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FULL PAPER

Characterisation of edge-sharing decahalogenodiosmate complexes in multiple oxidation states; synthesis, magnetochemistry, voltammetry and associated spectroelectrochemistry of $[PPh_4]_2[Os_2(\mu\text{-}X)_2X_8]$ (X = Br or Cl) †

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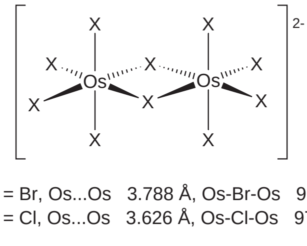
Organo-soluble salts of the edge-sharing bioctahedral $[Os_2(\mu\text{-}X)_2X_8]^{2-}$ complexes (X = Br or Cl) have been prepared by an improved procedure and investigated electrochemically. Their solution redox behaviour spans five levels, $[Os_2(\mu\text{-}X)_2X_8]^{z-}$ (*z* = 1–5), complementing pentavalent $[Os_2(\mu\text{-}Cl)_2Cl_8]$ known only in the solid phase. Chilled solutions of electrogenerated $[Os_2(\mu\text{-}X)_2X_8]^{3-}$ and $[Os_2(\mu\text{-}X)_2X_8]^{4-}$ have been characterised by UV/VIS/NIR spectroscopy (213 K; 45 000 to 5000 cm^{-1}). In contrast, $[Os_2(\mu\text{-}X)_2X_8]^{-}$ and $[Os_2(\mu\text{-}X)_2X_8]^{5-}$ rearrange rapidly to the face-sharing nonahalides, $[Os_2(\mu\text{-}X)_3X_6]^{-}$ and $[Os_2(\mu\text{-}X)_3X_6]^{4-}$, losing $\frac{1}{2}X_2$ or X^- as appropriate. The redetermined magnetic moments of the $[Os_2(\mu\text{-}X)_2X_8]^{2-}$ dimers (as their $[PPh_4]^+$ salts) are convergent at 1.52 and 1.48 μ_B per Os (296 K) for X = Br and Cl respectively. Cleavage reactions of $[Os_2(\mu\text{-}X)_2X_8]^{z-}$ (X = Br or Cl) are valence-dependent, leading to $[OsX_5L]^-$ (L = MeCN) for *z* = 2, $[OsX_6]^{2-}$ and *trans*-$[OsX_4L_2]^-$ for *z* = 3, and exclusively *trans*-$[OsX_4L_2]^-$ for *z* = 4.

The decahalogenodiosmate(IV) dianions, $[Os_2(\mu\text{-}X)_2X_8]^{2-}$ (X = Br or Cl), were discovered independently by two groups in 1984.[1,2] Until recently,[3–5] these edge-sharing structures were the only known class of bridged diosmium halide complexes $[Os_2X_n]^{z-}$. Aside from X-ray structural characterisation and detailed examination of their vibrational spectra,[6] the decahalogenodiosmate complexes have received surprisingly little attention. In particular, their solution behaviour is largely unexplored. We now describe improved syntheses of both complexes by the same route, together with a detailed account of their redox chemistry and associated spectroelectrochemistry. A preliminary report of this aspect has appeared.[4] We also present new magnetic measurements on the $[PPh_4]^+$ salts of $[Os_2(\mu\text{-}X)_2X_8]^{2-}$ complexes (X = Br or Cl), and describe some cleavage reactions which demonstrate the utility of the dimers as convenient precursors to monomeric halide complexes of Os^{IV} and/or Os^{III}.



X = Br, Os...Os 3.788 Å, Os-Br-Os 96.3°
X = Cl, Os...Os 3.626 Å, Os-Cl-Os 97.5°

Cotton *et al.*[1] reported that the reaction of tetravalent $[NBu_4]_2[OsBr_6]$ in hot trifluoroacetic acid yielded a black solid, which they formulated analytically as $[NBu_4]_2[Os_2Br_{10}]$. A highly crystalline material was obtained when the temperature was carefully maintained near 313 K and single-crystal X-ray diffraction disclosed the previously unreported edge-sharing bioctahedral structure. Krebs, Preetz and colleagues[2] originally prepared $[NEt_4]_2[Os_2(\mu\text{-}Cl)_2Cl_8]$ by a different approach, heating pentavalent $[NEt_4][OsCl_6]$ for a short period at 413 K. The double-bridged structure of metathetically derived $[NBu_4]_2[Os_2(\mu\text{-}Cl)_2Cl_8]$ was also confirmed by X-ray diffraction.[2] Later, Bruns and Preetz[7] prepared the same compound by heating tetravalent $[NEt_4][OsCl_5(CO)]$ to between 393 and 423 K. Our clarification of the stepwise $[OsX_6]^{2-}$–CF_3CO_2H condensation reactions[4,5] (see below) was followed by discovery of another logical but less convenient route to $[Os_2(\mu\text{-}X)_2X_8]^{2-}$, also applicable to both bromide and chloride. In this approach, Preetz and co-workers[8] showed that oxidative addition of X_2 to the metal–metal-bonded compounds $[NBu_4]_2[Os_2X_8]$ in the absence of excess of X^- produces $[NBu_4]_2[Os_2(\mu\text{-}X)_2X_8]$ rather than conversion to $[OsX_6]^{2-}$.

The general features of the $[NBu_4]_2[Os(\mu\text{-}X)_2X_8]$ (X = Br or Cl) structures are very similar. The metal centres are displaced from an ideal bioctahedral geometry, with the bridging Os–X_b–Os′ angle greater than 90° and X_b–Os–X'_b less than 90°. The resulting separation is quite long, at 3.788(3) and 3.626(1) Å for Br and Cl respectively. This displacement is presumed to reflect the dominant effect of electrostatic Os^{4+}/Os^{4+} repulsion over any bonding interactions that might occur by direct d-orbital overlap or superexchange, and the present paper is concerned with exploring the properties of these weakly coupled systems.

Results and Discussion

Synthesis

Our attempts to isolate authentic, pure samples of the $[Os_2(\mu\text{-}X)_2X_8]^{2-}$ (X = Br or Cl) complexes by prevailing literature methods were unsatisfactory. In our hands, treatment of $[NBu_4]_2[OsBr_6]$ in neat (= 100%) CF_3CO_2H under reflux, as directed in ref. 1, resulted in the separation of a highly reactive black precipitate which was shown to be previously unreported, analytically pure $[NBu_4][Os_2(\mu\text{-}Br)_3Br_6]$.[4,5] However, if the $[NBu_4]_2[OsBr_6]$–CF_3CO_2H mixture was warmed only to 313 K (as in the case of the structurally determined material[1]), high yields of $[NBu_4]_2[Os_2(\mu\text{-}Br)_2Br_8]$ could be collected. The genuine decabromodiosmate complex, which is very similar in appearance to $[NBu_4][Os_2(\mu\text{-}Br)_3Br_6]$ and shares the same Os^{IV}_2

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† *Non-SI unit employed*: $\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}, eV ≈ 1.60 × 10^{-19} J.

valency, was definitively characterised by its far-IR spectrum and C, H, N, Br elemental analysis. The X-ray powder diffraction pattern of this compound also matched that calculated from the known structure of $[NBu_4]_2[Os_2(\mu\text{-}Br)_2Br_8]$. The tetraphenylphosphonium salt of $[Os_2(\mu\text{-}Br)_2Br_8]^{2-}$ has been obtained in an identical manner, and is a valuable alternative derivative.

