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Refinement of the Crystal Structures of Ammonium Dihydrogen Phosphate and Ammonium Dihydrogen Arsenate

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The crystal structures of ADP, $NH_4H_2PO_4$, and ADA, $NH_4H_2AsO_4$, which crystallize in space group $I\bar{4}2d$ and are isomorphous with the tetragonal phase of KH_2PO_4, have been refined at room temperature with single-crystal X-ray diffractometer data. For ADP, $a = 7{\cdot}4997$ (4), $c = 7{\cdot}5494$ (12) Å and R equals 0·021 ($Rw = 0{\cdot}030$) for 312 observed reflections. For ADA, $a = 7{\cdot}6998$ (5), $c = 7{\cdot}7158$ (12) Å and R equals 0·015 ($Rw = 0{\cdot}019$) for 585 observed reflections. The O–H···O bonds are slightly shorter in ADP than in ADA while the reverse is true for the N–H···O bonds. The difference in the N–H···O bond lengths is consistent with the difference in the thermal-expansion behavior of the two compounds.

Introduction

Arsenates and phosphates isomorphous with the tetragonal form of KH_2PO_4 (KDP) are RbH_2PO_4 (RDP), $NH_4H_2PO_4$ (ADP), KH_2AsO_4 (KDA), RbH_2AsO_4 (RDA), CsH_2AsO_4 (CDA) and $NH_4H_2AsO_4$ (ADA). This series offers an opportunity of examining a structure type with various combinations of the cationic and anionic groups. The structural investigation of the series may help in the interpretation of their physical properties, among which we are mostly interested in the thermal-expansion behavior (Khan, 1966; Deshpande & Khan, 1963, 1965*a*, *b*, 1966; Deshpande, Khan & Pardikar, 1968). Careful neutron-diffraction studies at room temperature have been performed on KDP (Bacon & Pease, 1953) and ADP (Tenzer, Frazer & Pepinsky, 1958). Crystal structures of ADP, RDP, KDA and ADA were refined by Khan (1966) in an attempt to understand the thermal expansion characteristics of this group of crystals but this work was of limited accuracy because of the small number of observed data collected in each case by the film method and because of the modest computational facilities available at that time. In this paper we report the results of a careful study at room temperature ($\simeq 22$ °C) on ADP and ADA.

Ammonium dihydrogen phosphate has recently been found in bat guano in Murra-et-elevyn cave in Western Australia as a naturally occuring mineral and is called biphosphammite (Pryce, 1972).

Experimental

Commercially supplied crystalline powder of ADP was dissolved in water and recrystallized by slow evaporation. ADA was prepared by evaporating a 1:1 mixture of As_2O_5 and $(NH_4)_2CO_3$ in water. The crystals were ground to obtain spherical specimens of convenient size. Intensity data were collected on a four-circle automatic diffractometer using crystal-reflected monochromatic Ag $K\alpha$ radiation ($\lambda = 0{\cdot}5608$ Å). A list of the computer programs used in this work and a description of the procedures followed in data collection and processing is given in Baur & Khan (1970). In addition *ORTEP* (Johnson, 1965) was used. Detailed information on ADP and ADA is summarized in Table 1. Absorption corrections were applied for ADA because the minimum and maximum transmission factors differ by 3%. For ADP the difference was much less than 1% and, therefore, the absorption correction was neglected. Observed structure factors were obtained after application of the Lorentz–polarization corrections. The general equivalent positions are (0,0,0;

Table 1. $NH_4H_2PO_4$, *ADP*, *and* $NH_4H_2AsO_4$, *ADA*, *crystal data and information regarding the data collection*

	ADP	ADA
a	7·4997 (4) Å*	7·6998 (5) Å†
c	7·5494 (12)*	7·7158 (12)†
V	424·6 Å^3	457·4 Å^3
Z	4	4
F.W.	114·981	158·929
D_{calc}	1·798 g cm^{-3}	2·307 g cm^{-3}
D_{meas}	1·800 g cm^{-3}‡	2·313 g cm^{-3}‡
Space group	$I\bar{4}2d$	$I\bar{4}2d$
Diameter of the crystal	0·27 mm	0·25 mm
μ(Ag $K\alpha$)	2·9 cm^{-1}	40·7 cm^{-1}
μR	0·04	0·55
Number of non-unique reflections measured	3194	5456
$R(I)$ §	0·065	0·053
Number of unique reflections	401	735
Number of $I_{hkl} = 0 (I < 2\sigma)$	89	150
Number of reflections used in refinement	312	585
$2\theta_{max}$	60°	60°
$\sin\theta_{max}/\lambda$	0·89 Å^{-1}	0·89 Å^{-1}

* Deshpande & Khan (1963).

† Deshpande & Khan (1965*b*).

‡ Averaged from Groth (1908).

§ R between equivalent reflections $\sum w \left| \left(\frac{\sum wI}{\sum w} \right) - I \right| / \sum wI$.

Table 2. $NH_4H_2PO_4$, *ADP, and* $NH_4H_2AsO_4$, *ADA positional parameters in fractions of the cell edges and thermal parameters* ($\times 10^4$) *with their standard deviations*

The form of the temperature factor is $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$ for the P, As, N and O atoms. Isotropic temperature factors for the H atoms are listed under β_{11}.

	Site symmetry	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
(*a*) ADP										
P	$\bar{4}$	0	0	0	55 (1)	55 (1)	84 (1)	0	0	0
N	$\bar{4}$	0	0	$\frac{1}{2}$	110 (2)	110 (2)	88 (3)	0	0	0
O	1	0·0843 (1)	0·1466 (1)	0·1151 (1)	75 (2)	83 (2)	118 (2)	13 (1)	−22 (2)	−37 (2)
H(*n*)	1	−0·002 (5)	0·089 (3)	0·563 (2)	2·8 (5) Å^2					
H(*o*)	2	$\frac{1}{4}$	0·150 (6)	$\frac{1}{8}$	5 (1)					
(*b*) ADA										
As	$\bar{4}$	0	0	0	57 (1)	57 (1)	89 (1)	0	0	0
N	$\bar{4}$	0	0	$\frac{1}{2}$	112 (2)	112 (2)	89 (3)	0	0	0
O	1	0·0869 (2)	0·1578 (2)	0·1233 (2)	78 (2)	88 (2)	145 (2)	19 (1)	−28 (2)	−48 (2
H(*n*)	1	0·014 (5)	0·120 (3)	0·567 (3)	2·4 (6) Å^2					
H(*o*)	2	$\frac{1}{4}$	0·199 (9)	$\frac{1}{8}$	4·6 (2)					

