

The Structure of Tricesium Octabromodimolybdate; An Example of a Space-Group Ambiguity*

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When tetraacetatodimolybdenum is dissolved in aqueous hydrobromic acid and a solution of CsBr is added, a precipitate of microcrystalline $\text{Cs}_3\text{Mo}_2\text{Br}_8$ is formed. By a special technique, crystallographically useful single crystals were obtained and the substance has been structurally characterized. The structure consists of Cs^+ cations and $\text{Mo}_2\text{Br}_8^{3-}$ anions, the latter having the shape of an M_2X_9 confacial bioctahedron but with crystallographically disordered vacancies in the bridging positions. The dimensions of the $\text{Mo}_2\text{Br}_8^{3-}$ ion indicate that there is bonding interaction of medium strength between the molybdenum atoms. The crystals belong to the hexagonal system, with space groups $P\bar{6}2c$, $P6_3/mmc$ and $P6_3mc$ admissible on the basis of systematic absences. $P6_3mc$ was eliminated convincingly on the basis of unsatisfactory refinement, but no clear choice between the other two space groups was possible using diffraction data. The unit-cell parameters are $a=7.757$ (3), $c=17.804$ (7) Å, $Z=2$; $d_{\text{calc}}=4.40$; $d_{\text{obs}}=4.33$ g cm⁻³. The Mo-Mo distance is 2.439 (7); Mo-Br(terminal)=2.554 (3); Mo-Br(bridge)=2.672 (5) Å.

Introduction

In a previous study it has been shown that the reaction of $\text{Mo}_2(\text{CH}_3\text{CO}_2)_4$ with 12*N* HCl at 60° in presence of large alkali cations, M^+ ($\text{M}^+=\text{Rb}, \text{Cs}$) leads to the isolation of the compounds $\text{M}_3\text{Mo}_2\text{Cl}_8$. A crystallographic study (Bennett, Brencic & Cotton, 1969) of the rubidium compound produced the surprising result that the compound is structurally very similar to a number of $\text{M}_3^{\text{I}}\text{M}_2^{\text{II}}\text{X}_9$ compounds. The differences are: (1) $\text{Rb}_3\text{Mo}_2\text{Cl}_8$ contains $\text{Cl}_3\text{Mo}(\mu\text{-Cl})_2\text{MoCl}_3$ anions which are derived from a true D_{3h} bioctahedron by removal of one bridging chlorine ($\mu\text{-Cl}$). This deletion occurs randomly, so that the structure can be refined with an occupancy factor of 0.67 for the $\mu\text{-Cl}$ atoms. (2) The space group for $\text{Rb}_3\text{Mo}_2\text{Cl}_8$ was $P\bar{6}2c$, which is non-centric, rather than the centric $P6_3/mmc$ which is found for many $\text{M}_3^{\text{I}}\text{M}_2^{\text{II}}\text{X}_9$ compounds (see below).

In the course of further chemical studies of the reactions of $\text{Mo}_2(\text{CH}_3\text{CO}_2)_4$ with mineral acids, the stoichiometrically analogous bromo compound, $\text{Cs}_3\text{Mo}_2\text{Br}_8$, has been obtained and studied crystallographically. The crystallographic and structural work is reported here as it presents some features which are perhaps of more than routine interest. Again, from systematic absences and Laue symmetry, the three space groups $P\bar{6}2c$, $P6_3/mmc$ and $P6_3mc$ had to be considered. In this case again $P6_3mc$ could be eliminated convincingly. However, for $\text{Cs}_3\text{Mo}_2\text{Br}_8$, with a larger data set than for $\text{Rb}_3\text{Mo}_2\text{Cl}_8$, a convincing choice between $P\bar{6}2c$ and $P6_3/mmc$ could not be made on the basis of their performance in the refinement.

