métal du groupe IIa (Be, Mg ou Ca), et B, un métalloïde de la colonne V (N ou P). Ces composés possèdent une structure anti-α-Mn_2O_3 dont le paramètre varie avec la grosseur de chacun des types d'atome en présence, la distorsion de la structure étant principalement due à la différence d'électroaffinité entre A et B.

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The Crystal Structure of Monomethylammonium Perchlorate*

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The crystal structure of monomethylammonium perchlorate, $CH_3NH_3^+ClO_4^-$ has been determined by a three-dimensional X-ray analysis. The space group is $P2_1/n$ and the cell dimensions are: $a_0=10{\cdot}59$, $b_0=7{\cdot}67$, $c_0=12{\cdot}87$ Å, $\beta=101°26'$; there are two molecules per asymmetric unit. The structure has been solved by the heavy-atom technique and refined by least-squares methods. The average Cl–O and N–C bond lengths are 1·43 and 1·52 Å respectively. Each of the nitrogen atoms has six oxygen neighbours with distances varying from 2·86 to 3·14 Å probably forming bifurcated hydrogen bonds. Each of the two independent $CH_3NH_3^+$ cations in the structure is surrounded by twelve oxygen atoms with distances less than 3·5 Å.

Introduction

Little information is available in the literature on the crystal structure of monomethylammonium salts. Only two of these compounds, namely the tetragonal monomethylammonium chloride (Hughes & Lipscomb, 1946) and the monomethylammonium aluminum sulphate alum in the room temperature cubic phase (Okaya, Ahmed, Pepinsky & Vand, 1957) and in the low temperature orthorhombic phase (Fletcher & Steeple, 1964), have been examined by X-ray methods during the last twenty years.

In the chloride, the C–N axis of the cations lies on the fourfold symmetry axis; since this is physically impossible with normal valences, the cations must exhibit either internal rotation or orientation disorder in the crystal. In cubic monomethylammonium alum, the $CH_3NH_3^+$ ions are statistically arranged around the cube body diagonal. Therefore in both structures, the exact coordination around the methylammonium ion is not considered, the only determination being that in orthorhombic 'alum'.

The present crystal structure determination on monomethylammonium perchlorate was undertaken with the purpose of contributing towards a better knowledge of the crystallochemistry of the $CH_3NH_3^+$ ion.

Experimental

Crystals of monomethylammonium perchlorate, prepared by neutralization of an alcoholic solution of methylamine with an aqueous solution of perchloric acid, were kindly supplied by Dr Marzocchi of the

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Laboratorio di Spettroscopia Molecolare of Florence University. The crystals, grown from alcoholic solution, are colourless needles elongated in the [010] direction, stable in air and in the X-ray beam.

The cell parameters determined from Weissenberg and rotation photographs were refined by a least-squares method, employing data from a powder diffractogram. The results are:

$$a_0 = 10\cdot59 \pm 0\cdot01, \quad b_0 = 7\cdot67 \pm 0\cdot01,$$
$$c_0 = 12\cdot87 \pm 0\cdot01\ \text{Å}, \beta = 101°26' \pm 15'\ .$$

From the systematically absent reflexions the space group was determined as $P2_1/n$ (C_{2h}^5). For eight unit $CH_3NH_3^+ClO_4^-$ in the cell the calculated density is $D_x = 1\cdot71$ g.cm^{-3}, in agreement with the observed value of 1·69 g.cm^{-3} measured by flotation in a mixture of methylene iodide and carbon tetrachloride. The linear absorption coefficient for the Cu $K\alpha$ wave-length is $\mu = 60\cdot3$ cm^{-1}.

For the collection of the intensities a crystal of prismatic shape with a cross section of $0\cdot13 \times 0\cdot06$ mm^2 was used. The crystal was rotated about the b axis and equi-inclination Weissenberg photographs from $h0l$ to $h4l$ layers were taken with the use of Ni-filtered Cu $K\alpha$ radiation and the multiple film technique. In each layer, reflexions at high Bragg angles were too weak to be measured and were neglected. Of the 885 independent reflexions examined, 381 were in the observable range. Unidimensionally integrated intensities were measured with a microdensitometer and were roughly brought to a common relative scale on the basis of the exposure time of different layers. On account of the small cross section of the specimen, a sufficiently accurate correction was made for absorption by assuming the crystal to be a cylinder with a radius of 0·05 mm. Phillips's (1954) corrections for spot elongation and Lorentz–polarization factors to obtain the F^2's were applied.

Determination and refinement of the structure

A three-dimensional Patterson synthesis was first calculated. The $(\frac{1}{2}, v, \frac{1}{2})$ Harker line showed only a relevant peak, and this allowed the assignment of the same y coordinate to the two independent chlorine atoms in the structure. The sets of x and z coordinates obtained from the $(u, \frac{1}{2}, w)$ Harker plane were then correctly correlated with the positions of the peaks due to the Cl(1)–Cl(2) vectors. The approximate coordinates of remaining non-hydrogen atoms were found from a three-dimensional 'heavy-atom' Fourier synthesis calculated without the coefficients whose signs had a low probability of being correct. The atomic coordinates were improved by a second electron density map and the discrepancy index $R = \Sigma\, ||F_o| - |F_c|| / \Sigma\, |F_o|$ for all the observed structure factors was at this stage 0·20.

