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Structures of Chelates of Hydrazinecarboxylic Acid: Bis(hydrazinecarboxylato-*N'*,*O*)-zinc

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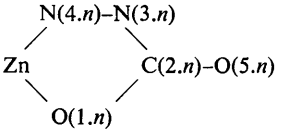
Crystals of bis(hydrazinecarboxylato-*N'*,*O*)-zinc, $Zn(N'H_2\text{–}NH\text{–}COO)_2$, are monoclinic, space group *Pc*, with unit cell constants: $a=6{\cdot}87$ (1), $b=5{\cdot}08$ (1), $c=9{\cdot}10$ (1) Å, $\beta=111{\cdot}2$ (1)°, $V=296{\cdot}5$ Å^3, $Z=2$. The structure has been determined by three-dimensional data (final $R=7{\cdot}9\%$). Both crystallographically independent hydrazinecarboxylato anions form, with the metal, pentatomic chelate rings



The complex around Zn is a square pyramid. The four basal corners are occupied by O(1·1), O(1·2), N(4·1), N(4·2), the apical position by O(5·2), belonging to an adjacent complex; the zinc atom is displaced 0·46 Å from the basal plane, toward the apex. The complexes form, *via* a bridging anion, chains parallel to [100]. Metal to oxygen bonds, $Zn\text{-}O_{av}=2{\cdot}04\pm0{\cdot}02$ Å, are only slightly shorter than those in the octahedral hexaquocation $Zn(OH_2)_6^{2+}$. The distances and angles in the chelate rings are practically equal to those found in octahedral complexes of the same ligand. Following a general rule for this ligand and for α-aminoacids, one part of the molecule including N(3), C(2), O(5), O(1) lies in the same plane or nearly so while N(4) is displaced from this plane.

Introduction

Several crystal structures of compounds of hydrazinecarboxylic acid with divalent metals have been determined in this Laboratory: 3*d* metals, and sometimes magnesium, form complex chelates of octahedral types, with different geometries, whereas calcium forms compounds with coordination numbers 7 and 8. The type of coordination in compounds of this acid are of interest in connexion with the possible geometries of compounds of α-aminoacids (Freeman, 1967).

Experimental

Preparation

Crystals of the compound can be obtained from solutions of $(N_2H_5)Zn(N'H_2\text{–}NH\text{–}COO)_3.H_2O$ after a long time. The crystals are plates or needles and are often twinned.

Crystal data

Compound: bis(hydrazinecarboxylato-*N'*,*O*)-zinc, $Zn(N'H_2\text{–}NH\text{–}COO)_2$, F.W.215·48;
Crystal class: monoclinic, domatic
Unit cell (radiation Cu Kα, $\bar{\lambda}=1{\cdot}5418$ Å)
$a=6{\cdot}87$ (1), $b=5{\cdot}08$ (1), $c=9{\cdot}10$ (1) Å
$\beta=111{\cdot}2$ (1)°
$V=296{\cdot}5$ Å^3; $Z=2$; $D_m=2{\cdot}38$, $D_x=2{\cdot}41$ g.cm^{-3}
μ(Cu Kα)$=57{\cdot}57$ cm^{-1}
Space group: *Pc*($C_s^{(2)}$, No. 7) from systematic absences and from structure determination (alternative space group *P*2/*c*).

Intensity data

Independent reflexions (665 out of 677 possible reflexions) of layers *h*0*l*, . . . ,*h*4*l* and *hk*0, . . . ,*hk*8 were recorded on integrated Weissenberg photographs and then measured with a microdensitometer.

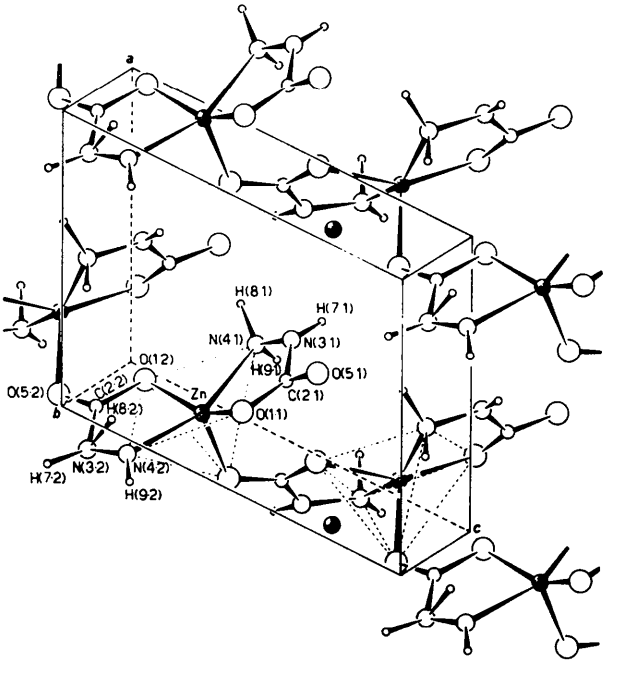


Fig. 1. Clinographic projection of the structure. The complexes around Zn at 0,1–*y*,¾ and at 1,1–*y*,¾ have been omitted.

Calculations

The usual corrections were applied to the intensities; no absorption correction was applied ($\mu\bar{R}_{[010]}=0{\cdot}34$ and $\mu\bar{R}_{[001]}=0{\cdot}23$). Atomic form factors according to Cromer & Mann (1968) were used. The structure was solved by Patterson and Fourier methods and refined by differential syntheses with anisotropic thermal parameters, following the procedure outlined in other works (*e.g.* Ferrari, Braibanti, Manotti Lanfredi & Tiripicchio, 1967).

The hydrogen atoms were identified in the difference map. (Final $R=7{\cdot}9\%$, with and without hydrogen atom contributions).

All the calculations were 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 1–7.

