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An X-Ray Diffraction Study on the Structure of Telluric Acid $Te(OH)_6$ in Aqueous Solution

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A 1.5 M $Te(OH)_6$ aqueous solution was investigated at 25 °C by the X-ray diffraction method. By analyses of a radial distribution curve and of the reduced intensities, the Te–OH bond distance was determined to be 1.935 ± 0.003 Å. Experimental data were explained satisfactorily by a model in which twelve water molecules were hydrogen bonded to each $Te(OH)_6$ octahedron.

A number of crystallographic studies of telluric acid and its salts have been performed, and the oxygen coordination of tellurium(VI) is well established in the solid state.[1,2] We have now initiated a series of X-ray structural investigations of tellurium(VI) compounds to study tellurium(VI) anions and their polymerization in solution. Initially, it is of importance to confirm the octahedral, monomeric structure of telluric acid in aqueous solution and to investigate its water coordination.

In the solid state, telluric acid is known to crystallize in at least three different phases, monoclinic[3,4] and cubic $Te(OH)_6$[5] and tetragonal $Te(OH)_6 \cdot 4H_2O$.[6] The structures were solved by X-ray and neutron diffraction methods and were shown to contain discrete $Te(OH)_6$ octahedra connected by hydrogen bonds, either directly or *via* water molecules, three-dimensional networks being formed.

EXPERIMENTAL

A sample solution was prepared by dissolving a weighed amount of commercial $Te(OH)_6$ (BDH) in a known volume of distilled water. The density of the solution was measured by a pycnometer. The composition of the sample solution is given in Table 1.

X-Ray scattering intensities were measured on a $\theta-\theta$ diffractometer of type described previously,[7] with a curved LiF monochromator mounted in the diffracted beam. A slit combination with divergent slits of 1/12°, 1/6° and 1° was employed for the range $1 \leqq \theta \leqq 7°$, $3 \leqq \theta \leqq 17°$ and $6 \leqq \theta \leqq 64°$, respectively (2θ is the scattering angle). Measurements were made in a step scanning mode every 0.1° ($1 \leqq \theta \leqq 24°$) and 0.25° ($19 \leqq \theta \leqq 64°$). Mo*K*α radiation ($\lambda = 0.7107$ Å) was used and the measurements were repeated twice so that the total number of counts per data point amounted to 80000 counts, *i.e.* the error due to counting statistics is 0.35 %. The sample solution was kept in a teflon vessel, which was placed in the airtight sample housing. The primary and reflected beams were passed through a Be window of the housing.

Experimental intensity data were corrected for background, absorption,[8] polarization[9] and Compton radiation,[10] and normalized to absolute scale with respect to a stoichiometric unit of volume, V, containing one Te atom as described previously.[10] The radial distribution function was calculated by a Fourier inversion, eqn. (1), where ρ_0 is the average

$$D(r) = 4\pi r^2 \rho_0 + \frac{2r}{\pi} \int_0^{s_{\max}} s \cdot i(s) M(s) \sin(rs) \mathrm{d}s \qquad (1)$$

Table 1. Composition of the sample solution (mol dm^{-3}) and the stoichiometric volume V per tellurium atom in the solution.

Te	1.500
O	59.22
H	109.4
density/g cm^{-3}	1.250
V/Å^3	1107
μ/cm^{-1}	7.98

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scattering density in the stoichiometric volume, s_{max} the maximum value of the variable s ($s=4\pi\sin\theta/\lambda$) available in the experiment, and $M(s)$ the modification function of $\{f_{Te}(0)^2/f_{Te}(s)^2\}\exp(-0.01\,s^2)$. The reduced intensity, $i(s)$, is given by formula (2). Here

$$i(s)=I(s)-\sum n_i\{(f_i(s)+\Delta f_i')^2+(\Delta f_i'')^2\} \qquad (2)$$

$I(s)$ is the corrected and scaled intensity and n_i represents the number of atoms "i" in the stoichiometric volume. The scattering factor, f_i, and the real and the imaginary parts of anomalous dispersion, $\Delta f_i'$, $\Delta f_i''$, for Te(0), O and H were obtained from the International Tables.[11] Values for incoherent scattering were taken from Cromer[12] for Te and O, and from Compton and Allison[13] for H, to which correction for the Breit-Dirac effect was applied. Theoretical reduced intensities, $i(s)_{calc}$, for pairs of atoms "i" and "j" were calculated according to eqn. (3),

$$i(s)_{calc}=\sum\sum n_{ij}\{(f_i+\Delta f_i')(f_j+\Delta f_j')+\Delta f_i''\Delta f_j''\}\frac{\sin(sr_{ij})}{sr_{ij}}\exp(-b_{ij}s^2) \qquad (3)$$

where r_{ij}, b_{ij} and n_{ij} are the distance, the temperature factor and the frequency factor of each atom pair "i–j".* Theoretical reduced intensities thus calculated were Fourier transformed to theoretical peak shapes using eqn (1). All calculations were carried out on an IBM 360/370 computer by means of the program KURVLR.[14]

