HAMILTON, W. C. (1959). *Acta Cryst.* **12**, 609–610.
HOWARD, T. & EVANS, J. R. (1960). *Z. Kristallogr.* **114**, 257–277.
HOWARD, T., EVANS, J. R. & BLOCK, S. (1966). *Inorg. Chem.* **5**, 1809–1814.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
KELMERS, A. D. (1961). *J. Inorg. Nucl. Chem.* **21**, 45–48.
SHELDRICK, G. M. (1976). *SHELX76*. A program for crystal structure determination. Univ. of Cambridge, England.
THÉOBALD, F. R. & THÉOBALD, J. G. (1984). *J. Phys. Chem. Solids*, **45**(6), 581–587.
TUDO, J. & JOLIBOIS, B. (1971). *C. R. Acad. Sci. Sér. C*, **273**, 466–468.

Acta Cryst. (1990). C**46**, 179–181

Crystal Chemistry of *cyclo*-Hexaphosphates. VI. Structure of Ammonium *cyclo*-Hexaphosphate Tellurate Dihydrate

BY M. T. AVERBUCH-POUCHOT AND A. DURIF

Laboratoire de Cristallographie, associé à l'Université J. Fourier, CNRS, 166 *X*, 38042 *Grenoble CEDEX, France*

(*Received* 10 *March* 1989; *accepted* 19 *May* 1989)

Abstract. $(NH_4)_6P_6O_{18}.Te(OH)_6.2H_2O$, M_r = 847·73, triclinic, $P\bar{1}$, a = 9·899 (4), b = 11·042 (7), c = 7·632 (9) Å, α = 109·53 (6), β = 106·74 (6), γ = 100·91 (4)°, V = 714·2 Å^3, Z = 1, D_x = 1·971 Mg m^{-3}, λ(Ag $K\bar{\alpha}$) = 0·5608 Å, μ = 0·790 mm^{-1}, F(000) = 426, T = 294 K, final R = 0·018 for 6013 observed reflections. Almost regular $Te(OH)_6$ octahedra and slightly distorted P_6O_{18} ring anions alternate in planes z = 0. These planes are interconnected by the ammonium groups and the water molecules through a three-dimensional network of hydrogen bonds. The water molecules are statistically located on two general positions. The hydrogen-bond scheme is described.

Introduction. Addition compounds between telluric acid and water-soluble phosphates have been extensively investigated by the authors. These adducts have been observed for almost all types of phosphates, condensed or not. A good review of the present state of this field has been recently reported by Boudjada (1985).

The title compound is the first example of a *cyclo*-hexaphosphate–tellurate.

Experimental. Crystals of the title compound can be prepared by slow evaporation at room temperature of an aqueous solution of telluric acid and ammonium *cyclo*-hexaphosphate with a stoichiometric ratio P/Te = 6. Crystals of $(NH_4)_6P_6O_{18}.Te(OH)_6.2H_2O$ appear as elongated monoclinic prisms.

Crystal size: 0·24 × 0·24 × 0·24 mm. Density not measured. Nonius CAD-4 diffractometer, graphite monochromator. 24 reflections (11·0 < θ < 15·0°) for refining unit-cell dimensions. ω scan, scan width: 1·20°, scan speed variable between 0·02 and 0·06° s^{-1}, total background measuring time: between 30 and 10 s. 9148 reflections collected, 3 < θ < 35°, ± h, ± k, l, $h_{\max}$ = 16, $k_{\max}$ = 20, $l_{\max}$ = 13. Two orientation ($63\bar{2}$ and $3\bar{7}\bar{1}$) and two intensity (361 and 633) control reflections without any significant variation. 8551 reflections obtained after averaging Friedel pairs ($R_{\rm int}$ = 0·01). Lorentz and polarization corrections, no absorption correction. Structure solved by direct methods (*MULTAN*77, Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1977). H atoms located by difference-Fourier syntheses. Anisotropic full-matrix least-squares refinements (on F), isotropic for H atoms. Unit weights. Final refinement cycles with 6013 reflections ($I > 9\sigma_I$). Final R = 0·018 (wR = 0·023), S = 0·498, max. Δ/σ = 0·05. Max. peak height in the final difference-Fourier synthesis: 0·684 e Å^{-3}. No extinction correction. For the total set of 8551 reflections the R value is 0·031. Scattering factors for neutral atoms and f', f'' from *International Tables for X-ray Crystallography* (1974). Enraf–Nonius (1977) *SDP* used for all calculations. Computer used: MicroVAXII.

