

The Crystal Structure of the Tellurate



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The crystal structure of $\text{Na}_2\text{K}_4[\text{Te}_2\text{O}_8(\text{OH})_2](\text{H}_2\text{O})_{14}$ has been determined. It belongs to the monoclinic space group $I2/m$ and there are two formula units in the unit cell, which has the dimensions $a=8.06$, $b=7.05$, $c=21.40$ Å, and $\beta=93.0^\circ$.

The structure was solved by means of three-dimensional Patterson and electron density summations, and the 805 independent $0kl-5kl$ reflections used in least squares refinements gave a final R value of 7.8 %.

The dinuclear $\text{Te}_2\text{O}_8(\text{OH})_2^{6-}$ ion consists of two oxygen octahedra sharing one edge, each having a tellurium atom at its centre. The bond distances are: $\text{Te}-\text{O}=1.90_1$ Å and 1.91_2 Å, $\text{Te}-\text{OH}=2.02_6$ Å and $\text{Te}-\text{O}_{\text{bridge}}=2.03_6$ Å. A large number of O-O distances ranging from 2.60 Å to 2.85 Å indicates considerable hydrogen bonding in the structure.

In a series of investigations of compounds containing tellurium coordinated to oxygen, the crystal structure of a new tellurate has been determined.

A variety of different crystalline phases of tellurates are formed when telluric acid and hydroxide solutions are mixed in different proportions. A recent study of $\text{K}_4[\text{Te}_2\text{O}_6(\text{OH})_4](\text{H}_2\text{O})_{7.3}$ ¹ showed that this structure is built up from dinuclear tellurate ions linked together through water molecules by hydrogen bonding. Crystals of this compound are easily obtained as described previously,¹ but in one of the preparations a few crystals showed a slightly different morphological appearance. They were initially thought to belong to the same phase, but their X-ray diffraction pattern was found to be completely different from that of $\text{K}_4[\text{Te}_2\text{O}_6(\text{OH})_4](\text{H}_2\text{O})_{7.3}$. It was therefore considered interesting to investigate the new phase and to make a comparison of these two tellurates, which crystallize from the same aqueous solution.

EXPERIMENTAL

The crystals of the new compound were formed as colourless plates, elongated along the b -axis. Their chemical composition was not obtained until the X-ray study had been completed, since attempts to prepare the pure compound in quantities sufficient for chemical analyses were unsuccessful.

The crystal used for the X-ray analysis was cut before mounting, the dimensions being $0.10 \times 0.07 \times 0.02$ mm³ (along the *a*-, *b*-, and *c*-axes, respectively). Weissenberg multiple films $0kl-5kl$ and the corresponding rotation photograph were recorded using $\text{CuK}\alpha$ radiation. From these films the unit cell was found to be monoclinic with the cell dimensions $a = 8.06 \pm 0.01$ Å, $b = 7.05 \pm 0.01$ Å, $c = 21.40 \pm 0.03$ Å and $\beta = 93.0 \pm 0.5^\circ$, giving a cell volume of 1214 Å³.

The intensities were estimated visually with a calibrated scale, prepared from timed exposures of a suitable reflection from the actual crystal. The six films recorded for each layer line were scaled together using the method of "figure of merit". A total of 805 independent reflections was measured.

The scales between the layer lines were initially given values in accordance with the exposure times.

STRUCTURE DETERMINATION

The only systematic absences occur when $h+k+l=2n+1$, suggesting one of the space groups $I2$, Im , or $I2/m$. From a three-dimensional Patterson summation $I2/m$ was deduced to be the correct one, since most of the peaks were situated in the sections $P(u0w)$ (cf. Fig. 1) and $P(u\frac{1}{2}w)$. However, statistics of the normalized structure factors gave $\langle |E| \rangle = 0.880$ and $\langle |E^2 - 1| \rangle = 0.722$. Compared with the corresponding theoretical values 0.798 and 0.968 for centrosymmetric and 0.886 and 0.736 for non-centrosymmetric structures, these values indicate either $I2$ or Im . This result clearly illustrates the failure of statistical methods when applied to structures containing heavy atoms and having many atoms in special positions.

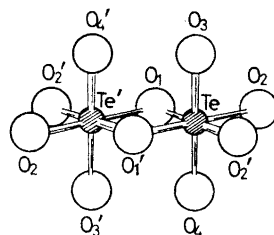
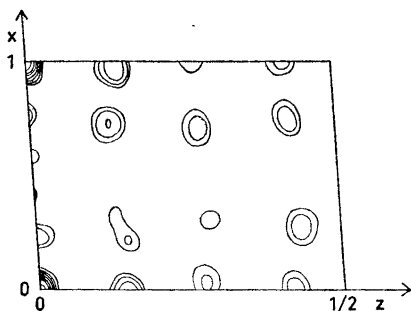


Fig. 1. The Patterson section $P(u0w)$. Fig. 2. The dinuclear $\text{Te}_2\text{O}_8(\text{OH})_2^{6-}$ ion.