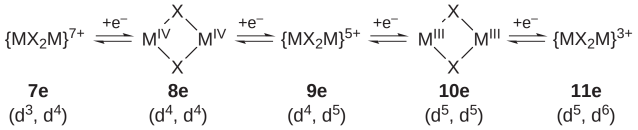
Turning to the decachlorodiosmate, we first attempted to prepare $[PPh_4]_2[Os_2(\mu\text{-}Cl)_2Cl_8]$ by a procedure paralleling that of Krebs and co-workers,[2] which starts from pentavalent $[NEt_4][OsCl_6]$.[9] However, heating $[PPh_4][OsCl_6]$ at 413 K under vacuum yielded a mixture of the desired product and $[PPh_4]_2[OsCl_6]$. Another published procedure for the synthesis of $[Os_2(\mu\text{-}Cl)_2Cl_8]^{2-}$ describes heating $[NEt_4][OsCl_5(CO)]$, but we were unable to make this starting material.[7] All our attempts to synthesize tetravalent $A[OsCl_5(CO)]$ ($A = [NBu_4]^+$ or $[PPh_4]^+$) resulted in the isolation of the tervalent salts instead. Electrochemical studies on $[NBu_4]_2[OsCl_5(CO)]$ reveal that the $Os^{III} \longrightarrow Os^{IV}$ oxidation is chemically irreversible,[5] which attests to the elusiveness of $[OsCl_5(CO)]^-$. Following an analogous strategy [*i.e.* thermal displacement of a volatile ligand to give a co-ordinatively unsaturated osmium(IV) centre], we found that heating $[NBu_4][OsCl_5(thf)]$[5] under vacuum gave mixtures of $[NBu_4]_2[Os_2(\mu\text{-}Cl)_2Cl_8]$ and $[NBu_4]_2[OsCl_6]$. Efforts to recrystallise these mixtures invariably resulted in decomposition of the green decachlorodiosmate complex (see below). Given the success of the CF_3CO_2H route to organo-soluble salts of $[Os_2(\mu\text{-}Br)_2Br_8]^{2-}$, it seemed worthwhile to pursue the decachloride by a similar procedure.

Heating a yellow solution of $[NBu_4]_2[OsCl_6]$ in neat CF_3CO_2H (to 413 K) produced a change to green over several hours. No products separated directly upon cooling (unlike the corresponding decabromide), but addition of diethyl ether led to the formation of a finely divided green precipitate. This proved to be a mixture of $[NBu_4]_2[Os_2(\mu\text{-}Cl)_2Cl_8]$, and some unchanged $[NBu_4]_2[OsCl_6]$, at least establishing that condensation occurs under these conditions. Corresponding treatment of the $[PPh_4]^+$ salt of $[OsCl_6]^{2-}$ led to slow but convenient separation of $[PPh_4]_2[Os_2(\mu\text{-}Cl)_2Cl_8]$, free of starting material and CF_3CO_2H. Near-quantitative yields (95% or more) of $[PPh_4]_2[Os_2(\mu\text{-}Cl)_2Cl_8]$ are now routinely obtained from this reaction, by prolonged heating of the $[PPh_4]_2[OsCl_6]$–CF_3CO_2H mixture at ≈413 K.

All attempts to recrystallise samples of the highly reactive decahalogenodiosmate(IV) compounds from dry dichloromethane resulted in their decomposition. Therefore, the spontaneous separation of the analytically pure $A_2[Os_2(\mu\text{-}X)_2X_8]$ compounds ($X = Br$, $A = [PPh_4]^+$ or $[NBu_4]^+$; $X = Cl$, $A = [PPh_4]^+$) from hot, neat CF_3CO_2H is of central importance to their preparation. Preetz and co-workers have done much to generalise the $[MX_6]^{z-}$–CF_3CO_2H methodology, and have applied it decisively to prepare salts of edge-sharing $[Re_2(\mu\text{-}X)_2X_8]^{2-}$,[10] $[Tc_2(\mu\text{-}X)_2X_8]^{2-}$,[11] $[Ir_2(\mu\text{-}Cl)_2Cl_8]^{2-}$,[12] and $[Pt_2(\mu\text{-}X)_2X_8]^{2-}$,[13] where X = Br or Cl throughout (except for Ir).

Magnetochemistry

The $[NBu_4]_2[Os_2(\mu\text{-}Br)_2Br_8]$ complex was initially described as 'almost diamagnetic' at room temperature (296 K),[1] with a magnetic moment of 0.26 μ_B per osmium (μ_{Os}). In contrast, the decachlorodiosmate complex was separately reported to have μ_{Os} (296 K) = 1.36 μ_B,[2] although the numerical values listed for magnetic susceptibility (χ_m) and for μ_{Os} are mutually inconsistent.‡ Given the very low moment reported for $[NBu_4]_2[Os_2(\mu\text{-}Br)_2Br_8]$, and the uncertainty associated with the published values of χ_m and μ_{Os} for $[NBu_4]_2[Os_2(\mu\text{-}Cl)_2Cl_8]$, we thought it important to re-examine the magnetic properties of these compounds.



Scheme 1 Electron-counting scheme for $[Os_2(\mu\text{-}X)_2X_8]^{z-}$ complexes

When room-temperature magnetic moments of freshly prepared samples of the $[PPh_4]_2[Os_2(\mu\text{-}X)_2X_8]$ compounds were measured a consistent picture emerged; μ_{Os} was found to be 1.52 and 1.48 μ_B for X = Br and Cl respectively. The variation of μ_{Os} with temperature (300–4.2 K) has also been examined,[14] and μ_{Os} confirmed to decrease towards zero with decreasing temperature for both edge-sharing dimers. Even monomeric low-spin osmium(IV) complexes have magnetic moments that tend to zero with decreasing temperature,[15] so no immediate conclusions can be drawn regarding the extent of the $Os \cdots Os$ interaction. We have taken the opportunity to carry out parallel magnetic susceptibility measurements (300–4.2 K) for $[PPh_4]_2[OsX_6]$ (X = Br or Cl),[14] and a detailed account of these magnetic studies on mono- and bi-nuclear osmium(IV) complexes sharing an octahalide co-ordination sphere will follow.

Electrochemistry

In our experience, halide- and pseudohalide-bridged binuclear transition-metal complexes are quite commonly capable of successive one-electron transfer steps spanning several oxidation levels.[16–22] The decahalogenodiosmate complexes are no exception although their voltammetric behaviour has not been considered elsewhere. Both $[Os_2(\mu\text{-}X)_2X_8]^{2-}$ complexes (X = Br or Cl) display *four* metal-centred redox processes, *i.e.* one oxidation and three reductions, as set out in Scheme 1. These processes are conveniently described in terms of the $n/(n + 1)$ incremental change in nett d-electron population; $[Os_2(\mu\text{-}X)_2X_8]^{2-}$, having two d^4 centres, is designated an eight-electron (8e) species, so that *reversible* one-electron reduction would correspond to the 8e/9e redox couple. Table 1 lists the properties of the observed couples as determined by cyclic voltammetry and alternating current voltammetry, and Fig. 1 illustrates the low-temperature cyclic voltammetric behaviour of $[PPh_4]_2[Os_2(\mu\text{-}Br)_2Br_8]$ and $[PPh_4]_2[Os_2(\mu\text{-}Cl)_2Cl_8]$. The reversible $Os^{IV}{}_2$–$Os^{IV}Os^{III}$ (8e/9e) and $Os^{IV}Os^{III}$–$Os^{III}{}_2$ (9/10e) reductions are shown in Fig. 3(a). Fig. 3(b) encompasses irreversible $Os^{III}{}_2$–$Os^{III}Os^{II}$ (10e $\longrightarrow$ 11e) reduction, while Fig. 3(c) encompasses the irreversible $Os^{V}Os^{IV}$–$Os^{IV}{}_2$ (7e $\longleftarrow$ 8e) oxidation. Unexpectedly, the same rearrangement product is formed upon scanning the most extreme reduction and the most extreme oxidation. The waves associated with the formation of this species are marked with asterisks in Fig. 3(b, c). These new couples, centred at +1.07, +0.35 and −1.27 V, coincide with those recorded for $[Os_2(\mu\text{-}Br)_3Br_6]^{z-}$.[4,5] Upon 10e/11e reduction (at *ca.* −1.9 V), the electrogenerated $[Os_2(\mu\text{-}Br)_2Br_8]^{5-}$ species expels Br^- immediately, forming the triple-bridged structure to satisfy the co-ordination requirements of each Os atom while moderating the overall negative charge. At low temperature, 11e $[Os_2(\mu\text{-}Br)_3Br_6]^{4-}$ is sufficiently long–lived to be detected by its oxidation to $[Os_2(\mu\text{-}Br)_3Br_6]^{3-}$ upon the return scan, providing a typical electrochemical step-chemical step-electrochemical step (ECE) voltammogram [Fig. 3(c)]. The formation of $[Os_2(\mu\text{-}Br)_3Br_6]^-$ upon oxidation of $[Os_2(\mu\text{-}Br)_2Br_8]^{2-}$ presumably involves oxidative elimination of $Br^{\bullet}$ (perhaps as $\frac{1}{2}$ Br_2). The voltammetric behaviour of $[PPh_4]_2[Os_2(\mu\text{-}Cl)_2Cl_8]$ under parallel conditions is very similar to that of the bromide complex, although oxidation to $Os^{V}Os^{IV}$ is more difficult to detect [Fig. 3(d)]. In this case, the 7e/8e couple appeared better defined in acetonitrile, partly because rearrangement of $[Os_2(\mu\text{-}Cl)_2Cl_8]^-$ to $[Os_2(\mu\text{-}Cl)_3Cl_6]^-$ was not detected on the voltammetric timescale in this solvent.

