Crystal Structure of Dicaesium Octa-μ_3-chloro-hexachloro-*octahedro*-hexa-tungstate(II) and -molybdate(II) Complexes

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The crystal structures of the title compounds have been determined from single-crystal photographic *X*-ray diffraction data by Patterson and Fourier techniques, and refined by block-diagonal least-squares methods. $Cs_2[(W_6Cl_8)Br_6]$: trigonal, *P*31*c*, *a* = 10·07 ± 0·03, *c* = 14·75 ± 0·01 Å; *Z* = 2; *R* = 0·11 for 665 observed reflections. $Cs_2[(Mo_6Cl_8)Br_6]$: trigonal, *P*31*c*, *a* = 10·06 ± 0·02, *c* = 14·70 ± 0·01 Å, *Z* = 2; *R* 0·12 for 598 observed reflections.

The anion consists of an octahedral cluster of metal atoms with the chlorine atoms bridging the octahedral faces and the bromine atoms axially co-ordinated to the M_6 core. The mean metal–metal distances are W–W 2·620 ± 0·007 and Mo–Mo 2·615 ± 0·006 Å. Other bonding distances are as expected. Implications of the structure concerning the vibrational spectrum are discussed. Cell dimensions are given for the range of isomorphous complexes $Cs_2[(M_6Cl_8)Y_6]$, M = Mo or W; Y = Cl, Br, or I.

THE molybdenum(II) and tungsten(II) halides are based on octahedral clusters of metal atoms with halogen atoms above each of the octahedral faces.[1,2] These formal $(M_6X_8)^{4+}$ units (M = Mo or W; X = Cl, Br, or I) can co-ordinate a further six ligands in the axial positions giving compounds of the type $[(M_6X_8)(\text{ligand})_6]^{x\pm}$.[1,2]

Oxidation of $(W_6Br_8)^{4+}$ with bromine leads[3,4] to $(W_6Br_8)^{6+}$ in which the mean W–W distance (2·64 Å) is almost the same as the Mo–Mo distance (2·61—2·64 Å) in $(Mo_6X_8)^{4+}$.[5-7] In contrast, the two-electron oxidation of the more weakly bound $(Nb_6X_{12})^{2+}$ increases the Nb–Nb distance[8] from 2·92 to 3·016 Å,[9] and decreases the Nb–(axial)Cl distance from 2·60 to 2·48 Å.

The similarity in metal–metal distances of $(Mo_6X_8)^{4+}$ and $(W_6X_8)^{6+}$ could be due either to a decrease in metal–metal bonding resulting from the two-electron

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oxidation compensated by the usual stronger tungsten–tungsten bonding compared with molybdenum–molybdenum bonding[10] (*e.g.* $K_3W_2Cl_9$: W–W 2·41;[11] $Cs_3Mo_2Cl_9$: Mo–Mo 2·66 Å[12]), or to an invariance in all $(M_6X_8)^{x+}$ clusters. Structural parameters for $(W_6Cl_8)^{4+}$ were required to differentiate between these hypotheses.

EXPERIMENTAL

The compounds $Cs_2[(M_6Cl_8)Y_6]$ (M = Mo or W; Y = Cl, Br, or I) were prepared by the method of Cotton *et al.*[13] Debye–Scherrer powder photographs (Philips camera, radius 57·3 mm, nickel-filtered Cu-K_α radiation, λ = 1·5418 Å[14]) showed all salts to be isomorphous, the samples being diluted with starch and containing aluminium powder as internal standard (a = 4·0494 Å).[15] The powder lines were indexed on the basis of a primitive hexagonal cell and the cell parameters refined by a least-squares procedure,[16] with weights $w = \sin\theta$. The lattice parameters and their estimated standard deviations are given in Table 1.

TABLE 1

Hexagonal lattice parameters (Å) for $Cs_2[(M_6Cl_8)Y_6]$

M	Mo		W	
Y	*a*	*c*	*a*	*c*
Cl	9·83(5)	14·31(3)	9·86(2)	14·30(1)
Br	10·06(2)	14·70(1)	10·07(3)	14·75(1)
I	10·33(3)	15·55(3)	10·34(4)	15·53(3)

