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The Crystal Structure of Compounds with $(N-P)_n$ Rings.
II. Sodium Trimetaphosphimate Tetrahydrate $Na_3(NHPO_2)_3 . 4H_2O$

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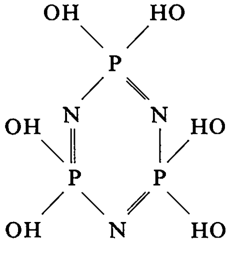
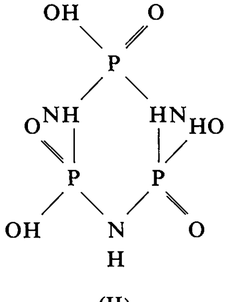
Sodium trimetaphosphimate tetrahydrate $Na_3(NHPO_2)_3 . 4H_2O$ crystallizes in the space group $P2_1/n$ with four formula units per cell. Unit-cell dimensions are $a=16{\cdot}976$, $b=7{\cdot}834$, $c=8{\cdot}918$ Å, $\beta=97{\cdot}08°$. The structure was refined by anisotropic least-squares analysis of 1450 independent reflexions to $R=0{\cdot}049$. A three-dimensional difference map clearly showed the maxima of the hydrogen atoms linked to the nitrogen atoms of the $(N\text{–}P)_3$ ring. The anions have the chair shape. Average values for the bond lengths and angles are P–N = 1·68, P–O = $1{\cdot}49_5$, s.d. 0·01 Å, P–N–P = 123°, N–P–N = 104.5°, O–P–O = 118°.

Introduction

The determination of the crystal structure of $Na_3 . (NHPO_2)_3 . 4H_2O$ is part of the experimental work carried out in this laboratory on a number of N–P ring systems. In the next paper the structure determination of $(NH)_4P_4O_8H_4 . 2H_2O$ is described (Migchelsen, Olthof & Vos, 1965). In an earlier paper the refinement of the crystal structure of $(NPCl_2)_4$–*K* form was reported (Hazekamp, Migchelsen & Vos, 1962). Further compounds under investigation are $(NPCl_2)_4$–*T* form, $[NP(NMe_2)_2]_6$, $N_3P_3FCl_5$ and $N_4P_4F_2Cl_6$.

Compounds with formula $[NP(OH)_2]_n$ are obtained by hydrolysis of phosphonitrilic chlorides $(NPCl_2)_n$. As early as 1895 Stokes (1895) realized that for acids of this type two tautomeric formulae, *e.g.* (I) and (II) for $n=3$, are possible. For the acids in solution Stokes preferred formula (II), as the basicities of the trimeric and tetrameric acid were found to be three and four on normal neutralization. Corbridge & Lowe (1954), who investigated solid salts by spectroscopic methods, thought the anions to be in the phosphonitrilate form corresponding to (I), however. More recent infrared spectroscopic work (Pustinger, Cave & Nielsen, 1959), on the contrary, strongly indicates that the anions in the solid state have the metaphosphimate form (II). Experimental evidence on the acids is less conclusive.


(I)


(II)

Experimental

Sodium trimetaphosphimate was prepared by the method of Stokes (1896). The substance was crystallized by dissolving it in an unsaturated aqueous sodium acetate solution, from which it was precipitated by adding ethanol very slowly. In this way crystals with four molecules of water per unit $Na_3(NHPO_2)_3$ were obtained. In one batch of crystals needles along different directions were present. For the X-ray work needles along the *b* and *c* axes were selected. In making the Weissenberg exposures only crystals with diameters of about 0·08 mm perpendicular to the rotation (needle) axis were used.

The unit cell is monoclinic, space group $P2_1/n$, with

$$a=16{\cdot}976\pm0{\cdot}009\ \text{Å} \qquad b=7{\cdot}834\pm0{\cdot}003\ \text{Å}$$
$$c=\ 8{\cdot}918\pm0{\cdot}006\ \text{Å} \qquad \beta=97{\cdot}08\pm0{\cdot}07°$$

There are 4 units $Na_3(NHPO_2)_3 . 4H_2O$ per cell. Accurate cell dimensions were obtained from back-reflexion photographs [$\lambda(\text{Cu}K\alpha_1)=1{\cdot}54050$, $\lambda(\text{Cu}K\alpha_2)=1{\cdot}54433$ Å].

The intensities of the relatively strong reflexions were measured on integrated equi-inclination Weissenberg photographs of seven layers about the [010] axis. Weak reflexions and high order reflexions with $\alpha_1-\alpha_2$ splitting were estimated visually from ordinary Weissenberg photographs of long exposure time. All films were taken with nickel-filtered Cu radiation. Use was made of the multiple film technique. Corrections for the Lorentz and polarization effects and for spot extension on upper layers of unintegrated Weissenberg photographs (Phillips, 1956) were applied. The intensities were not corrected for absorption as the errors due to absorption are fairly small ($\mu R\simeq0{\cdot}25$). The layers were put on the same relative scale by making another series of integrated Weissenberg photographs, four layers about the [001] axis.

