

Alternation of Ta-O and Te-O Layers in a Three-Dimensional Array: Crystal Structure of Ta₂Te₂O₉

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Single crystals of monoclinic Ta₂Te₂O₉ were grown by slow cooling of Ta₂O₅-TeO₂ melts. Ta₂Te₂O₉ crystallizes in space group *P*2₁/*c* (No. 14), *Z* = 4, with *a* = 7.100(1), *b* = 7.486(2), *c* = 14.625(5) Å and β = 102.98(2)°. The structure has been solved by X-ray single-crystal techniques up to a final *R* value of 0.061 using 1184 observed reflections. Ta₂Te₂O₉ is three-dimensional, with infinite puckered layers of composition (Te₄O₁₂)_n parallel to the *ab* plane, alternating along the *c* axis with infinite sheets constituted by nearly regular TaO₆ octahedra sharing corners. The two kinds of tellurium atoms are four- and five-fold oxygen coordinated, the nonbonded pair being directed towards the vacant positions of a trigonal bipyramid and a strongly deformed octahedron, respectively. The structure of Ta₂Te₂O₉ is compared with those known in the systems *M*₂O₅-TeO₂ (*M* = V, Nb). © 1987 Academic Press, Inc.

Introduction

During the last 20 years some systematic X-ray diffraction studies on the ternary oxides of Te(IV) and *M*(V) (*M* = V, Nb, Ta) have been performed (1-5). For *M* = V only the compound V₂Te₂O₉ could be isolated (1), while the phase equilibrium diagram for TeO₂-Nb₂O₅ showed the existence of several mixed oxides, namely, Nb₆TeO₁₇, Nb₂Te₃O₁₁, and Nb₂Te₄O₁₃ (2). As for the TeO₂-Ta₂O₅ system, four stable oxides with compositions Ta₂Te₃O₁₁, Ta₆Te₇O₂₉, and two forms of Ta₂Te₂O₉ were reported (3).

Only crystals of V₂Te₂O₉ and Nb₂Te₃O₁₁ have been obtained and their structures solved by X-ray diffraction (4, 5). In V₂Te₂O₉ the vanadium atoms occupy the centers of trigonal bipyramids which, sharing corners, form (VO₄)_n strings linked by Te₂O₅ groups, the tellurium atoms being bonded to three oxygens in a pyramidal array (4). Nb₂Te₃O₁₁ is constituted by infinite double chains of NbO₆ octahedra, sharing corners, which are connected by means of finite Te₃O₈ strings, to form a three-dimensional net (5).

The lack of structural information on the Ta₂O₅-TeO₂ system led the authors to attempt its study and, eventually, the growth of crystals of tantalum-tellurium oxides. This paper reports the synthesis and crystal structure of Ta₂Te₂O₉ and establishes a comparison with the other known struc-

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tures in the M₂O₅-TeO₂ (M = V, Nb) systems.

Experimental

1. Crystal Growth

Four mixtures of analytical-grade Ta₂O₅ and TeO₂ with molar ratios Ta : Te = 1 : 2.5, 1 : 2, 1 : 1.5, and 1 : 1 were prepared and heated in air up to 1173 K in covered porcelain crucibles to avoid the TeO₂ losses. After soaking for 3 hr, the melts were slowly cooled at 2 K hr⁻¹ down to 773 K and quenched to room temperature. The formation of colorless crystals was observed in all the samples, and those corresponding to the 1 : 1.5 initial molar ratio were chosen for X-ray single-crystal studies.

