Crystal Structure of Sperminium Diphosphate Hexahydrate†

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The crystal and molecular structure of sperminium (4,9-diazoniadodecane-1,12-diammonium) diphosphate hexahydrate has been determined by single-crystal X-ray methods. The crystals are monoclinic, space group *P*2/*c*, with $a = 1137.0(4)$, $b = 708.2(3)$, $c = 1513.4(3)$ pm, $\beta = 98.45(2)°$ and $Z = 2$. The compound consists of fully protonated, centrosymmetric sperminium ions, diphosphate ions ($P_2O_7{}^{4-}$) and water molecules. The diphosphate ion has two-fold symmetry with O(1) on a two-fold axis. The P–O–P bond angle is 143.7(1)°. The sperminium ion is hydrogen bonded mainly to the diphosphate ion.

Inorganic pyrophosphatase (E.C. 3.6.1.1.) of *Streptococcus faecalis*, an enzyme catalysing the hydrolysis of diphosphate ion $P_2O_7{}^{4-}$ to orthophosphate ions, requires Mg^{2+} ion for catalytic activity.[1] This ion is known to play a dual role; it is necessary for formation of substrate complexes, $[Mg(P_2O_7)]^{2-}$ and $[Mg_2(P_2O_7)]$, and it also acts as an allosteric activator.[2,3] However, protonated polyamines, such as sperminium (4,9-diazoniadodecane-1,12-diammonium) ion, may substitute for Mg^{2+} in the substrate complexes.[4] It has previously[5] been shown by calorimetric measurements that the stoichiometry of the sperminium–diphosphate interaction is 1:1 in aqueous solution. For the logarithmic stability constant of this 1:1 adduct a value of 2.1 ($T = 298.2$ K, $I = 1.0$ mol dm^{-3}) has been obtained by potentiometric techniques. Moreover, the adduct formation has been established to be an entropically driven process, the markedly positive enthalpy of interaction (26.5 kJ mol^{-1}) being overcompensated by a positive entropy change (160 J K^{-1} mol^{-1}).[5]

We now report the crystal and molecular structure of sperminium diphosphate crystallized as the hexahydrate from aqueous solution, and show that the diphosphate ion adopts a conformation similar to that in hydrated magnesium diphosphate.[6] Previously the crystal structure of the sperminium complex of monomeric hydrogenphosphate hexahydrate has been described.[7]

Experimental

Preparation of $C_{10}H_{30}N_4{}^{4+}P_2O_7{}^{4-}\cdot 6H_2O$.—Solutions of sodium diphosphate (2 mmol, Sigma) in water (20 cm^3) and spermine tetrahydrochloride $C_{10}H_{26}N_4\cdot 4HCl$ (2 mmol, Sigma) in ethanol (10 cm^3) were mixed and kept at −15 °C overnight. The precipitate obtained was dissolved in water and stored at 4 °C. In a few weeks crystals suitable for X-ray analysis were formed.

Thermal Analysis.—The thermogravimetric curve of the crystals was recorded under a nitrogen atmosphere on a Perkin-Elmer TGA7 instrument, using a scanning speed of 5 °C min^{-1}. Six water molecules were lost in a single step at 34–146 °C (Found: 22.4. Calc. 22.1%).

Infrared Spectroscopic Measurements.—A solid-state IR spectrum of the crystals was recorded on a Galaxy FT-IR spectrometer by applying the Nujol mull technique. The OH stretchings of hydrogen-bonded water molecules resulted in a broad signal at 3378 cm^{-1}. The NH stretchings were not clearly resolved owing to overlapping of OH and CH vibrations.

Crystal Structure Determination.—*Crystal data.* $C_{10}H_{42}N_4O_{13}P_2$, $M_r = 488.40$, monoclinic, space group *P*2/*c* (no. 13), $a = 1137.0(4)$, $b = 708.2(3)$, $c = 1513.4(3)$ pm, $\beta = 98.45(2)°$, $U = 1.205(1)$ nm^3 [by least-squares refinement of 25 automatically centred reflections ($38.2 < 2\theta < 47.8°$, $\lambda = 71.069$ pm)], $Z = 2$, $D_c = 1.345$ g cm^{-3}, $F(000) = 528$. Colourless plates. Approximate crystal dimensions 0.20 × 0.28 × 0.30 mm, μ(Mo-Kα) = 2.34 cm^{-1}, $T = 296(1)$ K.

