tropic stresses and isotropic strains. This has also been observed for Ag–Cd (Sen Gupta & Quader, 1966) and for Ag–In and Ag–Sn alloys (Adler & Wagner, 1962). Fig. 4 shows the variation of r.m.s. strains as a function of distance L normal to the reflecting planes for the Ag–5·35 Sb alloy, and the same general behaviour was shown by all the specimens and by several f.c.c. alloys of silver and copper. The rapid decrease with increasing L indicates the inhomogeneity of strains and the trend of the curves at higher L is quite consistent with the fact that owing to long range interactions of stresses around a dislocation, the positive and negative stresses balance at some average distance away from the source of stress reaching an asymptotic value.

The author is grateful to Prof. B. N. Srivastava, D.Sc., F.N.I., for his continued interest in the work and to the Council for Scientific and Industrial Research (New Delhi) for financial assistance.

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The Crystal and Molecular Structure of Bis(hydrazinecarboxylato-*N'*, *O*)manganese(II) Dihydrate

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(*Received* 26 *October* 1966)

The crystals of bis(hydrazinecarboxylato-*N'*,*O*)manganese(II) dihydrate, Mn(II)($N'H_2$–NH–COO$)_2$. $2H_2O$, are orthorhombic, space group *Pba*2. The structure, determined from three-dimensional data, consists of chains formed by two types of *trans,cis,cis*-octahedral chelates, bound together in the chain by bridging hydrazinecarboxylato groups. Some water molecules are coordinated to the metal and some are water of crystallization. Four corners of the coordination octahedra of the first type are occupied by hydrazinecarboxylato chelate groups and two by oxygen atoms of bridging hydrazinecarboxylato groups. The complexes of the second type have the same geometrical arrangement of donor atoms as the complexes of the first type except that two water molecules replace the bridging groups. Some of the hydrazinecarboxylato groups behave as tridentate (chelate and bridging) ligands and some as bidentate chelate ligands. The complexes can be compared with octahedral complexes of the same and of different stereochemical arrangements formed by hydrazinecarboxylic acid. The chains of complexes are held together in the crystal by strong hydrogen bonds either direct chain-to-chain or *via* water of crystallization.

Introduction

Determinations of the crystal structures of compounds formed by hydrazinecarboxylic acid, $N'H_2$–NH–COOH (hycH) with bivalent metals (Ferrari, Braibanti, Bigliardi & Lanfredi, 1965; Braibanti, Manotti Lanfredi & Tiripicchio, 1966; Braibanti, Bigliardi, Manotti Lanfredi & Tiripicchio, 1966; Braibanti, Tiripicchio, Manotti Lanfredi & Bigoli, 1966) have shown that this ligand invariably gives origin to chelates. The complexes which have been studied are of types *A*, *B* and *C* shown in Fig. 1. They are octahedral and can contain either three or two hyc's.

The crystal structure of the compound bis(hydrazinecarboxylato-*N'*,*O*)manganese(II) dihydrate,

$$\mathrm{Mn(hyc)_2.2H_2O},$$

has now been investigated.

Experimental

Crystals were prepared by evaporation of an aqueous solution of hydrazine hydrate and manganese(II) chloride into which carbon dioxide had been bubbled for one hour or more. The crystals are colourless, thick plates, very stable at room temperature and show piezoelectric effects. The composition has been determined by chemical analysis.

Crystal data

Compound: bis(hydrazinecarboxylato-*N'*,*O*)manganese(II) dihydrate,

$$\mathrm{Mn(II)(N'H_2–NH–COO)_2.2H_2O},\ \text{F.W. } 241{\cdot}074$$

Crystal habit: thick plates
Crystal class: orthorhombic, pyramidal
Unit cell (Cu $K\alpha$ radiation: $\lambda = 1{\cdot}5418$ Å):
$a = 11{\cdot}052 \pm 0{\cdot}010$, $b = 9{\cdot}862 \pm 0{\cdot}020$, $c = 7{\cdot}847 \pm 0{\cdot}005$ Å
$U = 855{\cdot}3$ Å^3, $Z = 4$ stoichiometric units
$D_m = 1{\cdot}893$ g.cm^{-3}, $D_x = 1{\cdot}872$ g.cm^{-3}
$\mu = 135{\cdot}8$ cm^{-1} (Cu $K\alpha$)
Reflexions: $0kl$ only if $k = 2n$, $h0l$ only if $h = 2n$
Space group: $Pba2$ (C^8_{2v}, no. 32), from systematic extinctions and piezoelectric observations.

The photographs for intensity measurements were taken in an integrating Weissenberg camera applying the multiple film technique. The intensities of reflexions $hk0$, $hk1$, ..., $hk6$ and $h0l$ were measured by a microdensitometer and the usual corrections were applied. Absorption corrections were applied as for cylindrical specimens ($\mu R = 2{\cdot}41$). Atomic form factors were calculated by Forsyth & Wells's (1959) method with the improved constants given by Moore (1963). All calculations were performed on the Olivetti Elea 6001/S of the Centro Calcolo Elettronico of the University of Parma.

Determination of the structure

The three-dimensional Patterson function $P(UVW)$ suggested that the manganese atoms are distributed over the two non-equivalent crystallographic positions: (*a*) $00z$; $\frac{1}{2}\frac{1}{2}z$ and (*b*) $0\frac{1}{2}z$; $\frac{1}{2}0z$. The light atom positions were found by means of several successive Fourier syntheses. The structure was refined by differential syntheses and the anisotropic thermal parameters were refined by the method of Nardelli & Fava (1960). ($R_{hkl} = 13{\cdot}2\%$, observed reflexions only). The final results are reported in Tables 1–4.

Table 1. *Final atomic coordinates with e.s.d.'s* (× 10⁴)

	X/a	Y/b	Z/c
Mn(*D*)	0000 (0)	5000 (0)	6771 (4)
O(1*D*)	0058 (12)	2840 (12)	6458 (19)
C(2*D*)	0945 (15)	2302 (15)	5572 (25)
N(3*D*)	1625 (13)	3214 (15)	4692 (24)
N(4*D*)	1471 (14)	4643 (13)	4958 (20)
O(5*D*)	1054 (12)	1110 (11)	5245 (19)
H_2O(6*D*)	1315 (12)	4726 (15)	8870 (21)
Mn(*C*)	0000 (0)	0000 (0)	3230 (4)
O(1*C*)	−1179 (13)	1697 (13)	2883 (16)
C(2*C*)	−0872 (14)	2657 (15)	1799 (29)
N(3*C*)	0257 (14)	2390 (22)	0913 (30)
N(4*C*)	0875 (12)	1214 (16)	1212 (22)
O(5*C*)	−1429 (15)	3689 (16)	1693 (23)
H_2O(7)	3668 (12)	4326 (14)	7892 (21)

Discussion of the structure

The structure, represented in Fig. 2, consists of two sets of complexes corresponding to the two sets of crystallographically non-equivalent metal atoms. Half the water molecules are directly coordinated to the metal and the other half appear as water of crystallization.

