Boron Halides as Reagents in Inorganic Syntheses. Part IV.[1] Preparation of Tris-μ-chloro-hexabromo-*triangulo*-trirhenium(III) (3 *Re–Re*) and Re_3I_9; Halogen Exchange Reactions with Re_3Cl_9 and the Crystal Structure of a Sublimation Product of Tris-μ-chloro-hexabromo-*triangulo*-trirhenium-(III) (3 *Re–Re*)

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The interaction of an excess of boron tribromide and rhenium trichloride in the condensed phase affords the new mixed halide $Re_3Br_6Cl_3$, identified by u.v. and far-i.r. spectra. Mass spectra confirm this approximate composition but do not provide a suitable method for characterising a mixed halide $Re_3(Br,Cl)$, because of redistribution equilibria; successive high temperature sublimation of $Re_3Br_6Cl_3$ affords as the most volatile component a compound which progressively approximates to Re_3Cl_9. Repeated sublimation of the mixed halide afforded a crystal suitable for *X*-ray study. This was identified by a complete single-crystal *X*-ray study as probably Re_3Br_8Cl (although the study does not distinguish this from mixtures of Re_3Br_9Cl and $Re_3BrC_6I_3$ or $Re_3Br_7Cl_2$). The structure of these halides is based on the triangular Re_3 systems in which terminal (preferentially) and bridging (subsequently) chloride ligands are replaced by bromide ligands. Interaction of boron tri-iodide and rhenium trichloride affords rhenium tri-iodide.

THE chemistry of metal clusters, and especially of the rhenium halides, has attracted much attention.[2,3] Various methods for preparing the neutral halides Re_3X_9 are available, but yields are never very great;[2]

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[1] Part III, P. M. Druce, M. F. Lappert, and P. N. K. Riley, *J.C.S. Dalton*, 1972, 438.

[2] J. E. Fergusson, *Co-ordination Chem. Rev.*, 1966, **1**, 459.

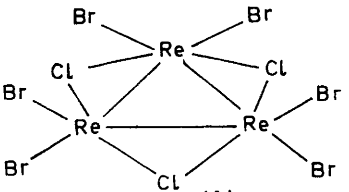
[3] F. A. Cotton, *Quart. Rev.*, 1966, **20**, 389.

their substitution reactions have not previously been examined.

In Part II,[4] we reported a general method for the synthesis of anhydrous bromides and iodides by exchange reactions between anhydrous metal chlorides and boron tribromide or tri-iodide. Here we describe such reactions of rhenium(III) chloride, with a view to determining relative reactivities of bridging and terminal chloride ligands in Re_3Cl_9.

In an attempt to synthesise rhenium(III) bromide, it was found that the interaction of rhenium chloride and an excess of boron tribromide in an evacuated sealed tube, afforded the black mixed halide $Re_3Br_6Cl_3$, in which the chloride ligands are still believed (i.r. and u.v. evidence) to occupy the bridging positions (I). The product sublimed at high temperature, *in vacuo*, and showed the presence of two electronic absorption bands, in the visible and near-i.r. regions ($\lambda_{max.}$ 555 and 745 nm in methanol). The presence of two such bands is a common feature of all compounds containing the triangular rhenium cluster.[5] In 2M-HCl, two absorptions at $\lambda_{max.}$ 519 and 744 nm were observed in an intensity ratio of *ca.* 3 : 1. The change in spectral shifts may be due to the formation of $[Re_3Br_6Cl_6]^{3-}$ in 2M-HCl.