A first refinement of the structure was performed with a least-squares program written by Albano, Bellon, Pompa & Scatturin (1963) for the IBM 1620 computer, using the block diagonal approximation and individual isotropic thermal parameters. The weighting scheme suggested by Cruickshank (1961), $\sqrt{w} = 1/(a + F_o + cF_o^2)$ with $a \simeq 2F_{\text{min}}$ and $a \simeq 2/F_{\text{max}}$, was employed for the structure factors and the unobserved reflexions were not included in the calculations. After three cycles the R index dropped to 0·14. At this stage the full-matrix least-squares refinement was undertaken with the program of Busing & Levy, adapted for the IBM 7090 computer by Stewart (1964). For the observed planes a weighting scheme like that specified by Hughes (1941) was used, with $\sqrt{w} = 1$ for reflexions with $F_o \le 4F_{\text{min}}$; $\sqrt{w} = 4F_{\text{min}}/F_o$ for $F_o > 4F_{\text{min}}$. To provide additional data in this new series of calculations the 'accidentally absent' reflexions were included with a value just below the lowest intensity observed in that part of the spectrum. These reflexions were weighted as follows: $\sqrt{w} = 1$ for reflexions with $F_o > F_{\text{min}}$, and $\sqrt{w} = 0$ when $F_c \le F_{\text{min}}$. Ten intense low order reflexions suspected to be affected by secondary extinction were excluded from the last cycle of refinement; they are marked by an E in Table 1. After one isotropic and three anisotropic cycles, each followed by a proper rescaling of F_o's, the R index for all observed structure factors reached the final value of 0·09.

The observed and calculated structure factors are listed in Table 1. For the calculations the scattering factor values from the self-consistent model as listed in *International Tables for X-ray Crystallography* (1962) for Cl, O, N and C were used.

Discussion of the structure

The atomic coordinates and anisotropic temperature factors, as from the last cycle of refinement, are given in Tables 2 and 3 with their standard deviations, estimated by the least-squares program using the formula:

$$\sigma_j = \sqrt{\frac{a^{jj}\, \Sigma\, w\Delta F^2}{m - n}},$$

where m is the number of reflexions, n is the number of parameters and a^{jj} is the jj element of the inverse matrix.

The high values reached by the temperature factors should indicate that in the structure the thermal motion is relevant and this fact may be responsible for the weakness of the diffraction effects at high Bragg angles.

The atomic arrangement projected along the b axis is shown in Fig. 1. The lists of bond lengths and bond angles with their standard deviations are included in Tables 4 and 5.

Both ClO_4 tetrahedra in the structure are slightly distorted. The O–Cl–O angles range from 105 to 112°. The average Cl–O distances are 1·44 and 1·42 Å respectively for Cl(1) and Cl(2) tetrahedra. These values are in agreement with those reported in the literature for Cl–O distances in perchlorates (Truter, Cruickshank & Jeffrey, 1960; Truter, 1961; Coulter, Gantzel & McCullough, 1963).

Table 1. *Observed and calculated structure factors* ($\times 10$) *for* $[CH_3NH_3]^+ClO_4^-$

Unobserved reflexions were assigned F_{obs} values corresponding to the minimum possible observable value and are designated with an asterisk. E signifies apparent extinction effect on $F^2{}_{obs}$.

