Discovery of Osmium(III) and Osmium(IV) Binuclear Nonahalide Complexes: the Synthesis, Voltammetry, and Spectro-electrochemistry of $(Bu_4N)_3[Os^{III}{}_2Br_9]$ and $(Bu_4N)[Os^{IV}{}_2Br_9]$, and their Relationship to the Corresponding Di-osmium Decahalides

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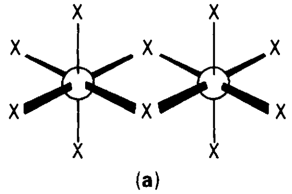
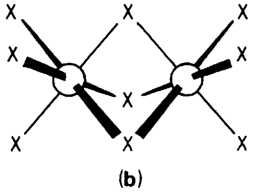
Redox-related $[Os^{IV}{}_2Br_9]^-$ and $[Os^{III}{}_2Br_9]^{3-}$ have been isolated and characterised for the first time, initially as tetra(n-butyl)ammonium salts, and compared with face-sharing $[Ru_2Br_9]^{z-}$ (z = 1, 2, 3) and edge-sharing $[Os_2X_{10}]^{z-}$ (X = Br, Cl; z = 2, 3, 4), by voltammetry and by spectroscopic studies which include the electrogenerated mixed-valence complexes, $[Os_2Br_9]^{2-}$ and $[Os_2Br_{10}]^{3-}$.

The triply halide-bridged structures $[M_2X_9]^{3-}$ and $[M_2X_9]^-$ are evidently well favoured and widely distributed among trivalent and tetravalent transition metals.[1,2] For osmium however, only doubly bridged $[Os_2Cl_{10}]^{2-}$ and $[Os_2Br_{10}]^{2-}$ (structure **a**) are known.[3—5] Di-osmium nonahalides (structure **b**) have not been isolated previously, despite efforts to identify them,[6] and despite the accessibility of neighbouring $[Re_2X_9]^-$,[7] $[Ir_2X_9]^{3-}$,[8] and $[Ru_2X_9]^{3-}$.[9,10] However, there is reportedly powder *X*-ray diffraction evidence for $Cs_3[Os_2Br_9]$ as an unstable component among the aerial decomposition products of solid $Cs_3[OsBr_6]\cdot H_2O$.[6]

Cotton *et al.* prepared crystals of $(Bu_4N)_2[Os_2Br_{10}]$ by heating $(Bu_4N)_2[OsBr_6]$ to only 40 °C in trifluoroacetic acid (TFA).[5] We find the halide-abstraction reaction reliably proceeds further under reflux to yield dark blue $(Bu_4N)[Os_2Br_9]$ as the exclusive product. Accordingly, $(Bu_4N)_2[Os_2Br_{10}]$ is best obtained by restricting both temperature and reaction time, and, once isolated, may be efficiently converted to $(Bu_4N)[Os_2Br_9]$ by the TFA procedure (Scheme 1; steps i and ii). The two binuclear Os^{IV} compounds, though similar in appearance, are clearly distinguished by appropriate analytical and physical measurements. Both have been prepared pure in good yield during these studies (as have the corresponding Ph_4P^+ salts). While $(Bu_4N)[Os_2Br_9]$ is a strong oxidant and considerably more reactive than the decabromide, it may be dissolved without decomposition in dry CH_2Cl_2 at 220 K. Addition of successive mole equivalents of Bu_4NBH_4 causes rapid stepwise reduction, culminating in quantitative separation of $(Bu_4N)_3[Os_2Br_9]$ as air-sensitive blue–black needles. The solid-state far-IR data for these systems (Table 1) are fully in accord with their assigned structures and oxidation states.



(**a**)



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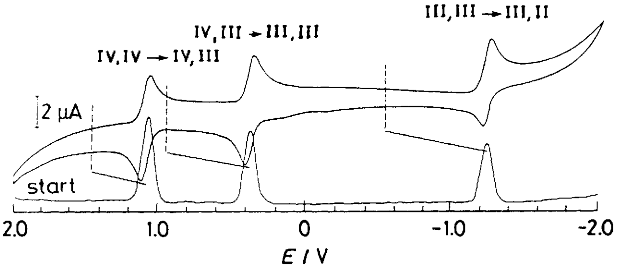
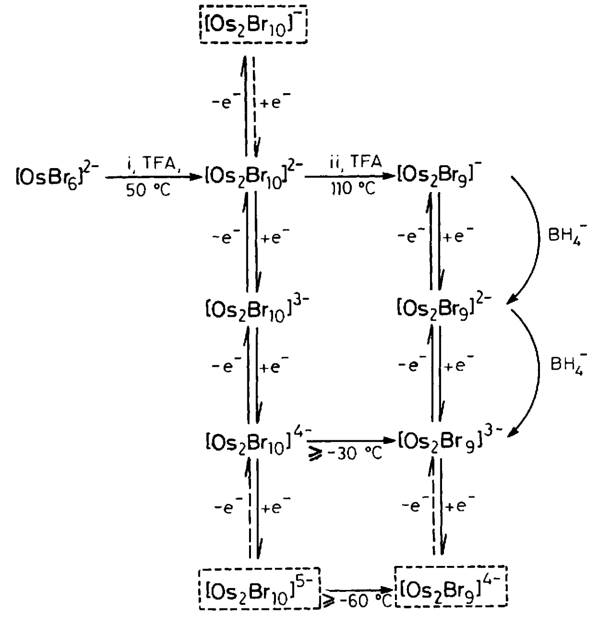


