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The Crystal Structure of Calcium Sodium Hypophosphite, $CaNa(H_2PO_2)_3$

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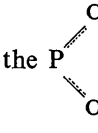
The crystal structure of $CaNa(H_2PO_2)_3$, a double salt of calcium and sodium hypophosphites, has been determined. The crystal belongs to the cubic system, space group $P2_13$, $Z=4$, with the lattice constant $a=9{\cdot}720\pm0{\cdot}003$ Å. Refinement of the structure was carried out by the full-matrix least-squares method including anisotropic thermal parameters. The final R value for 705 observed reflexions was 0·097. The structure consists of two kinds of octahedral groups, one with a calcium atom and the other with a sodium atom. Each oxygen atom of the hypophosphite ions is coordinated to each one of the calcium and sodium atoms to form the octahedra. The present structure is considered to be typical of the double salts of hypophosphorous acid. The structural similarities with langbeinite, $Mg_2K_2(SO_4)_3$, are discussed.

Introduction

In the course of a study on the structures of nucleic acid constituents, in which the infrared characteristic absorption bands of the  – groups in various hypophosphites were investigated, we found a new form of a hypophosphite, crystallized in the cubic system. The hypophosphites whose crystal structures have been studied so far are $NH_4H_2PO_2$ (orthorhombic; Zachariasen & Mooney, 1934), $Mg(H_2PO_2)_2.6H_2O$ (tetragonal; Pedrazuela, Garcia-Blanco & Rivoir, 1953), $Ca(H_2PO_2)_2$ (monoclinic; Loopstra, 1958) and KH_2PO_2 (monoclinic; Akimoto, 1965). The present crystal possesses the highest symmetry of these salts and it seemed to be interesting to determine its crystal structure. The result showed that the compound is actually a double salt of calcium and sodium hypophosphites having the chemical formula of $CaNa(H_2PO_2)_3$.

Experimental

The crystals of $CaNa(H_2PO_2)_3$ were obtained by slow evaporation of an aqueous solution prepared by adding $Ca(H_2PO_2)_2$ to the saturated aqueous solution of $Na(H_2PO_2).H_2O$. They crystallize in the form of a cubic dodecahedron with well developed {110} faces. The lattice constant was measured on a powder diffractometer with the use of silicon powder as an internal

standard. The 2θ values obtained for Cu $K\alpha$ radiation were calibrated against silicon. The density was measured by the flotation method by use of a mixed solution of methylene dibromide and benzene. Chemical analysis indicated the molar proportion of calcium and sodium to be approximately unity.

Crystal data

Calcium sodium hypophosphite, $CaNa(H_2PO_2)_3$, M.W. 258·0.

Cubic,
$a=9{\cdot}720\pm0{\cdot}003$ Å;
$U=918{\cdot}3$ Å^3;
$Z=4$,
$D_m=1{\cdot}90$ g.cm^{-3},
$D_x=1{\cdot}865$ g.cm^{-3},
μ(Cu $K\alpha$)$=113$ cm^{-1};
$F(000)=520$.
Absent spectra: $h00$ when h is odd, $0k0$ when k is odd, $00l$ when l is odd
Space group: $P2_13$.

The intensity data were collected from equi-inclination Weissenberg photographs with Cu $K\alpha$ radiation by use of the multiple-film method. The layers from $0kl$ to $5kl$ were recorded and the intensities were measured by visual comparison with a calibrated intensity scale. After correcting for Lorentz and polarization factors, the structure factors on various layers were correlated and scaled on a common base. A Wilson plot was then made to estimate the scale factor and an overall temperature factor. The value of B was found to be 0·66 Å^2.

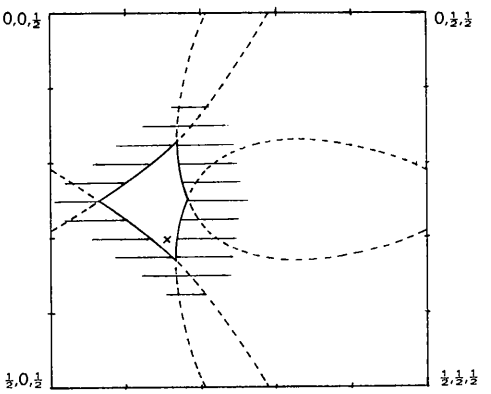


Fig. 1. Forbidden region (shown by horizontal lines) for the phosphorus atom calculated by assuming that the distance between the phosphorus atoms is greater than 4 Å. The final site is shown by a cross:

Determination and refinement of the structure

Since the $H_2PO_2^-$ group has no triad axis, the twelve $H_2PO_2^-$ groups contained in the unit cell should lie at the general positions [12(*b*) site of space group No. 198 in *International Tables for X-ray Crystallography* (1952)]. It is obvious that the phosphorus atoms should be found within a small region as shown in Fig. 1, if we assume the shortest P–P interatomic distances to be greater than 4 Å. The Harker section cut through $w=\frac{1}{2}$ showed peaks of considerable height which can be well accounted for in terms of the P–P vectors. The coordinates of the phosphorus atom were, therefore, determined as $x=0{\cdot}30$, $y=0{\cdot}16$, $z=0{\cdot}50$. A Fourier synthesis, phased on the phosphorus atoms, ($R=0{\cdot}53$), showed an excess symmetry, because the phosphorus atoms do not contribute to the imaginary part of the structure factors in cases where h,k and l are all even or all odd. As a result, it was hard to locate the oxygen atoms which must be found in the 12(*b*) sites. Therefore one of the peaks on the triad axis was taken as the sodium atom, and on the basis of the phosphorus and sodium contributions, the second Fourier synthesis was calculated. The R value was 0·45 at this stage. This map indicated one more atom on the triad axis and also several peaks around the phosphorus atom. Trials of locating the oxygen atoms led to a plausible structure, but because the chemical formula of the crystal was, at that time, thought to be NaH_2PO_2, the Fourier synthesis could not be interpreted in terms of this simple formula. The presence of the calcium ion was first noticed on a difference electron density map, which was later confirmed by chemical analysis. The structure of $CaNa(H_2PO_2)_3$ determined in this way ($R=0{\cdot}20$) was then subjected to the refinement by the method of least-squares. Eight cycles of the block-matrix followed by three cycles of the full-matrix [by *ORFLS*; Busing,

Table 1. *The final positional and thermal parameters*

Temperature factors are expressed in the form:

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

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
P	0·3011	0·1550	0·5177	0·0082	0·0041	0·0032	−0·0019	−0·0024	0·0017
	(4)	(4)	(4)	(4)	(3)	(3)	(3)	(3)	(3)
O(1)	0·3062	0·0637	0·6402	0·0081	0·0022	0·0024	0·0005	−0·0011	0·0014
	(10)	(8)	(8)	(11)	(7)	(7)	(7)	(8)	(6)
O(2)	0·2119	0·1150	0·4001	0·0100	0·0075	0·0027	0·0010	−0·0035	0·0008
	(12)	(11)	(9)	(13)	(11)	(9)	(11)	(9)	(8)
Ca	0·1727	0·1727	0·1727	0·0018	0·0018	0·0018	0·0002	0·0002	0·0002
	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(2)
Na	0·6282	0·6282	0·6282	0·0033	0·0033	0·0033	0·0001	0·0001	0·0001
	(5)	(5)	(5)	(4)	(4)	(4)	(4)	(4)	(4)

Martin & Levy, (1962)] least-squares calculations yielded the final R value of 0·097 for 705 observed reflexions.

In the latter calculations anisotropic thermal parameters were introduced for each atom and the following weighting scheme was adopted;

$$\sqrt{w} = F_o/20 \text{ , when } F_o \leq 20 \text{ ,}$$
$$\sqrt{w} = 20/F_o \text{ , when } F_o > 20 \text{ ,}$$
$$\sqrt{w} = 85 \times 20/F_o^2 \text{ , when } F_o \geq 85 \text{ .}$$

The atomic scattering factors for Ca^{2+}, Na^+, P and O were taken from *International Tables for X-ray Crystallography* (1962). The final atomic parameters and their standard deviations are listed in Table 1. A comparison of the observed and calculated structure factors is given in Table 2. The standard deviations in interatomic distances and angles were calculated by the *ORFFE* program (Busing, Martin & Levy, 1964) by use of the variance-covariance matrix elements put out from the last full-matrix least-squares cycle.

Discussion of the structure

Hypophosphite ion

The bond lengths and angles of the hypophosphite ion are shown in Table 3. The two P–O bonds are almost exactly equal in length, indicating the structure