Table 1. *Observed and calculated structure factors*

To obtain *F* on the absolute scale the values in the Table must be divided by 5

h	F_o	F_c
h,0,0		
2	292	313
4	469	-484
6	283	285
8	158	-145
10	287	-285
14	101	98
16	397	410
20	110	-116
h,0,1		
-19	125	-117
-17	225	229
-15	469	499
-13	115	109
-11	450	467
-9	101	-102
-7	392	-384
-5	254	-246
-3	335	-334
-1	81	72
7	761	-703
9	297	-300
11	335	-329
13	101	-90
19	120	140
21	105	122
h,0,2		
-20	115	-123
-18	153	-163
-16	163	161
-14	110	97
-12	225	-214
-10	450	453
-8	254	-248
-6	536	-542
-4	259	-286
-2	91	-63
0	311	-347
2	81	56
4	91	81
6	354	364
8	77	66
10	110	-97
12	72	-55
14	273	268
16	249	-255
18	105	-90
20	244	256
h,0,3		
-21	34	35
-17	206	-202
-15	139	-147
-13	158	-175
-11	148	-143
-9	440	427
-7	182	-164
-5	235	-227
-3	77	94
-1	536	501
1	685	-687
3	513	-462
5	168	153
7	129	118
15	134	-128
17	273	-272
19	105	-99
h,0,4		
-18	129	131
-14	359	-364
-10	148	158
-8	129	-130
-4	354	351
-2	158	153
0	259	239
2	493	-470
4	177	179
6	177	-176
8	321	-315
10	350	348
12	216	217
14	153	-145
h,0,5		
-19	139	161
-17	230	220
-11	220	221
-9	364	-373
-3	331	-333
-1	301	304
1	326	301
3	201	-202
5	206	215
7	254	-261
11	211	205
h,0,6		
-12	225	226
-10	153	172
-8	551	-568
-6	129	-148
-4	225	221
2	651	668
4	388	402
8	115	-109
h,0,7		
-15	182	190
-13	268	276
-11	302	312
-9	244	255
-7	277	-281
-1	163	-175
3	263	261
11	273	-281
13	220	-225
h,0,8		
-16	125	-147
-14	192	203
-6	153	-172
-4	469	-480
-2	277	-283
8	153	164
12	239	-257
h,0,9		
-9	139	-150
-7	192	207
-3	172	-182
9	192	194
h,0,10		
0	144	154
2	120	-127
4	172	-165
6	110	118
h,0,11		
3	115	-137
h,1,0		
1	110	-129
2	354	368
3	192	197
4	172	-185
5	335	-320
6	105	-92
7	125	-134
8	62	34
9	96	88
10	62	-57
11	168	-164
12	53	49
15	225	226
18	96	-99
19	67	74
20	62	-66
21	91	106
h,1,1		
-21	168	184
-17	120	-118
-16	216	-219
-15	120	136
-13	67	67
-12	277	282
-11	134	-122
-9	120	-109
-8	148	-143
-7	144	132
-6	340	-329
-5	273	250
-4	316	-325
-3	321	-346
-2	81	88
-1	398	-407
1	263	280
2	172	186
3	72	53
4	588	644
5	656	-646
6	383	363
7	196	-186
8	139	134
9	206	216
11	192	-184
12	168	-153
13	163	-170
14	168	-166
18	67	60
19	105	-111
20	62	68
h,1,2		
-21	96	-100
-19	48	-47
-17	144	-144
-16	91	-94
-15	201	-204
-14	77	-83
-13	187	193
-12	225	-223
-11	302	302
-10	416	-427
-9	283	272
-8	77	74
-7	469	458
-6	105	-85
-5	259	-230
-4	507	-462
-3	455	-434
-2	259	255
-1	38	-33
1	43	-36
2	331	-314
3	72	53
4	91	73
5	144	144
6	263	-252
8	48	47
9	158	135
10	216	217
13	388	-394
14	134	141
15	287	-303
16	96	98
18	153	-158
20	53	-51
h,1,3		
-21	43	-37
-20	77	-80
-17	91	102
-15	110	111
-14	211	-204
-11	388	-399
-10	254	251
-9	77	80
-8	139	121
-7	565	567
-6	187	186
-5	216	-219
-4	196	-177
-3	263	254
-2	426	-445
-1	646	716
0	206	-220
1	120	102
2	177	-186
3	283	-290
4	460	-453
5	220	-211
6	77	62
7	120	113
8	196	186
12	148	140
13	249	243
15	177	179
16	158	-163
19	187	-195
h,1,4		
-18	168	180
-16	148	154
-13	163	-160
-12	96	-101
-11	211	-215
-10	211	-209
-9	182	-192
-8	177	-184
-7	77	-75
-6	134	139
-5	249	244
-4	158	140
-3	163	153
0	259	256
2	196	179
4	489	-499
5	192	-180
6	96	-99
7	67	62
9	163	153
10	96	-99
11	158	163
12	268	272
13	196	193
14	196	195
17	81	-89
h,1,5		
-20	101	121
-13	211	-210
-12	139	-140
-10	125	-122
-9	192	187
-8	77	85
-7	307	-301
-6	110	-106
-4	263	258
-3	517	521
-2	527	527
-1	350	366
0	230	234
2	77	65
4	120	-111
5	96	91
6	302	-303
8	125	124
9	335	-346
12	115	-115
13	254	256
14	134	149
17	86	-92
h,1,6		
-19	153	176
-17	110	119
-16	101	110
-13	148	145
-9	66	-87
-8	86	81
-6	345	-349
-5	277	-263
-4	125	-134
-2	139	140
-1	235	230
0	110	-121
1	101	-109
3	139	-140
5	72	-69
6	148	-151
7	196	-203
10	211	-216
14	72	71
16	96	-108
h,1,7		
-18	53	65
-17	81	-83
-15	144	-152
-13	105	107
-5	168	-188
-4	263	-267
-3	144	155
-1	168	-157
1	196	-182
3	254	267
6	86	84
7	125	-135
10	96	96
15	96	-100
h,1,8		
-16	158	-181
-15	105	-108
-14	72	-75
-11	110	118
-5	177	180
0	168	-182
7	168	163
12	168	176
h,1,9		
-10	81	84
-9	134	-155
-5	259	270
-4	139	148
0	201	-206
1	230	234
2	110	-118
5	120	-125
8	110	108
h,1,10		
-8	67	-77
-6	67	-73
-5	72	-81
-3	120	139
1	81	-88
2	163	179
6	177	-196
h,1,11		
-6	48	62
-5	148	-174
-2	144	161
h,2,0		
0	311	-329
1	316	-331
2	148	163
3	378	388
4	62	101
5	168	206
6	392	-393
7	77	-78
8	144	-138
9	101	-96
12	102	102
13	144	-139
14	235	-235
16	153	-152
17	91	-75
18	172	171
21	86	105
h,2,1		
-21	72	-77
-20	105	-106
-16	120	-118
-14	277	-281
-12	311	311
-11	86	73
-9	187	186
-8	91	77
-6	316	304
-5	163	-139
-4	292	-289
-3	297	263
-2	340	-347
-1	277	-298
0	81	86
1	48	22
2	426	-436
3	206	195
4	565	574
6	134	141
8	187	-180
9	148	-136
14	302	-312
15	192	-193
16	139	-139
19	134	120
h,2,2		
-20	72	75
-19	91	-86
-18	81	-82
-17	72	73
-16	168	-169
-15	144	-137
-14	115	115
-13	297	-302
-12	168	164
-11	407	416
-10	201	-202
-9	163	151
-8	192	-204
-7	153	141
-6	392	389
-3	196	-179
-2	722	-768
-1	455	-485
0	350	-367
1	239	-225
2	354	359
3	115	-130
4	205	-195
5	192	177
6	77	-72
7	96	99
8	302	295
9	86	84
10	302	309
11	110	-107
13	120	113
14	105	-111
15	230	-231
16	86	83
17	144	-143
18	77	-76
19	81	84
20	72	-72
h,2,3		
-21	72	89
-17	172	-169
-16	62	-54
-15	225	-226
-14	177	-176
-12	177	-170
-11	62	-55
-10	192	182
-9	91	90
-7	273	273
-6	139	120
-5	211	214
-4	196	-181
-3	364	381
-2	196	-185
-1	283	262
0	354	-376
1	153	-146
2	168	160
3	144	150
5	163	147
6	101	87
7	263	257
8	259	256
9	307	307
10	144	128
11	134	135
12	72	56
13	96	-100
14	187	178
16	168	-173
19	110	-118
h,2,4		
-20	134	142
-17	120	-109
-14	110	108
-13	129	130
-11	158	-142
-10	86	-88
-9	172	155
-8	422	422
-7	196	190
-6	249	243
-5	91	83
-4	91	76
-1	81	77
2	91	-76
3	579	613
4	503	-557
5	144	-138
6	335	-342
7	239	-243
8	216	-204
9	211	206
12	158	-138
13	139	-135
15	139	130
18	72	-70
h,2,5		
-18	86	75
-14	91	70
-13	144	-136
-12	283	293
-11	283	-284
-6	57	-59
-5	148	-152
-4	268	-256
-3	187	-178
-2	62	-64
-1	163	-169
0	129	124
1	139	139
3	225	-222
4	297	302
5	225	-224
6	177	-164
7	158	157
8	239	-245
12	115	-101
13	101	96
16	129	132
h,2,6		
-19	62	-78
-18	77	-70
-16	86	94
-13	134	123
-12	235	-228
-11	201	209
-9	163	-166
-8	91	92
-7	110	109
-6	105	-93
-5	249	-248
-3	445	-460
-2	163	159
0	134	120
1	192	180
2	101	-98
5	268	276
6	254	260
10	182	-171
13	134	-124
15	72	-81
h,2,7		
-14	125	-108
-10	235	229
-6	120	113
-4	172	-176
