Acta Cryst. (1967). **22**, 366

X-ray Crystal Analysis of the Substrates of Aconitase. VII. The Structure of Lithium Ammonium Hydrogen Citrate Monohydrate*

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(*Received* 27 *April* 1966)

The structure of the diionized salt, lithium ammonium hydrogen citrate, $Li(NH_4)H(C_6O_7H_5).H_2O$, has been determined by the symbolic addition procedure. The data, collected by counter techniques, were refined by least squares to an R value of 0·043. The space group is $P2_1/a$ and the cell dimensions are $a=23{\cdot}195$, $b=6{\cdot}446$, $c=6{\cdot}508$ Å, $\beta=99{\cdot}02°$, with four molecules in the unit cell. The ionization in this crystalline form occurs in the central and one of the terminal carboxyl groups. The backbone of the citrate ion is fully extended in a plane roughly perpendicular to that of the hydroxyl group and the central carboxyl group. The lithium ion is tetrahedrally coordinated by oxygen atoms in four different citrate ions, the ammonium ion is surrounded by oxygen atoms, ten at distances less than 3·4 Å and the water molecule participates in three hydrogen bonds.

Introduction

The space group, cell dimensions, densities and method of crystallization of the isomorphous pair of salts, lithium ammonium hydrogen citrate monohydrate and lithium rubidium hydrogen citrate monohydrate, have been described by Love & Patterson (1960). The determination of the structure of the ammonium salt, $Li(NH_4)H(C_6O_7H_5).H_2O$, was undertaken to establish which of the three carboxyl groups are ionized and to find if the stereochemistry is similar to that of previously determined monoionized and triionized citrates (Glusker, van der Helm, Love, Dornberg, Minkin, Johnson & Patterson, 1965; Johnson, 1965*a*). Both cations in this salt contain only atoms with low atomic numbers, permitting an accurate analysis to be made.

Experimental

Crystals of both salts can be grown as needles by layering a stoichiometric aqueous solution under ethanol (Love & Patterson, 1960). The space group is $P2_1/a$ and the cell dimensions of the ammonium salt, measured on a General Electric XRD-5 goniometer, are given in Table 1. The density shows that this salt crystallizes as a monohydrate.

Table 1. *Cell data for* $Li(NH_4)H(C_6O_7H_5).H_2O$

a	$=23{\cdot}195\pm0{\cdot}011$ Å
b	$=6{\cdot}446\pm0{\cdot}002$
c	$=6{\cdot}508\pm0{\cdot}002$
β	$=99{\cdot}02°\pm0{\cdot}05°$
λ(Cu $K\alpha_1$)	$=1{\cdot}54050$ Å
ϱ(obs)	$=1{\cdot}617$ g.cm^{-3}*
ϱ(calc)	$=1{\cdot}611$ g.cm^{-3}
μ	$=13{\cdot}4$ cm^{-1}

* Love & Patterson, 1960.

* Work supported by grants AM 02884 and CA 06927 from the National Institutes of Health, U.S. Public Health Service. A preliminary report on this work was presented at a meeting of the American Crystallographic Association, Gatlinburg, Tennessee, June 27–July 2, 1965 (Paper G5).

Intensity data were collected on the diffractometer with the moving-crystal moving-counter technique ($\theta/2\theta$ scan) and Cu $K\alpha$ radiation. The crystal used, which was approximately a cube of side 0·22 mm, was cut from a needle with a solvent saw. For this crystal $\mu R\sim0{\cdot}18$ and therefore no corrections for absorption were thought to be necessary. 2102 reflections were accessible to measurement ($2\theta\leq165°$) and Lorentz and polarization corrections were applied to the data so obtained.

During the data reduction process the data were analyzed in the following way to determine whether the difference between the peak and background counts was significant.

If P is the peak count and mb the background count (where b is measured for $1/m$th of the time that P was measured)

$$I=P-mb$$

$$\sigma^2(I)=\left(\frac{\partial I}{\partial P}\right)^2\sigma^2(P)+\left(\frac{\partial I}{\partial b}\right)^2\sigma^2(b)=P+m^2b$$

(since $\sigma^2(P)=P$, *etc.*). If I is significant at a certain level (arbitrarily chosen as 1%)

$$\frac{I^2}{\sigma^2(I)}=\frac{(P-mb)^2}{(P+m^2b)}\geq(2{\cdot}33)^2\,.$$

If this condition is true the reflection is considered observed. On this basis 170 (8·1%) of the reflections were considered to be unobserved and these were given values of $I=(2{\cdot}33/3)\sqrt{(P+m^2b)}$, *i.e.* one-third of the value which is just significant. (It was subsequently shown from the structure refinement results that values of $|F_o|$ chosen for unobserved reflections in this way gave $\Sigma|F_o|/\Sigma|F_c|\simeq1$.) Least-squares weights were calculated on a similar basis taking into account errors introduced by counting statistics, instrumental in-

stability and filter factors (Johnson, 1965*a*). In the measurements m is chosen so that the length of time spent measuring the background is the minimum consistent with the condition that the variance of the background is always less than the variance of the peak, *i.e.* $m^2b < P$ (Mack & Spielberg, 1958).

Structure determination

The structure was solved by the symbolic addition procedure (Karle & Karle, 1963). The statistical averages and the distribution of the normalized structure factors are given in Table 2.

Table 2. *Statistical data for the symbolic addition procedure*

(*a*) Statistical averages for the normalized structure factors (E)

	$\langle\|E\|\rangle$	$\langle\|E^2-1\|\rangle$
Lithium ammonium citrate	0·822	0·936
Theoretical: centrosymmetric crystal	0·798	0·968
noncentrosymmetric crystal	0·886	0·736

(*b*) Distribution of structure factors

	Experimental	Theoretical
$E>3$	0·2 %	0·3 %
$E>2$	4·2 %	5·0 %
$E>1$	32·9 %	32·0 %

288 terms with E greater than 1·5 were used in the sign determination procedure. Signs of all of these were obtained with the intermediate use of one letter which was quickly found to be minus. A superposition of sections in the resulting Fourier map using E values as coefficients is shown in Fig. 1. It was subsequently shown that all the signs indicated by the symbolic addition procedure were correct and all the highest peaks in the E-map represented atomic positions. The first structure factor calculation gave $R=0{\cdot}28$ and the resulting Fourier map confirmed the atomic arrangement.

It was not possible at this stage or even after several cycles of refinement to distinguish between the ammonium ion and the water molecule. Therefore the $h0l$ data for the rubidium salt were estimated visually from Weissenberg photographs, and the rubidium ion, which replaces the ammonium ion, was located from the $|F|^2$ map.

Refinement of the structure

The structure was refined by block-diagonal least-squares and difference Fourier methods. In the least-squares the quantity $\Sigma w(k|F_o|-|F_c|)^2$ was minimized. The weights, which are listed in Table 4, were calculated from the counting statistics as explained earlier.

Table 3. *Final positional and temperature parameters*

Positional parameters are given as fractions of cell edges. Anisotropic temperature factors are expressed as

$$\exp\{-(h^2b_{11}+2hkb_{12}+2hlb_{13}+k^2b_{22}+2klb_{23}+l^2b_{33})\}.$$

Isotropic temperature factors are of the form $\exp(-B\sin^2\theta/\lambda^2)$ and are given in Å^2.