Experimental

Preparation of $\text{Cs}_3\text{Mo}_2\text{Br}_8$

Tricesium octabromodimolybdenum was prepared by mixing stoichiometric quantities of dimolybdenum tetracetate with cesium bromide, each dissolved in concentrated hydrobromic acid. The chemistry of this reaction is sensitive to conditions of temperature, concentration and purity of reagents. Further investigations are in progress and a detailed report will be published elsewhere in due course. Ordinarily, the reaction does not yield crystals suitable for X-ray diffraction studies. Recrystallization did not prove feasible because of the lack of a suitable solvent. Therefore the method of crystal growth by diffusion was applied. A U-shaped glass tube having a replaceable center part equipped with a fritted disc was constructed. Solutions of CsBr and of $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ in concentrated hydrobromic acid were put into separate ends of the U tube; the whole apparatus was then placed in a refrigerator. After three days several reddish-yellow plate-like crystals appeared on both surfaces of the fritted disk. The bulk microcrystalline material ordinarily obtained has been shown to be the same substance as that obtained in the form of larger crystals. The X-ray powder diffraction pattern of the bulk material can be satisfactorily indexed using the unit-cell and space-group data obtained from the larger crystals.

Collection of X-ray data

A Syntex P1, computer-controlled, four-circle diffractometer equipped with a graphite-crystal incident-beam monochromator was used to examine a crystal of dimensions $0.083 \times 0.033 \times 0.001$ cm, with faces later identified as (100), ($\bar{1}00$), ($0\bar{1}0$), ($1\bar{1}0$), (120), and ($\bar{1}20$).

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A hexagonal unit cell similar to that reported (Bennett, Brenic & Cotton, 1969) for $\text{Rb}_3\text{Mo}_2\text{Cl}_8$ was obtained. Least-squares refinement of fifteen centered reflections produced the orientation matrix for data collection and gave cell constants $a=b=7.757$ (3) and $c=17.804$ (7) Å. For $V=927.6$ (6) Å³ and $Z=2$ the calculated density is 4.40 g cm⁻³; this is in good agreement with the observed density of 4.33 g cm⁻³ measured by displacement in carbon tetrachloride.

Data were collected in the range $0^\circ < 2\theta \leq 45^\circ$ using Mo $K\alpha$ radiation. It later appeared that a larger data set would have been helpful. While the structure is adequately overdetermined (*ca.* 10:1), reflections beyond $2\theta=45^\circ$ might have improved the chances of distinguishing centric and noncentric space groups. These reflections would result primarily from scattering by inner core electrons, although this is probably also the case for many reflections with $2\theta < 45^\circ$, because the structure consists only of heavy atoms (Cs, Mo, and Br). At the time, data collection was terminated because of the sufficient overdeterminacy and because the last data shell ($40^\circ < 2\theta \leq 45^\circ$) showed a large drop-off in the fraction of reflections which are significantly above background. The θ - 2θ scan technique with a variable scan rate from 2.0 to $24.0^\circ/\text{min}$ was used. The scan range was from $2\theta_{\text{Mo } K\alpha 1} - 0.8^\circ$ to $2\theta_{\text{Mo } K\alpha 2} + 0.8^\circ$. Additional details about data collection have been described previously (Cotton, Frenz, Deganello & Shaver, 1973). In order to check the stability of the X-ray measurements three reflections were selected as standards and their intensities were recorded periodically throughout data collection. No significant change in these intensities was observed.

A total of 313 reflections were collected and the usual data reduction procedures were applied.* The parameter p used in the calculation of standard deviations on the intensities [$\sigma(F_o^2)$] was assigned the value 0.05. The high linear absorption coefficient ($\mu=253.5$ cm⁻¹ for Mo $K\alpha$ radiation) and the platelet shape of the crystal necessitated an absorption correction. A numerical correction gave transmission factors varying from 9 to 70% with an average of 61%. A comparison of observed and calculated structure factors showed that an extinction correction was unnecessary.