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

	x	y	z
Zn	0	2061 (3)	2500
O(1·1)	1416 (19)	4720 (13)	4218 (12)
C(2·1)	2992 (25)	3797 (23)	5338 (15)
N(3·1)	3889 (23)	1542 (21)	5028 (18)
N(4·1)	2764 (21)	0084 (18)	3699 (16)
O(5·1)	4095 (23)	5096 (19)	6521 (16)
O(1·2)	−0302 (18)	0122 (15)	0444 (11)
C(2·2)	−1731 (24)	1092 (21)	−0765 (15)
N(3·2)	−2757 (25)	3283 (27)	−0600 (18)
N(4·2)	−1935 (25)	4670 (20)	0858 (16)
O(5·2)	−2261 (20)	0081 (15)	−2100 (15)
H(7·1)	4750	0433	5725
H(8·1)	3733	−0500	3117
H(9·1)	2167	−1567	4000
H(7·2)	−3667	4133	−1583
H(8·2)	−0750	5667	0600
H(9·2)	−2417	6000	1200

Table 2. *Thermal parameters* (Å^2)

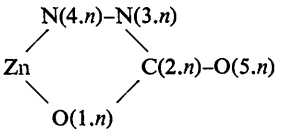
	B_{11} or B	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Zn	2·549	2·080	1·685	0·024	−0·043	0·046
O(1·1)	2·910	1·518	1·271	0·161	−0·666	−0·308
C(2·1)	2·609	2·599	2·850	1·146	−0·366	−1·503
N(3·1)	2·394	0·991	2·421	0·611	−0·807	−0·060
N(4·1)	2·078	1·907	1·394	0·152	−0·433	−0·926
O(5·1)	3·520	3·319	2·174	0·284	−0·374	−0·629
O(1·2)	2·395	1·621	0·807	0·871	−0·231	−0·508
C(2·2)	1·895	1·610	1·269	0·068	0·339	−0·170
N(3·2)	2·267	2·575	2·913	0·090	−1·112	0·288
N(4·2)	3·350	1·948	0·607	0·316	−0·341	0·421
O(5·2)	1·824	2·905	1·937	0·717	0·433	−0·593
H(7·1)	2·000					
H(8·1)	2·100					
H(9·1)	2·800					
H(7·2)	2·200					
H(8·2)	2·800					
H(9·2)	3·000					

Shifts of the last cycle:

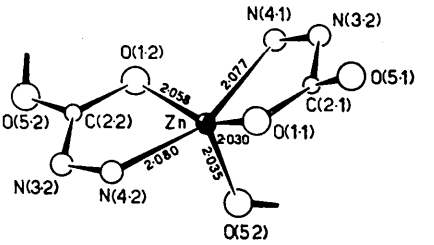
$$|\Delta B_{ij}|_{av}=0{\cdot}034,\ |\Delta B_{ij}|_{max}=0{\cdot}159$$

Discussion

The structure (Fig. 1) consists of square pyramidal complexes containing pentatomic chelate rings



where $n=1,2$ indicates the two groups, NH_2'–NH–COO^-, crystallographically independent. The basal corners of the pyramid are occupied by atoms O(1·1), O(1·2), N(4·1), N(4·2) and the apical position by O(5·2) of a carboxyl group chelating an adjacent metal. The distances in the complex (Fig. 2) around the zinc atom,



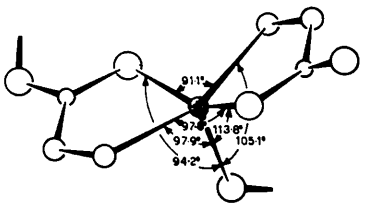
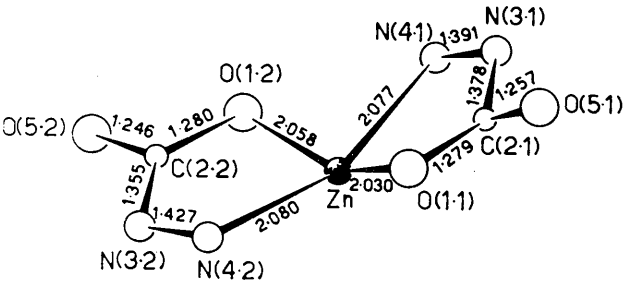


Fig. 2. Pyramidal complex around zinc. (Distances in Å.)



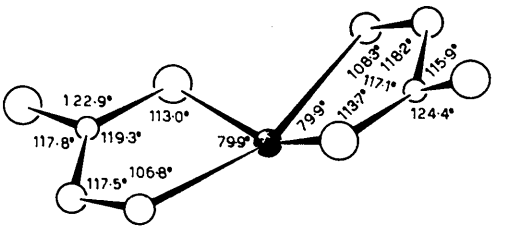


Fig. 3. Chelate rings. (Distances in Å.)

Zn–O(1·1) = 2·03, Zn–O(1·2) = 2·06, Zn–O(5·2) = 2·03 Å are, on the average, only a little shorter than those found in octahedral complexes, such as $Zn(OH_2)_6^{2+}$ (Ferrari, Braibanti, Manotti Lanfredi & Tiripicchio, 1967) where $Zn–OH_{2av}$ = 2·097 Å. The distance Zn–N(4·1) = 2·077 Å is significantly longer than Zn–O(1·1) = 2·030 Å and the distance Zn–N(4·2) = 2·080 Å is probably longer than Zn–O(1·2) = 2·058 Å; they follow the general rule that in chelate rings of hydrazinecarboxylic acid (Braibanti, Manotti Lan-

