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Structure of Anhydrous Titanyl Sulfate, Titanyl Sulfate Monohydrate and Prediction of a New Structure

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Abstract

(1) Titanyl sulfate, $TiOSO_4$, $M_r = 159.96$, orthorhombic, $P2_1ma$, $a = 10.942$ (1), $b = 5.158$ (1), $c = 25.726$ (2) Å, $U = 1452.0$ (3) Å^3, D_m (flotation) = 2.96 (2), $D_x = 2.93$ (1) g cm^{-3}, $Z = 16$, $\lambda(Mo\ K\alpha) = 0.7107$ Å, $\mu = 23.46$ cm^{-1}, $F(000) = 1248$, $T = 293$ K, final $R = 0.168$ for 2333 counter reflections. A combined X-ray and transmission electron microscopy study allowed the determination and refinement of this structure on a supercell of WPO_5 (a and b equal those above but c is $4 \times c$). The structure consists of an infinite array of corner-shared octahedra and tetrahedra and Ti—O distances range from 1.70 (2) to 2.05 (1) Å. (2) Titanyl sulfate monohydrate, $TiOSO_4.H_2O$, $M_r = 177.97$, orthorhombic, $P2_12_12_1$, $a = 9.818$ (1), $b = 5.133$ (1), $c = 8.614$ (2) Å, $U = 434.1$ (2) Å^3, $Z = 4$, D_m (flotation) = 2.71 (1), $D_x = 2.72$ (1) g cm^{-3}, $\lambda(Mo\ K\alpha) = 0.7107$ Å, $\mu = 23.46$ cm^{-1}, $F(000) = 352$, $T = 293$ K, final $R = 0.0190$ for 1985 counter reflections. The structure consists of $[TiO]_n^{2n+}$ chains parallel to the crystallographic b axis linked by sulfate tetrahedra to form the three-dimensional structure. The titanyl bridge is asymmetric [1.6870 (9) and 1.9641 (8) Å] and Ti—O distances range from 1.687 to 2.136 Å. A new struc-

ture derived from that of titanyl sulfate hydrate is predicted.

Introduction

As part of a general study of transition-element sulfate complexes (Gatehouse & Platts, 1993) interest focussed on titanyl sulfate ($TiOSO_4$) and its hydrates. These materials have been the subject of several studies as outlined in an earlier report (Naka, Tanaka, Suwa & Takeda, 1977) in which the unit-cell dimensions of $TiOSO_4$, from Weissenberg photographs, and a refinement of its powder diffraction pattern were given.

A structure determination of the monohydrate, $TiOSO_4.H_2O$, was reported some years ago (Lundgren, 1956), with the comments that the 'experimental intensity material was too poor to allow a complete structure determination' and that an 'idealised structure which should be slightly distorted according to $P2_12_12_1$' was being reported. This structure was, nevertheless, essentially the correct one. It has been claimed that a low-temperature or α-$TiOSO_4.H_2O$ can be prepared that is converted into the above form at about 403 K (Pervushin, Tolchev, Denisova, German & Kleshchev, 1989).

Observations on the structure of the dihydrate, $TiOSO_4.2H_2O$, have been reported (Reynolds &

Wiseman, 1967) but apparently crystals occur as bundles of very small fibres that decompose in air. From infrared spectra these authors suggested that the structure may be fundamentally different from that of the monohydrate and may be a basic sulfate, $Ti(OH)_2SO_4.H_2O$, similar to the zirconium compound of the same formula in which the metal atom bonds to four hydroxyl groups. No unit-cell dimensions have been reported for this compound.

We report here the single-crystal structure determination and a high-resolution electron microscopy study (carried out in order to explain the poor X-ray result) of anhydrous titanyl sulfate together with a refinement of the structure of titanyl sulfate monohydrate, the absolute configuration of which was also determined.

Experimental

Crystals of titanyl sulfate (up to 0.3 mm in length) and its monohydrate (up to 1.5 mm in length) were prepared by hydrothermal treatment (in sealed Carius tubes at 503–513 K) of solutions of hydrated anatase $(TiO_2.xH_2O)$ in aqueous sulfuric acid of approximate concentrations 80 and 65% (w/w), respectively. Freshly precipitated and oven dried (383 K for 2 days) hydrated anatase [prepared from K_2TiF_6 (Brauer, 1965)] was used, as commercially available precipitated TiO_2 was found to be insoluble under the conditions of the experiment. Crystals of both compounds, which appeared to be fully grown within a week, were removed from the Carius tube and washed with distilled water and appear to be stable to the atmosphere in the long term – some 12 to 18 months to date. The anhydrous titanyl sulfate crystals are clear colourless elongated prisms that extinguished perfectly when examined by polarized light. Titanyl sulfate monohydrate crystals formed as brittle elongated prisms, but whereas these are clear and colourless at their extremities, the centres of the crystals are white and appear to be multiply fractured. A spherical specimen was ground from a suitable crystal using a homemade Bond spheriser (Bond, 1951). Both data-collection crystals were repeatedly immersed in liquid nitrogen (77 K) to develop their 'mosaic structure' to minimize secondary-extinction effects.

