1089. *Polynuclear Halogeno-anions of Tervalent Rhenium.*

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The tervalent rhenium halogeno-anions $[Re_3Cl_{12}]^{3-}$, $[Re_3Cl_{11}]^{2-}$, $[Re_3Br_{12}]^{3-}$, $[Re_3Br_{11}]^{2-}$, and $[Re_3Br_{10}]^-$ have been prepared and studied.

THE range of transition-metal polynuclear halogeno-complexes is limited to those of niobium, tantalum, molybdenum, tungsten, and rhenium. The most recently discovered are those of tervalent rhenium. The chloro-anion obtained by dissolving rhenium trichloride in hydrochloric acid was considered[1] to be $[ReCl_4]^-$ but is now shown to be $[Re_3Cl_{12}]^{3-}$, containing a triangle of strongly bonded rhenium atoms.[2] Further structural work has confirmed the existence of the anions $[Re_3Cl_{11}]^{2-}$,[3] and $[Re_3Br_{11}]^{2-}$.[4]

The work to be described in this paper concerns the preparation and study of the chloro- and bromo-anions of rhenium(III) in order to eludicate the conditions under which the various anions form.

By varying the cation in the compounds, the following anions have been obtained from acid solution; $[Re_3Cl_{12}]^{3-}$, $[Re_3Cl_{11}]^{2-}$, $[Re_3Br_{12}]^{3-}$, $[Re_3Br_{11}]^{2-}$, $[Re_3Br_{10}]^-$, $[Re_3Cl_3(CNS)_9]^{3-}$, and $[Re_3Cl_3(CNS)_8]^{2-}$. Table 1 lists the compounds and their properties.

The predominant tendency of bromine to form the anion $[Re_3Br_{10}]^-$ is probably related to the steric strain in the anion $[Re_3Br_{12}]^{3-}$; the latter, as the cæsium salt, is isomorphous with the corresponding chloro-compound.[4] The anion $[Re_3Cl_{12}]^{3-}$ shows evidence of this strain, both in the long terminal in-plane Re–Cl bond distance, and in the splayed-out arrangement of the two groups of three out-of-plane chlorines.[2] This strain is somewhat relieved in the anion $[Re_3Cl_{11}]^{2-}$,[3] and even more so in $[Re_3Br_{11}]^{2-}$.[4] The strain in the bromo-compounds will be greater than in the chloro-anions, as seen from a comparison of the van der Waals radii of chlorine (1·80 Å) and bromine (1·95 Å).

[1] Orgel, "Quelques Prob. de Chemie Minerale," 10th Solvay Conf., 1956, 289.
[2] Robinson, Fergusson, and Penfold, *Proc. Chem. Soc.*, 1963, 116; Bertrand, Cotton, and Dollase, *Inorg. Chem.*, 1963, **2**, 1166.
[3] Fergusson, Penfold, and Robinson, *Nature*, 1964, **201**, 181.
[4] Elder and Penfold, *Nature*, 1965, **205**, 276.

TABLE 1.