The Patterson function indicated that the tellurium atoms are situated in the position $4(i)$ of $I2/m^*$ with $x=0.00$ and $z=0.07$. The signs of the structure factors calculated from these tellurium coordinates were applied to the $|F_o|$ values and a three-dimensional Fourier summation was made, using 769 reflections fulfilling the condition $0.3 < |F_o|/|F_c| < 3.0$. Eight potassium atoms

* Coordinates of equivalent positions in $I2/m$:

$(0,0,0; 1/2,1/2,1/2) \pm$
 $8(j): (x, \pm y, z); 4(i): (x, 0, z); 4(h): (0, y, 1/2); 4(g): (0, y, 0);$
 $(0,0,0; 1/2,1/2,1/2) +$
 $4(f): (1/4, \pm 1/4, 1/2); 4(e): (1/4, \pm 1/4, 0); 2(d): (0, 1/2, 1/2);$
 $2(c): (0, 0, 1/2); 2(b): (0, 1/2, 0); 2(a): (0, 0, 0);$

were found to occupy two positions 4(*i*) and all oxygen atoms bonded to the tellurium atom could be located in good agreement with the Patterson results.

After a preliminary refinement of the known atomic parameters a difference ($F_o - F_c$) synthesis was calculated. This was expected to show the oxygen atoms of the water molecules in the cell, and well defined peaks corresponding to four positions 4(*i*) and two positions 8(*j*) were found. However, one of the fourfold peaks had an electron density of $15 \text{ e}/\text{\AA}^3$, while all the others had densities (between 6 and $8.5 \text{ e}/\text{\AA}^3$) consistent with oxygen atoms. Since, in addition, the atom giving the high peak had six oxygen neighbours at distances of about 2.4 \AA , it was concluded that this peak corresponds to a sodium atom. Thus the unit cell was found to contain 4 tellurium, 8 potassium, 4 sodium and 48 oxygen atoms.

The presence of sodium atoms in the material was not suspected from the beginning, but the potassium hydroxide used in the preparation had, in fact, been stored for several months in a Pyrex flask and the crystallisation was carried out in a soda-glass vessel. Small amounts of sodium ions could, therefore, be present in the solution, making possible the formation of a sodium potassium tellurate. Subsequent attempts to prepare a pure sample of this phase, using hydroxide solutions with different ratios of sodium to potassium have failed. This may mean that the sodium-potassium compound is metastable under the preparation conditions used.

REFINEMENT OF THE STRUCTURE

A preliminary refinement of coordinates, isotropic temperature factors and separate scale factors for the six layer lines gave an *R* factor of 12 % ($R = \sum ||F_o| - |F_c|| / \sum |F_o|$). At this stage no absorption correction had

Table 1. Final atomic parameters for $\text{Na}_2\text{K}_4[\text{Te}_2\text{O}_8(\text{OH})_2](\text{H}_2\text{O})_{14}$. The anisotropic temperature factor is

$$\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + hka^*b^*U_{12} + hla^*c^*U_{13} + klb^*c^*U_{23})].$$