A single crystal section of each of $Cs_2[(W_6Cl_8)Br_6]$ (I) and $Cs_2[(Mo_6Cl_8)Br_6]$ (II) was cut as a hexagonal prism of height (c) 0·06 mm and section diagonal 0·06 mm. Non-integrated X-ray intensity data were collected by the multiple-film equi-inclination Weissenberg method with each crystal mounted about c and b. The upper-level photographs about c indicated trigonal symmetry; the reciprocal lattice was indexed initially on the basis of the H cell[17] and transformed to a primitive cell. Intensities were estimated visually and corrected for absorption,[18] Lorentz and polarization factors and scaled by internal correlation.[19]

Crystal Data.†—$Cs_2W_6Cl_8Br_6$ ($Cs_2Mo_6Cl_8Br_6$), M = 2132 (1604), Trigonal, a = 10·07 (10·06) ± 0·03, c = 14·75 (14·70) ± 0·01 Å, U 1294 (1283) Å^3, $D_m > 3·3$, $Z = 2$, D_c = 5·47 (4·15), $F(000)$ = 1800 (1416); μ(Cu-K_α radiation) = 903 (661) cm^{-1}; transmission coefficient range 0·029—0·143 (0·050—0·191). 665 (598) independent observed reflections. Space group $P\bar{3}1c$ (C^4_{3v}, No. 159).[20]

Structure Determination.—From the systematic absences, $\{hh2\bar{h}l\}$, $l = 2n + 1$, the possible space groups are $P31c$ (C^4_{3v}, No. 159)[20] or $P\bar{3}1c$ (D^2_{3d}, No. 163).[21] Structure (I) was initially solved in $P\bar{3}1c$, the tungsten co-ordinates being obtained from three-dimensional Patterson syntheses computed on both structures. For (I) calculation of structure factors for the tungsten atoms only gave R 0·39. A Fourier synthesis showed the remaining atoms to be consistent with $P\bar{3}1c$ except for the caesium atoms, located on the $00z$ axis as centrosymmetric pairs with a short interatomic distance of 1·5 Å, suggesting that a false centre of symmetry had been introduced and that $P31c$ was the correct choice.

With isotropic thermal parameters, all atoms were refined by a block-diagonal least-squares process (3 × 3, 6 × 6) (Local program SFLS 1, 2 by A.I.M. Rae) (R 0·155). Anisotropic thermal parameters of the form $\exp[-(h^2\beta_{11} + hk\beta_{12} + hl\beta_{13} + k^2\beta_{22} + kl\beta_{23} + l^2\beta_{33})]$ and a weighting scheme $w = (a + |F_o| + b|F_o|^2)^{-1}$ were introduced, a and b being redetermined as refinement proceeded, the function minimized being $\Sigma w(|F_o| - |F_c|)^2$. No corrections were made for extinction. Refinement terminated with all parameter shifts $< 0·2\sigma$ at R 0·133 and R' 0·154 $\{R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}\}$ with a = 21·0 and b = 0·0118.

TABLE 2

(*a*) Final atomic fractional cell parameters and isotropic thermal parameters; in this and the following Table, those parameters pertaining to the molybdenum derivative are given below the corresponding value for the tungsten analogue. Block-diagonal least-squares estimated standard deviations in the final digit are given in parentheses

Atom	*x*	*y*	*z*	B/Å^2
Cs(1)	1/3	2/3	0·246(2)	*
	1/3	2/3	0·245(1)	*
Cs(2)	0	0	0·034(1)	*
	0	0	0·034(1)	*
W(1)	0·5151(3)	0·3251(3)	0·3201(3)	*
	0·5128(4)	0·3253(4)	0·3202(3)	*
W(2)	0·6565(3)	0·4790(4)	0·1763(3)	*
	0·6578(3)	0·4793(4)	0·1756(3)	*
Br(1)	0·295(1)	0·326(1)	0·411(1)	*
	0·295(1)	0·328(1)	0·412(1)	*
Br(2)	0·631(1)	0·679(1)	0·081(1)	*
	0·628(1)	0·679(1)	0·080(1)	*
Cl(1)	0·369(2)	0·308(2)	0·176(2)	2·7(3)
	0·375(1)	0·314(1)	0·176(1)	2·3(2)
Cl(2)	0·650(2)	0·610(2)	0·318(1)	2·8(4)
	0·653(1)	0·610(1)	0·319(1)	2·4(2)
Cl(3)	2/3	1/3	0·441(3)	3·1(7)
	2/3	1/3	0·488(2)	2·1(3)
Cl(4)	2/3	1/3	0·033(3)	2·4(6)
	2/3	1/3	0·037(2)	2·7(4)

(*b*) * Anisotropic thermal parameters (× 10^4)