Discussion. Table 1 reports the final atomic coordinates.* The $Te(OH)_6$ group is located around the inversion center at 0,0,0. As usually observed in this kind of compound it corresponds to an almost regular octahedron with O—Te—O angles ranging from 87·88 to 89·80° and Te—O distances varying from 1·877 to 1·931 Å.

---

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52257 (50 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

0108-2701/90/020179-03$03.00

Table 1. *Final atomic coordinates and* B_{eq}/B_{iso} *values*

Starred atoms have been refined isotropically. E.s.d.'s are given in parentheses.

$$B_{eq} = (4/3)\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}/B_{iso}(Å^2)
Te	0	0	0	1·183 (2)
P(1)	0·75105 (4)	0·52787 (3)	0·27314 (5)	1·681 (6)
P(2)	0·66720 (4)	0·75207 (3)	0·21783 (4)	1·545 (5)
P(3)	0·65136 (3)	0·28090 (3)	0·89719 (5)	1·644 (5)
O(*E*11)	0·3009 (1)	0·4534 (1)	0·5580 (2)	2·39 (2)
O(*E*12)	0·0876 (1)	0·4360 (1)	0·6841 (2)	2·94 (3)
O(*L*12)	0·6783 (1)	0·6015 (1)	0·1395 (2)	2·45 (2)
O(*L*13)	0·3319 (1)	0·6274 (1)	0·8800 (2)	2·32 (2)
O(*E*21)	0·6601 (1)	0·7958 (1)	1·0524 (1)	2·29 (2)
O(*E*22)	0·2173 (1)	0·1628 (1)	0·5797 (2)	2·61 (2)
O(*E*31)	0·6443 (1)	0·1437 (1)	0·8916 (2)	2·69 (2)
O(*E*32)	0·7623 (1)	0·3484 (1)	0·8370 (2)	2·80 (2)
O(*L*23)	0·4913 (1)	0·2767 (1)	0·7623 (1)	2·48 (2)
O(1)	0·8447 (1)	0·8448 (1)	0·7888 (1)	2·21 (2)
O(2)	0·0828 (1)	0·8785 (1)	0·0957 (2)	2·32 (2)
O(3)	0·1113 (1)	−0·0082 (1)	0·8338 (1)	2·30 (2)
N(1)	0·4756 (2)	0·3085 (2)	0·3657 (2)	2·59 (3)
N(2)	0·0884 (2)	0·4149 (1)	0·1799 (2)	2·46 (2)
N(3)	0·8944 (2)	0·1655 (1)	0·5479 (2)	2·65 (3)
O(*W*1)	0·4013 (2)	0·9033 (2)	0·7466 (3)	3·33 (4)
O(*W*2)	0·4324 (7)	0·9216 (6)	0·578 (3)	4·0 (2)
H(1)	0·171 (2)	0·152 (2)	0·322 (3)	1·1 (4)*
H(2)	0·161 (2)	0·883 (2)	0·065 (3)	1·5 (5)*
H(3)	0·818 (2)	0·941 (2)	0·120 (3)	1·6 (5)*
H(1N1)	0·425 (3)	0·279 (3)	0·225 (4)	2·7 (6)*
H(2N1)	0·510 (3)	0·235 (3)	0·375 (4)	2·6 (6)*
H(3N1)	0·418 (3)	0·343 (3)	0·432 (4)	3·3 (7)*
H(4N1)	0·457 (3)	0·618 (3)	0·592 (1)	2·5 (6)*
H(1N2)	0·149 (3)	0·411 (2)	0·281 (3)	2·1 (5)*
H(2N2)	0·031 (3)	0·450 (3)	0·208 (4)	3·6 (7)*
H(3N2)	0·141 (3)	0·476 (2)	0·153 (3)	2·2 (6)*
H(4N2)	0·061 (3)	0·338 (3)	0·098 (4)	3·3 (7)*
H(1N3)	0·060 (3)	0·747 (2)	0·402 (4)	2·5 (6)*
H(2N3)	0·899 (3)	0·143 (3)	0·652 (4)	2·6 (6)*
H(3N3)	0·811 (3)	0·162 (3)	0·502 (4)	3·1 (7)*
H(4N3)	0·911 (3)	0·105 (3)	0·443 (4)	3·5 (7)*
H(1*W*1)	0·480 (4)	0·982 (4)	0·806 (5)	4 (1)*
H(2*W*1)	0·380 (5)	0·892 (4)	0·841 (6)	5 (1)*