Table 3. *Observed and calculated structure factors with phase angles*

– after F_o indicates an unobserved reflexion

h	k	l	$10F_o$	$10F_c$	α
0	1	0	138	163	0
0	2	0	144	168	0
0	3	0	201	211	180
0	4	0	208	224	0
0	5	0	178	182	0
0	6	0	110	111	0
0	1	1	396	408	110
0	2	1	152	191	250
0	3	1	182	215	359
0	4	1	263	273	16
0	5	1	86	77	162
0	6	1	109	108	184
0	0	2	135	137	230
0	1	2	302	325	229
0	2	2	314	347	4
0	3	2	208	205	336
0	4	2	167	159	176
0	5	2	177	173	180
0	6	2	39	19	349
0	1	3	475	525	352
0	2	3	220	212	357
0	3	3	238	226	188
0	4	3	149	140	152
0	5	3	40	64	151
0	6	3	128	130	7
0	0	4	319	337	7
0	1	4	334	319	38
0	2	4	421	398	166
0	3	4	191	188	137
0	4	4	61	52	68
0	5	4	221	214	26
0	6	4	20–	14	65
0	1	5	257	252	198
0	2	5	179	157	191
0	3	5	196	173	351
0	4	5	219	212	7
0	5	5	71	73	154
0	0	6	337	367	154
0	1	6	82	83	106
0	2	6	171	162	7
0	3	6	173	162	19
0	4	6	109	96	177
0	5	6	108	94	145
0	1	7	285	257	347
0	2	7	81	73	319
0	3	7	112	116	195
0	4	7	166	152	186
0	5	7	21	23	72
0	0	8	190	179	39
0	1	8	98	87	21
0	2	8	207	199	161
0	3	8	147	133	173
0	4	8	42	47	23
0	1	9	162	163	188
0	2	9	133	132	186
0	3	9	101	93	6
0	0	10	144	157	174
0	1	10	52	43	200
0	2	10	93	97	351
1	0	0	531	570	359
1	1	0	285	261	339
1	2	0	186	228	173
1	3	0	171	192	213
1	4	0	152	168	2
1	5	0	179	179	7
1	6	0	30	17	66
1	1	1	196	220	172
$\bar{1}$	1	1	716	767	169
1	2	1	249	265	156
$\bar{1}$	2	1	188	184	136
1	3	1	293	310	44
$\bar{1}$	3	1	97	117	31
1	4	1	202	200	357
$\bar{1}$	4	1	219	234	3
1	5	1	63	60	212
$\bar{1}$	5	1	54	31	210
1	6	1	145	148	176
$\bar{1}$	6	1	94	87	175
1	0	2	357	349	175
$\bar{1}$	0	2	405	447	203
1	1	2	263	273	129
$\bar{1}$	1	2	128	132	147
1	2	2	539	592	1
$\bar{1}$	2	2	356	377	346
1	3	2	222	222	26
$\bar{1}$	3	2	301	313	19
1	4	2	45	51	1
$\bar{1}$	4	2	105	107	180
1	5	2	183	168	149
$\bar{1}$	5	2	198	190	211
1	6	2	39	19	66
$\bar{1}$	6	2	35	22	203
1	1	3	426	465	23
$\bar{1}$	1	3	279	315	25
1	2	3	197	199	10
$\bar{1}$	2	3	247	261	11
1	3	3	202	178	174
$\bar{1}$	3	3	247	247	170
1	4	3	221	199	191
$\bar{1}$	4	3	163	162	178
$\bar{6}$	2	7	69	60	330
$\bar{6}$	3	7	48	53	194
$\bar{6}$	4	7	53	69	192
$\bar{6}$	0	8	71	52	328
$\bar{6}$	1	8	20–	11	149
$\bar{6}$	2	8	119	118	193
$\bar{6}$	3	8	69	76	174
$\bar{6}$	1	9	118	105	178
$\bar{6}$	2	9	93	75	204
$\bar{6}$	3	9	32	34	355
$\bar{6}$	0	10	81	77	160
$\bar{6}$	1	10	38	32	172
$\bar{6}$	2	10	58	67	19

h	k	l	$10F_o$	$10F_c$	α
1	5	3	48	26	178
$\bar{1}$	5	3	54	43	334
1	6	3	94	107	13
$\bar{1}$	6	3	120	122	350
1	0	4	390	455	1
$\bar{1}$	0	4	357	346	21
1	1	4	48	62	122
$\bar{1}$	1	4	202	222	37
1	2	4	70	48	238
$\bar{1}$	2	4	444	432	156
1	3	4	220	198	186
$\bar{1}$	3	4	163	144	120
1	4	4	272	249	351
$\bar{1}$	4	4	155	146	80
1	5	4	167	163	1
$\bar{1}$	5	4	141	146	18
$\bar{1}$	6	4	49	47	105
1	1	5	328	312	179
$\bar{1}$	1	5	335	341	171
1	2	5	107	91	182
$\bar{1}$	2	5	166	151	169
1	3	5	123	111	10
$\bar{1}$	3	5	161	152	3
1	4	5	196	170	346
$\bar{1}$	4	5	179	169	14
1	5	5	69	72	166
$\bar{1}$	5	5	33–	21	205
1	0	6	478	551	164
$\bar{1}$	0	6	300	315	194
1	1	6	103	92	159
$\bar{1}$	1	6	60	59	19
1	2	6	133	110	32
$\bar{1}$	2	6	196	184	7
1	3	6	141	134	1
$\bar{1}$	3	6	336	316	7
1	4	6	90	92	175
$\bar{1}$	4	6	109	97	146
1	5	6	118	122	214
$\bar{1}$	5	6	93	76	161
1	1	7	189	169	6
$\bar{1}$	1	7	250	250	6
1	2	7	139	133	1
$\bar{1}$	2	7	95	71	0
1	3	7	164	159	178
$\bar{1}$	3	7	107	103	190
1	4	7	136	134	186
$\bar{1}$	4	7	136	139	185
$\bar{1}$	5	7	40	38	4
1	0	8	127	135	52
$\bar{1}$	0	8	182	174	336
1	1	8	207	190	37
$\bar{1}$	1	8	102	97	143
1	2	8	210	212	169
$\bar{1}$	2	8	191	185	183
1	3	8	85	74	122
$\bar{1}$	3	8	161	158	178
1	4	8	28	35	25
$\bar{1}$	4	8	54	43	10
1	1	9	171	174	171
$\bar{1}$	1	9	148	153	183
1	2	9	78	72	173
$\bar{1}$	2	9	120	126	187
1	3	9	69	75	7
$\bar{1}$	3	9	93	92	356
$\bar{1}$	4	9	61	89	348
1	0	10	134	154	180
$\bar{1}$	0	10	125	145	159
1	1	10	29–	32	147
$\bar{1}$	1	10	148	151	178
$\bar{1}$	2	10	149	144	23
$\bar{1}$	3	10	29	27	0
$\bar{1}$	1	11	85	100	354
2	0	0	328	376	290
2	1	0	186	200	314
2	2	0	365	395	197
2	3	0	268	293	175
2	4	0	100	108	5
2	5	0	153	162	354
2	6	0	25	25	260
2	1	1	442	519	188
$\bar{2}$	1	1	396	414	187
2	2	1	195	206	190
$\bar{2}$	2	1	173	174	174
2	3	1	226	220	358
$\bar{2}$	3	1	133	154	12
2	4	1	161	160	359
$\bar{2}$	4	1	177	180	2
2	5	1	48	50	17
$\bar{2}$	5	1	92	80	167
2	6	1	149	150	166
$\bar{2}$	6	1	93	91	161
2	0	2	216	268	141
$\bar{2}$	0	2	696	761	151
2	1	2	132	147	148
$\bar{2}$	1	2	537	573	33
2	2	2	476	515	16
$\bar{2}$	2	2	282	302	16
2	3	2	202	202	31
$\bar{2}$	3	2	366	377	11
2	4	2	106	117	71
7	0	0	206	182	343
7	1	0	40	28	272
7	2	0	102	92	199
7	3	0	65	69	154
7	1	1	119	114	178
$\bar{7}$	1	1	128	115	177
7	2	1	76	68	180
$\bar{7}$	2	1	84	72	156
7	3	1	60	75	354
$\bar{7}$	3	1	40	32	353
7	0	2	80	88	229
$\bar{7}$	0	2	102	97	169
7	1	2	72	63	219