RESULTS AND DISCUSSION

The experimental distribution function, $D(r)-4\pi r^2\rho_0$, is shown in Fig. 1 b. Peaks are observed at 1.9, 2.5–3.2 and 3.8–4.8 Å. The first peak at 1.9 Å can be ascribed to the Te–OH bonds within telluric acid, estimated from the Te–OH distances found in the crystals.[3–5] The second peak is mainly due to the first neighbor H_2O-H_2O interaction in the bulk water structure.[15] Since the telluric acid is hydrogen bonded to neighboring water molecules in the solution, part of the peak is also due to such $OH-H_2O$ interactions. The broad peak in the range 3.8–4.8 Å ought to result mainly from the interaction between the Te atom and water molecules in the second coordination shell. Another contribution to the peak may come from the second neighbor H_2O-H_2O interaction of free water.

For a quantitative analysis, the least-squares method was applied to the reduced intensities multipled by s (Fig. 2), the function

$$U=\sum_{s_{min}}^{s_{max}} w(s)\{i(s)_{obs}-i(s)_{calc}\}^2$$

being minimized by means of the program NLPLSQ.[16] The lower and upper values of s_{min} and s_{max}, are used in the calculation. The weighting function, $w(s)$, used was proportional to $I(s)^{-2}\times\cos\theta$.

Among all possible interactions, the short Te–OH interaction within the $Te(OH)_6$ moiety should contribute predominantly to the observed $s\cdot i(s)$ values over the whole s-range, especially in the high s region. The long range interactions contribute mainly to the low s range, and diminish rapidly with increasing s value. In a first step of the refinements, therefore, the predominant Te–OH interaction was refined for the high s range. The parameters varied were the distance (r) and the temperature factor (b) of the Te–OH bond. The frequency factor (n) was in some cases treated as an independent parameter to confirm the coordination number 6 of the telluric acid molecule. Table 2 gives the results obtained for the $Te(OH)_6$ unit in the range of $6.5\leqq s\leqq 15$ Å^{-1}. As seen in Table 2 the Te atom is bonded to six OH groups probably forming an octahedron.* Fig. 2 a (dashed line) shows the theoretical $s\cdot i(s)$ curve calculated by using the parameter values given as C in Table 2. Fig. 2 b represents the difference between observed and calculated $s\cdot i(s)$ values. As seen in Fig. 2 b, the experimental $s\cdot i(s)$ curve over 6 Å^{-1} was reproduced satisfactorily by the $Te(OH)_6$ octahedron. Residual $s\cdot i(s)$ values below 6 Å^{-1} contain longer range interactions not considered, and could thus be used to construct a hydration model for telluric acid. The model used in the subsequent calculations had the following characteristics.

(1) A $Te(OH)_6$ molecule with octahedral coordination.

(2) A $Te(OH)_6$ molecule surrounded by N water molecules (the frequency factor $n_{ij}=N$).

(3) $N/6$ water molecules hydrogen-bonded directly to each OH-group of the telluric acid.

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*In some cases n_{ij} is identical to the coordination number.

*The octahedral coordination is further indicated by the improved R value in refinement C, in which oxygen–oxygen interactions of an octahedron have been included.