(As a is much greater than b or c the estimated standard deviations are difficult to present here. They are listed in Table 5 and indicate that, in Table 3, the last digit given for a parameter is only significant for x and b_{11} for the heavier atoms. All digits are listed because they were input to the final structure factor and angles and distances programs.)

	x	y	z	b_{11}	b_{12}	b_{13}	b_{22}	b_{23}	b_{33}
O(1)	0·3301	1·0476	0·6036	0·00116	−0·00054	0·00160	0·01757	−0·00686	0·01407
O(2)	0·4192	1·0486	0·5204	0·00088	−0·00062	0·00032	0·02005	−0·00480	0·01312
O(3)	0·3189	0·3124	−0·1139	0·00114	−0·00112	0·00206	0·01478	−0·00908	0·02398
O(4)	0·4075	0·4345	−0·1265	0·00090	−0·00002	0·00150	0·01203	−0·00539	0·02244
O(5)	0·4299	0·9704	0·0092	0·00118	−0·00074	0·00082	0·01941	0·00998	0·02000
O(6)	0·4799	0·7387	0·2146	0·00059	0·00002	0·00063	0·01296	0·00163	0·01940
O(7)	0·3894	0·5862	0·3466	0·00088	−0·00006	0·00063	0·01302	0·00504	0·01267
C(1)	0·3661	1·0095	0·4802	0·00087	0·00026	0·00052	0·00898	−0·00154	0·01044
C(2)	0·3401	0·9183	0·2715	0·00070	0·00078	0·00017	0·01441	−0·00404	0·01134
C(3)	0·3754	0·7427	0·1914	0·00061	0·00006	0·00042	0·00867	−0·00038	0·00861
C(4)	0·3368	0·6556	−0·0026	0·00068	0·00021	0·00004	0·01113	−0·00328	0·01213
C(5)	0·3584	0·4583	−0·0858	0·00084	0·00000	0·00020	0·01060	−0·00212	0·00939
C(6)	0·4334	0·8234	0·1344	0·00073	−0·00036	0·00054	0·00956	−0·00110	0·00918
O(W)	0·2833	0·4287	0·4027	0·00136	0·00164	0·00464	0·03019	0·02378	0·06041
N(1)	0·4996	0·6953	0·6917	0·00130	0·00020	0·00086	0·01277	0·00051	0·01421

	x	y	z	B	Attached to
Li	0·4429	0·1640	0·8024	1·91	
H(1)	0·3046	0·8671	0·2950	3·9	C(2)
H(2)	0·3343	1·0290	0·1631	2·6	C(2)
H(3)	0·2987	0·6265	0·0309	3·2	C(4)
H(4)	0·3339	0·7554	−0·1137	3·3	C(4)
H(5)	0·3528	0·5477	0·3701	5·1	O(7)
H(6)	0·3392	0·2105	−0·1533	6·1	O(3)
H(7)	0·5289	0·7775	0·6799	7·7	N(1)
H(8)	0·5151	0·5781	0·7070	6·5	N(1)
H(9)	0·4730	0·6819	0·5887	8·1	N(1)
H(10)	0·4767	0·7674	0·7881	7·8	N(1)
H(11)	0·2907	0·3166	0·4602	8·0	O(W)
H(12)	0·2469	0·4640	0·3966	5·7	O(W)

Table 4. *Observed and calculated structure factors and weights used in the least-squares refinement*

Each entry lists, in order, h, k, l, $10|F_o|$, $10|F_c|$ and the weight. The values of $10|F_o|$ do not have an extinction correction applied to them. Unobserved reflections are denoted by an asterisk.

H, 0, 0

2	311	379	73
4	622	-910	18
6	366	429	49
8	184	-187	460
10	199	170	384
12	498	525	83
14	252	233	232
16	16	16	49*
18	127	137	1181
20	235	-248	710
22	82	-82	985
24	45	45	953
26	93	-89	1726
28	6	-7	67*

H, 1, 0

1	155	-176	733
2	232	-266	373
3	89	-83	3769
4	344	-402	56
5	217	232	393
6	215	201	385
7	168	185	515
8	319	-335	62
9	731	870	13
10	352	-354	50
11	37	-31	1425
12	37	-47	1372
13	320	-313	177
14	46	-49	738
15	186	-185	1061
16	92	-82	1156
17	97	-105	1178
18	108	-117	1155
19	184	189	895
20	246	-254	218
21	176	179	807
22	8	0	38*
23	24	13	315
24	183	180	979
25	109	-106	1310
26	56	-56	1176
27	49	50	1769
28	41	41	1805
29	35	-29	3508

H, 2, 0

0	402	457	42
1	179	185	1687
2	324	-367	192
3	194	-195	1476
4	625	-777	18
5	192	203	419
6	546	-605	72
7	55	62	2025
8	215	-204	339
9	195	-186	369
10	132	-115	1640
11	74	-70	1817
12	128	131	1507
13	93	-139	1600
14	212	205	279
15	149	146	1269
16	230	-229	244
17	70	67	1055
18	90	-83	1112
19	85	-74	1090
20	40	31	853
21	53	-53	1011
22	61	56	1128
23	99	96	1060
24	62	62	1233
25	32	-32	1078
26	7	7	49*
27	69	-70	1968
28	89	86	3098

H, 3, 0

1	372	-389	144
2	281	291	230
3	227	240	306
4	113	119	1970
5	245	-253	272
6	132	134	1726
7	207	-212	324
8	80	-76	1698
9	96	93	1596
10	170	170	1193
11	279	-288	204
12	34	27	858
13	99	-106	1388
14	186	185	972
15	31	30	589
16	237	246	734
17	107	-114	1085
18	48	51	882
19	102	102	1053
20	121	-118	1067
21	80	78	1153
22	102	-101	1244
23	108	-105	1159
24	166	166	346
25	96	-92	1938
26	55	53	1780
27	10	-6	589

H, 4, 0

0	278	284	212
1	17	4	296
2	192	190	1107
3	16	-10	381
4	48	-28	1108
5	101	97	1588
6	97	94	1476
7	43	-50	1109
8	158	150	1178
9	175	174	319
10	37	-36	806
11	7	-5	49*
12	28	-31	553
13	110	-116	1140
14	125	124	1071
15	235	241	747
16	97	97	1198
17	95	-101	1043
18	184	-181	281
19	96	-99	1082
20	141	-142	1163
21	79	81	1361
22	41	36	1231
23	29	28	1085
24	6	9	67*
25	65	61	2736

H, 5, 0

1	73	-72	1217
2	139	145	1211
3	34	32	697
4	106	-108	1145
5	299	314	574
6	33	-37	476
7	211	214	253
8	85	-82	1065
9	63	-64	1014
10	184	-189	909
11	127	131	1083
12	102	-98	1114
13	27	22	499
14	149	153	974
15	48	-48	916
16	26	28	360
17	26	18	548
18	120	-124	1257
19	7	10	49*
20	66	-68	1597
21	45	41	1709
22	71	-68	2293
23	39	41	2955

H, 6, 0

0	65	-65	1138
1	68	65	1110
2	20	-6	213
3	32	34	609
4	47	50	915
5	9	5	30*
6	46	48	728
7	9	-6	30*
8	163	-163	984
9	52	-46	1106
10	133	-135	1148
11	46	-47	910
12	47	47	622
13	56	-55	1073
14	109	108	1326
15	6	3	67*
16	148	145	1405
17	13	-13	216
18	6	-5	67*
19	37	-34	1750
20	16	17	631

H, 7, 0

1	136	-133	1243
2	167	173	1138
3	32	-29	798
4	72	-75	1464
5	63	65	1316
6	82	-79	1371
7	6	-1	67*
8	61	63	1201
9	154	-154	1339
10	79	83	1610
11	15	13	315
12	95	96	1773
13	43	42	1406
14	6	3	67*
15	70	-72	2319

H, 8, 0

0	118	-116	2210
1	24	-20	1272
2	9	-5	277
3	52	50	2371
4	20	7	1019
5	42	46	1384
6	15	20	222

H, 0, 1

-28	62	-58	1579
-26	26	-30	714
-24	21	20	579
-22	22	-18	465
-20	251	-263	661
-18	168	-171	1082
-16	7	21	49*
-14	15	-17	436
-12	177	173	1303
-10	759	-913	12
-8	422	-452	37
-6	66	57	3156
-4	383	-448	46
-2	10	-28	407
0	123	118	3479
2	422	495	39
4	17	-20	948
6	11	10	522
8	344	-380	169
10	202	343	1257
12	170	177	1318
14	6	-26	67*
16	195	183	956
18	36	42	858
20	269	271	621
22	85	-92	1003
24	284	-284	636
26	34	-35	1242
28	11	-9	755

H, 1, 1

-29	67	-70	2652
-28	127	-127	1746
-27	105	-103	1770
-26	40	-37	1113
-25	30	28	643
-24	159	-159	1076
-23	218	218	825
-22	228	-234	769
-21	116	113	1073
-20	24	-27	362
-19	326	-333	502
-18	15	-6	178
-17	84	-77	1359
-16	149	146	1170
-15	34	-36	974
-14	116	-117	1581
-13	149	142	1477
-12	266	-261	796
-11	35	27	1590
-10	82	-85	2073
-9	305	-308	204
-8	116	-122	2252
-7	491	533	28
-6	169	174	1843
-5	265	-278	275
-4	414	-442	40
-3	424	-459	38
-2	237	227	110
-1	287	290	79
0	666	830	16
1	294	307	76
2	100	-115	3306
3	603	-768	19
4	476	-565	30
5	5	-9	96*
6	138	-145	2122
7	308	325	202
8	182	-177	1473
9	210	-201	1193
10	51	-60	1703
11	377	394	135
12	138	138	1439
13	86	76	1762
14	267	-263	718
15	244	-244	790
16	40	-38	911
17	223	-219	821
18	76	-76	1108
19	8	-19	38*
20	258	-261	653
21	133	131	1072
22	31	-33	466
23	113	120	1196
24	35	-30	798
25	14	10	222
26	129	-131	1475
27	118	-118	1853
28	52	-53	3161