Figure 1. Voltammetry of $(Bu_4N)[Os_2Br_9]$ at 215 K. The corresponding $[Ru_2Br_9]^{z/z-1}$ couples are indicated by dashed vertical lines. CV = cyclic voltammetry (v = 100 mV s^-), acV = alternating current voltammetry (v = 20 mV s^{-1}; ω = 200 Hz), conditions as in Table 2.

The low-temperature voltammetric data (Table 2) show that all these binuclear polyhalide complexes are capable of successive reversible one-electron transfers spanning four or



Scheme 1. All processes in CH_2Cl_2 except i and ii. Boxed complexes are short-lived.

Table 1. Far-IR data.

	Metal–halogen absorptions /cm$^{-1\,a,b}$	
Complex	$\nu(M{-}Br_{terminal})$	$\nu(M{-}Br_{bridging})$
$(Bu_4N)_2[Os^{IV}{}_2Br_{10}]$	235, 222, 198[c]	170vw[4]
$(Bu_4N)[Os^{IV}{}_2Br_9]$	*ca.* 230br[d]	183m
$(Bu_4N)_3[Os^{III}{}_2Br_9]$	223, 203	181m
$(Bu_4N)_3[Ru^{III}{}_2Br_9]$	258, 231[e]	178m

[a] Solids dispersed in polythene discs, and studied by FT IR. [b] m = medium, vw = very weak, all others are strong; br = broad. [c] This third band is absent in $[Os^{IV}{}_2Br_9]^-$ spectra. [d] Unresolved at 290 K but $(Ph_4P)[Os^{IV}{}_2Br_9]$ has ν 235, 220 cm^{-1}. [e] Scaling ν(Ru) by $[\mu_{RuBr}/\mu_{OsBr}]^{1/2}$ gives ν(Os) = 230, 205 cm^{-1}.

Table 2. Voltammetric data.

Complex	$E_{1/2}$/V for $M_2^{z,z}/M_2^{z,z\pm1}$ couples at 215 K[a,b]			
	V,IV←IV,IV	IV,IV⟷IV,III	IV,III⟷III,III	III,III→III,II
$(Bu_4N)_3[Ru_2Br_9]$	—	+1.46	+0.95	−0.52
$(Bu_4N)[Os_2Br_9]$[c]	—	+1.07	+0.35	−1.27
$(Bu_4N)_2[Os_2Br_{10}]$	+1.86	+0.30	−0.18	−1.88
$(Ph_4P)_2[Os_2Cl_{10}]$	+2.1[d]	+0.26	−0.24	−1.85
in situ[e] $[Os_2Cl_9]^{3-}$	—	+0.90	+0.20	−1.46

[a] In CH_2Cl_2/0.5 M $(Bu_4N)BF_4$ at a Pt working electrode *vs.* Ag/AgCl ref.; *cf.* $E_{1/2}$ = +0.55 V for $[Fe(C_5H_5)_2]^{+/0}$. [b] Couples fully reversible (⟷), or partially reversible (→), as indicated, under prevailing conditions. [c] $(Bu_4N)_3[Os_2Br_9]$ has identical voltammetry. [d] This wave measured in MeCN. [e] See text.

