

## Crystal Chemistry of Some Addition Compounds of Alkali Iodates with Telluric Acid

M. T. AVERBUCH-POUCHOT

*Laboratoire de Cristallographie, Centre National de la Recherche Scientifique, Laboratoire associé à l'USMG, 166 X, 38042 Grenoble Cédex, France*

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Five addition compounds of telluric acid with alkali iodates are described. Three of these compounds are orthorhombic and isotypic:  $\text{RbIO}_3 \cdot \text{Te}(\text{OH})_6$ ,  $\text{KIO}_3 \cdot \text{Te}(\text{OH})_6$ , and  $\text{NH}_4\text{IO}_3 \cdot \text{Te}(\text{OH})_6$ . The crystal structure of this class of compounds has been solved with the potassium salt whose unit-cell dimensions are  $a = 14.30(1) \text{ \AA}$ ,  $b = 6.734(5) \text{ \AA}$ ,  $c = 8.711(5) \text{ \AA}$ ,  $Pc2_1n (C_{2v}^2)$ ,  $Z = 4$ . Crystal data are given for the two isotypic salts. The crystal structures of two other compounds have been determined.  $2\text{KIO}_3 \cdot \text{Te}(\text{OH})_6$  is trigonal,  $R\bar{3}$ , with the unit cell dimensions  $a = 6.500(5) \text{ \AA}$ ,  $c = 25.717(8) \text{ \AA}$ ,  $Z = 3$  for the hexagonal description.  $\text{NH}_4\text{IO}_3 \cdot \text{Te}(\text{OH})_6 \cdot \text{H}_2\text{O}$  is triclinic ( $P\bar{1}$ ) with  $a = 10.99(1) \text{ \AA}$ ,  $b = 6.932(4) \text{ \AA}$ ,  $c = 6.559(4) \text{ \AA}$ ,  $\alpha = 88.89(5)^\circ$ ,  $\beta = 90.88(5)^\circ$ ,  $\gamma = 104.48(5)^\circ$ , and  $Z = 2$ . For these three different crystal structure determinations the final  $R$  values are, respectively, 0.047, 0.030, and 0.036. The first class of compounds described in this paper,  $\text{MIO}_3 \cdot \text{Te}(\text{OH})_6$  ( $M = \text{K}, \text{Rb}, \text{NH}_4$ ) is a new class of piezoelectric materials.

### Introduction

Telluric acid forms addition compounds with several kinds of inorganic salts: phosphates, arsenates, sulfates, and iodates. These addition compounds with phosphates, arsenates, and sulfates have been extensively studied by the author (1-8).

The present work deals with a structural characterization of three types of addition compounds of telluric acid with some alkali iodates. We describe the crystal structures of  $\text{KIO}_3 \cdot \text{Te}(\text{OH})_6$ ,  $\text{NH}_4\text{IO}_3 \cdot \text{Te}(\text{OH})_6 \cdot \text{H}_2\text{O}$ , and  $2\text{KIO}_3 \cdot \text{Te}(\text{OH})_6$ . Crystal data for  $\text{RbIO}_3 \cdot \text{Te}(\text{OH})_6$  and  $\text{NH}_4\text{IO}_3 \cdot \text{Te}(\text{OH})_6$ , both isotypic with  $\text{KIO}_3 \cdot \text{Te}(\text{OH})_6$ , are tab-

ulated. All these salts have already been described in early chemical literature (9-11) but have never been investigated from a structural point of view.

### Experimental

#### A. Chemical Preparations

All the compounds have been prepared at room temperature, by slow evaporation of a water solution containing telluric acid, diiodine pentoxide, and a salt of the corresponding associated cation. We report in Table I the various molecular ratios used for these preparations and the morphologies observed for the crystals.

TABLE I  
MOLECULAR RATIOS USED IN THE CHEMICAL PREPARATIONS AND MORPHOLOGIES OF THE  
OBTAINED CRYSTALS

Compounds	Te(OH) <sub>6</sub>	I <sub>2</sub> O <sub>5</sub>	KOH	NH <sub>4</sub> OH	Rb <sub>2</sub> CO <sub>3</sub>	NH <sub>4</sub> HCO <sub>3</sub>	Morphologies
2KIO <sub>3</sub> · Te(OH) <sub>6</sub>	1	1.5	3				Trigonal scalenohedron
KIO <sub>3</sub> · Te(OH) <sub>6</sub>	1	0.5	1				Orthorhombic bipyramidal prisms
NH <sub>4</sub> IO <sub>3</sub> · Te(OH) <sub>6</sub>	1	0.5		1			
RbIO <sub>3</sub> · Te(OH) <sub>6</sub>	1	0.5			0.5		
NH <sub>4</sub> IO <sub>3</sub> · Te(OH) <sub>6</sub> · H <sub>2</sub> O <sup>a</sup>	1	0.5				1	Triclinic pinacoid

<sup>a</sup> Some difficulties arose during the preparation of this last compound. The only successful synthesis requires ammonium bicarbonate.

### B. Crystal Data

Table II reports the main physical and crystallographic data for these five compounds.

Approximate unit cell dimensions and possible space groups have been determined by using film techniques. Unit-cell dimensions have been further refined by a least squares method from the angular data obtained with a powder diffractometer operating at a very low scan speed [ $1/8^\circ(\Theta) \cdot \text{min}^{-1}$ ] ( $\lambda = \text{CuK}\alpha$ ). Unit-cell dimensions obtained from these powder diagrams differ slightly from those refined with the angular data of the four circle diffractome-

ter. These last ones are reported in the summary and have been used throughout the crystal structure determination and for the final interatomic distance calculations. Tables III, IV, and V report indexed powder data for NH<sub>4</sub>IO<sub>3</sub> · Te(OH)<sub>6</sub>, NH<sub>4</sub>IO<sub>3</sub> · Te(OH)<sub>6</sub> · H<sub>2</sub>O, and 2KIO<sub>3</sub> · Te(OH)<sub>6</sub>. Intensities given in these tables are peak heights above the background.