$\frac{1}{2},\frac{1}{2},\frac{1}{2})+(x,y,z;\ \bar{x},\bar{y},z;\ \bar{y},x,\bar{z};\ y,\bar{x},\bar{z};\ \frac{1}{2}-x,y,\frac{1}{4}-z;\ \frac{1}{2}+x,\bar{y},\frac{1}{4}-z;\ \frac{1}{2}+y,x,\frac{1}{4}+z;\ \frac{1}{2}-y,\bar{x},\frac{1}{4}+z)$. This generally adopted setting is the same as first used by West (1930) for KDP and is obtained by a rotation of 90° about the $\bar{4}$ axis relative to the setting in *International Tables for X-ray Crystallography* (1965) for the space group $I\bar{4}2d$. In the least-squares refinement of the data extinction coefficients and the anisotropic temperature factors of the heavy atoms were adjusted, while the hydrogen atoms were refined with isotropic temperature factors. Anomalous dispersion corrections were made for the As atom in ADA. The initial atomic positions of the hydrogen atoms of the NH_4^+ groups, H(*n*), were taken as determined by Tenzer *et al.* (1958) in ADP. The hydrogen atoms, H(*o*), of the $(H_2XO_4)^-$ groups ($X=P^{5+}$ or As^{5+}) were refined in the position $(0,0,0;\ \frac{1}{2},\frac{1}{2},\frac{1}{2})+(\frac{1}{4},y,\frac{1}{8};\ \frac{3}{4},\bar{y},\frac{1}{8};\ \bar{y},\frac{1}{4},\frac{7}{8};\ y,\frac{3}{4},\frac{7}{8})$ starting with a value of y equal to y_{oxygen}. The atomic scattering factors for P, As, N, O^{-1} and H were taken from *International Tables for X-ray Crystallography* (1962) and $\Delta f'$ and $\Delta f''$ for the As atom for Ag $K\alpha$ radiation were used as given by Cromer (1965). The final parameters (Table 2) resulted in R of 0·021 ($Rw=0{\cdot}030$, extinction coefficient $C=0{\cdot}19\times10^{-4}$) for ADP and $R=0{\cdot}015$ ($Rw=0{\cdot}019$, $C=0{\cdot}69\times10^{-5}$) for ADA. The standard errors of an observation of unit weight are 0·38 for ADP and 0·47 for ADA. The maximum density in a difference map of ADA [with As, O, N and H(*n*) subtracted] is 0·16 e Å^{-3}. This maximum is in a location far removed from any atomic position and is slightly larger than the density at the H(*o*) position. The F_o and F_c values are given in Table 3(*a*) and (*b*).

Discussion of the results

A view of the crystal structure, based on the coordinates of ADP, is shown in Fig. 1. Table 4 gives selected interatomic distances and bond angles in the two structures. It was somewhat disappointing to note that in spite of low final R values the hydrogen atom positions determined here in ADP do not compare well with those found by Tenzer, Frazer & Pepinsky (1958) in their neutron-diffraction study. In ADA the atomic parameters of the hydrogen atoms must be even more inaccurate because of the presence of the As atom. Table 4, therefore, does not include atomic distances and angles involving the hydrogen atoms. The root-mean-square displacements of atoms along the principal axes of the thermal ellipsoids and their orientations relative to the crystallographic axes are listed in Table 5. The two structures differ only in the size of the tetrahedral group XO_4^{3-}. Both the tetrahedral groups PO_4^{3-} and AsO_4^{3-} are slightly flattened into the (001) plane as

Table 3. *Observed and calculated structure factors*

(*a*) F_o, F_c and σ's ($\times 5$) for $NH_4H_2PO_4$. Unobserved structure factors omitted.