Atom	β_{11}	β_{12}	β_{13}	β_{22}	β_{23}	β_{33}
Cs(1)	109(14)	55(7)	0	109(14)	0	121(11)
	109(9)	55(4)	0	109(9)	0	97(7)
Cs(2)	79(10)	39(5)	0	79(10)	0	77(7)
	104(7)	52(4)	0	104(7)	0	79(5)
W(1)	37(3)	35(6)	9(4)	37(4)	3(4)	28(2)
	60(3)	67(6)	10(5)	64(4)	13(4)	22(2)
W(2)	52(4)	57(7)	−10(5)	47(4)	3(4)	30(2)
	72(4)	82(7)	−1(5)	71(4)	11(5)	25(2)
Br(1)	74(10)	125(19)	11(13)	112(12)	−5(13)	55(6)
	98(6)	169(13)	46(9)	150(9)	16(9)	51(5)
Br(2)	85(10)	56(16)	2(13)	62(9)	28(12)	49(5)
	96(6)	79(10)	−2(8)	92(6)	35(7)	39(4)

A final difference Fourier showed no significant peaks. The inverse configuration was refined to convergence at R 0·114,

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† Data for the Mo compound (II) are given in parentheses where they differ from those of the W compound (I).

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TABLE 3

Selected interatomic distances (Å) and angles (°)

(*a*) Distances

(i) Within the anion

W(1$^{\rm I}$)–W(1$^{\rm II}$)	2·626(5) 2·614(6)
W(1$^{\rm I}$)–W(2$^{\rm I}$)	2·600(5) 2·606(7)
W(1$^{\rm I}$)–W(2$^{\rm III}$)	2·617(6) 2·614(7)
W(2$^{\rm I}$)–W(2$^{\rm III}$)	2·632(5) 2·624(5)
Br(1$^{\rm I}$)–Br(1$^{\rm II}$)	6·42(2) 6·44(2)
Br(1$^{\rm I}$)–Br(2$^{\rm I}$)	5·98(2) 5·97(2)
Br(1$^{\rm I}$)–Br(2$^{\rm III}$)	6·24(2) 6·27(2)
Br(2$^{\rm I}$)–Br(2$^{\rm III}$)	6·35(2) 6·38(2)

W(1$^{\rm I}$)–Cl(1$^{\rm I}$)	2·52(2) 2·50(2)
W(1$^{\rm I}$)–Cl(2$^{\rm I}$)	2·48(2) 2·48(1)
W(1$^{\rm I}$)–Cl(2$^{\rm III}$)	2·50(3) 2·47(1)
W(1$^{\rm I}$)–Cl(3$^{\rm I}$)	2·35(3) 2·41(2)
W(2$^{\rm I}$)–Cl(1$^{\rm I}$)	2·52(2) 2·48(1)
W(2$^{\rm I}$)–Cl(2$^{\rm I}$)	2·49(2) 2·49(1)
W(2$^{\rm I}$)–Cl(4$^{\rm I}$)	2·61(3) 2·55(2)
W(2$^{\rm I}$)–Cl(1$^{\rm II}$)	2·46(3) 2·45(1)
W(1$^{\rm I}$)–Br(1$^{\rm I}$)	2·57(1) 2·59(1)
W(2$^{\rm I}$)–Br(2$^{\rm I}$)	2·57(1) 2·58(1)

(ii) Cs environments. [Both Cs atoms and Cl(3) and Cl(4) occupy positions on C_3 symmetry axes. The ' co-ordination ' of the remaining atoms about the Cs is hence three-fold]

Cs(1$^{\rm I}$) · · · Br(1$^{\rm I, VII, XII}$)	4·06(2) 4·06(1)
Cs(1$^{\rm I}$) · · · Br(2$^{\rm I, VII, XII}$)	3·82(2) 3·78(1)
Cs(1$^{\rm I}$) · · · Cl(1$^{\rm I, VII, XII}$)	3·94(2) 3·91(1)
Cs(1$^{\rm I}$) · · · Cl(2$^{\rm I, VII, XII}$)	3·66(3) 3·70(2)
Cs(1$^{\rm I}$) · · · Cl(3$^{\rm IV}$)	4·50(5) 4·36(3)
Cs(1$^{\rm I}$) · · · Cl(4$^{\rm V}$)	4·22(5) 4·29(3)
Cs(2$^{\rm I}$) · · · Br(2$^{\rm III, VI, VII}$)	3·56(1) 3·58(1)
Cs(2$^{\rm I}$) · · · Br(1$^{\rm IV, VIII, IX}$)	3·63(1) 3·62(1)
Cs(2$^{\rm I}$) · · · Cl(1$^{\rm I, X, XI}$)	4·04(1) 4·08(1)