The observed extinctions rules for NH<sub>4</sub>IO<sub>3</sub> · Te(OH)<sub>6</sub>,  $h k 0$  only with  $h + k = 2n$  and  $0 k l$  only with  $l = 2n$ , lead to two possible space groups:  $Pc2_1n$  ( $C_{2v}^9$ ) or  $Pcmn$  ( $D_{2h}^{16}$ ). For 2KIO<sub>3</sub> · Te(OH)<sub>6</sub> the condition  $-h + k + l = 3n$  corresponds to five possible space groups,  $R3$ ,  $R\bar{3}$ ,  $R3m$ ,  $R\bar{3}m$ , and

TABLE II  
UNIT-CELL DIMENSIONS, FORMULA WEIGHTS, UNIT-CELL VOLUMES, AND CALCULATED DENSITIES FOR THE  
TITLE COMPOUNDS

Formula	<i>M</i>	Unit cells (Å)			<i>V</i> (Å <sup>3</sup> )	<i>Z</i>	S.G.	<i>D<sub>x</sub></i>
KIO <sub>3</sub> · Te(OH) <sub>6</sub>	443.64	14.22(1)	6.696(3)	8.672(5)	825.72	4	$Pc2_1n$	3.568
RbIO <sub>3</sub> · Te(OH) <sub>6</sub>	490.01	14.225(8)	6.893(3)	8.867(5)	869.43	4	$Pc2_1n$	3.743
NH <sub>4</sub> IO <sub>3</sub> · Te(OH) <sub>6</sub>	422.58	14.25(1)	6.842(3)	8.826(5)	860.52	4	$Pc2_1n$	3.261
Te(OH) <sub>6</sub> · 2KIO <sub>3</sub>	657.64	6.482(5)	25.664(8)		933.72	3	$R\bar{3}$	3.508
		$a_{Rh} = 9.336, \alpha_{Rh} = 40.63$						
Te(OH) <sub>6</sub> · NH <sub>4</sub> IO <sub>3</sub> · H <sub>2</sub> O	440.58	10.97(1)	6.916(5)	6.550(4)	481.37	2	$P\bar{1}$	3.039
		88.84(5)	90.81(5)	104.48(5)				

TABLE III  
INDEXED POWDER DATA FOR  $\text{NH}_4\text{IO}_3 \cdot \text{Te}(\text{OH})_6$

<i>hkl</i>	<i>d</i> <sub>calc</sub>	<i>d</i> <sub>obs</sub>	<i>I</i> <sub>obs</sub>	<i>hkl</i>	<i>d</i> <sub>calc</sub>	<i>d</i> <sub>obs</sub>	<i>I</i> <sub>obs</sub>
1 0 1	7.50	7.47	2	1 0 3	2.881	2.883	5
2 0 0	7.12	7.12	10	4 0 2	2.772	2.771	4
1 1 0	6.17	6.16	25	2 0 3	2.719	2.720	11
2 0 1	5.54	5.54	37	5 0 1	2.712	2.712	13
1 1 1	5.06	5.06	100	0 2 2	2.704	2.701	42
0 0 2	4.41	4.41	33	1 2 2	2.656	2.656	21
2 1 1	4.31	4.31	11	1 1 3	2.655	—	—
1 0 2	4.22	4.21	44	3 2 1	2.648	—	—
3 0 1	4.18	—	—	5 1 0	2.631	2.629	5
3 1 0	3.902	3.904	89	4 1 2	2.569	2.569	29
2 0 2	3.752	3.751	8	2 2 2	2.528	2.526	4
0 1 2	3.708	3.709	9	2 1 3	2.527	—	—
1 1 2	3.589	3.587	13	5 1 1	2.521	—	—
3 1 1	3.569	3.569	5	3 0 3	2.501	—	—
4 0 0	3.563	—	—	4 2 0	2.467	2.467	2
0 2 0	3.421	3.421	39	5 0 2	2.394	2.395	6
4 0 1	3.304	—	—	4 2 1	2.376	2.374	26
2 1 2	3.290	3.293	45	6 0 0	2.375	—	—
3 0 2	3.233	3.236	9	3 2 2	2.350	2.350	5
1 2 1	3.113	—	—	3 1 3	2.349	—	—
2 2 0	3.084	3.085	6	6 0 1	2.293	2.290	2
4 1 1	2.975	—	—	4 0 3	2.268	—	—
3 1 2	2.923	2.922	35	5 1 2	2.260	2.259	5
2 2 1	2.911	—	—	—	—	—	—

TABLE IV  
INDEXED POWDER DATA FOR  
 $\text{NH}_4\text{IO}_3 \cdot \text{Te}(\text{OH})_6 \cdot \text{H}_2\text{O}$

<i>hkl</i>	<i>d</i> <sub>calc</sub>	<i>d</i> <sub>obs</sub>	<i>I</i> <sub>obs</sub>	<i>hkl</i>	<i>d</i> <sub>calc</sub>	<i>d</i> <sub>obs</sub>	<i>I</i> <sub>obs</sub>
1 0 0	10.62	—	—	2 $\bar{2}$ 0	3.219	3.219	22
0 1 0	6.70	6.69	54	1 0 2	3.137	—	—
0 0 1	6.55	—	—	3 0 1	3.127	—	—
1 $\bar{1}$ 0	6.44	—	—	1 0 2	3.121	3.121	13
1 0 1	5.60	5.59	30	3 1 1	3.121	—	—
1 0 1	5.55	—	—	3 0 1	3.103	—	—
2 0 0	5.31	5.32	100	1 2 1	3.080	3.076	39
1 1 0	5.12	5.12	15	3 1 1	3.073	—	—
2 $\bar{1}$ 0	4.78	—	—	1 2 1	3.027	3.029	5
0 1 1	4.72	4.73	23	0 2 1	3.003	—	—
1 $\bar{1}$ 1	4.64	4.65	98	1 2 0	2.987	2.985	12
0 $\bar{1}$ 1	4.64	—	—	0 1 2	2.962	2.963	6
1 1 1	4.54	4.54	20	0 2 1	2.961	—	—
2 0 1	4.14	4.14	24	1 1 2	2.945	—	—
2 0 1	4.11	4.11	12	0 1 2	2.922	2.926	2
1 1 1	4.05	4.04	33	2 2 1	2.915	—	—
1 1 1	4.02	4.02	21	1 1 2	2.893	2.895	2
2 1 1	3.902	3.909	30	2 2 1	2.864	2.861	5
2 1 1	3.825	3.829	45	3 1 0	2.850	2.852	10
2 1 0	3.733	3.735	20	3 2 0	2.809	2.810	13
3 0 0	3.541	—	—	2 0 2	2.799	—	—
3 1 0	3.514	—	—	2 0 2	2.776	2.771	6
1 2 0	3.451	3.453	28	1 1 2	2.769	—	—
0 2 0	3.349	3.346	5	1 1 2	2.747	2.745	2
0 0 2	3.274	3.277	62	1 2 1	2.731	2.729	5
2 1 1	3.247	3.243	15	2 1 2	2.729	—	—
2 1 1	3.239	—	—	4 1 0	2.712	2.713	8
—	—	—	—	1 2 1	2.705	2.705	12

