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# Crystal Structure Refinement of Basic Tellurium Nitrate: A Reformulation as $(Te_2O_4H)^+(NO_3)^-$

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Basic tellurium nitrate crystallizes in the space group Pnma with $a = 14.607$ (1), $b = 8.801$ (1), and $c = 4.4633$ (4) Å. Full-matrix least-squares refinement of automatic diffractometer data converged to a residual $R = 0.036$ ($R_w = 0.046$) for 899 independent reflections. A detailed analysis of the structural data leads us to reformulate this compound as $(Te_2O_4H)^+(NO_3)^-$ with a basic structural element consisting of a charged two-dimensional puckered $Te_2O_4H^+$ network with discrete $NO_3^-$ anions, an example of a *positively*-charged network structure.

*[Keywords: Basic tellurium nitrate; Crystal structure refinement; Positively-charged network;* $(Te_2O_4H)^+(NO_3)^-$; $Te_2O_4 \cdot HNO_3$; *X-Ray diffraction]*

### *Verfeinerung der Kristallstruktur von basischem Telluriumnitrat. Eine Umformulierung in* $(Te_2O_4H)^+(NO_3)^-$

Basisches Telluriumnitrat kristallisiert in der Raumgruppe Pnma mit $a = 14{,}607$ (1), $b = 8{,}801$ (1) und $c = 4{,}4633$ (4) Å. Die verfeinernde Auswertung der Diffraktometerdaten konvergierte zu $R = 0{,}036$ ($R_w = 0.046$) für 899 unabhängige Reflexe. Eine detaillierte Analyse der Strukturdaten führte zu einer Umformulierung dieser Verbindung als $(Te_2O_4H)^+(NO_3)^-$, wobei die Basisstruktur aus einem geladenen, zweidimensionalen, gefalteten $Te_2O_4H^+$ Netzwerk mit getrennten $NO_3^-$ Anionen besteht. Es stellt dies ein Beispiel einer *positiv geladenen* Netzstruktur dar.

## Introduction

It is unusual that no examples of *positively*-charged networks exist in the crystal chemistry of inorganic structures considering the large number of known examples of negatively-charged networks (three-dimensional networks in zeolites, for example).

A search of the recent literature[1] does reveal several candidates for positively-charged one-, or two-dimensional networks among the struc-

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tures of complex compounds of the heavier elements of Groups V B, VI B, and VII B. However, in each case either a discrete anion does not exist or the anion forms covalent linkages which complete the primary coordination polyhedra about the metal atoms in the network. These structures will be briefly described.

$(Sb_6O_7)(SO_4)_2$ contains[2] cylindrical $Sb_6O_7$ units, but the bond distances to the $SO_4$ tetrahedra do not support the existence of discrete anions. Spiral one-dimensional chains of composition $(IO)_2$ are covalently linked[3] by $SO_4$ tetrahedra to form sandwich-like layers in $(IO)_2(SO_4)$. $(Te_2O_3)(SO_4)$ contains Te—O sheets which are intimately bonded to $SO_4$ tetrahedra[4]. In a similar manner[5], $(Te_2O_3)(HPO_4)$ contains bridging $HPO_4$ groups, while $(Te_8O_{10})(PO_4)_4$ has band-like units bridged by $PO_4$ tetrahedra[6].

The most likely candidate for discrete anions and a corresponding charged network is "basic" tellurium nitrate $Te_2O_4 \cdot HNO_3$, which has been reported[7] as containing a two-dimensional puckered network of Te and O atoms. As the details of this structure allow for the existence of discrete $NO_3^-$ groups, we undertook to perform a more accurate structure refinement using counter diffractometer data. This paper presents the results of this investigation.

## Experimental

### *Preparation*

Several grams of high purity Te (99.999%) ground to a coarse powder were dissolved in a sufficient amount of concentrated $HNO_3$ and heated gently at 50-60 °C until no further reaction occured. An additional small amount of $HNO_3$ was added and the process repeated. When the Te had completely reacted, heating was stopped and the supernatant liquid decanted while still hot. Boiling the solution caused the product to decompose into $\alpha$-$TeO_2$ (paratellurite, the tetragonal form of $TeO_2$) which contaminated the product. The hot solution was set aside in a closed container and permitted to cool. $Te_2O_4 \cdot HNO_3$ crystallized from this supersaturated solution over a period of several days yielding masses consisting of needles several mm in length and up to 1 mm in cross section. Crystals were isolated from the solution, washed thoroughly with 95% ethanol, dried at 100 °C, and placed in tightly sealed vials.