The two sets of complexes are of types *C* and *D* (Fig. 3); both are *trans,cis,cis*-complexes strictly related to the complexes *C* found in the structure of Cd(hyc)₂ (Braibanti, Tiripicchio, Manotti Lanfredi & Bigoli, 1966) where they are the only complexes present; in the

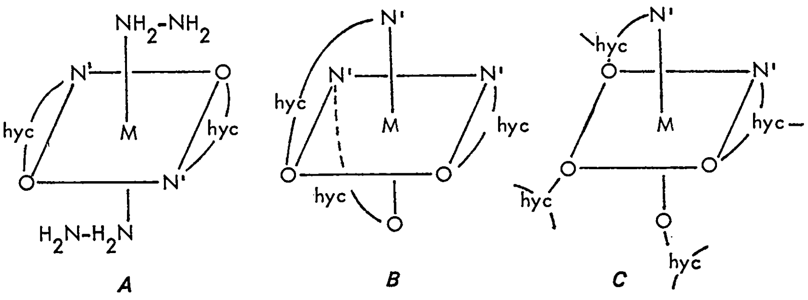
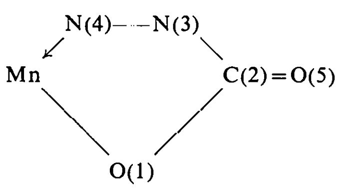


Fig. 1. Types of complex found in compounds of hyc. *A*: *trans*-[M(II)(N₂H₄)₂]hyc₂. *B*:*cis*-[M(II)hyc₃]⁻. *C*: *trans,cis,cis*-[Cdhyc₂ (O-hyc)₂].

latter they are bound in layers through tridentate hyc groups, which form chelates and at the same time bridge two complexes. In the manganese compound, however, the layer structure becomes a chain structure, each chain being formed by alternate *C* and *D* complexes.

The *D* complexes possess the same geometrical arrangement *trans,cis,cis* as *C* complexes but the two positions occupied by $\mathrm{O{-}hyc}\langle$ of adjacent chains are taken by two water molecules. Comparisons can also be made with other octahedral complexes *A* and *B* to see how many different arrangements can be found with this ligand.

The main bond lengths in the complexes are quoted in Table 5 and the corresponding bond angles in Table 6. The complex *C* is drawn in perspective in Fig. 4 and the complex *D* in Fig. 5; the chelate rings formed by the atoms



are there easily recognized.

In both complexes the Mn–O(1) bonds within the same ring are shorter than the Mn–N(4) bonds and this is probably due to the electrostatic attraction of the negatively charged oxygen atom. Such differences between metal–oxygen and metal–nitrogen bonds have not been observed in the complexes of neutral semicarbazide molecules (Nardelli, Fava Gasparri, Boldrini & Giraldi Battistini, 1965) where the bonds in each of the two pairs Cu–O 1·97, Cu–N 1·99 Å and Zn–O 2·06, Zn–N 2·07 Å are equal. Furthermore, in the complex *D*, Mn(*D*)–OH_2(6*D*), 2·213 Å, formed with an uncharged water molecule, is longer than Mn(*D*)–O(1*D*), 2·145 Å, and in the complex *C*, Mn(*C*)–O(5*D*), 2·248 Å, formed with the C=O group of an adjacent hyc, is also longer than Mn(*C*)–O(1*C*), 2·138 Å.

The nitrogen–nitrogen bonds of the hydrazine radical, N(3*C*)–N(4*C*), 1·366 Å and N(3*D*)–N(4*D*), 1·435 Å are shorter than the corresponding distance in the N_2H_4 molecule [N–N, 1·47 Å; Ferrari, Braibanti, Bigliardi & Lanfredi (1965)].

The carbon–oxygen bonds C(2*C*)–O(1*C*), 1·317 Å and C(2*D*)–O(1*D*), 1·314 Å are longer than the bonds C(2*C*)–O(5*C*), 1·192 Å and C(2*D*)–O(5*D*), 1·209 Å in the hydrazine radical of *C* and *D* respectively and cor-

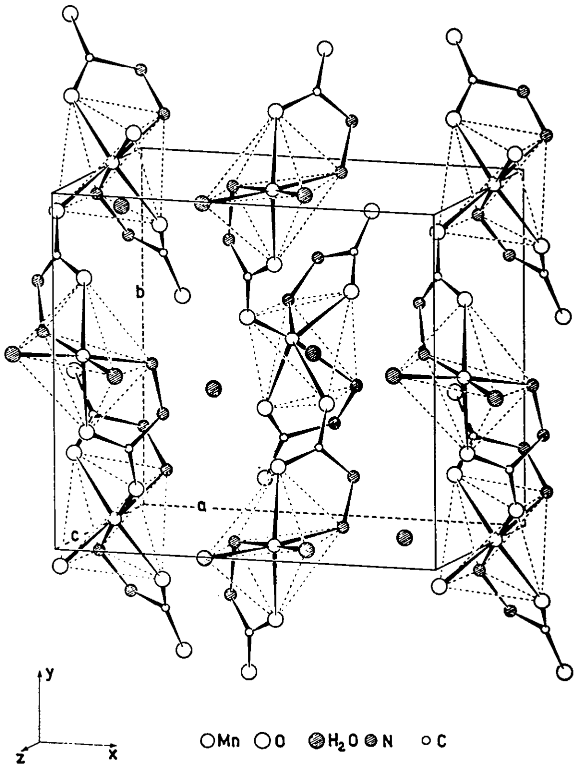


Fig. 2. Clinographic projection of the structure of $Mn(II)hyc_2.2H_2O$.