Refinement of X-ray data*

Systematic extinctions of $l \neq 2n$ for $hh2hl$ (except 221, see below) and no conditions for $hkil$ or $hh0l$ are con-

* The following crystallographic computer programs were used on the IBM 360: *DATARED* by Frenz for data reduction; *AGNOST* by Cahen, which is based on Coppens's *DATAPP* and the Tompa analytical subroutines of Cullen's program, for absorption corrections; *JIMDAP* by Ibers, a version of Zalkin's *FORDAP*, for Fourier summations; *NUCLS* by Ibers & Doedens, based on Busing & Levy's *ORFLS*, for least-squares refinement; *SADIAN* by Baur for calculating atomic distances and angles; *RSCAN* by Doedens for structure-factor analysis; *ORTEP* by Johnson for plotting; *ORFFE* by Busing, & Martin Levy and modified by Brown, Johnson, & Thiessen, for calculating errors or derived parameters; and *LIST* by Snyder for listing the data.

sistent with three space groups: noncentric $P6_3mc$ (No. 186), noncentric $P6_2c$ (No. 190), and centric $P6_3/mmc$ (No. 194). Because of the similarity in cell constants and the identical systematic absences for the present work and that of $\text{Rb}_3\text{Mo}_2\text{Cl}_8$, it was assumed that the analogy extended to the crystal and molecular structure. Hence space group $P6_2c$ was selected and refinement was begun with Cs, Mo, and Br atoms in positions derived from the structure of $\text{Rb}_3\text{Mo}_2\text{Cl}_8$. Only the 202 reflections with $F_o^2 > 3\sigma(F_o^2)$ were used in the full-matrix least-squares refinement on F_c in which the quantity minimized was $\sum w(|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes and w is $4F_o^2/\sigma^2(F_o^2)$. Scattering factors were from Cromer's (1973) tabulation. Included in calculations of F_c (Ibers & Hamilton, 1964) were anomalous dispersion effects for all atoms (Cromer & Liberman, 1970).

Individual isotropic refinement resulted in conventional and weighted agreement factors of $R_1=0.083$ and $R_2=0.098$. As discussed later, reflections 221 and 2,2,15, which were omitted from refinement because the space-group symmetry requires them to be absent, had observed intensities significantly above background. No satisfactory explanation for their high intensities could be deduced. Three cycles of anisotropic refinement gave R values of 0.053 and 0.068. With the rejection of two additional reflections (F_o vs. F_c for 002 and 061 were 133 vs. 93 and 37 vs. 9) the agreement factors were reduced to 0.043 and 0.052. In view of the large data set (relative to the number of variables) and the fact that the calculated structure factors for the two rejected reflections are largely independent of the various space group refinements (see below), the intensities of these reflections were considered to be spurious.

In the final stage of refinement in the noncentric space group $P6_2c$ there existed a high correlation between anisotropic temperature factors β_{11} and β_{12} for both Br(1) and Br(2); the correlation coefficients were 0.69 and 0.95 respectively. In addition, the errors in the x coordinates for each of the Br atoms were an order of magnitude greater than those in other parameters. Since these observations suggested the possibility of a space group of higher symmetry, refinements were carried out in the centric space group $P6_3/mmc$.

In all previous studies of $\text{M}_2\text{X}_9^{3-}$ structures the centric space group has been assumed. These include $\text{Cs}_3\text{Cr}_2\text{Cl}_9$ (Wessel & IJdo, 1957), $\text{Cs}_3\text{Cr}_2\text{Br}_9$, $\text{Cs}_3\text{Mo}_2\text{Cl}_9$, $\text{Cs}_3\text{Mo}_2\text{Br}_9$ (Saillant, Wentworth, Streib, Foltz & Wentworth, 1971), $\text{K}_2\text{W}_2\text{Cl}_9$ (Watson & Waser, 1958), $\text{Cs}_3\text{Ti}_2\text{Cl}_9$ (Powell & Wells, 1935; Hoard & Goldstein, 1935), $\text{Cs}_3\text{Bi}_2\text{I}_9$ (Lindquist, 1968), and $[(\text{CH}_3)_4\text{N}]_2\text{Sb}_3\text{Br}_9 \cdot \text{Br}_2$ (Hubbard & Jacobson, 1972). In none of the reports of these structures is there an indication that the noncentric space group was tested.