h	k	l	$10F_o$	$10F_c$	α
$\bar{2}$	4	2	82	87	182
2	5	2	130	122	182
$\bar{2}$	5	2	99	85	152
2	6	2	52	47	19
$\bar{2}$	6	2	49	41	111
2	1	3	188	201	351
$\bar{2}$	1	3	356	372	2
2	2	3	161	150	150
$\bar{2}$	2	3	203	215	4
2	3	3	194	186	186
$\bar{2}$	3	3	174	168	163
2	4	3	203	193	177
$\bar{2}$	4	3	264	249	182
2	5	3	81	92	6
$\bar{2}$	5	3	64	39	2
$\bar{2}$	6	3	88	89	359
2	0	4	435	484	359
$\bar{2}$	0	4	280	313	8
2	1	4	93	97	8
$\bar{2}$	1	4	243	248	28
2	2	4	160	130	180
$\bar{2}$	2	4	310	309	196
2	3	4	158	143	165
$\bar{2}$	3	4	279	203	173
2	4	4	154	152	7
$\bar{2}$	4	4	92	84	326
2	5	4	169	158	348
$\bar{2}$	5	4	130	124	3
$\bar{2}$	6	4	21	12	80
2	1	5	399	366	100
$\bar{2}$	1	5	292	304	168
2	2	5	144	138	186
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2	3	5	64	68	352
$\bar{2}$	3	5	207	195	23
2	4	5	151	138	5
$\bar{2}$	4	5	68	50	351
2	5	5	16	7	195
$\bar{2}$	5	5	27	22	135
2	0	6	136	139	185
$\bar{2}$	0	6	227	258	144
2	1	6	162	142	135
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2	2	6	207	198	6
$\bar{2}$	2	6	248	238	18
2	3	6	170	149	31
$\bar{2}$	3	6	95	67	329
2	4	6	72	63	177
$\bar{2}$	4	6	81	81	141
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2	1	7	131	136	11
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$\bar{2}$	2	8	187	185	173
2	3	8	97	102	171
$\bar{2}$	3	8	164	162	193
2	4	8	54	55	43
2	1	9	130	153	177
$\bar{2}$	1	9	152	149	181
2	2	9	54	63	177
$\bar{2}$	2	9	71	42	226
$\bar{2}$	3	9	84	79	346
$\bar{2}$	4	9	65	90	354
$\bar{2}$	0	10	152	164	173
$\bar{2}$	1	10	113	105	159
$\bar{2}$	2	10	76	81	14
$\bar{2}$	3	10	58	62	7
$\bar{2}$	1	11	103	104	353
$\bar{2}$	2	11	67	70	348
3	0	0	382	443	30
3	1	0	218	239	328
3	2	0	293	323	172
3	3	0	122	119	238
3	4	0	84	67	8
3	5	0	214	212	346
3	6	0	37	37	39
3	1	1	334	348	185
$\bar{3}$	1	1	291	331	190
3	2	1	119	123	191
$\bar{3}$	2	1	316	338	191
3	3	1	166	159	345
$\bar{3}$	3	1	174	180	351
3	4	1	120	112	27
$\bar{3}$	4	1	164	182	357
3	5	1	31–	33	146
$\bar{3}$	5	1	56	39	114
3	6	1	105	124	168
$\bar{3}$	6	1	101	104	168
3	0	2	264	293	171
7	1	2	67	57	95
7	2	2	106	116	346
$\bar{7}$	2	2	98	94	6
7	3	2	106	97	6
7	4	2	48	56	180
7	1	3	85	106	3
$\bar{7}$	1	3	154	142	1
7	2	3	93	76	35
7	3	3	54	67	175
7	4	3	30	63	161
7	0	4	129	117	328
7	1	4	33	24	63
7	2	4	126	129	203

