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Synthesis and X-ray Crystal Structure of the Ethylenediammonium Monohydric Phosphate

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Ethylenediammonium Monohydric Phosphate의 합성 및 X-선 결정구조

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Abstract

The title compound, $(H_3NCH_2CH_2NH_3)HPO_4$ (**I**), has been synthesized by hydrothermal technique for the first time and its novel structure analyzed by X-ray single crystallography. The compound (**I**) crystallizes in the monoclinic system, $P2_1/c$ space group with a = 10.209(1), b = 7.891(1), c = 8.039(1) Å, β = 92.138(9)°, V = 647.2(2) Å^3, Z = 4, R_1 = 0.0295 and ωR_2 = 0.0811 for 1141 independent reflections. The compound (**I**) is interconnected to give a three-dimensional network through hydrogen-bonding interactions.

요 약

$(H_3NCH_2CH_2NH_3)HPO_4$ (**I**) 화합물을 수열법으로 최초로 합성하고 단결정 X-선 회절법으로 구조를 규명하였다. 이 화합물은 단사정계, 공간군 $P2_1/c$, a = 10.209(1), b = 7.891(1), c = 8.039(1) Å, β = 92.138(9)°, V = 647.2(2) Å^3, Z = 4로 결정화되었으며; 1141 개의 독립적인 회절 반점에 대한 최종 신뢰도 인자 R_1 및 ωR_2 값은 각각 0.0295 및 0.0811이었다. 화합물 (**I**)은 수소결합으로 연결된 3차원의 그물 구조를 갖는다.

1. Introduction

More than thirty years ago, Roy C. Mast and Ralph E. Oesper reported the preparation of some kinds of phosphate of aliphatic diamines,[1)] in which the title compound, $(H_3NCH_2CH_2NH_3)HPO_4$, was included. In that literature those compounds were prepared at the room temperature and normal pressure. And only the chemical composition and some physical properties of the compounds were investigated. Up to now no one has further studied this kind of compounds, so that its single crystal structure, chemical properties and main use have been unknown. Here we report the synthesis of the ethylenediammonium monohydric phosphate (**I**), $(H_3NCH_2CH_2NH_3)HPO_4$, by the hydrothermal method and its crystal structure by single crystal X-ray diffractometer.

2. Experimental Section

Preparation and Analysis of $(H_3NCH_2CH_2NH_3)HPO_4$, (I). The title compound, $(H_3NCH_2CH_2NH_3)HPO_4$, was prepared hydrothermally at 150°C and under the autogenous pressure over 5 days from a

homogeneous mixture of ethylenediamine(en), H_3PO_4, CeO_2, ethylene glycol (EG) and NH_4F in the mole ratio 3 : 5.5 : 2.4 : 55 : 1 in a Teflon-lined stainless steel autoclave. The product was colourless-transparent big single crystal mixed other polycrystal containing element Ce and other amorphous materials. And the other materials will be studied in other paper.

IR spectrum of the crystal was recorded on a Bio-Rad Digilab FTS-165 infrared spectrophotometer using KBr wafer method. Ethylenediamine was assigned by the relevant IR absorption bands.[2] EDS spectrum obtained on a Philips XL-30S FEG scanning electron microscope/EDAX Phoenix energy dispersive X-ray spectrometer showed the presence of C, N, O, and P elements. The analyses of the carbon, hydrogen, nitrogen, and oxygen contents were made on a CE EA-1110 elemental analyzer. The composition of the crystal (**I**) was deduced from the elemental analyses; the formula of $(H_3NCH_2CH_2NH_3)HPO_4$ is consistent with results of the single crystal X-ray diffraction analysis. *Anal. Calcd for* $C_2H_{11}N_2O_4P$: C, 15.19; H, 7.01; N, 17.72; O, 40.48; P, 19.59%. *Found*: C, 15.00; H, 7.04; N, 17.36; O, 39.54%.