Anion	Cation	Molar conductivity at 25°* (ohm⁻¹ cm.² mole⁻¹ M) $c = 1 \times 10^{-3}$ M	Mol. wt.* Obs.	Calc.	Absorption spectra Solid (λ in mμ)		Solution λ (mμ)	ε	λ (mμ)	ε	λ (mμ)	ε
$[Re_3Cl_{12}]^{3-}$	$[Coen_3]^{3+}$	195 (1)	insoluble		515	790	515	1840	750	565 (1)		
	$[Ph_3MeAs]^+$	59·7 (2)	430 (5)	1947	530	780	515	1340	750	480 (5)		
	$[Ph_3PH]^+$	72 (2)	400 (5)	1776	530	790	515	1430	750	570 (5)		
	$[Me_4N]^+$	unstable in solution			530	750	unstable in solution					
	$[Et_4N]^+$	61·3 (2)	insoluble		530	760	540	1290	780	460 (2)		
	Cs^+	insol.	insoluble		530	780	515	1284	750	348 (7)		
$[Re_3Cl_{11}]^{2-}$	$[bipyH]^+$	63·4 (2)	insoluble		520	770	515	1710	750	480 (2)		
	$[Ph_4As]^+$	149 (3)	470 (5)	1715	530	780	510	1630	750	590 (5)		
	$[Ph_3benzylP]^+$	115·7 (1)	insoluble		530	790	512	1480	775	590 (1)		
	$[o\text{-}phenH]^+$	125·5 (4)	insoluble		520(sh)	770	513	1670	765	522 (4)		
$[Re_3Br_{12}]^{3-}$	$[Coen_3]^{3+}$	insol.	insoluble		490, 570	750, 770	insoluble*					
	Cs^+	insol.	insoluble		550	780	525	1740	760	550 (6)		
	Rb^+	insol.	insoluble		550	790	530	1820	760	570 (6)		
	Cs^+	insol.	insoluble		550	780	530	1800	760	570 (6)		
$[Re_3Br_{11}]^{2-}$	$[Ph_3PH]^+$	17·4 (2)	850 (5)	1622	550	810	530	1710	750	590 (5)		
$[Re_3Br_{10}]^-$	$[Ph_4As]^+$	17·1 (2)	860 (5)	1741	540	750	540	1850	850	540 (5)		
	$[Ph_3benzylP]^+$	19·6 (2)	864 (5)	1712	550	760	550	1670	770	530 (5)		
	$[Ph_3EtP]^+$	18·3 (2)	—		550	790	540	1680	790	570 (5)		
	$[Ph_3MeAs]^+$	55·0 (2)	unstable in suitable solvent		425, 615	950	620	2784	975	850 (5)		
$[Re_3Cl_3(CNS)_9]^{3-}$	$[Ph_4As]^+$	38·5 (2)	unstable in suitable solvent		430, 610	950	610	2340	965	700 (5)		
$[Re_3Cl_3(CNS)_8]^{2-}$	Re_3Cl_9	1·3 (2)	—		500	750	513	1334	750	513 (7)		
	Re_3Br_9	1·45 (2)	—		550	820	530	1700	740	490 (6)		

Solvents: (1) dimethylformamide, (2) nitrobenzene, (3) nitromethane, (4) dimethyl sulphoxide, (5) acetone, (6) hydrobromic acid, (7) hydrochloric acid.
* Insoluble indicated where no satisfactory solvent could be found.

Table 2 lists the estimated cation volumes. It is evident that the larger the cation the more likely is it to find less halogens in the anion. It appears therefore that crystal-packing requirements of anions and cations can influence the type of compound formed.

TABLE 2.

Cation	Effective volume (Å^3)	Cation	Effective volume (Å^3)
Rb^+	14	Ph_3EtP^+	480
Cs^+	21	$bipyH^+$	490
Me_4N^+	62	$o\text{-phenH}^+$	720
Et_4N^+	256	Ph_4As^+	840
Ph_3PH^+	400	$Ph_3benzylP^+$	860
Ph_3MeAs^+	460		

Attempts to prepare bromo-anions of the tetramethyl- and tetraethyl-ammonium cations gave intractable tars. Also, the very large cation benzyltribiphenylarsonium did not form a compound.

Radiochlorine exchange experiments on the anion $[Re_3Cl_{12}]^{3-}$ indicate a rapid exchange of three chlorines (terminal, in-plane), and a slower exchange of six others (terminal, out-of-plane). Similar results are obtained by studying the addition of thiocyanate to rhenium trichloride. The lability of nine of the twelve chlorine atoms suggests that the basic unit in the chloro-compounds is Re_3Cl_3. The same basic unit appears probable for the bromo-compounds and is confirmed by the close similarity of two bands in the visible and near-infrared spectra of the chloro- and bromo-anions. The bands, chloro- (515—530, 750—790 mμ), bromo- (540—570, 750—810 mμ), and thiocyanato- (610—615, 950 mμ), also have comparable molar extinction coefficients 1200—1800 and 400—600 (3:1). In addition, the two compounds $Cs_3Re_3Cl_{12}$ and $Cs_3Re_3Br_{12}$ are isomorphous, having identical X-ray powder photographs, and the two compounds Re_3Cl_9 $(Ph_3P)_3$ and $Re_3Br_9(Ph_3P)_3$ (see below) are also isomorphous.