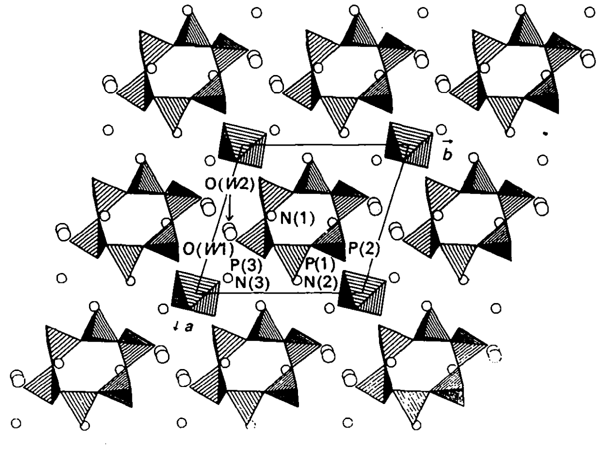

Fig. 1. Projection along the *c* axis of the atomic arrangement of $(NH_4)_6P_6O_{18}.Te(OH)_6.2H_2O$. The H atoms have been omitted.

Table 2. *Main interatomic distances* (Å) *and bond angles* (°) *in the atomic arrangement of* $(NH_4)_6P_6O_{18}.Te(OH)_6.2H_2O$

E.s.d.'s are given in parentheses.

The P_6O_{18} ring anion

$P(1)O_4$ tetrahedron

P(1)	O(*E*11)	O(*E*12)	O(*L*12)	O(*L*13)
O(*E*11)	1·487 (1)	2·561 (2)	2·539 (2)	2·452 (1)
O(*E*12)	119·42 (7)	1·479 (1)	2·508 (2)	2·534 (1)
O(*L*12)	110·41 (7)	108·83 (8)	1·603 (1)	2·462 (2)
O(*L*13)	105·20 (7)	110·79 (7)	100·51 (6)	1·5983 (9)

$P(2)O_4$ tetrahedron

P(2)	O(*L*12)	O(*E*21)	O(*E*22)	O(*L*23)
O(*L*12)	1·606 (1)	2·473 (2)	2·532 (1)	2·469 (2)
O(*E*21)	106·24 (6)	1·484 (1)	2·557 (2)	2·532 (2)
O(*E*22)	110·38 (7)	119·38 (7)	1·4773 (9)	2·498 (2)
O(*L*23)	100·67 (7)	110·21 (7)	108·35 (7)	1·602 (1)

$P(3)O_4$ tetrahedron

P(3)	O(*L*13)	O(*E*31)	O(*E*32)	O(*L*23)
O(*L*13)	1·602 (1)	2·465 (1)	2·544 (2)	2·500 (1)
O(*E*31)	105·70 (7)	1·489 (1)	2·561 (2)	2·525 (2)
O(*E*32)	111·36 (6)	119·37 (8)	1·477 (1)	2·483 (2)
O(*L*23)	102·49 (6)	109·37 (6)	107·27 (7)	1·604 (1)

P(1)—O(*L*12)—P(2)	127·31 (6)	P(2)—P(1)—P(3)	114·30 (2)
P(1)—O(*L*13)—P(3)	135·33 (9)	P(1)—P(2)—P(3)	115·18 (1)
P(2)—O(*L*23)—P(3)	132·40 (9)	P(1)—P(3)—P(2)	96·11 (1)

P(1)—P(2)	2·8758 (6)
P(1)—P(3)	2·9603 (4)
P(2)—P(3)	2·9334 (5)

The TeO_6 octahedron

Te—O(1)	1·9045 (8)	O(1)—Te—O(2)	87·88 (4)
Te—O(2)	1·931 (1)	O(1)—Te—O(3)	90·20 (4)
Te—O(3)	1·877 (1)	O(2)—Te—O(3)	91·37 (4)

Te—O(1)—H(1)	112 (1)
Te—O(2)—H(2)	103 (2)
Te—O(3)—H(3)	112 (2)

The NO_n polyhedra

N(1)—O(*E*11)	2·939 (2)	N(2)—O(*E*11)	2·877 (2)
N(1)—O(*E*11)	2·860 (2)	N(2)—O(*E*12)	2·795 (2)
N(1)—O(*L*13)	3·176 (2)	N(2)—O(*E*32)	3·281 (2)
N(1)—O(*E*21)	2·793 (1)	N(2)—O(*E*32)	2·812 (2)
N(1)—O(*L*23)	3·125 (2)	N(2)—O(1)	3·131 (2)
N(1)—O(1)	2·965 (2)	N(2)—O(2)	3·018 (1)
N(1)—O(*W*1)	2·833 (3)		
N(1)—O(*W*2)	2·975 (8)		

