The Crystal Structure of Strontium Dipicolinate Tetrahydrate, Sr.C$_7$H$_3$NO$_4$.4H$_2$O

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The crystal structure of strontium dipicolinate tetrahydrate has been determined and refined on the basis of data collected by an automatic diffractometer. Crystals are monoclinic, space group $C2/c$, with cell dimensions $a=10\cdot698$, $b=12\cdot827$, $c=8\cdot394$ Å, $\beta=98\cdot75°$; there are four molecules per unit cell. The structure was determined by interpretation of the Patterson function and was refined by least-squares methods to an R index of 0·044. The dipicolinate ion is coordinated to the strontium ion as a tridentate ligand. The strontium ion is coordinated to eight oxygen atoms and one nitrogen atom. Two of the eight oxygen atoms belong to carboxyl groups of the same dipicolinate ion; two others belong to carboxyl groups of two additional dipicolinate ions; the four remaining oxygen atoms are in water molecules. The structure consists of a continuous ribbon of alternately oriented dipicolinate ions, coordinately bonded to strontium ions. There are four hydrogen bonds per asymmetric unit between carboxyl oxygen atoms and water oxygen atoms. Three of them are between oxygen atoms in the same dipicolinate ribbon. The fourth links two oxygen atoms in adjacent ribbons.

Introduction

The heat resistance and metabolic dormancy of bacterial spores are thought to rest on, yet undefined, morphological structures in association with the biologically unusual spore component calcium dipicolinate (Ca.DPA) (Murrell, Ohye & Gordon, 1969). Insight as to the role of Ca.DPA has been sought through replacement of Ca^{2+} or DPA^{2-} by other metal or ligand ions for sporulation (Slepecky, 1961; Fukuda, Gilvarg & Lewis, 1969) and for Ca.DPA-induced germination (Riemann & Ordal, 1961; Jaye & Ordal, 1965; Lewis, 1969). For example, Sr^{2+} substitutes for Ca^{2+}, and 4H-pyran-2,6-dicarboxylate (PDC) substitutes for DPA. The presence of a dimeric linkage Ca–O, O'–Ca' in the crystals of Ca.DPA.3H$_2$O (Strahs & Dickerson, 1968) and the isostructural Ca.PDC.3H$_2$O (Palmer & Lee, 1969), and the complete interchangeability of these compounds in sporulation and germination, have led to a hypothesis that Ca.DPA serves as a readily mobilizable structure-locking component of the dormant bacterial spore (Lewis, 1969). A search for similar linkages in active and inactive analogues of Ca.DPA has led to the finding (reported here) of a related polymeric linkage in the crystalline tetrahydrate of the active compound strontium dipicolinate (Sr.DPA.4H$_2$O).

Experimental

Crystals of strontium dipicolinate tetrahydrate were grown from saturated water solutions. The crystals are bipyramids, slightly elongated along **c**. The density, measured by suspension in a mixture of benzene and dibromomethane, is 1·89 g.cm^{-3}. There are four molecules in the unit cell.

Zero- and upper-level Weissenberg and precession photographs indicated Laue symmetry 2/m. Reflections hkl were observed only when $h+k=2n$, and $h0l$ reflections were observed only when $l=2n$. These restrictions are compatible with either space group Cc or $C2/c$. The structure was successfully solved in $C2/c$. The unit-cell dimensions were refined by high-angle θ–2θ scans with a 1° take-off angle. The crystal data are summarized in Table 1.

Table 1. *Crystal data*

Sr.C$_7$H$_3$NO$_4$.4H$_2$O	F.W. 324·74
Monoclinic	Space group $C2/c$
$a=10\cdot698$ (5) Å	$Z=4$
$b=12\cdot827$ (6)	$F(000)=322\cdot56$
$c=\ \ 8\cdot394$ (4)	$\varrho_m=1\cdot89$ g.cm^{-3}
$\beta=98\cdot75$ (1)°	$\varrho_c\ =1\cdot878$ g.cm^{-3}
λ Cu $K\alpha_1=1\cdot54051$ Å	

Intensity data were obtained from a small crystal, measuring about 0·1 mm on a side. A four-circle diffractometer, equipped with a full-circle goniostat and controlled by a time-sharing computer, was used. The Ni-filtered Cu radiation was detected by a scintillation counter equipped with a single-channel pulse-height analyzer. Data were recorded for angles up to $2\theta=145°$ using the θ–2θ scanning technique. The scan rate was 1° min^{-1} (in 2θ). Backgrounds were measured 0·5° on each side of the scan limits. The net intensity I was calculated by the expression $I=C-(B_1+B_2)(T_c/2T_b)$, where C is the total scan count in time T_c, and B_1 and B_2 are the two backgrounds each counted for $T_b=$ 10 sec.

Three standard reflections were measured every 48 reflections; no significant change in their intensities

was noted. 2804 reflections were measured, of which 1135 were independent. Eight reflections had $I < \sigma(I)$ and were given zero weight in the least-squares refinement of the parameters.

Variances $\sigma^2(I)$ were calculated from $\sigma^2(I) = [C + (T_c/2T_b)^2 (B_1 + B_2) + (0.05I)^2]$, where the factor 0.05 was arbitrarily chosen to accommodate systematic errors. The intensities and their standard devia-

Table 2. *Positional and thermal parameters* ($Å^2$)

Standard deviations are in parentheses. Symmetry of the special positions of Sr, N, and C(4) restricts $B_{12} = B_{23} = 0$. Anisotropic temperature factor has the form: $T = \exp[-\frac{1}{4} \sum \sum B_{ij}h_ih_j/(b_ib_j)]$, where h_i is the ith Miller index, b_i is the ith reciprocal axis length, and i and j are cycled 1 through 3. Isotropic temperature factor has the form: $T = \exp[-B(\sin\theta/\lambda)^2]$.

