

Structure of an Adduct Between Diammonium Dihydrogendiphosphate and Telluric Acid: $(\text{NH}_4)_2\text{H}_2\text{P}_2\text{O}_7 \cdot \text{Te}(\text{OH})_6$

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Abstract. Telluric acid–diammonium dihydrogendiphosphate (1/1), $\text{Te}(\text{OH})_6 \cdot (\text{NH}_4)_2\text{H}_2\text{P}_2\text{O}_7$, $M_r = 441.677$, monoclinic, $P2_1/n$, $a = 7.651$ (2), $b = 21.790$ (10), $c = 6.689$ (2) Å, $\beta = 113.85$ (3)°, $V = 1020$ (1) Å³, $Z = 4$, $D_x = 2.876$ Mg m⁻³, $\lambda(\text{Ag } K\alpha) = 0.5608$ Å, $\mu = 1.766$ mm⁻¹, $F(000) = 864$, $T = 294$ K, final $R = 0.033$ for 3602 reflections. The title compound is the second example of an adduct between telluric acid and a diphosphate. Thick layers containing infinite $[\text{H}_2\text{P}_2\text{O}_7]_n$ chains and layers of $\text{Te}(\text{OH})_6$ octahedra alternate perpendicular to the b axis. The hydrogen-bond scheme which includes very short bonds inside the $[\text{H}_2\text{P}_2\text{O}_7]_n$ chains is described. Crystal data for the isotypic Rb salt are given.

Introduction. During the past 20 years the authors have characterized a great number of addition compounds between telluric acid and various alkali phosphates, condensed or not. A good review of the present state of crystal chemistry of this class of adducts was recently given by Boudjada (1985). The main feature of these compounds is the coexistence within the atomic arrangement of both $\text{Te}(\text{OH})_6$ groups and phosphoric anions as independent units (not sharing O atoms). Among this important class of addition compounds $\text{K}_3\text{HP}_2\text{O}_7 \cdot \text{Te}(\text{OH})_6 \cdot \text{H}_2\text{O}$ (Averbuch-Pouchot & Durif, 1983) was up to now the only one involving a diphosphate group. In the present work we report the chemical preparation and crystal structure determination for the second example of coexistence of $\text{Te}(\text{OH})_6$ octahedra and diphosphate groups in an atomic arrangement: $\text{Te}(\text{OH})_6 \cdot (\text{NH}_4)_2\text{H}_2\text{P}_2\text{O}_7$.

The corresponding Rb salt, $\text{Te}(\text{OH})_6 \cdot \text{Rb}_2\text{H}_2\text{P}_2\text{O}_7$, is isotypic, with the following unit-cell dimensions: $a = 7.652$ (2), $b = 21.758$ (10), $c = 6.674$ (2) Å, $\beta = 114.12$ (5)°.

Experimental. Stout prismatic crystals of $\text{Te}(\text{OH})_6 \cdot (\text{NH}_4)_2\text{H}_2\text{P}_2\text{O}_7$ can be easily obtained by slow evaporation at room temperature of an aqueous solution prepared with the stoichiometric ratio of the

two components. Crystal size $0.48 \times 0.24 \times 0.35$ mm. Density not measured. Philips PW1100 diffractometer, graphite monochromator. 18 reflections ($10.0 < \theta < 16.0^\circ$) for refining unit-cell dimensions. ω scan, scan width 1.20° , scan speed $0.03^\circ \text{ s}^{-1}$, total background measuring time 10 s. 4592 non-zero reflections among 6525 scanned reflections collected ($3 < \theta < 30.0^\circ$), 4304 unique reflections after averaging $\pm h, k, l$; $h_{\text{max}} = 13$, $k_{\text{max}} = 38$, $l_{\text{max}} = 11$. Two orientation and intensity control reflections (440 and $\bar{4}40$) measured every 4 h show no significant variation. Lorentz and polarization corrections, no absorption correction.

