The Crystal Structures of $Cs_3Cr_2Br_9$, $Cs_3Mo_2Cl_9$, and $Cs_3Mo_2Br_9$

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The crystal structures of $Cs_3Cr_2Br_9$, $Cs_3Mo_2Cl_9$, and $Cs_3Mo_2Br_9$ have been determined from three-dimensional X-ray data. Each crystallizes in the space group D_{6h}^4-$P6_3/mmc$ with $Z = 2$ and is isomorphous with $Cs_3Cr_2Cl_9$. The unit cell parameters, observed and calculated densities, conventional residuals, R, and metal–metal internuclear distances are given. The structures were refined using 150, 192, and 213 unique reflections for $Cs_3Cr_2Br_9$, $Cs_3Mo_2Cl_9$, and $Cs_3Mo_2Br_9$, respectively. Within the bioctahedral anions, metal–metal bonding is indicated only in the enneahalodimolybdates, in agreement with magnetic data. Within the $Cr_2Br_9^{3-}$ anion, a very clear repulsive force exists between the metal atoms.

Our interest in the chemistry of the enneahalodi-metalates was originally provoked by the significant differences which arise in the structures of the $Cr_2Cl_9^{3-}$ and $W_2Cl_9^{3-}$ ions. Although each can be described as two octahedra sharing a common trigonal face, the metal–metal internuclear distance is smaller in the anion containing the inherently larger metal atoms. This distance is only 2.41 Å in $K_3W_2Cl_9$,[2] while in Cs_3-Cr_2Cl_9[3] it is 3.12 Å. In the former a clear attraction exists between the adjacent metal atoms. However, in $Cr_2Cl_9^{3-}$ a net repulsion appears to exist[4] since the chromium atoms do not lie exactly at the centers of their octahedra but are displaced away from each other. Significant differences in the chemistry of these anions have been attributed[5,6] to the presence of metal-to-metal bonding in the $W_2Cl_9^{3-}$ anion and its absence in the chromium analog. This state of affairs naturally led to a study of the corresponding enneahalodimolyb-dates, since intermediate physical and chemical properties would be expected. Magnetic studies[7] have indicated that strong metal-to-metal interactions occur in $Cs_3Mo_2Cl_9$, such that only temperature-independent paramagnetism is observed. However, in the case of $Cs_3Mo_2Br_9$, the existence of a weak temperature-dependent paramagnetism can be attributed to a somewhat weaker interaction between the transition metal atoms.

The structures of these enneahalodimolybdates have now been determined. In addition, the structure of $Cs_3Cr_2Br_9$ was determined for comparative purposes.

Experimental Section

Crystals of $Cs_3Cr_2Br_9$, $Cs_3Mo_2Cl_9$, and $Cs_3Mo_2Br_9$ were prepared as described earlier.[6,7] The crystals of all three compounds were hexagonal prisms, elongated along c. Preliminary precession and Weissenberg photographs (using Mo Kα radiation, λ 0.71069 Å, and Cu Kα radiation, λ 1.54178 Å) showed that crystals of all three have $6/mmm$ Laue symmetry with the only general condition $l = 2n$ for $h, h, 2\bar{h}, l$, which limited the possible space groups to $P6_3mc$, $P\bar{6}2c$, and $P6_3/mmc$. Furthermore they had similar unit cell dimensions and intensity distributions, indicating that they were isomorphous. Finally a comparison of cell dimensions and intensities indicated that the structures were isomorphous with $Cs_3Cr_2Cl_9$,[3] and we therefore assumed $P6_3/mmc$ to be the correct space group.