|	10^4x	10^4y	10^4z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Sr	0	125·4 (2)	$\frac{1}{4}$	2·48 (2)	1·40 (2)	1·37 (2)	0	−0·00 (1)	0
N	0	2184 (3)	$\frac{1}{4}$	2·1 (1)	1·7 (1)	1·9 (1)	0	0·14 (9)	0
O(1)	1409 (2)	2503 (2)	6553 (3)	5·8 (1)	2·4 (1)	2·22 (9)	−1·06 (9)	−0·85 (9)	−0·36 (8)
O(2)	651 (2)	1087 (2)	5215 (2)	3·63 (8)	1·87 (8)	2·02 (8)	−0·50 (6)	0·04 (7)	−0·03 (6)
O(3)	−2314 (2)	791 (2)	2941 (3)	3·28 (9)	2·4 (1)	2·5 (1)	0·63 (8)	0·20 (7)	0·22 (8)
O(4)	−2073 (2)	−1007 (2)	1226 (3)	3·6 (1)	3·3 (1)	2·25 (9)	−0·24 (8)	0·26 (8)	−0·08 (8)
C(1)	876 (2)	2048 (2)	5324 (3)	2·7 (1)	2·0 (1)	1·9 (1)	−0·22 (8)	0·12 (8)	0·02 (9)
C(2)	436 (2)	2713 (2)	3838 (3)	2·26 (9)	1·8 (1)	2·1 (2)	−0·05 (7)	0·32 (8)	−0·02 (3)
C(3)	474 (3)	3789 (2)	3881 (4)	3·1 (1)	1·8 (1)	2·8 (1)	−0·19 (9)	0·4 (1)	−0·35 (9)
C(4)	0	4338 (4)	$\frac{1}{4}$	3·1 (2)	1·5 (1)	3·3 (2)	0	0·6 (1)	0
H(1)	0	500 (4)	$\frac{1}{4}$	2·9 (16)					
H(2)	86 (4)	422 (4)	489 (6)	3·9 (9)					
H(3)	−253 (5)	122 (4)	253 (6)	4·4 (14)					
H(4)	−234 (4)	84 (4)	394 (6)	3·6 (9)					
H(5)	−254 (4)	−67 (4)	167 (6)	3·6 (9)					
H(6)	−185 (5)	−158 (5)	188 (7)	5·9 (13)					
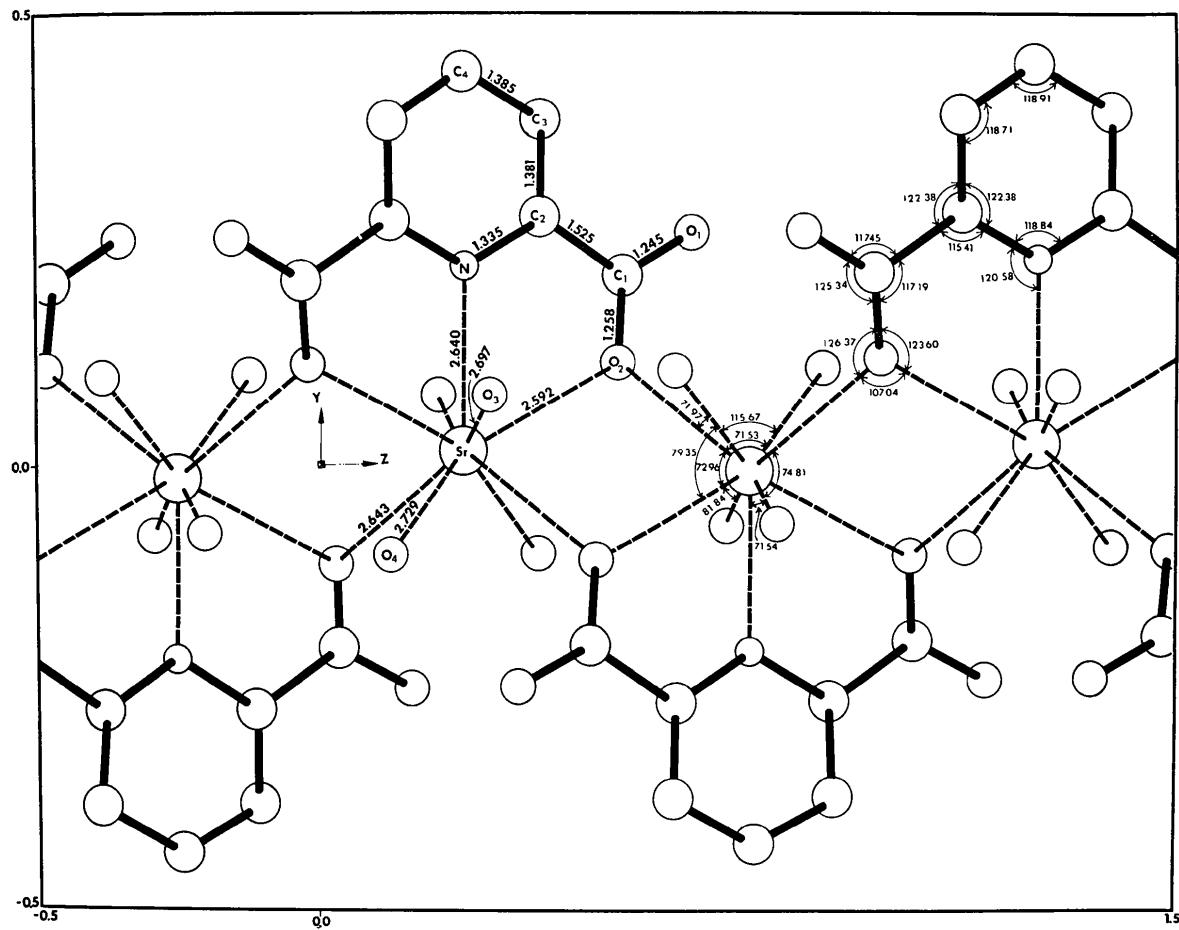
Fig. 1. Projection of structure down a. Sr, N, and C(4) lie on a twofold axis. The numbering of atoms, bond lengths, and bond angles is also shown.

tions were corrected for Lorentz and polarization factors, but not for absorption ($\mu = 7{\cdot}54\ \mathrm{cm}^{-1}$).

A full-matrix least-squares program was used which minimizes the function $\sum w(\Delta F)^2/\sum wF_o^2$; F_o and F_c are the observed and calculated structure factors, $\Delta F = |F_o| - |F_c|$, and w is a weighting factor taken equal to $1/\sigma^2(F)$. The value of $\sigma(F)$ was calculated by the expression $\sigma(F) = F_o - [F_o^2 - \sigma(F_o^2)]^{1/2}$, when $I > \sigma(I)$, and w was set equal to zero when $I \le \sigma(I)$. The least-squares program accommodates both real and imaginary parts of the dispersion correction.

