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LETTER TO THE EDITOR

Crystal Structure of Sodium Cyclooctaphosphate Hexahydrate, $Na_8P_8O_{24} \cdot 6H_2O$

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Sodium cyclooctaphosphate hexahydrate crystallizes in the triclinic system, $P\bar{1}$, with the following monomolecular unit cell:

$$a = 6.622(2), \quad b = 10.031(4), \quad c = 11.250(4)\ \text{Å}$$
$$\alpha = 104.06(5), \quad \beta = 101.21(5), \quad \gamma = 90.88(5)°.$$

The crystal structure was solved by using 1932 unique reflections with a final R value 0.036. The P_8O_{24} ring is centrosymmetrical. Sodium atoms with a five- or sixfold coordination and water molecules through H-bonds maintain the tridimensional cohesion of this very simple arrangement. The hydrogen-bond system is remarkable because one of the water molecules is connected only to bonding oxygen atoms of the phosphate ring. A comparison of the geometrical features of the P_8O_{24} ring observed in the title compound with those previously investigated is given.

Introduction

As early as 1968, Schülke (*1, 2*) reported a process for the production of convenient amounts of sodium cyclooctaphosphate hexahydrate, $Na_8P_8O_{24} \cdot 6H_2O$. In spite of this possibility offered to explore cyclooctaphosphate chemistry by using this salt as a starting material, the few cyclooctaphosphates thoroughly investigated until now have been characterized either during elaborations of phase equilibrium diagrams or during the investigations of various systems by flux methods. So, a series of four isotypic compounds $Cu_3M_2P_8O_{24}$ were characterized during the elaboration of the MPO_3–$Cu_2P_4O_{12}$ phase equilibrium diagrams for M = Rb (*3, 4, 6*), Cs (*5, 6*), and Tl (*3, 6*), and for the ammonium salt during an investigation of the CuO–P_2O_5–$(NH_4)_2O$ system (*7, 8*). Other compounds of general formula $M_2K_2P_8O_{24}$ (M = Al, Fe (*9*), Ga (*10*), V (*11*)) were discovered during investigations of the corresponding K_2O–P_2O_5–M_2O_3 systems by flux methods. In all cases, the true nature of the anion was recognized during the structural investigations.

We report in the present work the crystal

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TABLE I

CRYSTAL DATA AND EXPERIMENTAL PARAMETERS USED FOR THE INTENSITY DATA COLLECTION AND THE CRYSTAL STRUCTURE DETERMINATION

I. Crystal data	
Formula: $Na_8P_8O_{24} \cdot 6H_2O$	F_w = 923.778
Crystal system: triclinic	Space group: $P\bar{1}$
a = 6.622(2), b = 10.031(4)	V = 709(1) Å^3
c = 11.250(4) Å, α = 104.06(5)	
β = 101.21(5), γ = 90.88(5)°	Z = 1
Refinement of unit cell parameters:	25 reflections ($8 < \theta < 13°$)
ρcal. = 2.162 g cm^{-3}	$F(000)$ = 460
Linear absorption factor:	μ(AgKα) = 0.389 mm^{-1}
Morphology: irregular prism	Crystal size: 0.48 × 0.04 × 0.07 mm
II. Intensity measurements	
Temperature: 293 K	Wavelength: AgKα (0.5608 Å)
Diffractometer: Nonius CAD4	Scan mode: ω
Monochromator: graphite plate	Scan width: 1.20°
Max. scan time: 120 sec	Theta range: 2–25°
Measurement area: $\pm h$, $\pm k$, l	$h$max. = 10, $k$max. = 15, $l$max. = 16
Total background measuring time:	40 sec
Total number of scanned reflections:	6440
Total number of nonzero reflections:	2003
Total number of independent reflections:	1932
One intensity and one orientation reference reflections: no variation	
III. Structure determination	
Lorentz and polarization corrections	No absorption correction
Program used: SDP (*13*)	Computer used: Micro-Vax II
Determination:	Direct methods with MULTAN (*14*)
Hydrogen atoms from difference-Fourier syntheses	
Unique reflections included:	1819 with $I > 3\sigma(I)$
Weighting scheme: unitary	Refined parameters: 232
Unweighted agreement factor R:	0.036
Weighted agreement factor Rw:	0.042
Esd: 1.360	Largest shift/error = 0.00
Drawings made with STRUPLO (*15*)	

structure of $Na_8P_8O_{24} \cdot 6H_2O$. The main interest of this investigation rests on the existence of a P_8O_{24} ring anion in the atomic arrangement.