A number of adducts of the trihalides of rhenium have been prepared. Monodentate ligands, pyridine and triphenylphosphine, give complexes $Re_3Cl_9L_3$. Bidentate ligands, acetylacetone and dithiocarbamate,[5] give $Re_3Cl_6(L)_3$. On the basis of absorption spectra these compounds can be formulated as trinuclear structures. Table 3 lists the experimental data. Substitution of the terminal halogens by the organic ligands does not change the broad features of the spectra, indicating that the same basic unit is present. Small changes of the bands from one compound to the next cannot be commented on until a more detailed spectral investigation is carried out. The low molecular-weight values for the complexes must indicate

TABLE 3.

Complex	Λ_M (25°) (ohm^{-1} mole^{-1} cm.^{2}) $c = 1 \times 10^{-3}M$	Mol. wt. Obs.	Mol. wt. Calc.	Solid		Absorption spectra (λ in mμ, ε in parentheses) Solution			
$Re_3Cl_9(PPh_3)_3$	6·8(1)	425(4)	1665	530	750	516 (1698)	755	(654)(4)
$Re_3Cl_6(acac)_3$	3·9(2)	780(4)	1071	530	770	535 (1780)	825	(540)(4)
$Re_3Cl_6(dithiocarbamate)_3$	1·7(2)	monomer[5]		510	770	500sh(1550)	835	(680)(4)
$Re_2Cl_4(2,2'\text{-bipyridyl})$ [6]	62·3(3)*	—		530	910	515 (1640)	820	(530)(4)
$Re_2Cl_4(o\text{-phen})$ [6]	59·0(2)*	—		530	870	520 (1780)	810	(610)(4)
$Re_3Cl_3(SCN)_3(dithiocarb.)_3$	3·8(2)	532(5)	1282	540	820	500 (1800)	815	(450)(5)
$Re_3Br_9(PPh_3)_3$	9·4(2)*	†		570	850	550 (1950)	800	(590)(2)
$Re_3Br_9(py)_3$	1·5(2)	†		620	850	550 (1610)	860	(520)(2)
$Re_3Br_6(dithiocarbamate)_3$	2·0(2)	474(5)	1482			not obs.	770	(810)(5)
$Re_2Br_4(o\text{-phen})$	insol.	insol.		550	900	insoluble		
$[Ph_4As]_2[Re_3Cl_{11}PPh_3]$	44·6(2)	520(4)	1997	520	750	515 (1730)	750	(600)(4)
$[Ph_3benzylP][Re_3Br_{10}(py)_2]$	23·1(2)	—	—	550	790br	540 (1910)	810br	(590)(4)
$[Ph_3PH][Re_3Br_{10}(py)_2]$	20·2(2)	860(4)	1780	550	770br	540 (1870)	790	(580)(4)

Solvents: (1) nitromethane, (2) nitrobenzene, (3) dimethylformamide, (4) acetone, (5) chloroform.
* Unstable. † Unstable in solution.

[5] Colton, Levitus, and Wilkinson, *J.*, 1960, 5275.

considerable dissociation in solution. However, this does not affect the spectral features in solution.

The complexes Re_2Cl_4–o-phenanthroline and Re_2Cl_4–2,2'-bipyridyl described[6] as containing mixed valency states of rhenium (I and III) have the same absorption spectra as the trinuclear complexes. It appears, therefore, that the tervalent rhenium in the compounds is trinuclear. Further supporting evidence is the isolation of (o-phenH]$_2$Re$_3$Cl$_{11}$ and [bipyH]$_3$Re$_3$Cl$_{12}$ from the complexes when treated with acid.

The salts [cation]Re$_3$Br$_{10}$ can be converted into [cation]Re$_3$Br$_{10}$L$_2$ with pyridine. Presumably, on crystallisation, the crystals can cope with two extra neutral ligands in the eleventh and twelfth positions around the rhenium triangle. However, the infrared spectra of all the compounds, obtained from aqueous or ethanolic acid, did not show bands characteristic of associated solvent molecules. The complexes containing inorganic cations had spectral traces in the 2·5—15 μ range virtually as straight lines. Further evidence for the absence of solvent molecules comes from the crystal structure study of the Re$_3$Br$_{11}$$^{2-}$ anion.[4]

The work described above shows clearly that a wide variety of anions can form, that there is changing co-ordination environment of certain rhenium atoms in the triangle, and that the basic unit in all these complexes is Re$_3$X$_3$ with the halogens probably bridging.