Table 2. *Anisotropic thermal parameters* (Å^2)

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mn(*D*)	2·318	2·205	2·599	−0·064	0	0
O(1*D*)	2·562	2·545	1·993	−0·359	0·003	0·020
C(2*D*)	1·015	1·654	1·630	−1·060	−0·005	0·166
N(3*D*)	1·115	1·334	1·488	−0·155	0·318	−0·139
N(4*D*)	1·848	0·710	1·298	−0·522	−0·647	−0·784
O(5*D*)	1·982	1·868	2·178	−0·157	−0·271	−0·086
H_2O(6*D*)	1·763	1·735	1·917	0·425	0·075	0·359
Mn(*C*)	2·286	2·199	2·561	0·136	0	0
O(1*C*)	1·810	2·419	2·176	0·722	0·264	0·447
C(2*C*)	1·632	1·426	2·308	−0·401	−0·100	0·310
N(3*C*)	0·239	2·098	2·840	0·161	0·111	1·126
N(4*C*)	1·048	2·593	1·642	−0·039	0·191	−0·175
O(5*C*)	2·859	2·880	3·558	−0·451	0·630	−0·515
H_2O(7)	2·076	2·859	3·941	−0·182	0·540	−0·603

Average and maximum shift in the last cycle:

Mn	$\lvert\Delta_{av}\rvert = 0{\cdot}102$	$\lvert\Delta_{max}\rvert = 0{\cdot}271$
Light atoms:	$\lvert\Delta_{av}\rvert = 0{\cdot}083$	$\lvert\Delta_{max}\rvert = 0{\cdot}353$

