Crystal Structures of Two Rhenium(III) Cluster Halides: $Cs_3Re_3Br_{12}$ and $CsRe_3Cl_3Br_7(H_2O)_2$

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Summary Crystal structures, of both $Cs_3Re_3Br_{12}$ and $CsRe_3Cl_3Br_7(H_2O)_2$ are based on anions with Re_3 triangles, the latter compound being the first example of a mixed halide, and the first example containing an anion bearing only a single charge for structures in this class.

CRYSTAL structures are known for at least nine halides or halogeno-anions of rhenium(III) containing units of general formula $(Re_3X_{9+n}L_{3-n})^{n-}$ where X is Cl, Br, or I, and L is a neutral ligand which is sometimes absent. For each one, the structural basis is a triangle of Re atoms linked by formally double bonds. Detailed comparisons have been made of the main structural features,[1,2] and preparative methods and ranges of stability for this whole class of compounds have been summarised.[3]

The preparation of $CsRe_3Cl_3Br_7(H_2O)_2$ from $ReCl_3$, HBr and CsBr has been described by Hickford and Fergusson[4] who incorrectly assigned it the formula $Cs_2Re_3Cl_4Br_7$ on the basis of bulk chemical analysis. The crystals are orthorhombic with $a = 14{\cdot}08(2)$, $b = 15{\cdot}64(2)$, $c = 8{\cdot}60(1)$ Å, $U = 1894$ Å^3, $Z = 4$, $D_c = 4{\cdot}9$, $\mu = 736$ cm.$^{-1}$ for Cu-K_α radiation, space group $Pna2_1$. *X*-Ray intensity data were obtained by visual estimation of integrated equi-inclination Weissenberg photographs of the levels (*hk*0—6) obtained with Cu-K_α radiation. 1755 independent reflections (1706 observed) were used in the structure refinement. Positions of metal and halogen atoms were obtained by standard procedures and the presence of two water molecules associated with each anion was strongly indicated in an electron-density difference map by residual peaks of height appropriate to oxygen atoms. Full-matrix least-squares refinement with all atoms treated isotropically led to $R = 0{\cdot}120$ for all data.

The crystal structure is an assemblage of discrete ions and the anion structure is represented in the Figure. All the bridging atoms are chlorines (in disagreement with the original suggestion[4]) and, of the three in-plane terminal ligands, one is bromine and two are water molecules. The ion can therefore be formulated $Re_3Cl^b_3Br^o_6Br^i(H_2O)^i_2$ where X^b, X^o, and X^i denote bridging, out-of-plane, and terminal in-plane ligands, respectively. The idealised symmetry of the whole anion is C_{2v} and that of the $Re_3Cl_3Br^o_6$ core is D_{3h}. Although there are crystallographically significant departures from these idealised symmetries, we attribute them mainly to intermolecular packing forces.

Crystals of $Cs_3Re_3Br_{12}$ (ref. 5) are orthorhombic, $a = 11{\cdot}17(3)$, $b = 14{\cdot}74(3)$, $c = 14{\cdot}68(1)$ Å, $U = 2418$ Å^3, $Z = 4$, $D_c = 5{\cdot}32$, $\mu = 850$ cm.$^{-1}$ for Cu-K_α radiation. The space group *Ama*2, one of three possibilities from systematic absences, was initially assigned by analogy with the apparently isostructural $Cs_3Re_3Cl_{12}$.[6,7] Intensity data for 1106 reflections (1029 observed) in the levels (0—7*kl*) and (*h*0—2*l*) were obtained as for the mixed halide. Initial atom parameters from $Cs_3Re_3Cl_{12}$ were refined as above to $R = 0{\cdot}092$ for all data. The bromide is confirmed to be isostructural with the chloride and the anion shows no significant departures from its idealised symmetry D_{3h}.

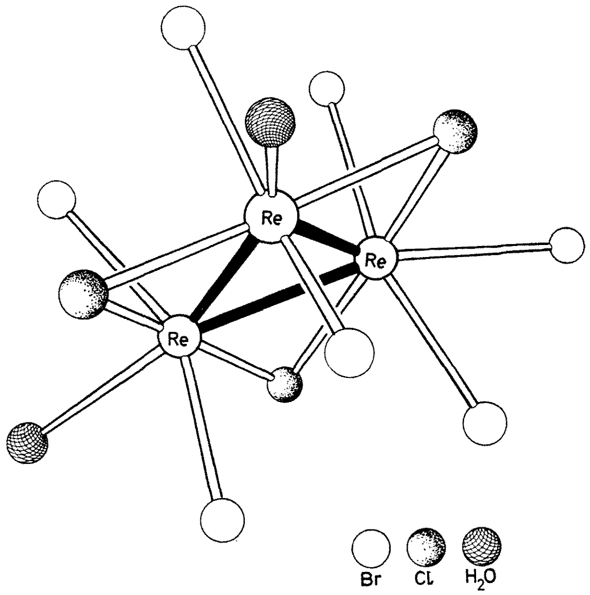

FIGURE. *Structure of the anion* $Re_3Cl_3Br_7(H_2O)_2^-$.

The listed dimensions for the two anions are averaged in terms of their idealised symmetries and we include data for $Cs_3Re_3Cl_{12}$ for comparison with the bromide. The dimensions cannot profitably be discussed in detail because of the relatively high standard deviations in atom positions which are caused (a) by the inadequate (spherical approximation) corrections for high crystal absorption and (b) by the inexact model used for atomic scattering. For Cu-K_α

radiation the imaginary corrections $\Delta f''$ to the scattering factors of Re, Cs, and Br are high but could not be applied because, at the time of data collection, the reflections were not indexed absolutely and Friedel's Law was assumed. It has been shown[8] that neglect of these corrections can lead to large errors in relative positions of atoms in polar space-groups such as in these two structures. From empirical estimates of these errors together with the least-squares estimates of random errors we deduce the following upper limits for standard deviations in individual bond lengths in both compounds. Re–Re, 0·006; Re–Br, 0·02; Re–Cl, 0·03; Re–O, 0·2 Å.

Important observations are possible for the Re–Re bond lengths. In $Re_3Br_{12}^{3-}$ they range from 2·497 to 2·500 Å and in $Re_3Cl_3Br_7(H_2O)_2^-$ from 2·449 to 2·455 Å. Thus, within each compound the bonds are equal to within one standard deviation but the difference of 0·05 Å between the two compounds is highly significant. The shortening observed in the mixed halide is associated with the replacement of in-plane terminal halogens by water molecules and has also been observed[1,2] in $Re_3Cl_{11}(H_2O)^{2-}$ and $Re_3Br_9(H_2O)_3$.

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