Scattering factors for all atoms except hydrogen were taken from the tables published by Cromer & Waber (1965). The scattering factors for hydrogen were those published by Stewart, Davidson & Simpson (1965). The real and imaginary dispersion corrections for strontium are $-0{\cdot}73$ and $2{\cdot}0$ respectively (Cromer, 1965).

Determination of the structure

Since there are four molecules in the unit cell, they occupy either general positions in *Cc* or a special position in *C*2/*c*. A straightforward interpretation of a three-dimensional Patterson function indicated that Sr and two other heavy atoms lie on twofold axes and thus occupy special positions (*e*) in *C*2/*c*. Approximate values for the *y* parameters of these three atoms were obtained from the Patterson function.

A least-squares refinement of the parameters for these three atoms, followed by a Fourier difference calculation, led to the determination of approximate parameters for all heavy atoms in the asymmetric unit. Three cycles of least-squares refinement with isotropic temperature factors led to an *R* index, defined as $R = \sum|\Delta F|/\sum|F_o|$, of 0·108. When anisotropic temperature factors were used, *R* decreased to 0·051. A dif-

Table 3. *Observed and calculated structure factors* (× 10) *for strontium dipicolinate tetrahydrate*

FCA(0,0,0) = 3226.

L	FOB	FCA
H,K= 0, 0		
2	970	708
4	512	460
6	342	316
8	458	456
10	196	208
H,K= 0, 2		
0	377	334
1	113	110
2	880	689
3	740	604
4	732	643
5	95	88
6	454	430
7	29	21
8	246	242
9	84	81
10	141	147
H,K= 0, 4		
0	367	347
1	231	215
2	942	749
3	182	170
4	417	374
5	142	137
6	345	329
7	25	12
8	229	226
9	20	21
H,K= 0, 6		
0	348	315
1	421	362
2	335	302
3	174	161
4	499	453
5	165	155
6	366	351
7	182	181
8	153	152
9	111	116
H,K= 0, 8		
0	577	547
1	303	270
2	250	232
3	38	37
4	115	106
5	172	163
6	185	176
7	152	149
8	245	248
H,K= 0, 10		
0	395	407
1	165	156
2	117	106
3	372	352
4	309	296
5	245	233
6	178	178
7	168	174
H,K= 0, 12		
0	184	182
1	228	207
2	293	285
3	258	250
4	126	107
5	163	165
6	84	87
H,K= 0, 14		
0	83	86
1	253	249
2	182	179
3	224	220
4	170	166
H,K= 1, 1		
-10	197	205
-9	70	67
-8	267	262
-7	191	162
-6	121	114
-5	66	61
-4	637	574
-3	55	41
-2	476	405
-1	417	410
0	642	777
1	6	3
2	445	382
3	251	244
4	789	691
5	16	10
6	485	459
7	322	310
8	291	291
9	20	20
10	200	210
H,K= 1, 3		
-10	166	174
-9	19	12
-8	249	243
-7	54	54
-6	462	440
-5	14	12
-4	173	169
-3	317	295
-2	708	644
-1	104	104
0	377	426
1	697	552
2	783	646
3	762	629
4	311	295
5	41	40
6	372	351
7	30	27
8	292	290
9	53	52
H,K= 1, 5		
-9	72	68
-8	261	260
-7	91	92
-6	550	525
-5	226	210
-4	585	522
-3	350	323
-2	566	537
-1	299	296
0	422	484
1	207	204
2	827	684
3	223	205
4	380	342
5	335	301
6	282	269
7	240	238
8	201	201
9	136	139
H,K= 1, 7		
-9	169	173
-8	229	227
-7	101	96
-6	367	356
-5	145	144
-4	352	331
-3	280	260
-2	483	454
-1	224	236
0	309	335
1	314	294
2	362	343
3	222	206
4	218	209
5	234	224
6	170	164
7	30	24
8	198	200
9	109	109
H,K= 1, 9		
-8	190	193
-7	161	162
-6	143	139
-5	252	243
-4	526	499
-3	331	323
-2	269	263
-1	292	302
0	382	403
1	137	133
2	236	218
3	59	57
4	440	415
5	227	216
6	217	212
7	163	164
8	139	137
H,K= 1, 11		
-7	258	258
-6	81	82
-5	161	161
-4	75	76
-3	170	166
-2	190	168
-1	282	293
0	288	307
1	253	246
2	130	122
3	313	303
4	143	139
5	38	39
6	219	209
7	170	168
H,K= 1, 13		
-5	217	217
-4	43	41
-3	205	209
-2	167	167
-1	136	130
0	71	66
1	170	163
2	227	222
3	195	197
4	150	139
5	169	170
H,K= 1, 15		
-3	167	166
-2	40	35
-1	196	199
0	70	70
1	261	262
2	88	90
3	260	249
H,K= 2, 0		
-10	220	229
-8	546	532
-6	258	248
-4	716	670
-2	228	219
0	848	865
2	362	316
4	791	705
6	624	608
8	223	225
H,K= 2, 2		
-10	211	218
-9	14	7
-8	161	158
-7	122	98
-6	333	323
-5	84	77
-4	618	571
-3	300	294
-2	713	682
-1	98	94
0	230	250
1	177	183
2	333	313
3	368	332
4	473	444
5	221	210
6	325	313
7	144	125
8	319	326
9	69	72
H,K= 2, 4		
-10	195	199
-9	94	93
-8	308	305
-7	101	99
-6	530	509
-5	28	22
-4	272	262
-3	149	139
-2	505	522
-1	117	129
0	621	715
1	47	48
2	1191	958
3	130	111
4	488	440
5	36	27
6	311	300
7	123	117
8	238	238
9	76	80
H,K= 2, 6		
-9	95	97
-8	123	120
-7	131	128
-6	318	313
-5	184	176
-4	382	366
-3	289	289
-2	590	627
-1	236	246
0	480	550
1	180	181
2	506	472
3	204	188
4	202	193
5	206	250
6	218	201
7	106	106
8	225	229
9	101	107
H,K= 2, 8		
-8	231	233
-7	92	93
-6	216	212
-5	133	131
-4	217	211
-3	354	350
-2	276	282
-1	232	247
0	432	461
1	331	319
2	319	306
3	66	58
4	348	325
5	306	299
6	228	225
7	86	87
8	118	125
H,K= 2, 10		
-8	146	146
-7	145	153
-6	46	47
-5	334	327
-4	382	376
-3	345	342
-2	223	226
-1	299	314
0	256	262
1	309	303
2	110	102
3	479	450
4	208	200
5	170	165
6	236	230
7	131	131
H,K= 2, 12		
