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The Structure of Lithium Dipotassium Trimetaphosphate Monohydrate*

BY EDWARD DAVID EANES†
The Johns Hopkins University, Baltimore, Md., U.S.A.

AND HELEN M. ONDIK
National Bureau of Standards, Washington, D.C., U.S.A.

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$LiK_2P_3O_9.H_2O$ is monoclinic, space group $P2_1/c$, with cell dimensions:

$$a=8\cdot669\pm0\cdot003,\ b=14\cdot497\pm0\cdot004,\ c=7\cdot634\pm0\cdot006\ \text{Å};\ \beta=99°\ 53'\pm3',\ Z=4\ .$$

The structure was determined from a three-dimensional Patterson function, and refined by electron-density syntheses and complete matrix least squares. The final R value for 1,011 independent observed reflections is 0·099.

The trimetaphosphate anion consists of three orthophosphate tetrahedra joined at corners to form a six-membered ring of alternate phosphorus and oxygen atoms in a chair configuration. The phosphate tetrahedra are nearly regular. The two potassium ions have irregular coordination figures. One is surrounded by six oxygen atoms from five different anions and the water molecule. The other is surrounded by eight oxygens, two oxygens from each of four different anions. The lithium ion is found at the center of a fairly regular tetrahedron formed by three oxygens and the water. The cation polyhedra are linked at edges and corners to produce equal cohesion in all directions, thus accounting for the lack of cleavage.

Introduction

X-ray, spectroscopic, and chemical evidence (Van Wazer, 1958; Simon & Steger, 1954*a*, *b*) indicates that the trimetaphosphate anion is a ring formed by three phosphate tetrahedra sharing corner oxygen atoms. The X-ray structure work on trimetaphosphate salts previously reported (Caglioti, Giacomello & Bianchi, 1942; Raistrick, 1949) merely indicated the possible existence of such a ring. As part of a study of trimetaphosphate salts, the determination of the structure of $LiK_2P_3O_9.H_2O$ was undertaken in order to provide accurate information concerning this anion.

Experimental data

To prepare the lithium dipotassium salt, sodium trimetaphosphate sesquihydrate (Ondik & Gryder, 1960) was first converted to $Ag_3P_3O_9$, using an excess of $AgNO_3$ to prevent the formation of double salts. A slurry of the silver salt was metathesized with LiCl and KCl in a 1:2 molar ratio. After filtering to remove the AgCl, the product was precipitated from solution by adding ethanol. Single crystals were obtained by inserting one ml. of a 2% aqueous solution under 20 ml. of ethanol in a test tube and permitting diffusion to take place at 60 °C. for a few days.

The crystals are lath-like in habit, with approximately the following dimensions: 0·01 × 0·08 × 0·70 mm. Precession photographs were taken to determine the cell dimensions and space group. The cell dimensions were refined by a least squares treatment of powder data recorded on a Geiger Counter diffractometer, using Cu $K\alpha_1$ radiation (1·5405 Å). The final values are:

$$a=8\cdot669\pm0\cdot003,\ b=14\cdot497\pm0\cdot004,$$
$$c=7\cdot634\pm0\cdot006\ \text{Å};\ \beta=99°\ 53'\pm3'.$$

The limits given are the standard errors computed by the least squares program. The space group is $P2_1/c$, since $h0l$ reflections occur only with l even, and $0k0$ only with k even. The density measured pycnometrically is 2·33 g.cm.$^{-3}$. The calculated number of formula units per cell is 3·88. With $Z=4$, the calculated density is 2·40 g.cm.$^{-3}$. The difficulty in completely removing air trapped in the mass of loosely-packed, lath-like crystals would account for the rather low experimental value for the density.

The length of the crystals is parallel to [001] and the dominant form is the (100) pinacoid. The crystals are colorless, biaxial positive with $2V$ estimated at 42°. The optic normal is parallel to b. The acute bisectrix γ makes an angle of 12° with c in the obtuse angle β. The indices of refraction, measured in white transmitted light using oil immersion techniques, are:

$$n_\alpha=1\cdot486,\ n_\beta=1\cdot490,\ n_\gamma=1\cdot500,\ \text{all}\ \pm0\cdot002$$

(A. Van Valkenburg, priv. comm.).

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† Present address, National Institutes of Health, Bethesda, Maryland.

Integrated equi-inclination Weissenberg photographs were taken of layers $l=0$ to 6 and of the $0kl$ layer, with Cu $K\alpha$ radiation. The usual multiple-film techniques were used. A densitometer-comparator was used to measure the intensities, supplemented by visual estimation of the very weak spots. Lorentz and polarization factor corrections were made, but absorption corrections were considered unnecessary because of the small size of the crystals. A fragment approximately $0·01 \times 0·08 \times 0·08$ mm. was used in obtaining the $0kl$ data.

Determination of the structure

Neither trimetaphosphate anions nor individual P or O atoms could be expected to occupy centers of symmetry, the special positions of $P2_1/c$, and the intensity data did not indicate that the K^+ ions should occupy them. That these atoms occupy 4-fold general positions was verified upon examination of a three-dimensional Patterson function. Trial parameters for K, P, and O were derived from the Patterson. Direct reference to the Harker sections $P(x,\frac{1}{2},z)$ and $P(0,y,\frac{1}{2})$ did not prove fruitful because of extreme amounts of overlap and parameters were deduced using various sets of non-Harker peaks.