As shown in Table 1, statistics on the distribution of intensities favor the centric space group. However, it is known that a centric distribution can be obtained

even for a noncentrosymmetric crystal when certain symmetry or near-symmetry elements are present in the cell (Stout & Jensen, 1968). This test is, therefore, by itself inconclusive.

Table 1. *Distribution of |E| values*

	Observed	Theoretical (centric)	Theoretical (noncentric)
Av. E	0.720	0.798	0.886
Av. E ²	0.948	1.000	1.000
Av. E ² -1	1.077	0.968	0.736
E > 1(%)	27.5	27.5	37.0
E > 2(%)	6.1	5.0	1.8
E > 3(%)	0.32	0.30	0.01

Using the centric space group, three cycles of anisotropic least-squares refinement resulted in *R* values of 0.046 and 0.056. All correlation coefficients were less than 0.56 and the errors in the *x* coordinates were normal. Variables included a scale factor, an occupancy factor for Br(1), and positional and anisotropic temperature parameters not fixed by space-group symmetry. Thus refinement in *P* $\bar{6}2c$ included 25 variables, while *P*_{6₃/mnc required 20 variables. On the basis of Hamilton's *R*-factor ratio test (Hamilton, 1965) for a ratio of 1.068, the hypothesis that the centric space group is correct can be rejected on the 0.995 confidence level, *i.e.*, if this were the only criterion for judgement we would be quite sure that the space group is noncentric. Structure factors based on the parameters derived from the noncentric refinement were calculated for 500 Freidel pairs of reflections within the bounds of the experiment. Of these, only twelve pairs having $k|F_c| > 10$ differed by more than 10%. Examination of these twelve pairs on the diffractometer showed that most of the intensities were barely above background and that the difference between pairs was random and not generally significant. No attempt has been made to test for a piezoelectric effect; the often}

unreliable nature of this experiment did not encourage us to seek or construct facilities for the test. Thus one is left with the choice between the statistical test on the *R* values suggesting the noncentric space group on the one hand and the least-squares correlation coefficients as well as the intensity distribution suggesting the centric space group on the other. A summary of results obtained from refinement in both space groups is given in Table 2.

Table 2. *Comparison of refinements in two space groups*

	Noncentric <i>P</i> $\bar{6}2c$	Centric <i>P</i> _{6₃/mnc}
<i>R</i> values <i>R</i> ₁	0.0428	0.0455
<i>R</i> ₂	0.0519	0.0555
Correlation coefficients between β_{11} and β_{12}	Br(1) 0.69 Br(2) 0.95	<0.5 <0.5
Error in <i>x</i> coordinate	Br(1) 0.0028 Br(2) 0.0014	0.0004 0.0002
Occupancy factor for Br(1)	0.70	0.70
Bond distances (Å)		
Mo—Mo	2.438 (7)	2.439 (7)
Mo—Br(1)	2.679 (6)	2.672 (5)
Mo—Br(2)	2.554 (3)	2.554 (3)
Br(1)—Br(2)	3.560 (15)	3.494 (3)
Br(1)—Br(2')	3.435 (15)	3.494 (3)
Br(1)—Br(1')	3.634 (10)	3.640 (9)
Br(2)—Br(2')	3.639 (4)	3.638 (5)

For the sake of completeness, refinement was also attempted in the third possible space group *P*_{6₃mc. Isotropic refinement gave *R*₁=0.185 and *R*₂=0.239 and produced many high correlations among parameters. Anisotropic refinement diverged and caused non-positive-definite temperature factors for two atoms. Thus space group *P*_{6₃mc is definitely unacceptable.}}

