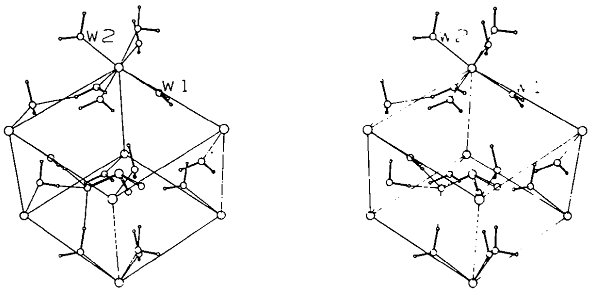

Fig. 1. A stereoscopic view of the $MgSO_3.6H_2O$ unit cell.

Table 3. *Hydrogen-bonding distances* (Å) *and angles* (°)

A	*B*	*C*	$d(A-C)$	$d(A-B)$	$d(B\cdots C)$	$\angle(A-B\cdots C)$
$W(1)-$	$H(1)\cdots$	$W(2^{ii})$	2·872 (3)	0·958 (4)	1·941 (4)	163·6 (3)
$W(1)-$	$H(2)\cdots$	$O(^{iii})$	2·726 (3)	0·967 (4)	1·759 (3)	178·3 (4)
$W(2)-$	$H(3)\cdots$	O	2·687 (3)	0·989 (3)	1·701 (3)	173·8 (3)
$W(2)-$	$H(4)\cdots$	$O(^{iv})$	2·701 (3)	0·980 (3)	1·731 (3)	169·4 (3)
$H(1)-$	$W(1)-$	$H(2)$	1·551 (4)	—	—	107·4 (3)
$H(3)-$	$W(2)-$	$H(4)$	1·553 (4)	—	—	104·1 (3)

Symmetry codes: (ii) $x-1, y, z$; (iii) $x, y-1, z$; (iv) $y, z, x-1$.

molecule is distorted from this favorable orientation owing to the strong hydrogen bonds between $W(2)$ and the SO_3^{2-} ion. The SO_3^{2-} ion takes part in nine of the twelve hydrogen bonds in the cell, each sulfite oxygen being bonded in the oxygen plane through $W(1)-H(2)\cdots O$ and $W(2)-H(4)\cdots O$ and perpendicular to it through $W(2)-H(3)\cdots O$ (*cf.* Fig. 1). The other three hydrogen bonds are between water molecules in different $Mg(H_2O)_6^{2+}$ units.

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The Structures of Magnesium Tellurate(IV) Hexahydrate, $MgTeO_3.6H_2O$, and Magnesium Selenate(IV) Hexahydrate, $MgSeO_3.6H_2O$

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Abstract. $MgTeO_3.6H_2O$ and $MgSeO_3.6H_2O$ isomorphous, $M_r = 307·9$, 259·4, rhombohedral, $R3$, $a = 6·011$ (3), 5·965 (2) Å, $\alpha = 97·36$ (4), 97·28 (2)°, $V = 211·3$ (1), 206·7 (1) Å^3, $Z = 1$, $D_x = 2·42$ (1), 2·08 (1) g cm^{-3}, Mo $K\alpha$, $\lambda = 0·71069$ Å, $\mu = 37·4$, 49·8 cm^{-1}, $F(000) = 148$, 130, $T = 293$ K, 819, 695 diffractometer reflections, $R = 0·029$, 0·021. The structures are isomorphous with $MgSO_3.6H_2O$. The dimen-

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sions of the TeO_3^{2-} and SeO_3^{2-} ions are Te—O = 1·859 (4), Se—O = 1·697 (3) Å and ∠O—Te—O = 98·6 (1), O—Se—O = 101·4 (1)°.

Introduction. In order to evaluate the electronic structure of the SO_3^{2-} and TeO_3^{2-} ions, SCF Hartree–Fock calculations have been started on these systems (Strömberg, Gropen, Wahlgren & Lindqvist, 1983). Successful geometry optimizations have been performed for SO_3^{2-} and HSO_3^- using the structures of Na_2SO_3 (Larsson & Kierkegaard, 1969) and $CsHSO_3$ (Johansson, Lindqvist & Vannerberg, 1980) for crystal potential-field calculations.