Assuming the anion to be a ring, P–P ring vectors were identified. These peaks corresponded to vectors between P atoms which form a triangle about 3 Å on an edge. A set of four K_I–K_{II} peaks established the two K^+ ion positions. Two sets of K–P vectors were used to locate the ring within the asymmetric unit. These sets each contain two peaks separated by a vector equal to one of the P–P ring vectors. The peaks have relative weights and are at suitable distances for K–P interactions. Oxygen parameters were established by considering appropriate P–O vectors which would form fairly regular oxygen tetrahedra about the P atoms giving rise to a ring configuration.

Several cycles of $hk0$ structure factor calculations and electron density syntheses partially refined the x and y values. An isolated peak appeared which was correctly assumed to be the water molecule. With an assumed B of 1·5 for each atom, the x and y values were refined by a complete-matrix least squares procedure. The resulting $R(hk0)$ equalled 0·11. The $0kl$ data were used to refine the z parameters, first by Fourier methods, and then by least squares. The $R(0kl)=0·14$. Several least squares cycles using all 1,011 independent observed reflections, varying both position and temperature parameters, resulted in an $R(hkl)$ of 0·10.

To locate the Li^+ ion, a three-dimensional difference synthesis was computed, using the (F_o-F_c) values obtained from the last least squares cycle. The largest peak was one of density 2·0 e.Å^{-3}, the maximum value of the rest of the synthesis being 0·5 e.Å^{-3}. This peak is at the center of a fairly regular tetrahedron formed by three oxygen atoms and a water molecule. Inclusion of the Li parameters in a final least squares refinement changed the $R(hkl)$ negligibly (to 0·099). In this refinement the total number of parameters varied was 72, including x, y, z, and B for each atom and a scale factor for each level of data. The final parameters are reported in Table 1.

The structure factors listed in Table 2 are the F_o and sF_c values obtained from the least squares program. The s refers to the scale factors given in Table 1. The final electron density projections $\varrho(y,z)$ and $\varrho(x,y)$, (Fig. 1), clearly show the overlap which prevented location of the Li^+ ion earlier in the structure analysis.

Form factors for P^0 and K^+ calculated by Tomiie & Stam (1958), for O^0 from the tables of Berghuis *et al.* (1955), and for Li^+ from the tables of Freeman (1959)

Table 1. *Final structure parameters*

	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$	B	$\sigma(B)$
P_I	0·4895	0·0005	0·1558	0·0003	0·2125	0·0005	0·99	0·07
P_{II}	0·1705	0·0005	0·1789	0·0003	0·2742	0·0005	1·04	0·07
P_{III}	0·2413	0·0005	0·0441	0·0003	0·0142	0·0005	0·90	0·07
K_I	0·8266	0·0005	0·2162	0·0003	0·9510	0·0004	1·70	0·07
K_{II}	0·4580	0·0005	0·0993	0·0003	0·6753	0·0004	1·54	0·07
Li	0·0723	0·0030	0·1195	0·0017	0·6427	0·0026	0·60	0·38
O_I	0·1331	0·0014	0·1155	0·0008	0·1019	0·0013	1·39	0·20
O_{II}	0·4054	0·0014	0·1010	0·0008	0·0406	0·0012	1·26	0·20
O_{III}	0·3420	0·0013	0·2164	0·0008	0·2561	0·0012	1·18	0·19
O_{IV}	0·5422	0·0015	0·0879	0·0009	0·3590	0·0013	1·80	0·22
O_V	0·5993	0·0015	0·2238	0·0009	0·1531	0·0012	1·77	0·21
O_{VI}	0·1807	0·0017	0·1231	0·0009	0·4361	0·0013	2·04	0·23
O_{VII}	0·0583	0·0017	0·2424	0·0011	0·7402	0·0014	2·65	0·25
O_{VIII}	0·7349	0·0015	0·0415	0·0009	0·8768	0·0013	1·78	0·22
O_{IX}	0·1818	0·0016	0·0398	0·0009	0·8258	0·0014	1·86	0·23
H_2O	0·8498	0·0019	0·0917	0·0011	0·5725	0·0015	3·27	0·30

Scale factors

$hk0$	$hk1$	$hk2$	$hk3$	$hk4$	$hk5$	$hk6$	$0kl$
0·71	0·59	0·58	0·65	0·72	0·81	0·87	0·61

