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Hydrogen Bond Studies

52.* Neutron Diffraction Study of Hydrazinium Bis(dihydrogen phosphate), $N_2H_6(H_2PO_4)_2$

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The crystal structure of hydrazinium bis(dihydrogen phosphate), $N_2H_6(H_2PO_4)_2$, has been refined from three-dimensional neutron diffraction data. A correction for extinction effects was included in the least-squares refinement. The positional parameters of the heavy atoms are in good agreement with those obtained by Liminga in a previous X-ray investigation. The structure is composed of $H_2PO_4^-$ and $N_2H_6^{2+}$ ions. The $H_2PO_4^-$ ions are linked by O–H···O bonds to form layers. The $N_2H_6^{2+}$ ions create a three-dimensional network by forming N–H···O bonds with these layers.

The crystal structures of $N_2H_5H_2PO_4$ and $N_2H_6(H_2PO_4)_2$ have been determined by Liminga.[1,2] The X-ray diffraction method used in these structure determinations could only give the approximate positions of the hydrogen atoms and thus did not reveal the details of the hydrogen bonding arrangement. Neutron diffraction has now been used to obtain accurate hydrogen positions in the above cases. The result of the neutron diffraction study of $N_2H_5H_2PO_4$ has been reported recently.[3] This paper reports on the results of the corresponding study of $N_2H_6(H_2PO_4)_2$.

CRYSTAL DATA

Hydrazinium bis(dihydrogen phosphate), $N_2H_6(H_2PO_4)_2$. F.W. 228.04. Monoclinic; $a = 4.4831(4)$,** $b = 8.0389(6)$, $c = 10.7014(8)$ Å, $\beta = 99.678(8)°$. $V = 380.18$ Å^3 at 25°C.[2] $D_m = 1.94$ g cm^{-3},[2] $Z = 2$, $D_x = 1.992$ g cm^{-3}. Space group $P2_1/c$.

Calculated neutron absorption coefficient: 1.82 cm^{-1}.

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** Numbers in parentheses here and throughout this paper are the estimated standard deviations in the least significant digits.

EXPERIMENTAL

Hydrazinium bis(dihydrogen phosphate) was prepared from hydrazine hydrate and phosphoric acid as described earlier.[2] Large single crystals were grown from an aqueous solution. A crystal, having a volume of 124 mm^3 and mounted with the a^* axis parallel to the phi axis, was used for data collection on the computer controlled Hilger & Watts four-circle diffractometer at the Swedish Atomic Energy Company R2 reactor at Studsvik. Using a neutron wavelength of 1.097 Å a portion of reciprocal space extending out to sin $\theta/\lambda = 0.75$ Å^{-1} was examined. The experimental method was as used for $N_2H_5H_2PO_4$,[3] differing only in the following details.

The crystal shape was described by six rational crystal boundary planes in the calculation of the absorption correction. The resulting transmission factors were in the range 0.39 – 0.52. The linear absorption coefficient of 1.82 cm^{-1} was calculated using a value of 34 barns for the incoherent scattering cross-section for hydrogen.

The measured intensities were corrected for small systematic variations in the intensities of the two standard reflections. The source of these variations could later be traced to long-term drift in the monitor counting chain.

The space group absent reflections were excluded from the data and the values of F^2 for the few reflections measured more than once were averaged. The total number of independent * reflections thus obtained was 1468 of which 1109 had F^2 values larger than twice their standard deviations.