2. Data Collection

A flat crystal of dimensions 0.1 × 0.1 × 0.025 mm was mounted in a Nonius CAD-4 diffractometer. The cell dimensions were initially refined by least-squares fitting of the 2θ values of 25 reflections. The intensities of all 1327 unique reflections with 1 < θ < 25° and hkl range -8.0.0 to 8.8.17 were measured with monochromatic MoK_α radiation and an ω/2θ scan technique. There was no appreciable change in the periodically monitored standard reflections. The intensities were corrected for Lorentz and polarization effects, and 1184 of these were considered as observed with I > 1σ(I). Scattering factors for neutral atoms and anomalous dispersion correction for Te and Ta were taken from "International Tables for X-Ray Crystallography" (6). The powder pattern was recorded using a Siemens Kristalloflex 810 diffractometer and a D-500 goniometer, with CuK_α radiation, at a scanning rate of 0.1°2θ min⁻¹ with Si, a = 5.43088(4) Å, as an internal standard. The same pattern was indexed using the parameters determined at the four-circle diffractometer. A further refinement of the cell

TABLE I

CRYSTAL DATA AND CONSTANTS OF Ta₂Te₂O₉

Formula weight: 761.09
Crystal system: Monoclinic
Space group: P2 ₁ /c (No. 14)
a = 7.100(1) Å
b = 7.486(2) Å
c = 14.625(5) Å
β = 102.98(2)°
V = 757.5(4) Å ³
Z = 4
ρ _s = 6.67 Mg · m ⁻³
F(0 0 0) = 1288
Temperature: 295 K
Radiation MoK _α : 0.71069 Å
Absorption factor (MoK _α): 36.14 mm ⁻¹
R = 0.061

constants was tried from 20 nonaxial powder reflections using the program L-SUCRE (7).

3. Structure Determination

The heavy atoms were located from a three-dimensional Patterson map. The positions of the oxygen atoms were obtained from Fourier synthesis. An empirical absorption correction (8) was applied at the end of the isotropic refinement. Mixed full-matrix least-squares refinement with anisotropic thermal parameters for the Ta and Te atoms and isotropic for the O atoms led to R = 0.061. The maximum and average shift-to-error ratios were 0.002 and 0.0003, respectively. Most of the calculations were carried out with X-RAY 80 (9).

Results and Discussion

Crystal data and constants for Ta₂Te₂O₉ are given in Table I. The cell parameters are those refined in the four-circle diffractometer, since it was not possible to improve them from the powder data. Table II lists the d-spacings and intensities measured in the powder diffractogram. The observed reflections correspond to those given by Bart and Petrini (3) for the oxide