### *Infrared Data*

Infrared spectra were recorded on a Perkin-Elmer Model 283 Spectrometer operating in transmittance mode (12 min scan, response 1, expansion 10 × ). The sample was prepared by grinding single crystals and suspending the powder in a Nujol mull since it reacted with KBr.

### *X-Ray Diffraction Data*

X-ray precession photographs of a single crystal confirmed orthorhombic symmetry[7]. Subsequent analysis showed the space group to be Pnma, in which the structural refinement was carried out.

The lattice parameters were determined in a PICK-II least-squares refinement program, using 46 reflections within the angular range $45^\circ < 2\theta < 48^\circ$; the reflections were automatically centered on a Picker FACS-I four-circle diffractometer using Mo $K_{\alpha 1}$ radiation ($\lambda = 0.70930$ Å). At 22 °C the lattice parameters were found to be $a = 14.607$ (1), $b = 8.801$ (1), $c = 4.4633$ (4) Å, where the figures in parentheses represent the standard deviations in the last reported figure. The calculated volume is 583.8 Å$^3$, giving a calculated density, with $Z = 4$, of 4.425 g cm$^{-3}$.

A small euhedral crystal with dimensions $0.65 \times 0.25 \times 0.25$ mm ($V = 4.0 \times 10^{-2}$ cm$^{-3}$) was chosen for data collection. Precise dimensions of the crystal were determined for use in an absorption correction program written by *N. W. Alcock* and *B. Lee* for a crystal of general shape. Input for this program included three pairs of faces on the crystal which were found to be normal to major reciprocal lattice rows as judged by precession photographs and the orientation angles of the crystal coordinate system with respect to the diffractometer coordinate system which were obtained from the program PICK-II.

Diffraction intensities were measured using Zr-filtered Mo $K_\alpha$ radiation at a take-off angle of 1.5° with the diffractometer operating in the $\omega$ scan mode. 10-second background counts were taken at the both ends of a $1.4^\circ$ $\theta$-$2\theta$ offset corrected for dispersion. Of the 1551 independent data investigated in the angular range $2\theta < 71^\circ$, 899 were considered observable according to the criterion $|F_0| > 1.5\,\sigma_F$, where $\sigma_F$ is defined as $0.02\,|F_0| + [C + k^2B]^{1/2}/2|F_0|\mathrm{Lp}$; the total scan count is $C$, $k$ is the ratio of scanning time to the total background time, and $B$ is the total background count. Three reflections were systematically monitored; the maximum variation in intensity observed was never greater than $\pm 2\%$ over the data collected period.

Intensity data were corrected for *Lorentz* and polarization factors, and absorption corrections ($\mu = 105$ cm$^{-1}$, Mo $K_\alpha$) were made using the program already cited. The maximum absorption correction was 35% of $|F_0|$.

### *Refinement of the Structure*

Full-matrix least-squares refinement[8] using the positional parameters reported by *Swink* and *Carpenter*[7] for the seven atoms as a trial structure, a $1/\sigma^2$ weighting scheme, zerovalent scattering factors[9] for Te, O, and N, isotropic temperature factors, and corrections for secondary extinction and anomalous dispersion, yielded a residual $R = 0.052$ and a weighted residual $R_w = 0.064$. The final anisotropic refinement, based on a data : parameter ratio of 17 with 53 independently varied parameters, yielded $R = 0.036$ and $R_w = 0.046$ (figure of merit —1.0453) for the observed data. The maximum extinction correction[10] in the final refinement was 24% of $|F_0|$ for the 002 reflection.

Table 1 presents the positional and anistropic temperature parameters from the final anisotropic refinement. A table of observed and calculated structure factors can be requested from the authors.

## Results and Discussion

Our refinement confirms the space group assignment and structural details reported by *Swink* and *Carpenter*[7]. The four-coordinated tellurium atom forms a puckered two-dimensional network (illustrated in