The single crystal used for data collection for $Cs_3Cr_2Br_9$ was a hexagonal rod approximately 0.1 mm in cross section and 0.3 mm in length. Following earlier unsuccessful attempts to protect the air-sensitive crystals with shellac, the crystal was imbedded in paraffin in a 0.2-mm thin-walled glass capillary. The capillary was mounted and oriented such that the c axis of the crystal was along the goniometer head axis (φ). The data were collected on a Datex automated GE XRD-6 diffractometer equipped with a quarter-circle orienter and scintillation counter, using Mo Kα radiation, λ 0.71069 Å. The pulse height analyzer was set to admit 90% of the Mo Kα peak. The crystal to source distance of 5.73 in., crystal to counter distance of 7.0 in., and 2° aperture receiving collimator, standard for this instrument, were used. The takeoff angle was 2°. The hexagonal cell dimensions, $a = 7.507$ (6) and $c = 18.680$ (15) Å at a room temperature of 23°, were obtained by least-squares fit with diffractometer 2θ values from eight reflections having well-defined peaks at large 2θ. For three of these the α_1 (λ 0.70926 Å) and α_2 (λ 0.71354 Å) peaks were resolved and both 2θ values were used. The observed density $\rho_{obsd} = 4.25$ g cm^{-3}, measured by volume displacement of methylene iodide, compares well with $\rho_{calcd} = 4.20$ g cm^{-3} for the two molecules per unit cell that would be required by the isomorphous structure anticipated above. Redundant intensity data were collected (60° φ interval) for $2\theta \leq 45°$. Reflections were scanned through a range of 2° in 2θ at a speed of 1°/min. Stationary-counter, stationary-crystal background counts of 20 sec were taken at the upper and lower limits of each scan. A 0.03-mm Zr β filter was used for all measurements and an additional attenuation filter made up of Zr and Al foils was used to keep the stronger reflections below a 10,000-cps counter saturation rate. The intensities of the 049 and the 409 reflections were remeasured periodically during the data collection as a check on electronic and crystal stability and showed no systematic trends. The raw data were corrected for Lorentz and polarization effects in the usual manner and standard errors were based on counting statistics as described by Johnson,[8] $F_o^2 = Lpq[N - k(b_1 + b_2)]$, where Lp are Lorentz and polarization corrections, q is the filter factor, N is the scan count, k is a factor to scale each of the background counts to half the scan time, and b_1 and b_2 are the background counts. A 5% error was assigned to the filter factor based on a manual calibration. The expression used to calculate standard deviations was $\sigma(F_o^2) = Lpq[0.0025C^2 + N + k^2(b_1 + b_2)]^{1/2}$, where $C = N - k(b_1 + b_2)$. After scaling the attenuated data, the unique intensity data (30° φ interval) were obtained by averaging the equivalent reflections in a manner similar to the one described by Corfield, Doedens, and Ibers.[9] Of 252 unique reflections 152 were considered observed by the criterion $F_o^2 \geq 2.33\sigma(F_o)^2$. Absorption ($\mu = 265$ cm^{-1}) corrections were made using the cylindrical approximation.[10] The absorption coefficients ranged from 7.324 to 8.386.

The single crystal of $Cs_3Mo_2Cl_9$ used for data collection was a hexagonal prism having approximately the same dimensions as the $Cs_3Cr_2Br_9$ crystal described above. $Cs_3Mo_2Cl_9$, however, is air stable and the crystal was simply mounted on a thin glass rod which was then oriented such that the c axis was along the

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goniometer head axis (φ). The cell dimensions at a room temperature of 23°, $a = 7.357$ (5) and $c = 17.545$ (12) Å, were obtained by least-squares fit with 2θ values from nine reflections, all of which had resolved α_1 and α_2 peaks. From powder photographs, Grey and Smith[11] found $a = 7.346$ (3) and $c = 17.506$ (14) Å while Bennett, Brencic, and Cotton[12] listed $a = 7.33$ (4) and $c = 17.23$ (10) Å. The observed density of $\rho_{obsd} = 3.65$ g cm^{-3}, obtained by volume displacement of CH_2I_2, again compared well with $\rho_{calcd} = 3.68$ g cm^{-3} for $Z = 2$ as would be required by the anticipated isomorphous structure. The intensity data were collected on the GE equipment described above; however, this set was collected in a manual mode of operation due to equipment malfunction. Because of the increased time and human effort this involved, only a unique set of data was collected for $2\theta \leq 42°$. The preliminary data processing was the same as for $Cs_3Cr_2Br_9$ and yielded 249 unique reflections, 197 of which were considered observed by the criterion $F_o^2 > 1.5\sigma(F_o)^2$. Absorption ($\mu = 95.6$ cm^{-1}) corrections were made using the cylindrical approximation.[10] The absorption coefficients ranged from 2.191 to 2.327.