N(3)—O(*E*12)	2·877 (2)
N(3)—O(*E*22)	3·142 (2)
N(3)—O(*E*22)	3·289 (2)
N(3)—O(*E*32)	3·216 (2)
N(3)—O(2)	2·873 (2)
N(3)—O(*W*1)	2·903 (2)
N(3)—O(*W*2)	2·954 (7)

The hydrogen bonds

O(N)—H···O	O(N)—H	H···O	O(N)—H···O	O(N)···O
O(1)—H(1)···O(*E*22)	0·83 (2)	1·84 (2)	174 (2)	2·689 (2)
O(2)—H(2)···O(*E*31)	0·87 (3)	1·95 (3)	149 (2)	2·736 (2)
O(3)—H(3)···O(*E*21)	0·81 (2)	1·82 (2)	172 (3)	2·622 (1)
N(1)—H(1N1)···O(*E*21)	0·95 (2)	1·85 (2)	172 (3)	2·793 (2)
N(1)—H(2N1)···O(*W*2)	0·95 (3)	2·03 (3)	172 (3)	2·975 (8)
N(1)—H(3N1)···O(*E*11)	0·92 (3)	2·03 (3)	167 (3)	2·939 (2)
N(1)—H(4N1)···O(*E*11)	0·84 (2)	2·04 (3)	167 (3)	2·860 (2)
N(2)—H(1N2)···O(*E*11)	0·85 (3)	2·04 (2)	165 (2)	2·877 (2)
N(2)—H(2N2)···O(*E*12)	0·79 (3)	2·02 (3)	171 (2)	2·795 (2)
N(2)—H(3N2)···O(*E*32)	0·89 (3)	1·95 (3)	160 (2)	2·812 (2)
N(2)—H(4N2)···O(2)	0·80 (2)	2·25 (2)	160 (3)	3·018 (1)
N(3)—H(1N3)···O(*E*12)	0·88 (2)	2·02 (2)	164 (3)	2·877 (2)
N(3)—H(2N3)···O(2)	0·90 (3)	1·98 (3)	172 (2)	2·873 (2)
N(3)—H(3N3)···O(*W*1)	0·78	2·18 (2)	153 (3)	2·903 (2)
N(3)—H(3N3)···O(*W*2)	0·78	2·23 (3)	154 (3)	2·954 (7)
N(3)—H(4N3)···O(3)	0·93 (3)	1·95 (3)	156 (3)	2·826 (2)
O(*W*1)—H(1*W*1)···O(*E*31)	0·92 (3)	1·94 (4)	171 (4)	2·853 (2)
O(*W*1)—H(2*W*1)···O(*E*31)	0·85 (5)	2·27 (5)	172 (4)	3·112 (3)

The P_6O_{18} ring anion develops around the inversion center at $\frac{1}{2},\frac{1}{2},0$ and so is built up by only three independent corner-sharing PO_4 tetrahedra. If compared with other similar phosphoric groups having $\bar{1}$ internal symmetry it appears relatively little distorted. Here the P—O—P angles spread from 96·11 to 115·18° while in $Cs_6P_6O_{18}.6H_2O$, for instance, the same angles vary from 93·2 to 142·5° (Averbuch-Pouchot, 1989). The main geometrical features of these two groups are reported in Table 2.

During the structure determination the formula was originally thought to correspond to a tetrahydrate with two general positions occupied by water molecules, but during refinement very high thermal factors were observed for these water molecules and, in addition, an abnormally short distance between them. In fact, as already observed in $Na_2Cd_2P_6O_{18}.14H_2O$ (Averbuch-Pouchot, 1990), the water molecules are statistically distributed on two general positions denoted here as O(*W*1) and O(*W*2). After refinements of the occupancy rates of these two positions: O(*W*1) 0·783 (4), O(*W*2) 0·236 (4), the title compound appears to be really a dihydrate and the thermal factors decrease to values one can expect for this type of salt.

The main interatomic distances observed in this arrangement and the geometry of the hydrogen-bond scheme are reported in Table 2.

Fig. 1 is a projection along the *c* axis of this atomic arrangement, drawn using the *STRUPLO* program (Fischer, 1985).