A comparison of the geometries of the rings observed in the previously investigated compounds with that found in the title compound is given in the last section of the present work.

Experimental

As said above, the chemical preparation of the title compound was previously described by Schülke (*1*, *2*), but the atomic arrangement has not yet been determined, probably because of the difficulties to grow suitable crystals for an X-ray investigation. The relatively low solubility (*12*) and the crystal morphology (irregular very thin prisms) can explain why the growth of a crystal was long and difficult. In the present

TABLE II

FINAL ATOMIC COORDINATES AND $B_{eq.}$ ($B_{iso.}$ FOR H ATOMS) IN $Na_8P_8O_{24} \cdot 6H_2O$

Atoms	x	y	z	$B_{eq.}$
P(1)	0.5972(2)	0.2260(1)	0.8110(1)	0.87(2)
P(2)	0.6811(2)	0.3570(1)	0.0881(1)	0.86(2)
P(3)	0.9672(2)	0.2443(1)	0.2610(1)	0.90(2)
P(4)	0.7811(2)	−0.0188(1)	0.6984(1)	0.92(2)
Na(1)	0.2514(4)	−0.0269(2)	0.5870(2)	1.71(4)
Na(2)	0.0804(3)	0.2855(2)	0.7643(2)	1.87(4)
Na(3)	0.4936(3)	0.3408(2)	0.3648(2)	1.58(4)
Na(4)	0.1851(3)	0.4392(2)	0.1073(2)	1.49(4)
O(E11)	0.2672(6)	0.6684(4)	0.2128(3)	1.47(7)
O(L12)	0.4382(5)	0.7324(4)	0.0478(3)	1.13(6)
O(L14)	0.2760(5)	0.9088(4)	0.1836(3)	1.14(6)
O(E12)	0.6101(6)	0.8144(4)	0.2704(3)	1.43(7)
O(L23)	0.8224(6)	0.2379(4)	0.1274(3)	1.28(6)
O(E21)	0.8170(6)	0.4718(4)	0.0769(3)	1.46(7)
O(E22)	0.5238(6)	0.3848(4)	0.1666(3)	1.49(7)
O(E31)	0.1261(6)	0.3614(4)	0.2918(3)	1.46(7)
O(E32)	0.8409(5)	0.2343(4)	0.3552(3)	1.30(6)
O(L34)	0.0684(6)	0.1013(4)	0.2168(3)	1.34(7)
O(E41)	0.0933(6)	0.9485(4)	0.3683(3)	1.60(7)
O(E42)	0.4045(6)	0.1065(4)	0.3743(4)	1.78(8)
O(W1)	0.8598(6)	0.7896(5)	0.0390(4)	2.22(8)
O(W2)	0.9666(7)	0.6119(4)	0.4026(4)	2.22(9)
O(W3)	0.5369(8)	0.5917(5)	0.4235(4)	2.61(9)
				$B_{iso.}$
H(1W1)	0.06(1)	0.144(8)	0.960(7)	2(2)
H(2W1)	0.25(2)	0.18(1)	−0.017(9)	5(3)
H(1W2)	0.02(2)	0.65(1)	0.490(9)	5(3)
H(2W2)	0.03(1)	0.554(7)	0.380(6)	1(2)
H(1W3)	0.45(1)	0.612(9)	0.364(8)	3(2)
H(2W3)	0.62(2)	0.61(1)	0.40(1)	6(3)

Note. The estimated standard deviations are given in parentheses.

$$B_{eq.} = \tfrac{1}{3} \sum_i \sum_j a_i \cdot b_j \cdot \beta_{ij}.$$

case, this growth was run by carefully controlled crystallization in water at room temperature. The main crystal data, the parameters used for the intensity data collection, the strategy used for the crystal structure determination, and its results are summarized in Table I. Final atomic coordinates and $B_{eq.}$ are listed in Table II thermal parameters, and anisotropic in Table III.

