Reductive Nitrosylation of Tetraoxometallates. Part 16.[1] Generation and Reactivity of the $Os(NO)^{3+}$ Moiety. Synthesis, Characterisation, and Electrochemistry of Oxalato- and Halogeno-nitrosyl Derivatives of Osmium; Crystal and Molecular Structure of Bis(1,10-phenanthrolinium) Pentabromonitrosylosmate Dihydrate†

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Osmium tetraoxide smoothly reacts with $NH_2OH{\cdot}HCl$ in the presence of oxalate ion furnishing solid complexes $A[Os(NO)(C_2O_4)_2]{\cdot}H_2O$ (A = K, **1a**; PPh_4, **1b**; or $AsPh_4$, **1c**). The complex anion possesses a square-pyramidal structure, as is evident from analytical, spectroscopic (IR, UV/VIS), and thermoanalytical data. The complexes react with concentrated HX (X = Cl, Br or I) forming besides $[Os(NO)(C_2O_4)Cl_3]^{2-}$ **3**, $[Os(NO)Br_4(H_2O)]^-$ **4a** and $[Os(NO)Br_4]^-$ **4b**; $[Os(NO)X_5]^{2-}$ (X = Cl, **2a**; Br, **2b**; or I, **2c**) as the main product. The latter (X = Cl or I) reacts with phen (1,10-phenanthroline) producing $[Os(NO)X_3(phen)]$, whereas the bromo complex furnishes $[Hphen]_2[Os(NO)Br_5]{\cdot}2H_2O$, **5c**. The crystal and molecular structure of **5c** has been determined by Patterson and Fourier methods and refined to $R = 0.052$ for 1221 unique reflections with $I > 3\sigma(I)$. The crystals are monoclinic, space group $P2_1/c$, $a = 7.371(1)$, $b = 13.646(1)$, $c = 14.001(2)$ Å, $\beta = 99.88(1)°$ and $Z = 2$. The structure consists of $[Hphen]^+$ cations, disordered $[Os(NO)Br_5]^{2-}$ anions, and two water molecules of crystallisation; the anions have approximate octahedral geometry with a near linear nitrosyl ligand in the axial positions. Cyclic voltammograms of compounds **2a** and **2b** show a reversible oxidative response in MeCN at E°_{298} +0.94 and +0.96 V respectively, while **2c** shows an irreversible oxidation peak at +1.08 V in dimethylformamide, indicating the ease of oxidation of $Os(NO)^{3+} \longrightarrow Os(NO)^{4+}$ (confirmed by ESR study), increasing in the series $Cl^- < Br^- < I^-$.

In recent years, nitrosyl complexes of transition elements, especially those with rarer platinum metals, have attracted increasing attention because of their interesting electron-transfer properties,[2] pollution-controlling abilities[3] and catalytic uses in organic syntheses.[4] Compared to 3d metals and to molybdenum, ruthenium and rhenium, the osmium nitrosyl system has been much less studied,[5] and only three reports have so far been made on the reductive nitrosylation of OsO_4 using $NH_2OH{\cdot}HCl$ (in the presence of NCS^- [6a,b] or N_3^- [6c]). Moreover, the same reductive reaction of tetraoxometalates, *viz.* MO_4^{n-} (M = Cr or Mo when $n = 2$, V when $n = 3$ and Os when $n = 0$), and subsequent isolation of pure metal nitrosyl derivatives[7] have so far been shown to occur only when another reducing agent, for instance, CN^-, NCS^- or N_3^-, is used in the reaction medium along with NH_2OH, a reductant as well as a source of the NO group. It has been demonstrated,[7f] only in a single case (MoO_4^{2-} as substrate), that $C_2O_4^{2-}$ ions can also function as a member in the 'twin reagent' group mentioned above. In the present paper, we report a reductive nitrosylation reaction of OsO_4 using $NH_2OH{\cdot}HCl$ and $C_2O_4^{2-}$ in a slightly acidic medium under aqueous aerobic conditions. The process generates the moiety $Os(NO)^{3+}$, as confirmed by the isolation of complexes $A[Os(NO)(C_2O_4)_2]{\cdot}H_2O$ (A = K, **1a**; PPh_4, **1b**; or $AsPh_4$, **1c**) from the reaction medium.

Studies on the reactivities of osmium nitrosyl systems towards electrophiles and nucleophiles have received only scant attention,[8] owing probably to their lack of reactivity or because of the non-availability of suitable starting compounds. Herein is also described the reactivity of the oxalatonitrosyl derivatives as mentioned above, towards typical nucleophiles and electrophiles. Such a study *via* the interaction of halogen acids paves the way for synthesising halogenonitrosylosmates(II) precipitable with various cations, or, neutral complexes with 1,10-phenanthroline(phen), obtained directly or *via* thermolysis. One interesting compound in the series, $[HPhen]_2[Os(NO)Br_5]{\cdot}2H_2O$, has been structurally characterised by three-dimensional X-ray crystallography.