Table 2. *Comparison of observed and calculated structure factors*

h	k	F_o	sF_c
		hk0	
0	2	32	-31
	4	42	-38
	6	71	-64
	8	11	-5
	10	17	15
	12	24	-22
	14	34	-31
	16	42	-42
	18	23	25
1	0	36	-44
	1	42	-43
	2	24	-24
	3	68	-68
	4	61	58
	5	26	22
	6	18	18
	7	21	-21
	9	20	-18
	10	15	-12
	12	24	-27
	13	20	-19
	14	10	-6
	15	41	42
	16	38	36
2	0	20	-18
	1	5	-3
	2	30	-27
	3	5	-6
	4	77	-75
	5	16	14
	6	27	-26
	7	31	-32
	8	45	43
	9	32	-32
	10	20	20
	11	14	14
	12	58	58
	13	10	-10
	14	10	9
	15	34	37
	16	14	-14
	17	15	-19
3	0	150	-163
	1	28	-28
	2	6	4
	3	16	-15
	4	68	66
	5	22	23
	6	10	-8
	7	50	46
	8	19	13
	9	9	7
	10	19	-15
	11	10	-11
	12	10	-8
	13	26	-20
	14	14	14
	16	20	20
4	0	7	7
	1	12	-7
	2	51	53
	3	76	85
	4	7	-7
	5	41	-40
	6	22	18
	7	28	27
	8	13	-15
	10	46	-45
	13	33	34
	14	9	-10
	15	24	-30
	16	15	-16
5	0	27	27
	1	21	-19
	2	18	-14
	3	11	-12
	4	28	29
	5	26	-27
	6	9	-11
	7	25	24
	8	14	-14
	10	14	17
	12	19	-20
	15	12	-10
6	0	45	41
	1	9	8
	2	51	-52
	4	19	-17
	5	23	-22
	6	31	33
	7	22	-20
	8	10	-10
	9	10	-9
	10	17	14
	12	13	14
	14	14	17
	15	11	10
7	1	24	-20
	2	10	8
	4	10	-7
	5	30	28
	6	25	-17
	10	29	28
	11	8	8
	13	24	-25
	14	8	-9
8	0	10	-10
	1	24	21
	2	28	24
	5	24	18
	6	17	14
	7	9	-7
	10	26	-31
	11	12	8
	12	5	-4
9	0	35	-32
	1	21	-15
	2	32	30
	6	23	-22
	8	7	6
	9	9	-5
	10	9	8
10	0	18	-21
	1	7	6
	2	13	-12
	3	10	7
	5	24	-26
	6	21	17
	7	5	5
		hk1	
0	1	33	36
	2	34	-35
	3	14	13
	4	80	79
	5	62	60
	7	29	-29
	8	25	-23
	10	23	21
	11	49	-47
	14	10	-6
1	1	18	-17
	3	44	45
	4	81	-83
	5	22	-22
	6	36	33
	7	12	-11
	8	11	-13
	9	17	15
	10	27	24
	12	44	-43
	13	17	4
	16	24	20
$\bar{1}$	1	26	29
	2	19	18
	3	36	-34
	4	37	34
	5	29	25
	6	17	13
	7	25	-23
	8	35	36
	12	28	-25
	18	9	-15
2	1	59	-69
	3	11	10
	4	34	-29
	6	7	-6
	7	42	40
	8	45	-43
	12	24	20
	13	24	20
	15	20	17
$\bar{2}$	1	21	-21
	3	63	-65
	4	30	27
	5	26	-23
	6	21	-21
	7	25	24
	8	22	-19
	9	8	11
	10	9	-7
	11	46	43
	12	30	30
	16	8	-14
3	1	35	35
	4	26	-26
	5	50	-51
	8	58	57
	10	28	-22
	11	28	26
	15	15	-12
$\bar{3}$	1	14	-14
	2	29	29
	3	8	9
	4	37	-39
	5	38	-35
	6	47	-43
	7	30	29
	8	31	29
	9	18	-17
	10	35	-34
	11	20	23
4	4	35	37
	5	35	34
	7	21	22
	9	49	-50
	11	10	-12
	12	24	21
	16	11	-11
$\bar{4}$	1	29	29
	2	13	12
	3	52	55
	4	30	-30
	5	11	-14
	6	20	20
	7	9	-11
	8	46	-46
	9	19	-19
	10	19	22
	11	20	-18
	17	12	-14
5	1	33	34
	3	32	-33
	6	32	-32
	7	42	-44
	9	37	38
	11	14	15
	15	16	-14
$\bar{5}$	1	22	-16
	3	36	36
	4	8	-13
	5	22	20
	6	25	28
	8	25	23
	11	31	-27
	12	30	-29
6	1	30	-28
	2	26	-23
	3	13	-13
	4	9	13
	5	33	31
	8	28	-26
	10	17	17
	11	13	-16
	13	22	18
$\bar{6}$	1	15	-15
	2	32	-31
	3	24	-21
	4	42	42
	9	26	27
	11	13	18
7	2	31	31
	3	26	21
	5	35	-32
	9	24	22
	10	9	12
	12	7	-6
$\bar{7}$	1	10	-15
	2	10	-15
	3	32	-32
	5	37	34
	8	14	18
	10	9	-14
	14	10	15
8	2	14	-13
	6	32	27
	7	18	12
	9	16	-14
	11	23	-22
$\bar{8}$	1	37	36
	5	26	-26
	6	14	-14
	10	8	-16
	11	12	15
	12	18	19
9	4	17	-14
	5	14	-12
	6	15	-18
$\bar{9}$	2	31	28
	7	16	16
	8	13	14
	9	21	-19
10	2	28	-24
	3	25	-23
$\overline{10}$	5	26	-24
	6	18	17
$\overline{11}$	1	12	-14
		hk2	
0	0	20	-26
	1	16	-17
	2	49	46
	3	32	-28
	5	28	25
	6	30	-27
	7	48	45
	12	43	-40
	13	14	-16
	17	7	9
1	0	23	23
	1	72	80
	2	13	-11
	3	56	-56
	4	30	-25
	6	9	10
	9	28	-26
	13	14	12
	14	19	15
	15	18	20
	16	14	-15
$\bar{1}$	0	54	65
	1	15	-14
	3	46	45
	4	28	-24
	6	18	-15
	9	29	24
	10	9	8
	12	10	-13
	14	19	17
	16	32	-30
	17	16	-17
	18	6	12
2	0	50	-54
	2	36	36
	3	31	-31
	4	24	-23
	5	13	12
	6	16	11
	7	8	9
	8	18	-17
	9	18	-18
	10	25	22
	12	28	23
	14	9	-15
	16	21	18
	17	13	13
$\bar{2}$	0	77	-91
	1	78	-83
	2	45	-45
	4	41	38
	5	18	-14
	6	25	20
	7	10	-10
	10	18	16
	13	10	-11
	14	9	14
	16	23	22
	17	11	13
3	0	15	-16
	2	9	11
	3	39	41
	6	51	49
	8	32	-29
	9	16	15
	10	30	-29
	11	10	-9
	12	24	21
	13	10	10
	14	9	-13
	17	12	-13
$\bar{3}$	0	21	20
	1	23	-23
	2	34	32
	3	21	18
	4	82	-84