LOCATION OF HYDROGEN ATOMS AND REFINEMENT

A three-dimensional difference map for which the calculated structure factors were based on the heavy atom positions from the X-ray study [2] revealed the positions of the hydrogen atoms. The structure was refined using the full-matrix least-squares program LINUS.[4] The function minimized was $\sum w(|F_o^2| - |F_c^2|)^2$. The 1109 reflections with $F^2 > 2\sigma_c(F^2)$ were given weights according to the formula $1/w = \sigma_c^2(F^2) + (kF^2)^2$ with the $k = 0.05$ and $\sigma_c(F^2)$ based on counting statistics. The parameters refined were 33 positional parameters, 66 anisotropic thermal parameters, an overall scale factor, and one isotropic extinction parameter. In the last cycle of the refinement all parameters shifted by less than 0.01 σ; the final agreement factors for the 1109 observed reflections were

$$R = \frac{\sum| |F_o^2| - |F_c^2| |}{\sum|F_o^2|} = 0.071$$

$$R_w = \left\{\frac{\sum w(|F_o^2| - |F_c^2|)^2}{\sum w|F_o^4|}\right\}^{1/2} = 0.095$$

The corresponding conventional R-factor based on F was 0.049. The standard deviation of an observation of unit weight, $S = [\sum w(|F_o^2| - |F_c^2|)^2/(m-n)]^{1/2}$ was 1.07. In this expression w is the weight of an observation, m is the number of observations and n the number of refined parameters.

The final positional and thermal parameters are presented in Table 1; the root-mean-square displacements along principal axes of thermal ellipsoids are given in Table 2. The refined value of the isotropic extinction parameter is $g = 7943(345)$. This value corresponds to a mosaic spread parameter of approx-

* $0kl$ and $0k\bar{l}$ reflections were treated as independent reflections since the value of $\bar{T}$, later used in calculating an extinction correction, differs for these symmetry-related reflections.

Table 1. Final positional and thermal parameters for $N_2H_6(H_2PO_4)_2$. The positional parameters are given as fractional coordinates $\times 10^5$. The anisotropic thermal parameters ($\times 10^5$) are defined as $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$. The second line given each heavy atom parameter compares the neutron results with the X-ray results of Liminga.[2] The value given first is Δ (defined as the X-ray parameter minus the neutron parameters) followed by $|\Delta|/\sigma$ where σ is the combined standard deviation (see text).

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
P	280(37)	16517(19)	17481(14)	1057 (61)	486(18)	250(10)	−15(28)	175(19)	42(11)
	−44 1.1	−38 1.8	6 0.4	1073 10.6	139 5.1	100 7.1	16 0.5	117 4.3	−7 0.4
O(1)	7285(41)	30999(21)	9601(15)	2264 (76)	696(21)	373(11)	138(31)	415(22)	220(12)
	−189 2.5	−8 0.2	−31 1.0	1058 5.7	214 4.7	165 5.2	54 0.6	95 1.5	−29 0.9
O(2)	−9985(45)	22793(20)	29997(15)	3170 (84)	548(20)	316(11)	−36(33)	519(22)	13(11)
	−194 2.4	−36 1.0	−17 0.6	960 5.1	238 5.3	149 6.6	−96 1.1	69 1.1	−49 1.5
O(3)	−27075(41)	6801(29)	9931(17)	1307 (69)	1403(33)	454(13)	−423(39)	144(22)	−257(16)
	136 1.8	−91 1.9	20 0.6	1513 8.3	158 2.6	152 4.6	120 1.2	162 2.5	−22 0.5
O(4)	26194(35)	4436(19)	21433(15)	1232 (62)	559(19)	396(11)	86(27)	153(20)	107(11)
	−69 1.0	−9 0.2	−58 2.1	1455 9.0	204 4.6	130 5.7	−26 0.3	155 2.5	−18 0.5
N	49778(23)	8209(13)	47357 (9)	1635 (44)	727(13)	327 (7)	22(19)	229(12)	−59(7)
	−93 1.2	−38 1.0	−38 1.3	1537 7.9	149 2.9	151 4.9	23 0.3	183 2.6	19 0.5
H(1)	−15353(83)	34903(38)	29932(29)	3750(166)	771(38)	553(22)	−26(65)	561(48)	−15(23)
H(2)	−45176(73)	5363(45)	14077(34)	2041(135)	1091(47)	756(28)	−272(62)	311(46)	0(28)
H(3)	43084(94)	7327(50)	37525(30)	4190(193)	1356(54)	447(22)	238(84)	252(50)	52(26)
H(4)	33419(86)	15088(45)	51406(34)	3051(150)	1022(44)	705(27)	479(69)	365(48)	−168(28)
H(5)	71388(91)	13384(49)	49811(39)	3145(174)	1139(47)	906(34)	−539(75)	628(60)	−68(33)