L	FO	FC	SIG
H=	0,	K=	0
4	45	45	10
8	82	84	18
H=	1,	K=	0
1	140	140	22
3	15	15	5
5	16	16	6
7	30	30	9
9	29	29	9
11	7	8	17
H=	1,	K=	1
2	205	213	30
6	63	64	14
10	34	34	11
H=	2,	K=	0
0	207	215	30
2	90	85	17
4	87	87	18
6	23	23	7
8	50	50	12
10	6	5	20
12	14	16	13
H=	2,	K=	1
1	92	87	17
3	59	57	12
5	25	24	7
7	39	40	10
9	15	15	10
11	7	7	18
H=	2,	K=	2
0	128	127	22
4	109	109	21
8	42	42	11
12	17	17	12
H=	3,	K=	0
1	68	65	14
3	98	97	19
5	72	72	15
11	12	11	13
13	8	6	20
H=	3,	K=	1
0	65	60	13
2	140	139	25
4	34	33	8
6	78	80	17
8	10	10	11
10	23	22	9
H=	3,	K=	2
1	95	83	17
3	88	86	18
5	56	56	13
7	22	23	8
9	13	13	10
11	11	12	14
H=	3,	K=	3
2	114	112	22
6	56	57	13
10	28	27	10
H=	4,	K=	0
2	33	31	8
4	139	143	26
6	9	10	9
8	19	19	9
12	20	19	12
H=	4,	K=	1
1	25	26	7
3	48	47	11
5	45	44	11
7	19	19	8
9	8	8	14
11	7	6	20
H=	4,	K=	2
0	86	84	17
2	39	38	9
4	86	87	18
6	19	19	8
8	32	32	10
10	7	8	18
12	16	15	13
H=	4,	K=	3
1	71	70	15
3	24	25	7
5	17	17	8
7	25	25	9
9	16	16	10
H=	4,	K=	4
0	121	121	24
4	37	39	10
8	43	44	12
12	10	10	17
H=	5,	K=	0
1	24	25	7
3	24	25	7
5	41	41	10
7	22	22	8
H=	5,	K=	1
0	55	53	12
2	84	84	17
4	32	33	9
6	52	53	12
8	13	13	10
10	21	21	11
H=	5,	K=	2
1	43	43	10
3	38	38	9
5	31	32	9
7	12	12	10
9	16	16	10
11	9	9	17
H=	5,	K=	3
0	57	56	13
2	84	85	18
4	37	38	10
6	42	41	11
8	16	16	10
10	26	25	11
H=	5,	K=	4
1	34	34	9
3	32	32	9
5	16	15	8
7	15	15	10
9	14	15	12
11	7	8	22
H=	5,	K=	5
2	61	63	14
6	46	47	12
10	16	16	13
H=	6,	K=	0
0	64	64	14
2	67	68	15
4	69	70	15
6	32	33	9
8	27	27	10
10	10	9	16
12	15	13	14
H=	6,	K=	1
1	15	15	7
3	58	59	13
5	30	30	9
7	8	8	14
9	10	10	14
11	13	12	14
H=	6,	K=	2
0	96	97	20
4	41	41	10
8	36	36	11
H=	6,	K=	3
1	67	68	15
3	20	21	8
5	15	15	9
7	30	30	10
9	18	17	11
H=	6,	K=	4
0	75	76	16
2	37	37	10
4	38	38	10
6	19	19	9
8	33	32	11
10	8	6	16
H=	6,	K=	5
1	29	29	9
3	16	16	9
5	23	23	9
7	21	21	10
9	7	7	20
H=	6,	K=	6
0	14	13	9
4	63	64	15
8	10	11	16
H=	7,	K=	0
1	58	60	13
3	6	5	13
7	32	31	10
9	16	14	13
H=	7,	K=	1
0	17	18	8
2	62	63	14
4	12	12	9
6	36	36	10
10	19	19	11
H=	7,	K=	2
1	45	46	11
3	16	16	8
5	16	16	9
7	19	18	10
9	15	16	12
H=	7,	K=	3
0	8	9	11
2	55	56	13
4	8	7	12
6	33	32	10
10	19	17	12
H=	7,	K=	4
1	14	14	9
3	35	35	10
5	23	23	9
7	8	8	17
H=	7,	K=	5
0	12	12	9
2	43	43	11
4	9	9	13
6	36	36	11
10	10	9	17
H=	7,	K=	6
1	6	6	17
3	32	32	10
5	31	31	10
H=	7,	K=	7
2	32	32	10
6	27	27	11
H=	8,	K=	0
0	52	54	12
2	22	22	8
4	42	42	11
6	15	15	10
8	23	24	11
10	9	7	18
H=	8,	K=	1
1	20	20	9
3	27	28	9
5	27	27	10
7	9	10	16
9	8	7	17
H=	8,	K=	2
0	59	60	14
2	6	7	14
4	34	34	10
6	11	11	12
8	26	26	11
10	7	7	23
H=	8,	K=	3
1	37	37	10
3	19	20	9
5	16	16	10
7	19	18	10
9	12	12	15
H=	8,	K=	4
0	49	49	12
2	11	12	11
4	33	33	10
6	9	8	15
8	23	22	11
H=	8,	K=	5
1	22	23	10
3	18	18	10
5	11	11	14
7	13	13	13
9	8	7	20
H=	8,	K=	6
0	24	23	10
4	38	39	11
8	9	9	17
H=	8,	K=	7
1	11	11	13
3	21	22	11
5	15	15	12
H=	8,	K=	8
0	18	17	11
4	29	28	11
H=	9,	K=	0
1	12	13	10
3	27	27	9
5	16	16	10
9	7	8	24
H=	9,	K=	1
0	25	25	9
2	39	40	11
4	20	20	10
6	30	30	11
8	12	11	14
H=	9,	K=	2
1	25	25	9
3	25	25	10
5	22	22	10
7	13	12	13
9	10	9	17
H=	9,	K=	3
0	22	23	9
2	37	37	11
4	19	18	10
6	27	27	10
8	11	10	15
H=	9,	K=	4
1	24	23	10
3	13	13	11
5	12	12	14
7	13	13	14
H=	9,	K=	5
0	9	8	15
2	40	39	11
4	7	7	20
6	21	21	11
H=	9,	K=	6
1	23	22	10
3	12	12	13
5	10	9	15
7	9	9	19
H=	9,	K=	7
2	27	27	11
6	13	13	14
H=	9,	K=	8
1	14	14	13
3	13	13	14
5	8	8	20
H=	9,	K=	9
4	22	22	12
H=	10,	K=	0
0	29	29	10
2	23	22	10
4	33	34	11
6	13	13	13
8	13	12	14
H=	10,	K=	1
1	21	21	10
3	7	8	17
5	12	13	13
7	14	14	13
H=	10,	K=	2
0	24	24	10
4	35	35	11
8	13	12	15
H=	10,	K=	3
1	7	8	18
3	21	21	10
5	16	16	12
H=	10,	K=	4
0	30	30	11
2	12	12	12
4	23	23	11
6	8	8	19
8	13	14	16
H=	10,	K=	5
1	15	15	12
3	14	14	13
5	7	6	22
H=	10,	K=	6
0	40	40	12
4	7	7	21
H=	10,	K=	7
1	17	16	12
H=	10,	K=	8
0	22	22	12
H=	11,	K=	0
3	24	24	10
5	14	14	13
H=	11,	K=	1
2	28	29	11
6	17	16	13
H=	11,	K=	2
1	10	9	14
3	17	17	11
5	14	15	13
7	9	9	18
H=	11,	K=	3
2	24	24	11
6	20	20	12
H=	11,	K=	4
1	15	15	12
5	9	9	19
H=	11,	K=	5
2	21	21	11
4	8	5	17
H=	11,	K=	6
1	17	17	13
3	7	6	23
H=	11,	K=	7
2	18	17	13
H=	12,	K=	0
0	34	33	11
2	9	9	18
4	10	10	16
H=	12,	K=	1
1	19	18	12
3	7	7	22
H=	12,	K=	2
0	18	18	12
4	20	20	12
H=	12,	K=	3
1	9	8	17
3	19	18	12
5	16	15	14
H=	12,	K=	4
0	10	10	17
4	22	22	12
H=	12,	K=	5
1	7	8	22
3	8	8	21
H=	13,	K=	0
1	15	15	14
H=	13,	K=	1
2	17	17	13
H=	13,	K=	2
1	12	11	0

Table 3 (*cont.*)

(*b*) F_o, F_c and σ's (× 5) for $NH_4H_2AsO_4$. Unobserved structure factors omitted.