-2	302	-303
-1	77	74
2	110	125
3	91	-95
4	120	-110
6	148	152
7	115	101
8	211	209
12	101	-95
h,2,8		
-14	96	-99
-13	168	-168
-10	196	207
-9	249	254
-7	125	111
-6	235	-229
-5	125	128
-2	211	218
-1	139	-139
0	148	-133
1	120	-135
2	148	-147
5	148	-132
7	139	140
9	163	162
12	110	112
h,2,9		
-13	125	-135
-12	201	-204
-10	81	-73
-8	177	180
-4	91	93
-3	110	122
-2	158	155
2	158	-159
6	148	-141
10	153	155
h,2,10		
-11	57	-65
-8	86	-81
-7	72	75
-6	110	114
-4	187	179
-3	96	93
-1	235	244
3	72	-82
5	72	74
6	72	-74
7	96	-103
h,2,11		
-4	89	-101
-1	86	-97
0	91	94
1	96	-108
h,3,0		
1	53	-46
2	86	88
3	168	-167
4	77	85
6	201	182
7	91	-79
8	201	-193
9	244	-235
10	368	-367
12	105	-103
13	96	87
16	86	-76
20	144	149
h,3,1		
-20	77	-81
-16	144	122
-14	96	-95
-13	148	-142
-12	216	-210
-11	62	63
-9	436	446
-8	249	-246
-7	407	-436
-6	388	-400
-5	388	-391
-3	230	228
-2	216	191
-1	469	-511
0	172	190
2	158	-146
3	474	515
4	192	-188
5	115	116
6	316	311
7	120	106
10	283	-275
12	134	125
13	153	148
14	230	226
17	101	-102
19	196	184
h,3,2		
-20	105	112
-16	148	-141
-15	182	181
-14	72	75
-13	86	-86
-12	77	-76
-11	110	-108
-9	168	166
-8	345	337
-4	43	27
-3	182	182
-1	331	339
0	249	233
2	201	189
3	81	84
4	139	127
5	177	-169
6	168	179
7	72	42
10	115	92
11	134	-134
12	110	102
14	134	-141
15	144	140
16	86	-79
18	148	-138
h,3,3		
-19	244	239
-18	115	111
-16	163	155
-15	187	-193
-14	182	176
-11	134	120
-10	57	49
-9	182	-165
-7	120	-101
-6	235	-236
-5	350	348
-4	72	-65
-3	196	203
-2	125	116
-1	307	-309
1	172	-177
4	168	157
6	139	-137
7	479	-512
8	277	-274
9	91	-94
10	91	-75
11	402	413
14	96	86
15	134	-133
17	77	64
19	134	-130
h,3,4		
-18	211	203
-14	105	-92
-13	148	132
-10	101	-83
-9	172	-170
-8	277	-272
-7	196	-194
-6	172	157
-5	120	-106
-4	91	73
-2	91	-73
0	177	170
2	101	-96
3	292	286
4	321	-320
5	359	363
6	62	-63
7	125	-114
8	239	-245
9	206	-192
11	101	88
12	230	226
18	67	77
h,3,5		
-12	177	169
-11	235	-225
-10	196	179
-9	148	-141
-8	148	-134
-7	192	-178
-6	91	-82
-3	144	-124
-1	81	-67
1	350	366
3	168	152
5	311	-309
6	163	157
8	225	-215
10	206	-191
14	163	-155
15	96	98
17	96	90
h,3,6		
-18	163	-169
-14	158	162
-11	139	120
-10	163	151
-8	158	134
-7	230	-223
-4	196	196
-3	172	-161
-2	220	-212
-1	230	-223
1	105	93
2	422	442
4	148	143
6	91	-87
8	148	134
12	163	-155
14	110	-106
h,3,7		
-17	153	-162
-15	77	74
-14	105	107
-13	96	85
-9	230	220
-7	316	322
-5	244	-241
-3	340	-347
-2	230	-238
-1	101	-91
1	91	-85
2	311	318
3	182	-177
5	168	160
6	115	-102
7	158	141
9	110	114
10	115	115
13	144	-148
h,3,8		
-15	53	59
-14	110	-114
-13	105	100
-8	177	170
-6	235	229
-4	148	-135
2	163	-150
3	168	158
6	182	173
8	115	101
10	168	158
h,3,9		
-13	148	-108
-12	67	135
-9	91	99
-4	115	-241
-1	134	-118
0	110	-71
3	244	-118
5	125	-54
8	67	-195
9	120	-236
h,3,10		
-8	57	-54
-6	192	-195
-3	259	-236
0	110	116
1	144	140
3	101	-100
4	96	-93
h,4,0		
1	62	74
2	86	73
3	62	64
4	134	-127
5	129	-118
6	268	269
7	129	125
8	513	529
9	168	160
10	139	139
11	244	251
12	297	-298
15	110	97
16	77	-62
18	211	-214
h,4,1		
-19	91	84
-18	67	-60
-16	81	-76
-15	69	-106
-11	201	-188
-10	168	-171
-9	268	260
-7	416	419
-6	354	370
-5	158	153
-4	321	334
-3	96	-76
-2	43	49
0	259	279
1	541	572
2	105	97
3	48	-42
4	53	-37
5	91	-84
7	196	-194
9	96	81
11	105	104
13	101	-87
14	144	-137
15	96	87
17	139	-122
18	96	-78
19	125	-129
h,4,2		
-18	148	139
-16	96	81
-15	158	151
-14	101	-86
-13	77	-66
-12	72	-70
-11	129	-132
-10	287	-293
-9	120	112
-8	81	82
-7	235	235
-5	129	117
-4	96	-81
-2	259	258
-1	182	-184
0	77	64
1	201	192
2	383	-391
3	374	-404
4	211	-207
5	297	-303
6	134	136
7	172	163
8	182	-169
9	168	158
10	139	-127
12	235	233
14	120	122
h,4,3		
-19	57	-49
-18	110	105
-17	192	174
-14	72	-68
-13	125	-108
-12	201	-206
-11	153	144
-9	196	-202
-8	86	-81
-7	239	-237
-4	105	102
1	287	291
2	86	-87
3	144	-136
4	244	-232
5	72	55
6	81	75
7	120	113
9	321	-318
10	101	100
11	230	-235
12	153	140
13	177	168
14	77	69
17	62	57
18	101	-115
h,4,4		
-17	115	98
-16	129	115
-13	211	-205
-11	297	-304
-10	311	311
-9	110	102
-8	220	-210
-6	187	-181
-5	134	-125
-3	101	93
-1	326	321
0	153	-157
2	220	217
3	168	-159
4	183	179
5	134	-122
7	115	-107
8	134	-112
9	168	-156
10	101	-95
13	96	88
15	163	143
16	101	-94
17	81	-83
h,4,5		
-18	57	56
-16	182	159
-9	196	195
-7	86	74
-6	168	-162
-5	168	-146
-2	144	124
-1	96	-86
0	254	253
1	283	-283
3	254	256
8	196	-192
9	153	143
10	206	-208
14	158	143
16	81	90
h,4,6		
-16	249	-230
-12	120	110
-11	101	95
-10	259	-254
-9	153	-139
-8	96	67
-7	277	-280
-6	239	232
-5	163	-152
-4	134	132
0	239	-239
3	148	145
4	273	276
5	201	202
6	148	-143
7	120	-111
9	129	-125
10	225	227
11	120	101
h,4,7		
-15	134	-127
-14	77	-62
-10	259	217
-9	153	-155
-7	196	198
-5	211	211
-4	120	109
-3	101	98
-2	115	106
0	110	94
1	129	-129
2	125	120
3	153	-153
4	134	121
6	134	123
7	134	-115
11	115	98
h,4,8		
-14	96	-99
-12	77	-66
-11	96	72
-10	134	-119
-8	168	-170
-6	168	167
-5	129	131
-2	148	-142
0	129	120
1	120	-118
4	249	-255
5	115	-99
7	187	-159
h,4,9		
-12	72	-80
-11	81	-68
-10	196	-189
-8	110	-93
-5	77	69
-4	81	76
1	129	124
3	196	167
5	125	-120
6	206	-200
h,4,10		
-8	148	166
-6	86	-78
-4	129	-121
-2	72	64
-1	81	69
1	153	147
h,5,0		
2	187	-199
3	311	-324
4	125	130
5	359	367
7	201	196
8	120	-126
10	81	-76
11	239	241
12	139	-122
15	163	-148
h,5,1		
-16	77	-78
-14	196	-201
-13	129	122
-11	105	96
-9	220	-217
-8	196	-201
-7	115	111
-6	398	408
-4	589	612
-3	469	-493
-2	62	-47
-1	48	-56
0	172	-193
1	148	151
2	81	-68
3	81	-58
4	91	-71
5	86	-85
6	91	-85
8	105	96
9	105	95
10	297	302
12	153	153
13	139	-135
16	81	-79
17	115	118
18	43	-43
h,5,2		
-18	81	-76
-17	72	61
-14	115	-112
-13	177	-168
-11	158	-152
-9	110	-99
-8	101	-98
-7	125	-117
-5	331	335
-4	211	-210
-3	249	255
-2	101	-99
-1	105	-104
0	148	147
1	67	-65
2	105	105
3	120	-113
4	168	165
5	445	-452
6	110	106
7	239	-246
8	120	122
17	62	-61
h,5,3		
-15	129	125
-14	187	196
-12	172	-175
-10	331	-336
-9	230	235
-7	144	134
-4	101	-99
-3	105	106
1	101	-97
6	230	-233
7	86	71
10	105	105
11	235	-247
12	134	-127
16	216	198
17	129	-149
h,5,4		
-17	86	-89
-15	91	91
-13	125	129
-9	148	-144
-7	201	184
-4	163	-156
-3	307	-311
-2	120	-120
-1	96	-89
0	144	-138
2	101	-78
5	225	229
8	144	131
13	172	-174
14	115	107
15	91	85
16	43	41
h,5,5		
-16	81	-69
-15	91	-76
-13	110	-107
-12	81	73
-10	96	83
-8	144	137
-6	368	368
-5	144	-145