A comparison of $\sum w(|F_o| - |F_c|)^2$ as a function of indices, $\lambda^{-1} \sin \theta$, $|F_o|$, *etc.* showed no significant trends in the data after refinement in *P* $\bar{6}2c$ or *P*_{6₃/mnc. In the last cycles of refinement in both *P*_{6₃/mnc and *P* $\bar{6}2c$ no parameter shifted by more than 0.01 times its standard deviation. A list of $|F_o|$ and $|F_c|$ values for refinement in *P*_{6₃/mnc is given in Table 3.}}}

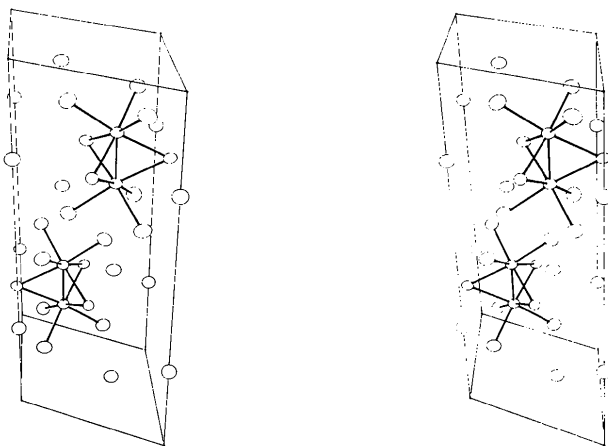


Fig. 1. The unit cell of Cs₃Mo₂Br₈ presented as a stereoscopic pair. The origin of the unit cell is the front, upper left-hand corner, with *x* pointing into the plane of the paper, *y* pointing to the right, and *z* pointing downward.

Table 3. *Values of 10|F_o| and 10|F_c| (in electrons) for Cs₃Mo₂Br₈ after refinement in space group P_{6₃/mnc}*

