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Crystal structure of dipotassium octakis(μ_3-bromo)hexabromo-*octahedro*-hexamolybdenate, $K_2[Mo_6Br_{14}]$

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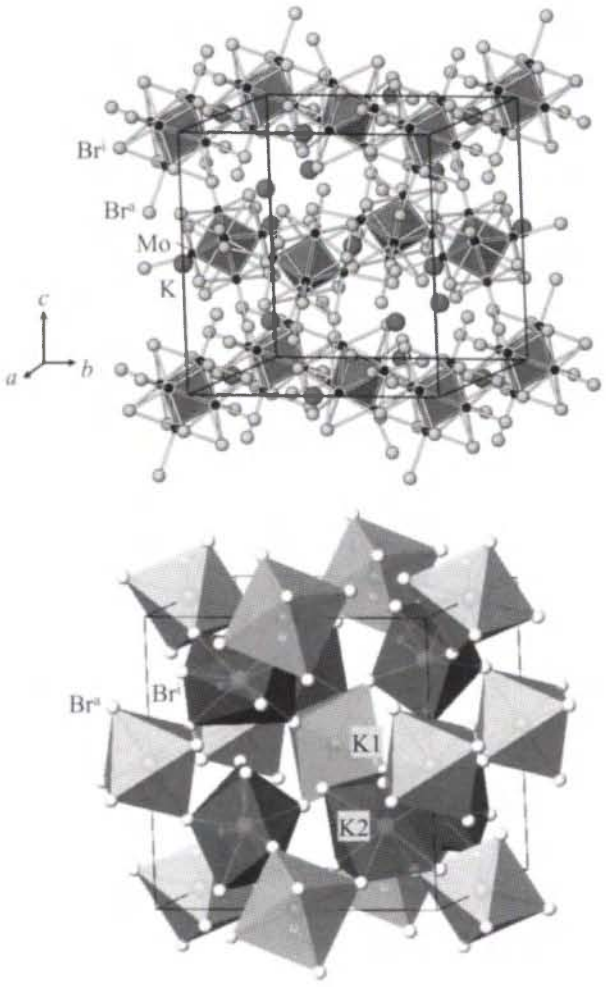

Abstract

$Br_{14}K_2Mo_6$, cubic, $Pn\bar{3}$ (no. 201), a = 13.800(2) Å, V = 2628.1 Å^3, Z = 4, $R_{gt}(F)$ = 0.077, $wR_{ref}(F^2)$ = 0.186, T = 293 K.

Source of material

A silica tube (∅ = 15 mm, D = 1 mm, L = 90 mm) charged with 462 mg (0.300 mmol) Mo_6Br_{12} (Alfa, 98+ %) and 72 mg (0.600 mmol) KBr (ACROS 98 %) was heated in the temperature gradient 925/915 K for one week. Orange plate-shaped crystals were formed in the low temperature zone and Mo in the high temperature zone.

Experimental details

Refinements gave an occupancy of the K2 cation close to ⅔, before the parameter was fixed at this value. The large R values may be due to the inferior crystal quality.

Discussion

$K_2[(Mo_6Br^i_8)Br^a_6]$ consists of K^+ cations and $[(Mo_6Br^i_8)Br^a_6]^{2-}$ cluster anions, being isotypic with $M_2[W_6Br_{14}]$ (M = K, Cu, Tl) [1-3] and $M_2[Mo_6Br_{14}]$ (M = Cu, Tl) [4,5]. The $[(Mo_6Br^i_8)Br^a_6]^{2-}$ anions deviate only slightly from $m\bar{3}m$ symmetry: $\bar{d}$(Mo—Mo) = 2.631 Å, $\bar{d}$(Mo—Br^i) = 2.598 Å, $\bar{d}$(Mo—Br^a) = 2.606 Å, $\bar{d}$(Br^i—Br^a) = 3.704 Å, $\bar{d}$(Br^i—Br^i) = 3.674 Å, ∠Mo–Br^i–Mo = 59.7°. The Mo atoms are shifted outside the Br^i_8 cube by Δ = 0.0238 Å. The K1 atoms sixfold coordinated by Br^a atoms with $\bar{d}$(K—Br) = 3.281 Å, while K2 eightfold coordinated by Br^a and Br^i atoms with d(K—Br) = 3.232 Å (4×) and 3.451 Å (4×), respectively.

Table 1. Data collection and handling.

Crystal:	orange plate, size 0.04 × 0.24 × 0.33 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	243.68 cm^{-1}
Diffractometer, scan mode:	Bruker P4, $\theta/2\theta$
$2\theta_{max}$:	54.96°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	3833, 1016
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 659
$N(param)_{refined}$:	37
Programs:	SHELXS-97 [6], SHELXL-97 [7]

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*		0.12410(9)	−0.03159(9)	0.04222(9)	0.0231(6)	0.0286(7)	0.0264(7)	0.0001(5)	−0.0014(5)	−0.0001(4)
Br(1)	8*e*		0.1334(1)	x	x	0.0389(7)	U_{11}	U_{11}	−0.0085(6)	U_{12}	U_{12}
Br(2)	24*h*		0.1952(1)	0.0486(1)	−0.1124(1)	0.0289(8)	0.0357(8)	0.0371(8)	−0.0019(6)	0.0048(6)	0.0035(6)
Br(3)	24*h*		0.2982(1)	−0.0777(2)	0.0989(1)	0.0267(8)	0.068(1)	0.048(1)	0.0020(8)	−0.0048(7)	0.0168(9)
K(1)	4*c*		½	0	0	0.043(2)	U_{11}	U_{11}	−0.008(3)	U_{12}	U_{12}
K(2)	6*d*	0.67	¼	¾	¾	0.033(5)	0.057(7)	0.038(5)	0	0	0

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