Table 2. *Observed and calculated structure factors*

H	K	L	F(OBS)	F(CAL)
2	0	0	63.76	67.12
4	0	0	68.10	76.90
6	0	0	74.61	89.20
8	0	0	9.42	7.99
10	0	0	0.00	2.22
12	0	0	15.29	13.46
1	1	0	97.34	69.33
2	1	0	4.88	4.12
3	1	0	40.56	49.68
4	1	0	27.58	30.80
5	1	0	4.30	3.94
6	1	0	11.30	10.98
7	1	0	17.43	17.17
8	1	0	52.24	52.22
9	1	0	17.70	15.43
10	1	0	4.44	2.15
11	1	0	26.31	24.99
12	1	0	16.40	15.27
1	2	0	24.09	26.07
2	2	0	29.56	38.78
3	2	0	31.78	31.13
4	2	0	16.24	18.31
5	2	0	46.19	45.98
6	2	0	9.40	8.80
7	2	0	15.15	15.10
8	2	0	0.00	0.49
9	2	0	40.68	41.21
10	2	0	21.49	20.98
11	2	0	15.92	14.83
12	2	0	4.00	4.39
1	3	0	125.24	164.72
2	3	0	32.67	37.87
3	3	0	0.00	0.49
4	3	0	20.94	22.74
5	3	0	71.83	82.36
6	3	0	14.69	15.81
7	3	0	51.33	52.01
8	3	0	34.42	36.06
9	3	0	18.97	17.05
10	3	0	0.00	1.73
1	4	0	47.27	60.58
2	4	0	27.70	31.40
3	4	0	13.12	9.86
4	4	0	7.40	7.48
5	4	0	35.59	33.60
6	4	0	8.72	11.17
7	4	0	30.33	32.78
8	4	0	13.92	15.99
9	4	0	15.56	14.87
10	4	0	15.66	15.73
11	4	0	12.05	14.87
1	5	0	9.54	12.91
2	5	0	12.65	13.20
3	5	0	30.99	28.93
4	5	0	40.58	42.38
5	5	0	16.14	16.59
6	5	0	3.17	6.34
7	5	0	18.36	16.72
8	5	0	26.35	24.98
9	5	0	0.00	2.91
10	5	0	23.18	22.98
11	5	0	10.23	12.94
1	6	0	42.94	45.40
2	6	0	28.05	28.22
3	6	0	34.60	31.36
4	6	0	16.02	14.46
5	6	0	17.41	15.60
6	6	0	64.63	54.05
7	6	0	64.18	51.58
8	6	0	24.35	21.26
9	6	0	5.04	2.47
10	6	0	13.07	9.29
1	7	0	5.85	4.47
2	7	0	10.71	9.96
3	7	0	27.14	27.32
4	7	0	4.22	1.21
5	7	0	14.10	13.76
6	7	0	9.34	6.62
7	7	0	11.06	8.49
8	7	0	31.15	26.22
9	7	0	18.72	15.79
10	7	0	8.05	6.98
1	8	0	19.19	18.19
2	8	0	0.00	1.62
3	8	0	31.90	29.25
4	8	0	29.66	26.31
5	8	0	20.28	20.00
6	8	0	28.21	24.31
7	8	0	18.48	17.52
8	8	0	15.25	13.56
9	8	0	24.35	24.89
1	9	0	46.41	45.80
2	9	0	59.04	56.79
3	9	0	15.41	14.63
4	9	0	22.64	19.16
5	9	0	34.36	30.11
6	9	0	0.00	1.49
7	9	0	31.21	29.42
8	9	0	27.80	27.39
1	10	0	9.46	7.45
2	10	0	23.24	22.18
3	10	0	11.46	11.20
4	10	0	7.20	6.49
5	10	0	5.37	4.33
6	10	0	10.37	4.33
7	10	0	15.11	15.48
1	11	0	0.00	1.17
2	11	0	11.14	10.70
3	11	0	7.32	8.38
4	11	0	9.64	8.38
5	11	0	5.12	5.00
1	12	0	17.74	17.31
2	12	0	20.26	23.34
3	12	0	29.48	34.07
1	1	1	36.12	37.97
2	1	1	62.45	69.07
3	1	1	36.20	38.07
4	1	1	58.41	64.86
5	1	1	46.81	53.20
6	1	1	26.49	26.11
7	1	1	3.69	0.73
8	1	1	32.00	32.25
9	1	1	35.79	34.26
10	1	1	14.67	11.47
11	1	1	20.78	18.27
12	1	1	15.52	16.32
2	2	1	43.76	43.77
3	2	1	49.94	55.65
4	2	1	30.45	31.82
5	2	1	36.10	33.49
6	2	1	10.55	12.06
7	2	1	30.81	29.98
8	2	1	60.13	57.01
9	2	1	31.82	31.80
10	2	1	16.14	14.32
11	2	1	10.86	10.34
12	2	1	21.95	23.80
2	3	1	51.96	55.82
3	3	1	12.27	14.04
4	3	1	91.83	92.76
5	3	1	59.04	56.03
6	3	1	24.84	22.99
7	3	1	6.32	5.48
8	3	1	30.35	30.33
9	3	1	15.68	14.08
10	3	1	28.53	28.41
11	3	1	16.22	18.79
12	3	1	6.84	6.72
2	4	1	41.69	40.24
3	4	1	28.57	27.86
4	4	1	45.42	42.96
5	4	1	29.78	26.76
6	4	1	12.43	10.54
7	4	1	18.44	18.58
8	4	1	33.70	32.70
9	4	1	18.28	17.72
10	4	1	15.50	15.44
11	4	1	2.40	3.33
2	5	1	25.83	27.40
3	5	1	46.61	43.02
4	5	1	19.73	20.40
5	5	1	37.51	37.01
6	5	1	8.25	8.16
7	5	1	44.17	44.82
8	5	1	19.83	17.06
9	5	1	5.77	6.08
10	5	1	26.27	26.91
11	5	1	14.24	14.16
2	6	1	29.68	31.72
3	6	1	50.36	47.56
4	6	1	59.30	62.04
5	6	1	17.72	18.30
6	6	1	24.31	20.50
7	6	1	20.18	16.88
8	6	1	0.00	5.85
9	6	1	40.37	37.24
10	6	1	8.09	6.83
2	7	1	5.04	4.70
3	7	1	19.47	17.80
4	7	1	6.86	5.52
5	7	1	12.81	10.31
6	7	1	25.28	22.10
7	7	1	23.93	20.13
8	7	1	0.00	3.22
9	7	1	17.17	14.62
10	7	1	15.17	15.50
2	8	1	37.27	37.25
3	8	1	14.59	14.34
4	8	1	25.71	24.61
5	8	1	21.06	19.11
6	8	1	35.71	29.50