Table 1 (*cont.*)

h	F_o	F_c
-4	196	-194
-2	163	-169
-1	259	273
0	144	132
1	134	-132
2	160	-154
5	292	302
6	392	403
8	182	184
12	77	-70
h,5,6		
-14	81	-75
-13	192	-177
-12	101	107
-11	86	84
-9	259	269
-7	148	142
-6	168	160
-5	192	187
-4	81	-79
-1	105	-99
1	139	-129
3	148	-144
7	192	193
8	91	-93
h,5,7		
-14	134	-142
-12	307	-307
-11	153	143
-8	129	130
-6	115	-98
-4	96	97
-1	172	-172
1	134	-119
2	158	-147
10	72	-69
h,5,8		
-13	43	-64
-12	57	-60
-11	172	-179
-10	101	91
-6	86	-75
-5	86	-79
-4	101	94
-3	192	175
-1	148	138
0	163	-158
1	105	-99
4	81	73
7	168	-187
8	62	61
9	67	-76
h,5,9		
-8	211	-211
-7	120	113
-5	125	115
-2	120	113
4	110	115
h,6,0		
0	364	-374
3	144	-146
4	62	52
5	77	73
7	187	193
8	101	92
9	139	-140
10	187	175
13	220	230
15	105	-91
16	101	-90
17	101	-120
h,6,1		
-12	101	-92
-11	148	-142
-8	139	-142
-7	125	114
-6	196	-193
-5	230	237
-4	187	193
-2	177	173
-1	48	34
0	182	-187
2	139	135
3	62	-52
4	110	117
5	110	-102
6	115	-104
8	115	-119
10	96	-92
11	148	154
13	62	65
14	67	67
16	96	-91
h,6,2		
-16	67	54
-14	53	53
-13	172	72
-11	91	84
-10	134	-156
-8	216	-217
-7	172	-165
-5	239	-238
-4	144	146
-3	172	170
-1	81	75
0	153	138
1	368	-376
3	110	113
4	62	62
5	67	78
6	206	-222
7	239	-233
8	249	-249
9	125	-120
13	96	-85
15	53	43
16	172	186
h,6,3		
-17	77	100
-16	148	-149
-15	153	137
-13	77	68
-12	172	180
-11	110	101
-10	158	-147
-9	216	-209
-8	115	-113
-7	268	-270
-6	144	-141
-5	158	-162
-4	192	-190
-3	62	53
-1	129	133
1	259	263
3	124	132
4	244	244
5	120	116
6	115	124
7	120	-122
9	206	-204
10	129	120
11	163	-165
12	101	98
14	120	-118
15	120	119
h,6,4		
-16	72	67
-15	110	-101
-13	153	139
-12	67	75
-11	177	179
-9	115	-113
-7	172	171
-6	134	-123
-5	364	376
-4	316	-323
-2	91	-86
-1	163	-167
0	182	181
1	307	308
2	259	262
3	163	164
7	101	92
9	105	92
10	182	-177
11	91	84
12	230	-200
13	134	-111
14	43	34
h,6,5		
-15	67	63
-13	110	83
-10	134	132
-9	125	121
-6	86	83
-4	201	204
-3	115	-120
-2	168	-172
-1	168	-169
0	268	-268
3	220	218
4	182	-181
7	57	46
8	72	68
13	72	-69
h,6,6		
-8	120	110
-1	101	-102
2	153	-153
5	211	-205
6	110	102
7	125	105
9	216	195
11	91	-87
h,6,7		
-12	86	-86
-11	91	-74
-10	277	-237
-9	62	-52
-8	168	168
-7	86	76
-4	125	-132
-2	101	97
-1	72	74
0	53	49
3	125	-127
4	67	-66
6	115	-94
8	110	108
h,6,8		
-10	34	30
-8	81	-63
-7	139	126
-5	115	-104
-3	62	-52
-1	125	108
3	81	-69
5	81	65
h,6,9		
-5	46	-44
-4	72	-73
-3	53	-44
-2	86	-83
-1	38	-35
1	62	54
h,7,0		
1	96	-101
2	287	-305
4	168	-168
6	211	-212
7	148	136
9	72	65
10	168	163
11	105	-111
h,7,1		
-15	72	-76
-12	177	-179
-10	105	-106
-9	244	-248
-8	235	234
-6	105	-99
-4	120	-120
-2	216	233
-1	144	126
1	158	-154
2	268	-267
3	244	-236
4	201	-213
8	96	87
10	91	-89
11	225	226
13	96	100
14	134	143
h,7,2		
-15	34	-38
-14	57	-55
-13	96	-96
-12	110	-105
-11	105	-90
-8	177	-172
-4	72	65
-3	96	93
-1	254	257
0	220	230
1	91	88
2	110	111
3	105	-104
4	153	-145
6	101	100
7	110	109
10	125	-137
11	62	61
12	62	56
13	153	144
14	62	65
h,7,3		
-15	62	-77
-14	43	-41
-13	57	45
-11	115	108
-7	144	-140
-6	105	-94
-5	129	121
-3	86	91
-2	168	164
-1	129	-117
3	134	126
4	115	104
8	139	-137
9	57	-47
10	129	-129
11	148	-137
12	129	128
13	48	-42
h,8,0		
1	134	135
2	144	-148
4	77	-77
6	91	82
8	77	-69
9	196	207
11	67	67
12	91	88
h,8,1		
-11	62	63
-7	72	-70
-6	77	65
-5	105	108
-4	134	126
-2	110	115
-1	125	-126
1	101	96
2	254	254
6	110	-102
7	91	88
12	115	-123
h,8,2		
-12	129	-125
-11	86	-94
-10	105	99
-8	115	113
-5	134	-142
-3	158	-158
-1	201	185
0	86	-91
1	115	128
3	67	-73
5	105	-102
7	62	56
9	67	-74
11	153	-164
h,8,3		
-12	72	74
-11	48	-43
-9	57	-65
-7	67	62
-6	134	-123
-4	158	-156
-1	72	-69
0	139	151
1	72	-72
4	91	86
5	72	-62
6	91	100
9	163	155
10	77	-76
h,9,0		
2	81	-86
3	182	185
4	125	-133
6	91	95
7	177	-186
h,9,1		
-8	48	-53
-2	67	56
2	105	103
3	53	-49
4	196	218
6	134	-140
7	53	48
8	110	-127
h,9,2		
-9	57	-80
-6	48	-48
-5	129	-119
-3	216	-221
2	129	-125
4	110	112
5	77	74
7	48	-49
h,9,3		
-8	67	-76
-6	168	166
-2	244	-231
0	129	123
2	177	169
3	53	54
4	105	-102
5	115	119
h,10,0		
0	192	239
1	125	-161

