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Structure of Dithallium Tungstate (VI)

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Abstract. Tl_2WO_4, trigonal, $P\bar{3}m1$, $a = 6\cdot278\ (1)$, $c = 8\cdot099\ (2)$ Å, $Z = 2$, $D_x = 7\cdot89$ Mg m^{-3}. The crystals were prepared by heating an intimate mixture of Tl_2CO_3 and WO_3 at 973 K for 3 h in a platinum crucible. Colourless and transparent platy crystals were obtained. The substance is isostructural with glaserite, with mean W—O, Tl(1)—O, Tl(2)—O and Tl(3)—O distances of 1·78, 2·70, 3·29 and 3·25 Å respectively.

Introduction. From Weissenberg and precession photographs, the crystals were found to have trigonal Laue symmetry $\bar{3}m$. Since systematic absences were not observed, the Laue symmetry restricts the possible space groups to $P3m1$, $P321$ and $P\bar{3}m1$. $P\bar{3}m1$ gave a satisfactory result for the structure refinement. A platy crystal with approximate dimensions 0·25 × 0·22 × 0·056 mm was used for intensity collection. The ω–2θ technique was used to measure, on a Philips automated four-circle diffractometer, the graphite-monochromated Mo $K\alpha$ reflection intensities up to $2\theta = 80°$. The scan speed was 4° min^{-1} in ω and scanning was repeated twice when the total counts were less than 10 000. The scan width was determined according to $(1\cdot4 + 0\cdot2 \tan\theta)°$. Intensities were corrected for the Lorentz–polarization factor. Absorption corrections ($\mu = 80\cdot32$ mm^{-1}) were also made using a local version of the program *ACACA* (Wuensch & Prewitt, 1965). Corrections for isotropic secondary extinction were carried out in the course of the structure refinement (the crystal was assumed to be a sphere 0·15 mm in diameter). Intensities of 146 independent reflections, whose $|F|$'s were larger than $3\sigma(|F|)$, were obtained and used for the structure determination.

The positions of the Tl and W atoms were obtained from the Patterson map and those of the O atoms were then found on Fourier and difference Fourier maps synthesized with phases derived from the Tl and W atoms. The structure was refined with the full-matrix least-squares program *LINUS* (Coppens & Hamilton, 1970) and anisotropic temperature factors for Tl and W atoms. After correction for isotropic secondary extinction, the calculation converged to give an R value of 0·059 for the 146 observed reflections; the extinction parameter (G) was $0\cdot012\ (8) \times 10^{-4}$. The weighting scheme of Hughes (1941) was adopted: $w = 1\cdot0$ if $F_o < 176\cdot0$, and $w = (176\cdot0/F_o)^2$ if $176\cdot0 \le F_o$. The atomic scattering factors for neutral atoms and the dispersion-correction factors were taken from *International Tables for X-ray Crystallography* (1974). The final positional and thermal parameters are listed in Table 1.* Interatomic distances and bond angles are given in Table 2.

Discussion. The crystallographic data and phase transformations of Tl_2WO_4 had been given by Sleight, Bierlein & Bierstedt (1975). They reported that the phase transformations of Tl_2WO_4 were observed at 284, 310 and 835 K, and that the space group of the phase below 284 K (δ phase) was $Pna2_1$; that of the phase between 284 and 310 K (γ phase) was probably $P\bar{3}m1$; and that of the phase above 835 K (α phase) was presumably $P6_3/mmc$. They also reported that the δ

Table 1. *Final atomic parameters of* Tl_2WO_4

	x	y	z	B (Å^2)
Tl(1)	0	0	0	2·12*
Tl(2)	0	0	$\frac{1}{2}$	3·72*
Tl(3)	$\frac{2}{3}$	$\frac{1}{3}$	0·1717 (5)	3·67*
W	$\frac{2}{3}$	$\frac{1}{3}$	0·6855 (7)	1·61*
O(1)	$\frac{2}{3}$	$\frac{1}{3}$	0·475 (8)	2·4 (14)
O(2)	0·181 (16)	−0·181	0·228 (6)	5·4 (13)