imately 7 sec or a domain size of 0.9 μm depending upon whether a Zachariasen [5] Type I or Type II description is chosen. The observed and calculated structure factors are presented in Table 3 together with the calculated extinction corrections defined as

$$E=\left[1+\frac{2\bar{T}|F_c^2|g\lambda^3}{V^2\sin 2\theta}\right]^{-1/2}$$

Table 2. Root-mean-square amplitudes of vibration (in units of 10^{-3} Å).

Atom	Axis 1	Axis 2	Axis 3
P	94(3)	118(3)	131(2)
O(1)	102(3)	142(3)	183(2)
O(2)	111(3)	134(2)	184(2)
O(3)	106(3)	148(2)	227(3)
O(4)	109(3)	124(2)	159(2)
N	117(2)	138(2)	158(1)
H(1)	156(4)	159(4)	203(4)
H(2)	134(5)	193(4)	207(4)
H(3)	158(4)	197(5)	218(5)
H(4)	139(5)	193(4)	214(4)
H(5)	148(5)	201(4)	234(4)

Table 3. Observed and calculated neutron structure factors for $N_2H_6(H_2PO_4)_2$. The five columns are, in order, the indices k and l, $100|F_o|$, $100\,|F_c|$ (in units of 10^{-12} cm) and $100\,E$. The entry for the extinction correction, E, is not included for $E > 0.99$. The values of F_o have been divided by $E^{1/2}$. A negative value for F_o indicates an unobserved reflection which was not included in the least-squares refinement.

where $|F_c^2|$ is on an absolute scale, λ is in Å, and the cell volume V is in Å^3. The mean path length through the crystal for the reflection concerned is given by $\overline{T}$, calculated using the expression $\overline{T} \sim -\ln(A^*)/\mu$, where A^* is the transmission factor and μ the linear absorption coefficient in cm^{-1}. The observed $|F_o|$ values in Table 3 are corrected for extinction: $|F_o|_{corr} = |F_o|/E^{1/2}$

The neutron scattering lengths used were in units of 10^{-12} cm: $\overline{b_P} = 0.51$, $\overline{b_O} = 0.577$, $b_N = 0.94$, $\overline{b_H} = -0.372$. The calculations were carried out on the CDC 3600 computer in Uppsala using the programs described briefly by Jönsson and Liminga.[3]

COMPARISON OF NEUTRON AND X-RAY PARAMETERS

A comparison of the positional and thermal parameters of the heavy atoms with the X-ray results of Liminga [2] is included in Table 1. The table gives the difference Δ (defined as X-ray parameter minus neutron parameter) followed by $|\Delta|/\sigma$, where σ is the combined standard deviation defined as

$$\sigma = (\sigma^2_{X-ray} + \sigma^2_{neutron})^{1/2}$$

Table 4. Covalent bond lengths and angles.

A. Bond lengths (Å). Distances given within brackets are corrected for thermal riding motion

	Neutron		X-ray [2]
P–O(1)	1.501(2)	[1.510]	1.504(3)
P–O(2)	1.571(2)	[1.579]	1.572(3)
P–O(3)	1.560(2)	[1.574]	1.556(3)
P–O(4)	1.519(2)	[1.523]	1.515(3)
O(2)–H(1)	1.003(3)	[1.012]	
O(3)–H(2)	0.995(4)	[0.998]	
N–N	1.435(2)		1.432(6)
N–H(3)	1.047(3)	[1.069]	
N–H(4)	1.067(3)	[1.086]	
N–H(5)	1.046(4)	[1.070]	