Results and Discussion

(*a*) *Oxalato Complexes: Synthesis, Characterisation and Probable Structure.*—Osmium tetraoxide smoothly reacts with an excess of $NH_2OH{\cdot}HCl$ and $C_2O_4^{2-}$ in an acidic medium giving crystalline salts of oxalatonitrosyl complexes **1a**–**1c**, and the analytical, molar conductance (Table 1, 1:1 electrolytes[9]), infrared (Tables 1 and 2), and thermoanalytical data (one lattice held water molecule in each case, endothermally expelled at *ca.* 80 °C) suggest that the compounds are five-co-ordinate. The oxalate group vibrations as obtained from the infrared

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Non-SI units employed: mmHg ≈ 133 Pa, G = 10^{-4} T.

Table 1 Analytical[a] and physical data for the complexes

	Complex	Analysis (%)					Selected IR data (cm^{-1})			
		C	H	N	X (Cl, Br, I)	P	ν(NO)	ν(Os–N)(NO)	ν(Os–X)	Λ_M/S cm^2 mol^{-1}
1a	$K[Os(NO)(C_2O_4)_2]\cdot H_2O$[b]	10.4 (10.6)	0.50 (0.45)	3.0 (3.1)	—	—	1825vs	620w	—	118[c]
1b	$[PPh_4][Os(NO)(C_2O_4)_2]\cdot H_2O$	45.0 (44.6)	2.8 (2.9)	1.7 (1.9)	—	4.0 (4.1)	1812s	615w	—	125[d]
1c	$[AsPh_4][Os(NO)(C_2O_4)_2]\cdot H_2O$	42.6 (42.1)	2.7 (2.8)	1.7 (1.8)	—	—	1810s	612w	—	116[d]
2a	$[PPh_4]_2[Os(NO)Cl_5]$	53.2 (53.5)	3.7 (3.7)	1.2 (1.3)	16.7 (16.5)	5.7 (5.8)	1790s 1772s	615w	317m 290s 222m	235[d]
2b	$[PPh_4]_2[Os(NO)Br_5]$	44.5 (44.4)	3.0 (3.1)	1.1 (1.1)	31.1 (30.8)	4.6 (4.8)	1795s	612w	214m	245[d]
2c	$[PPh_4]_2[Os(NO)I_5]$	37.4 (37.6)	2.4 (2.6)	0.9 (0.9)	41.9 (41.4)	3.8 (4.0)	1812s	—	182m 169w	235[d]
3	$[PPh_4]_2[Os(NO)(C_2O_4)Cl_3]$	54.7 (54.9)	3.6 (3.7)	1.2 (1.3)	9.9 (9.7)	5.5 (5.7)	1785s	610w	308m 291m 220m	240[d]
4a	$[PPh_4][Os(NO)Br_4(H_2O)]\cdot 0.5H_2O$	32.0 (31.8)	2.4 (2.5)	1.5 (1.5)	35.4 (35.6)	3.3 (3.4)	1835s	615w	225m 214w	130[d]
4b	$[PPh_4][Os(NO)Br_4]\cdot 0.5H_2O$	32.5 (32.4)	2.3 (2.4)	1.5 (1.6)	36.3 (36.0)	3.3 (3.5)	1820s	620w	218m 212w	125[d]
4c	$H[Os(NO)Br_4(H_2O)]$	—	0.5 (0.5)	2.5 (2.4)	57.2 (57.0)	—	1850s	625w	225w 215m	250[c]
5a	$[H_2phen][Os(NO)Br_5]$	18.0 (17.6)	1.25 (1.30)	5.2 (5.3)	49.8 (50.2)	—	1822s 1795s	620w	220m	190[e]
5b	$[Hphen]_2[Os(NO)Br_5]\cdot H_2O$	28.8 (29.0)	2.0 (1.9)	7.0 (7.0)	40.0 (40.3)	—	1805s	615w	215m	140[e]
5c	$[Hphen]_2[Os(NO)Br_5]\cdot 2H_2O$	28.3 (28.3)	2.2 (2.2)	6.9 (6.8)	39.3 (39.4)	—	1812s	620w	215m	135[e]
5d	$H_2[Os(NO)Br_5]$	—	0.3 (0.3)	2.2 (2.1)	64.3 (64.5)	—	1855s	610w	220m	382[c]
6a	$[Os(NO)Cl_3(phen)]$	28.5 (28.4)	1.5 (1.6)	8.2 (8.3)	21.3 (21.0)	—	1805s	615w	300(sh) 287s 242m	10[e]
6b	$[Os(NO)I_3(phen)]$	18.8 (18.4)	1.0 (1.0)	5.7 (5.4)	50.1 (48.8)	—	1850s	610w	177m 163m	12[d]
6c	$[Os(NO)Br_3(phen)]$	22.5 (22.4)	1.25 (1.20)	6.6 (6.5)	37.5 (37.7)	—	1848s	608w	214m	8[e]
7	$[Os(NO)Br_3(py)_2]\cdot 2H_2O$	18.4 (18.4)	2.1 (2.1)	6.5 (6.4)	36.9 (36.7)	—	1810s	615w	216m	8[d]

[a] Calculated values in parentheses. [b] K 8.8 (8.6%). [c] In water. [d] In MeCN. [e] In dmf.