Table 1. *Fractional atomic coordinates and anisotropic thermal parameters**

| Atom | $10^4x$ | $10^4y$ | $10^4z$ | $B_{11}$ | $B_{22}$ | $B_{33}$ | $B_{12}$ | $B_{13}$ | $B_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Te | 1665.0 (3) | 638.0 (4) | 196.8 (8) | 1.14 (2) | 0.66 (2) | 1.01 (2) | —0.10 (1) | —0.14 (1) | 0.04 (1) |
| O (1) | 2108 (4) | 346 (6) | 4128 (10) | 1.59 (22) | 1.33 (18) | 0.82 (18) | 0.19 (12) | —0.07 (14) | 0.11 (12) |
| O (2) | 2303 (5) | 1/4 | 9295 (16) | 1.18 (24) | 0.15 (19) | 1.92 (24) | 0 | 0.11 (21) | 0 |
| O (3) | 886 (6) | 1/4 | 2116 (17) | 1.10 (27) | 1.44 (27) | 1.92 (28) | 0 | 0.61 (22) | 0 |
| O (4) | 3804 (6) | 1/4 | 5156 (17) | 1.86 (30) | 1.36 (27) | 2.32 (32) | 0 | —0.98 (26) | 0 |
| O (5) | 4701 (5) | 1255 (8) | 8149 (16) | 2.65 (30) | 2.18 (27) | 3.08 (29) | 0.60 (23) | —0.85 (24) | 1.18 (21) |
| N | 4396 (7) | 1/4 | 7150 (20) | 1.26 (34) | 1.85 (36) | 1.54 (30) | 0 | —0.21 (25) | 0 |

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* Numbers in parantheses are e.s.d.'s in the last significant figure. The *B*'s are defined by the general factor exp $\left[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}kla^*c^*)\right]$.

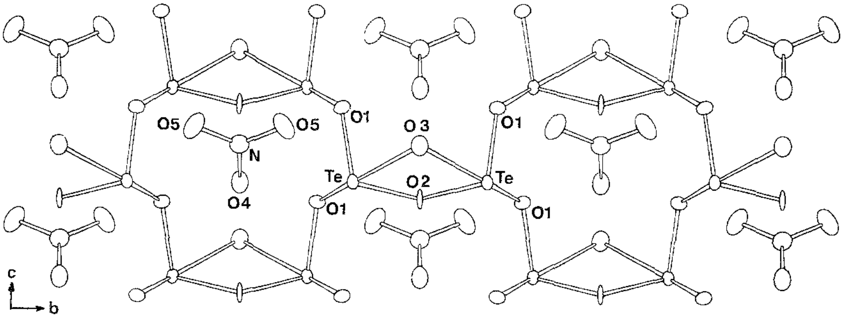

Fig. 1. The puckered two-dimensional Te—O network projected onto the *bc* plane

Table 2. *Bond distances, angles and polyhedral edge lengths for the tellurium and nitrogen polyhedra**

| | | Bond Distance (Å) | | Bond Angle (°) | Edge Length (Å) |
|---|---|---|---|---|---|
| Te Polyhedron | | | | | |
| Te—O (1) | | 1.888 (5) | | | |
| Te—O (2) | | 1.928 (4) | | | |
| Te—O (1′) | | 2.046 (5) | | | |
| Te—O (3) | | 2.173 (4) | | | |
| O (1)—Te—O (2) | | | | 98.3 (3) | 2.886 (7) |
| O (1)—Te—O (1′) | | | | 81.9 (1) | 2.581 (6) |
| O (1)—Te—O (3) | | | | 85.2 (3) | 2.756 (8) |
| O (2)—Te—O (1′) | | | | 83.6 (2) | 2.649 (6) |
| O (2)—Te—O (3) | | | | 72.2 (2) | 2.425 (9) |
| O (1′)—Te—O (3) | | | | 150.5 (2) | 4.081 (9) |
| N Polyhedron | | | | | |
| N—O (4) | | 1.241 (11) | | | |
| N—O (5) | 2 × | 1.264 (7) | | | |
| O (4)—N—O (5) | | | 2 × | 119.9 (5) | 2.169 (9) |
| O (5)—N—O (5) | | | | 120.1 (9) | 2.191 (13) |

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* Numbers in parentheses are e.s.d.'s in the last significant figure.

Figure 1, a projection of the structure onto the *bc* plane); its coordination polyhedron consists of four oxygen atoms at an average distance of 2.009 Å and exhibits the lone-pair geometric distortion characteristic[11] of $Te^{4+}$.