7	8	1	22.09	17.61
8	8	1	21.08	17.40
9	8	1	15.62	15.60
2	9	1	38.52	36.91
3	9	1	39.79	36.08
4	9	1	29.30	27.49
5	9	1	34.22	29.75
6	9	1	13.11	10.70
7	9	1	11.70	9.97
8	9	1	21.11	19.84
2	10	1	11.04	10.85
3	10	1	11.52	11.52
4	10	1	27.02	23.37
5	10	1	14.41	14.54
6	10	1	16.26	13.27
7	10	1	15.54	15.64
2	11	1	6.66	5.66
3	11	1	12.41	11.19
4	11	1	8.88	7.37
5	11	1	20.44	20.82
2	12	1	23.81	27.17
3	12	1	13.86	15.88
2	2	2	31.88	31.05
3	2	2	21.21	22.01
4	2	2	43.84	39.70
5	2	2	37.50	38.82
6	2	2	37.05	37.84
7	2	2	11.99	15.10
8	2	2	20.92	19.37
9	2	2	27.48	26.60
10	2	2	19.25	16.94
11	2	2	24.82	26.22
12	2	2	1.72	3.99
3	3	2	12.55	13.12
4	3	2	3.53	2.53
5	3	2	54.18	50.12
6	3	2	23.36	22.59
7	3	2	35.67	37.35
8	3	2	53.41	52.58
9	3	2	21.39	21.53
10	3	2	5.23	6.31
11	3	2	15.70	19.18
3	4	2	28.01	23.07
4	4	2	66.89	63.42
5	4	2	35.55	34.81
6	4	2	23.45	24.34
7	4	2	39.73	35.71
8	4	2	11.18	9.53
9	4	2	0.00	3.43
10	4	2	30.49	32.78
11	4	2	14.27	18.72
3	5	2	37.41	34.51
4	5	2	75.18	79.23
5	5	2	17.70	15.70
6	5	2	13.56	14.53
7	5	2	5.61	8.52
8	5	2	15.46	12.76
9	5	2	15.52	15.44
10	5	2	13.36	14.87
11	5	2	9.22	10.17
3	6	2	22.48	22.79
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9	7	2	30.39	31.35
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4	8	2	15.33	13.76
5	8	2	35.29	32.85
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7	8	2	10.84	9.70
8	8	2	12.61	12.90
9	8	2	13.34	16.72
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8	9	2	16.08	21.81
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4	10	2	15.50	15.47
5	10	2	10.96	11.68
6	10	2	12.09	13.60
7	10	2	13.66	17.24
3	11	2	8.05	11.31
4	11	2	32.02	33.53
5	11	2	6.92	6.38
3	3	3	64.93	57.23
4	3	3	43.34	40.13
5	3	3	34.26	27.24
6	3	3	19.05	15.35
7	3	3	22.62	19.30
8	3	3	22.30	21.63
9	3	3	20.56	21.19
10	3	3	12.59	13.87
11	3	3	21.53	28.51
4	4	3	21.75	18.49
5	4	3	32.77	26.64
6	4	3	28.97	26.34
7	4	3	53.25	52.55
8	4	3	16.81	18.13
9	4	3	0.00	7.46
10	4	3	13.88	16.50
11	4	3	6.44	7.96
4	5	3	7.20	5.84
5	5	3	39.57	34.72
6	5	3	26.82	26.14
7	5	3	45.24	40.92
8	5	3	29.34	28.54
9	5	3	14.53	13.00
10	5	3	12.65	15.27
11	5	3	3.33	8.77
4	6	3	11.94	7.51
5	6	3	39.16	37.69
6	6	3	18.58	19.17
7	6	3	12.33	11.77
8	6	3	17.07	16.41
9	6	3	11.38	12.03
10	6	3	15.11	17.06
4	7	3	11.26	9.66
5	7	3	30.00	31.42
6	7	3	45.64	44.51
7	7	3	8.64	9.87
8	7	3	21.13	21.62
9	7	3	15.09	19.58
4	8	3	29.80	30.05
5	8	3	18.50	16.93
6	8	3	6.67	7.38
7	8	3	8.39	11.91
8	8	3	22.58	26.59
4	9	3	18.56	19.84
5	9	3	7.77	6.40
6	9	3	9.30	10.14
7	9	3	9.93	11.34
5	10	3	12.25	13.46
6	10	3	12.73	16.24
4	11	3	3.79	3.45
5	11	3	10.65	16.57
4	4	4	68.80	64.57
5	4	4	66.32	64.31
6	4	4	13.24	12.70
7	4	4	18.18	16.09
8	4	4	16.55	17.31
9	4	4	16.53	14.48
10	4	4	23.41	27.32
11	4	4	7.18	12.98
5	5	4	23.34	21.58
6	5	4	48.16	43.86
7	5	4	26.71	25.89
8	5	4	10.69	10.10
9	5	4	11.76	12.72
10	5	4	20.18	22.97
5	6	4	17.72	14.24
6	6	4	13.34	13.01
7	6	4	30.31	28.33
8	6	4	15.60	16.13
9	6	4	8.55	8.32
10	6	4	7.61	11.05
5	7	4	21.53	21.92
6	7	4	13.30	12.50
7	7	4	18.48	17.85
8	7	4	12.15	12.97
9	7	4	25.67	32.22
5	8	4	13.41	12.45
6	8	4	25.02	21.84
7	8	4	21.85	21.18
8	8	4	8.19	12.15
5	9	4	9.91	10.50
6	9	4	15.19	15.10
7	9	4	6.78	11.35
5	10	4	4.28	4.78
6	10	4	3.25	7.36
5	5	5	9.16	5.69
6	5	5	13.98	13.19
7	5	5	30.18	29.96
8	5	5	7.73	8.27
9	5	5	19.41	18.69
10	5	5	21.47	26.02
6	6	5	27.92	24.83
7	6	5	18.26	15.93
8	6	5	0.00	5.08
9	6	5	19.11	21.89
6	7	5	29.58	29.17
7	7	5	12.73	11.62
8	7	5	13.58	13.71
9	7	5	9.00	13.65
6	8	5	14.57	16.88
7	8	5	11.92	14.17
8	8	5	13.48	18.86
6	9	5	6.64	8.23
7	9	5	6.64	12.36

