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# $(NH_4)_4P_4O_{12} \cdot 2Te(OH)_6 \cdot 2H_2O$, the First Example of a Tetrametaphosphate-Tellurate

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Ammonium tetrametaphosphate-tellurate dihydrate, $(NH_4)_4P_4O_{12} \cdot 2Te(OH)_6 \cdot 2H_2O$, is triclinic with the following unit cell dimensions: $a = 11.845(6)$, $b = 8.554(5)$, $c = 7.433(5)$ Å, $\alpha = 66.28(5)$, $\beta = 95.91(5)$, $\gamma = 76.00(5)°$ space group: $P\bar{1}$ and $Z = 1$. The crystal structure has been determined with a final $R$ value of 0.021. As in the previously described phosphate-tellurates, monophosphate-tellurate and trimetaphosphate-tellurates, the phosphoric anion (here the $P_4O_{12}$ ring) is independent of the octahedral $Te(OH)_6$ group. A complete pattern of the hydrogen bonds is given.

## Introduction

A good number of phosphate-tellurates have already been described. Up to now they were distributed in two main classes: monophosphate-tellurates (*1–5*) and trimetaphosphate-tellurates (*6–8*). A common feature for all these compounds is the coexistence in the same atomic arrangement of two different kinds of anions: a phosphoric anion and a $TeO_6$ octahedral group, as independent units.

In monophosphate-tellurates the phosphoric group is the $PO_4$ tetrahedron whereas in trimetaphosphate-tellurates it is the $P_3O_9$ ring.

In the present work we describe the first example of a tetrametaphosphate-tellurate: $(NH_4)_4P_4O_{12} \cdot 2Te(OH)_6 \cdot 2H_2O$.

## Chemical Preparation and Crystal Chemistry

Single crystals up to 5 mm in length are readily grown by evaporating at room temperature a solution of ammonium tetrametaphosphate and telluric acid in the proper ratio. Crystals are stout triclinic prisms.

The ammonium tetrametaphosphate was prepared by neutralization of tetrametaphosphoric acid by ammonium dicarbonate and precipitation of $(NH_4)_4P_4O_{12}$ by methyl alcohol.

X-Ray diffraction studies by film techniques show this compound to be triclinic. Refinement of the four circle diffractometer angular data leads to the following values for the unit cell dimensions: $a =$



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11.845(6), $b$ = 8.554(5), $c$ = 7.433(5) Å, $\alpha$ = 66.28(5), $\beta$ = 95.91(5), $\gamma$ = 76.00(5)°, with $Z$ = 1 and $D_x$ = 2.250.

Crystal structure determination confirms that the correct space group is the centrosymmetrical $P\bar{1}$.

This compound is stable at room temperature.

## Crystal Structure Determination

The crystal used for the diffraction data collection was a prism fragment approximately cubic (0.32 × 0.32 × 0.40 mm³). From 3 to 25° ($\theta$) 5167 independent reflections were measured using an $\omega$-scan. Each reflection was scanned at constant speed (0.02°/sec) in an angular domain of 1.40°. Background was measured during 10 sec at each extremity of this domain. No significant variation of the intensity standard reflections ($\bar{8}20$ and $82\bar{0}$) was observed during the data collection. Being given the radiation used ($\lambda Ag K_\alpha$: 0.5608 Å) no absorption correction was applied.

The crystal structure was solved by conventional methods: study of a three-dimensional Patterson function followed by successive Fourier syntheses. In order to save time, a set of 3713 reflections such that $F_o > 2\sigma(F_o)$ was extracted from the initial complete set of 5167 reflections and used for the refinement cycles.

With a few least-squares refinement cycles, taking into account anisotropic thermal factors, the conventional $R$ value decreased to 0.022. At this stage a difference Fourier synthesis clearly revealed all the hydrogen atoms. Subsequent least-squares refinement cycles taking into account the hydrogen atoms with their isotropic thermal factors led to a final $R$ value of 0.021. With the final coordinates this same $R$ factor is 0.026 for the complete set of 5167 reflections.

Table I reports the final atomic coordinates and Table II the anisotropic thermal coefficients for the nonhydrogen atoms. Throughout this work a unitary weighting scheme was used. Atomic scattering factors corresponding to neutral atoms (*9*) were used. The S.D.P. system (*10*) was used for Fourier syntheses, least-squares refinement, and bond distances calculations.