Table 2. *Final atomic coordinates and estimated standard deviations*

Atom	*x*	s.d.	*y*	s.d.	*z*	s.d.
P(1)	0·3661	0·0001	0·2171	0·0002	0·3993	0·0002
P(2)	0·3281	0·0001	0·1176	0·0002	0·7042	0·0002
P(3)	0·4377	0·0001	0·4029	0·0002	0·6682	0·0002
N(1)	0·3049	0·0003	0·1366	0·0007	0·5163	0·0006
N(2)	0·3669	0·0003	0·3085	0·0007	0·7602	0·0006
N(3)	0·4009	0·0003	0·3961	0·0007	0·4846	0·0006
O(1)	0·4328	0·0003	0·0950	0·0006	0·3883	0·0005
O(2)	0·3894	0·0003	−0·0164	0·0006	0·7422	0·0005
O(3)	0·5107	0·0003	0·2953	0·0006	0·6927	0·0005
O(4)	0·3150	0·0003	0·2667	0·0007	0·2566	0·0005
O(5)	0·2504	0·0003	0·0976	0·0006	0·7669	0·0005
O(6)	0·4420	0·0003	0·5852	0·0006	0·7167	0·0005
Na(1)	0·4356	0·0002	0·8232	0·0003	0·5282	0·0003
Na(2)	0·3632	0·0002	0·7328	0·0004	0·8793	0·0003
Na(3)	0·5272	0·0002	1·0405	0·0004	0·8230	0·0003
O_I	0·3046	0·0003	0·7127	0·0007	0·4681	0·0006
O_{II}	0·6299	0·0003	1·4571	0·0007	0·9000	0·0006
O_{III}	0·5176	0·0003	0·7792	0·0007	0·9594	0·0005
O_{IV}	0·6655	0·0003	1·0841	0·0007	0·9123	0·0006

Determination of the structure

The approximate coordinates of all independent atoms except the hydrogen atoms could be found from a three-dimensional Patterson synthesis. First the [010] and [001] projections were refined by successive cycles of structure factor calculations and difference Fourier syntheses. The scale factor was determined by comparison of the calculated and observed structure factors. For all atoms the temperature factor was assumed to be $\exp[-1{\cdot}5\sin^2\theta/\lambda^2]$. $R(hk0)$ decreased from 0·49 to 0·14 and $R(h0l)$ from 0·42 to 0·12. No positions for the hydrogen atoms were obtained.

For the three-dimensional refinement 1450 independent reflexions were available. Schoone's program (Schoone, 1961) for least-squares refinement on the computer ZEBRA was used to obtain refined atomic coordinates and isotropic temperature factors for the individual atoms. After ten cycles the index R was 0·064. Thereafter four cycles of anisotropic least-squares calculations were kindly carried out by Dr J. S. Rollett (Rollett, 1961) on the Mercury computer at Oxford. The weighting scheme was $w=[1+(|F_o|-61)^2/41^2]^{-1}$. The atomic scattering functions were substantially those now recommended in *International Tables for X-ray Crystallography* (1962). The index R decreased to 0·049. The observed and calculated structure factors are listed in Table 1.

Final coordinates are listed in Table 2 with their standard deviations as derived from the least-squares residuals; vibrational parameters are given in Table 3. An attempt was made to correct the coordinates of the phosphorus, nitrogen and oxygen atoms of the metaphosphimate group for the effects of torsional oscillation of the group, considered as a rigid body (Cruickshank, 1956). This was not successful, however. The bad agreement between observed and calculated vibrational parameters showed that the metaphosphimate

Table 3. *Thermal parameters* (*in* Å$^2 \times 10^5$)

Standard deviations calculated by the least-squares program are given in brackets

	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
P(1)	1147(50)	1145(50)	884(47)	−357(88)	171(95)	0(73)
P(2)	1047(50)	798(50)	1396(50)	−329(83)	144(97)	1053(73)
P(3)	958(40)	602(47)	1112(39)	−213(83)	76(95)	356(73)
N(1)	1616(170)	1680(203)	1473(179)	−621(302)	−246(314)	970(278)
N(2)	1506(170)	1266(183)	1049(173)	−385(278)	390(307)	1142(267)
N(3)	1476(160)	1476(190)	1567(176)	−394(306)	887(331)	388(273)
O(1)	2025(150)	1825(168)	1825(160)	232(274)	−1150(292)	718(246)
O(2)	1885(150)	1059(157)	2271(171)	404(246)	563(271)	1153(241)
O(3)	1347(140)	1456(157)	1605(149)	334(246)	183(266)	147(225)
O(4)	2803(170)	3247(205)	1834(171)	−2264(311)	926(322)	−2012(283)
O(5)	1975(140)	2095(197)	2489(171)	−1266(176)	−49(327)	2227(252)
O(6)	1925(140)	1158(157)	1641(149)	−348(297)	−858(268)	524(236)
Na(1)	1616(80)	1624(93)	1740(88)	−751(139)	−297(149)	818(136)
Na(2)	3511(110)	2183(104)	2505(107)	−1192(176)	−658(180)	954(168)
Na(3)	2594(90)	1728(93)	2252(96)	−148(148)	404(163)	687(152)
O_{I}	2095(170)	3594(205)	2376(179)	−557(315)	1448(341)	−671(273)
O_{II}	3372(200)	2906(208)	2739(204)	−543(320)	1806(324)	−624(325)
O_{III}	2773(170)	2207(179)	1908(165)	872(302)	341(307)	671(267)
O_{IV}	2683(190)	3225(224)	4917(240)	−366(343)	−1270(405)	980(330)

group could not be considered as a rigid body oscillating around its centre of mass. This is likely to be ascribed to the strong intermolecular forces in the crystal. Bond lengths and angles in Table 4 are thus not corrected for rotational effects.

During the refinement the hydrogen atoms were not taken into account. An attempt was made to determine their positions from a difference Fourier synthesis of 420 low order reflexions with $(\sin\theta)/\lambda < 0{\cdot}4$ Å^{-1}. Among others three important peaks, one in the neighbourhood of each of the nitrogen atoms, were observed at a distance of about 1 Å from the respective nitrogen atoms. The heights are between 0·3 and 0·4 e.Å^{-3}, which is approximately four times as large as the e.s.d. in the electron density. It could thus be concluded that the anions have the metaphosphimate form with hydrogen atoms directly linked to the nitrogen atoms.

Accuracy

Standard deviations in bond lengths and valence angles, as calculated from the e.s.d. in the atomic coordinates listed in Table 2, are 0·006 Å for P–N, 0·005 Å for P–O and 0·3° for the angles. Moreover systematic errors of two kinds may be present. Firstly, the positions of the heavy atoms may be slightly in error as the hydrogen atoms were not considered during the refinement. This effect was investigated by another cycle of anisotropic least-squares refinement in which the hydrogen atoms were taken into account with fixed positions. The index R changed only from 0·049 to 0·046. The maximum observed changes are 0·004 Å in the bond lengths and 0·6° in the angles. Secondly, errors due to rotational effects were roughly estimated at 0·004 Å for the bond lengths and 0·2° for the angles.

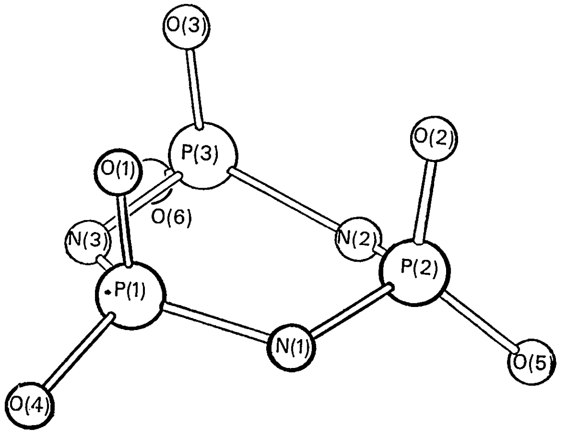


Fig. 1. The trimetaphosphimate anion.