of this ion to be $\begin{matrix} H & O \\ & >P< \\ H & O \end{matrix}$ –. The bond angle, O–P–O, is significantly larger than the tetrahedral angle. This may be a result of the repulsions between the oxygen atoms. In Table 3 the dimensions of the hypophosphite ion observed in its various salts are compared. It is seen that the P–O bond lengths are found within the range of 1·485 Å ~ 1·52 Å and the values obtained in the present determination are the shortest ones.

Environment of the calcium and sodium ions

As shown in Fig. 3, every calcium and sodium ion is coordinated to six oxygen atoms arranged in a nearly regular octahedron. Since the calcium and sodium ions lie on the triad axis, there were only two kinds of distinct Ca–O or Na–O distances involved in each octahedron. These distances and the bond angles are listed in Table 4.

The crystal structure

The normal projection of the crystal structure on (001) and the perspective view of the structure along [$\bar{1}$10] are shown in Figs. 2 and 3, respectively. The latter Figure illustrates the structure around the body diagonal showing how the hypophosphite ions are coordinated to the metal ions. It is seen that the crystal structure consists of two kinds of octahedral groups, one with the calcium ions and the other with the sodium ions. Each oxygen atom of the hypophosphite ions is coordinated to both calcium and sodium ions so that the octaheda are joined together by sharing one of their edges, and form a three-dimensional framework. The feature is best represented by the stereoscopic drawing shown in Fig. 5. Figs. 3 and 5 were drawn on a CalComp

Table 3. *Comparison of the dimensions of the hypophosphite ion found in its various salts*

	$CaNa(H_2PO_2)_3$ Present study	$NH_4(H_2PO_2)$ Zachariasen & Mooney, 1934	$Mg(H_2PO_2)_2.6H_2O$ Pedrazuela *et al.* 1953	$Ca(H_2PO_2)_2$ Loopstra, 1958	KH_2PO_2 Akimoto, 1965
P–O(1)	1·485 ± 0·008 Å	1·51 ± 0·11	1·52	1·49	1·50
P–O(2)	1·487 ± 0·011	1·51*	1·52*	1·52	1·50*
O–P–O	118·6 ± 0·6°	120 ± 8	109	117·3	115·7

* Equivalent to P–O(1).