Data collection and processing. Data were collected at room temperature with a Rigaku AFC5S diffractometer in the ω–2θ scan mode with an ω scan rate of 8.0° min^{-1} and a scan width of $(1.57 + 0.30 \tan\theta)$, using graphite-monochromated Mo-Kα radiation. Weak reflections [$I < 10\sigma(I)$] were rescanned up to two times. Of 2435 reflections ($2\theta_{max} = 50°$), 2313 were unique and 1718 with $I > 3\sigma(I)$ were used in the final refinement. The data obtained were corrected for Lorenz and polarization effects. Corrections for crystal decay and absorption were not applied, but a correction for secondary extinction was done.

Structure analysis and refinement. The structure was solved by direct methods and refined by least-squares techniques to an R value of 0.033 $\{R' = 0.042, w = [\sigma^2(F_o)]^{-1}\}$. The heavy atoms were refined anisotropically and the hydrogen atoms isotropically with fixed thermal parameters. The residual electron density varied from 0.39 to −0.28 e Å^{-3}.

Neutral atomic scattering and dispersion factors were taken from ref. 8. Calculations were performed using the TEXSAN[9] crystallographic software, and molecular illustrations were drawn by ORTEP.[10] The final atomic positional coordinates are listed in Table 1.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

The Structure of the Compound.—The compound is formed of

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

sperminium cations, diphosphate anions and water molecules. A part of the structure with the atomic numbering of the asymmetric unit is shown in Fig. 1. The bond distances and angles around the heavy atoms are listed in Table 2.

The diphosphate ion has two-fold symmetry with O(1) on a two-fold symmetry axis. The short P–O bond distances fall in the range from 150.6(2) to 151.5(2) pm, the long P–O distance being 161.3(1) pm. The bond angle of the P–O–P bridge is 143.7(1)°. The bonding around the phosphorus atoms is tetrahedral, but somewhat distorted. The bonding parameters

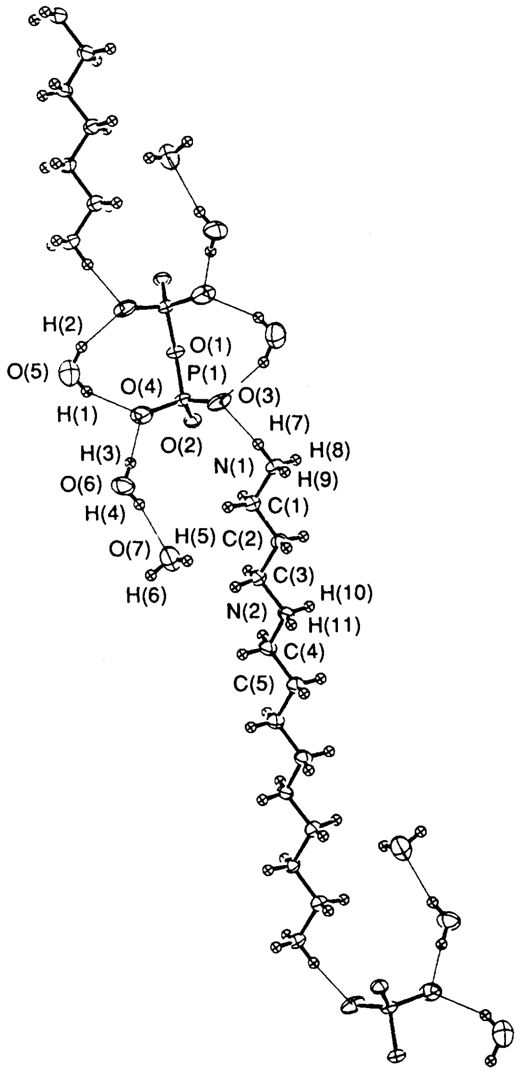

Fig. 1 An ORTEP drawing of the structural unit including the atomic labelling scheme. The asymmetric unit is completely labelled. The labels for CH hydrogens are omitted for clarity. Here and in Fig. 2, 50% probability ellipsoids are shown

