maximum and minimum peaks in the final difference Fourier map are near Ta sites. All calculations were performed on a MicroVAXII computer using *TEXSAN* software (Molecular Structure Corporation, 1985).

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coordinated by four Te_2 groups. The Ta atom in the TaI_6^- complex anion is octahedrally coordinated by I^- anions.

Comment

Transition metal chalcogenides with chain structures have attracted growing interest in recent years (Whittingham & Jackson, 1982) owing to their physical properties, such as superconductivity, magnetic ordering at low temperatures, charge-density wave properties and anisotropic behaviour (Li *et al.*, 1990; Minton & Brill, 1987). Recently, the study of compounds with MQ_4 chains (M = Ta, Nb; Q = chalcogen) has increased markedly. The compounds $(M\mathrm{Te}_4)I$ (Huang, 1994) and $(M\mathrm{Se}_4)_yX$ ($y = 2, 3, 3.33, 4$; X = Br, I) (King, 1994) have been synthesized and structurally characterized. A compound with TaI_6 complex anions, $(\mathrm{TaTe}_4)_4I_2(\mathrm{TaI}_6)$, has been obtained (Liu *et al.*, 1996). In this paper, we report the structure of a new compound, $(\mathrm{TaTe}_4)_6I_4(\mathrm{TaI}_6)$.

The structure of the title compound can be considered as consisting of $[\mathrm{TaTe}_4]_n$ chains, TaI_6^- complex anions and I^- anions. The TaI_6^- complex anions and I^- anions are relatively isolated.

The configuration of the $[\mathrm{TaTe}_4]_n$ chain is shown in Fig. 1, in which each Ta atom is coordinated by four Te_2 groups in the form of a rectangular antiprism. The dichalcogen group acts as a ligand and bridges two neighbouring metal atoms along the chain, as found in the binary compound VS_4 (Allmann *et al.*, 1964). The Ta—Te bond lengths are in the range 2.831 (1)–2.866 (1) Å, while the $(\mathrm{TaTe}_4)_4I_2(\mathrm{TaI}_6)$ compound exhibits longer Ta—Te bond lengths, from 2.81 to 2.96 Å. The Te—Te bond lengths of the Te_2 groups are in the range 2.752 (1)–2.812 (1) Å, which
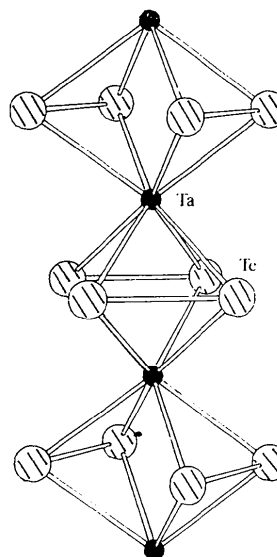
A New One-Dimensional Compound: $(\mathrm{TaTe}_4)_6I_4(\mathrm{TaI}_6)$

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Abstract

The title compound, hexakis(tetratelluriotantalum) tetraiodide hexaiodotantalate, has a $[\mathrm{TaTe}_4]_n$ chain structure with TaI_6^- complex anions and I^- anions between the chains. The $[\mathrm{TaTe}_4]_n$ chain contains rectangular antiprismatic TaTe_8 polyhedra, each Ta atom being

Fig. 1. The structure of a $[\mathrm{TaTe}_4]_n$ chain.

is very close to the range 2.760–2.803 Å found for (TaTe₄)₄I₂(TaI₆). All the Ta—Te—Ta bond angles of the [TaTe₄]ₙ chain in (TaTe₄)₆I₄(TaI₆) and (TaTe₄)₄I₂(TaI₆) are about 73°. The Ta—Ta distances are about 3.40 Å in the title compound.

In the TaI₆⁻ complex anion, the Ta atom is octahedrally coordinated by six I atoms, but there are three symmetrically independent Ta—I bonds with bond lengths of 2.704 (1), 2.757 (1) and 2.759 (1) Å.