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‡ In ref. 2 the figure of 1.36 μ_B (per Os) does not correspond to the quoted susceptibility, of $\chi_m = 2970 \times 10^{-6}$ cm³ mol⁻¹. Based on the latter $\mu_{eff} = 1.87$ per Os. Alternatively, accepting μ_{eff} (per Os) = 1.36 μ_B implies $\chi_m = 780 \times 10^{-6}$ cm³ mol⁻¹.

Table 1 Voltammetric data for $[Os_2(\mu\text{-}X)_2X_8]^{2-}$ complexes[a]

	V,IV/IV,IV (7e/8e)	IV,IV/IV,III (8e/9e)			IV,III/III,III (9e/10e)			III,III/III,II (10e/11e)
Complex	E_{pa}/V	$E_{\frac{1}{2}}$/V	ΔE_p/mV	I_{pa}/I_{pc}	$E_{\frac{1}{2}}$/V	ΔE_p/mV	I_{pa}/I_{pc}	E_{pc}/V
$[PPh_4]_2[Os_2Br_{10}]$	+1.86 (irr)	+0.30 (rev)	80	1.0	−0.18 (rev)	80	1.0	−1.88 (irr)
$[PPh_4]_2[Os_2Cl_{10}]$	+2.10 (irr)[b]	+0.26 (qrev)	110	1.0	−0.24 (qrev)	120	1.0	−1.85 (irr)

[a] Measured in CH_2Cl_2 containing 0.50 mol dm^{-3} $[NBu_4][PF_6]$ at 213 K, *vs.* Ag–AgCl reference electrode, against which ferrocene–ferrocenium occurs at +0.55 V. Scan rate = 100 mV s^{-1}. By convention the couples are listed as reductions, the numbers in parentheses referring to the electron-counting scheme used in the text. rev = Reversible, qrev = quasi-reversible and irr = irreversible, as determined by cyclic voltammetry where a reversible process is defined as one where $I_{pr}/I_{pf} = 1.0$ and ΔE_p is constant with increasing scan rate, whereas for a quasi-reversible process $I_{pr}/I_{pf} = 1.0$ and ΔE_p increases with increasing scan rate. $E_{\frac{1}{2}} = (E_{pa} + E_{pc})/2$, $\Delta E_p = E_{pf} - E_{pr}$ at a scan rate = 100 mV s^{-1}; I_{pa}/I_{pc} ratio determined by the method given in ref. 23. The subscripts pf and pr refer to the appropriate numerical maxima (*E* or *I*) of the forward and reverse peaks respectively, of a cyclic voltammetric response. [b] More reliably observed in MeCN containing 0.10 mol dm^{-3} $[NBu_4][PF_6]$ at 233 K, *vs.* Ag–AgCl.

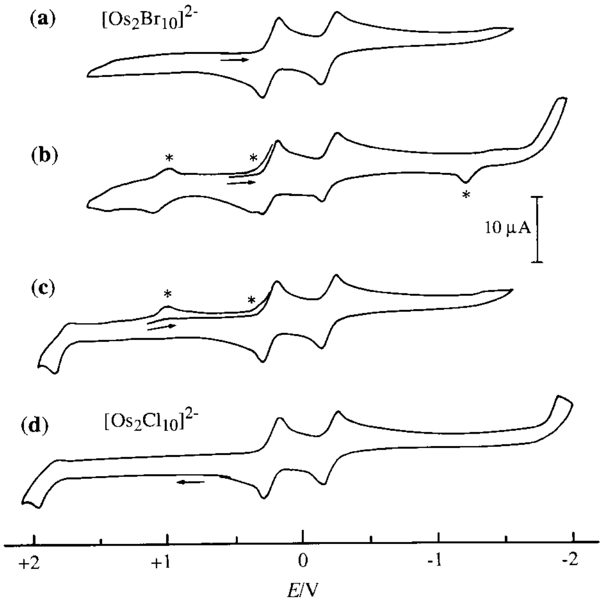

Fig. 1 Cyclic voltammetry of $[NBu_4]_2[Os_2(\mu\text{-}X)_2X_8]$. (a), (b), (c) X = Br, in CH_2Cl_2 containing 0.5 mol dm^{-3} $[NBu_4][PF_6]$ at 213 K, scan rate = 100 mV s^{-1}. Asterisk indicates additional waves corresponding to $[Os_2(\mu\text{-}Br)_3Br_6]^{z-}$ (see text), observed after scanning over the irreversible 10e/11e reduction or the irreversible 7e/8e oxidation. (d) X = Cl, in MeCN containing 0.1 mol dm^{-3} $[NBu_4][PF_6]$ at 233 K, scan rate = 100 mV s^{-1}

The 8e/9e and 9e/10e reductions, which are only 0.5 V apart, can be formally designated as consecutive Os^{IV}–Os^{III} couples. A greater separation (*ca.* 1.75 V) is found between the 7e/8e and 8e/9e couples, since the 7e/8e oxidation is first of a pair of Os^{V}–Os^{IV} processes. Equally, we observe a large separation between the 9e/10e and 10e/11e couples, the latter being the first formal Os^{III}–Os^{II} couple. The grouping of couples into related pairs, alternating with wider voltage separations between such pairs, is the characteristic pattern in binuclear transition-metal electrochemistry.[16–22] Under conditions where the 7e/8e and 10e/11e couples become reversible,§ and their $E_{\frac{1}{2}}$ values reliable, we can infer that their respective 6e/7e and 11e/12e partners probably lie some 0.5 V further on, just beyond the voltage limits of the present electrolyte medium. Although 6e $[Os_2(\mu\text{-}Cl)_2Cl_8]$ (very reactive in solution) is not accessible in our measurements, it has been prepared as a solid by the two-phase reaction of OsF_6 with BCl_3 at low temperature, and characterised crystallographically.[24] This means that six oxidation states of the edge-sharing dimer have been defined in all, ranging from Os^{V}_2 to $Os^{III}Os^{II}$.

