

- RIETVELD, H. M. (1969). *J. Appl. Cryst.* **2**, 65–71.
 ROBERTSON, B. E. & CALVO, C. (1968). *Can. J. Chem.* **46**, 605–612.
 SCHNEIDER, S. & COLLIN, R. L. (1973). *Inorg. Chem.* **12**, 2136–2139.
 SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
 STEPHENS, J. S. & CALVO, C. (1969). *Can. J. Chem.* **47**, 2215–2225.
 TONDON, V. K. & CALVO, C. (1981). *Indian J. Pure Appl. Phys.* **19**, 756–758.
 WERNER, P. E., SALOMÉ, S., MALMROS, G. & THOMAS, J. O. (1979). *J. Appl. Cryst.* **12**, 107–109.
 ZACHARIASEN, W. H. (1930). *Z. Kristallogr.* **73**, 1–6.

Acta Cryst. (1984). **C40**, 1999–2001

Structure of the Adduct of Orthotelluric Acid and Potassium Iodate, $\text{Te}(\text{OH})_6 \cdot \text{KIO}_3$

BY J. PODLAHOVÁ AND J. LOUB†

Department of Inorganic Chemistry, Charles University, Albertov 2030, 12840 Praha 2, Czechoslovakia

F. PECHAR

Institute of Geology and Geotechnics, Czechoslovak Academy of Sciences, Holešovická 41, 18209 Praha 8, Czechoslovakia

AND V. PETŘÍČEK

Institute of Physics, Czechoslovak Academy of Sciences, Na Slovance 2, 18040 Praha 8, Czechoslovakia

(Received 23 May 1984; accepted 28 August 1984)

Abstract. $M_r = 443.65$, $Pn2_1a$, $a = 8.702$ (2), $b = 6.719$ (1), $c = 14.279$ (3) Å, $V = 834.9$ (3) Å³, $Z = 4$, $D_m = 3.50$ (1), $D_x = 3.528$ Mg m⁻³, Mo Kα, $\lambda = 0.71069$ Å, $\mu = 7.94$ mm⁻¹, $F(000) = 808$, $T = 296$ K, $R = 0.031$, 1315 unique reflections. The orthotelluric acid molecules and the iodate anions are connected by hydrogen bonds, so that they form a three-dimensional network. The orthotelluric acid is in a slightly distorted octahedral arrangement and the iodate ion is a trigonal pyramid. The K atom is surrounded by six O atoms.

Introduction. The title compound was studied as part of an investigation of the adducts of orthotelluric acid with various organic or inorganic compounds, see, for example, Loub, Haase & Mergehenn (1979), Boudjada, Boudjada & Guitel (1983).

Experimental. Crystals prepared by mixing 0.02 M aqueous solutions of orthotelluric acid and iodic acid in 1:1 molar ratio, adding potassium hydroxide solution to pH 5.3 and crystallization at 296 K (Weinland & Prause, 1901). D_m by the pycnometric method at 296 K in xylene; colourless prismatic crystals stable in air and to X-rays, spherical crystal, max. dimensions 5 mm, $2R = 0.36$ mm; Hilger & Watts four-circle diffractometer controlled by computer M 7000; ω - 2θ scan; lattice parameters refined using 19 reflections with $\theta = 5.3$ to 28.7° ; absorption correction applied ($5.94 < A^* < 7.04$); max. $\sin\theta/\lambda = 0.703$ Å⁻¹, $h_{\max} = 12$, $k_{\max} = 9$,

$l_{\max} = 19$; 2 standard reflections after every 30 measured reflections with no significant variation; 1315 measured unique reflections, 49 unobserved with $I < 1.96 \sigma(I)$; heavy-atom method, F magnitudes in full-matrix least-squares refinement; all positional and anisotropic thermal parameters of non-H atoms refined; $wR = 0.053$, $w = 1/\sigma^2(F_o)$; max. $\Delta/\sigma = 0.20$, max. and min. heights in final difference map 1.45 and -1.83 e Å⁻³ at 0.81 and 0.13 Å from I atom, corrected for secondary extinction, $I_o^{\text{cor}} = I_o(1 + 2.06 \times 10^{-5}I_o)$; atomic scattering factors and corrections for anomalous dispersion of Te, I and K from *International Tables for X-ray Crystallography* (1974); programs *TLS* (Sklenář, 1973) and *ORTEP* (Johnson, 1965).‡

Discussion. The final atomic parameters are given in Table 1. The intramolecular and selected intermolecular bond distances and angles are given in Table 2. The molecule is depicted in Fig. 1. The projection of the structure along **a** is depicted in Fig. 2. The systematic absences point either to centrosymmetric space group $Pnma$ or to noncentrosymmetric space group $Pn2_1a$. Refinement in the centrosymmetric group led to the R value of 0.16, non-positive-definite temperature factors of almost all atoms and unreliable bond angles in tellurate octahedra and iodate tetrahedra. Hence, the

‡ Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39695 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

† To whom correspondence should be addressed.

final structure determination and refinement were carried out in the noncentrosymmetric space group with the equivalent positions $x, y, z; -x, \frac{1}{2}+y, -z; \frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}+z; \frac{1}{2}+x, y, \frac{1}{2}-z$. The coincidence of the bands of infrared and Raman spectra holds also for the noncentrosymmetric group.