The first two points indicate the considerable effect of both steric and crystal-packing interactions in determining the composition and structures of the anions. The third point is dependent on the short and hence strong Re–Re bonds in the triangle. Two of the bonds become even shorter in the Re$_3$Br$_{11}$$^{2-}$ anion where some strain has been relieved.[4] The bridging halogens in Re$_3$X$_3$, and also in the [Mo$_6$Cl$_8$]$^{4+}$ cage structure of molybdenum dichloride, are forced to form bridging angles of 60° (bridging angle in Fe$_2$Cl$_6$ is 98°).[7] This severe bond-angle deformation again points to the strong bonding in the metal–metal clusters.

EXPERIMENTAL

Rhenium trichloride[8] was prepared by thermal decomposition of silver rhenichloride in a high vacuum at 300° (Found: Cl, 36·0; Re, 63·9. Calc. for ReCl$_3$: Cl, 36·25; Re, 63·75%). Rhenium tribromide[9] was prepared similarly from silver rhenibromide (Found: Br, 56·7; Re, 43·1. Calc. for ReBr$_3$: Br, 56·35; Re, 43·65%).

Dimethylformamide was dried over phosphorus pentoxide and fractionally distilled in a high vacuum. Nitrobenzene was dried over molecular sieves and used without further treatment. Nitromethane was initially dried over phosphorus pentoxide and finally with alumina and distilled. Dimethyl sulphoxide was dried over molecular sieves and fractionally distilled. Acetone was dried over anhydrous calcium sulphate and fractionally distilled.

The cations, cæsium, rubidium, tetramethyl- and tetraethyl-ammonium, and tetraphenyl-arsonium, as halide salts, were obtained as commercial reagents and used after recrystallisation. Cobalt trisethylenediamine halides were prepared by the method of Work.[10] Benzyltriphenyl-phosphonium chloride was prepared according to Arksnes and Songsted,[11] and ethyltriphenyl-arsonium bromide according to Michaelis.[12] Ethyltriphenylphosphonium bromide was prepared from the reaction of triphenylphosphine with ethyl bromide.[13] The cations o-phenanthrolinium, 1,1'-bipyridylium, and triphenylphosphonium were obtained by dissolving the parent substance in the required halogen acid. Benzyltrisbiphenylarsonium iodide was obtained by treating trisbiphenylarsine with benzyl iodide for 24 hr. under reflux. The white crystals of the iodide were converted into the *chloride* by boiling with silver chloride (Found: C, 78·4; H, 5·1. C$_{43}$H$_{34}$AsCl requires C, 78·2; H, 5·15%).

Preparation of Trinuclear Rhenium Chloro- and Bromo-salts.—A slight molar excess of the cation halide dissolved in ethanol or the appropriate halogen acid was added to the trihalide

    [6] Colton, Levitus, and Wilkinson, *J.*, 1960, 4121.
    [7] Hassel and Viervoll, *Tidsskr. Kjemi Bergvesen Met.*, 1943, **3**, 97.
    [8] Biltz, Geilmann, and Wrigge, *Annalen*, 1934, **511**, 301.
    [9] Klemm and Schüth, *Z. anorg. Chem.*, 1934, **220**, 193.
   [10] Work, *Inorg. Synth.*, **2**, 221.
   [11] Arksnes and Songsted, *Acta Chem. Scand.*, 1962, **16**, 1426.
   [12] Michaelis, *Annalen*, 1902, **321**, 166.
   [13] Deacon, Jones, and Rogasch, *Austral. J. Chem.*, 1963, **16**, 360.

dissolved in aqueous or ethanolic halogen acid. In general the rhenium salt precipitated out of solution quantitatively, but occasionally concentration of the solution was necessary.

