INORGANIC COMPOUNDS

Titanium(III) Tris(metaphosphate)

WILLIAM T. A. HARRISON

Department of Chemistry, University of Houston, Houston, TX 77204-5641, USA

THURMAN E. GIER AND GALEN D. STUCKY

Department of Chemistry, University of California, Santa Barbara, CA 93106-9510, USA

Abstract

The synthesis and single crystal structure of titanium(III) tris(metaphosphate), $Ti(PO_3)_3$, are reported. $Ti(PO_3)_3$ is isostructural with other $M(PO_3)_3$ phases, where M = Al, V, Sc or Rh.

Comment

Monoclinic $Ti(PO_3)_3$ is isostructural with $Al(PO_3)_3$ (van der Meer, 1975), $V(PO_3)_3$ (Middlemiss, Hawthorne & Calvo, 1976), $Sc(PO_3)_3$ (Domanskii, Shepelev, Smolin & Litvin, 1982) and $Rh(PO_3)_3$ (Rittner & Glaum, 1994). Each Ti atom in $Ti(PO_3)_3$ forms six Ti—O—P bonds to six different neighboring P atoms. The three distinct TiO_6 octahedra in $Ti(PO_3)_3$ are all very similar [average Ti(1)—O = 2.033 (2), average Ti(2)—O = 2.029 (2), average Ti(3)—O = 2.029 (2) Å] and have very close to regular MO_6 geometry. These average Ti—O bond distances are in accordance with those expected on the basis of ionic radii sums (Shannon, 1976): $r(Ti^{III})$ = 0.81, $r(O^{2-})$ = 1.21 Å; Ti—O = 2.02 Å. This regular Ti^{III} MO_6 geometry is quite distinct from the 'second-order Jahn–Teller distortion' of TiO_6 groups typically observed in Ti^{IV}-containing phases such as $KTiOPO_4$ (Stucky, Phillips & Gier, 1989).

The nine crystallographically distinct P atoms are all tetrahedrally coordinated by O atoms: each P atom makes two P—O—Ti bonds and two P—O—P' linkages. The two types of P—O bond show a characteristic difference in average bond length [average P—O_P = 1.482 (2) and average P—O_{Ti} = 1.582 (1) Å], as was also observed in previous structural studies of $M(PO_3)_3$ phases (Middlemiss, Hawthorne & Calvo, 1976; Domanskii, Shepelev, Smolin & Litvin, 1982).

A systematic trend may also be observed in the three types of bond angles of the PO_4 groups, depending on which species the bridging O atom is linked to:

the average O_{Ti}—P—O_{Ti} bond angle is 117.7°, with a standard deviation about the mean of 0.9° (9 values considered). For comparison, the average O_{Ti}—P—O_P bond angle is 108.9° (s.d. about the mean = 1.9°; 18 values) and for O_P—P—O_P, θ_{ave} = 102.3° (s.d. about the mean = 2.9°; 9 values). Thus, O_{Ti}—P—O_{Ti} bond angles are systematically larger than O_{Ti}—P—O_P or O_P—P—O_P angles at a high confidence level. The distinction between O_{Ti}—P—O_P and O_P—P—O_P angles is less marked, but is probably a real effect.

Of the 27 O atoms, 18 [O(1)–O(18)] link Ti and P atoms, with average Ti—O—P = 145.1° (s.d. of the mean = 6.7°). The remaining nine O atoms [O(19)–O(27)] link adjacent P atoms into infinite $[PO_3]_n$ chains: average P—O—P = 141.7° (s.d. of the mean = 4.7°). There appear to be no significant trends involving these bond angles: the smallest and largest Ti—O—P angles are 133.3 (2) and 162.3 (2)°, respectively; corresponding values for the P—O—P angles are 135.8 (2) and 148.1 (3)°, respectively.