h	k	l	$10F_o$	$10F_c$	α
$\bar{3}$	0	2	258	302	159
3	1	2	67	53	318
$\bar{3}$	1	2	113	120	110
3	2	2	174	184	344
$\bar{3}$	2	2	349	356	24
3	3	2	378	319	344
$\bar{3}$	3	2	222	221	16
3	4	2	127	130	205
$\bar{3}$	4	2	84	75	144
3	5	2	101	92	206
$\bar{3}$	5	2	105	93	186
$\bar{3}$	6	2	33–	13	352
3	1	3	302	310	359
$\bar{3}$	1	3	323	336	354
3	2	3	104	108	2
$\bar{3}$	2	3	34	30	187
3	3	3	134	129	197
$\bar{3}$	3	3	165	159	172
3	4	3	233	215	164
$\bar{3}$	4	3	195	182	181
3	5	3	57	45	1
$\bar{3}$	5	3	78	67	51
$\bar{3}$	6	3	76	92	2
3	0	4	386	479	11
$\bar{3}$	0	4	311	338	12
3	1	4	158	158	101
$\bar{3}$	1	4	169	187	320
3	2	4	203	175	173
$\bar{3}$	2	4	234	226	163
3	3	4	180	178	171
$\bar{3}$	3	4	227	213	192
3	4	4	66	52	346
$\bar{3}$	4	4	64	60	357
3	5	4	85	90	21
$\bar{3}$	5	4	140	132	347
$\bar{3}$	6	4	11	21	256
3	1	5	194	173	179
$\bar{3}$	1	5	274	281	183
3	2	5	163	147	175
$\bar{3}$	2	5	229	221	176
3	3	5	118	124	357
$\bar{3}$	3	5	129	136	7
3	4	5	94	94	16
$\bar{3}$	4	5	119	124	344
$\bar{3}$	5	5	36	15	127
3	0	6	65	77	69
$\bar{3}$	0	6	292	317	159
3	1	6	101	92	128
$\bar{3}$	1	6	170	167	165
3	2	6	303	296	10
$\bar{3}$	2	6	193	179	31
3	3	6	136	111	1
$\bar{3}$	3	6	96	76	102
3	4	6	35	18	127
$\bar{3}$	4	6	119	117	165
$\bar{3}$	5	6	168	169	171
3	1	7	229	213	0
$\bar{3}$	1	7	175	183	0
3	2	7	102	81	11
$\bar{3}$	2	7	88	78	11
3	3	7	93	95	176
$\bar{3}$	3	7	92	105	173
$\bar{3}$	4	7	105	119	173
$\bar{3}$	5	7	26	16	339
3	0	8	185	174	355
$\bar{3}$	0	8	234	266	8
3	1	8	44	34	349
$\bar{3}$	1	8	54	51	345
3	2	8	108	108	186
$\bar{3}$	2	8	87	86	151
$\bar{3}$	3	8	162	157	165
$\bar{3}$	4	8	76	74	25
$\bar{3}$	1	9	163	158	181
$\bar{3}$	2	9	54	54	186
$\bar{3}$	3	9	89	77	353
$\bar{3}$	4	9	69	89	3
$\bar{3}$	0	10	178	185	192
$\bar{3}$	1	10	78	66	237
$\bar{3}$	2	10	52	57	336
$\bar{3}$	3	10	44	52	354
$\bar{3}$	1	11	90	90	357
$\bar{3}$	2	11	60	63	349
4	0	0	319	347	3
4	1	0	227	232	12
4	2	0	180	182	172
4	3	0	34	43	30
4	4	0	107	116	347
4	5	0	196	179	1
4	1	1	241	254	166
$\bar{4}$	1	1	260	275	169
4	2	1	200	214	174
$\bar{4}$	2	1	91	94	187
4	3	1	121	120	16
$\bar{4}$	3	1	159	158	16
4	4	1	169	163	355
$\bar{4}$	4	1	110	115	350
4	5	1	49	37	183
$\bar{4}$	5	1	27–	10	175
4	0	2	245	259	191
$\bar{4}$	0	2	360	391	178
7	3	4	71	86	179
7	4	4	18–	30	254
7	1	5	71	75	183
7	2	5	55	49	161
7	3	5	57	65	19
7	0	6	146	131	171
7	1	6	88	72	152
7	2	6	72	62	16
7	3	6	48	43	51
7	1	7	106	107	357
7	2	7	70	55	357
7	3	7	33	33	180
7	0	8	97	76	2

h	k	l	$10F_o$	$10F_c$	α
4	1	2	104	107	271
$\bar{4}$	1	2	257	254	168
4	2	2	226	227	357
$\bar{4}$	2	2	139	135	7
4	3	2	225	235	340
$\bar{4}$	3	2	180	180	1
4	4	2	71	69	229
$\bar{4}$	4	2	95	92	165
4	5	2	101	101	200
$\bar{4}$	5	2	144	132	177
4	1	3	253	258	9
$\bar{4}$	1	3	274	291	8
4	2	3	58	57	59
$\bar{4}$	2	3	130	104	1
4	3	3	127	119	164
$\bar{4}$	3	3	151	144	178
4	4	3	125	120	181
$\bar{4}$	4	3	151	161	181
4	5	3	16	21	312
$\bar{4}$	5	3	38	24	35
4	0	4	180	180	24
$\bar{4}$	0	4	384	393	22
4	1	4	115	114	343
$\bar{4}$	1	4	152	133	134
4	2	4	189	180	149
$\bar{4}$	2	4	165	170	133
4	3	4	117	103	187
$\bar{4}$	3	4	147	137	177
4	4	4	78	73	32
$\bar{4}$	4	4	121	127	28
$\bar{4}$	5	4	89	92	9
4	1	5	159	155	174
$\bar{4}$	1	5	212	214	174
4	2	5	158	148	154
$\bar{4}$	2	5	133	134	171
4	3	5	128	134	10
$\bar{4}$	3	5	79	83	345
4	4	5	76	100	3
$\bar{4}$	4	5	129	137	355
$\bar{4}$	5	5	35	39	205
4	0	6	227	203	182
$\bar{4}$	0	6	241	257	163
4	1	6	49	22	114
$\bar{4}$	1	6	160	139	179
4	2	6	185	169	6
$\bar{4}$	2	6	180	158	20
4	3	6	103	104	26
$\bar{4}$	3	6	106	110	338
$\bar{4}$	4	6	70	69	172
$\bar{4}$	5	6	98	103	188
4	1	7	152	148	8
$\bar{4}$	1	7	157	158	359
4	2	7	67	64	23
$\bar{4}$	2	7	77	77	47
$\bar{4}$	3	7	146	156	187
$\bar{4}$	4	7	38–	97	176
$\bar{4}$	5	7	26	44	220
$\bar{4}$	0	8	121	127	1
$\bar{4}$	1	8	82	80	41
$\bar{4}$	2	8	125	140	163
$\bar{4}$	3	8	76	79	164
$\bar{4}$	4	8	39	18	289
$\bar{4}$	1	9	126	120	178
$\bar{4}$	2	9	97	87	141
$\bar{4}$	3	9	66	62	39
$\bar{4}$	4	9	67	79	10
$\bar{4}$	0	10	184	162	206
$\bar{4}$	1	10	54	39	197
$\bar{4}$	2	10	89	91	315
$\bar{4}$	3	10	44	46	0
$\bar{4}$	1	11	88	102	1
$\bar{4}$	2	11	25–	48	12
5	0	0	302	325	346
5	1	0	96	101	0
5	2	0	117	110	202
5	3	0	195	195	187
5	4	0	97	89	341
5	5	0	72	32	349
5	1	1	222	214	191
$\bar{5}$	1	1	202	209	180
5	2	1	103	95	185
$\bar{5}$	2	1	77	55	212
5	3	1	104	100	36
$\bar{5}$	3	1	152	160	16
5	4	1	164	155	359
$\bar{5}$	4	1	101	98	4
5	5	1	43	48	122
$\bar{5}$	5	1	50	38	98
5	0	2	223	231	172
$\bar{5}$	0	2	262	254	156
5	1	2	88	70	347
$\bar{5}$	1	2	147	132	223
5	2	2	149	150	16
$\bar{5}$	2	2	176	173	22
5	3	2	94	92	357
$\bar{5}$	3	2	56	51	340
5	4	2	82	82	151
$\bar{5}$	4	2	80	78	132
$\bar{5}$	5	2	128	125	228
5	1	3	155	157	354
7	1	8	65	43	304
7	2	8	46	47	188
7	1	9	74	62	192
7	2	9	49	35	210
8	0	0	89	98	17
8	1	0	24	39	352
8	1	1	117	118	188
8	2	1	54	56	202
8	0	2	120	107	175
8	1	2	88	76	139
8	2	2	43	30	17
8	1	3	60	62	12
8	2	3	57	33	348