B. Angles (degrees)

O(1)–P–O(2)	110.4(1)	110.4(1)
O(1)–P–O(3)	108.5(1)	108.4(2)
O(1)–P–O(4)	115.5(1)	115.5(2)
O(2)–P–O(3)	106.6(1)	106.5(2)
O(2)–P–O(4)	106.7(1)	107.2(1)
O(3)–P–O(4)	108.8(1)	108.5(2)
P–O(2)–H(1)	114.2(2)	
P–O(3)–H(2)	117.2(3)	
N–N–H(3)	108.5(3)	
N–N–H(4)	106.4(2)	
N–N–H(5)	108.4(2)	
H(3)–N–H(4)	110.1(3)	
H(3)–N–H(5)	112.1(3)	
H(4)–N–H(5)	111.3(3)	

The agreement between the positional parameters is satisfactory; no error is greater than 2.5 times the combined standard deviation. Bond lengths and angles are compared in Table 4.

The hydrogen positions found in the X-ray study [2] by combining information from the difference Fourier synthesis with chemical evidence differ from the coordinates found in the neutron diffraction study by 0.04 – 0.16 Å.

The agreement between the X-ray and neutron obtained thermal parameters is less satisfactory than the agreement between positional parameters. This is partly due to systematic errors in the X-ray data since no experimental scaling was performed. The X-ray data were collected on a Weissenberg camera with the crystal rotating around the *a* axis. It is therefore probably no coincidence that the largest discrepancies occur for the β_{11} values. It should also be pointed out, however, that the usual assumption of a spherical electron distribution affects the thermal parameters determined using X-rays.[6,7]

DISCUSSION OF THE STRUCTURE

The structure is illustrated in Figs. 1 – 3 and also in a more detailed stereoscopic view by Liminga (Fig. 9 in Ref. 8). The structure consists of $N_2H_6^{2+}$ and $H_2PO_4^-$ ions. The $H_2PO_4^-$ ions are linked together by O – H···O hydrogen bonds to form infinite layers parallel to the *ab*-plane. The phosphate layers are cross-linked *via* $N_2H_6^{2+}$ ions by N – H···O hydrogen bonds, thus forming a three-dimensional network. The distances quoted in the text are not corrected for thermal motion.

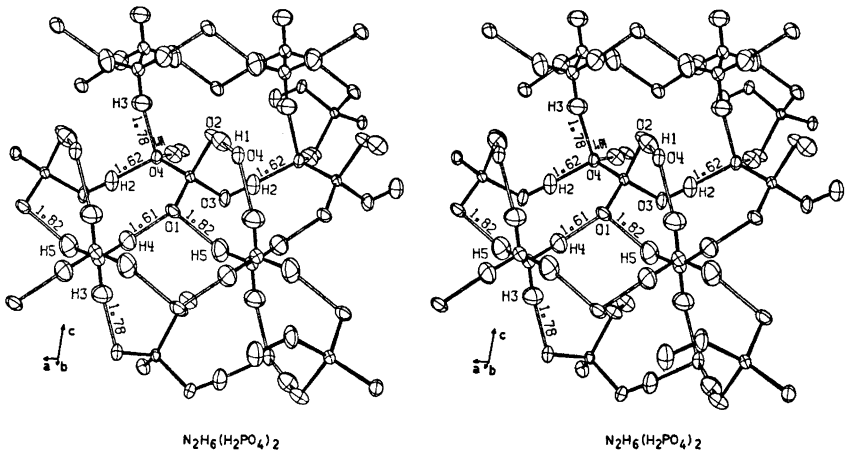

Fig. 1. A stereoscopic pair of figures showing part of the structure. Covalent bonds are filled and H···O and H···N contacts which take part in hydrogen bonds are open. The ellipsoids are scaled to 50 % probability. The orientation is similar to that of Fig. 9 in Ref. 8.

