Crystal structure of dithallium(I) octa-μ_3-bromohexabromo-*octahedro*-hexamolybdate, $Tl_2[(Mo_6Br_8)Br_6]$

W. Xu, Y.-Q. Zheng* and P. Wang

Ningbo University, Institute for Solid State Chemistry, Municipal Key Laboratory of Inorganic Materials Chemistry, Ningbo, Zhejiang, 315211 P. R. China

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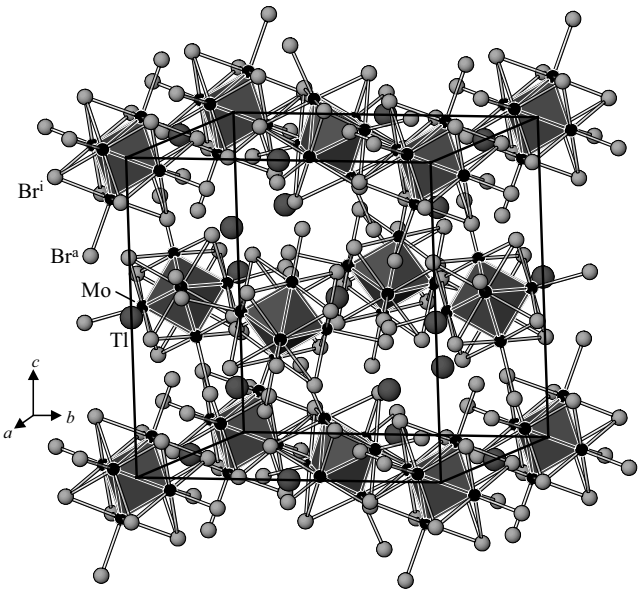

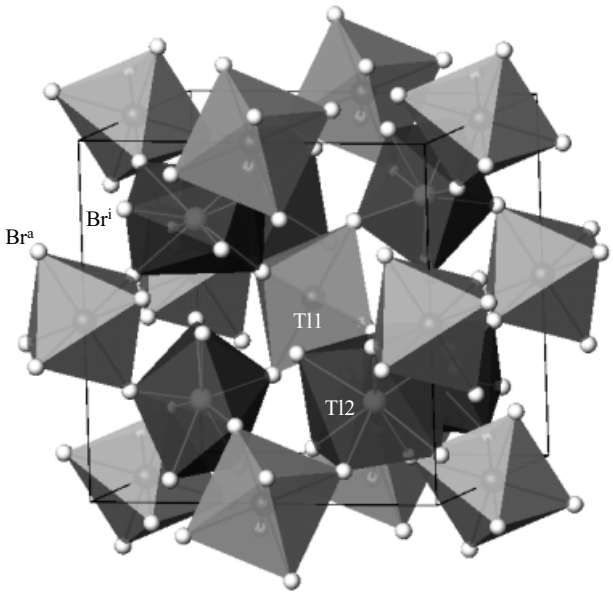

Abstract

$Br_{14}Mo_6Tl_2$, cubic, $Pn\bar{3}$ (no. 201),
a = 13.813(1) Å, V = 2635.4 Å^3, Z = 4,
$R_{gt}(F)$ = 0.080, $wR_{ref}(F^2)$ = 0.147, T = 295 K.

Source of material

A silica tube ($\varnothing_{outer}$ = 15 mm, d = 1 mm, l = 90 mm) charged with 340 mg (0.221 mmol) Mo_6Br_{12} (Alfa 98+ %) and 126 mg (0.442 mmol) TlBr (ACROS 99.999%) was heated in the temperature gradient 925/915 K for 4 weeks. Orange block-like crystals were formed in the low temperature zone and Mo in the high temperature zone.

Experimental details

The large R values are caused by the poor quality of the used crystal chosen as the best sample from a series of syntheses. Moreover, the strong absorption empirically corrected via ψ scans has probably affected the refinement result.

Discussion

The initial structure refinement with a full occupancy of Tl(2) at the 6*d* site gave a large displacement U_{eq}(Tl(2)), which was roughly four times larger than U_{eq}(Tl(1)). The subsequent refinement was performed with U_{eq}(Tl(2)) = U_{eq}(Tl(1)), leading to the occupancy of Tl(2) position close to 2/3. Therefore, the final refinement was carried out with a *s.o.f.*(Tl(2)) fixed at 2/3.

Being isotypic with $Tl_2[W_6Br_{14}]$ [1], $Tl_2[(Mo_6Br^i_8)Br^a_6]$ consists of Tl^+ cations and $[(Mo_6Br^i_8)Br^a_6]^{2-}$ cluster anions (figure, top). The $[(Mo_6Br^i_8)Br^a_6]^{2-}$ anions deviate only slightly from $m\bar{3}m$ symmetry: $\bar{d}$(Mo—Mo) = 2.635 Å, $\bar{d}$(Mo—Br^i) = 2.597 Å, $\bar{d}$(Mo—Br^a) = 2.590 Å, $\bar{d}$(Br^i—Br^a) = 3.696 Å, $\bar{d}$(Br^i—Br^i) = 3.675 Å, ∠Mo–Br^i–Mo = 59.7°. The Mo atoms are shifted outside the Br^i_8 cube by Δ = 0.01 Å. The Tl(1) atoms are sixfold coordinated by Br^a atoms with $\bar{d}$(Tl—Br) = 3.296 Å, while Tl(2) are eightfold coordinated by Br^a and Br^i atoms with $\bar{d}$(Tl—Br) = 3.227 Å (4×) and 3.473 Å (4×), respectively (figure, bottom).

Table 1. Data collection and handling.

Crystal:	orange block, size 0.16 × 0.28 × 0.31 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	361.54 cm^{-1}
Diffractometer, scan mode:	Bruker P4, $\theta/2\theta$
$2\theta_{max}$:	54.9°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	3830, 1016
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 666
$N(param)_{refined}$:	37
Program:	SHELXL-97 [2]

* Correspondence author (e-mail: zhengcm@nbu.edu.cn)

Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	Occ.	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo	24*h*		0.1239(1)	–0.0319(1)	0.0430(1)	0.0493(9)	0.055(1)	0.0549(9)	0.0006(7)	–0.0011(7)	0.0017(7)
Br(1)	8*e*		0.1332(1)	*x*	*x*	0.069(1)	U_{11}	U_{11}	–0.010(1)	U_{12}	U_{12}
Br(2)	24*h*		0.1956(1)	0.0472(2)	–0.1117(2)	0.056(1)	0.066(1)	0.068(1)	–0.0011(9)	0.0075(9)	0.005(1)
Br(3)	24*h*		0.2975(2)	–0.0776(2)	0.0997(2)	0.053(1)	0.105(2)	0.081(2)	0.005(1)	–0.006(1)	0.017(1)
Tl(1)	4*c*		1/2	0	0	0.0750(7)	U_{11}	U_{11}	–0.0013(6)	U_{12}	U_{12}
Tl(2)	6*d*	0.67	1/4	3/4	3/4	0.068(2)	0.086(2)	0.068(2)	0	0	0

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