Table 3. *Observed and calculated structure factors*

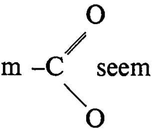
h	k	l	10F_o	10F_c
2	0	0	1015	1515
4	0	0	469	523
6	0	0	579	722
8	0	0	699	906
10	0	0	338	364
12	0	0	311	250
14	0	0	201	151
1	1	0	—	49
2	1	0	192	165
3	1	0	282	240
4	1	0	215	186
5	1	0	310	318
6	1	0	235	242
7	1	0	259	265
8	1	0	162	66
9	1	0	211	166
10	1	0	—	28
11	1	0	—	110
12	1	0	—	131
13	1	0	—	80
14	1	0	—	165
0	2	0	544	408
1	2	0	—	66
2	2	0	210	204
3	2	0	229	223
4	2	0	176	227
5	2	0	227	281
6	2	0	478	578
7	2	0	150	131
8	2	0	405	464
9	2	0	229	194
10	2	0	—	75
11	2	0	—	20
12	2	0	—	51
13	2	0	—	94
14	2	0	—	229
1	3	0	277	263
2	3	0	—	101
3	3	0	240	183
4	3	0	172	122
5	3	0	406	445
6	3	0	136	129
7	3	0	—	55
8	3	0	240	261
9	3	0	194	170
10	3	0	178	128
11	3	0	—	33
12	3	0	—	19
13	3	0	—	93
0	4	0	750	788
1	4	0	143	121
2	4	0	793	913
3	4	0	143	116
4	4	0	788	892
5	4	0	—	102
6	4	0	548	595
7	4	0	—	53
8	4	0	351	368
9	4	0	141	98
10	4	0	282	249
11	4	0	—	7
12	4	0	264	185
13	4	0	—	68
1	5	0	442	393
2	5	0	187	207
3	5	0	167	130
4	5	0	—	23
5	5	0	—	72
6	5	0	—	70
7	5	0	—	101
8	5	0	203	167
9	5	0	—	34
10	5	0	192	194
11	5	0	—	42
12	5	0	—	27
13	5	0	—	76
0	6	0	391	418
1	6	0	381	430
2	6	0	230	254
3	6	0	277	279
4	6	0	272	294
5	6	0	254	318
6	6	0	438	487
7	6	0	137	77
8	6	0	330	301
9	6	0	182	124
10	6	0	145	92
11	6	0	—	43
12	6	0	136	104
1	7	0	—	5
2	7	0	—	37
3	7	0	214	192
4	7	0	231	268
5	7	0	—	61
6	7	0	—	58
7	7	0	—	97
8	7	0	217	188
9	7	0	—	24
10	7	0	—	58
11	7	0	154	112
0	8	0	491	488
1	8	0	239	263
2	8	0	424	485
3	8	0	203	250
4	8	0	295	303
5	8	0	155	135
6	8	0	191	106
7	8	0	151	115
8	8	0	238	176
9	8	0	—	34
10	8	0	246	234
11	8	0	—	33
1	9	0	—	21
2	9	0	—	121
3	9	0	—	43
4	9	0	—	55
5	9	0	—	43
6	9	0	—	48
7	9	0	—	61
8	9	0	—	24
9	9	0	—	34
10	9	0	—	89
0	10	0	244	156
1	10	0	201	143
2	10	0	267	229
3	10	0	186	175
4	10	0	270	262
5	10	0	—	1
6	10	0	208	165
7	10	0	—	77
8	10	0	170	143
1	11	0	—	46
2	11	0	226	190
3	11	0	—	38
4	11	0	—	21
5	11	0	—	39
6	11	0	155	149
7	11	0	—	52
0	12	0	181	104
1	12	0	—	78
2	12	0	205	156
3	12	0	—	66
4	12	0	152	182
0	0	1	534	803
2	0	1	250	267
4	0	1	290	261
6	0	1	295	385
8	0	1	245	238
10	0	1	187	189
12	0	1	247	194
14	0	1	—	61
1	1	1	709	852
2	1	1	536	639
3	1	1	757	870
4	1	1	173	145
5	1	1	499	548
6	1	1	251	295
7	1	1	335	340
8	1	1	170	105
9	1	1	343	389
10	1	1	—	98
11	1	1	256	262
12	1	1	—	25
13	1	1	206	155
14	1	1	—	48
0	2	1	575	573
1	2	1	323	317
2	2	1	370	383
3	2	1	173	186
4	2	1	562	637
5	2	1	210	147
6	2	1	266	234
7	2	1	187	172
8	2	1	210	143
9	2	1	—	66
10	2	1	—	81
11	2	1	162	124
12	2	1	114	93
13	2	1	—	27
14	2	1	—	47
1	3	1	480	533
2	3	1	236	219
3	3	1	390	428
4	3	1	204	167
5	3	1	471	531
6	3	1	—	72
7	3	1	366	399
8	3	1	190	219
9	3	1	247	191
10	3	1	208	148
11	3	1	215	151
12	3	1	—	12
13	3	1	186	166
0	4	1	435	440
1	4	1	314	347
2	4	1	194	241
3	4	1	214	241
4	4	1	299	325
5	4	1	245	248
6	4	1	221	214
7	4	1	197	128
8	4	1	205	157
9	4	1	154	109
10	4	1	173	105
11	4	1	—	49
12	4	1	183	163
13	4	1	—	56
1	5	1	644	759
2	5	1	168	132
3	5	1	354	410
4	5	1	186	126
5	5	1	368	457
6	5	1	—	107
7	5	1	466	542
8	5	1	201	183
9	5	1	275	311
10	5	1	172	160
11	5	1	—	92
12	5	1	—	23
13	5	1	—	92
0	6	1	256	346
1	6	1	—	34
2	6	1	172	210
3	6	1	—	23
4	6	1	291	277
5	6	1	—	18
6	6	1	267	273
7	6	1	—	82
8	6	1	151	141
9	6	1	—	81
10	6	1	—	18
11	6	1	—	48
12	6	1	—	79
1	7	1	330	417
2	7	1	—	70
3	7	1	216	205
4	7	1	155	120
5	7	1	221	159
6	7	1	—	118
7	7	1	260	230
8	7	1	233	185
9	7	1	164	202
10	7	1	—	91
11	7	1	—	138
0	8	1	204	159
1	8	1	—	104
2	8	1	151	154
3	8	1	—	69
4	8	1	196	148
5	8	1	—	106
6	8	1	—	16
7	8	1	—	51
8	8	1	—	105
9	8	1	—	19
10	8	1	160	134
11	8	1	—	36
1	9	1	234	270
2	9	1	173	119
3	9	1	350	359
4	9	1	—	35
5	9	1	347	329
6	9	1	—	96
7	9	1	235	215
8	9	1	—	33
9	9	1	133	113
10	9	1	—	37
0	10	1	155	177
1	10	1	171	94
2	10	1	208	159
3	10	1	—	101
4	10	1	147	106
5	10	1	—	49
6	10	1	—	75
7	10	1	—	50
8	10	1	—	101
1	11	1	227	191
2	11	1	—	24
3	11	1	134	120
4	11	1	—	36
5	11	1	—	83
6	11	1	—	18
7	11	1	—	104
0	12	1	—	62
1	12	1	—	34
2	12	1	—	54
3	12	1	—	39
4	12	1	—	43
0	0	2	747	711
2	0	2	783	806
4	0	2	496	511
6	0	2	298	282
8	0	2	332	342
10	0	2	289	248
12	0	2	217	160
14	0	2	—	132
1	1	2	473	523
2	1	2	824	916
3	1	2	677	705
4	1	2	289	311
5	1	2	525	601
6	1	2	260	291
7	1	2	423	465
8	1	2	—	51
9	1	2	240	247
10	1	2	147	104
11	1	2	138	176
12	1	2	123	148
13	1	2	122	121
14	1	2	—	86
0	2	2	900	872
1	2	2	601	551
2	2	2	508	581
3	2	2	515	557
4	2	2	445	466
5	2	2	252	226
6	2	2	297	342
7	2	2	262	298
8	2	2	256	231
9	2	2	—	30
10	2	2	160	158
11	2	2	164	154
12	2	2	176	127
13	2	2	—	18
1	3	2	346	382
2	3	2	320	278
3	3	2	531	598
4	3	2	187	145