X-ray Single Crystallography. A colourless block crystal (0.34×0.30×0.24 mm) of the title compound was coated with epoxy glue in order to prevent degradation of the specimen under ambient conditions. The epoxy-coated crystal was mounted on an Siemens P4 four-circle X-ray diffractometer with graphite-monochromated MoKα radiation (λ = 0.71073 Å). Accurate unit cell dimensions were refined using 39 reflections with 2θ ranges 10.63~29.33°. Three standard reflections were measured every 97 reflections; no remarkable decays were observed. The reflections used with the intensities $|I| > 2\sigma|IT|$ were Lorentz and polarization corrected; a semi-empirical absorption correction based on the psi-scans was applied. A total of 1617 reflections was collected in the 2θ range 4.0~50.0° in the θ-2θ scan mode.[3]

All calculations in the structural solution and refinements were performed using the Siemens SHELXTL crystallographic software package.[4] The space group was assigned on the basis of the systematic absences and intensity statistics, and was confirmed by successful refinements. The structure was solved by the direct method[5] and refined by successive least-squares methods followed by difference Fourier maps. All the non-hydrogen atoms

Table 1. Crystallographic and experimental data for (I)

Empirical formula	$C_2H_{11}N_2O_4P$
Formula weight	158.10
Temperature	294(2) K
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 10.209(1) Å b = 7.892(1) Å c = 8.039(1) Å β = 92.138(9)°
Volume	647.2(2) Å^3
Z	4
Density (calculated)	1.623 g/cm^3
Absorption coefficient	0.376 mm^{-1}
F(000)	336
θ range for data collection	2.00 to 24.99°
Limiting indices	$-12 \le h$ 12, $-1 \le k \le 9$, $-9 \le l \le 1$
Reflections collected/unique	1617/1141 (R_{int} = 0.0170)
Data/restraints/parameters	1141/0/86
Goodness-of-fit on F^2	1.075
Final R indices [$I>2\sigma(I)$]	R_1 = 0.0295, wR_2 = 0.0811
R indices (all data)	R_1 = 0.0331, wR_2 = 0.0833
Largest diff. peak and hole	0.235 and −0.333 eÅ^{-3}

Table 2. Atomic coordinates and equivalent isotropic displacement parameters for (I)

atom	x	y	z	U_{eq} (Å^2)
P(1)	0.7527(1)	0.0697(1)	0.3998(1)	0.018(1)
O(1)	0.7678(1)	−0.1152(2)	0.3465(2)	0.022(1)
O(2)	0.6108(1)	0.1248(2)	0.3895(2)	0.031(1)
O(3)	0.8395(1)	0.1867(2)	0.3033(2)	0.032(1)
O(4)	0.8030(2)	0.0655(2)	0.5892(2)	0.038(1)
N(11)	0.4680(2)	0.2944(2)	0.6100(2)	0.023(1)
C(12)	0.4372(2)	0.4563(2)	0.5246(2)	0.025(1)
N(21)	0.0793(2)	0.3019(2)	0.4221(2)	0.022(1)
C(22)	0.0559(2)	0.4473(2)	0.5335(2)	0.026(1)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

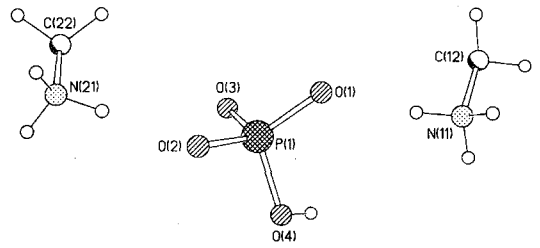

Fig. 1. The asymmetric unit of the crystal (I), $(H_3NCH_2CH_2NH_3)HPO_4$.

were refined anisotropically; all the hydrogen atoms were fixed at calculated positions with isotropic thermal parameters were included in the final structure-factor calculations. The final difference of electron density map contained no significant features. The crystallographic and experimental data are summarized in Table 1. Table 2 contains atomic positions and equivalent temperature factors for non-hydrogen atoms.