TABLE I

ATOMIC COORDINATES FOR $(NH_4)_4P_4O_{12} \cdot 2Te(OH)_6 \cdot 2H_2O$[a]

| Atom | $x(\sigma)$ | $y(\sigma)$ | $z(\sigma)$ | $B_{eq}$ |
|---|---|---|---|---|
| Te | 0.16716(2) | 0.22073(2) | 0.17234(3) | 1.25 |
| P(1) | 0.41044(6) | 0.70065(8) | 0.0467(1) | 1.32 |
| P(2) | 0.38906(6) | 0.58965(9) | 0.7185(1) | 1.38 |
| O(1) | 0.2224(2) | 0.1315(3) | 0.9815(3) | 1.99 |
| O(2) | 0.0102(2) | 0.2265(3) | 0.0942(4) | 2.11 |
| O(3) | 0.1721(2) | −0.0082(3) | 0.3725(4) | 2.20 |
| O(4) | 0.8519(2) | 0.5441(3) | 0.0287(3) | 1.97 |
| O(5) | 0.3243(2) | 0.1977(3) | 0.2688(3) | 2.36 |
| O(6) | 0.1096(2) | 0.3212(3) | 0.3509(3) | 2.36 |
| O(L1) | 0.6285(2) | 0.3998(3) | 0.0739(3) | 1.75 |
| O(L2) | 0.4783(2) | 0.5323(3) | 0.2452(3) | 1.78 |
| O(E11) | 0.3027(2) | 0.7892(3) | 0.1049(3) | 2.16 |
| O(E12) | 0.4915(2) | 0.8061(3) | 0.9435(3) | 2.02 |
| O(E21) | 0.6144(2) | 0.2355(3) | 0.4415(3) | 2.19 |
| O(E22) | 0.6939(2) | 0.5108(3) | 0.3015(3) | 1.95 |
| O(W) | 0.1648(2) | 0.6070(3) | 0.3474(4) | 2.54 |
| N(1) | 0.5801(3) | 0.8363(4) | 0.3550(4) | 2.20 |
| N(2) | 0.9562(3) | 0.8846(4) | 0.2814(4) | 2.53 |
| | | | | $B_{iso}$ |
| H(1) | 0.245(5) | 0.006(6) | 0.056(7) | 4.5 |
| H(2) | 0.044(4) | 0.671(5) | 0.903(6) | 2.5 |
| H(3) | 0.247(4) | 0.931(6) | 0.402(7) | 4.1 |
| H(4) | 0.198(4) | 0.456(5) | 0.885(6) | 2.6 |
| H(5) | 0.375(3) | 0.204(5) | 0.179(6) | 2.0 |
| H(6) | 0.129(4) | 0.418(6) | 0.339(7) | 4.2 |
| H(1W) | 0.199(5) | 0.563(6) | 0.473(7) | 4.7 |
| H(2W) | 0.209(4) | 0.665(6) | 0.252(7) | 4.4 |
| H(1N1) | 0.385(4) | 0.235(6) | 0.684(7) | 3.5 |
| H(2N1) | 0.512(4) | 0.808(5) | 0.404(6) | 3.0 |
| H(3N1) | 0.372(4) | 0.150(6) | 0.557(7) | 4.2 |
| H(4N1) | 0.421(4) | 0.063(6) | 0.732(7) | 4.0 |
| H(1N2) | 0.031(4) | 0.014(6) | 0.756(7) | 3.6 |
| H(2N2) | 0.017(4) | 0.815(6) | 0.286(7) | 3.8 |
| H(3N2) | 0.075(4) | 0.124(6) | 0.631(7) | 4.4 |
| H(4N2) | 0.090(5) | 0.104(7) | 0.805(8) | 6.4 |

[a] $B_{eq}$ are given for nonhydrogen atoms, $B_{iso}$ for hydrogen atoms.

## Structure Description

As in the described phosphate-tellurates one observes in this arrangement the coex-

TABLE II

ANISOTROPIC THERMAL PARAMETERS FOR NONHYDROGEN ATOMS[a]