H	K	L	FC	FC
0	0	2	79	-113
		4	1282	-1395
		6	100	113
		8	369	376
		10	139*	-121
		12	145*	-60
1	0	1	48*	-68
		-1	873E	968
		3	69*	77
		-3	230	207
		5	283	-283
		-5	535	-525
		7	316	-373
		-7	107*	13
		9	313	279
		-9	846	955
		11	535	599
		-11	144*	-6
		13	134*	-113
		-13	389	-432
		15	94*	-109
		-15	106*	-6
2	0	0	658E	756
		2	1592E	1843
		-2	1572E	-1739
		4	87*	-41
		-4	181	-171
		6	307	-322
		-6	98*	36
		8	229	240
		-8	118*	-40
		10	337	360
		-10	138*	74
		12	139*	-112
		-12	145*	77
		14	109*	-89
		-14	128*	-83
3	0	1	462	474
		-1	709	679
		3	88*	39
		-3	645	-573
		5	106*	-108
		-5	150	128
		7	146	-164
		-7	338	293
		9	142*	-176
		-9	130*	70
		11	249	195
		-11	519	-541
		13	120*	93
		-13	140*	-62
4	0	0	656	-660
		2	287	-232
		-2	239	-210
		4	107*	101
		-4	94*	-52
		6	217	218
		-6	108*	108
		8	226	-253
		-8	125*	47
		10	271	293
		-10	167	166
		12	127*	113
		-12	190	-171
		-14	125*	-74
5	0	1	285	272
		-1	662	-597
		3	112*	47
		-3	100*	-103
		5	126*	101
		-5	211	181
		7	140*	-46
		-7	321	-303
		9	145*	-43
		-9	254	-230
		11	130*	-32
		-11	145*	-47
		-13	135*	76
6	0	0	164	-180
		2	119*	-125
		-2	111*	-1
		4	130*	-118
		-4	115*	16
		6	141*	-36
		-6	124*	8
		8	267	-234
		-8	137*	111
		10	132*	34
		-10	145*	-87
		-12	307	-248
7	0	1	127*	141
		-1	703	-657
		3	166	175
		-3	124*	-42
		5	143*	164
		-5	130*	-11
		7	144*	-150
		-7	138*	17
		9	131*	81
		-9	144*	31
		-11	142*	18
8	0	0	137*	155
		2	141*	-33
		-2	274	-250
		4	145*	78
		-4	248	-231
		6	142*	17
		-6	249	222
		8	220	-213
		-8	196	146
		-10	338	-261
		-12	126*	-28
9	0	1	145*	-159
		-1	490	-460
		3	450	417
		-3	143*	95
		5	139*	52
		-5	237	206
		7	249	-289
		-7	145*	45
		-9	140*	11
		-11	125*	-46
10	0	0	144*	-71
		2	177	198
		-2	411	-384
		4	131*	35
10	0	-4	145*	168
		6	111*	23
		-6	356	276
		-8	136*	-71
		-10	163	-146
		-12	94*	52
11	0	-1	135*	-29
		-3	136*	149
		-5	134*	47
		-3	136*	149
		-5	134*	47
		-7	126*	39
		-9	112*	0
		-11	116	-104
12	0	-4	206	212
		-6	110*	8
		-8	97*	-121
		-10	69*	-19
0	1	1	37*	26
		2	955E	1357
		3	352	390
		4	140	-131
		5	482	-527
		6	109	-131
		7	225	-241
		8	120*	55
		9	219	219
		10	139*	152
1	1	0	368	491
		1	141	177
		-1	147	169
		2	99	126
		-2	140	-189
		3	72*	98
		-3	759	-830
		4	659	-722
		-4	486	-570
		5	188	180
		-5	87*	-62
		6	137	-156
		-6	216	256
		7	181	-181
		-7	233	237
		8	192	179
		-8	119*	91
		9	423	-406
		-9	129*	38
		10	141*	9
		-10	137*	-1
		11	209	254
		-11	388	-417
2	1	0	809E	-1082
		1	62*	15
		-1	184	199
		2	907E	1000
		-2	645	-747
		3	80*	-57
		-3	122	-105
		4	271	-255
		-4	177	177
		5	99*	39
		-5	377	-436
		6	341	-326
		-6	99*	88
		7	162	-160
		-7	144	139
		8	240	-235
		-8	119*	-59
		9	137*	33
		-9	129*	86
		10	230	246
		-10	137*	25
3	1	0	133	119
		1	341	353
		-1	763	-828
		2	83*	6
		-2	75*	24
		3	90*	-38
		-3	485	-466
		4	98*	-60
		-4	88	63
		5	107*	-1
		-5	236	-180
		6	186	-201
		-6	103*	79
		7	125*	51
		-7	227	201
		8	134*	16
		-8	121*	-12
		9	176	-158
		-9	155	-149
		10	144*	-5
		-10	138*	-9
4	1	0	550	-603
		1	174	-167
		-1	132	-162
		2	95*	9
		-2	232	222
		3	101*	105
		-3	266	254
		4	244	244
		-4	95*	10
		5	117*	-61
		-5	102*	-16
		6	125*	-108
		-6	109*	-54
		7	133*	19
		-7	117*	68
		8	445	-445
		-8	125*	37
		9	143*	9
		-9	133*	56
		10	143*	-146
		-10	140*	-155
		11	136*	15
		-11	144*	-2
5	1	0	100*	54
		1	221	-227
		-1	759E	-784
		2	107*	70
		-2	115	116
		3	113*	64
		-3	184	212
		4	147	146
		-4	105*	20
		5	126*	-53
		-5	330	283
5	1	6	133*	-23
		-6	117*	-1
		7	140*	-120
		-7	164	143
		8	143*	-44
		-8	131*	47
		9	143*	6
		-9	268	-261
		10	138*	13
		-10	142*	-25
		11	143*	-47
		-11	144*	75
6	1	0	113*	30
		1	116*	-45
		-1	111*	64
		2	266	-251
		-2	140	-122
		3	124*	109
		-3	113*	-18
		-4	116*	18
		4	130*	113
		5	136*	-54
		-5	120*	127
		6	339	332
		-6	125*	96
		7	143*	-16
		-7	131*	88
		8	143*	-28
		-8	136*	-27
		9	140*	19
		-9	141*	-63
		10	344	-382
		-10	245	-236
		-11	143*	-9
7	1	0	125*	41
		1	569	-581
		-1	124*	-55