TABLE II
 POWDER PATTERN OF Ta₂Te₂O₉

<i>hkl</i>	<i>d</i> _o (Å)	<i>d</i> _c (Å)	<i>I</i> / <i>I</i> _o	<i>hkl</i>	<i>d</i> _o (Å)	<i>d</i> _c (Å)	<i>I</i> / <i>I</i> _o	<i>hkl</i>	<i>d</i> _o (Å)	<i>d</i> _c (Å)	<i>I</i> / <i>I</i> _o
002	7.16	7.13	2	12 $\bar{4}$	2.563	2.558	13	041	1.855	1.856	8
011	6.66	6.63	18	22 $\bar{2}$	2.533	2.529	4	313		1.853	
10 $\bar{2}$	5.66	5.64	3	031	2.458	2.458	6	126	1.837	1.835	5
012	5.18	5.16	21	10 $\bar{6}$	2.423	2.420	8	108	1.830	1.827	11
111	4.57	4.55	16	213	2.408	2.404	9	042		1.810	
11 $\bar{2}$	4.51	4.50	17	21 $\bar{5}$	2.369	2.364	4	140	1.807	1.807	17
102		4.49		130		2.347		322		1.806	
013	4.04	4.01	10	13 $\bar{1}$	2.349	2.345	7	141		1.805	
112	3.86	3.85	2	115	2.331	2.327	5	117	1.792	1.791	24
020	3.75	3.74	8	131		2.288		027		1.788	
021	3.63	3.62	82	13 $\bar{2}$	2.284	2.282	15	32 $\bar{5}$		1.784	
004	3.57	3.56	44	12 $\bar{5}$		2.279		008		1.781	
10 $\bar{4}$	3.51	3.50	24	31 $\bar{1}$		2.252		206	1.782	1.780	32
200	3.47	3.46	18	224	2.249	2.251	11	233		1.779	
20 $\bar{2}$	3.44	3.43	26	31 $\bar{2}$		2.246		141		1.779	
120		3.292		033	2.211	2.209	8	14 $\bar{2}$		1.776	
12 $\bar{1}$	3.299	3.286	74	310		2.204		304		1.764	
014		3.217		20 $\bar{6}$	2.206	2.202	7	23 $\bar{5}$	1.765	1.763	7
113	3.218	3.216	100	132	2.184	2.181	5	135	1.750	1.748	3
21 $\bar{1}$		3.207		302	2.064	2.063	12	043	1.743	1.741	3
114	3.179	3.174	27	125		2.049		22 $\bar{7}$		1.734	
12 $\bar{2}$		3.118		034	2.046	2.044	5	018	1.734	1.733	8
21 $\bar{2}$	3.128	3.118	46	116		2.027		216		1.732	
211		2.943		230	2.025	2.024	9	400		1.730	
023	2.949	2.940	6	32 $\bar{1}$		1.997		142	1.729	1.727	11
122		2.874		32 $\bar{2}$	1.995	1.993	4	41 $\bar{2}$		1.727	
202	2.878	2.869	27	231		1.968		411		1.718	
20 $\bar{4}$	2.824	2.818	8	017	1.969	1.965	6	314	1.717	1.717	21
114	2.719	2.714	21	31 $\bar{5}$		1.959		33 $\bar{1}$		1.715	
11 $\bar{5}$	2.687	2.682	19	233	1.958	1.957	8	317		1.687	
015	2.670	2.664	7	22 $\bar{6}$		1.898		33 $\bar{3}$	1.687	1.686	5
21 $\bar{4}$	2.642	2.638	3	321	1.899	1.897	13	410		1.685	
024		2.581		30 $\bar{6}$		1.879		234	1.670	1.668	6
123	2.583	2.580	16	324	1.879	1.878	36	044	1.658	1.657	5
22 $\bar{1}$		2.576		035		1.878		143		1.657	

of initial stoichiometry Ta₆Te₇O₂₉, which they obtained as a powder. The light excess of TeO₂ probably upsets its partial sublimation at the synthesis temperature, the reaction leading to a product with the actual stoichiometry Ta₂Te₂O₉.

Table III lists the final atomic parameters and Table IV gives bond lengths and angles. The two kinds of tantalum atoms are both coordinated to six oxygen atoms occupying the vertexes of distorted octahedra. The

Ta–O distances range from 1.88 to 2.07 Å, with average values of 1.97 Å for Ta(1) and 1.96 Å for Ta(2), very close to those of 1.96–1.98 Å found in comparable oxides (10–12). If a distortion parameter for TaO₆ octahedra is defined as $\Delta = 10^3 \sum [(r_i - r_m)/r_m]^2$, where r_i are the distances Ta–O and r_m the average distance, the obtained values for Ta(1) and Ta(2) octahedra are 5 and 8, respectively, being of the same order as those calculated for LaTaO₄ (10), $\Delta = 7$;