TABLE V  
INDEXED POWDER DATA FOR  $2\text{KIO}_3 \cdot \text{Te}(\text{OH})_6$

<i>hkl</i>	<i>d</i> <sub>calc</sub>	<i>d</i> <sub>obs</sub>	<i>I</i> <sub>obs</sub>	<i>hkl</i>	<i>d</i> <sub>calc</sub>	<i>d</i> <sub>obs</sub>	<i>I</i> <sub>obs</sub>
0 0 3	8.55	8.55	23	2 1 7	1.836	1.836	1
1 0 1	5.48	5.48	16	3 0 3	1.828	1.827	1
0 1 2	5.14	—	—	2.0.11	1.794	1.795	2
0 0 6	4.28	4.27	100	1.1.12	1.785	1.785	7
1 0 4	4.22	—	—	1 2 8	1.770	—	—
0 1 5	3.788	3.787	65	0.1.14	1.743	1.743	2
1 1 0	3.241	3.241	12	3 0 6	1.714	1.714	2
1 0 7	3.069	3.071	2	0.0.15	1.711	—	—
1 1 3	3.031	3.030	2	2.1.10	1.635	1.635	1
0 0 9	2.851	2.851	12	2 2 0	1.620	1.620	1
0 2 1	2.790	2.787	3	0.2.13	1.615	—	—
0 1 8	2.785	—	—	2 2 3	1.592	—	—
2 0 2	2.742	—	—	1.2.11	1.570	1.570	2
1 1 6	2.583	2.584	11	3 0 9	1.564	1.565	1
0 2 4	2.571	—	—	1 3 1	1.554	1.554	1
2 0 5	2.462	2.463	9	3 1 2	1.545	—	—
1.0.10	2.334	2.334	4	1.0.16	1.542	1.543	1
0 2 7	2.229	2.229	3	2.0.14	1.535	1.535	1
0.1.11	2.154	2.154	6	2 2 6	1.515	1.515	1
1 1 9	2.141	2.138	7	1.1.15	1.513	—	—
0.0.12	2.139	—	—	1 3 4	1.513	—	—
2 1 1	2.114	2.114	1	3 1 5	1.490	1.490	2
2 0 8	2.112	—	—	0.1.17	1.458	1.458	4
1 2 2	2.093	2.092	1	2.1.13	1.445	—	—
2 1 4	2.014	—	—	1 3 7	1.433	1.434	1
1 2 5	1.961	1.961	5	0.0.18	1.426	1.426	4
0.2.10	1.894	1.893	4	2 2 9	1.409	1.409	2.63
3 0 0	1.871	1.871	5	3.0.12	1.408	—	—
1.0.13	1.862	—	—	—	—	—	—

R32. The crystal structure determinations showed the correct space groups to be  $Pc2_1n$  and  $R\bar{3}$ , respectively. The triclinic  $\text{NH}_4\text{IO}_3 \cdot \text{H}_2\text{O}$  appeared to be centrosymmetric,  $P1$ , during the structure determination.

For  $\text{KIO}_3 \cdot \text{Te}(\text{OH})_6$ , thermal decomposition occurs at 449 K. During the DTA analysis no thermal event is observed between room temperature and the decomposition.

### Crystal Structure Determinations

Parameters used for the three X-ray diffraction data collections are reported in Table VI. In all cases, the Lorentz and polarization corrections have been made, but in view of the wavelength used, no absorption correction has been applied. The three crystal structure determinations have been run by classical methods: a three-dimensional Patterson function, followed by suc-

TABLE VI  
INSTRUMENTAL PARAMETERS USED FOR THE THREE DIFFRACTION DATA COLLECTIONS

Parameters	$KIO_3 \cdot Te(OH)_6$	$2KIO_3 \cdot Te(OH)_6$	$NH_4IO_3 \cdot Te(OH)_6 \cdot H_2O$
Apparatus	Philips PW 1100	Philips PW 1100	Philips PW 1100
Monochromator	Graphite plate	Graphite plate	Graphite plate
Wave length	Ag( $K\alpha$ )	Ag( $K\alpha$ )	Ag( $K\alpha$ )
Scan mode	$\Omega$	$\Omega$	$\Omega$
Scan speed ( $^\circ$ /sec)	0.02	0.02	0.02
Total background measurement (sec)	20	20	20
Scan width ( $^\circ$ )	1.2	1.2	1.4
Theta range ( $^\circ$ )	3–30	3–30	3–25
Intensity reference reflections	444, 444	636, 636	622, 622
Number of collected reflections	2219 ( $h, k, l$ )	2743 ( $\pm h, \pm k, l$ )	3199 ( $\pm h, \pm k, l$ )
Crystal size (mm)	0.18 × 0.18 × 0.18	0.19 × 0.18 × 0.20	0.24 × 0.24 × 0.19
$\mu$ ( $cm^{-1}$ )	41.2	42.0	33.3

cessive Fourier syntheses. Throughout the least squares refinements a unitary weighting scheme has been used. In the last refinements, reflections which are too weak, i.e., badly measured, or overly strong (attenuator) i.e., badly corrected, are rejected.

(a)  $KIO_3 \cdot Te(OH)_6$

After some refinement iterations the final  $R$  value is 0.047 for a set of 2106 reflections such that  $F_{obs} > 115$  (on a scale ranging from 0 to 3255),  $|F_{obs}|^2 > 6 \sigma_F$ , and  $||F_{obs}| - |F_{calc}|| < 116$ . Final atomic parameters and anisotropic thermal factors are reported in Tables VII and VIII.<sup>1</sup>

(b)  $NH_4IO_3 \cdot Te(OH)_6 \cdot H_2O$

In this case the final  $R$  value for the complete set of 3199 reflections is 0.046. After a reject of 387 reflections there are 374 corresponding to  $F_{obs} < 3 \sigma_F$  and 13 strong ones

for which  $||F_{obs}| - |F_{calc}|| > 145$  on a  $F$  scale ranging from 0 to 1586; the  $R$  value decreases to 0.036 for the remaining 2812 reflections. Final atomic coordinates and anisotropic thermal factors are reported in Tables IX and X.

