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Halogen Ordering in Tricaesium Tribromohexachlorodichromate

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Abstract. $Cs_3Cr_2Br_3Cl_6$, $M_r = 955{\cdot}16$, hexagonal, $P6_3/mmc$, $a = 7{\cdot}336\,(1)$, $c = 18{\cdot}181\,(3)$ Å, $V = 847{\cdot}3$ Å^3, $Z = 2$, $D_x = 3{\cdot}74$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}7107$ Å, $\mu = 15{\cdot}5$ mm^{-1}, $F(000) = 840$, room temperature, final $R = 0{\cdot}050$ for 326 independent reflections. The title compound is isostructural with $Cs_3Cr_2Cl_9$. The structure is based on a closest packing of $Cs(Cl,Br)_3$ layers with chromium atoms ordered in octahedral interstices to form isolated pairs of face-shared octahedra, $[Cr_2Br_3Cl_6]^{3-}$. Bromine selectively occupies the terminal halogen positions.

Introduction. Enneahalodimetalates, $A_3M_2X_9$, of the d^3 transition elements Cr,Mo,W have closely related hexagonal structures containing binuclear complex anions $[M_2X_9]^{3-}$ formed by pairs of octahedra sharing a common face. The M–M separation across the shared face varies greatly as a function of M, owing to increasing strength of metal–metal bonding from Cr to Mo to W. The variation in M–M bonding has a strong influence on the energy levels of the binuclear clusters and the resulting effects on the magnetic and spectral properties have been extensively studied as a function of different A cations (alkali elements and substituted ammonium salts) and halogens (Cl, Br and I). However, there are no reported structural studies of mixed-halogen compounds, $A_3M_2X_xY_{9-x}$. The caesium chromium compounds form a suitable system for this type of study because they are readily prepared as single crystals by high-temperature preparative methods, and the structures and properties of the end-member chloride and bromide compounds have been previously characterized (Wessel & IJdo, 1957; Saillant, Jackson, Streib, Folting & Wentworth, 1971; Saillant & Wentworth, 1968; Grey & Smith, 1970; Black, Dunsmuir, Forrest & Lane, 1974). We report here the results of a structure refinement for the mixed-halide complex $Cs_3Cr_2Br_3Cl_6$.

Experimental. $Cs_3Cr_2Br_3Cl_6$ was prepared by reacting together stoichiometric quantities of CsBr and $CrCl_3$ (3:2 molar ratio) in a sealed evacuated silica tube, placed in a furnace with a temperature gradient. The sample was held for 6 d at 1070 K then slowly cooled. The mixed-halide compound formed a zone of dark-blue hexagonal plates and columns at the end of the tube. Analysis by electron microprobe gave (average of five analyses): Cr, 10·6 (1); Cl, 22·0 (2); Br, 25·0(1) wt%; *cf.* theoretical for $Cs_3Cr_2Br_3Cl_6$: Cr, 10·89; Cl, 22·27; Br, 25·10 wt%.

Preliminary X-ray diffraction study with precession method showed crystals had $6/mmm$ Laue symmetry with extinction condition $l = 2n + 1$ for $hh\bar{2h}l$, consistent with $P6_3mc$, $P\bar{6}2c$ and $P6_3/mmc$. Small hexagonal platelet 0·14 mm wide by 0·05 mm thick; Siemen's AED diffractometer. Cell parameters refined using 2θ values for 13 reflections ($19 < \theta < 23°$). θ–2θ scan, scan width $(2{\cdot}4° + \Delta\theta)$, $\Delta\theta = \Delta\lambda/2d \cos\theta$ to allow for α_1/α_2 separation, scan speed $= 0{\cdot}033°\,s^{-1}$. 3174 reflections measured for $h = 0$ to 8, $k = -8$ to 8, $l = -21$ to 21, 2θ 5–50°. One standard reflection measured every 2 h, less than 1·0% intensity variation. Data corrected for absorption, transmission coefficients between 0·17 and 0·50. Reduction and averaging of intensities yielded 326 unique observed reflections with $R_{\rm int} = 0{\cdot}024$. Normalized structure-factor distributions consistent with centrosymmetric structure. Wessel & IJdo's (1957) coordinates for $Cs_3Cr_2Cl_9$ in $P6_3/mmc$ used as starting parameters with both terminal and bridging halogens assigned as Cl. Refinement of coordinates and isotropic thermal parameters converged at $R = 0{\cdot}14$. Temperature factor for terminal halogens negative ($U = -0{\cdot}01$ Å^2), that for bridging halogen normal ($U = +0{\cdot}01$ Å^2). Br atoms then assigned to terminal halogen sites [6Br + 6Cl statistically distributed at 12(k) site]. Refinement on F with all data, anisotropic thermal parameters, converged at $R = 0{\cdot}054$ (unit weights). For comparison, refinement with Br randomly distributed over both terminal and bridging halogen positions converged at $R = 0{\cdot}060$. Population parameters refined for Cl and Br in both terminal and bridging sites, subject to constraints of combined full occupancy of both sites. Refinement of this model converged at $R = 0{\cdot}050$ for