Tris(ethylenediamine)cobalt(III) *tri-μ-chloro-nonachlorotrirhenate*(III) crystallised from 5M-hydrochloric acid (Found: C, 6·4; H, 2·8; Cl, 34·75; Re, 45·4. $C_6H_{24}Cl_{12}CoN_6Re_3$ requires C, 5·9; H, 2·0; Cl, 34·8; Re, 45·6%).

Tris(methyltriphenylarsonium) tri-μ-chloro-nonachlorotrirhenate(III) crystallised from acetone as purple-red plates (Found: C, 35·6; H, 3·4; Cl, 21·6; Re, 28·8. $C_{57}H_{54}As_3Cl_{12}Re_3$ requires C, 35·1; H, 2·8; Cl, 21·85; Re, 28·6%).

Tris(tetramethylammonium) tri-μ-chloro-nonachlorotrirhenate(III) occurs as a hygroscopic powder when recrystallised from hydrochloric acid (Found: C, 12·6; H, 4·75; Cl, 35·0; Re, 45·8. $C_{12}H_{36}Cl_{12}N_3Re_3$ requires C, 11·95; H, 3·0; Cl, 35·35; Re, 46·3%).

Tris(tetraethylammonium) tri-μ-chloro-nonachlorotrirhenate(III) was obtained from hydrochloric acid as red hygroscopic needles (Found: Cl, 30·3; Re, 40·4. $C_{24}H_{60}Cl_{12}N_3Re_3$ requires Cl, 31·0; Re, 40·6%).

Tris(triphenylphosphonium) tri-μ-chloro-nonachlorotrirhenate(III) crystallised from ethanol (Found: C, 36·1; H, 3·3; Cl, 23·6; Re, 31·3. $C_{54}H_{48}P_3Cl_{12}Re_3$ requires C, 36·5; H, 2·6; Cl, 24·0; Re, 31·45%).

Tris-(2,2′-bipyridylium) tri-μ-chloro-nonachlorotrirhenate(III) crystallised from acetone (Found: C, 24·7; H, 2·3; Re, 38·4. $C_{30}H_{27}Cl_{12}N_6Re_3$ requires C, 24·75; H, 1·85; Re, 38·4%).

Bis(benzyltriphenylphosphonium) tri-μ-chloro-octachlorotrirhenate(III) was prepared from hydrochloric acid–acetone (1:1) mixture and recrystallised from hot ethanol (Found: C, 36·8; H, 3·9; Cl, 23·15; Re, 33·8. $C_{50}H_{44}Cl_{11}P_2Re_3$ requires C, 36·25; H, 2·7; Cl, 23·55; Re, 33·7%).

Bis-(o-phenanthrolinium) tri-μ-chloro-octachlorotrirhenate(III) (Found: C, 22·85; H, 2·45; Cl, 29·5; Re, 42·5. $C_{24}H_{18}Cl_{11}N_4Re_3$ requires C, 22·0; H, 1·4; Cl, 29·8; Re, 42·6%).

Bis(tetraphenylarsonium) tri-μ-chloro-octachlorotrirhenate(III) crystallised from acidic ethanol (Found: C, 33·8; H, 2·3; Cl, 23·2; Re, 31·6. $C_{48}H_{40}As_2Cl_{11}Re_3$ requires C, 33·6; H, 2·3; Cl, 22·8; Re, 32·6%).

Tris(ethylenediamine)cobalt(III) *tri-μ-bromo-nonabromotrirhenate*(III) was prepared from hydrobromic acid and ethanol (10:1) (Found: C, 4·4; H, 1·9; Br, 56·4; Re, 31·05. $C_6H_{24}Br_{12}CoN_6Re_3$ requires C, 4·1; H, 1·4; Br, 54·7; Re, 31·75%).

Trisrubidium tri-μ-bromo-nonabromotrirhenate(III) crystallised from hydrobromic acid (Found: Br, 54·5; Rb, 16·3; Re, 31·4. $Rb_3Br_{12}Re_3$ requires Br, 54·1; Rb, 14·4; Re, 31·5%).