TEM specimens were prepared by crushing a few crystals in ethanol in an agate mortar and collecting some of the resulting suspension on a holey-carbon-coated copper grid. These were examined in the NAMAC*/CSIRO Philips CM30 equipped with a TWIN lens (spherical aberration coefficient, C_s = 2 mm) and double-tilt holders, operated at 300 keV.

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Results

(1) Titanyl sulfate

X-ray study. Space group $P2_1ma$ or $Pmma$ ($hk0$: $h = 2n$); $P2_1ma$ by refinement; cell parameters determined with a Philips PW1100 four-circle diffractometer equipped with a graphite monochromator and are the means of 12 measurements made on the positions of 24 reflections ($16 < 2\theta < 38°$) as orientation checks during data collection. Intensity measurements were made with a crystal with dimensions $0.09 \times 0.28 \times 0.08$ mm using the diffractometer and Mo $K\alpha$ radiation monochromated with a flat graphite crystal. A unique data set was collected out to $2\theta(Mo\ K\alpha) = 70°$ using the ω-scan technique with a symmetric scan range of $\pm(0.70 + 0.2\tan\theta)°$ in 2θ from the calculated Bragg angle, at a scan speed of $0.02° s^{-1}$. 6981 unique reflections measured, 2333 $[I > 3\sigma(I)]$ used in analysis; index range $0 < h < 17$, $0 < k < 8$, $0 < l < 41$. Three standard reflections measured at 2 h intervals; no decomposition occurred. Data were processed as described previously (Canty, Chaichit & Gatehouse, 1980). Absorption correction applied (indexed crystal faces) maximum and minimum transmission factors 0.8291 and 0.7660 respectively; no extinction correction necessary. Initial attempts to solve this structure with a subcell with $c/4$ were frustrated by space-group anomalies. A preliminary examination by TEM confirmed that that real cell should have a quadrupled c axis and a data set was collected on this basis. The structure solution presented here was obtained by Patterson and Fourier methods and refined by full-matrix least-squares methods. Function minimized in full-matrix least-squares refinement on F, $\sum w(|F_o| - |F_c|)^2$, where $w = [\sigma^2(F_o)]^{-1}$.

Ti and S positions were determined from the Patterson synthesis and oxygen sites located in difference Fourier syntheses. However, refinement of the structure with all coordinates free to vary proved impractical with the diffraction intensities as measured using the cell above. The details of the diffraction pattern as seen by electron microscopy (see below) indicated that a high degree of refinement was not going to be possible.

However, refinement was continued by fixing the sulfate ion S—O distances and the O—S—O angles so that a single S—O distance [1.447 (1) Å] was refined for the sulfate ions. Refinement of positional and isotropic thermal parameters for all atoms resulted in $R = 0.168$ and $wR = 0.182$ and goodness of fit 5.71. Not an impressive result; however, to illustrate that the intensities are sensitive to the presence of O atoms at this level of refinement O(1) was omitted and a cycle of refinement resulted in $R = 0.1733$ and $wR = 0.1888$. At convergence one oxygen

