming chains parallel to [001]. Calcium ions alternate along the chain at 3·70 and 3·87 Å from one another. The coordination polyhedron around calcium is a distorted pentagonal bipyramid with a centred face; calcium–oxygen bonds ($Ca–O_{av}$ = 2·44 Å) are a result of a balance between electrostatic forces and steric constrictions. The two crystallographically independent anions form pentatomic rings with Ca; part of the ring, namely –NH–COO, forms a rather rigid body whereas Ca and $–NH_2$ are out of the plane of the rigid portion of the molecule. Distances and angles in the anions are compared with distances and angles found in octahedral chelates of the same ligand with 3*d*-transition metals. Strong hydrogen bonds are formed by H_2O within the same chain; weak hydrogen bonds hold the chains together in the structure.

Introduction

The crystal and molecular structures of several hydrazinecarboxylates have been determined in this laboratory (Braibanti, Manotti Lanfredi, Tiripicchio & Bigoli, 1970; Bigoli, Braibanti, Tiripicchio & Tiripicchio Camellini, 1970). All these compounds concern complexes of 3*d*-metals and sometimes magnesium. They present various types of octahedral coordination but all of them contain pentatomic chelate rings.



which are strictly analogous to the rings formed by α-amino acids with the same metals (Freeman, 1967). The structures of compounds of hydrazinecarboxylic acid can constitute valid substitutive examples for non-obtainable or non-crystallizable compounds of α-amino acids.

Experimental

Preparation

Crystals of the compound can be obtained by evaporation of an aqueous solution of calcium hydroxide and hydrazine treated by carbon dioxide. The crystals have a prismatic habit and decompose slowly in the air.

Crystal data

Compound: Calcium hydrazinecarboxylate monohydrate, $Ca(N'H_2–NH–COO)_2.H_2O$, F.W. 208·2.
Crystal class: triclinic pinacoidal.
Unit cell (radiation Cu $K\alpha$, $\lambda = 1·5418$ Å, from rotation and Weissenberg photographs around [010]):
$a = 7·67$ (1), $b = 7·86$ (1), $c = 6·37$ (1) Å;
$\alpha = 84·02$ (45), $\beta = 72·88$ (55), $\gamma = 78·65$ (25)°.
$V = 359·3$ Å^3, $Z = 2$; $D_x = 1·92$, $D_m = 1·92$ g.cm^{-3};
μ(Cu $K\alpha$) = 72·7 cm^{-1}.
Space group: $P\bar{1}(C_i(1)$, No. 2).

Intensity data

Intensities were recorded photographically on an integrating Weissenberg camera and measured by a microdensitometer. The crystal was rotated around [010] and 1113 independent reflexions out of 1358 possible were observed in layers $h0l$, $h1l$, . . ., $h6l$.

The intensities were corrected as usual; absorption corrections were applied as for cylindrical specimens ($\mu\bar{R} = 0·49$). Atomic form factors according to Cromer & Mann (1968) have been used.

The structure, solved by Patterson and Fourier methods, has been refined by differential syntheses using anisotropic thermal parameters. The hydrogen atoms have been identified in the difference synthesis ($R = 10·7$% without hydrogen contributions and $R = 10·3$% with hydrogen contributions). All the calculations have been performed on the computer, Olivetti Elea 6001/S of Centro di Calcolo Elettronico, of the University of Parma.

The results of the structure determination are summarized in Tables 1 to 4.

Discussion

The structure consists of chains parallel to [001] (Fig. 1) formed by a sequence of cations and anions. The main interatomic distances and angles in a chain are quoted in Table 5. The anions $NH_2–NH–COO^-$ not only surround the cations Ca^{2+} in a cage but also share oxygen atoms between two calcium ions and form bridges. The calcium ions alternate along the chain at distances

3·70 and 3·87 Å from one another; these distances are shorter than those found in $CaCl_2$.glycylglycylglycine.$3H_2O$ (Van der Helm & Willoughby, 1969).

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

	x	*y*	*z*
Ca	1193 (1)	0512 (2)	1933 (1)
O(1.1)	1280 (6)	0802 (7)	5765 (6)
C(2.1)	2532 (7)	1420 (9)	6201 (5)
N(3.1)	3729 (7)	2174 (9)	4537 (8)
N(4.1)	3775 (8)	2046 (8)	2299 (7)
O(5.1)	2758 (6)	1424 (7)	8095 (6)
O(1.2)	−1223 (6)	1859 (7)	0264 (5)
C(2.2)	−1890 (7)	3455 (13)	0317 (11)
N(3.2)	−1748 (8)	4360 (10)	1950 (8)
N(4.2)	−0555 (9)	3561 (9)	3235 (7)
O(5.2)	−2638 (7)	4321 (9)	−1090 (8)
O(6)	3674 (6)	−1816 (8)	2506 (7)
H(7.1)	4874	2521	4518
H(8.1)	3649	3157	1539
H(9.1)	4899	1188	1583
H(7.2)	−2406	5500	2218
H(8.2)	−1167	3650	4657
H(9.2)	0633	4311	2933
H(10)	3000	−2583	2013
H(11)	4892	−1682	2093

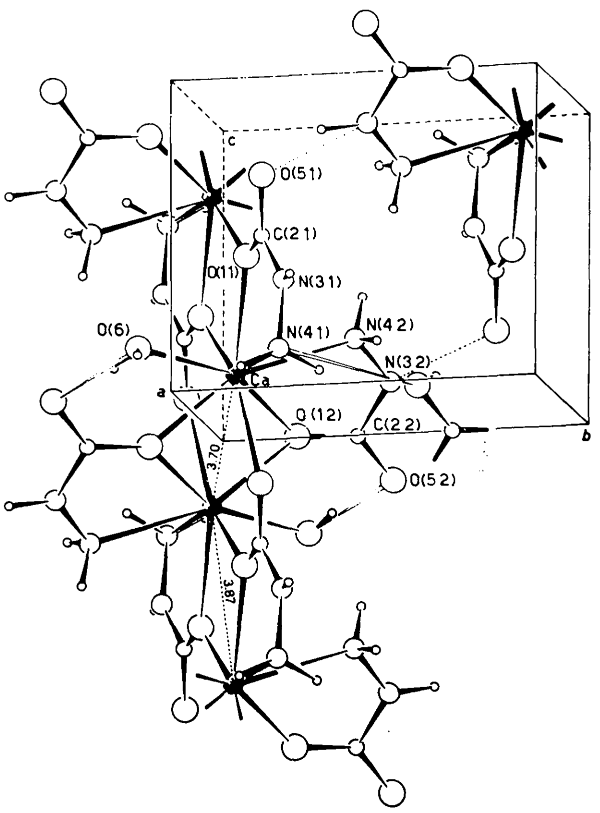


Fig. 1. Clinographic projection of the structure of calcium hydrazinecarboxylate monohydrate, with Ca···Ca distances along chains parallel to [001].

The polyhedron of donor atoms around calcium (Fig. 2) is not related to any polyhedra observed in compounds of the same acid with 3*d*-metals. It can be roughly described as a pentagonal bipyramid with a centred face and is analogous to that observed in $CaCl_2$.glycylglycylglycine.$3H_2O$. The resulting coordination number is 8, formed by six O atoms and two N atoms. One O belongs to the water molecule which therefore enters the coordination sphere of the cation. The two bond distances between calcium and nitrogen, crystallographically independent, are equal (Ca–N = 2·59 Å), but the bonds between calcium and oxygen range from 2·37 to 2·50 Å with an average value of 2·44 Å. Apparently the calcium–oxygen bonds, both in length and arrangement, are a result of a balance between the electrostatic attraction of the cations to the anions and steric constrictions.

Table 2. *Thermal parameters* (Å^2)

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ca	1·882	1·498	0·691	−0·199	−0·675	0·140
O(1.1)	2·623	2·173	1·477	−0·766	−0·901	0·048
C(2.1)	2·324	1·484	1·333	−0·014	−0·817	0·046
N(3.1)	3·041	2·547	1·478	−1·020	−0·801	0·448
N(4.1)	2·582	2·364	1·435	−0·374	−0·568	0·248
O(5.1)	3·156	3·247	1·421	−0·884	−1·082	0·013
O(1.2)	2·629	1·825	2·155	0·284	−1·402	−0·158
C(2.2)	2·931	1·841	2·327	−0·348	−1·191	0·470
N(3.2)	5·515	3·169	3·229	0·261	−2·452	−0·521
N(4.2)	3·546	2·176	2·317	−0·152	−1·458	0·039
O(5.2)	5·898	1·979	4·167	−0·380	−3·669	0·804
O(6)	2·697	2·933	2·964	0·068	−1·248	−0·568

In the last cycle for all the atoms the average shift $|\Delta B_{ij}|_{\rm av}$, and the maximum shift $|\Delta B_{ij}|_{\rm max}$, were $|\Delta B_{ij}|_{\rm av}=0·037$, $|\Delta B_{ij}|_{\rm max}=0·183$.

	B		*B*
H(7.1)	2·50	H(8.2)	2·70
H(8.1)	2·10	H(9.2)	2·70
H(9.1)	2·20	H(10)	3·10
H(7.2)	3·50	H(11)	3·20

Table 3. *Observed and calculated structure factors*

Columus are h, k, l, $10F_o$ and $10F_c$. – after F_o indicates an unobserved reflexion.