-6	168	170
-5	177	177
-4	104	81
-3	156	153
-2	94	93
-1	351	341
0	30	18
1	254	229
2	185	200
3	253	247
4	222	201
5	120	121
6	68	74
H,K= 2, 14		
-4	95	90
-3	189	188
-2	150	154
-1	181	181
0	115	120
1	254	250
2	121	114
3	170	171
4	57	57
H,K= 3, 1		
-10	152	159
-9	131	131
-8	306	303
-7	77	55
-6	413	398
-5	46	44
-4	854	793
-3	23	18
-2	213	227
-1	1129	1157
0	248	280
1	111	127
2	634	570
3	140	127
4	391	371
5	126	121
6	241	231
7	174	168
8	159	164
9	30	36
H,K= 3, 3		
-10	216	222
-9	107	108
-8	240	230
-7	174	171
-6	361	354
-5	203	201
-4	179	188
-3	90	93
-2	613	671
-1	185	216
0	538	601
1	235	248
2	275	279
3	39	37
4	377	364
5	24	23
6	307	297
7	112	111
8	271	278
9	28	35
H,K= 3, 5		
-9	132	134
-8	248	248
-7	134	133
-6	270	264
-5	161	155
-4	243	240
-3	320	329
-2	602	661
-1	381	426
0	583	647
1	295	293
2	537	518
3	38	37
4	415	387
5	68	63
6	441	437
7	102	105
8	273	281
9	128	130
H,K= 3, 7		
-9	28	29
-8	140	140
-7	140	141
-6	209	205
-5	312	313
-4	176	180
-3	240	246
-2	328	353
-1	197	197
0	417	441
1	320	316
2	369	349
3	388	374
4	389	374
5	296	285
6	261	253
7	25	24
8	233	235
H,K= 3, 9		
-8	155	159
-7	92	93
-6	203	204
-5	44	45
-4	469	468
-3	217	224
-2	150	154
-1	225	240
0	237	252
1	359	362
2	466	446
3	163	157
4	332	318
5	203	197
6	200	200
7	149	152
H,K= 3, 11		
-7	144	145
-6	136	137
-5	179	180
-4	171	158
-3	83	86
-2	178	183
-1	324	335
0	174	180
1	104	105
2	116	116
3	317	305
4	111	112
5	204	200
6	130	133
H,K= 3, 13		
-5	115	119
-4	102	94
-3	185	185
-2	173	173
-1	225	220
0	103	102
1	199	197
2	74	74
3	122	124
4	94	91
5	90	95
H,K= 3, 15		
-2	89	88
-1	139	144
0	77	77
1	184	186
2	38	41
H,K= 4, 0		
-10	103	108
-8	449	440
-6	404	401
-4	653	652
-2	859	928
0	896	891
2	747	727
4	341	321
6	548	564
8	189	205
H,K= 4, 2		
-10	180	186
-9	24	25
-8	210	212
-7	84	69
-6	372	368
-5	290	286
-4	383	385
-3	118	122
-2	378	431
-1	354	402
0	775	812
1	119	129
2	732	685
3	288	278
4	386	373
5	17	11*
6	128	122
7	19	13
8	205	214
9	12	4
H,K= 4, 4		
-9	47	46
-8	194	194
-7	41	42
-6	338	335
-5	35	38
-4	459	470
-3	250	264
-2	497	561
-1	220	240
0	210	231
1	62	63
2	241	248
3	47	53
4	500	485
5	78	73
6	389	398
7	69	68
8	272	279
H,K= 4, 6		
-9	83	89
-8	153	155
-7	162	162
-6	184	186
-5	175	172
-4	189	190
-3	154	167
-2	201	228
-1	167	174
0	229	245
1	323	331
2	311	308
3	170	163
4	324	323
5	196	192
6	181	173
7	71	68
8	109	195
H,K= 4, 8		
-8	191	193
-7	189	190
-6	179	176
-5	20	21
-4	217	225
-3	165	170
-2	221	226
-1	50	52
0	201	204
1	276	282
2	104	97
3	58	46
4	251	242
5	159	155
6	294	288
7	155	158
H,K= 4, 10		
-7	142	144
-6	132	134
-5	298	295
-4	173	173
-3	136	139
-2	180	183
-1	163	165
0	275	286
1	212	212
2	365	361
3	357	347
4	69	69
5	155	157
6	141	140
H,K= 4, 12		
-6	178	181
-5	171	173
-4	195	185
-3	170	173
-2	141	142
-1	332	310
0	152	151
1	109	95
2	134	134
3	191	187
4	168	165
5	176	172
H,K= 4, 14		
-4	103	103
-3	247	246
-2	178	183
-1	194	195
0	169	169
1	222	221
2	154	150
3	192	187
H,K= 5, 1		
-10	113	118
-9	123	124
-8	237	238
-7	49	51
-6	251	250
-5	81	85
-4	250	265
-3	74	78
-2	363	409
-1	307	332
0	543	575
1	33	27
2	628	660
3	250	258
4	262	264
5	189	188
6	347	363
7	18	14
8	218	234
H,K= 5, 3		
-9	37	38
-8	193	194
-7	70	69
-6	243	245
-5	156	164
-4	335	352
-3	125	130
-2	360	396
-1	124	134
0	416	439
1	41	40
2	181	191
3	272	273
4	440	440
5	117	115
6	251	251
7	123	106
8	193	205
H,K= 5, 5		
-9	99	102
-8	213	213
-7	123	123
-6	357	361
-5	79	78
-4	425	451
-3	109	112
-2	420	453
-1	194	203
0	238	260
1	366	384
2	350	349
3	293	285
4	375	375
5	190	192
6	199	201
7	90	89
8	188	197
H,K= 5, 7		
-8	183	184
-7	173	173
-6	242	246
-5	154	154
-4	309	323
-3	224	239
-2	241	256
-1	100	111
0	265	279
1	265	267
2	154	157
3	23	23
4	243	244
5	110	104
6	165	164
7	138	141
H,K= 5, 9		
-8	189	188
-7	210	210
-6	248	247
-5	69	72
-4	244	243
-3	177	181
-2	233	243
-1	167	179
0	259	272
1	162	169
2	414	412
3	119	118
4	107	107
5	103	102
6	185	183
H,K= 5, 11		
-6	60	59
-5	259	257
-4	73	72
-3	175	180
-2	215	224
-1	279	281
0	195	196
1	50	48
2	122	124
3	135	135
4	139	135
5	164	165
H,K= 5, 13		
-5	144	148
-4	96	97
-3	129	130
-2	92	90
-1	118	116
0	159	159
1	179	182
2	107	109
3	226	224
H,K= 6, 0		
-8	275	274
-6	143	147
-4	234	250
-2	843	926
0	243	253
2	304	321
4	258	260
6	478	514
8	218	234
H,K= 6, 2		
-9	27	25
-8	220	223
-7	5	8*
-6	293	302
-5	203	206
-4	304	318
-3	258	263
-2	126	138
-1	111	114
0	299	314
1	102	99
2	388	405
3	134	137
4	373	385
5	17	4
6	255	264
7	15	9
8	170	178
H,K= 6, 4		
-9	27	27
-8	182	184
-7	49	48
-6	309	313
-5	13	9
-4	370	400
-3	59	63
-2	374	401
-1	29	30
0	524	553
1	16	16
2	338	349
3	109	114
4	289	290
5	30	25
6	157	161
7	79	81
8	243	252
H,K= 6, 6		
-9	102	106
-8	162	163
-7	100	100
-6	323	326
-5	88	89
-4	307	317
-3	227	238
-2	144	152
-1	152	157