Table 1. *Atomic parameters for* TiOSO$_4$ *(with e.s.d.'s in parentheses)*

	x	y	z	U_{iso} (Å²)
Ti(1)	0.4397	0.0	0.0996 (3)	0.008 (1)
Ti(2)	0.4228 (8)	0.0	0.3572 (2)	0.002 (1)
Ti(3)	0.9453 (10)	0.0	0.1511 (3)	0.013 (1)
Ti(4)	0.9347 (10)	0.0	0.3928 (2)	0.006 (1)
Ti(5)	0.3227 (11)	0.5	0.0176 (4)	0.022 (2)
Ti(6)	0.3190 (7)	0.5	0.2690 (2)	0.005 (1)
Ti(7)	0.8072 (11)	0.5	0.2291 (3)	0.018 (2)
Ti(8)	0.8070 (8)	0.5	0.4731 (3)	0.016 (2)
S(1)	0.2331 (10)	0.0	0.1920 (3)	0.012 (3)
S(2)	0.2079 (9)	0.0	0.4488 (3)	0.005 (1)
S(3)	0.7321 (10)	0.0	0.0575 (3)	0.012 (2)
S(4)	0.7089 (9)	0.0	0.3010 (3)	0.002 (1)
S(5)	0.0428 (11)	0.5	0.0731 (4)	0.014 (2)
S(6)	0.0369 (10)	0.5	0.3192 (3)	0.005 (1)
S(7)	0.5300 (10)	0.5	0.1798 (3)	0.011 (2)
S(8)	0.5151 (10)	0.5	0.4365 (3)	0.013 (2)
O(1)	0.1009 (10)	0.0	0.1913 (7)	0.004 (4)
O(2)	0.0765 (9)	0.0	0.4425 (6)	0.000 (3)
O(3)	0.2787 (16)	0.0	0.1392 (4)	0.002 (4)
O(4)	0.2656 (14)	0.0	0.3982 (4)	0.006 (4)
O(5)	0.6078 (13)	0.0	0.0767 (11)	0.058 (13)
O(6)	0.5981 (14)	0.0	0.3317 (8)	0.036 (9)
O(7)	0.8161 (22)	0.0	0.1009 (8)	0.039 (9)
O(8)	0.8139 (15)	0.0	0.3352 (7)	0.021 (6)
O(9)	−0.0432 (20)	0.5	0.0304 (7)	0.043 (10)
O(10)	−0.0653 (14)	0.5	0.2834 (7)	0.022 (6)
O(11)	0.4796 (25)	0.5	0.2318 (5)	0.027 (8)
O(12)	0.4642 (19)	0.5	0.4884 (5)	0.014 (5)
O(13)	0.6621 (10)	0.5	0.1826 (11)	0.052 (12)
O(14)	0.6472 (10)	0.5	0.4396 (8)	0.023 (7)
O(15)	0.1663 (13)	0.5	0.0529 (10)	0.036 (8)
O(16)	0.1502 (13)	0.5	0.2901 (7)	0.014 (5)
O(17)	0.0241 (18)	0.2709 (4)	0.1046 (4)	0.082 (13)
O(18)	0.0314 (15)	0.2708 (4)	0.3515 (3)	0.059 (9)
O(19)	0.2765 (14)	0.2291 (4)	0.2187 (4)	0.142 (21)
O(20)	0.2448 (12)	0.2291 (4)	0.4772 (3)	0.089 (14)
O(21)	0.4891 (16)	0.2709 (4)	0.1523 (5)	0.084 (13)
O(22)	0.4745 (15)	0.2709 (4)	0.4090 (4)	0.087 (14)
O(23)	0.7522 (18)	0.2292 (4)	0.0261 (4)	0.174 (27)
O(24)	0.7119 (15)	0.2291 (4)	0.2685 (3)	0.058 (10)
O(25)	0.4005 (14)	0.2751 (32)	0.0651 (5)	0.007 (2)
O(26)	0.3900 (16)	0.2611 (43)	0.3195 (6)	0.017 (3)
O(27)	0.8869 (18)	0.2951 (39)	0.1831 (6)	0.017 (3)
O(28)	0.8712 (13)	0.2940 (31)	0.4222 (5)	0.005 (2)

Table 2. *Bond lengths* (Å) *and selected bond angles* (°) *for* TiOSO$_4$ *(with e.s.d.'s in parentheses)*

Ti(1)—O(25)	1.73 (2)	Ti(2)—O(26)	1.70 (2)
—O(25)^a	1.73 (2)	—O(26)^a	1.70 (2)
—O(5)	1.93 (2)	—O(22)	2.01 (1)
—O(21)	2.02 (1)	—O(22)^a	2.01 (1)
—O(21)^a	2.02 (1)	—O(4)	2.02 (2)
—O(3)	2.04 (2)	—O(6)	2.03 (2)
Ti(3)—O(27)	1.84 (2)	Ti(4)—O(28)	1.83 (2)
—O(27)^a	1.84 (2)	—O(28)^a	1.83 (2)
—O(7)	1.91 (2)	—O(8)	1.99 (2)
—O(1)^b	1.99 (2)	—O(2)^b	2.01 (2)
—O(17)^b	2.03 (1)	—O(18)^b	2.05 (1)
—O(17)^c	2.03 (1)	—O(18)^c	2.05 (1)
Ti(5)—O(25)	1.89 (2)	Ti(6)—O(16)	1.93 (2)
—O(25)^r	1.89 (2)	—O(26)	1.95 (2)
—O(9)^d	1.92 (2)	—O(26)^r	1.95 (2)
—O(15)	1.94 (2)	—O(19)	1.96 (1)
—O(23)^f	1.95 (1)	—O(19)^r	1.96 (1)
—O(23)^g	1.95 (1)	—O(11)	2.00 (3)
Ti(7)—O(27)	1.81 (2)	Ti(8)—O(28)	1.83 (2)
—O(27)^r	1.81 (2)	—O(28)^r	1.83 (2)
—O(10)^b	1.98 (2)	—O(14)	1.95 (2)
—O(13)	1.99 (2)	—O(12)^a	1.98 (2)
—O(24)	2.02 (1)	—O(20)^a	2.01 (1)
—O(24)^r	2.02 (1)	—O(20)^i	2.01 (1)

