REGULAR STRUCTURAL PAPERS

Acta Cryst. (1993). C**49**, 361–363

Ammonium *cyclo*-Octaphosphate–Telluric Acid Dihydrate Adduct

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(*Received* 19 *May* 1992; *accepted* 7 *September* 1992)

Abstract

As in all previously investigated adducts of telluric acid with monovalent inorganic or organic cation phosphates, the phosphoric anions (here P_8O_{24} rings) and the $Te(OH)_6$ groups coexist as independent entities inside the atomic arrangement. In addition, the present structure is the first example of a *cyclo*-octaphosphate containing two crystallographically independent P_8O_{24} ring anions, both centrosymmetrical. The hydrogen-bonding scheme is reported.

Comment

The structural investigation of the title compound was undertaken mainly to obtain new information about the geometrical features of higher phosphoric-ring-anion conformations, a domain still not investigated in depth. A second reason was to verify a well established rule about the formation of adducts between telluric acid [$Te(OH)_6$] and any kind of monovalent cation phosphate (Li excepted) condensed or not.

The development of the structural chemistry of *cyclo*-octaphosphates did not start seriously before 1990 and only a few P_8O_{24} ring-anion conformations are known at present. The only reported structures are $Cu_3(NH_4)_2P_8O_{24}$ (Laügt & Guitel, 1975), $Na_8P_8O_{24}.6H_2O$ (Schülke, Averbuch-Pouchot & Durif, 1992*a*), $Ga_2K_2P_8O_{24}$ (Palkina, Maksimova, Kusznetsov & Chudinova, 1979) and $Te(OH)_6.K_8P_8O_{24}.2H_2O$ (Schülke, Averbuch-Pouchot & Durif, 1992*b*). As shown in Fig. 1, the atomic arrangement in the title compound has a typical layer organization. Layers containing the phosphoric ring anions and the $Te(OH)_6$ groups alternate perpendicular to the [101] direction, with corrugated layers including the ammonium groups and the water molecules. Two crystallographically independent P_8O_{24} ring anions coexist inside this arrangement; these are located around inversion centers at $(0, 0, \frac{1}{2})$ and $(\frac{1}{2}, \frac{1}{2}, 0)$. The main geometrical features of these two rings are reported in Table 2. Among the six similar rings observed previously, three are centrosymmetrical, two have $2/m$ internal symmetry and one has no symmetry. In such rings (which are still not sufficiently numerous for a comparison of their geometries to lead to a valuable discussion), the P—P—P angles vary from 92.1 to 147.8° while in the title compound the range of values is smaller (103.72–119.87°).

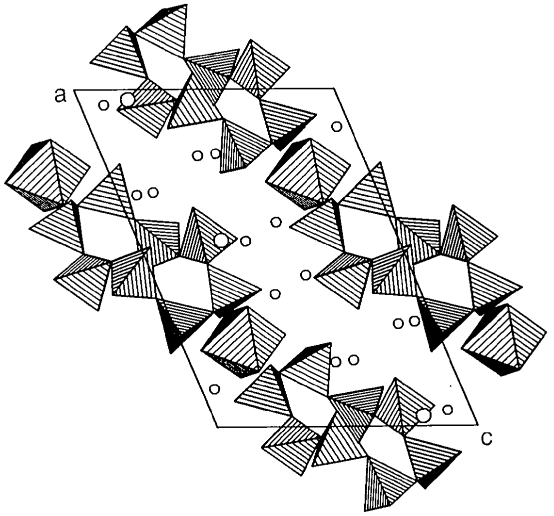

Fig. 1. Projection along the **b** direction of the atomic arrangement of $Te(OH)_6.(NH_4)_8P_8O_{24}.2H_2O$. Hatched octahedra are the $Te(OH)_6$ groups, small circles denote the N atoms and larger ones the water molecules.

The ammonium groups build a three-dimensional network of NO_6, NO_7 and NO_8 polyhedra, with N—N distances ranging from 3.424 to 4.852 Å. Inside these various NO_n polyhedra, the N—O distances are in the range 2.729–3.453 Å. The $Te(OH)_6$ group observed in this arrangement is, as usual, an almost regular TeO_6 octahedron with Te—O distances ranging from 1.905 to 1.917 Å and O—Te—O angles of 88.4 to 89.8°. The Te—O—H angles vary from 109 to 117°.