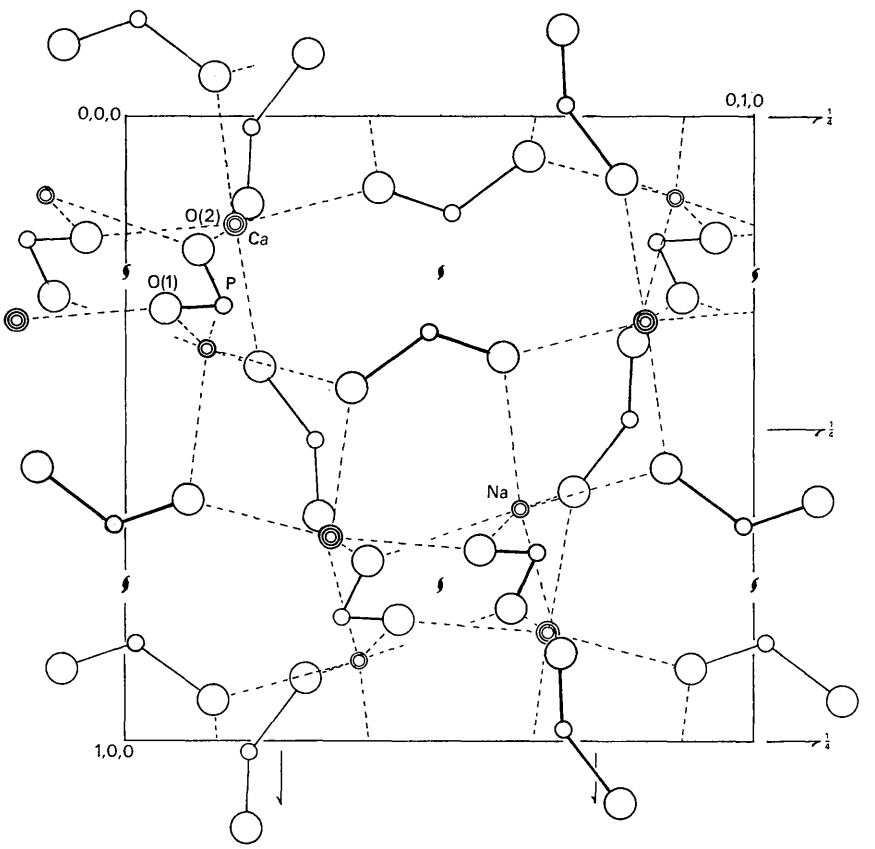

Fig. 2. The crystal structure of $CaNa(H_2PO_2)_3$ projected on (001).

Table 4. *Coordination around the calcium and sodium ions*

Ca octahedron			
Ca–O(1)	2·329 (0·008) Å	$O(1)^6$–Ca–$O(1)^{11}$	88·0 (0·3)°
Ca–O(2)	2·312 (0·009)	$O(2)^2$–Ca–$O(2)^3$	96·6 (0·4)
		$O(2)^1$–Ca–$O(1)^6$	82·9 (0·3)
		$O(2)^1$–Ca–$O(1)^7$	170·8 (0·4)
		$O(2)^1$–Ca–$O(1)^{11}$	92·6 (0·3)
Na octahedron			
Na–O(1)	2·422 (0·009)	$O(1)^9$–Na–$O(1)^{10}$	93·7 (0·3)
Na–O(2)	2·515 (0·011)	$O(2)^4$–Na–$O(2)^{12}$	103·7 (0·4)
		$O(1)^5$–Na–$O(2)^4$	76·9 (0·3)
		$O(1)^5$–Na–$O(2)^8$	170·4 (0·4)
		$O(1)^5$–Na–$O(2)^{12}$	85·3 (0·3)

1	x	y	z
2	z	x	y
3	y	z	x
4	$0·5+x$	$0·5-y$	$1·0-z$
5	$1·0-x$	$0·5+y$	$1·5-z$
6	$0·5-x$	$-y$	$-0·5+z$
7	$-0·5+z$	$0·5-x$	$-y$
8	$1·0-z$	$0·5+x$	$0·5-y$
9	$1·5-z$	$1·0-x$	$0·5+y$
10	$0·5+y$	$1·5-z$	$1·0-x$
11	$-y$	$-0·5+z$	$0·5-x$
12	$0·5-y$	$1·0-z$	$0·5+x$