L	FO	FC	SIG	L	FO	FC	SIG	L	FO	FC	SIG	L	FO	FC	SIG	L	FO	FC	SIG	L	FO	FC	SIG	L	FO	FC	SIG
H=	-13,	K=	-4	-1	62	63	15	-9	37	36	15	8	139	141	25	10	51	50	16	6	69	70	16	4	69	69	16
-1	21	20	23	H=	-9,	K=	-3	-7	61	61	15	12	27	28	18	H=	5,	K=	2	10	30	29	18	6	13	14	25
H=	-13,	K=	-3	-10	26	25	21	-5	46	47	13	H=	1,	K=	0	1	121	119	21	H=	7,	K=	6	8	36	36	17
-2	39	38	17	-6	60	59	16	-3	52	51	12	1	251	247	36	3	99	99	18	1	44	44	13	H=	10,	K=	1
H=	-13,	K=	-2	-2	87	87	18	-1	127	130	22	3	67	83	15	5	75	75	15	3	65	66	15	1	57	57	15
-3	23	22	22	H=	-9,	K=	-2	H=	-6,	K=	-2	5	79	80	15	7	54	54	14	5	52	53	15	3	41	41	14
-1	29	29	19	-9	15	17	31	-12	22	22	23	7	88	88	17	9	37	37	15	7	24	24	18	5	30	30	16
H=	-13,	K=	-1	-7	33	32	16	-8	75	76	17	9	53	54	14	11	20	21	22	9	15	15	28	7	28	27	18
-2	41	40	17	-5	49	50	15	-4	111	111	20	11	20	23	21	H=	5,	K=	3	H=	7,	K=	7	9	21	21	23
H=	-12,	K=	-5	-3	58	59	15	H=	-6,	K=	-1	13	15	12	27	0	52	52	11	2	86	86	18	H=	10,	K=	2
-3	21	21	22	-1	53	52	14	-11	22	22	21	H=	1,	K=	1	2	178	181	30	6	49	49	15	0	68	68	16
-1	27	27	19	H=	-9,	K=	-1	-9	28	29	16	2	342	345	49	4	33	33	11	H=	8,	K=	0	4	73	73	17
H=	-12,	K=	-4	-10	27	27	21	-7	40	41	14	6	162	165	28	6	105	105	20	0	114	116	21	8	31	31	19
-4	46	46	17	-6	64	64	16	-5	81	81	16	10	60	61	15	8	13	12	23	4	107	107	20	H=	10,	K=	3
H=	-12,	K=	-3	-4	17	16	18	-3	112	113	20	H=	2,	K=	0	10	46	46	16	8	49	48	15	1	38	38	14
-5	30	30	19	-2	96	95	19	-1	78	78	15	0	345	354	48	H=	5,	K=	4	H=	8,	K=	1	3	51	51	15
-3	35	35	17	H=	-8,	K=	-8	H=	-5,	K=	-5	2	108	103	18	1	93	93	17	1	67	66	14	5	40	40	15
-1	20	21	22	-4	54	53	16	-10	32	33	18	4	219	224	35	3	92	92	17	3	65	66	15	7	19	19	23
H=	-12,	K=	-2	H=	-8,	K=	-7	-6	98	99	19	6	27	27	11	5	72	72	15	5	61	62	15	H=	10,	K=	4
-4	44	43	17	-7	22	21	20	-2	134	135	24	8	100	101	19	7	47	46	14	7	40	40	15	0	70	70	16
H=	-12,	K=	-1	-5	34	34	16	H=	-5,	K=	-4	12	34	34	17	9	29	29	16	9	19	19	21	4	58	57	16
-5	19	19	24	-3	45	46	13	-11	17	18	25	H=	2,	K=	1	11	18	18	23	11	13	13	34	8	31	32	20
-3	26	26	19	-1	40	39	15	-9	29	28	16	1	194	185	31	H=	5,	K=	5	H=	8,	K=	2	H=	10,	K=	5
-1	39	38	16	H=	-8,	K=	-6	-7	47	47	14	3	121	115	20	2	137	139	24	0	121	123	22	1	42	43	15
H=	-11,	K=	-8	-8	35	35	18	-5	74	73	15	5	100	98	18	6	96	96	19	4	93	93	18	3	32	32	16
-1	24	24	22	-4	70	70	16	-3	91	91	17	7	82	82	16	10	35	34	17	8	51	51	16	5	28	28	17
H=	-11,	K=	-7	-2	10	5	22	-1	91	91	17	9	45	45	14	H=	6,	K=	0	H=	8,	K=	3	7	24	23	20
-2	40	39	17	H=	-8,	K=	-5	H=	-5,	K=	-3	11	22	22	19	0	176	179	30	1	75	76	16	H=	10,	K=	6
H=	-11,	K=	-6	-9	22	22	22	-10	45	45	16	13	13	13	33	2	77	78	15	3	56	55	14	0	74	74	18
-5	21	20	22	-7	26	25	17	-8	13	12	23	H=	2,	K=	2	4	140	143	25	5	45	46	14	4	33	33	17
-3	27	27	19	-5	37	36	14	-6	107	108	20	0	276	273	42	6	38	38	12	7	41	40	15	H=	10,	K=	7
-1	31	31	17	-3	54	54	15	-4	33	33	11	4	225	228	37	8	69	69	16	9	26	25	19	1	35	35	17
H=	-11,	K=	-5	-1	60	60	15	-2	174	170	29	8	90	91	18	10	14	12	25	H=	8,	K=	4	3	23	24	20
-6	36	35	18	H=	-8,	K=	-4	H=	-5,	K=	-2	12	35	34	17	12	26	25	21	0	112	114	21	5	21	22	23
-2	49	48	16	-8	47	46	16	-11	21	21	21	H=	3,	K=	0	H=	6,	K=	1	4	77	77	17	H=	10,	K=	8
H=	-11,	K=	-4	-4	77	77	17	-9	36	37	15	1	39	40	8	1	80	79	15	8	47	47	16	0	45	45	17
-7	20	19	23	H=	-8,	K=	-3	-7	52	52	14	3	196	192	32	3	113	114	20	H=	8,	K=	5	4	36	35	18
-5	26	26	18	-9	27	26	18	-5	73	72	15	5	145	146	25	5	80	81	16	1	58	59	14	H=	10,	K=	9
-3	32	32	17	-7	37	38	15	-3	102	101	18	7	47	49	12	7	39	39	13	3	53	53	14	1	18	18	25
-1	34	35	16	-5	43	43	14	-1	124	122	21	9	28	29	14	9	29	29	16	5	36	37	15	H=	11,	K=	0
H=	-11,	K=	-3	-3	60	59	14	H=	-5,	K=	-1	11	28	29	18	11	22	22	23	7	27	26	17	1	40	40	15
-6	42	42	17	-1	79	80	16	-10	52	50	15	13	17	16	28	H=	6,	K=	2	9	23	22	21	3	38	39	15
-4	11	7	29	H=	-8,	K=	-2	-8	11	11	25	H=	3,	K=	1	0	198	206	33	H=	8,	K=	6	5	30	30	17
-2	57	57	16	-8	51	51	16	-6	111	113	20	0	85	80	15	4	111	110	20	0	80	80	17	7	20	20	24
H=	-11,	K=	-2	-4	92	93	18	-4	32	31	11	2	266	266	41	8	76	76	17	4	70	70	17	H=	11,	K=	1
-7	23	22	20	H=	-8,	K=	-1	-2	198	200	33	4	41	41	10	12	22	22	23	8	36	34	17	2	66	66	16
-5	31	31	17	-11	17	13	25	H=	-4,	K=	-4	6	148	152	26	H=	6,	K=	3	H=	8,	K=	7	6	38	38	17
-3	35	35	16	-9	20	21	22	-12	24	23	21	8	12	11	19	1	129	131	23	1	42	41	15	H=	11,	K=	2
-1	38	38	15	-7	39	39	15	-8	84	83	18	10	56	55	15	3	54	54	13	3	47	48	15	1	39	38	15
H=	-11,	K=	-1	-5	60	61	15	-4	123	124	22	H=	3,	K=	2	5	45	45	13	5	33	33	16	3	35	36	16
-6	40	39	17	-3	67	67	15	H=	-4,	K=	-3	1	132	127	22	7	59	60	15	7	21	19	21	5	30	30	18
-2	66	64	16	-1	69	69	15	-11	19	18	23	3	157	155	26	9	37	36	15	H=	8,	K=	8	7	22	21	22
H=	-10,	K=	-9	H=	-7,	K=	-7	-9	41	41	14	5	119	118	21	11	14	13	30	0	59	58	16	H=	11,	K=	3
-1	20	19	24	-6	51	50	16	-7	67	66	15	7	58	58	13	H=	6,	K=	4	4	54	53	16	2	60	60	16
H=	-10,	K=	-8	-2	82	83	18	-5	67	67	14	9	37	37	14	0	147	150	26	H=	9,	K=	0	6	40	40	18
-4	36	35	18	H=	-7,	K=	-6	-3	86	85	16	11	26	26	18	2	37	36	12	1	46	46	13	H=	11,	K=	4
H=	-10,	K=	-7	-9	17	16	25	-1	158	158	27	13	14	14	33	4	110	112	20	3	71	73	16	1	34	34	16
-5	20	21	24	-7	23	24	19	H=	-4,	K=	-2	H=	3,	K=	3	6	19	19	17	5	52	52	15	3	32	32	16
-3	25	25	19	-5	52	52	15	-12	31	30	18	2	226	226	36	8	62	61	16	7	20	21	20	5	26	26	19
-1	36	36	16	-3	66	66	15	-8	81	83	17	6	124	127	22	H=	6,	K=	5	9	19	18	23	7	20	19	23
H=	-10,	K=	-6	-1	45	44	13	-6	13	13	18	10	54	54	16	1	72	72	15	H=	9,	K=	1	H=	11,	K=	5
-4	34	33	17	H=	-7,	K=	-5	-4	176	179	30	H=	4,	K=	0	3	72	72	15	0	21	21	15	2	49	49	16
H=	-10,	K=	-5	-10	30	30	20	-2	39	38	9	0	154	150	25	5	59	61	14	2	97	98	19	6	35	35	19
-7	24	24	20	-6	68	68	16	H=	-4,	K=	-1	2	16	14	9	7	39	39	15	4	17	16	18	H=	11,	K=	6
-5	28	28	18	-2	107	108	20	-11	26	25	17	4	238	242	39	9	23	22	19	6	63	62	16	1	30	30	18
-3	32	31	16	H=	-7,	K=	-4	-9	37	37	14	6	68	69	15	H=	6,	K=	6	10	27	28	21	3	26	26	19
-1	42	43	15	-11	15	16	31	-7	54	55	13	12	37	35	17	0	72	70	15	H=	9,	K=	2	5	20	20	24
H=	-10,	K=	-4	-9	18	20	23	-5	98	97	18	H=	4,	K=	1	4	121	123	23	1	56	56	14	H=	11,	K=	7
-8	32	32	19	-7	34	34	15	-3	141	140	24	1	117	115	20	8	34	33	16	3	61	62	15	2	39	38	17
-4	57	56	16	-5	61	61	15	-1	112	110	19	3	143	143	24	H=	7,	K=	0	5	48	48	15	H=	11,	K=	8
H=	-10,	K=	-3	-3	79	76	16	H=	-3,	K=	-3	5	95	95	18	1	113	114	21	7	29	29	17	1	26	25	20
-7	20	20	22	-1	65	65	14	-10	55	55	15	7	53	53	13	3	57	58	13	9	18	18	24	H=	12,	K=	0
-5	41	41	16	H=	-7,	K=	-3	-6	122	125	22	9	38	38	14	5	44	45	13	H=	9,	K=	3	0	70	70	17
-3	50	50	15	-10	34	34	18	-2	230	229	37	11	27	25	18	7	53	53	14	0	12	11	20	4	30	30	18
-1	35	36	14	-6	82	82	17	H=	-3,	K=	-2	H=	4,	K=	2	9	37	36	16	2	86	86	18	H=	12,	K=	1
H=	-10,	K=	-2	-4	14	13	17	-13	13	13	37	0	227	223	36	11	14	14	32	4	10	10	28	1	39	39	16
-8	32	31	18	-2	127	129	23	-11	27	27	18	2	39	38	9	H=	7,	K=	1	6	60	60	16	3	26	26	18
-4	73	73	17	H=	-7,	K=	-2	-9	39	39	14	4	176	180	30	0	29	29	11	10	26	24	21	5	19	18	22
H=	-10,	K=	-1	-11	15	15	29	-7	54	55	13	6	13	13	17	2	139	142	24	H=	9,	K=	4	H=	12,	K=	2
-9	21	20	23	-9	30	31	17	-5	114	113	20	8	82	82	17	4	21	21	13	1	61	61	15	0	51	50	16
-7	28	28	18	-7	46	47	14	-3	164	161	27	12	30	30	20	6	89	89	18	3	37	38	14	4	43	42	16
-5	30	32	16	-5	56	55	14	-1	144	138	24	H=	4,	K=	3	10	38	37	16	5	36	36	15	H=	12,	K=	3
-3	40	41	15	-3	65	65	14	H=	-3,	K=	-1	1	162	163	27	H=	7,	K=	2	7	33	33	17	1	23	23	20
-1	55	56	15	-1	96	97	18	-10	57	56	15	3	92	92	17	1	99	100	18	9	20	20	23	3	36	36	17
H=	-9,	K=	-9	H=	-7,	K=	-1	-8	11	11	22	5	64	63	14	3	68	68	14	H=	9,	K=	5	5	29	29	19
-2	42	41	17	-10	37	37	17	-6	144	148	25	7	65	65	15	5	52	52	13	2	76	76	17	H=	12,	K=	4
H=	-9,	K=	-8	-6	90	89	18	-4	41	41	10	9	42	42	14	7	46	46	14	4	10	8	27	0	36	35	17
-5	26	26	19	-4	21	21	14	-2	276	274	43	11	19	20	23	9	32	32	16	6	48	48	16	4	47	46	17
-3	28	27	18	-2	138	141	24	H=	-2,	K=	-2	H=	4,	K=	4	11	14	15	33	H=	9,	K=	6	H=	12,	K=	5
-1	33	34	17	H=	-6,	K=	-6	-12	35	34	17	0	222	229	36	H=	7,	K=	3	1	53	53	15	1	27	28	20
H=	-9,	K=	-7	-8	34	33	16	-8	89	90	18	4	123	125	22	0	18	17	14	3	31	30	16	3	22	22	22
-6	39	38	17	-4	121	123	23	-4	226	229	37	8	82	82	17	2	125	126	22	5	23	22	18	H=	12,	K=	6
-2	59	59	16	H=	-6,	K=	-5	H=	-2,	K=	-1	12	26	24	19	4	14	13	18	7	28	27	18	0	39	39	18
H=	-9,	K=	-6	-11	14	15	34	-13	13	13	33	H=	5,	K=	0	6	83	83	17	H=	9,	K=	7	2	12	10	33
-7	27	26	19	-9	21	21	21	-11	23	23	18	1	133	134	23	10	34	34	17	2	60	60	16	H=	13,	K=	0
-5	21	21	20	-7	39	39	14	-9	46	46	14	3	89	87	16	H=	7,	K=	4	4	10	3	29	1	32	32	18
-3	32	31	16	-5	61	62	15	-7	80	80	16	5	79	78	16	1	63	63	14	6	38	37	17	3	17	17	27
-1	54	54	15	-3	71	71	15	-5	97	95	17	7	60	63	14	3	73	73	15	H=	9,	K=	8	H=	13,	K=	1
H=	-9,	K=	-5	-1	70	70	15	-3	129	122	22	9	36	36	14	5	61	62	15	1	37	37	16	2	40	38	17
-6	45	45	16	H=	-6,	K=	-4	-1	201	192	32	11	20	19	21	7	37	36	14	3	29	29	18	H=	13,	K=	2
-2	79	80	17	-10	11	6	30	H=	-1,	K=	-1	H=	5,	K=	1	9	18	19	23	5	24	23	20	1	28	28	19
H=	-9,	K=	-4	-8	61	60	16	-10	62	62	15	0	53	51	11	11	16	15	30	H=	9,	K=	9	3	21	20	23
-9	21	21	24	-6	20	19	16	-6	157	161	27	2	198	201	33	H=	7,	K=	5	2	44	43	16	H=	13,	K=	3
-7	32	33	17	-4	111	113	21	-2	354	355	50	4	32	31	11	0	11	10	21	H=	10,	K=	0	2	37	37	18
-5	33	33	15	-2	37	36	11	H=	0,	K=	0	6	110	112	20	2	104	105	20	0	81	82	17	H=	13,	K=	4
-3	40	40	14	H=	-6,	K=	-3	4	90	85	16	8	12	11	24	4	9	8	27	2	23	23	15	1	21	21	24

