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A Refinement of the Crystal Structure of Putrescine Diphosphate with Neutron Diffraction Data*

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The crystal structure of putrescine diphosphate, $[NH_3(CH_2)_4NH_3]^{2+}.2[H_2PO_4]^-$, has been refined, based upon neutron diffraction data measured at 85 K. Crystal data: space group $P2_1/a$; $a = 7{\cdot}890\,(7)$, $b = 9{\cdot}725\,(8)$, $c = 8{\cdot}132\,(8)$ Å, $\beta = 110{\cdot}26\,(5)°$; $Z = 2$. The final unweighted R value based on F^2 is 0·038 for 1691 unique reflections, and all bond distances have been determined with precision better than 0·002 Å. The amino groups on putrescine are protonated, and each is hydrogen bonded to three neighboring phosphate groups. The ammonium and phosphate groups are both roughly tetrahedral; however, small differences are observed in these groups between chemically equivalent covalent bond distances and angles. These differences may be ascribed to effects of hydrogen bonding and non-bonded contacts. The N and P coherent neutron scattering amplitudes have been refined to yield values of 0·927 (3) and 0·503 (3) $\times$ 10^{-12} cm respectively.

Introduction

Putrescine (1,4-diamino-*n*-butane) is an aliphatic diamine found in all prokaryotic and eukaryotic cells. The crystal structures of the salts with Cl^- (Ashida & Hirokawa, 1963), $C_4H_{10}O_4P^-$ (Furberg & Solbakk, 1972) and PF_6^- (Goldberg, 1974) have previously been determined by X-ray diffraction techniques. The general features of the crystal structure of putrescine diphosphate have been elucidated from X-ray photographic data (Woo & Rich, 1975; Woo, Seeman & Rich, 1978). We have now determined accurate hydrogen-atom positions and refined this structure with single-crystal neutron diffraction data measured at 85 K. This work has been undertaken as part of a study of the bonding and lone-pair electrons in putrescine diphosphate by a combination of X-ray and neutron diffraction techniques.

Data collection

A crystal of putrescine diphosphate with volume 7·75 mm³ was mounted on an aluminum pin oriented approximately along the $[10\bar{1}]$ direction. The sample was placed in a specially constructed closed-cycle helium refrigerator‡ and mounted on an automated four-circle diffractometer (Dimmler, Greenlaw, Kelley, Potter, Rankowitz & Stubblefield, 1976; McMullan, Andrews, Koetzle, Reidinger, Thomas & Williams, 1976) at the Brookhaven High Flux Beam Reactor with a crystal-monochromated neutron beam of wavelength 1·047 Å. The temperature of the sample during data collection was 85 ± 1 K. Cell dimensions refined by a least-squares procedure based on setting angles of 29 high-angle ($2\theta > 50°$) reflections are listed in Table 1, and agree well with the more precise values determined by X-ray diffraction at the same temperature. Intensities were measured for reflections in four octants of reciprocal space ($hkl,h\bar{k}l,\bar{h}kl,\bar{h}\bar{k}l$), with $2\theta < 90°$, employing a $\theta/2\theta$ step-scan technique. The scan range was varied according to $\Delta 2\theta = 0{\cdot}75°\,(1{\cdot}0 + 5{\cdot}3\tan\theta)$ for the high-angle data ($50° \le 2\theta \le 90°$) and $\Delta 2\theta = 3{\cdot}0°$ for the low-angle data, and the step size was adjusted to give approximately 75 steps in each scan. Counts were accumulated for about four seconds per step, with the exact interval determined by monitoring the flux in the incident neutron beam. As a general check on experimental stability, the intensities of two standard reflections were remeasured every 50 reflections. These did not vary to any significant degree during the entire period of data collection.