In the hydrogen-bond network it is worth reporting that there are no hydrogen bonds between the $Te(OH)_6$ groups, all of whose O atoms are bonded to O atoms of the phosphoric anions. The same can be said of the two water molecules. Among the six independent O atoms of the $Te(OH)_6$ group, only two [O(4) and O(5)] act as acceptors in the N—H···O bonds.

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The interatomic distances and bond angles in the various NO_n polyhedra and in the hydrogen-bond network have been deposited.

Experimental

Crystal data

$(NH_4)_8P_8O_{24}.Te(OH)_6.2H_2O$
$M_r = 1041.752$
Triclinic
$P\bar{1}$
$a = 15.146$ (6) Å
$b = 11.049$ (6) Å
$c = 12.189$ (6) Å
$\alpha = 117.15$ (4)°
$\beta = 109.72$ (4)°
$\gamma = 90.54$ (4)°
$V = 1676$ (4) Å^3
$Z = 2$

$D_x = 2.064$ Mg m^{-3}
Ag $K\alpha$ radiation
$\lambda = 0.5608$ Å
Cell parameters from 18 reflections
$\theta = 10$–12°
$\mu = 0.741$ mm^{-1}
$T = 295$ K
Elongated prism
0.35 × 0.24 × 0.16 mm
Colorless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
Absorption correction: none
12440 measured reflections
11957 independent reflections
6268 observed reflections [$I>4\sigma(I)$]
$R_{\rm int} = 0.014$
$\theta_{\rm max} = 30°$

$h = -22 \rightarrow 22$
$k = -16 \rightarrow 16$
$l = 0 \rightarrow 18$
2 orientation standard reflections monitored every 400 reflections
intensity variation: none
2 intensity standard reflections
frequency: 60 min
intensity variation: none

Refinement

Refinement on F
Final $R = 0.031$
$wR = 0.033$
$S = 1.559$
6268 reflections
611 parameters
H atoms refined with $B_{\rm iso}$
$w = 1$
$(\Delta/\sigma)_{\rm max} = 0.20$ [B of H(3N5)]