can be seen from the values of the angles O(*u*)–X–O(*u*) and O(*u*)–X–O(*l*) (Table 4), where O(*u*) is the upper oxygen of a given tetrahedral group, and O(*l*) the lower one as viewed along the *c* axis. This may be caused by a pull exerted by the hydrogen bonds which are positioned in the (001) plane between the different tetrahedra. The hydrogen bonds connect the tetrahedra in such a way as to form a three-dimensional network (Fig. 1), which is topologically equivalent to the cristobalite framework. The P correspond to Si, and the hydrogen bonds to the oxygen atoms in cristobalite (Wells, 1970). The NH_4^+ cations (or the alkali ions in the isomorphous alkali compounds) provide additional binding but are not part of the cristobalite-type framework. The size of the ion substituting for NH_4^+ in the alkali isomorph of this structure type is linearly related to the *c*/*a* values (Fig. 2). It can be seen that the changes in the *a* cell constant are smaller than the changes in the *c* cell constant (Table 6). This can be understood because the O–H···O bonds are lying essentially in the *ab* plane. The role of these O–H···O bonds is also reflected in the thermal-expansion behavior of the alkali atom isomorph of KDP. The coefficient of thermal expansion $\bar{\alpha}_a$ along the *a* axis in these crystals is always smaller than the coefficient of expansion $\bar{\alpha}_c$ along the *c* axis (Table 6).