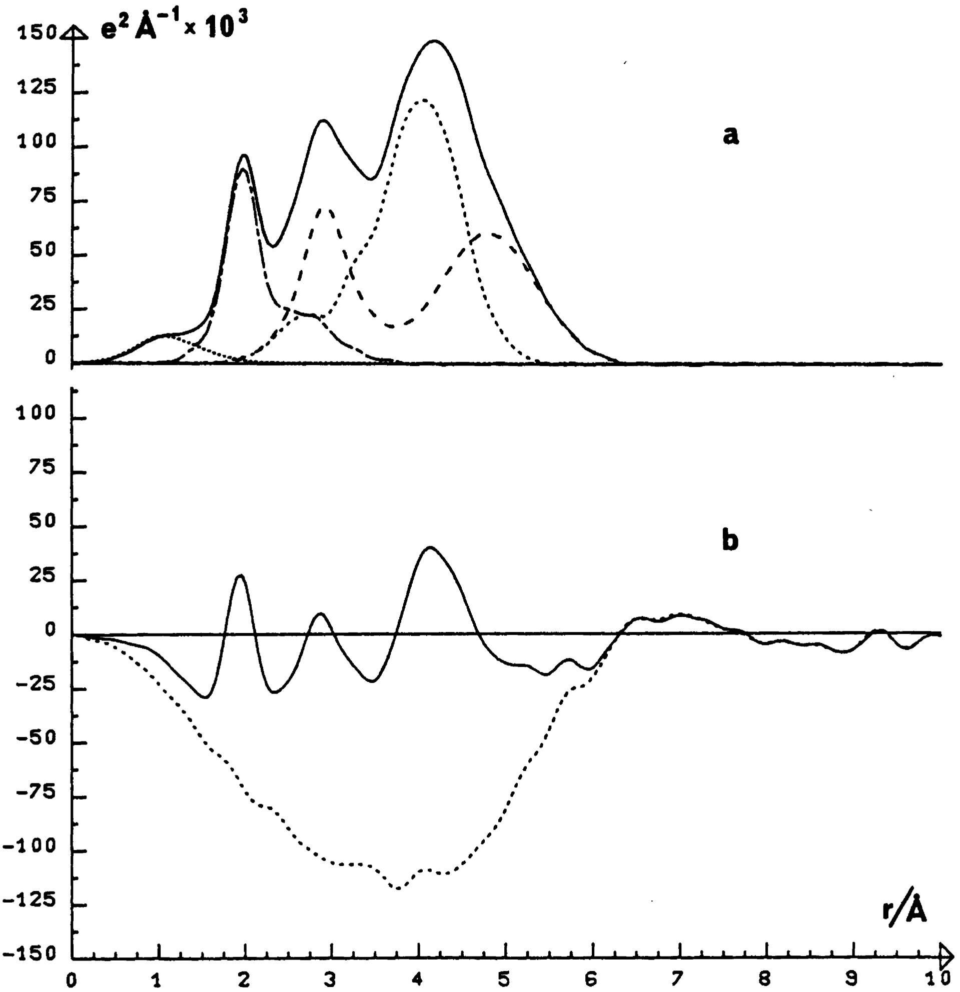

Fig. 1. a. Theoretical peak shapes: Te−OH and *cis* OH−OH interactions (—·—); free water structure (— — —); Te−H_2O, OH−H_2O(1), OH−H_2O(2) and OH−H_2O(3) interactions (---); the O−H interactions within H_2O molecules and OH groups (···); their sum (——). b. The $D(r)-4\pi r^2\rho_0$ curve. The solid and dashed lines show, respectively, the observed and difference curves between experimental and theoretical values.

(4) Free water structure treated as a pentamer, $(H_2O)_5$, forming a tetrahedron.

(5) Interactions between the $Te(OH)_6$ molecules were neglected since the $s \cdot i(s)$ curve showed no peak in the small angle region which indicated "a quasi lattice" structure in solution.

In order to estimate the number of water molecules bonded to the $Te(OH)_6$ molecule, we carried out preliminary refinements including interactions (1−4) for a wider s range ($3.5 \leqq s \leqq 15.0$ Å^{-1}). The results indicated clearly that there are twelve water molecules hydrogen-bonded to each $Te(OH)_6$ molecule. Based on these, we constructed the water coordination model shown in Fig. 3. In the model, a trigonal orientation of water molecules was chosen since this orientation is preferred in the case of high valent metals like Cr^{3+} [17] and Fe^{3+}.[18] The Te−O(OH)−O(H_2O) bond angle was assumed