TABLE III
ATOMIC PARAMETERS FOR Ta₂Te₂O₉ COORDINATES
AND THERMAL PARAMETERS

Atom	X/A	Y/B	Z/C	UEQ
O(1)	0.4008(28)	0.1606(27)	0.3355(14)	102(41)
Ta(1)	0.9438(2)	0.2019(1)	0.0664(1)	25(4)
Ta(2)	0.6315(2)	0.0035(1)	0.4006(1)	23(4)
Te(1)	0.1262(2)	0.1403(2)	0.3162(1)	51(5)
Te(2)	0.5364(2)	0.0614(2)	0.1643(1)	63(6)
O(2)	0.0000(0)	0.0000(0)	0.0000(0)	100(61)
O(3)	0.7120(29)	0.0639(27)	0.0872(14)	105(42)
O(4)	1.1726(28)	0.3284(26)	0.0518(14)	72(38)
O(5)	0.7198(30)	0.0420(28)	0.2794(15)	117(41)
O(6)	0.4773(29)	-0.1920(27)	0.3291(14)	99(42)
O(7)	0.7881(30)	0.1970(26)	0.4529(14)	97(42)
O(8)	1.0942(29)	0.0924(27)	0.1887(14)	98(40)
O(9)	0.5000(0)	0.0000(0)	0.5000(0)	54(56)
O(10)	0.8947(33)	0.4065(32)	0.1448(16)	194(49)

Note. UEQ = (1/3), SUM(UIJ.AI*.AJ*.AI.AJ.COS(AI.AJ)).10**4.

LiTa₃O₈ (11), $\Delta = 8, 3,$ and 1 for Ta(1), Ta(2), and Ta(3); and Ca₂TiTa₅O₁₅ (12), $\Delta = 14$ and 1 for Ta(1) and Ta(2).

The tellurium atoms, Te(1) and Te(2), are bonded to three nearest oxygen atoms with a configuration based on a trigonal pyramid. However, there are other oxygen atoms at larger distances which could also be considered as coordinated. A suitable criterion widely applied (13, 14) to explain oxygen coordination of Te(IV) is the bond valence theory. If only the three shortest Te(1)-O of Table V, between 1.86 and 1.91 Å, are considered, the sum of the bond valences equals 3.76, a rather low value for the tellurium valence. However, taking into account the additional bonds, one for Te(1), at 2.91 Å, and two for Te(2), at 2.97 and 3.03 Å, the sums of the bond valences for both Te atoms become close to 4. Then, the coordination polyhedron for Te(1) can be described as a ψ -trigonal bipyramid with the lone pair directed towards one of the equatorial vertexes. As for Te(2), its polyhedron can be considered as a very distorted octahedron, where the inert pair occupies one

of the vertexes. Figure 1 shows the asymmetric unit and the coordination polyhedra of the heavy atoms.

Considering the Te(IV) free electron pair as a sphere with a volume similar to that of an oxygen atom (15), the average volume per oxygen atom for Ta₂Te₂O₉ is sound and equal to that calculated for Nb₂Te₃O₁₁ (5), 17.2 Å³.

The presence of the stereochemically active lone pair of Te(IV) is often shown in its nonsymmetrical coordination polyhedra. The most simple unit is the ψ -trigonal pyramid TeO₃, although other isolated units containing two or more tellurium atoms have also been found, such as Te₂O₅ or Te₃O₈ (16).

In three-dimensional Ta₂Te₂O₉ the Te atoms are linked through O(1) and O(5) to give infinite puckered layers of composition (Te₄O₁₂)_n parallel to the **ab** plane (Fig. 2), containing Te(1) and Te(2) four- and five-fold coordinated, respectively. On the other hand, the TaO₆ octahedra share corners, forming infinite bidimensional sheets also parallel to the **ab** plane. These layers alternate along the **c** axis with those constituted by tellurium atoms, via common oxygens, thus forming a three-dimensional array. A view of the unit cell is shown in Fig. 3.

It is interesting to compare the structure of Ta₂Te₂O₉ with those reported for the known oxides V₂Te₂O₉ and Nb₂Te₃O₁₁ in the M₂O₅-TeO₂ (M = V, Nb, Ta) systems. In these oxides, a gradual increase of the tellurium coordination can be observed from V₂Te₂O₉ to Ta₂Te₂O₉. In V₂Te₂O₉ all the tellurium atoms are threefold coordinated, the trigonal pyramids sharing corners to give isolated Te₂O₅ units; the three- and fourfold coordinated Te atoms of Nb₂Te₃O₁₁ form Te₃O₈ groups, whereas in Ta₂Te₂O₉ the two kinds of Te polyhedra, trigonal bipyramid and distorted octahedron, constitute bidimensional nets of composition (Te₄O₁₂)_n.