Crystal structure solved using a direct method (*MULTAN77*: Main, Lessinger, Woolfson, Germain & Declercq, 1977) for heavy atoms and successive Fourier syntheses. H atoms located by difference Fourier syntheses. Anisotropic full-matrix least-squares refinement (on F), isotropic for H atoms. Unit weights. Scattering factors for neutral atoms and f' , f'' from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B). Enraf-Nonius (1977) *SDP* used for all calculations on a MicroVAX II computer. Drawings prepared using the program *STRUPLO84* (Fischer, 1985). No secondary-extinction correction. Results after final refinements with 3602 reflections [$I > 4\sigma(I)$]: final $R = 0.033$ ($wR = 0.037$), $S = 1.219$, maximum $\Delta/\sigma = 0.05$, maximum peak height in the final difference Fourier synthesis = $1.089 \text{ e } \text{Å}^{-3}$. Table 1 reports the final atomic coordinates with equivalent isotropic temperature factors for non-H atoms and isotropic temperature factors for H atoms.*

Discussion. The main interatomic distances and bond angles observed in the present atomic arrangement are reported in Table 2.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54864 (31 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: PA0258]

Table 1. Final atomic coordinates and isotropic temperature factors (Å²)

Equivalent isotropic temperature factors for non-H atoms;
 $B_{eq} = (4/3) \sum \beta_i a_i^2$.

| | x | y | z | B_{eq}/B_{iso} |
|--------|------------|-------------|-------------|------------------|
| Te | 0.0 | 0.0 | 0.0 | 1.336 (3) |
| P(1) | 0.5303 (1) | 0.78307 (4) | 0.0156 (1) | 1.77 (1) |
| P(2) | 0.6269 (1) | 0.87860 (3) | 0.3455 (1) | 1.55 (1) |
| O(1) | 0.2736 (3) | 0.0041 (1) | 0.1386 (4) | 2.34 (4) |
| O(2) | 0.5283 (3) | 0.5602 (1) | 0.3058 (4) | 2.41 (4) |
| O(3) | 0.0070 (3) | 0.9349 (1) | 0.1943 (4) | 2.48 (4) |
| O(E11) | 0.8934 (4) | 0.6882 (1) | 0.3071 (4) | 2.75 (5) |
| O(E21) | 0.4441 (3) | 0.7479 (1) | 0.1443 (4) | 2.52 (4) |
| O(E31) | 0.6798 (4) | 0.7445 (1) | -0.0341 (4) | 2.54 (5) |
| O(E12) | 0.7366 (3) | 0.4315 (1) | 0.1111 (4) | 2.09 (4) |
| O(E22) | 0.4202 (3) | 0.8946 (1) | 0.2678 (4) | 2.64 (5) |
| O(E32) | 0.6820 (3) | 0.8359 (1) | 0.5498 (4) | 2.46 (4) |
| O(L12) | 0.6626 (3) | 0.8371 (1) | 0.1664 (3) | 2.08 (4) |
| N(1) | 0.5767 (4) | 0.6837 (1) | 0.5463 (5) | 2.36 (5) |
| N(2) | 0.6392 (4) | 0.0666 (2) | 0.3292 (5) | 2.90 (6) |
| H(1N1) | 0.056 (7) | 0.792 (3) | 0.937 (8) | 3 (1) |
| H(2N1) | 0.835 (3) | 0.06 (1) | 0.168 (9) | 6 (2) |
| H(3N1) | 0.078 (8) | 0.792 (3) | 0.137 (9) | 3 (1) |
| H(4N1) | 0.507 (9) | 0.339 (3) | 0.43 (1) | 5 (2) |
| H(1N2) | 0.52 (1) | 0.042 (3) | 0.25 (1) | 6 (2) |
| H(2N2) | 0.89 (1) | 0.577 (4) | 0.04 (1) | 6 (2) |
| H(3N2) | 0.73 (1) | 0.050 (4) | 0.31 (1) | 7 (2) |
| H(4N2) | 0.629 (9) | 0.102 (3) | 0.25 (1) | 5 (2) |
| H(1) | 0.317 (8) | 0.963 (3) | 0.177 (9) | 4 (2) |
| H(2) | 0.062 (8) | 0.052 (3) | 0.325 (9) | 3 (1) |
| H(3) | 0.89 (1) | 0.938 (3) | 0.25 (1) | 6 (2) |
| H(P1) | 0.777 (8) | 0.221 (3) | 0.456 (9) | 4 (2) |
| H(P2) | 0.206 (8) | 0.194 (3) | 0.423 (9) | 3 (1) |