		2	131*	-38
		-2	124*	-3
		3	187	187
		-3	739	762
		4	139*	113
		-4	127*	-97
		5	196	190
		-5	130*	107
		6	144*	83
		-6	134*	114
		7	143*	-109
		-7	255	-242
		8	138*	-95
		-8	141*	82
		9	196	-186
		-9	144*	-6
		-10	144*	-55
8	1	0	159	-179
		1	139*	4
		-1	235	-250
		2	141*	-51
		-2	135*	-94
		3	264	275
		-3	135*	57
		4	144*	-76
		-4	338	334
		5	144*	-13
		-5	167	171
		6	140*	147
		-6	141*	149
		7	135*	-111
		-7	143*	-74
		-8	187	-171
		-9	143*	6
		-10	141*	-67
9	1	0	143*	18
		1	278	-296
		-1	389	418
		2	144*	55
		-2	142*	-141
		3	143*	-113
		-3	178	194
		4	141*	10
		-4	143*	-47
		5	232	280
		-5	187	-185
		-6	144*	189
		-7	144*	-33
		-8	141*	-11
		-9	138*	-11
		-10	132*	-114
10	1	0	142*	-157
		1	140*	-139
		-1	143*	-42
		2	138*	-40
		-2	204	205
		3	134*	81
		-3	143*	71
		-4	272	274
		-5	142*	-16
		-6	140*	-72
11	1	-3	134*	-64
		-4	133*	68
		-5	131*	-2
		-6	128*	49
0	2	1	47	-71
		2	105	-91
		3	301	319
		4	117	110
		5	446	497
		6	99*	76
		7	550	-589
		8	232	-139
		9	198	-231
		10	135*	69
		11	186	183
		12	134*	59
1	2	0	567E	-682
		1	67	74
		-1	238	-296
		2	1054	1169
		-2	844	-907
		3	95	73
		-3	64*	-64
		4	758	676
		-4	643	675
		5	92*	116
		-5	93	-96
		6	917	-830
		-6	430	398
1	2	7	112*	64
		-7	107*	-16
		-8	117*	-168
		8	122*	-83
		9	159	-148
		-9	402	-420
		10	136*	94
		-10	134*	1
		11	277	-302
		-11	137*	-30
		12	132*	27
		-12	135*	-4
		13	122*	58
		-13	183	214
2	2	0	477	-572
		1	89	106
		-1	169	179
		2	717	-698
		-2	701	747
		3	91	93
		-3	485	-492
		4	89*	74
		-4	236	242
		5	192	188
		-5	315	314
		6	108*	36
		-6	99*	47
		7	117*	-12
		-7	652	669
		8	247	-209
		-8	118*	-3
		9	161	-140
		-9	234	-258
		10	137*	-196
		-10	134*	-53
		11	136*	-11
		-11	149	-150
		12	129*	95
		-12	136*	-61
3	2	00	152	168
		1	320	-310
		-1	647	-696
		2	362	-331
		-2	104	122
		3	90*	96
		-3	370	365
		4	481	494
		-4	120	115
		5	106*	50
		-5	134	152
		6	192	153
		-6	103*	-13
		7	123*	131
		-7	193	-180
		8	192	-149
		-8	120*	38
		9	136*	114
		-9	149	-152
		10	137*	-30
		-10	134*	8
		11	133*	-166
		-11	315	340
		-12	135*	-12
4	2	0	496	488
		1	90*	-76
		-1	291	302
		2	396	-425
		-2	412	401
		3	101*	119
		-3	151	162
		4	108*	-8
		-4	94*	-5
		5	115*	52
		-5	314	315
		6	276	233
		-6	108*	-2
		7	130*	31
		-7	238	-253
		8	135*	99
		-8	123*	-105
		9	137*	-27
		-9	134	-138
		10	380	-307
		-10	163	-200
		-11	138*	84
		-12	134*	141
5	2	0	164	165
		1	680	-636
		-1	352	321
		2	106*	-33
		-2	99*	5
		3	112*	-19
		-3	615	626
		4	118*	-135
		-4	105*	28
		5	124*	86
		-5	110*	-80
		6	219	178
		-6	115*	87
		7	135*	36
		-7	121*	-107
		8	137*	27
		-8	128*	-0
		9	135*	33
		-9	185	179
		-10	137*	-45
		-11	137*	114
		-12	132*	6
6	2	0	182	187
		1	114*	-136
		-1	110*	132
		2	118*	22
		-2	111*	-5
		3	123*	116
		-3	112*	68
		4	128*	-106
		-4	115*	79
		5	132*	146
		-5	118*	-133
		6	136*	89
		-6	123*	-40
		7	137*	-49
		-7	128*	-159
		8	354	276
		8	201	-180
		-9	136*	65
		-10	138*	90
6	2	-11	135*	-25
		-12	225	217
7	2	0	123*	42
		1	126*	-55
		-1	589	530
		2	129*	-49
		-2	122*	-49
		3	209	-193
		-3	123	46
		4	135*	-77
		-4	125*	29
		5	137*	56
		-5	127*	-108
		6	137*	135
		-6	174	202
		7	134*	150
		-7	134*	-15
		-8	186	-187
		-9	137*	45
		-10	136*	-98
		-11	131*	-33
8	2	0	133*	-46
		1	378	-331
		-1	132*	-96
		2	136*	2
		-2	180	147
		3	137*	-32
		-3	132*	142
		4	137*	-29
		-4	133*	35
		5	355	305
		-5	134*	7
		6	132*	-26
		-6	136*	-100
		-7	137*	-56
		-8	137*	-24
		-9	135*	-20
		-10	165	172
9	2	0	137*	-152
		1	137*	132
		-1	173	146
		2	137*	29
		-2	137*	-127
		3	135*	-119
		-3	137*	-94
		4	132*	-4
		-4	274	271
		-5	137*	-72
		-6	137*	-11
		-7	136*	-15
		-8	240	-253
0	3	1	49*	-11
		2	116	120
		3	177	-193
		4	100*	-36
		5	390	445
		6	141	-138
		7	210	223
		8	149*	-8
		9	205	-165
		10	164*	-70
1	3	0	54*	-55
		1	65*	-6
		-1	59*	75
		2	241	207
		-2	167	-190
		3	92*	-72
		-3	86*	-79
		4	612	682
		-4	418	556
		5	118*	97
		-5	112*	-56
		6	130*	75
		-6	162	-194
		7	141*	-0
		-7	136*	38