Structure Description

This very simple atomic arrangement is represented by Fig. 1 in a projection along the **a** direction. The P_8O_{24} ring anion develops around the inversion center located in (0, 0, 0). It so has a $\bar{1}$ internal symmetry and is consequently built by four independent PO_4 tetrahedra. As shown in the view reported in Fig. 1, this ring has in projection a

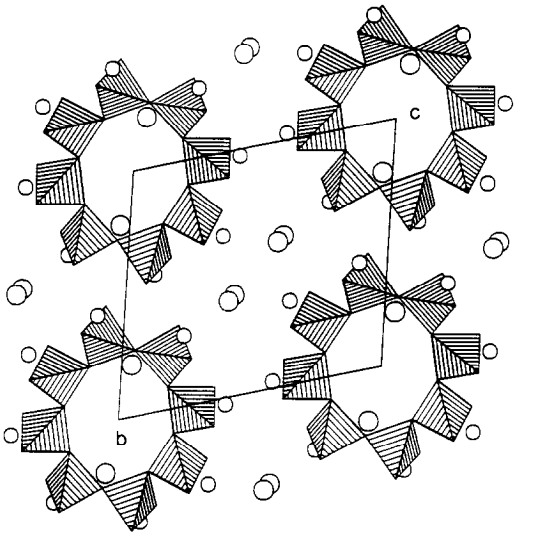

FIG. 1. Projection along the **a** direction of the atomic arrangement of $Na_8P_8O_{24} \cdot 6H_2O$. The smaller empty circles represent the sodium atoms, the larger ones the water molecules.

TABLE III

ANISOTROPIC THERMAL PARAMETERS IN $Na_8P_8O_{24} \cdot 6H_2O$

Atoms	$\beta(1,1)$	$\beta(2,2)$	$\beta(3,3)$	$\beta(1,2)$	$\beta(1,3)$	$\beta(2,3)$
P(1)	0.0047(2)	0.0025(1)	0.00196(8)	0.0021(2)	0.0015(2)	0.0010(1)
P(2)	0.0044(2)	0.0026(1)	0.00192(8)	0.0018(2)	0.0011(2)	0.0010(1)
P(3)	0.0046(2)	0.0023(1)	0.00239(8)	0.0014(2)	0.0017(2)	0.0012(1)
P(4)	0.0043(2)	0.0024(1)	0.00254(8)	0.0014(2)	0.0013(2)	0.0014(1)
Na(1)	0.0085(5)	0.0049(2)	0.0038(2)	0.0008(5)	0.0010(5)	0.0016(3)
Na(2)	0.0085(4)	0.0063(2)	0.0046(2)	0.0042(5)	0.0056(4)	0.0038(3)
Na(3)	0.0084(4)	0.0044(2)	0.0036(2)	0.0004(5)	0.0027(4)	0.0016(3)
Na(4)	0.0069(4)	0.0040(2)	0.0042(2)	0.0000(5)	0.0028(4)	0.0026(3)
O(E11)	0.0094(8)	0.0036(3)	0.0039(3)	0.0014(9)	0.0059(7)	0.0027(5)
O(L12)	0.0061(7)	0.0037(3)	0.0018(2)	−0.0009(8)	0.0014(6)	−0.0004(5)
O(L14)	0.0066(7)	0.0034(3)	0.0024(2)	0.0046(7)	0.0015(7)	0.0017(4)
O(E12)	0.0071(7)	0.0045(4)	0.0025(3)	0.0024(9)	−0.0006(7)	0.0007(5)
O(L23)	0.0083(7)	0.0029(3)	0.0026(2)	0.0044(8)	0.0004(7)	0.0009(5)
O(E21)	0.0086(8)	0.0031(3)	0.0039(3)	−0.0007(8)	0.0008(7)	0.0028(5)
O(E22)	0.0071(7)	0.0057(4)	0.0030(3)	0.0060(8)	0.0050(6)	0.0025(5)
O(E31)	0.0072(7)	0.0042(3)	0.0036(3)	−0.0007(8)	0.0029(7)	0.0020(5)
O(E32)	0.0073(7)	0.0037(3)	0.0032(2)	0.0027(8)	0.0048(6)	0.0021(5)
O(L34)	0.0087(7)	0.0031(3)	0.0032(3)	0.0053(8)	0.0017(7)	0.0021(5)
O(E41)	0.0092(7)	0.0045(3)	0.0045(3)	0.0023(9)	0.0072(7)	0.0046(5)
O(E42)	0.0076(8)	0.0035(4)	0.0049(3)	0.0007(9)	−0.0006(8)	−0.0007(6)
O(W1)	0.0097(8)	0.0067(4)	0.0052(3)	−0.002(1)	0.0031(8)	0.0021(6)
O(W2)	0.017(1)	0.0051(4)	0.0041(3)	0.005(1)	0.0039(9)	0.0016(6)
O(W3)	0.026(1)	0.0055(4)	0.0033(3)	−0.003(1)	0.005(1)	0.0027(5)