3. Results and Discussion

An asymmetric unit of the title compound with the atomic numbering scheme, $(H_3NCH_2CH_2NH_3)HPO_4$, is illustrated in Fig. 1. Selected bond distances and angles, and hydrogen bonding parameters are listed in Tables 3 and 4, respectively.

The title material is a typical ionic crystal, which is made up of HPO_4^{2-} anions and $H_3NCH_2CH_2NH_3^{2+}$ cations. From its asymmetric unit as shown in Fig. 1, we can consider that the combination of monohydric phosphate HPO_4^{2-} and doubly protonated ethylenediamine $H_3NCH_2CH_2NH_3^{2+}$ is based on the ionic bond. As listed in Table 3, the P-O distances and O-P-O angles of HPO^{2-} anion are also in agreement with those in the previously reported phosphate structures.[6,7] The geometrical data for $H_3NCH_2CH_2NH_3^{2+}$ cation are not unusual.

Table 4. Hydrogen bonding parameters (Å, °) for (I)

D-H···A	D-H	H···A	D···A	D-H···A
O(4)-H(4)O(3)^{i}	0.82	1.89	2.622(2)	148.5
N(11)-H(11a)O(2)	0.89	1.81	2.693(2)	171.2
N(11)-H(11b)O(1)^{ii}	0.89	1.94	2.824(2)	173.6
N(11)-H(11c)O(2)^{i}	0.89	1.82	2.709(2)	174.5
N(21)-H(21a)O(3)^{iii}	0.89	1.86	2.749(2)	174.4
N(21)-H(21b)O(1)^{ii}	0.89	1.95	2.802(2)	160.1
N(21)-H(21c)O(1)^{iv}	0.89	1.90	2.788(2)	172.1

Symmetry code : (i) x, $-y+1/2$, $z+1/2$, (ii) $x+1$, $-y$, $-z+1$, (iii) $x-1$, y, z, (iv) $-x+1$, $y+1/2$, $-z+1/2$.

Fig. 2 and Fig. 3 illustrate the crystal packing of the $H_3NCH_2CH_2NH_3^{2+}$ cation and the HPO_4^{2-} anions of the title compound. From Fig. 2 we shall suggest that HPO_4^{2-} anions are linked to each other by a moderate O-H···O hydrogen bond {O(4)-H(4)··· O(3); 2.622(2) Å, 148.5°}, represented as dotted lines, to form two kinds of zigzag chain, which are parallel to the *bc* crystallographic plane. And the one kind of the HPO_4^{2-} anions chain is made up of P(I)-P(III)-P(V)-P(VII), and the another chain P(II)-P(IV)-P(VI)-P(VIII), which alternately arrange along the *a* axis direction.

According to the Fig. 3 we shall think that there are two kinds of the ethylenediammonium cation between the every two HPO_4^{2-} chains, one of which is made up of N(11)-C(12)-C(12)-N(11), and another N(21)-C(22)-C(22)-N(21). And the two kinds of $H_3NCH_2CH_2NH_3^{2+}$ cation alternately arrange along the *a* axis direction, too. As listed in Table 4, it is

Table 3. Bond lengths (Å) and angles (°) for (I)

P(1)-O(1)	1.531(1)	P(1)-O(2)	1.512(1)
P(1)-O(3)	1.514(1)	P(1)-O(4)	1.589(1)
N(11)-C(12)	1.479(2)	C(12)-C(12)^{i}	1.521(4)
N(21)-C(22)	1.481(2)	C(22)-C(22)^{ii}	1.496(2)
O(1)-P(1)-O(2)	111.40(8)	O(1)-P(1)-O(3)	111.82(8)
O(1)-P(1)-O(4)	102.45(7)	O(2)-P(1)-O(3)	112.04(8)
O(2)-P(1)-O(4)	109.43(8)	O(3)-P(1)-O(4)	109.25(9)
N(11)-C(12)-C(12)^{i}	110.2(2)	N(21)-C(22)-C(22)^{ii}	110.6(2)

Symmetry code : (i) $-x+1$, $-y+1$, $-z+1$, (ii) $-x$, $-y+1$, $-z+1$.