| Atom | X | Y | Z | U_{11} | U_{22} | U_{33} | U_{12} | U_{13} | U_{23} |
|----------------|-------------|------------|-------------|------------|-----------|-----------|------------|------------|------------|
| Te | -0.0109(2) | 0 | 0.07317(5) | 0.007(2) | 0.0062(5) | 0.0029(6) | 0 | -0.003(1) | 0 |
| K ₁ | 0.2950(10) | 0 | 0.5041(3) | 0.066(8) | 0.059(4) | 0.030(3) | 0 | 0.007(7) | 0 |
| K ₂ | 0.2341(10) | 0 | 0.7975(3) | 0.054(7) | 0.041(3) | 0.039(4) | 0 | 0.032(7) | 0 |
| Na | 0.0219(14) | 0 | 0.3461(4) | 0.020(9) | 0.024(4) | 0.034(5) | 0 | -0.042(10) | 0 |
| O ₁ | 0 | 0.1033(20) | 0 | 0.059(17) | 0.015(6) | 0.010(7) | 0 | 0.002(16) | 0 |
| O ₂ | -0.0409(10) | 0.2020(14) | 0.1305(5) | 0.060(11) | 0.020(5) | 0.018(5) | 0.000(11) | 0.035(11) | -0.009(8) |
| O ₃ | 0.2252(17) | 0 | 0.0602(5) | -0.032(11) | 0.014(5) | 0.006(6) | 0 | 0.018(10) | 0 |
| O ₄ | 0.2612(25) | 0 | -0.0581(10) | 0.012(17) | 0.027(6) | 0.060(14) | 0 | -0.026(21) | 0 |
| O ₅ | 0.2909(21) | 0 | 0.2066(7) | -0.020(12) | 0.045(5) | 0.025(8) | 0 | 0.018(13) | 0 |
| O ₆ | 0.7363(30) | 0 | 0.3567(13) | 0.006(19) | 0.070(15) | 0.123(22) | 0 | -0.008(27) | 0 |
| O ₇ | 0.0000(10) | 0.2177(16) | 0.2551(6) | 0.016(11) | 0.042(7) | 0.052(6) | -0.016(12) | -0.004(13) | 0.009(11) |
| O ₈ | 0.0207(16) | 0.2402(15) | 0.4209(7) | 0.043(12) | 0.036(6) | 0.071(10) | -0.025(13) | 0.032(15) | -0.043(12) |
| O ₉ | 0.3194(31) | 0 | 0.3754(10) | 0.053(20) | 0.049(11) | 0.065(14) | 0 | -0.015(24) | 0 |

Table 2. Observed and calculated structure factors for $\text{Na}_2\text{K}_4[\text{Te}_2\text{O}_8(\text{OH})_2](\text{H}_2\text{O})_{14}$. The columns are l , $|F_o|$ and F_c , respectively.