The gap between related couples in binuclear complexes (ΔE) is a recognised index of the degree of electronic interaction between the two metal centres.[25,26] Generally speaking, the larger the gap the greater the presumed interaction. The separation of the 8e/9e and 9e/10e couples in the two $[Os_2(\mu\text{-}X)_2X_8]^{2-}$ complexes is virtually the same, *i.e.* 0.48 V for X = Br and 0.50 V for X = Cl. In confacial $[Os_2(\mu\text{-}X)_3X_6]^{3-}$, where the metal–metal interaction is distinctly stronger, ΔE takes the values 0.72 and 0.93 V for X = Br and Cl respectively.[5] Comproportionation constants, $K_c = 10^{\Delta E/(2.3RT/F)}$, are often quoted for binuclear complexes as a means of conveying the stability of the mixed-valence species towards redox disproportionation [equation (1)].[27] For the $[Os_2(\mu\text{-}X)_2X_8]^{2-}$–$[Os_2(\mu\text{-}X)_2X_8]^{4-}$ system K_c takes

$$\{Os^{III}(\mu\text{-}X)_2Os^{III}\}^{4+} + \{Os^{IV}(\mu\text{-}X)_2Os^{IV}\}^{6+} \xrightleftharpoons{K_c} 2\,\{Os^{IV}(\mu\text{-}X)_2Os^{III}\}^{5+} \qquad (1)$$

the values 2.3×10^{11} for X = Br and 6.8×10^{11} for X = Cl. Such large numbers imply considerable stability of $[Os_2(\mu\text{-}X)_2X_8]^{3-}$ towards redox disproportionation (assuming retention of gross structure). However in practice the trianion can react by pathways not encompassed in this equilibrium, and is prone to valence disproportionation coupled to ligand transfer. Electrogenerated $[Os_2(\mu\text{-}X)_2X_8]^{3-}$ readily gives way to a mixture of $[OsX_6]^{2-}$ and tervalent products, through asymmetric cleavage of the double-halide bridge in the mixed-valence dimer. Salts of the $[Os_2(\mu\text{-}X)_2X_8]^{3-}$ anions (X = Br or Cl) have not been isolated to date, and this underlines the value of their characterisation *in situ* by optical spectroelectrogeneration as described below.

Several other edge-sharing 5d/5d decahalogenodimetalate complexes are now known, *e.g.* $[Re_2(\mu\text{-}X)_2X_8]^{2-}$ (X = Br or Cl)[10] and $[Ir_2(\mu\text{-}Cl)_2Cl_8]^{2-}$.[12] All these systems present informative voltammetry, and further investigations in our laboratory will be reported shortly.

Optical spectroelectrochemistry

Spectroelectrogeneration. The moderate potentials associated with the 8e/9e and 9e/10e couples, and their chemical reversibility at low temperature, suggested an opportunity to electrogenerate previously unreported $[Os_2(\mu\text{-}X)_2X_8]^{3-}$ and $[Os_2(\mu\text{-}X)_2X_8]^{4-}$ complexes. Undertaking such experiments in an optically transparent semi-thin-layer electrogenerative (OSTLE) cell led to characterisation of these species *in situ*, by means of their electronic spectra.

Employing solutions in CH_2Cl_2–$[NBu_4][PF_6]$ at 213 K within the chilled OSTLE cell, of pathlength 0.5 mm, it proved possible successively to electrogenerate $[Os_2(\mu\text{-}Br)_2Br_8]^{3-}$ and $[Os_2(\mu\text{-}Br)_2Br_8]^{4-}$, and to cycle between the 8e, 9e and 10e species without loss of material or spectral degradation. The optical changes accompanying the first and second steps

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§ At present any subsequent electron-transfer process detected at more extreme potentials than either of the 7e/8e or 10e/11e couples have little chemical significance in relation to the $[Os_2(\mu\text{-}X)_2X_8]^{z-}$ complexes, since the former couples are irreversible. However, should conditions be found where the 7e/8e or 10e/11e processes were to become reversible, then the corresponding pairs to these couples are expected outside the +2.0 to −2.0 V window available under the experimental conditions described in Table 1.

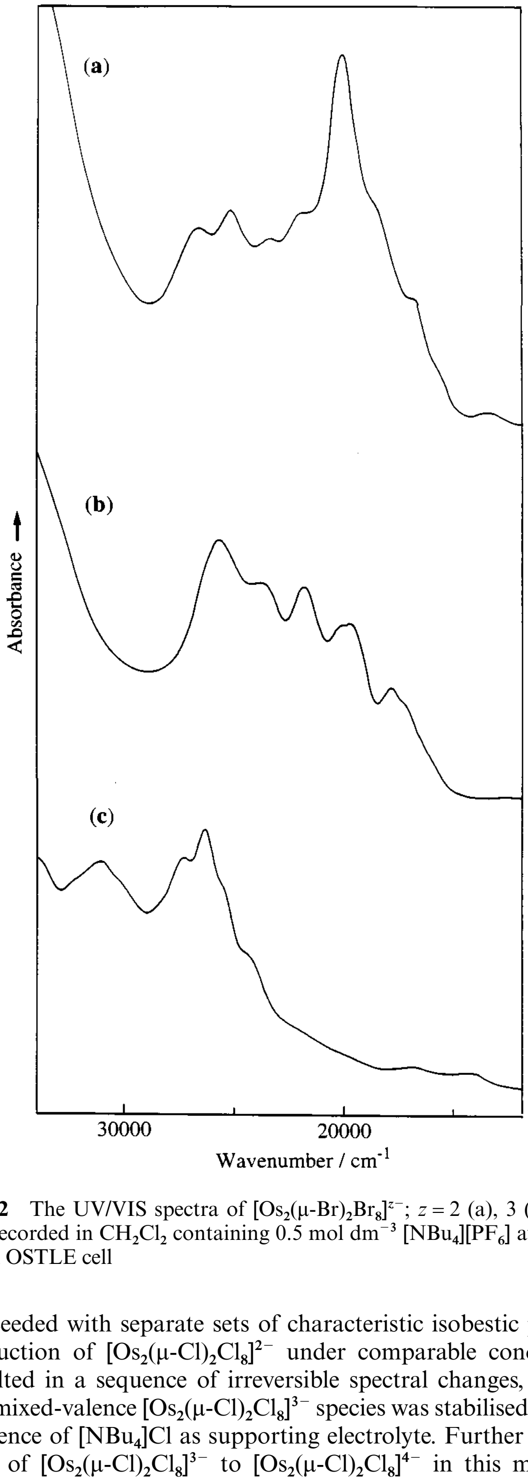


Fig. 2 The UV/VIS spectra of $[Os_2(\mu\text{-}Br)_2Br_8]^{z-}$; $z = 2$ (a), 3 (b) or 4 (c), recorded in CH_2Cl_2 containing 0.5 mol dm^{-3} $[NBu_4][PF_6]$ at 213 K in an OSTLE cell

proceeded with separate sets of characteristic isobestic points. Reduction of $[Os_2(\mu\text{-}Cl)_2Cl_8]^{2-}$ under comparable conditions resulted in a sequence of irreversible spectral changes, unless the mixed-valence $[Os_2(\mu\text{-}Cl)_2Cl_8]^{3-}$ species was stabilised by the presence of $[NBu_4]Cl$ as supporting electrolyte. Further reduction of $[Os_2(\mu\text{-}Cl)_2Cl_8]^{3-}$ to $[Os_2(\mu\text{-}Cl)_2Cl_8]^{4-}$ in this medium was undertaken several times, but in each case electrolysis proceeded smoothly only to ≈50% conversion before abrupt decomposition. Even so, it is possible to identify the most prominent band of the emerging $[Os_2(\mu\text{-}Cl)_2Cl_8]^{4-}$ spectrum (at ≈34 500 cm^{-1}) from the orderly early phase of the electrolysis.