		8	178	-194
		-8	147*	-121
		9	161*	114
		-9	157*	-25
		-10	163*	-29
2	3	0	230E	389
		1	93	106
		-1	77*	-75
		2	108	-112
		-2	93	72
		3	103*	23
		-3	95	-107
		4	114*	11
		-4	103*	50
		5	125*	-54
		-5	520E	630
		6	136*	120
		-6	126*	-47
		7	231	246
		-7	138*	-79
		8	157*	134
		-8	148*	-23
		9	163*	-90
		-9	176	-160
		-10	163*	9
3	3	0	340	-385
		1	215	-226
		-1	318	367
		2	300	-368
		-2	97*	186
		3	115*	-3
		-3	315	333
		4	349	350
		-4	111*	7
		5	134*	-25
		-5	120*	-137
		6	478	532
		-6	130*	-121
		7	154*	-47
		-7	157	-140
		8	194	-204
		-8	150*	-4
		9	165*	71
		-9	177	192
		-10	163*	-35
4	3	0	380	427
		1	129	-119
		-1	209	-232
		2	121*	94
		-2	112*	-106
		3	131*	127
4	3	-3	223	239
		4	352	-360
		-4	121*	-64
		5	148*	110
		-5	222	248
		6	153*	-2
		-6	137*	-47
		7	160*	-38
		-7	413	-464
		8	336	335
		-8	154*	-57
		9	164*	35
		-9	164*	-136
		-10	164*	101
5	3	0	126*	123
		1	130*	42
		-1	632	695
		2	230	-118
		-2	126*	-61
		3	234	-238
		-3	128*	-105
		4	554	-507
		-4	132*	-11
		5	155*	39
		-5	341	-366
		6	380	330
		-6	145*	89
		7	164*	71
		-7	152*	20
		8	204	189
		-8	183	-215
		-9	182	167
		-10	165*	-20
6	3	0	141*	72
		1	270	-282
		-1	199	206
		2	166	132
		-2	140*	16
		3	369	-377
		-3	308	317
		4	158*	-155
		-4	144*	11
		5	261	253
		-5	417	-462
		6	199	-173
		-6	154*	-71
		7	164*	79
		-7	222	-246
		-8	162*	-13
		-9	184	180
		-10	183	143
7	3	0	154*	-46
		1	175	188
		-1	153*	21
		2	159*	58
		-2	152*	41
		3	162*	-58
		-3	239	-216
		4	237	-231
		-4	182	182
		5	165*	-90
		-5	158*	-83
		6	197	-181
		-6	230	-243
		-7	163*	75
		-8	199	-187
		-9	164*	50
8	3	0	162*	42
		1	167*	139
		-1	284	314
		2	164*	59
		-2	161*	-6
		3	424	-425
		-3	165*	-170
		4	163*	-11
		-4	163*	-51
		-5	217	-260
		6	165*	-37
		-7	164*	145
9	3	-1	164*	-96
		-2	168*	150
		-3	164*	-13
		-4	164*	0
		-5	164*	31
		-6	232	-252
		-7	160*	56
0	4	1	21*	-33
		2	88	106
		3	50	-47
		4	224	206
		5	211	-218
		6	128	-101
		7	320	277
		8	65*	-1
		9	121	104
		10	70*	2
		11	102	-76
		12	64*	-35
1	4	0	49	39
		1	28*	-46
		-1	25*	0
		2	327	-308
		-2	266	263
		3	54	-77
		-3	92	-91
		4	400	-332
		-4	260	-257
		5	52*	-6
		-5	120	110
		6	502	471
		-6	306	-268
		7	62*	13
		-7	130	118
		-8	65*	82
		8	66*	48
		9	69*	26
		-9	68*	6
		10	69*	-68
		-10	70*	20
		11	67*	5
		-11	69*	-8
		-12	65*	-0
2	4	0	33*	-35
		1	117	-103
		-1	106	119
		2	105	83
		-2	80	-85
2	4	3	45*	2
		-3	293	306
		4	117	96
		-4	66	-63
		5	122	-126
		-5	204	-209
		6	60*	-37
		-6	55*	-29
		7	65*	-20
		-7	520	-495
		8	68*	36
		-8	65*	27
		9	138	127
		-9	153	143
		10	69*	45
		-10	70*	10
		-11	135	126
3	4	0	230	239
		1	206	196
		01	76	83
		2	47*	33
		-2	42*	-28
		3	51*	-27
		-3	129	-117
		4	746	-712
		-4	239	-247
		5	59*	-65
		-5	53*	13
		6	91	57
		-6	57*	42
		7	67*	-22
		-7	62*	54
		8	260	240
		-8	94	-92
		9	69*	-34
		-9	68*	29
		-10	70*	-1
		-11	68*	-51
4	4	0	108	-121
		1	206	-188
		-1	246	256
		2	196	205
		-2	143	-152
		3	342	-317
		-3	151	129
		4	60*	-0
		-4	53*	12
		5	80	66
		-5	628	-680
		6	150	-169
		-6	60*	18
		7	69*	-49
		-7	64*	77
		8	70*	-8
		-8	68	65
		-9	279	278
		-10	69*	52
5	4	0	71	59
		1	164	169
		-1	55*	37
		2	286	300
		-2	98	-108
		3	62*	37
		-3	197	-217
		4	211	-222
		-4	59*	49
		5	67*	-48
		-5	91	-109
		6	318	-342
		-6	196	-197
		7	70*	-21
		-7	102	141
		-8	74	-89
		-9	70*	-26
		-10	182	165
6	4	0	62*	-37
		1	249	268
		-1	242	222
		2	65*	63
		-2	61*	10
		3	276	-298
		-3	230	-250
		4	68*	36
		-4	63*	10
		5	198	-215
		-5	156	-150
		6	69*	-76
		-6	67*	9
		-7	285	298
		-8	69*	39
		-9	69*	16
		-10	68*	-5
7	4	0	67*	-0
		1	68*	47
		-1	67*	-21
		2	69*	52
		-2	66*	56
		3	69*	-37
		-3	67*	-111
		4	70*	93
		-4	67*	-77
		5	69*	3
		-5	68*	30
		-6	193	-189
		-7	70*	48
		-8	216	207
		-9	68*	-46
		-10	126	110
8	4	0	69*	-20
		1	198	219
		-1	69*	18
		2	69*	17
		-2	69*	30
		3	85	116
		-3	69*	-106
		-4	70*	33
		-5	70*	60
		-6	69*	-55
		-7	69*	64
9	4	-2	69*	33
		-3	69*	30
		-4	113	-125
		-5	68*	-4
		-6	67*	67
		-7	65*	8
		-8	165	167