h	k	l	$10F_o$	$10F_c$	α
$\bar{5}$	1	3	189	184	353
5	2	3	129	109	357
$\bar{5}$	2	3	187	173	341
5	3	3	121	117	167
$\bar{5}$	3	3	127	116	188
5	4	3	94	101	188
$\bar{5}$	4	3	125	128	175
$\bar{5}$	5	3	37	6	0
5	0	4	202	196	355
$\bar{5}$	0	4	233	223	29
5	1	4	223	213	349
$\bar{5}$	1	4	90	100	59
5	2	4	118	108	186
$\bar{5}$	2	4	191	203	158
5	3	4	60	52	177
$\bar{5}$	3	4	133	126	154
$\bar{5}$	4	4	81	80	43
$\bar{5}$	5	4	74	92	18
5	1	5	169	167	186
$\bar{5}$	1	5	203	209	186
5	2	5	52	40	191
$\bar{5}$	2	5	77	71	214
5	3	5	61	86	4
$\bar{5}$	3	5	54	73	339
$\bar{5}$	4	5	92	94	17
$\bar{5}$	5	5	26	28	184
5	0	6	140	145	183
$\bar{5}$	0	6	176	160	202
5	1	6	60	55	222
$\bar{5}$	1	6	77	59	144
5	2	6	65	83	353
$\bar{5}$	2	6	129	132	335
$\bar{5}$	3	6	115	109	351
$\bar{5}$	4	6	64	50	226
$\bar{5}$	5	6	63	73	193
$\bar{5}$	1	7	128	124	354
$\bar{5}$	2	7	82	68	336
$\bar{5}$	3	7	95	109	190
$\bar{5}$	4	7	76	92	179
$\bar{5}$	0	8	89	74	356
$\bar{5}$	1	8	43	48	110
$\bar{5}$	2	8	168	181	183
$\bar{5}$	3	8	96	114	187
$\bar{5}$	4	8	32	27	226
$\bar{5}$	1	9	124	114	180
$\bar{5}$	2	9	88	63	180
$\bar{5}$	3	9	32	39	14
$\bar{5}$	0	10	112	88	181
$\bar{5}$	1	10	65	33	94
$\bar{5}$	2	10	61	53	359
$\bar{5}$	3	10	53	54	359
$\bar{5}$	1	11	82	80	0
6	0	0	189	177	330
6	1	0	51	43	322
6	2	0	164	163	220
6	3	0	124	129	199
6	4	0	57	60	296
6	1	1	152	163	175
$\bar{6}$	1	1	154	151	177
6	2	1	49	38	106
$\bar{6}$	2	1	147	130	154
6	3	1	92	92	8
$\bar{6}$	3	1	85	94	7
6	4	1	71	76	359
$\bar{6}$	4	1	103	109	7
6	0	2	133	127	182
$\bar{6}$	0	2	119	114	179
6	1	2	91	81	131
$\bar{6}$	1	2	28–	6	171
6	2	2	150	143	348
$\bar{6}$	2	2	218	220	7
6	3	2	114	108	23
$\bar{6}$	3	2	108	105	29
$\bar{6}$	4	2	43	28	104
6	1	3	145	134	8
$\bar{6}$	1	3	181	158	358
6	2	3	137	131	1
$\bar{6}$	2	3	95	72	23
6	3	3	49	70	173
$\bar{6}$	3	3	80	75	186
$\bar{6}$	4	3	84	84	179
6	0	4	192	191	6
$\bar{6}$	0	4	98	90	345
6	1	4	50	50	333
$\bar{6}$	1	4	54	37	274
6	2	4	58	64	266
$\bar{6}$	2	4	130	137	182
$\bar{6}$	3	4	119	133	167
$\bar{6}$	4	4	33	36	12
6	1	5	102	106	174
$\bar{6}$	1	5	149	154	186
$\bar{6}$	2	5	76	71	176
$\bar{6}$	3	5	53	74	358
$\bar{6}$	4	5	65	71	6
$\bar{6}$	0	6	248	220	183
$\bar{6}$	1	6	49	36	160
$\bar{6}$	2	6	77	64	354
$\bar{6}$	3	6	114	92	30
$\bar{6}$	4	6	52	42	179
$\bar{6}$	1	7	102	100	359
8	0	4	117	113	2
8	1	4	50	52	29
8	2	4	69	76	167
8	1	5	74	82	176
8	2	5	38	37	190
8	0	6	90	76	199
8	1	6	58	25	198
8	2	6	33	33	359
8	1	7	61	65	0
8	2	7	26	32	5
8	0	8	66	76	349
8	1	8	33	23	303