Data correction and refinements

Background corrections were made by the program *PEAK* (Takusagawa, 1977), written for a PDP-11/40 computer with interactive graphics display (Vector General, Inc., 1973; Bernstein *et al.*, 1974). Reflections with weak net intensity or unusual background curves were displayed and the most suitable backgrounds estimated manually. Absorption corrections for ob-

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‡ Air Products and Chemicals, Inc. DISPLEX® Model CS-202.

served intensities were made by a semi-empirical method* (North, Phillips & Mathews, 1968) based on ψ-scan intensity data for several reflections. The standard deviation of each reflection was estimated as follows: $\sigma^2(I) = T + B + [0{\cdot}03(T - B)]^2 + (0{\cdot}03B)^2$, where T and B are total and background counts, respectively, and the factor 0·03 represents an estimate of non-statistical errors. Squared observed structure factors were obtained as $F_o^2 = I \sin 2\theta$ and averaged for symmetry-related reflections. The agreement factor obtained on averaging is $R_c = \sum (\sum_i^n |\langle F_o^2 \rangle - F_{oi}^2|)/\sum n\langle F_o^2 \rangle =$ 0·023, where the first summation is over all independent reflections, and the second over n equivalent observations (in this case, usually $n = 2$).

The atomic coordinates from the X-ray determination (Woo, Seeman & Rich, 1978) were used as initial values for a full-matrix least-squares refinement minimizing $\sum w(F_o^2 - k^2F_c^2)^2$ and using *FLINUS*, a local version of *ORFLS* (Busing, Martin & Levy, 1962). Weights were chosen as $w = 1/\sigma^2(F_o^2) = 1/[\sigma^2(I)\sin^2 2\theta]$. A scale factor k, coherent neutron scattering lengths of N and P and the Zachariasen (1967) isotropic extinction parameter g were varied, together with positional and anisotropic thermal parameters for all atoms. The extinction correction, applied to F_c^2, is given by

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

Table 1. *Crystal data for putrescine diphosphate,* $C_4H_{14}N_2^{2+}.2H_2PO_4^-$ ($T = 85$ K)

	Neutron	X-ray*
a	7·890 (7) Å	7·879 (3) Å
b	9·725 (8)	9·734 (4)
c	8·132 (8)	8·126 (3)
β	110·26 (5)°	110·19 (9)°
V	585·4 Å^3	584·9 Å^3
D_m	1·613 g cm^{-3}	
Space group	$P2_1/a$, $Z = 2$	
μ	2·348 cm^{-1}†	

* The cell parameters obtained by X-ray diffraction (Mo $K\alpha_1$; $\lambda = 0{\cdot}70926$ Å) were used for bond-length and bond-angle calculations.

† Mass-absorption coefficients of C, N, O and P were obtained from *International Tables for X-ray Crystallography* (1962). For H, 23·9 cm^2 g^{-1} was used for the effective mass-absorption coefficient due to incoherent scattering, corresponding to an incoherent cross-section of 40 barn.

Table 2. *Experimental and refinement parameters*

Crystal weight	0·0125 g
Crystal volume	7·75 mm^3
Number of faces	18
Total number of reflections measured	3208 (hkl, $h\bar{k}l$, $\bar{h}kl$, $\bar{h}\bar{k}l$)
Number of independent reflections	1691
Number of reflections with $I > 3\sigma(I)$	1362
$R = \sum\lvert F_o^2 - k^2F_c^2\rvert/\sum F_o^2$	
all reflections	0·038
$F_o^2 > 3\sigma(F_o^2)$	0·035
$R_w = (\sum w\lvert F_o^2 - k^2F_c^2\rvert^2/\sum wF_o^4)^{1/2}$	
all reflections	0·046
$F_o^2 > 3\sigma(F_o^2)$	0·043
$S = [\sum w\lvert F_o^2 - k^2F_c^2\rvert^2/(m-n)]^{1/2}$*	
all reflections	1·027
$F_o^2 > 3\sigma(F_o^2)$	1·075

* m is the number of reflections and n the number of variable parameters.