Table 2 Some important and characteristic infrared oxalate bands (cm^{-1}) of the complexes **1a**–**1c**

	1a	**1b**	**1c**
$\nu_{asym}(CO)$	1700vs 1670s	1700vs 1675s	1700vs 1675s
$\nu_{asym}(CO)$ + $\nu_{sym}(C-C)$	1375s	1380m 1350m	1365m 1340m
$\nu_{sym}(CO)$ + δ(O–C=O)	1230w 895w	895w	895w
δ(O–C=O) + ν(MO)	810m	*	*
ν(MO) + ν(CC)	535w	*	*
ring def. + ν(O–C=O)	455w	455w	*

* Obscured.

spectra (Table 2) are compatible with that of a chelate, undergoing appropriate shifts from those of the free oxalate group.[10] The ν(NO) vibration of the nitrosyl group occurs (Table 1) in the same region as that for the thiocyanato and azido complexes,[6b,c] which also contain the $Os(NO)^{3+}$ moiety.

Assuming the NO^+ formalism,[11] the oxidation state of osmium in the present series of complexes, containing the above moiety, should be II, which is consistent with the observed diamagnetism [as required by a $\{Os(NO)\}^{6,*}$ species]. The local symmetry of the $OsNO_4$ chromophore (a 16-electron system) is expected to be C_{4v} (the strict symmetry with a linear Os–N–O axis and equivalent oxalate co-ordintion is not expected to be much different), leading to the ground-state molecular orbital (MO) configuration, $e^4b_2{}^2$,[11] and, as such, two UV/VIS bands corresponding to the transitions $b_2 \longrightarrow e$ and $b_2 \longrightarrow b_1$ are expected for five-co-ordinate systems, and are experimentally observed at *ca.* 500 and *ca.* 300 nm respectively, in the electronic spectra of complexes **1a**–**1c** (Table 3). For six-co-ordinate C_{4v} systems three bands are expected.[11]

Based on the above evidence, an axial NO[11] and equatorial oxalato (O_4) groups leading to a square-pyramidal geometry may be a reasonable assumption for the structure of the anion **I** present in **1a**–**1c**.

(*b*) *Reactivity of the Oxalatonitrosyl Complexes.*—Anion **I**, representing a 16-electron system, shows apparent inertness towards expansion of its co-ordination number *via* nucleophilic addition, using pyridine (py), EPh_3 (E = P or As) or $Ph_2PCH_2CH_2PPh_2$ (dppe). However, preparation of a ruthenium compound, $H_2[Ru(NO)(C_2O_4)_2]$, was reported[12]

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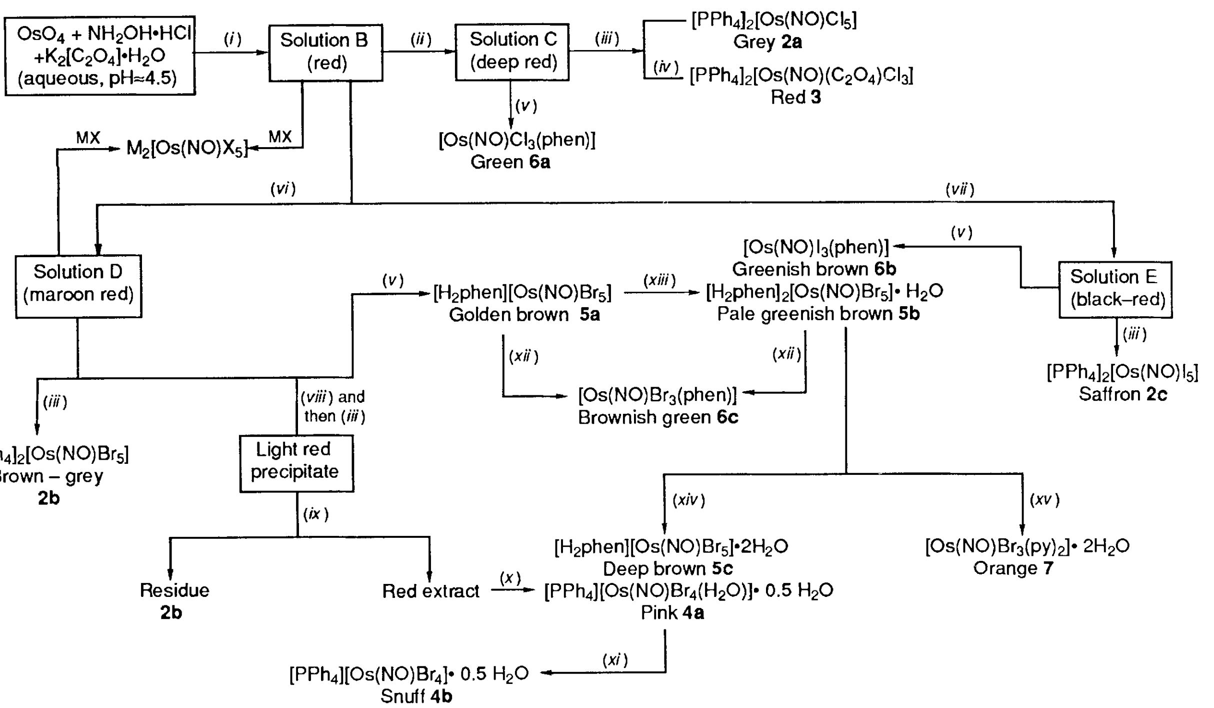
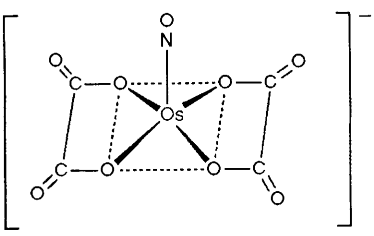
* The numerical superscript indicates the number of valence electrons in Os and NO orbitals.