* Calculated from the anisotropic thermal parameters according to $B = 4(B_{11}a^2 + B_{22}b^2 + B_{33}c^2 + B_{12}ab\cos\gamma)/3$.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34454 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 2. *Interatomic distances* (Å) *and bond angles* (°)

Symmetry code

(0)	x,y,z	(ix)	$\bar{x}, \bar{y}, 1-z$
(i)	$x-y, x, 1-z$	(x)	$y, y-x, 1-z$
(ii)	$1-x, \bar{y}, 1-z$	(xi)	$1-y, x-y, z$
(iii)	$1+y, x, 1-z$	(xii)	$1-x+y, \bar{x}, z$
(iv)	$\bar{x},\bar{y},\bar{z}$	(xiii)	$1+x, 1+y, z$
(v)	$\bar{y}, x-y, z$	(xiv)	$1-x+y, 1-x, z$
(vi)	$y, y-x, \bar{z}$	(xv)	$1-x, \bar{y}, \bar{z}$
(vii)	$y-x, \bar{x}, z$	(xvi)	$1+y, 1-x+y, \bar{z}$
(viii)	$x-y, x, \bar{z}$		

W—O(1^{0})	1·70 (6)	W—O($2^{\mathrm{i,ii,iii}}$)	1·80 (8) ×3
Tl(1)—O($2^{\mathrm{0,iv,v,vi,vii,viii}}$)	2·70 (7) ×6		
Tl(2)—O($1^{\mathrm{0,i,v,vii,ix,x}}$)	3·630 (4) ×6		
Tl(2)—O($2^{\mathrm{0,i,v,vii,ix,x}}$)	2·95 (7) ×6		
Tl(3)—O(1^{0})	2·46 (6)		
Tl(3)—O($2^{\mathrm{0,v,xi,xii,xiii,xiv}}$)	3·18 (6) ×6		
Tl(3)—O($2^{\mathrm{viii,xv,xvi}}$)	3·64 (6) ×3		
O(1)—W—O(2)	112·9 (18) ×3	O(2)—W—O(2)	105·9 (30) ×3

phase showed ferroelectric behaviour and was isostructural with $(NH_4)_2SO_4$ (Schlemper & Hamilton, 1966). The α phase was considered to be isostructural with the high-temperature phase of K_2SO_4 (van den Berg & Tuinstra, 1978). However, no structural investigation of the γ phase has been made.

Projections along the **c** and [110] axes are shown in Figs. 1 and 2. The W atom is tetrahedrally surrounded by four O atoms. The apex of a given WO_4 tetrahedron relative to those of neighbouring tetrahedra points in the opposite direction to the c axis (Fig. 1). The W—O distances are 1·70 (6) and 1·80 (8) Å (mean 1·78 Å). The O—W—O angles are 105·9 (30) and 112·9 (18)°. Tl(1) is octahedrally surrounded by six O atoms, with a Tl(1)—O distance of 2·70 (7) Å. The Tl(2) atom is surrounded by twelve O atoms, with Tl(2)—O distances of 2·95 (7) and 3·630 (4) Å (mean 3·29 Å). Tl(3) is surrounded by ten O atoms, with Tl(3)—O distances of 2·46 (6), 3·18 (6) and 3·64 (6) Å. One of the Tl(3)—O distances is fairly short (2·46 Å) when compared to the other Tl—O distances.