The [TaTe₄]ₙ chains are held together by I⁻ anions and TaI₆⁻ complex anions, as illustrated in Fig. 2. Their stacking order is –TaI₆–[TaTe₄]ₙ–I–[TaTe₄]ₙ–I–[TaTe₄]ₙ– along the b axis. The shortest contacts between isolated I⁻ anions and Te atoms in adjacent [TaTe₄]ₙ chains are about 3.2 Å, but the shortest contact between an I atom of a TaI₆⁻ complex anion and a Te atom of a [TaTe₄]ₙ chain is larger than 3.4 Å.
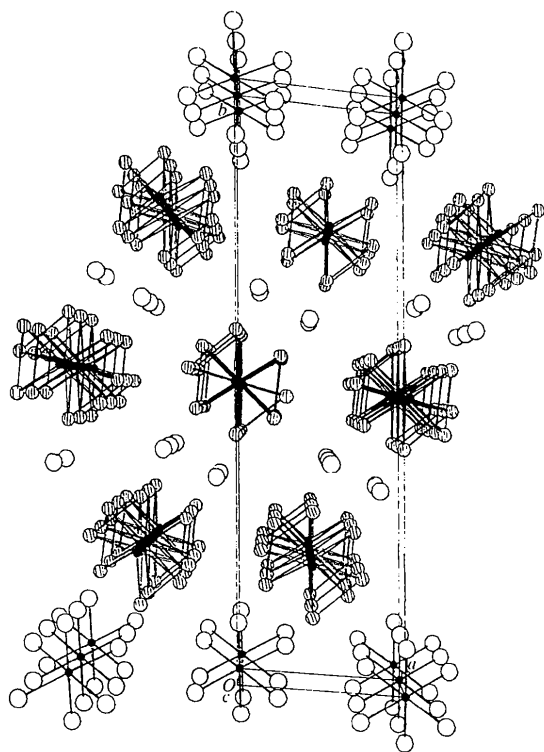

Fig. 2. A view of (TaTe₄)₆I₄(TaI₆) along the c axis, showing the stacking of the [TaTe₄]ₙ chains, TaI₆⁻ complex anions and I⁻ anions. Filled circles represent Ta atoms, shaded circles represent Te atoms and large open circles represent I atoms.

Experimental

The title compound was obtained by a solid-state reaction at high temperature from a Ta:Te:I mixture in the molar ratio 1:1:1; the I and Te elements act as reactants and melting reagents. Some needle-shaped crystals were formed on the wall of the tube when the mixture was heated at 1173 K for one day and then naturally cooled to 823 K.

Crystal data

(TaTe₄)₆I₄(TaI₆)
M_r = 5598.08
Triclinic
$P\bar{1}$
a = 7.712 (2) Å
b = 26.454 (8) Å
c = 6.777 (2) Å
α = 91.06 (2)°
β = 102.02 (2)°
γ = 94.69 (2)°
V = 1346.8 (6) Å³
Z = 1
D_x = 6.90 Mg m⁻³
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 12–20°
μ = 32.468 mm⁻¹
T = 296 K
Needle
0.50 × 0.03 × 0.02 mm
Black

Data collection

Rigaku AFC-5R diffractometer
ω scans
Absorption correction: refined from ΔF (DIFABS; Walker & Stuart, 1983)
T_{min} = 0.292, T_{max} = 0.522
10 867 measured reflections
10 215 independent reflections

5959 reflections with $I \geq 3\sigma(I)$
R_{int} = 0.036
θ_{max} = 33.1°
h = 0 → 13
k = −44 → 44
l = −11 → 11
3 standard reflections every 150 reflections
intensity variation: ±2%

Refinement

Refinement on F
R = 0.032
wR = 0.055
S = 1.44
5959 reflections
188 parameters
w = $1/\sigma^2(F)$