The data for $Cs_3Mo_2Br_9$ were collected on a newly installed Picker FACS-1 PDP8/S computer automated full-circle diffractometer with scintillation counter. Copper Kα radiation (λ 1.54178 Å) was used initially because a Cu target X-ray tube was the only one available at the time. From a hexagonal rod-shaped crystal which was 0.08 mm in cross section and 0.3 mm in length, cell dimensions of $a = 7.648$ (3) and $c = 18.339$ (16) Å were obtained at a room temperature of 24°. The cell dimensions and orientation matrix were fitted to the diffractometer angles from six reflections having large 2θ values using the least-squares program supplied by Picker for the PDP8/S computer. Grey and Smith[11] found $a = 7.644$ (5) and $c = 18.350$ (20) Å from measurements of powder photographs. The observed density of $\rho_{obsd} = 4.59$ g cm^{-3}, also obtained by volume displacement of CH_2I_2, again compared well with $\rho_{calcd} = 4.66$ g cm^{-3} for $Z = 2$ as would be required by the anticipated isomorphous structure. Although intensity data were collected with the Cu Kα radiation and used for preliminary refinement, final cycles of refinement were based on the intensity data (whose structure factors are given in Table III) which were subsequently collected using Mo radiation monochromatized by using the 002 reflection from highly oriented graphite. In addition a considerably smaller crystal (0.06-mm cross section $\times$ 0.15-mm length) was used and an absorption ($\mu = 275$ cm^{-1}) correction was carried out using the cylindrical approximation.[10] The absorption coefficients ranged from 3.709 to 4.167. This compound is also air stable and the crystal was mounted on a thin glass rod in a stable goniometer head of our own design which has translational adjustments only. A crystal to source distance (target–monochromator–sample) of 9.25 in., standard for this instrument, a crystal to detector distance of approximately 9.8 in., a receiving aperture of 1.5 $\times$ 1.5 mm, and a takeoff angle of 2.4° were used. Cell dimensions were checked for the new crystal and radiation; they were found to be in good agreement with the above results, and therefore they were not given further refinement. Twofold redundant intensity data were collected for $2\theta \leq 55°$. Reflections were scanned through a 2θ range of 2° plus $\alpha_1 - \alpha_2$ dispersion at a speed of 1°/min. Stationary-counter, stationary-crystal background counts of 20 sec were taken at the upper and lower 2θ limits for each scan. No attenuators were required. The raw data were processed as described above to give 309 unique observed intensities, 213 of which were considered to be observed by the criterion $F_o^2 > 1.5\sigma(F_o)^2$. At the conclusion of the experiment a careful check of the instrumental and crystal alignment was carried out, and it was found that the reflections were still centered in the rather small receiving aperture. During the data collection the intensities of the 0012, 220, and 060 reflections were remeasured after every 13 reflections and showed no systematic trends.

With the exception of the calculations on the PDP8/S, all computations were done on the CDC 3600 computer. Cell dimensions and errors were determined using the least-squares program by Heaton, Gvildys, and Mueller.[13] A version of the

Busing, Martin, and Levy full-matrix least-squares program[14] was employed for the structure refinement, and their function and error program[15] was used for the calculation of bond distances, bond angles, and their standard deviations. The function minimized during refinement was $\Sigma w(|F_o|^2 - |F_c|^2)^2$ with $w = 1/\sigma^2$ (F_o^2).

Fourier summations and Patterson functions were computed using the Fortran version of ERFR2.[16] The atomic scattering factors of Cromer and Waber[17] for the neutral Cr, Mo, Br, Cl, and Cs atoms were used and were corrected for the real and imaginary parts of the anomalous dispersion.[18]

Structure Determinations and Refinements

The crystal structure of $Cs_3Cr_2Br_9$ was solved by simply assuming coordinates identical with those in the $Cs_3Cr_2Cl_9$ structure.[2] Refining only the scale factor, a residual, $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, of 0.36 was obtained. Further refinement on all variable coordinates and isotropic temperature factors quickly reduced R to 0.075. In addition to this rather satisfactory refinement, the space group assignment was checked by computing a three-dimensional Patterson map which did give vector peaks in agreement with peaks computed for the above structure, as computed in a specially written program. A plot of $|F_o|$ vs. $|F_c|$ showed a marked deviation for the two most intense reflections, 220 and 006. This deviation was attributed to extinction and these two reflections were removed. Further refinement was carried out using anisotropic thermal parameters. Some initial difficulty was experienced when the temperature factors turned negative, but this problem was solved by multiplying the shifts in the thermal parameters by 0.5. Three cycles of anisotropic refinement reduced R to 0.048. Three further cycles applying full shifts yielded the final values of $R_F = 0.048$, $R_{F_2} = \Sigma|F_o^2 - F_c^2|/\Sigma F_o^2 = 0.087$, and $R_{wF^2} = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w (F_o^2)^2]^{1/2} = 0.118$ for the 150 observations used in the refinement. The number of parameters varied was 19 including the overall scale factor. The standard error of an observation of unit weight was 1.70. The observed and calculated structure factors for all 252 unique reflections are given in Table I[19] for which $R_F = 0.084$.