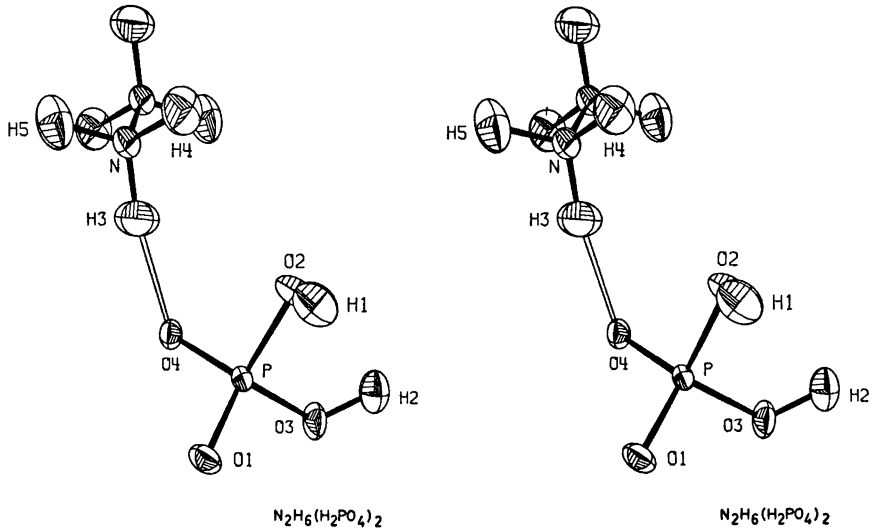

Fig. 2. A stereoscopic illustration of an asymmetric unit of $N_2H_6(H_2PO_4)_2$. The ellipsoids are scaled to 50 % probability.

The phosphate layers

The geometry of the $H_2PO_4^-$ ion (*cf.* Table 4) agrees very well with the X-ray values and confirms the assignment of the hydrogen atoms by Liminga.[2] The O–H distances are 1.003(3) and 0.995(4) Å. The P–O and P–OH distances agree well with earlier reported values. A summary of such values has been given by Liminga.[1]

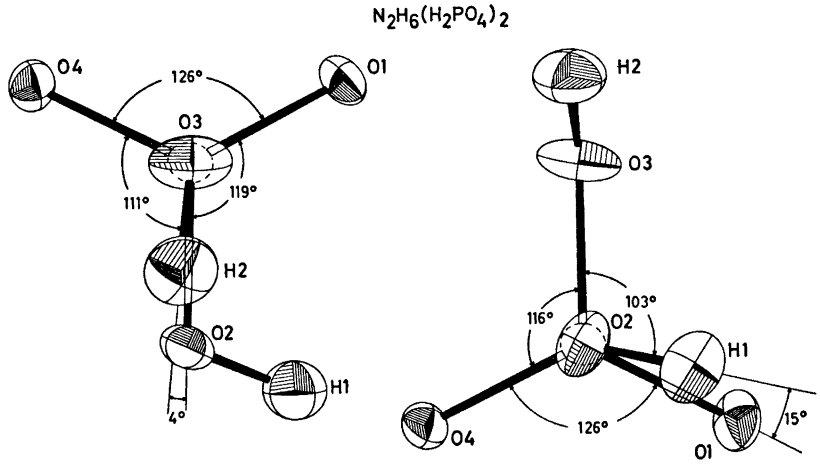

Fig. 3. The $H_2PO_4^-$ ion viewed along the O3–P and O2–P bonds.

The conformation of the phosphate ion is illustrated in Fig. 3. The phosphate ion is viewed along the P–O(2) and the P–O(3) bonds. The two hydrogen atoms occupy very similar positions. H(1) lies close to the plane formed by P–O(1)–O(2); H(2) is even closer to the P–O(2)–O(3) plane. Both hydrogen atoms have one short hydrogen-oxygen distance: H(1) is at a distance of 2.570(4) Å from O(1) and H(2) is as near as 2.540(4) Å to O(2). The other non-bonding hydrogen-oxygen distances within the phosphate ion are all well over 3 Å. The O(2)–H(1)···O(1) angle is 76.0° and the O(3)–H(2)···O(2) angle is 76.9°.