Table 2. Main interatomic distances (Å), bond angles (°) and hydrogen-bond geometry (Å, °)

| P ₂ O ₇ group | | | | | | | |
|-------------------------------------|-----------|-------------------|-----------|-----------|-----------|------------|---------|
| P(1)O ₄ tetrahedron | | | | | | | |
| P(1) | O(E11) | O(E21) | O(E31) | O(L12) | | | |
| O(E11) | 1.501 (2) | 2.544 (4) | 2.490 (4) | 2.514 (3) | | | |
| O(E21) | 116.5 (1) | 1.491 (3) | 2.534 (4) | 2.529 (4) | | | |
| O(E31) | 108.8 (1) | 112.3 (1) | 1.560 (3) | 2.456 (4) | | | |
| O(L12) | 107.6 (1) | 109.1 (1) | 101.4 (1) | 1.613 (2) | | | |
| P(2)O ₄ tetrahedron | | | | | | | |
| P(2) | O(E12) | O(E22) | O(E32) | O(L12) | | | |
| O(E12) | 1.502 (2) | 2.545 (3) | 2.533 (4) | 2.472 (3) | | | |
| O(E22) | 116.3 (1) | 1.493 (2) | 2.480 (3) | 2.548 (4) | | | |
| O(E32) | 111.5 (1) | 108.5 (2) | 1.563 (2) | 2.508 (3) | | | |
| O(L12) | 105.1 (1) | 110.3 (1) | 104.4 (1) | 1.610 (3) | | | |
| P(1)—P(2) | 2.903 (1) | P(1)—O(E31)—H(P1) | 113 (6) | | | | |
| P(1)—O(L12)—P(2) | 128.5 (2) | P(2)—O(E32)—H(P2) | 116 (4) | | | | |
| NO _n polyhedra | | | | | | | |
| N(1)O ₁₀ polyhedron | | | | | | | |
| N(1)—O(2) | 3.080 (4) | N(1)—O(E21) | 2.830 (4) | | | | |
| N(1)—O(3) | 2.894 (4) | N(1)—O(E21) | 3.010 (4) | | | | |
| N(1)—O(E11) | 3.402 (5) | N(1)—O(E31) | 2.909 (4) | | | | |
| N(1)—O(E31) | 3.262 (4) | N(1)—O(E32) | 3.411 (4) | | | | |
| N(1)—O(E22) | 2.978 (4) | N(1)—O(E32) | 3.496 (3) | | | | |
| N(2)O ₆ polyhedron | | | | | | | |
| N(2)—O(1) | 2.903 (4) | N(2)—O(2) | 3.027 (5) | | | | |
| N(2)—O(3) | 3.242 (3) | N(2)—O(E11) | 2.780 (4) | | | | |
| N(2)—O(E12) | 3.071 (4) | N(2)—O(E22) | 3.029 (5) | | | | |
| Te(OH) ₆ group | | | | | | | |
| Te—O(1) | 1.919 (2) | Te—O(1)—H(1) | 106 (4) | | | | |
| Te—O(2) | 1.919 (3) | Te—O(2)—H(2) | 106 (4) | | | | |
| Te—O(3) | 1.909 (2) | Te—O(3)—H(3) | 112 (4) | | | | |
| O(N)—H...O | | | | | | | |
| N(1)—H(1N1)...O(E21) | 0.87 (6) | H...O | 1.99 (5) | O(N)—O | 2.830 (4) | O(N)—H...O | 163 (5) |
| N(1)—H(1N1)...O(E22) | 0.78 (7) | | 2.28 (6) | | 2.978 (3) | | 148 (7) |
| N(1)—H(3N1)...O(E31) | 0.80 (6) | | 2.17 (6) | | 2.909 (4) | | 154 (5) |
| N(1)—H(4N1)...O(3) | 0.87 (7) | | 2.24 (7) | | 2.894 (4) | | 132 (6) |
| N(2)—H(1N2)...O(1) | 1.03 (6) | | 1.88 (7) | | 2.903 (4) | | 171 (7) |
| N(2)—H(2N2)...O(E22) | 0.99 (9) | | 2.04 (8) | | 3.029 (5) | | 175 (6) |
| N(2)—H(3N2)...O(2) | 0.85 (9) | | 2.28 (9) | | 3.027 (5) | | 148 (7) |
| N(2)—H(2N2)...O(E11) | 0.94 (7) | | 1.90 (7) | | 2.780 (4) | | 155 (7) |
| O(1)—H(1)...O(E22) | 0.95 (6) | | 1.68 (6) | | 2.628 (4) | | 173 (4) |
| O(2)—H(2)...O(E12) | 0.89 (5) | | 1.87 (5) | | 2.710 (3) | | 157 (6) |
| O(3)—H(3)...O(E12) | 1.06 (9) | | 1.64 (9) | | 2.672 (4) | | 164 (6) |
| O(E31)—H(P1)...O(E11) | 0.71 (6) | | 1.86 (5) | | 2.523 (3) | | 156 (7) |
| O(E32)—H(P2)...O(E21) | 1.03 (6) | | 1.58 (6) | | 2.594 (4) | | 168 (6) |