Scheme 1 (*i*) Heating at 80 °C for 1 h; (*ii*) boiling with concentrated HCl for 2 h; (*iii*) aqueous PPh_4Cl; (*iv*) concentration of the filtrate; (*v*) aqueous phen; (*vi*) boiling with concentrated HBr for 1.5 h; (*vii*) heating with concentrated HI for 10 min; (*viii*) dilution to three times its volume with water; (*ix*) extraction with EtOH; (*x*) evaporation under reduced pressure; (*xi*) attempted crystallisation from MeCN–Et_2O; (*xii*) thermolysis (300–320 °C) under a nitrogen atmosphere followed by crystallisation of the residue; (*xiii*) washing with water; (*xiv*) crystallisation from dmso–water; (*xv*) pyridine in MeOH at 80 °C; M = K or Cs and X = Cl or Br



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and it has long been known (needs further confirmation, however)[13a] that $K_2[Ru(NO)(C_2O_4)_2Cl]$ exists (also prepared otherwise[14]) which reacts with py furnishing $K[Ru(NO)(C_2O_4)_2(py)]$. It may be recalled here that the $Re(NO)^{2+}$ moiety containing a $\{M(NO)\}^6$ configuration also produces five-co-ordinate uninegative 16-electron species, $[Re(NO)X_3(H_2O)]^-$ (X = NCS or N_3, see ref. 15) which, again, do not react with unidentate nucleophiles like py, ER_3, or R_2S (R = alkyl or aryl), to afford any six-co-ordinate 18-electron system.

However, a strong electrophile, H^+, is found to induce reactivity in the otherwise inert oxalato complexes, towards nucleophilic substitution by X^- (X = Cl, Br or I), *via* rupture of at least one of the metal–oxalato chelate rings. Hot concentrated halogen acids (HX) react with the anion **I** present in solution B (see Experimental section) forming $[Os(NO)X_5]^{2-}$ **2a–2c**, and in one case (X = Cl), $[Os(NO)(C_2O_4)Cl_3]^{2-}$ **3**, both isolable as hitherto unknown PPh_4 salts (Scheme 1) and, in the case of the former, also as K and Cs salts for X = Cl or Br.* Although $[Os(NO)X_5]^{2-}$ (when X = F, structurally characterised; see below) was reported earlier as alkali-metal salts,[16] the methods of preparation were rather cumbersome and the products were also not very pure.[8] The assistance of H^+ ion is necessary for these reactions to occur, since X^- in the absence of H^+ fails to effect the reaction. Interestingly, the product **3** is exclusively obtained when solution B is boiled with HCO_2H (but not with $MeCO_2H$). This suggests that a minimum level of H^+ in the medium is a prerequisite for the above substitution reaction, and that rendered by HCO_2H is optimal for the synthesis of **3**. However, when HCl reacts with the isolated compound **1b**, instead of solution B, the products obtained are identical with those from the said solution, but HBr under the same condition affords an

Table 3 Electronic spectral data (Gaussian analysed)

Complex	λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})
1a[a]	490 (26), 306 (155)
1b[b]	505 (33), 320 (340)
1c[b]	500 (30), 322 (313)
2a[b]	562 (10), 495 (5), 434 (23), 366 (25)
2b[b]	572 (5), 532 (7), 465 (30), 392 (30)
2c[b]	602 (8), 307 (2395)
3[b]	544 (30), 438 (12), 296 (380)
4a[b]	588 (12), 510 (10), 458 (15), 386 (12)
4b[b]	555 (15), 446 (16)
4c[a]	568 (11), 516 (7), 478 (12), 384 (28)
5a[c]	516 (78), 476 (60), 400 (22), 336 (2225)
5b[c]	574 (98), 433 (270), 395 (1060), 348 (117), 313 (1125), 304 (2517)
5c[c]	*d*
5d[a]	532 (10), 454 (10), 384 (17)
6a[c]	585 (10), 500 (5), 438 (15), 347 (203)
6b[b]	585 (110), 405 (700), 353 (165), 306 (3100)
6c[c]	552 (250), 452 (125), 392 (1375), 312 (970), 302 (1770)
7[b]	580 (10), 504 (15), 452 (18), 392 (40)

Intraligand transitions are not listed.
[a] In water. [b] In acetonitrile. [c] In dmf. [d] Same as above.

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* Their colours, molar conductance, and spectroscopic (IR and UV/VIS) data are comparable with those of corresponding reported compounds.[8]

additional product, $H[Os(NO)Br_4(H_2O)]$ **4c** as hygroscopic red crystals.

So, the above reaction can be classed as H^+-induced X^--assisted nucleophilic substitution on a central $Os(NO)^{3+}$ framework; the halogen acids (HX), however, fail to attack the NO *centre via* protonation of NO or otherwise.