	5	40	-36
	6	26	23
	7	26	-22
	9	15	-13
	10	9	8
	12	43	41
	13	10	13
	14	31	-30
4	1	18	-19
	4	25	22
	5	25	23
	6	19	-15
	7	27	-29
	8	16	-17
	9	19	17
$\bar{4}$	0	23	-23
	1	19	21
	2	15	16
	3	15	11
	4	50	47
	6	28	24
	7	15	9
	8	22	-21
	9	21	-20
	10	33	-30
	11	10	10
	12	31	-26
	14	15	-16
	16	24	26
5	2	29	-27
	3	12	14
	5	31	-33
	7	30	-32
	8	17	14
	14	27	24
$\bar{5}$	0	74	76
	1	40	36
	2	17	18
	4	32	-32
	6	21	-20
	7	39	39
	16	24	-23
6	1	9	13
	3	35	-31
	5	17	14
	6	35	-34
	8	26	25
	10	29	25
	13	7	-10
$\bar{6}$	0	67	-66
	1	24	21
	2	26	-23
	3	9	13
	4	36	29
	6	21	-15
	8	20	18
	11	9	13
	14	27	27
7	1	52	43
	6	10	14
	7	30	26
	10	8	-16
$\bar{7}$	0	28	26
	1	46	-44
	2	32	-29
	5	17	-16
	6	17	-14
	11	12	-13
	12	8	12
	14	20	19
8	0	27	25
	1	9	-12
	2	21	17
	6	9	-10
	7	8	11
$\bar{8}$	1	20	-15
	2	20	14
	3	14	11
	4	26	19
	7	24	-25
	8	9	-10
	12	16	-12
9	5	21	-19
	6	25	22
	7	15	-15
	8	9	-10
$\bar{9}$	0	26	26
	6	25	19
	7	13	13
	10	24	-21
10	1	25	-22
	2	10	-10
	3	8	6
$\overline{10}$	1	24	21
$\overline{11}$	1	20	18
		hk3	
0	1	37	39
	2	19	18
	3	12	-11
	4	64	-62
	5	30	-27
	6	48	47
	7	39	-39
	9	24	22
	10	13	-15
	11	21	20
	13	19	-19
	15	8	-14
1	1	63	-66
	2	18	-16
	3	28	-28
	4	13	-12
	5	82	83
	7	26	23
	8	39	-40
	9	47	-45
	13	21	20
	16	10	16
	17	5	12
$\bar{1}$	1	4	5
	2	24	25
	3	9	-9
	4	36	35
	5	43	36
	6	28	24
	8	14	-13
	10	15	-16
	11	53	-50
	12	29	26
	16	20	-20
2	2	19	17
	3	22	23
	4	9	10
	5	51	-50
	6	20	-19
	7	14	15
	10	25	22
	11	52	53
	13	13	-16
$\bar{2}$	1	35	37
	2	35	-34
	5	58	-54
	6	42	-40
	7	29	-28
	8	64	62
	9	69	67
	10	27	-26
	17	9	-10
3	2	23	-28
	3	17	16
	4	52	53
	5	11	12
	7	32	29
	8	27	29
	9	29	-30
	10	16	15
	11	32	-27
	14	25	-28
$\bar{3}$	1	11	-15
	2	6	-8
	4	29	27
	5	19	-18
	6	50	-49
	7	36	36
	8	50	-50
	10	28	26
	12	10	16
4	1	28	25
	2	11	15
	3	20	19
	5	23	-24
	6	33	-35
	7	33	-32
	9	37	39
	11	23	-23
	13	12	-16
$\bar{4}$	3	26	26
	8	29	29
	9	29	-30
	10	16	17
	12	26	-24
5	2	28	-33
	3	20	-19
	4	38	-39
	10	18	-24
$\bar{5}$	2	17	19
	4	16	21
	5	29	31
	6	30	32
$\bar{5}$	8	25	-23
	9	30	-32
	10	19	22
	12	9	14
6	1	19	-20
	2	31	32
	3	10	-10
	4	23	-22
	5	10	14
	6	10	16
	7	13	-16
	8	13	-16
	9	18	20
	11	13	14
$\bar{6}$	1	27	-27
	2	29	29
	3	9	-15
	4	47	-44
	5	30	27
	6	28	30
	7	9	-15
	9	10	14
	12	12	-16
	13	10	16
	14	6	11
7	1	9	13
	3	19	-19
	6	39	38
	9	29	-22
	10	14	13
	11	20	20
$\bar{7}$	2	16	-19
	6	13	-17
	8	13	-15
	9	20	22
	10	22	-22
	12	24	24
	13	14	16
8	3	32	29
	4	14	17
	9	22	-24
$\bar{8}$	3	25	24
	6	13	-16
	8	22	19
	11	25	-24
	12	15	-11
9	1	7	12
	2	26	-22
	6	17	-19
$\bar{9}$	1	22	20
	2	18	-15
	3	12	14
	4	32	32
	5	14	-17
	10	15	15
$\overline{10}$	1	14	-15
	7	16	17
		hk4	
0	0	30	35
	1	43	44
	2	44	-41
	3	28	-26
	4	28	26
	5	20	-15
	6	33	31
	7	32	-31
	8	25	-25
	10	24	-24
	15	25	29
1	0	30	-29
	1	53	-53
	2	14	12
	3	39	-38
	4	17	-14
	6	28	-27
	7	43	-41
	8	12	12
	12	24	24
	13	24	-24
	15	12	13
	16	5	11
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	8	34	-30
	13	15	-17
	15	14	-17
2	0	53	-53
	1	30	37
	3	40	35
	8	34	33
	10	16	-19
	12	15	18
	14	7	13
$\bar{2}$	0	4	4
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	3	28	31
	4	6	8
	5	25	-21
	6	22	23
	7	36	34
	11	27	-30
	12	9	10
	13	38	40
	15	17	-19
3	1	36	-36
	2	28	28
	3	36	37
	5	25	22
	6	43	-42
	7	44	43
	15	34	-42
$\bar{3}$	0	35	-35
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	3	32	-29
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	11	16	-17
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	1	18	21
	2	12	-14
	3	37	37
	4	34	33
	5	41	-45
	6	15	18
	9	9	-12
	10	25	-29
	11	8	-15
	12	17	-23
	13	27	29
$\bar{4}$	1	18	18
	2	39	39
	3	12	12
	4	50	-47
	7	28	-26
	8	25	22
	10	16	-20
5	0	56	51
	3	36	-39
	7	24	-21
	9	23	-24
	10	28	29
$\bar{5}$	0	35	-33
	5	47	49
	9	20	20
	12	8	-12
	13	27	-31
	14	6	-11
6	0	18	-13
	2	30	-35
	6	34	30
$\bar{6}$	0	65	61
	1	37	28
	2	35	-34
	4	9	-16
	10	12	21