0	338	359
1	165	173
2	366	379
3	70	70
4	290	292
5	200	204
6	87	86
7	92	96
H,K= 6, 8		
-8	146	144
-7	132	130
-6	83	81
-5	22	25
-4	230	235
-3	303	308
-2	390	398
-1	237	243
0	273	286
1	114	115
2	132	132
3	95	96
4	139	140
5	129	126
6	200	204
H,K= 6, 10		
-7	151	156
-6	141	142
-5	309	303
-4	99	101
-3	181	179
-2	240	240
-1	241	243
0	76	78
1	286	289
2	238	238
3	240	237
4	144	148
5	118	117
H,K= 6, 12		
-5	187	187
-4	110	110
-3	138	141
-2	55	53
-1	226	220
0	156	157
1	193	185
2	73	74
3	186	185
4	94	96
H,K= 6, 14		
-2	43	46
-1	136	140
0	82	84
H,K= 7, 1		
-9	124	125
-8	184	186
-7	15	14
-6	324	331
-5	95	98
-4	291	312
-3	100	101
-2	347	367
-1	70	66
0	136	141
1	35	33
2	334	343
3	37	38
4	201	207
5	176	178
6	220	224
7	17	16
H,K= 7, 3		
-9	83	83
-8	210	211
-7	93	96
-6	152	155
-5	79	77
-4	300	319
-3	52	51
-2	257	273
-1	163	167
0	371	382
1	88	86
2	176	189
3	19	24
4	282	288
5	86	87
6	209	214
7	20	22
H,K= 7, 5		
-8	189	187
-7	137	138
-6	250	249
-5	162	168
-4	219	227
-3	195	203
-2	303	314
-1	91	92
0	480	490
1	72	74
2	349	353
3	94	98
4	313	326
5	144	153
6	173	180
7	103	104
H,K= 7, 7		
-8	137	136
-7	108	107
-6	113	114
-5	103	104
-4	229	227
-3	168	175
-2	225	229
-1	115	121
0	326	329
1	250	253
2	201	240
3	153	160
4	214	215
5	67	67
6	210	213
H,K= 7, 9		
-7	77	78
-6	248	241
-5	106	106
-4	169	166
-3	189	186
-2	231	230
-1	161	164
0	160	163
1	73	76
2	348	347
3	233	233
4	154	160
5	178	178
H,K= 7, 11		
-5	120	119
-4	135	134
-3	122	124
-2	190	189
-1	216	216
0	46	44
1	219	219
2	52	52
3	124	123
4	122	120
H,K= 7, 13		
-3	81	81
-2	34	35
-1	119	119
0	114	116
1	112	121
H,K= 8, 0		
-8	161	160
-6	332	340
-4	321	337
-2	571	585
0	255	270
2	454	462
4	342	343
6	173	175
H,K= 8, 2		
-9	60	61
-8	182	180
-7	45	47
-6	262	265
-5	70	71
-4	332	343
-3	43	47
-2	263	275
-1	142	148
0	308	308
1	159	159
2	295	302
3	86	86
4	178	182
5	29	30
6	208	212
7	12	12*
H,K= 8, 4		
-8	200	200
-7	35	33
-6	162	159
-5	67	65
-4	211	211
-3	86	90
-2	245	250
-1	166	169
0	411	417
1	11	10*
2	229	230
3	40	37
4	293	278
5	34	35
6	179	185
H,K= 8, 6		
-8	137	137
-7	105	105
-6	138	134
-5	108	109
-4	166	164
-3	183	182
-2	135	137
-1	70	72
0	230	226
1	170	174
2	127	128
3	136	136
4	185	188
5	95	97
6	190	195
H,K= 8, 8		
-7	67	66
-6	84	81
-5	85	86
-4	140	135
-3	105	104
-2	184	182
-1	84	86
0	95	101
1	35	39
2	205	206
3	199	200
4	167	168
5	102	106
H,K= 8, 10		
-5	156	156
-4	122	124
-3	73	75
-2	194	190
-1	146	149
0	72	72
1	244	243
2	156	157
3	134	136
4	116	121
H,K= 8, 12		
-3	143	150
-2	56	57
-1	144	146
0	159	163
1	122	124
H,K= 9, 1		
-8	128	128
-7	62	52
-6	265	257
-5	16	9
-4	136	132
-3	239	244
-2	260	262
-1	40	40
0	329	328
1	25	27
2	348	348
3	15	8
4	185	189
5	133	135
6	166	171
H,K= 9, 3		
-8	154	151
-7	11	8
-6	104	100
-5	54	50
-4	279	276
-3	53	53
-2	244	241
-1	79	78
0	209	204
1	99	104
2	198	198
3	108	110
4	223	220
5	115	111
6	182	185
H,K= 9, 5		
-7	56	56
-6	180	175
-5	84	84
-4	287	281
-3	161	161
-2	228	224
-1	162	160
0	228	229
1	128	127
2	125	126
3	107	104
4	259	262
5	103	104
H,K= 9, 7		
-7	164	164
-6	120	118
-5	95	92
-4	195	189
-3	13	13
-2	180	178
-1	96	93
0	129	127
1	178	178
2	151	146
3	131	129
4	111	110
H,K= 9, 9		
-5	122	123
-4	84	83
-3	101	101
-2	161	159
-1	134	133
0	202	202
1	33	31
2	218	214
3	86	87
H,K= 9, 11		
-3	158	160
-2	130	130
-1	64	66
0	99	97
1	121	123
H,K= 10, 0		
-6	191	185
-4	202	199
-2	286	279
0	200	198
2	223	221
4	331	325
H,K= 10, 2		
-7	34	36
-6	157	149
-5	4	6*
-4	128	124
-3	12	7*
-2	213	211
-1	61	60
0	246	244
1	103	99
2	235	230
3	15	13
4	106	105
5	61	58
H,K= 10, 4		
-7	27	27
-6	181	177
-5	39	39
-4	283	273
-3	14	7
-2	179	174
-1	8	9*
0	213	211
1	11	8*
2	184	186
3	61	58
4	232	233
5	81	78
H,K= 10, 6		
-6	145	142
-5	46	47
-4	191	185
-3	99	99
-2	162	160
-1	99	101
0	220	211
1	102	101
2	167	153
3	109	106
4	95	93
H,K= 10, 8		
-5	104	106
-4	148	145
-3	101	98
-2	187	181
-1	169	154
0	72	68
1	26	26
2	153	152
3	87	83
H,K= 10, 10		
-3	113	115
-2	132	133
-1	159	159
0	153	153
H,K= 11, 1		
-7	32	31
-6	160	152
-5	19	21
-4	135	128
-3	95	96
-2	197	190
-1	51	44
0	179	175
1	45	43
2	110	109
3	66	62
4	139	140
H,K= 11, 3		
-6	126	122
-5	63	62
-4	185	177
-3	17	8
-2	168	164
-1	33	35
0	120	114
1	52	50
2	195	190
3	17	15
4	146	142
H,K= 11, 5		
-6	138	139
-5	70	69
-4	212	202
-3	84	84
-2	138	135
-1	85	88
0	258	250
1	68	68
2	202	197
3	74	75
H,K= 11, 7		
-4	118	115
-3	65	66
-2	171	165
-1	155	147
0	129	121
1	53	55
2	180	176
H,K= 12, 0		
-4	308	296
-2	196	190
0	153	148
2	145	144
H,K= 12, 2		
-5	18	18
-4	112	103
-3	32	30
-2	183	173
-1	52	51
0	163	159
1	63	62
2	156	155
H,K= 12, 4		
-4	145	141
-3	49	46
-2	148	144
-1	26	24
0	180	172
1	48	46
2	139	138
H,K= 12, 6		
-3	71	71
-2	91	87
-1	84	84
0	151	146
H,K= 13, 1		
-3	59	57
-2	129	123
-1	16	8
0	175	166