| | | | | | | | | | | | | | | |
|----|-----|------|-----|-----|------|-----|-----|------|----|----|-----|----|----|-----|
| 2 | 117 | 125 | 10 | - | 10 | 1 | 3 | L | 16 | - | -5 | 14 | 75 | -75 |
| 4 | 44 | -32 | 12 | 69 | 69 | -18 | - | -23 | 18 | 30 | -28 | 16 | 39 | -39 |
| 6 | 156 | -146 | 14 | 171 | 176 | -16 | - | 15 | 20 | 94 | -59 | 16 | 19 | -16 |
| 8 | 74 | -61 | 16 | 58 | 51 | -14 | 124 | 142 | 22 | 75 | -42 | | | |
| 10 | - | 26 | 18 | 32 | -30 | -12 | 119 | 108 | 24 | 52 | -45 | | | |
| 12 | 151 | 138 | | | | -10 | 37 | -27 | -2 | 84 | -88 | | | |
| 14 | 44 | 239 | 1 | 75 | 74 | -4 | 153 | -150 | -4 | 34 | -28 | | | |
| 16 | 177 | 111 | 3 | - | -20 | -4 | 161 | -156 | -2 | 59 | 57 | | | |
| 18 | 74 | -65 | 5 | 55 | -53 | -2 | 72 | -57 | 0 | 75 | 79 | | | |
| 20 | 65 | -67 | 7 | 143 | -152 | 0 | 166 | 51 | 2 | 47 | 70 | | | |
| 22 | 82 | -75 | 9 | 64 | -54 | 2 | 115 | 104 | 0 | 90 | -61 | | | |
| 24 | 66 | 52 | 11 | 64 | 34 | 4 | 58 | -56 | 8 | 93 | -79 | | | |
| 26 | 78 | 85 | 13 | 64 | 70 | 6 | 94 | -91 | 10 | - | -16 | | | |
| | | | 15 | 71 | 65 | 8 | 174 | -178 | 12 | 78 | 65 | | | |
| | | | | | | 10 | 62 | -63 | 14 | 66 | 76 | | | |
| | | | 0 | 1 | 1 | 12 | 111 | 104 | | | | | | |
| | | | 2 | 58 | 49 | 14 | 76 | 78 | | | | | | |
| | | | 4 | 29 | -23 | 16 | - | -4 | | | | | | |
| | | | 6 | 73 | -81 | 18 | 51 | -69 | | | | | | |
| | | | 8 | 90 | -91 | 20 | 90 | -89 | | | | | | |
| | | | 10 | - | -1 | 22 | 16 | -79 | | | | | | |
| | | | 12 | 60 | 62 | 24 | 32 | -28 | | | | | | |
| | | | 14 | 124 | 119 | | | | | | | | | |
| | | | 16 | 42 | -41 | -19 | 74 | -82 | | | | | | |
| | | | 18 | 104 | -117 | -17 | 74 | -6 | | | | | | |
| | | | 20 | 112 | -177 | -15 | 87 | 93 | | | | | | |
| | | | 22 | 77 | 81 | -13 | 88 | 52 | | | | | | |
| | | | 24 | 77 | 85 | -11 | 55 | -40 | | | | | | |
| | | | 26 | 77 | 85 | -9 | 55 | -40 | | | | | | |
| | | | 28 | 77 | 85 | -7 | 55 | -40 | | | | | | |
| | | | 30 | 77 | 85 | -5 | 55 | -40 | | | | | | |
| | | | 32 | 77 | 85 | -3 | 55 | -40 | | | | | | |
| | | | 34 | 77 | 85 | -1 | 55 | -40 | | | | | | |
| | | | 36 | 77 | 85 | 1 | 55 | -40 | | | | | | |
| | | | 38 | 77 | 85 | 3 | 55 | -40 | | | | | | |
| | | | 40 | 77 | 85 | 5 | 55 | -40 | | | | | | |
| | | | 42 | 77 | 85 | 7 | 55 | -40 | | | | | | |
| | | | 44 | 77 | 85 | 9 | 55 | -40 | | | | | | |
| | | | 46 | 77 | 85 | 11 | 55 | -40 | | | | | | |
| | | | 48 | 77 | 85 | 13 | 55 | -40 | | | | | | |
| | | | 50 | 77 | 85 | 15 | 55 | -40 | | | | | | |
| | | | 52 | 77 | 85 | 17 | 55 | -40 | | | | | | |
| | | | 54 | 77 | 85 | 19 | 55 | -40 | | | | | | |
| | | | 56 | 77 | 85 | 21 | 55 | -40 | | | | | | |
| | | | 58 | 77 | 85 | 23 | 55 | -40 | | | | | | |
| | | | 60 | 77 | 85 | 25 | 55 | -40 | | | | | | |
| | | | 62 | 77 | 85 | 27 | 55 | -40 | | | | | | |
| | | | 64 | 77 | 85 | 29 | 55 | -40 | | | | | | |
| | | | 66 | 77 | 85 | 31 | 55 | -40 | | | | | | |
| | | | 68 | 77 | 85 | 33 | 55 | -40 | | | | | | |
| | | | 70 | 77 | 85 | 35 | 55 | -40 | | | | | | |
| | | | 72 | 77 | 85 | 37 | 55 | -40 | | | | | | |
| | | | 74 | 77 | 85 | 39 | 55 | -40 | | | | | | |
| | | | 76 | 77 | 85 | 41 | 55 | -40 | | | | | | |
| | | | 78 | 77 | 85 | 43 | 55 | -40 | | | | | | |
| | | | 80 | 77 | 85 | 45 | 55 | -40 | | | | | | |
| | | | 82 | 77 | 85 | 47 | 55 | -40 | | | | | | |
| | | | 84 | 77 | 85 | 49 | 55 | -40 | | | | | | |
| | | | 86 | 77 | 85 | 51 | 55 | -40 | | | | | | |
| | | | 88 | 77 | 85 | 53 | 55 | -40 | | | | | | |
| | | | 90 | 77 | 85 | 55 | 55 | -40 | | | | | | |
| | | | 92 | 77 | 85 | 57 | 55 | -40 | | | | | | |
| | | | 94 | 77 | 85 | 59 | 55 | -40 | | | | | | |
| | | | 96 | 77 | 85 | 61 | 55 | -40 | | | | | | |
| | | | 98 | 77 | 85 | 63 | 55 | -40 | | | | | | |
| | | | 100 | 77 | 85 | 65 | 55 | -40 | | | | | | |
| | | | 102 | 77 | 85 | 67 | 55 | -40 | | | | | | |
| | | | 104 | 77 | 85 | 69 | 55 | -40 | | | | | | |