UV/VIS spectra of $[Os_2(\mu\text{-}X)_2X_8]^{z-}$ complexes (z = 2, 3 or 4). Electronic spectra in the range 15 000 to 45 000 cm^{-1} are dominated by intense halide-to-metal charge-transfer (XMCT) bands, due essentially to $X(\pi)\rightarrow Os(d_\pi)$ excitations. For the established $Os^{IV}{}_2$ complexes[6] the absorption manifold is found some 6000 cm^{-1} lower for $[Os_2(\mu\text{-}Br)_2Br_8]^{2-}$ than for $[Os_2(\mu\text{-}Cl)_2Cl_8]^{2-}$, as required for the XMCT assignment [Figs. 2(a), 3(a)]. In addition, the intense absorption envelopes show more structure for the bromo complex. This is a familiar observation, and the extra splitting is attributable to the larger spin–orbit coupling constant of Br *vs.* Cl.[28]

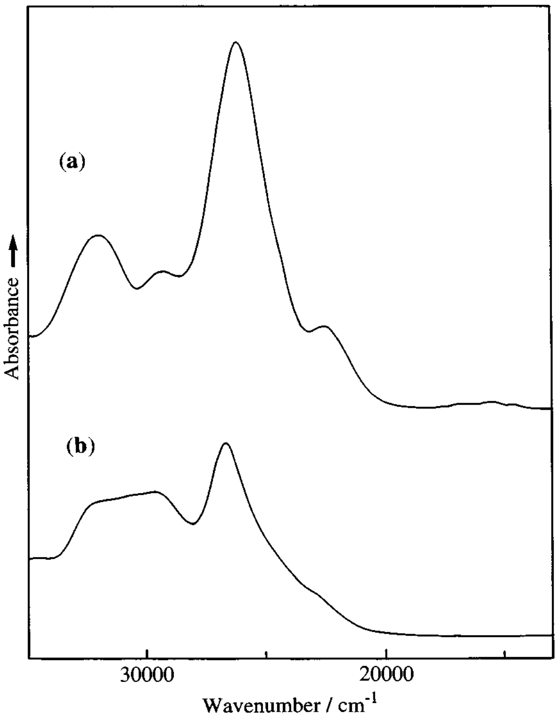


Fig. 3 The UV/VIS spectra of $[Os_2(\mu\text{-}Cl)_2Cl_8]^{z-}$; $z = 2$ (a) or 3 (b), recorded in CH_2Cl_2 containing 0.1 mol dm^{-3} $[NBu_4]Cl$ at 213 K in an OSTLE cell. Note that the spectrum of $[Os_2(\mu\text{-}Cl)_2Cl_8]^{2-}$ is identical to that recorded in the presence of $[NBu_4][PF_6]$ electrolyte

For the electrochemically reduced compounds, the corresponding charge-transfer (CT) assignment of the major spectral features is supported by several observations. Both $[Os_2(\mu\text{-}X)_2X_8]^{3-}$ and $[Os_2(\mu\text{-}X)_2X_8]^{4-}$ yield Cl/Br shifts of *ca.* 5000–7000 cm^{-1} in the intense absorption envelope (Table 2), as required by the relative optical electronegatives of Cl and Br ligands. Upon two-electron reduction of $[Os_2(\mu\text{-}X)_2X_8]^{2-}$ to $[Os_2(\mu\text{-}X)_2X_8]^{4-}$, *i.e.* comparing the fully tetravalent and fully tervalent states, the absorption manifold moves to higher energy, by ≈8000 cm^{-1} overall (Fig. 2). This is also consistent with the XMCT assignment, since the optical electronegativity of the bimetallic core should decrease upon reduction from $\{Os(\mu\text{-}X)_2Os\}^{6+}$ to $\{Os(\mu\text{-}X)_2Os\}^{4+}$. The shifts in the XMCT spectra between $[OsX_6]^{2-}$ and $[OsX_6]^{3-}$ (Os^{IV} and Os^{III}) are ≈8300 cm^{-1} for X = Cl and ≈8200 cm^{-1} for X = Br.

In referring to $X(\pi)\rightarrow Os(d_\pi)$ charge transfer we have not yet distinguished between terminal (X_t) and bridging halides (X_b). The CT manifold in $[Os_2(\mu\text{-}X)_2X_8]^{2-}$ (X = Br or Cl) spans ≈10 000 cm^{-1} [Figs. 2(a), 3(a)]; this broad envelope of transitions could conceivably encompass different varieties of CT. X-Ray photoelectron spectral studies on a range of halide-bridged complexes of the type $[M_2(\mu\text{-}Cl)_2Cl_8]$ and $[M_2(\mu\text{-}Cl)_3Cl_6]^{3-}$ (M = Cr, Mo, W or Rh) suggest that the $X_b(\pi)$ levels lie lower than the $X_t(\pi)$ levels,[29] by an eV or so, in accord with the joint stabilisation of $X_b(\pi)$ by two metal cations. This being the case, if CT excitations from the bridging halide ligands are observed, they should appear at higher energy. Indeed, Bruns and Preetz[6] have described the UV/VIS region of the $Os^{IV}{}_2$ spectra in terms of $X_b(\pi)\rightarrow Os(d_\pi)$ and $X_t(\pi)\rightarrow Os(d_\pi)$ CT transitions. Spectroelectrochemical definition of fully reduced $[Os_2(\mu\text{-}Cl)_2Cl_8]^{4-}$ is incomplete (as noted above), but $[Os_2(\mu\text{-}Br)_2Br_8]^{4-}$ certainly reveals a broad CT envelope with several components, consistent with contributions from different kinds of $X(\pi)\rightarrow Os(d_\pi)$ CT. In our view, further measurements and theoretical analysis are required before specific assignments can be secured. This is particularly so because one needs first to identify the orientation of the binuclear metal LUMO, and then to distinguish between axial and equatorial $X(\pi)\rightarrow Os(d_\pi)$ CT

Table 2 The UV/VIS/NIR spectral data for $[Os_2(\mu\text{-}X)_2X_8]^{z-}$ complexes

Complex	Band maxima/cm^{-1} (ε/dm^3 mol^{-1} cm^{-1})														
$[Os_2Br_{10}]^{2-}$ [a]	4880		5300				9660	10 980	13 150	19 940	21 600	23 320	25 130	26 450	34 150
	(170)		(320)				(120)	(90)	(350)	(6000)	(3600)	(3040)	(3430)	(3140)	(4560)
$[Os_2Br_{10}]^{3-}$ [a]	4850	4990	5270	5530	6660	7900	9900	11 980	17 720	19 510	21 630	23 700	25 520		
	(310)	(320)	(320)	(340)	(330)	(140)	(60)	(70)	(2010)	(3010)	(3610)	(3680)	(4340)		
$[Os_2Br_{10}]^{4-}$ [a]	7780			5630					14 040	16 790			26 270	27 220	31 000
	(80)			(50)					(220)	(310)			(4410)	(4000)	(3930)
$[Os_2Cl_{10}]^{2-}$ [b]		5000	5400				9950	14 630	15 590	16 880	22 600		26 230	29 480	32 130
		(120)	(340)				(600)	(210)	(230)	(310)	(4390)		(16 360)	(6680)	(8280)
$[Os_2Cl_{10}]^{3-}$ [b]		5000	6000		7100	8750	10 100						26 620 [c]	29 690	32 250
		(450)	(490)		(600)	(420)	(220)						(9080)	(7080)	(6900)

[a] Recorded in CH_2Cl_2 containing 0.50 mol dm^{-3} $[NBu_4][PF_6]$ at 213 K in an OSTLE cell. [b] Recorded in CH_2Cl_2 containing 0.10 mol dm^{-3} $[NBu_4][Cl]$ at 213 K in an OSTLE cell. [c] *cf.* band for $[OsCl_{10}]^{4-}$ at 34 500 cm^{-1}.

processes as a possible alternative source of the spectral complexity.[30]

We can now compare the CT spectra of mixed-valence $[Os_2(\mu\text{-}X)_2X_8]^{3-}$ (X = Br or Cl) with the spectra of the homovalent Os^{IV}_2 and Os^{III}_2 species. The electronic nature of the 11e complex, *i.e.* whether essentially localised or delocalised, is naturally of special interest. Inspection reveals that the intense UV/VIS absorption spans the entire region covered by the Os^{IV}_2 and the Os^{III}_2 CT manifolds. Indeed, comparing $[Os_2(\mu\text{-}Br)_2Br_8]^{3-}$ with $[Os_2(\mu\text{-}Br)_2Br_8]^{2-}$ and $[Os_2(\mu\text{-}Br)_2Br_8]^{4-}$ (Fig. 2) we see that the intervening spectrum suggests a superposition of the last two. In accord with this impression, the lower energy bands collapse upon further reduction of $[Os_2(\mu\text{-}Br)_2Br_8]^{3-}$ while the higher components of the manifold increase in importance.