5	3	2	350	400
6	3	2	243	237
7	3	2	172	113
8	3	2	216	198
9	3	2	221	170
10	3	2	176	156
11	3	2	238	247
12	3	2	—	81
13	3	2	155	129
0	4	2	281	255
1	4	2	—	58
2	4	2	478	470
3	4	2	—	26
4	4	2	500	523
5	4	2	—	78
6	4	2	151	146
7	4	2	—	48
8	4	2	164	127
9	4	2	—	49
10	4	2	257	233
11	4	2	—	60
12	4	2	183	148
13	4	2	—	58
1	5	2	459	514
2	5	2	131	68
3	5	2	587	650
4	5	2	—	68
5	5	2	359	337
6	5	2	—	95
7	5	2	236	164
8	5	2	178	154
9	5	2	235	273
10	5	2	—	57
11	5	2	289	260
12	5	2	—	29
0	6	2	381	433
1	6	2	137	91
2	6	2	357	384
3	6	2	—	47
4	6	2	250	253
5	6	2	—	78
6	6	2	—	84
7	6	2	—	19
8	6	2	183	200
9	6	2	—	44
10	6	2	204	208
11	6	2	—	57
12	6	2	—	51
1	7	2	193	211
2	7	2	176	156
3	7	2	260	252
4	7	2	213	187
5	7	2	244	244
6	7	2	—	75
7	7	2	203	188
8	7	2	130	143
9	7	2	144	126
10	7	2	—	37
11	7	2	—	92
0	8	2	301	305
1	8	2	—	123
2	8	2	170	140
3	8	2	—	75
4	8	2	195	251
5	8	2	145	131
6	8	2	260	243
7	8	2	—	19
8	8	2	—	39
9	8	2	—	99
10	8	2	—	33
1	9	2	229	295
2	9	2	—	111
3	9	2	278	275
4	9	2	—	54
5	9	2	295	296
6	9	2	—	115
7	9	2	220	194
8	9	2	—	8
9	9	2	79	94
0	10	2	—	94
1	10	2	—	89
2	10	2	158	136
3	10	2	130	115
4	10	2	229	182
5	10	2	—	64
6	10	2	142	137
7	10	2	—	73
8	10	2	—	64
1	11	2	160	163
2	11	2	—	43
3	11	2	159	149
4	11	2	—	33
5	11	2	108	90
6	11	2	—	36
0	12	2	143	156
1	12	2	—	39
2	12	2	96	85
3	12	2	—	19
4	12	2	—	31
0	0	3	301	305
2	0	3	878	825
4	0	3	1289	1365
6	0	3	460	529
8	0	3	353	329
10	0	3	322	351
12	0	3	164	125
1	1	3	—	54
2	1	3	249	238
3	1	3	354	350
4	1	3	—	37
5	1	3	174	180
6	1	3	145	108
7	1	3	154	182
8	1	3	—	111
9	1	3	135	107
10	1	3	—	41
11	1	3	163	135
12	1	3	—	59
13	1	3	—	40
0	2	3	393	345
1	2	3	183	151
2	2	3	574	545
3	2	3	286	305
4	2	3	540	605
5	2	3	—	92
6	2	3	270	276
7	2	3	242	200
8	2	3	108	109
9	2	3	—	74
10	2	3	236	278
11	2	3	—	85
12	2	3	232	250
13	2	3	—	42
1	3	3	—	81
2	3	3	196	203
3	3	3	386	446
4	3	3	174	149
5	3	3	229	240
6	3	3	—	46
7	3	3	—	58
8	3	3	180	178
9	3	3	—	75
10	3	3	141	141
11	3	3	145	105
12	3	3	—	32
13	3	3	—	66
0	4	3	665	690
1	4	3	215	171
2	4	3	551	573
3	4	3	197	194
4	4	3	390	477
5	4	3	163	107
6	4	3	380	423
7	4	3	176	112
8	4	3	309	324
9	4	3	125	101
10	4	3	235	246
11	4	3	—	79
12	4	3	186	189
1	5	3	209	188
2	5	3	270	290
3	5	3	220	255
4	5	3	157	116
5	5	3	211	231
6	5	3	197	218
7	5	3	—	17
8	5	3	132	122
9	5	3	—	25
10	5	3	—	35
11	5	3	—	61
12	5	3	80	77
0	6	3	490	530
1	6	3	234	265
2	6	3	440	474
3	6	3	181	154
4	6	3	246	253
5	6	3	195	219
6	6	3	195	132
7	6	3	—	33
8	6	3	259	273
9	6	3	148	128
10	6	3	248	261
11	6	3	—	69
1	7	3	163	169
2	7	3	186	171
3	7	3	125	98
4	7	3	174	139
5	7	3	169	124
6	7	3	—	102
7	7	3	178	194
8	7	3	115	133
9	7	3	—	61
10	7	3	—	61
11	7	3	—	53
0	8	3	168	156
1	8	3	177	148
2	8	3	217	202
3	8	3	186	150
4	8	3	306	332
5	8	3	—	82
6	8	3	297	337
7	8	3	112	133
8	8	3	113	145
9	8	3	—	15
10	8	3	—	57
1	9	3	—	125
2	9	3	—	37
3	9	3	—	34
4	9	3	—	29
5	9	3	—	23
6	9	3	—	60
7	9	3	—	45
8	9	3	—	27
9	9	3	—	58
0	10	3	258	269
1	10	3	—	66
2	10	3	230	222
3	10	3	—	70
4	10	3	219	185
5	10	3	—	27
6	10	3	193	193
7	10	3	—	63
1	11	3	—	97
2	11	3	—	101
3	11	3	—	50
4	11	3	—	19
5	11	3	—	53
0	12	3	—	192
1	12	3	—	52
2	12	3	—	100
0	0	4	348	215
2	0	4	337	448
4	0	4	352	429
6	0	4	236	210
8	0	4	118	118
10	0	4	140	164
12	0	4	127	114
1	1	4	787	894
2	1	4	89	104
3	1	4	257	250
4	1	4	211	249
5	1	4	260	290
6	1	4	—	68
7	1	4	435	498
8	1	4	119	91
9	1	4	282	316
10	1	4	—	91
11	1	4	148	154
12	1	4	80	84
13	1	4	—	144
0	2	4	74	7
1	2	4	223	209
2	2	4	—	53
3	2	4	111	108
4	2	4	105	58
5	2	4	165	163
6	2	4	—	45
7	2	4	—	70
8	2	4	—	37
9	2	4	—	78
10	2	4	93	48
11	2	4	83	79
12	2	4	64	47
1	3	4	283	225
2	3	4	114	110
3	3	4	464	558
4	3	4	101	108
5	3	4	411	458
6	3	4	100	54
7	3	4	259	239
8	3	4	—	92
9	3	4	175	185
10	3	4	—	65
11	3	4	96	126
12	3	4	69	56
0	4	4	274	282
1	4	4	105	65
2	4	4	230	230
3	4	4	107	57
4	4	4	166	154
5	4	4	—	44
6	4	4	164	163
7	4	4	—	86
8	4	4	165	175
9	4	4	—	40
10	4	4	116	97
11	4	4	—	39
12	4	4	—	27
1	5	4	446	511
2	5	4	—	58
3	5	4	401	419
4	5	4	124	111
5	5	4	329	341
6	5	4	—	56
7	5	4	234	276
8	5	4	125	108
9	5	4	209	221
10	5	4	102	82
11	5	4	150	193
0	6	4	142	133
1	6	4	100	50
2	6	4	—	42
3	6	4	—	26
4	6	4	96	57
5	6	4	102	71
6	6	4	—	77
7	6	4	114	78
8	6	4	77	65
9	6	4	95	77
10	6	4	72	62
11	6	4	—	15
1	7	4	214	217
2	7	4	238	263
3	7	4	219	213
4	7	4	—	59
5	7	4	211	245
6	7	4	129	132
7	7	4	197	219
8	7	4	93	93
9	7	4	67	106
10	7	4	48	58
0	8	4	198	238
1	8	4	100	58
2	8	4	—	75
3	8	4	—	54
4	8	4	87	98
5	8	4	89	51
6	8	4	106	101
7	8	4	81	38
8	8	4	66	65
9	8	4	—	21
1	9	4	254	299
2	9	4	107	102
3	9	4	248	259
4	9	4	—	45
5	9	4	178	150
6	9	4	—	22
7	9	4	122	149
8	9	4	—	5
0	10	4	85	56
1	10	4	—	46
2	10	4	—	29