TABLE VII

ATOMIC PARAMETERS AND  $B_{eq.} \left( \frac{1}{3} \sum_{ij} a_i a_j \beta_{ij} \right)$   
FOR  $KIO_3 \cdot Te(OH)_6$

Atom	$x(\sigma)$	$y(\sigma)$	$z(\sigma)$	$B_{eq.} (\sigma)$
I	0.75960(3)	0.0074(2)	0.36542(6)	1.10(2)
Te	0.08053(4)	0.0000(0) <sup>a</sup>	0.22241(6)	0.63(2)
K	0.0954(2)	0.0162(5)	0.7209(3)	1.62(6)
O(1)	0.1423(5)	-0.021(1)	0.0276(8)	1.13(6)
O(2)	0.0211(5)	0.036(1)	0.4201(9)	1.21(6)
O(3)	0.4744(6)	0.369(2)	0.3618(11)	2.90(8)
O(4)	0.1897(6)	0.128(2)	0.3024(11)	1.04(5)
O(5)	0.0280(8)	0.255(2)	0.1623(12)	2.04(6)
O(6)	0.6257(7)	0.242(1)	0.2227(10)	1.34(6)
O(7)	0.3067(5)	0.526(2)	0.3272(8)	1.49(6)
O(8)	0.2985(7)	0.260(2)	0.0637(12)	1.56(6)
O(9)	0.3493(7)	0.656(2)	0.0539(13)	2.70(8)

<sup>a</sup> Fixed coordinate.

Note. The  $Pc2_1n$  space group used here is a nonstandard one. Coordinates for the general positions are  $x, y, z; x, \frac{1}{2} + y, \frac{1}{2} - x, y, \frac{1}{2} + z; \frac{1}{2} + x, \frac{1}{2} + y, \frac{1}{2} - z$ .

<sup>1</sup> Supplementary material is available from the author.

TABLE VIII  
ANISOTROPIC THERMAL PARAMETERS FOR  $\text{KIO}_3 \cdot \text{Te}(\text{OH})_6$  (THERMAL FACTOR IS  
 $T = h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hl\beta_{13} + kl\beta_{23}$ )

Atoms	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
I	0.00082(1)	0.00493(7)	0.00310(4)	0.0009(1)	0.00002(5)	0.0012(3)
Te	0.00093(1)	0.00453(7)	0.00212(4)	0.0005(1)	-0.00005(5)	-0.0017(3)
K	0.0037(1)	0.0080(4)	0.0050(2)	-0.0005(6)	0.0017(3)	-0.0017(8)
O(1)	0.0015(2)	0.005(2)	0.0026(6)	0.0020(9)	0.0011(6)	-0.002(1)
O(2)	0.0018(3)	0.011(2)	0.0028(7)	-0.0016(12)	0.0010(7)	-0.003(2)
O(3)	0.0010(3)	0.017(2)	0.0043(9)	-0.0005(14)	0.0003(9)	0.007(3)
O(4)	0.0014(3)	0.009(2)	0.0054(9)	-0.0023(12)	0.0013(9)	-0.005(2)
O(5)	0.0033(4)	0.008(2)	0.0050(10)	0.0053(14)	-0.0004(12)	-0.001(2)
O(6)	0.0027(4)	0.004(1)	0.0039(8)	0.0028(11)	0.0012(10)	-0.001(2)
O(7)	0.0013(2)	0.012(2)	0.0025(6)	0.0011(14)	-0.0006(6)	0.000(2)
O(8)	0.0020(3)	0.010(2)	0.0051(10)	0.0020(13)	0.0002(10)	-0.003(2)
O(9)	0.0016(3)	0.014(2)	0.0065(10)	-0.0031(14)	-0.0006(10)	0.009(3)

### (c) $\text{Te}(\text{OH})_6 \cdot 2\text{KIO}_3$

From the original data collection (2743 reflections) a set of 991 independent reflections has been obtained and used for the crystal structure determination. The final  $R$  value for the complete set of 991 reflections is 0.035. This same factor decreases to 0.030 for a set of 952 reflections corresponding to the elimination of 34 reflections such that  $F < 2\sigma_F$  and 5 reflections such that  $||F_{\text{obs}}| - |F_{\text{cal}}|| > 140$  on a scale ranging from 0 to 1200. Final atomic coordinates and  $B_{\text{eq}}$  are reported in Table XI while an-

TABLE IX  
FINAL ATOMIC COORDINATES AND  $B_{\text{eq}}$  FOR  
 $\text{NH}_4\text{IO}_3 \cdot \text{Te}(\text{OH})_6 \cdot \text{H}_2\text{O}$

Atoms	$x(\sigma)$	$y(\sigma)$	$z(\sigma)$	$B_{\text{eq}}$ ( $\sigma^2$ )
I	0.78437(4)	0.22754(6)	0.21609(6)	0.992(5)
Te	0.30046(4)	0.41653(6)	0.28120(6)	0.997(5)
O(1)	0.2441(5)	0.6494(8)	0.2067(8)	1.603(8)
O(2)	0.4742(5)	0.5552(9)	0.2313(10)	2.017(8)
O(3)	0.3630(5)	0.1909(8)	0.3553(9)	1.992(8)
O(4)	0.3173(6)	0.5105(9)	0.5556(8)	2.140(8)
O(5)	0.2875(7)	0.3538(9)	-0.0016(8)	2.366(8)
O(6)	0.1335(6)	0.2623(9)	0.3353(10)	2.287(8)
O(7)	0.1776(5)	0.9718(8)	0.9223(9)	1.881(8)
O(8)	0.0647(5)	0.5981(9)	0.7827(10)	2.199(8)
O(9)	0.2113(6)	0.8744(8)	0.5271(8)	1.840(8)
O(W)	0.4704(6)	0.0172(10)	0.7944(11)	2.709(9)
N	-0.0035(7)	0.815(1)	0.246(1)	2.173(8)

isotropic thermal factors are given in Table XII.

## Structure Descriptions

### A. $\text{KIO}_3 \cdot \text{Te}(\text{OH})_6$

Figure 1 is a projection of the atomic arrangement along the  $\mathbf{b}$  axis. This projection is centrosymmetric. The main feature is the existence of chains of  $\text{IO}_6$  groups parallel to the  $\mathbf{c}$  axis at  $y = 0$  and  $0.5$ ,  $\text{IO}_6$  groups being connected by the oxygen atoms O(7). In this type of linkage the bonding oxygen O(7) shared between two  $\text{IO}_6$  groups, participates to a long I-O bond (2.843 Å) with the first one and to a short bond (1.813 Å) with the second one. Rows of alternating Te and K polyhedra are parallel to the  $\text{IO}_6$  chains, each  $\text{IO}_6$  chain being surrounded by six Te-K rows arranged around it in an almost hexagonal way. Note that bonding oxygen O(7) does not participate in the coordination of Te and K atoms. The two other oxygen atoms involved in I-O long distances, O(6) and O(4), belong to the coordination of the Te atoms, while the last two corresponding to the short I-O distances, O(8) and O(9), belong to the  $\text{KO}_6$  polyhedron.