1	0	0	319	321
2	0	0	316	-326
3	0	0	133	-145
4	0	0	371	-374
5	0	0	151	-154
6	0	0	65	-57
7	0	0	60	48
8	0	0	164	163
9	0	0	37	30
0	0	1	180	199
1	0	1	36	28
$\bar{1}$	0	1	225	241
2	0	1	38	4
$\bar{2}$	0	1	278	-284
3	0	1	476	-496
$\bar{3}$	0	1	152	155
4	0	1	37	-34
$\bar{4}$	0	1	29-	2
5	0	1	133	133
$\bar{5}$	0	1	212	-218
6	0	1	53	41
$\bar{6}$	0	1	37-	-30
7	0	1	163	167
$\bar{7}$	0	1	78	-66
8	0	1	64	61
$\bar{8}$	0	1	59	-40
9	0	1	28	-16
0	0	2	275	-328
1	0	2	190	-218
$\bar{1}$	0	2	181	198
2	0	2	242	-240
$\bar{2}$	0	2	192	206
3	0	2	238	-237
$\bar{3}$	0	2	54	50
4	0	2	27-	-1
$\bar{4}$	0	2	126	137
5	0	2	43	35
$\bar{5}$	0	2	62	42
6	0	2	151	145
$\bar{6}$	0	2	53	-49
7	0	2	118	104
$\bar{7}$	0	2	83	-79
8	0	2	58	-47
$\bar{8}$	0	2	69	-61
9	0	2	69	-61
0	0	3	253	-289
1	0	3	197	208
$\bar{1}$	0	3	132	-148
2	0	3	274	291
$\bar{2}$	0	3	68	-67
3	0	3	316	334
$\bar{3}$	0	3	110	-114
4	0	3	126	130
$\bar{4}$	0	3	119	126
5	0	3	74	-64
$\bar{5}$	0	3	153	162
6	0	3	50	-46
$\bar{6}$	0	3	60	53
7	0	3	169	-169
$\bar{7}$	0	3	50	17
8	0	3	148	-139
9	0	3	28-	12
0	0	4	119	117
1	0	4	43	52
$\bar{1}$	0	4	115	-113
2	0	4	169	196
$\bar{2}$	0	4	80	-88
3	0	4	290	303
$\bar{3}$	0	4	172	-178
4	0	4	172	-186
$\bar{4}$	0	4	115	-124
5	0	4	64	-65
$\bar{5}$	0	4	99	89
6	0	4	42	38
$\bar{6}$	0	4	50	49
7	0	4	126	-129
8	0	4	39	-30
9	0	4	42	42
0	0	5	277	299
1	0	5	121	128
$\bar{1}$	0	5	135	136
2	0	5	130	140
$\bar{2}$	0	5	200	-201
3	0	5	172	-193
$\bar{3}$	0	5	107	-108
4	0	5	242	-268
$\bar{4}$	0	5	95	-90
5	0	5	139	-161
$\bar{5}$	0	5	69	-61
6	0	5	134	-142
7	0	5	96	97
8	0	5	130	121
9	0	5	15-	60
0	0	6	66	55
1	0	6	134	144
$\bar{1}$	0	6	82	71
2	0	6	86	-97
$\bar{2}$	0	6	99	93
3	0	6	225	-250
$\bar{3}$	0	6	98	57
4	0	6	55	-48
$\bar{4}$	0	6	21-	7
5	0	6	36-	1
6	0	6	71	61
7	0	6	98	87
8	0	6	27	34
0	0	7	91	-76
1	0	7	48	-31
$\bar{1}$	0	7	30-	-12
2	0	7	74	-55
$\bar{2}$	0	7	66	76
3	0	7	67	-56
4	0	7	43	29
5	0	7	94	96
6	0	7	115	116
7	0	7	17-	55
1	0	8	16-	-30
2	0	8	20-	21
3	0	8	111	132
4	0	8	18-	113
0	1	0	7-	378
1	1	0	45	13
$\bar{1}$	1	0	182	166
2	1	0	252	267
$\bar{2}$	1	0	136	-146
3	1	0	114	-107
$\bar{3}$	1	0	132	-127
4	1	0	358	-345
$\bar{4}$	1	0	262	-276
5	1	0	209	-190
$\bar{5}$	1	0	171	-186
6	1	0	48-	7
$\bar{6}$	1	0	101	-90
7	1	0	181	164
$\bar{7}$	1	0	49-	-1
8	1	0	150	133
$\bar{8}$	1	0	135	146
9	1	0	48	37
$\bar{9}$	1	0	57	92
0	1	1	151	-181
0	1	$\bar{1}$	53	-52
1	1	1	33	36
$\bar{1}$	1	1	198	-218
1	1	$\bar{1}$	538	629
$\bar{1}$	1	$\bar{1}$	195	-211
2	1	1	237	-226
$\bar{2}$	1	1	137	141
2	1	$\bar{1}$	587	652
$\bar{2}$	1	$\bar{1}$	51	50
3	1	1	202	-203
$\bar{3}$	1	1	303	331
3	1	$\bar{1}$	253	238
$\bar{3}$	1	$\bar{1}$	395	-424
4	1	1	57	47
$\bar{4}$	1	1	88	92
4	1	$\bar{1}$	252	-256
$\bar{4}$	1	$\bar{1}$	120	-134
5	1	1	41-	3
$\bar{5}$	1	1	120	-132
5	1	$\bar{1}$	227	-222
$\bar{5}$	1	$\bar{1}$	151	156
6	1	1	48-	6
$\bar{6}$	1	1	55	-55
6	1	$\bar{1}$	58	-40
$\bar{6}$	1	$\bar{1}$	49	42
7	1	1	75	45
$\bar{7}$	1	1	49-	-10
7	1	$\bar{1}$	82	-69
$\bar{7}$	1	$\bar{1}$	78	73
8	1	1	70	44
$\bar{8}$	1	1	40-	-15
8	1	$\bar{1}$	46-	-14
$\bar{8}$	1	$\bar{1}$	57	53
9	1	1	40-	3
9	1	$\bar{1}$	19-	62
$\bar{9}$	1	$\bar{1}$	33-	-1
0	1	2	195	-220
0	1	$\bar{2}$	123	-125
1	1	2	71	-75
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1	1	$\bar{2}$	269	303
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2	1	2	35	-22
$\bar{2}$	1	2	127	137
2	1	$\bar{2}$	390	415
$\bar{2}$	1	$\bar{2}$	400	-448
3	1	2	70	-52
$\bar{3}$	1	2	244	267
3	1	$\bar{2}$	39-	15
$\bar{3}$	1	$\bar{2}$	311	-311
4	1	2	283	272
$\bar{4}$	1	2	101	114
4	1	$\bar{2}$	64	-54
$\bar{4}$	1	$\bar{2}$	78	74
5	1	2	277	250
$\bar{5}$	1	2	49-	-6
5	1	$\bar{2}$	72	-51
$\bar{5}$	1	$\bar{2}$	196	210
6	1	2	48-	4
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$\bar{6}$	1	2	130	-118
$\bar{6}$	1	$\bar{2}$	207	231
7	1	2	55	-31
$\bar{7}$	1	2	83	-63
7	1	$\bar{2}$	94	-81
$\bar{7}$	1	$\bar{2}$	85	98
8	1	2	95	-71
$\bar{8}$	1	2	60	-88
8	1	$\bar{2}$	36-	-29
$\bar{8}$	1	$\bar{2}$	47-	-4
9	1	2	128	-108
$\bar{9}$	1	2	36-	-24
0	1	3	209	-225
0	1	$\bar{3}$	199	-205
1	1	3	391	423
$\bar{1}$	1	3	392	-426
1	1	$\bar{3}$	215	-247
$\bar{1}$	1	$\bar{3}$	166	-169
2	1	3	176	171
$\bar{2}$	1	3	220	-240
2	1	$\bar{3}$	103	-109
$\bar{2}$	1	$\bar{3}$	35-	8
3	1	3	233	251
$\bar{3}$	1	3	154	-169
3	1	$\bar{3}$	108	107
$\bar{3}$	1	$\bar{3}$	58	41
4	1	3	280	258
$\bar{4}$	1	3	73	76
4	1	$\bar{3}$	126	120
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5	1	3	48	-36
$\bar{5}$	1	3	134	138
5	1	$\bar{3}$	124	114
$\bar{5}$	1	$\bar{3}$	139	146
6	1	3	160	-140
$\bar{6}$	1	3	60	66
6	1	$\bar{3}$	83	76
$\bar{6}$	1	$\bar{3}$	49-	9
7	1	3	145	-138
$\bar{7}$	1	3	55	61
7	1	$\bar{3}$	40-	-17
$\bar{7}$	1	$\bar{3}$	120	-119
8	1	3	76	-52
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9	1	3	42-	35
$\bar{9}$	1	$\bar{3}$	33-	-21