Infrared Spectra.—Far-i.r. absorption maxima (cm^{-1}) were observed as follows: Re_3Cl_9: 378sh, 369sh, 359s, 350sh, 322m, 240—300vw, 220m; Re_3Br_9: 289vw, 264s, 256m, 239s, 213s, 206sh, 180m, 152m, 134w, 118w; $Re_3Br_6Cl_3$: 289m, 276vw, 263m, 252s, 230m, 220vw, 212s, 204sh, 186w, and 151w; $Cs_3Re_3Cl_{12}$: 358s, 352s, 345sh, 336s, 323s, 310sh, 234sh, 226s, 208s, 168m, 144w, and 116w. These data show that $Re_3Br_6Cl_3$ is (i) not a mixture, in appropriate stoicheiometry of the binary halides, and (ii) indicate that the bromide ligands probably occupy terminal positions, in accordance with the proposed structure (I). Thus, we note that the higher energy absorptions of $Re_3Br_6Cl_3$ are broadly similar to those of Re_3Br_9. Furthermore, by analogy with the assignments[6] on $[ReCl_6]^{2-}$ and $[ReBr_6]^{2-}$, it is likely that terminal ReCl and ReBr stretching modes are found between 320 and 380 cm^{-1} and between 220 and 290 cm^{-1}, respectively. No Raman spectra were obtained owing to the deep colour of the compounds.



(I)

Mass Spectra.—Samples were introduced *via* the direct insertion probe and spectra run after ½ h, except in the case of '$Re_3Br_6Cl_3$'. Specimens examined were Re_3Cl_9 and Re_3Br_9 as standards, the sample believed on previous evidence to be $Re_3Br_6Cl_3$, and three successive sublimates of the latter compound. Sublimation conditions were those (*ca.* 360 °C, 10^{-3} mmHg) used to obtain a crystal suitable for *X*-ray analysis.

Mass spectrometry of rhenium(III) halides has previously shown that the vapours of the chlorides and bromides are trimeric;[7] and that heating a mixture of Re_3Cl_9 and Re_3Br_9 at 250—500 °C and then subliming in a mass spectrometer reveals all the mixed species $[Re_3(Br,Cl)_9]^+$.[8,9] Furthermore, sublimation of Re_3Br_9, under *ca.* 2 atm. HCl pressure under transport conditions at 250—500 °C, affords a product approximating to $ReBr_{2\cdot 50}Cl_{0\cdot 43}$.[8]

Our experiments show that (i) the spectrum of Re_3Cl_9 agrees well with that found by Rinke and Schäfer[8,9] and reasonably with that of Büchler *et al.*;[7] (ii) the spectrum of Re_3Br_9 disagrees significantly in the percentages of the major ions: $[Re_3Br_9]^+$, 27·2 (*cf.*[7] 58·9) $[Re_3Br_8]^+$, 9·8 (*cf.*[7] 21·1) $[ReBr_3]^+$, 25·0 (*cf.*[7] 0·9), and $[ReBr_2]^+$, 14·2% (*cf.*[7] 0·1%); (iii) the sample of $Re_3Br_6Cl_3$ was not mass spectrometrically pure, but the most abundant parent ion approximated most closely to $[Re_3Br_6Cl_3]^+$; (iv) successive high-temperature sublimation of the mixed halide leads to more volatile components which are progressively richer in chloride at the expense of bromide. As to (ii), the differences may, in part, be caused by different experimental conditions, but we believe our results to be substantially correct because of repeated measurements and because the percentages of $[ReBr_3]^+$ and $[ReBr_2]^+$ in the various mixed halides are rather similar. It is clear that high-temperature sublimation is not a satisfactory way to purify a mixed $Re_3(Br,Cl)_9$, because of the existence of redistribution equilibria.

Crystal-Structure Analysis.—In order to obtain a crystal good enough for *X*-ray analysis, it was necessary to submit the sample of $Re_3Br_6Cl_3$ to four high-temperature resublimations. The resulting crystals were found to be monoclinic, space-group *C*2/*m*, with $a = 15\cdot 56$, $b = 10\cdot 50$, $c = 9\cdot 37$ Å, $\beta = 116° 50'$, and $Z = 4$. The structure was elucidated by Fourier and full-matrix least-squares refinement methods from the intensities of 528 independent reflections measured from precession data (Mo-K_α radiation) for the layers 0—6 *kl* and *hk* 0—3. The molecule has C_{3v} symmetry within experimental error and has crystallographically required mirror symmetry (see the Figure). Atomic co-ordinates and vibration parameters are given in Table 1 and important bond lengths and angles in Table 2.

