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Preparation and Structure of the Hexabromobis(μ-bromo)(μ-hydrido)dimolybdenum(III) Ion, $[Mo_2Br_8H]^{3-}$

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Dinuclear complexes of molybdenum(III) containing a μ-hydrido ligand with the general formula $[Mo_2X_8H]^{3-}$ (X = Cl, Br, I) were the subject of structural, spectroscopic and theoretical studies [1–9]. These complexes are formed by oxidative addition of HX to the dinuclear molybdenum(II) unit, Mo_2^{4+}. The chloro complex, $[Mo_2Cl_8H]^{3-}$, was thoroughly investigated by X-ray and neutron techniques and the position of the μ-H atom in the dimer was accurately determined [7]. Recently, we have reported the preparation and structure of the iodo complex, $[Mo_2I_8H]^{3-}$ [8]. The cesium salt of the bromo complex $Cs_3[Mo_2Br_8H]$, **1**, was prepared several years ago and its structure was determined by X-ray crystallography [2]. The dimeric ion in this compound was constrained to occupy, in a disordered fashion, a position of D_{3h} symmetry ($\bar{6}m2$ site), thus obscuring important structural details. The real symmetry of the $[Mo_2X_8H]^{3-}$ ion is C_{2v}, as found in other compounds were no disorder exists in the crystal [4–8]. The Mo–Mo distance in $Cs_3[Mo_2Br_8H]$, 2.439(7) Å, deviates significantly from the range of 2.377(7)–2.408(2) Å previously found for the chloro and iodo complexes [6, 8].

We describe here the preparation and structure of the tetramethylammonium salt of a bromo complex $[Mo_2Br_8H]^{3-}$ in which the dimer is not disordered.

Experimental

Crystals of $(H_7O_3)[(CH_3)_4N]_2[Mo_2Br_8H]$, **2**, were obtained by dissolving $Mo_2(O_2CCH_3)_4$ (0.25 g) and Me_4NBr (0.7 g) in 20 ml of 8 M HBr at 70 °C, followed by slow evaporation of the solution under a stream of nitrogen. Dark yellow-brown crystals were deposited after 48 h.

The crystals are orthorhombic, space-group $P2_12_12_1$ with a = 25.437(3) Å, b = 10.291(1) Å, c = 10.681(1) Å, V = 2796(1) Å^3 and Z = 4.

A total of 2072 reflections were collected in the range of $3° < 2\theta < 45°$, of which 1411 were found to have $I > 3\sigma(I)$ and were therefore used in refining of the structural parameters. The structure was refined by least-squares methods to a conventional R factor of 5.60%.

TABLE I. Positional Parameters and e.s.d.s for $(H_7O_3)(Me_4N)[Mo_2Br_8H]$.[a]

Atom	x	y	z
Mo(1)	−0.6570(1)	−0.2175(3)	−0.7033(3)
Mo(2)	−0.6074(1)	−0.2586(4)	−0.5181(3)
Br(1)	−0.5868(2)	−0.4065(4)	−0.7133(4)
Br(2)	−0.5806(2)	−0.0563(4)	−0.6519(5)
Br(3)	−0.7229(2)	−0.0334(4)	−0.6838(5)
Br(4)	−0.7292(1)	−0.3820(4)	−0.7512(4)
Br(5)	−0.6404(2)	−0.1665(5)	−0.9416(4)
Br(6)	−0.6376(2)	−0.4605(4)	−0.3959(4)
Br(7)	−0.6322(2)	−0.1162(4)	−0.3342(4)
Br(8)	−0.5074(1)	−0.2782(5)	−0.4564(5)
OW(1)	−0.298(1)	−0.168(3)	−0.929(3)
OW(2)	−0.305(1)	−0.340(3)	−1.088(3)
OW(3)	−0.204(1)	−0.162(4)	−0.861(3)
N(1)	−0.990(1)	−0.252(3)	−0.942(3)
N(2)	−0.845(1)	−0.269(4)	−0.459(3)
C(10)	−0.937(2)	−0.210(5)	−0.881(5)
C(11)	−0.984(2)	−0.270(5)	−1.076(5)
C(12)	−1.026(2)	−0.139(5)	−0.921(4)
C(13)	−1.012(2)	−0.368(4)	−0.879(4)
C(20)	−0.854(2)	−0.178(4)	−0.576(4)
C(21)	−0.859(2)	−0.404(4)	−0.498(4)
C(22)	−0.876(2)	−0.238(5)	−0.350(5)
C(23)	−0.788(2)	−0.269(5)	−0.426(4)

[a] e.s.d.s. in the least significant digits are shown in parentheses.

Results and Discussion

Table I presents the positional parameters of $(H_7O_3)(Me_4N)_2[Mo_2Br_8H]$, and the important bond distances and angles are given in Table II. The

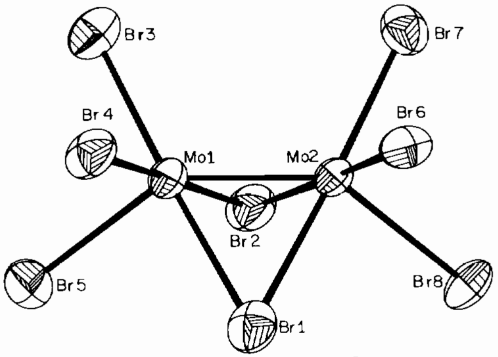

Fig. 1. The structure of $[Mo_2Br_8H]^{3-}$. Atoms are represented by their ellipsoids of vibration at the 50% probability level. The μ-H atom was not located.