Table 4. *Interatomic distances and angles in* $NH_4H_2PO_4$, *ADP, and* $NH_4H_2AsO_4$, *ADA*

O(*u*) and O(*l*) represent respectively the upper and lower oxygen atoms of a given tetrahedral group as viewed along the *c* axis. O(*f*) and O(*s*) represent, respectively, the oxygen atoms of the flat and steep disphenoids around the N atom.

		ADP	ADA
4 ×	X—O(X = P or As)	1·537 (1) Å	1·682 (1) Å
4 ×	O(*u*)–X–O(*u*)	111·17 (4)°	111·08 (7)°
2 ×	O(*u*)–X–O(*l*)	108·63 (4)	108·67 (6)
2 ×	O(*u*)–O(*u*)	2·536 (1) Å	2·774 (2) Å
4 ×	O(*u*)–O(*l*)	2·497 (1)	2·733 (2)
	O—H···O	2·490 (1)	2·512 (2)
4 ×	N—H···O(*f*)	2·909 (1)	2·889 (1)
4 ×	N—H···O(*s*)	3·170 (1)	3·220 (2)
4 ×	O(*f*)–N···O(*f*)	97·04 (2)°	96·58 (4)°
2 ×	O(*f*)–N···O(*f*)	139·01 (2)	140·42 (5)
2 ×	O(*s*)–N···O(*s*)	47·16 (2)	50·92 (4)
4 ×	O(*s*)–N···O(*s*)	147·14 (2)	144·60 (4)

Table 5. *R.m.s. thermal displacements along principal axes and their orientations relative to the crystallographic axes*

	Axis	Displacement	[100]	[010]	[001]
$NH_4H_2PO_4$, ADP					
P	1	0·126 (1) Å	0°	90°	90°
	2	0·126	90	0	90
	3	0·156 (1)	90	90	0
N	1	0·156 (3)	90	90	0
	2	0·177 (2)	0	90	90
	3	0·177	90	0	90
O	1	0·130 (1)	86 (7)	33 (3)	57 (2)
	2	0·138 (1)	161 (2)	77 (7)	103 (4)
	3	0·208 (1)	108 (1)	120 (1)	36 (1)
$NH_4H_2AsO_4$, ADA					
As	1	0·131 (1) Å	0°	90°	90°
	2	0·131	90	0	90
	3	0·164 (1)	90	90	0
N	1	0·164 (3)	90	90	0
	2	0·183 (2)	0	90	90
	3	0·183	90	0	90
O	1	0·135 (2)	106 (7)	29 (2)	67 (3)
	2	0·143 (2)	155 (5)	97 (7)	114 (3)
	3	0·235 (2)	108 (1)	108 (1)	34 (1)

The O–H···O bonds are shorter in ADP than in ADA. The difference is about ten times the combined errors in the two values. The inherent limitations of the X-ray method did not warrant a refinement of the hydrogen atoms in the 16-fold general position and therefore it was refined in the eightfold position located on a twofold axis. Of course there can be no doubt that atom H(*o*) in the O–H···O bond is best described as disordered with one half of each of it residing in a general position on both sides of the eightfold special position. This is obvious from the neutron diffraction results of Tenzer *et al.* (1958) on room-temperature ADP, and of Bacon & Pease (1955) on room-temperature KDP, who both preferred the half-proton disordered model over a model in which the protons vibrate anisotropically parallel to the O–H–O vector. The actual situation must be even more complicated, as is discussed in the following paper (Baur, 1973).

Every NH_4^+ ion in the structure is coordinated by eight oxygen atoms forming two interpenetrating tetragonal disphenoids. One of the disphenoids is flat and the other steep with respect to the *c* axis. The N–O(*f*) lengths are shorter by about 0·30 Å than the N–O(*s*) lengths where O(*f*) and O(*s*) refer to the oxygen atoms of the flat and steep disphenoids respectively (Table 4). In KDP, however, the corresponding bond lengths from K^+ to the two sets of oxygen atoms have values which are much closer: 2·819 Å in the flat disphenoid, 2·888 Å in the steep disphenoid (Bacon & Pease, 1953). This comparison shows very clearly that in ADP (and ADA) there is a tendency for the NH_4^+ groups to engage in four hydrogen bonds within the flat disphenoid. Neutron-diffraction work on ADP by Tenzer *et al.* (1958) provides a direct evidence of the N–H···O(*f*) bonds. This is a specific example of the tendency of the NH_4^+ ions towards displaying smaller coordination numbers than the corresponding alkali compounds (Khan & Baur, 1972). The effect of these N–H···O bonds is reflected in the cell parameters and in the thermal expansion behavior of ADP and ADA. The *c*/*a* values for the two compounds are too large to lie on the straight line connecting the alkali isomorphs in Fig. 2. Unlike the alkali compounds the two ammonium compounds expand with temperature mainly in the *ab* plane. The $\bar{\alpha}_a$ values are about 20 times as large as the $\bar{\alpha}_c$ values (Table 6). As pointed out by Deshpande & Khan (1963), the N–H···O bonds which have a larger component in the *ab* plane tend to enforce the binding in this plane, so that the bonding in the **c** direction will be relatively weaker. This situation appears, therefore, to be responsible for the higher *c*/*a* values of ADP and ADA. With the increase in temperature, the initial structural constraints introduced by the presence of the N–H···O bonds are likely to decrease and the cristobalite framework of the hydrogen bonded XO_4 groups will tend to assume a structure more similar to that for the alkali isomorphs with smaller *c*/*a* values. This is accomplished by a relatively small expansion along the *c* axis and a much larger expansion in the *ab* plane as the temperature is increased. As *c*/*a* is lowered the coordination number of the ammonium ion tends towards eight, as in the alkali dihydrogen phosphates and arsenates. This is analogous to the increasing coordination numbers of NH_4^+ with rising temperature in the transition of $(NH_4)_2SO_4$ (Schlemper & Hamilton, 1966; Khan & Baur, 1972) and is an indication of the increasing alkali ion character of NH_4^+ with increasing temperature.