	12	15	17
	13	6	-12
7	1	12	-14
	2	17	18
	4	30	-28
	5	38	42
	10	12	12
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	3	22	-24
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	6	29	22
	8	19	-19
	9	12	-17
8	0	31	-26
	2	31	27
	7	20	18
$\bar{8}$	0	44	44
	4	15	-18
	5	21	-22
	7	18	20
	11	18	-19
9	1	14	-12
	2	9	8
	3	8	6
$\bar{9}$	0	34	-35
	2	21	21
	3	22	24
	4	15	22
	7	11	13
$\overline{10}$	2	19	15
	4	39	-38
		hk5	
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	2	46	-48
	3	15	15
	4	21	-21
	5	9	8
	6	19	20
	7	11	11
	8	34	-37
	9	28	-29
	10	8	13
	11	34	-35
	12	27	-29
	13	8	12
1	1	42	-44
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	8	48	-48
	12	11	13
	14	26	26
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	2	16	16
	3	11	-10
	4	44	36
	6	26	22
	7	58	-55
	9	46	43
	10	28	26
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	3	24	-24
	6	18	21
	7	20	21
	8	28	28
	10	8	-13
	11	8	14
	13	34	33
	14	12	-14
$\bar{2}$	1	9	-9
	2	15	-17
	3	52	-47
	4	31	31
	5	52	46
	6	35	29
	7	32	28
	8	18	20
	9	33	-30
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	14	7	-13
	15	10	12
3	1	21	-23
	2	39	40
	4	32	35
	5	12	16
	8	34	36
	12	14	22
	13	16	-20
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	6	48	-43
	7	24	-19
	8	37	37
	9	41	39
	10	37	-35
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	12	8	12
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	2	28	-26
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	5	17	17
	12	11	-8
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	4	10	-12
	5	11	13
	6	19	-19
	7	40	42
	8	19	-23
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	13	21	-22
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	5	23	-25
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	7	10	15
$\bar{6}$	2	12	17
	4	52	48
	7	15	15
	8	33	-36
	10	17	23
	11	21	-23
	12	15	13
	13	13	15
7	1	43	-35
	2	26	22
	3	38	36
	6	14	18
$\bar{7}$	2	12	-13
	3	12	-14
	4	12	-21
	7	27	-25
	9	24	24
	10	11	14
	11	14	14
	12	27	-26
8	1	20	19
	4	11	-10
$\bar{8}$	3	27	-23
	4	19	17
	5	32	26
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	8	22	-20
	9	19	-17
$\bar{9}$	2	12	4
	8	48	50
		hk6	
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	1	15	13
	2	61	52
	3	57	-54
	6	25	-24
	9	19	-18
	11	24	26
	12	12	-11
	13	14	-16
	14	12	-15
1	0	49	-44
	1	58	56
	2	18	13
	5	61	-56
	6	51	44
	7	11	-11
	8	11	-11
	9	11	-15
	10	23	-22
	13	17	16
$\bar{1}$	0	28	-42
	1	35	36
	3	57	56
	4	42	41
	10	23	-23
	12	19	-25
	14	29	31
2	0	41	32
	1	43	-39
	3	21	19
	4	69	-60
	5	7	10
	10	40	43
	12	27	26
	13	5	8
$\bar{2}$	1	42	-48
	2	29	-28
	3	9	-7
	5	62	59
	6	27	-24
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	9	17	17
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	7	11	16
	9	28	30
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	3	34	36
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	6	27	23
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	13	26	23
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	1	29	-29
	5	28	26
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	7	35	-34
	11	15	14
$\bar{4}$	0	27	26
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	2	22	25
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	4	16	-18
	5	22	-25
	8	20	-19
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	1	15	11
	3	37	-35
	4	28	26
	5	7	-13
	6	7	-13
	7	6	12
$\bar{5}$	0	27	24
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	3	13	13
	5	11	-13
	7	24	26
	10	18	-22
6	0	49	-40
	1	40	28
	5	23	20
	6	5	7
	8	10	11
$\bar{6}$	0	45	-42
	1	8	11
	2	11	12
	5	23	29
	6	17	-17
	7	29	31
	8	7	11
	11	22	19
7	1	18	16
	3	5	-8
$\bar{7}$	1	11	15
	2	24	-25
	5	7	-15
	6	7	-9
	7	7	-14
	8	23	16
$\bar{8}$	1	47	-40
	2	10	-14
	3	7	-13
	4	34	30
	6	12	-13
	7	25	-24
$\bar{9}$	0	38	32
	3	25	22
	4	17	-17
	6	10	11