Table 3. *Atomic coordinates and thermal parameters*

Thermal parameters are of the form $\exp[-2\pi^2(h^2a^{*2}U_{11} + \cdots + 2hka^*b^*U_{12} + \cdots)]$.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
N	0·55276 (6)	0·86879 (4)	0·23217 (5)	0·00897 (20)	0·00819 (16)	0·00880 (16)	−0·00020 (14)	0·00403 (12)	−0·00087 (12)
C(1)	0·63489 (9)	0·85718 (6)	0·42680 (7)	0·01165 (30)	0·01038 (22)	0·00919 (21)	0·00292 (20)	0·00363 (18)	0·00004 (17)
C(2)	0·60013 (9)	0·98528 (6)	0·51848 (7)	0·01010 (30)	0·01145 (23)	0·00935 (23)	0·00080 (20)	0·00328 (18)	−0·00214 (18)
H(1)	0·59006 (20)	0·96205 (13)	0·18963 (16)	0·02460 (73)	0·01693 (50)	0·02194 (53)	−0·00258 (46)	0·01021 (44)	0·00265 (41)
H(2)	0·41275 (20)	0·86460 (15)	0·18750 (17)	0·01492 (65)	0·02633 (58)	0·02205 (54)	−0·00045 (50)	0·00529 (42)	−0·00059 (47)
H(3)	0·59605 (22)	0·79072 (14)	0·16893 (17)	0·02715 (77)	0·01996 (53)	0·02128 (54)	0·00477 (49)	0·01112 (46)	−0·00512 (43)
H(4)	0·57892 (25)	0·76571 (14)	0·46778 (19)	0·04140 (98)	0·01780 (54)	0·02693 (62)	−0·00176 (56)	0·01650 (57)	0·00429 (47)
H(5)	0·78008 (22)	0·84266 (18)	0·45924 (19)	0·01715 (73)	0·03766 (76)	0·02626 (61)	0·00938 (57)	0·00369 (47)	−0·00316 (54)
H(6)	0·67068 (23)	0·96867 (17)	0·65933 (17)	0·02599 (77)	0·03701 (72)	0·01505 (52)	0·00728 (61)	0·00204 (44)	−0·00356 (50)
H(7)	0·66398 (24)	1·07422 (15)	0·48010 (21)	0·02660 (86)	0·02128 (55)	0·03565 (72)	−0·00586 (53)	0·01554 (56)	−0·00323 (51)
P	0·84554 (11)	1·11257 (7)	0·12071 (9)	0·00626 (34)	0·00546 (25)	0·00752 (27)	−0·00011 (23)	0·00389 (21)	0·00056 (21)
O(1)	0·66424 (10)	1·11850 (7)	0·14335 (8)	0·00855 (31)	0·00894 (24)	0·01390 (27)	0·00103 (22)	0·00697 (20)	0·00062 (21)
O(2)	0·83878 (10)	1·13725 (6)	−0·06604 (8)	0·00894 (32)	0·00844 (24)	0·00823 (23)	0·00028 (21)	0·00434 (19)	0·00058 (19)
O(3)	0·97695 (12)	1·21636 (8)	0·24878 (9)	0·01789 (38)	0·01919 (32)	0·00988 (25)	−0·01108 (27)	0·00630 (23)	−0·00359 (23)
O(4)	0·92057 (11)	0·96440 (7)	0·18293 (9)	0·01470 (37)	0·01126 (26)	0·01687 (29)	0·00599 (25)	0·01060 (23)	0·00583 (23)
H(8)	1·05599 (20)	1·27515 (14)	0·20139 (17)	0·02067 (69)	0·02276 (57)	0·02276 (54)	−0·00615 (49)	0·00956 (44)	−0·00095 (44)
H(9)	1·01680 (21)	0·93124 (14)	0·13728 (18)	0·02112 (74)	0·02183 (55)	0·02648 (59)	0·00605 (48)	0·01321 (47)	0·00362 (45)

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* The semi-empirical absorption correction was employed because the sample was irregular in shape. An attempt was made to describe the crystal by 18 rational boundary planes, and analytical absorption corrections were calculated based on this description. Refinements based on the analytically corrected data, with anisotropic extinction (Becker & Coppens, 1975), gave results which agreed to within experimental error with those based on the empirical correction; these are reported here.