The crystal structures of all known $A_2^+B^{6+}O_4$ compounds of which the A^+ cation is larger than K^+ are classified into two types, *i.e.* K_2WO_4 (Koster, Kools & Rieck, 1969) and $(NH_4)_2SO_4$ (Schlemper & Hamilton, 1966). The crystal structure of γ-Tl_2WO_4 is different from those of the known structures in $A_2^+B^{6+}O_4$ compounds. This substance is isostructural with the glaserite structure type (Eysel, 1973) which was found only in $(A,C)_2BX_4$ compounds (A is a medium-sized and C a large cation). In Fig. 3, the lattice parameters of the glaserite structure-type compounds are plotted against the sum of the cation ionic radii, $(\bar{r}_{A,C} + r_B)$; all are distributed nearly along a line. It is considered that γ-Tl_2WO_4 is the first example of the glaserite structure type, $(A,C)_2BX_4$, in which the A and C cations are identical.

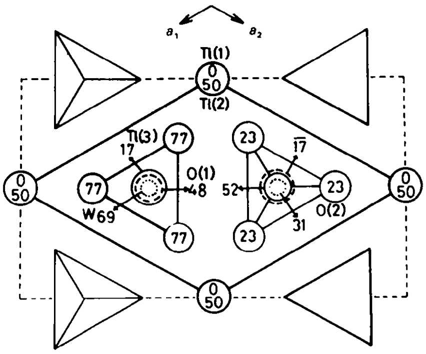

Fig. 1. Projection of the structure of Tl_2WO_4 along the c axis; numbers give, in decimal fractions of the c length, the heights of the atoms (×10^2). Large circles denote Tl, medium circles denote O, and small circles denote W.

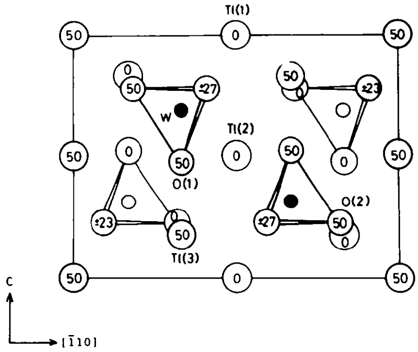

Fig. 2. Projection of the structure of Tl_2WO_4 along the [110] axis; numbers give, in decimal fractions of the [110] length, the heights of the atoms (×10^2). The atoms are depicted as in Fig. 1 (small open and solid circles denote W).

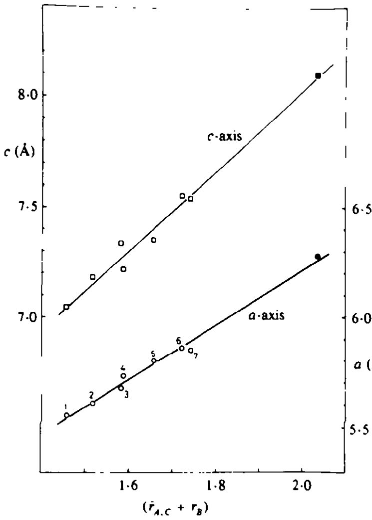

Fig. 3. A plot of the lattice parameters against the sum of the radii of different cations for the glaserite structure-type compounds. r_A, r_B and r_C are ionic radii of the cations A, B and C in $(A,C)_2BO_4$ respectively. $\bar{r}_{A,C}$ is the average of r_A and r_C. The solid circle and the solid square indicate Tl_2WO_4. (1) $Na_{1.33}K_{0.67}SO_4$ (JCPDS 20-926); (2) $NaKSO_4$ (JCPDS 20-927); (3) $Na_{0.5}K_{1.5}SO_4$ (JCPDS 20-928); (4) $Na_{1.4}K_{0.6}CrO_4$ (Eysel, 1973); (5) $NaKCrO_4$ (JCPDS 26-1468); (6) $Na_{0.5}K_{1.5}CrO_4$ (JCPDS 22-855); (7) $Na_{0.5}K_{1.5}SeO_4$ (JCPDS 26-923).