Triscæsium tri-μ-bromo-nonabromotrirhenate(III). The initial precipitate analysed close to the composition $CsRe_3Br_{10}$ but after washing with concentrated hydrobromic acid a purer sample was obtained (Found: Br, 51·2; Re, 31·8. $Cs_3Br_{12}Re_3$ requires Br, 50·2; Re, 29·2%).

Biscæsium tri-μ-bromo-octabromotrirhenate(III) crystallised from hydrobromic acid (Found: Br, 51·7; Cs, 15·0; Re, 32·4. $Cs_2Br_{11}Re_3$ requires Br, 51·6; Cs, 15·6; Re, 32·8%).

Tetraphenylarsonium tri-μ-bromo-heptabromotrirhenate(III) crystallised from ethanolic hydrobromic acid (4:1) (Found: C, 17·0; H, 1·85; Br, 46·9; Re, 31·75. $C_{24}H_{20}AsBr_{10}Re_3$ requires C, 16·5; H, 1·15; Br, 45·9; Re, 32·0%).

Triphenylphosphonium tri-μ-bromo-heptabromotrirhenate(III) was obtained from 4:1 ethanol–hydrobromic acid (Found: C, 13·35; H, 1·35; Br, 48·5; Re, 34·25. $C_{18}H_{16}Br_{10}PRe_3$ requires C, 13·3; H, 1·1; Br, 49·3; Re, 34·4%).

Ethyltriphenylphosphonium tri-μ-bromo-heptabromotrirhenate(III) (Found: C, 14·2; H, 1·9; Br, 47·8; Re, 33·4. $C_{20}H_{20}Br_{10}PRe_3$ requires C, 14·5; H, 1·2; Br, 48·45; Re, 33·8%).

Benzyltriphenylphosphonium tri-μ-bromo-heptabromotrirhenate(III) was obtained as a red-brown powder (Found: C, 17·65; H, 1·8; Br, 46·15; Re, 32·0. $C_{25}H_{22}Br_{10}PRe_3$ requires C, 17·45; H, 1·3; Br, 46·7; Re, 32·55%).

Bis(tetraphenylarsonium) tri-μ-chloro-octachloro(triphenylphosphine)trirhenate(III). The complex salt $[Ph_4As]_2Re_3Cl_{11}$ was recrystallised from acetone containing one mole of triphenyl-phosphine. A second recrystallisation was carried out without further phosphine present. (Found: C, 40·3; H, 4·0; Cl, 19·05; Re, 27·9. $C_{66}H_{55}As_2Cl_{11}PRe_3$ requires C, 40·1; H, 3·3; Cl, 19·75; Re, 28·2%).

Triphenylphosphonium tri-μ-bromo-heptabromobis(pyridine)trirhenate(III). One mole of the complex $[Ph_3PH]Re_3Br_{10}$ was dissolved in acetone to which was added two moles of pyridine. The solution was evaporated to dryness *in vacuo*, leaving brown plates which were washed with ethanol and ether, and dried (Found: C, 17·8; H, 2·1; Br, 44·8; Re, 31·2. $C_{28}H_{26}Br_{10}N_2PRe_3$ requires C, 18·8; H, 1·4; Br, 44·9; Re, 31·3%).

Benzyltriphenylphosphonium tri-μ-bromo-heptabromobis(pyridine)trirhenate(III). The same procedure as above was used (Found: C, 22·3; H, 2·45; Br, 42·4; Re, 30·0. $C_{35}H_{32}Br_{10}N_2PRe_3$ requires C, 22·55; H, 1·7; Br, 42·85; Re, 29·85%).

Tris(methyltriphenylarsonium) tri-μ-chloro-nonathiocyanatotrirhenate(III), prepared as for the chloro- and bromo-salts, using thiocyanic acid and rhenium trichloride, was obtained as a dark brown-green powder (Found: C, 36·5; H, 2·9; Re, 26·3; S, 12·6. $C_{66}H_{54}As_3Cl_3N_9Re_3S_9$ requires C, 36·9; H, 2·5; Re, 26·0; S, 13·4%).