Table 3 (*cont.*)

h	k	l	$10F_o$	$10F_c$
3	10	4	—	70
4	10	4	67	39
5	10	4	57	44
6	10	4	57	81
1	11	4	80	84
2	11	4	—	41
3	11	4	86	99
4	11	4	—	21
0	0	5	730	752
2	0	5	436	389
4	0	5	279	265
6	0	5	362	398
8	0	5	271	276
10	0	5	182	150
12	0	5	80	82
1	1	5	434	443
2	1	5	238	226
3	1	5	296	278
4	1	5	170	132
5	1	5	226	182
6	1	5	—	53
7	1	5	236	256
8	1	5	167	186
9	1	5	170	177
10	1	5	—	8
11	1	5	133	176
12	1	5	—	55
0	2	5	427	408
1	2	5	262	240
2	2	5	309	285
3	2	5	216	201
4	2	5	233	200
5	2	5	175	165
6	2	5	219	251
7	2	5	97	84
8	2	5	208	204
9	2	5	—	79
10	2	5	134	130
11	2	5	—	24
12	2	5	74	131
1	3	5	348	360
2	3	5	229	249
3	3	5	238	251
4	3	5	141	93
5	3	5	244	266
6	3	5	181	215
7	3	5	214	234
8	3	5	—	43
9	3	5	149	159
10	3	5	—	26
11	3	5	—	56
12	3	5	—	67
0	4	5	362	336
1	4	5	129	118
2	4	5	283	243
3	4	5	—	96
4	4	5	283	289
5	4	5	—	73
6	4	5	348	405
7	4	5	—	73
8	4	5	229	239
9	4	5	—	33
10	4	5	—	8
11	4	5	—	34
1	5	5	295	282
2	5	5	153	171
3	5	5	222	216
4	5	5	—	58
5	5	5	237	290
6	5	5	—	76
7	5	5	206	256
8	5	5	118	83
9	5	5	120	86
10	5	5	96	123
11	5	5	—	80
0	6	5	365	409
1	6	5	164	140
2	6	5	199	168
3	6	5	161	140
4	6	5	184	153
5	6	5	—	64
6	6	5	153	161
7	6	5	—	84
8	6	5	165	181
9	6	5	—	35
10	6	5	95	90
1	7	5	116	108
2	7	5	141	111
3	7	5	126	176
4	7	5	144	145
5	7	5	150	130
6	7	5	—	60
7	7	5	—	57
8	7	5	112	107
9	7	5	—	51
0	8	5	225	243
1	8	5	130	133
2	8	5	194	217
3	8	5	111	95
4	8	5	159	193
5	8	5	134	133
6	8	5	139	113
7	8	5	—	64
8	8	5	104	133
1	9	5	175	205
2	9	5	110	115
3	9	5	167	157
4	9	5	—	32
5	9	5	101	51
6	9	5	—	45
7	9	5	—	65
0	10	5	134	116
1	10	5	—	62
2	10	5	110	111
3	10	5	85	85
4	10	5	84	77
5	10	5	—	65
1	11	5	—	84
0	0	6	580	556
2	0	6	315	304
4	0	6	225	183
6	0	6	294	340
8	0	6	195	226
10	0	6	117	135
1	1	6	256	240
2	1	6	118	90
3	1	6	114	81
4	1	6	119	94
5	1	6	—	36
6	1	6	129	121
7	1	6	110	145
8	1	6	—	83
9	1	6	121	130
10	1	6	—	71
11	1	6	—	22
0	2	6	388	345
1	2	6	162	139
2	2	6	300	304
3	2	6	149	97
4	2	6	256	264
5	2	6	114	124
6	2	6	238	264
7	2	6	—	69
8	2	6	180	202
9	2	6	—	63
10	2	6	99	110
11	2	6	—	41
1	3	6	211	196
2	3	6	154	141
3	3	6	138	79
4	3	6	—	89
5	3	6	160	168
6	3	6	—	56
7	3	6	162	170
8	3	6	—	76
9	3	6	—	42
10	3	6	—	85
11	3	6	—	40
0	4	6	274	227
1	4	6	151	98
2	4	6	278	270
3	4	6	126	80
4	4	6	286	323
5	4	6	—	56
6	4	6	175	209
7	4	6	—	23
8	4	6	135	128
9	4	6	—	12
10	4	6	94	132
1	5	6	137	120
2	5	6	—	90
3	5	6	132	75
4	5	6	—	97
5	5	6	—	12
6	5	6	—	72
7	5	6	—	54
8	5	6	—	64
9	5	6	80	104
10	5	6	—	24
0	6	6	214	250
1	6	6	83	98
2	6	6	209	221
3	6	6	103	64
4	6	6	219	244
5	6	6	—	75
6	6	6	186	220
7	6	6	—	22
8	6	6	107	129
9	6	6	—	84
1	7	6	135	156
2	7	6	—	104
3	7	6	120	125
4	7	6	—	56
5	7	6	—	68
6	7	6	—	31
7	7	6	—	58
8	7	6	—	68
0	8	6	182	184
1	8	6	—	31
2	8	6	142	152
3	8	6	—	59
4	8	6	142	138
5	8	6	—	40
6	8	6	98	91
7	8	6	—	49
1	9	6	—	34
2	9	6	—	34
3	9	6	67	96
4	9	6	—	46
5	9	6	58	94
0	10	6	75	136
1	10	6	—	53
2	10	6	—	157

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

			$-A_{hh}$	$-A_{kk}$	$-A_{ll}$	A_{hk}	A_{hl}	A_{kl}
Mn(*D*)	obs.	52·9	551	559	354	−5	0	0
	calc.	55·4	561	568	373	−2	0	0
O(1*D*)	obs.	12·1	117	111	78	−1	4	−3
	calc.	12·8	117	114	81	−2	4	−3
C(2*D*)	obs.	9·3	96	90	58	−10	−4	0
	calc.	9·8	96	94	61	−8	−4	−1
N(3*D*)	obs.	11·5	117	112	71	7	5	5
	calc.	11·9	116	111	75	7	3	6
N(4*D*)	obs.	11·3	104	100	69	−12	−6	−2
	calc.	11·4	105	101	71	−11	−6	−2
O(5*D*)	obs.	12·8	116	129	74	1	−2	−2
	calc.	13·3	118	135	79	1	−1	−2
H_2O(6*D*)	obs.	12·7	117	97	76	−1	5	2
	calc.	13·1	120	97	80	−1	4	1
Mn(*C*)	obs.	52·8	545	561	355	13	0	0
	calc.	55·3	557	569	371	10	0	0
O(1*C*)	obs.	12·3	114	115	79	11	−4	−8
	calc.	13·1	119	117	83	10	−2	−8
C(2*C*)	obs.	9·6	102	98	55	−1	2	3
	calc.	9·8	102	97	57	−1	2	3
N(3*C*)	obs.	10·3	104	84	55	9	−4	8
	calc.	10·8	102	87	60	8	−3	8
N(4*C*)	obs.	10·7	114	84	63	−1	−3	−4
	calc.	11·0	116	88	65	0	−3	−5
O(5*C*)	obs.	11·2	95	98	62	6	−3	0
	calc.	11·5	99	96	65	8	−2	1
H_2O(7)	obs.	11·3	108	95	63	−3	−10	−2
	calc.	11·7	109	99	67	−2	−9	−2
e.s.d.		0·5	7	7	4	4	3	3

respondingly the form  $-\mathrm{C}\begin{matrix}{}^{/\!/\,\mathrm{O}}\\{}_{\backslash\,\mathrm{O}}\end{matrix}$ seems to give the largest contribution to the resonance bond state of the carboxylato group.