A structure suitable as an experimental basis for geometry optimizations of TeO_3^{2-} should contain this ion on a threefold axis of symmetry. A recent compilation of tellurate(IV) structures (Daniel, Moret, Maurin & Philippot, 1982; Philippot, 1981) shows that only a few of the known structures contain free TeO_3^{2-} ions *e.g.* $Na_2TeO_3.5H_2O$ (Philippot, Maurin & Moret, 1979), $K_2TeO_3.3H_2O$ (Johansson & Lindqvist, 1978), $BaTeO_3.H_2O$ (Rottersten-Nielsen, Grönbaek-Hazell & Rasmussen, 1971) and $Li_2TeO_3.LiOH$ (Cachau-Herreillat, Norbert, Maurin, Fourcade & Philippot, 1983). However, none of these structures contain TeO_3^{2-} ions with threefold symmetry.

The powder diagram of $MgTeO_3.6H_2O$ has been reported by Samplavskaya, Ivankova & Karapet'yahts (1966), without reference to space group or cell dimensions. A comparison of their data and the powder patterns of $MgSO_3.6H_2O$ and $MgSeO_3.6H_2O$ indicates that the three compounds are isomorphous. If so, this would constitute the first case in which isomorphism between sulfite and tellurate(IV) compounds has been demonstrated.

$MgSO_3.6H_2O$ (Flack, 1973) and $MgSeO_3.6H_2O$ (Weiss, Wendling & Grandjean, 1966) have been determined previously from X-ray data in space group $R3$ with S and Se on the threefold axis. A neutron diffraction refinement of $MgSO_3.6H_2O$ (Andersen & Lindqvist, 1984) has given the details of the hydrogen-bond structure in this compound.

In the present work, the crystal structure of $MgTeO_3.6H_2O$ has been determined to confirm the probable isomorphism in the series $MgXO_3.6H_2O$, X = S, Se and Te. In addition, a refinement of the structure of $MgSeO_3.6H_2O$ has been performed, since the previous work is of relatively low precision [σ(Se—O) ≃ 0·1 Å].

Experimental. Crystals of $MgTeO_3.6H_2O$, $MgSeO_3.6H_2O$ obtained from aqueous solutions of K_2TeO_3, K_2SeO_3 saturated with $Mg(OH)_2$, colorless octahedra of corner-to-corner dimensions 0·05, 0·09 mm mounted on a Syntex $P2_1$ diffractometer, graphite-monochromatized Mo $K\alpha$ radiation, lattice parameters refined from setting angles of 11, 15 reflections in the interval $7 < 2\theta < 23°$; 925 ($2\theta < 80°$; $h \geq k$, $-7 \leq h \leq 7$, $-7 \leq k \leq 7$, $-10 \leq l \leq 10$), 703 ($2\theta < 60°$; $h \geq k$, $-5 \leq h \leq 8$, $-8 \leq k \leq 5$, $0 \leq l \leq 8$) reflections* measured in scan interval $2{\cdot}0 \leq 2\theta \leq 3{\cdot}0°$, and evaluated by profile analysis according to Lehmann & Larsen (1974) (program *LELA*; Lindqvist & Ljungström, 1979) giving 819, 695 (295, 264 unique) intensities with $I > 3\sigma(I)$; standard reflections in both cases 133, 022, stable, Lp corrections (*XTL*, Syntex, 1973), no absorption corrections; structures verified from Patterson and Fourier maps (*XTL*; Syntex, 1973), H not located for $MgTeO_3.6H_2O$, H located from difference maps for $MgSeO_3.6H_2O$, full-matrix least-squares refinements of 819, 695 non-averaged reflections (Busing, Martin & Levy, 1962; Coppens & Hamilton, 1970), anisotropic temperature factors for non-H atoms, minimizing $\sum w(|F_o| - |F_c|)^2$, $wR = 0{\cdot}032$, 0·025, $S = 0{\cdot}27$, 0·32, $w = [\sigma^2(F_o) + 0{\cdot}0025\, F_o^2]^{-1}$, $\sigma^{-2}(F_o)$ (σ based on counting statistics) giving satisfactory weight analyses, $\Delta/\sigma < 0{\cdot}5\%$, scattering factors and anomalous-dispersion factors from *International Tables for X-ray Crystallography* (1974).

Discussion. Atomic coordinates, equivalent isotropic temperature factors and cell dimensions are given in Table 1 for $MgTeO_3.6H_2O$ and $MgSeO_3.6H_2O$, along with the values found for $MgSO_3.6H_2O$ (Andersen & Lindqvist, 1984). Coordination distances and angles are given in Table 2.