Addition of phen to solution C or E (Scheme 1) produces $[Os(NO)X_3(phen)]$ (X = Cl, **6a**; or I, **6b**), and to solution D furnishes $[H_2phen][Os(NO)Br_5]$ **5a**, which on washing with water changes to $[Hphen]_2[Os(NO)Br_5]\cdot H_2O$ **5b**, affording an acidic (pH *ca.* 2.0) washing which on treatment with PPh_4Cl gives $[PPh_4]_2[Os(NO)Br_5]$ presumably *via* reaction (1) (see, also, Scheme 1). Both **5a** and **5b**, when heated under dinitrogen, in a glass tube at *ca.* 300 °C evolve only very little HBr (trapping the issuing gas in standard KOH solution), the bulk inside the hot zone being $[Os(NO)Br_3(phen)]$ **6c**, while a sublimate, $[H_2phen]Br_2$ (in both cases), condenses at the cooler part of the tube. It is noteworthy that addition of PPh_4Cl to solution D gives **2b**, whereas if PPh_4Cl is added to a solution prepared by diluting solution D with water an additional product **4a** is obtained as pink crystals (Scheme 1), which on further crystallisation produces $[PPh_4][Os(NO)Br_4]\cdot 0.5H_2O$ **4b**.

$$\begin{aligned}&2[H_2phen][Os(NO)Br_5] + H_2O \longrightarrow\\ &\qquad [Hphen]_2[Os(NO)Br_5] + \underset{\mathbf{5d}}{H_2[Os(NO)Br_5]}\\ &\qquad\qquad\qquad \big\downarrow \scriptstyle PPh_4Cl\\ &\qquad\qquad [PPh_4]_2[Os(NO)Br_5] \qquad (1)\end{aligned}$$

(*c*) *Reactivity of the Halogenonitrosyl Derivatives.*—The reactivity of the isolated halogenonitrosyl derivatives can be represented by Scheme 2. So it appears that the product **5b** is a reactive species, compared with the insensitivity of the PPh_4-salt **2b** towards nucleophilic attack. Compound **5b** contains the $[Hphen)]^+$ cation where only one of the two nitrogen centres are supposed to be protonated. Since there exists a dearth of structural data on osmium-mononitrosyl systems, it was thought worthwhile structurally to characterise **5c**, the crystals obtained from **5b** [see section (*e*)].

$$\mathbf{5b} \xrightarrow{(i)} K_2[Os(NO)Br_5] \xrightarrow{(ii)} \mathbf{2b}$$

$$\xrightarrow{(iii)} \text{Compound decomposes}$$

$$\xrightarrow{(iv)} Ag_2[Os(NO)Br_5]$$

$$\xrightarrow{(v)} \text{Yellow solution} \; \big\downarrow (ii) \; [PPh_4]_2[Os(NO)(NO_2)_4(OH)] \; (K^+ \text{ salt})^{13b}$$

$$\xrightarrow{(vi)} \text{No reaction}$$

$$\xrightarrow{(vii)} [Os(NO)Br_3(py)_2]\cdot 2H_2O \; \mathbf{7}$$

$$\xrightarrow{(viii)} \mathbf{7}$$

$$\mathbf{2a}\text{–}\mathbf{2c} \xrightarrow{(v)} \text{No reaction}$$

$$\xrightarrow{(ix)} \text{No reaction}$$

Scheme 2 (*i*) Dilute KOH, aqueous solution; (*ii*) $PPh_4Cl(aq)$; (*iii*) strong aqueous KOH; (*iv*) dmf solution, $AgNO_3$; (*v*) $NaNO_2(aq)$, heat; (*vi*) PPh_3 (or dppe), MeOH; (*vii*) py in MeOH, 60–70 °C; (*viii*) py + PPh_3 (or dppe) in MeOH, 70 °C; (*ix*) py or PPh_3