Bis(tetraphenylarsonium) tri-μ-chloro-octathiocyanatotrirhenate(III) was obtained as a yellow-green powder (Found: C, 35·4; H, 2·9; Re, 29·8; S, 13·0. $C_{56}H_{40}As_2Cl_3N_8Re_3S_8$ requires C, 35·5; H, 2·2; Re, 29·45; S, 13·55%).

The two compounds $[Ph_3MeAs]_3Re_3Cl_3(CNS)_9$ and $[Ph_4As]_2Re_3Cl_3(CNS)_8$ react with further thiocyanate when heated under reflux, to give products which do not contain halogen. The same products are obtained from treating rhenium tribromide with thiocyanate. The compounds analysed closely to (cation)$_3$Re$_3$(CNS)$_{12}$ (*e.g.*, Found: C, 37·0; H, 3·4; Re, 25·3; S, 17·6. Calc. for $C_{69}H_{54}As_3N_{12}Re_3S_{12}$: C, 37·3; H, 2·4; Re, 25·1; S, 17·3%). The spectral bands in the visible and near infrared were somewhat similar to those for the trinuclear halogeno-species, and the compounds were 3:1 electrolytes in nitrobenzene {56·4 ohm^{-1} mole^{-1} cm.^{2} for $[Ph_3MeAs]_3Re_3(CNS)_{12}$}. This suggests that the trinuclear species extends to the fully substituted compound with thiocyanate, if indeed the compounds still contain tervalent rhenium. This point was not pursued further.

Spectrophotometric titration of thiocyanate complexes. The addition of thiocyanic acid (0·038M in acetone) to rhenium trichloride (trimer) (0·26 × 10^{-5} moles) in acetone was followed spectrophotometrically by observing the changes at 750 and 965 mμ. An end-point was determined after the addition of 0·63 ml. of acid (9·25 moles). The reaction is slow, and a rough estimate of exchange rate was carried out spectrophotometrically at 965 mμ. A total of nine moles of thiocyanic acid (0·62 ml.; 0·038M) was added to rhenium trichloride (trimer) (0·26 × 10^{-5} moles). The number of thiocyanate ions which reacted per rhenium trichloride were: 3 after ¾ min., 4 after 1·3 min., and 9 after 26 min.

Tri-μ-chloro-trichlorotris(acetylacetonato)trirhenium(III). A solution of rhenium trichloride (0·1 g.) and acetylacetone (0·5 ml.) dissolved in ethanol (10 ml.) was heated under reflux for 3 hr. The solution was evaporated to dryness, leaving a red powder which was obtained as black-red plates (0·1 g.) by slow recrystallisation from acetone (Found: C, 15·1; H, 4·55; Cl, 20·3; Re, 51·6. $C_{30}H_{27}Cl_6O_6Re_3$ requires C, 15·3; H, 2·0; Cl, 19·9; Re, 52·2%).

Tri-μ-chloro-hexachlorotris(triphenylphosphine)trirhenium(III). Excess triphenylphosphine (0·4 g.) was added to a solution of rhenium trichloride (0·3 g.) in acetone (30 ml.). The solution was heated under reflux for ½ hr. and concentrated until crystals formed. The red compound was recrystallised from acetone (yield 0·5 g.) (Found: C, 39·5; H, 2·7; Cl, 19·0; P, 5·7; Re, 33·9. $C_{54}H_{45}Cl_9P_3Re_3$ requires C, 39·0; H, 2·7; Cl, 19·2; P, 5·6; Re, 33·6%).

Tri-μ-bromo-hexabromotris(triphenylphosphine)trirhenium(III). An acetone solution (containing one drop of hydrobromic acid) of rhenium tribromide (0·1 g.) and triphenylphosphine (0·2 g.) was warmed on a water-bath for 15 min. The residue obtained from evaporation to dryness was recrystallised from hot acetone. The compound was hygroscopic (yield 0·1 g.) (Found: C, 31·0; H, 3·6; Br, 34·3; Re, 27·2. $C_{54}H_{45}Br_9P_3Re_3$ requires C, 30·75; H, 2·2; Br, 34·5; Re, 27·0%).