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occupancies of 0·94 (2) Cl + 0·06 Br at bridging site and 0·56 (1) Cl +0·44 Br at terminal site. This model is statistically significant at >99% confidence level (Hamilton, 1965), corresponds to composition $Cs_3Cr_2Br_{2.8(2)}Cl_{6.2(2)}$, which agrees with composition from microprobe data within e.s.d.'s. Refinement also attempted in $P6_3mc$, with Br atoms ordered in terminal sites at one end of binuclear anions, *i.e.* Cl_3–Cr–Cl_3–Cr–Br_3. Refinement of coordinates and isotropic thermal-vibration parameters converged at higher *R* of 0·074 and resulting *U* values for terminal Br and terminal Cl atoms +0·066 and –0·026 Å². This confirms that a statistical distribution of Br atoms over all terminal halogen sites gives best fit to X-ray diffraction data.

In final refinement (*R* = 0·050 above), 21 parameters varied, max. Δ/σ 0·02. Largest peak in final difference map 1·35 e Å^{-3}, near Cs(1). No correction for secondary extinction. Scattering factors for neutral atoms and anomalous-dispersion coefficients from *International Tables for X-ray Crystallography* (1974). Computing carried out with *SHELX*76 (Sheldrick, 1976).

Discussion. Atomic coordinates are given in Table 1.* Selected bond lengths and angles are given in Table 2. A representation of the halogen close-packing, viewed approximately along [11$\bar{2}$0], is shown in Fig. 1. The grouping of the halogens associated with four $[M_2X_9]^{3-}$ complex anions is illustrated. They form closest-packed layers with a six-layer stacking sequence of the type *hcchcc*. In each layer, one anion site in four is occupied by caesium. The two types of caesium sites, associated with the *h* and *c* layers, are shown in Fig. 1. In the *h* layers, Cs(1) is completely encased by 12 halogens from three surrounding $[Cr_2X_9]^{3-}$ units. It bonds to six bridging halogens in the same plane, and to three terminal halogens above and three below. In the *c* layers Cs(2) has cuboctahedral coordination, involving bonds to six terminal and three bridging halogens from three surrounding $[Cr_2X_9]^{3-}$ units and three terminal halogens from a fourth unit, collinear with Cs(2). Whereas Cs(1) is forced by symmetry to be coplanar with its six equatorial halogens, Cs(2) is displaced from the plane of its equatorial halogens, 0·27 Å along [0001] towards the terminal halogens of the collinear $[Cr_2X_9]^{3-}$ complex anion. This results in long bonds from Cs(2) to the three bridging halogens, Cs(2)–X(1) = 3·907 (4) Å.

In Fig. 1 one of the binuclear anions is represented by a ball-and-stick model to show the chromium coordination. As in the end-member chloride and

Table 1. *Atomic coordinates and equivalent isotropic thermal parameters* (Å²) *with e.s.d.'s in parentheses*

$$U_{eq} = \tfrac{1}{3}\,\mathrm{trace}\,\tilde{\mathbf{U}}.$$

	x	*y*	*z*	U_{eq}
Cs(1)	0	0	$\frac{1}{4}$	0·040 (2)
Cs(2)	$\frac{1}{3}$	$\frac{2}{3}$	0·0770 (1)	0·049 (1)
Cr	$\frac{1}{3}$	$\frac{2}{3}$	0·8373 (3)	0·035 (3)
X(1)*	0·5164 (4)	0·0328	$\frac{1}{4}$	0·019 (3)
X(2)*	0·8241 (2)	0·6482	0·0914 (1)	0·030 (2)

* X(1) = 0·94 (2) Cl + 0·06 Br, X(2) = 0·56 (1) Cl + 0·44 Br.