The structure of $Ti(PO_3)_3$ comprises infinite $[PO_3]_n$ chains, crosslinked by Ti atoms into a three-dimensional network. Ti—O—P—O'—Ti' and Ti—O—P—O'—P''—O''—Ti' links are present, and the smallest identifiable loop unit is a five-membered ring or '5-ring' of configuration —Ti—P—P'—Ti'—P''— (O atoms omitted). An interesting feature is the presence of two types of metaphosphate chain in the structure: the first, a three-membered chain or '3-chain', consists of the P(1)-, P(2)- and P(6)-centered PO_4 groups, linked *via* P(1)—O(19)—P(2)—O(20)—P(6)—O(21)—P(1)' bonds. This 3-chain propagates in the [100] direction and is illustrated in Fig. 2. The second $[PO_3]_n$ chain ('6-chain') consists of P(3), P(4), P(5), P(7), P(8) and P(9), linked *via* P(3)—O(22)—P(5)—O(24)—P(8)—O(25)—P(9)—O(26)—P(4)—O(23)—P(7)—O(27)—P(3)'. The 6-chain also propagates along [100] and is shown in Fig. 3. Each Ti atom makes two Ti—O—P linkages to adjacent 3-chains and four Ti—O—P bonds to nearby 6-chains. Both the 3-chain and the 6-chain show a zigzag configuration when projected onto [001]; the repeat distance of the 3-chain is half that of the 6-chain.

As observed for $V(PO_3)_3$ (Middlemiss, Hawthorne & Calvo, 1976), $Ti(PO_3)_3$ shows a superlattice effect in the *b* direction, based upon a *b*/3 subcell ($b_{sub} \simeq 6.45$ Å). The reason for the subcell effect is not immediately apparent in this complex structure. A symmetry analysis, using the program *MISSYM* (Le Page, 1988), indicated that positional shifts of up to 0.5 Å for the Ti and P atoms, and up to 0.75 Å for the O atoms were necessary for any translational pseudosymmetry to become apparent. This potential transformation to the subcell configuration may occur *via* concerted polyhedral rotations;

the [PO$_3$]$_n$ 3-chains and 6-chains would then become equivalent and the three TiO$_6$ octahedra would reduce to one distinct species. The newly described compound In(PO$_3$)$_3$ (Palinka, Maksimova, Chibiskova, Chudinova & Karmanovskaya, 1993) appears to crystallize in the $b/3$ subcell. In In(PO$_3$)$_3$, there are 13 asymmetric atoms: one In, three P and nine O. Just one type of [PO$_3$]$_n$ chain is present in In(PO$_3$)$_3$ and the P—O—P chain angle is substantially reduced to 116(2)°, compared to the average value of 141° found for Ti(PO$_3$)$_3$.
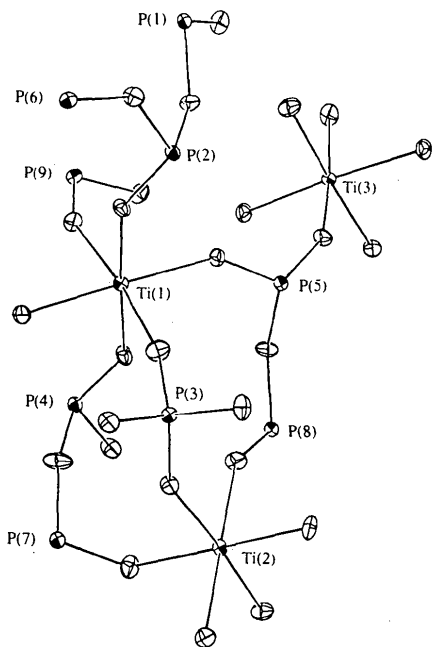

Fig 3. Polyhedral view of the 6-chain in Ti(PO$_3$)$_3$, with polyhedral centers labelled (viewed down [010], with the chain centers at $y \simeq 0.1$).

Experimental

0.120 g of Ti$_2$O$_3$ and 1 g of polyphosphoric acid (major component H$_4$P$_2$O$_7$) were sealed into a small gold tube by flame welding. Using water as the external support fluid, the tube was heated to 973 K (3000 atm; $\simeq 3 \times 10^8$ Pa) in a hydrothermal bomb and held for 3 h. The soak period was followed by cooling at 5 K h^{-1} to 473 K and then a furnace quench. 0.26 g of blue crystals were recovered from the tube (91% yield) by standard filtration and drying techniques. These crystals are indefinitely stable in air at ambient conditions.

