

tion with the sodium ion. The relevant room-temperature volume ranges, expressed as  $A$ -ion equivalents are:  $45.360 < V_{W^{6+}} < 47.665$  and  $48.583 < V_{Na^+} < 49.112 \text{ \AA}^3$ . It is to be expected, therefore, that the  $WO_6$  octahedron will be sufficiently large for the tungsten ion to be stabilized at a polar, off-centre position. In order to bring the average  $B$ -ion valence down to five, the  $W^{6+}$  ion could be combined with the  $Ti^{4+}$  ion in a 1:1 ratio. The observed room-temperature volume range of the titanium ion (see Fig. 3) is consistent with stabilization in a perovskite structure, but the volume of the  $Ti^{4+}$  octahedron is likely to be too small for the titanium ions to be *ferroelectrically active*. Thus, the compound  $Na(Ti_{1/2}W_{1/2})O_3$  is likely to have properties similar to  $Pb(Sc_{1/2}Ta_{1/2})O_3$ , in which the dielectric response varies between that of a normal and a relaxor ferroelectric (Thomas, 1989).

The polyhedral analysis offers a versatile framework for the observation and rationalization of structural trends. It can be applied to all crystallographic systems with electronic and mechanical properties dependent upon equilibria between structurally related phases.

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## The Structure of $K_2TeO_3$ – an Experimental and Theoretical Study

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#### Abstract

The single-crystal structure of  $K_2TeO_3$  is presented with  $M_r = 253.8$ , trigonal,  $P\bar{3}$ ,  $a = 6.279(2)$ ,  $c =$

$7.069(4) \text{ \AA}$ ,  $V = 241.4(2) \text{ \AA}^3$ ,  $Z = 2$ ,  $D_x = 3.492(3) \text{ Mg m}^{-3}$ ,  $Mo K\alpha$ ,  $\lambda = 0.71069 \text{ \AA}$ ,  $\mu = 7.77 \text{ mm}^{-1}$ ,  $F(000) = 228$ ,  $T = 293 \text{ K}$ , 572 observed reflections gave  $R = 0.049$ . The structure consists of

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free  $\text{TeO}_3^{2-}$  ions with the Te atom on the threefold axis. The Te—O bond distance, corrected for thermal motion using the riding model, is 1.836 (6) Å and the angle O—Te—O is 101.5 (2)°. The next-closest Te—O distance is 3.902 (5) Å. Restricted Hartree–Fock self-consistent field (RHF–SCF) calculations using a frozen-orbital effective-core-potential description for Te are presented for the  $\text{TeO}_3^{2-}$  ion with and without the inclusion of the crystal field. The optimized Te—O bond distance in  $\text{K}_2\text{TeO}_3$  was 0.03 Å longer than in experiment.

### Introduction

The oxygen coordination around tellurium(IV) is very irregular in the chain and network structures often formed by these compounds. Only a few of the single-crystal structures contain pyramidal tellurite ions,  $\text{TeO}_3^{2-}$ , with a pure  $C_3$  axis, but the O atoms are then frequently H bonded to water of crystallization. This report of the structure of  $\text{K}_2\text{TeO}_3$ , together with the recently determined structure of  $\text{Cs}_2\text{TeO}_3$  (Loopstra & Goubitz, 1986), is the first accurate determination of a symmetrical ( $C_{3v}$ )  $\text{TeO}_3^{2-}$  ion in a simple ionic environment.

A problem with alkali tellurites(IV) is their hygroscopicity. The crystals need to be handled in dry air and glove boxes. These difficulties are probably the reason why so little structural information is available. In the present investigation, crystals were prepared by a melt synthesis.

A theoretical investigation of the oxygen coordination in tellurium(IV) compounds has begun in our laboratory. In the first stage of this rather extensive study, comparison with experiment is valuable in order to obtain an estimate of the accuracy of the methods, and to test the basis sets chosen.