TABLE X  
ANISOTROPIC THERMAL FACTORS FOR  $\text{NH}_4\text{IO}_3 \cdot \text{Te}(\text{OH})_6 \cdot \text{H}_2\text{O}$  (TEMPERATURE FACTOR IS  
 $T = h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hl\beta_{13} + kl\beta_{23}$ )

Atoms	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
I	0.00262(3)	0.00486(6)	0.00540(7)	0.00207(6)	0.00013(7)	0.0012(1)
Te	0.00277(3)	0.00580(6)	0.00436(7)	0.00278(7)	0.00150(7)	0.0025(1)
O(1)	0.0051(4)	0.0093(9)	0.0064(9)	0.0072(9)	0.000(1)	0.003(2)
O(2)	0.0034(4)	0.0100(10)	0.0152(13)	0.0018(10)	0.003(1)	0.004(2)
O(3)	0.0050(4)	0.0090(9)	0.0138(12)	0.0074(9)	0.005(1)	0.009(2)
O(4)	0.0069(4)	0.0160(10)	0.0061(9)	0.0135(10)	-0.003(1)	-0.006(2)
O(5)	0.0103(6)	0.0085(10)	0.0040(9)	0.0027(13)	0.002(1)	-0.001(2)
O(6)	0.0035(4)	0.0111(11)	0.0180(14)	0.0010(11)	0.002(1)	0.009(2)
O(7)	0.0057(4)	0.0088(9)	0.0099(11)	0.0060(10)	0.002(1)	-0.003(2)
O(8)	0.0032(4)	0.0097(10)	0.0189(15)	0.0007(11)	0.000(1)	0.003(2)
O(9)	0.0067(5)	0.0082(9)	0.0064(9)	0.0053(10)	-0.001(1)	0.006(2)
O(W)	0.0041(4)	0.0148(13)	0.0203(16)	0.0030(13)	0.003(1)	0.005(3)
N	0.0057(5)	0.009(1)	0.013(1)	0.004(1)	0.000(2)	0.001(2)

TABLE XI  
FINAL ATOMIC COORDINATES AND  $B_{\text{eq}}$  FOR  
 $\text{Te}(\text{OH})_6 \cdot 2\text{KIO}_3$

Atom	$x(\sigma)$	$y(\sigma)$	$z(\sigma)$	$B_{\text{eq}}(\sigma)$
Te	0.0000(0)	0.0000(0)	0.0000(0)	0.90(2)
I	0.0000(0)	0.0000(0)	0.17835(2)	0.87(2)
K	0.0000(0)	0.0000(0)	0.4047(1)	2.50(6)
O(1)	0.2550(6)	0.0219(6)	0.0413(2)	1.91(5)
O(2)	0.2444(5)	-0.0048(5)	0.2110(1)	1.56(5)

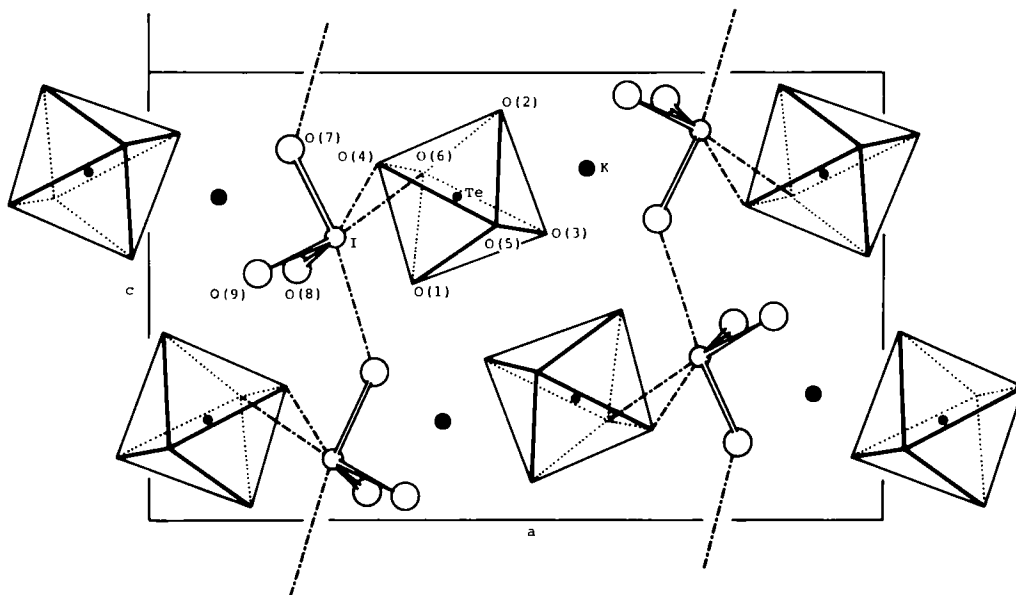


FIG. 1. Projection along the  $b$  direction of the atomic arrangement of  $\text{KIO}_3 \cdot \text{Te}(\text{OH})_6$ . Short I-O distances are denoted by continuous lines, long ones by dashed lines.

TABLE XII  
ANISOTROPIC THERMAL PARAMETERS FOR  $\text{Te}(\text{OH})_6 \cdot 2\text{KIO}_3$  (TEMPERATURE FACTOR IS  
 $T = h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hk\beta_{13} + kl\beta_{23}$ )

Atoms	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Te	0.0065(0)	0.0065(1)	0.00040(1)	0.0065(0)	0.0000(0)	0.0000(0)
I	0.00618(7)	0.00618(7)	0.00040(1)	0.00618(0)	0.0000(0)	0.0000(0)
K	0.0099(0)	0.0099(3)	0.00188(4)	0.0099(0)	0.0000(0)	0.0000(0)
O(1)	0.0137(6)	0.0150(6)	0.00088(5)	0.0171(8)	-0.0028(3)	-0.0012(3)
O(2)	0.0094(5)	0.0122(6)	0.00077(5)	0.0122(7)	-0.0012(3)	0.0003(3)

Main interatomic distances and bond angles are reported in Table XIII.

### B. $2\text{KIO}_3 \cdot \text{Te}(\text{OH})_6$

Figure 2 reports a projection of the atomic arrangement on the  $(a, c)$  plane.