Fig. 1. View of the asymmetric unit of Ti(PO$_3$)$_3$ with Ti and P atoms labelled. Displacement ellipsoids are shown at 50% probability levels.
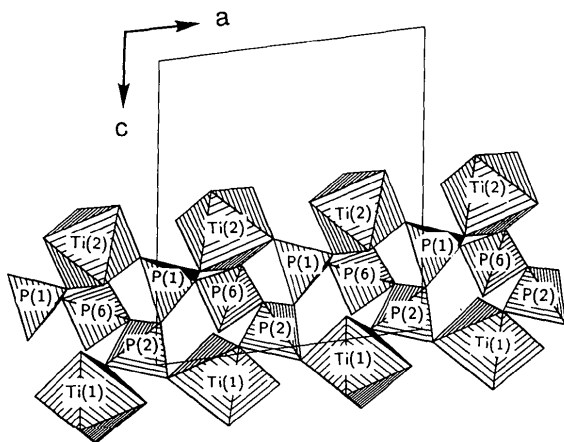
Crystal data

Ti$_3$P$_9$O$_{27}$	Mo $K\alpha$ radiation
$M_r = 854.43$	$\lambda = 0.71073$ Å
Monoclinic	Cell parameters from 25
Ic	reflections
$a = 9.551$ (2) Å	$\theta = 6.5–10.5°$
$b = 19.355$ (3) Å	$\mu = 2.04$ mm^{-1}
$c = 10.730$ (2) Å	$T = 298$ K
$\beta = 97.874$ (3)°	Irregular lump
$V = 1964.6$ Å^3	0.60 × 0.60 × 0.60 mm
$Z = 12$	Brilliant blue
$D_x = 2.889$ Mg m^{-3}	

Data collection

Huber automated diffrac-tometer	$\theta_{max} = 32.5°$
	$h = -14 \rightarrow 14$
$\theta/2\theta$ scans	$k = 0 \rightarrow 29$
Absorption correction:	$l = 0 \rightarrow 16$
ψ scan	3 standard reflections
$T_{min} = 0.75$, $T_{max} = 1.00$	monitored every 100
4531 measured reflections	reflections
4531 independent reflections	intensity variation: <2%
3487 observed reflections	
$[I > 3\sigma(I)]$	

Refinement

Refinement on F	$\Delta\rho_{max} = 0.71$ e Å^{-3}
$R = 0.027$	$\Delta\rho_{min} = -0.43$ e Å^{-3}
$wR = 0.024$	Extinction correction:
$S = 1.068$	Larson (1967)

Fig 2. Polyhedral view of the 3-chain in Ti(PO$_3$)$_3$, with polyhedral centers labelled (viewed down [010], with the chain centers at $y \simeq 0.2$).
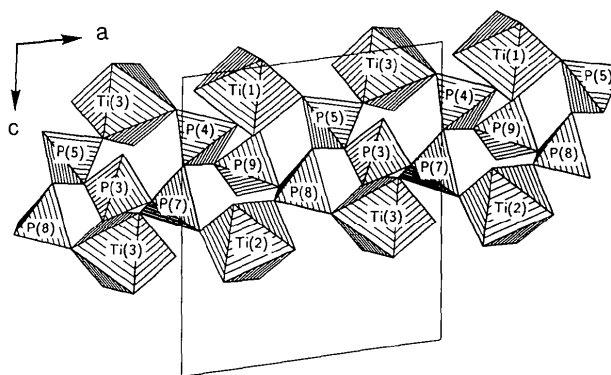
3487 reflections
353 parameters
Chebychev polynomial
fit using the method of
Carruthers & Watkin
(1979)
$(\Delta/\sigma)_{max} = 0.010$

Extinction coefficient:
189 (6)
Atomic scattering factors
from *International Tables
for X-ray Crystallography*
(1974, Vol. IV, Table
2.2B)