The coordinates for the appropriate atoms from the final refinement of $Cs_3Cr_2Br_9$ were assumed for the initial refinement of the $Cs_3Mo_2Cl_9$ structure. After three cycles of least-squares refinement, the residual was $R = 0.34$. Three additional cycles on all variable coordinates and isotropic thermal parameters reduced R to 0.104. At this point it was noticed that the data contained two 3,2,13 reflections. The redundant data were removed together with the 110, 220, 300, 600, and 006 reflections which appeared to be affected by extinc-

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(19) Listings of observed and calculated structure factors (Tables I–III) will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit $3.00 for photocopy or $2.00 for microfiche.

TABLE IV

ATOMIC AND THERMAL PARAMETERS

Atom[a]	Point symmetry	x	y	z	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$[b]
					$Cs_3Cr_2Br_9$					
Br (k)	m	0.8233 (4)	1.6465	0.0915 (2)	77 (9)	52 (14)	12 (1)	26	3	5 (4)
Br (h)	mm	0.5149 (5)	1.0298	0.25	73 (14)	35 (19)	10 (2)	17	0	0
Cs (b)	$\bar{6}m2$	0.0	0.0	0.25	50 (14)	50	11 (3)	25	0	0
Cs (f)	$3m$	0.3333	0.6667	0.0756 (3)	70 (10)	70	12 (2)	35	0	0
Cr (f)	$3m$	0.3333	0.6667	0.8388 (6)	30 (20)	30	9 (4)	15	0	0
					$Cs_3Mo_2Cl_9$					
Cl (k)	m	0.8208 (8)	1.6415	0.0973 (5)	170 (26)	86 (28)	18 (4)	43	−5	−10 (9)
Cl (h)	mm	0.5016 (11)	1.0032	0.25	96 (29)	89 (38)	18 (5)	45	0	0
Cs (b)	$\bar{6}m2$	0.0	0.0	0.25	99 (12)	99	19 (3)	50	0	0
Cs (f)	$3m$	0.3333	0.6667	0.0743 (2)	140 (9)	140	13 (2)	70	0	0
Mo (f)	$3m$	0.3333	0.6667	0.8257 (3)	85 (11)	85	12 (2)	42	0	0
					$Cs_3Mo_2Br_9$					
Br (k)	m	0.8244 (2)	1.6489	0.0942 (1)	147 (6)	89 (8)	12 (1)	45	6	12 (3)
Br (h)	mm	0.4994 (3)	0.9988	0.25	134 (8)	108 (12)	8 (1)	54	0	0
Cs (b)	$\bar{6}m2$	0.0	0.0	0.25	95 (8)	95	14 (1)	48	0	0
Cs (f)	$3m$	0.3333	0.6667	0.0730 (2)	170 (6)	170	11 (1)	85	0	0
Mo (f)	$3m$	0.3333	0.6667	0.8268	77 (7)	77	8 (1)	38	0	0

[a] The Wyckoff notation is given in parentheses and is used to differentiate the halogens. The bridging halogens are in position (h) and the terminal halogens are in position (k). [b] The anisotropic thermal parameters are in the form $\exp -[h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. The point symmetries of the special positions impose the following restrictions on the β_{ij}: position (k) (m), $\beta_{12} = \frac{1}{2}\beta_{22}$, $\beta_{13} = \frac{1}{2}\beta_{23}$; position (h) (mm), $\beta_{12} = \frac{1}{2}\beta_{22}$, $\beta_{13} = \beta_{23} = 0$; position (b) $(\bar{6}m2)$, $\beta_{11} = \beta_{22} = 2\beta_{12}$, $\beta_{13} = \beta_{23} = 0$; position (f) $(3m)$, $\beta_{11} = \beta_{22} = 2\beta_{12}$, $\beta_{13} = \beta_{23} = 0$.

tion. At this point the absorption correction described above was carried out and anisotropic thermal parameters were introduced. Again three cycles of anisotropic refinement with half-shifts applied to the thermal parameters reduced R_F to 0.076. Three further cycles allowing full shifts yielded the final values of $R_F = 0.071$, $R_{F^2} = 0.128$, and $R_{wF^2} = 0.188$ for 192 reflections included in the refinement. The standard error of an observation of unit weight was 2.28. The observed and calculated structure factors for all 249 unique reflections are given in Table II[19] for which $R_F = 0.109$.

