

Redetermination of tantalum pentabromide, (TaBr₅)₂

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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{Ta}-\text{Br}) = 0.002$ Å; R factor = 0.042; wR factor = 0.109; data-to-parameter ratio = 29.6.

Crystals of di- μ -bromido-bis[tetrabromidotantalum(V)], (TaBr₅)₂, were obtained by recrystallization at 773 K. A first crystal structure study of (TaBr₅)₂ was reported by Rolsten [*J. Am. Chem. Soc.* (1958), **80**, 2952–2953], who analysed the powder diffraction pattern and came to the conclusion that it crystallizes isotypically with (NbBr₅)₂ in a primitive orthorhombic cell. These findings are not in agreement with our current results of a monoclinic C -centred structure. (TaBr₅)₂ is isotypic with α -(NbCl₅)₂. The crystal structure contains [TaBr₆] octahedra sharing common edges forming [TaBr₅]₂ dimers. Two crystallographically independent dimers with symmetries m and $2/m$ and Ta··Ta distances of 4.1574 (11) and 4.1551 (15) Å, respectively, are present in the structure.

Related literature

For a previous study of (TaBr₅)₂, see: Rolsten (1958*a*), who also reported the crystal structure of (NbBr₅)₂ (Rolsten, 1958*b*). (TaBr₅)₂ is isotypic with α -(NbCl₅)₂, the structure of which was first described by Zalkin & Sands (1958) and was redetermined by Hoenle & von Schnering (1990). For a summary of all possible stackings of double octahedral molecules in pentahalides of Nb and Ta, see: Müller (1978). Experimental details can be found in Brauer's handbook (Brauer, 1962). For data analysis, see: Spek (2009).

Experimental

Crystal data

Ta ₂ Br ₁₀	$V = 2263.2$ (6) Å ³
$M_r = 1161.00$	$Z = 6$
Monoclinic, $C2/m$	Mo $K\alpha$ radiation
$a = 19.433$ (3) Å	$\mu = 40.93$ mm ⁻¹
$b = 18.775$ (2) Å	$T = 293$ K
$c = 6.2034$ (10) Å	$0.14 \times 0.09 \times 0.04$ mm
$\beta = 90.716$ (13)°	

Data collection

Stoe IPDS 2 diffractometer	17962 measured reflections
Absorption correction: numerical (X -SHAPE; Stoe & Cie, 1999)	2605 independent reflections
$T_{\min} = 0.014$, $T_{\max} = 0.089$	1678 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.125$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.042$	88 parameters
$wR(F^2) = 0.109$	$\Delta\rho_{\text{max}} = 1.71$ e Å ⁻³
$S = 0.95$	$\Delta\rho_{\text{min}} = -1.53$ e Å ⁻³
2605 reflections	

Data collection: *X-Area* (Stoe & Cie, 2002); cell refinement: *X-RED* (Stoe & Cie, 2002); data reduction: *X-RED*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2005); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WM2384).

References

- Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.
- Brandenburg, K. (2005). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
- Brauer, G. (1962). *Handbuch der präparativen Anorganischen Chemie*, Band II, p. 1152. Stuttgart: F. Enke-Verlag.
- Hoenle, W. & von Schnering, H. G. (1990). *Z. Kristallogr.* **191**, 139–140.
- Müller, U. (1978). *Acta Cryst.* **A34**, 256–267.
- Rolsten, R. F. (1958*a*). *J. Am. Chem. Soc.* **80**, 2952–2953.
- Rolsten, R. F. (1958*b*). *J. Phys. Chem.* **62**, 126–127.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
- Stoe & Cie (1999). *X-SHAPE*. Stoe & Cie, Darmstadt, Germany.
- Stoe & Cie (2002). *X-Area* and *X-RED*. Stoe & Cie, Darmstadt, Germany.
- Zalkin, A. & Sands, D. E. (1958). *Acta Cryst.* **11**, 615–619.

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Comment

(TaBr₅)₂ was first described by Rolsten (Rolsten, 1958*a*). He compared the powder diffraction pattern of (TaBr₅)₂ with orthorhombic NbBr₅ (space group *Pbam*) and came to the conclusion that the structures are alike. The structure of (NbBr₅)₂ was already known from single-crystal structure analysis (Rolsten, 1958*b*). However, the apparent isotypism between (TaBr₅)₂ and (NbBr₅)₂ is not in agreement with our result that shows (TaBr₅)₂ to crystallize in the monoclinic space group *C2/m*.

The crystal structures of all pentahalides besides the fluorides contain [MX₆] octahedra (*M* = Nb, Ta; *X* = Cl, B, I) sharing common edges forming [MX₅]₂ dimers. These double octahedra can be stacked in different ways, resulting in different structure types. In the title compound, the stacking of the (TaBr₅)₂ layers along *b* can be described as *A₁B₁A₁B₁...*. Within one layer the molecules are stacked in a "2 1" stacking scheme (Fig. 1). A summary of all possible stacking possibilities has been given by Müller (1978). The [TaBr₆] octahedra are distorted due to the repulsive forces of the highly charged metal atoms centering the octahedra with *d*(Ta—Ta) = 4.1574 (11) Å for the (Ta1Br₅)₂ dimer (*m* symmetry) and 4.1551 (15) Å for the (Ta2Br₅)₂ dimer (*2/m* symmetry).