The conformation differs from the situation in $N_2H_5H_2PO_4$.[3]

Hydrogen bonding within the layers. The hydrogen bond system of the phosphate group is illustrated in Fig. 1. The oxygen atoms O(2), O(3), and O(4) but not O(1) participate in hydrogen bonds within the layers. O(2) and O(3) each acts as a donor in one O–H···O bond whereas O(4) acts as an acceptor in two O–H···O bonds and one N–H···O bond. O(1) only participates in N–H···O bonds between the phosphate layers and the hydrazinium (2+) ions. The hydrogen bond lengths are listed in Table 5.

Table 5. Hydrogen bonds and angles (X–H···O) (Å and degrees).

X	H	O	X···O	X–H	H···O	<X–H···O	<H···O–P
O(2)	H(1)	O(4)	2.643(2)	1.003(3)	1.643(3)	174.7(3)	112.7(2)
O(3)	H(2)	O(4)	2.609(2)	0.995(4)	1.616(4)	175.3(4)	117.9(2)
N	H(3)	O(4)	2.814(2)	1.047(3)	1.776(4)	170.7(4)	111.6(2)
N	H(4)	O(1)	2.634(2)	1.067(3)	1.608(4)	159.5(3)	134.3(2)
N	H(5)	O(1)	2.825(2)	1.046(4)	1.823(4)	158.9(4)	105.5(2)

The O–H···O bonds are both almost linear with the angle O(2)–H(1)···O(4) 174.7(3)° and O(3)–H(2)···O(4) 175.3(4)°. The corresponding O–H···O hydrogen bonds in $N_2H_5H_2PO_4$[3] are shorter because of the smaller coordination number of the acceptor oxygens.[2,8] The difference in O···O distances is 0.034(3) Å and the corresponding difference in O···H distance is 0.027(5) Å (Table 5). The interaction with H(2) is somewhat stronger than the interaction with H(1), but this is too small to produce a significant difference in the O–H distances (O(3)–H(2): 0.995(4) Å; O(2)–H(1): 1.003(3) Å).

All short interatomic distances are listed in Table 6. The short O(3)···O(3) distance of 2.910(4) Å between adjacent layers does not represent a hydrogen bond.

The hydrazinium (2+) ion

The hydrazinium(2+) ion which lies on a centre of symmetry has an N–N distance of 1.435(2) Å. This is close to that of the X-ray investigation (1.432(6) Å). An earlier neutron diffraction study of the hydrazinium(2+) ion in $N_2H_6SO_4$ gave a value of 1.426(3) Å.[9]

Table 6. Short intermolecular distances. All intermolecular distances involving hydrogen atoms ≤ 2.9 Å and distances not involving hydrogen atoms ≤ 3.4 Å are listed. Atoms not in the asymmetric unit are accompanied by a subscript. The first three digits in the subscript describe lattice translations; the fourth digit specifies one of the symmetry transformations below.

1. x, y, z
2. $x, 1/2-y, 1/2+z$
3. $-x, -y, -z$
4. $-x, 1/2+y, 1/2-z$

Ex. 6452 means that the coordinates have been transformed by 2 and translated by $(6-5)a+(4-5)b+(5-5)c$.

