DALTON

Redox chemistry of the $[Re_3(\mu\text{-}Cl)_3X_9]^{3-}$ halides (X = Cl or Br); isolation and structural characterization of the $[\{Re_3(\mu\text{-}Cl)_3Br_6(H_2O)(\mu\text{-}O)\}_2]^{2-}$ cluster anion†

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The *triangulo* Re_3^{9+} cluster $[Re_3(\mu\text{-}Cl)_3X_9]^{3-}$ (X = Cl **1a** or Br **1b**) in concentrated aqueous hydrohalogenic acid solutions underwent a facile one-electron reduction by various reducing agents ($VCl_2{\cdot}4H_2O$, $Sn–SnCl_2$ or Hg) to give the air-sensitive Re_3^{8+} anion $[Re_3(\mu\text{-}Cl)_3X_{9-n}(H_2O)_n]^{(4-n)-}$ (X = Cl **2a** or Br **2b**), where *n* may be 1; the diamagnetism and EPR silence of this compound indicate that it may exist as a dimer with a direct or indirect rhenium–rhenium bond linking two Re_3^{8+} trimetal cores. Oxidation of **2** by molecular oxygen in 6 mol dm^{-3} HX (X = Cl or Br) solutions yielded **1** quantitatively, whereas in the absence of acid and in aprotic solvents oxo-derivatives are formed; from **2b** the hexanuclear anion $[\{Re_3(\mu\text{-}Cl)_3Br_6(H_2O)(\mu\text{-}O)\}_2]^{2-}$ **3b** was obtained whose structural characterization, as its $[PPh_4]^+$ salt **3c**, shows that two μ-O ligands bridge two oxidized Re_3^{10+} units. The structure of the Re_3^{9+} cluster $[Co(en)_3][Re_3(\mu\text{-}Cl)_3Br_8(H_2O)]Br$ has been also determined by X-ray diffraction. The redox couple $xRe_3^{9+}–(Re_3^{8+})_x$, where *x* = 1 or 2, derived upon mixing 6 mol dm^{-3} HX (X = Cl or Br) solutions of **1** with an excess of mercury, catalyses efficiently the reduction of molecular oxygen to water.

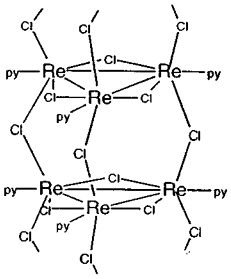
Rhenium in its 3+ oxidation state forms the $[Re_3Cl_{12}]^{3-}$ **1a** and $[Re_2Cl_8]^{2-}$ ions the discovery of which landmarked the development of transition-metal chemistry.[1,2] The first exhibits metalloaromaticity[3] having a *triangulo* Re_3^{9+} structure with three Re=Re bonds[4] and the second contains a Re≡Re bond.[2] Attempts to reduce **1a** started ever since its discovery but still there is uncertainty surrounding the composition of the species formed. Early studies[5] on the electrochemical reduction of **1a** (aqueous HCl–NaCl at a dropping mercury electrode) report the formation of a purple, not characterized compound, where a six-electron reduction wave was observed.

Recent investigations[6] in a room-temperature eutectic ($AlCl_3$–1-ethyl-3-methylimidazolium chloride) at a glassy carbon electrode revealed a reversible one-electron reaction with a value of $E_{\frac{1}{2}}$ *ca.* −0.34 V (referenced to the Al^{3+}–Al couple) although this is dependent upon the pCl of the melt indicating that loss of Cl^- from the cluster occurs during reduction to form $[Re_3Cl_{12-n}]^{(4-n)-}$ **2a** where *n* may be 1 [equation (1)]. The

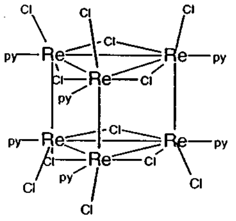
$$\underset{\textbf{1a}}{[Re_3Cl_{12}]^{3-}} + e^- \rightleftharpoons \underset{\textbf{2a}}{[Re_3Cl_{12-n}]^{(4-n)-}} + nCl^- \qquad (1)$$

electronic spectrum of **2a** in the melt[6] is similar to that of the electrochemically prepared species in aqueous HCl,[5,7] whose anaerobic reaction with sulfuric acid produced the capped bridged μ_3-sulfato derivative $[Re_3(\mu\text{-}Cl)_3Cl_3(\mu_3\text{-}O_3SO)]^{3-}$ containing the singly reduced Re_3^{8+} cluster.[7]

Reaction of Re_3Cl_9 with aromatic amines of different basicity induces one-, two- or three-electron reduction producing complexes of the type $[\{Re_3Cl_{9-n}(amine)_n\}_x]$ (*n* = 1, 2 or 3) containing the $Re_3^{(9-n)+}$ core.[8] With pyridine (py) a complex of stoichiometry $[\{ReCl_2(py)\}_n]$ has been isolated for which, on the basis of detailed spectroscopic and supporting chemical evidence, two possible structures have been proposed. In the first the complex is represented as a 'polymer of trimers' **I** with polymerization occurring through Re–Cl–Re bridges.[9] In the second, the compound actually is the hexanuclear 30-electron Re_6^{12+} cluster $[Re_6Cl_{12}(py)_6]$ of the trigonal-prismatic type **II** containing three Re≡Re and six Re–Re bonds,[10] like the well documented $[Re_6Br_{14}]^{2-}$ and $[Tc_6Cl_{12}]^{2-}$ clusters, prepared respectively from the reduction of hydrohalogenic solutions of ReO_4^- and $TcCl_6^{2-}$, under high hydrogen pressure.[11,12] The hypo-