(*d*) *Physico-chemical Characterisation of the Reaction Products.*—(*i*) *General characterisation and infrared data.* The compounds **2a**–**2c**, **3**, **5b** and **5c** are all 2:1 electrolytes,[9] **5a** is a 2:2 electrolyte, while **4a** and **4b** behave as 1:1 electrolytes[9] (Table 1). This is in conformity with the molecular formulae suggested. The acids (**4c** and **5d**) show expected molar conductance values in water,[9] taking into account that they are weak acids. Compounds **6a**–**6c** and **7** are practically non-electrolytes, showing only a marginal dissociation of X^- (Table 1). The ν(NO) vibrations occur in the region where the co-ordinated NO group of the $Os(NO)^{3+}$ moiety is expected to absorb. However, in some cases (**2a**, **5a** and **6a**) there is an outright splitting of the ν(NO) band (separation *ca.* 15–30 cm^{-1}) which may be ascribed[17] to a large change in the bond-dipole moment of the NO group during its vibration, and hence a sensitivity to the external electric field. The complex anions present in **2a**–**2c**, **4a** and **5a**–**5d** are all six-co-ordinte. Assuming NO to be axial and M–N–O to be linear,* the molecules should have C_{4v} symmetry. Since M–N(NO) bonds have reasonable double-bond character, the metal ion is expected to be raised out of the equatorial plane towards the nitrosyl ligand; the three ν(OsCl) infrared bands of **2a** may be assigned to $\nu_{asym}(OsCl_4)$, $\nu_{sym}(OsCl_4)$ and $\nu(OsCl)^-$ (*trans*) vibrations, in order of decreasing wavenumber.[18–20] However, for the bromo complexes **2b** and **5a**–**5d** where spectra are recorded, as usual, up to 200 cm^{-1}, a single band possibly due to $\nu_{asym}(OsBr)$ is seen, others being outside the scan range. For iodo complex **2c** the spectrum was recorded up to 150 cm^{-1} and both $\nu_{asym}(OsI)$ and $\nu_{sym}(OsI)$ are observed (Table 1); $\nu(OsI)^-$ (*trans*) possibly occurs below 150 cm^{-1} and the bromo compounds **4a** and **4c** show only two ν(OsBr) bands for obvious reasons. The five-co-ordinate species **4b** should possess C_{4v} symmetry and quite reasonably show only two Os–Br bands, corresponding to both symmetric and asymmetric $\nu(OsBr_4)$ vibrations. Other halogeno complexes are of lower symmetry and show the expected number of bands (the chloro complexes **3** and **6a**); again for the bromo and iodo complexes all the bands are not shown (Table 1), some obviously occurring below the scan range.

(*ii*) *Magnetic susceptibility and electronic spectra.* The C_{4v} species described above, containing the $\{Os(NO)\}^6$ moiety, should have $e^4b_2{}^2$ MO configuration,[11] both in the five- and six-co-ordinate systems. The diamagnetism of all the isolated complexes further supports their formulation. Accordingly, in the six-co-ordinate systems three electronic absorption bands corresponding to the transitions $b_2 \longrightarrow e$, $b_2 \longrightarrow b_1$ and $b_2 \longrightarrow a_1$ are expected.[11] However, for the chloro and bromo complexes (C_{4v}), except the acid **5d**, four bands of low intensity appear (Table 3). This can be rationalised if it is assumed: (1) the energy of $a_1(\sigma^*_{NO})$ is sufficiently lowered so that the transition $b_2 \longrightarrow a_1(\sigma^*_{NO})$ may be accessible at a comparatively lower energy (*ca.* 350 nm) or (2) the strict symmetry of the molecules is lower than C_{4v}, so that the degeneracy of the 'e' MO is lifted giving rise to four electronic transitions without involving the normally high-energy $a_1(\sigma^*_{NO})$ MO[11] The acid **5d** however shows the expected three bands. For the iodo complex, however, only two broad bands are observed; the high-energy intense one (307 nm), possibly being a ligand-to-metal charge transfer (l.m.c.t.) ($I^- \rightarrow Os^{II}$) transition, may mask the other weak intensity bands.

As expected, the five-co-ordinate anion present in the

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* There is no exception to this behaviour in the structurally confirmed cases containing $\{M(NO)\}^n$ moieties where n = 4–6.[11] However, the slight deviation from the linearity we observe for **5c** is due mainly to the disorder in the structure (see below).

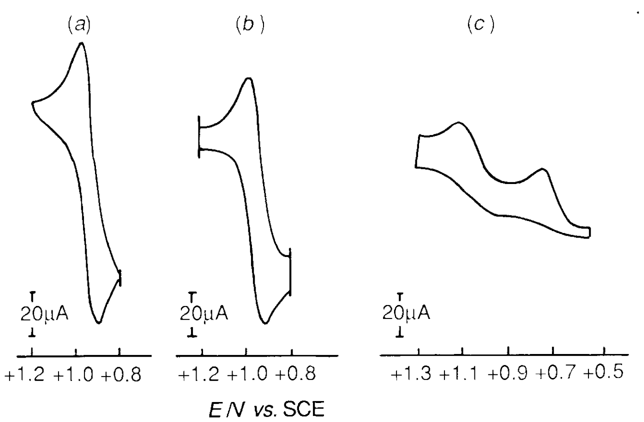

Fig. 1 Segmented cyclic voltammograms of $[PPh_4]_2[Os(NO)X_5]$, X = Cl (*a*), Br (*b*) or I (*c*), in dmso (scan rate 50 mV s^{-1}). All in 0.1 mol dm^3 NEt_4ClO_4 at a platinum electrode

Table 4 Cyclic voltammetric data at 298 K for the complexes **2a** and **2b** in MeCN *vs.* s.c.e. (values *vs.* ferrocene–ferrocenium are shown in parentheses). Scan rate 50 mV s^{-1}

	Compound	
	2a	**2b**
E_{pc}/V	+0.90 (+0.52)	+0.92 (+0.54)
E_{pa}/V	+0.98 (+0.60)	+1.00 (+0.62)
E°_{298}/V	+0.94 (+0.56)	+0.96 (+0.58)
ΔE_p/mV	80	80
i_{pc}/i_{pa}	0.98	0.98

compound **4b** shows only two bands representing the electronic transitions $b_2 \longrightarrow e$ and $b_2 \longrightarrow b_1$; the energy of the a_1 orbital has been estimated[11] to be lowered in five-co-ordinate systems and hence the third band shown by six-co-ordinate species should be unobserved here. This observation lends further support to the formulations of the five-co-ordinate species. Curiously, the structurally confirmed compound **5c** shows six bands as against not more than four bands (**6c**, however, shows five) being observed for the low-symmetry compounds **3**, **6a**–**6c** and **7**.