The [H₂P₂O₇]²⁻ group. The diphosphate anion observed in this arrangement has no internal symmetry and so is built by two independent PO₄ tetrahedra. The averages of the P—O distances in the two tetrahedra are identical (1.541 Å). Among the set of P—O distances one can distinguish three types of values: the longest ones (1.613 and 1.610 Å) corresponding to the P—O—P bonding, the two intermediate ones (1.560 and 1.563 Å) corresponding to the P—OH bonds, and the shortest ones ranging from 1.491 to 1.502 Å for the four P—O bonds. These phosphoric groups, interconnected by strong hydrogen bonds, assemble themselves so as to build infinite chains spreading in thick layers perpendicular to the *b* direction ($z = \frac{1}{4}$ and $\frac{3}{4}$). In the crystal chemistry of dihydrogendiphosphates it is commonly observed that this type of linkage through strong hydrogen bonds leads, most of the time, to the formation of infinite chains and sometimes infinite ribbons. Chains similar to those observed in the title compound have been described for K₂H₂P₂O₇ (Larbot, 1971; Larbot, Duran, Norbert & Cot, 1983), (NH₄)₂H₂P₂O₇ (Averbuch-Pouchot & Durif, 1992a) and (NH₃C₂H₄OH)₂H₂P₂O₇ (Averbuch-Pouchot & Durif, 1992b), while ribbons have been observed for the Ag salt Ag₂H₂P₂O₇ (Averbuch-Pouchot & Durif, 1992c). Fig. 1 is a projection along the *b* axis of a section of that atomic arrangement (0.05 < *y* < 0.45) showing the development of two of these chains crossing the unit cell.

The Te(OH)₆ group. The Te atom is located on the inversion centre at 0,0,0. As is usual, TeO₆ appears

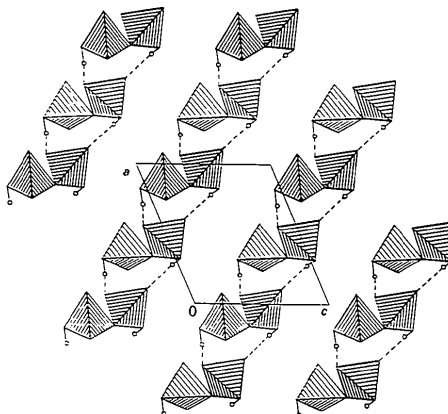


Fig. 1. Projection along the *b* axis of a layer of phosphoric groups showing the organization of the [H₂P₂O₇]²⁻_n chains. The ammonium groups lining the represented layer have been omitted. (0.05 < *y* < 0.45.)