The isomorphism between the three structures is evident, thus constituting the first example of isomorphous sulfite and tellurate(IV) compounds. The reasons that such isomorphism does not generally occur are the differences in chemistry, mainly the great tendency of TeO_3^{2-} to be stabilized in condensed chain or network structures. In the present case, the TeO_3^{2-} ion is shielded from polarization and condensation by the large $Mg(H_2O)_6^{2+}$ ions.

The present set of bond distances and angles for the SO_3^{2-}, SeO_3^{2-} and TeO_3^{2-} ions (Table 2) may be regarded as reference values, since there are no strong ionic or covalent interactions between the anions and other units in the structure. They are in rather good agreement with the previous reference values published by Wells (1975), who compiled earlier structural works.

A comparison of $MgSO_3.6H_2O$ with other sulfites was performed in the previous paper (Andersen & Lindqvist, 1984). Concerning selenites, there are not many structures known containing free SeO_3^{2-} ions, but the previously published values for $MgSeO_3.6H_2O$

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* Lists of structure factors and anisotropic temperature factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39129 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Comparison of fractional coordinates, equivalent isotropic temperature factors* (*Hamilton*, 1959) *and unit-cell dimensions for* I $MgTeO_3.6H_2O$, II $MgSeO_3.6H_2O$ *and* III $MgSO_3.6H_2O$ (*Andersen & Lindqvist*, 1984)

W denotes a water-molecule oxygen atom.

		x	y	z	B_{eq}(Å^2)
Mg	I	0·0000 (2)	0·0000 (2)	0·0000 (2)	1·30 (1)
	II*	0	0	0	1·26 (1)
	III*	0	0	0	1·49 (1)
Te	I*	0·5305	0·5305	0·5305	1·67 (1)
Se	II	0·5218 (2)	0·5218 (2)	0·5218 (2)	1·55 (1)
S	III	0·5021 (6)	0·5021 (6)	0·5021 (6)	2·18 (2)
O	I	0·5741 (5)	0·4886 (5)	0·2282 (6)	1·95 (5)
	II	0·5728 (4)	0·4893 (4)	0·2469 (4)	1·89 (4)
	III	0·5598 (3)	0·4826 (3)	0·2565 (3)	2·12 (2)
W(1)	I	−0·3232 (5)	−0·1273 (6)	0·0561 (6)	2·25 (6)
	II	−0·3195 (5)	−0·1275 (6)	0·0641 (6)	2·21 (5)
	III	−0·3165 (3)	−0·1254 (3)	0·0765 (4)	2·45 (3)
W(2)	I	0·3279 (5)	0·1385 (5)	−0·0443 (5)	1·79 (5)
	II	0·3299 (5)	0·1424 (6)	−0·0440 (5)	1·74 (4)
	III	0·3288 (3)	0·1464 (3)	−0·0496 (3)	1·98 (2)

Cell dimensions:		a (Å)	α (°)	V (Å^3)
	I	6·011 (2)	97·36 (3)	211·3 (1)
	II	5·965 (2)	97·28 (2)	206·7 (1)
	III	5·933 (2)	96·28 (2)	204·8 (2)

* Fixed to define origin.

Table 2. *Coordination distances* (Å) *and angles* (°) *in* $MgXO_3.6H_2O$, X = Te, Se *and* S

	Te	Se	S*
Mg−*W*(1)	2·080 (3)	2·061 (3)	2·059 (2)
Mg−*W*(2)	2·102 (3)	2·104 (3)	2·112 (2)
X−O	1·859 (4)	1·697 (3)	1·528 (2)
O···O	2·818 (4)	2·625 (4)	2·413 (3)
W(1)−Mg−*W*(1^{i})†	91·0 (2)	92·4 (1)	93·8 (1)
W(1)−Mg−*W*(2)	177·6 (2)	176·3 (1)	174·9 (1)
W(2)−Mg−*W*(2^{i})	87·6 (1)	87·1 (1)	86·6 (1)
O−*X*−O	98·6 (1)	101·4 (1)	104·3 (2)

* Andersen & Lindqvist (1984).
† Symmetry code: (i) z, x, y.