An attempt was made to refine the structure of $Cs_3Mo_2Br_9$ using the intensity data obtained with Cu Kα radiation. However, the residual could not be reduced below 10% and the Mo atom thermal parameter was always negative. The refinements using the intensity data obtained with Mo Kα radiation on the other hand proceeded quite smoothly. The respective coordinates from the $Cs_3Mo_2Cl_9$ structure were used as the starting parameters for the refinement of the $Cs_3Mo_2Br_9$ structure. The refinement converged in five least-squares cycles varying all variable coordinates and the isotropic thermal parameters to give a residual of 0.063 for 213 reflections having $F_o^2 > 1.5\sigma F_o^2$. At this point an absorption correction was carried out (see above) and anisotropic thermal parameters were introduced. Three cycles, applying half-shifts to the thermal parameters, followed by three further cycles with full shifts, yielded the final values of $R_F = 0.044$, $R_{F^2} = 0.062$, and $R_{wF^2} = 0.099$. The standard error of an observation of unit weight was 0.82. The observed and calculated structure factors for all 309 unique reflections are given in Table III[19] for which $R_F = 0.075$.

Discussion

The Structures.—The final atomic and thermal parameters are given in Table IV, while interatomic distances and angles are given in Table V. The standard errors were computed using the variance–covari-

TABLE V

BOND DISTANCES AND ANGLES WITHIN THE $Cr_2Br_9^{3-}$, $Mo_2Cl_9^{3-}$, AND $Mo_2Br_9^{3-}$ ANIONS

Distance, Å

	$Cr_2Br_9^{3-}$	$Mo_2Cl_9^{3-}$	$Mo_2Br_9^{3-}$
Metal–metal	3.317 (21)[d]	2.655 (11)	2.816 (9)
Metal–halogen (k)[a]	2.417 (6)	2.384 (6)	2.544 (3)
Metal–halogen (h)[a]	2.577 (9)	2.487 (12)	2.624 (5)
Halogen (k)–halogen (k)[b]	3.527 (3)	3.401 (6)	3.620 (2)
Halogen (h)–halogen (h)[b]	3.417 (5)	3.643 (8)	3.834 (4)
Halogen (k)–halogen (k)[c]	5.921 (10)	5.357(18)	5.715 (7)

Angle, Deg

	$Cr_2Br_9^{3-}$	$Mo_2Cl_9^{3-}$	$Mo_2Br_9^{3-}$
Halogen (h)–metal–halogen (k)	91.4 (1)	87.4 (2)	87.65 (7)
Halogen (h)–metal–halogen (h)	83.0 (3)	94.2 (1)	93.89 (11)
Halogen (k)–metal–halogen (k)	93.7 (3)	91.0 (3)	90.73 (15)

Some Interionic Distances, Å

	$Cs_3Cr_2Br_9$	$Cs_3Mo_2Cl_9$	$Cs_3Mo_2Br_9$
Cs (b)–Cs (b) along c	9.34	8.77	9.17
Cs (b)–Cs (b) along a	7.51	7.36	7.65
Cs (b)–Cs (f)	5.422 (4)	5.248 (3)	5.480 (3)
Cs (b)–halogen (h)	3.758 (2)	3.679 (2)	3.824 (1)
Cs (b)–halogen (k)	3.748 (4)	3.520 (7)	3.684 (3)
Cs (f)–halogen (h)	4.024 (5)	3.755 (4)	3.922 (4)
Cs (f)–halogen (k)	3.768 (4)	3.704 (6)	3.846 (3)
Halogen (k)–halogen (k)[e]	4.120 (8)	4.109 (16)	4.164 (6)

[a] The Wyckoff notation for the special positions is used to distinguish the two kinds of halogen atoms. The bridging halogens are in position (h) and the terminal halogens are in position (k). [b] These distances are between atoms at the same level in z. [c] Distance between terminal halogens at either end of the anion. [d] Standard deviations are given in parentheses. [e] Closest approach between two terminal halogens in two anions.

ance matrix from the final cycles of least-squares refinement. Table VI contains some pertinent distances and angles for $Cs_3Cr_2Cl_9$ and $K_3W_2Cl_9$. The structure shown in Figure 1 pertains to the three isomorphous compounds and contains twelve terminal halogen atoms in the (k) position, using the Wyckoff notation, point symmetry m, another six bridging halogen atoms in the (h) position, mm, four Cs atoms in the (f) position, $3m$, and two in the (b) position, $\bar{6}m2$, and the four transition metal atoms in the (f) position of the space group. The