Throughout the structure analysis no significant

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[4] Part II, P. M. Druce and M. F. Lappert, *J. Chem. Soc.* (*A*), 1971, 3595.

[5] B. H. Robinson and J. E. Fergusson, *J. Chem. Soc.*, 1964, 5683.

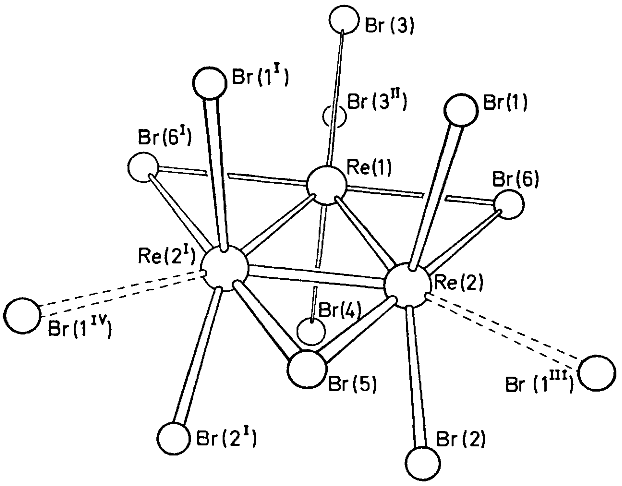
[6] D. M. Adams, J. Chatt, J. M. Davidson, and J. Gerratt, *J. Chem. Soc.*, 1963, 2189; L. A. Woodward and M. J. Ware, *Spectrochim. Acta*, 1964, **20**, 711; D. M. Adams and H. A. Gebbie, *ibid.*, 1963, **19**, 925.

[7] A. Büchler, P. E. Blackburn, and J. L. Stauffer, *J. Phys. Chem.*, 1966, **70**, 685.

[8] K. Rinke, M. Klein, and H. Schäfer, *J. Less-Common Metals*, 1967, **12**, 497.

[9] K. Rinke and H. Schäfer, *Angew. Chem.*, 1965, **77**, 131.

difference between the electron-density maxima representing the halogen atoms could be found, however, and a model based on Re_3Br_9 refined satisfactorily to a discrepancy index $R = 0{\cdot}116$. Moreover, the replacement of bromine by chlorine in this model produced higher R values and unreasonably small (usually negative) isotropic temperature factors for chlorine on further refinement. When occupation numbers were included with the refinement of the positional and isotropic vibration parameters, convergence at $R = 0{\cdot}113$ was obtained and the occupation number of one of the bridging bromine atoms Br(6) was significantly low having the value 74% ± 6%. Since the atomic number of bromine (35) is approximately twice that of chlorine (17), the situation corresponds to a disordered site having 50% occupancy of bromine and 50% of chlorine. Hence, as Br(6) has a symmetry-related position in the molecule, the overall composition of Re_3Br_8Cl is implied. The mass spectrum of the sample from which the crystal data was taken, also indicates that this is the correct formula, and it is therefore apparent that redistribution of the $Re_3Br_6Cl_3$ occurred during the resublimation. It should be noted that Re_3Br_9 has different crystal data [10] from those found here.



The molecular structure of the sublimation product of $Re_3Br_6Cl_3$: the bridging positions are here labelled Br(5) and Br(6), but there is evidence that some bromine–chlorine disorder occurs at these sites

TABLE 1

Atomic co-ordinates and isotropic vibration parameters

Atom	x/a	y/b	z/c	B
Re(1)	0·3537(5)	0·0000(—)	0·3812(8)	1·3(1)
Re(2)	0·2364(3)	0·1167(4)	0·1467(5)	1·1(1)
Br(1)	0·3357(10)	0·1623(12)	−0·0003(17)	2·4(2)
Br(2)	0·1132(9)	0·1597(11)	0·2262(15)	2·4(2)
Br(3)	0·4959(13)	0·0000(—)	0·3239(21)	2·0(3)
Br(4)	0·2751(16)	0·0000(—)	0·5422(26)	3·0(3)
Br(5)	0·1182(21)	0·0000(—)	−0·0998(31)	3·8(4)
Br(6)	0·3572(14)	0·2414(17)	0·3849(24)	3·8(3)