(*b*) Angles

W(1$^{\rm I}$)–W(2$^{\rm I}$)–W(1$^{\rm II}$)	60·4(1) 60·1(2)	W(1$^{\rm II}$)–W(1$^{\rm I}$)–Br(1$^{\rm I}$)	135·7(3) 135·6(3)
W(2$^{\rm I}$)–W(1$^{\rm II}$)–W(1$^{\rm I}$)	59·5(1) 60·1(2)	W(1$^{\rm III}$)–W(1$^{\rm I}$)–Br(1$^{\rm I}$)	139·6(3) 139·6(3)
W(1$^{\rm II}$)–W(1$^{\rm I}$)–W(2$^{\rm I}$)	60·1(1) 60·0(2)	W(2$^{\rm I}$)–W(1$^{\rm I}$)–Br(1$^{\rm I}$)	130·3(3) 130·2(3)
W(2$^{\rm I}$)–W(1$^{\rm I}$)–W(2$^{\rm III}$)	60·6(1) 60·4(2)	W(2$^{\rm III}$)–W(1$^{\rm I}$)–Br(1$^{\rm I}$)	134·1(3) 134·0(3)
W(1$^{\rm I}$)–W(2$^{\rm I}$)–W(2$^{\rm III}$)	60·0(1) 60·0(2)	W(1$^{\rm I}$)–W(2$^{\rm I}$)–Br(2$^{\rm I}$)	132·0(3) 131·0(2)
W(1$^{\rm I}$)–W(2$^{\rm III}$)–W(2$^{\rm I}$)	59·4(1) 59·7(2)	W(1$^{\rm II}$)–W(2$^{\rm I}$)–Br(2$^{\rm I}$)	135·4(3) 135·6(2)
W(2$^{\rm I}$)–W(1$^{\rm I}$)–W(1$^{\rm III}$)	90·3(2) 90·2(2)	W(2$^{\rm II}$)–W(2$^{\rm I}$)–Br(2$^{\rm I}$)	137·8(3) 139·0(3)
W(1$^{\rm II}$)–W(2$^{\rm I}$)–W(2$^{\rm III}$)	89·8(2) 90·0(2)	W(2$^{\rm III}$)–W(2$^{\rm I}$)–Br(2$^{\rm I}$)	134·8(3) 134·3(2)
W(1$^{\rm II}$)–W(1$^{\rm I}$)–W(2$^{\rm III}$)	89·9(2) 90·2(2)		
Cl(1$^{\rm I}$)–W(1$^{\rm I}$)–Cl(2$^{\rm I}$)	92·0(7) 91·6(5)	Cl(1$^{\rm I}$)–W(2$^{\rm I}$)–Cl(1$^{\rm I}$)	92·0(7) 90·0(5)
Cl(1$^{\rm I}$)–W(1$^{\rm I}$)–Cl(3$^{\rm I}$)	172·1(8) 173·4(5)	Cl(1$^{\rm I}$)–W(2$^{\rm I}$)–Cl(1$^{\rm II}$)	176·2(7) 175·7(5)
Cl(1$^{\rm I}$)–W(1$^{\rm I}$)–Cl(2$^{\rm III}$)	88·6(7) 89·5(5)	Cl(1$^{\rm I}$)–W(2)$^{\rm I}$–Cl(4$^{\rm I}$)	88·3(7) 88·6(5)
Cl(2$^{\rm I}$)–W(1$^{\rm I}$)–Cl(3$^{\rm I}$)	89·6(8) 89·1(5)	Cl(2$^{\rm I}$)–W(2$^{\rm I}$)–Cl(1$^{\rm II}$)	90·1(7) 90·0(5)
Cl(2$^{\rm I}$)–W(1$^{\rm I}$)–Cl(2$^{\rm III}$)	176·0(7) 176·1(5)	Cl(2$^{\rm I}$)–W(2$^{\rm I}$)–Cl(4$^{\rm I}$)	177·3(7) 175·9(5)
Cl(2$^{\rm III}$)–W(1$^{\rm I}$)–Cl(3$^{\rm I}$)	89·3(8) 89·1(5)	Cl(1$^{\rm II}$)–W(2$^{\rm I}$)–Cl(4$^{\rm I}$)	89·4(7) 88·6(5)