We here present the results of RHF–SCF calculations on the tellurite ion,  $\text{TeO}_3^{2-}$ , both free and in the surroundings of the crystal field in  $\text{K}_2\text{TeO}_3$  and  $\text{MgTeO}_3 \cdot 6\text{H}_2\text{O}$ . The frozen-orbital effective-core-potential (ECP) method (Pettersson, Wahlgren & Gropen, 1983) is used to reduce the size of the calculations. This method has been shown to reproduce all-electron results very well in a number of molecules containing transition metals (Pettersson *et al.*, 1983) and heavy main-group elements (Strömberg, Gropen & Wahlgren, 1983b).

An estimate of the geometry of a free  $\text{TeO}_3^{2-}$  ion, which is frequently used in semi-quantitative treatments of the stereochemistry of tellurium(IV) (Brown, 1974) may also be obtained by these calculations.

### Experimental

Crystals of  $\text{K}_2\text{TeO}_3$  were prepared from a melt of stoichiometric amounts of  $\text{TeO}_2$  and  $\text{K}_2\text{O}$  kept in a gold

crucible under anhydrous atmosphere at 973 K. A white irregular prism of dimensions 0.2 × 0.1 × 0.1 mm was obtained from the cold melt. It was mounted in a glass capillary to avoid decomposition in air. Data were collected on a Syntex  $P2_1$  diffractometer with graphite-monochromatized  $\text{Mo K}\alpha$  radiation. Lattice parameters from setting of 14 reflections with  $9.5 < 2\theta < 26.2^\circ$ . 640 reflections were measured with  $2\theta < 80.8^\circ$  ( $hkl$ :  $0 < h < 8$ ,  $0 < k < 9$ ,  $0 < l < 12$ ), of which 572 had  $I < 3\sigma(I)$ ; intensities from profile analyses of  $\omega/2\theta$  scans (*cf.* Lindqvist & Ljungström, 1979) according to Lehmann & Larsen (1974),  $\omega/2\theta$ -scan intervals 2.0–3.0°; standard reflection 210, stable; no systematic absences, Laue group  $P3m$ ; Lp correction (*XTL*; Syntex, 1973), semi-empirical absorption correction (Kopfmann & Huber, 1968; North, Phillips & Mathews, 1968), transmission factors between 0.29 and 0.45; Patterson methods (*XTL*; Syntex, 1973); final cycle of full-matrix refinement including third cumulants and isotropic extinction parameter (Finger & Prince, 1975), minimizing  $\sum w(|F_o| - |F_c|)^2$ ,  $R = 0.049$ ,  $wR = 0.078$ , final  $\Delta/\sigma = 0.004$ , weights  $w = 1/(\sigma^2 + 0.0016F_o^2)$  ( $\sigma$  based on counting statistics) gave acceptable weight analysis,  $S = 1.75$ ; scattering factors including anomalous-dispersion terms from *International Tables for X-ray Crystallography* (1974). Final difference synthesis featured a maximum and a minimum of 3.1 and  $-3.2 \text{ e } \text{Å}^{-3}$ , respectively, in the vicinity of the Te atom.

### Quantum-chemical calculations

RHF–SCF calculations (using the *MOLECULE-ALCHEMY* program package)\* have been accomplished for the tellurite ion as a free ion (in vacuum) and also enclosed in the crystal structure of  $\text{K}_2\text{TeO}_3$  and  $\text{MgTeO}_3 \cdot 6\text{H}_2\text{O}$  (Andersen, Lindqvist & Moret, 1984). The number of electrons in tellurium is large but few of them are actually involved in chemical processes like the formation of bonds. This fact is utilized in the effective-core-potential (ECP) method which substantially reduces the computer time for systems like the tellurites. In the frozen-orbital ECP method (Pettersson *et al.*, 1983), the inner-core orbitals of tellurium (1s to 3d) are replaced by a local potential whose parameters are determined by calculations on the atom. It should be noted that the method does not contain any empirically determined parameters. The outermost core shell (4s–4d) participates in the calculation in the form of frozen orbitals, and is thus not varied in the SCF calculations.