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0	1	$\bar{4}$	81	75
1	1	4	69	73
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1	1	$\bar{4}$	45-	6
$\bar{1}$	1	$\bar{4}$	106	117
2	1	4	246	264
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2	1	$\bar{4}$	90	-88
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3	1	$\bar{4}$	109	-103
$\bar{3}$	1	$\bar{4}$	155	164
4	1	4	199	-192
$\bar{4}$	1	4	88	-83
4	1	$\bar{4}$	50-	23
$\bar{4}$	1	$\bar{4}$	66	58
5	1	4	152	-137
$\bar{5}$	1	4	62	66
5	1	$\bar{4}$	57	38
$\bar{5}$	1	$\bar{4}$	144	-142
6	1	4	148	-131
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6	1	$\bar{4}$	57	43
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8	1	4	46-	25
$\bar{8}$	1	$\bar{4}$	46-	-31
9	1	4	70	65
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0	1	5	190	190
0	1	$\bar{5}$	282	306
1	1	5	85	68
$\bar{1}$	1	5	220	223
1	1	$\bar{5}$	50-	10
$\bar{1}$	1	$\bar{5}$	180	192
2	1	5	141	139
$\bar{2}$	1	5	59	-46
2	1	$\bar{5}$	146	-138
$\bar{2}$	1	$\bar{5}$	50	42
3	1	5	61	25
$\bar{3}$	1	5	93	-88
3	1	$\bar{5}$	112	-106
$\bar{3}$	1	$\bar{5}$	49-	16
4	1	5	166	-169
$\bar{4}$	1	5	70	-61
4	1	$\bar{5}$	142	-134
$\bar{4}$	1	$\bar{5}$	71	-37
5	1	5	292	-292
$\bar{5}$	1	5	74	-82
5	1	$\bar{5}$	74	-62
$\bar{5}$	1	$\bar{5}$	139	-150
6	1	5	112	-103
6	1	$\bar{5}$	188	-206
7	1	5	157	139
7	1	$\bar{5}$	46-	21
8	1	5	124	96
$\bar{8}$	1	$\bar{5}$	150	165
9	1	5	46	48
0	1	6	50-	-4
0	1	$\bar{6}$	67	61
1	1	6	109	-117
$\bar{1}$	1	6	49-	42
1	1	$\bar{6}$	147	149
$\bar{1}$	1	$\bar{6}$	50-	-1
2	1	6	136	-135
$\bar{2}$	1	6	84	65
2	1	$\bar{6}$	127	125
$\bar{2}$	1	$\bar{6}$	169	-175
3	1	6	51-	9
$\bar{3}$	1	6	92	78
3	1	$\bar{6}$	43-	16
$\bar{3}$	1	$\bar{6}$	225	-238
4	1	6	109	92
$\bar{4}$	1	6	26-	30
4	1	$\bar{6}$	72	-81
$\bar{4}$	1	$\bar{6}$	77	-66
5	1	6	49-	23
$\bar{5}$	1	$\bar{6}$	48-	-9
6	1	6	69	45
$\bar{6}$	1	$\bar{6}$	46	44
7	1	6	110	95
$\bar{7}$	1	$\bar{6}$	107	107
8	1	6	57	52
$\bar{8}$	1	$\bar{6}$	17-	80
0	1	7	166	-150
0	1	$\bar{7}$	50	38
1	1	7	131	-122
$\bar{1}$	1	7	40-	-24
1	1	$\bar{7}$	124	112
$\bar{1}$	1	$\bar{7}$	117	-106
2	1	7	127	-112
$\bar{2}$	1	7	83	88
2	1	$\bar{7}$	90	103
$\bar{2}$	1	$\bar{7}$	133	-131
3	1	7	46-	-14
$\bar{3}$	1	$\bar{7}$	97	-82
4	1	7	126	112
$\bar{4}$	1	$\bar{7}$	77	-49
5	1	7	109	97
$\bar{5}$	1	$\bar{7}$	60	61
6	1	7	92	88
$\bar{6}$	1	$\bar{7}$	102	118
7	1	7	28-	14
1	1	8	23-	-14
2	1	8	67	77
$\bar{2}$	1	$\bar{8}$	21-	16
3	1	8	161	181
$\bar{3}$	1	$\bar{8}$	21-	63
4	1	8	77	93
5	1	8	17-	-41
0	2	0	6-	-14
1	2	0	217	-221
$\bar{1}$	2	0	849	929
2	2	0	347	-349
$\bar{2}$	2	0	218	222
3	2	0	256	-256
$\bar{3}$	2	0	263	-266
4	2	0	57	-53
$\bar{4}$	2	0	42	6
5	2	0	196	-188
$\bar{5}$	2	0	104	-107
6	2	0	73	64
$\bar{6}$	2	0	72	-90
7	2	0	149	158
$\bar{7}$	2	0	37	24
8	2	0	32-	8
$\bar{8}$	2	0	41	43
9	2	0	24-	39
0	2	1	207	273
0	2	$\bar{1}$	73	-71
1	2	1	119	-135
$\bar{1}$	2	1	66	-61
1	2	$\bar{1}$	56	-56
$\bar{1}$	2	$\bar{1}$	88	-93
2	2	1	417	-403
$\bar{2}$	2	1	120	143
2	2	$\bar{1}$	395	419
$\bar{2}$	2	$\bar{1}$	344	-325
3	2	1	389	338
$\bar{3}$	2	1	66	59
3	2	$\bar{1}$	117	118
$\bar{3}$	2	$\bar{1}$	190	-192
4	2	1	127	116
$\bar{4}$	2	1	125	125
4	2	$\bar{1}$	42	-27
$\bar{4}$	2	$\bar{1}$	197	-199
5	2	1	29-	-6
$\bar{5}$	2	1	56	77
5	2	$\bar{1}$	42	-35
$\bar{5}$	2	$\bar{1}$	80	-67
6	2	1	153	141
$\bar{6}$	2	1	109	-123
6	2	$\bar{1}$	147	-160
$\bar{6}$	2	$\bar{1}$	108	127
7	2	1	33-	-15
$\bar{7}$	2	1	61	-68
7	2	$\bar{1}$	42	-62
$\bar{7}$	2	$\bar{1}$	88	105
8	2	1	33-	-14
$\bar{8}$	2	1	23-	-33
8	2	$\bar{1}$	[illegible]	46
$\bar{8}$	2	$\bar{1}$	62	74
9	2	1	50	-37
9	2	$\bar{1}$	33	76
$\bar{9}$	2	$\bar{1}$	14-	16
0	2	2	377	-433
0	2	$\bar{2}$	112	110
1	2	2	462	-524
$\bar{1}$	2	2	280	-292
1	2	$\bar{2}$	217	234
$\bar{1}$	2	$\bar{2}$	293	-305
2	2	2	34	22
$\bar{2}$	2	2	56	-59
2	2	$\bar{2}$	260	291
$\bar{2}$	2	$\bar{2}$	305	-301
3	2	2	290	280
$\bar{3}$	2	2	207	224
3	2	$\bar{2}$	204	232
$\bar{3}$	2	$\bar{2}$	38	-13
4	2	2	263	243
$\bar{4}$	2	2	109	116
4	2	$\bar{2}$	90	95
$\bar{4}$	2	$\bar{2}$	48	-41
5	2	2	329	295
$\bar{5}$	2	2	62	84
5	2	$\bar{2}$	52	-50
$\bar{5}$	2	$\bar{2}$	41	34
6	2	2	90	71
$\bar{6}$	2	2	33-	44
6	2	$\bar{2}$	160	-180
$\bar{6}$	2	$\bar{2}$	125	139
7	2	2	48	-48
$\bar{7}$	2	2	45	-63
7	2	$\bar{2}$	97	-106
$\bar{7}$	2	$\bar{2}$	93	101
8	2	2	98	-94
8	2	$\bar{2}$	26	11
$\bar{8}$	2	2	31-	32
9	2	2	98	-111
$\bar{9}$	2	$\bar{2}$	17-	-59
0	2	3	189	-198
0	2	$\bar{3}$	210	-230
1	2	3	26	17
$\bar{1}$	2	3	240	-245
1	2	$\bar{3}$	132	-123
$\bar{1}$	2	$\bar{3}$	481	-556
2	2	3	318	315
$\bar{2}$	2	3	160	-171
2	2	$\bar{3}$	40	-33
$\bar{2}$	2	$\bar{3}$	41	30
3	2	3	250	238
$\bar{3}$	2	3	57	-60
3	2	$\bar{3}$	205	221
$\bar{3}$	2	$\bar{3}$	327	330
4	2	3	100	86
$\bar{4}$	2	3	34-	27
4	2	$\bar{3}$	139	142
$\bar{4}$	2	$\bar{3}$	203	193
5	2	3	59	-51
$\bar{5}$	2	3	109	127