Ranges of angles in the titanium octahedra

O—Ti(1)—O	81.0 (6)–110.5 (10), 167.7 (9)–168.2 (6)
O—Ti(2)—O	83.5 (7)–105.0 (13), 167.4 (8)–171.3 (8)
O—Ti(3)—O	80.9 (6)–111.2 (12), 167.8 (7)–168.9 (10)
O—Ti(4)—O	81.1 (5)–111.9 (10), 167.0 (7)–171.2 (8)
O—Ti(5)—O	85.5 (8)–96.4 (6), 167.9 (11)–172.2 (7)
O—Ti(6)—O	78.3 (12)–101.2 (7), 167.8 (8)–169.7 (8)
O—Ti(7)—O	71.4 (13)–100.0 (7), 169.1 (7)–171.9 (10)
O—Ti(8)—O	71.1 (10)–100.5 (5), 171.5 (6)–176.4 (9)

Symmetry codes: (a) x, $-y$, z; (b) $1+x$, y, z; (c) $1+x$, $-y$, z; (d) $\frac{1}{2}+x$, $1-y$, $-z$; (e) x, $1-y$, z; (f) $-\frac{1}{2}+x$, $1-y$, $-z$; (g) $\frac{1}{2}-x$, y, $-z$; (h) $\frac{1}{2}+x$, $1-y$, $1-z$; (i) $\frac{1}{2}+x$, y, $1-z$.

atom, O(2), persisted in having a non-positive-definite thermal parameter.* 178 parameters were refined in the final cycles and at convergence the largest shift to e.s.d. ratio was 0.44 for the U_{11} coordinate of O(2). Final parameters and their estimated standard deviations are given in Table 1 and selected interatomic distances and angles in Table 2.† The atomic scattering factors used were for neutral atoms and were corrected for anomalous dispersion (Ibers & Hamilton, 1974). All calculations were carried out on the Monash University DEC VAX 11/780 and Macintosh IIci computers; the major program used was *SHELX*76 (Sheldrick, 1976).

Discussion. It appears that the first structural model for compounds of the type $A^V B^V O_5$ was deduced by Chahboun, Groult, Hervieu & Raveau

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* The largest feature in the final difference Fourier synthesis was 1 e Å^{-3} near Ti(3).

† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55873 (22 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL0545]

(1986) from X-ray powder and TEM data for β-NbPO$_5$ and β-TaPO$_5$. This model was subsequently refined from X-ray data for β-NbPO$_5$ (Leclaire, Chahboun, Groult & Raveau, 1986) and later shown to be the structure of WPO$_5$ (Wang, Wang & Lii, 1989) for which the characteristic unit cell is orthorhombic with $a \approx 11.2$, $b \approx 5.2$ and $c \approx 6.5$ Å. Insurmountable difficulties encountered in trying to solve the titanyl sulfate structure using the characteristic unit cell resulted in a data set being collected with the unit cell 10.942, 5.158 and 25.726 (4×6.432) Å from which a structure has been derived that has gone some way towards explaining the complex diffraction pattern observed in the TEM study.

The structure, an infinite array of corner-shared octahedra and tetrahedra, may be considered to be made up of ribbons of octahedra and tetrahedra as shown in Fig. 1. These ribbons are corner shared to one another and are parallel to [010] as may be seen in Fig. 2. The resulting structure (Fig. 2) has four- and five-sided holes or tunnels; the four-sided holes can be seen to be progressively more distorted as one views them in going from one subcell to the next in the c-axis direction. These can be seen for the WPO$_5$ structure (with the characteristic subcell $11.2 \times 5.2 \times 6.5$ Å) (Fig. 3) as being relatively undistorted.

The shortest Ti—O distances in each of the octahedra range from 1.70 (2) to 1.93 (2) Å whereas the longest ones range from 1.95 (1) to 2.05 (1) Å (Table 2). This considerable variation in Ti—O distances results in distortions in the structure and presumably in the supercell formation and other diffraction pattern complexities.

Electron diffraction study. Figs. 4(a) and 4(b) show [010] zone-axis selected-area electron diffraction patterns (SADP) from two different crystals. In Fig. 4(a), the rows of 00l reflections are canted away from the exact c^* direction by about 2°, indicating that the normal '4c' supercell in this crystal is incommensurable with the basic WPO$_5$-like substructure. This canting is delineated about the 0,0,12 reflection. In Fig. 4(b), besides the correct 4c superstructure in the