Table 1 Atomic positional parameters for sperminium diphosphate hexahydrate

Atom	*x*	*y*	*z*
P(1)	0.422 10(5)	0.216 32(8)	1.158 29(3)
O(1)	1/2	0.145 3(3)	1.250 0
O(2)	0.386 9(1)	0.034 6(2)	1.108 56(9)
O(3)	0.499 7(2)	0.339 1(2)	1.109 6(1)
O(4)	0.314 9(2)	0.316 4(3)	1.184 0(1)
O(5)	0.250 9(2)	0.285 0(3)	1.346 7(2)
O(6)	0.146 3(2)	0.493 6(3)	1.086 2(1)
O(7)	0.093 2(2)	0.463 7(3)	0.900 9(1)
N(1)	0.478 9(2)	0.273 5(3)	0.927 3(1)
N(2)	0.192 8(2)	0.142 0(3)	0.655 4(1)
C(1)	0.353 5(2)	0.226 7(4)	0.891 5(1)
C(2)	0.333 4(2)	0.231 9(3)	0.790 5(1)
C(3)	0.210 1(2)	0.160 9(4)	0.754 6(1)
C(4)	0.079 2(2)	0.045 6(4)	0.619 2(2)
C(5)	0.060 6(2)	0.040 1(4)	0.518 4(2)
H(1)	0.250(3)	0.299(5)	1.293(2)
H(2)	0.331(3)	0.299(4)	1.378(2)
H(3)	0.203(2)	0.430(4)	1.117(2)
H(4)	0.141(2)	0.480(4)	1.034(2)
H(5)	0.129(3)	0.555(4)	0.877(2)
H(6)	0.022(3)	0.501(4)	0.897(2)
H(7)	0.491(2)	0.284(3)	0.987(2)
H(8)	0.529(2)	0.183(3)	0.911(2)
H(9)	0.496(2)	0.380(4)	0.906(2)
H(10)	0.190(2)	0.265(3)	0.631(2)
H(11)	0.251(2)	0.079(3)	0.638(1)
H(12)	0.303(2)	0.320(3)	0.916(1)
H(13)	0.341(2)	0.104(4)	0.914(2)
H(14)	0.387(2)	0.157(3)	0.768(1)
H(15)	0.344(2)	0.356(4)	0.771(1)
H(16)	0.151(2)	0.253(3)	0.768(2)
H(17)	0.196(2)	0.044(4)	0.778(2)
H(18)	0.083(2)	−0.082(4)	0.646(2)
H(19)	0.017(2)	0.109(3)	0.641(2)
H(20)	0.121(2)	−0.021(4)	0.497(2)
H(21)	0.070(2)	0.165(4)	0.494(2)

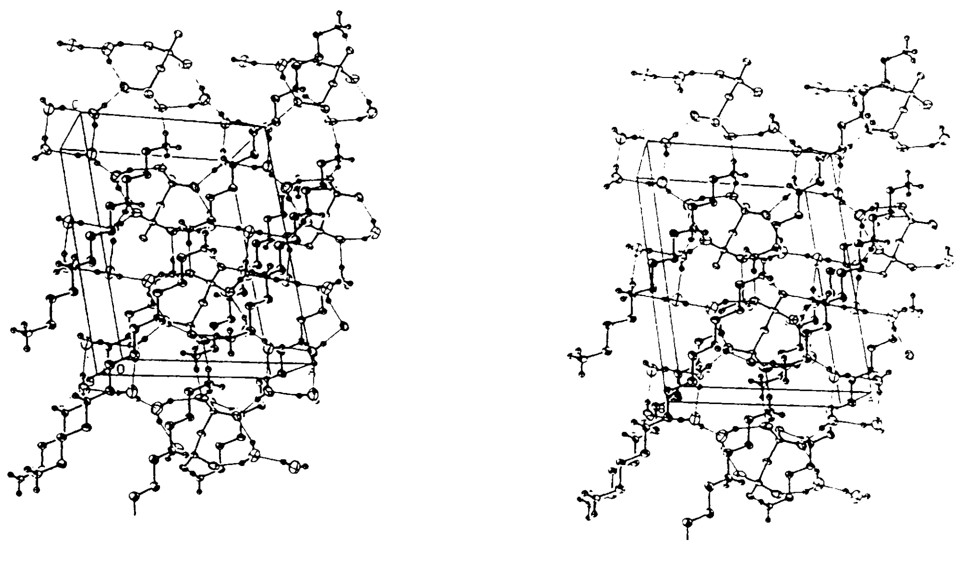

Fig. 2 Stereoview of the unit cell. Hydrogen bonds are shown as thin lines. For clarity CH hydrogens are omitted and N and C atoms are shaded

Table 2 Bond distances (pm) and angles (°) in the amine and diphosphate molecules (standard deviations in parentheses)