Note. The estimated standard deviations are given in parentheses. The temperature factor form used here is

$$T = h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hl\beta_{13} + kl\beta_{23}.$$

TABLE IV

MAIN INTERATOMIC DISTANCES (Å) AND BOND ANGLES (°) IN THE $[P_8O_{24}]^{8-}$ GROUP

		The $P(1)O_4$ tetrahedron		
P(1)	O(E11)	O(L12)	O(L14)	O(E12)
O(E11)	1.484(4)	2.552(6)	2.513(5)	2.566(5)
O(L12)	111.3(2)	1.606(4)	2.449(5)	2.471(4)
O(L14)	108.6(2)	99.2(2)	1.609(4)	2.534(5)
O(E12)	119.7(2)	106.1(2)	109.9(2)	1.484(3)
		The $P(2)O_4$ tetrahedron		
P(2)	O(L12)	O(L23)	O(E21)	O(E22)
O(L12)	1.615(3)	2.436(5)	2.569(5)	2.477(5)
O(L23)	97.6(2)	1.621(4)	2.544(5)	2.527(5)
O(E21)	111.3(2)	109.4(2)	1.495(4)	2.586(6)
O(E22)	106.2(2)	109.1(2)	120.8(2)	1.480(4)
		The $P(3)O_4$ tetrahedron		
P(3)	O(L23)	O(E31)	O(E32)	O(L34)
O(L23)	1.604(3)	2.523(4)	2.551(5)	2.376(4)
O(E31)	109.0(2)	1.493(4)	2.568(6)	2.537(5)
O(E32)	110.9(2)	118.6(2)	1.493(4)	2.537(5)
O(L34)	95.7(2)	110.1(2)	110.1(2)	1.601(4)
		The $P(4)O_4$ tetrahedron		
P(4)	O(L14)	O(L34)	O(E41)	O(E42)
O(L14)	1.619(3)	2.385(5)	2.556(5)	2.536(4)
O(L34)	94.8(2)	1.620(4)	2.539(6)	2.552(5)
O(E41)	110.3(2)	109.1(2)	1.494(4)	2.560(6)
O(E42)	110.0(2)	110.9(2)	119.0(2)	1.476(4)

P(1)–P(2)	3.011(2)	P(1)–O(L12)–P(2)	138.4(2)
P(1)–P(4)	2.880(2)	P(1)–O(L14)–P(4)	126.3(2)
P(2)–P(3)	2.891(2)	P(2)–O(L23)–P(3)	127.3(2)
P(3)–P(4)	2.902(2)	P(3)–O(L34)–P(4)	128.5(2)
		P(2)–P(1)–P(4)	123.92(6)
		P(1)–P(2)–P(3)	120.97(5)
		P(2)–P(3)–P(4)	147.76(5)
		P(1)–P(4)–P(3)	146.70(6)

Note. Estimated standard deviations are given in parentheses.

strong pseudo-symmetry $2/m$. The pseudo-mirror includes the two centrosymmetric O(L12) atoms, while the pseudo-twofold axis almost perpendicular to the mirror includes the two centrosymmetric O(L34) atoms. All the geometrical values observed in this ring and listed in Table IV are in accordance with all previous data reported in condensed phosphate crystal chemistry.

Among the four independent sodium atoms, one of them [Na(1)] has a fivefold coordination built by external oxygen atoms

TABLE V

MAIN INTERATOMIC DISTANCES (Å) IN THE COORDINATION POLYHEDRA OF THE SODIUM ATOMS

Na(1)–O(E12)	2.380(4)	Na(1)–O(E41)	2.528(4)
Na(1)–O(E32)	2.428(5)	Na(1)–O(E42)	2.420(4)
Na(1)–O(E41)	2.431(4)		
Na(2)–O(E11)	2.405(4)	Na(2)–O(E41)	2.571(4)
Na(2)–O(E12)	2.354(4)	Na(2)–O(W1)	2.470(5)
Na(2)–O(E21)	2.635(4)	Na(2)–O(W2)	2.324(5)
Na(3)–O(E22)	2.419(5)	Na(3)–O(E42)	2.447(5)
Na(3)–O(E31)	2.441(4)	Na(3)–O(W3)	2.439(5)
Na(3)–O(E32)	2.560(4)	Na(3)–O(W3)	2.362(5)
Na(4)–O(E11)	2.318(4)	Na(4)–O(E22)	2.326(4)
Na(4)–O(E21)	2.445(5)	Na(4)–O(E31)	2.483(5)
Na(4)–O(E21)	2.433(4)	Na(4)–O(W1)	2.453(4)