Even though the CT manifold shifts *ca.* 8000 cm^{-1} overall between $[Os_2(\mu\text{-}Br)_2Br_8]^{2-}$ and $[Os_2(\mu\text{-}Br)_2Br_8]^{4-}$ (as noted above), there is very little movement of the leading (low energy) edge of the manifold upon the first one-electron reduction of $[Os_2(\mu\text{-}Br)_2Br_8]^{2-}$ to $[Os_2(\mu\text{-}Br)_2Br_8]^{3-}$. The same remark holds for the analogous chloride series. If a localised electronic structure prevails, with distinct osmium-(IV) and -(III) chromophores, then these observations are readily explained by assuming the lower energy bands are associated with Os^{IV} and the higher bands with Os^{III}. The non-linear shift in the $X_t(\pi)\rightarrow Os(d_\pi)$ absorption edge upon stepwise reduction then follows naturally from progression through the trapped states $\{Os^{IV}(\mu\text{-}X)_2Os^{IV}\}^{6+}$, $\{Os^{IV}(\mu\text{-}X)_2Os^{III}\}^{5+}$ and $\{Os^{III}(\mu\text{-}X)_2Os^{III}\}^{4+}$.

Purely empirical correlations can be drawn between the disjointed shifts in optical CT energies and the accompanying pattern of reduction potentials, without theorising over the nature of the $\{Os(\mu\text{-}X)_2Os\}^{z+}$ core. The small shift between the 8e/9e and 9e/10e couples (*ca.* −0.5 V) and the relatively large further shift to reach the 10e/11e couple (*ca.* −1.6 V) match the non-uniform movement of the charge-transfer manifold. Rational correlations between optical charge-transfer $[X(\pi)\rightarrow Os(d_\pi)]$ energies and the underlying metal-centred reduction potentials E°_{red} $(d^n/d^{(n+1)})$ are well established for simple $[MX_6]^{z-}$ and $[MX_{6-n}L_n]^{z-}$ monomers.[31,32]

VIS/NIR Spectra of $[Os_2(\mu\text{-}X)_2X_8]^{z-}$ complexes (*z* = 2, 3, or 4). This region of the spectrum (4500–15 000 cm^{-1}) is potentially rich in single-ion crystal field transitions, as well as low wavenumber metal–metal manifold transitions in both even (8 and 10e) and odd-electron systems (9e).

Bruns and Preetz[6] recorded the spectra of the $[Os_2(\mu\text{-}X)_2X_8]^{2-}$ (X = Cl or Br) complexes in polyethylene films at 10 K, and offered detailed assignments. For comparison, the spectra in cold, concentrated CH_2Cl_2 solutions are presented in Figs. 4(a) and 5(a), clearly showing a series of sharp, weak bands. For $[Os_2(\mu\text{-}Br)_2Br_8]^{2-}$ the features at 4880, 9660 and 10 980 cm^{-1} are in similar positions to those reported for $[OsBr_6]^{2-}$ single-ion transitions,[33] and were so assigned by Bruns and Preetz.[6] However two well defined bands at 5300 and 13 150 cm^{-1}, peculiar to the dimer, tend to dominate this region. These were proposed to arise from pairwise transitions or from double excitations, both characteristic of binuclear systems.[6] The VIS/NIR spectrum of $[Os_2(\mu\text{-}Cl)_2Cl_8]^{2-}$ [Fig. 5(a)] bears a striking resemblance to that of $[Os_2(\mu\text{-}Br)_2Br_8]^{2-}$ [Fig. 4(a)], and its features are similarly assigned. The quality of the spectra derived from chilled CH_2Cl_2 solutions, and the close correspondence with the rigorous earlier measurements, encouraged us to proceed to *in situ* NIR spectroelectrochemistry of the decahalides in otherwise inaccessible oxidation levels.

The spectral progression obtained upon one-electron reduction of $[Os_2(\mu\text{-}Br)_2Br_8]^{2-}$ is presented in Fig. 6(a). A complex series of new VIS/NIR bands steadily emerges. In particular, the original sharp single-ion band at 5300 cm^{-1} is overtaken by the broader more intense spectrum of $[Os_2(\mu\text{-}Br)_2Br_8]^{3-}$ [Fig. 4(b)]. Considerable structure is present within the NIR envelope, but before discussing this further it is helpful to examine the spectrum of $[Os_2(\mu\text{-}Br)_2Br_8]^{4-}$ also reported here for the first time [Fig. 4(c)]. In marked contrast to $[Os_2(\mu\text{-}Br)_2Br_8]^{3-}$, the Os^{III}_2 spectral region below 10 000 cm^{-1} is featureless except for the pair of weak bands at 4780 and 5630 cm^{-1} (ε < 100 dm^3 mol^{-1} cm^{-1}). Octahedral osmium(III) complexes typically display two such low-energy, low-intensity bands, due to characteristic transitions within the spin–orbit coupled components of the $^2T_{2g}$ ground state.[34] For example, axially symmetric *trans*-$[OsBr_4(MeCN)_2]^-$ has a doublet absorption at *ca.* 4800 and 6200 cm^{-1}.[5] The bands now discovered for $[Os_2(\mu\text{-}Br)_2Br_8]^{4-}$ are similarly assigned as single-ion intraconfigurational transitions.

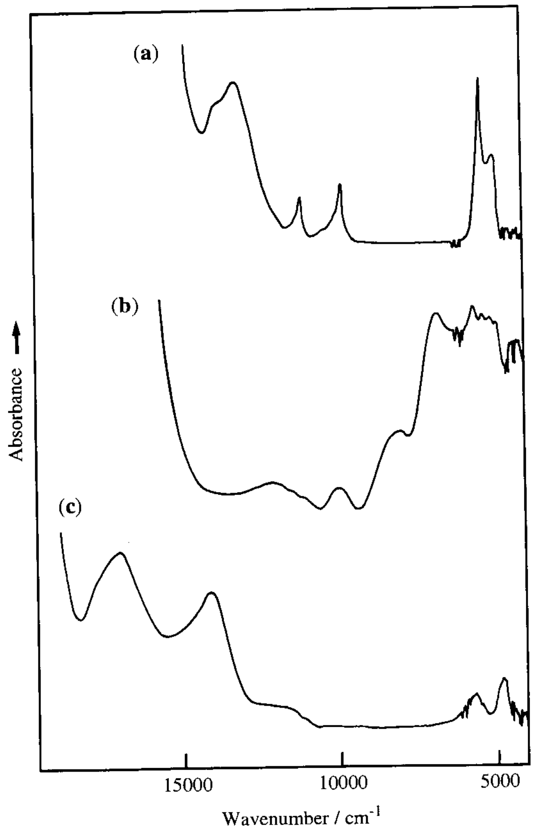


Fig. 4 The VIS/NIR spectra of $[Os_2(\mu\text{-}Br)_2Br_8]^{z-}$; *z* = 2 (a), 3 (b) or 4 (c), recorded in CH_2Cl_2 containing 0.5 mol dm^{-3} $[NBu_4][PF_6]$ at 213 K in an OSTLE cell