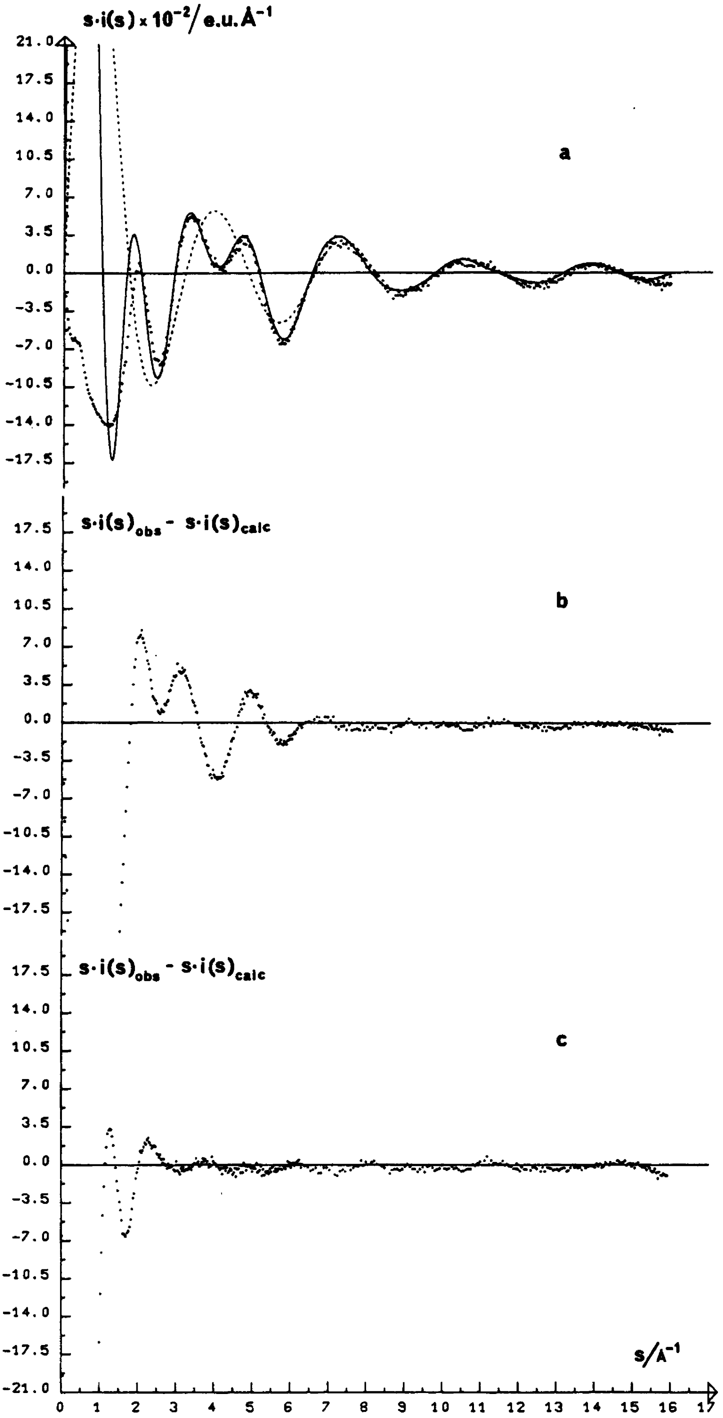

Fig. 2. a. The reduced intensity, $i(s)$, multiplied by s. Dots denote observed values. Dashed and solid lines show theoretical curves calculated from parameter values given in Tables 2 and 3, respectively. b. Residual $s \cdot i(s)$ curve obtained by subtracting the theoretical curve (dashed line) from the observed one (dots). c. Residual $s \cdot i(s)$ curve obtained by subtracting the theoretical curve (solid line) from the observed one (dots).

Table 2. Results of the least-squares refinements for the Te – OH interaction obtained from the range $6.5 \leqq s \leqq 15.0$ Å^{-1}. In refinements B and C an octahedral configuration for $Te(OH)_6$ was assumed. Standard deviations are given in parentheses, indicating the parameters refined in models A, B and C, respectively. The units of r and b are Å and Å^2, respectively.

	A	B	C[b]
Te – OH			
r	1.923(5)	1.923(5)	1.921(3)
b	0.0024(4)	0.0025(2)	0.0025(2)
n	6.0(3)	6	6
cis OH – OH			
r	–	–	2.717(= 1.921 ×$\sqrt{2}$)
b	–	–	0.010(3)
n	–	–	12
R-factor[a]			
	0.302	0.302	0.286

[a] R-factor was defined as

$$\left[\sum_{s_{\min}}^{s_{\max}} s^2\{i(s)_{\text{obs}} - i(s)_{\text{calc}}\}^2 \Big/ \sum_{s_{\min}}^{s_{\max}} s^2 i(s)_{\text{obs}}{}^2\right]^{\frac{1}{2}}.$$

[b] The *trans* OH – OH interaction is not included since its contribution for $s \geqq 6.5$ Å^{-1} is of low significance.

to be 120° for simplicity. Based on this model, final calculations were carried out as follows:

(1) The $Te(OH)_6$ octahedron. The parameters r and b of the Te – OH interaction were refined independently. *Cis* $H_2O - H_2O$ interaction was also included, for which only the temperature factor was refined independently, while the distance was estimated from the geometry.