$\text{Te}(\text{OH})_6$  groups are located at the origin of the unit cell while  $\text{IO}_6$  groups lie in planes  $z \sim 0.16, 0.50,$  and  $0.83$ . Potassium  $\text{KO}_6$  polyhedra are located between  $\text{Te}(\text{OH})_6$  and  $\text{IO}_6$  layers. Details of an  $\text{IO}_6$  layer are

TABLE XIII

MAIN INTERATOMIC DISTANCES AND BOND ANGLES  
IN  $\text{KIO}_3 \cdot \text{Te}(\text{OH})_6$

		$\text{IO}_6$ group			
		I-O(7)	1.813(4)		
		I-O(8)	1.859(6)		
		I-O(9)	1.772(5)		
O(7)-I-O(8)	105.0(2)	O(7)-O(8)	2.914(9)		
O(7)-I-O(9)	93.3(2)	O(7)-O(9)	2.608(7)		
O(8)-I-O(9)	99.0(2)	O(8)-O(9)	2.762(6)		
		I-O(4)	3.109(6)		
		I-O(6)	2.777(5)		
		I-O(7)	2.843(4)		
Te	O(1)	O(2)	$\text{Te}(\text{OH})_6$ group		O(6)
			O(3)	O(4)	O(5)
O(1)	1.918(4)	176.7(2)	89.6(2)	88.8(2)	90.2(2)
O(2)	3.853(6)	1.936(4)	92.9(2)	88.7(2)	87.6(2)
O(3)	2.692(7)	2.783(7)	1.903(5)	178.2(2)	89.9(3)
O(4)	2.682(7)	2.693(7)	3.817(7)	1.915(5)	90.9(3)
O(5)	2.740(7)	2.689(8)	2.719(9)	2.753(8)	1.948(6)
O(6)	2.709(7)	2.776(7)	2.624(7)	2.763(7)	3.859(7)
		$\text{KO}_6$ polyhedron			
		K-O(1)	2.766(4)	K-O(5)	2.690(6)
		K-O(2)	2.831(5)	K-O(8)	2.624(6)
		K-O(3)	2.855(8)	K-O(9)	2.937(8)

given by Figure 3 in projection along the  $c$  axis. In such a layer each  $\text{IO}_6$  group whose geometrical features are reported in Table XIV shares all its oxygen atoms with the three nearest  $\text{IO}_6$  groups, so that each oxygen atom is involved in one short and one long I-O bond.

### C. $\text{NH}_4\text{IO}_3 \cdot \text{Te}(\text{OH})_6 \cdot \text{H}_2\text{O}$

Here, contrary to the two other structures, the  $\text{IO}_6$  groups do not share any oxygen atoms. The three oxygen atoms involved in the short I-O bonds are connected to the ammonium groups. The three longer I-O bonds involve the two oxygen atoms O(1) and O(4) and the water molecules O(W).

Figure 4 reports this atomic arrangement in projection along the  $c$  axis, while Table

TABLE XIV

MAIN INTERATOMIC DISTANCES AND BOND ANGLES  
IN  $2\text{KIO}_3 \cdot \text{Te}(\text{OH})_6$

		$\text{Te}(\text{OH})_6$ group			
		Te-O(1)	1.912(3) ( $\times 6$ )		
O(1)-Te-O(1)	180.0(4)	( $\times 3$ )	O(1)-O(1)	3.825(6)	
O(1)-Te-O(1)	92.18(15)	( $\times 6$ )	O(1)-O(1)	2.756(6)	
O(1)-Te-O(1)	87.82(15)	( $\times 6$ )	O(1)-O(1)	2.653(6)	
		$\text{IO}_6$ group			
		I-O(2)	1.811(3)	( $\times 3$ )	
O(2)-I-O(2)	100.2(1)( $\times 3$ )	O(2)-O(2)	2.779	( $\times 3$ )	
		I-O(2)	2.899(3)	( $\times 3$ )	
		$\text{KO}_6$ polyhedron			
		K-O(1)	2.714(3)	( $\times 3$ )	
		K-O(2)	2.801(3)	( $\times 3$ )	

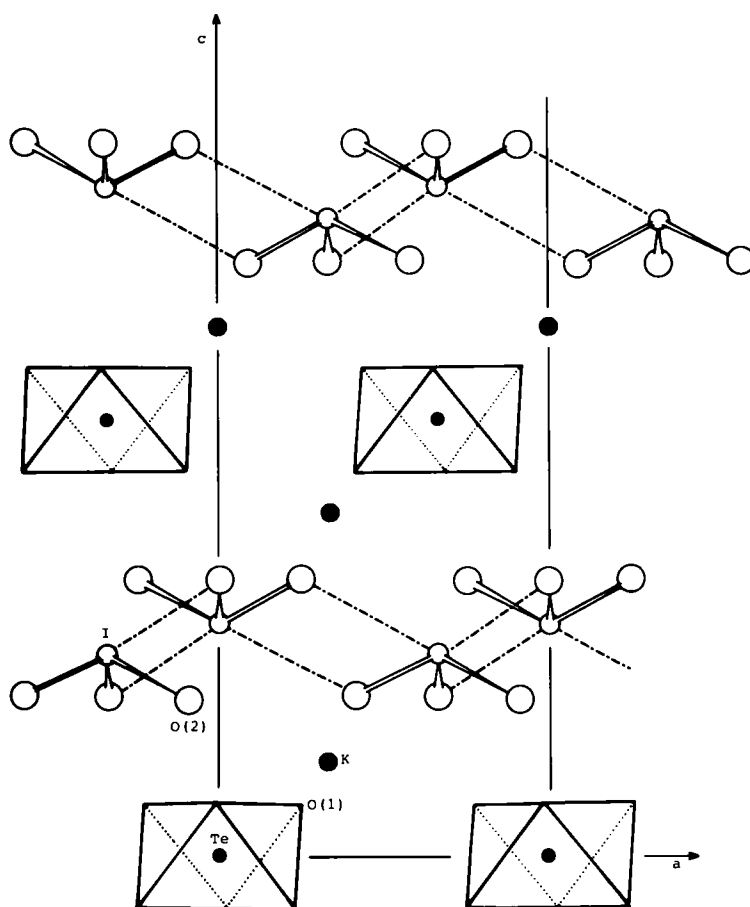


FIG. 2. Projection on the  $(a, c)$  plane of the atomic arrangement of  $2\text{KIO}_3 \cdot \text{Te}(\text{OH})_6$ . Short I-O distances are denoted by continuous lines, long ones by dashed lines.