I



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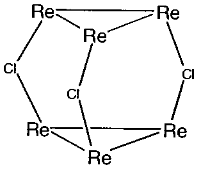
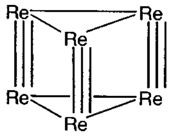
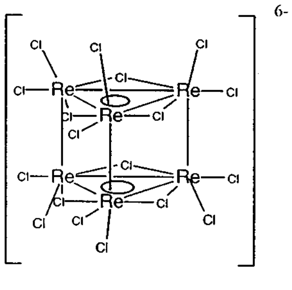
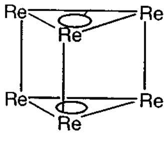






III



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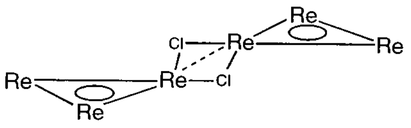
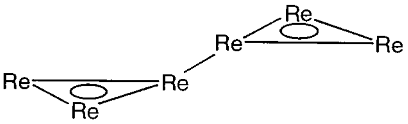
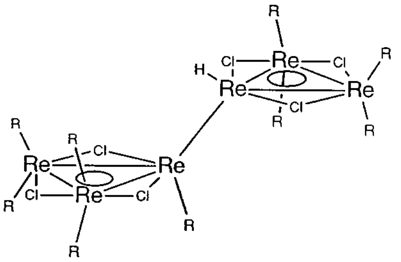
† Mnemosyne: Sir Geoffrey Wilkinson, FRS, Nobel Laureate 1973, and his legacy to the culture of Chemistry.



IV



V



VI R = –CH_2SiMe_3

thetical isomer having the 'dimer of trimers' prismatic arrangement **III** with six Re=Re and three Re–Re bonds could be possible and isolable according to theoretical predictions.[13] We have been interested for some time in the activation of small molecules by exploiting the redox reactivity of metal–metal multiple bonds[14] contained in the halide clusters of Re, Mo and W; also, in isolating the $[Re_6Cl_{18}]^{6-}$ cluster having structure **III** by the three-electron reductive coupling of **1**, which is consistent with ideas concerning the electronic structures of such species.[15]

Here, we describe further attempts to define the nature of complex **2** and its ability to activate molecular oxygen.

Results and Discussion

Reduction of the $[Re_3(\mu\text{-}Cl)_3X_9]^{3-}$ 1 anion (X = Cl 1a or Br 1b)

The interaction of 6 mol dm^{-3} hydrochloric acid solutions of Re_3Cl_9 where it exists[16] as the anion $[Re_3(\mu\text{-}Cl)_3Cl_9]^{3-}$ **1a** with an excess of $VCl_2{\cdot}4H_2O$ gives the reduced, air-sensitive purple complex $[Re_3(\mu\text{-}Cl)_3Cl_{9-n}(H_2O)_n]^{(4-n)-}$ **2a** where n may be 1 [equation (2)]. The visible spectrum of this compound is identical to those

$$\underset{\textbf{1a}}{[Re_3Cl_{12}]^{3-}} + V^{2+} + nH_2O \xrightarrow{6\ \mathrm{mol\ dm^{-3}\ HCl}} \underset{\textbf{2a}}{[Re_3Cl_{12-n}(H_2O)_n]^{(4-n)-}} + nCl^- + V^{3+} \quad (2)$$

generated electrochemically in aqueous 6 mol dm^{-3} HCl[5,7] and similar to that prepared in a eutectic melt.[6] Complex **2a** can also be obtained by using as reductants a mixture of Sn and $SnCl_2{\cdot}2H_2O$. The simultaneous presence of both reagents is necessary. Otherwise, for unknown reasons, the reaction does not proceed to completion (30 to 50%) and the results are not reproducible. Electrochemical synthesis is preferred to chemical since separation of **2a** from the reducing agents is tedious, but with both methods a high acid concentration (>3 mol dm^{-3}) is required to prevent solvolysis, due to the high lability of the terminal chloride ligands.[17] This decreases the solubility of the added counter cation salt(s) which co-crystallize with **2a**, limiting the diagnostic value of the analytical results.