The average volume expansion coefficient, $\bar{\alpha}_v$, is influenced by the N–H···O bonds since the $\bar{\alpha}_v$ values for ADP and ADA are smaller than for the alkali iso-

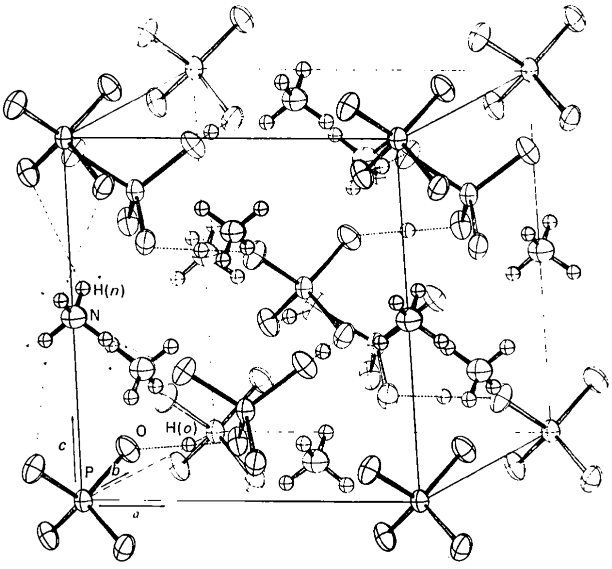

Fig. 1. A perspective view of the unit cell of $NH_4H_2PO_4$, ADP. Atoms are drawn at their 50% probability level with hydrogen atoms H(*n*) and H(*o*) included with a small arbitrary value of the isotropic temperature factor equal to 0·1 Å^2.

Table 6. *Lattice parameters at room temperature* (22°C) *and average linear and volume expansion coefficients* ($\bar{\alpha}_a$, $\bar{\alpha}_c$ and $\bar{\alpha}_v$) *for KDP-type crystals*

Crystal	*a*(Å)	*c*(Å)	$\bar{\alpha}_a$(× 10^6 °C^{-1})	$\bar{\alpha}_c$(× 10^6 °C^{-1})	α_v(× 10^6 °C^{-1})	Reference
ADP	7·4997 (4)	7·5494 (12)	39·3	1·9	80·5	Deshpande & Khan (1963)
ADA	7·6998 (5)	7·7158 (12)	22·3	1·0	45·6	Deshpande & Khan (1965*b*)
KDP	7·4520 (4)	6·9670 (4)	26·9	46·6	100·4	Sirdeshmukh & Deshpande (1967)
KDA	7·6290 (4)	7·1612 (9)	24·9	50·1	99·9	Deshpande & Khan (1965*a*)
RDP	7·6057 (9)	7·2998 (14)	27·8	52·0	107·6	Deshpande & Khan (1966)
RDA	7·7950 (7)	7·4732 (11)	20·8	46·9	88·5	Deshpande, Khan & Pardikar (1968)
CDA*	7·98 (1)	7·87 (2)				Ferrari, Nardelli & Cingi (1956)

* Room temperature not known.

morphs (Table 6). Among the two ammonium salts, the average expansion coefficient for ADA is significantly smaller than for ADP. The difference between the $\bar{\alpha}_v$ values measured by Deshpande & Khan (1963, 1965*b*) has also been confirmed in an independent study by Haussühl (1964).

The N–H···O bonds are shorter in ADA than in ADP by 0·020 Å, which is a highly significant difference. This difference is the only structural feature which can be correlated with the difference in the thermal expansion behavior of ADP and ADA. It probably is safe to assume that during the thermal expansion of the structure the PO_4^{3-}/AsO_4^{3-} and NH_4^+ groups will change their individual size and shape much less than their relative positions. In other words the thermal-expansion behavior will be governed mostly by the strengths of the hydrogen bonds connecting one group to another. Since O–H···O bonds in ADA are longer (weaker) than in ADP the smaller value of the volume expansion coefficient of ADA can only be attributed to the shorter (stronger) N–H···O bonds in this structure. The O–H···O bonds are longer by 0·022 Å and the N–H···O bonds are shorter by 0·020 Å in ADA, but there are twice as many N–H···O bonds as O–H···O bonds in the structure and therefore their effect may be reflected in the smaller volume-expansion coefficient.

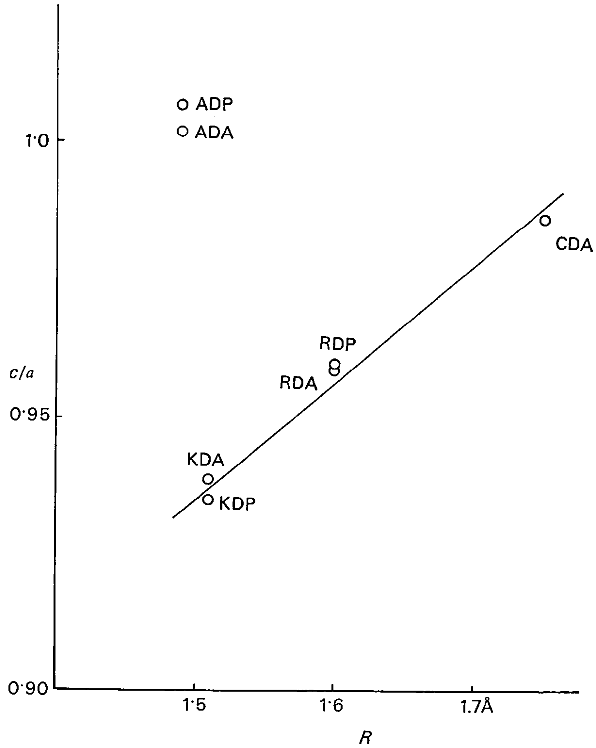

Fig. 2. The *c/a* ratios *vs.* ionic radii of K^+, Rb^+, Cs^+ and NH_4^+ cations in KDP-type structures. Ionic radii for the alkali atoms in eightfold coordination are from Shannon & Prewitt (1969) and for NH_4^+ ions in fourfold coordination from Khan & Baur (1972).