TABLE IV
INTERATOMIC BOND DISTANCES (Å) AND ANGLES (°) IN Ta₂Te₂O₉

Ta(1)–O(2) ⁱ	1.887(1)	Ta(2)–O(7)	1.88(2)
Ta(1)–O(7) ⁱⁱ	1.93(2)	Ta(2)–O(9)	1.897(1)
Ta(1)–O(4)	1.93(2)	Ta(2)–O(4) ⁱⁱⁱ	1.92(2)
Ta(1)–O(10)	1.99(2)	Ta(2)–O(6)	1.98(2)
Ta(1)–O(3)	2.02(2)	Ta(2)–O(5)	2.03(2)
Ta(1)–O(8)	2.04(2)	Ta(2)–O(1)	2.07(2)
Te(1)–O(10) ^{iv}	1.86(2)	Te(2)–O(6) ^{vi}	1.85(2)
Te(1)–O(8) ^v	1.86(2)	Te(2)–O(3)	1.86(2)
Te(1)–O(1)	1.91(2)	Te(2)–O(5)	1.89(2)
Te(1)–O(5) ^v	2.91(2)	Te(2)–O(1)	2.97(2)
		Te(2)–O(1) ^v	3.03(2)
O(2) ⁱ –Ta(1)–O(7) ⁱⁱ	91.0(6)	O(7) –Ta(2)–O(9)	92.7(7)
O(2) ⁱ –Ta(1)–O(4)	93.2(6)	O(7) –Ta(2)–O(4) ⁱⁱⁱ	93.7(8)
O(2) ⁱ –Ta(1)–O(10)	175.9(6)	O(7) –Ta(2)–O(6)	172.0(9)
O(2) ⁱ –Ta(1)–O(3)	86.6(6)	O(7) –Ta(2)–O(5)	88.6(9)
O(2) ⁱ –Ta(1)–O(8)	90.0(6)	O(7) –Ta(2)–O(1)	94.8(8)
O(7) ⁱⁱ –Ta(1)–O(4)	92.6(8)	O(9) –Ta(2)–O(4) ⁱⁱⁱ	98.8(6)
O(7) ⁱⁱ –Ta(1)–O(10)	93.1(9)	O(9) –Ta(2)–O(6)	94.9(7)
O(7) ⁱⁱ –Ta(1)–O(3)	90.1(8)	O(9) –Ta(2)–O(5)	166.8(6)
O(7) ⁱⁱ –Ta(1)–O(8)	176.8(9)	O(9) –Ta(2)–O(1)	83.4(6)
O(4) –Ta(1)–O(10)	87.0(9)	O(4) ⁱⁱⁱ –Ta(2)–O(6)	87.5(8)
O(4) –Ta(1)–O(3)	177.3(8)	O(4) ⁱⁱⁱ –Ta(2)–O(5)	94.2(9)
O(4) –Ta(1)–O(8)	90.4(8)	O(4) ⁱⁱⁱ –Ta(2)–O(1)	171.1(8)
O(10) –Ta(1)–O(3)	93.0(9)	O(6) –Ta(2)–O(5)	83.5(9)
O(10) –Ta(1)–O(8)	85.9(9)	O(6) –Ta(2)–O(1)	83.7(8)
O(3) –Ta(1)–O(8)	86.9(8)	O(5) –Ta(2)–O(1)	83.4(8)
O(10) ^{iv} –Te(1)–O(8) ^v	97.2(10)	O(6) ^{vi} –Te(2)–O(3)	94.1(9)
O(10) ^{iv} –Te(1)–O(1)	100.3(9)	O(6) ^{vi} –Te(2)–O(5)	93.6(9)
O(10) ^{iv} –Te(1)–O(5) ^v	71.0(8)	O(6) ^{vi} –Te(2)–O(1)	71.1(8)
O(8) ^v –Te(1)–O(1)	93.1(9)	O(6) ^{vi} –Te(2)–O(1) ^{iv}	174.4(7)
O(8) ^v –Te(1)–O(5) ^v	82.7(8)	O(3) –Te(2)–O(5)	96.8(9)
O(1) –Te(1)–O(5) ^v	169.6(8)	O(3) –Te(2)–O(1)	153.7(7)
		O(3) –Te(2)–O(1) ^{iv}	83.8(8)
		O(5) –Te(2)–O(1)	63.7(8)
		O(5) –Te(2)–O(1) ^{iv}	81.4(7)
		O(1) –Te(2)–O(1) ^{iv}	108.7(6)