Table 1. Atomic coordinates ($\times 10^4$) and isotropic thermal parameters with e.s.d.'s in parentheses

$$B_{eq} = (4 \sum_i \sum_j \beta_{ij} a_i a_j) / 3.$$

	x	y	z	$B_{eq}(\text{\AA}^2)$
Te	2223.7 (4)	2500	0806.0 (3)	1.00 (1)
I	1344.7 (5)	7573 (2)	2595.8 (3)	1.11 (1)
K	2202 (2)	2626 (7)	4056 (2)	2.13 (4)
O(1)	4195 (7)	2853 (12)	0216 (4)	1.9 (2)
O(2)	0274 (6)	2296 (13)	1413 (4)	1.5 (1)
O(3)	3040 (7)	3729 (12)	1915 (4)	1.8 (1)
O(4)	1353 (7)	1169 (11)	-0264 (4)	1.7 (1)
O(5)	1636 (8)	5024 (12)	0317 (5)	2.2 (2)
O(6)	2791 (6)	-0114 (10)	1267 (4)	1.5 (1)
O(7)	3285 (6)	7625 (17)	3055 (4)	2.0 (1)
O(8)	0517 (7)	6013 (11)	3492 (5)	1.7 (1)
O(9)	0642 (6)	9967 (11)	2985 (5)	1.7 (1)

Table 2. Bond distances (\AA) and angles ($^\circ$), for $\text{I}\cdots\text{O} < 3.1 \text{\AA}$, for $\text{K}\cdots\text{O} < 3.2 \text{\AA}$ and for possible H bonds $\text{O}\cdots\text{O} < 3.0 \text{\AA}$

Te—O(1)	1.926 (6)	O(1)—Te—O(3)	88.8 (3)
Te—O(2)	1.910 (5)	O(1)—Te—O(4)	93.5 (3)
Te—O(3)	1.922 (6)	O(1)—Te—O(5)	88.3 (3)
Te—O(4)	1.924 (6)	O(1)—Te—O(6)	91.9 (3)
Te—O(5)	1.902 (7)	O(2)—Te—O(3)	89.1 (3)
Te—O(6)	1.937 (7)	O(2)—Te—O(4)	88.7 (3)
		O(2)—Te—O(5)	89.5 (3)
		O(2)—Te—O(6)	90.5 (3)
		O(3)—Te—O(5)	91.1 (3)
		O(3)—Te—O(6)	90.9 (3)
		O(4)—Te—O(5)	90.9 (3)
		O(4)—Te—O(6)	87.1 (3)
		O(7)—I—O(8)	97.3 (4)
		O(7)—I—O(9)	100.7 (4)
I—O(7)	1.812 (5)	O(8)—I—O(9)	99.5 (3)
I—O(8)	1.805 (7)	O(7)—I—O(6 ^{ix})	79.2 (3)
I—O(9)	1.810 (7)	O(9)—I—O(6 ^{ix})	82.2 (3)
I—O(6 ^{ix})	2.757 (7)	O(8)—I—O(7 ⁱⁱⁱ)	82.2 (3)
I—O(7 ⁱⁱⁱ)	2.820 (5)	O(9)—I—O(7 ⁱⁱⁱ)	76.8 (4)
		O(6 ^{ix})—I—O(7 ⁱⁱⁱ)	101.4 (3)
K—O(1 ⁱⁱⁱ)	2.820 (6)	O(1 ⁱⁱⁱ)—K—O(4 ^{ix})	103.8 (2)
K—O(2 ⁱⁱ)	2.765 (6)	O(1 ⁱⁱⁱ)—K—O(5 ^x)	97.8 (2)
K—O(4 ^{ix})	2.863 (8)	O(1 ⁱⁱⁱ)—K—O(8)	65.2 (2)
K—O(5 ^x)	2.708 (8)	O(1 ⁱⁱⁱ)—K—O(9 ⁱ)	77.2 (2)
K—O(8)	2.823 (8)	O(2 ⁱⁱ)—K—O(4 ^{ix})	73.9 (2)
K—O(9 ⁱ)	2.714 (7)	O(2 ⁱⁱ)—K—O(5 ^x)	75.4 (2)
		O(2 ⁱⁱ)—K—O(8)	119.8 (2)
		O(2 ⁱⁱ)—K—O(9 ⁱ)	107.2 (2)
		O(4 ^{ix})—K—O(5 ^x)	98.5 (2)
		O(4 ^{ix})—K—O(8)	69.8 (2)
		O(5 ^x)—K—O(9 ⁱ)	97.8 (2)
		O(8)—K—O(9 ⁱ)	96.3 (2)
Possible hydrogen bonds			
O(1)—O(8 ^{vi})	2.766 (9)	O(2)—O(9 ⁱ)	2.755 (9)
O(3)—O(8 ⁱⁱ)	2.708 (9)	O(4)—O(5 ^{vi})	2.715 (9)
O(4)—O(7 ^{vi})	2.611 (9)	O(6)—O(9 ⁱⁱⁱ)	2.702 (8)