5	2	$\bar{3}$	34	66
$\bar{5}$	2	$\bar{3}$	189	201
6	2	3	245	-229
$\bar{6}$	2	3	117	126
6	2	$\bar{3}$	34	-8
$\bar{6}$	2	$\bar{3}$	72	88
7	2	3	178	-162
$\bar{7}$	2	3	33	50
7	2	$\bar{3}$	77	-92
$\bar{7}$	2	$\bar{3}$	33-	-17
8	2	3	43	-39
$\bar{8}$	2	$\bar{3}$	88	-91
9	2	3	28-	16
$\bar{9}$	2	$\bar{3}$	15-	-113
0	2	4	94	-87
0	2	$\bar{4}$	147	-152
1	2	4	178	173
$\bar{1}$	2	4	52	41
1	2	$\bar{4}$	46	46
$\bar{1}$	2	$\bar{4}$	84	-96
2	2	4	309	284
$\bar{2}$	2	4	33-	-21
2	2	$\bar{4}$	153	-163
$\bar{2}$	2	$\bar{4}$	41	40
3	2	4	37	-29
$\bar{3}$	2	4	67	-65
3	2	$\bar{4}$	50	-62
$\bar{3}$	2	$\bar{4}$	53	37
4	2	4	77	59
$\bar{4}$	2	4	56	-66
4	2	$\bar{4}$	102	109
$\bar{4}$	2	$\bar{4}$	148	140
5	2	4	49	21
$\bar{5}$	2	4	43	-30
5	2	$\bar{4}$	42	13
$\bar{5}$	2	$\bar{4}$	68	-74
6	2	4	172	-159
$\bar{6}$	2	4	46	65
6	2	$\bar{4}$	52	63
$\bar{6}$	2	$\bar{4}$	79	-73
7	2	4	163	-146
$\bar{7}$	2	$\bar{4}$	53	41
8	2	4	55	-48
$\bar{8}$	2	$\bar{4}$	63	-74
9	2	4	85	101
0	2	5	99	93
0	2	$\bar{5}$	92	97
1	2	5	58	56
$\bar{1}$	2	5	170	170
1	2	$\bar{5}$	111	-98
$\bar{1}$	2	$\bar{5}$	291	319
2	2	5	143	-132
$\bar{2}$	2	5	124	129
2	2	$\bar{5}$	35-	-8
$\bar{2}$	2	$\bar{5}$	83	83
3	2	5	134	-127
$\bar{3}$	2	5	122	-122
3	2	$\bar{5}$	89	-97
$\bar{3}$	2	$\bar{5}$	51	25
4	2	5	147	-143
$\bar{4}$	2	5	103	-112
4	2	$\bar{5}$	63	-67
$\bar{4}$	2	$\bar{5}$	101	-110
5	2	5	68	-41
$\bar{5}$	2	5	47	-55
5	2	$\bar{5}$	24-	2
$\bar{5}$	2	$\bar{5}$	163	-177
6	2	5	194	172
$\bar{6}$	2	$\bar{5}$	42	-75
7	2	5	64	59
$\bar{7}$	2	$\bar{5}$	64	-70
8	2	5	47	51
$\bar{8}$	2	$\bar{5}$	19-	40
9	2	5	70	94
0	2	6	53	37
0	2	$\bar{6}$	76	69
1	2	6	213	-191
$\bar{1}$	2	6	41	41
1	2	$\bar{6}$	111	109
$\bar{1}$	2	$\bar{6}$	42	25
2	2	6	226	-210
$\bar{2}$	2	6	36	42
2	2	$\bar{6}$	134	128
$\bar{2}$	2	$\bar{6}$	34-	29
3	2	6	74	-74
$\bar{3}$	2	6	97	94
3	2	$\bar{6}$	34	10
$\bar{3}$	2	$\bar{6}$	125	-125
4	2	6	103	26
$\bar{4}$	2	6	7-	54
4	2	$\bar{6}$	80	-126
$\bar{4}$	2	$\bar{6}$	221	-216
5	2	6	162	142
$\bar{5}$	2	$\bar{6}$	31-	3
6	2	6	95	80
$\bar{6}$	2	$\bar{6}$	112	106
7	2	6	46	41
$\bar{7}$	2	$\bar{6}$	82	93
8	2	6	23-	22
0	2	7	89	-84
0	2	$\bar{7}$	50	-8
1	2	7	99	-83
$\bar{1}$	2	7	57	-50
1	2	$\bar{7}$	82	83
$\bar{1}$	2	$\bar{7}$	137	-124
2	2	7	111	-92
$\bar{2}$	2	7	15-	37
2	2	$\bar{7}$	14-	95
$\bar{2}$	2	$\bar{7}$	113	-106
3	2	7	32-	1
$\bar{3}$	2	$\bar{7}$	109	-101
4	2	7	189	163
$\bar{4}$	2	$\bar{7}$	91	-77
5	2	7	182	153
$\bar{5}$	2	$\bar{7}$	59	54
6	2	7	68	52
$\bar{6}$	2	$\bar{7}$	14-	95
7	2	7	19-	-14
1	2	8	12-	0
2	2	8	78	98
3	2	8	127	137
4	2	8	113	128
5	2	8	11-	21
0	3	0	184	-219
1	3	0	157	224
$\bar{1}$	3	0	347	361
2	3	0	135	-165
$\bar{2}$	3	0	479	452
3	3	0	330	-337
$\bar{3}$	3	0	20-	1
4	3	0	90	-86
$\bar{4}$	3	0	23-	21
5	3	0	54	36
$\bar{5}$	3	0	142	-112
6	3	0	230	224
$\bar{6}$	3	0	168	-146
7	3	0	118	111
$\bar{7}$	3	0	90	-71
8	3	0	34	-21
$\bar{8}$	3	0	60	-54
9	3	0	16-	10
0	3	1	119	-116
0	3	$\bar{1}$	70	90
1	3	1	237	-332
$\bar{1}$	3	1	230	-217
1	3	$\bar{1}$	180	277
$\bar{1}$	3	$\bar{1}$	13-	22
2	3	1	328	-375
$\bar{2}$	3	1	82	55
2	3	$\bar{1}$	254	301
$\bar{2}$	3	$\bar{1}$	199	-191
3	3	1	142	141
$\bar{3}$	3	1	164	142
3	3	$\bar{1}$	304	-335
$\bar{3}$	3	$\bar{1}$	20-	41
4	3	1	133	124
$\bar{4}$	3	1	161	142
4	3	$\bar{1}$	159	-168
$\bar{4}$	3	$\bar{1}$	126	-102
5	3	1	168	163
$\bar{5}$	3	1	80	75
5	3	$\bar{1}$	36	18
$\bar{5}$	3	$\bar{1}$	55	-53
6	3	1	164	163
$\bar{6}$	3	1	142	-129
6	3	1	123	-127
$\bar{6}$	3	$\bar{1}$	193	160
7	3	1	43	33
$\bar{7}$	3	1	104	-89
7	3	$\bar{1}$	25-	-27
$\bar{7}$	3	$\bar{1}$	38	32
8	3	1	25-	-7
$\bar{8}$	3	1	10-	-29
8	3	$\bar{1}$	50	47
$\bar{8}$	3	$\bar{1}$	19-	14
9	3	1	68	-63
0	3	2	115	-151
0	3	$\bar{2}$	122	149
1	3	2	280	-350
$\bar{1}$	3	2	262	-289
1	3	$\bar{2}$	73	87
$\bar{1}$	3	$\bar{2}$	221	-250
2	3	2	285	-306
$\bar{2}$	3	2	20-	-22
2	3	$\bar{2}$	49	55
$\bar{2}$	3	$\bar{2}$	190	-188
3	3	2	171	170
$\bar{3}$	3	2	264	258
3	3	$\bar{2}$	93	98
$\bar{3}$	3	$\bar{2}$	226	-223
4	3	2	314	300
$\bar{4}$	3	2	193	184
4	3	$\bar{2}$	24-	9
$\bar{4}$	3	$\bar{2}$	212	-192
5	3	2	229	219
$\bar{5}$	3	2	124	112
5	3	$\bar{2}$	26-	-17
$\bar{5}$	3	$\bar{2}$	162	135
6	3	2	25-	11
$\bar{6}$	3	2	24	25
6	3	$\bar{2}$	65	-63
$\bar{6}$	3	$\bar{2}$	192	160
7	3	2	118	-116
$\bar{7}$	3	2	39	-36
7	3	$\bar{2}$	71	-65
$\bar{7}$	3	$\bar{2}$	61	52
8	3	2	136	-128
8	3	$\bar{2}$	16-	8
$\bar{8}$	3	$\bar{2}$	49	38
9	3	2	110	-103
0	3	3	237	246
0	3	$\bar{3}$	221	-246
1	3	3	55	59
$\bar{1}$	3	3	21-	-24
1	3	$\bar{3}$	135	-154
$\bar{1}$	3	$\bar{3}$	189	-218
2	3	3	158	185
$\bar{2}$	3	3	242	-255
2	3	$\bar{3}$	64	57
$\bar{2}$	3	$\bar{3}$	21-	-24
3	3	3	71	76
$\bar{3}$	3	3	48	-40
3	3	$\bar{3}$	211	238
$\bar{3}$	3	$\bar{3}$	23-	46
4	3	3	79	76
$\bar{4}$	3	3	26-	-14
4	3	$\bar{3}$	184	207
$\bar{4}$	3	$\bar{3}$	135	145
5	3	3	24-	-1
$\bar{5}$	3	3	45	38
5	3	$\bar{3}$	88	103