ference map led to the determination of approximate parameters for all six hydrogen atoms. Three additional cycles of least-squares refinement led to an R index of 0·049.

An inspection of the results revealed that the very intense reflections had $F_o \ll F_c$. An extinction correction of the form $F_{corr} = SF[1 + (EF)I]F_o$ (Zachariasen, 1963), where SF is the scale factor, and EF the extinction factor, was applied to the data and led to a significant improvement between calculated and observed structure factors.

An extinction factor of 6×10^{-7} resulted in a final R index of 0·044.

The effects of using scattering factors for neutral Sr and O versus Sr^{2+} and $O(2)^-$ were compared and found to be essentially the same. Values listed for positional and thermal parameters and their standard deviations (Table 2), and observed and calculated structure factors (Table 3), were calculated with atomic scattering factors for Sr^{2+}, $O(2)^-$, and O(1) neutral.

Discussion of the structure

The numbering system used in this study and the interatomic distances and angles for the heavy atoms are shown in Fig. 1. Bond distances involving the hydrogen atoms are listed in Table 4. The estimated standard deviations of the distances are 0·003 Å for Sr–O, 0·004 Å for Sr–N, C–N, C–C, & C–O, and 0·10 Å for H–C and H–O bonds; corresponding e.s.d.'s in the angles involving heavy atoms are about 0·10°.

Table 4. *Bond distances*
and angles involving hydrogen atoms

E.s.d.'s are 0·10 Å and 3·0°.

H(1)–C(4)	0·84 Å	H(1)–C(4)–C(3)	120°
H(2)–C(3)	1·04	H(2)–C(3)–C(4)	117
H(3)–O(3)	0·67	H(2)–C(3)–C(2)	123
H(4)–O(3)	0·84	H(3)–O(3)–H(4)	112
H(5)–O(4)	0·80	H(5)–O(4)–H(6)	106
H(6)–O(4)	0·92		