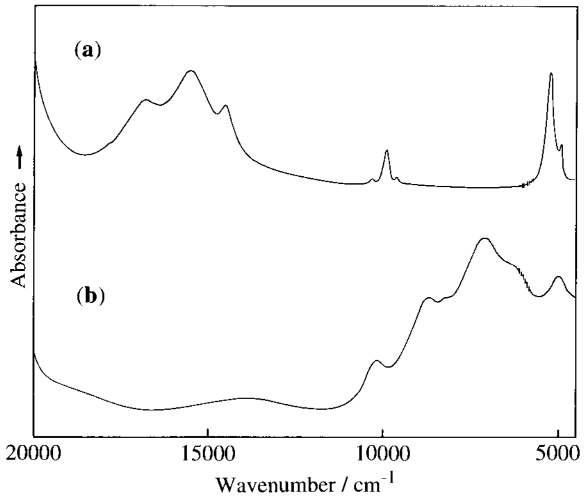


Fig. 5 The VIS/NIR spectra of $[Os_2(\mu\text{-}Cl)_2Cl_8]^{z-}$ *z* = 2 (a) or 3 (b), recorded in CH_2Cl_2 containing 0.1 mol dm^{-3} $[NBu_4]Cl$ at 213 K in an OSTLE cell

Returning to the $[Os_2(\mu\text{-}Br)_2Br_8]^{3-}$ species, in the 4500–6000 cm^{-1} domain the band structure suggests a superposition

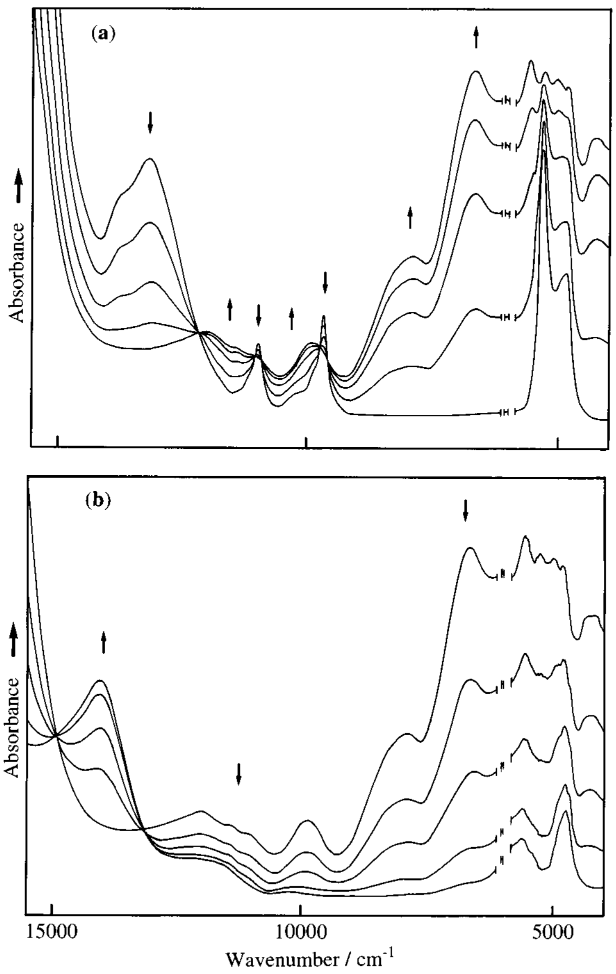
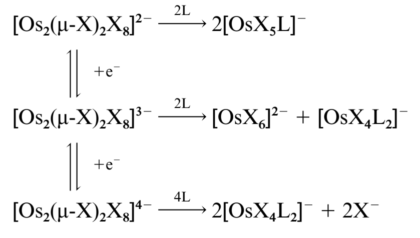


Fig. 6 The NIR spectral changes accompanying the reduction of $[Os_2(\mu\text{-}Br)_2Br_8]^{z-}$ in CH_2Cl_2 containing 0.5 mol dm^{-3} $[NBu_4][PF_6]$ at 213 K in an OSTLE cell. (a) $z = 2-/3-$ reduction, (b) $z = 3-/4-$ reduction. The discontinuities in the spectra near 6000 cm^{-1} arise due to uncorrected solvent overtones which have been omitted

of the sharp single-ion features from the spectra of $[Os_2(\mu\text{-}Br)_2Br_8]^{2-}$ (Os^{IV}_2) and $[Os_2(\mu\text{-}Br)_2Br_8]^{4-}$ (Os^{III}_2). In other words, the NIR spectrum is consistent with the presence of coexisting discrete osmium-(IV) and -(III) centres. The broad absorption envelope in the $[Os_2(\mu\text{-}Br)_2Br_8]^{3-}$ spectrum, apparently stretching all the way from 4500 to 9000 cm^{-1} but with maxima near 6500 and 8000 cm^{-1} (Table 2), is then attributable to intervalence charge transfer (IVCT) in the localised mixed-valence system. It is worth noting that most of this domain, say from 6500 to 9000 cm^{-1}, is transparent in *both* the homovalent (*i.e.* Os^{IV}_2 and Os^{III}_2) chromophores. In much the same way the NIR spectrum of $[Os_2(\mu\text{-}Cl)_2Cl_8]^{3-}$ has features akin to the single-ion transitions observed for $[Os_2(\mu\text{-}Cl)_2Cl_8]^{2-}$ and transient $[Os_2(\mu\text{-}Cl)_2Cl_8]^{4-}$, as well as broad strong features attributable to IVCT transitions (Fig. 5). In short, the systematic spectral resemblance between $[Os_2(\mu\text{-}Cl)_2Cl_8]^{3-}$ and $[Os_2(\mu\text{-}Br)_2Br_8]^{3-}$ is unmistakable throughout this region, and consistent with their characterisation as strictly analogous, weakly coupled $\{5d^4, 5d^5\}$ dimers. As discussed above, the behaviour of the intense charge-transfer manifold in the UV/VIS spectra also supports the localised mixed-valence description of $[Os_2(\mu\text{-}X)_2X_8]^{3-}$.

Reactivity

The spectroelectrochemical experiments described above have delineated the restricted conditions under which the $[Os_2(\mu\text{-}X)_2X_8]^{z-}$ species (z = 2, 3 or 4) are maintained in solution, *i.e.* chilled non-co-ordinating solvents under an inert atmosphere are required, as well as a suitably polarised electrode in the case of the reduced species. Otherwise, edge-sharing $[Os_2(\mu\text{-}X)_2X_8]^{z-}$ complexes react rapidly to give a variety of monomeric products. In the presence of potential ligands, cleavage of the bimetallic structure is inevitable but the identity of the ultimate product(s) depends on the oxidation level of the bimetallic core prior to bridge cleavage. This can be illustrated by the product distribution when solutions of the 8e, 9e and 10e dimers in MeCN are separately allowed to react with the solvent, as outlined below (Scheme 2).