\* The *MOLECULE-ALCHEMY* program package incorporates the *MOLECULE* integral program written by Jan Almlöf and the *ALCHEMY* program package written by P. Bagus, B. Liu, M. Yoshimine and D. McLean, and modified by P. Bagus and U. Wahlgren. The program *ECPINT* has been written by L. Pettersson and U. Wahlgren, University of Stockholm.

The basis set of Strömberg, Gropen & Wahlgren (1983a) is reduced from fifteen *s*, eleven *p* and six *d* Cartesian Gaussian-type functions to six *s*, five *p* and three *d* functions. One diffuse *s* function and *d* functions are included for polarization as described by Strömberg, Wahlgren & Lindqvist (1985). The 9*s*, 5*p*-type basis set of Huzinaga (1971) was used on oxygen. It was contracted to 4*s*, 3*p*. A diffuse *p* function (exponent of 0.064) was added in order better to describe the negative oxygen. Details of the basis sets used for the sulfite and the selenite systems, results from which are included for comparison, are given by Strömberg *et al.* (Strömberg, Wahlgren, Pettersson & Siegbahn, 1984; Strömberg, Strömberg, Wahlgren, Karvinen & Niinistö, 1986).

The electrostatic field imposed on  $TeO_3^{2-}$  by the crystal environment was simulated following a technique suggested by Ewald (1921) which has been used by Almlöf & Wahlgren (1973). The initial charges on Te and O in  $TeO_3^{2-}$  were taken from an SCF run without a crystal field. The charges on the O and H atoms within the water molecules in  $MgXO_3 \cdot 6H_2O$  were set to -0.68 and +0.34 respectively. The crystal field was calculated using all the atoms in the unit cell and an (in principle) infinite number of unit cells. The H-atom positions in the magnesium tellurites and selenites were extrapolated from the neutron diffraction solution of the sulfite analogue. The numerical electrostatic potential thus obtained was modelled by 34 point charges whose magnitude was determined by a least-squares procedure. The charges were placed at the lattice sites for K ions and Te atoms within 7 Å of the tellurite group. These point charges were then included in the actual SCF calculations. New charges on Te and O atoms were obtained, a new potential modelled, and so forth, until convergence was reached.

The optimization of the Te—O distance and the O—Te—O angle was made both with and without the crystal field. The equilibrium geometries for the different cases were found by using ordinary grid techniques. The geometry of the tellurite ion was in all cases optimized with the  $C_3$  axis retained.

### Results and discussion

Atomic coordinates and equivalent isotropic temperature factors are given in Table 1\* and selected distances and angles in Table 2. The structure consists of isolated  $TeO_3^{2-}$  ions with the Te atom on the threefold axis. A stereoscopic picture of the packing in the unit cell is shown in Fig. 1. The K atoms are octahedrally

\* A list of structure factors and a table of anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51774 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Coordinates for  $K_2TeO_3$  and equivalent isotropic temperature factors according to Hamilton (1959)

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{eq}(\text{Å}^2)$
Te	$\frac{1}{3}$	$\frac{2}{3}$	0.14428 (7)	1.16 (1)
K1	0	0	0	1.65 (2)
K2	0	0	$\frac{1}{2}$	1.69 (2)
K3	$\frac{1}{3}$	$\frac{2}{3}$	0.6246 (4)	2.13 (2)
O	0.2690 (12)	0.3816 (9)	0.2595 (5)	2.86 (9)

Table 2. Selected distances (Å) and angles (°) in  $K_2TeO_3$

Te—O	$3 \times 1.836$ (6)*	K1—O	$6 \times 2.813$ (6)
Te—O	$3 \times 3.902$ (6)	K2—O	$6 \times 2.728$ (6)
O—Te—O	101.5 (2)	K3—O	$3 \times 2.785$ (6)
		K3—O	$3 \times 3.050$ (5)

\* Corrected for thermal motion using riding-motion model.

coordinated to six O atoms with distances ranging from 2.728 (4) to 3.050 (5) Å, which is within the normal range.

