Crystal structure of tetrakis(4-methoxybenzylammonium) cyclotetraphosphate tetrahydrate, $(C_8H_{12}NO)_4[P_4O_{12}] \cdot 4H_2O$

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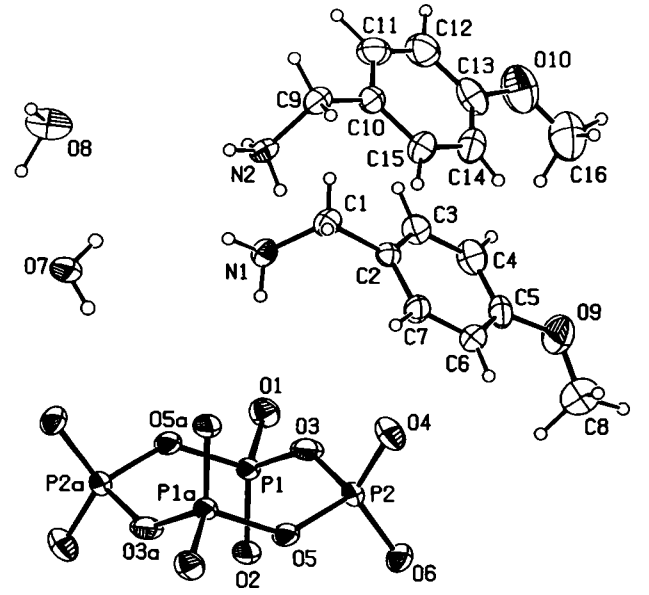
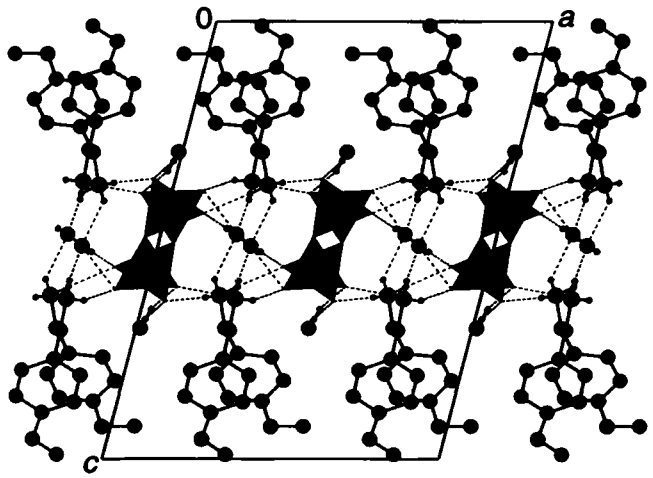
Received March 24, 2005, accepted and available on-line April 28, 2005; CCDC no. 1267/1516





Abstract

$C_{32}H_{56}N_4O_{20}P_4$, monoclinic, $P12_1/a1$ (no. 14),
$a = 13.412(2)$ Å, $b = 9.160(2)$ Å, $c = 18.128(3)$ Å,
$\beta = 104.41(1)°$, $V = 2157.0$ Å^3, $Z = 2$,
$R_{gt}(F) = 0.039$, $wR_{ref}(F) = 0.043$, $T = 296$ K.

Source of material

Single crystals of the title compound were prepared at room temperature by slow evaporation of a mixture of an aqueous solution of cyclotetraphosphoric acid and an ethanolic solution of 4-methoxybenzylamine. The first solution was cooled to 0 °C and the second one was added drop-wise under agitation. The cyclotetraphosphoric acid was prepared by passing a solution of $Na_4P_4O_{12} \cdot 4H_2O$, prepared according to the Ondik process [1,2], through an ion-exchange resin in its H-state (Amberlite IR 120).

Discussion

Three chemical species types are present in the asymmetric unit: a P_4O_{12} ring anion, two 4-methoxybenzylammonium cations and two water molecules (figure, top). The phosphate anion is centrosymmetrical and thus built up by only two independent PO_4 tetrahedra. This ring is distorted with P–P–P angles ranging between 84.10(2)° and 95.90(2)°. In spite of this distortion, the observed geometrical characteristics of the P_4O_{12} ring (P—O distances and P–O–P or O–P–O angles as well as P—P distances) are in accordance with those observed in other cyclotetraphosphoric anions with the same internal centre of symmetry [3,4]. P_4O_{12} anion alternates with the OW1 water molecule to form, via H-bonds, ribbons running along the [010] direction. These ribbons are themselves linked by the second water molecule OW2 and the ammonium groups through H-bonds to form thick anionic layers parallel to the *a,b* plane (figure, bottom). The 4-methoxybenzylammonium cations are located between the anionic layers, compensating their negative charge. Two independent organic cations coexist in this structure; their phenyl rings are planar with a maximum atomic deviation of 0.0036 Å and are nearly parallel with a dihedral angle 3.32°. The conformation of the methoxy and methylamine side substituents with respect to the benzene ring is usually described by the torsion angles C–O–C–C (t_1) and N–C–C–C (t_2). These angles exhibit the values of $t_1 = -166.7(3)°$ and $t_2 = 92.2(3)°$ in the first methoxybenzylammonium cation and $t_1 = -174.7(4)°$ and $t_2 = 100.0(3)°$ in the second one, respectively. Consequently, in each organic cation the methoxy and methylamine substituents have not the same conformation and lie out of the planes of their carrier phenyl rings.