$$[Os_2(\mu\text{-}X)_2X_8]^{2-} \xrightarrow{2L} 2[OsX_5L]^-$$

$$\Big\Updownarrow {+e^-}$$

$$[Os_2(\mu\text{-}X)_2X_8]^{3-} \xrightarrow{2L} [OsX_6]^{2-} + [OsX_4L_2]^-$$

$$\Big\Updownarrow {+e^-}$$

$$[Os_2(\mu\text{-}X)_2X_8]^{4-} \xrightarrow{4L} 2[OsX_4L_2]^- + 2X^-$$

Scheme 2

Warming of an MeCN solution of $[Os_2(\mu\text{-}X)_2X_8]^{2-}$ from 233 K to room temperature results in symmetric cleavage of the double-bridged structure to yield monomeric tetravalent complexes of the type $[OsX_5(MeCN)]^-$ (X = Br or Cl).[5,35] This cleavage reaction can be extended to other co-ordinating solvents such as tetrahydrofuran or acetone.[5] If one-electron reduction to the $Os^{IV}Os^{III}$ complex is performed prior to MeCN cleavage of the bridge two quite different monomers are formed upon warming. These products are $[OsX_6]^{2-}$ and *trans*-$[OsX_4(MeCN)_2]^-$,[5,35] present in solution in a one-to-one ratio. In this case asymmetric cleavage has occurred, producing tetra- and ter-valent monomers, with the halide ligands distributed to provide optimum stabilisation of the respective oxidation states. In contrast, electrogeneration of $[Os_2(\mu\text{-}X)_2X_8]^{4-}$ by low-temperature two-electron reduction of $[Os_2(\mu\text{-}X)_2X_8]^{2-}$, followed by warming, yields 2 equivalents of $[OsX_5(MeCN)]^{2-}$. The latter gives way in time to *trans*-$[OsX_4(MeCN)_2]^-$, since the halide ligand *trans* to MeCN is relatively labile in tervalent $[OsX_5(MeCN)]^{2-}$.[5,35] These experiments, summarised in Scheme 2, serve to highlight the utility of the $[Os_2(\mu\text{-}X)_2X_8]^{z-}$ complexes as precursors to a range of tetra- and ter-valent monomers.

Conclusion

Organo-soluble salts of $[Os_2(\mu\text{-}X)_2X_8]^{2-}$ (X = Br or Cl) can be conveniently prepared in pure form through controlled warming of the appropriate salt of $[OsX_6]^{2-}$ in neat CF_3CO_2H. Some preliminary reactions have illustrated the versatility of the decahalogenodiosmate anions as precursors to a range of monomeric complexes of Os^{III} and Os^{IV}. The low-temperature voltammetry of the $[Os_2(\mu\text{-}X)_2X_8]^{2-}$ complexes reveals a series of one-electron, metal-based processes, corresponding to an oxidation and three reductions. The chemically reversible 8e/9e and 9e/10e reductions have permitted the *in situ* solution characterisation of the $[Os_2(\mu\text{-}X)_2X_8]^{3-}$ and $[Os_2(\mu\text{-}X)_2X_8]^{4-}$ species. The 7e/8e oxidation and the 10e/11e reduction are irreversible, leading to the formation of the triple-bridged $[Os_2(\mu\text{-}X)_3X_6]^{z-}$ species through contrasting mechanisms. The electronic spectra of the homovalent $[Os_2(\mu\text{-}X)_2X_8]^{z-}$ dimers (X = Br or Cl, z = 2 or 4) can be attributed to a series of charge-transfer transitions from the halide(π) orbital array to vacancies in the metal d_π set, and single-ion type transitions within the spin–orbit coupled components of the respective ground states. In addition to these transitions, the localised mixed-valence $[Os_2(\mu\text{-}X)_2X_8]^{3-}$ (X = Br or Cl) species display broad weak IVCT transitions at low energy. More specific electronic assignments are unwarranted until further experimental and/or theoretical studies are brought to bear. In wider terms, this work illustrates the value of concerted application of voltammetry, electrosynthesis and optical spectroelectrochemistry in extending and systematising the descriptive chemistry of binuclear complexes of the heavy transition metals.

Experimental

Synthetic methods

Ammonium salts of the hexahalogenoosmates (X = Br or Cl) were obtained from Strem Chemicals Incorporated, as was $[PPh_4]Br$; $[PPh_4]Cl$, $[NBu_4]X$ (X = Br or Cl) and CF_3CO_2H were from the Aldrich Chemical Company. All of the above reagents were used as supplied except for CF_3CO_2H, which was distilled from P_2O_5 prior to use, and stored under N_2 away from the light.

The organo-soluble salts of the hexahalogenoosmates were prepared simply by dissolving ammonium salts in the appropriate dilute hydrohalogenic acid (sometimes filtering is necessary to remove traces of insoluble material), and adding the bromide or chloride salt of the appropriate cation. The organic salt of $[OsX_6]^{2-}$ precipitated immediately, and was collected by filtration. The crude material was washed thoroughly with distilled water and diethyl ether. Recrystallisation was achieved from dichloromethane–diethyl ether, or acetonitrile–diethyl ether, and the products dried *in vacuo*. Yields were 90% or more.

Bis(tetraphenylphosphonium) di-μ-chlorooctachlorodiosmate(IV). The salt $[PPh_4]_2[OsCl_6]$ (1.07 g, 0.99 mmol) was dissolved in neat CF_3CO_2H (15.0 cm^3), and the resulting solution warmed (oil-bath temperature 313 K) with stirring under N_2. After heating for 5 d a considerable quantity of fine green precipitate had formed. The mixture was allowed to cool to room temperature, the precipitate filtered off and washed extensively with *n*-hexane and diethyl ether. The product was then dried *in vacuo* at 373 K (0.67 g, 95%) (Found: C, 41.0; H, 2.7; P, 4.3. $C_{24}H_{20}Cl_5OsP$ requires C, 40.78; H, 2.85; P, 4.38%). Far-IR spectrum (polyethylene disc): 330s, 300s, 262s, 171w and 156w cm^{-1}.

Bis(tetraphenylphosphonium) di-μ-bromooctabromodiosmate(IV). The salt $[PPh_4]_2[Os_2(\mu\text{-}Br)_2Br_8]$ was prepared by a similar procedure to that described above. Warming $[PPh_4]_2[OsBr_6]$ (0.12 g) in neat CF_3CO_2H (5.0 cm^3) for 26 h produced 0.48 g (95%) of $[PPh_4]_2[Os_2(\mu\text{-}Br)_2Br_8]$ (Found: C, 29.6; H, 2.0; P, 3.1. $C_{24}H_{20}Br_5OsP$ requires C, 31.03; H, 2.17; P, 3.33%).

Bis(tetra-*n*-butylammonium) di-μ-bromooctabromodiosmate(IV). The $[NBu_4]^+$ salt of $[Os_2(\mu\text{-}Br)_2Br_8]^{2-}$ was prepared in much the same way as $[PPh_4]_2[Os_2(\mu\text{-}Br)_2Br_8]$. The salt $[NBu_4]_2[OsBr_6]$ (0.28 g) in neat CF_3CO_2H (3.0 cm^3) gave 0.14 g (70%) of $[NBu_4]_2[Os_2(\mu\text{-}Br)_2Br_8]$ after 8 h warming (Found: C, 19.8; H, 4.2; Br, 47.9; N, 1.5. $C_{16}H_{36}Br_5Os$ requires C, 23.09; H, 4.36; Br, 48.01; N, 1.68%. Note: the carbon figure was repeatedly found to be low). Far-IR spectrum (polyethylene disc): 235s, 222s and 198m cm^{-1}.

Other measurements

Elemental analyses were performed by the Microanalytical Services Unit at the Research School of Chemistry, The Australian National University (ANU). The spectroscopic instrumentation, electrochemical and spectroelectrochemical apparatus has been described previously, as has electrolyte preparation and solvent purification.[31] The discs for far-IR spectra were prepared by evaporating the solvent from a suspension of compound and polyethylene (in *n*-hexane), grinding up the remaining residue, and pressing. The far-IR spectra were recorded on a Perkin-Elmer 1800 FTIR spectrometer. Magnetic susceptibility data were collected using a Quantum Design MPMS SQUID magnetometer. Calibration for field and temperature were as set by the manufacturer, and checked against a standard palladium sample (field) and $CuSO_4 \cdot 5H_2O$ and $Hg[Co(NCS)_4]$ (temperature). Powdered samples (*ca.* 30 mg) of the complexes were contained in a calibrated gelatine capsule and held in the centre of a plastic straw which was attached to the end of the sample rod. An applied field of 1 T was used. The derived magnetic susceptibilities were corrected for diamagnetism of the ligands, counter ion and osmium(IV) using Pascal's tables.[36]

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