c^* direction (it is commensurate in this crystal), very weak extra 'satellite' reflections are present in between the 00l rows (two are marked S in the pattern) but their spacing suggests the presence of a new additional superstructure in the **a** direction, incommensurable (but parallel) with the TiOSO$_4$ **a** repeat. The spacing of the satellite reflections suggests a primary wavevector $g = 2.63a$, about 29.4 Å in real space for this superstructure. The images from the [010] zone axis (Fig. 5a) confirm the basic structure, comprising a herringbone arrangement of connected TiO$_6$ octahedra and SO$_4$ tetrahedra, and the four times longer c repeat in TiOSO$_4$. However, the incommensurate superstructure in the SADP of Fig. 4(b), which was obtained from this crystal, does not appear in the image as might be expected from such weak satellite reflections. Fig. 5(b) shows a rare
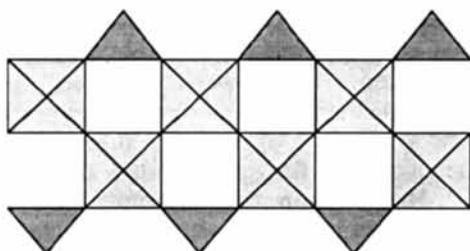
Fig. 1. Ribbon of octahedra and tetrahedra – the basic building unit of the titanyl sulfate structures.
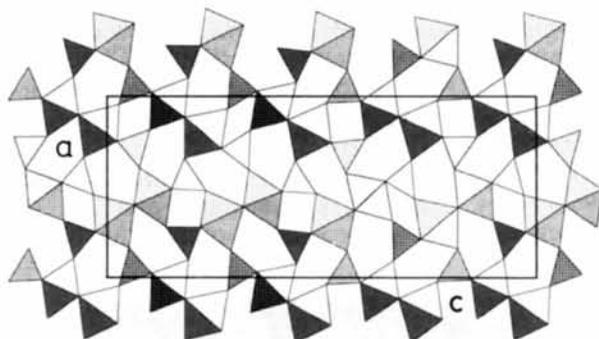
Fig. 2. The structure of titanyl sulfate viewed along (010).
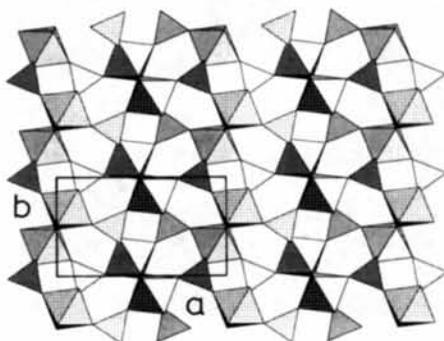
Fig. 3. The structure of WPO$_5$ (Wang, Wang & Lii, 1989) viewed along (001).
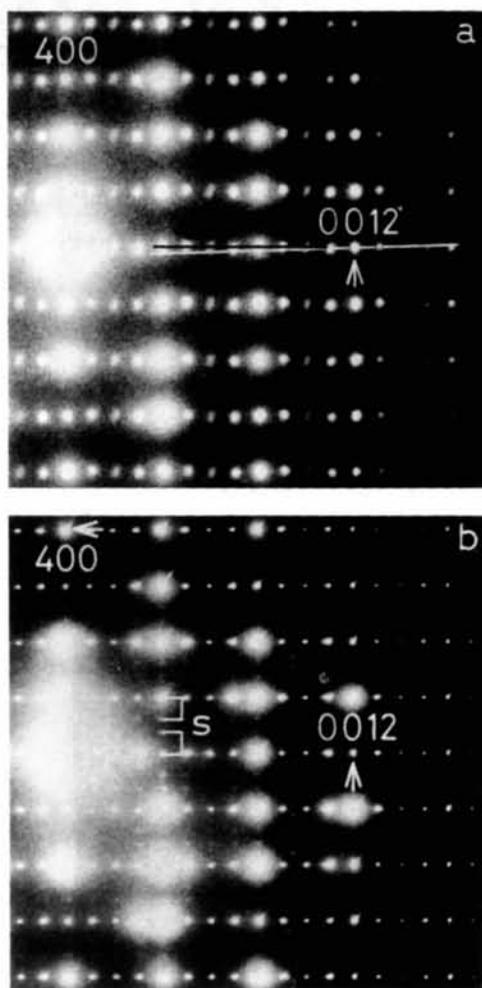
Fig. 4. (a) SADP from the [010] zone axis of titanyl sulfate, showing the rows of 00l reflections to be canted away from the subcell c^* direction by about 2°. (b) SADP from a different titanyl sulfate crystal in the same orientation showing additional weak and incommensurate reflections ('satellites') present between the basic 00l rows.

defect, but one that would further complicate the structure solution. It is effectively a 180° rotation about the *a* axis, which maintains the basic connectivity of the structure albeit with some distortion of the bonds, visible here as strain contrast. Fig. 6 shows a [001] zone-axis SADP, and here again there is evidence for disorder in the form of streaking of

100 Å

the reflections in the **a*** direction. We could confirm the structural similarity with WPO₅ by direct comparison of images in the relevant orientations. Fig. 7 shows a [001] zone-axis image and the corresponding SADP from WPO₅, corresponding to Fig. 6. Although we did multislice image simulations for both WPO₅ and TiOSO₄ in this orientation, the results were in good agreement with these experimental images and are not considered here. It is therefore clear that refinement of the X-ray data was limited by the complex diffraction effects discussed above.