P···H(2)$_{5454}$	2.632(3)	O(2)···H(5)$_{4551}$	2.522(4)
P···H(5)$_{4542}$	2.653(4)	O(2)···H(3)$_{4551}$	2.682(4)
P···H(2)$_{6551}$	2.686(3)	O(2)···H(3)	2.685(5)
P···H(3)	2.729(4)	O(2)···H(4)	2.814(4)
P···H(4)$_{5542}$	2.866(4)	O(3)···O(4)$_{4551}$	2.609(2)[a]
O(1)···N$_{5554}$	3.353(2)	O(3)···O(3)$_{4563}$	2.910(4)
O(1)···H(4)$_{5542}$	1.608(4)[a]	O(3)···N$_{4542}$	3.214(3)
O(1)···H(5)$_{4542}$	1.823(4)[a]	O(3)···H(5)$_{4542}$	2.626(5)
O(1)···N$_{5542}$	2.634(2)[a]	O(3)···H(1)$_{5454}$	2.683(4)
O(1)···N$_{4542}$	2.825(2)[a]	O(3)···H(2)$_{4563}$	2.834(4)
O(1)···N$_{6554}$	3.086(2)	O(4)···N	2.814(2)[a]
O(1)···O(2)$_{5542}$	3.147(2)	O(4)···H(2)$_{6551}$	1.616(4)[a]
O(1)···O(4)$_{5554}$	3.308(2)	O(4)···H(1)$_{5454}$	1.643(3)[a]
O(2)···O(4)$_{5554}$	2.643(2)[a]	O(4)···H(3)	1.776(4)[a]
O(2)···N$_{4551}$	3.034(2)	H(1)···H(2)$_{4554}$	2.575(5)
O(2)···O(4)$_{4551}$	3.213(2)	H(1)···H(3)$_{5554}$	2.739(5)
O(2)···N	3.214(2)	H(1)···H(5)$_{4551}$	2.880(5)
O(2)···O(3)$_{5554}$	3.285(3)	H(2)···H(3)$_{4551}$	2.654(5)
		H(2)···H(4)$_{4542}$	2.822(5)
		H(4)···H(5)$_{4551}$	2.761(6)

[a] Distances corresponding to hydrogen bonds.

The conformation of the $N_2H_6^{2+}$ ion can be seen in Figs. 1 – 2. The dihedral angles are 60.3(3), 58.1(4), and 61.3(3)° corresponding to a staggered conformation.

The N – H bond lengths are 1.047(3), 1.067(3), and 1.046(4) Å. The significant differences are a result of hydrogen bond interactions of differing strengths. This is illustrated in Fig. 4 where the N – H distance is plotted against the corresponding O···H distance in N – H···O hydrogen bonds. The straight line was obtained by a weighted least-squares fit using eight single hydrogen bonds found in $N_2H_6SO_4$,[9] $N_2H_5H_2PO_4$,[3] and $N_2H_6(H_2PO_4)_2$ (this investigation).

Hydrogen bonding. The $N_2H_6^{2+}$ ion can only donate hydrogen bonds. In the present case each ion acts as a donor in three independent bonds of the type N – H···O. These bonds cross-link the phosphate layers to produce a three-dimensional network (illustrated in Fig. 1). Table 5 gives a detailed description of the N – H···O bonds.

The N – H···O(4) bond is close to linear with an N – H···O angle of 170.7(4)° whereas the two hydrogen bonds to O(1) are bent through 159.5(3)° and 158.9(4)°. The bond N – H(4)···O(1) is by far the strongest and accordingly the N – H(4) is longer (1.067(3) Å) than N – H(3) (1.047(3) Å). See also Fig. 4.

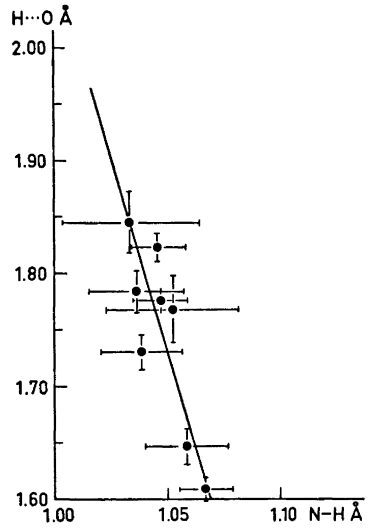

Fig. 4. An illustration of the relation between N−H and H···O distances in hydrogen bonds found in $N_2H_6SO_4$,[9] $N_2H_5H_2PO_4$,[3] and $N_2H_6(H_2PO_4)_2$. Three times the standard deviations of the experimental values are included in the figure. The straight line was obtained by a weighted least-squares fit.

There are two additional N···O distances of approximately the same magnitude as the sum of the van der Waals radii (N···O(1) 3.086(2) Å and N···O(2) 3.034(2) Å). These do not involve any hydrogen bond interaction as all possible H···O distances are too large.

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