Description of the structure

As was mentioned in the previous paragraph a three-dimensional difference map showed the anions to be in the metaphosphimate form: $[NHPO_2]_3^{3-}$. In Fig. 1 the anion is illustrated. The six-membered ring is in the chair form; the distances of the nitrogen atoms to

Table 4. *Interatomic distances and bond angles in the trimetaphosphimate anion*

P(1)–N(3)	1·668 Å	P(1)–O(1)	1·495 Å
P(1)–N(1)	1·683	P(1)–O(4)	1·500
P(2)–N(1)	1·680	P(2)–O(2)	1·487
P(2)–N(2)	1·685	P(2)–O(5)	1·503
P(3)–N(2)	1·705	P(3)–O(3)	1·492
P(3)–N(3)	1·680	P(3)–O(6)	1·491
P(1)–N(1)–P(2)	124·4°	N(3)–P(1)–O(1)	109·8°
P(2)–N(2)–P(3)	121·0	N(3)–P(1)–O(4)	107·7
P(3)–N(3)–P(1)	122·6	N(1)–P(1)–O(1)	109·4
N(3)–P(1)–N(1)	104·1	N(1)–P(1)–O(4)	106·6
N(1)–P(2)–N(2)	104·6	N(1)–P(2)–O(2)	111·1
N(2)–P(3)–N(3)	104·8	N(1)–P(2)–O(5)	105·8
O(1)–P(1)–O(4)	118·3	N(2)–P(2)–O(2)	108·8
O(2)–P(2)–O(5)	117·6	N(2)–P(2)–O(5)	108·1
O(3)–P(3)–O(6)	119·3	N(2)–P(3)–O(3)	107·8
		N(2)–P(3)–O(6)	106·7
		N(3)–P(3)–O(3)	109·1
		N(3)–P(3)–O(6)	108·2

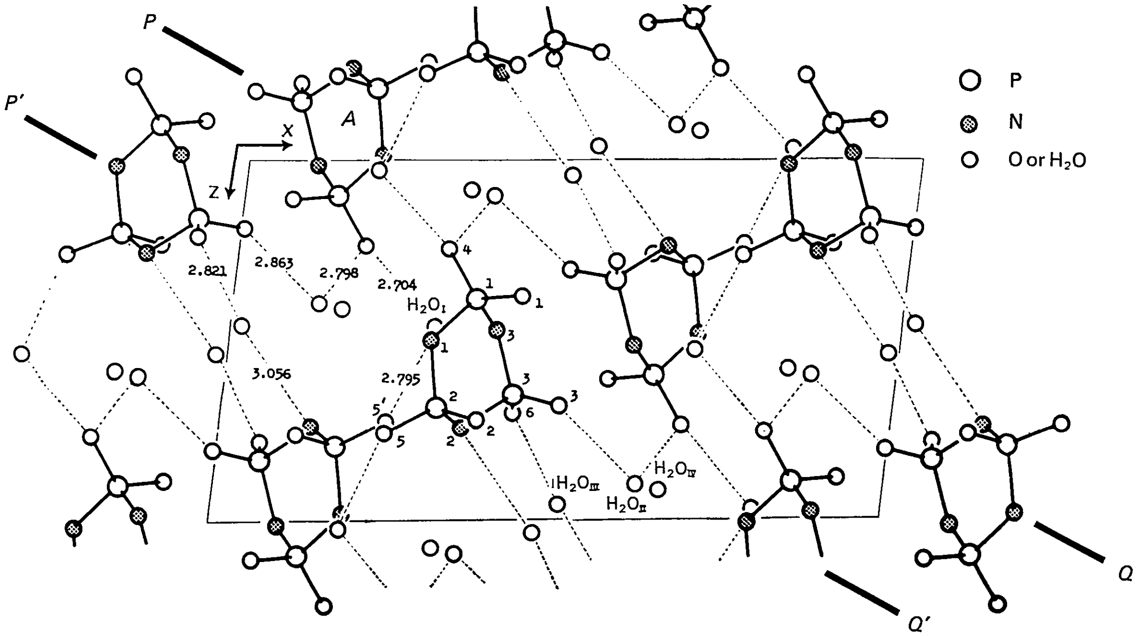


Fig. 2. The structure viewed along [010]; the y axis points downwards. (The sodium atoms are shown in Fig. 5).

the plane through the three phosphorus atoms are 0·394, 0·449 and 0·442 Å. As may be seen from the bond lengths and valence angles in Table 4 the phosphorus, nitrogen and oxygen atoms of the anion have the approximate symmetry $3m$ (C_{3v}). The triangles of the three phosphorus and the three nitrogen atoms have P–P distances of 2·97, 2·94 and 2·95 Å and N–N distances of 2·66, 2·68 and 2·64 Å respectively.

Although the positions of the three hydrogen atoms linked to N(1), N(2) and N(3) could not be determined accurately from the difference map, the positions of their maxima indicate that they are located differently relative to the (N–P)$_3$ ring. Both at N(2) and N(3) pyramids are present with an angle P–N–P of about 122° and two angles P–N–H of approximately 109°. At N(1) a very flat pyramid with the hydrogen atom lying close to the plane through N(1), P(1) and P(2) is found; a hydrogen atom at N(1) related to those at N(2) and N(3) by $3m$ symmetry would lie in a negative area of the difference map at a distance of 1·1 Å from the observed maximum. All hydrogen atoms are at the same side of the molecule as O(4), O(5) and O(6). The difference in location of the hydrogen reduces the approximate symmetry of the anion from $3m$ to m. The remaining pseudo mirror plane is the best plane through N(1), P(3), O(3) and O(6). The distances of all atoms of the anion to this plane are listed in Table 5. Also the atoms (ions) in the near surroundings of the metaphosphimate group are approximately related by the pseudo mirror plane mentioned above. This suggests that the differences observed for the hydrogen atoms are due to intermolecular forces. A planar configuration at N(2) and N(3), as observed at N(1), would bring the hydrogen atoms linked to these nitrogen atoms close to the sodium cations, whereas in the present positions the hydrogen atoms take part in weak hydrogen bonds, N(2)–H · · · O(5′) = 3·00 Å and N(3)–H · · · $(H_2O)_I$ = 2·96 Å. The nitrogen and oxygen atoms involved in these hydrogen bonds are indicated by numbers in Fig. 2. The hydrogen atom attached to N(1) has quite large distances to the surrounding atoms (ions).

The arrangement of the anions in [010] projection is illustrated in Fig. 2. The Figure shows that the atoms N(1) and P(3) of 'molecule' A, and of all molecules related to it by the glide plane n, nearly coincide with

Table 5. *Distances to the best plane through* N(1), P(3), O(3) *and* O(6)

P(1)	−1·487 Å	O(1)	−1·708 Å
P(2)	+1·488	O(2)	+1·733
P(3)	−0·010	O(3)	+0·003
N(1)	+0·002	O(4)	−2·450
N(2)	+1·352	O(5)	+2·492
N(3)	−1·330	O(6)	+0·005

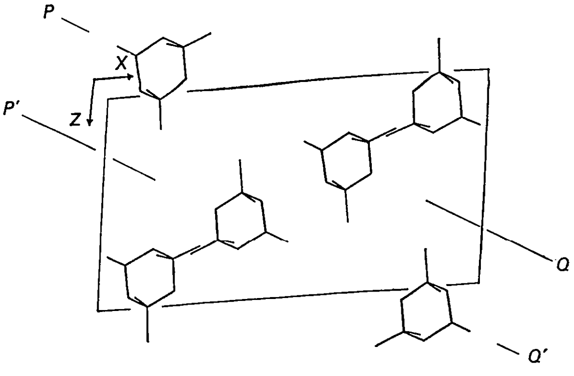


Fig. 3. The anions in [010] projection after rotation around the lines N(1)P(3) (see text).

a plane, tentatively called *V*, passing through *PQ* and perpendicular to the plane of projection. The atoms N(1) and P(3) of the molecules centrosymmetrically related to those on *V* are on a plane *V′* parallel to *V* and passing through *P′Q′*. The dihedral angle between *V*(or *V′*) and the pseudo mirror planes of the molecules is 15°; the lines of intersection almost coincide with the lines N(1)P(3). Rotation of all molecules about these lines through an angle of 15°, in symmetrically related directions, makes the pseudo mirror planes coincide either with *V* or *V′*. In this way Fig. 3 is obtained from Fig. 2. The arrangement of the anions in Fig. 3 shows some analogy with the crystal structure of the trimeric phosphonitrilic compounds in which the molecules lie on symmetry planes in the space group *Pnma* (Wilson & Carroll, 1960; Dougill, 1963). The glide plane *n* for the metaphosphimate anions corresponds to the glide plane *a* for the phosphonitrilic molecules.