(2) *Titanyl sulfate monohydrate*

Intensity measurements were made with the spherical specimen described above using the diffractometer and Mo $K\alpha$ radiation monochromated with a flat graphite crystal. Cell parameters were obtained as the means of 20 measurements made on 25 reflections $38.6 < 2\theta < 39.9°$ as orientation checks during data collection. Data were collected out to $\theta(\text{Mo } K\alpha) = 45°$ using the ω-scan technique with a symmetric scan range of $\pm(0.75 + 0.15\tan\theta)°$ in 2θ from the calculated Bragg angle, at a scan speed of $0.02° \text{ s}^{-1}$. No reflection was sufficiently large to warrant the insertion of an attenuation filter. 2055 unique reflections measured ($R_{\text{int}} = 0$, no duplications), 1985 $[I > 2.5\sigma(I)]$ used in analysis; index range $0 < h < 19, 0 < k < 10, 0 < l < 17$. Three standard reflections measured at 2 h intervals; no decomposition occurred. The data were processed in a manner described previously (Canty, Chaichit & Gatehouse, 1980). A spherical absorption correction was applied (crystal radius 0.113 mm); no extinction correction was necessary.

The coordinates previously reported (Lundgren, 1956) were used as the starting point for this refinement which proceeded smoothly. After several

Fig. 5. (*a*) Composite high-resolution image and corresponding SADP from the [010] zone axis of titanyl sulfate, showing the characteristic herringbone appearance of the structure, and the weak contrast modulation resulting from the long *c* repeat. A single 10.9 × 25.7 Å unit cell is outlined above the structure axes and an enlargement of the thin edge is included. (*b*) An image showing a rare stacking defect in a [010] zone-axis image from titanyl sulfate.

Fig. 6. [001] zone-axis pattern from titanyl sulfate. All reflections are slightly streaked in the **a*** direction, indicating the presence of structural disorder in this fragment.

cycles of full-matrix least-squares adjustment of positional and isotropic thermal parameters, first the Ti and S and then the O atoms were refined anisotropically. At this stage the H atoms of the water molecule were readily discernible and were included in the refinement with independent isotropic thermal parameters. The refinement converged after several further cycles and using the test of whether the coordinates or their inverted values gave rise to the lower R factor the absolute configuration of the structure was determined ($R = 0.0190$, $wR = 0.0289$ and goodness of fit = 0.9732 *versus* $R = 0.0273$, $wR = 0.0310$ and goodness of fit = 1.6039).

At convergence the conventional $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.0190$, $wR = 0.0289$ [$wR = \sum w^{1/2}(||F_o| - |F_c||)/\sum w^{1/2}|F_o|$] and $w = [\sigma^2(F_o)]^{-1}$. 82 parameters were varied in the final cycles and at convergence the largest shift to e.s.d. ratio was 0.028 for the U_{11} coordinate of H(2). The largest feature in the final difference Fourier synthesis was 0.7 e Å^{-3} near S and O(2). Final parameters and their estimated standard deviations are given in Table 3 [these differ from those originally reported (Lundgren, 1956) owing to the determination of the absolute configuration followed by transformation of the

Table 3. *Atomic parameters for* $TiOSO_4.H_2O$ *(with e.s.d.'s in parentheses)*

	x	y	z	U^* (Å^2)
Ti	0.37425 (2)	0.22658 (3)	0.70950 (2)	0.00685 (3)
S	0.17395 (2)	0.76008 (5)	0.58652 (3)	0.00734 (4)
O(1)	0.47791 (8)	0.96890 (17)	0.73808 (11)	0.0135 (2)
O(2)	0.02950 (9)	0.71710 (21)	0.61355 (12)	0.0172 (2)
O(3)	0.29219 (9)	0.25807 (21)	0.91792 (9)	0.0162 (2)
O(4)	0.25851 (11)	0.57182 (17)	0.66777 (12)	0.0167 (2)
O(5)	0.20906 (8)	0.02796 (16)	0.63905 (11)	0.0125 (2)
O(6)	0.07681 (11)	0.73800 (23)	0.97764 (10)	0.0180 (2)
H(1)	0.0224 (30)	0.8307 (61)	0.9299 (29)	0.034 (7)
H(2)	0.0369 (33)	0.6041 (69)	0.9223 (36)	0.051 (9)

* Equivalent isotropic U is defined as one third of the trace of the orthogonalized U_{ij} tensor. H atoms are included with isotropic U.