Table 2. *Fractional atomic coordinates with their standard deviations*

	x	$10^4\sigma(x)$	y	$10^4\sigma(y)$	z	$10^4\sigma(z)$
Cl(1)	0·3818	4	0·6895	8	0·1503	3
Cl(2)	0·5469	5	0·3037	9	0·3911	4
O(1)	0·3866	13	0·8086	21	0·2403	9
O(2)	0·3539	12	0·7916	21	0·0533	10
O(3)	0·2847	15	0·5603	19	0·1493	14
O(4)	0·5023	13	0·6110	18	0·1556	12
O(5)	0·5764	13	0·1911	20	0·4844	11
O(6)	0·4278	15	0·3859	20	0·3910	13
O(7)	0·5383	14	0·1864	23	0·3014	12
O(8)	0·6416	13	0·4265	22	0·3906	12
N(1)	0·1883	15	0·6663	23	0·3615	11
N(2)	0·8715	12	0·3280	29	0·1068	12
C(1)	0·1016	20	0·7075	38	0·4410	16
C(2)	0·7744	22	0·3547	38	0·1766	18

The two independent N–C distances in the methylammonium ions are 1·54 and 1·51 Å. These values are somewhat larger than the expected normal single-bond lengths between carbon and quaternary nitrogen atoms: 1·49, 1·50 and 1·51 Å in spermine phosphate (Iitaka & Huse, 1965), 1·47 Å in tetramethylammonium perchlorate (McCullough, 1964), 1·47 Å in monomethylammonium chloride (Hughes & Lipscomb, 1946), 1·51 Å in monomethylammonium alum (Fletcher & Steeple, 1964); but the difference seems not to be significant considering their standard deviations.

The shortest distances among the nitrogen atoms of the methylammonium ions and oxygen atoms of ClO_4 tetrahedra are listed in Table 6. The directions of the N–H···O bonds cannot be deduced simply, but it seems likely from stereochemical considerations that there are bifurcated hydrogen bonds in the following manner:

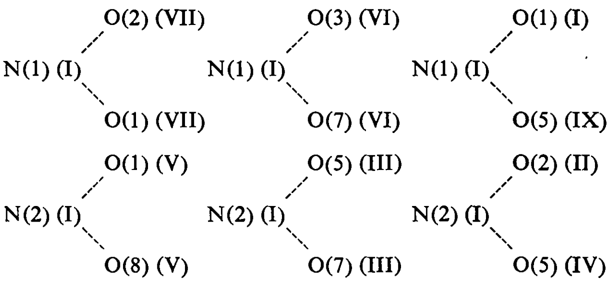

Table 3. *Anisotropic thermal parameters*

$$\exp\left[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})\right].$$

(σ) applies to the rightmost digit of the quantity in question.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cl(1)	0·0063 (6)	0·0161 (16)	0·0058 (4)	0·0012 (8)	0·0002 (3)	−0·0010 (7)
Cl(2)	0·0060 (5)	0·0217 (16)	0·0050 (4)	0·0005 (9)	−0·0004 (3)	0·0006 (8)
O(1)	0·0131 (17)	0·0223 (45)	0·0047 (10)	−0·0007 (21)	−0·0006 (10)	−0·0030 (17)
O(2)	0·0130 (16)	0·0370 (48)	0·0028 (10)	−0·0004 (22)	0·0001 (10)	0·0053 (19)
O(3)	0·0124 (19)	0·0170 (44)	0·0117 (15)	−0·0043 (25)	−0·0012 (14)	−0·0015 (20)
O(4)	0·0098 (18)	0·0199 (43)	0·0103 (15)	0·0019 (19)	0·0009 (14)	−0·0039 (18)
O(5)	0·0102 (16)	0·0272 (40)	0·0083 (13)	0·0003 (21)	−0·0002 (11)	0·0025 (22)
O(6)	0·0093 (16)	0·0272 (49)	0·0154 (16)	0·0058 (22)	0·0011 (13)	0·0017 (22)
O(7)	0·0152 (19)	0·0330 (49)	0·0060 (14)	0·0027 (26)	0·0002 (13)	−0·0038 (25)
O(8)	0·0072 (19)	0·0467 (57)	0·0085 (13)	−0·0035 (27)	0·0000 (13)	−0·0001 (19)
N(1)	0·0117 (19)	0·0238 (50)	0·0031 (10)	−0·0025 (31)	0·0019 (10)	0·0030 (22)
N(2)	0·0058 (16)	0·0502 (56)	0·0055 (12)	−0·0052 (29)	−0·0001 (11)	−0·0008 (25)
C(1)	0·0085 (22)	0·0660 (88)	0·0058 (16)	0·0068 (36)	0·0006 (14)	−0·0060 (32)
C(2)	0·0106 (22)	0·0415 (77)	0·0110 (22)	0·0032 (36)	0·0065 (17)	0·0009 (30)