H, 2, 1

-28	36	-33	2413
-27	67	67	2021
-26	97	91	1809
-25	6	-4	67*
-24	50	-52	907
-23	75	-76	1151
-22	22	-17	566
-21	146	145	1031
-20	139	141	920
-19	106	-97	1116
-18	45	49	881
-17	213	-222	832
-16	164	164	1033
-15	42	-44	865
-14	227	224	892
-13	408	-417	115
-12	111	107	1510
-11	204	197	1092
-10	153	141	1499
-9	435	445	34
-8	163	152	1476
-7	168	165	1557
-6	280	-282	238
-5	395	-406	131
-4	469	484	31
-3	650	-728	17
-2	473	494	30
-1	274	-277	255
0	499	-554	27
1	160	156	1796
2	157	155	1887
3	411	444	39
4	107	-101	2299
5	311	-328	198
6	188	-192	1364
7	111	-101	2068
8	37	-24	1694
9	45	-34	2001
10	134	-131	1591
11	19	21	355
12	90	-84	1423
13	138	-136	1429
14	7	3	49*
15	145	-144	1132
16	158	-159	1054
17	85	79	1132
18	148	-153	971
19	125	-121	1036
20	170	177	917
21	11	5	178
22	42	43	844
23	28	31	609
24	111	-112	1476
25	93	-91	1521
26	6	6	67*
27	24	-27	1591

H, 3, 1

-27	5	6	96*
-26	74	75	2200
-25	7	-7	49*
-24	46	50	1114
-23	87	88	1387
-22	115	-110	1235
-21	120	120	1056
-20	223	220	773
-19	109	-120	1023
-18	187	188	835
-17	76	-75	1141
-16	61	-66	1141
-15	170	173	996
-14	16	-24	278
-13	7	-8	49*
-12	97	102	1337
-11	32	-28	758
-10	214	-208	981
-9	263	266	771
-8	59	-62	1542
-7	23	-20	773
-6	310	301	187
-5	194	-179	1236
-4	485	-507	28
-3	167	163	1449
-2	21	23	693
-1	65	63	1913
0	189	168	1349
1	237	238	976
2	59	-52	1992
3	31	-37	1254
4	194	-194	369
5	250	-254	256
6	328	-333	168
7	248	250	856
8	6	-3	67*
9	34	-31	856
10	276	270	710
11	155	-155	1140
12	320	332	161
13	137	135	1128
14	102	-104	1213
15	52	46	1074
16	93	-98	960
17	31	-27	589
18	24	31	385
19	9	14	30*
20	141	144	1088
21	53	56	960
22	145	145	1174
23	7	12	49*
24	34	31	1205
25	58	-56	1979
26	66	60	2579

H, 4, 1

-25	54	-54	2402
-24	87	-89	1957
-23	13	8	433
-22	41	-41	1203
-21	130	124	1220
-20	8	0	38*
-19	114	116	1184
-18	93	-93	1051
-17	33	35	610
-16	78	-73	1160
-15	31	27	610
-14	21	25	391
-13	70	-69	1100
-12	119	-116	1202
-11	158	159	1054
-10	92	-94	1231
-9	206	205	924
-8	57	-56	1126
-7	87	88	1409
-6	139	-133	1278
-5	201	-193	1010
-4	101	-95	1601
-3	170	-173	1144
-2	88	90	1451
-1	23	8	663
0	20	-9	405
1	351	359	146
2	56	48	1094
3	534	588	72
4	154	155	1196
5	333	-350	49
6	34	-32	738
7	154	-150	1163
8	105	105	1451
9	131	137	1324
10	176	176	993
11	103	-107	1102
12	27	27	522
13	117	122	1090
14	49	-51	751
15	208	210	784
16	105	106	1037
17	31	29	533
18	106	107	1137
19	40	32	740
20	29	-24	698
21	84	82	1512
22	31	-33	969
23	65	-65	1989
24	29	-30	1926

H, 5, 1

-23	60	61	3112
-22	105	-108	1972
-21	6	-9	67*
-20	29	-30	881
-19	6	-1	67*
-18	77	80	1261
-17	37	37	939
-16	44	-43	855
-15	98	-102	894
-14	90	-91	970
-13	147	-147	1064
-12	51	46	961
-11	30	-28	657
-10	18	14	232
-9	15	-11	213
-8	124	127	1102
-7	76	76	999
-6	228	227	762
-5	52	43	908
-4	98	-95	1023
-3	179	-179	975
-2	120	118	1148
-1	65	64	1034
0	219	226	834
1	59	-59	378
2	23	19	304
3	189	-182	925
4	164	-160	1005
5	17	24	316
6	38	-37	821
7	161	162	947
8	222	232	796
9	102	105	1187
10	89	86	1022
11	108	-105	994
12	37	35	612
13	48	-49	738
14	22	-13	306
15	48	44	1109
16	111	-111	1189
17	8	-6	38*
18	132	-134	1358
19	76	-77	1570
20	37	-36	943
21	15	13	543
22	60	59	2947

H, 6, 1

-20	51	53	3418
-19	80	-79	2248
-18	137	140	1652
-17	109	-106	1619
-16	52	-48	1527
-15	60	-62	1195
-14	26	-25	836
-13	85	-79	1405
-12	142	142	1039
-11	106	111	1113
-10	102	100	1045
-9	82	74	1070
-8	76	-67	1089
-7	51	-54	983
-6	18	-16	213
-5	9	-3	30*
-4	54	-57	819
-3	193	-192	820
-2	81	81	880
-1	153	-153	993
0	95	93	1007
1	173	172	879
2	166	-167	907
3	97	94	1042
4	62	61	940
5	100	-99	1034
6	8	7	38*
7	46	43	805
8	218	-219	817
9	49	-51	735
10	138	-134	1180
11	171	-169	1060
12	16	3	232
13	22	-21	501
14	19	-19	504
15	14	11	266
16	32	30	1217
17	6	-5	67*
18	57	55	2341
19	46	-48	2531

H, 7, 1

-15	5	1	96*
-14	53	48	2158
-13	34	-31	1370
-12	17	-11	498
-11	11	4	211
-10	152	-150	1292
-9	72	66	1432
-8	185	-189	1053
-7	45	47	1043
-6	33	-33	818
-5	49	45	1123
-4	36	39	826
-3	34	-35	888
-2	7	7	49*
-1	12	-14	167
0	7	-9	49*
1	23	-19	455
2	115	-117	1266
3	25	-27	604
4	93	-92	1584
5	22	22	535
6	79	-75	1519
7	91	91	1464
8	118	-115	1614
9	7	6	49*
10	23	21	697
11	149	-151	1580
12	79	80	2158
13	5	1	96*
14	4	-6	151*

H, 8, 1

-6	16	22	336
-5	21	25	669
-4	49	53	1375
-3	61	-63	2006
-2	50	-55	2054
-1	64	-67	2394
0	27	-32	728
1	22	-20	586
2	62	63	1872
3	16	17	321
4	45	46	1060
5	58	61	1711

H, 0, 2

-28	181	172	1420
-26	102	-102	1589
-24	218	213	842
-22	184	188	923
-20	226	-234	783
-18	379	-401	120
-16	129	-118	1265
-14	241	244	830
-12	292	293	700
-10	12	-3	285
-8	774	-925	12
-6	578	-646	21
-4	630	-770	18
-2	101	92	3016
0	200	197	433
2	656	-799	16
4	205	-198	1322
6	256	-239	268
8	141	-150	1691
10	311	-309	183
12	34	24	964
14	215	210	848
16	32	42	740
18	38	44	722
20	8	2	38*
22	34	-28	710
24	29	-26	976
26	69	66	2407