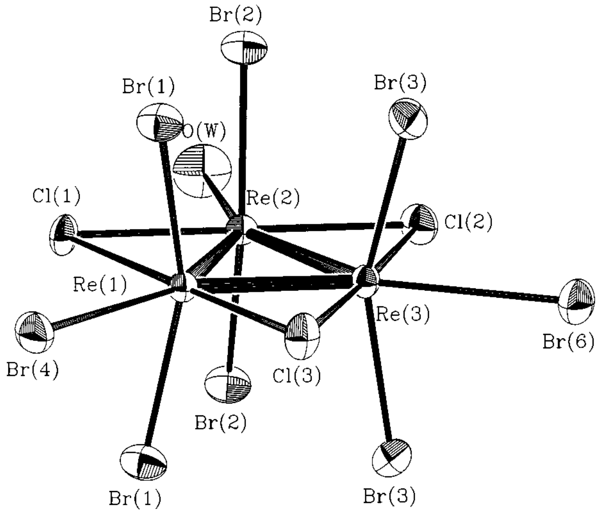


Fig. 1 Structure of the anion $[Re_3(\mu\text{-}Cl)_3Br_8(H_2O)]^{2-}$ of complex **1c**

Table 1 Selected bond lengths (Å) and angles (°) for $[Re_3(\mu\text{-}Cl)_3Br_8(H_2O)]^{2-}$ with estimated standard deviations (e.s.d.s) in parentheses

Re(1)–Cl(3)	2.356(5)	Re(2)–Cl(2)	2.412(5)
Re(1)–Cl(1)	2.419(5)	Re(2)–Br(2)	2.436(2)
Re(1)–Br(1)	2.452(2)	Re(2)–Re(3)	2.452(1)
Re(1)–Re(2)	2.458(1)	Re(3)–Cl(3)	2.402(5)
Re(1)–Re(3)	2.480(1)	Re(3)–Cl(2)	2.425(5)
Re(1)–Br(4)	2.821(2)	Re(3)–Br(3)	2.449(2)
Re(2)–O(W)	2.30(2)	Re(3)–Br(6)	2.838(3)
Re(2)–Cl(1)	2.411(5)		
Re(1)–Re(2)–Re(3)	60.69(3)	Re(2)–Re(1)–Br(4)	154.26(7)
Re(1)–Re(3)–Re(2)	59.77(3)	Re(1)–Re(3)–Br(6)	159.04(6)
Re(2)–Re(1)–Re(3)	59.66(3)	Re(1)–Re(3)–O(W)	151.1(5)
Re(2)–Cl(1)–Re(1)	61.2(1)	Br(1)–Re(1)–Br(1′)	156.72(8)
Re(2)–Cl(2)–Re(3)	60.9(1)	Br(2)–Re(2)–Br(2′)	154.70(8)
Re(1)–Cl(3)–Re(3)	62.8(1)	Br(3)–Re(3)–Br(3′)	155.84(9)

Primed atoms are related by the symmetry transformation $-x + 1, y, z$.

However, we were unable to reproduce our previous electrochemical synthesis of complex **2a** in 6 mol dm^{-3} HCl (mercury-pool cathode and platinum-wire anode, at a steady potential of −0.400 V relative to the saturated calomel electrode SCE)[7] when we employed a platinum cathode instead of mercury. This, coupled with careful examination of the results obtained by Münze[5] where the reduction potential should be substantially more negative (around −0.560 V as compared to −0.400 V required under our conditions) indicated that the process is a chemical–electrochemical reaction where the **1** ⟶ **2** transformation has been induced by mercury and the resulting Hg_2Cl_2–Hg couple was cycling from the electrons supplied during the electrolysis [equations (3) and (4)]. Indeed, addition of

$$2[Re_3Cl_{12}]^{3-} + 2Hg + 2Cl^- + nH_2O \longrightarrow 2[Re_3Cl_{12-n}(H_2O)_n]^{(4-n)-} + 2nCl^- + Hg_2Cl_2 \quad (3)$$

$$Hg_2Cl_2 + 2e^- \longrightarrow 2Hg + 2Cl^- \quad (4)$$

mercury strictly under anaerobic conditions to an aqueous 6 mol dm^{-3} HCl solution of **1a** smoothly reduces it to **2a** with concurrent formation of insoluble Hg_2Cl_2.

The mixed halide $[Re_3(\mu\text{-}Cl)_3Br_9]^{3-}$ **1b** formed[18] by dissolution of Re_3Cl_9 in 6 mol dm^{-3} HBr solutions is similarly reduced giving the derivative $[Re_3(\mu\text{-}Cl_3)Br_{9-n}(H_2O)_n]^{(4-n)-}$ **2b**.

Although complexes **2a** and **2b** should be paramagnetic, their Cs^+ and $[PPh_4]^+$ salts are diamagnetic and their solutions in aqueous 6 mol dm^{-3} HX or dichloromethane respectively are EPR silent (T = 5 to 300 K). This implies that **2** may exist as a dimer with a direct or indirect Re–Re bond linking the two

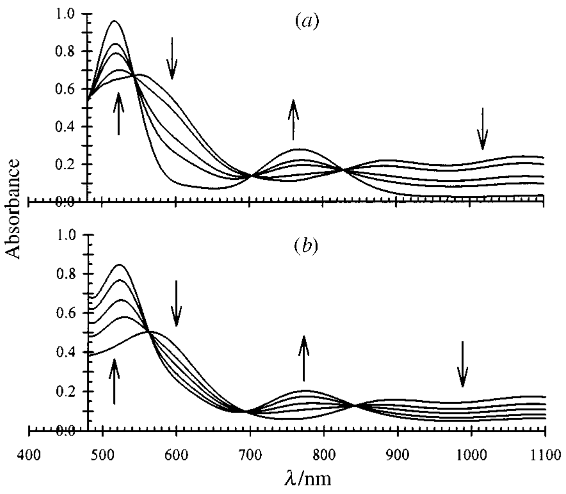


Fig. 2 The UV/VIS spectra showing the oxidation by atmospheric oxygen of complex **2** to **1** in aqueous 6 mol dm^{-3} HX [X = Cl (*a*) or Br (*b*)]