Note. (i) $1 + x, y, z$; (ii) $x, \frac{1}{2} - y, -\frac{1}{2} + z$; (iii) $2 - x, -\frac{1}{2} + y, \frac{1}{2} - z$; (iv) $1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$; (v) $1 - x, y, z$, (vi) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$.

TABLE V
BOND VALENCE FOR Te–O IN Ta₂Te₂O₉

$d(\text{Te–O})$ (Å): S^a	d_1 S_1	d_2 S_2	d_3 S_3	d_4 S_4	d_5 S_5	ΣS
Te(1)	1.86 1.31	1.86 1.31	1.91 1.14	2.91 0.13		3.89
Te(2)	1.85 1.35	1.86 1.31	1.89 1.21	2.97 0.11	3.03 0.10	4.08

$$^a S = 1.333(d/1.854)^{-5.2}.$$

In the same way, pentacoordinated vanadium atoms in V₂Te₂O₉ (4) occupy the centers of trigonal bipyramids, which share corners to give infinite monodimensional (VO₄)_n strings. Nb in Nb₂Te₃O₁₁ (5) and Ta in Ta₂Te₂O₉ occur in almost octahedral environments, showing a higher oxygen coordination, as expected on the basis of the differences in ionic radii between V⁵⁺ (0.54 Å) and Nb⁵⁺, Ta⁵⁺ (0.64 Å). NbO₆ octahedra share corners to give double infinite

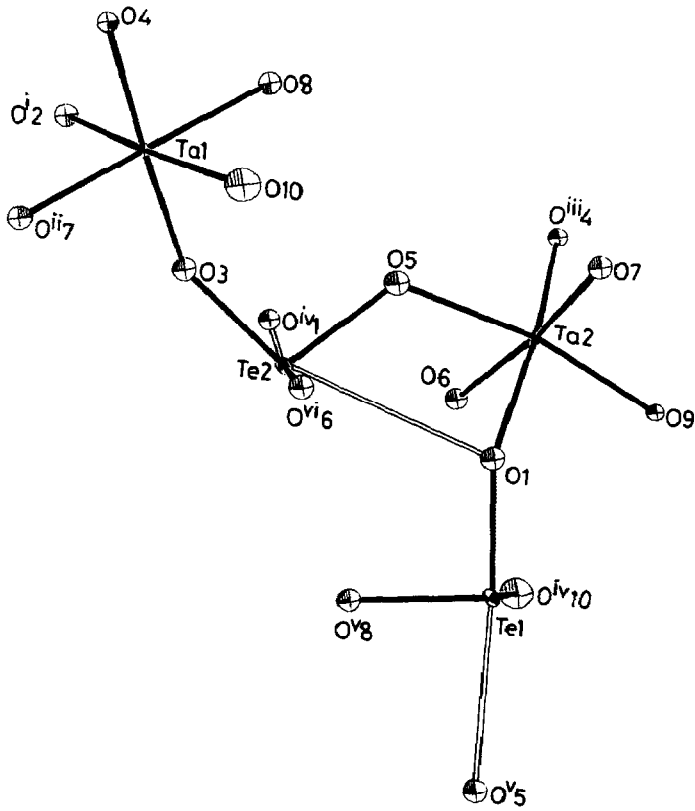


FIG. 1. Coordination polyhedra of the heavy atoms. The unfilled Te-O bonds correspond to distances close to 3 Å.