H, 1, 2

-29	4	-1	151*
-28	6	-8	67*
-27	138	-134	1449
-26	77	-70	1618
-25	15	8	335
-24	47	-48	1108
-23	20	-15	635
-22	116	116	1080
-21	38	-22	754
-20	73	-72	1091
-19	275	275	622
-18	133	-141	1142
-17	168	-162	1020
-16	13	22	171
-15	120	-124	1348
-14	57	57	1427
-13	95	84	1642
-12	158	-161	1406
-11	183	-176	1231
-10	137	-133	1590
-9	359	-360	151
-8	112	-117	2126
-7	124	115	2001
-6	133	137	2037
-5	326	333	59
-4	137	142	2175
-3	83	83	2627
-2	42	-45	2407
-1	339	363	175
0	661	696	16
1	895	-1173	9
2	379	408	45
3	509	-546	83
4	258	248	271
5	487	528	28
6	63	59	1905
7	316	318	188
8	27	-23	992
9	124	120	1689
10	295	284	197
11	123	-114	1445
12	187	194	1069
13	189	-201	974
14	163	172	990
15	215	-217	801
16	228	236	769
17	41	44	725
18	64	72	989
19	151	151	886
20	70	-67	1158
21	55	49	1178
22	31	26	689
23	64	-66	1336
24	33	-28	807
25	5	1	96*
26	43	-44	1977
27	12	17	810

H, 2, 2

-28	9	-7	456
-27	49	49	1851
-26	81	-81	1703
-25	10	10	21
-24	24	19	549
-23	89	81	1322
-22	76	70	1278
-21	43	40	802
-20	167	-160	950
-19	72	-65	1056
-18	227	-224	746
-17	179	-176	911
-16	330	336	503
-15	14	7	188
-14	266	270	698
-13	297	302	181
-12	58	-55	1468
-11	15	24	278
-10	461	480	95
-9	49	-37	1419
-8	135	-128	1626
-7	163	155	1434
-6	342	-334	52
-5	172	185	1486
-4	348	356	160
-3	314	-299	192
-2	595	630	19
-1	328	311	180
0	680	773	15
1	6	13	67*
2	228	237	317
3	218	-221	1122
4	277	-269	231
5	508	546	26
6	113	107	1632
7	99	-96	1673
8	252	265	829
9	29	30	835
10	313	-320	171
11	305	328	589
12	52	39	1066
13	7	-22	49*
14	273	281	192
15	168	-167	939
16	15	-6	113
17	20	-12	341
18	100	-103	1266
19	44	-51	791
20	152	-155	1024
21	84	83	1206
22	32	-29	631
23	232	236	885
24	6	0	67*
25	56	-56	2345
26	33	-31	2353

H, 3, 2

-27	71	69	3320
-26	66	-69	2325
-25	57	55	1616
-24	14	-2	312
-23	22	-16	807
-22	156	156	1047
-21	98	99	1173
-20	136	138	953
-19	9	17	30*
-18	22	21	355
-17	95	-100	1195
-16	121	-131	1158
-15	87	94	1055
-14	130	130	1172
-13	66	-58	1151
-12	38	43	975
-11	25	-23	593
-10	151	149	1210
-9	347	362	146
-8	47	55	1210
-7	139	136	1389
-6	134	-130	1456
-5	195	195	1156
-4	246	240	861
-3	263	258	792
-2	227	-223	995
-1	185	-176	1217
0	232	-225	276
1	281	-285	216
2	14	11	251
3	114	103	1570
4	18	-13	410
5	243	241	868
6	332	-342	161
7	199	198	1041
8	137	-132	1239
9	144	152	1253
10	146	-152	1188
11	25	23	405
12	126	-125	1166
13	104	-99	1072
14	208	214	804
15	124	-122	1058
16	175	-178	907
17	44	43	713
18	243	-246	744
19	104	103	1167
20	64	61	1145
21	73	71	1315
22	90	90	1674
23	6	4	67*
24	40	-36	1890
25	78	-77	3736

H, 4, 2

-25	4	2	151*
-24	13	14	346
-23	29	28	1129
-22	87	86	1621
-21	85	-83	1309
-20	60	-59	1199
-19	20	10	314
-18	71	-68	1114
-17	104	-105	1174
-16	118	116	1101
-15	8	3	38*
-14	97	96	1149
-13	286	290	582
-12	97	-89	1022
-11	105	-105	1083
-10	132	-123	1088
-9	152	-154	1089
-8	81	-82	1270
-7	139	-145	1078
-6	166	-164	1100
-5	126	-123	1305
-4	167	-162	1147
-3	61	-50	1342
-2	198	-202	1020
-1	128	123	1252
0	64	56	1330
1	87	90	1425
2	92	86	1343
3	137	-141	1261
4	94	-93	1328
5	116	-115	1276
6	136	-139	1087
7	224	-221	830
8	145	-148	1075
9	125	-126	1123
10	29	-27	520
11	40	-40	669
12	78	77	1080
13	104	106	1066
14	122	119	1075
15	45	-40	829
16	7	-4	49*
17	132	-132	1114
18	8	14	38*
19	22	27	470
20	87	83	1606
21	5	16	96*
22	10	16	324
23	30	28	2681

H, 5, 2

-23	30	-32	2365
-22	117	115	1935
-21	15	-12	511
-20	25	-18	940
-19	49	50	1080
-18	128	-123	1278
-17	87	85	1264
-16	113	-111	1238
-15	104	-103	1124
-14	25	-23	308
-13	87	-90	1083
-12	122	-119	1079
-11	166	-167	925
-10	8	-13	38*
-9	96	-85	923
-8	77	73	1046
-7	76	80	1021
-6	22	-18	267
-5	38	-43	606
-4	41	41	670
-3	69	-69	1091
-2	219	-228	794
-1	112	-115	1081
0	6	4	38*
1	118	-122	1168
2	249	255	686
3	17	23	149
4	76	-77	994
5	10	7	24*
6	81	-78	1106
7	240	-252	694
8	265	270	647
9	24	23	315
10	89	90	956
11	159	156	965
12	73	-74	935
13	75	-70	1111
14	125	133	1158
15	55	-55	1187
16	50	-49	1460
17	50	-50	1453
18	80	-80	2003
19	10	5	253
20	58	58	2585
21	24	22	1927

H, 6, 2

-19	60	-58	2614
-18	59	58	2260
-17	6	-5	67*
-16	21	-19	652
-15	26	-31	720
-14	70	-67	1420
-13	42	47	653
-12	21	14	338
-11	65	72	1042
-10	19	-20	291
-9	21	-23	407
-8	228	233	793
-7	22	14	252
-6	111	109	999
-5	46	41	683
-4	205	-211	850
-3	76	-79	1056
-2	81	-74	1091
-1	89	89	986
0	166	165	891
1	178	179	883
2	53	52	910
3	100	-102	1067
4	8	-9	38*
5	28	28	421
6	85	80	1001
7	109	106	1220
8	38	-37	745
9	38	38	819
10	76	-80	1374
11	90	85	1260
12	49	-46	1491
13	16	13	374
14	39	42	1227
15	26	-23	928
16	36	-34	1478
17	5	-1	96*

H, 7, 2

-14	58	55	3057
-13	36	-38	1576
-12	45	42	2252
-11	37	40	1073
-10	14	8	313
-9	65	62	1709
-8	16	13	468
-7	32	34	946
-6	7	-1	49*
-5	44	41	1389
-4	6	6	67*
-3	20	15	453
-2	72	70	1375
-1	45	-40	1359
0	96	96	1528
1	124	121	1391
2	14	-12	180
3	94	95	1605
4	61	-60	1405
5	7	-5	49*
6	33	-33	1363
7	45	-44	1661
8	70	-71	1967
9	22	-22	996
10	5	-6	96*
11	78	79	2417
12	14	-15	299

H, 0, 3

-28	87	81	2381
-26	231	226	903
-24	82	83	1343
-22	184	-182	923
-20	29	29	534
-18	383	415	405
-16	67	-69	1268
-14	285	280	665
-12	373	395	132
-10	241	-227	259
-8	480	515	89
-6	138	133	1641
-4	97	-92	2158
-2	351	366	157
0	112	-111	2098
2	554	-587	22
4	326	358	175
6	317	323	179
8	236	-245	252
10	152	172	1186
12	87	-73	1321
14	286	-299	575
16	77	-70	1010
18	250	253	667
20	171	176	1044
22	89	-83	1451
24	6	-7	67*