References

AVERBUCH-POUCHOT, M. T. (1989). *C. R. Acad. Sci.* **308**(II), 1699–1702.

AVERBUCH-POUCHOT, M. T. (1990). *Acta Cryst.* **C46**, 10–13.

BOUDJADA, N. (1985). Thesis, Univ. of Grenoble, France.

Enraf–Nonius (1977). *Structure Determination Package*, version RSX11M. Enraf–Nonius, Delft, The Netherlands.

FISCHER, R. X. (1985). *J. Appl. Cryst.* **18**, 258–262.

International Tables for X-ray Crystallography (1974). Vol. IV, Table 2.2B. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1977). *MULTAN77. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Acta Cryst. (1990). **C46**, 181–186

Structural Phase Transitions in Chevrel Phases Containing Divalent Metal Cations. II. Structure Refinement of Triclinic $EuMo_6S_8$ and $BaMo_6S_8$ at Low Temperature

By F. Kubel* and K. Yvon†

Laboratoire de Cristallographie aux Rayons X, Université de Genève, 24 quai Ernest-Ansermet, CH-1211 Genève 4, Switzerland

(*Received* 8 *February* 1989; *accepted* 12 *May* 1989)

Abstract. Single-crystal X-ray (λ = 0·71069 Å) diffraction data above and below the lattice transformation temperature, T_l, are reported for $EuMo_6S_8$ (T_l = 110 K) and $BaMo_6S_8$ (T_l = 175 K): $EuMo_6S_8$, M_r = 984·1, T = 112 K: rhombohedral, $R\bar{3}$, a = 6·5378 (5) Å, α = 88·809 (11)°, V = 279·26 (7) Å^3, Z = 1, D_x = 5·862 Mg m^{-3}, μ = 13·33 mm^{-1}, F(000) = 443, R (wR) = 0·038 (0·075) for 25 variables and 977 independent reflections; T = 40 K: triclinic, $P\bar{1}$, a = 6·4692 (16), b = 6·5651 (13), c = 6·5986 (10) Å, α = 89·179 (15), β = 89·184 (16), γ = 88·009 (20)°, V = 280·02 (18) Å^3, Z = 1, D_x = 5·836 Mg m^{-3}, μ = 13·33 mm^{-1}, R (wR) = 0·058 (0·061) for 71 variables and 1637 independent reflections. $BaMo_6S_8$, M_r = 969·5, T = 177 K: rhombohedral, $R\bar{3}$, a = 6·6441 (6) Å, α = 88·562 (8)°, V = 293·02 (8) Å^3, Z = 1, D_x = 5·494 Mg m^{-3}, μ = 10·71 mm^{-1}, F(000) = 436, R (wR) = 0·060 (0·043) for 25 variables and 858 independent reflections; T = 173 K: triclinic, $P\bar{1}$, a = 6·5896 (4), b = 6·6500 (5), c = 6·6899 (5) Å, α = 88·731 (7), β = 88·818 (7), γ = 88·059 (7)°, V = 292·86 (7) Å^3, Z = 1, D_x = 5·497 Mg m^{-3}, μ = 10·71 mm^{-1}, R (wR) = 0·070 (0·060) for 30 variables and 1686 independent reflections. For $EuMo_6S_8$ the bond and contact distances of the triclinic modification differ from those of the rhombohedral modification by up to 0·0410 (14) (Mo—Mo), 0·032 (6) (Mo—S), 0·033 (3) (Eu—S) and 0·084 (4) Å (S—S). For $BaMo_6S_8$ they differ by up to 0·33 (2) (Mo—Mo), 0·021 (5) (Mo—S), 0·028 (4) (Ba—S) and 0·066 (6) Å (S—S). The cell volume of $EuMo_6S_8$ at the rhombohedral-to-triclinic phase transition increases by about 0·83 (15) Å^3 whereas that of $BaMo_6S_8$ remains constant within experimental resolution (0·2 Å^3).

Introduction. Chevrel phase sulfides MMo_6S_8 containing divalent metal cations such as M = Eu, Sr, Ba undergo structural phase transitions below room temperature (Baillif, Dunand, Muller & Yvon, 1981; Baillif, Junod, Lachal, Muller & Yvon, 1981; Lachal, Baillif, Junod & Muller, 1983). Structural parameters

---

* Now at Département de Chimie Minérale, Analytique et Appliquée, Université de Genève.

† Also at Institut für Physikalische und Theoretische Chemie, Technische Universität, Graz, Austria.

0108-2701/90/020181-06$03.00