Re_3^{8+} clusters, supported (**IV**) or unsupported (**V**) by halide bridges. The lability of the terminal halide ligands may facilitate dimerization by lowering the anionic charge, decreasing intercluster repulsion. Such a dimeric arrangement **VI** has been encountered in the hexanuclear Re_6^{16+} hydrido alkyl $[Re_6(\mu\text{-}Cl)_6H\{CH_2SiMe_3\}_9]$ where two Re_3^{8+} subclusters are joined by a long Re–Re bond [2.993(1) Å],[19] as shown in **II**. The singly bonded rhenium atoms are formally in the II oxidation state while the others in the III state.

Attempts to obtain suitable crystals of complex **2** for X-ray crystallography using a range of counter cations $\{Li^+, Na^+, K^+, Rb^+, Cs^+, Ca^{2+}, Sr^{2+}, Y^{3+}, La^{3+}, [PH_4]^+, [PPh_4]^+, [AsPh_4]^+, (H_2en)^{2+}(en = H_2NCH_2CH_2NH_2), Hpy^+, [NR_xH_{4-x}]^+ [R = C_nH_{2n+1}, n = 1–4, x = 0–4]\}$ and mixtures of solvents were not successful; when $[Co(en)_3]^{3+}$ was employed a redox reaction occurred with **2** and the Re_3^{9+} clusters $[Co(en)_3][Re_3Cl_{12}]$ and $[Co(en)_3][Re_3(\mu\text{-}Cl)_3Br_8(H_2O)]Br$ **1c** have been isolated. The structure of **1c** has been determined by X-ray diffraction and is shown in Fig. 1; bond lengths and angles are given in Table 1. The rhenium and chlorine atoms lie on the symmetry plane of the anion. The Re_3 triangle is almost perfectly equilateral, except from the side opposite to Re(2), where a water molecule is bound, which is longer by 0.025(1) Å (average), and the respective angle is also larger by 0.98(3)° (average). A similar perturbation is observed in the triangles formed by the bridging chlorine and rhenium atoms, where the Re(1)–Cl(3)–Re(3) angle is larger by 1.8(1)° (average).

Reaction of the reduced species with molecular oxygen

Exposure of a purple solution of complex **2a** to atmospheric oxygen results in its quantitative conversion into the oxidized **1a** state as shown by visible spectroscopy and analytical determinations. The characteristic peaks of **2a** at 1072, 883 and 554 nm slowly diminish and peaks at 763 and 513 nm due to **1a** appear with isosbestic points at 828, 704 and 508 nm maintained throughout the reaction and a lack of any other detectable absorbances except those of the oxidized and reduced forms, Fig. 2. Similar reactivity is exhibited by **2b**. Complex **1a** does not react with O_2 under the same conditions whereas oxidation of **1b** occurs very slowly and partially with cluster disruption giving monomeric species of rhenium(IV).[18]

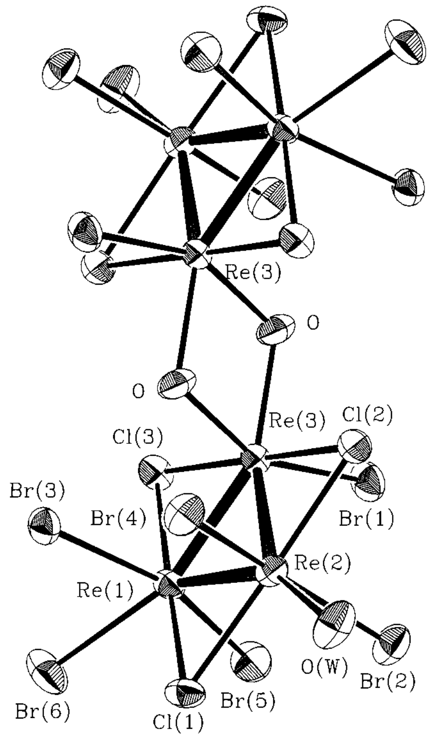


Fig. 3 Structure of the anion $[\{Re_3(\mu\text{-}Cl)_3Br_6(H_2O)(\mu\text{-}O)\}_2]^{2-}$ **3b**

Table 2 Selected bond lengths (Å) and angles (°) for $[\{Re_3(\mu\text{-}Cl)_3Br_6(H_2O)(\mu\text{-}O)\}_2]^{2-}$ with e.s.d.s in parentheses