TABLE VI
BOND DISTANCES AND ANGLES WITHIN THE
$Cr_2Cl_9{}^{3-}$ AND $W_2Cl_9{}^{3-}$ ANIONS[a]

	$Cr_2Cl_9{}^{3-}$	$W_2Cl_9{}^{3-}$
Distance, Å		
Metal–metal	3.12	2.41
Metal–halogen (k)[b]	2.34	2.40
Metal–halogen (h)	2.52	2.48
Halogen (k)–halogen (k)	3.40	3.44
Halogen (h)–halogen (h)	3.43	3.76
Angle, Deg		
Halogen (h)–metal–halogen (k)	90.5	84.8
Halogen (h)–metal–halogen (h)	85.8	98.4
Halogen (k)–metal–halogen (k)	93.3	91.4

[a] Taken from the data for $Cs_3Cr_2Cl_9$ in ref 3 and the data for $K_3W_3Cl_9$ in ref 2. [b] Wyckoff position is given in parentheses. Although $K_2W_2Cl_9$ is not isomorphous with the Cs salts of the other enneahalodimetalates and the Wyckoff positions do not, therefore, correspond, we have retained the same system throughout to facilitate comparisons of the different anions.

anions are centered at $(^1/_3, {}^2/_3, {}^3/_4)$ and $(^2/_3, {}^1/_3, {}^1/_4)$ with the point symmetry $\bar{6}m2$ required by the space group.

The Cr atoms in $Cs_3Cr_2Br_9$ are displaced away from the centers of their octahedra such that the metal–metal internuclear distance is 3.32 (2) Å. Although similar in direction to that found in $Cs_3Cr_2Cl_9$, the magnitude of the displacement and its effects in the bromide are unexpected, as shown in Table VII. The

TABLE VII
SOME PERTINENT DISTANCES IN THE ENNEAHALODIMETALATES
WHICH HAVE BEEN STRUCTURALLY CHARACTERIZED

	$\overline{MM}$,[a] Å	$\overline{MB}$,[b] Å	$\overline{MT}$,[c] Å
$Cs_3Cr_2Cl_9$	3.12	1.56	1.27
$Cs_3Cr_2Br_9$	3.31	1.66	1.30
$Cs_3Mo_2Cl_9$	2.66	1.33	1.36
$Cs_3Mo_2Br_9$	2.82	1.41	1.46
$K_3W_2Cl_9$	2.41	1.21	1.35

[a] Metal-to-metal internuclear distance. [b] The distance between the transition metal atom and the midpoint of the plane of bridging halogen atoms. [c] The distance between the transition metal atom and the midpoint of the plane of terminal halogen atoms.

distance between the midpoint of the plane of the bridging Br atoms and the Cr atom ($\overline{MB}$) is 1.66 Å while the corresponding distance to the midpoint of the plane of the terminal Br atoms ($\overline{MT}$) is 1.30 Å. This displacement results in a Cr–terminal Br bond distance of 2.417 (6) Å and a Cr–bridging Br bond distance of 2.577 (9) Å. In the totally bridged $CrBr_3$[20] structure the Cr–Br bond length is 2.57 Å. It is of some interest to note that the distance between the chromium atoms and the bridging bromine atoms is approximately the sum of their ionic radii. Consequently, the structure could be described alternatively as pyramidal $CrBr_3$ units separated by layers of Br^- ions. This description may have more than a semantic value. Many attempts in this laboratory to prepare alkylammonium salts of $Cr_2Br_9{}^{3-}$ in either acetonitrile, dichloromethane, or chloroform solutions[21] have ended in failure, which suggests, but by no means proves, that the $Cs_3Cr_2Br_9$ stoichiometry finds a great deal of its stability through packing in the lattice. Since it is now clear that there

(20) H. Brakken, *Kgl. Nor. Vidensk. Selsk., Forh.*, **5**, No. 11 (1932). Uncertainties in bond lengths are not available.