TABLE 2

Bond lengths (Å) and angles

Bonds

Re(1)–Re(2)	2·46(1)	Re(1)–Br(6)	2·54(2)
Re(2)–Re(2)$^{\mathrm{I}}$	2·45(1)	Re(2)–Br(6)	2·54(2)
Re(1)–Br(4)	2·33(3)	Re(2)–Br(5)	2·52(2)
Re(2)–Br(2)	2·39(2)	Re(1)–Br(3)$^{\mathrm{II}}$	2·69(2)
Re(1)–Br(3)	2·50(2)	Re(2)–Br(1)$^{\mathrm{III}}$	2·67(2)
Re(2)–Br(1)	2·53(2)		

Angles

Angle	Mean	Range	Number in range
Re–Re–Re	60·0	59·8(2)—60·1(1)	2
Re–Re–Br(bridging)	61·0	60·9(3)—61·0(5)	3
Re–Br(bridging)–Re	58·1	57·9(5)—58·3(6)	2
Re–Re–Br(terminal)	100·8	100·3(4)—101·0(4)	6
Br(terminal)–Re–Br(terminal)	155·3	154·7(4)—155·9(7)	2
Br(bridging)–Re–Br(terminal)	89·8	88·2(8)—91·3(9)	6

Superscripts refer to the symmetry operations:

None x, y, z
I $x, -y, z$
II $1 - x, y, 1 - z$
III $\frac{1}{2} - x, \frac{1}{2} - y, -z$
IV $\frac{1}{2} - x, y - \frac{1}{2}, -z$

The terminal bromine atoms Br(3), Br(1), and Br(1)^1 on one side of the rhenium triangle are involved in intermolecular bridging and thereby form a polymeric structure in which the rhenium atom interacts with a fifth bromine atom. Similar polymerisation occurs in Re_3Cl_9[11] and Re_3I_9.[12] The molecular parameters agree closely with those established for the Re_3Br_9 moiety in $(QnH)_2Re_4Br_{15}$ (where Qn = quinoline, ref. 13) except for the lengths of the Re–Br(terminal) bonds which form two distinct sets in the present compound because of the intermolecular bonding. It is interesting, however, that the average of these two sets (2·44 Å) is close to the average Re–Br(terminal) distance (2·45 Å) in $(QnH)_2Re_4Br_{15}$ (ref. 13) in which no intermolecular bridging occurs.

Reaction with Boron Tri-iodide.—The reaction of rhenium trichloride with boron tri-iodide afforded different products, depending on reaction conditions. When heated together in an evacuated sealed tube, a 1 : 1 mixture produced a black product, analysing (Cl, I) as $Re_3Cl_6I_3$. The compound was too insoluble in organic solvents for measurement of its u.v. spectrum. It was not examined further.

When rhenium trichloride and a large excess of boron tri-iodide were heated together, a black, microcrystalline solid was obtained which appeared to be (by analysis) Re_3I_9 (containing no chlorine). The compound was insoluble in organic solvents. Far-i.r. absorption maxima (cm^{-1}) were observed as follows: 226m, 188s, 176m, 164m. Absorption in this region would be appropriate for terminal ReI_2 stretching modes of Re_3I_9.

The formulation of the above product as Re_3I_9 is tentative and there is no evidence that it is a triangular cluster compound. However, quite clearly BI_3, unlike BBr_3, is capable of replacing bridging as well as terminal chloride ligands of Re_3Cl_9.

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[10] J. Jelinek and W. Rüdorff, *Naturwiss.*, 1964, **51**, 85; F. A. Cotton, S. J. Lippard, and J. T. Mague, *Inorg. Chem.*, 1965, **4**, 508.

[11] F. A. Cotton and J. T. Mague, *Inorg. Chem.*, 1964, **3**, 1402.