Neighbouring phosphimate anions are 'connected' by sodium cations and by hydrogen bridges. Figs. 4 and 5 show that all sodium atoms are approximately octahedrally coordinated by six oxygen atoms, either from the phosphimate groups or from the water molecules. It may be seen that Na(1) is surrounded by five oxygen atoms of three different phosphimate groups and one water molecule; Na(2) and Na(3) are surrounded by three oxygen atoms from three and two

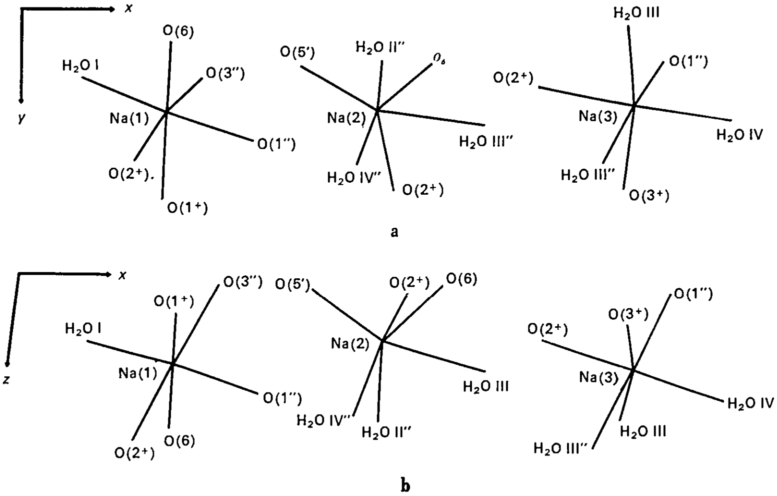


Fig. 4. Coordination octahedra of the sodium atoms (*a*) in [010] projection and (*b*) in [001] projection. The oxygen atoms O(1⁺), O(2⁺), O(3⁺) are of the metaphosphimate group adjacent to that of O(6) in the positive y direction, O(1″) and O(3″) are related to O(1) and O(3) by the centre at ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$), O(5′) is related to O(5) by the screw axis [$\frac{1}{4}$, y, $\frac{3}{4}$]. The molecules (H_2O)″ are related to H_2O by the centre at ($\frac{1}{2}$, 1, 1).

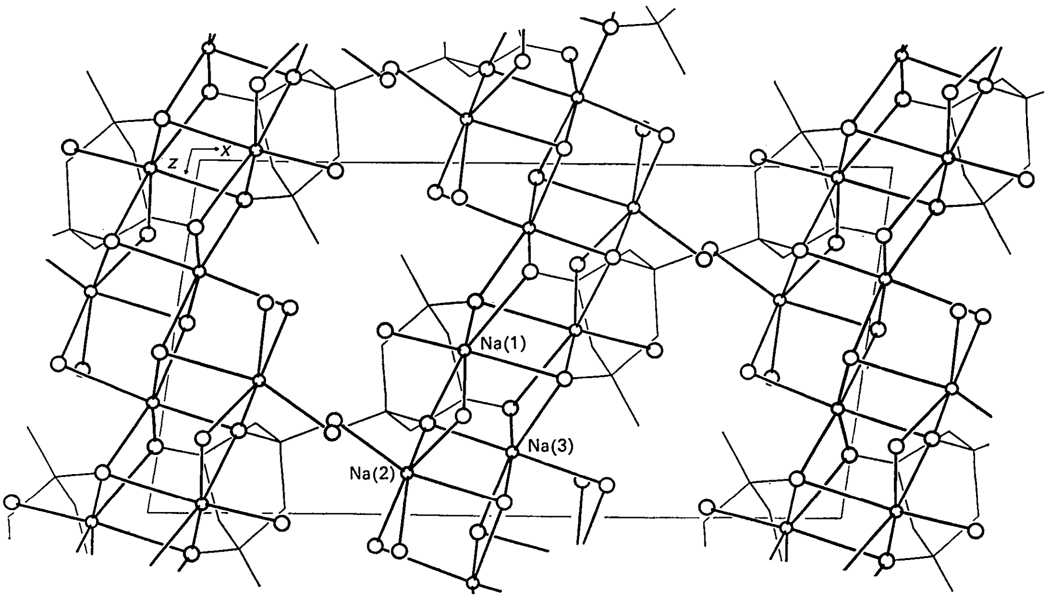


Fig. 5. Chains of sodium coordination octahedra in [010] projection, the y axis points downwards. The octahedra are given by strong lines, the location of the metaphosphimate groups is indicated by thin lines.

rings respectively, and by three water molecules. The Na · · · O and O · · · O distances are given in Table 6. They are consistent with corresponding values in other sodium salts, *e.g.* in the monoclinic and triclinic form of sodium tetrametaphosphimate tetrahydrate where Na · · · O ranges from 2·258 to 2·648 Å and O · · · O from 2·725 to 4·345 Å (Ondik, 1961, 1964).

The irregular octahedra of Fig. 4 share edges with neighbours so that a chain is formed stretching in the *z* direction. Fig. 5 shows the projection of this chain on the (010) plane. Neighbouring chains contain oxygen atoms of the same metaphosphimate group, as is schematically shown in Fig. 6. In this way a three-dimensional network is formed.

The sodium atoms of a chain are at the corners of equilateral triangles; the plane of the triangles is approximately parallel to the plane of the phosphorus atoms in $(N\text{–}P)_3$ rings adjacent to the chain. Na · · · Na distances are listed in Table 6.

Fig. 2 shows that the metaphosphimate ions are also linked by hydrogen bonds, *via* water molecules. The positions of the hydrogen atoms of the water molecules, as deduced from the location of the hydrogen bonds indicated by dotted lines in the figure, correspond to positive areas in the three-dimensional difference map. Peaks representing the positions of the hydrogen atoms of $(H_2O)_{\text{IV}}$ were not observed. This may be due to the fact that the location of this water molecule is not fixed by hydrogen bonds as O_{IV} has no short distances to neighbouring oxygen or nitrogen atoms.

The P–N bonds in the metaphosphimate anion, 1·68 Å on the average, are approximately 0·1 Å longer than those in the phosphonitrilic derivatives. This is in agreement with the formulae shown in the introduction. The P–N and P–O bond lengths and the valence angles will further be discussed in the paper on $(NH)_4P_4O_8H_4 \cdot 2H_2O$ (Migchelsen, Olthof & Vos, 1965).

Calculations were carried out on the digital computer ZEBRA with programs devised by Dr D. W. Smits, Dr J. C. Schoone and Dr D. Rogers; the least-squares analysis was carried out by Dr J. S. Rollett on the Mercury Computer at Oxford. We wish to thank Prof. E. H. Wiebenga for his interest throughout the course of this investigation and Mr H. Schurer for operating the ZEBRA. The work was supported by the Netherlands Organization for the Advancement of Pure Research (Z.W.O.).