| Atoms | $\beta(1,1)$ | $\beta(2,2)$ | $\beta(3,3)$ | $\beta(1,2)$ | $\beta(1,3)$ | $\beta(2,3)$ |
|---|---|---|---|---|---|---|
| Te | 0.00233(1) | 0.00455(1) | 0.00707(2) | −0.00125(2) | −0.00047(2) | −0.00344(3) |
| P(1) | 0.00257(4) | 0.00435(7) | 0.0078(1) | −0.00037(9) | 0.0003(1) | −0.0043(1) |
| P(2) | 0.00265(4) | 0.00548(8) | 0.0062(1) | −0.00119(9) | −0.0010(1) | −0.0024(1) |
| O(1) | 0.0043(2) | 0.0064(2) | 0.0104(4) | 0.0007(3) | −0.0013(4) | −0.0071(4) |
| O(2) | 0.0025(1) | 0.0067(2) | 0.0166(5) | −0.0009(3) | −0.0032(4) | −0.0067(5) |
| O(3) | 0.0033(1) | 0.0062(3) | 0.0129(5) | −0.0020(3) | −0.0018(4) | 0.0020(6) |
| O(4) | 0.0041(1) | 0.0049(2) | 0.0116(4) | −0.0009(3) | 0.0029(4) | −0.0018(5) |
| O(5) | 0.0030(1) | 0.0154(4) | 0.0098(4) | −0.0059(3) | −0.0017(4) | −0.0075(6) |
| O(6) | 0.0064(2) | 0.0100(3) | 0.0133(4) | −0.0077(3) | 0.0076(4) | −0.0130(5) |
| O(L1) | 0.0039(1) | 0.0086(2) | 0.0083(3) | −0.0038(3) | 0.0011(4) | −0.0083(4) |
| O(L2) | 0.0029(1) | 0.0076(3) | 0.0077(3) | 0.0001(3) | −0.0008(4) | −0.0026(5) |
| O(E11) | 0.0041(1) | 0.0065(2) | 0.0145(4) | 0.0011(3) | 0.0036(4) | −0.0086(5) |
| O(E12) | 0.0039(1) | 0.0069(2) | 0.0117(4) | −0.0038(3) | 0.0002(4) | −0.0033(5) |
| O(E21) | 0.0039(1) | 0.0068(3) | 0.0099(4) | −0.0008(3) | −0.0016(4) | 0.0022(6) |
| O(E22) | 0.0037(1) | 0.0097(3) | 0.0097(4) | −0.0044(3) | −0.0011(4) | −0.0079(5) |
| O(W) | 0.0056(2) | 0.0121(3) | 0.0114(4) | −0.0069(4) | −0.0008(5) | −0.0091(5) |
| N(1) | 0.0044(2) | 0.0096(3) | 0.0105(4) | −0.0031(4) | −0.0003(5) | −0.0068(6) |
| N(2) | 0.0051(2) | 0.0139(4) | 0.0115(5) | −0.0081(4) | 0.0023(5) | −0.0096(7) |

[a] The formula used for the calculation is: $T = \beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl$.

istence of two independent types of anions, $P_4O_{12}$ rings and $Te(OH)_6$ groups.

Figure 1 gives a projection of this arrangement on the $(b, c)$ plane. Hydrogen atoms of the $Te(OH)_6$ groups are not represented.

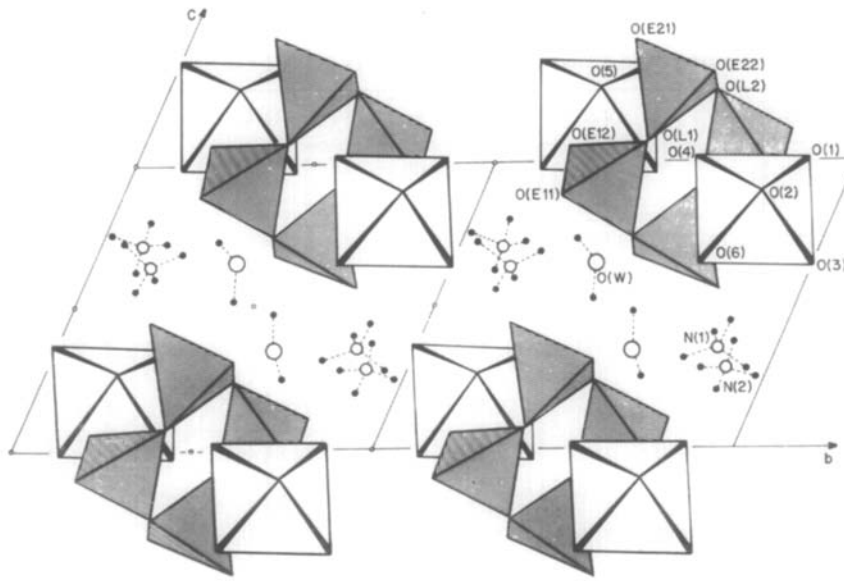


FIG. 1. Projection along the $a$ axis of the atomic arrangement of $(NH_4)_4P_4O_{12} \cdot 2Te(OH)_6 \cdot 2H_2O$. Hydrogen atoms bonded to the oxygen atoms of the $TeO_6$ groups are not represented here.