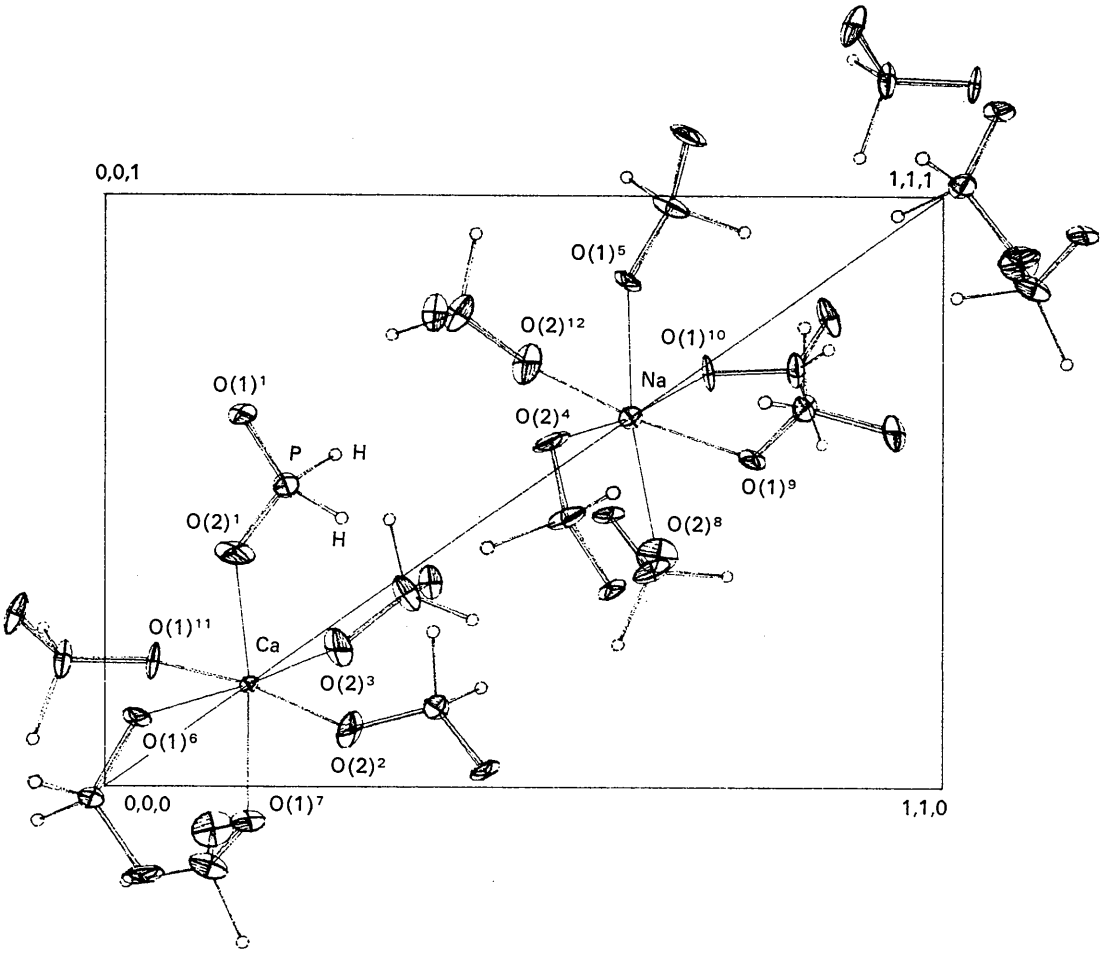

Fig. 3. Perspective view of $CaNa(H_2PO_2)_3$ along [$\bar{1}$10] showing the structure around the body diagonal. Hydrogen atoms are at the assumed positions. The thermal ellipsoids enclose 50% probability.

plotter using the *ORTEP* program of Johnson (1965). The surface of each ellipsoid encloses 50% of normally distributed displacements of a vibrating atom in Fig. 3 and 30% in Fig. 5.

The crystal structure of $CaNa(H_2PO_2)_3$ in some respects resembles that of langbeinite, $Mg_2K_2(SO_4)_3$, which is a typical structure found in a number of double sulphates with cubic symmetry. Langbeinite crystallizes in space group $P2_13$ with the lattice constant $a=9{\cdot}920$ Å. The unit cell contains twice as many metal ions as $CaNa(H_2PO_2)_3$ and both the two magnesium ions and the two potassium ions lie at the 4(*a*) sites (Zemann & Zemann, 1957) As shown in Fig. 4, the magnesium ions are coordinated to six oxygen atoms whereas the coordination of the potassium ions is not regular, one of the two kinds of potassium ion being surrounded by twelve oxygen atoms while the other is surrounded by nine oxygen atoms. Similarity between the two structures will be seen in Figs. 3 and 4. Since the sulphate ion has two more oxygen atoms and one additional formal charge comparing with the hypophosphite ion, the spaces surrounded by hydrogen atoms in $CaNa(H_2PO_2)_3$ are occupied by metal ions.

Isomorphism

The present structure may be considered to be one of the typical structures of the double salts of hypophosphorous acid. Replacement of the cations by metal ions other than calcium and sodium has been attempted and it was found that $MgNa(H_2PO_2)_3$ was an isomorphous crystal. This compound crystallizes in the same space group, $P2_13$, with the lattice constant, $a=9{\cdot}266$ Å and the powder pattern looks very similar to that of $CaNa(H_2PO_2)_3$. In Table 5 their powder data are compared.

The authors would like to express their sincere thanks to Professor M. Tsuboi for his valuable discussions and to Mr T. Akimoto, who found the present crystal, for his assistance at the early stage of the structure deter-