Table 3 (*cont.*)

$\bar{5}$	3	$\bar{3}$	206	206
6	3	3	185	-184
$\bar{6}$	3	3	131	103
6	3	$\bar{3}$	24-	-14
$\bar{6}$	3	$\bar{3}$	86	79
7	3	3	57	-44
7	3	$\bar{3}$	105	-94
$\bar{7}$	3	$\bar{3}$	24-	-34
8	3	3	25-	-12
$\bar{8}$	3	$\bar{3}$	121	-122
9	3	3	67	-56
0	3	4	38	5
0	3	$\bar{4}$	104	-106
1	3	4	273	263
$\bar{1}$	3	4	25-	33
1	3	$\bar{4}$	163	-173
$\bar{1}$	3	$\bar{4}$	74	55
2	3	4	22-	42
$\bar{2}$	3	4	119	-111
2	3	$\bar{4}$	171	-180
$\bar{2}$	3	$\bar{4}$	102	113
3	3	4	160	-181
$\bar{3}$	3	4	137	-127
3	3	$\bar{4}$	35	43
$\bar{3}$	3	$\bar{4}$	50	49
4	3	4	62	60
$\bar{4}$	3	4	25-	-4
4	3	$\bar{4}$	77	82
$\bar{4}$	3	$\bar{4}$	234	247
5	3	4	89	-97
$\bar{5}$	3	4	83	-63
5	3	$\bar{4}$	34	38
$\bar{5}$	3	$\bar{4}$	92	116
6	3	4	48	-57
$\bar{6}$	3	4	8-	5
6	3	$\bar{4}$	80	68
$\bar{6}$	3	$\bar{4}$	105	-100
7	3	4	76	72
$\bar{7}$	3	$\bar{4}$	55	-57
8	3	4	24-	27
$\bar{8}$	3	$\bar{4}$	15-	-66
9	3	4	69	76
0	3	5	76	68
0	3	$\bar{5}$	98	-84
1	3	5	26-	17
$\bar{1}$	3	5	122	107
1	3	$\bar{5}$	178	-167
$\bar{1}$	3	$\bar{5}$	234	242
2	3	5	171	-167
$\bar{2}$	3	5	238	203
2	3	$\bar{5}$	82	-73
$\bar{2}$	3	$\bar{5}$	66	68
3	3	5	156	-178
$\bar{3}$	3	5	24-	-4
3	3	$\bar{5}$	119	-111
$\bar{3}$	3	$\bar{5}$	26-	14
4	3	5	250	-297
$\bar{4}$	3	5	93	-69
4	3	$\bar{5}$	23-	-18
$\bar{4}$	3	$\bar{5}$	26-	58
5	3	5	66	-75
5	3	$\bar{5}$	16-	36
$\bar{5}$	3	$\bar{5}$	25-	-65
6	3	5	205	240
$\bar{6}$	3	$\bar{5}$	94	-91
7	3	5	97	117
$\bar{7}$	3	$\bar{5}$	138	-123
8	3	5	65	70
9	3	5	14-	32
0	3	6	25-	-30
0	3	$\bar{6}$	183	174
1	3	6	197	-184
$\bar{1}$	3	6	70	59
1	3	$\bar{6}$	136	122
$\bar{1}$	3	$\bar{6}$	25-	24
2	3	6	61	-58
$\bar{2}$	3	6	94	75
2	3	$\bar{6}$	84	63
$\bar{2}$	3	$\bar{6}$	53	-56
3	3	6	65	48
$\bar{3}$	3	6	103	93
3	3	$\bar{6}$	54	-42
$\bar{3}$	3	$\bar{6}$	25-	-81
4	3	6	26-	-28
$\bar{4}$	3	$\bar{6}$	185	-175
5	3	6	72	73
$\bar{5}$	3	$\bar{6}$	23-	-48
6	3	6	116	134
$\bar{6}$	3	$\bar{6}$	18-	33
7	3	6	74	72
8	3	6	29	-31
0	3	7	112	-98
0	3	$\bar{7}$	76	70
1	3	7	170	-142
$\bar{1}$	3	7	73	-73
1	3	$\bar{7}$	13-	91
$\bar{1}$	3	$\bar{7}$	51	-37
2	3	7	44	-31
$\bar{2}$	3	7	102	-104
3	3	7	66	67
$\bar{3}$	3	$\bar{7}$	94	-98
4	3	7	123	120
$\bar{4}$	3	$\bar{7}$	16-	-29
5	3	7	182	167
$\bar{5}$	3	$\bar{7}$	11-	41
6	3	7	85	73
7	3	7	13-	-19
2	3	8	9-	105
3	3	8	11-	28
4	3	8	10-	40
0	4	0	131	-141
1	4	0	280	-354
$\bar{1}$	4	0	207	191
2	4	0	239	-274
$\bar{2}$	4	0	421	394
3	4	0	168	-176
$\bar{3}$	4	0	173	158
4	4	0	157	-141
$\bar{4}$	4	0	115	-97
5	4	0	169	166
$\bar{5}$	4	0	132	-123
6	4	0	229	223
$\bar{6}$	4	0	145	-134
7	4	0	88	87
$\bar{7}$	4	0	75	-86
8	4	0	58	57
9	4	0	15-	-18
0	4	1	191	-237
0	4	$\bar{1}$	185	236
1	4	1	284	-334
$\bar{1}$	4	1	261	275
1	4	$\bar{1}$	179	222
$\bar{1}$	4	$\bar{1}$	146	141
2	4	1	38	-35
$\bar{2}$	4	1	173	147
2	4	$\bar{1}$	18-	14
$\bar{2}$	4	$\bar{1}$	20-	-11
3	4	1	104	-97
$\bar{3}$	4	1	87	82
3	4	$\bar{1}$	65	-74
$\bar{3}$	4	$\bar{1}$	23-	-4
4	4	1	63	-66
$\bar{4}$	4	1	131	123
4	4	$\bar{1}$	59	-58
$\bar{4}$	4	$\bar{1}$	90	-74
5	4	1	91	79
$\bar{5}$	4	1	73	62
5	4	$\bar{1}$	132	-131
$\bar{5}$	4	$\bar{1}$	202	-173
6	4	1	113	99
$\bar{6}$	4	1	45	-42
6	4	$\bar{1}$	50	-64
$\bar{6}$	4	$\bar{1}$	92	-91
7	4	1	96	85
$\bar{7}$	4	1	78	-83
7	4	$\bar{1}$	59	61
$\bar{7}$	4	$\bar{1}$	26-	20
8	4	1	58	-57
8	4	$\bar{1}$	93	92
$\bar{8}$	4	$\bar{1}$	13-	65
9	4	1	73	-79
0	4	2	157	-197
0	4	$\bar{2}$	158	192
1	4	2	30	-30
$\bar{1}$	4	2	192	-203
1	4	$\bar{2}$	72	86
$\bar{1}$	4	$\bar{2}$	45	-55
2	4	2	111	109
$\bar{2}$	4	2	24-	-1
2	4	$\bar{2}$	22-	21
$\bar{2}$	4	$\bar{2}$	116	-98
3	4	2	265	261
$\bar{3}$	4	2	58	55
3	4	$\bar{2}$	61	66
$\bar{3}$	4	$\bar{2}$	24-	-22
4	4	2	146	141
$\bar{4}$	4	2	124	124
4	4	$\bar{2}$	53	-69
$\bar{4}$	4	$\bar{2}$	27-	27
5	4	2	47	51
$\bar{5}$	4	2	92	90
5	4	$\bar{2}$	142	-158
$\bar{5}$	4	$\bar{2}$	28-	26
6	4	2	70	56
$\bar{6}$	4	2	25-	-2
6	4	$\bar{2}$	62	-68
$\bar{6}$	4	$\bar{2}$	28-	2
7	4	2	114	-99
$\bar{7}$	4	2	11-	-17
7	4	$\bar{2}$	25-	4
$\bar{7}$	4	$\bar{2}$	26-	50
8	4	2	143	-125
8	4	$\bar{2}$	14-	16
$\bar{8}$	4	$\bar{2}$	14-	68
9	4	2	45	-44
0	4	3	24	33
0	4	$\bar{3}$	196	-207
1	4	3	107	118
$\bar{1}$	4	3	59	-68
1	4	$\bar{3}$	25-	-8
$\bar{1}$	4	$\bar{3}$	245	-280
2	4	3	207	234
$\bar{2}$	4	3	121	-134
2	4	$\bar{3}$	89	99
$\bar{2}$	4	$\bar{3}$	267	-280
3	4	3	36	30
$\bar{3}$	4	3	72	-80
3	4	$\bar{3}$	111	113
$\bar{3}$	4	$\bar{3}$	27-	32
4	4	3	135	-121
$\bar{4}$	4	3	77	-81
4	4	$\bar{3}$	138	146
$\bar{4}$	4	$\bar{3}$	265	251
5	4	3	134	-126
$\bar{5}$	4	3	52	-29
5	4	$\bar{3}$	28	24
$\bar{5}$	4	$\bar{3}$	104	101
6	4	3	89	-81
$\bar{6}$	4	3	61	62
6	4	$\bar{3}$	46	-42
$\bar{6}$	4	$\bar{3}$	27-	47
7	4	3	48	26
7	4	$\bar{3}$	45	-43
$\bar{7}$	4	$\bar{3}$	24-	26
8	4	3	67	57
$\bar{8}$	4	$\bar{3}$	10-	-59
9	4	3	40	44
0	4		117	111
0	4	$\bar{4}$	28-	-9
1	4	4	189	178
$\bar{1}$	4	4	42	23
1	4	$\bar{4}$	182	-171
$\bar{1}$	4	$\bar{4}$	27-	-33
2	4	4	47	-37
$\bar{2}$	4	4	40	36
2	4	$\bar{4}$	55	-61
$\bar{2}$	4	$\bar{4}$	28-	4
3	4	4	102	-112
$\bar{3}$	4	4	28-	-32
3	4	$\bar{4}$	50	42
$\bar{3}$	4	$\bar{4}$	144	164
4	4	4	72	-76
$\bar{4}$	4	4	63	-54
4	4	$\bar{4}$	27-	33
$\bar{4}$	4	$\bar{4}$	124	124
5	4	4	168	-174
$\bar{5}$	4	4	80	-72
5	4	$\bar{4}$	137	117
$\bar{5}$	4	$\bar{4}$	27-	52
6	4	4	135	-136
6	4	$\bar{4}$	65	66
$\bar{6}$	4	$\bar{4}$	26-	-73
7	4	4	28-	12
$\bar{7}$	4	$\bar{4}$	116	-130
8	4	4	151	141
9	4	4	89	97
0	4	5	85	82
0	4	$\bar{5}$	113	-98
1	4	5	28-	-9
$\bar{1}$	4	5	156	143
1	4	$\bar{5}$	61	-61
$\bar{1}$	4	$\bar{5}$	63	64
2	4	5	147	-141
$\bar{2}$	4	5	216	193
2	4	$\bar{5}$	143	-137
$\bar{2}$	4	$\bar{5}$	283	286
3	4	5	232	-246
$\bar{3}$	4	5	106	92
3	4	$\bar{5}$	103	-100
$\bar{3}$	4	$\bar{5}$	161	168
4	4	5	87	-92
$\bar{4}$	4	5	88	-79
4	4	$\bar{5}$	33	-23
$\bar{4}$	4	$\bar{5}$	27-	34
5	4	5	114	119
5	4	$\bar{5}$	10-	45
$\bar{5}$	4	$\bar{5}$	26-	-41
6	4	5	68	80
$\bar{6}$	4	$\bar{5}$	86	-95
7	4	5	68	86
$\bar{7}$	4	$\bar{5}$	11-	-102
8	4	5	109	105
9	4	5	11-	7
0	4	6	99	-85
0	4	$\bar{6}$	91	83
1	4	6	138	-122
$\bar{1}$	4	6	25-	30
1	4	$\bar{6}$	128	98
$\bar{1}$	4	$\bar{6}$	49	32
2	4	6	104	-94
$\bar{2}$	4	6	70	79
2	4	$\bar{6}$	21-	-11
$\bar{2}$	4	$\bar{6}$	26-	22
3	4	6	28-	-7
$\bar{3}$	4	6	9-	32
3	4	$\bar{6}$	126	-123
$\bar{3}$	4	$\bar{6}$	26-	7
4	4	6	27-	56
$\bar{4}$	4	$\bar{6}$	134	-115
5	4	6	82	79
$\bar{5}$	4	$\bar{6}$	135	-134
6	4	6	118	117
$\bar{6}$	4	$\bar{6}$	7-	-19
7	4	6	67	59
8	4	6	19	-21
0	4	7	63	-60
0	4	$\bar{7}$	11-	50
1	4	7	126	-104
$\bar{1}$	4	7	9-	-59
$\bar{1}$	4	$\bar{7}$	15-	-9
2	4	7	24-	-13
$\bar{2}$	4	$\bar{7}$	72	-74
3	4	7	89	82
$\bar{3}$	4	$\bar{7}$	13-	-95
4	4	7	84	83
5	4	7	63	60
6	4	7	22	-17
7	4	7	8-	-51
0	5	0	157	160
1	5	0	119	-167
$\bar{1}$	5	0	42	31
2	5	0	200	-250
$\bar{2}$	5	0	218	203
