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Redetermination of tantalum pentabromide, $(TaBr_5)_2$

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Key indicators: single-crystal X-ray study; T = 293 K; mean σ(Ta–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)], $(TaBr_5)_2$, were obtained by recrystallization at 773 K. A first crystal structure study of $(TaBr_5)_2$ 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 $(NbBr_5)_2$ in a primitive orthorhombic cell. These findings are not in agreement with our current results of a monoclinic C-centred structure. $(TaBr_5)_2$ is isotypic with α-$(NbCl_5)_2$. The crystal structure contains $[TaBr_6]$ octahedra sharing common edges forming $[TaBr_5]_2$ dimers. Two crystallographically independent dimers with symmetries m and $2/m$ and Ta$\cdots$Ta distances of 4.1574 (11) and 4.1551 (15) Å, respectively, are present in the structure.

Related literature

For a previous study of $(TaBr_5)_2$, see: Rolsten (1958*a*), who also reported the crystal structure of $(NbBr_5)_2$ (Rolsten, 1958*b*). $(TaBr_5)_2$ is isotypic with α-$(NbCl_5)_2$, 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_2Br_{10}
M_r = 1161.00
Monoclinic, $C2/m$
a = 19.433 (3) Å
b = 18.775 (2) Å
c = 6.2034 (10) Å
β = 90.716 (13)°
V = 2263.2 (6) Å^3
Z = 6
Mo $K\alpha$ radiation
μ = 40.93 mm^{-1}
T = 293 K
0.14 × 0.09 × 0.04 mm

Data collection

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

Refinement

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

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).

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S1. Comment

$(TaBr_5)_2$ was first described by Rolsten (Rolsten, 1958*a*). He compared the powder diffraction pattern of $(TaBr_5)_2$ with orthorhombic $NbBr_5$ (space group *Pbam*) and came to the conclusion that the structures are alike. The structure of $(NbBr_5)_2$ was already known from single-crystal structure analysis (Rolsten, 1958*b*). However, the apparent isotypism between $(TaBr_5)_2$ and $(NbBr_5)_2$ is not in agreement with our result that shows $(TaBr_5)_2$ to crystallize in the monoclinic space goup *C*2/*m*.

The crystal structures of all pentahalides besides the fluorides contain $[MX_6]$ octahedra (M = Nb, Ta; X = Cl, B, I) sharing common edges forming $[MX_5]_2$ dimers. These double octahedra can be stacked in different ways, resulting in different structure types. In the title compound, the stacking of the $(TaBr_5)_2$ layers along *b* can be described as $A_1B_1A_1B_1\cdots$. 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 $[TaBr_6]$ 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 $(Ta1Br_5)_2$ dimer (*m* symmetry) and 4.1551 (15) Å for the $(Ta2Br_5)_2$ dimer (2/*m* symmetry).

$(TaBr_5)_2$ is isotypic with α-$(NbCl_5)_2$ (Zalkin & Sands, 1958; Hoenle & von Schnering, 1990).

S2. Experimental

$TaBr_5$ was synthesized according to an experimental procedure reported in Brauer's handbook (Brauer, 1962). Orange polyhedric crystals were obtained by recrystallization of $TaBr_5$ 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 $TaBr_5$ were selected under a microscope in an argon-filled glove box.

S3. 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 1.29Å from Ta1 and the density minimum lies at the Br4 atom.