| | | | 106 | 77 | 85 | 71 | 55 | -40 | | | | | | |
| | | | 108 | 77 | 85 | 73 | 55 | -40 | | | | | | |
| | | | 110 | 77 | 85 | 75 | 55 | -40 | | | | | | |
| | | | 112 | 77 | 85 | 77 | 55 | -40 | | | | | | |
| | | | 114 | 77 | 85 | 79 | 55 | -40 | | | | | | |
| | | | 116 | 77 | 85 | 81 | 55 | -40 | | | | | | |
| | | | 118 | 77 | 85 | 83 | 55 | -40 | | | | | | |
| | | | 120 | 77 | 85 | 85 | 55 | -40 | | | | | | |
| | | | 122 | 77 | 85 | 87 | 55 | -40 | | | | | | |
| | | | 124 | 77 | 85 | 89 | 55 | -40 | | | | | | |
| | | | 126 | 77 | 85 | 91 | 55 | -40 | | | | | | |
| | | | 128 | 77 | 85 | 93 | 55 | -40 | | | | | | |
| | | | 130 | 77 | 85 | 95 | 55 | -40 | | | | | | |
| | | | 132 | 77 | 85 | 97 | 55 | -40 | | | | | | |
| | | | 134 | 77 | 85 | 99 | 55 | -40 | | | | | | |
| | | | 136 | 77 | 85 | 101 | 55 | -40 | | | | | | |
| | | | 138 | 77 | 85 | 103 | 55 | -40 | | | | | | |
| | | | 140 | 77 | 85 | 105 | 55 | -40 | | | | | | |
| | | | 142 | 77 | 85 | 107 | 55 | -40 | | | | | | |
| | | | 144 | 77 | 85 | 109 | 55 | -40 | | | | | | |
| | | | 146 | 77 | 85 | 111 | 55 | -40 | | | | | | |
| | | | 148 | 77 | 85 | 113 | 55 | -40 | | | | | | |
| | | | 150 | 77 | 85 | 115 | 55 | -40 | | | | | | |
| | | | 152 | 77 | 85 | 117 | 55 | -40 | | | | | | |
| | | | 154 | 77 | 85 | 119 | 55 | -40 | | | | | | |
| | | | 156 | 77 | 85 | 121 | 55 | -40 | | | | | | |
| | | | 158 | 77 | 85 | 123 | 55 | -40 | | | | | | |
| | | | 160 | 77 | 85 | 125 | 55 | -40 | | | | | | |
| | | | 162 | 77 | 85 | 127 | 55 | -40 | | | | | | |
| | | | 164 | 77 | 85 | 129 | 55 | -40 | | | | | | |
| | | | 166 | 77 | 85 | 131 | 55 | -40 | | | | | | |
| | | | 168 | 77 | 85 | 133 | 55 | -40 | | | | | | |
| | | | 170 | 77 | 85 | 135 | 55 | -40 | | | | | | |
| | | | 172 | 77 | 85 | 137 | 55 | -40 | | | | | | |
| | | | 174 | 77 | 85 | 139 | 55 | -40 | | | | | | |
| | | | 176 | 77 | 85 | 141 | 55 | -40 | | | | | | |
| | | | 178 | 77 | 85 | 143 | 55 | -40 | | | | | | |
| | | | 180 | 77 | 85 | 145 | 55 | -40 | | | | | | |
| | | | 182 | 77 | 85 | 147 | 55 | -40 | | | | | | |
| | | | 184 | 77 | 85 | 149 | 55 | -40 | | | | | | |
| | | | 186 | 77 | 85 | 151 | 55 | -40 | | | | | | |
| | | | 188 | 77 | 85 | 153 | 55 | -40 | | | | | | |
| | | | 190 | 77 | 85 | 155 | 55 | -40 | | | | | | |
| | | | 192 | 77 | 85 | 157 | 55 | -40 | | | | | | |
| | | | 194 | 77 | 85 | 159 | 55 | -40 | | | | | | |
| | | | 196 | 77 | 85 | 161 | 55 | -40 | | | | | | |
| | | | 198 | 77 | 85 | 163 | 55 | -40 | | | | | | |
| | | | 200 | 77 | 85 | 165 | 55 | -40 | | | | | | |
| | | | 202 | 77 | 85 | 167 | 55 | -40 | | | | | | |
| | | | 204 | 77 | 85 | 169 | 55 | -40 | | | | | | |
| | | | 206 | 77 | 85 | 171 | 55 | -40 | | | | | | |
| | | | 208 | 77 | 85 | 173 | 55 | -40 | | | | | | |
| | | | 210 | 77 | 85 | 175 | 55 | -40 | | | | | | |
| | | | 212 | 77 | 85 | 177 | 55 | -40 | | | | | | |
| | | | 214 | 77 | 85 | 179 | 55 | -40 | | | | | | |
| | | | 216 | 77 | 85 | 181 | 55 | -40 | | | | | | |
| | | | 218 | 77 | 85 | 183 | 55 | -40 | | | | | | |
| | | | 220 | 77 | 85 | 185 | 55 | -40 | | | | | | |
| | | | 222 | 77 | 85 | 187 | 55 | -40 | | | | | | |
| | | | 224 | 77 | 85 | 189 | 55 | -40 | | | | | | |
| | | | 226 | 77 | 85 | 191 | 55 | -40 | | | | | | |
| | | | 228 | 77 | 85 | 193 | 55 | -40 | | | | | | |
| | | | 230 | 77 | 85 | 195 | 55 | -40 | | | | | | |
| | | | 232 | 77 | 85 | 197 | 55 | -40 | | | | | | |
| | | | 234 | 77 | 85 | 199 | 55 | -40 | | | | | | |
| | | | 236 | 77 | 85 | 201 | 55 | -40 | | | | | | |
| | | | 238 | 77 | 85 | 203 | 55 | -40 | | | | | | |
| | | | 240 | 77 | 85 | 205 | 55 | -40 | | | | | | |
| | | | 242 | 77 | 85 | 207 | 55 | -40 | | | | | | |
| | | | 244 | 77 | 85 | 209 | 55 | -40 | | | | | | |
| | | | 246 | 77 | 85 | 211 | 55 | -40 | | | | | | |
| | | | 248 | 77 | 85 | 213 | 55 | -40 | | | | | | |
| | | | 250 | 77 | 85 | 215 | 55 | -40 | | | | | | |
| | | | 252 | 77 | 85 | 217 | 55 | -40 | | | | | | |