(*iii*) *Thermoanalytical studies.* The percentage composition of water molecules in the complexes **4a**, **4b**, **5b**, **5c** and **7** has been assessed from weight loss data obtained from their thermogravimetric analysis (TGA) curves. For **4b** an exothermic peak at 85–90°C, in its differential thermal analysis (DTA) curve corresponds to the loss of 0.5 molecules of H_2O per molecule of complex (from TGA) indicating that the water molecule is held only in the lattice. For **4a** two endothermic peaks, at 90 and 150°C, correspond to the loss of 0.5 and one molecule of H_2O per molecule of complex, respectively, showing clearly that the former is lattice held and the latter is co-ordinated, conforming nicely with the formulation of the complexes. Compounds **5c** and **7** show two DTA peaks corresponding to the loss of two molecules of lattice held water (TGA) in each case, but in the case of the latter the water molecules are lost at slightly higher temperatures, *viz.* 110 and 130°C. Admittedly, 130°C is a little too high for the loss of a crystal water.

(*iv*) *Electrochemistry of complexes* **2a**–**2c**. Cyclic voltammetry was carried out in acetonitrile solutions at a platinum working electrode. All potentials are referenced to the saturated calomel electrode (SCE) and the notations used have the following meanings, E_{p_c} = cathodic peak potential, E_{p_a} = anodic peak potential, $\Delta E_p = E_{pa} - E_{pc}$, i_{pc} = cathodic peak current, and i_{pa} = anodic peak current. The formal potential, E°_{298}, is taken as the average of E_{pa} and E_{pc}. Tetraethylammonium perchlorate was used as an inert electrolyte in each case. The formal potentials are also expressed (as parentheses in the relevant table) relative to the E°_{298} of ferrocene–ferrocenium *vs.* SCE, separately measured under identical experimental conditions, solvents and inert electrolytes as used for the measurement of the sample solutions.

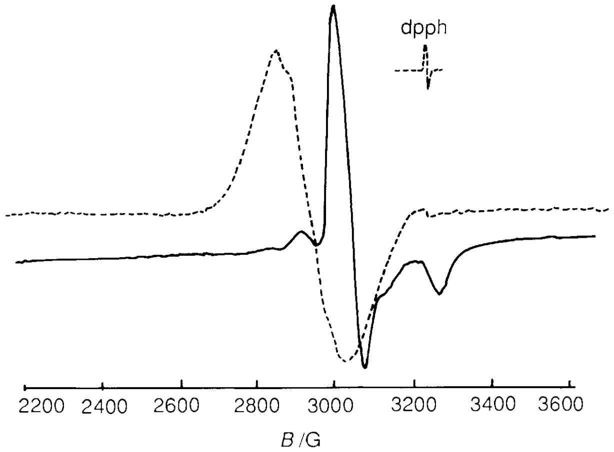

Fig. 2 X-Band ESR spectra of a frozen MeCN solution of electro-oxidised $[PPh_4]_2[Os(NO)X_5]$, X = Cl (——) or Br (– – – –)

The complexes **2a** and **2b** display a nearly reversible cyclic response [Fig. 1(*a*) and 1(*b*)] at a potential +0.94 (+0.56) and +0.96 (+0.58) V respectively assigned to the electrode process (2). The details of the voltammetric parameters are

$$\underset{\{Os(NO)\}^6}{Os(NO)^{3+}} \rightleftharpoons \underset{\{Os(NO)\}^5}{Os(NO)^{4+}} + e^- \qquad (2)$$

in Table 4. Exhaustive electrolysis (coulometry) at a higher positive potential (by *ca.* 200 mV than the region where the corresponding anodic responses are observed) gives however a continuous coloumb count, perhaps owing to the onset of an unidentified reaction after the one-electron oxidation of the metal centre. This one-electron oxidation was further corroborated by discontinuing the electrolysis at a coloumb count corresponding to one-electron change and recording the ESR spectra of the resulting frozen (at 77 K) solutions (Fig. 2). If it is assumed that the electron transfer is the only change occurring in the molecules at this stage then the configuration of the oxidised molecules, *i.e.* $Os(NO)^{4+}$, should be $e^4b_2^1$;* the higher $\langle g\rangle_{av}$† than the spin-only value may be due to a high negative (essentially a t_{2g}^5 configuration) spin–orbit coupling constant of the 5d metal ion [$g = g_e - (n\lambda/\Delta E)$].[21a] Though the anisotropic g-tensor features are quite apparent from the spectrum, there appears no metal hyperfine splitting due to ^{189}Os [$I = \frac{3}{2}$; natural abundance of ^{187}Os ($I = \frac{1}{2}$) is too low (1.6%) for its effect to be observed] for the bromo-complex (solution relatively unstable and undergoes sharp colour change at room temperature, compared to the chloro complex), while the chloro-complex shows an ill defined quartet (Fig. 2) (some of the features possibly being embedded within the broad derivative curve), which may be due to metal hyperfine coupling.