Table 1. *Fractional atomic coordinates and equivalent
isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Ti(1)	0.2542 (1)	0.17080 (5)	0.0795 (1)	0.0080
Ti(2)	0.2551 (1)	0.16151 (4)	0.5818 (1)	0.0080
Ti(3)	0.7705 (1)	0.00510 (4)	0.0597 (1)	0.0081
P(1)	0.5633 (2)	0.22220 (6)	−0.2718 (1)	0.0080
P(2)	0.4391 (1)	0.28195 (6)	−0.0587 (1)	0.0083
P(3)	0.2452 (1)	0.27210 (6)	0.3441 (1)	0.0082
P(4)	0.0816 (1)	0.05295 (6)	0.2105 (1)	0.0087
P(5)	0.5735 (1)	0.11371 (6)	0.2114 (1)	0.0079
P(6)	0.2719 (2)	0.39317 (6)	−0.1958 (1)	0.0083
P(7)	−0.0512 (2)	0.11363 (6)	0.4232 (1)	0.0085
P(8)	0.4538 (2)	0.05212 (6)	0.4298 (1)	0.0084
P(9)	0.2522 (1)	0.06182 (6)	−0.1668 (1)	0.0083
O(1)	0.2729 (4)	0.2355 (2)	0.2293 (4)	0.0173
O(2)	0.3064 (4)	0.2522 (2)	−0.0241 (4)	0.0113
O(3)	0.0430 (4)	0.1921 (2)	0.0470 (4)	0.0122
O(4)	0.2138 (4)	0.0856 (2)	0.1808 (3)	0.0120
O(5)	0.4635 (4)	0.1436 (2)	0.1162 (3)	0.0131
O(6)	0.2125 (4)	0.1147 (2)	−0.0786 (3)	0.0125
O(7)	0.4359 (4)	0.2128 (2)	0.6335 (4)	0.0135
O(8)	0.1985 (4)	0.2318 (2)	0.4478 (3)	0.0115
O(9)	0.1606 (4)	0.2208 (2)	0.7085 (4)	0.0138
O(10)	0.3543 (4)	0.1074 (2)	0.4541 (3)	0.0136
O(11)	0.2977 (4)	0.0850 (2)	0.7134 (3)	0.0145
O(12)	0.0688 (4)	0.1167 (2)	0.5277 (4)	0.0157
O(13)	0.7322 (4)	0.0756 (2)	−0.0797 (4)	0.0162
O(14)	0.6975 (4)	0.0803 (2)	0.1673 (3)	0.0121
O(15)	0.8353 (4)	−0.0631 (2)	−0.0639 (4)	0.0143
O(16)	0.8152 (4)	−0.0605 (2)	0.2066 (4)	0.0129
O(17)	0.9776 (4)	0.0326 (2)	0.1027 (4)	0.0139
O(18)	0.5774 (4)	−0.0396 (2)	0.0273 (4)	0.0139
O(19)	0.5143 (4)	0.2272 (2)	−0.1366 (4)	0.0122
O(20)	0.3985 (4)	0.3403 (2)	−0.1622 (4)	0.0133
O(21)	0.6429 (4)	0.1510 (2)	−0.2604 (4)	0.0135
O(22)	0.1267 (4)	0.3291 (2)	0.3126 (4)	0.0136
O(23)	0.0073 (5)	0.1043 (2)	0.2949 (4)	0.0166
O(24)	0.5039 (4)	0.0600 (2)	0.2960 (3)	0.0128
O(25)	0.3740 (4)	0.0193 (2)	−0.0892 (3)	0.0137
O(26)	0.1220 (4)	−0.0102 (2)	0.3046 (4)	0.0136
O(27)	0.3837 (4)	0.3118 (2)	0.4008 (4)	0.0138

Table 2. *Selected geometric parameters* (Å)