TABLE III

MAIN INTERATOMIC DISTANCES AND BOND ANGLES IN THE $P_4O_{12}$ RING

| | | $P(1)O_4$ tetrahedron | | |
|---|---|---|---|---|
| P(1) | O(L1) | O(E11) | O(E12) | O(L2) |
| O(L1) | 1.575(2) | 2.521(3) | 2.549(3) | 2.341(3) |
| O(E11) | 109.3(1) | 1.516(2) | 2.652(4) | 2.396(3) |
| O(E12) | 110.4(1) | 121.1(1) | 1.529(2) | 2.561(3) |
| O(L2) | 97.3(1) | 103.1(1) | 113.0(1) | 1.543(2) |
| | | $P(2)O_4$ tetrahedron | | |
| P(2) | O(L1) | O(E21) | O(E22) | O(L2) |
| O(L1) | 1.613(2) | 2.566(3) | 2.397(3) | 2.593(3) |
| O(E21) | 112.2(1) | 1.477(2) | 2.610(3) | 2.393(3) |
| O(E22) | 101.3(1) | 123.6(1) | 1.485(2) | 2.494(3) |
| O(L2) | 108.2(1) | 102.6(1) | 108.4(1) | 1.588(2) |
| P(1)–P(2) | 2.961(1) | | P(1)–O(L1)–P(2) | 136.5(2) |
| P(1)–P(2) | 2.767(1) | | P(1)–O(L2)–P(2) | 124.1(2) |
| P(1)–P(2)–P(1) | 86.64(3) | | P(2)–P(1)–P(2) | 93.36(3) |

TABLE IV

MAIN INTERATOMIC DISTANCES AND BOND ANGLES IN THE $Te(OH)_6$ GROUP[a]

| Te | O(1) | O(2) | O(3) | O(4) | O(5) | O(6) |
|---|---|---|---|---|---|---|
| O(1) | 1.961(2) | 2.771(4) | 2.853(4) | 2.668(3) | 2.667(3) | 3.905(3) |
| O(2) | 92.5(1) | 1.873(2) | 2.442(3) | 2.788(3) | 3.728(3) | 2.632(4) |
| O(3) | 95.1(1) | 80.5(1) | 1.906(2) | 3.805(3) | 2.771(4) | 2.667(4) |
| O(4) | 87.3(1) | 95.2(1) | 175.1(1) | 1.903(2) | 2.647(3) | 2.720(4) |
| O(5) | 88.5(1) | 175.3(1) | 94.8(1) | 89.5(1) | 1.858(2) | 2.737(4) |
| O(6) | 177.2(1) | 87.1(1) | 87.6(1) | 89.9(1) | 92.0(1) | 1.945(3) |

| | O–H (Å) | H---O (Å) | O–H---O (°) |
|---|---|---|---|
| O(1)–H(1) ..... O(E11) | 0.94(6) | 1.68(6) | 157(5) |
| O(2)–H(2) ..... O(4) | 0.96(5) | 1.79(5) | 164(4) |
| O(3)–H(3) ..... O(E21) | 0.87(6) | 1.79(6) | 157(5) |
| O(4)–H(4) ..... O(E22) | 0.91(5) | 1.97(5) | 171(4) |
| O(5)–H(5) ..... O(E12) | 0.93(4) | 1.91(4) | 165(4) |
| O(6)–H(6) ..... O(W) | 0.89(6) | 1.79(6) | 172(5) |

[a] Numerical data for the hydrogen bond involving oxygen atoms belonging to this group.

TABLE V

MAIN INTERATOMIC DISTANCES AND BOND ANGLES IN THE TWO $NH_4O_6$ POLYHEDRA[a]