Table 3. *Hydrogen coordinates and hydrogen-bond geometry* (Å, °) *for* $MgSeO_3.6H_2O$, *and a comparison of* O···O *hydrogen-bond distances in* $MgXO_3.6H_2O$, X = Te, Se *and* S

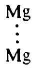
	x	y	z	B_{iso}(Å^2)
H(1)	0·585 (8)	0·955 (8)	0·068 (8)	3·3 (9)
H(2)	0·644 (8)	0·772 (8)	0·135 (8)	5·6 (1·1)
H(3)	0·421 (8)	0·270 (8)	0·066 (8)	5·4 (1·1)
H(4)	0·362 (8)	0·175 (8)	0·816 (8)	3·9 (9)

A *B* *C*	*A*−*B*	*B*···*C*	∠*A*−*B*···*C*
W(1)−H(1)···*W*(2^{ii})†	0·80 (5)	2·09 (5)	160 (5)
W(1)−H(2)···O(^{iii})	0·80 (5)	1·91 (5)	167 (5)
W(2)−H(3)···O(^{iv})	0·99 (5)	1·67 (5)	179 (5)
W(2)−H(4)···O(^{v})	0·92 (5)	1·79 (5)	167 (5)

O···O	Te	Se	S*
W(1)···*W*(2^{ii})	2·845 (4)	2·856 (5)	2·872 (3)
W(1)···O(^{iii})	2·682 (5)	2·695 (4)	2·726 (3)
W(2)···O(^{iv})	2·646 (4)	2·662 (4)	2·687 (3)
W(2)···O(^{v})	2·690 (4)	2·698 (4)	2·701 (3)

* Andersen & Lindqvist (1984).
† Symmetry code: (ii) $1+x, y, z$; (iii) $x, y, z-1$; (iv) $x-1, y-1, z-1$; (v) $y-1, z-1, x$.

Table 4. *Distances* (Å) *along the threefold axis in* $MgXO_3.6H_2O$, X = Te, Se *and* S

Distance		Te	Se	S*
	Mg···*X*	4·763 (4)	4·658 (3)	4·561 (3)
	Mg···*X*^{i}†	4·216 (2)	4·269 (2)	4·522 (3)
	Mg···Mg^{i}	8·979 (5)	8·927 (5)	9·083 (5)

* Andersen & Lindqvist (1984).
† Symmetry code: (i) $x+1, y+1, z+1$.

(Weiss, Wendling & Grandjean, 1966; *cf.* also Wells, 1975) agree well with the present results.

Philippot (1981) has reviewed the literature with respect to accurate tellurate(IV) structures, and refined the three-coordinated Te—O distance (R_o) to 1·854 Å, according to Brown's (1974) valence-bond formula $S = S_o(R/R_o)^{-N}$. Trömel (1980) has developed the valence-bond theory further. His considerations, which refer to a free TeO_3^{2-} ion without any backbonding to Te^{IV}, gave a value of 1·815 Å, significantly shorter than the present experimental value.

The hydrogen-bond structure determined for $MgSeO_3.6H_2O$ is in agreement with that found from neutron diffraction data for $MgSO_3.6H_2O$ (Andersen & Lindqvist, 1984), except for some minor differences probably due to the different dimensions of the XO_3^{2-} ions (*cf.* Table 3). There is, however, an unbroken tendency indicating slightly stronger hydrogen bonding in the order S < Se < Te. This tendency is significant from S to Te and especially for the strongest hydrogen bond $W(2)$–O^{IV} through all three structures. This effect, as well as the increasing 'back-side' distances, 3·49 (5), 3·57 (4) and 3·69 (5) Å for Te···O, Se···O and S···O, respectively, leads to the conclusion that the stereochemical activity of the lone pair is decreasing in the order $S^{IV} > Se^{IV} > Te^{IV}$ in the XO_3^{2-} ions. Accordingly, the electronegativity of the oxygen atoms increases in the order S < Se < Te, also in agreement with the O···O distances within the XO_3^{2-} ions (*cf.* Table 2).

Table 4 shows the distribution of atoms along the threefold symmetry axis, and displays the most significant differences between the three isomorphous structures. There is obviously 'more space', *i.e.* higher stereochemical activity, accompanying the $3s^2$ free-electron pair of S^{IV} than for the $4s^2$ and $5s^2$ pairs on

Se^{IV} and Te^{IV}, respectively. However, the rather large difference also includes the evident geometrical factor that the smaller covalent radius of S^{IV} results in a larger O—*X*—O bond angle (*cf.* Table 2).

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