h	k	l	10 F _o	10 F _c	h	k	l	10 F _o	10 F _c	h	k	l	10 F _o	10 F _c
0	0	0	210	210	0	0	0	210	210	0	0	0	210	210
1	0	0	180	180	1	0	0	180	180	1	0	0	180	180
2	0	0	150	150	2	0	0	150	150	2	0	0	150	150
3	0	0	120	120	3	0	0	120	120	3	0	0	120	120
4	0	0	90	90	4	0	0	90	90	4	0	0	90	90
5	0	0	60	60	5	0	0	60	60	5	0	0	60	60
6	0	0	30	30	6	0	0	30	30	6	0	0	30	30
7	0	0	0	0	7	0	0	0	0	7	0	0	0	0
8	0	0	0	0	8	0	0	0	0	8	0	0	0	0
9	0	0	0	0	9	0	0	0	0	9	0	0	0	0
10	0	0	0	0	10	0	0	0	0	10	0	0	0	0
11	0	0	0	0	11	0	0	0	0	11	0	0	0	0
12	0	0	0	0	12	0	0	0	0	12	0	0	0	0
13	0	0	0	0	13	0	0	0	0	13	0	0	0	0
14	0	0	0	0	14	0	0	0	0	14	0	0	0	0
15	0	0	0	0	15	0	0	0	0	15	0	0	0	0
16	0	0	0	0	16	0	0	0	0	16	0	0	0	0
17	0	0	0	0	17	0	0	0	0	17	0	0	0	0
18	0	0	0	0	18	0	0	0	0	18	0	0	0	0
19	0	0	0	0	19	0	0	0	0	19	0	0	0	0
20	0	0	0	0	20	0	0	0	0	20	0	0	0	0
21	0	0	0	0	21	0	0	0	0	21	0	0	0	0
22	0	0	0	0	22	0	0	0	0	22	0	0	0	0
23	0	0	0	0	23	0	0	0	0	23	0	0	0	0
24	0	0	0	0	24	0	0	0	0	24	0	0	0	0
25	0	0	0	0	25	0	0	0	0	25	0	0	0	0
26	0	0	0	0	26	0	0	0	0	26	0	0	0	0
27	0	0	0	0	27	0	0	0	0	27	0	0	0	0
28	0	0	0	0	28	0	0	0	0	28	0	0	0	0
29	0	0	0	0	29	0	0	0	0	29	0	0	0	0
30	0	0	0	0	30	0	0	0	0	30	0	0	0	0
31	0	0	0	0	31	0	0	0	0	31	0	0	0	0
32	0	0	0	0	32	0	0	0	0	32	0	0	0	0
33	0	0	0	0	33	0	0	0	0	33	0	0	0	0
34	0	0	0	0	34	0	0	0	0	34	0	0	0	0
35	0	0	0	0	35	0	0	0	0	35	0	0	0	0
36	0	0	0	0	36	0	0	0	0	36	0	0	0	0
37	0	0	0	0	37	0	0	0	0	37	0	0	0	0
38	0	0	0	0	38	0	0	0	0	38	0	0	0	0
39	0	0	0	0	39	0	0	0	0	39	0	0	0	0
40	0	0	0	0	40	0	0	0	0	40	0	0	0	0
41	0	0	0	0	41	0	0	0	0	41	0	0	0	0
42	0	0	0	0	42	0	0	0	0	42	0	0	0	0
43	0	0	0	0	43	0	0	0	0	43	0	0	0	0
44	0	0	0	0	44	0	0	0	0	44	0	0	0	0
45	0	0	0	0	45	0	0	0	0	45	0	0	0	0
46	0	0	0	0	46	0	0	0	0	46	0	0	0	0
47	0	0	0	0	47	0	0	0	0	47	0	0	0	0
48	0	0	0	0	48	0	0	0	0	48	0	0	0	0
49	0	0	0	0	49	0	0	0	0	49	0	0	0	0
50	0	0	0	0	50	0	0	0	0	50	0	0	0	0

Table 4. *Positional and anisotropic thermal parameters and their standard deviations for Cs₃Mo₂Br₈**

The form of the thermal ellipsoid is $\exp [-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Values of β are multiplied by 10^4 . Numbers in parentheses in this and other tables are estimated standard deviations in the last significant digits.

Positions (Wyckoff notation)	Symmetry	<i>x</i>	<i>y</i>	<i>z</i>	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	
Cs(1)	2(<i>b</i>)	$\bar{6}m2$	0	0	$\frac{1}{2}$	226 (8)	β_{11}	23 (2)	$\beta_{11}/2$	0	0
Cs(2)	4(<i>f</i>)	3 <i>m</i>	$\frac{1}{2}$	$\frac{1}{2}$	0.5720 (1)	248 (6)	β_{11}	16 (1)	$\beta_{11}/2$	0	0
Mo	4(<i>f</i>)	3 <i>m</i>	$\frac{1}{2}$	$\frac{1}{2}$	0.1815 (2)	181 (7)	β_{11}	14 (1)	$\beta_{11}/2$	0	0
Br(1)†	6(<i>h</i>)	<i>mm</i>	0.5103 (4)	2 <i>x</i>	$\frac{1}{2}$	369 (2)	156 (2)	14 (2)	$\beta_{22}/2$	0	0
Br(2)	12(<i>k</i>)	<i>m</i>	0.1770 (2)	2 <i>x</i>	0.0999 (2)	240 (7)	154 (7)	38 (1)	$\beta_{22}/2$	10 (5)	$\beta_{13}/2$

* For space group $P6_3/mmc$.