Table 2. *Bond lengths* (Å) *and bond angles* (°) *for* $Cs_3Cr_2Br_3Cl_6$ *with corresponding values for* $Cs_3Cr_2Cl_9$ *and* $Cs_3Cr_2Br_9$ *for comparison*

	$Cs_3Cr_2Br_3Cl_6$	$Cs_3Cr_2Cl_9$*	$Cs_3Cr_2Br_9$†
Bond lengths			
Cr–Cr	3·175 (9)	3·14 (3)	3·32 (2)
Cr–X(1)	2·483 (5)	2·47 (2)	2·577 (9)
Cr–X(2)	2·384 (4)	2·31 (1)	2·417 (6)
X(1)–X(1′)	3·306 (9)	3·31 (4)	3·417 (5)
X(2)–X(2′)	3·465 (5)	3·37 (3)	3·527 (3)
X(1)–X(2)	3·485 (4)	3·41 (1)	
Cs(1)–X(1)	3·674 (1)	3·614 (1)	3·758 (2)
Cs(1)–X(2)	3·648 (3)	3·59 (1)	3·748 (4)
Cs(2)–X(1)	3·912 (4)	3·83 (2)	4·024 (5)
Cs(2)–X(2)	3·680 (1)	3·62 (1)	3·768 (4)
Cs(2)–X(2′)	3·658	3·62 (1)	3·727 (6)
Bond angles			
Cr–X(1)–Cr	79·5 (2)	78·8 (9)	80·1 (4)
X(1)–Cr–X(1′)	83·5 (2)	84·0 (7)	83·0 (3)
X(2)–Cr–X(2′)	93·2 (1)	93·5 (6)	93·7 (3)
X(1)–Cr–X(2)	91·4 (1)	91·1 (6)	91·4 (1)

* From coordinates in Table 3, obtained by refinement of structure-factor data reported by Wessel & IJdo (1957).

† From Saillant *et al.* (1971).

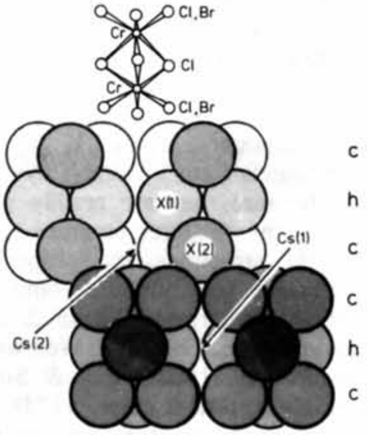

Fig. 1. Packing of anions in $Cs_3Cr_2Br_3Cl_6$ viewed along [11$\bar{2}$0]. Groups of anions are separated slightly to emphasize the $[Cr_2X_9]^{3-}$ complex anions. The Cs(1) and Cs(2) sites in the anion layers are indicated by arrows. The anion layer stacking sequence is shown. One $[Cr_2X_9]^{3-}$ cluster is shown as a ball-and-stick model to illustrate the chromium coordination.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42786 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

bromide complexes, the Cr—*X* bonds to the bridging halogens, 2·48 Å, are considerably longer than those to the terminal halogens, 2·38 Å. The chromium atoms are displaced away from one another across the shared octahedral face, resulting in a Cr—Cr separation of 3·17 Å, *cf.* 2·88 Å for chromium atoms centrally located in the octahedra.