P(1)–O(1)	161.3(1)	N(2)–C(4)	149.2(3)
P(1)–O(2)	151.5(2)	C(1)–C(2)	151.3(3)
P(1)–O(3)	150.6(2)	C(2)–C(3)	151.3(3)
P(1)–O(4)	151.0(2)	C(4)–C(5)	151.0(3)
N(1)–C(1)	148.6(3)	C(5)–C(5$^{\mathrm{I}}$)	151.8(5)
N(2)–C(3)	149.2(3)		
O(1)–P(1)–O(2)	103.53(9)	P(1)–O(1)–P(1$^{\mathrm{II}}$)	143.7(1)
O(1)–P(1)–O(3)	108.32(8)	N(1)–C(1)–C(2)	110.9(2)
O(1)–P(1)–O(4)	106.67(8)	C(1)–C(2)–C(3)	110.4(2)
O(2)–P(1)–O(3)	112.24(9)	C(2)–C(3)–N(2)	111.7(2)
O(2)–P(1)–O(4)	111.3(1)	N(2)–C(4)–C(5)	111.6(2)
O(3)–P(1)–O(4)	114.1(1)	C(4)–C(5)–C(5$^{\mathrm{I}}$)	111.4(2)

Symmetry codes: I $-x, -y, 1 - z$; II $1 - x, y, 2.5 - z$.

Table 3 Distances (pm) and angles (°) related to hydrogen-bond formation (standard deviations in parentheses)

	O–H	H···X	O···X	O–H···X
O(5)–H(1)···O(4)	82(3)	191(3)	267.8(3)	156(3)
O(5)–H(2)···O(3$^{\mathrm{II}}$)	97(3)	193(3)	284.2(3)	156(3)
O(6)–H(3)···O(4)	87(3)	170(3)	257.0(2)	175(3)
O(6)–H(4)···O(7)	79(3)	201(3)	278.8(3)	168(3)
O(7)–H(5)···O(5$^{\mathrm{III}}$)	87(3)	190(3)	273.7(3)	161(3)
O(7)–H(6)···O(6$^{\mathrm{IV}}$)	84(3)	197(3)	277.5(3)	159(3)
N(1)–H(7)···O(3)	90(3)	188(3)	277.4(3)	171(2)
N(1)–H(8)···O(2$^{\mathrm{V}}$)	92(2)	186(2)	276.2(3)	168(2)
N(1)–H(9)···O(3$^{\mathrm{VI}}$)	86(2)	200(3)	281.7(3)	158(2)
N(2)–H(10)···O(6$^{\mathrm{III}}$)	94(2)	188(2)	280.5(3)	166(2)
N(2)–H(11)···O(2$^{\mathrm{VII}}$)	87(2)	186(2)	272.0(2)	173(2)

Symmetry codes: II $1 - x, y, 2.5 - z$; III $x, 1 - y, -0.5 + z$; IV $-x, 1 - y, 2 - z$; V $1 - x, -y, 2 - z$; VI $1 - x, 1 - y, 2 - z$; VII $x, -y, -0.5 + z$.

of the diphosphate ion thus closely resemble those reported for hydrated magnesium diphosphate, $Mg_2P_2O_7 \cdot 2H_2O$.[6] However, the P–O–P bond angle is significantly greater than in the latter crystals, for which a value of 127.5(2)° has been observed.[6] A deviation of this magnitude is not unexpected, since this particular bond angle has been shown[11,12] to vary from 130 to 180 depending on the nature of the counter ion.

The sperminium ion is in a linear chain conformation with normal bonding parameters. The deviation from the linear arrangement is greatest at the C(2)–C(3)–N(2)–C(4) fragment, which exhibits a torsion angle of 171.4(2)°. The sperminium ion is hydrogen bonded mainly to the diphosphate ion (Fig. 2). Of the five NH hydrogens belonging to one asymmetric unit, four are bonded to oxygen atoms of diphosphate ion and only one interacts with an oxygen atom of a water molecule. The hydrogen-bonding parameters are shown in Table 3.

The hydrogen-bonding pattern of the water molecules, in turn, consists of three different modes of interactions: (*i*) bonding of the first water molecule [O(5)] to atoms O(3$^{\mathrm{II}}$) and O(4) of the diphosphate ion, (*ii*) bonding of the second water molecule [O(6)] to O(4) of the diphosphate ion and to an oxygen of the third water molecule [O(7)], and (*iii*) bonding of the third water molecule [O(7)] to two other water molecules [O(5$^{\mathrm{III}}$) and O(6$^{\mathrm{IV}}$)]. The water molecules containing O(6) and O(7) form a square-like array.

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