The Te—O bond length was corrected using the riding-motion model (Busing & Levy, 1964; Busing, Martin & Levy, 1964). The experimental *X*—O bond distances given for  $K_2SeO_3$  and  $MgSeO_3 \cdot 6H_2O$  and for the sulfite analogues in Table 4 are also corrected in this way. The effect of the corrections is a general lengthening of the bonds, and the largest effects are seen in the tellurite cases. Application of a non-correlated-motion model (Finger & Prince, 1975) to these crystal-structure solutions gives unreasonably long *X*—O distances for the selenite and sulfite analogues. The correction by the riding-motion model seems to be the most appropriate.

The Te—O bond length of 1.84 Å, which corresponds well with that found in  $Cs_2TeO_3$ , is shorter than the distances found in other structures containing isolated  $TeO_3^{2-}$  ions as shown in Table 3. The Te—O bond length (uncorrected as well as corrected) is about 0.02–0.04 Å shorter in  $K_2TeO_3$  than in the other compounds. However, all the other structures contain water of crystallization with hydrogen bonding between

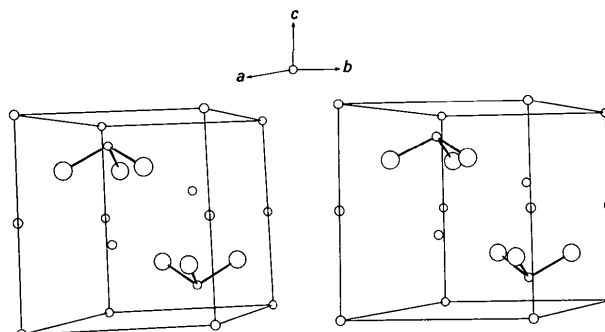


Fig. 1. Stereoscopic view of the structure (ORTEP; Johnson, 1965).

Table 3. Experimental Te—O bond distances less than 3.0 Å in structures with isolated  $\text{TeO}_3^{2-}$  units

	$R_{\text{Te-O}}(\text{Å})$	Reference
$\text{BaTeO}_3 \cdot \text{H}_2\text{O}$	1.847 (7), 1.858 (6), 1.859 (6)	(a)
$\text{K}_2\text{TeO}_3 \cdot 3\text{H}_2\text{O}$	1.848 (8), $2 \times 1.852$ (6)	(b)
$\text{Na}_2\text{TeO}_3 \cdot 5\text{H}_2\text{O}$	1.850 (3), 1.858 (3), 1.862 (3)	(c)
$\text{Li}_2\text{TeO}_3 \cdot \text{LiOH}$	$2 \times 1.857$ (5), 1.860 (5)	(d)
$\text{MgTeO}_3 \cdot 6\text{H}_2\text{O}$	$3 \times 1.862$ (4)	(e) (g)
$\text{Cs}_2\text{TeO}_3$	$3 \times 1.84$ (2)	(f)
$\text{K}_2\text{TeO}_3$	$3 \times 1.836$ (6)	(g)

References: (a) Rottensten Nielsen, Grønbaek Hazell & Rasmussen (1971); (b) Johansson & Lindqvist (1978); (c) Philippot, Maurin & Moret (1979); (d) Cachau-Herreillat, Norbert, Maurin, Fourcade & Philippot (1983); (e) Andersen, Lindqvist & Moret (1984); (f) Loopstra & Goubitz (1986); (g) this work, corrected for thermal motion by riding model.

Table 4. Calculated geometries for  $\text{XO}_3^{2-}$  ( $X$  is Te, Se or S) with and without the inclusion of the crystal field

Some experimental geometries are also given for comparison; all experimental  $X$ —O distances have been corrected using the riding-motion model.