| | N–H (Å) | H–O (Å) | N–O (Å) | $\widehat{N\text{–}H\ldots O}$ (°) |
|---|---|---|---|---|
| N(1)–H(1N1) ..... O(E22) | 0.82(6) | 2.20(6) | 2.986(4) | 160(5) |
| N(1)–H(2N1) ..... O(E21) | 0.96(5) | 1.99(5) | 2.937(4) | 166(4) |
| N(1)–H(3N1) ..... O(5) | 0.89(6) | 2.00(6) | 2.778(4) | 146(5) |
| N(1)–H(4N1) ..... O(E12) | 0.84(6) | 2.01(6) | 2.809(4) | 158(5) |
| N(1) O(E12) | | | 3.260(4) | |
| N(1) O(L2) | | | 3.451(4) | |
| N(2)–H(1N2) ..... O(2) | 0.85(6) | 2.11(6) | 2.951(4) | 167(5) |
| N(2)–H(2N2) ..... O(W) | 0.80(6) | 2.03(6) | 2.822(5) | 169(5) |
| N(2)–H(3N2) ..... O(6) | 0.77(7) | 2.24(6) | 2.899(5) | 144(6) |
| N(2)–H(4N2) ..... O(1) | 0.76(8) | 2.06(8) | 2.796(4) | 165(7) |
| N(2) O(2) | | | 3.322(5) | |
| N(2) O(3) | | | 3.020(4) | |

| | H–N–H (°) | $\widehat{O\text{–}N\text{–}O}$ (°) |
|---|---|---|
| O(E22) ... H(1N1)–N(1)–H(2N1) ... O(E21) | 112(5) | 106.9(1) |
| O(E22) ... H(1N1)–N(1)–H(3N1) ... O(5) | 113(5) | 111.7(1) |
| O(E22) ... H(1N1)–N(1)–H(4N1) ... O(E12) | 104(5) | 126.1(1) |
| O(E21) ... H(2N1)–N(1)–H(3N1) ... O(5) | 112(5) | 80.0(1) |
| O(E21) ... H(2N1)–N(1)–H(4N1) ... O(E12) | 125(5) | 110.1(1) |
| O(5)... H(3N1)–N(1)–H(4N1) ... O(E12) | 88(5) | 112.2(1) |
| O(2)... H(1N2)–N(2)–H(2N2) ... O(W) | 106(5) | 107.0(1) |
| O(2)... H(1N2)–N(2)–H(3N2) ... O(6) | 105(5) | 138.0(2) |
| O(2)... H(1N2)–N(2)–H(4N2) ... O(1) | 105(6) | 111.0(1) |
| O(W)... H(2N2)–N(2)–H(3N2) ... O(6) | 126(6) | 94.4(1) |
| O(W)... H(2N2)–N(2)–H(4N2) ... O(1) | 106(6) | 106.8(1) |
| O(6)... H(3N2)–N(2)–H(4N2) ... O(1) | 107(6) | 96.0(1) |

[a] Numerical data for the hydrogen bond involving hydrogen atoms of the $NH_4$ group.

TABLE VI

GEOMETRY OF THE $H_2O$ GROUP AND HYDROGEN BOND CHARACTERISTICS FOR THE PROTONS OF THIS GROUP

| | O(W)–H (Å) | H..O (Å) | O(W)–O (Å) | O(W)–H..O (°) |
|---|---|---|---|---|
| O(W)–H(1W) ..... O(E22) | 0.86(6) | 1.77(6) | 2.606(3) | 162(6) |
| O(W)–H(2W) ..... O(E11) | 0.97(6) | 1.86(6) | 2.814(4) | 169(5) |
| O(W) — O(6) | | | 2.670(4) | |
| O(W) — O(2) | | | 3.241(4) | |
| O(W) — O(3) | | | 3.392(4) | |

H(1W)–O(W)–H(2W) 116(5)°

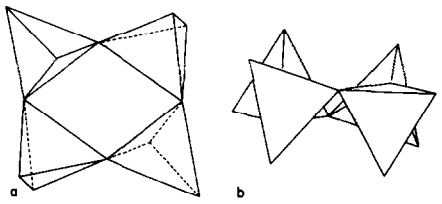


FIG. 2. (a) Projection of the $P_4O_{12}$ ring anion on the R.M.S. plane. (b) Projection of the same group along a perpendicular direction.

### The $P_4O_{12}$ Ring

The $P_4O_{12}$ ring is centrosymmetric and located around the $(\frac{1}{2}, \frac{1}{2}, 0)$ inversion center. In Fig. 2a we give a projection of this group on the R.M.S. plane while Fig. 2b is a projection of the same group along a perpendicular direction. All geometrical features of this group are reported in Table III. They do not differ significantly from what was already observed in tetrametaphosphates.