(21) As a point of reference, alkylammonium salts of the $Cr_2Cl_9{}^{3-}$ anion can be prepared in any of these solvents.[6]
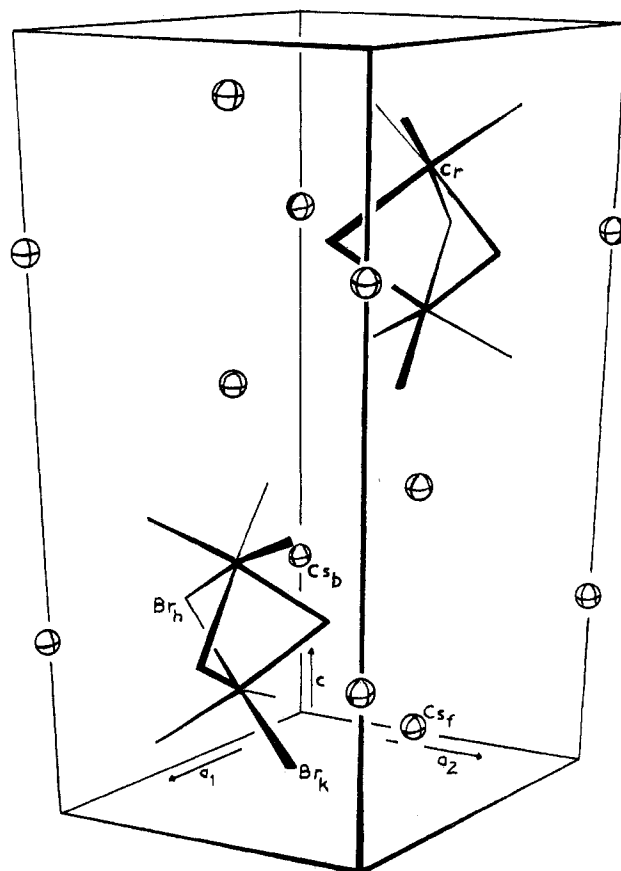

Figure 1.—The unit cell of $Cs_3M_2X_9$. The atoms are labeled for $Cs_3Cr_2Br_9$. Wyckoff positions are given as subscripts.

is a long Cr–bridging Br bond, it would seem likely then that Cr–solvent interactions could easily prevent the formation of the $Cr_2Br_9{}^{3-}$ ion in solutions.[22]

The Mo–Mo internuclear distances in $Cs_3Mo_2Cl_9$ and $Cs_3Mo_2Br_9$ are 2.655 (11)[23] and 2.816 (9) Å, respectively. In both cases the Mo atoms are fairly close to the centers of their octahedra, but in each case a slight displacement toward the plane of bridging halogen atoms has occurred (Table VII). In the $Mo_2Cl_9{}^{3-}$ anion the Mo–bridging Cl bond distance is 2.487 (12) Å while the bond length between the terminal Cl and the Mo atom is 2.384 (6) Å. A comparison of these bond lengths with those found[24] in the totally bridged $\alpha\text{-}MoCl_3$ is possible. The pairwise interactions of the Mo atoms in the crystal lattice of $\alpha\text{-}MoCl_3$ cause the smallest Mo–Mo separation to be 2.76 (1) Å while the two distinct Mo–Cl bond distances are 2.40 (3) and 2.45 (3) Å. An interesting comparison may also be made with the $Mo_2Cl_8{}^{3-}$ anion which has the typical enneahalodimetalate structure but with one of the bridging atoms missing.[12] In this ion the Mo–bridging Cl bond length is 2.50 (2) Å, while the Mo–terminal Cl bond distance is

(22) The existence of $[(C_2H_5)_4N]_3Cr_2Br_9$ has been mentioned but details of its preparation were not given: P. D. W. Boyd, P. W. Smith, and A. G. Wedd, *Aust. J. Chem.*, **22**, 653 (1969). Presumably, however, this compound was prepared by crystallization from a nonaqueous solvent.

(23) The crystal structure of $Cs_3Mo_2Cl_9$ was recently briefly discussed in a paper which appeared during the preparation of this article. Although the structure was not described in detail, the Mo–Mo, Mo–bridging Cl, and Mo–terminal Cl internuclear distances were given as 2.68, 2.52, and 2.39 Å, respectively, without reference to the uncertainties in these distances: P. W. Smith and A. G. Wedd, *J. Chem. Soc.*, 2447 (1970).

(24) H. Schafer, H. G. Schnering, J. Tillack, F. Kuhnen, H. Wöhrle, and H. Bauman, *Z. Anorg. Allg. Chem.*, **353**, 281 (1967).

2.38 (1) Å. The decrease in the formal oxidation state of each Mo atom $(3+ \rightarrow 2.5+)$ should normally lead to longer metal–halogen bond lengths, but also the loss of a Cl atom would significantly relieve Cl$\cdots$Cl repulsions. Apparently these effects almost exactly cancel so that the Mo–Cl bond distances in $Mo_2Cl_9{}^{3-}$ and $Mo_2Cl_8{}^{3-}$ are essentially the same. The two types of Mo–Br bond lengths in the $Mo_2Br_9{}^{3-}$ anion lie above and below the Mo–Br distance[25] of 2.57 Å in the totally bridged $MoBr_3$.