$\Delta\rho_{\rm max} = 1.17$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.65$ e Å^{-3}
Extinction correction: Stout & Jensen (1968)
Extinction coefficient: $g = 3.57\times10^{-8}$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$$B_{\rm eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
Te	0.25287 (2)	0.24049 (3)	0.23927 (2)	1.487 (3)
P(1)	0.88347 (6)	0.17593 (8)	0.74808 (7)	1.52 (2)
P(2)	0.94176 (6)	0.92558 (9)	0.25150 (8)	1.70 (2)
P(3)	0.95336 (6)	0.22344 (9)	0.41665 (8)	1.78 (2)
P(4)	0.19383 (6)	−0.24344 (9)	0.47118 (8)	1.76 (2)
P(5)	0.45265 (6)	0.71825 (9)	0.92356 (8)	1.64 (2)
P(6)	0.70275 (6)	0.27937 (9)	−0.02002 (8)	1.79 (2)
P(7)	0.38639 (6)	0.67924 (8)	0.25312 (7)	1.46 (2)
P(8)	−0.55797 (6)	−0.56921 (8)	−0.26390 (7)	1.36 (2)
O(1)	0.3590 (2)	0.3856 (3)	−0.6880 (2)	2.45 (6)
O(2)	0.1652 (2)	0.3648 (3)	−0.7502 (3)	2.95 (7)
O(3)	0.2294 (2)	0.2064 (3)	−0.9376 (2)	2.78 (6)
O(4)	−0.1472 (2)	−0.0957 (3)	−0.1693 (2)	2.37 (6)
O(5)	0.6585 (2)	0.8831 (3)	0.7724 (3)	3.20 (8)
O(6)	0.7241 (2)	0.7275 (3)	0.5851 (2)	2.68 (6)
O(*E*11)	0.0777 (2)	−0.2738 (3)	−0.8929 (2)	2.27 (6)
O(*E*12)	0.8153 (2)	0.0467 (3)	0.6932 (3)	2.92 (7)
O(*L*12)	0.9691 (2)	0.1356 (3)	0.6975 (2)	3.30 (6)
O(*L*14)	0.1620 (2)	0.7370 (2)	0.3243 (2)	1.81 (5)
O(*E*21)	−0.0606 (2)	−0.0610 (3)	−0.8651 (2)	2.45 (6)
O(*E*22)	−0.1433 (3)	−0.1501 (5)	−0.7595 (3)	5.8 (1)
O(*L*23)	0.9687 (3)	0.0711 (3)	0.3816 (3)	5.1 (1)
O(*E*31)	0.9499 (3)	0.6893 (4)	0.5128 (4)	4.9 (1)
O(*E*32)	−0.1162 (2)	0.2274 (3)	−0.7005 (2)	2.55 (6)
O(*L*34)	0.0878 (2)	0.7365 (3)	0.4713 (3)	3.23 (7)
O(*E*41)	−0.2326 (2)	0.3668 (3)	−0.4675 (2)	2.72 (6)
O(*E*42)	−0.2489 (3)	0.1042 (3)	0.4269 (3)	3.29 (8)
O(*L*56)	0.3839 (2)	−0.3301 (3)	−0.0231 (2)	2.83 (6)
O(*L*58)	0.4926 (2)	−0.4214 (2)	−0.1350 (2)	1.83 (5)
O(*E*51)	0.5358 (2)	−0.1788 (3)	0.0391 (3)	3.36 (8)
O(*E*52)	0.3949 (2)	−0.2569 (3)	−0.1857 (2)	2.75 (6)
O(*L*67)	0.6573 (2)	0.2395 (2)	−0.1746 (2)	1.85 (5)
O(*E*61)	0.7232 (2)	0.1509 (3)	0.9832 (2)	3.04 (6)
O(*E*62)	0.2210 (2)	0.5937 (4)	0.9432 (3)	3.77 (9)
O(*L*78)	0.5153 (2)	0.3395 (2)	−0.2274 (2)	1.73 (5)
O(*E*71)	0.5905 (2)	0.2228 (3)	0.6042 (2)	2.11 (5)
O(*E*72)	0.6735 (2)	0.4599 (3)	−0.1889 (2)	2.07 (5)
O(*E*81)	0.5583 (2)	0.5671 (3)	0.3848 (2)	2.10 (5)
O(*E*82)	0.3492 (2)	0.3830 (3)	0.7343 (2)	2.09 (5)
O(*W*1)	0.4474 (3)	0.0114 (5)	0.6797 (3)	5.4 (1)
O(*W*2)	0.9697 (3)	0.4980 (5)	0.1931 (4)	5.2 (1)
N(1)	0.3952 (3)	0.0482 (4)	0.4397 (4)	3.40 (9)
N(2)	0.1134 (3)	0.4554 (4)	0.0508 (3)	2.99 (8)
N(3)	0.1923 (3)	0.1621 (4)	0.5598 (3)	2.69 (8)
N(4)	0.6878 (2)	0.6619 (3)	0.0712 (3)	2.31 (7)
N(5)	−0.4495 (3)	0.3203 (4)	−0.5881 (3)	3.05 (7)
N(6)	0.6953 (3)	0.0292 (4)	0.1378 (3)	2.92 (8)
N(7)	0.0465 (3)	0.8182 (4)	0.9089 (3)	2.80 (7)
N(8)	0.1983 (3)	0.5328 (4)	0.6332 (3)	2.91 (8)

Table 2. *Main interatomic distances* (Å) *and bond angles* (°) *in the two independent* P_8O_{24} *ring anions*

The first P_8O_{24} ring anion

$P(1)O_4$ tetrahedron

P(1)	O(*E*11)	O(*E*12)	O(*L*12)	O(*L*14)
O(*E*11)	1.475 (2)	2.556 (3)	2.519 (4)	2.467 (4)
O(*E*12)	119.8 (2)	1.479 (3)	2.495 (5)	2.526 (5)
O(*L*12)	109.9 (2)	108.1 (2)	1.600 (3)	2.456 (4)
O(*L*14)	106.6 (2)	110.2 (2)	100.3 (2)	1.599 (3)