Re(1)–Cl(3)	2.405(5)	Re(2)–Cl(2)	2.418(5)
Re(1)–Cl(1)	2.418(5)	Re(2)–Re(3)	2.436(1)
Re(1)–Br(5)	2.433(2)	Re(2)–Br(2)	2.456(2)
Re(1)–Re(3)	2.458(1)	Re(2)–Br(4)	2.469(2)
Re(1)–Re(2)	2.465(1)	Re(3)–O	2.18(1)
Re(1)–Br(3)	2.500(2)	Re(3)–O′	2.03(1)
Re(1)–Br(6)	2.698(2)	Re(3)–Cl(3)	2.405(5)
Re(2)–O(W)	2.25(1)	Re(3)–Cl(2)	2.413(5)
Re(2)–Cl(1)	2.413(5)	Re(3)–Br(1)	2.432(2)
Re(3)–Re(2)–Re(1)	60.22(4)	E(2)–Re(1)–Br(6)	149.66(8)
Re(2)–Re(3)–Re(1)	60.48(4)	Re(3)–Re(2)–O(W)	150.3(5)
Re(3)–Re(1)–Re(2)	59.30(3)	Br(1)–Re(3)–O	82.9(4)
Re(2)–Cl(1)–Re(1)	61.4(1)	Br(1)–Re(3)–O′	151.6(4)
Re(2)–Cl(2)–Re(3)	60.6(1)	O–Re(3)–O′	68.7(6)
Re(1)–Cl(3)–Re(3)	61.5(1)	Re(3)–O–Re(3′)	111.3(6)

Primed atoms are related by the symmetry transformation $-x + 1, -y + 1, -z + 2$.

In the absence of acid and in aprotic organic solvents (CH_2Cl_2, C_4H_8O) complexes **2a** and **2b** are instantly oxidized by molecular oxygen to give oxo species. From tetrahydrofuran (thf) solutions of **2b** the hexanuclear orange compound $[PPh_4]_2[\{Re_3(\mu\text{-}Cl)_3Br_6(H_2O)(\mu\text{-}O)\}_2]\cdot 6thf$ **3c** has been isolated and its structure determined by X-ray diffraction is shown in Fig. 3; bond lengths and angles are given in Table 2. The distinction between μ-O and μ-OH ligands is made as follows. (*i*) If hydroxide ligands were present the compound would consist of Re_3^{8+} clusters, whereas charges higher than eight are expected by virtue of its synthesis (reaction of the water-stable **2b** with O_2). (*ii*) The reduction of **3b** to **1b** indicates the existence in the anion **3b** of *trimeric* rhenium units with charges higher than nine. (*iii*) The presence of a band at 665 cm^{-1} in the IR spectrum is consistent with a μ-oxo ligand.[20] (*iv*) The tight binding of the oxo ligands to both rhenium atoms: the asymmetry observed (within the limit)[21] [Re(3)–O 2.18(1) and Re(3)–O′ 2.03(1) Å] is dictated by the terminal in- and out-of-plane positions of the oxides in the cluster. Longer distances are consistently and always observed for ligands occupying the former site in these Re_3^{n+} clusters both in mono- and di-meric arrangements.[7,22]

The anion **3b** of the salt **3c** consists of two oxidized Re_3^{10+} clusters which are bridged by two oxide ions and is centrosymetric at the bisection point of the diagonals of the rhombs defined by the Re(3)–O–Re(3′)–O′ atoms. Both Re_3^{10+} cores form a nearly perfect equilateral triangle with a maximum difference of 0.031(1) Å in the Re–Re bond lengths and a maximum deviation of 0.7(4)° from the ideal 60° angle. The triangles formed by the bridging chlorine atoms are also isosceles. In the crystal lattice there are six tetrahydrofuran molecules, not interacting with the anion. The oxo-bridged Re–O–Re atoms are formally in the IV oxidation state whereas the others are in the III. This constitutes the second example of oxidation of the Re_3^{9+} core, the other being the $[Re_3(\mu_3\text{-}H)_2(\mu\text{-}NMe_2)_2(NMe_2)_6]$ complex[23] obtained from the reaction of the $[Re_3Cl_9(thf)_3]$ with an excess of $Li[NMe_2]_2$.

A potential in the range +1.7 to +1.5 *versus* SCE is exhibited for the reversible one-electron oxidation in cyclic voltammetric studies of the $[Re_3Cl_9(CNR)_3]$ (X = Cl or Br) adducts in $NBu^n{}_4PF_6$–CH_2Cl_2 solutions.[24]

Dinuclear bis(μ-oxo) complexes are of interest because of their relevance to enzyme bimetal sites[25,26] and are found for tri- and/or tetra-valent manganese,[27] technetium,[28] iron,[29] ruthenium[30] and osmium.[31] With rhenium there are several examples of structurally characterized dinuclear metal–metal bonded complexes containing the Re_2^{8+} or Re_2^{7+} cores of the general type $[Re_2(\mu\text{-}O)_2L_2]^{n-}$ {n = 3 or 4, L = $C_2O_4^{2-}$,[32] ethylenediaminetetraacetate(-4),[33] tris(2-pyridylmethyl)amine,[34] [(6-methyl-2-pyridyl)methyl]bis(2-pyridylmethyl)amine[34]} or $[Re_2(\mu\text{-}O)_2X_2(tacn)_2]^{2+}$ (X = Cl or I, tacn = 1,4,7-triazacyclononane)[35] and their redox properties have been studied. If **2** is a dimer, formation of **3** indicates that dioxygen activation and reduction may occur at the dirhenium centre linking the two reduced Re_3^{8+} cores, thus demonstrating the ability of bimetallic sites to induce facile four-electron reductions.[25] This mechanism is not favoured in mononuclear complexes (even electron rich) for symmetry reasons despite the high exothermicity of this reaction.[36]