where $\bar{T}$ is the effective mean path length approximated from the calculated absorption A, by $\bar{T} \sim -\ln A/\mu$, and $\bar{V} = V^2/\lambda^3$. The smallest E value was found to be 0·47 for the reflection $20\bar{4}$, and the value of g is $1{\cdot}677 \times 10^{-4}$. Finally, a correction was applied for the effects of a small number of neutrons in the incident beam with wavelength $\lambda/2$, by means of a least-squares procedure, minimizing $L = \sum w[F_o^2(hkl) - F_c^2(hkl) - k' F_c^2(2h,2k,2l)]^2$. The value of k' is 0·0031 (3), which may be compared with the result $k' = 0{\cdot}023$ (4), obtained under similar conditions in a study of quinolinic acid (Takusagawa & Koetzle, 1978). The data-collection and structure-refinement procedures for putrescine diphosphate are summarized in Table 2. Final positional and thermal parameters for all atoms are listed in Table 3.* Neutron scattering lengths used are $b_C = 0{\cdot}665 \times 10^{-12}$ cm (Bacon, 1972), $b_H = -0{\cdot}374$ and $b_O = 0{\cdot}580 \times 10^{-12}$ cm (Shull, 1972), $b_N = 0{\cdot}927$ (3) and $b_P = 0{\cdot}503$ (3) $\times 10^{-12}$ cm.

Discussion

The structure of the putrescinium and dihydrogenphosphate ions in the crystalline state is illustrated in Fig. 1 (Johnson, 1976) and bond distances and angles are shown in Fig. 2. The structure and its implications as a model for bonding of diamines to nucleic acids have been discussed by Woo *et al.* (1978). The discussion here will mainly be restricted to aspects of the observed hydrogen-bonding scheme.

The amino groups on putrescine are protonated, and each group is hydrogen bonded to three $H_2PO_4^-$ anions as indicated in Fig. 3(*a*). The environment of the phosphate group is shown in Fig. 3(*b*). By contrast to the situation observed here, in urea–phosphoric acid (Kostansek & Busing, 1972) the amide groups on urea are formally unprotonated, but one proton is shared almost equally between the urea and phosphoric acid moieties, by means of a short O···H···O bond with a single-minimum potential-energy surface.

The two halves of the putrescinium cation are related by a center of symmetry. Torsion angles are listed in Table 4 and indicate that the cation takes the *gauche* conformation at the C(1)–C(2) bond, and the *anti* conformation at the central C(2)–C(2)′ bond as required by crystallographic symmetry.

The crystal structure of putrescine diphosphate, illustrated in Fig. 4, consists of layers of $H_2PO_4^-$ anions, connected by means of hydrogen bonds through putrescinium cations. In this respect the packing is similar to that observed in hydrazinium bis(dihydrogenphosphate) (Liminga, 1966; Kvick, Jönsson & Liminga, 1972). The structure contains five distinct hydrogen bonds, one for each proton covalently attached to N or O. Hydrogen-bond parameters are included in Fig. 3. As expected, O–H···O bonds between phosphate groups are found to be considerably stronger than N–H···O bonds between ammonium and phosphate groups (mean H···O distances are 1·55 and 1·82 Å respectively). In the phosphate group, atoms O(1) and O(2) accept two and three hydrogen bonds, respectively, while the hydroxyl oxygens O(3) and O(4) act as donors, but accept no hydrogen bonds. A similar situation was found to exist in urea–phosphoric acid (Kostansek & Busing, 1972), acetic acid–phosphoric acid (Jönsson, 1972), and hydrazinium bis(dihydrogenphosphate) (Kvick *et al.*, 1972). By contrast, in phosphoric acid (Cole, 1966), hydrazinium dihydrogenphosphate (Jönsson & Liminga, 1971) and phosphoric acid hemihydrate

Table 4. *Torsion angles in the putrescinium cation (IUPAC–IUB Commission on Biochemical Nomenclature,* 1970)

H(1)–N–C(1)–C(2)	50·3 (1)°
H(2)–N–C(1)–C(2)	−70·2 (1)
H(3)–N–C(1)–C(2)	169·3 (1)
N–C(1)–C(2)–C(2)′	60·9 (1)
H(4)–C(1)–C(2)–C(2)′	−59·8 (1)
H(5)–C(1)–C(2)–C(2)′	−179·9 (1)
C(1)–C(2)–C(2)′–C(1)′	180*
H(6)–C(2)–C(2)′–C(1)′	60·8 (1)
H(7)–C(2)–C(2)′–C(1)′	−57·2 (1)

* Fixed by crystallographic symmetry.