3	5	0	233	-254
$\bar{3}$	5	0	336	324
4	5	0	88	-95
$\bar{4}$	5	0	50	-53
5	5	0	214	213
$\bar{5}$	5	0	94	-88
6	5	0	49	55
$\bar{6}$	5	0	53	-48
7	5	0	24-	17
$\bar{7}$	5	0	54	-72
8	5	0	62	67
0	5	1	126	-141
0	5	$\bar{1}$	273	293
1	5	1	44	-74
$\bar{1}$	5	1	108	115
1	5	$\bar{1}$	165	223
$\bar{1}$	5	$\bar{1}$	77	55
2	5	1	55	57
$\bar{2}$	5	1	23	20
2	5	$\bar{1}$	238	-262
$\bar{2}$	5	$\bar{1}$	97	98
3	5	1	54	-46
$\bar{3}$	5	1	64	54
3	5	$\bar{1}$	115	-134
$\bar{3}$	5	$\bar{1}$	146	-134
4	5	1	143	137
$\bar{4}$	5	1	70	67
4	5	$\bar{1}$	84	-96
$\bar{4}$	5	$\bar{1}$	209	-189
5	5	1	99	95
$\bar{5}$	5	1	24	-11
5	5	$\bar{1}$	116	-132
$\bar{5}$	5	$\bar{1}$	126	-116
6	5	1	25-	8
$\bar{6}$	5	1	21	9
6	5	$\bar{1}$	39	20
$\bar{6}$	5	$\bar{1}$	72	-76
7	5	1	45	41
7	5	$\bar{1}$	54	64
$\bar{7}$	5	$\bar{1}$	61	70
8	5	1	59	-56
8	5	$\bar{1}$	94	113
9	5	1	34	-46
0	5	2	131	-145
0	5	$\bar{2}$	71	77
1	5	2	58	-66
$\bar{1}$	5	2	115	-122
1	5	$\bar{2}$	132	146
$\bar{1}$	5	$\bar{2}$	188	181
2	5	2	41	43
$\bar{2}$	5	2	131	-141
2	5	$\bar{2}$	65	83
$\bar{2}$	5	$\bar{2}$	74	54
3	5	2	262	249
$\bar{3}$	5	2	90	-93
3	5	$\bar{2}$	23-	-18
$\bar{3}$	5	$\bar{2}$	180	-160
4	5	2	235	223
$\bar{4}$	5	2	73	75
4	5	$\bar{2}$	24-	-35
$\bar{4}$	5	$\bar{2}$	194	-179
5	5	2	46	-35
$\bar{5}$	5	2	63	68
5	5	$\bar{2}$	85	-97
$\bar{5}$	5	$\bar{2}$	143	-129
6	5	2	93	-89
$\bar{6}$	5	2	31	40
6	5	$\bar{2}$	37	-14
$\bar{6}$	5	$\bar{2}$	31	26
7	5	2	109	-102
7	5	$\bar{2}$	19-	15
$\bar{7}$	5	$\bar{2}$	90	98
8	5	2	77	-72
9	5	2	18	21
0	5	3	170	170
0	5	$\bar{3}$	159	-159
1	5	3	124	127
$\bar{1}$	5	3	98	97
1	5	$\bar{3}$	23-	6
$\bar{1}$	5	$\bar{3}$	53	-53
2	5	3	34	-21
$\bar{2}$	5	3	28	-18
2	5	$\bar{3}$	168	166
$\bar{2}$	5	$\bar{3}$	64	-61
3	5	3	64	47
$\bar{3}$	5	3	150	-164
3	5	$\bar{3}$	106	114
$\bar{3}$	5	$\bar{3}$	25-	-24
4	5	3	118	-110
$\bar{4}$	5	3	96	-94
4	5	$\bar{3}$	64	73
$\bar{4}$	5	$\bar{3}$	48	63
5	5	3	246	-236
$\bar{5}$	5	3	19-	-4
5	5	$\bar{3}$	32	-41
$\bar{5}$	5	$\bar{3}$	51	53
6	5	3	61	-56
6	5	$\bar{3}$	90	-94
$\bar{6}$	5	$\bar{3}$	114	105
7	5	3	31	-32
$\bar{7}$	5	$\bar{3}$	50	68
8	5	3	23-	0
9	5	3	69	88
0	5	4	339	324
0	5	$\bar{4}$	163	-163
1	5	4	61	54
$\bar{1}$	5	4	133	121
1	5	$\bar{4}$	249	-245
$\bar{1}$	5	$\bar{4}$	25-	8
2	5	4	37	-24
$\bar{2}$	5	4	42	-18
2	5	$\bar{4}$	30	29
$\bar{2}$	5	$\bar{4}$	59	45
3	5	4	32	20
$\bar{3}$	5	4	90	-78
3	5	$\bar{4}$	38	39
$\bar{3}$	5	$\bar{4}$	116	109
4	5	4	181	-183
$\bar{4}$	5	4	129	-124
4	5	$\bar{4}$	32	26
$\bar{4}$	5	$\bar{4}$	24-	25
5	5	4	116	-119
5	5	$\bar{4}$	104	97
$\bar{5}$	5	$\bar{4}$	70	67
6	5	4	25-	-32
$\bar{6}$	5	$\bar{4}$	19	-17
7	5	4	30	35
8	5	4	125	125
9	5	4	12-	30
0	5	5	30	27
0	5	$\bar{5}$	62	-54
1	5	5	69	-54
$\bar{1}$	5	5	122	110
1	5	$\bar{5}$	94	-83
$\bar{1}$	5	$\bar{5}$	35	-17
2	5	5	108	-101
$\bar{2}$	5	5	45	43
2	5	$\bar{5}$	138	-116
$\bar{2}$	5	$\bar{5}$	261	238
3	5	5	280	-257
$\bar{3}$	5	5	71	68
3	5	$\bar{5}$	20-	-6
$\bar{3}$	5	$\bar{5}$	144	128
4	5	5	35	-31
4	5	$\bar{5}$	14-	0
$\bar{4}$	5	$\bar{5}$	23-	-16
5	5	5	132	143
$\bar{5}$	5	$\bar{5}$	19-	-9
6	5	5	70	79
$\bar{6}$	5	$\bar{5}$	11-	-136
7	5	5	144	138
8	5	5	51	55
0	5	6	144	-123
0	5	$\bar{6}$	121	114
1	5	6	26	-29
$\bar{1}$	5	6	22	-16
1	5	$\bar{6}$	67	60
$\bar{1}$	5	$\bar{6}$	186	169
2	5	6	23-	-10
$\bar{2}$	5	6	55	59
2	5	$\bar{6}$	86	-86
$\bar{2}$	5	$\bar{6}$	94	79
3	5	6	30	-29
$\bar{3}$	5	$\bar{6}$	18-	-22
4	5	6	33	13
$\bar{4}$	5	$\bar{6}$	15-	-24
5	5	6	26	37
6	5	6	88	76
7	5	6	23	-22
0	5	7	7-	-67
1	5	7	15-	-8
2	5	7	73	69
3	5	7	155	134
4	5	7	123	105
5	5	7	39	31
6	5	7	41	-41
0	6	0	25	-7
1	6	0	93	-122
$\bar{1}$	6	0	19-	29
2	6	0	54	-69
$\bar{2}$	6	0	79	67
3	6	0	68	-63
$\bar{3}$	6	0	146	152
4	6	0	65	71
$\bar{4}$	6	0	26-	19
5	6	0	163	164
$\bar{5}$	6	0	41	-48
6	6	0	52	51
$\bar{6}$	6	0	35	-53
7	6	0	38	37
8	6	0	18-	-8
0	6	1	151	-178
0	6	$\bar{1}$	274	262
1	6	1	25	-39
$\bar{1}$	6	1	76	-93
1	6	$\bar{1}$	53	49
$\bar{1}$	6	$\bar{1}$	190	181
2	6	1	46	48
$\bar{2}$	6	1	24-	4
2	6	$\bar{1}$	93	-118
$\bar{2}$	6	$\bar{1}$	116	87
3	6	1	45	-39
$\bar{3}$	6	1	26-	-1
3	6	$\bar{1}$	42	-51
$\bar{3}$	6	$\bar{1}$	117	-95
4	6	1	47	40
$\bar{4}$	6	1	26-	9
4	6	$\bar{1}$	183	-199
$\bar{4}$	6	$\bar{1}$	67	-77
5	6	1	139	124
$\bar{5}$	6	1	47	57
5	6	$\bar{1}$	134	-143
$\bar{5}$	6	$\bar{1}$	27	-14
6	6	1	88	75
$\bar{6}$	6	1	40	69
6	6	$\bar{1}$	48	46
$\bar{6}$	6	$\bar{1}$	60	-81
7	6	1	48	-42
7	6	$\bar{1}$	82	78
8	6	1	60	-63
8	6	$\bar{1}$	7-	74
0	6	2	51	-70
0	6	$\bar{2}$	103	93
1	6	2	131	158
$\bar{1}$	6	2	85	-105
1	6	$\bar{2}$	154	124
$\bar{1}$	6	$\bar{2}$	143	121
2	6	2	210	240
$\bar{2}$	6	2	136	-172
2	6	$\bar{2}$	58	55
$\bar{2}$	6	$\bar{2}$	136	-116
3	6	2	48	57
$\bar{3}$	6	2	93	-109
3	6	$\bar{2}$	56	-64
$\bar{3}$	6	$\bar{2}$	220	-211
4	6	2	29	21
$\bar{4}$	6	2	50	62
4	6	$\bar{2}$	102	-103
$\bar{4}$	6	$\bar{2}$	77	-67
5	6	2	46	-39
$\bar{5}$	6	2	72	106
5	6	$\bar{2}$	102	-100
$\bar{5}$	6	$\bar{2}$	30	-40
6	6	2	145	-136
6	6	$\bar{2}$	24-	-10
$\bar{6}$	6	$\bar{2}$	20-	19
7	6	2	137	-126
7	6	$\bar{2}$	29	26
8	6	2	69	-73
9	6	2	7-	13
0	6	3	120	136
0	6	$\bar{3}$	125	108
1	6	3	282	297
$\bar{1}$	6	3	43	-43
1	6	$\bar{3}$	149	122
$\bar{1}$	6	$\bar{3}$	61	-62
2	6	3	96	100
$\bar{2}$	6	3	40	-42
2	6	$\bar{3}$	171	138
$\bar{2}$	6	$\bar{3}$	290	-265
3	6	3	23-	-12
$\bar{3}$	6	3	99	-126
3	6	$\bar{3}$	126	116
$\bar{3}$	6	$\bar{3}$	190	-185
4	6	3	135	-125
$\bar{4}$	6	3	62	-73
4	6	$\bar{3}$	26-	20
$\bar{4}$	6	$\bar{3}$	26-	-11
5	6	3	137	-129
$\bar{5}$	6	3	8-	-7
5	6	$\bar{3}$	49	-41
$\bar{5}$	6	$\bar{3}$	68	83
6	6	3	21-	1
6	6	$\bar{3}$	75	-74
$\bar{6}$	6	$\bar{3}$	63	88
7	6	3	39	-32
8	6	3	22-	20
0	6	4	148	156
0	6	$\bar{4}$	89	-69
1	6	4	34	29
$\bar{1}$	6	4	30	29
1	6	$\bar{4}$	74	-53
$\bar{1}$	6	$\bar{4}$	26-	0
2	6	4	38	26
$\bar{2}$	6	4	48	-43
2	6	$\bar{4}$	26-	-10
$\bar{2}$	6	$\bar{4}$	26-	-3
3	6	4	34	-29
$\bar{3}$	6	4	22-	-22
3	6	$\bar{4}$	25-	-1
$\bar{3}$	6	$\bar{4}$	25-	29
4	6	4	160	-176
$\bar{4}$	6	4	11-	-76
4	6	$\bar{4}$	94	81
$\bar{4}$	6	$\bar{4}$	84	63
5	6	4	79	-93
5	6	$\bar{4}$	49	56
$\bar{5}$	6	$\bar{4}$	60	72
6	6	4	26-	-15
7	6	4	92	96
8	6	4	104	123
0	6	5	25-	-12
0	6	$\bar{5}$	31	-16
1	6	5	89	-84
$\bar{1}$	6	5	50	43
1	6	$\bar{5}$	125	-100
$\bar{1}$	6	$\bar{5}$	87	-58
2	6	5	150	-148
$\bar{2}$	6	5	40	43
2	6	$\bar{5}$	138	-115
$\bar{2}$	6	$\bar{5}$	98	65
3	6	5	121	-106
3	6	$\bar{5}$	53	-44
$\bar{3}$	6	$\bar{5}$	170	159
4	6	5	85	82
$\bar{4}$	6	$\bar{5}$	18-	23
5	6	5	54	58
6	6	5	25-	14
7	6	5	83	77
8	6	5	20	14
0	6	6	78	-86
0	6	$\bar{6}$	11-	116
1	6	6	23-	-9
$\bar{1}$	6	6	38	-57
$\bar{1}$	6	$\bar{6}$	137	129
2	6	6	24	17
$\bar{2}$	6	$\bar{6}$	11-	84
3	6	6	39	33
4	6	6	100	99
5	6	6	94	84
6	6	6	20-	9
7	6	6	40	-39
2	6	2	10-	77
3	6	7	124	133
4	6	7	85	88