factor weights according to the formula $w=(a+|F_o|+c|F_o|^2+d|F_o|^3)^{-1}$, with $a=120$, $c=0.004$, and $d=0.00006$, were applied.⁴ The final weight analysis (cf. Table 3) has an abnormally high value of $w \cdot \Delta^2$ for the $|F_o|$ interval corresponding to the strongest reflections. These are, however, probably effected by primary and secondary extinction not accounted for.

Table 3. Weight analysis. The quantities $w \cdot \Delta^2$ have been normalized giving the sum of the values for the ten $|F_o|$ intervals equal to 10.0. N is the number of reflections in each interval.

| $ F_o $ interval | $w \cdot \Delta^2$ | N |
|------------------|--------------------|-----|
| 0.0— 38.8 | 1.04 | 80 |
| 38.8— 49.4 | 1.10 | 81 |
| 49.4— 58.7 | 0.75 | 81 |
| 58.7— 67.0 | 0.95 | 81 |
| 67.0— 75.1 | 0.72 | 83 |
| 75.1— 83.2 | 0.81 | 78 |
| 83.2— 93.8 | 0.71 | 81 |
| 93.8—107.8 | 1.10 | 81 |
| 107.8—131.0 | 0.89 | 81 |
| 131.0—294.0 | 1.93 | 81 |

A three-dimensional ($F_o - F_c$) Fourier summation was calculated to check the refinement results. Good agreement was obtained and the largest differences, corresponding to about $2.5 \text{ e}/\text{\AA}^3$, occurred on the line (0,0,z).

Because of the presence of the sodium atoms and the many special positions, the structure was also refined as if it belonged to the space group $I2$, in spite of the very clear indications of $I2/m$ in the Patterson function. The coordinates were moved out of their centric positions, but in the refinement they were shifted back again, leading to matrix singularities. Since Im is considered quite impossible, this result offers extra proof for the correctness of the structure determination.

All calculations have been carried out on an IBM 360/50 computer. The following programs were used:⁵ Lp and absorption correction—DATAP2; E statistics—GAASA; Patterson and Fourier summations—DRF; Refinements—LALS; Distances and angles—DISTAN.

DESCRIPTION OF THE STRUCTURE

The structure contains dinuclear tellurium ions consisting of two TeO_6 octahedra sharing an edge. Distances and angles within this ion are given in Table 4 in accordance with the notation of Fig. 2. As can be seen, six of the twelve Te—O distances are significantly longer ($2.02_6 - 2.03_6 \text{ \AA}$) than the others ($1.90_1 - 1.91_2 \text{ \AA}$). These six distances would then correspond to oxygen single bonds, O_1 being shared between two tellurium atoms and O_4 belonging to a hydroxyl group. The formula of the complex tellurium ion should then be $\text{Te}_2\text{O}_8(\text{OH})_2^{6-}$, which is in accordance with the fact that it is neutralized by two Na^+ and four K^+ ions. The chemical composition of the compound should thus be given as $\text{Na}_2\text{K}_4[\text{Te}_2\text{O}_8(\text{OH})_2](\text{H}_2\text{O})_{14}$.