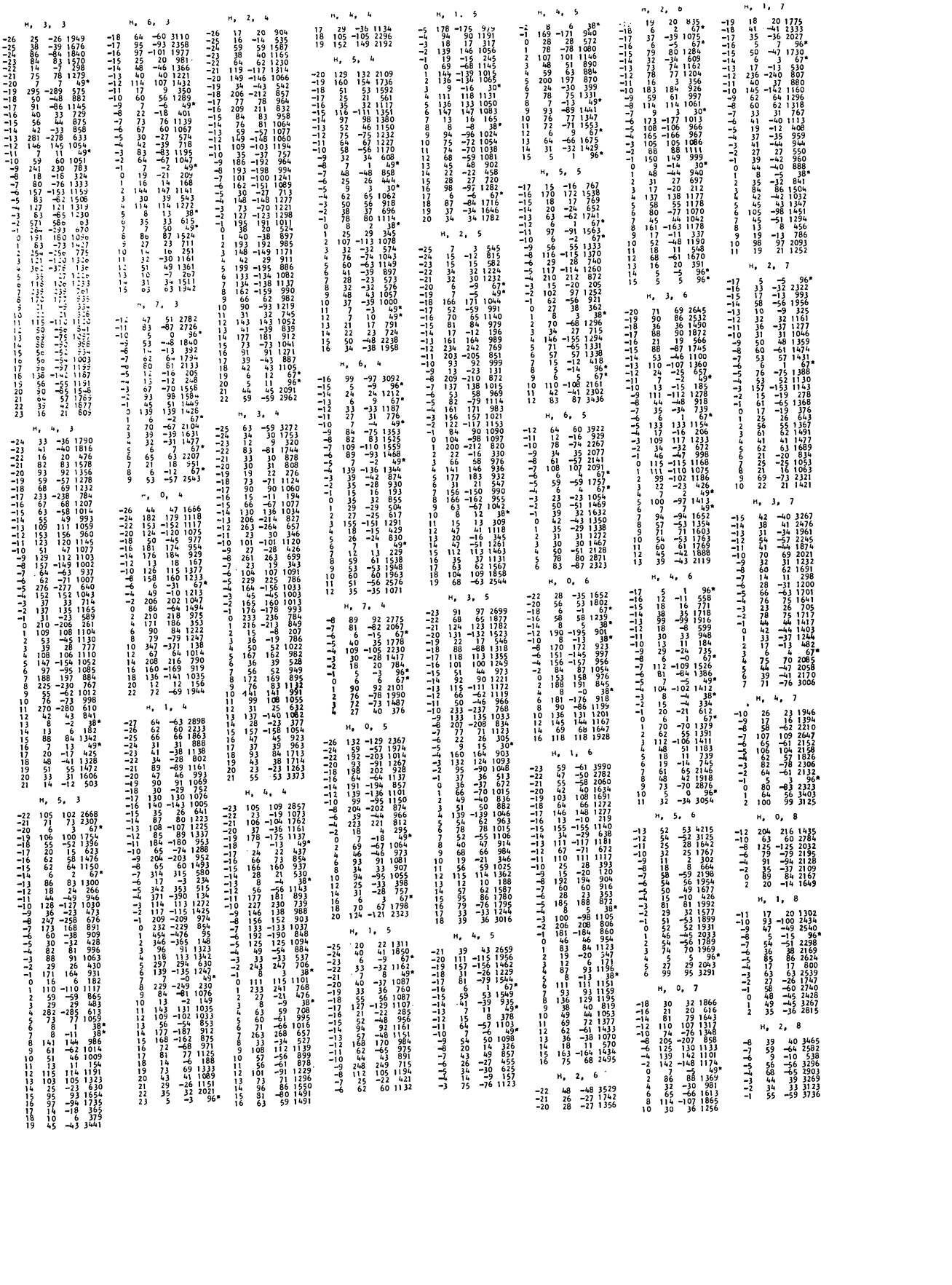
H, 1, 3

-28	138	137	1945
-27	15	-16	485
-26	46	45	1507
-25	6	6	67*
-24	7	-6	49*
-23	170	170	1025
-22	148	152	1020
-21	41	-44	1013
-20	29	24	534
-19	126	-130	1063
-18	95	-99	1038
-17	231	234	765
-16	22	-19	416
-15	44	40	1021
-14	7	2	49*
-13	126	-122	1355
-12	214	210	939
-11	76	-73	1649
-10	192	-192	1107
-9	277	270	218
-8	220	-228	1008
-7	6	5	67*
-6	55	-51	1919
-5	60	-61	1691
-4	260	-261	870
-3	188	190	1331
-2	140	142	1659
-1	6	11	67*
0	115	80	2003
1	292	292	211
2	218	-231	1079
3	265	-261	243
4	10	-8	241
5	164	-167	1403
6	17	31	477
7	229	228	919
8	72	-74	1351
9	92	93	1366
10	280	290	654
11	114	-112	1251
12	106	108	1240
13	81	85	1217
14	64	-75	1072
15	57	57	951
16	180	181	851
17	104	-107	1075
18	107	114	924
19	109	111	1093
20	35	31	717
21	7	12	49*
22	68	65	1386
23	101	-100	1514
24	6	3	67*
25	46	47	2655

H, 2, 3

-28	19	-18	2532
-27	31	-28	2305
-26	22	23	925
-25	20	-16	613
-24	130	-130	1273
-23	13	-17	133
-22	158	-163	1027
-21	189	183	910
-20	167	-172	919
-19	47	48	831
-18	29	-15	360
-17	104	-99	1107
-16	84	87	1186
-15	131	-134	1115
-14	24	-25	580
-13	138	144	1200
-12	249	-254	768
-11	170	178	1134
-10	346	-352	503
-9	54	-52	1405
-8	116	-113	1464
-7	109	103	1700
-6	140	-139	1512
-5	276	-276	750
-4	14	23	193
-3	18	-17	579
-2	141	115	1560
-1	273	268	767
0	175	167	397
1	7	-13	49*
2	80	-74	1727
3	144	-145	1484
4	49	-44	1447
5	112	112	1571
6	119	113	1503
7	145	142	1227
8	101	-102	1520
9	37	32	863
10	126	120	1273
11	7	-9	49*
12	46	35	947
13	128	-130	935
14	156	-153	967
15	82	73	1120
16	113	114	1069
17	60	65	924
18	184	178	923
19	7	-0	49*
20	79	-76	1194
21	41	33	1030
22	161	-165	1225
23	6	-1	67*
24	69	-71	3195

Table 4 (*cont.*)



The scattering factors for O, N, C and Li^+ were taken from *International Tables for X-ray Crystallography* (1962). For oxygen atoms in the ionized carboxyl groups the average of scattering factors for O and O^- were used. For hydrogen the values given by Stewart, Davidson & Simpson (1965) were used. Unobserved reflections were included in the refinement and 70% of the indicated shifts were used in each cycle.

Three cycles of isotropic refinement with the heavier atoms alone reduced R to 0·18 and then three cycles of anisotropic refinement gave $R=0{\cdot}108$. At this point a difference map showed all the hydrogen atoms. Refinement was continued with isotropic temperature factors for the lithium ion and the hydrogen atoms until the shifts were all less than half the estimated standard deviations of the parameters. C(3) is effectively isotropic using the criterion of Kraut & Jensen (1963) although anisotropic parameters were used in the final structure factor calculations. At this point R was 0·055 for all data, 0·052 for observed data alone and 0·043 for all data after an extinction correction,

$$|F_o'| = \frac{|F_o|}{\sqrt{1-k|F_o|^2}},$$

was applied with $k=5{\cdot}4\times10^{-5}$. The final positional and temperature factor parameters listed in Table 3 were used to compute the final structure factors given in Table 4. The estimated standard deviations are listed in Table 5. The principal axes of the anisotropic temperature factors and their directions cosines relative to the orthonormal **E** system (Patterson, 1952) are listed in Table 6. The γ matrix is

$$\begin{bmatrix} 23{\cdot}18126 & 0 & -0{\cdot}79815 \\ 0 & 6{\cdot}44600 & 0 \\ -0{\cdot}79815 & 0 & 6{\cdot}45887 \end{bmatrix}$$

Table 5. *Estimated standard deviations*

(*a*)	Positional parameters	
	O(1)–O(7)	0·0013 Å
	C(1)–C(6)	0·0016
	N(1)	0·0016
	O(*W*)	0·0022
	Li	0·0030
	H(1)–H(12)	0·033
(*b*)	Temperature parameters	
	O(1)–O(7)	0·048 Å²
	C(1)–C(6)	0·052
	N(1)	0·057
	O(*W*)	0·098
	Li	0·045
	H(1)–H(12)	0·84
(*c*)	Bond lengths	
	O-----O	0·0018 Å
	O–C, O-----N	0·0021
	C–C	0·0023
	Li-----O	0·0033
	H–C, H–O, H–N	0·033
	H-----H	0·047

Table 5 (*cont.*)

(*d*)	Bond angles	
	O–C–C, C–C–C	0·12°
	H–O–C, H–C–C	1·8
	H–N–H, H–O–H, H–C–H	4
	O–Li–O	0·15

so that E_2 coincides with b and E_1 and E_3 lie in the ac plane. A stereodiagram of the thermal ellipsoids is shown in Fig. 2 (Johnson, 1965*b*).