(TaBr₅)₂ is isotopic with α -(NbCl₅)₂ (Zalkin & Sands, 1958; Hoenle & von Schnering, 1990).

Experimental

TaBr₅ was synthesized according to an experimental procedure reported in Brauer's handbook (Brauer, 1962). Orange polyhedral crystals were obtained by recrystallization of TaBr₅ in a silica ampoule. The ampoule was heated with 50 K per hour to 773 K and annealed for 12 h, after which it was slowly cooled to room temperature with 2 K per hour. Single crystals of TaBr₅ were selected under a microscope in an argon-filled glove box.

Refinement

PLATON (Spek, 2009) indicates higher (pseudo)-symmetry and suggests a change of the crystal system from monoclinic *C* to orthorhombic *C*, but the experimentally determined unit cell angles differ with 0.72° considerably from orthogonality. The maximum residual density lies 1.29 Å from Ta1 and the density minimum lies at the Br4 atom.

Figures

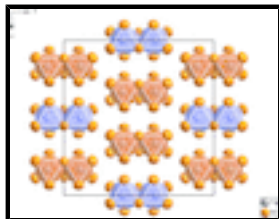


Fig. 1. Unit cell of TaBr₅ in a view along [001]. Double octahedral molecules are coloured in orange or blue for depth perception. Thermal ellipsoids are given on the 99% probability level.

di- μ -bromido-bis[tetrabromidotantalum(V)]

Crystal data

Ta ₂ Br ₁₀	$F(000) = 2976$
$M_r = 1161.00$	none
Monoclinic, $C2/m$	$D_x = 5.111 \text{ Mg m}^{-3}$
Hall symbol: $-C 2y$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
$a = 19.433 (3) \text{ \AA}$	Cell parameters from 7929 reflections
$b = 18.775 (2) \text{ \AA}$	$\theta = 2.1\text{--}27.1^\circ$
$c = 6.2034 (10) \text{ \AA}$	$\mu = 40.93 \text{ mm}^{-1}$
$\beta = 90.716 (13)^\circ$	$T = 293 \text{ K}$
$V = 2263.2 (6) \text{ \AA}^3$	Polyhedron, orange
$Z = 6$	$0.14 \times 0.09 \times 0.04 \text{ mm}$

Data collection

Stoe IPDS 2 diffractometer	2605 independent reflections
Radiation source: fine-focus sealed tube graphite	1678 reflections with $I > 2\sigma(I)$
Detector resolution: 0 pixels mm^{-1}	$R_{\text{int}} = 0.125$
oscillation scans	$\theta_{\text{max}} = 27.3^\circ$, $\theta_{\text{min}} = 1.5^\circ$
Absorption correction: numerical ($X\text{-SHAPE}$; Stoe & Cie, 1999)	$h = -24 \rightarrow 24$
$T_{\text{min}} = 0.014$, $T_{\text{max}} = 0.089$	$k = -24 \rightarrow 24$
17962 measured reflections	$l = -7 \rightarrow 7$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.042$	$w = 1/[\sigma^2(F_o^2) + (0.0563P)^2]$
$wR(F^2) = 0.109$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.95$	$(\Delta/\sigma)_{\text{max}} = 0.001$
	$\Delta\rho_{\text{max}} = 1.71 \text{ e \AA}^{-3}$

2605 reflections

$$\Delta\rho_{\min} = -1.53 \text{ e } \text{\AA}^{-3}$$

88 parameters

Extinction correction: SHELXL97 (Sheldrick, 2008),

$$F_c^* = kF_c [1 + 0.001 \times F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$$

0 restraints

Extinction coefficient: 0.00064 (4)