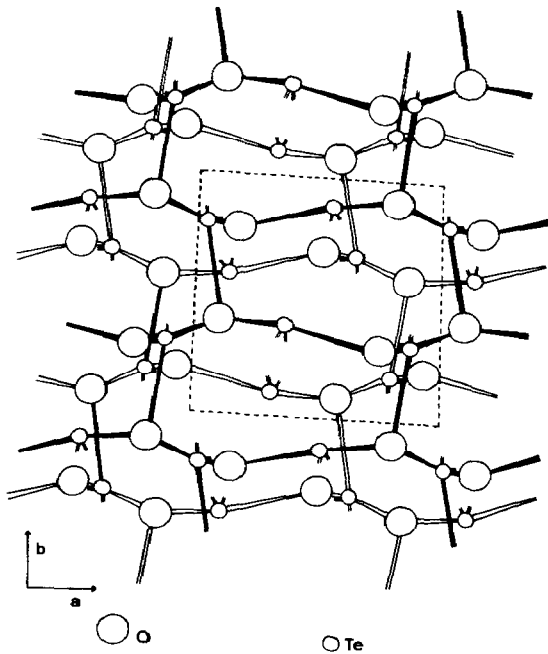


FIG. 2. Schematic representation of the bidimensional Te-O nets, projected on the *ab* plane. Only O(1) and O(5) are shown. Solid bonds correspond to the upper layer. Dashed lines show the repeating unit of composition Te_4O_{12} .

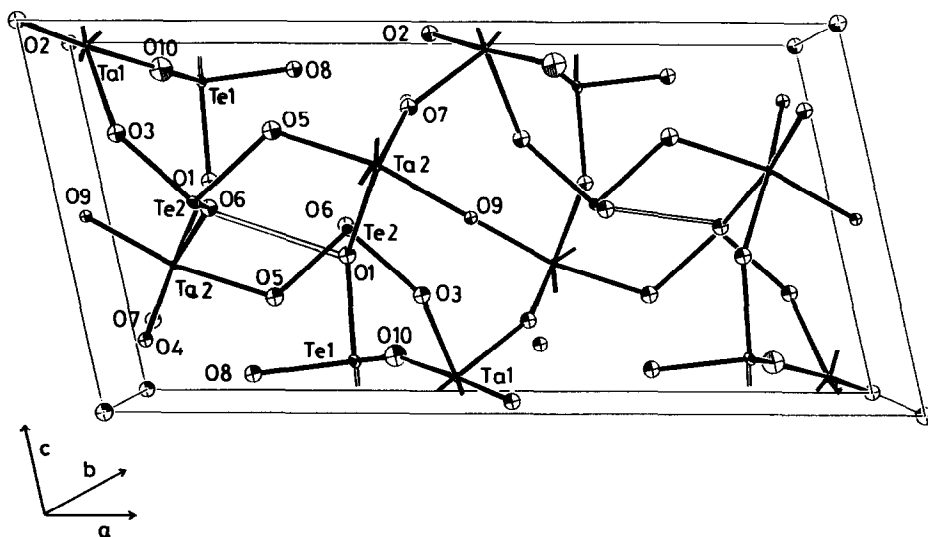


FIG. 3. A view of the unit cell. The unfilled Te-O bonds correspond to distances close to 3 Å.

monodimensional chains, whereas TaO_6 , sharing corners, form a bidimensional network. The different stacking of polyhedra along the sequence chains—double chains—layers can be explained as a consequence of the gradual increasing of the ionic character of M -O bonds from $M = \text{V}$ to $M = \text{Ta}$.

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