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TABLE II. Important Bond Lengths (Å) and Angles (deg) for $(H_7O_3)(Me_4N)[Mo_2Br_8H]$.

Lengths			
Mo(1)–Mo(2)	2.384(4)	Mo(2)–Br(2)	2.616(5)
Mo(1)–Br(1)	2.644(5)	Mo(2)–Br(6)	2.571(5)
Mo(1)–Br(2)	2.615(5)	Mo(2)–Br(7)	2.529(5)
Mo(1)–Br(3)	2.538(5)	Mo(2)–Br(8)	2.637(4)
Mo(1)–Br(4)	2.548(5)	OW(1)–OW(2)	2.45(4)
Mo(1)–Br(5)	2.633(5)	OW(1)–OW(3)	2.50(4)
Mo(2)–Br(1)	2.635(5)		
Angles			
Br(1)–Mo(1)–Br(2)	88.4(2)	Br(1)–Mo(2)–Br(7)	177.1(2)
Br(1)–Mo(1)–Br(3)	177.4(2)	Br(1)–Mo(2)–Br(8)	87.8(2)
Br(1)–Mo(1)–Br(4)	89.4(2)	Br(2)–Mo(2)–Br(6)	176.9(2)
Br(1)–Mo(1)–Br(5)	89.9(2)	Br(2)–Mo(2)–Br(7)	91.6(2)
Br(2)–Mo(1)–Br(3)	90.0(2)	Br(2)–Mo(2)–Br(8)	86.9(2)
Br(2)–Mo(1)–Br(4)	177.8(2)	Br(6)–Mo(2)–Br(7)	90.0(2)
Br(2)–Mo(1)–Br(5)	87.5(2)	Br(6)–Mo(2)–Br(8)	95.7(2)
Br(3)–Mo(1)–Br(4)	92.1(2)	Br(7)–Mo(2)–Br(8)	95.2(2)
Br(3)–Mo(1)–Br(5)	92.1(2)	Mo(1)–Br(1)–Mo(2)	53.7(1)
Br(4)–Mo(1)–Br(5)	93.1(2)	Mo(1)–Br(2)–Mo(2)	54.2(1)
Br(1)–Mo(2)–Br(2)	88.6(2)	OW(2)–OW(1)–OW(3)	107(1)
Br(1)–Mo(2)–Br(6)	89.7(2)		

TABLE III. Dimensions of the $[Mo_2Br_8H]^{3-}$ Anion in the Cs^+ and Me_4N^+ Salts.[a]

	$Cs_3[Mo_2Br_8H]$	$(H_7O_3)(Me_4N)_2$-$[Mo_2Br_8H]$, 2
Mo–Mo (Å)	2.439(7)	2.384(4)
Mo–Br_t (Å)	2.554(3)	2.546[9][b]
		2.635[2][c]
Mo–Br_b (Å)	2.672(5)	2.627[7]

[a] Numbers in brackets are grand average values obtained by the expression $[(\Sigma\Delta i^2)/n(n-1)]^{1/2}$. [b] Bonds *trans* to μ-Br. [c] Bonds *trans* to μ-H.

dinuclear anion is shown in Fig. 1. With $Z = 4$ in space group $P2_12_12_1$ there is no crystallographic symmetry imposed upon the dimer. The overall symmetry of the $[Mo_2Br_8H]^{3-}$ ion is nearly C_{2v}. There are three different sets of Mo–Br distances with some significant scattering within the sets. The grand average values for the various sets for $[Mo_2Br_8H]^{3-}$ in the cesium and Me_4N^+ salts are presented in Table III.

The Mo–Br bond distances are in the order that was previously found for other $[Mo_2X_8H]^{3-}$ ions (X = Cl, I), namely Mo–$Br_{t,H}$ > Mo–Br_b > Mo–$Br_{t,Br}$. The difference of *ca.* 0.09 Å between Mo–$Br_{t,H}$ and Mo–$Br_{t,Br}$ is due to the greater *trans* effect of the μ-H relatively to μ-Br.

The Mo–Mo distance, 2.384(4) Å, falls within the range of 2.377(7) Å and 2.408(2) Å found in $[Mo_2Cl_8H]^{3-}$ and $[Mo_2I_8H]^{3-}$ respectively. The variation in this distance when two μ-Cl atoms are replaced with larger μ-Br or μ-I is relatively small. This fact is predicted by theoretical studies that suggest that the Mo–H–Mo is a three-center 4-electron system with a strong interaction. The elimination of this interaction by replacing the μ-H atom with μ-Br results in a dramatic change in the Mo–Mo separation, from 2.384(4) Å in $[Mo_2Br_8H]^{3-}$ to 2.816(1) Å in $[Mo_2Br_8]^{3-}$ [10].

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