Tri-μ-bromo-hexabromotris(pyridine)trirhenium(III). Excess of pyridine added to a salt of the anion $[Re_3Br_{10}]^-$ gave, on removal of solvent, green hygroscopic needles (Found: C, 10·7; H, 1·3; Br, 47·3. $C_{15}H_{15}Br_9N_3Re_3$ requires C, 11·9; H, 1·0; Br, 47·55%).

Tri-μ-chloro-trichlorotris(diethyldithiocarbamato)rhenium(III) was prepared according to the method of Colton, Levitus, and Wilkinson[5] (Found: C, 14·3; H, 3·7; Re, 45·6. Calc. for $C_{15}H_{30}Cl_6N_3Re_3S_6$: C, 14·8; H, 2·5; Re, 46·0%).

Tri-μ-bromo-tribromotris(diethyldithiocarbamato)rhenium(III). A solution of rhenium tribromide (0·1 g.) and sodium diethyldithiocarbamate (0·1 g.), dissolved in acetone, was filtered and evaporated to dryness *in vacuo*. The brown residue was recrystallised from chloroform a number of times (Found: Br, 32·25; Re, 37·0. $C_{15}H_{30}Br_6N_3Re_3S_6$ requires Br, 32·45; Re, 37·6%).

Tri-μ-chloro-trithiocyanatotris(diethyldithiocarbamato)rhenium(III). The complex, Re$_6$Cl$_6$-(dithiocarbamato)$_3$ (0·1 g.) and silver thiocyanate (1·0 g.) were heated under reflux in acetone for 12 hr. The red solution was filtered and evaporated to dryness. The residue crystallised

from chloroform as brown-red crystals (0·11 g.) (Found: C, 16·8; H, 3·8; Cl, 8·8; Re, 43·4; S, 7·3. $C_{18}H_{30}Cl_3N_3Re_3S_9$ requires C, 16·85; H, 2·35; Cl, 8·3; Re, 43·6; S, 7·5%).

The complexes formulated as Re_2Cl_4(o-phenanthroline) and Re_2Cl_4(2,2′-bipyridyl) were prepared according to Colton, Levitus, and Wilkinson.[6] Treatment of these compounds with hydrochloric acid, in the presence of excess of o-phenanthroline and 2,2′-bipyridyl, respectively, gave products with identical *X*-ray powder photographs to [o-phenH]$_2$Re$_3$Cl$_{11}$ and [bipyH]$_3$Re$_3$Cl$_{12}$. In both cases only 85% of the rhenium was obtained as the salt, confirming at least two different types of rhenium atoms in the original compounds.

Radiochemical exchange. Pure $Cs_3Re_3Cl_{12}$ (0·4479 g.) was dissolved in 2·17M-hydrochloric acid (100 ml.) to which was added [36]Cl as hydrochloric acid. After certain time intervals, aliquots (10 ml.) of the solution were taken and the rhenium quantitatively precipitated as [Ph$_3$PH]$_3$Re$_3$Cl$_{12}$ (0·0575 g.). The material was washed thoroughly with a solution of triphenyl-phosphonium chloride and finally with hydrochloric acid. It was dissolved in acetone and counted in a Geiger–Muller dip-type cell. The results are as follows:

Aliquot	1	2	3	4	5	6	7	8	9	10
Time (min.)	2·75	4	5	10	20	40	60	90	120	240
Counts (min.)	335	668	716	843	877	917	976	1010	1071	1092
Fraction of exchange	0·24	0·45	0·485	0·57	0·59	0·62	0·66	0·68	0·725	0·74

After 3 days. $F = 0·74$.
After heating under reflux for 8 hr. $F = 0·75$.

Physical Measurements.—Conductivities were measured on a Phillips GM 4249 conductivity bridge using a dip-type conductivity cell.

Molecular weights were determined isopiestically in acetone, using purified azobenzene as standard.

Rhenium was determined colorimetrically as the rhenium α-furildioxime complex.[14] Halogens were determined either gravimetrically as silver halide or potentiometrically by titrating with silver nitrate. Sulphur was determined as barium sulphate. Carbon and hydrogen were determined at the microanalytical laboratory, University of Otago, New Zealand.

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[14] Martin, Meloche, and Webb, *Ind. Eng. Chem., Analyt.* 1957, **29**, 527.