Ti(1)—O(1)	2.025 (4)	P(3)—O(8)	1.477 (4)
Ti(1)—O(2)	2.029 (4)	P(3)—O(22)	1.583 (4)
Ti(1)—O(3)	2.042 (4)	P(3)—O(27)	1.578 (4)
Ti(1)—O(4)	2.041 (3)	P(4)—O(4)	1.485 (4)
Ti(1)—O(5)	2.052 (4)	P(4)—O(17^{iv})	1.472 (4)
Ti(1)—O(6)	2.007 (4)	P(4)—O(23)	1.576 (4)
Ti(2)—O(7)	2.003 (4)	P(4)—O(26)	1.598 (4)
Ti(2)—O(8)	1.999 (4)	P(5)—O(5)	1.479 (4)
Ti(2)—O(9)	2.077 (4)	P(5)—O(14)	1.481 (4)
Ti(2)—O(10)	2.056 (4)	P(5)—O(22^{iii})	1.585 (4)
Ti(2)—O(11)	2.049 (4)	P(5)—O(24)	1.585 (4)
Ti(2)—O(12)	1.993 (4)	P(6)—O(13^{v})	1.480 (4)
Ti(3)—O(13)	2.020 (4)	P(6)—O(16^{vi})	1.480 (4)
Ti(3)—O(14)	2.040 (3)	P(6)—O(20)	1.587 (4)
Ti(3)—O(15)	2.027 (4)	P(6)—O(21^{v})	1.580 (4)
Ti(3)—O(16)	2.024 (4)	P(7)—O(12)	1.490 (4)
Ti(3)—O(17)	2.039 (4)	P(7)—O(15^{vii})	1.481 (4)
Ti(3)—O(18)	2.023 (4)	P(7)—O(23)	1.566 (4)

P(1)—O(7^i)	1.485 (4)	P(7)—O(27^v)	1.577 (4)
P(1)—O(9^{ii})	1.476 (4)	P(8)—O(10)	1.478 (4)
P(1)—O(19)	1.588 (4)	P(8)—O(18^{viii})	1.487 (4)
P(1)—O(21)	1.570 (4)	P(8)—O(24)	1.582 (4)
P(2)—O(2)	1.485 (4)	P(8)—O(25^{viii})	1.578 (4)
P(2)—O(3^{iii})	1.488 (4)	P(9)—O(6)	1.479 (4)
P(2)—O(19)	1.582 (4)	P(9)—O(11^i)	1.482 (4)
P(2)—O(20)	1.594 (4)	P(9)—O(25)	1.568 (4)
P(3)—O(1)	1.477 (4)	P(9)—O(26^{ix})	1.592 (4)

Symmetry codes: (i) $x, y, z - 1$; (ii) $\frac{1}{2}+x, \frac{1}{2}-y, z-1$; (iii) $\frac{1}{2}+x, \frac{1}{2}-y, z$; (iv) $x - 1, y, z$; (v) $x - \frac{1}{2}, \frac{1}{2} - y, z - 1$; (vi) $x - \frac{1}{2}, \frac{1}{2} + y, z - \frac{1}{2}$; (vii) $x - 1, -y, \frac{1}{2} + z$; (viii) $x, -y, \frac{1}{2} + z$; (ix) $x, -y, z - \frac{1}{2}$.

Several $h0l$ reflections ($\bar{1}05$, $\bar{1}03$, $\bar{3}03$, $\bar{5}07$, *etc.*) weakly violate the $h0l$, $l = 2n$ absence condition of space group Ic, indicating that the true symmetry of $Ti(PO_3)_3$ is possibly lower (space group $I1$) than the Ic model used here. In space group $I1$, there are 78 independent atoms (6 Ti, 18 P, 54 O): a refinement in this space group converged to similar residuals to those obtained for the Ic model. The spread of bond distances and angles for the $I1$ model was somewhat greater than that found in the Ic model, but there were no particular features observed in the lower symmetry model which would explain the symmetry reduction. *MISSYM* (Le Page, 1988) indicated that the $I1$-model atomic positions were displaced by less that 0.05 Å from the equivalent positions of the related atoms in space group Ic.

Data collection, cell refinement and data reduction: *UCLA Crystallographic Package* (Strouse, 1982). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *CRYSTALS* (Watkin, Carruthers & Betteridge, 1990). Molecular graphics: *ORTEPII* (Johnson, 1976); *STRUPLO* (Fischer, 1985). Software used to prepare material for publication: local routines.

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Octahydridosilasesquioxane Determined by Neutron Diffraction

KARL WILHELM TÖRNROOS

Structural Chemistry, Stockholm University, 106 91 Stockholm, Sweden

Fig. 1. Structure of the title compound displaying mean-square displacement ellipsoids at 90% probability.