[12] M. J. Bennett, F. A. Cotton, and B. M. Foxman, *Inorg. Chem.*, 1968, **7**, 1563.

[13] F. A. Cotton and S. J. Lippard, *Inorg. Chem.*, 1965, **4**, 59.

Comments on Relative Reactivities of Bridging and Terminal Cl^- *in* Re_3Cl_9.—There has been little success in replacing halide bridges of cluster compounds such as $(Nb_6Cl_{12})^{2+}$, $(Mo_6Cl_6)^{4+}$, or $(Re_3Cl_3)^{6+}$, by other bridging ligands. Chloride exchange work on the trinuclear complex $(Re_3Cl_{12})^{3-}$, has shown that the bridging halides are inactive.[5] The compounds $Re_3Br_6Cl_3$ and Re_3Br_8Cl are the first neutral mixed halides of rhenium. The compound $Cs_3[Re_3Cl_3Br_7](H_2O)_2$ has been prepared from Re_3Cl_9, HBr, and CsBr; its structure is based on an anion with Re_3 triangles.[14] There is mass spectral evidence for some mixed trirhenium nonahalide cations.[7-9] It is interesting, in the present work, that the rhenium clusters should retain their integrity in the Cl–Br exchanges, and it is clear that displacement of chloride is easier in terminal rather than bridging sites. It is possible that an extensive chemistry of rhenium cluster derivatives awaits exploration.

EXPERIMENTAL

All manipulations were carried out *in vacuo*, or in an atmosphere of dry nitrogen. Boron tribromide and boron tri-iodide were purified as described previously.[4] Rhenium(III) chloride [15] and bromide,[16] and caesium tetrachlororhenate(III),[17] were prepared by standard methods.

I.r. spectra (400—80 cm^{-1}) were recorded with an R.I.I.C. Fourier interferometer FS-620, using samples dispersed in polythene discs. U.v. spectra were obtained with a Unicam SP 800 spectrophotometer, and mass spectra with an A.E.I. MS9 spectrometer operating at 70 eV between 160—180 °C. High-temperature sublimations were performed using a Wood's metal bath.

The Reaction of Boron Tribromide with Rhenium(III) *Chloride*.—Boron tribromide (5·6 g, 22 mmol) and rhenium(III) chloride (1·6 g, 2·0 mmol) were heated in an evacuated sealed tube (280—300°, 25 h). Removal of excess boron tribromide and sublimation, (>360°, 0·01 mmHg) of the reaction products afforded a black solid (2·1 g, 90·6%) with analysis corresponding to *hexabromotrichlororhenium*(III) (Found: Br, 41·6; Cl, 9·1. $Br_6Cl_3Re_3$ requires Br, 41·9; Cl, 9·3%).

The Reactions of Boron Tri-iodide with Rhenium(III) *Chloride*.—Boron tri-iodide (0·74 g, 1·9 mmol) and rhenium(III) chloride (0·5 g, 0·6 mmol) were heated in an evacuated sealed tube (200°, 14 h). After removal of excess boron tri-iodide (20°, 0·01 mmHg), the remaining black solid analysed as *hexachlorotri-iodorhenium*(III) (Found: Cl, 18·8; I, 33·2. $Cl_6I_3Re_3$ requires Cl, 18·5; I, 33·0%).

Boron tri-iodide (3·2 g, 8·2 mmol) in a large excess, and rhenium(III) chloride (1·02 g, 1·3 mmol), when similarly treated (310°, 28 h), yielded a black solid (1·4 g), analysing as Re_3I_9 (Found: Cl, 0·0; I, 66·1. Calc. for I_9Re_3: I, 67·2%).

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[15] W. Biltz, W. Geilmann, and F. W. Wrigge, *Annalen*, 1934, **511**, 301.

[16] R. J. Thompson, R. E. Foster, and J. L. Booker, *Inorg. Synth.*, 1967, **10**, 58.

[17] W. Geilmann and F. W. Wrigge, *Z. anorg. Chem.*, 1935, **223**, 144.