	$r_{X-O}(\text{Å})$	$\theta_{O-X-O}(\text{°})$	$q_X^*$ (a.u.)	$q_O$
$\text{TeO}_3^{2-}$ , free	1.857	106.2	+1.18	-1.06
$\text{K}_2\text{TeO}_3$	1.869	102.0	+1.36	-1.12
$\text{MgTeO}_3 \cdot 6\text{H}_2\text{O}$	1.879	101.0	+1.54	-1.18
$\text{SeO}_3^{2-}$ , free	1.672	106.5	+0.82	-0.94
$\text{K}_2\text{SeO}_3$	1.683	103.8	+0.94	-0.98
$\text{MgSeO}_3 \cdot 6\text{H}_2\text{O}$	1.692	102.8	+1.06	-1.02
$\text{SO}_3^{2-}$ , free	1.520	107.0	+0.79	-0.93
$\text{K}_2\text{SO}_3$	1.524	106.3	+0.88	-0.96
$\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$	1.535	104.2	+1.00	-1.00
$\text{K}_2\text{TeO}_3$ , exp. <sup>(a)</sup>	1.836 (6)	101.5 (2)	—	—
$\text{MgTeO}_3 \cdot 6\text{H}_2\text{O}$ , exp. <sup>(b)</sup>	1.862 (4)	98.6 (1)	—	—
$\text{K}_2\text{SeO}_3$ , exp. <sup>(c)</sup>	1.694 (8)	102.9 (4)	—	—
$\text{MgSeO}_3 \cdot 6\text{H}_2\text{O}$ , exp. <sup>(b)</sup>	1.700 (3)	101.4 (1)	—	—
$\text{K}_2\text{SO}_3$ , exp. <sup>(d)</sup>	1.530 (1)	105.2 (1)	—	—
$\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$ , exp. <sup>(e)</sup>	1.528 (4)	104.3 (2)	—	—

References: (a) this work; (b) Andersen, Lindqvist & Moret (1984); (c) Eriksson & Helander (1989); (d) Andersen & Strömberg (1986); (e) Andersen & Lindqvist (1984).

\* Charges obtained from a Mulliken population analysis.

them and the O atoms in the tellurite group. This is probably the reason for the longer Te—O bonds found in these crystals compared with those in the water-free ones.

The calculated theoretical geometries for the  $\text{TeO}_3^{2-}$  ion with and without the crystal-field surroundings are presented in Table 4 together with similar results for selenites and sulfites. The effects of the crystal field on the tellurite ion are: (1) a general lowering of all orbital energies; (2) a lengthening of the Te—O bonds by 0.01–0.02 Å; (3) a reduction of the O—Te—O angles; and (4) a slightly more polarized Te—O bond, as is seen in the charges,  $q$ , in Table 4. It should be noted that, in the free  $\text{TeO}_3^{2-}$ , the highest occupied molecular orbital, which is doubly occupied, has a positive orbital energy and may not be stable on the removal of one electron. This is resolved when the crystal field is included.

The calculated geometries for all the anions  $\text{XO}_3^{2-}$  ( $X = \text{Te, Se or S}$ ) are in good agreement with the experimental results as illustrated in Fig. 2. The deviations from experimental  $X$ —O bond lengths are at most 0.033 Å. The bond angles differ by about 2° at the most, especially for the  $\text{MgTeO}_3 \cdot 6\text{H}_2\text{O}$  and  $\text{MgSeO}_3 \cdot 6\text{H}_2\text{O}$  compounds. This is presumably due to deficiencies in the description of the hydrogen bonding in crystal structures that have been solved using X-ray diffraction techniques. Their H-atom positions had to be extrapolated from the neutron diffraction results for the corresponding sulfite structure, e.g. all  $\text{O} \cdots \text{H} - \text{O}$  angles were set to 180°. However, the calculations correctly reproduce the relative importance of the crystal field by using this simple electrostatic model.