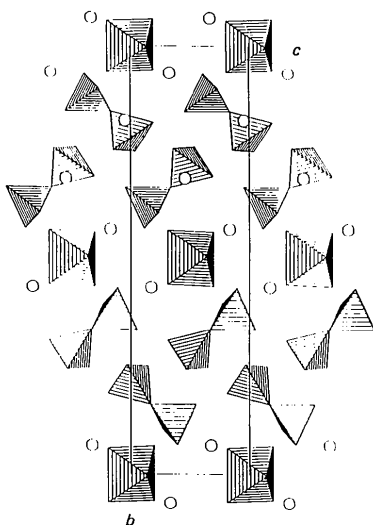


Fig. 2. Projection along the *a* direction of the atomic arrangement of $\text{Te}(\text{OH})_6 \cdot (\text{NH}_4)_2\text{H}_2\text{P}_2\text{O}_7$. Hatched octahedra represent the $\text{Te}(\text{OH})_6$ groups and empty circles are the NH_4 groups. H atoms have been omitted for clarity.

as an almost regular octahedron with, in the present study, $\text{Te}-\text{O}$ distances ranging from 1.909 to 1.919 Å and $\text{Te}-\text{O}-\text{H}$ angles varying from 106 to 112°. As shown by Fig. 2 these $\text{Te}(\text{OH})_6$ groups are located in planes $y=0$ and $\frac{1}{2}$ and so form layers alternating with the phosphoric ones.

The $(\text{NH}_4)_n$ polyhedra. The two NH_4 groups appear as moderately distorted tetrahedra with $\text{N}-\text{H}$ distances ranging from 0.78 to 0.87 Å in $\text{N}(1)\text{H}_4$ and from 0.85 to 1.03 Å in $\text{N}(2)\text{H}_4$. $\text{H}-\text{N}-\text{H}$ angles spread from 96 to 127° in the first group and from 96 to 133° in the second with, in

both cases, an average value of 109°. Within a range of 3.50 Å $\text{N}(1)\text{H}_4$ has ten O neighbours while $\text{N}(2)\text{H}_4$ has only six.

The hydrogen bonds. Among the main geometrical features of the hydrogen-bond network reported in Table 2 it must be noted that all the hydrogen bonds involving H atoms of the $\text{Te}(\text{OH})_6$ or NH_4 groups are classical with $\text{N}-\text{O}$ or $\text{O}-\text{O}$ distances ranging from 2.628 to 3.029 Å, while those connecting the $\text{P}_2\text{O}_7\text{H}_2^{2-}$ groups correspond to much shorter distances (2.523 and 2.594 Å), comparable to the $\text{O}-\text{O}$ distances inside a PO_4 tetrahedron. This fact explains the formation of $[\text{P}_2\text{O}_7\text{H}_2^{2-}]_n$ chains or ribbons commonly observed in the dihydrogendiphosphates. Such entities are today sometimes designated as 'macroanions'.

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Hydrothermal Synthesis and Structures of Two Layered Dioxovanadium(V) Phosphates $A(\text{VO}_2)\text{PO}_4$ ($A = \text{Ba}, \text{Sr}$)

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Abstract. Barium dioxovanadium(V) phosphate, $\text{Ba}(\text{VO}_2)\text{PO}_4$, $M_r = 315.256$, monoclinic, $P2_1/c$, $a =$

5.616 (2), $b = 10.062$ (1), $c = 8.727$ (1) Å, $\beta = 90.90$ (2)°, $V = 493.1$ (2) Å³, $Z = 4$, $D_x = 4.247$ g cm⁻³, $\lambda(\text{Mo K}\alpha) = 0.70930$ Å, $\mu = 100.49$ cm⁻¹, $F(000) = 568$, $T = 297$ K, $R = 0.0239$

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