TABLE 3 (*Continued*)

The roman superscripts in this and the following Table define the transformations of the asymmetric unit given in Table 2 as follows:

I	x, y, z	VII	$y - x, 1 - x, z$
II	$1 + y - x, 1 - x, z$	VIII	$\bar{x}, y - x, z - \frac{1}{2}$
III	$1 - y, x - y, z$	IX	$x - y, \bar{y}, z - \frac{1}{2}$
IV	$y, x, z - \frac{1}{2}$	X	$\bar{y}, x - y, z$
V	$y, x, \frac{1}{2} + z$	XI	$y - x, \bar{x}, z$
VI	$x - 1, y - 1, z$	XII	$1 - y, 1 + x - y, z$

TABLE 4

Equations of best least-squares planes in the form $lX + mY + nZ = p$ (X,Y,Z, being defined in the text) and atomic deviations [(Å)]. The parameters corresponding to the molybdenum derivative are given in parentheses. Roman superscripts are defined in the footnote to Table 3

	l	*m*	*n*	*p*
Plane (I): W(1^{i})			1 (1)	4·722 (4·708)
Cl(2^{i}) −0·03 (−0·02)]				
Plane (II): W(2$^{\rm I}$)			1 (1)	2·600 (2·580)
[Cl(1^{i}) 0·00 (0·01)]				
Plane (III): W(1$^{\rm I}$), W(1$^{\rm II}$), W(2$^{\rm I}$)	−0·509 (−0·500)	0·792 (0·793)	0·338 (0·337)	2·051 (2·042)
[Cl(1$^{\rm I}$) −0·14 (−0·11), Cl(1$^{\rm II}$) −0·01 (−0·05), Cl(3$^{\rm I}$) −0·11 (−0·08)]				
Plane (IV): W(1$^{\rm I}$), W(2$^{\rm I}$), W(2$^{\rm III}$)	0·940 (0·942)	0·055 (0·048)	0·336 (0·333)	5·049 (5·022)
[Cl(2$^{\rm I}$) 0·08 (0·09), Cl(2$^{\rm III}$) 0·05 (0·05), Cl(4$^{\rm I}$) 0·00 (0·03)]				
Plane (V): W(1$^{\rm I}$), Cl(1$^{\rm I}$), Cl(2$^{\rm I}$), Cl(3$^{\rm I}$), Cl(2$^{\rm III}$)	0·805 (0·814)	0·042 (0·034)	−0·591 (−0·580)	0·259 (0·321)
[W(1$^{\rm I}$) −0·10 (−0·09), Cl(1$^{\rm I}$) 0·06 (0·05), Cl(2$^{\rm I}$) 0·01 (−0·01), Cl(2$^{\rm III}$) −0·02 (−0·01), Cl(3$^{\rm I}$) 0·07 (0·05)]				
Plane (VI): W(2$^{\rm I}$), Cl(1$^{\rm I}$), Cl(2$^{\rm I}$), Cl(1$^{\rm II}$), Cl(4$^{\rm I}$)	−0·466 (−0·454)	0·682 (0·687)	−0·564 (−0·567)	−0·625 (−0·571)
[W(2$^{\rm I}$) 0·05 (0·07), Cl(1$^{\rm I}$) −0·02 (−0·01), Cl(2$^{\rm I}$) −0·02 (−0·01), Cl(1$^{\rm II}$) −0·02 (−0·01), Cl(4$^{\rm I}$) −0·01 (−0·02)]				
Plane (VII): W(1$^{\rm I}$) W(1$^{\rm III}$), W(2$^{\rm I}$), W(2$^{\rm II}$), Br(1$^{\rm I}$), Br(1$^{\rm III}$), Br(2$^{\rm I}$), Br(2$^{\rm II}$)	0·369 (0·373)	0·725 (0·725)	0·582 (0·579)	6·094 (6·092)
[W(1$^{\rm I}$) 0·01 (0·00), W(1$^{\rm III}$) −0·01 (0·00), W(2$^{\rm I}$) −0·01 (0·00), W(2$^{\rm II}$) 0·01 (0·00), Br(1$^{\rm I}$) −0·02 (−0·03), Br(1$^{\rm III}$) −0·20 (−0·21), Br(2$^{\rm I}$) 0·03 (−0·04), Br(2$^{\rm II}$) 0·13 (0·18)]				

R' 0·155 and rejected on the basis of a ratio test.[22,23] Refinement of (II) proceeded similarly and terminated at R 0·121 and R' 0·160, with $a = 3{\cdot}79$ and $b = 0{\cdot}066$.