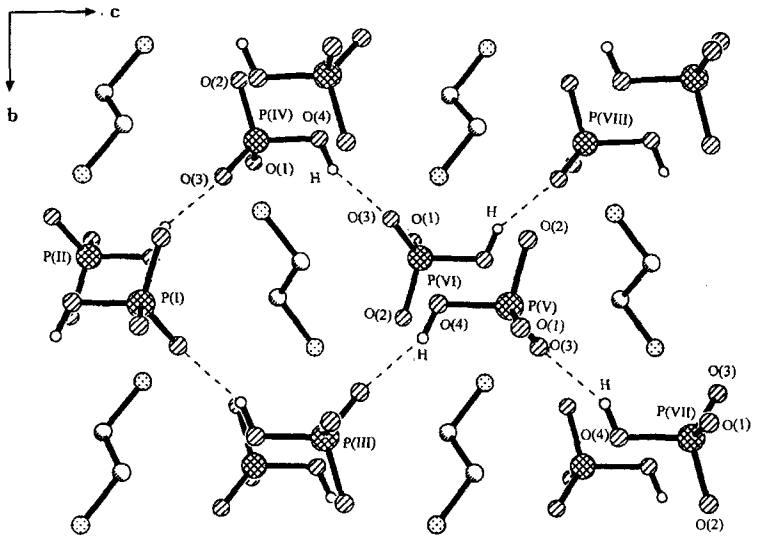

Fig. 2. A view of the crystal structure along the *a* axis, showing the zigzag chains of HPO_4^{2-} and the hydrogen bonds between two HPO_4^{2-} anions, using the dotted lines to stand for the hydrogen bonds.

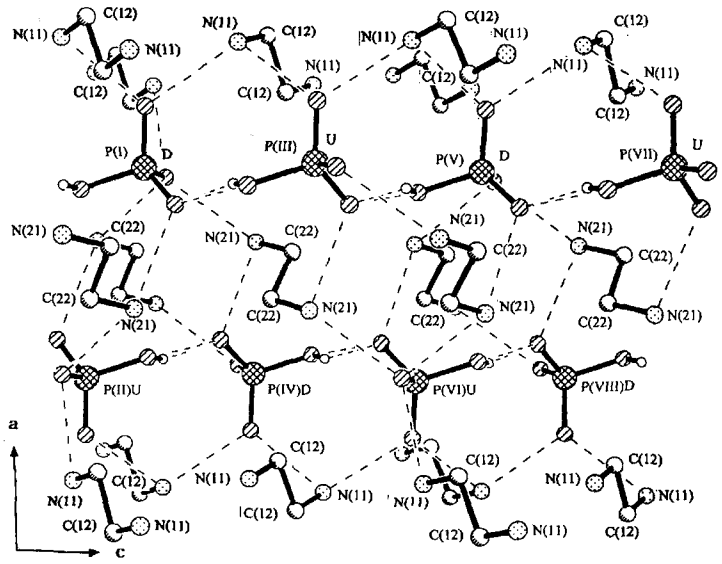

Fig. 3. A view of the crystal structure along the *b* axis, showing the arrangement of chains of anions and cations. *P(II), P(III), P(VI) and P(VII) marked with "D" showing their down position;* P(I), P(IV), P(V) and P(VIII) marked with "U" showing their up position.

noteworthy that there are other moderate N-H···O hydrogen bonds between the oxygen atom of the HPO_4^{2-} anion and the nitrogen atom of the $H_3NCH_2CH_2NH_3^{2+}$ cation. So that the acting force between ions is not only ionic bonding but also hydrogen bonding. In summary, the compound (**I**) is interconnected to give a three-dimensional network through hydrogen-bonding interactions.

4. Supplementary Material

Tables of crystallographic details, atomic coordi-

nates, interatomic distances and angles, torsional angles, hydrogen atom coordinates, anisotropic displacement parameters, and structure factors are available from C. H. Kim.

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