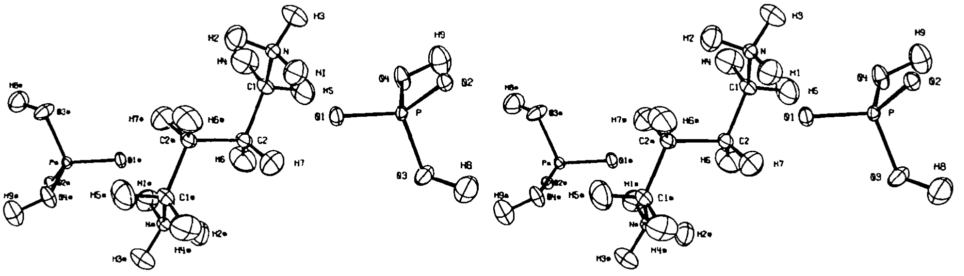

Fig. 1. Stereoscopic illustration of putrescine diphosphate. Thermal ellipsoids are drawn at the 74% probability level.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33281 (30 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

(Dickens, Prince, Schroeder & Jordan, 1974) the hydroxyl O atoms on the phosphate moieties act as both hydrogen-bond donors and acceptors.

The ammonium and phosphate groups in putrescine diphosphate are each roughly tetrahedral. Mean P—O and P—O(H) bond distances are 1·511 (8) and 1·568 (8) Å, respectively, in good agreement with average values taken from several other structures containing $H_2PO_4^-$ anions (Baur & Khan, 1970). In the present work, small differences are observed between chemically equivalent covalent bond distances and angles. These differences may be ascribed to effects of hydrogen bonding and non-bonded contacts. For example, bond P—O(2) is slightly longer than P—O(1) [1·520 (2) *vs* 1·506 (2) Å], presumably because O(2) accepts three hydrogen bonds, while O(1) accepts two bonds, as mentioned above. Baur & Khan (1970) have pointed out that P—O distances in phosphates tend to show some variation, dependent upon local environment. Both N—H and O—H covalent bond distances in the present structure correlate inversely with hydrogen-bond strengths, as measured by the corresponding O···H distances.

A short contact [2·238 (3) Å] occurs between H(3) and H(9), two of the protons involved in hydrogen bonds to O(2). The angle H(3)···O(2)···H(9) is 80·1 (1)°, so that the coordination around O(2) is quite distorted from an ideal tetrahedral arrangement.

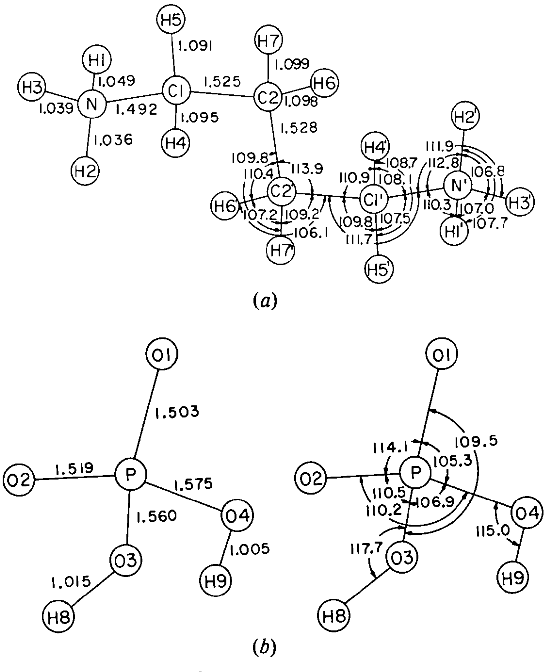

Fig. 2. Bond distances (Å) and angles (°) of (*a*) the putrescinium cation and (*b*) the dihydrogenphosphate anion. Standard deviations in bond distances and angles are 0·001 ~ 0·002 Å and 0·07 ~ 0·15° respectively.