fredi, Tiripicchio & Bigoli, 1970) the metal–nitrogen bonds M–N(4) are longer than the metal oxygen bonds M–O(1). This is very likely due to the negative charge borne by O(1), and in agreement with the general lengthening of the bond C(2)–O(1) with respect to C(2)–O(5). Also in the present compound C(2·*n*)–O(1·*n*) is slightly longer (probably significantly) than C(2·*n*)–O(5·*n*). The zinc ion is displaced toward the apex from the average plane passing through O(1·1), 0(1·2), N(4·1), N(4·2), whose equation is $-5{\cdot}6445\,x-2{\cdot}3812\,y+5{\cdot}4671\,z=0{\cdot}4068$. Deviations of the atoms from this plane are Δ[O(1·1)] = −0·024, Δ[O(1·2)] = −0·023, Δ[N(4·1)] = +0·035, Δ[N(4·2)] = +0·042 and Δ[Zn] = +0·469 Å.

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}
Zn	obs	80·7	775	865	880	−21	222	1
	calc	81·7	779	867	882	−23	224	2
O(1·1)	obs	15·1	121	161	154	−9	30	−9
	calc	15·2	118	161	152	−12	28	−7
C(2·1)	obs	9·9	88	96	98	9	14	16
	calc	9·8	85	95	96	10	13	−19
N(3·1)	obs	12·2	98	125	103	−2	17	9
	calc	12·5	99	126	104	−2	18	8
N(4·1)	obs	12·5	113	128	120	2	28	−4
	calc	12·8	113	127	121	1	29	−2
O(5·1)	obs	12·6	106	116	117	4	29	−10
	calc	12·7	107	117	117	5	30	−10
O(1·2)	obs	16·1	135	151	166	10	38	−13
	calc	16·5	135	152	166	10	38	−13
C(2·2)	obs	11·7	113	105	145	−8	41	−3
	calc	11·7	113	105	145	−6	41	−4
N(3·2)	obs	11·1	91	95	101	−6	15	9
	calc	11·1	88	93	96	−7	11	10
N(4·2)	obs	12·9	105	130	136	0	37	6
	calc	13·0	101	131	136	−2	36	8
O(5·2)	obs	14·9	146	141	151	11	56	−16
	calc	15·1	146	143	141	10	56	−14
e.s.d.'s		0·4	6	6	6	4	4	4

Table 6. *Bond distances involving hydrogen atoms*

N(3·1)–H(7·1)	0·89 Å	H(7·1)–N(3·1)–C(2·1)	127·6°
N(4·1)–H(8·1)	1·03	H(7·1)–N(3·1)–N(4·1)	107·4
N(4·1)–H(9·1)	1·01	H(8·1)–N(4·1)–H(9·1)	107·4
N(3·2)–H(7·2)	0·99	H(8·1)–N(4·1)–N(3·1)	109·9
N(4·2)–H(8·2)	1·06	H(9·1)–N(4·1)–N(3·1)	111·0
N(4·2)–H(9·2)	0·86	H(8·1)–N(4·1)–Zn	120·4
		H(9·1)–N(4·1)–Zn	99·2
		H(7·2)–N(3·2)–C(2·2)	116·4
		H(7·2)–N(3·2)–N(4·2)	122·3
		H(8·2)–N(4·2)–H(9·2)	97·6
		H(8·2)–N(4·2)–N(3·2)	96·3
		H(9·2)–N(4·2)–N(3·2)	130·6
		H(8·2)–N(4·2)–Zn	97·0
		H(9·2)–N(4·2)–Zn	118·2

Table 7. *Shortest intermolecular contacts*

O(1·1)–N(4·2)	3·093 (18) Å
O(1·1)–O(1·2^{i})	3·106 (14)
O(1·1)–N(3·2^{ii})	3·103 (23)
O(1·1)–C(2·2^{ii})	3·039 (18)
O(1·2)–N(4·1)	2·951 (17)
O(1·2)–N(3·1^{iii})	3·153 (22)
O(1·2)–N(4·1^{iii})	3·064 (20)
O(1·2)–C(2·1^{iii})	3·043 (20)
O(5·1)–N(4·2^{v})	3·002 (25)
O(5·2)–O(1·2^{iii})	3·000 (18)
O(5·2)–N(4·2^{iii})	3·104 (16)

Asymmetric unit transformations:

i $x, -y, \frac{1}{2}+z$
ii $x, 1-y, \frac{1}{2}+z$
iii $x, -y, z-\frac{1}{2}$
iv $x, 1-y, z-\frac{1}{2}$
v $x+1, 1-y, z+\frac{1}{2}$

The coordination in this compound is different from the square pyramidal arrangement found in bis-(L-serinato)zinc (Van der Helm, Nicholas & Fisher, 1970) where one of the chelate ligands occupies, with oxygen, one corner of the basal plane and, with nitrogen, the apex of the pyramid.