Note. Estimated standard deviations are given in parentheses.

of the phosphate ring. The three remaining ones have a sixfold coordination including both water molecules and external oxygen atoms building moderately distorted octahedra. The Na–O distances vary from 2.318 to 2.635 Å. Table V reports the main interatomic distances in these polyhedra.

In the three-dimensional hydrogen-bond network (see Table VI), hydrogen atoms belonging to O(W2) and O(W3) water molecules are involved, as can be expected, in bonds connecting these water molecules either to external oxygen atoms of the phosphoric ring or to other water molecules. The situation of the two hydrogen atoms of the O(W1) water molecule is different; both are connected to bonding oxygen atoms, O(L12) and O(L14) belonging to two different phosphoric rings. This fact is rather unusual in condensed phosphate chemistry, where bonding oxygen atoms are almost never involved in associated cation coordination or in hydrogen bonds.

The P_8O_{24} Ring Anion

As said above, only two structural studies of cyclooctophosphates have been reported before this study. What we consider as the main geometrical features of a ring framework, P–P distances, P–O–P and P–P–P angles for the three P_8O_{24} rings presently known are reported in Table VII. In front of so few examples, any kind of discussion similar to what was possible with a good number of examples for other smaller rings, P_6O_{18} for instance (*16*), seems here fruitless.

TABLE VI

MAIN INTERATOMIC DISTANCES (Å) AND ANGLES (°) IN THE HYDROGEN-BOND NETWORK

O(W)–H···O	O(W)–H	H···O	O(W)–H···O	O(W)–O
O(W1)–H(1W1)···O(L14)	0.87(9)	2.42(8)	123(7)	2.980(5)
O(W1)–H(2W1)···O(L12)	0.81(10)	2.36(11)	122(10)	2.867(6)
O(W2)–H(1W2)···O(E32)	0.95(9)	1.91(8)	160(10)	2.825(5)
O(W2)–H(2W2)···O(E31)	0.73(7)	2.12(7)	166(8)	2.838(5)
O(W3)–H(1W3)···O(E11)	0.88(9)	2.08(9)	172(9)	2.947(6)
O(W3)–H(2W3)···O(W2)	0.69(13)	2.29(12)	151(13)	2.909(7)

H(1W1)–O(W1)–H(2W1)	100.5(10)
H(1W2)–O(W2)–H(2W2)	107.1(8)
H(1W3)–O(W3)–H(2W3)	94.1(12)

Note. Estimated standard deviations are given in parentheses.

TABLE VII

MAIN GEOMETRICAL FEATURES OBSERVED IN P_8O_{24} RING-ANIONS

Formula	P–P–P (°)	P–O–P (°)	P–P (Å)	Symmetry	Ref.
$K_2Ga_2P_8O_{24}$	131.4	123.1	2.818	$2/m$	(*20*)
	138.0	134.4	2.933		
		136.0	2.947		
$Cu_3(NH_4)_2P_8O_{24}$	119.9	129.1	2.888	$\bar{1}$	(*5*)
	92.1	134.8	2.928		
	112.2	146.3	2.930		
	123.3	134.9	3.018		
$Na_8P_8O_{24} \cdot 6H_2O$	123.9	138.4	3.011	$\bar{1}$	
	121.0	126.3	2.880		
	147.8	127.3	2.891		
	146.7	128.5	2.902		

Nevertheless, one can note that among the three rings presently investigated one has a $2/m$ internal symmetry and two are centrosymmetrical. Among the numerical data reported in Table VII the P–P distances ranging from 2.818 to 3.018 Å and the P–O–P angles spreading from 123.1 to 146.3° are within the ranges commonly observed in the cyclophosphate crystal chemistry. The values reported for the P–P–P angles can appear as very dispersed, spreading from 92.1 to 146.7°, but are in fact quite comparable to the range of values observed in cyclohexaphosphates (85.9 to 142.8°) (*16*).

A list of observed and calculated structure factors can be obtained on request.

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