Table 6. *Principal axes of thermal ellipsoids*

	B	l_1	l_2	l_3
O(1)	3·93Å²	0·299	−0·734	0·610
	2·28	0·881	0·457	0·118
	1·29	−0·366	0·502	0·784
O(2)	3·75	0·096	−0·893	0·439
	2·07	0·758	−0·221	−0·614
	1·57	0·645	0·391	0·656
O(3)	5·08	0·273	−0·512	0·814
	1·98	0·955	0·039	−0·295
	1·52	0·119	0·858	0·500
O(4)	4·11	0·130	−0·382	0·915
	1·91	0·782	0·607	0·143
	1·43	−0·610	0·697	0·378
O(5)	5·03	−0·181	0·704	0·687
	2·59	0·894	−0·173	0·413
	1·38	0·410	0·689	−0·598
O(6)	3·28	0·033	−0·234	−0·972
	2·09	−0·003	0·972	−0·235
	1·22	0·999	0·011	0·031
O(7)	2·97	0·059	−0·724	−0·687
	1·86	0·971	−0·118	0·208
	1·25	−0·231	−0·679	0·697
C(1)	1·96	−0·640	−0·556	0·530
	1·81	0·704	−0·149	0·694
	1·27	−0·307	0·818	0·487
C(2)	3·07	0·336	0·791	−0·512
	1·52	0·553	0·274	0·787
	1·20	0·762	−0·547	−0·346
C(3)	1·50	0·086	0·778	−0·622
	1·39	0·390	0·548	0·740
	1·25	0·917	−0·307	−0·256
C(4)	2·60	−0·291	−0·615	0·733
	1·42	0·700	−0·659	−0·275
	1·35	0·652	0·432	0·622
C(5)	2·08	−0·400	−0·706	0·584
	1·76	0·903	−0·413	0·118
	1·28	0·158	0·575	0·803
C(6)	1·85	−0·515	0·704	−0·489
	1·43	−0·661	0·037	0·750
	1·33	0·546	0·709	0·446
N(1)	2·77	0·930	0·200	0·308
	2·31	−0·345	0·190	0·919
	2·09	0·125	−0·961	0·246
O(W)	12·30	−0·150	−0·477	−0·866
	2·93	−0·331	0·850	−0·410
	2·06	0·932	0·226	−0·285

In this analysis and that of lithium glycolate (Gabe & Taylor, 1966) the peak height of the lithium ion is as high as that of some of the heavier atoms while the temperature factor of the lithium ion is similar to that of the rest of the structure. This is presumably because the scattering factors of positively charged ions fall off more slowly than those for the non-ionized atoms, giving rise to a very sharp peak. The electron count is, however, approximately 2 as expected.

Description of the structure

The bond lengths and angles in the citrate ion are shown in Fig. 3. These show that it is the central carboxyl group and one of the terminal carboxyl groups which are ionized in this crystal. The fact that the terminal carboxyl group O(4)C(5)O(3) is not ionized is shown by the distances 1·219 and 1·306 Å for C(5)O(4) and C(5)O(3) and also by the presence of the hydrogen atom H(6) at 0·87 Å from O(3). This result is in agreement with a reinterpretation of the nuclear magnetic resonance data of Loewenstein & Roberts (1960) by Martin (1961). However, those measurements were made on solutions and the present study is of a particular crystalline form of the citrate.

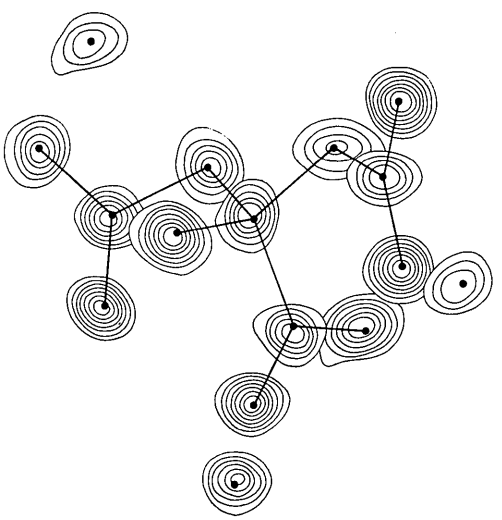


Fig. 1. Superposition of sections in the *E* map (viewed down the *c* axis).

The carbon–carbon bond lengths are shorter near the terminal carboxyl groups than near the central carboxyl group as found in other citrates. The distances are 1·516, 1·499 for C(1)C(2), C(4)C(5) compared with 1·535 for both C(3)C(2) and C(3)C(4). The distance C(3)C(6) to the central carboxyl group is 1·541 Å (±0·002 Å), a value which is lower than that found for monoionized sodium dihydrogen citrate (1·556± 0·005 Å) or triionized magnesium citrate (1·555± 0·002 Å).

The equations of planes through selected portions of the citrate ion are listed in Table 7. The carbon chain of C(1) to C(5) is fully extended with the terminal carboxyl groups turned out of the plane through these five carbon atoms. The central carboxyl group and the hydroxyl group are in a plane almost perpendicular to the plane of the backbone. The hydroxyl oxygen, O(7), is only 2·584 Å from one of the oxygen atoms [O(6)] of the central carboxyl group, a distance which is consistently short in the citrates (*e.g.* 2·638 Å in sodium dihydrogen citrate and 2·595 Å in magnesium citrate).

The lithium and ammonium ions lie near $x=\frac{1}{2}$ and 0 while the water lies near $x=\frac{1}{4}$ and $\frac{3}{4}$. The citrate ions pack between these as shown in Fig. 4. The marked cleavage of the crystal perpendicular to the *a* axis is explained by the loose packing around the water molecule.

There are eight different hydrogen atoms available for hydrogen bond formation, two in the citrate ion, two in the water molecule and four in the ammonium ion. The hydrogen bonds formed by these are listed in Table 8. There is a very short hydrogen bond, 2·552 Å, between two citrate ions with O(1) as acceptor from

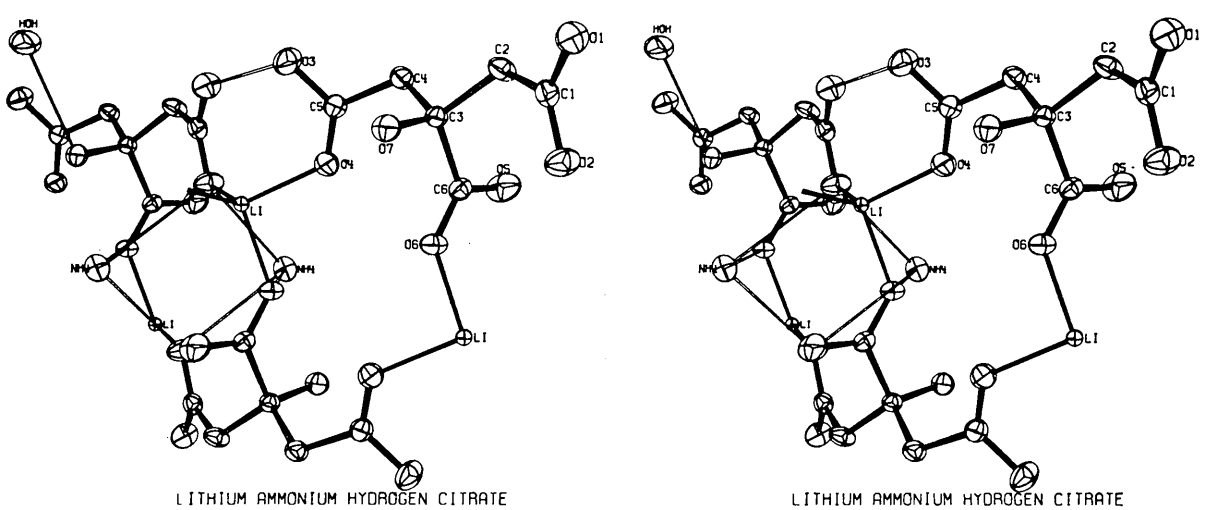


Fig. 2. Stereodiagram of thermal ellipsoids (courtesy of C. K. Johnson, Oak Ridge National Laboratory). Viewed down the *c* axis.