The dipicolinate ion is coordinated to the strontium ion as a tridendate ligand. The coordination around the strontium ion consists of nine atoms: four carboxyl oxygen atoms, four water oxygen atoms, and nitrogen. The four carboxyl oxygen atoms belong to three dipicolinate ions, and each carboxyl oxygen atom is in turn bonded to two strontium ions. This leads to continuous ribbons composed of oppositely oriented
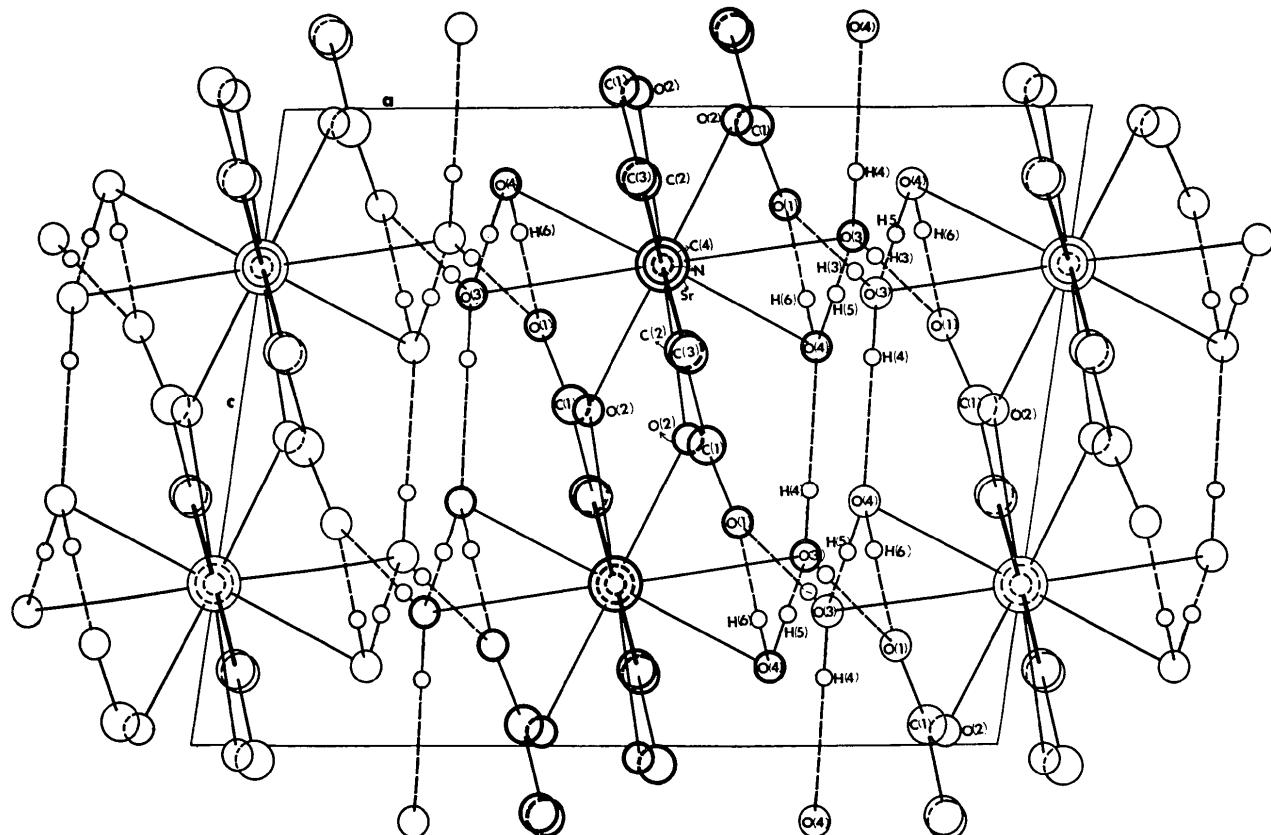

Fig. 2. Projection of structure onto the (101) plane. The six-membered rings are seen edge-on in a direction parallel to the C(2)–C(3) bond. The nitrogen atoms lie directly above (or below) the strontium ions. The atoms shown as thick circles belong to one ribbon of dipicolinate ions. The origin of the unit cell is the upper left-hand corner.

dipicolinate ions bonded together through strontium ions, as shown in Fig. 1. The discrete dimers that occur in Ca.DPA.3H$_2$O (Strahs & Dickerson, 1968) are not present in Sr.DPA.4H$_2$O.

The dipicolinate ribbons run parallel to the c axis; adjacent ribbons in the a-axis direction are related by the twofold screw axes parallel to the b axis. Consequently, carboxyl groups of adjacent ribbons are bonded to strontium ions translated $\pm\frac{1}{2}y$ from those shown in Fig. 1. This results in sheets composed of water molecules, carboxyl oxygen atoms, and strontium ions parallel to the ac plane. One such sheet is shown edgeon in Fig. 1.

The packing and bonding in strontium dipicolinate are illustrated in Figs. 1 and 2.
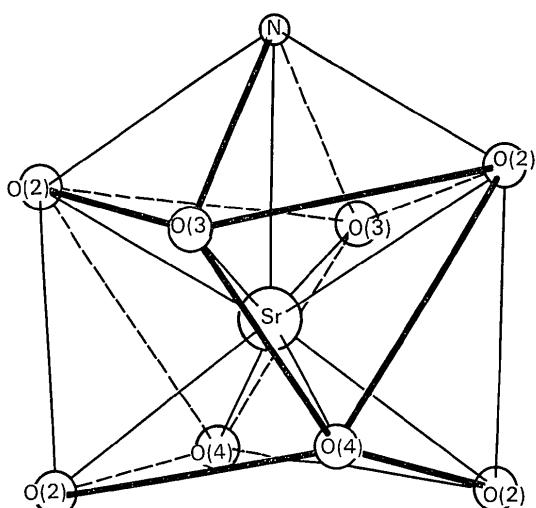
Fig. 3. Packing of nine atoms around the strontium ion to form monocapped square antiprism. O(2) designates carboxyl oxygen atoms; O(3) and O(4) are water oxygen atoms.
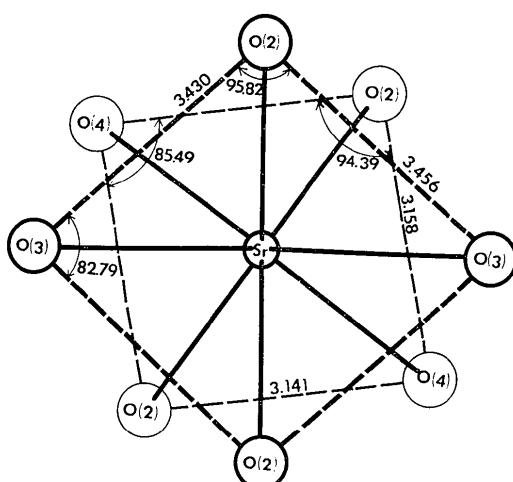
Fig. 4. Arrangement of oxygen atoms around the strontium ion as viewed down the twofold N–Sr axis. The interatomic distances and angles between the oxygen atoms are shown.