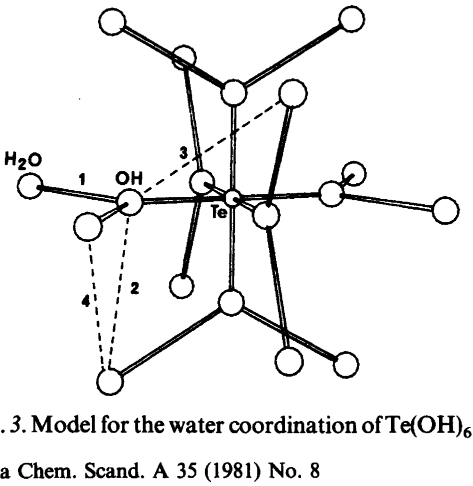

Fig. 3. Model for the water coordination of $Te(OH)_6$.

(2) The interaction between the Te atom and hydration water molecules, abbreviated $Te - H_2O$. Parameters r and b were refined independently.

(3) The interaction between the OH group of the $Te(OH)_6$ and hydration water molecules. Those abbreviated $OH - H_2O(1)$, $OH - H_2O(2)$ and $OH - H_2O(3)$ were taken into account, while other pairs over 5 Å were neglected since no discrete peak was observed in the distribution curve. Only temperature factors of the interactions were treated as independent parameters. The distances were estimated from the model geometry and values of r_{Te-OH} and r_{Te-H_2O}.

(4) Free water structure. The distance of the first neighbor $H_2O - H_2O$ interaction was refined, while that of the second neighbor interaction was fixed to the value calculated from the geometry. The temperature factors were refined independently.

The above model was refined in the interval $2.5 \leqq s \leqq 15.0$ Å^{-1} and the results are given in Table 3.

As a comparison, a refinement was carried out in the same s interval, but based on the $Te(OH)_6$ octahedron only. The R value became as high as 52 %, due to the high influence of the long distances to the low order data. On the other hand, there is no significant difference between the refined parameter values. The contribution of *trans* OH – OH was not significant (*cf.* Table 3), while the negative temperature factor of *cis* OH – OH indicated further contributions in the same distance range, *i.e.* $OH - H_2O(1)$ and free $H_2O - H_2O(1)$.

Figs. 2a (solid line) and 2c show the theoretical $s \cdot i(s)$ curve, calculated using parameter values in Table 3, and the difference curve, respectively. The theoretical peak for each interaction is shown in Fig. 1a, together with the residual distribution curve obtained by subtracting the sum of theoretical peaks from the original curve. As is apparent from Table 3, the temperature factor of interaction $OH - H_2O(2)$ is too small. This may be caused by the oversimplified model for free water structure, since no interaction with respect to interstitial water molecules, which appears around 3. 1 – 3. 2 Å,[15] has been included in the model.

Introduction of interactions between coordination water molecules below 5 Å, *e.g.* $H_2O - H_2O(4)$ in Fig. 3, seemed to improve the relatively small temperature factor of interaction $OH - H_2O(3)$. However, the results of such calculations yielded

Table 3. Final results of the least-squares refinement for the coordination model (Fig. 3) obtained for the range $2.5 \leqq s \leqq 15$ Å^{-1}. Standard deviations are given in parentheses. Parameter values marked with an asterisk were estimated from the geometries of the models. The units of r and b are Å and Å^2, respectively.

Te–OH	*r*	1.935(3)	[1.944(12)][a]
	b	0.0028(3)	[0.0051(11)]
	n	6	[6]
cis OH–OH	*r*	2.736*	[2.750]
	b	0.011(4)	[−0.0073(18)]
	n	12	[12]
Te–H_2O	*r*	3.92(2)	[3.889*] (*trans* OH–OH)
	b	0.042(1)	[2.0(6)]
	n	12	[3]
OH–H_2O(1)	*r*	2.58*	
	b	0.011(1)	
	n	12	
OH–H_2O(2)	*r*	3.24*	
	b	0.000(3)	
	n	12	
OH–H_2O(3)	*r*	4.37*	
	b	0.008(2)	
	n	24	
free H_2O–H_2O(1)	*r*	2.89(2)	
	b	0.007(1)	
	n	4	
free H_2O–H_2O(2)	*r*	4.72*	
	b	0.105(4)	
	n	6	
R-factor		0.132	0.532

[a] Values within brackets refer to the refinement of only $Te(OH)_6$ octahedron.