Scattering factors employed were for the zerovalent atoms,[24] corrections for anomalous dispersion being applied to the caesium ($\Delta f'$, $\Delta f''$), tungsten and molybdenum atoms ($\Delta f'$).[25] Observed and calculated structure factors are given in Supplementary Publication No. SUP 20608 (4 pp.,

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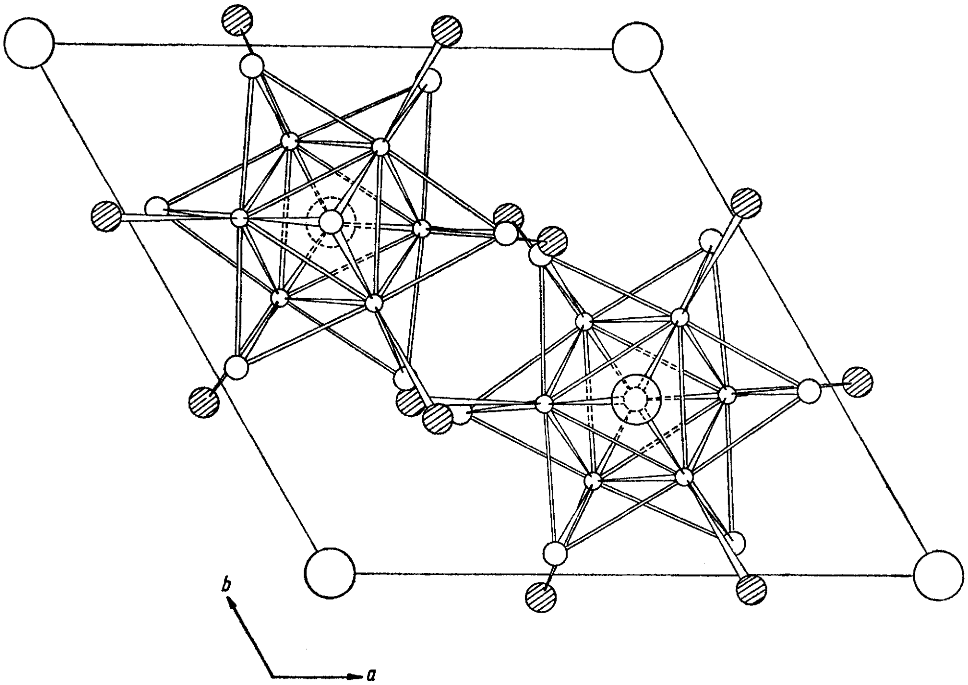

FIGURE 1 Projection of the unit cell on the *ab* plane

1 microfiche).* Final atomic parameters are given in Table 2. Interatomic distances and angles are given in Table 3.[26] Least-squares planes with atomic deviations are given in Table 4, referred to an orthogonal frame (X,Y,Z) Å defined by $X = ax + by \cos\gamma$, $Y = by \sin\gamma$, and $Z = cz$.

The structure is depicted in general view in Figure 1; the atom numbering system is defined in Figure 2.

Computation was carried out on the DEC PDP 10 computer at this University.

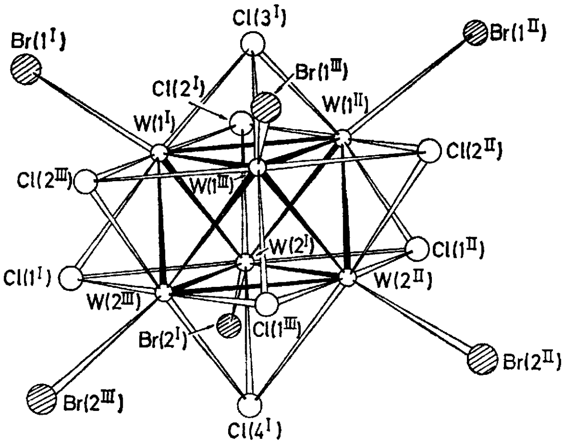

FIGURE 2 A perspective view of the $[(M_6Cl_8)Br_6]^{2-}$ anion with the atomic numbering system

DISCUSSION

Since the two derivatives are closely isostructural, the general discussion of both will be conducted in terms of (I).