† The final occupancy factor was 0.70 (1)

A disturbing feature of this work is the presence of the 221 reflection, a reflection expected to be extinguished by the *c* glide plane. Of the 38 unique reflections examined in the class $hh2hl$ with $l=2n+1$, 36 reflections are definitely unobserved. The 2,2,15 reflection with $I=134$ and $\sigma(I)=36$ (where I is the observed intensity corrected only for background and $\sigma(I)$ is the standard deviation based on counting statistics alone) is of marginal significance. However the 221 reflection has $I=512$ and $\sigma(I)=58$. Another crystal mounted in a different orientation showed a diffuse spot on precession films for this reflection, thus ruling out most causes of spurious reflections, *e.g.* Renninger effects. If we accept this reflection as genuine, the crystal must not contain a *c* glide plane, although the successful refinement in space group $P6_3/mmc$ suggests that the actual crystal symmetry must be very close to satisfying the *c* glide condition. In space groups not including the *c* glide plane the hkl and khl reflections are no longer equivalent and since both forms had not been collected, refinement in these space groups was precluded. However, had this been possible it is doubtful that it would have clarified the situation. A poor refinement would substantiate the results obtained from the present refinement but not explain the presence of the 221 reflection; on the other hand, a good refinement would explain the presence of the 221 reflection but would still leave ambiguous the question of space group since the structure successfully refined in space group $P6_3/mmc$. Because the crystal which was used to collect data later decomposed and since no other suitable crystals were available or readily obtainable, it was decided that the achievement of what seemed likely to be only another ambiguous result was not worth the large amount of effort and cost involved. In any event it is doubtful that the molecular structure could change significantly from that reported here. Nor is it likely that the confirmation of the presence or absence of the glide plane would clarify the ambiguity between centric and noncentric space groups.

Results

The final positional and thermal parameters obtained from refinement in $P6_3/mmc$ are presented in Table 4.

Root-mean-square vibrational amplitudes are given in Table 5. Interatomic distances and angles are presented in Tables 2 and 6, respectively. Fig. 1 is a stereo pair showing the contents of the unit cell.

Table 5. *Root-mean-square amplitudes of vibration (Å)*

	Min.	Intermed.	Max.
Cs(1)	0.193 (7)	0.227 (4)	0.227 (4)
Cs(2)	0.161 (5)	0.238 (3)	0.238 (3)
Mo	0.148 (7)	0.203 (4)	0.203 (4)
Br(1)	0.152 (9)	0.189 (10)	0.317 (8)
Br(2)	0.187 (4)	0.237 (6)	0.257 (6)

Table 6. *Bond angles in the Mo₂Br₈³⁻ ion*

Mo—Br(1)—Mo'	54.3 (2)°
Br(1)—Mo—Br(1')	100.8 (1)
Br(1)—Mo—Br(2)	83.90 (6)
Br(1)—Mo—Br(2')	172.5 (2)
Br(2)—Mo—Br(2')	90.8 (1)

Discussion

Leaving aside the space-group ambiguity, which has been fully discussed in the Experimental section, and causes no significant uncertainty in the structural parameters, the structure of Cs₃Mo₂Br₈ is very similar to that of Rb₂Mo₂Cl₈. According to all the criteria previously proposed (Cotton & Ucko, 1972) for evaluating the nature and magnitude of the direct metal-to-metal interaction in confacial bioctahedra, the Mo—Mo interaction is unquestionably of a bonding nature, but slightly less strong than that in Mo₂Cl₈³⁻. Thus in Mo₂Cl₈³⁻ the Mo—Mo distance is 2.38 (1) Å, while in Mo₂Br₈³⁻ it is 2.439 (7) Å.

An interesting comparison can be made between the pair Mo₂X₈³⁻ (X=Cl, Br) on the one hand and the pair Mo₂X₉³⁻ (X=Cl, Br) (Saillant *et al.*, 1971) on the other. Both of the nonhalo anions have much longer Mo—Mo distances (2.66, 2.82 Å) than their octahalo analogs (2.38, 2.44 Å), and according to all criteria (Cotton & Ucko, 1972) have markedly weaker Mo—Mo bonding interactions. The metal-to-halogen bonds in the two sets of compounds are presumably very similar since corresponding bond distances differ very little, except for the Mo—Br(bridge) bond distances. In

$\text{Mo}_2\text{Br}_9^{3-}$ the distance is 2.624 Å, while in $\text{Mo}_2\text{Br}_8^{3-}$ it is 2.679 Å.