The differences in the lengths of the O–H···O and N–H···O bonds in the two isomorphous crystal structures can be interpreted by considering the electrostatic charge balance. The oxygen atoms which are coordinating one X^{5+} ion in the two XO_4^{3-} groups are also the acceptors of N–H···O bonds and serve as donors as well as acceptors in the O–H···O bonds. Pauling (1929) introduced the concept of the electrostatic bond strength defined as the valence of a cation divided by its coordination number. According to Pauling the sum of the bond strengths around the anions is approximately equal to their valence (with opposite sign). Recently Brown & Shannon (1973) have derived bond-strength *versus* bond-length relationships for bonds between oxygen and various cations in many crystal structures by requiring that the sums of the bond strengths around the ions be equal to their valence. The bond strengths of a P–O bond in ADP and of an As–O bond in ADA are found to be almost identical (≃ 1·24 v.u.) when calculated from the equation and the proper empirical constants given by Brown & Shannon (1973). The total electrostatic balance at the oxygen atoms is then achieved through the hydrogen bonds, which means that the sum of the bond strengths provided by the N–H···O and O–H···O bonds must be constant in ADP and ADA. Since the N–H···O bond length is longer in ADP than in ADA, the O–H···O bond length is accordingly shorter in ADP than in ADA, thus maintaining the balance of bond strengths at the oxygen atom.

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References

Bacon, G. E. & Pease, R. S. (1953). *Proc. Roy. Soc.* A**220**, 397–421.

Bacon, G. E. & Pease, R. S. (1955). *Proc. Roy. Soc.* A**230**, 359–381.

Baur, W. H. (1973). *Acta Cryst.* B**29**, 2726–2731.

Baur, W. H. & Khan, A. A. (1970). *Acta Cryst.* B**26**, 1584–1597.

Brown, I. D. & Shannon, R. D. (1973). *Acta Cryst.* A**29**, 266–282.

Cromer, D. T. (1965). *Acta Cryst.* **18**, 17–23.

Deshpande, V. T. & Khan, A. A. (1963). *Acta Cryst.* **16**, 936–938.

Deshpande, V. T. & Khan, A. A. (1965*a*). *Acta Cryst.* **18**, 977–978.

Deshpande, V. T. & Khan, A. A. (1965*b*). *Curr. Sci.* **34**, 633–634.

Deshpande, V. T. & Khan, A. A. (1966). *Nature, Lond.* **209**, 608.

Deshpande, V. T., Khan, A. A. & Pardikar, P. G. (1968). *Ind. J. Pure Appl. Phys.* **6**, 97–98.

Ferrari, A., Nardelli, M. & Cingi, M. (1956). *Gazz. Chim. Ital.* **86**, 1174–1180.

Groth, P. (1908). *Chemische Krystallographie*, Vol. II, pp. 796–797. Leipzig: Wilhelm Engelmann.

Haussühl, S. (1964). *Z. Kristallogr.* **120**, 401–414.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
International Tables for X-ray Crystallography (1965). Vol. I. Birmingham: Kynoch Press.
JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
KHAN, A. A. (1966). Ph.D. thesis, Osmania Univ.
KHAN, A. A. & BAUR, W. H. (1972). *Acta Cryst.* B**28**, 683–693.
PAULING, L. (1929). *J. Amer. Chem. Soc.* **51**, 1010–1026.
PRYCE, M. W. (1972). *Miner. Mag.* **38**, 965–967.
SCHLEMPER, E. O. & HAMILTON, W. C. (1966). *J. Chem. Phys.* **44**, 4498–4509.
SHANNON, R. D. & PREWITT, C. T. (1969). *Acta Cryst.* B**25**, 925–946.
SIRDESHMUKH, D. B. & DESHPANDE, V. T. (1967). *Acta Cryst.* **22**, 438–439.
TENZER, L., FRAZER, B. C. & PEPINSKY, R. (1958). *Acta Cryst.* **11**, 505–509.
WELLS, A. F. (1970). *Models in Structural Inorganic Chemistry*, p. 19. Oxford Univ. Press.
WEST, J. (1930). *Z. Kristallogr.* **74**, 306–332.

Acta Cryst. (1973). B**29**, 2726

Reconstruction of Local Atomic Environments in the Disordered Hydrogen-Bonded Crystal Structures of Paraelectric Ammonium Dihydrogen Phosphate and Potassium Dihydrogen Phosphate

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In crystal structures in which one equivalent position is randomly occupied by different atomic species of different sizes the adjoining atoms must exhibit positional disorder. A special case is the statistical presence or absence of hydrogen atoms as observed in $NH_4H_2PO_4$ (ADP) and KH_2PO_4 (KDP), where the bond lengths in the phosphate group will vary locally depending on whether it is a P–O or a P–O–H [P–O(*h*)] bond. The ideal shape of an individual $PO_2(OH)_2$ group is predicted on the basis of the extended electrostatic valence rule and the O–P–O on P–O dependence in orthophosphate groups: P–O 1·501 Å, P–O(*h*) 1·573 Å, O(*h*)–P–O(*h*) 105·8°, O(*h*)–P–O 109·2° and O–P–O 113·9°. This calculated $PO_2(OH)_2$ group is fitted into unit cells of the same dimensions but lower symmetry than those of the paraelectric $I\bar{4}2d$ structures of ADP and KDP. These hypothetical local environments in C_{2v}^{19} (*I*-centered) and $P2_12_12_1$ are compatible with the observed averaged structure deduced from X-ray diffraction data for ADP. The hydrogen-atom positions as calculated for the least electrostatic energy in the local environments agree with their positions as determined from neutron-diffraction data. The local environments display interatomic distances which differ from the distances in the averaged structure individually as well as in their average values. Therefore, the bond lengths derived from the refinement of averaged disordered structures should be viewed with extreme caution. The distance between the averaged atomic positions can be different from the average of the individual distances. The situation resembles the case of the effects which thermal motion has on the estimation of bond distances. In these instances a valid correction is only possible if we have information on the nature of the thermal motion or on the type of disorder in the crystal structure. Such information is generally not available.

Introduction

In many crystal structures, and particularly in those of minerals, disorder is present. It can be evident in the random occupation of one equipoint by several atomic kinds. An example is the partial substitution of Al for Si in tetrahedral coordination in feldspars. Because the bond lengths Si–O, 1·61 Å, and Al–O, 1·75 Å (Smith & Bailey, 1963) differ by 0·14 Å the positions of the oxygen atoms must be affected by this substitution. At a given tetrahedral site occupied by Al the oxygen atoms will have a larger distance to the central cation than at a location where Si is the central atom. If the distribution of the Al and Si atoms is disordered then the X-ray data refinement will yield an averaged structure. The atomic positions of the averaged structure are the centroids of the atomic distributions in many asymmetric units. Therefore, the coordinates of the *averaged* positions are coordinates of *apparent* sites which most likely are not occupied in any single unit cell of the structure. In the averaged structure the atomic positions in the different unit cells superpose and cause a smearing out of the observed electron densities, which usually is not distinguishable from the effects of anisotropic thermal motion of the atoms. The thermal ellipsoid contains then the effects of both thermal motion and positional disorder. In any given asymmetric unit the local environment around an Al atom will be different from the environment in the averaged structure and from the local environment