Formally the pentatomic chelate rings are maintained but, strictly speaking, each anion cannot be said either to chelate one Ca^{2+} or bridge two Ca^{2+}.

There are in the structure two independent anions (Fig. 3). The distances and angles in them are compared (Table 6) with distances and angles of a model ring taken from the compounds of transition metals. The main difference, occurring in the model ring, concerns the carboxylate group where C(2)–O(1) and C(2)–O(5) are equal for the calcium compound and different for the transition metal compounds. This clearly indicates the ionic character of the bond between carboxylate and calcium.

Altogether the structures of the two independent anions do not differ from one another although their chemical functions are not exactly the same. In fact, in the ring 1, the atoms O(1.1), O(5.1) and N(4.1) are all involved in bonds with Ca while in the ring 2, only atoms O(1.2) and N(4.2) are bound to Ca and O(5.1) forms one strong hydrogen bond (2.59 Å) with the water molecule of an adjacent polyhedron of the same chain. Even with respect to the planarity of the pentatomic ring or of part of the anion, the two independent molecules behave analogously. The analysis of the planarity (Table 7) shows how atoms O(1.1), C(2.1), N(3.1), O(5.1) lie in the same plane and atoms O(1.2), C(2.2), N(3.2), O(5.2) nearly so. These groups of atoms constitute a rigid body in each molecule. Atoms Ca and N(4.1) and, even more, atoms Ca and N(4.2) are significantly out of the plane of the rigid portion of the molecule. Here the calcium and nitrogen atoms are on the same side of each respective ring. Situations like these have been found for other compounds of hydrazinecarboxylic acid and α-amino acids (Freeman, 1967) as well cases where N(4) and the metal atom are on opposite sides of the rigid portion. It can be deduced that in these ligands the bonds Me–O(1) and N(3)–N(4) (or C′–N in α-amino acids) can be slightly, but significantly, distorted.

The distances involving hydrogen atoms are reasonable (Table 8). The positions of the hydrogen atoms are in accordance with an approximate sp^2 configuration of atoms N(3.1) and N(3.2) and a sp^3 configuration of atoms N(4.1) and N(4.2). The structure of the water molecule O(6) is not clearly defined because it forms two strong hydrogen bonds $O(6)\cdots O(5.2^{i}) = 2{\cdot}59$ and $O(6)\cdots(5.2^{v}) = 2{\cdot}72$ Å with angle 125·8° between them. The hydrogen atoms have been found along the O···O directions or nearby. It is not possible, therefore, to establish the class of this water molecule, according to Chidambaram, Sequeira & Sikka (1964). The two hydrogen bonds of the water molecule join groups of the

Table 4. *Atomic peak heights* (e.$Å^{-3}$), *curvatures* (e.$Å^{-5}$) *and e.s.d.'s*

		ϱ	$-A_{hh}$	$-A_{kk}$	$-A_{ll}$	A_{hk}	A_{hl}	A_{kl}
Ca	obs.	50·0	537	350	633	−68	−184	−36
	calc.	50·8	537	352	625	−69	−182	−37
O(1.1)	obs.	13·9	129	88	145	−18	−48	−11
	calc.	14·0	129	89	144	−17	−47	−11
C(2.1)	obs.	10·8	112	74	147	−13	−43	−7
	calc.	11·1	113	74	147	−13	−43	−7
N(3.1)	obs.	10·7	101	68	104	−14	−37	−8
	calc.	11·0	101	69	104	−13	−37	−7
N(4.1)	obs.	11·6	110	74	124	−17	−24	−6
	calc	11·7	111	74	122	−19	−23	−7
O(5.1)	obs.	13·4	129	85	142	−19	−44	−8
	calc.	13·7	131	87	139	−18	−43	−7
O(1.2)	obs.	13·8	124	87	145	−9	−46	−13
	calc.	13·9	124	86	146	−9	−45	−12
C(2.2)	obs.	9·4	95	58	89	1	−24	4
	calc.	9·5	95	59	89	1	−23	4
N(3.2)	obs.	9·3	81	60	92	−7	−38	−9
	calc.	9·6	83	59	91	−8	−37	−8
N(4.2)	obs.	10·6	91	67	112	−17	−33	−9
	calc.	10·8	92	67	111	−18	−32	−9
O(5.2)	obs.	11·3	93	73	107	−12	−48	−1
	calc.	11·6	94	72	107	−13	−46	−2
O(6)	obs.	12·5	114	78	123	−12	−36	−10
	calc.	12·8	112	78	124	−12	−35	−10
e.s.d.		0·2	3	2	4	2	2	2

		ϱ			ϱ
H(7.1)	obs.	1·1	H(8.2)	obs.	1·1
	calc.	1·3		calc.	1·1
H(8.1)	obs.	1·4	H(9.2)	obs.	1·1
	calc.	1·2		calc.	1·1
H(9.1)	obs.	0·8	H(10)	obs.	0·8
	calc.	0·8		calc.	1·0
H(7.2)	obs.	0·3	H(11)	obs.	1·0
	calc.	0·6		calc.	1·2

same chain. The connexions between chains are given by a weak hydrogen bond N(4·1)···O(5.2^{vi}) = 2.91 Å. Other contacts are quoted in Table 9; among these is the bond N(3.2^{vii})···O(5.1) = 3·25 Å. Although the hydrogen atom lies along the line, the bond cannot be considered to be a hydrogen bond because the

Table 5. *Main bond distances and angles* (*)

Ca——O(1.1)	2·497 (8) Å	O(1.1) —Ca——N(4.1)	64·1 (1)°
Ca—N(4.1)	2·588 (14)	Ca ——O(1.1)-C(2.1)	123·1 (3)
O(1.1)-C(2.1)	1·266 (9)	O(1.1) —C(2.1)-N(3.1)	118·3 (4)
C(2.1)-N(3.1)	1·352 (8)	C(2.1)—N(3.1)-N(4.1)	121·1 (6)
N(3.1)-N(4.1)	1·430 (8)	N(3.1) —N(4.1)-Ca	112·6 (4)
C(2.1)-O(5.1)	1·269 (7)	O(1.1)—C(2.1)-O(5.1)	125·7 (5)
N(4.1)-O(1.1)	2·700 (10)	O(5.1)—C(2.1)-N(3.1)	115·9 (5)
Ca——O(1.2)	2·416 (13)	O(1.2)—Ca——N(4.2)	63·7 (2)
Ca——N(4.2)	2·592 (13)	Ca——O(1.2)-C(2.2)	123·6 (4)
O(1.2)-C(2·2)	1·258 (13)	O(1.2)—C(2.2)-N(3.2)	118·2 (6)
C(2.2)-N(3.2)	1·361 (11)	C(2.2)—N(3.2)-N(4.2)	118·5 (7)
N(3.2)-N(4.2)	1·417 (11)	N(3.2) —N(4.2)-Ca	112·4 (4)
C(2.2)-O(5.2)	1·272 (10)	O(1.2)—C(2.2)-O(5.2)	125·2 (7)
N(4.2)-O(1.2)	2·646 (11)	O(5.2)—C(2.2)-N(3.2)	116·6 (9)
Ca——O(6)	2·449 (13)	O(1.1)—Ca——O(6)	75·0 (2)
Ca——O(1.2^{i})	2·437 (11)	O(6)——Ca——O(1.2^{i})	74·0 (2)
Ca——O(1.1^{ii})	2·373 (9)	O(1.2;)—Ca——O(1.2)	80·6 (2)
Ca——O(5.1^{iii})	2·486 (9)	N(4.2) —Ca——O(1.1)	70·7 (2)
		O(1.1^{ii}) -Ca——O(5.1^{iii})	145·4 (1)
		O(1.1^{ii}) -Ca——O(1.1)	74·7 (1)
		O(1.1^{ii}) -Ca——O(6)	95·8 (2)
		O(1.1^{ii}) -Ca——O(1.2^{i})	78·3 (2)
		O(1.1^{ii}) -Ca——O(1.2)	80·8 (2)
		O(1.1^{ii}) -Ca——N(4.2)	91·0 (2)
		O(5.1^{iii})-Ca——O(1.1)	139·6 (2)
		O(5.1^{iii})-Ca——O(6)	97·9 (2)
		O(5.1^{iii})-Ca——O(1.2^{i})	75·3 (2)
		O(5.1^{iii})-Ca——O(1.2)	73·2 (1)
		O(5.1^{iii})-Ca——N(4.2)	97·4 (2)