Table 5. *Main bond distances and angles*

Zn——O(1·1)	2·030 (9) Å	O(1·1)–Zn——O(1·2)	151·9 (5)°
Zn——N(4·1)	2·077 (14)	O(1·1)–Zn——N(4·1)	79·9 (5)
Zn——O(1·2)	2·058 (10)	O(1·1)–Zn——N(4·2)	97·6 (4)
Zn——N(4·2)	2·080 (13)	O(1·1)–Zn——O(5·2^{i})	113·8 (5)
Zn——O(5·2^{i})	2·035 (14)	O(1·2)–Zn——N(4·1)	91·1 (5)
C(2·1)–O(1·1)	1·279 (18)	O(1·2)–Zn——N(4·2)	79·9 (5)
C(2·1)–O(5·1)	1·257 (18)	O(1·2)–Zn——O(5·2^{i})	94·2 (5)
N(4·1)–N(3·1)	1·391 (19)	N(4·1)–Zn——N(4·2)	155·8 (6)
C(2·1)–N(3·1)	1·378 (19)	N(4·1)–Zn——O(5·2^{i})	105·1 (5)
C(2·2)–O(1·2)	1·280 (17)	N(4·2)–Zn——O(5·2^{i})	97·9 (6)
C(2·2)–O(5·2)	1·246 (17)	C(2·1)–O(1·1)–Zn	113·7 (7)
N(4·2)–N(3·2)	1·427 (20)	N(3·1)–C(2·1)–O(1·1)	117·1 (12)
C(2·2)–N(3·2)	1·355 (20)	N(3·1)–C(2·1)–O(5·1)	115·9 (15)
		O(5·1)–C(2·1)–O(1·1)	124·4 (12)
		C(2·1)–N(3·1)–N(4·1)	118·2 (14)
		N(3·1)–N(4·1)–Zn	108·3 (9)
		C(2·2)–O(1·2)–Zn	113·0 (8)
		N(3·2)–C(2·2)–O(1·2)	119·3 (12)
		N(3·2)–C(2·2)–O(5·2)	117·8 (13)
		O(5·2)–C(2·2)–O(1·2)	122·9 (12)
		C(2·2)–N(3·2)–N(4·2)	117·5 (14)
		N(3·2)–N(4·2)–Zn	106·8 (8)

The two hydrazinecarboxylato anions (Fig. 3) are practically equal; corresponding angles and distances repeat values found in octahedral complexes (Table 8). The slight lengthening of C(2)–O(5) and shortening of C(2)–O(1) suggest, however, that the ionic character of the carboxylato group is more pronounced here than in the octahedral complexes.

Table 8. *Comparison between octahedral and pyramidal complexes of hydrazinecarboxylic acid.*

$$t = \frac{\Delta\bar{d}(\text{or } \Delta\bar{\alpha})}{(\sigma_1^2+\sigma_2^2)^{1/2}}$$

	Mean octahedral $\bar{d}$	$Zn(N'H_2\text{–}NH\text{–}COO)_2$ $\bar{d}$	t
O(1)–C(2)	1·293 (6) Å	1·280 (12) Å	0·97
O(5)–C(2)	1·224 (6)	1·251 (12)	2·01
C(2)–N(3)	1·381 (7)	1·367 (14)	0·89
N(3)–N(4)	1·422 (7)	1·408 (14)	0·89
	$\bar{\alpha}$	$\bar{\alpha}$	
O(1)–C(2)–N(3)	116·74 (45)°	118·20 (85)°	1·52
C(2)–N(3)–N(4)	119·14 (42)	117·85 (99)	1·20
O(1)–C(2)–O(5)	124·11 (50)	123·65 (85)	0·47
O(5)–C(2)–N(3)	118·97 (49)	116·99 (98)	1·81

The only differences between the two chelate rings concern the planarities of the rings or of parts of them. (Table 9). In ring 1 the atom C(2·1) is 0·09 Å above the average plane passing through O(1·1), C(2·1), N(3·1), O(5·1) and the group cannot be said to be exactly planar, though it is nearly so. The zinc ion is +0·25 Å and N(4·1)+0·05 Å out of this plane. On the other hand in ring 2, the atoms O(1·2), C(2·2), N(3·2) and O(5·2) lie on the same plane, thus mantaining the general feature of hydrazinecarboxylato chelates where these four atoms form a rigid planar group. In ring 2 the zinc ion is above the plane of the rigid portion of the molecule (Δ[Zn] = +0·16 Å) whereas N(4·2) is below this plane (Δ[N(4·2)] = −0·22 Å). It is a typical feature of the hydrazinecarboxylato chelates, that the metal atom and N(4), the flexible points of the whole ring, are displaced either to the same or to opposite sides of the rigid portion of the ring. The same behaviour is shown by α-aminoacids (Freeman, 1967).

The positions of the hydrogen atoms, and the angles involving them, confirm a nearly sp^2 configuration for atoms N(3·1) and N(3·2) and a nearly sp^3 configuration for atoms N(4·1) and N(4·2).

Table 9. *Analysis of planarity of chelate rings*

Ring 1

Equation of plane:

$$-5{\cdot}1906x - 2{\cdot}3802y + 6{\cdot}3743z = 0{\cdot}8486$$

	Atoms in				Atoms out	
	O(1·1)	C(2·1)	N(3·1)	O(5·1)	N(4·1)	Zn
$\Delta\cdot10^4$(Å)	−193	+965	−296	−314	+545	2540
$\sigma\cdot10^4$(Å)	129	180	173	163	155	7

$$\sum(\Delta/\sigma)^2 = 40{\cdot}96$$

Atoms 'in' are not in the same plane

Ring 2

Equation of plane:

$$-5{\cdot}5189x - 2{\cdot}8638y + 4{\cdot}2943z = 0{\cdot}3211$$

	Atoms in				Atoms out	
	O(1·2)	C(2·2)	N(3·2)	O(5·2)	N(4·2)	Zn
$\Delta\cdot10^4$(Å)	+13	−70	+26	+17	−2221	+1623
$\sigma\cdot10^4$(Å)	118	159	176	135	164	9

$$\sum(\Delta/\sigma)^2 = 0{\cdot}24$$

Atoms 'in' lie in the same plane
Angle between planes 16·34°

There are several intermolecular contacts in the range 2·95–3·14 Å; but none of them involves hydrogen atoms and consequently they are not hydrogen bonds. The structure, therefore, can be described as an arrangement of chains of complexes, parallel to [100], bridged by one ligand molecule. The chains are held together by van der Waals contacts.

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