It was of interest to compare the bond lengths in the mixed-halide complex with those for the pure end members. An excellent refinement has been reported for $Cs_3Cr_2Br_9$ (Saillant *et al.*, 1971). However, for $Cs_3Cr_2Cl_9$, the reported atom positions were determined from electron density maps and were not refined, so e.s.d.'s were not given for the interatomic distances (Wessel & IJdo, 1957). We carried out a least-squares refinement of the structure of $Cs_3Cr_2Cl_9$, using the *h*0*l* structure-factor data reported by Wessel & IJdo (1957). Refinement of coordinates and an overall temperature factor converged at $R = 0{\cdot}12$. The final coordinates and e.s.d.'s are given in Table 3. Relevant bond lengths and angles for the chloride and bromide complexes are compared with those for $Cs_3Cr_2Br_3Cl_6$ in Table 2. For the latter compound the bond lengths associated with the bridging halogen, Cr—*X*(1) and *X*(1)—*X*(1), agree closely with the corresponding values for $Cs_3Cr_2Cl_9$, whereas the distances associated with the terminal halogens, Cr—*X*(2) and *X*(2)—*X*(2), are intermediate between the corresponding values for the chloride and bromide complexes. This is consistent with ordering of bromine in the terminal halogen sites as determined from the refinement. The question of whether the bromines are ordered in the three terminal sites at one end of the binuclear anions or statistically distributed over all six terminal sites has not been resolved. As discussed above, refinement of the ordered model in $P6_3mc$ was unsuccessful. However, it is possible that the ordering occurs in microdomains and the X-ray intensity data correspond to an averaged model over all microdomains. The ordered model with three bromine atoms at one end (3–0 configuration) maintains the local threefold symmetry of the binuclear units (C_{3v}) whereas the statistical model includes configurations of the type 2–1 (two bromines at one end and one at the other) and the local threefold symmetry would be lost (highest point symmetry C_s). An analysis of vibrational and electronic spectra has been made to distinguish between these models and the results are consistent with the 3–0 configuration. These studies will be reported elsewhere.

Table 3. *Atomic coordinates for* $Cs_3Cr_2Cl_9$ *from refinement of data of Wessel & IJdo* (1957)

	x	*y*	*z*
Cs(1)	0	0	$\frac{1}{4}$
Cs(2)	$\frac{1}{3}$	$\frac{2}{3}$	0·0773 (3)
Cr	$\frac{1}{3}$	$\frac{2}{3}$	0·8375 (9)
Cl(1)	0·514 (2)	0·028	$\frac{1}{4}$
Cl(2)	0·822 (1)	0·644	0·0928 (5)

References

Black, J. D., Dunsmuir, J. T. R., Forrest, I. W. & Lane, A. P. (1974). *Inorg. Chem.* **14**, 1257–1262.

Grey, I. E. & Smith, P. W. (1970). *Aust. J. Chem.* **24**, 73–81.

Hamilton, W. C. (1965). *Acta Cryst.* **18**, 502–510.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

Saillant, R., Jackson, R. B., Streib, W. E., Folting, K. & Wentworth, R. A. D. (1971). *Inorg. Chem.* **10**, 1453–1457.

Saillant, R. & Wentworth, R. A. D. (1968). *Inorg. Chem.* **7**, 1606–1611.

Sheldrick, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

Wessel, G. J. & IJdo, D. J. W. (1957). *Acta Cryst.* **10**, 466–468.

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Structure of Hexaaquamanganese(II) Tetrabromozincate

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Abstract. $[Mn(H_2O)_6][ZnBr_4]$, $M_r = 548{\cdot}02$, orthorhombic, *Pbam* {Hall symbol $\bar{P}22_{ab}$ [*Acta Cryst.* (1981), A**37**, 517–525]}, $a = 12{\cdot}444\ (3)$, $b = 12{\cdot}952\ (3)$, $c = 8{\cdot}002\ (1)$ Å, $V = 1289{\cdot}7$ Å^3, $Z = 4$, $D_x = 2{\cdot}82$ Mg m^{-3}, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71069$ Å, $\mu = 16{\cdot}04$ mm^{-1}, $F(000) = 1020$, $T = 208$ K, $R = 0{\cdot}052$ for 897 reflections. Prepared from a saturated equimolar aqueous solution of $MnBr_2$ and $ZnBr_2$. The crystal consists of octahedral $Mn(H_2O)_6^{2+}$ [av. Mn—O = 2·18 (1) Å] and tetrahedral $ZnBr_4^{2-}$ [av. Zn—Br = 2·413 (3) Å] ions linked by hydrogen bonds (3·30–3·68 Å).

Introduction. Recent studies of the binary bromides crystallized from saturated solution has highlighted how little is known about the structures of these compounds.

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