The rather strong Mo–Mo interaction in $\text{Mo}_2\text{Br}_8^{3-}$ reduces the Mo–Br–Mo angle to the remarkably low value of 54.3 (2)°. This is smaller than any previously observed bridge angle in a confacial bioctahedron. So far as we know it is the smallest angle ever reported at a bridging halogen atom in any compound.

Related to this uniquely low bridge angle is the parameter d'/d'' [the ratio of the distance (d') of the metal atom to the plane of the set of bridging halogen atoms to the distance (d'') of the metal atom from the plane of the terminal set of halogen atoms]. The smaller this ratio, the stronger the M–M attraction must be. The value in this structure is 1.22 Å/1.45 Å = 0.84. This is the smallest value yet observed. Previously the smallest was that in $\text{Mo}_2\text{Cl}_8^{3-}$, namely 0.89. This is further evidence for a strong Mo–Mo bond in $\text{Mo}_2\text{Br}_8^{3-}$ although it should not be taken to imply that it is stronger than that $\text{Mo}_2\text{Cl}_8^{3-}$.

The very short Mo–Mo distance in $\text{Mo}_2\text{Br}_8^{3-}$ would lead one to predict that the ion would have only one unpaired electron. Even in $\text{Mo}_2\text{Cl}_8^{3-}$, where Mo–Mo = 2.66 Å, there is only a small temperature-independent paramagnetism, although $\text{Mo}_2\text{Br}_9^{3-}$ (Mo–Mo = 2.82 Å) appears to possess unpaired electrons (Saillant & Wentworth, 1969).

Undoubtedly the greater deformation of the (incomplete) bioctahedra in the $\text{Mo}_2\text{X}_8^{3-}$ structures, compared to the $\text{Mo}_2\text{X}_9^{3-}$ ones occurs because, in effect, there is only $\frac{2}{3}$ as much resistance to compression along the threefold axis. A comparison may also be made with the recently reported structure of molybdenum(III) bromide (Babel, 1972). This consists of infinite stacks of MoBr_6 octahedra, sharing opposite faces. The Mo–Mo distances are alternately 2.92 and 3.14 Å. The Mo–Br distances range from 2.53 to 2.57 Å. The planes of the triangular sets of Br atoms are separated by 3.68 Å as compared to only 2.67 Å between the planes of the terminal and bridging sets in $\text{Mo}_2\text{Br}_8^{3-}$. This shows very dramatically the great structural influence of the Mo–Mo bonding coupled with the incompleteness of the bridging set of bromine atoms.

Note added in proof: – Powder samples of $\text{Cs}_3\text{Mo}_2\text{Br}_8$ and $\text{Cs}_3\text{Mo}_2\text{Cl}_8$ were examined for second harmonic generation (SHG) since lack of an inversion center is a necessary condition for SHG (Bergman & Kurtz, 1970). Negative results were obtained for each compound. In each case both 1.06 μ to green (0.54 μ) conversion and 1.32 μ to red (0.66 μ) conversion were examined. Increasing

the power of the laser resulted only in burning the sample. These results tend to indicate that the crystals are centric; if they are, in fact acentric, the harmonic is either very weak or it is being absorbed. While the indication of the centric space group is quite acceptable in the present case, its significance is uncertain for the chloro compound where refinement definitely favored the acentric space group. Since the SHG criterion thus appears to be inconclusive, the space group ambiguity is considered to be still unresolved. We thank Drs. J. G. Bergman and B. F. Levine of Bell Laboratories for performing these experiments for us.

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