XV gives the main interatomic distances and bond angles.

## Discussion

### $\text{Te}(\text{OH})_6$ Groups

As in all previously described addition compounds involving telluric acid, the three  $\text{Te}(\text{OH})_6$  groups described in this work are almost regular octahedra. Table XVI reports for these three arrangements a short comparison of some features of the

$\text{Te}(\text{OH})_6$  groups. The connections of these groups with the  $\text{IO}_6$  groups are similar in the case of  $\text{KIO}_3 \cdot \text{Te}(\text{OH})_6$  and  $\text{NH}_4\text{IO}_3 \cdot \text{Te}(\text{OH})_6 \cdot \text{H}_2\text{O}$ : the  $\text{Te}(\text{OH})_6$  groups share two oxygen atoms with an  $\text{IO}_6$  group. The two oxygen atoms correspond to long I-O bonds of the iodine group. The four remaining oxygen atoms are shared with the associated cation polyhedra.

In rhomboedral  $2\text{KIO}_3 \cdot \text{Te}(\text{OH})_6$ ,  $\text{Te}(\text{OH})_6$  groups and  $\text{IO}_6$  do not share oxygen atoms. The six oxygen atoms of the telluric group belong to the coordination of the potassium polyhedra.



TABLE XV  
MAIN INTERATOMIC DISTANCES AND BOND ANGLES  
IN  $\text{NH}_4\text{IO}_3 \cdot \text{Te}(\text{OH})_6 \cdot \text{H}_2\text{O}$

		IO <sub>6</sub> group				
		I-O(7)	1.804(4)			
		I-O(8)	1.791(4)			
		I-O(9)	1.818(4)			
O(7)-I-O(8)	99.58(19)	O(7)-O(8)	2.746(6)			
O(7)-I-O(9)	98.50(18)	O(7)-O(9)	2.745(5)			
O(8)-I-O(9)	98.60(20)	O(8)-O(9)	2.737(6)			
		I-O(1)	2.920(3)			
		I-O(4)	2.821(4)			
		I-O(W)	2.888(4)			
		Te(OH) <sub>6</sub> group				
Te	O(1)	O(2)	O(3)	O(4)	O(5)	O(6)
O(1)	1.921(3)	2.766(5)	3.832(5)	2.657(5)	2.629(5)	2.755(6)
O(2)	91.5(2)	1.940(4)	2.635(5)	2.722(6)	2.654(6)	3.850(6)
O(3)	177.8(2)	86.3(2)	1.911(4)	2.753(5)	2.784(6)	2.689(6)
O(4)	87.6(2)	89.8(2)	92.0(2)	1.917(4)	3.819(5)	2.719(6)
O(5)	86.7(2)	87.2(2)	93.6(2)	173.5(2)	1.909(4)	2.770(6)
O(6)	92.8(2)	175.7(2)	89.4(2)	90.5(2)	92.9(2)	1.912(4)
		NH <sub>4</sub> O <sub>3</sub> polyhedron				
		N-O(9)	2.922(7)	N-O(6)	3.087(7)	
		N-O(8)	2.783(6)	N-O(6)	3.151(7)	
		N-O(7)	2.890(7)	N-O(1)	3.222(6)	
		N-O(7)	2.936(7)			

### IO<sub>6</sub> Groups

In agreement with all was previously found concerning crystal structures of monovalent iodates (see Table XVII), in the three compounds described here the iodine atoms are surrounded by six oxygen atoms: three at a short distance ( $\text{I-O} \approx 1.80$

Å) and three at a longer distance ( $\text{I-O} \approx 2.80$  Å). The umbrella neighborhood of iodine explained by its lone pair is now well known and has been the subject of extensive studies (19-23).

The main difference one can observe between one iodate and another is the way the IO<sub>6</sub> groups link through their long I...O bonds. The three title compounds are all different in this bonding. In  $\text{NH}_4\text{IO}_3 \cdot \text{Te}(\text{OH})_6 \cdot \text{H}_2\text{O}$  the iodine IO<sub>6</sub> groups are independent (Fig. 4). In  $2\text{KIO}_3 \cdot \text{Te}(\text{OH})_6$  the iodine groups link, forming infinite bidimensional hexagonal layers perpendicular to the ternary axis at  $z \approx 0.17, 0.50, 0.83$  (Fig. 3). In the third one,  $\text{KIO}_3 \cdot \text{Te}(\text{OH})_6$ , one observes independent monodimensional infinite chains of IO<sub>6</sub> groups parallel to the *c* axis (Fig. 1).

Comparing these results with those previously observed in the atomic arrangements of monovalent iodates we could not find any example for independent IO<sub>6</sub> groups or infinite chains, while three examples of infinite layers are already known in  $\text{KIO}_3$ ,  $\alpha\text{-LiIO}_3$  and  $\text{AgIO}_3$ . Three dimensional linkages are found in  $\text{NH}_4\text{IO}_3$  and in  $\alpha\text{-RbIO}_3$ .

With regard to their physical properties, all of them have at least one noncentrosymmetric variety which is notably piezoelectric. In the case of the title compounds only one series,  $[\text{K}(\text{Rb}, \text{NH}_4)\text{IO}_3 \cdot \text{Te}(\text{OH})_6]$ , exhibits a strong piezoelectric effect.

TABLE XVI  
COMPARISON OF THE  $\text{Te}(\text{OH})_6$  GROUPS

Formula	$\text{Te-O} \langle$	Te-O	$\rangle \text{O-Te-O} \langle$	$\rangle \text{O-Te-O} \langle \langle$
$\text{KIO}_3 \cdot \text{Te}(\text{OH})_6$	1.903-1.948	1.926	86.9-92.9	176.7
$2\text{KIO}_3 \cdot \text{Te}(\text{OH})_6$	1.912	1.912	92.18	180.0
$\text{NH}_4\text{IO}_3 \cdot \text{Te}(\text{OH})_6 \cdot \text{H}_2\text{O}$	1.909-1.940	1.918	86.3-93.6	173.5

Note. The first column reports the largest and shortest Te-O distances, whose averages are given in the second column. The third and fourth columns give the O-Te-O angles having the largest deviations from the theoretical values in a regular octahedron.