Table 4. *Bond lengths* (Å) *and selected bond angles* (°) *for* $TiOSO_4.H_2O$ *(with e.s.d.'s in parentheses)*

Ti—O(1)^a	1.6870 (9)	O(1)^a—Ti—O(1)^b	90.98 (1)
—O(1)^b	1.9641 (8)	O(1)^a—Ti—O(3)	100.23 (4)
—O(3)	1.9744 (8)	O(1)^a—Ti—O(5)	97.65 (4)
—O(5)	2.0095 (8)	O(1)^a—Ti—O(6)^c	94.01 (5)
—O(6)^c	2.0623 (9)	O(1)^a—Ti—O(4)	174.98 (4)
—O(4)	2.1356 (10)	O(1)^b—Ti—O(3)	92.33 (4)
		O(1)^b—Ti—O(5)	170.81 (4)
S—O(4)	1.4536 (10)	O(1)^b—Ti—O(6)^c	89.69 (4)
—O(2)	1.4540 (9)	O(1)^b—Ti—O(4)	84.63 (4)
—O(5)^d	1.4880 (9)	O(3)—Ti—O(5)	89.24 (4)
—O(3)^e	1.4928 (8)	O(3)—Ti—O(6)^c	165.57 (4)
		O(3)—Ti—O(4)	82.41 (4)
O(4)—S—O(2)	112.28 (6)	O(5)—Ti—O(6)^c	86.58 (4)
O(4)—S—O(5)^d	109.61 (5)	O(5)—Ti—O(4)	86.60 (4)
O(4)—S—O(3)^e	107.44 (6)	O(6)^c—Ti—O(4)	83.56 (4)
O(2)—S—O(5)^d	108.51 (5)		
O(2)—S—O(3)^e	111.32 (6)	Ti^d—O(1)—Ti^e	167.40 (5)
O(5)^d—S—O(3)^e	107.57 (6)		

Symmetry codes: (a) $x, y - 1, z$; (b) $1 - x, y - \frac{1}{2}, \frac{3}{2} - z$; (c) $\frac{1}{2} - x, 1 - y, z - \frac{1}{2}$; (d) $x, y + 1, z$; (e) $1 - x, \frac{1}{2} + y, \frac{3}{2} - z$.

coordinates to positive values] and selected interatomic distances and angles in Table 4. The atomic scattering factors used were for neutral atoms and were corrected for anomalous dispersion (Ibers & Hamilton, 1974). All calculations were carried out on the Monash University DEC VAX 11/780 computers; the major program used was *SHELX*76 (Sheldrick, 1976).

Discussion

The structure and the numbering scheme used for $TiOSO_4.H_2O$ are shown in Fig. 8; the basic ribbons of octahedra and tetrahedra are the same as for $TiOSO_4$ (Fig. 1); the linking between these ribbons is shown in Fig. 9. The structure may be described as chains of titanyl groups, $[TiO]_n^{2n+}$, running parallel to the crystallographic b axis (this corresponds to the needle axis of the crystal), which are linked by sulfate groups to form the three-dimensional structure. Each Ti atom is in a distorted octahedral coordination of two (mutually *cis*) bridging oxide ions, three sulfate oxygens and one water molecule. The titanyl bridge is quite asymmetric [1.6870 (9) and 1.9641 (8) Å] in common with that in other polymeric titanyl compounds, *e.g.* KTiOPO$_4$ [Ti(1) 1.718 (4) and 1.993 (4) Å; Ti(2) 1.738 (4) and 2.101 (4) Å]

Fig. 7. [001] zone-axis pattern from WPO$_5$ corresponding to Fig. 6 for titanyl sulfate.

(Tordjman, Masse & Guitel, 1974), CsTiOAsO₄ [Ti(1) 1.714 (4) and 1.966 (4) Å; Ti(2) 1.748 (4) and 2.122 (5) Å] (Protas, Marnier, Boulanger & Menaert, 1989) and CaTiOSiO₄ [1.766 (4) and 1.974 (6) Å] (Speer & Gibbs, 1976). It appears that this structure exhibits the shortest titanium-to-bridging oxide distance yet recorded [1.6870 (9) Å] and is the only example of a purely *cis*-bridged chain of TiO₆ octahedra.

Overall Ti—O distances range from 1.6870 (9) to 2.136 (1) Å, the wide variation being reflected in the
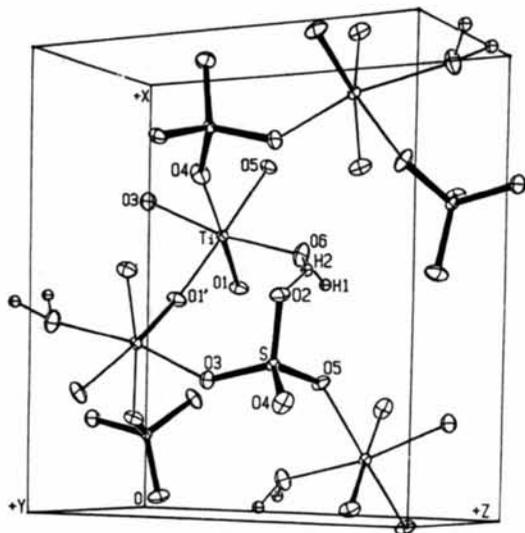
angles within the Ti octahedra (Table 4). The Ti atom is displaced from the octahedron centre by the short Ti—O(1) bond as shown in Fig. 8 with all four O(1)—Ti—O(equatorial) angles being significantly greater than 90°. The sulfate group is quite regularly tetrahedral in geometry, with the average sulfur–oxygen distance being 1.47 (2) Å and the average interbond angle at sulfur being very close to the ideal at 109 (2)°. Three sulfate O atoms are bonded to titanium the fourth being involved in hydrogen bonding to the water molecule (Fig. 8).