The deviations between the calculated and experimental  $X$ —O bond lengths are greatest for the tellurites, where  $r_{\text{Te-O}}$  is too long in both cases. This may be caused essentially by four factors: the basis sets, the ECP, the electrostatic treatment of the surroundings and the relativistic effects. The basis sets are of the same quality as those for the sulfites and selenites. The ECP of tellurium as well as the electrostatic potential are constructed and tested in a similar manner to that for the selenite. Test calculations on  $\text{TeO}_2$  (Strömberg

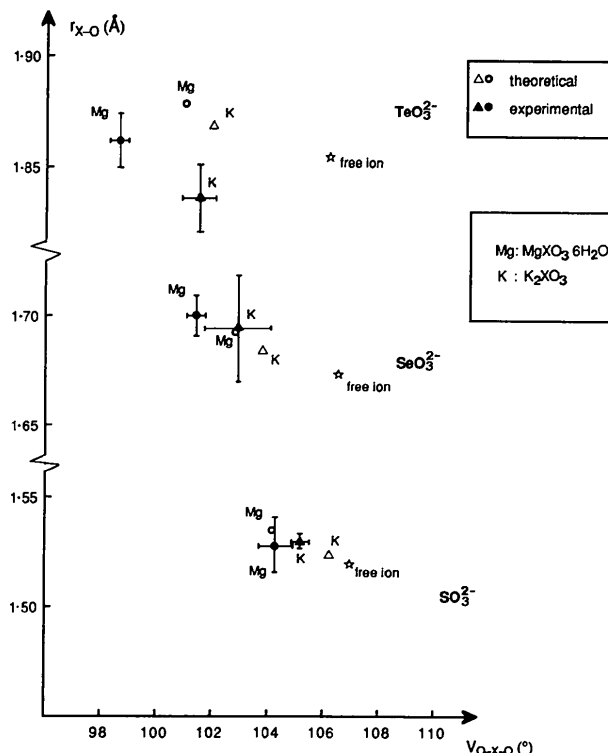


Fig. 2. Comparison between calculated and experimental geometries for tellurite, selenite and sulfite structures. The bars represent the  $3\sigma$  value. Theoretical results are represented by unfilled symbols and experimental results by filled symbols. Mg stands for  $\text{MgXO}_3 \cdot 6\text{H}_2\text{O}$  and K for  $\text{K}_2\text{XO}_3$ , where  $X$  is S, Se or Te.

*et al.*, 1983b) indicate that only a small error, a shortening of around 0.01 Å, can be expected from the ECP treatment on tellurium. We have not considered or included relativistic effects in these calculations but they could be of importance for such a heavy element as tellurium. There are, however, no references in the literature concerning these effects on bond lengths in tellurium compounds.

If the difference between the calculated and experimental Te—O bond distances in  $K_2TeO_3$ , is used to extrapolate the geometry of a hypothetical (experimental) free tellurite ion, we obtain a Te—O distance of 1.83 Å. The value, extrapolated from experimental results, employed for example by Brown (1974) in the valence-bond theory, is slightly shorter, 1.813 Å.

These quantum-chemical calculations and comparison with experiments give us a good starting point for our further studies of the stereochemistry of tellurium(IV)—oxygen compounds.

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## Absolute Chirality and Crystal Structure of Barium Nitrite Monohydrate, $Ba(NO_2)_2 \cdot H_2O$

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### Abstract

The absolute chirality of barium nitrite monohydrate,  $Ba(NO_2)_2 \cdot H_2O$  [ $M_r = 247.4$ , hexagonal, space group  $P6_1$ ,  $a = 7.070$  (1),  $c = 17.886$  (2) Å,  $V = 774.3$  Å<sup>3</sup>,  $R = 0.017$  for 1792 observed reflections] has been determined at room temperature through a combination of X-ray diffraction and optical study. For a

crystal that is optically dextrorotatory in the visible region of the spectrum, the space group is found to be  $P6_1$ . Classical polarizability theory is successfully used to calculate the optical rotation and refractive indices in this crystal and results in good agreement with experiment are obtained. Using the results of these calculations and the principles of anisotropic polarizability theory, a correlation between the sign of the observed optical rotation and the arrangement of the atoms in the crystal structure is established. The

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