Alternatively complex **3** could be formed bimolecularly, by a not clearly envisaged pathway, following initial dioxygen interaction with the Re_3^{8+} monomer. A rare example of net four- and six-electron redox reactions at a Re_2^{4+} centre containing an electron-rich triple bond possessing the $\sigma^2\pi^4\delta^2\delta^{*2}$ ground-state configuration has been found to occur in the reaction of $[Re_2X_4(\mu\text{-}dppm)_2]$ (X = Cl or Br, dppm = $Ph_2PCH_2PPh_2$) with molecular O_2 to give the $[Re_2(\mu\text{-}O)(\mu\text{-}X)OX_3(\mu\text{-}dppm)_2]$ and $[Re_2(\mu\text{-}O)O_2X_4(\mu\text{-}dppm)_2]$ complexes, where the Re≡Re bond has been oxygenated with complete retention of the ligand set of the parent compounds.[37] Other instances are the conversion of the Ru_2R_6[38] alkyl to give $[Ru_2(\mu\text{-}O)_2R_6]$ and of $Mo_2(S_2CNEt_2)_4$ to give $[Mo_2O_3(S_2CNEt_2)_4]$[39] upon their reaction with molecular O_2.

Quantitative oxidation of complex **2** to **1** occurs not only by molecular O_2 but also with stoichiometric amounts of H_2O_2, NaOCl, Bu^nO_2H as demonstrated by independent control experiments. This shows that any possible oxygen-containing intermediate products (*e.g.* $^{\bullet}OH$, $^{\bullet}O_2H$, $^{\bullet}OCl$) which may be formed from partial reduction of O_2 would be eventually reduced to O^{2-}. Also, reduction of **3** to **1** is facile and quantitative upon interaction of a tetrahydrofuran solution of **3** with a mixture of aqueous 6 mol dm^{-3} HX and Hg.

From the above it could be said that O_2 is reduced by complex **2** to O^{2-}, which under the reaction conditions (aqueous 6 mol dm^{-3} HX, Hg) forms water and therefore the redox couple $[xRe_3^{9+}\text{–}(Re_3^{8+})_x$, x = 1 or 2] catalyses the chemically and biochemically important reaction: $O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$. Indeed, the catalytic system [O_2 (P_{O_2} = 1 atm, 101 325 Pa; room temperature), Hg, 6 mol dm^{-3} HX(aq), **1**] consumes gas continuously and is active indefinitely (we have terminated the reaction after 3 months) provided that there is an excess of reductant (mercury) present and the acidity of the mixture does not drop below 1 mol dm^{-3}. No trace amounts of Hg_2Cl_2 could be detected under the same conditions in the absence of **1**.

Experimental

All reactions including electroreductions[7,40] were carried out under purified Ar or under vacuum, except otherwise stated. Reagents were of analytical grade, thoroughly purified and carefully deoxygenated. Demineralized (by ion exchange) and doubly distilled water was used. The compounds Re_3Cl_9,[41] $VCl_2\cdot 4H_2O$,[40] $VBr_2\cdot 6H_2O$[40] were prepared as referenced. Spectra were recorded with a Hitachi U-2000 (UV/VIS), Perkin-Elmer 883 (IR), Bruker ER 200D-SRC (EPR) spectrometers and magnetic measurements using a Mettler magnetic balance with a Newport electromagnet. Microanalyses were performed in this Laboratory.

Reductions of $[Re_3(\mu\text{-}Cl)_3Cl_9]^{3-}$ 1a

(*a*) With $VCl_2\cdot 4H_2O$. To a solution of 6 mol dm^{-3} HCl (20 cm^3) containing Re_3Cl_9 (0.500 g, 0.569 mmol) was added a solution of $VCl_2\cdot 4H_2O$ (0.754 g, 3.89 mmol) in 6 mol dm^{-3} HCl (20 cm^3) and the mixture was stirred for *ca.* 2 h. The Cs^+, $AsPh_4^+$ and H_3O^+ salts of the product **2a** were isolated as follows.

(*i*) To a portion (10 cm^3) of the reaction mixture was added CsCl (5.0 g) with stirring. The red-black precipitate was filtered off, washed twice (2 × 2 cm^3) with a solution of CsCl (2.5 g) in 6 mol dm^{-3} HCl (4 cm^3), absolute ethanol (3 × 6 cm^3) and dried *in vacuo* (0.14 g).

(*ii*) Similarly, to a portion of the reaction mixture (10 cm^3) was added $[AsPh_4]Cl$ (0.050 g, 0.131 mmol) suspended in water (5 cm^3). The precipitate formed was filtered off, washed with tetrahydrofuran (3 × 5 cm^3), extracted with absolute methanol, filtered and the solvent removed *in vacuo* (0.21 g).

(*iii*) A portion of the parent reaction mixture (10 cm^3) was taken and evaporated *in vacuo*. The residue was dissolved in 0.1 mol dm^{-3} HCl (10 cm^3), placed on an anion exchange resin (Dowex 50 W X 2, 100–200 mesh, 0.5 g), washed with 0.6 mol dm^{-3} HCl (4 × 10 cm^3) and the product eluted with 0.9 mol dm^{-3} HCl (25 cm^3).