$P(2)O_4$ tetrahedron

P(2)	O(*L*12)	O(*E*21)	O(*E*22)	O(*L*23)
O(*L*12)	1.581 (3)	2.534 (5)	2.469 (5)	2.382 (5)
O(*E*21)	111.5 (2)	1.484 (3)	2.533 (6)	2.540 (4)
O(*E*22)	108.3 (2)	118.6 (2)	1.462 (4)	2.435 (5)
O(*L*23)	97.9 (2)	112.1 (2)	106.4 (2)	1.578 (3)

$P(3)O_4$ tetrahedron

P(3)	O(*L*23)	O(*E*31)	O(*E*32)	O(*L*34)
O(*L*23)	1.577 (4)	2.437 (5)	2.527 (5)	2.461 (5)
O(*E*31)	105.8 (2)	1.477 (4)	2.563 (4)	2.411 (6)
O(*E*32)	111.4 (2)	120.2 (2)	1.481 (3)	2.512 (4)
O(*L*34)	102.7 (2)	104.4 (2)	110.7 (2)	1.573 (4)

$P(4)O_4$ tetrahedron

P(4)	O(*L*14)	O(*L*34)	O(*E*41)	O(*E*42)
O(*L*14)	1.595 (3)	2.416 (5)	2.468 (4)	2.533 (3)
O(*L*34)	97.4 (1)	1.620 (3)	2.486 (4)	2.544 (4)
O(*E*41)	106.8 (1)	106.7 (2)	1.476 (3)	2.549 (4)
O(*E*42)	111.8 (2)	111.2 (2)	120.3 (2)	1.462 (3)

P(1)—O(*L*12)—P(2)	130.0 (2)	P(2)—P(1)—P(4)	110.26 (5)
P(2)—O(*L*23)—P(3)	137.0 (3)	P(1)—P(2)—P(3)	118.74 (4)
P(3)—O(*L*34)—P(4)	134.6 (1)	P(2)—P(3)—P(4)	105.65 (4)
P(4)—O(*L*14)—P(1)	136.4 (2)	P(1)—P(4)—P(3)	106.81 (4)

P(1)—P(2)	2.884 (1)	P(3)—P(4)	2.946 (1)
P(2)—P(3)	2.936 (1)	P(4)—P(1)	2.965 (1)

The second P_8O_{24} ring anion

$P(5)O_4$ tetrahedron

P(5)	O(*L*56)	O(*L*58)	O(*E*51)	O(*E*52)
O(*L*56)	1.598 (4)	2.424 (4)	2.501 (5)	2.508 (5)
O(*L*58)	98.6 (2)	1.600 (3)	2.441 (3)	2.517 (4)
O(*E*51)	108.9 (2)	104.9 (2)	1.476 (2)	2.582 (4)
O(*E*52)	109.5 (2)	110.0 (1)	122.3 (2)	1.472 (3)

$P(6)O_4$ tetrahedron

P(6)	O(*L*56)	O(*L*67)	O(*E*61)	O(*E*62)
O(*L*56)	1.589 (3)	2.454 (4)	2.551 (4)	2.436 (5)
O(*L*67)	100.4 (1)	1.606 (2)	2.469 (4)	2.537 (3)
O(*E*61)	112.9 (2)	106.6 (1)	1.471 (3)	2.573 (5)
O(*E*62)	104.5 (2)	110.0 (2)	120.6 (2)	1.490 (3)

$P(7)O_4$ tetrahedron

P(7)	O(*L*67)	O(*L*78)	O(*E*71)	O(*E*72)
O(*L*67)	1.590 (3)	2.454 (4)	2.455 (4)	2.536 (4)
O(*L*78)	99.7 (2)	1.619 (3)	2.522 (4)	2.519 (4)
O(*E*71)	106.3 (1)	109.0 (1)	1.477 (2)	2.564 (3)
O(*E*72)	111.2 (1)	108.6 (1)	120.1 (2)	1.482 (3)