$(\Delta/\sigma)_{max}$ = 0.03
$\Delta\rho_{max}$ = 2.72 e Å⁻³
$\Delta\rho_{min}$ = −3.43 e Å⁻³
Extinction correction: none
Scattering factors from International Tables for X-ray Crystallography (Vol. IV)

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

$$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta^{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Ta(1)	0	0	0	1.53 (2)
Ta(2)	0.56694 (7)	0.78515 (2)	0.39077 (8)	1.36 (2)
Ta(3)	0.56294 (7)	0.78528 (2)	−0.10886 (6)	1.35 (2)
Ta(4)	0.00266 (6)	0.49963 (2)	0.74959 (7)	1.11 (1)
I(1)	−0.0024 (1)	0.08577 (3)	0.2370 (1)	1.94 (3)
I(2)	0.2799 (1)	0.04268 (4)	−0.1537 (2)	2.31 (3)
I(3)	0.2342 (1)	−0.03693 (4)	0.3057 (2)	2.50 (3)
I(4)	0.4413 (1)	0.62246 (3)	0.1021 (1)	1.97 (3)
I(5)	0.1320 (1)	0.66423 (3)	0.5393 (1)	1.94 (3)
Te(1)	0.7802 (1)	0.72966 (3)	0.1857 (1)	1.60 (3)
Te(2)	0.8316 (1)	0.83452 (3)	0.2049 (1)	1.59 (3)
Te(3)	0.3070 (1)	0.73317 (3)	0.0780 (1)	1.48 (3)
Te(4)	0.3461 (1)	0.83986 (3)	0.0947 (1)	1.49 (3)
Te(5)	0.5613 (1)	0.87225 (3)	0.6466 (1)	1.59 (3)
Te(6)	0.2731 (1)	0.80083 (3)	0.5713 (1)	1.53 (3)
Te(7)	0.8556 (1)	0.76847 (3)	0.7115 (1)	1.52 (3)
Te(8)	0.5579 (1)	0.69860 (3)	0.6332 (1)	1.57 (3)
Te(9)	−0.2909 (1)	0.51596 (3)	0.9293 (1)	1.48 (3)
Te(10)	0.0028 (1)	0.58684 (3)	1.0055 (1)	1.52 (3)
Te(11)	0.2602 (1)	0.55149 (3)	0.5630 (1)	1.48 (3)
Te(12)	0.2184 (1)	0.44484 (3)	0.5443 (1)	1.47 (3)