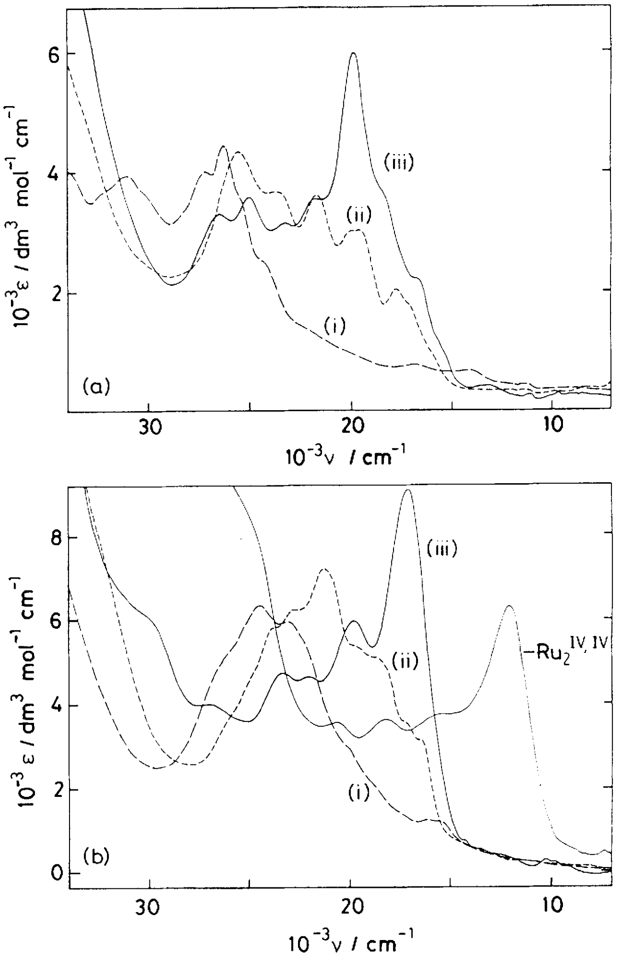


Figure 2. Electronic absorption spectra, recorded in an OTTLE cell at 215 K (see text). (a) $[Os_2Br_{10}]^{z-}$ spectra: (i) $Os_2^{III,III}$; (ii) $Os_2^{IV,III}$; (iii) $Os_2^{IV,IV}$. (b) $[M_2Br_9]^{z-}$ spectra: (i) $Os_2^{III,III}$; (ii) $Os_2^{IV,III}$; (iii) $Os_2^{IV,IV}$.

five oxidation levels, as first demonstrated for $[Ru_2Br_9]^{z-}$.[11,12] Figure 1 compares the response of $[Os_2Br_9]^{z-}$ which is shifted cathodically, as expected,[13] and has a noticeably larger separation between successive iv/iii couples. The most reduced species, $[Os_2Br_9]^{4-}$, is very reactive even at 215 K.

Apparently the electrochemistry of $[Os_2Cl_{10}]^{2-}$ and $[Os_2Br_{10}]^{2-}$ has not been considered previously. In accord with their greater overall ligation, the decahalides prove systematically easier to oxidize and harder to reduce than their nonahalide counterparts (by ≥0.5 V at every stage). Consequently the $Os_2^{IV,IV\rightarrow V,IV}$ couple is accessible in solution, even though electrogenerated $[Os_2X_{10}]^-$ is shortlived under the prevailing conditions. It is noteworthy that neutral $[Os_2Cl_{10}]$ is also known, in the crystalline state, and confirmed to have structure (**a**).[14]

The first two voltammetric reductions of $[Os_2Br_{10}]^{2-}$ are fully reversible in CH_2Cl_2 at 215 K. Accordingly, the new species $[Os_2Br_{10}]^{3-}$ and $[Os_2Br_{10}]^{4-}$ were electrogenerated and their electronic spectra recorded in a cryostatted optically transparent thin-layer electrode (OTTLE) cell (Figure 2a). However the third reduction is coupled with rapid expulsion of Br^- by $[Os_2Br_{10}]^{5-}$, forming $[Os_2Br_9]^{4-}$ which is readily detected on the voltammetric return scan. Above 240 K, the di-osmium(iii) complex $[Os_2Br_{10}]^{4-}$ gives way quantitatively to $[Os_2Br_9]^{3-}$ in a parallel reaction, as in Scheme 1. Moreover, the corresponding electroreduction of $(Bu_4N)_2[Os_2Cl_{10}]$ appears to lead directly to the hitherto unknown $[Os_2Cl_9]^{3-}$, provisionally identified in solution by its voltammetry and optical spectrum (ν_{max} 28 670 and 32 090 cm^{-1}).

Electronic spectra for the $[Os_2^{III,III}]$, $[Os_2^{IV,III}]$, and $[Os_2^{IV,IV}]$ states of structures (**a**) and (**b**) are contrasted in Figure 2. The UV-VIS region is dominated in each case by an intense manifold of halide-to-metal charge-transfer transitions whose centre of gravity moves to lower energy on stepwise oxidation of the metal centres (and on replacement of Os by Ru in **b**). Resemblance with the corresponding $[Ru_2Br_9]^{z-}$ envelope[11,15] is most evident at the (iv,iv) level, where metal–metal interaction is expected to be lessened by d-orbital contraction (Figure 2b). For $(Bu_4N)[Os_2Br_9]$, μ_{eff}(295 K) is 1.51 μ_B per Os atom, according to preliminary variable-temperature measurements.[16]

Several weaker features are seen in the 10 000 to 3 000 cm^{-1} region for these complexes but, in particular, mixed-valence $[Os_2Br_9]^{2-}$ is characterised by a well resolved broad band at 4 700 cm^{-1} (ε 780 dm^3 mol^{-1} cm^{-1}) which is more distinct than any corresponding feature of $[Os_2Br_{10}]^{3-}$. Detailed studies are in progress on the crystal structures, spectra, and magnetic properties of the newly discovered di-osmium nonahalides in successive oxidation states.

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