Table 4. *Bond lengths with standard deviations*

(I) x, y, z
(II) $1-x, 1-y, -z$
(III) $\frac{3}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$
(IV) $\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$
(V) $\frac{3}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z$
(VI) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$
(VII) $\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$
(VIII) $x-\frac{1}{2}, \frac{3}{2}-y, \frac{1}{2}+z$
(IX) $1-x, 1-y, 1-z$

Cl(1)(I) – O(1)(I)	1·47 ± 0·01 Å	
– O(2)(I)	1·45	0·01
– O(3)(I)	1·43	0·02
– O(4)(I)	1·40	0·01
N(1)(I) – C(1)(I)	1·54 ± 0·02	

Cl(2)(I) – O(5)(I)	1·46 ± 0·01 Å	
– O(6)(I)	1·41	0·02
– O(7)(I)	1·45	0·02
– O(8)(I)	1·38	0·02
N(2)(I) – C(2)(I)	1·51 ± 0·02	

Table 5. *Bond angles in* ClO_4 *tetrahedra and their standard deviations*

O(1) (I) – Cl(1) (I) – O(2) (I)	108·2 ± 0·9°	
– O(3) (I)	110·5	0·8
– O(4) (I)	109·9	0·8
O(2) (I) – Cl(1) (I) – O(3) (I)	110·1	0·8
– O(4) (I)	107·6	0·8
O(3) (I) – Cl(1) (I) – O(4) (I)	110·5	0·9
O(5) (I) – Cl(2) (I) – O(6) (I)	108·1 ± 0·8	
– O(7) (I)	104·9	0·9
– O(8) (I)	111·8	0·8
O(6) (I) – Cl(2) (I) – O(7) (I)	111·2	0·9
– O(8) (I)	110·3	1·0
O(7) (I) – Cl(2) (I) – O(8) (I)	110·6	0·9

The resultant system of hydrogen bonding is rather complex.

Table 6. N–O *distances less than* 3·5 Å

N(1) (I)	– O(1) (I)	3·06 Å	N(2) (I)	– O(1) (V)	2·91 Å
	– O(1) (VII)	3·08		– O(2) (II)	2·97
	– O(2) (VII)	3·14		– O(5) (IV)	2·93
	– O(3) (VI)	3·04		– O(5) (III)	3·11
	– O(5) (IX)	3·06		– O(7) (III)	3·07
	– O(7) (VI)	2·86		– O(8) (V)	3·08
	– O(3) (I)	3·20		– O(3) (II)	3·49
	– O(6) (I)	3·29		– O(6) (IV)	3·38
	– O(8) (IX)	3·41			

The interatomic distances less than 3·5 Å among methyl carbon atoms and the neighbours oxygen atoms are listed in Table 7. These distances appear to be normal, although C(1)(I) shows five contacts [with O(2)(VII), O(2)(VIII), O(8)(IX), O(7)(VI) and O(3)(VI)] and C(2)(I) two contacts [with O(2)(II) and O(7)(III)], which are slightly less than the sum of the van der Waals radii for a methyl group and oxygen, *i.e.* 3·4 Å. The environments of the two non-equivalent $CH_3NH_3^+$ ions are shown in Fig. 2. Each of them is surrounded by twelve oxygen atoms at distances less than 3·5 Å.

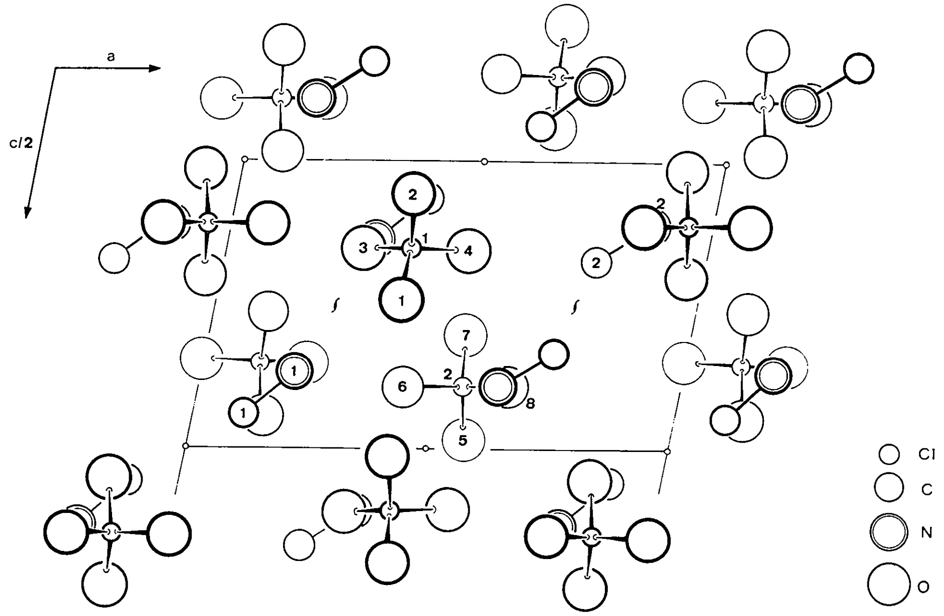

Fig. 1. Projection of the structure along the *b* axis.