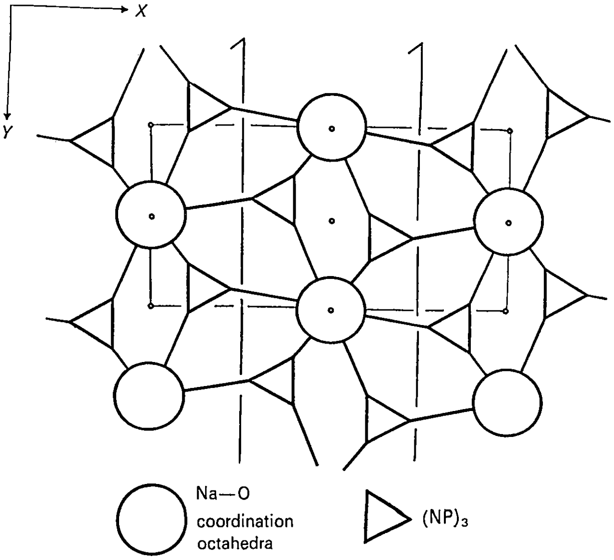


Fig. 6. Schematic representation in [001] projection of the chains shown in Fig. 5 and the metaphosphimate groups.

Table 6. *Interatomic distances in the* Na *coordination polyhedra*

For numbering of oxygen atoms and water molecules, see Fig. 4.

Na(1″) and Na(3″) are related to Na(1) and Na(3) by the symmetry centre at (½, 1, ½) and at (½, 1, 1) respectively.

Na(1)–O(1^+)	2·465 Å	Na(2)–O(6)	2·388 Å	Na(3)–O(3^+)	2·309 Å
Na(1)–O(2^+)	2·490	Na(2)–$(H_2O)_{\text{II}}''$	2·458	Na(3)–$(H_2O)_{\text{III}}$	2·397
Na(1)–O(6)	2·504	Na(2)–$(H_2O)_{\text{III}}$	2·655	Na(3)–$(H_2O)_{\text{III}}''$	2·589
Na(1)–O(1″)	2·355	Na(2)–O(5′)	2·433	Na(3)–O(1″)	2·335
Na(1)–O(3″)	2·453	Na(2)–O(2^+)	2·385	Na(3)–O(2^+)	2·403
Na(1)–$(H_2O)_{\text{I}}$	2·385	Na(2)–$(H_2O)_{\text{IV}}''$	2·444	Na(3)–$(H_2O)_{\text{IV}}$	2·409
O(1^+)–O(1″)	3·205 Å	O(6)–O(5′)	3·287 Å	O(3^+)–O(1″)	3·311 Å
O(1^+)–O(3″)	3·311	O(6)–O(2^+)	3·261	O(3^+)–O(2^+)	3·259
O(1^+)–O(2^+)	3·440	O(6)–$(H_2O)_{\text{II}}''$	3·783	O(3^+)–$(H_2O)_{\text{III}}''$	3·250
O(1^+)–$(H_2O)_{\text{I}}$	3·820	O(6)–$(H_2O)_{\text{III}}$	2·821	O(3^+)–$(H_2O)_{\text{IV}}$	3·494
O(6)–O(1″)	3·488	O(5′)–O(2^+)	3·839	O(1″)–O(2^+)	3·422
O(6)–O(3″)	3·947	O(5′)–$(H_2O)_{\text{II}}''$	3·664	O(1″)–$(H_2O)_{\text{III}}$	3·455
O(6)–O(2^+)	3·261	O(5′)–$(H_2O)_{\text{IV}}''$	4·144	O(1″)–$(H_2O)_{\text{IV}}$	3·292
O(6)–$(H_2O)_{\text{I}}$	3·174	O(2^+)–$(H_2O)_{\text{III}}$	3·165	O(2^+)–$(H_2O)_{\text{III}}$	3·165
O(1″)–O(3″)	3·270	O(2^+)–$(H_2O)_{\text{IV}}''$	3·370	O(2^+)–$(H_2O)_{\text{III}}$ ″	3·464
O(1″)–O(2^+)	3·422	$(H_2O)_{\text{II}}''$–$(H_2O)_{\text{III}}$	3·470	$(H_2O)_{\text{III}}$–$(H_2O)_{\text{III}}''$	3·600
O(3″)–$(H_2O)_{\text{I}}$	3·606	$(H_2O)_{\text{II}}''$–$(H_2O)_{\text{IV}}''$	2·983	$(H_2O)_{\text{III}}$–$(H_2O)_{\text{IV}}$	3·528
O(2^+)–$(H_2O)_{\text{I}}$	3·418	$(H_2O)_{\text{IV}}''$–$(H_2O)_{\text{III}}$	3·605	$(H_2O)_{\text{III}}''$–$(H_2O)_{\text{IV}}$	3·605
Na(1)–Na(2)	3·572 Å	Na(2)–Na(3)	3·763 Å	Na(2)–Na(3″)	3·529 Å
Na(1)–Na(3)	3·349	Na(1)–Na(1″)	3·603	Na(3)–Na(3″)	3·455
				Na(1″)–Na(3)	3·441

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The Crystal Structure of Compounds with $(N-P)_n$ Rings.
III. $(NH)_4P_4O_8H_4.2H_2O$, Tetrametaphosphimic Acid Dihydrate.

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The crystal structure of $(NH)_4P_4O_8H_4 . 2H_2O$ has been determined by three-dimensional X-ray methods. The compound crystallizes in the orthorombic space group $P2_12_12$. The cell dimensions are $a=13\cdot98$, $b=8\cdot32$, $c=5\cdot04$ Å. There are two formula units on special positions with symmetry 2 in the unit cell. Anisotropic least-squares refinement was carried out with 482 independent reflexions. R is 0·064. Hydrogen atoms could not be found in the three-dimensional difference map, but comparison of the bond lengths and angles with those in $Na_3(NHPO_2)_3 . 4H_2O$ and in the phosphonitrilic derivatives strongly indicates that the nitrogen atoms of the ring are linked to hydrogen atoms. The values observed for P–O are best explained by considering the compound as an acid salt $2(H_3O)^+[(NH)_4P_4O_8H_2]^{2-}$. Neighbouring anions are linked by short $O \cdots H \cdots O$ bonds of 2·46 Å to two-dimensional sheets perpendicular to the c axis. The hydrogen atom of the $O \cdots H \cdots O$ bond is either in the centre of the bond or statistically distributed between two possible positions. The sheets are connected to a three-dimensional network by $N-H \cdots O$ bonds of 2·79 and 2·81 Å. The anions have the tub configuration with approximate symmetry $\bar{4}$. The P–N bonds are equal within experimental error. The average value is 1·66 Å. There are two kinds of P–O bond. The oxygen atoms of two independent P–O bonds of 1·52 Å are involved in the short $O \cdots H \cdots O$ bonds. The oxygen atoms of the two remaining P–O bonds of $1\cdot48_5$ Å are not directly linked to hydrogen. The standard deviation in the individual bond lengths is 0·01 Å. Average values for the angles are P–N–P = 125·6, N–P–N = 107·3, O–P–O = 116·1°, s.d. 0·5°.

Introduction

As was mentioned in the introduction to the previous paper on $Na_3(NHPO_2)_3 . 4H_2O$ (Olthof, Migchelsen & Vos, 1965), a study of the structure of $(NH)_4P_4O_8H_4 . 2H_2O$ is interesting in connexion with the position of the hydrogen atoms. A preliminary X-ray study was carried out by Corbridge (1953). Infrared spectroscopic work by Steger & Lunkwitz (1961) suggests that the nitrogen atoms in the $(N-P)_4$ ring are linked to hydrogen atoms.

Experimental

Tetrametaphosphimic acid dihydrate was prepared by hydrolysis of $(NPCl_2)_4$ (Stokes, 1896) and recrystallized from water. Although many attempts were made to grow crystals of reasonable dimensions, only very thin long needles along the c axis were obtained. Finally crystals with diameters of about 0·04 mm were grown by very slow evaporation of water from saturated aqueous solutions. The crystals were not of good quality, however. Preliminary photographs were taken of a great number of crystals, but in all cases Weissenberg exposures with strongly extended spots in the φ-direction were obtained. This indicates that the crystals show distortion around the c axis. Because of this effect and the small cross-section of the available crystals, long exposure times were required. Therefore only little use was made of integrated Weissenberg photographs.