were used throughout. All computing was performed on a high speed digital computer. The least squares refinement of the cell dimensions was done using a program written by Dr Charles Burnham of The Geophysical Laboratory, Carnegie Institution of Washington. The Lorentz and polarization corrections, structure factor and Fourier calculations were done using programs written at the National Bureau of Standards. The least squares refinement and calculation of interatomic distances and angles were done using programs written at Oak Ridge by Busing & Levy (1959*a*, *b*).

Description of the structure

In a Raman study of solutions of sodium trimetaphosphate (Simon & Steger, 1954), the ring exhibited $\bar{6}m2(D_{3h})$ symmetry. In the lithium dipotassium salt the triangles formed by the three phosphorus atoms and the three ring oxygens are almost equilateral (P–P distances: 2·90, 2·90, 2·92 Å; O–O distances: 2·49, 2·46, 2·47 Å). The angle between the normals to the planes of the two triangles is only 3·3° (standard deviation, σ, $= \pm 0{\cdot}4°$), indicating that the two planes are nearly parallel. The ring oxygens, however, are appreciably displaced from the plane of the phosphorus atoms, O_{I} by 0·29 Å, O_{II} by 0·38 Å, and O_{III} by 0·42 Å. Therefore, in the lithium dipotassium salt, the trimetaphosphate anion does not even approach $\bar{6}m2$ symmetry but does exhibit pseudo $3m(C_{3v})$ symmetry, the chair (or *trans*-) form of a six-membered ring. The chair form of the ring can best be seen outlined on the electron density map of Fig. 1(*a*).

The anion, as viewed along *a* and *c*, is outlined in Fig. 1, and as viewed along *b*, in Fig. 2. Distances and angles within the anion (Table 3) are given with the same atom designation as in Fig. 2. These values are consistent with values reported in other condensed phosphate structures (Romers, Ketelaar & MacGillavry, 1951; Corbridge, 1956; MacArthur & Beevers, 1957; Davies & Corbridge, 1958; Corbridge, 1960; Ondik, Block & MacGillavry, 1961; Jost, 1961). Features common to these structures include the short P–O terminal bonds and the longer P–O bridge bonds, the displacement of the phosphorus from the center of the tetrahedron toward the terminal oxygens and the regularity of the tetrahedral edges.

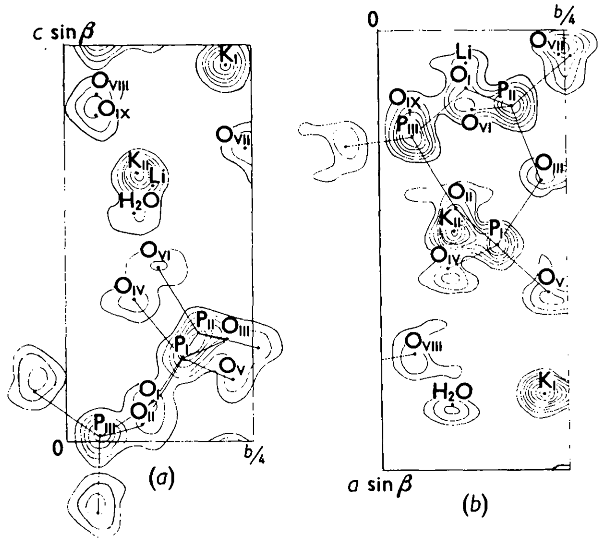

Fig. 1. Final electron density projections $\varrho(y, z)$ and $\varrho(x, y)$ for the asymmetric unit. Contours are drawn at arbitrary intervals. The atomic positions are those obtained from the final least squares refinement.

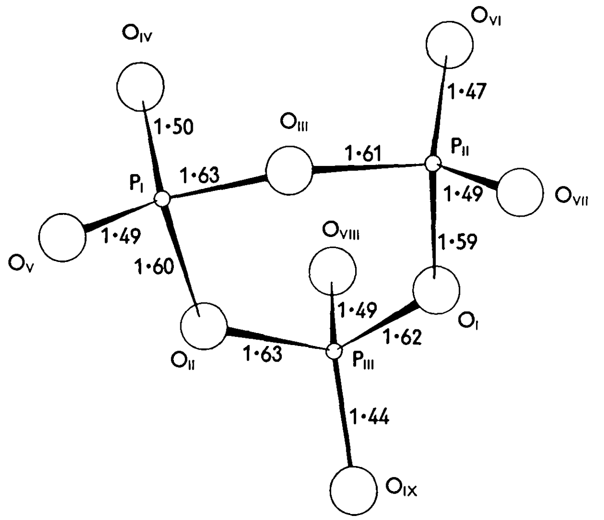

Fig. 2. The trimetaphosphate anion viewed along [010], with bond distances in Å.