The structure consists of hexagonal close-packed layers of $[(W_6Cl_8)Br_6]^{2-}$ anions with the caesium ions located in trigonal holes in the array. The anions occur on crystallographic three-fold axes and are related by the $(1\bar{1}0)$ glide plane. The caesium ions occupy special positions on the three-fold axes (Figure 1).

The stereochemistry of the anion is based on the $(W_6Cl_8)^{4+}$ cluster consisting of an octahedron of tungsten atoms with chlorine atoms bridging each triangular octahedral face. Each metal atom further co-ordinates a bromine in an axial position forming an outer octahedron of bromine atoms (Figure 2).

The four independent W–W bond lengths in the W_6 octahedron range from 2·600 ± 0·005 to 2·632 ± 0·005, mean 2·620 ± 0·007 Å. The molybdenum derivative does not have a significantly different Mo–Mo distance (2·606 ± 0·007 to 2·624 ± 0·005, mean 2·615 ± 0·006 Å). Both are shorter than the distances in the metals (W 2·74, Mo 2·73 Å)[27b] being closely comparable with the Mo–Mo distances of 2·61 in '$(Mo_6Cl_8)Cl_4$'[5] and 2·62 Å in $Hg[(Mo_6Cl_8)Cl_6]$.[6] In $[(Mo_6Br_8)Br_4(H_2O)_2]$, substitution of the inner chlorine atoms by bromine results in slightly longer Mo–Mo distances of 2·63 and 2·64 Å;[7] by analogy $(W_6Br_8)^{4+}$ could reasonably be expected to exhibit the same behaviour. Hence, from a consideration of the W–W distances in the $(W_6Cl_8)^{4+}$ cluster (W–W 2·62 Å) and in the oxidised $(W_6Br_8)^{6+}$ cluster (W–W 2·64 Å)[4] there appears to be no significant weakening of the W–W bonds following a two-electron oxidation of the $(W_6X_8)^{4+}$ cluster.

About each metal atom, the disposition of the chlorine atoms is approximately square planar [planes (V) and (VI) Table 4]; the metal–chlorine distances show a wide variation probably due to the low relative scattering of

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* For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. are sent as full size copies).

[26] M. E. Pippy and F. R. Ahmed, Div. Pure and Appl. Phys., NRC, Ottawa, Canada, Program NRC 12, BONDSCAN.

[27] *Chem. Soc. Special Publ.* (*a*) No. 11, 1958; (*b*) No. 18, 1965.

the chlorine atoms (W–Cl 2·35—2·61, mean 2·49 ± 0·03; Mo–Cl 2·41—2·55, mean 2·48 ± 0·02 Å) but the mean values agree well with those found in ' $(Mo_6Cl_8)Cl_4$ ' (2·47 ± 0·03 Å) [5] and $Hg[(Mo_6Cl_8)Cl_6]$ (2·48 ± 0·02 Å).[6] There are two independent but equal metal–terminal-bromine distances: mean W–Br 2·57 ± 0·01, and mean Mo–Br 2·58 ± 0·01, *cf.* 2·58 ± 0·03 in $[(W_6Br_8)Br_4Br_{4/2}]$ [4] and 2·58 ± 0·002 Å $[(Mo_6Br_8)Br_4(H_2O)_2]$.[7] Here again the two-electron oxidation of the cluster does not appear to affect the strength of the metal–terminal-halide bond.

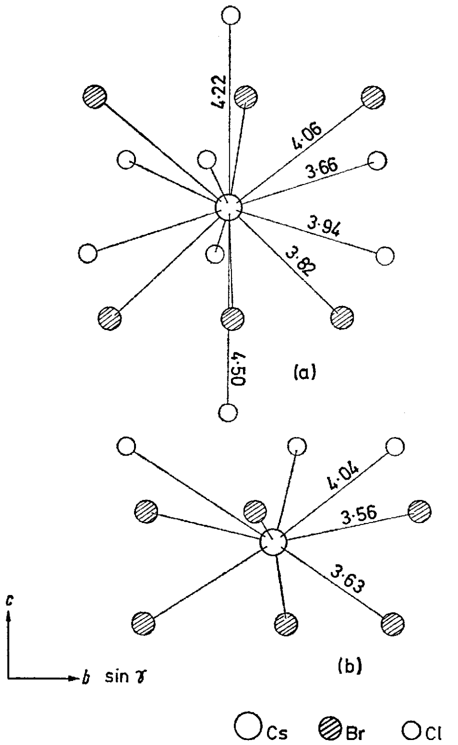

FIGURE 3 ' Co-ordination environment ' of the caesium atoms: (a) Cs(1), and (b) Cs(2)