Table 1. Data collection and handling.

Crystal:	colorless prism, size 0.35 × 0.55 × 0.65 mm
Wavelength:	Ag K_α radiation (0.5608 Å)
μ:	1.40 cm^{-1}
Diffractometer, scan mode:	Enraf-Nonius CAD4, $\omega/2\theta$
$2\theta_{max}$:	49.92°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	7512, 7270
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 4\,\sigma(I_{obs})$, 3638
$N(param)_{refined}$:	271
Programs:	SIR92 [5], teXsan [6]

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Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{iso}
H(1)	4e	0.1912	0.1774	0.4734	0.061
H(2)	4e	0.2743	0.1319	0.5133	0.064
H(3)	4e	1.0286	1.0791	0.6575	0.139
H(4)	4e	1.0192	0.9006	0.6810	0.125
H(5)	4e	0.6792	0.6310	0.6310	0.059
H(6)	4e	0.6939	0.4978	0.5899	0.056
H(7)	4e	0.7673	0.6008	0.6062	0.082
H(8)	4e	0.7092	0.4562	0.7203	0.053
H(9)	4e	0.8089	0.4096	0.6915	0.058
H(10)	4e	0.6991	0.6498	0.8038	0.094
H(11)	4e	0.7901	0.8097	0.8940	0.088
H(12)	4e	1.0698	0.9835	0.8715	0.135
H(13)	4e	1.0903	1.0176	0.9721	0.167
H(14)	4e	1.1212	0.8439	0.9388	0.151

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(15)	4e	1.0483	0.7234	0.8219	0.091
H(16)	4e	0.9544	0.5616	0.7327	0.077
H(17)	4e	0.7193	0.1487	0.6242	0.046
H(18)	4e	0.7655	0.0292	0.5929	0.069
H(19)	4e	0.8237	0.1444	0.6375	0.056
H(20)	4e	0.7173	-0.0551	0.6955	0.047
H(21)	4e	0.8371	-0.0473	0.7088	0.056
H(22)	4e	0.9293	0.1653	0.7871	0.050
H(23)	4e	0.9280	0.3196	0.8869	0.083
H(24)	4e	0.9216	0.3680	1.0116	0.166
H(25)	4e	0.8374	0.5127	1.0382	0.191
H(26)	4e	0.8806	0.5124	0.9465	0.176
H(27)	4e	0.6284	0.2404	0.8792	0.097
H(28)	4e	0.6259	0.0822	0.7707	0.089