### $Te(OH)_6$ Octahedron

As shown in Fig. 1 one $Te(OH)_6$ octahedron is located on each side of a $P_4O_{12}$ ring. So the framework of anions can be described as $Te(OH)_6$–$P_4O_{12}$–$Te(OH)_6$ blocks spreading in arrays in (011) planes. Between these planes we found water molecules and $NH_4$ groups. The main features of the geometry of the almost regular $Te(OH)_6$ octahedron are reported in Table IV. In the same table a complete hydrogen bonding pattern is given for all the oxygen atoms involved in the coordination polyhedron of tellurium. Four of them are connected by hydrogen bonds to external oxygen atoms of the $P_4O_{12}$ ring, one of them to the water molecule, and the last one to one oxygen atom belonging to the second $Te(OH)_6$ group of the $Te(OH)_6$–$P_4O_{12}$–$Te(OH)_6$ block previously described. Figure 3 gives in a projection along the *a* axis an idea of the geometry for this set of bonds.

### $NH_4$ Groups and $NO_6$ Polyhedra

The two nonequivalent $NH_4$ groups are almost regular tetrahedra with N–H distances ranging from 0.82 to 0.96 Å for $N(1)H_4$ and from 0.76 to 0.85 Å for $N(2)H_4$. Nitrogen atoms and their hydrogen neighbors are represented in Fig. 1, while Fig. 4 depicts the hydrogen bonding pattern in which they are involved. The corresponding detailed numerical values are gathered in Table V. Each nitrogen atoms has four oxygen neighbors with N–O < 3 Å while the remaining two show larger N–O distances.

Numerical details concerning these polyhedra are reported in Table V.

### The Water Molecule

The main characteristics of this group are reported in Table VI, in which we also include the shortest O(W)–O distances observed in this arrangement.

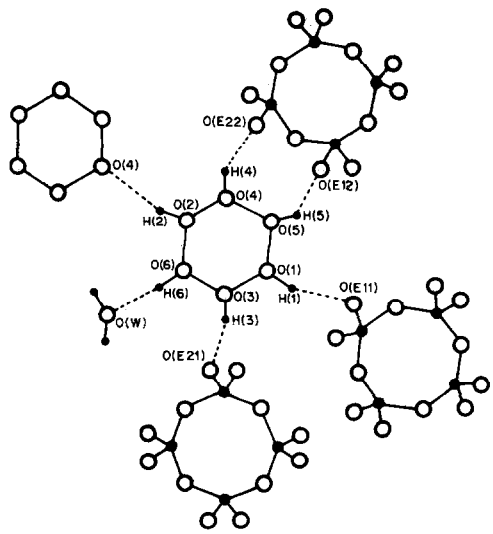


FIG. 3. Schematic drawing of the hydrogen bonding pattern involving oxygen atoms belonging to $TeO_6$ groups. These groups are schematized by hexagons, $P_4O_{12}$ rings by octagons.

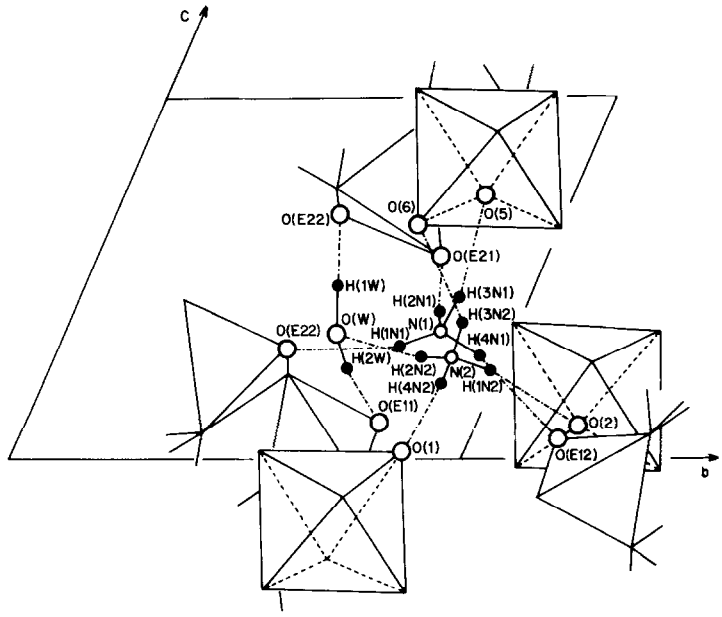


FIG. 4. Projection along the *a* axis of the hydrogen bonding pattern involving $NH_4$ groups and water molecules.

## Conclusion

As in all the previously described phosphate-tellurates (*1–8*) we observe the coexistence, as independent units, of the phosphoric anion (here $P_4O_{12}$) and of the $Te(OH)_6$ group.

Experiments are in progress for the study of the other alkali tetrametaphosphate-tellurates.

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