Consideration of the bromine octahedron reveals a distortion of the cluster, the metal octahedron showing a parallel but much smaller distortion. The overall intrinsic O_h symmetry of the anion is degraded to C_3 in the crystal, there being a contraction in the *c* axial direction and a twist of the two (upper and lower) trigonal faces relative to each other. In projection (Figure 1) the angle at the centre of the trigonal face between $Br(1^{III})$ and $Br(2^{II})$ has opened out to 63·8 ± 0·2° (I) [64·4 ± 0·1° in (II)], as opposed to 60° for the undistorted configuration. [The corresponding distortion in the metal octahedron is 60·6 ± 0·1° in (I) and 60·3 ± 0·2° in (II)]. This spreading of the metal–bromine bonds is caused by interactions of the bromine atoms with one of the caesium atoms [Cs(2)]. This distortion is also observed as a squashing of the octahedron of bromine atoms; for an undistorted octahedron resting on a trigonal face of side *a* and of height *h*, the ratio $r = a/h$ is 1·22. In the bromine octahedron *r* is 1·31 in (I) and 1·32 in (II) [for the metal cluster, it is 1·24 (I), 1·23 (II)].

The ' co-ordination ' of Cs(2) [Figure 3(b)] consists of three bromine contacts at 3·56 Å in (I) [Br(2)] [3·58 Å in (II)], three more at 3·63 Å [3·62 Å in (II)] and three chlorine contacts at 4·04 Å [4·08 Å in (II)]. The caesium–bromine distances are significantly shorter than the distance (3·71 Å) found for caesium bromide.[27a] The other independent caesium atom [Cs(1), Figure 3(a)] has twelve neighbouring atoms at distances of <4·1 Å (Table 3), *cf.* 3·57 (CsCl) and 3·71 Å (CsBr).[27a]

In contrast to the $(Nb_6X_{12})^{2+}$ cluster where changes in bond length of up to 0·12 Å accompany a similar oxidation process, a comparison of the metal–metal and metal–terminal-bromine distances in the reduced and oxidized $(M_6X_8)^{n+}$ clusters reveals no significant structural change. According to the theory of Cotton and Haas,[28] the M.O. energy diagram for $(M_6X_{12})^{2+}$ accommodates all 16 electrons available for metal–metal bonding in bonding orbitals. The removal of two electrons by oxidation weakens the bonding within the cluster leading to increased metal–metal distances. A similar description of the $(M_6X_8)^{4+}$ cluster system [28] accommodates the 24 electrons available for metal–metal bonding in the bonding $A_{1g}(d_{z^2})$, $T_{1u}(d_{xz},d_{yz})$, $T_{1g}(d_{xz},d_{yz})$, and $E_g(d_{x^2-y^2})$ orbitals and the non-bonding $T_{2u}(d_{x^2-y^2})$ orbital, the latter being uppermost although its energy may be slightly lowered by configuration interaction with the antibonding $T_{2u}(d_{xz},d_{yz})$ orbital. This bonding scheme is vindicated by the current result; the two electrons involved in the oxidation process will be removed from the non-bonding level and the effect on the observed bond length should be minimal.

The far-i.r. spectra of a series of $[(W_6X_8)Y_6]^{2-}$ derivatives have recently been reported.[29] In the O_h approximation to the anion, there are 54 normal vibrations; of these only the five T_{1u} species should be i.r.-active, these being assigned as two W–X stretching, one W–W stretching, one W–Y stretching, and one X–W–Y bending (fundamentals). Because of the degradation of the anion symmetry from O_h to C_3 in the present complexes, splitting of these bands should occur, being particularly associated with those modes involving the bromine (Y) atoms. Tentative empirical assignments were made for the vibrational spectra of the $[(W_6X_8)Y_6]^{2-}$ species by the comparison of systematic differences in changing X and Y. For the compounds $A_2[(W_6Cl_8)Y_6]$ (A = Cs or Et_4N; Y = Cl, Br, or I), the band assigned as the W–Y bending mode was split by up to 22 cm^{-1} for (I). From the tabulated frequencies and reproduced spectra of $A_2[(W_6Cl_8)Br_6]$ it is evident that the strong band at 169 cm^{-1} assigned as the W–Br stretching vibration has a distinct shoulder at 158 cm^{-1}. The crystal structure of (I) adds credence to these assignments by demonstrating that these extra bands in the vibrational spectrum may arise from the observed reduction of symmetry of the anion.

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