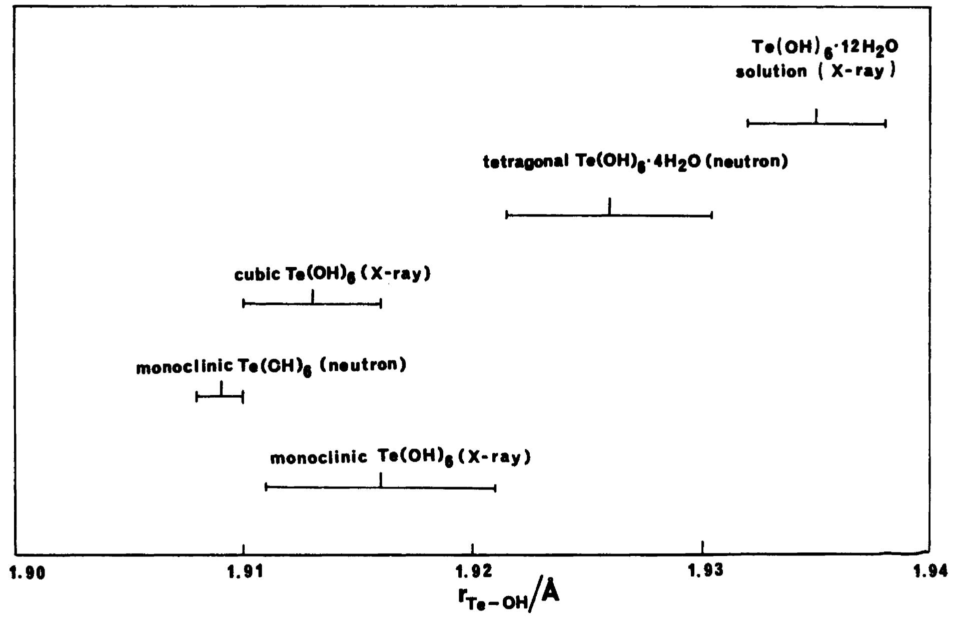

Fig. 4. A comparison of Te–OH bond lengths in $Te(OH)_6$ in solution and in the solid state.

unreasonable values for other parameters, which indicates that the water molecules are not situated rigidly according to Fig. 3. This is also suggested by the fact that only diffuse peaks appear in the residual distribution curve over 5 Å (Fig. 1b). No further details were included in the model, since the main part of the experimental $s \cdot i(s)$ values was explained by the predominant interactions considered in Table 3 (Fig. 2c).

The Te – OH bond distance within the $Te(OH)_6$ molecule in solution has been found to be 1.935(3) Å. Fig. 4 shows a comparison of the Te – OH bond lengths found in solution and in solids. The Te – OH distance found in solution is somewhat longer than those in monoclinic and cubic $Te(OH)_6$ crystals.[3–5] A long Te – OH bond length was also found in the tetragonal $Te(OH)_6 \cdot 4H_2O$. It thus seems probable that the Te – OH bond lengthens when water molecules are hydrogen-bonded to the telluric acid.

In Raman spectroscopic measurements on a Cary 82 argon ion laser spectrophotometer using the 4880 Å line, a peak due to the totally symmetric Te – OH stretching frequency appeared at 650 (±2) cm^{-1} for the sample solution, which is significantly smaller than the corresponding peak (663 ± 2 cm^{-1}) for solid $Te(OH)_6$. These frequencies agree well within experimental errors with those reported previously,[19] *i.e.* 647 and 670 cm^{-1} in solution and in solid, respectively. By using these values, the force constant of the Te – OH bond for the octahedral $Te(OH)_6$ was determined from the approximate frequency formula[20] to be $F_r = 3.99 \times 10^5$ dyn/cm (solution) and 4.15×10^5 dyn/cm (solids), which indicates that the Te – OH bond is slightly weaker in solution than in the solid state. This result corresponds well to the elongation of the Te – OH bond in solution as mentioned above.

Short hydrogen bonds between the OH units of the telluric acid and nearest neighbor water molecules were observed in solution, which indicates strong $OH - H_2O$ bonds. Short hydrogen bonds are also reported in the crystals.[3–6]

Nearest neighbor water molecules are separated from the central Te atom by 3.92 Å in solution, comparable with those found in the crystals, *e.g.* 3.91 – 3.94 Å in monoclinic $Te(OH)_6$.[3]

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