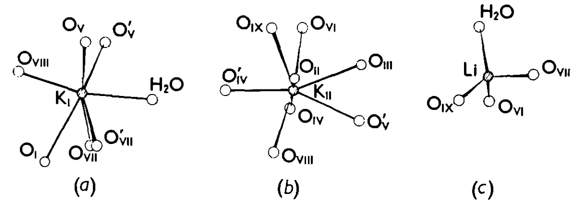

Fig. 3. The cation coordination figures viewed along [001].

The coordination about the cations is shown in Fig. 3, and the distances in Table 4. The K_{I} coordination figure (Fig. 3(*a*)) is formed by five terminal oxygen atoms, each from a different ring, the water molecule, and a bridge oxygen O_{I}. This polyhedron shares edges with its symmetry equivalents across the glide plane, forming chains along [001] (Fig. 4(*a*)). Oxygen atoms from four different anions are coordinated to K_{II} (Fig. 3(*b*)). Two anion rings contribute two terminal oxygen atoms each and the other two rings contribute one terminal and one bridge oxygen each. Two of these K_{II}–O polyhedra share an edge across a center of symmetry.

The lithium coordination figure is formed by three terminal oxygens, each from a different ring, and the

Table 3. *Interatomic distances and bond angles in the trimetaphosphate anion*

P_{I}–O_{II}	1·596 Å	O_{II}–O_{III}	2·470 Å	O_{II}–P_{I}–O_{III}	99·9°
P_{I}–O_{III}	1·631	O_{II}–O_{IV}	2·517	O_{II}–P_{I}–O_{IV}	108·7
P_{I}–O_{IV}	1·500	O_{II}–O_{V}	2·497	O_{II}–P_{I}–O_{V}	107·8
P_{I}–O_{V}	1·494	O_{III}–O_{IV}	2·574	O_{III}–P_{I}–O_{IV}	110·6
P_{II}–O_{I}	1·589	O_{III}–O_{V}	2·491	O_{III}–P_{I}–O_{V}	105·6
P_{II}–O_{III}	1·610	O_{IV}–O_{V}	2·618	O_{IV}–P_{I}–O_{V}	122·0
P_{II}–O_{VI}	1·466	O_{I}–O_{III}	2·462	O_{I}–P_{II}–O_{III}	100·6
P_{II}–O_{VII}	1·493	O_{I}–O_{VI}	2·511	O_{I}–P_{II}–O_{VI}	110·5
P_{III}–O_{I}	1·616	O_{I}–O_{VII}	2·451	O_{I}–P_{II}–O_{VII}	105·3
P_{III}–O_{II}	1·626	O_{III}–O_{VI}	2·515	O_{III}–P_{II}–O_{VI}	109·6
P_{III}–O_{VIII}	1·488	O_{III}–O_{VII}	2·514	O_{III}–P_{II}–O_{VII}	108·2
P_{III}–O_{IX}	1·441	O_{VI}–O_{VII}	2·571	O_{VI}–P_{II}–O_{VII}	120·7
$\sigma = \pm 0·013$ Å		O_{I}–O_{II}	2·492	O_{I}–P_{III}–O_{II}	100·4
		O_{I}–O_{VIII}	2·540	O_{I}–P_{III}–O_{VIII}	109·8
P_{I}–P_{II}	2·902 Å	O_{I}–O_{IX}	2·472	O_{I}–P_{III}–O_{IX}	107·8
P_{I}–P_{III}	2·901	O_{II}–O_{VIII}	2·531	O_{II}–P_{III}–O_{VIII}	108·6
P_{II}–P_{III}	2·921	O_{II}–O_{IX}	2·476	O_{II}–P_{III}–O_{IX}	107·5
$\sigma = \pm 0·007$ Å		O_{VIII}–O_{IX}	2·546	O_{VIII}–P_{III}–O_{IX}	120·8
		$\sigma = \pm 0·016$ Å			
				P_{II}–O_{I}–P_{III}	131·4
				P_{I}–O_{II}–P_{III}	128·3
				P_{I}–O_{III}–P_{II}	127·1
				$\sigma = \pm 0·6°$	

water oxygen (Fig. 3(*c*)). It is almost a regular tetrahedron, as evidenced by the Li–O distances, and the O–O distances which vary from 2·98 to 3·27 Å ($\sigma = \pm 0·02$ Å) (Table 4). The Li^+ ion temperature factor, 0·60, the smallest of all the *B* values in Table 1, indicates that the ion is within a rigid coordination figure.

Through edge and corner sharing, the K_I, K_{II}, and Li polyhedra are linked to form a complex network roughly parallel to the *ab* plane as is shown in Fig. 4(*b*). Only the terminal oxygens and the water are involved in this linkage and to simplify Fig. 4(*b*) only these atoms are shown. The network combined with the K_I polyhedral chains form a complex three-dimensional linkage of the polyhedra. The resulting cohesion is fairly uniform in all directions, accounting for the absence of cleavage.