0 constraints

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Ta1	1.0000	0.38934 (4)	0.5000	0.0296 (2)
Ta2	0.66677 (3)	0.38928 (3)	0.97909 (7)	0.02938 (18)
Br1	0.61422 (10)	0.5000	1.2034 (3)	0.0326 (4)
Br2	0.61078 (9)	0.30802 (8)	1.2210 (2)	0.0430 (4)
Br3	0.56469 (8)	0.40167 (8)	0.7436 (2)	0.0406 (3)
Br4	0.72279 (9)	0.30797 (8)	0.7378 (2)	0.0430 (4)
Br5	0.71903 (11)	0.5000	0.7544 (3)	0.0321 (4)
Br6	0.89789 (8)	0.40192 (8)	0.7271 (2)	0.0421 (3)
Br7	0.76900 (8)	0.40188 (8)	1.2143 (2)	0.0415 (3)
Br8	1.05614 (9)	0.30768 (8)	0.7446 (2)	0.0451 (4)
Br9	1.05245 (11)	0.5000	0.7294 (3)	0.0323 (4)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ta1	0.0289 (4)	0.0278 (4)	0.0320 (4)	0.000	0.0032 (3)	0.000
Ta2	0.0292 (3)	0.0280 (3)	0.0310 (3)	0.0002 (2)	0.00055 (19)	-0.00014 (18)
Br1	0.0353 (11)	0.0314 (9)	0.0312 (8)	0.000	0.0070 (7)	0.000
Br2	0.0464 (10)	0.0408 (8)	0.0419 (7)	-0.0076 (6)	0.0083 (6)	0.0062 (5)
Br3	0.0338 (8)	0.0460 (8)	0.0419 (7)	-0.0012 (6)	-0.0074 (5)	-0.0021 (5)
Br4	0.0465 (10)	0.0396 (7)	0.0431 (7)	0.0060 (7)	0.0079 (6)	-0.0087 (6)
Br5	0.0343 (11)	0.0316 (9)	0.0305 (8)	0.000	0.0067 (7)	0.000
Br6	0.0353 (8)	0.0457 (8)	0.0455 (7)	-0.0017 (6)	0.0125 (6)	0.0023 (6)
Br7	0.0349 (8)	0.0453 (8)	0.0440 (7)	0.0008 (6)	-0.0079 (5)	0.0031 (6)
Br8	0.0464 (10)	0.0400 (7)	0.0487 (8)	0.0075 (7)	-0.0038 (6)	0.0096 (6)
Br9	0.0360 (11)	0.0305 (8)	0.0303 (8)	0.000	-0.0039 (7)	0.000

supplementary materials

Geometric parameters (Å, °)

Ta1—Br8 ⁱ	2.4087 (15)	Ta2—Br3	2.4598 (16)
Ta1—Br8	2.4087 (15)	Ta2—Br7	2.4613 (17)
Ta1—Br6	2.4591 (14)	Ta2—Br5	2.7075 (12)
Ta1—Br6 ⁱ	2.4591 (14)	Ta2—Br1	2.7084 (12)
Ta1—Br9	2.7100 (13)	Br1—Ta2 ⁱⁱⁱ	2.7084 (12)
Ta1—Br9 ⁱⁱ	2.7100 (13)	Br5—Ta2 ⁱⁱⁱ	2.7075 (12)
Ta2—Br4	2.4075 (14)	Br9—Ta1 ⁱⁱ	2.7100 (13)
Ta2—Br2	2.4092 (15)		
Br8 ⁱ —Ta1—Br8	100.93 (9)	Br2—Ta2—Br3	93.59 (6)
Br8 ⁱ —Ta1—Br6	93.41 (6)	Br4—Ta2—Br7	93.53 (6)
Br8—Ta1—Br6	93.60 (6)	Br2—Ta2—Br7	93.39 (6)
Br8 ⁱ —Ta1—Br6 ⁱ	93.60 (6)	Br3—Ta2—Br7	169.06 (5)
Br8—Ta1—Br6 ⁱ	93.41 (6)	Br4—Ta2—Br5	89.51 (5)
Br6—Ta1—Br6 ⁱ	168.98 (8)	Br2—Ta2—Br5	169.14 (5)
Br8 ⁱ —Ta1—Br9	169.48 (6)	Br3—Ta2—Br5	85.79 (6)
Br8—Ta1—Br9	89.59 (5)	Br7—Ta2—Br5	85.77 (6)
Br6—Ta1—Br9	85.78 (6)	Br4—Ta2—Br1	169.22 (5)
Br6 ⁱ —Ta1—Br9	85.77 (6)	Br2—Ta2—Br1	89.43 (5)
Br8 ⁱ —Ta1—Br9 ⁱⁱ	89.59 (5)	Br3—Ta2—Br1	85.76 (6)
Br8—Ta1—Br9 ⁱⁱ	169.48 (6)	Br7—Ta2—Br1	85.90 (6)
Br6—Ta1—Br9 ⁱⁱ	85.77 (6)	Br5—Ta2—Br1	79.71 (4)
Br6 ⁱ —Ta1—Br9 ⁱⁱ	85.78 (6)	Ta2—Br1—Ta2 ⁱⁱⁱ	100.26 (6)
Br9—Ta1—Br9 ⁱⁱ	79.90 (6)	Ta2—Br5—Ta2 ⁱⁱⁱ	100.31 (6)
Br4—Ta2—Br2	101.35 (6)	Ta1—Br9—Ta1 ⁱⁱ	100.10 (6)
Br4—Ta2—Br3	93.34 (6)		

Symmetry codes: (i) $-x+2, y, -z+1$; (ii) $-x+2, -y+1, -z+1$; (iii) $x, -y+1, z$.

Fig. 1