The analysis of the planarity (Table 7) shows that each chelate ring as a whole is non-planar. Some of the atoms, however, around Mn(*C*), namely O(1*C*), C(2*C*), N(3*C*) lie in the same plane as O(5*C*), while N(4*C*) and Mn(*C*) are out of this plane. The same situation had been found also in complexes of type *C* with cadmium (Braibanti, Tiripicchio, Manotti Lanfredi & Bigoli, 1966), in complexes of type *A* (Ferrari, Braibanti, Bigliardi & Lanfredi, 1965), and in complexes of type *B* (Braibanti, Manotti Lanfredi & Tiripicchio, 1966). The metal atom, in particular, is always out of the plane. In the complex around Mn(*D*), the chelate ring is again non-planar but no group of four atoms lying in the same plane has been found. The chelate rings formed by semicarbazide with zinc and

Table 5. *Bond lengths* (*with e.s.d.'s*)

Mn(*D*)-O(1*D*)	2·145 ±	0·018 Å	Mn(*C*)-O(1*C*)	2·138 ±	0·014 Å
Mn(*D*)-N(4*D*)	2·189	0·016	Mn(*C*)-N(4*C*)	2·208	0·016
Mn(*D*)-H$_2$O(6*D*)	2·213	0·016	Mn(*C*)-O(5*D*)	2·248	0·014
O(1*D*) -C(2*D*)	1·314	0·022	O(1*C*) -C(2*C*)	1·317	0·023
C(2*D*) -N(3*D*)	1·360	0·023	C(2*C*) -N(3*C*)	1·452	0·025
N(3*D*) -N(4*D*)	1·435	0·023	N(3*C*) -N(4*C*)	1·366	0·026
C(2*D*) -O(5*D*)	1·209	0·019	C(2*C*) -O(5*C*)	1·192	0·023

Table 6. *Bond angles with e.s.d.'s*

O(1*D*)——Mn(*D*)-H$_2$O(6*D*)	86·8 ±	0·7°	O(1*C*) -Mn(*C*)-N(4*C*)	75·6 ±	0·5°
O(1*D*)——Mn(*D*)-N(4*D*)	75·2	0·6	N(4*C*) -Mn(*C*)-O(5*D*)	90·8	0·5
O(1*D*)——Mn(*D*)-H$_2$O(6*D*) ($\bar{x}$, $1-y$, z)	103·1	0·7	O(1*C*) -Mn(*C*)-O(5*D*)	91·4	0·5
O(1*D*)——Mn(*D*)-N(4*D*) ($\bar{x}$, $1-y$, z)	96·2	0·6	O(5*D*) -Mn(*C*)-O(5*D*) ($\bar{x}$, $\bar{y}$, z)	90·6	0·5
N(4*D*)——Mn(*D*)-H$_2$O(6*D*)	88·6	0·6	N(4*C*) -Mn(*C*)-N(4*C*) ($\bar{x}$, $\bar{y}$, z)	88·4	0·6
N(4*D*)——Mn(*D*)-N(4*D*) ($\bar{x}$, $1-y$, z)	98·9	0·6	O(1*C*) -Mn(*C*)-O(5*D*) ($\bar{x}$, $\bar{y}$, z)	98·9	0·5
H$_2$O(6*D*)-Mn(*D*)-H$_2$O(6*D*) ($\bar{x}$, $1-y$, z)	83·8	0·6	O(1*C*) -Mn(*C*)-N(4*C*) ($\bar{x}$, $\bar{y}$, z)	93·8	0·5
Mn(*D*)——O(1*D*) -C(2*D*)	118·9	1·1	Mn(*C*)-O(1*C*) -C(2*C*)	119·2	1·1
O(1*D*)——C(2*D*) -N(3*D*)	114·4	1·4	O(1*C*) -C(2*C*) -N(3*C*)	113·6	1·5
C(2*D*)——N(3*D*) -N(4*D*)	120·7	1·5	C(2*C*) -N(3*C*) -N(4*C*)	120·1	1·8
N(3*D*)——N(4*D*) -Mn(*D*)	109·9	1·1	N(3*C*) -N(4*C*) -Mn(*C*)	111·4	1·2
O(1*D*)——C(2*D*) -O(5*D*)	125·4	1·6	O(1*C*) -C(2*C*) -O(5*C*)	121·7	1·8
O(5*D*)——C(2*D*) -N(3*D*)	118·7	1·7	O(5*C*) -C(2*C*) -N(3*C*)	124·4	1·9

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

Best plane through		Complex *D*	Complex *C*	
		N(3)C(2)O(1)O(5)	N(4)N(3)C(2)O(1)O(5)	N(3)C(2)O(1)O(5)
m_1		0·62730	0·52038	0·53336
m_2		−0·02884	0·43295	0·42530
m_3		0·77824	0·73603	0·73119
d		3·91903	1·70974	1·66617
Δ	O(1)	−0·0158 Å	0·0019 Å	0·0048 Å
	C(2)	0·0733	−0·0377	−0·0335
	N(3)	−0·0185	−0·0142	0·0116
	O(5)	−0·0168	0·0214	0·0102
	N(4)	(−0·0035)	0·0119	(0·0543)
$\Sigma\,(\Delta/\sigma_{\perp})^2$		19·953	6·252	3·714
$\chi_{95\%}{}^2$		3·841	5·991	3·841
Δ	N(4)	−0·0035 Å	0·0119 Å	0·0543 Å
	Mn	0·0737	0·1558	0·1871

Equation of plane: $m_1X+m_2Y+m_3Z=d$
$\sigma_{\perp}=[m_1{}^2\sigma^2(X)+m_2{}^2\sigma^2(Y)+m_3{}^2\sigma^2(Z)]^{\frac{1}{2}}$ (Å).