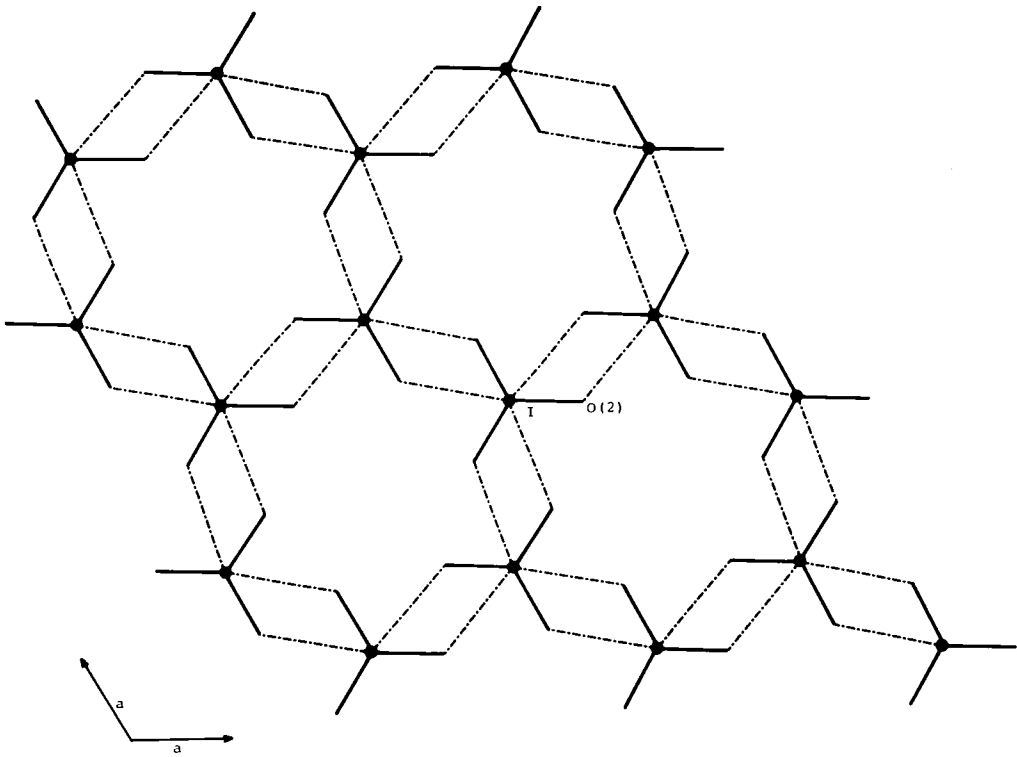


FIG. 3. Details of the  $\text{IO}_6$  layer located in  $z \sim 0.16$ . Only oxygen atoms involved in  $\text{IO}_6$  groups are figured.

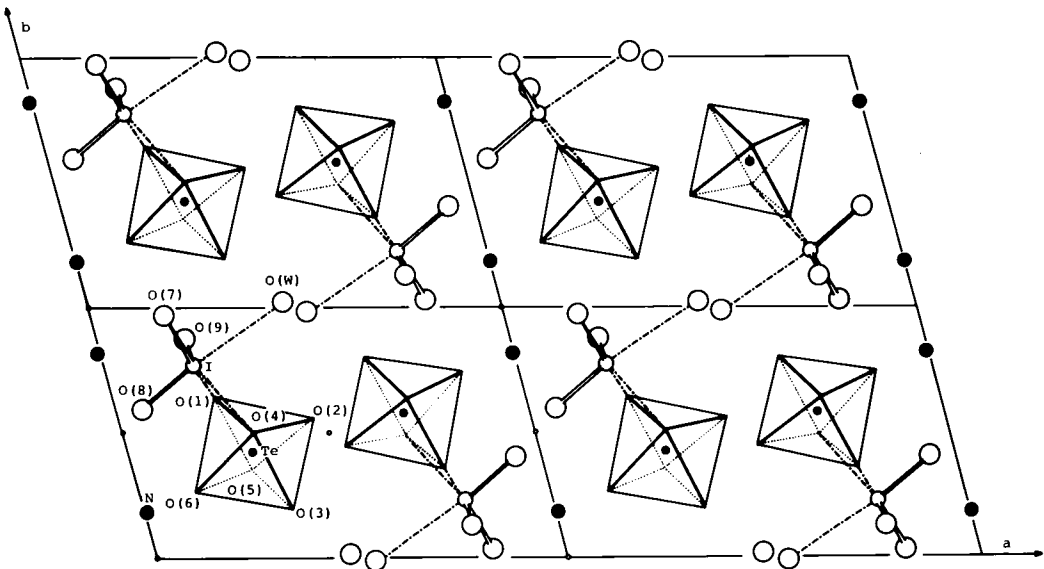


FIG. 4. Projection along the  $c$  axis of the atomic arrangement of  $\text{NH}_4\text{IO}_3 \cdot \text{Te}(\text{OH})_6 \cdot \text{H}_2\text{O}$ .

TABLE XVII

IO<sub>6</sub> GROUPS: COMPARISON OF THE MAIN GEOMETRICAL FEATURES OF THE IO<sub>6</sub> GROUPS AS OBSERVED IN SOME ALKALI AND SILVER IODATES AND IN THE TITLE COMPOUNDS

Compounds	I-O	I · · · O	>O-I-O<	Space group	Ref.
NH <sub>4</sub> IO <sub>3</sub>	1.802	2.809	102.3-105.6	<i>Pc2<sub>1</sub>n</i>	(12)
α-LiIO <sub>3</sub>	1.817	2.873	98.65(×3)	<i>P6<sub>3</sub></i>	(3)
	1.809	2.892	99.54(×3)		(14)
β-LiIO <sub>3</sub>	1.79	2.98	96-102	<i>P4<sub>2</sub>/n</i>	(15)
α-RbIO <sub>3</sub>	1.807	2.753	99.63(×3)	<i>R3m</i>	(16)
AgIO <sub>3</sub>	1.80	2.84	96.3-101.0	<i>Pbc2<sub>1</sub></i>	(17)
	1.83	2.74	95.8-99.9		
KIO <sub>3</sub>	1.787	2.742	99.52	<i>P1</i>	(18)
KIO <sub>3</sub> · Te(OH) <sub>6</sub>	1.815	2.910	93.3-105.0	<i>Pc2<sub>1</sub>n</i>	
2KIO <sub>3</sub> · Te(OH) <sub>6</sub>	1.811	2.889	100.2	<i>R3̄</i>	
NH <sub>4</sub> IO <sub>3</sub> · Te(OH) <sub>6</sub> · H <sub>2</sub> O	1.804	2.876	98.5-99.6	<i>P1̄</i>	

Note. The first two columns report the average I-O distances; the third column gives the largest and smallest O-I-O angles for the short I-O bonds.

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