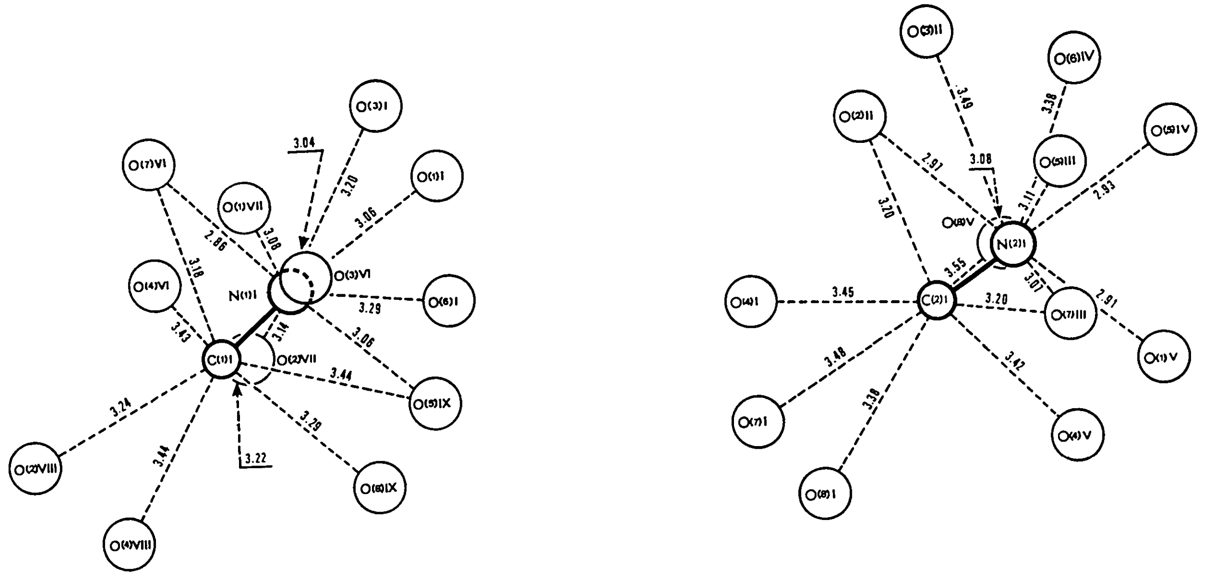

Fig. 2. The environments of the two non-equivalent $[NH_3CH_3]^+$ ions projected along the *b* axis. Distances in Å.

Table 7. *Distances less than* 3·5 Å *between methyl carbon atoms and neighbouring atoms*

C(1) (I) – O(2) (VII)	3·22 Å	C(2) (I) – O(2) (II)	3·20 Å
– O(2) (VIII)	3·24	– O(4) (V)	3·42
– O(3) (VI)	3·27	– O(4) (I)	3·45
– O(4) (VI)	3·43	– O(7) (III)	3·20
– O(4) (VIII)	3·44	– O(7) (I)	3·48
– O(5) (IX)	3·44	– O(8) (I)	3·38
– O(7) (VI)	3·18		
– O(8) (IX)	3·29		

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A New Method of Locating Heavy Atoms Bound to Protein Crystals

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It is shown that heavy atoms bound isomorphously to protein crystals can be located by using a direct method (Sayre's equation) to phase X-ray diffraction reflections in centrosymmetric projections. This method has been tested successfully with three derivatives of carboxypeptidase A, one of which contains four heavy atoms per protein molecule. Quite possibly several heavy atoms can be located in this manner with greater ease and assurance than by difference Patterson methods alone and thus the method may be especially useful in the X-ray study of proteins larger than 125,000 molecular weight, where binding of more than one or two heavy atoms will probably be both common and necessary.

Multiple isomorphous replacement phasing of X-ray diffraction data is the method which has proven most useful for determining protein structures. Its application requires the preparation of several isomorphous heavy atom derivatives of the native protein and the determination of the positions of these heavy atoms in the derivative crystals. The difference Patterson synthesis (Green, Ingram & Perutz, 1954), which is used to locate heavy atoms when no estimate of the protein phases is available, is quite adequate if only one or two heavy atoms are bound per asymmetric unit. However, by this method the location of larger numbers of heavy atoms becomes increasingly difficult.

It is shown here that a direct phase determination using Sayre's equation may be applied to reflections in centrosymmetric zones to locate heavy atoms bound isomorphously to protein crystals. The method has been successfully tested with three heavy atom derivatives of carboxypeptidase A_α (CPA_α), one of which contains eight mercury atoms per unit cell (four per molecule), and hence may prove to be a useful and powerful alternative to the difference Patterson syntheses for locating large numbers of heavy atoms.

The method

Sayre's (1952) equation expresses a relationship between the signs (phases) of certain structure factors for centrosymmetric structures of non-overlapping atoms:

$$s(F_{\mathbf{h}}) = s \sum_{\mathbf{k}} (F_{\mathbf{k}} F_{\mathbf{h}-\mathbf{k}}),$$

where $s(\,)$ means 'sign of' and $F_{\mathbf{h}}$, $F_{\mathbf{k}}$ and $F_{\mathbf{h}-\mathbf{k}}$ are the structure factors of reflections $\mathbf{h}(=hkl)$, $\mathbf{k}$, and $\mathbf{h}-\mathbf{k}$. Using this equation, and assuming the signs of a few structure factors, the signs of other structure factors can be predicted and these in turn can be used to pre-

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