Refined values of the N and P neutron scattering amplitudes are b_N = 0·927 (3) and b_P = 0·503 (3) × 10^{-12} cm. These values are slightly smaller than those of b_N = 0·940 and b_P = 0·51 × 10^{-12} cm in the compilation by Shull (1972). However, the same trends were observed in urea–phosphoric acid (Kostansek & Busing, 1972) where only the value of b_O was fixed at 0·577 × 10^{-12} cm and all other scattering amplitudes were allowed to refine. Results of a number of other structure refinements with single-crystal data have indicated (Kvick, Koetzle, Thomas & Takusagawa, 1974) that b_N is actually somewhat smaller than the generally accepted value of 0·94 × 10^{-12} cm.

The observed thermal parameters have been fit to general rigid-body motions described by **T**, **L** and **S** tensors (Schomaker & Trueblood, 1968). When the entire putrescinium cation is taken as a rigid body, the largest principal axis of **L** corresponds to a mean-square libration of $\mathbf{L}_1$ = 30·9 (°)², approximately about the long axis of the cation, and the r.m.s. error of fit is $\langle \Delta U_{ij}^2 \rangle^{1/2}$ = 0·0046 Å². When the H atoms are excluded from the rigid body, the corresponding results are $\mathbf{L}_1$ = 27·6 (°)² and $\langle \Delta U_{ij}^2 \rangle^{1/2}$ = 0·0003 Å². Motions of the **P** and O atoms in the anion conform very closely to a

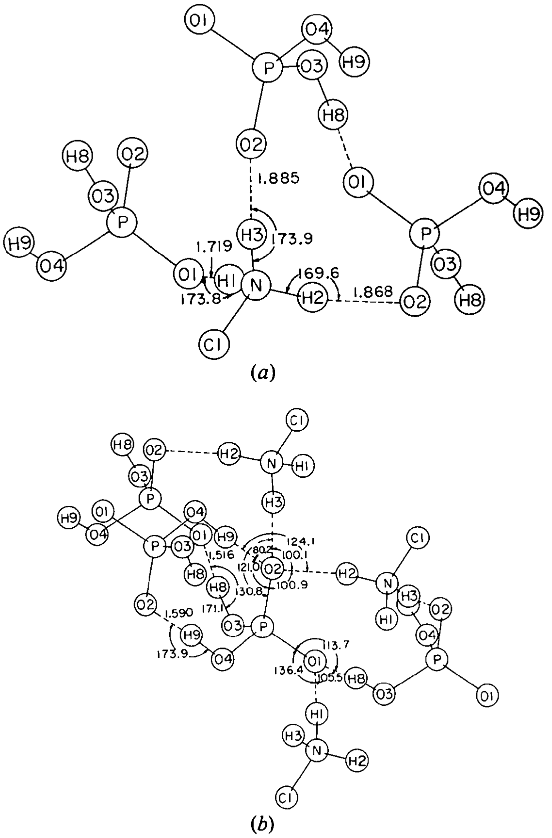

Fig. 3. Hydrogen bonding: (*a*) ammonium group, (*b*) phosphate group.