Symmetry code: (i) $x, y-1, z$; (ii) $\frac{1}{2}+x, y, \frac{1}{2}-z$; (iii) $x-\frac{1}{2}, y, \frac{1}{2}-z$; (iv) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}+z$; (v) $\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}+z$; (vi) $\frac{1}{2}-x, y-\frac{1}{2}, z-\frac{1}{2}$; (vii) $-x, y-\frac{1}{2}, -z$; (viii) $\frac{1}{2}+x, y-1, \frac{1}{2}-z$; (ix) $x, y+1, z$; (x) $x-\frac{1}{2}, y+1, \frac{1}{2}-z$; (xi) $-x, \frac{1}{2}+y, -z$.

The average value of the Te—O distances, 1.92 (1) \AA , suggests bonding of the hydrogens to the Te—O oxygen atoms. For comparison, the mean Te—O distance in orthotelluric acid, $\text{Te}(\text{OH})_6$, is 1.91 (3) \AA (cubic, Mullica, Korp, Milligan, Beall & Bernal, 1980) and 1.915 (7) \AA (monoclinic, Lindqvist, 1970). The mean O—Te—O angle is 90 (2) $^\circ$, which indicates a very slightly distorted octahedral structure of the orthotellurate groups. The mean I—O distance of 1.809 (4) \AA and the mean O—I—O angle of 99 (2) $^\circ$ are in accordance with a trigonal pyramidal arrangement of the IO_3^- anion; two neighbouring oxygen atoms are located at a mean distance of 2.79 (4) \AA . The corresponding parameters in KIO_3 are I—O 1.79 (2) \AA and O—I—O 100 (1) $^\circ$ (Iljuchin, Kalinin, Ivanova-Korfini & Pachomov, 1979).

The environment of the K atom consists of six oxygen atoms (four from Te, two from I) with a mean K—O distance of 2.78 (6) \AA . This value is comparable with that of 2.8 (1) \AA in KTeO_3OH for CN 6 (Lindqvist, 1972) but differs from the mean value of 3.0 (1) \AA for CN 6 in KIO_3 (Iljuchin *et al.*, 1979).

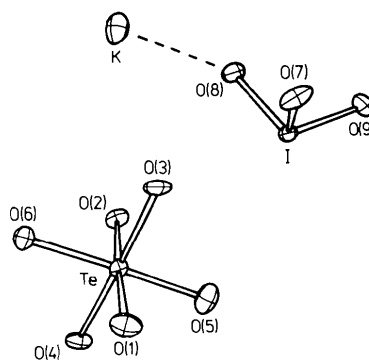


Fig. 1. The $\text{Te}(\text{OH})_6\text{KIO}_3$ adduct. The Te, I, K and O atoms are represented by thermal ellipsoids at the 50% level (Johnson, 1965).

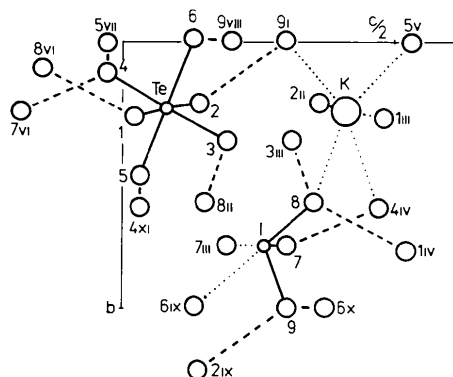


Fig. 2. A view of part of the structure of the $\text{Te}(\text{OH})_6\text{KIO}_3$ adduct along a . Possible hydrogen bonds are indicated by dashed lines, the neighbouring oxygen atoms of I and K by dotted lines.