(*b*) With Sn. To a solution of 6 mol dm^{-3} HCl (35 cm^3) were added Re_3Cl_9 (0.539 g, 0.614 mmol), $SnCl_2\cdot 2H_2O$ (0.531 g, 2.36 mmol) and metallic Sn (0.594 g). The mixture was stirred (*ca.* 20 h), filtered from the remaining Sn (0.410 g) and $[AsPh_4]Cl$ (1.800 g, 4.298 mmol) was added. The mixture was heated in a steam-bath (*ca.* 20 min), cooled to room temperature and the product filtered from the precipitate and isolated as described above. The yield is not given since the complex partially precipitates with the excess of $[AsPh_4]Cl$.

(*c*) With Hg. To a solution of 6 mol dm^{-3} HCl (20 cm^3) containing Hg (1.4 cm^3, 0.10 g, 0.50 mmol) was added Re_3Cl_9 (0.176 g, 0.200 mmol) and the mixture stirred vigorously (*ca.* 30 min). The resulting purple solution was filtered from the insoluble Hg_2Cl_2 and the remaining Hg and $[PPh_4]Cl$ (0.795 g, 2.01 mmol) was added to the filtrate. The deep purple residue was filtered off, washed with 6 mol dm^{-3} HCl (3 × 5 cm^3) and dried *in vacuo* (0.40 g).

Reduction of $[Re_3(\mu\text{-}Cl)_3Br_9]^{3-}$ 1b with Hg

The compound Re_3Cl_9 (0.517 g, 0.589 mmol) was dissolved in 6 mol dm^{-3} HBr (20 cm^3) and the solution was stirred at *ca.* 40 °C for 20 min. To this solution was added Hg (2.6 cm^3, 0.19 g, 0.95 mmol), the mixture was stirred (*ca.* 20 min) and filtered from Hg_2Br_2 and residual Hg. To the clear purple filtrate was added $[PPh_4]Br$ (0.957 g, 2.28 mmol) and the deep purple solid formed was filtered off, washed with 6 mol dm^{-3} HBr (3 × 5 cm^3) and dried *in vacuo* (1.13 g).

Reaction of complex 2a with $[Co(en)_3]Cl_3$

To a solution (20 cm^3) of complex **2a**, prepared from a solution of **1a** (1.714 mmol dm^{-3}) as described, was added $[Co(en)_3]Cl_3$ (0.773 g, 2.24 mmol). The red orange residue, $[Co(en)_3]$-

Table 3 Summary of crystal, intensity collection and refinement data

Empirical formula	$C_6H_{26}Br_9Cl_3CoN_6ORe_3$	$C_{72}H_{92}Br_{12}Cl_6O_{10}P_2Re_6$
M	1641.40	3468.31
T/°K	298	298
λ/Å	0.710 70	0.710 69
Space group	*Pmna*	$P\bar{1}$
a/Å	15.852(1)	11.830(2)
b/Å	13.810(1)	13.925(3)
c/Å	13.414(1)	17.318(3)
U/Å^3	2936.5(3)	2450.6(8)
α/°		113.183(6)
β/°		86.524(7)
γ/°		110.264(7)
Z	4	1
D_c, D_m/Mg m^{-3}	3.713, 3.69	2.350, 2.327
μ/mm^{-1}	25.415	12.515
Maximum absorption correction	4.46	2.27
θ Range/°	1.99–25.98	1.70–25.00
Reflections collected	2370	3924
Independent reflections (R_{int} = 0.0000)	2370	3924
Ranges h, k, l	0–19, 0–17, 0–16	−13 to 13, −14 to 13, 0–17
$F(000)$	2920	1606
Δ/σ_{max}	0.001	0.004
a, b in weighting scheme[a]	0.1713, 18.4149	0.0724, 14.9893
Maximum, minimum residual electron density e Å^{-3}	9.664, −7.995	2.028, −1.492
Data, restraints, parameters	2370, 0, 149	3924, 0, 416
Goodness of fit on F^2	1.046	1.041
$R1$, $wR2$ [$I > 2\sigma(I)$]Br[b]	0.0652, 0.1871	0.0464, 0.1133
(all data)	0.0652, 0.1871	0.0508, 0.1174

[a] $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ and $P = [\max(F_o^2, 0) + 2F_c^2]/3$. [b] $R1$ based on F, $wR2$ on F^2.

[Re(μ-Cl)$_3$Cl$_9$], was filtered off, washed with cold 6 mol dm^{-3} HCl (2 × 5 cm^3), acetone (3 × 5 cm^3) and dried *in vacuo* (0.0386 g, 92% based on Re$_3$Cl$_9$) (Found: C, 5.7; H, 2.2; Cl, 34.6; Co, 4.9; N, 7.0; Re, 45.4. $C_6H_{24}Cl_{12}CoN_6Re_3$ requires C, 5.9; H, 2.0; Cl, 34.8; Co, 4.8; N, 6.9; Re, 45.6%).

Reaction of complex 2b with [Co(en)$_3$]Br$_3$

To a solution (20 cm^3) of complex **2b**, prepared from a solution of **1b** (1.858 mmol dm^{-3}) as described, was added [Co(en)$_3$]Br$_3$ (1.103 g, 2.30 mmol). The red-orange residue, [Co(en)$_3$][Re(μ-Cl)$_3$Br$_8$(H$_2$O)]Br, was filtered off, washed with cold 6 mol dm^{-3} HBr (2 × 5 cm^3), acetone (3 × 5 cm^3) and dried *in vacuo* (0.0538 g, 89% based on Re$_3$Cl$_9$) (Found: C, 4.0; H, 1.5; Br, 43.6; Cl, 6.6; Co, 3.6; N, 5.3; Re, 33.9. $C_6H_{26}Br_9Cl_3CoN_6ORe_3$ requires C, 4.4; H, 1.6; Br, 43.8; Cl, 6.5; Co, 3.6; N, 5.1; Re, 34.0%).