Table 7. *Planarity of groups in the citrate ion*

The equations are expressed in the form

$$lX+mY+nZ=D$$

where distances are expressed in Å and X, Y, Z are coordinates in the E system.

(*a*) Equations of planes

Designations and description of planes	Atoms in plane	*l*	*m*	*n*	*D*
(1) Center backbone	C(2)C(3)C(4)	−0·4754	−0·6541	0·5883	−6·6451
(2) Full backbone	C(1)C(2)C(3)C(4)C(5)	−0·5914	−0·6007	0·5379	−7·2807
(3) Hydroxyl	O(7)C(3)C(6)	−0·0464	0·6954	0·7171	3·6041
(4) Ionized end carboxyl	O(1)O(2)C(1)C(2)	0·1113	−0·9180	0·3807	−4·0130
(5) Central carboxyl	O(5)O(6)C(6)C(3)	−0·0141	0·6472	0·7622	3·6917
(6) Non-ionized end carboxyl	O(3)O(4)C(5)C(4)	0·1914	−0·3233	0·9267	−0·1345

(*b*) Deviations Δ (Å) from these planes

	Δ(1)		Δ(2)		Δ(3)		Δ(4)		Δ(5)		Δ(6)
C(2)	0·000	C(1)	0·091	O(7)	0·000	O(1)	−0·004	O(5)	0·000	O(3)	−0·001
C(3)	0·000	C(2)	−0·012	C(3)	0·000	O(2)	−0·004	O(6)	0·000	O(4)	−0·002
C(4)	0·000	C(3)	−0·148	C(6)	0·000	C(1)	0·011	C(6)	0·001	C(5)	0·004
		C(4)	−0·030			C(2)	−0·003	C(3)	0·000	C(4)	−0·001
		C(5)	0·100								
C(1)	0·189			O(5)	0·080			O(7)	0·100	H(6)	0·056
C(5)	0·236			O(6)	−0·082			H(5)	0·089		
C(6)	−1·245	C(6)	−1·505	H(5)	−0·003						
O(1)	0·958	O(1)	0·939								
O(2)	−0·418	O(2)	−0·653								
O(3)	1·188	O(3)	1·113								
O(4)	−0·398	O(4)	−0·663								
O(5)	−2·348	O(5)	−2·519								
O(6)	−1·087	O(6)	−1·518								
O(7)	1·148	O(7)	0·873								
H(1)	0·722	H(1)	0·781								
H(2)	−0·853	H(2)	−0·787								
H(3)	0·701	H(3)	0·753								
H(4)	−0·852	H(4)	−0·814								
H(5)	1·829	H(5)	1·632								
H(6)	1·219	H(6)	1·065								

(*c*) Angles between these planes

Planes		Angle	
(2)	(5)	89°16′	Full backbone/Central carboxyl
(2)	(4)	46 20	Full backbone/Ionized end carboxyl
(2)	(6)	35 25	Full backbone/Non-ionized end carboxyl
(3)	(5)	4 13	Hydroxyl/Central carboxyl
(1)	(2)	7 54	Center backbone/Full backbone
(1)	(3)	89 23	Center backbone/Hydroxyl

Table 8. *Hydrogen bonds*

Donor (*D*) (at *x*, *y*, *z*)	Acceptor (*A*)	*D*---*A* (Å)	H—*D* (Å)	H---*A* (Å)	∠*A*---H—*D* (°)	∠H—*D*---*A* (°)
O(7)—H(5)----O(*W*)	*x*, *y*, *z*	2·739	0·92	1·83	171	6
O(3)—H(6)----O(1)	*x*, *y*−1, *z*−1	2·552	0·87	1·88	132	33
N(1)—H(7)----O(2)	1−*x*, 2−*y*, 1−*z*	2·999	0·87	2·21	149	22
N(1)—H(8)----O(6)	1−*x*, 1−*y*, 1−*z*	2·887	0·84	2·10	156	17
N(1)—H(9)----O(7)	*x*, *y*, *z*	3·205	0·84	2·38	167	10
N(1)—H(10)---O(5)	*x*, *y*, 1+*z*	3·328	1·00	2·33	173	5
O(*W*)–H(11)---O(1)	*x*, *y*−1, *z*	2·912	0·82	2·11	167	10
O(*W*)–H(12)---O(1)	½−*x*, *y*−½, 1−*z*	2·734	0·87	1·87	177	2

Table 9. *Coordination around the ammonium ion*

Distances

		N---O	H---O	∠N—H---O	Oxygen Parameters
N(1)H(7)	O(2)	2·999 Å	2·21 Å	149°	$1-x, 2-y, 1-z$
N(1)	O(5)	3·179	2·65	120	
N(1)H(8)	O(6)	2·887	2·10	156	$1-x, 1-y, 1-z$
N(1)	O(7)	3·191	2·53	137	
N(1)	O(4)	3·382	3·03	108	
N(1)H(9)	O(7)	3·205	2·38	167	x, y, z
N(1)	O(6)	3·079	2·49	128	
N(1)	O(2)	3·042	2·68	108	
N(1)H(10)	O(5)	3·328	2·33	173	$x, y, 1+z$
N(1)	O(4)	3·095	2·79	98	

Angles

H(7)N(1)H(8)	104°
H(7)N(1)H(9)	118
H(7)N(1)H(10)	106
H(8)N(1)H(9)	104
H(8)N(1)H(10)	127
H(9)N(1)H(10)	99

Table 10. *Coordination around the lithium ion*

Li–O Distances

	Oxygen parameters				Oxygen function in carboxyl group
Li–O(5)	x	$y-1$	$1+z$	1·894 Å	Ionized
O(6)	$1-x$	$1-y$	$1-z$	1·917	Ionized
O(2)	x	$y-1$	z	1·977	Ionized
O(4)	x	y	$1+z$	2·012	Carbonyl

O–O Distances		O–Li–O angles	
O(6)O(4)	2·978 Å	O(6)–Li–O(4)	98·5°
O(6)O(2)	3·011	O(6)–Li–O(2)	101·3
O(5)O(4)	3·139	O(5)–Li–O(4)	107·0
O(5)O(2)	3·192	O(5)–Li–O(2)	111·1
O(5)O(6)	3·295	O(2)–Li–O(4)	118·4
O(2)O(4)	3·426	O(5)–Li–O(6)	120·7

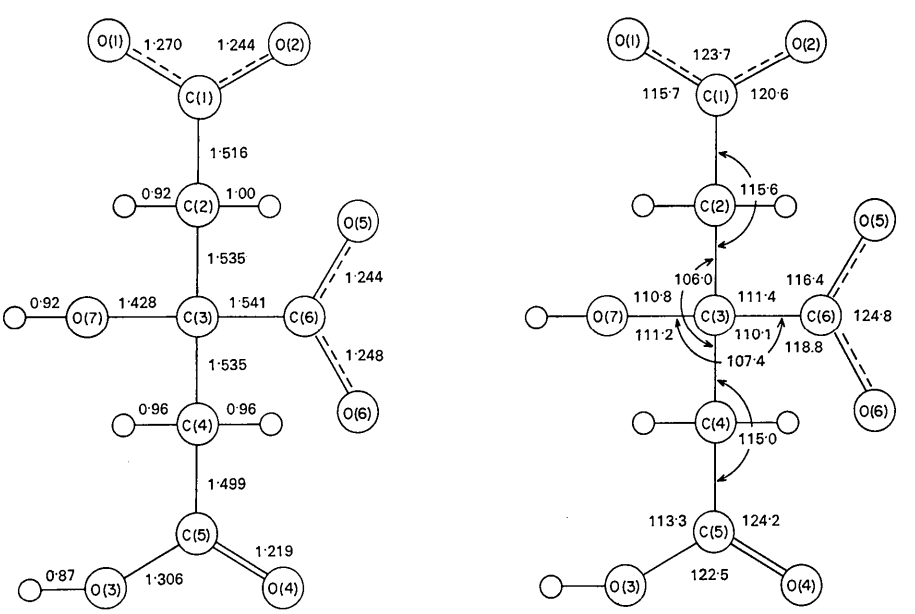


Fig. 3. (*a*) Bond lengths and (*b*) angles in the citrate ion.