The bond distances and angles found for the dipicolinate group agree well with those reported for Ca.DPA.3H$_2$O (Strahs & Dickerson, 1968). The nine atoms consisting of the pyridine ring, C(1), C(1') and Sr are coplanar as required by the twofold axis passing through Sr, N, and C(4). The four atoms C(1), C(2), O(1), and O(2) are also coplanar; the out-of-plane distances of these atoms from their least-squares plane are given in Table 5. The dihedral angle between these two planes, i.e., the twist about the C(1)–C(2) bond, is 9·1°.

Table 5. Planarity of the carboxyl group
in Sr.DPA.4H$_2$O

The values are the out-of-plane distances of atoms of the carboxyl group and C(2) from their least-squares plane. The dihedral angle between the plane of the pyridine ring and the carboxyl group is 9·1°.

C(1)	0·006 Å
C(2)	−0·002
O(1)	−0·002
O(2)	−0·002

Two different Sr–O(2) distances occur in the crystal. The distance between the strontium ion and the carboxyl oxygen atoms of the same dipicolinate ion is slightly shorter (2·592 Å) than the distance between the strontium ion and the two carboxyl oxygen atoms from different dipicolinate ions (2·643 Å). Another manifestation of this is shown by the angle 115·4° for C(1)–C(2)–N. A similar value for this angle (114·9°) was found in Ca.DPA. The approximate equivalence of the C–O bond lengths indicates an ionic structure for the carboxyl group and about 50% double-bond character for the C–O bonds. The nine atoms coordinated to strontium form a distorted, monocapped square antiprism. The arrangement of these nine atoms around the strontium ion is shown in Fig. 3. The interatomic distances and angles between the oxygen atoms of the antiprism are shown in Fig. 4.

There are four hydrogen bonds per asymmetric unit in the crystal. They are shown as dashed lines in Fig. 2. The positions of the hydrogen atoms forming the hydrogen bonds are also shown. The hydrogen-bond distances are given in Table 6, and from their magnitudes it is concluded they are relatively strong.

Table 6. Hydrogen bond distances and angles

	O–O distance	Angle
O(1)–H(3)–O(3)	2·743 Å	165°
O(3)–H(4)–O(4)	2·744	169
O(3)–H(5)–O(4)	2·752	132
O(1)–H(6)–O(4)	2·695	168

Each water molecule is involved in three hydrogen bonds and one coordinate bond to Sr (Fig. 2). Of the four crystallographically distinct hydrogen bonds, one occurs between oxygen atoms of the same antiprism, O(3)–O(4), one between oxygen atoms of adjacent

antiprisms but belonging to the same dipicolinate ribbon, O(3)–O(4), one between O(1) and O(4) where again both oxygen atoms belong to the same dipicolinate ribbon, and one between O(3) and O(1) where the two oxygen atoms belong to adjacent ribbons. This latter hydrogen bond is the only bond between atoms of adjacent dipicolinate ribbons.

Each carboxyl oxygen atom is involved in three bonds. O(2) has two coordinate bonds to strontium ions and a covalent bond to C(1); O(1) is covalently bonded to C(1) and forms hydrogen bonds with two water molecules. The carboxyl oxygen atoms in $Ca.DPA.3H_2O$ (Strahs & Dickerson, 1968) also form three bonds.

The shortest contact distances between heavy atoms of different molecules are 3·398 Å for C(4)–O(3) and 3·488 Å for C(4)–O(4). All other contact distances are greater than 3·5 Å. The Sr–Sr distance is 4·209 Å.

The anisotropic thermal parameters shown in Table 2 are all quite small, including those for the water oxygen atoms. These values suggest that the heavy atoms are rather firmly bound in the crystal. Although the coordination of the cations in $Sr.DPA$ and $Ca.DPA$ is different in the crystalline state, it is evident that both compounds are capable of forming strong bonds to polar groups. This fact probably accounts for the ability of strontium dipicolinate to replace calcium dipicolinate in certain spores (Slepecky, 1961) with only a small reduction in heat resistance and metabolic inertness.

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Etude Structurale du Violurate de Cuivre, $(C_4O_4N_3H_2)_2Cu. 4H_2O$

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Copper(II) violurate tetrahydrate crystallizes in the triclinic system, space group $P\bar{1}$ with one molecule in the unit cell of dimensions $a = 12·66$, $b = 5·14$, $c = 6·36$ Å, $\alpha = 102°$, $\beta = 112°$, $\gamma = 93°$. The violurate anions are almost planar. The copper coordination has been shown to be a distorted octahedron. It consists of two water molecules [O(5) atoms at 2·06 Å] and two oxime nitrogen [N(3) atoms at 1·97 Å] in a planar square configuration and of two more distant neighbours, ketonic oxygen [O(3) atoms at 2·21 Å]. The molecules are linked together by a hydrogen bond network.

L'acide violurique, dont la structure a été déterminée de façon précise (Craven & Mascarenhas, 1964), est représenté par la formule développée suivante:
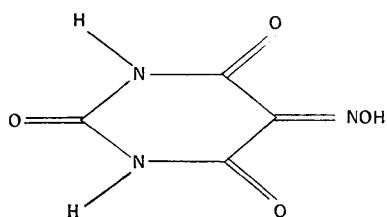
Cet acide donne des sels très bien cristallisés et de colorations variées pouvant servir à des tests pour l'identification de cations minéraux (van Ligten & van Velthuyzen, 1964).

L'étude structurale de ces composés a été abordée par Gillier (1965) avec le violurate de rubidium et le violurate dihydraté de potassium.

En choisissant des métaux bivalents, il était, en outre, intéressant d'établir le mode de fixation des cations aux anions violurates. Nous avons indiqué antérieurement les configurations moléculaires des violurates de strontium et de cuivre (Hamelin, 1967, 1968).