Table 4. Distances and angles in the dinuclear tellurate ion $\text{Te}_2\text{O}_8(\text{OH})_2^{6-}$.

| | | | |
|----------------------------------|------------|-------------------------------------|-----------|
| Te—Te' | 3.146(5) Å | O ₁ —Te—O ₁ ' | 78.8(6)° |
| Te—O ₁ | 2.036(9) | O ₁ —Te—O ₂ | 92.0(4) |
| Te—O ₂ | 1.912(11) | O ₁ —Te—O ₃ | 88.7(5) |
| Te—O ₃ | 1.901(14) | O ₁ —Te—O ₄ | 87.8(6) |
| Te—O ₄ | 2.026(21) | O ₂ —Te—O ₂ | 96.3(6) |
| | | O ₂ —Te—O ₃ | 97.7(6) |
| | | O ₂ —Te—O ₄ | 85.3(7) |
| | | O ₃ —Te—O ₄ | 175.4(7) |
| O ₁ —O ₁ ' | 2.59(3) Å | O ₂ —O ₂ ' | 2.85(2) Å |
| O ₁ —O ₂ | 2.84(1) | O ₂ —O ₃ | 2.87(2) |
| O ₁ —O ₃ | 2.75(2) | O ₂ —O ₄ | 2.67(2) |
| O ₁ —O ₄ | 2.82(2) | O ₃ —O ₄ ' | 2.99(2) |

A comparison of the anion in $\text{K}_4[\text{Te}_2\text{O}_6(\text{OH})_4](\text{H}_2\text{O})_{7.3}^1$ with that of $\text{Na}_2\text{K}_4[\text{Te}_2\text{O}_8(\text{OH})_2](\text{H}_2\text{O})_{14}$ shows good agreement between the bond distances:

| | Te—O (Å) | Te—OH (Å) | Te—O _{bridge} (Å) |
|---|---------------------------------------|---------------------------------------|---------------------------------------|
| $\text{Te}_2\text{O}_6(\text{OH})_4^{4-}$ | 1.86 ₁ , 1.89 ₄ | 1.98 ₅ , 2.00 ₅ | 1.98 ₅ , 2.02 ₉ |
| $\text{Te}_2\text{O}_8(\text{OH})_2^{6-}$ | 1.90 ₁ , 1.91 ₂ | 2 × 2.02 ₆ | 2 × 2.03 ₆ |

There are no significant differences in the various Te—O bond types, but a small expansion of all the bonds in $\text{Te}_2\text{O}_8(\text{OH})_2^{6-}$ is indicated, as might be expected from the higher charge of this ion. The structure of $\text{K}_4[\text{Te}_2\text{O}_6(\text{OH})_4](\text{H}_2\text{O})_{7.3}$ has also been compared¹ with those of $\text{KTeO}(\text{OH})_5 \cdot \text{H}_2\text{O}$,⁶ $\text{KTeO}_2(\text{OH})_3$,⁷ $\text{KTeO}_3(\text{OH})$,⁸ and $\text{K}_4[\text{I}_2\text{O}_8(\text{OH})_2](\text{H}_2\text{O})_8$.⁹

All O—O distances below 3.4 Å in the cell, except those within the $\text{Te}_2\text{O}_8(\text{OH})_2^{6-}$ ion, are listed in Table 5. Only those shorter than 3.0 Å, however, are considered to be possible for hydrogen bonding. For most of the 56 hydrogen atoms belonging to the water molecules (O₅—O₉) in the cell, very probable locations can be deduced. The hydrogen atoms of O₅, O₆, O₈, and O₉ are likely to be situated as proposed in Table 5, but for O₇ the situation is not so clear.

Table 5. Distances and angles indicating hydrogen bonds in the structure of $\text{Na}_2\text{K}_4[\text{Te}_2\text{O}_8(\text{OH})_2](\text{H}_2\text{O})_{14}$ (cf. Fig. 3).

| | | | |
|---|-----------|--|-----------|
| O ₅ —O ₃ | 2.73(2) Å | O ₈ —O ₃ (2 ×) | 2.66(2) Å |
| O ₅ —O ₇ (2 ×) | 2.70(2) | O ₈ —O ₄ (2 ×) | 2.85(2) |
| O ₆ —O ₂ (2 ×) | 2.63(2) | O ₉ —O ₂ (2 ×) | 2.80(2) |
| O ₇ —O ₂ | 2.68(2) | (O ₈ —O ₈ (2 ×)) | 3.18(3) |
| (O ₇ —O ₅ (2 ×)) | 3.03(2) | (O ₈ —O ₉ (2 ×)) | 3.12(3) |
| (O ₇ —O ₇) | 3.07(3) | | |
| O ₃ —O ₅ —O ₇ | 112.7(6)° | (O ₃ ···H—O ₅ —H···O ₇) | |
| (O ₇ —O ₅ —O ₇) | 94.8(8) | | |
| O ₂ —O ₆ —O ₂ | 106.0(9) | (O ₂ ···H—O ₆ —H···O ₂) | |
| (O ₂ —O ₇ —O ₅) | 73.2(6) | | |
| (O ₂ —O ₇ —O ₇) | 87.6(3) | (O ₂ ···H—O ₇ —H···(O ₅ , O ₇)) | |
| O ₂ —O ₇ —O ₅ | 112.8(7) | | |
| O ₃ —O ₈ —O ₄ | 99.0(5) | (O ₃ ···H—O ₈ —H···O ₄) | |
| O ₂ —O ₉ —O ₂ | 97.4(9) | (O ₂ ···H—O ₉ —H···O ₂) | |