Synthesis of [PPh$_4$]$_2$[{Re$_3$(μ-Cl)$_3$Br$_6$(H$_2$O)(μ-O)}$_2$]·6thf 3c

To a mixture of the tetraphenylphosphonium salt of complex **2b** and [PPh$_4$]Br (0.78 g) was added tetrahydrofuran (30 cm^3) and air was passed for *ca.* 10 s. The red-orange solution was filtered from the white [PPh$_4$]Br formed, concentrated under reduced pressure to *ca.* 15 cm^3 and the orange crystals were filtered off, washed with cold tetrahydrofuran (2 × 5 cm^3) and dried *in vacuo* (0.50 g). IR: 665 cm^{-1} (Re–O–Re) (Found: C, 26.1; H, 2.7; Br, 27.2; Cl, 6.1; P, 1.7; Re, 31.4. $C_{72}H_{92}Br_{12}Cl_6O_{10}P_2Re_6$ requires C, 26.4; H, 2.9; Br, 27.0; Cl, 6.0; P, 1.7; Re, 31.5%).

Reaction of '[Re$_3$(μ-Cl)$_3$Cl$_{9-n}$(H$_2$O)$_n$]$^{(4-n)-}$' 2a with O$_2$

To a 6 mol dm^{-3} HCl solution (10 cm^3) of complex **2a**, prepared from a 0.938 mmol dm^{-3} solution of **1a** as described, air was passed for *ca.* 10 s and subsequently CsCl (12 g) was added. The red Cs$_3$[Re$_3$Cl$_{12}$] was filtered off, washed with cold 6 mol dm^{-3} HCl (2 × 2 cm^3), acetone (3 × 5 cm^3) and dried *in vacuo* (0.0126 g, 97% based on Re$_3$Cl$_9$) (Found: Cl, 30.6; Cs, 28.9; Re, 40.5. Calc. for Cl$_{12}$Cs$_3$Re$_3$: Cl, 30.8; Cs, 28.8; Re, 40.4%).

Reaction of '[Re$_3$(μ-Cl)$_3$Br$_{9-n}$(H$_2$O)$_n$]$^{(4-n)-}$' 2b with O$_2$

To a 6 mol dm^{-3} HBr solution of complex **2b**, prepared from a 0.826 mmol dm^{-3} solution of **1b** as described, air was passed for *ca.* 10 s. The solution changed from purple to red and CsBr (9 g) was added. The red Cs$_2$[Re$_3$(μ-Cl)$_3$Br$_8$(H$_2$O)] was filtered off, washed with cold 6 mol dm^{-3} HBr (2 × 2 cm^3), acetone (3 × 5 cm^3) and dried *in vacuo* (0.0107 g, 96% based on the Re$_3$Cl$_9$) (Found: Br, 40.4; Cl, 6.9; Cs, 16.5; Re, 35.5. Calc. for H$_2$Br$_8$Cl$_3$Cs$_2$ORe$_3$: Br, 40.5; Cl, 6.7; Cs, 16.8; Re, 35.4%).

X-Ray crystallography

Slow crystallization from 6 mol dm^{-3} HBr yielded red-orange crystals of complex **1c**. A crystal with approximate dimensions 0.15 × 0.25 × 0.50 mm was mounted in a capillary. Orange crystals of **3c**, which formed during the preparation, with dimensions 0.15 × 0.35 × 0.70 mm were mounted in a capillary filled with drops of mother-liquor. Diffraction measurements were made on a P2$_1$ Nicolet diffractometer using Zr-filtered Mo-Kα radiation. Unit-cell dimensions were determined and refined by using the angular settings of 25 automatically centred reflections in the range 11 < 2θ < 23 and they appear in Table 3. Intensity data were recorded using a θ–2θ scan. For **1c**, $2\theta_{max}$ = 52°, scan speed 4.5° min^{-1} and scan range 1.85 plus $\alpha_1\alpha_2$ separation. For **3c**, $2\theta_{max}$ = 50°, scan speed 4.5° min^{-1} and scan range 2.5 plus $\alpha_1\alpha_2$ separation. Three standard reflections monitored every 97 showed less than 3% variation and no decay. Lorentz-polarization and ψ-scan absorption corrections were applied using CRYSTAL LOGIC software.[42] The structures were solved by direct methods using SHELXS 86[43] and refined by full-matrix least-squares techniques on F^2 with SHELXL 93.[44] Hydrogen atoms on the carbon atoms for the complex **1c** were introduced at calculated positions as riding on bonded atoms and refined isotropically; the remaining H atoms were not included in the refinement. For **3c** only the H atoms of the [PPh$_4$]$^+$ cation were included at calculated positions; the rest were not refined. All non-hydrogen atoms for both complexes were refined anisotropically (except the C$_4$H$_8$O solvent molecules of **3c** which were refined isotropically).

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