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
P(1)	4e	0.49722(3)	0.14800(4)	0.41951(2)	0.0249(2)	0.0244(2)	0.0390(2)	0.0012(2)	0.0038(2)	-0.0006(2)
P(2)	4e	0.49919(3)	0.17511(4)	0.58298(2)	0.0303(2)	0.0254(2)	0.0402(2)	0.0038(2)	0.0078(2)	-0.0049(2)
O(1)	4e	0.43576(9)	0.2430(1)	0.36003(7)	0.0462(7)	0.0360(6)	0.0496(7)	0.0074(5)	0.0067(5)	0.0088(5)
O(2)	4e	0.61073(8)	0.1504(1)	0.43866(7)	0.0254(5)	0.0392(6)	0.0606(7)	-0.0025(5)	0.0103(5)	-0.0064(5)
O(3)	4e	0.45533(8)	0.1745(1)	0.49321(7)	0.0266(5)	0.0649(8)	0.0415(7)	0.0075(5)	0.0038(5)	-0.0019(6)
O(4)	4e	0.40759(9)	0.1959(1)	0.61280(7)	0.0529(8)	0.0504(7)	0.0624(8)	0.0118(6)	0.0292(7)	-0.0035(6)
O(5)	4e	0.54364(8)	0.0143(1)	0.60143(7)	0.0288(5)	0.0259(5)	0.0679(8)	0.0008(4)	-0.0049(5)	-0.0042(5)
O(6)	4e	0.58859(9)	0.2721(1)	0.60655(7)	0.0436(6)	0.0301(6)	0.0574(7)	-0.0053(5)	0.0012(5)	-0.0066(5)
O(7)	4e	0.22493(8)	0.1035(1)	0.48678(7)	0.0348(6)	0.0462(7)	0.0650(8)	0.0090(5)	0.0004(6)	-0.0002(6)
O(8)	4e	1.0112(1)	1.0070(2)	0.7015(1)	0.100(1)	0.061(1)	0.129(2)	0.0068(9)	0.066(1)	0.005(1)
O(9)	4e	0.9742(2)	0.8807(2)	0.9260(1)	0.112(2)	0.096(1)	0.078(1)	-0.021(1)	0.008(1)	-0.022(1)
O(10)	4e	0.7787(2)	0.3737(3)	0.9548(1)	0.141(2)	0.126(2)	0.086(2)	0.029(2)	0.025(1)	-0.010(1)
N(1)	4e	0.7211(1)	0.5590(2)	0.62621(8)	0.0421(8)	0.0482(8)	0.0478(9)	0.0012(7)	0.0095(7)	-0.0095(7)
N(2)	4e	0.7707(1)	0.0897(2)	0.63409(9)	0.0318(7)	0.0377(7)	0.063(1)	-0.0025(6)	0.0093(7)	0.0015(7)
C(1)	4e	0.7629(1)	0.4892(2)	0.7011(1)	0.050(1)	0.0385(9)	0.058(1)	-0.0011(8)	0.0067(8)	-0.0020(9)
C(2)	4e	0.8211(1)	0.5946(2)	0.75914(9)	0.0418(9)	0.0349(8)	0.0412(9)	0.0030(7)	0.0094(7)	0.0048(7)
C(3)	4e	0.7731(2)	0.6696(2)	0.8064(1)	0.052(1)	0.059(1)	0.056(1)	0.0086(9)	0.0174(9)	-0.001(1)
C(4)	4e	0.8261(2)	0.7626(2)	0.8602(1)	0.081(2)	0.061(1)	0.056(1)	0.014(1)	0.020(1)	-0.009(1)
C(5)	4e	0.9289(2)	0.7859(2)	0.8680(1)	0.089(2)	0.045(1)	0.039(1)	-0.006(1)	-0.002(1)	-0.0004(9)
C(6)	4e	0.9783(2)	0.7137(3)	0.8215(1)	0.050(1)	0.080(1)	0.053(1)	-0.014(1)	0.0060(9)	0.006(1)
C(7)	4e	0.9239(1)	0.6172(2)	0.7672(1)	0.043(1)	0.067(1)	0.049(1)	-0.0009(9)	0.0122(8)	-0.0050(9)
C(8)	4e	1.0708(3)	0.9309(4)	0.9256(2)	0.098(2)	0.110(2)	0.109(2)	-0.019(2)	0.021(2)	-0.003(2)
C(9)	4e	0.7777(1)	0.0075(2)	0.7062(1)	0.0448(9)	0.041(1)	0.066(1)	-0.0001(8)	0.0001(8)	0.0093(9)
C(10)	4e	0.7810(1)	0.1058(2)	0.7716(1)	0.049(1)	0.044(1)	0.053(1)	0.0018(8)	0.0005(8)	0.0144(9)
C(11)	4e	0.6941(2)	0.1322(3)	0.7974(1)	0.055(1)	0.085(2)	0.079(2)	-0.004(1)	0.022(1)	0.017(1)
C(12)	4e	0.6966(2)	0.2217(3)	0.8572(2)	0.075(2)	0.102(2)	0.077(2)	0.005(2)	0.029(1)	0.009(2)
C(13)	4e	0.7857(2)	0.2883(3)	0.8943(1)	0.100(2)	0.068(1)	0.053(1)	0.027(1)	0.023(1)	0.013(1)
C(14)	4e	0.8732(2)	0.2660(3)	0.8698(1)	0.070(1)	0.065(1)	0.063(1)	-0.001(1)	-0.003(1)	-0.003(1)
C(15)	4e	0.8713(2)	0.1752(2)	0.8090(1)	0.051(1)	0.064(1)	0.065(1)	0.003(1)	0.004(1)	-0.003(1)
C(16)	4e	0.8618(4)	0.4517(4)	0.9900(2)	0.169(4)	0.108(3)	0.095(2)	0.010(3)	0.007(2)	-0.007(2)

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