* Asymmetric units

i	$-x$	$-y$	$-z$
ii	$-x$	$-y$	$1-z$
iii	x	y	$-1+z$
iv	$1-x$	$-y$	$-z$
v	$1-x$	$-y$	$1-z$
vi	$-x$	$1-y$	$-z$
vii	$-x$	$1-y$	$1-z$

Table 6. *Comparison of distances and angles in compounds of hydrazinecarboxylic acid*

Distance	Octahedral* complexes mean $\bar{d}$	S_b/σ^2	$\chi^2_{95\%}$	$Ca(N'H_2-NH.COO)_2.H_2O$ mean $\bar{d}$	t†
O(1)-C(2)	1·293 (6) Å	17·60	18·48	1·268 (5)	3·2
O(5)-C(2)	1·224 (6)	16·62			5·6
C(2)-N(3)	1·381 (7)	17·16		1·355 (6)	2·8
N(3)-N(4)	1·422 (7)	10·05		1·425 (6)	0·3
Angles	$\bar{\alpha}$			$\bar{\alpha}$	
O(1)-C(2)-N(3)	116·74 (45)	17·65	18·48	18·27 (30) Å	2·6
C(2)-N(3)-N(4)	119·14 (42)	18·66		20·00 (50)	1·3
O(1)-C(2)-O(5)	124·11 (50)	20·59		25·53 (40)	2·2
O(5)-C(2)-N(3)	118·97 (49)	20·37		16·06 (40)	4·5

* Weighted means have been calculated following Hamilton (1964) p. 115. The weighted mean was accepted if $\frac{Sb}{\sigma^2} \le \chi^{-}_{1\%}$.

Values are taken from Ferrari, Braibanti, Bigliardi & Lanfredi (1965), Braibanti, Manotti Lanfredi & Tiripicchio (1967), Braibanti, Tiripicchio, Manotti Lanfredi & Camellini (1967), Braibanti, Tiripicchio, Manotti Lanfredi & Bigoli (1968), Braibanti, Manotti Lanfredi, Tiripicchio & Bigoli (1969), Braibanti, Manotti Lanfredi, Tiripicchio & Bigoli (1970).

† $t = \frac{\Delta \bar{d}}{(\sigma_1^2 + \sigma_2^2)^{1/2}}$.

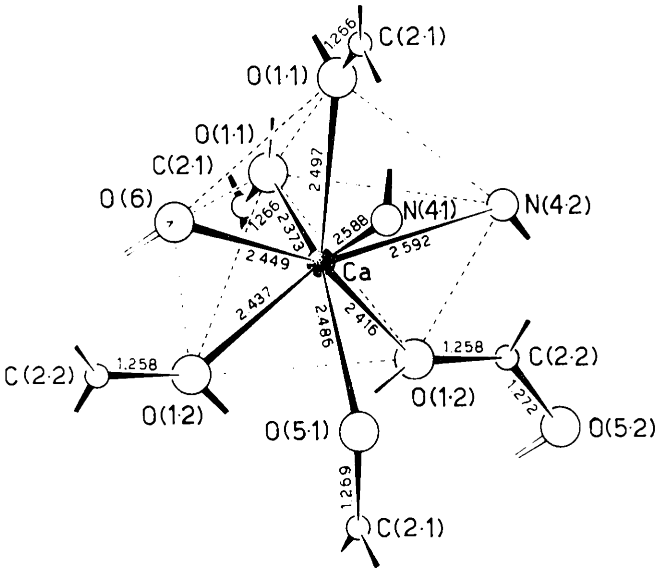

Fig. 2. Coordination polyhedron around Ca^{2+}.

N···O distance is well beyond the accepted values for distances in bonds of this kind (Wallwork, 1962).

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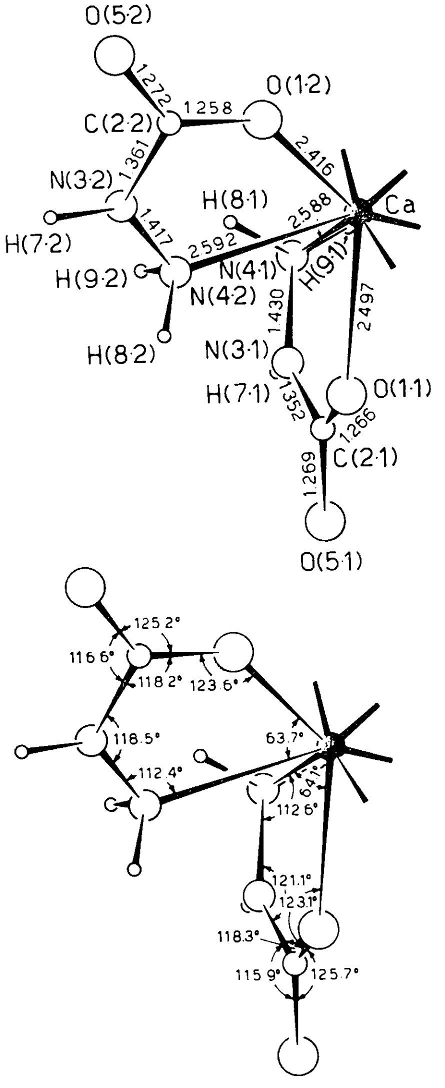

Fig. 3. Chelate rings, 1 and 2.

Table 7. *Analysis of the planarity of the chelate molecules*

(*A*) Ring 1

Plane $-3\cdot2671x+6\cdot2069y+0\cdot4153z=0\cdot3177$

	in				out	
Atoms	O(1.1)	C(2.1)	N(3.1)	O(5.1)	N(4.1)	Ca
Δ . 10^4 (Å)	+13	+60	+18	+13	−1856	−3094
σ . 10^4 (Å)	48	60	60	48	56	
$\sum(\Delta/\sigma)^2$		1·24				

(*A*) The hypothesis of the planarity of atoms 'in' can be accepted with confidence.

(*B*) Ring 2

Plane $-6\cdot2075x-2\cdot5552y+1\cdot8489z=0\cdot3355$

	in				out	
Atoms	O(1.2)	C(2.2)	N(3.2)	O(5.2)	N(4.2)	Ca
Δ . 10^4 (Å)	+25	+135	+40	−36	−3028	−8495
σ . 10^4 (Å)	42	58	58	51	62	
$\sum(\Delta/\sigma)^2$		6·75				

(*B*) The hypothesis of the planarity of atoms 'in' can be accepted with caution: deviation Δ of C(2.2) is possibly significant, but the deviations Δ of atoms 'out' are much greater and highly significant.

Angle between planes (*A*) and (*B*): 73·64°.

Table 8. *Bond distances and angles involving hydrogen atoms*

Interatomic bonds			
N(3.1)-H(7.1)	0·966 Å	H(7.1)—N(3.1)-C(2.1)	129·1°
N(4.1)-H(8.1)	0·955	H(7.1)—N(3.1)-N(4.1)	107·0
N(4.1)-H(9.1)	1·005	H(8.1)—N(4.1)-H(9.1)	115·1
		H(8.1)—N(4.1)-N(3.1)	112·3
		H(9.1)—N(4.1)-N(3.1)	108·9
		H(8.1)—N(4.1)-Ca	107·3
		H(9.1)—N(4.1)-Ca	99·9
N(3.2)-H(7.2)	0·943	H(7.2)—N(3.2)-C(2.2)	121·4
N(4.2)-H(8.2)	0·892	H(7.2)—N(3.2)-N(4.2)	120·1
N(4.2)-H(9.2)	1·139	H(8.2)—N(4.2)-H(9.2)	105·9
		H(8.2)—N(4.2)-N(3.2)	109·3
		H(9.2)—N(4.2)-N(3.2)	109·1
		H(8.2)—N(4.2)-Ca	117·5
		H(9.2)—N(4.2)-Ca	101·9
O(6)—H(10)	0·993	H(10)—O(6)—H(11)	132·7
O(6)—H(11)	0·917		
Hydrogen bonds			
O(6)—O(5.2$^{\mathrm{i}}$)	2·594 (15) Å	O(5.2$^{\mathrm{i}}$)-O(6)—O(5.1$^{\mathrm{v}}$)	125·8 (3)°
O(6)—O(5.1$^{\mathrm{v}}$)	2·723 (18)	O(5.2$^{\mathrm{i}}$)-H(10)-O(6)	158·6
N(4.1)-O(5.2$^{\mathrm{vi}}$)	2·909 (17)	O(5.2$^{\mathrm{ii}}$)-O(6)—H(10)	13·4
		O(5.1$^{\mathrm{v}}$)-H(11)-O(6)	167·7
		O(5.1$^{\mathrm{v}}$)-O(6)—H(11)	8·2
		H(10)—O(6)—Ca	84·6
		O(5.2$^{\mathrm{i}}$)-O(6)—Ca	97·4 (2)
		H(11)—O(6)—Ca	122·2
		O(5.1$^{\mathrm{v}}$)-O(6)—Ca	124·7 (3)
		N(4.1)—H(8.1)-O(5.2$^{\mathrm{vi}}$)	157·2
		H(8.1)—N(4.1)-O(5.2$^{\mathrm{vi}}$)	15·5

Asymmetric units: see Table 5.

Table 9. *Shortest intermolecular contacts*

N(4.1)-O(6)	3·039 (20) Å	N(4.1)-O(6$^{\mathrm{iv}}$)	3·112 (11) Å
N(4.1)-O(5.1$^{\mathrm{iii}}$)	3·110 (11)	N(3.1)-O(6$^{\mathrm{v}}$)	3·078 (16)
N(4.2)-O(1.1)	2·947 (13)	O(5.1)-O(1.2$^{\mathrm{ii}}$)	3·007 (16)
O(1.2)-O(5.1$^{\mathrm{iii}}$)	2·924 (17)	O(1.1)-O(1.2$^{\mathrm{ii}}$)	3·105 (11)
O(1.2)-O(6$^{\mathrm{i}}$)	2·939 (14)	O(1.2)-O(1.1$^{\mathrm{iii}}$)	3·037 (10)
O(1.1)-O(6)	3·012 (11)	O(5.1)-N(3.2$^{\mathrm{vii}}$)	3·250 (21)

Asymmetric units: see Table 5.

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