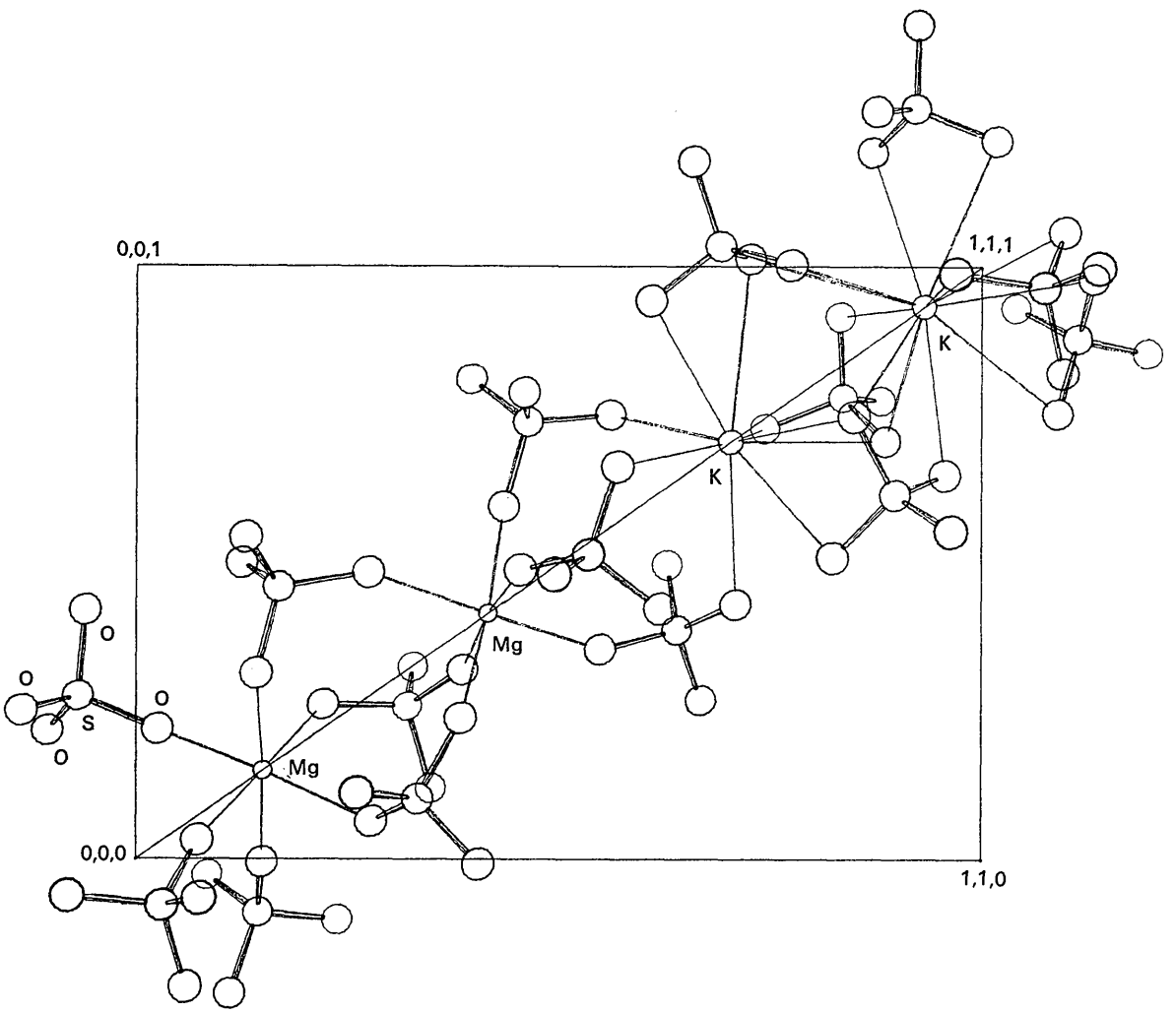

Fig. 4. Perspective view of langbeinite, $Mg_2K_2(SO_4)_3$, along [$\bar{1}$10] showing the structure around the body diagonal.

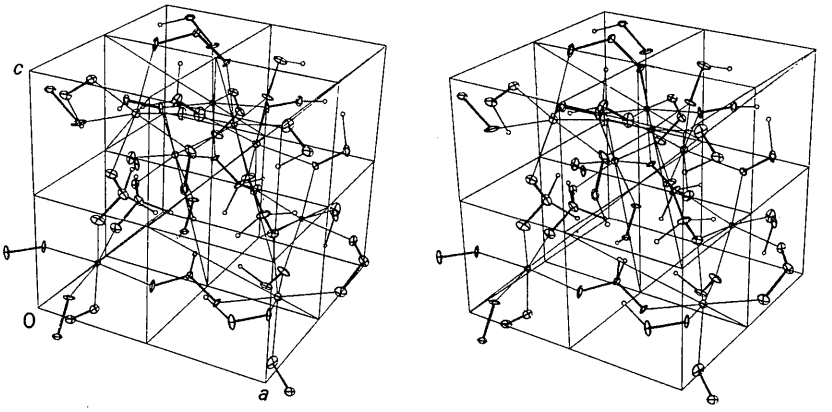

Fig. 5. Stereoscopic drawing of the crystal structure of $CaNa(H_2PO_2)_3$. The thermal ellipsoids enclose 30% of probability.

Table 5. *Powder data*

$CaNa(H_2PO_2)_3$			$MgNa(H_2PO_2)_3$		
hkl	d_{obs}	I/I_o	*hkl*	d_{obs}	I/I_o
110	6·857	45	110	6·55	79
111	5·604	14	111	5·35	27
200	4·849	20	200	4·63	20
210	4·330	5	210	4·14	8
211	3·967	57	211	3·78	92
220	3·439	9	220	3·28	17
221	3·240	21	221	3·09	19
310	3·075	100	310	2·930	100
311	2·929	13	311	2·794	13
222	2·802	3	222	2·675	6
320	2·693	8	320	2·570	17
321	2·598	30	321	2·477	36
400	2·430	6	400	2·317	10
322, 410	2·357	12	322, 410	2·247	12
330, 411	2·291	16	330, 411	2·184	23
420	2·1691	1	331	2·126	5
421	2·1210	7	420	2·072	7
422	1·9827	3	421	2·022	11
431, 510	1·9067	19	422	1·891	7
333, 511	1·8667	9	431, 510	1·817	23
432, 520	1·8040	4	333, 511	1·783	19
521	1·7750	4	521	1·691	11
441, 522	1·6916	7	441, 522	1·613	11
433, 530	1·6669	6	433, 530	1·589	14
531	1·6420	6	531	1·566	7
442, 600	1·6207	7	442, 600	1·544	8
532, 611	1·5773	6	532, 611	1·503	10
443, 540 621	1·5154	3	542, 630	1·381	12
542, 630	1·4481	5			
631	1·4326	3			

mination. They also wish to express their thanks to C. Itho Electronic Computing Service for the use of a CDC 3600 computer.

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