The nitrogen atom lies on a mirror plane at the center of a triangle of oxygen atoms at an average distance of 1.256 Å. The O—N—O angles

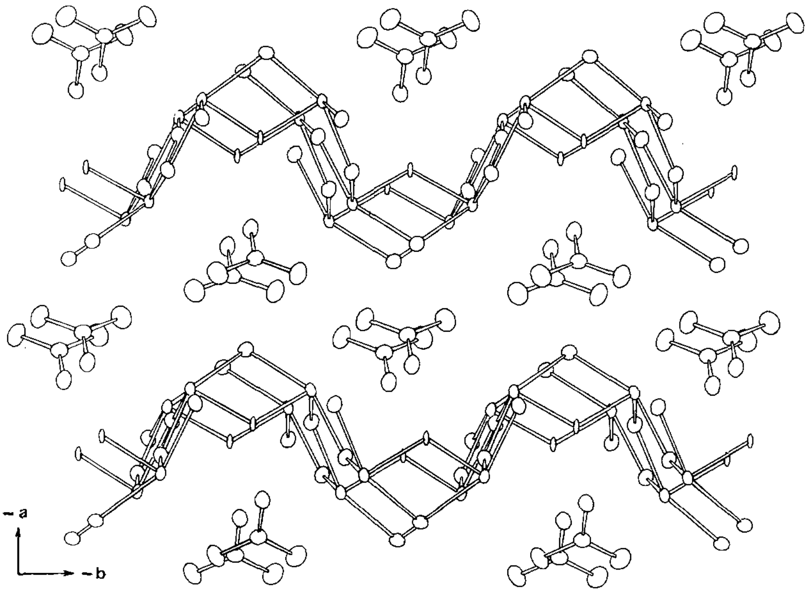

Fig. 2. A projection of the structure of $(Te_2O_4H)^+(NO_3)^-$ projected onto the *ab* plane (slightly skewed for clarity) showing the stacking pattern of Te—O layers and $NO_3^-$ groups

Table 3. *Bond distances, angles and polyhedral edge lengths for oxygen polyhedra**

| | | Bond Distance (Å) | Bond Angle (°) | Edge Length (Å) |
|---|---|---|---|---|
| i) O (1) Polyhedron | | | | |
| O (1)—Te | | 1.888 | | |
| O (1)—Te′ | | 2.046 | | |
| Te—O (1)—Te′ | | | 125.1 (3) | 3.492 (2) |
| ii) O (2) Polyhedron | | | | |
| O (2)—Te | 2 × | 1.928 | | |
| Te—O (2)—Te | | | 116.4 (4) | 3.277 (2) |
| iii) O (3) Polyhedron | | | | |
| O (3)—Te | 2 × | 2.173 | | |
| Te—O (3)—Te | | | 97.9 (3) | 3.277 (2) |

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* Numbers in parentheses are e.s.d.'s in the last significant figure.

define a planar geometry within experimental error. These angles and distances compare well with tabulated[12] values for $NO_3^-$. Table 2 presents the relevant bond distances about Te and N while Table 3 lists the corresponding values for the oxygen atoms in the two-dimensional net. Fig. 2, a view approximately perpendicular to that in Fig. 1, illustrates the location of the $NO_3^-$ ions between puckered Te—O sheets.

The infrared spectrum agrees with published data[13] including the broad peak at ~ 3,250 cm$^{-1}$ which *Swink* and *Carpenter* attribute to a hydrogen bonding interaction with an O—H···O distance of about 2.75 Å. Three relatively sharp bands at 1,370 (sh), 812, and 715 cm$^{-1}$ are characteristic of a free nitrate ion[14].

We now turn to the problem of locating the hydrogen atom and the nature of the nitrate group. By calculating[15] the bond strengths (in valence units) for each of the Te—O bonds in the net and summing about each of the oxygen atoms, it is found that 0 (3) is decidely underbonded (1.18 v.u.) compared to O (1) and O (2) (1.88 and 2.02 v.u., respectively). This strongly suggests that the hydrogen atom is bonded to 0 (3) forming an OH group and giving rise to a positively-charged net. The charge, of course, is balanced by the discrete $NO_3^-$ ion. We choose to represent this compound as $(Te_2O_4H)^+(NO_3)^-$ due to (1) the symmetric nature of the nitrate group and (2) the location of the hydrogen atom on the Te—O network.

The possibility of hydrogen bonding is more difficult to pin down. *Swink* and *Carpenter*[7] suggest that a "nitrate" hydrogen [on O (4)] forms a hydrogen bond to O (2). The above argument rules this out. Since neither O (1) nor O (2) is sufficiently under-bonded to act as a hydrogen bond acceptor, any hydrogen bonding must occur from O (3)—H to a nitrate oxygen: O (5) at 2.94 or 3.12 Å, or O (4) at 3.21 Å. As the N—O (5) distance is slightly shorter than N—O (4), it is tempting to assign O (4) as the acceptor atom.

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