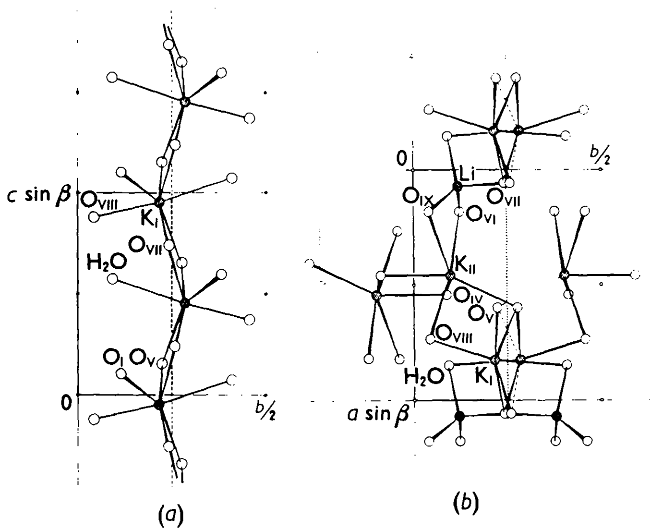

Fig. 4. Linkage of the cation coordination figures. The asymmetric unit is outlined by the heavier line. (*a*) The glide-equivalent K_I and coordinated O atoms forming vertical chains along *c*. (*b*) Network parallel to (001) formed by the cations and oxygens. Only coordination figures in adjacent units joined directly to those in the asymmetric unit are shown. O_I, O_{II} and O_{III} have been omitted to simplify the picture since they do not link cation polyhedra. The dashed lines indicate that the coordination involves oxygen atoms that are related by a *c* translation to those in the asymmetric unit.

Table 4. *Interatomic distances in the cation coordination polyhedra*

K_{I}–O_{I}	3·076 Å	K_{II}–O_{II}	2·896 Å
K_{I}–O_{V}	2·703	K_{II}–O_{III}	2·956
K_{I}–O_{V}'	2·873	K_{II}–O_{IV}	2·640
K_{I}–O_{VII}	2·804	K_{II}–O_{IV}'	2·726
K_{I}–O_{VII}'	2·779	K_{II}–O_{V}'	2·858
K_{I}–O_{VIII}	2·684	K_{II}–O_{VI}	2·777
K_{I}–H_2O	2·931	K_{II}–O_{VIII}	2·748
$\sigma = \pm 0·014$ Å		K_{II}–O_{IX}	2·956
		$\sigma = \pm 0·013$ Å	
Li–O_{VI}	1·968 Å		
Li–O_{VII}	1·939		
Li–O_{IX}	1·930		
Li–H_2O	1·955		
$\sigma = \pm 0·026$ Å			

The hydrogens of the water molecule are probably bonded to the O_{IV} and O_{VIII} atoms (H_2O–O_{IV}, 2·875 Å; H_2O–O_{VIII}, 2·772 Å; $\sigma = \pm 0·020$). The O_{IV}–H_2O–O_{VIII} angle is 92°, which would indicate that the hydrogen bonds are probably non-linear. No exact hydrogen positions could be derived from the difference synthesis, but the map did contain positive areas consistent with the postulated hydrogen bonds.

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The Crystal Structure of Sulphanilic Acid Mono-Hydrate

By A. I. M. Rae and E. N. Maslen

Department of Physics, University of Western Australia, Nedlands, Western Australia

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The crystal structure of sulphanilic acid mono-hydrate has been solved by a combination of Patterson and Fourier syntheses on two projections. These have been refined using difference syntheses to accuracies of 12·3% (*hk*0) and 14·6% (0*kl*) in *R*. The molecules have been shown to pack with their benzene rings in parallel layers 3·4 Å apart. The charged groups and water molecule are connected by a series of hydrogen bonds and this system is compared with that existing in sulphamic acid.

1. Introduction

The crystal structure of sulphanilic acid mono-hydrate, $NH_3^+C_6H_4SO_3^-,H_2O$, is of interest in relation to a programme of work on the structural properties of charged groups which is in progress in this laboratory. That sulphanilic acid exists in the zwitterion configuration in solution is known from a variety of chemical evidence, of which the work on dissociation constants by Kumler (1955) is perhaps the most conclusive. It is reasonable in the light of work on similar structures—particularly sulphamic acid—to presume that this configuration persists in the solid state.

Structural investigations on sulphamic acid ($NH_3^+SO_3^-$), by X-ray diffraction (Kanda & King, 1951; Osaki *et al.*, 1955) and neutron diffraction (Sass, 1960) have revealed the interactions of the charged groups and the details of the hydrogen bond system in that molecule.

The present work was undertaken in order to investigate the changes, if any, which take place in these interactions when the charged groups are separated by a benzene ring.

2. Experimental

Two crystalline habits for sulphanilic acid have been reported (Hodgman *et al.*, 1955)—elongated monoclinic laths and rhombic plates. Crystals of the first form were obtained by precipitation from a hot saturated aqueous solution and the rhombic crystals when a cold solution was allowed to evaporate. Both forms were initially transparent, but decomposed quickly to white microcrystalline aggregates when exposed to air.

Although Hodgman *et al.* (1955) indicate that the monoclinic crystals contain two molecules of water of crystallization per molecule compared with one for the rhombic form, X-ray photography showed that both forms are chemically identical. They have the same space group, cell dimensions and distribution of intensities, differing only in the development of their crystal faces. A density measurement—see below—showed that the crystals contain one molecule of water per molecule.

The cell dimensions were measured using the back-reflection technique, modified for the Weissenberg camera. A crystal, mounted about a non-unique axis,