The Question of Metal–Metal Bonding.—According to a useful criterion of Cotton,[4] in a polynuclear molecule containing bridging groups, "a metal–metal bond may be said to exist if the metal atoms approach each other more closely than the bridging geometry would appear to require; whereas, when the metal–metal distance is a relatively long one which does not differ significantly from what would be expected in the absence of any attractive force between the metal atoms, we may assume that nothing more than weak electron spin coupling exists." The application of this criterion clearly eliminates the possibility of metal–metal bonding in those enneahalodichromates which have been structurally characterized. From magnetic studies,[6] the total electron coupling energy has been estimated as 0.1 kcal/mol, a quantity neither chemically significant nor sufficiently large to constitute a chemical bond in the usual sense. On the other hand, the squashed structure of the $W_2Cl_9{}^{3-}$ anion is a clear result of the W atoms moving away from the centers of their octahedra toward each other (Table VII). An extremely crude estimate[7] of the total electron coupling energy suggests that it exceeds 25 kcal/mol. There is little doubt that a strong metal–metal bond exists. One approach to the bonding would involve direct overlap of the half-filled t_{2g} orbitals on the adjacent metal atoms, resulting in three bonding interactions. However, several alternative formulations are also possible and not easily eliminated. For example, direct overlap of only the trigonally directed d_{z^2} orbitals on the adjacent W atoms would lead to a single interaction. The remaining electrons could be located either in localized pairs or in singly occupied, localized orbitals with intraionically coupled spins. In any event, Bennett, Brencic, and Cotton[12] have indicated that submaximal overlap of the metal orbitals probably exists since the close approach of the metal atoms is at least partially counteracted by the resistance of the W–Cl–W angles to excessive compression, the presence of Cl$\cdots$Cl nonbonded contacts, and the resistance of W–Cl bonds to stretching. Be-

cause of the likelihood of submaximal overlap, Cotton[26] stressed the terms "bonding interactions" rather than "bonds."

In each of the enneahalodimolybdates, there is a slight but significant shift of the adjacent Mo atoms toward each other (Table VII). If these shifts are due to metal–metal bonds in accordance with Cotton's criterion, then the number of bonding interactions should lie between 0 and 3, since the shifts are in the opposite direction to those found in the enneahalodichromates and far less than that found in the $W_2Cl_9{}^{3-}$ anion. The total electron coupling energy[7] in the $Mo_2Cl_9{}^{3-}$ anion has been estimated to be at least 25 kcal/mol while that in the corresponding bromide is about 8–10 kcal/mol. While these are again crude estimates, their orders of magnitude are undoubtedly correct and far too large to be dismissed as the result of a long-range coupling of electron spins. Consequently, the shifts of the adjacent Mo atoms in both $Mo_2Cl_9{}^{3-}$ and $Mo_2Br_9{}^{3-}$ are due to bonding interactions between the metal atoms. The approach to the bonding in either anion need not differ appreciably from those formulations which were described as possibilities for the $W_2Cl_9{}^{3-}$ anion. The smaller shifts of the Mo atoms from the centers of their octahedra (relative to those observed in the $W_2Cl_9{}^{3-}$ anion) presumably would be the result of decreased overlap, which in turn would lead to smaller energy differences in the molecular orbitals. With sufficiently small energy differences, a thermal population of the antibonding, metal-to-metal molecular orbitals could be expected and would presumably explain the small temperature-dependent paramagnetism of the $Mo_2Br_9{}^{3-}$ ion.

A comparison of the internuclear separations of the metal atoms in the $Mo_2Cl_9{}^{3-}$ and $Mo_2Cl_8{}^{3-}$ anions is of interest. The loss of a bridging Cl atom in the latter results in a significant movement of the Mo atoms toward each other and a short Mo–Mo distance of 2.38 (1) Å. The decreased internuclear separation is believed[12] to result from a fourth bonding interaction which is obtained from the overlap of the two additional Mo orbitals, i.e., those used to bind the now-missing Cl atom, as well as a result of a significant decrease in Cl$\cdots$Cl repulsions due to the loss of this Cl atom.

(25) D. Babel and W. Rudorff, *Naturwissenschaften*, **51**, 85 (1964).

(26) F. A. Cotton, private communication.