Table 2. *Selected geometric parameters (Å, °)*

Ta(1)—I(3)	2.704 (1)	Ta(3)—Te(8')	2.850 (1)
Ta(1)—I(2')	2.757 (1)	Ta(4)—Te(9'')	2.831 (1)
Ta(1)—I(1)	2.759 (1)	Ta(4)—Te(1''')	2.843 (1)
Ta(2)—Te(6)	2.845 (1)	Ta(4)—Te(10'')	2.853 (1)
Ta(2)—Te(8)	2.847 (1)	Ta(4)—Te(10)	2.860 (1)
Ta(2)—Te(2)	2.855 (1)	I(5)—Te(11)	3.215 (2)
Ta(3)—Te(4)	2.840 (1)	Te(9)—Te(10)	2.774 (1)
Ta(3)—Te(1)	2.842 (1)	Te(11)—Te(12)	2.811 (2)
Ta(2)—Ta(3'')	3.397 (1)	I(5)—Te(8)	3.262 (2)
I(1)—Te(5''')	3.415 (2)	Te(6)—Te(7''')	3.586 (1)
I(2)—Te(2')	3.433 (2)	Te(9)—Te(9'')	3.593 (2)
I(3')—Ta(1)—I(1)	90.66 (4)	Te(6)—Ta(2)—Te(8)	78.41 (4)
I(3')—Ta(1)—I(1')	89.34 (4)	Te(6)—Ta(2)—Te(4)	77.15 (4)
I(2)—Ta(1)—I(2')	180	Te(6)—Ta(2)—Te(2)	144.17 (4)
Te(3)—Ta(3)—Te(8')	90.36 (3)	Te(11''')—Ta(4)—Te(12)	79.07 (4)
Te(3)—Ta(3)—Te(2)	107.22 (4)	Te(11''')—Ta(4)—Te(11)	107.20 (3)
Te(7')—Ta(3)—Te(1)	77.05 (3)	Te(11''')—Ta(4)—Te(10)	133.01 (4)
Te(7')—Ta(3)—Te(5')	80.39 (4)	Te(9)—Ta(4)—Te(12''')	76.62 (3)
Te(1)—Ta(3)—Te(8')	84.38 (4)	Te(12)—Ta(4)—Te(10'')	85.47 (4)
Te(1)—Ta(3)—Te(2)	58.15 (3)	Te(12)—Ta(4)—Te(10)	143.79 (3)
Te(9'')—Ta(4)—Te(12)	79.08 (4)	Te(2)—Te(1)—Ta(2)	61.22 (3)
Ta(3)—Te(3)—Ta(2)	73.03 (3)	Te(12)—Te(11)—I(5)	156.13 (4)
Te(8)—Te(7)—Ta(3'')	60.93 (5)	Ta(2)—Te(7)—Ta(3'')	73.52 (3)

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

The structure was solved by direct methods (*MITHRIL*; Gilmore, 1983) and difference Fourier techniques, and refined by full-matrix least-squares methods (Peterse & Palm, 1966). Refined absorption corrections were compared to the cylindrical corrections and were deemed reliable for this fine needle crystal. The maximum and minimum peaks in the final difference Fourier map are near Ta sites. All calculations were performed on a MicroVAXII computer using *TEXSAN* software (Molecular Structure Corporation, 1985).

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Carbon Dioxide at 1.0 GPa

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Abstract

An X-ray diffraction study of single-crystal CO_2 has been undertaken at 1.00 (5) GPa pressure. The crystal exhibits $Pa\bar{3}$ symmetry with a cell edge of 5.4942 (2) Å and a C—O bond length of 1.168 (1) Å (corrected for thermal motion effects). The study demonstrates that an earlier claim of a new dry ice II phase at this pressure is unfounded.

Comment

Carbon dioxide is one of the most important gaseous compounds relevant to geological processes, both for the earth and other planetary bodies. As such, an understanding of its high-pressure phases and properties is of interest. For instance, an interpretation of near-surface emission spectra obtained from Jupiter requires a knowledge of the phases that could possibly exist there. The CO_2 gas phase, stable at room conditions, transforms directly to solid dry ice at 194.5 K and room pressure. The structure of a single crystal of dry ice has most recently been determined by Simon & Peters (1980) at 150 K, crystallizing in space group $Pa\bar{3}$ with the C atoms occupying special position $4a$ and the O atoms occupying $8c$.

With application of pressure while maintaining room temperature, however, the gas transforms to a liquid at around 7.5 MPa, and then to a solid at around 0.5 GPa (Bridgman, 1914). Liu (1983) claimed that this solid represents a new phase, which he called dry ice II, stable to 2.3 GPa, above which the solid transforms to dry ice. The evidence for the existence of the dry ice II phase was a 'poor quality' powder pattern. With further application of pressure above 10 GPa, dry ice appears to transform to a *Cmca* structure (Aoki *et al.*, 1994), again based on powder work. We report here the first single-crystal X-ray diffraction study of the structure of CO_2 at pressure, undertaken to determine the phase observed by Liu (1983). The results demonstrate that Liu's claim of the new dry ice II phase is unfounded.

The single-crystal X-ray analysis demonstrates that CO_2 exhibits cubic $Pa\bar{3}$ symmetry immediately upon

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