$P(8)O_4$ tetrahedron

P(8)	O(*L*58)	O(*L*78)	O(*E*81)	O(*E*82)
O(*L*58)	1.595 (2)	2.434 (3)	2.524 (3)	2.521 (3)
O(*L*78)	99.5 (1)	1.595 (3)	2.524 (4)	2.492 (4)
O(*E*81)	110.2 (2)	110.2 (2)	1.482 (3)	2.541 (5)
O(*E*82)	109.8 (1)	107.9 (2)	117.7 (1)	1.486 (3)

P(5)—O(*L*56)—P(6)	136.5 (2)	P(8)—P(5)—P(6)	106.75 (4)
P(6)—O(*L*67)—P(7)	134.9 (1)	P(5)—P(6)—P(7)	103.72 (4)
P(7)—O(*L*78)—P(8)	126.3 (2)	P(6)—P(7)—P(8)	114.55 (4)
P(5)—O(*L*58)—P(8)	131.0 (1)	P(5)—P(8)—P(7)	119.87 (3)

P(5)—P(6)	2.960 (1)	P(7)—P(8)	2.868 (1)
P(6)—P(7)	2.952 (1)	P(8)—P(5)	2.908 (1)

The title compound was prepared in several stages. Firstly, the phosphoric acid $H_8P_8O_{24}$ was prepared from an aqueous solution of sodium *cyclo*-octaphosphate (Schülke, 1968*a*,*b*) using an ion-exchange resin (Amberlite IRN 77). The resulting acid was then neutralized by ammonium carbonate and the aqueous solution of $(NH_4)_8P_8O_{24}$ so obtained was added to an aqueous solution of telluric acid in stoichiometric ratio. Crystals of the title compound were obtained by slow evaporation of the resulting solution at room temperature.

During the data collection, a pseudo-body-centred distribution of the diffracted intensities was observed. This phenomenon is clearly explained by the results of the structure determination; in this atomic arrangement, the main components [$Te(OH)_6$ groups and two independent P_8O_{24} rings] are centred on $\pm(\frac{1}{4},\frac{1}{4},\frac{1}{4})$, $(0,0,\frac{1}{2})$ and $(\frac{1}{2},\frac{1}{2},0)$.

It was noticed that a pseudo-monoclinic unit cell (dimensions $a = 21.72$, $b = 11.06$, $c = 15.16$ A, $\beta = 112.46°$) can be derived from the triclinic one used for the structure determination. However, the angles α and γ could not be refined to values acceptably close to 90° with such a setting and careful examination of the intensity repartition did not reveal a possible monoclinic symmetry.

The crystal structure was solved using direct methods (Main, Lessinger, Woolfson, Germain & Declercq, 1977). Table 1 gives the final atomic coordinates and B_{eq} values for the non-H atoms of this arrangement. The corresponding data for the H atoms have been deposited. The figure was drawn using *STRUPLO* (Fischer, 1985).

Lists of structure factors, anisotropic thermal parameters, coordinates of the unique molecule, H-atom coordinates and main interatomic bond distances and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55533 (57 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: PA1019]

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Acta Cryst. (1993). C**49**, 363–365

Structure of a New Sodium Thiosulfate Hydrate

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(*Received* 13 *February* 1992; *accepted* 4 *September* 1992)

Abstract

A new crystal form of sodium thiosulfate hydrate with the stoichiometry $Na_2S_2O_3.\frac{2}{3}H_2O$ is reported.

Comment

During the synthesis of sodium dithionite ($Na_2S_2O_4$) following the 'formate process' (Ostertag *et al.*, 1979), a small amount of sodium thiosulfate was produced as a side product. The latter was removed from the sodium dithionite solid by washing with methanol at *ca* 323 K. On cooling the resulting methanol solution to room temperature, a white precipitate consisting of various crystalline forms of sodium thiosulfate was formed. In addition to the previously reported pentahydrate and anhydrous α-$Na_2S_2O_3$ forms, powder diffractometry showed an

0108-2701/93/020363-03$06.00