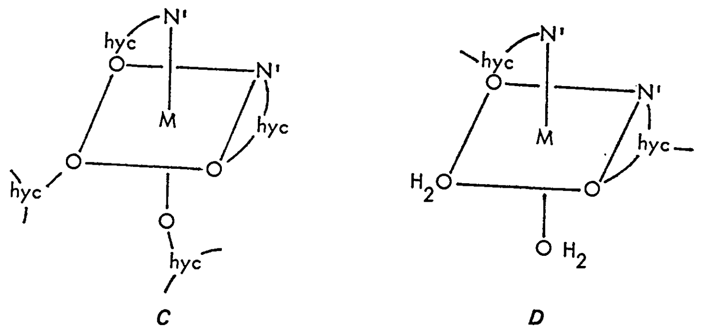


Fig. 3. Types of complexes in the crystal structure of Mn(II)hyc$_2$.2H$_2$O. *C*: *trans,cis,cis*-[Mn(hyc)$_2$(O-hyc)$_2$]. *D*: *trans,cis,cis*-[Mn(hyc)$_2$(OH$_2$)$_2$].

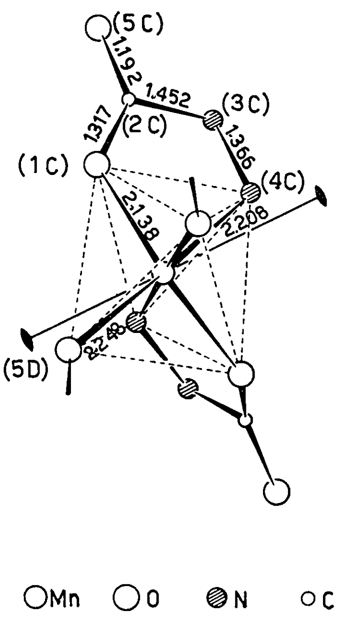


Fig. 4. Complex of *C* type. Atoms O(5*D*) belong to hyc groups of complexes of *D* type.

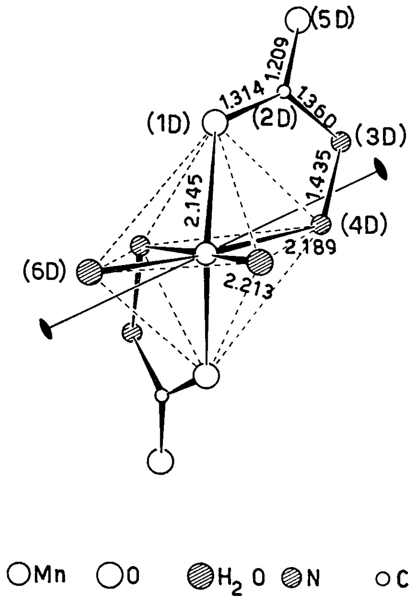


Fig. 5. Complex of *D* type.

copper (Nardelli, Fava Gasparri, Boldrini & Giraldi Battistini, 1965) are also non-planar with the metal atom lying out of the plane of the chelate ring. Again the metal atom is out of the plane in the copper(II) complex with hydroxyquinoline (Palenik, 1964*a*) and in the corresponding zinc compound (Palenik, 1964*b*). The absence of planarity indicates that the rings possess no 'aromatic' character.

Table 8. *Hydrogen bonds* (*with e.s.d.'s*)

$O(5C)\cdots N(4D)$ $(\bar{x}, 1-y, z)$	$3{\cdot}045 \pm 0{\cdot}024$ Å
$N(3D)\cdots O(1C)$ $(\frac{1}{2}+x, \frac{1}{2}-y, z)$	$2{\cdot}813 \pm 0{\cdot}021$
$O(5C)$ $(\bar{x}, 1-y, z)\cdots N(4C)$ $(\frac{1}{2}-x, \frac{1}{2}+y, z)$	$3{\cdot}005 \pm 0{\cdot}022$
$H_2O(7)\cdots H_2O(6D)$	$2{\cdot}740 \pm 0{\cdot}020$
$H_2O(7)\cdots O(5D)$ $(\frac{1}{2}-x, \frac{1}{2}+y, z)$	$2{\cdot}739 \pm 0{\cdot}023$
$H_2O(7)\cdots N(4C)$ $(\frac{1}{2}-x, \frac{1}{2}+y, 1+z)$	$3{\cdot}234 \pm 0{\cdot}026$

The intermolecular distances (Table 8) indicate that the water molecule $H_2O(7)$ forms rather strong hydrogen bonds, $H_2O(7)\cdots OH_2(6D) = 2{\cdot}740$ Å and $H_2O(7)\cdots O(5D) = 2{\cdot}739$ Å, with two complexes belonging to different chains (Fig. 6). Other hydrogen bonds are formed either between different chains, $N(3D)\cdots O(1C) = 2{\cdot}813$ Å, which is particularly strong, and $O(5C)\cdots N(4C) = 3{\cdot}005$ Å or between complexes of the same chain, $O(5C)\cdots N(4D) = 3{\cdot}045$ Å. The network of hydrogen bonds is responsible for the stability of the crystals.

We wish to thank the Consiglio Nazionale delle Ricerche, Rome, for financial aid.

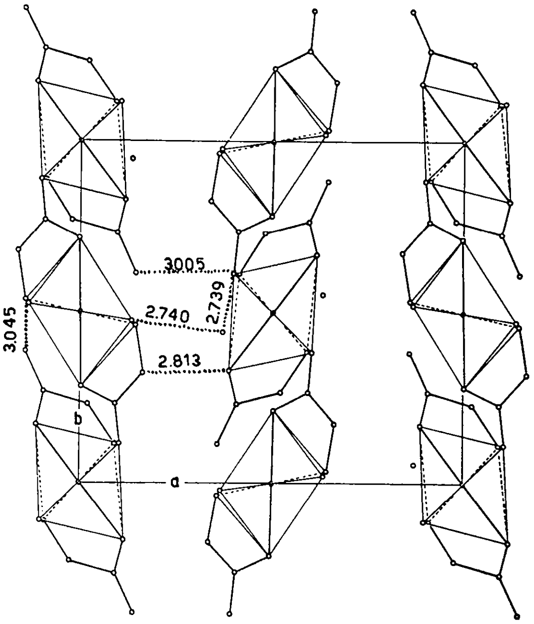


Fig. 6. Interchain and intrachain hydrogen bonds.

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