Abstract

The structure of $H_8Si_8O_{12}$ has been determined by neutron diffraction at 29 K and compared with X-ray determinations at 9.5 and 100 K. There are only small geometrical differences, but it can be concluded that the deviation from the ideal molecular symmetry, O_h ($m\bar{3}m$), increases with decreasing temperature and that the large vibration amplitudes for the O atoms observed in the X-ray analyses are also present in the neutron structure. Static disorder of the O atoms is excluded. The molecular deformation is caused by the rigid $HSiO_3$ tetrahedra performing a cooperative torsional movement inducing vibrational deformations of the flexible Si—O—Si angles.

Comment

This investigation has been carried out in order to locate the atomic positions, particularly those of the H atoms, and to try to establish whether static disorder of the O atoms may be present in the crystal structure of $H_8Si_8O_{12}$, as shown in Fig. 1. The compound was prepared as described by Agaskar (1991). The X-ray experiments revealed notably large anisotropic mean-square displacements of the O atoms, principally in a direction orthogonal to the Si—O—Si plane, as well as along the bisector of the Si—O—Si angle. The structural information gained from this neutron diffraction experiment, including the anisotropic atomic displacement parameters for the H atoms, is of use in a current study of the electron-density deformation of this compound. For that study, X-ray data have been collected at 100 K (Auf der Heyde, Bürgi, Bürgy & Törnroos, 1991) and at 9.5 K (Törnroos, Schwarzenbach, Delley & Larsen, 1994).
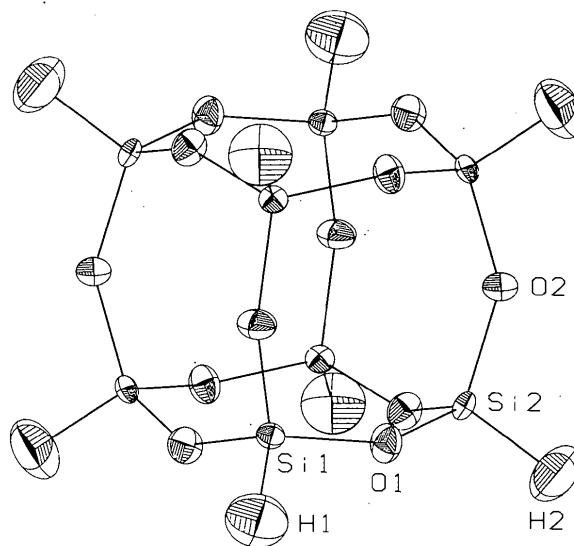
The temperature in the neutron diffraction experiment, 29 K, was the minimum temperature attainable with the cryo-instrument at the site.

The crystallographic symmetry of the $H_8Si_8O_{12}$ structure is C_{3i} ($\bar{3}$), but the molecule has non-crystallographic symmetry of T_h ($m\bar{3}$). It may, however, ideally be of O_h symmetry. The reasons for the departure from the O_h symmetry are intriguing, but the soft Si—O—Si angles seem crucial in this context as they provide flexible connections between the relatively rigid $HSiO_3$ tetrahedra. The geometrical parameters best describing this deviation from the ideal O_h symmetry are the O(1,5) non-bonded distances (across faces of the Si_8 cube) and the two Si⋯Si body diagonals in the Si_8 cube. These are given for all three determinations in Table 4. The largest differences in the three experiments occur at the O(1,5) non-bonded distances. For these ideally equal distances, the difference increases consistently with decreasing temperature. For the Si⋯Si body diagonals this tendency is insubstantial considering the e.s.d.'s. The distances of the Si⋯Si cube edge are the same to within experimental error for the X-ray data, but differ significantly towards larger values in the neutron structure determination. We thus note that the Si⋯Si and also possibly the Si—O

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Si(1)	0	0	0.32152 (18)	0.0049 (5)
Si(2)	0.31958 (19)	0.20905 (19)	0.44037 (10)	0.0048 (3)
O(1)	0.19471 (14)	0.11230 (15)	0.35740 (8)	0.0083 (3)
O(2)	0.31997 (15)	0.06903 (14)	0.50720 (8)	0.0080 (3)
H(1)	0	0	0.22521 (25)	0.0222 (8)
H(2)	0.49339 (26)	0.32175 (27)	0.40885 (16)	0.0218 (5)