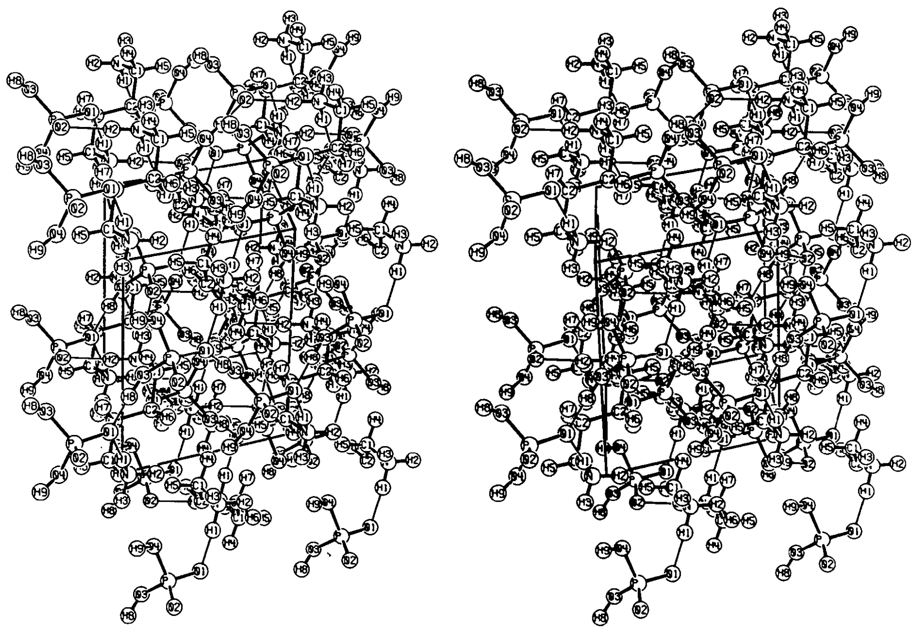

Fig. 4. The crystal structure as viewed down **c**, with **a** horizontal.

Table 5. *Bond distances corrected for effects of thermal motion*

Hydrogen atoms have not been included in the rigid-body fit, which was carried out separately for the anion and cation.

N–C(1)	1·497 Å	C(2)–H(6)	1·102 Å
N–H(1)	1·054	C(2)–H(7)	1·103
N–H(2)	1·041	P–O(1)	1·507
N–H(3)	1·039	P–O(2)	1·522
C(1)–C(2)	1·526	P–O(3)	1·566
C(1)–H(4)	1·100	P–O(4)	1·581
C(1)–H(5)	1·096	O(3)–H(8)	1·017
C(2)–C(2)′	1·533	O(4)–H(9)	1·007

rigid-body model, and $\langle \Delta U_{ij}^2 \rangle^{1/2} = 0{\cdot}0005$ Å^2. Bond distances corrected for effects of thermal motion are listed in Table 5.

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The Crystal and Molecular Structure of a 1:1 Adduct of Hexamethylenetetramine Oxide and Formic Acid

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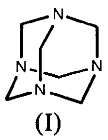
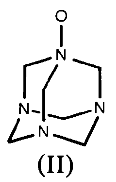
The 1:1 adduct $(CH_2)_6N_4O.HCOOH$ is monoclinic, space group $P2_1/c$, with $a = 6{\cdot}845\ (4)$, $b = 6{\cdot}847\ (4)$, $c = 20{\cdot}07\ (2)$ Å, $\beta = 104{\cdot}8\ (1)^\circ$, $Z = 4$. The structure was refined with 2031 visual reflections to $R = 0{\cdot}105$. Moving away from the quaternary to the tertiary N atoms in hexamethylenetetramine oxide, the average lengths of the three non-equivalent C—N bonds vary in the order long–short–normal relative to that in hexamethylenetetramine. The two molecular components are linked by an $\geqq$NO···H—O hydrogen bond and the two C—O bonds in the formic acid moiety are unequal in length.

Introduction

Recently it has been shown that hexamethylenetetramine, $(CH_2)_6N_4$ (I), reacts with 30% H_2O_2 in a neutral medium to give hexamethylenetetramine oxide, $(CH_2)_6N_4O$ (II), as the principal product (Lam & Mak, 1978).


(I)


(II)

Besides $(CH_2)_6N_4O$, two crystalline adducts of composition $(CH_2)_6N_4O.H_2O_2.H_2O$ and $(CH_2)_6N_4O.HCOOH$ were isolated under different reaction conditions. In the present work, the last compound was subjected to X-ray analysis. The objective was threefold: to study the effect of the *N*-oxide function on $(CH_2)_6N_4O$ cage geometry, to establish the mode of attachment of the formic acid moiety to the $(CH_2)_6N_4O$ skeleton, and to determine whether there is indeed proton transfer in the hydrogen bonding, *i.e.* whether the formic acid molecule has given up a proton to a donor atom of $(CH_2)_6N_4O$ and become a formate ion.

Experimental

The adduct was prepared as described by Lam & Mak (1978). The crystals were colorless prisms elongated along **b** and well developed on the (100) face. As the compound is very hygroscopic, roughly spherical single crystals of diameter 0·6 mm were mounted in quartz capillaries filled with paraffin wax for the X-ray measurements. Cell dimensions were determined from high-angle reflections on all three zero-layer Weissenberg photographs calibrated with superimposed NaCl powder lines and refined by minimizing the sum of the residuals $|\sin^2\theta_m - \sin^2\theta_c|$.

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