There are eight distances O_7-O_2 of 2.68 Å suggesting an eight-fold position $O_7-H\cdots O_2$ for one of the hydrogen atoms of O_7 . For the other one there are only four distances O_5-O_7 of 2.70 Å left, and the four remaining hydrogen atoms might be directed towards symmetry-related O_7 or O_5 atoms (*cf.* Table 5). Exact predictions concerning the location of the hydrogen on O_4 are difficult, but it is probably linked to O_3 within the anion. Probable hydrogen bonding is marked out in Fig. 3, which shows a projection of the structure along the b -axis.

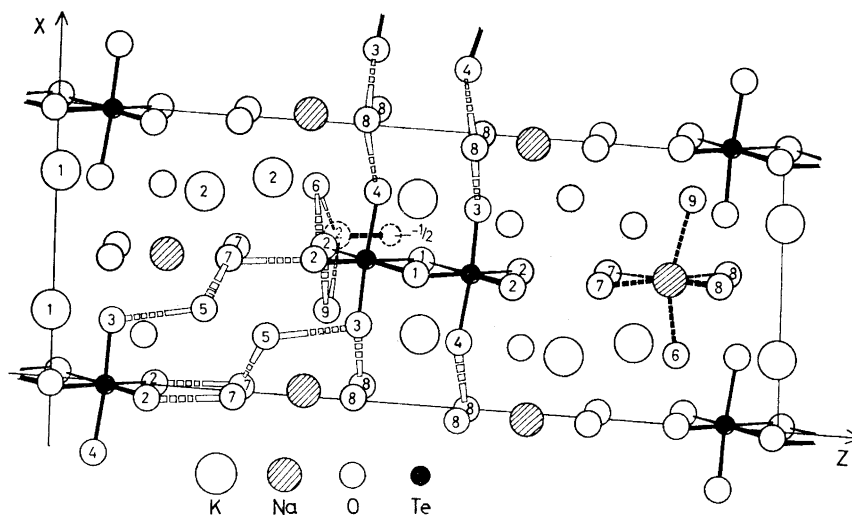


Fig. 3. The structure of $Na_2K_4[Te_2O_8(OH)_2](H_2O)_{14}$ projected along the b -axis. Atoms related by the mirror plane have been shifted relative to one another for the sake of clarity.

The sodium atoms are six-coordinated with $Na-O$ distances ranging from 2.31 Å to 2.48 Å with a mean value of 2.41 Å (*cf.* Table 6 and Fig. 3). This is in good agreement with the values (2.25–2.78 Å) given in the *International*

Table 6. Coordination distances for the sodium and potassium atoms.

| | | | |
|------------------|---------------|------------------|-----------|
| | $Na-O_6$ | | 2.31(3) Å |
| | $Na-O_8$ (2×) | | 2.37(2) |
| | $Na-O_9$ | | 2.45(3) |
| | $Na-O_7$ (2×) | | 2.48(1) |
| K_1-O_9 | 2.83(2) Å | K_2-O_7 (2×) | 2.83(2) Å |
| K_1-O_6 | 2.98(3) | K_2-O_2 (2×) | 2.89(2) |
| K_1-O_1 (2×) | 2.98(1) | K_2-O_3 (2×) | 2.94(2) |
| K_1-O_8 (2×) | 3.04(2) | K_2-O_4 | 3.10(2) |
| K_1-O_5 (2×) | 3.36(2) | K_2-O_6 | 3.30(3) |
| (K_1-O_2) (2×) | 3.72(2) | K_2-O_5 | 3.43(2) |
| (K_1-O_4) (2×) | 3.72(1) | (K_2-O_8) (2×) | 3.67(2) |
| | | (K_2-O_6) (2×) | 3.77(1) |

*Tables.*² The definite coordination of the potassium atoms is not obvious (see Table 6). However, K_1 has eight oxygen atoms at distances ranging from 2.83 to 3.36 Å while K_2 has nine at distances between 2.83 and 3.43 Å.

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