Infrared (broad bands at 2500–3500 cm^{-1} , *vs*) and Raman (2800–3300 cm^{-1} , *w*) spectra suggest that the three-dimensional network of the compound is held together by hydrogen bonding. Unfortunately, the positions of the hydrogen atoms could not be determined and thus the discussion of the hydrogen bonding is necessarily limited and speculative. The following hydrogen-bonding types seem to appear in the structure. (i) All the tellurate oxygen atoms except O(5) carry hydrogen atoms that act as donors to the iodate oxygen atoms [mean O...O distance 2.7 (5) Å]. (ii) The O(4) and O(5^{vii}) atoms are involved in bifurcated hydrogen bonding $\text{O} \cdots \begin{array}{c} \text{H} \cdots \\ \text{H} \end{array} \cdots \text{O}$. (iii) The O(5) atom can take part only in this type of hydrogen bonding. (iv) The iodate oxygen atoms can act as acceptors for one hydrogen atom [O(7)] or two hydrogen atoms [O(8) and O(9)].

From the point of view of the polar-axis direction, $wR = 0.0526$, which corresponds to a structure with the atomic coordinates given in Table 1, is lower than

$wR = 0.0534$ calculated for the structure with the coordinates related through the centre of inversion, assuming $\alpha = 10^{-6}$ (Rogers, 1981).

References

- BOUDJADA, N., BOUDJADA, A. & GUITEL, J. C. (1983). *Acta Cryst.* **C39**, 656–658.
 ILJUCHIN, V. V., KALININ, V. R., IVANOVA-KORFINI, I. I. & PACHOMOV, V. I. (1979). *Koord. Khim.* **5**, 1549–1557.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.
 JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
 LINDQVIST, O. (1970). *Acta Chem. Scand.* **24**, 3178–3188.
 LINDQVIST, O. (1972). *Acta Chem. Scand.* **26**, 4107–4120.
 LOUB, J., HAASE, W. & MERGEHENN, R. (1979). *Acta Cryst.* **B35**, 3039–3041.
 MULLICA, D. F., KORP, J. D., MILLIGAN, W. O., BEALL, G. W. & BERNAL, I. (1980). *Acta Cryst.* **B36**, 2565–2570.
 ROGERS, D. (1981). *Acta Cryst.* **A37**, 734–741.
 SKLENĀŘ, I. (1973). *TLS*. Institute of Physics, Czechoslovak Academy of Sciences, Prague.
 WEINLAND, R. F. & PRAUSE, H. (1901). *Z. Anorg. Chem.* **28**, 45–70.

Acta Cryst. (1984). **C40**, 2001–2005

The Structure of γ -Bismuth Molybdate, Bi_2MoO_6 , by Powder Neutron Diffraction

BY RAYMOND G. TELLER, JAMES F. BRAZDIL AND ROBERT K. GRASSELLI

Sohio Research Center, 4440 Warrensville Center Road, Cleveland, Ohio 44128, USA

AND JAMES D. JORGENSEN

Argonne National Laboratory, Argonne, Illinois 60439, USA

(Received 7 February 1984; accepted 30 August 1984)

Abstract. $M_r = 609.89$, orthorhombic, $Pna2_1$, $a = 5.4822$ (3), $b = 16.1986$ (8), $c = 5.5091$ (3) Å, $V = 489.23$ (3) Å³, $Z = 4$, $D_x = 8.28$ g cm⁻³, $R_p = 0.050$. The structure has been determined with room-temperature time-of-flight powder neutron diffraction data. Results of a Rietveld refinement indicate that the structure of the mineral koechlinite, as determined by single-crystal X-ray diffraction, is an adequate representation of the structure of the synthetic material if some adjustments in oxygen-atom positions are made.

Introduction. Bismuth molybdates, $\text{Bi}_2\text{O}_3-n\text{MoO}_3$, have been the subject of intense interest for several decades because they are very selective catalysts for alkene oxidation (Grasselli & Burrington, 1981). As these processes are industrially important, many kinetic and structural studies aimed at elucidating the mechanism of olefin oxidation have been performed. Although too numerous to cite individually, there are several studies

that are especially worthy of note: the initial discovery of the activity of these materials for selective oxidation (Veatch, Callahan, Milberger & Foreman, 1960), the realization that lattice oxygen of certain reducible metal oxides can serve as a more versatile and selective oxidizing agent than molecular oxygen for alkene oxidation and ammoxidation, and that the reduced oxides can, in turn, be reoxidized by gaseous oxygen to regenerate the active sites (Callahan & Grasselli, 1963; Callahan, Grasselli, Milberger & Strecker, 1970), mechanistic tracer experiments confirming the pioneering work by Standard Oil (Ohio) workers that the reducible metal oxides themselves are the active catalytic agents (Keulks, 1970; Keulks & Krenzke, 1976) and a number of more recent studies that establish the nature of the intermediate on the catalyst surface (Burrington & Grasselli, 1979) and the importance of catalyst oxidation state which regulates the catalyst activity and selectivity (Brazdil, Suresh & Grasselli, 1980).