A considerably less distorted structure than that of TiOSO₄ with the *AOBO₄* stoichiometry can be derived from the titanyl sulfate hydrate structure by simply envisaging removal of the water molecule and linking the unshared oxygen on the nearby tetrahedron with the now vacant site on the octahedron (Fig. 9). The resulting structure (Fig. 10) is an oxygen-deficient ReO₃ (*ABO₆*) with the stoichiometry *ABO₅*. The unit cell of this structure has been estimated to be *a* = 5.60, *b* = 6.80, *c* = 11.20 Å and the space-group symmetry conforms to *Pmm2*. A search of the ICSD files (Bergerhoff, Kilger, Witthauer, Hundt & Sievers, 1992) has not revealed a composition and unit cell that matches these parameters – further work is being carried out to produce such a compound (Gatehouse & Williams, 1992).

The structure determination of α-TiOSO₄ (a phase containing about 7 wt% Fe₂O₃) from powder X-ray diffraction data was described recently (Grey & Stranger, 1992). The structure contains ribbons of octahedra and tetrahedra of the same type as in the titanyl sulfates described above but only a single octahedron wide.

Fig. 8. Titanyl sulfate hydrate – structure and numbering scheme.

Fig. 9. The structure of titanyl sulfate monohydrate viewed along (010).

Fig. 10. Diagram of the new *ABO₅* structure derived from the structure of titanyl sulfate monohydrate.

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Kikuchi Patterns, Index System and Inflation Properties of an $Al_{70}Co_{15}Ni_{15}$ Decagonal Quasicrystal*

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Abstract

The general principle of the projection method and an index scheme for decagonal phases are described systematically. Kikuchi-line patterns over a large angular range from an $Al_{70}Co_{15}Ni_{15}$ decagonal quasicrystal with a periodicity of 4 Å along the tenfold axis were obtained by connecting a series of large-angle convergent-beam electron diffraction patterns. Computer-simulated electron diffraction patterns of major zone axes and Kikuchi-line patterns covering the whole orientation triangle show good agreement with the patterns recorded experimentally. After discussion of the inflation and deflation properties, appropriate quasilattice parameters of $a = 6.6$ Å (or 2.5 Å), $c = 4.0$ Å for an $Al_{70}Co_{15}Ni_{15}$ decagonal quasicrystal are chosen that are suitable for atomic decoration of the quasilattice of the decagonal phase.

1. Introduction

Decagonal quasicrystals having tenfold rotational symmetry and one-dimensional translational symmetry along the tenfold axis have been reported in rapidly solidified alloys of Al–Mn (Bendersky, 1985; Chattopadhyay, Lele, Ranganathan, Subbanna & Thangaraj, 1985), Al–Fe (Fung, Yang, Zhou, Zhao, Zhan & Shen, 1986), Al–Co (Dong, Li & Kuo, 1987; Suryanarayana & Menon, 1987), Al–Pd (Idziak, Heiney & Bancel, 1987) and Al–Ni (Li & Kuo, 1988).

The period along the tenfold axis was about 12 Å for Al–Mn and 16 Å for Al–Co, Al–Fe and Al–Pd. In addition, a periodicity of 4 Å along the tenfold axis has been reported in Al–Ni (Li & Kuo, 1988) and in the stable decagonal phases of AlCoCu and AlCoNi (Tsai, Inoue & Masumoto, 1989). In the system AlCoCu, He, Wu & Kuo (1988) found decagonal quasicrystals with periodicities of 4, 8, 12 and 16 Å corresponding to two-, four-, six- and eight-layer stackings, respectively.

The cut-and-projection method (Elser, 1985; Katz & Duneau, 1986; Jaric, 1986) affords an adequate indexing of diffraction patterns for the icosahedral quasicrystalline phase. Based on this method, an indexing scheme was described for the decagonal phase (Ho, 1986) and used by Koopmans, Schurer, van der Woude & Bronsveld (1987) and Thangaraj, Subbanna, Ranganathan & Chattopadhyay (1987) in the interpretation of their data for the Al–Mn decagonal phase. These authors support the concept of the derivation of an indexing model that has a periodic axis c by a distortion of the icosahedral vertex basis, to a pentagonal-bipyramid (PB) edge-vector basis (Ho, 1986). Choy, FitzGerald & Kalloniatis (1988) provided a more straightforward index system, which uses a planar pentagonal basis set plus the periodic axis. These two index systems are equivalent. Mandal & Lele (1989, 1991) generated the direct and reciprocal space of a one-dimensionally periodic quasicrystal by simultaneous distortion of the six-dimensional hypercubic cell along one of its edges and also of the icosahedron (formed by projection of the six-dimensional basis