H(6)O(3). O(1) is also the acceptor of two other hydrogen bonds, both from water molecules, and it should be noted that the distance O(1)C(1), 1·270 Å, is longer than other similar distances in the citrate ion.

The marked anisotropy of the water molecule shown in Table 6 is probably an indication of disorder. The water molecule is surrounded by four oxygens, forming hydrogen bonds to three of them (see Table 8) and packing against O(3). The effect of the disorder, assuming two possible sites, is to shorten the hydrogen bond to O(7) in one position and to shorten the longer of the two hydrogen bonds to O(1) in the other position. The distances and angles given in Table 8 are for an average position of the water molecule.

The coordination around the ammonium ion is described in Table 9. Four citrate ions are gathered round the ammonium ion at minimum distances of 2·887, 2·999, 3·042 and 3·095 Å and distances to other atoms in these citrate ions account for the ten closest oxygen distances as shown in Fig. 5.

The lithium ion is surrounded by four oxygen atoms in four different citrate ions. The distances of the lithium ion to the faces of the tetrahedron range from 0·56–0·75 Å. Table 10 contains a list of the distances and angles in the coordination tetrahedron. O(1), which takes part in three hydrogen bonds, is the only oxygen atom without an attached hydrogen atom which does not coordinate to the lithium ion. There is one ring formed by chelation which includes the short hydrogen bond [Li O(4)C(5)O(3)H(6)···O(1)C(1)O(2)] and one ring involving two lithium ions [Li O(5)C(6)O(6)Li′–O(5′)C(6′)O(6′)] (Fig. 4).

Computations

All computations were done on an IBM 1620 computer with programs written in this laboratory. For a list of these programs see Johnson (1965*a*). The Symbolic Addition Procedure Program (ICR No. 15) was written by E. J. Gabe and M. R. Taylor and the Data Reduction Program (ICR No. 16) by E. J. Gabe.

We are grateful to Dr M. R. Taylor for assistance in the data collection and to Dr C. K. Johnson for providing the diagram of the stereo pair in Fig. 2.

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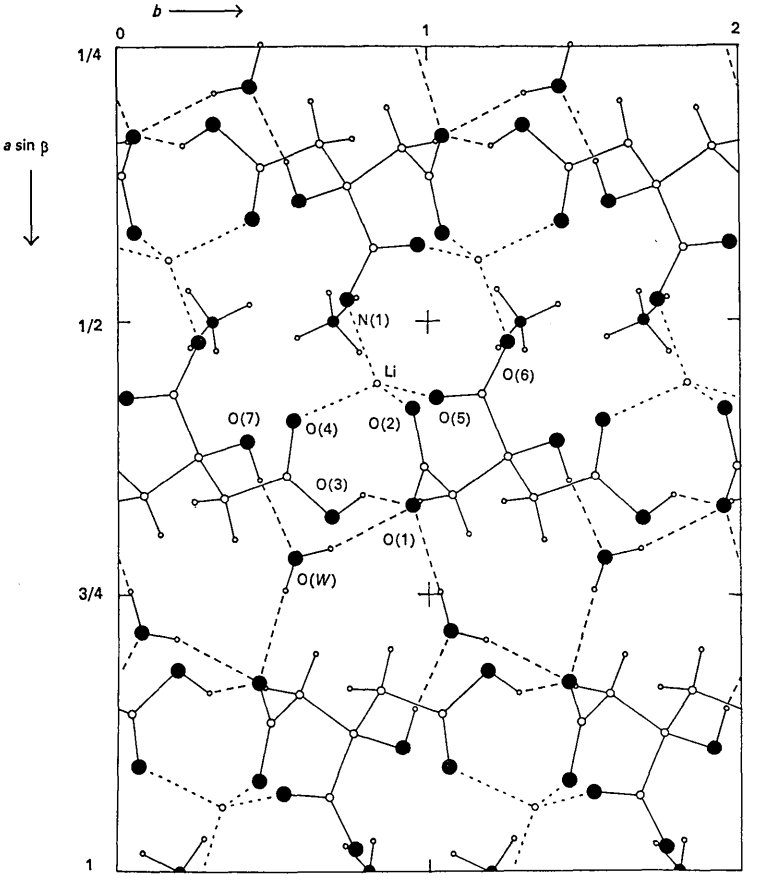

Fig. 4. General packing of the molecule.

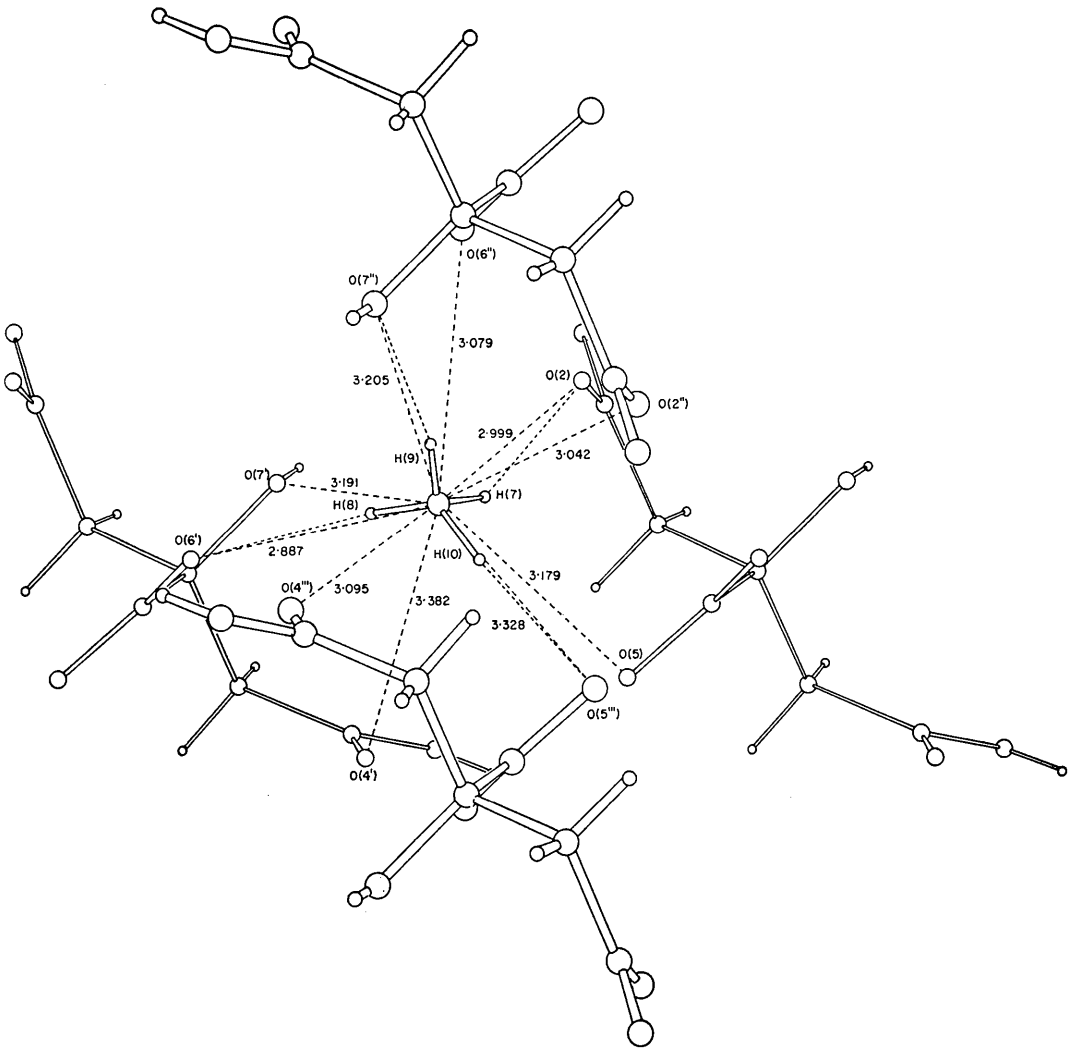

Fig. 5. Packing around the ammonium ion.

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