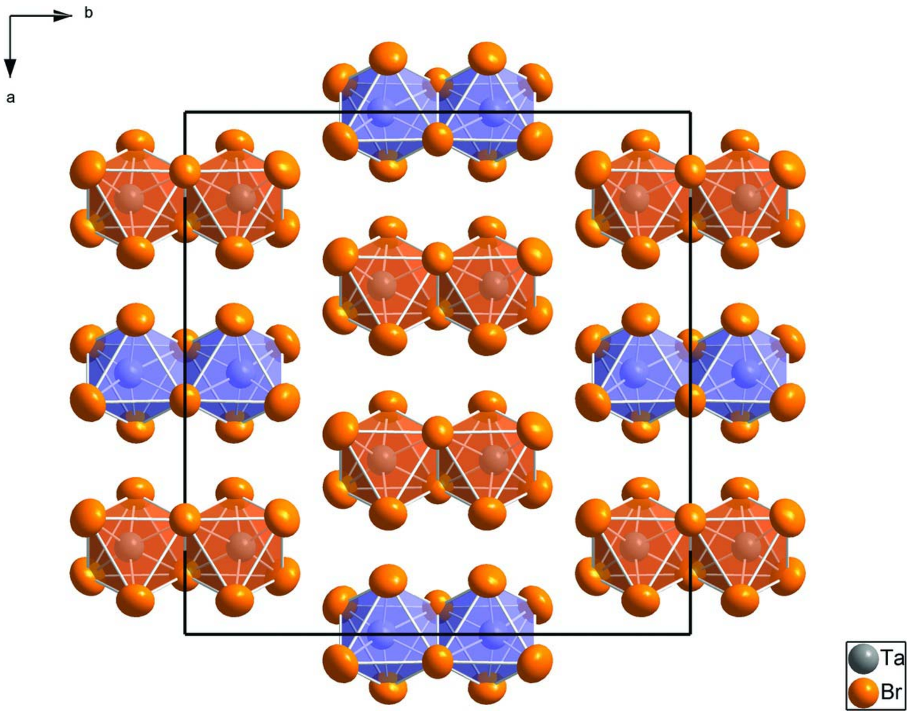

Figure 1

Unit cell of $TaBr_5$ 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_2Br_{10}
$M_r = 1161.00$
Monoclinic, $C2/m$
Hall symbol: -C 2y
$a = 19.433$ (3) Å
$b = 18.775$ (2) Å
$c = 6.2034$ (10) Å
$\beta = 90.716$ (13)°
$V = 2263.2$ (6) Å^3
$Z = 6$
$F(000) = 2976$
none
$D_x = 5.111$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 7929 reflections
$\theta = 2.1$–27.1°
$\mu = 40.93$ mm^{-1}
$T = 293$ K
Polyhedron, orange
0.14 × 0.09 × 0.04 mm

Data collection

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

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.109$
$S = 0.95$
2605 reflections
88 parameters
0 restraints
0 constraints
Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map
$w = 1/[\sigma^2(F_o^2) + (0.0563P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.71$ e Å^{-3}
$\Delta\rho_{min} = -1.53$ e Å^{-3}
Extinction correction: SHELXL97 (Sheldrick, 2008), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.00064 (4)

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 (Å²)

	x	y	z	U_{iso}*/U_{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 (Å²)

	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

Geometric parameters (Å, º)

Ta1—Br8$^{\mathrm{i}}$	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$^{\mathrm{i}}$	2.4591 (14)	Ta2—Br1	2.7084 (12)
Ta1—Br9	2.7100 (13)	Br1—Ta2$^{\mathrm{iii}}$	2.7084 (12)
Ta1—Br9$^{\mathrm{ii}}$	2.7100 (13)	Br5—Ta2$^{\mathrm{iii}}$	2.7075 (12)
Ta2—Br4	2.4075 (14)	Br9—Ta1$^{\mathrm{ii}}$	2.7100 (13)
Ta2—Br2	2.4092 (15)		

Br8$^{\mathrm{i}}$—Ta1—Br8	100.93 (9)	Br2—Ta2—Br3	93.59 (6)
Br8$^{\mathrm{i}}$—Ta1—Br6	93.41 (6)	Br4—Ta2—Br7	93.53 (6)
Br8—Ta1—Br6	93.60 (6)	Br2—Ta2—Br7	93.39 (6)
Br8$^{\mathrm{i}}$—Ta1—Br6$^{\mathrm{i}}$	93.60 (6)	Br3—Ta2—Br7	169.06 (5)
Br8—Ta1—Br6$^{\mathrm{i}}$	93.41 (6)	Br4—Ta2—Br5	89.51 (5)
Br6—Ta1—Br6$^{\mathrm{i}}$	168.98 (8)	Br2—Ta2—Br5	169.14 (5)
Br8$^{\mathrm{i}}$—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$^{\mathrm{i}}$—Ta1—Br9	85.77 (6)	Br2—Ta2—Br1	89.43 (5)
Br8$^{\mathrm{i}}$—Ta1—Br9$^{\mathrm{ii}}$	89.59 (5)	Br3—Ta2—Br1	85.76 (6)
Br8—Ta1—Br9$^{\mathrm{ii}}$	169.48 (6)	Br7—Ta2—Br1	85.90 (6)
Br6—Ta1—Br9$^{\mathrm{ii}}$	85.77 (6)	Br5—Ta2—Br1	79.71 (4)
Br6$^{\mathrm{i}}$—Ta1—Br9$^{\mathrm{ii}}$	85.78 (6)	Ta2—Br1—Ta2$^{\mathrm{iii}}$	100.26 (6)
Br9—Ta1—Br9$^{\mathrm{ii}}$	79.90 (6)	Ta2—Br5—Ta2$^{\mathrm{iii}}$	100.31 (6)
Br4—Ta2—Br2	101.35 (6)	Ta1—Br9—Ta1$^{\mathrm{ii}}$	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*.