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Octacarbonylbis[μ-(pentacarbonylmanganio)indium(III)]-diiron

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Abstract. $Fe_2(CO)_8[InMn(CO)_5]_2$, M_r = 955·40, tetragonal, $I4_1/a$, a = 13·283 (2), c = 30·123 (3) Å, U = 5314·8 Å^3, Z = 8, D_c = 2·387 Mg m^{-3}, $F(000)$ = 3616, Mo $K\alpha$ radiation, λ = 0·71069 Å, μ(Mo $K\alpha$) = 3·56 mm^{-1}. The structure was refined with 2821 unique reflections ($I > 3\sigma$) to R = 0·027. No Fe–Fe bond is present in the four-membered In_2Fe_2 ring.

Introduction. We have prepared a number of compounds of the type $M''(CO)_8[\mu\text{-}M(X)M'(CO)_5]$ [M = Ge, X = Br, $M' = M''$ = Mn (Preut & Haupt, 1979); M = Sn, X = Cl, Br, $M' = M''$ = Mn (Preut & Haupt, 1976; Haupt, Preut & Wolfes, 1978)] and of the type $M_2''(CO)_8[\mu\text{-}MM'(CO)_5]_2$ [M = Ga, $M' = M''$ = Mn; M = In, $M' = M''$ = Mn, Re (Preut & Haupt, 1974, 1975)] and we now report on the similar compound $Fe_2(CO)_8[InMn(CO)_5]_2$, which has been prepared in a bomb tube by reaction of $Fe(CO)_5$, In metal and $Hg[Mn(CO)_5]$ in the presence of xylene at a temperature of 443–453 K.

Data were collected from a crystal 0·30 [100] × 0·23 [010] × 0·30 [001] mm. Cell parameters were determined by least squares from the positions of 11 reflexions on a Hilger & Watts Y 290 four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation and a scintillation counter. The intensities of 5817 reflexions ($I > 3\sigma$) with $2 \leq \theta \leq 30{\cdot}0°$ were measured by the $\omega/2\theta$ scan technique, with a scan width $\Delta 2\theta = (1{\cdot}34 + 0{\cdot}34 \tan\theta)°$ from background to background and a scan speed of 0·02° s^{-1} in 2θ. Backgrounds were measured at either end of the scan range for 8 s. Five standard reflexions were measured every fifty reflexions, and showed only random deviations from their mean intensities. Lp but no absorption corrections were applied, and after averaging of equivalent reflexions the data set contained 2821 reflexions for the analysis. The structure was solved by Patterson and Fourier methods and refined by full-matrix least

Table 1. *Positional parameters* (×10^4) *with e.s.d.'s in parentheses*

	x	y	z
In(1)	4552 (0)	6362 (0)	2814 (0)
Mn(1)	4034 (0)	4446 (0)	2813 (0)
Fe(1)	5000 (0)	7500 (0)	2114 (0)
Fe(2)	5000 (0)	7500 (0)	3514 (0)
C(1)	3697 (3)	3111 (3)	2811 (2)
C(2)	3074 (4)	4743 (3)	2380 (2)
C(3)	5021 (4)	4349 (4)	2385 (2)
C(4)	3102 (4)	4812 (4)	3241 (2)
C(5)	4982 (4)	4301 (4)	3256 (2)
C(6)	4676 (5)	6538 (4)	3902 (2)
C(7)	6252 (4)	7060 (4)	3397 (2)
C(8)	6203 (4)	6992 (3)	2225 (2)
C(9)	5397 (4)	8461 (3)	1733 (1)
O(1)	3516 (4)	2279 (3)	2800 (2)
O(2)	2486 (3)	4892 (3)	2125 (3)
O(3)	5620 (3)	4282 (4)	2115 (1)
O(4)	2543 (4)	5038 (4)	3511 (3)
O(5)	5534 (3)	4189 (4)	3534 (2)
O(6)	4493 (4)	5943 (4)	4160 (2)
O(7)	7055 (3)	6781 (4)	3346 (2)
O(8)	6998 (3)	6623 (3)	2270 (2)
O(9)	5646 (3)	9085 (3)	1497 (1)

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