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* That this sort of configuration exists in solution is corroborated by comparing the electronic absorption spectra of the electro-oxidised chloro complex $[Os(NO)^{4+}]$ with that of an authentic $\{M(5d)NO\}^5$ system, *viz.* $\{Re(NO)\}^5$ complexes;[21b] both systems show two clear-cut electronic spectral bands. Since the bromo complex rapidly changes colour there may exist mixtures of species which shows greater number of bands.

† (X = Cl) $g_{\perp}$ 2.16, $g_{\parallel}$ = 2.09, $\langle g\rangle_{av}$ = 2.14; (X = Br) $g_{\perp}$ 2.26, $g_{\parallel}$ = 2.16, $\langle g\rangle_{av}$ = 2.23.

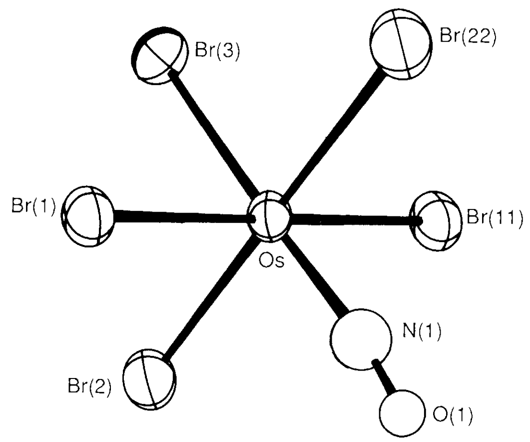

Fig. 3 View of the anion $[Os(NO)Br_5]^{2-}$ along the *b*-axis with atom numbering

Table 5 Positional parameters for $[Hphen]_2[Os(NO)Br_5]\cdot 2H_2O$ **5c**, with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*
Os*	0.0	0.5	0.5
Br(1)	0.1727(3)	0.3913(1)	0.6288(2)
Br(2)	0.0547(3)	0.3754(2)	0.3779(2)
Br(3)*	0.2917(4)	0.5818(3)	0.4841(4)
O(1)*	0.352	0.601	0.483
N(1)*	0.218	0.559	0.496
N(2)	−0.359(2)	−0.012(1)	0.304(2)
N(3)	−0.190(2)	0.106(1)	−0.451(1)
C(1)	−0.440(3)	−0.063(2)	0.232(2)
C(2)	−0.1508(3)	−0.155(2)	0.242(2)
C(3)	−0.491(2)	−0.194(2)	0.328(2)
C(4)	−0.401(2)	−0.140(1)	0.409(2)
C(5)	−0.373(2)	−0.176(2)	0.505(2)
C(6)	−0.294(2)	−0.120(2)	0.575(2)
C(7)	−0.230(2)	−0.023(1)	0.561(2)
C(8)	−0.147(3)	0.041(2)	0.637(2)
C(9)	−0.085(2)	0.131(1)	0.616(2)
C(10)	−0.188(2)	0.162(1)	0.518(2)
C(11)	−0.248(2)	0.018(1)	0.475(2)
C(12)	0.337(2)	−0.044(2)	0.393(2)
C(2)	−0.183(2)	0.153(1)	0.250(1)

* Occupancy factor 0.5.

Table 6 Selected bond distances (Å) and angles (°) for $[Hphen]_2[Os(NO)Br_5]\cdot 2H_2O$ **5c**

Os–Br(1)	2.540(2)	N(2)–C(1)	1.30(3)
Os–Br(2)	2.528(2)	N(2)–C(12)	1.34(3)
Os–Br(3)	2.478(7)	N(3)–C(10)	1.28(2)
Os–N(1)	1.81(0)	N(3)–C(11)	1.33(2)
N(1)–O(1)	1.19(0)		
Br(1)–Os–Br(2)	89.7(1)	Br(2)–Os–Br(3)	89.7(1)
Br(1)–Os–Br(3)	89.8(1)	Br(2)–Os–N(1)	91.5(8)
Br(1)–Os–N(1)	86.8(7)	Os–N(1)–O(1)	172(0)

The iodo complex **2c**, however, shows two irreversible peaks in MeCN solution (Fig. 1), of which, in comparison to **2a** and **2b**, that at 1.08 V may be ascribed to the oxidation reaction of the otherwise reversible electrode process shown in equation (2). Though the true $E°$ in the case of **5c** is not obtained, from the position of the oxidation peak it is quite apparent that $E°$ of the electrode process [equation (2)] becomes more and more positive as X^- changes from Cl^- *via* Br^- to I^-. However, since the onset of the second peak of **2c** occurs quite close to the first, at present it is not possible to assign the first peak convincingly.

(*e*) *Molecular Structure of* $[Hphen]_2[Os(NO)Br_5]\cdot 2H_2O$ **5c**.—Final atomic coordinates, selected bond lengths and angles are given in Tables 5 and 6 respectively. The co-ordination sphere of the formally osmium(II) ion with atom labelling is shown in Fig. 3. The crystal structure consists of discrete $[Os(NO)Br_5]^{2-}$ anions, $[HPhen]^+$ cations, and two water molecules of crystallisation. None of the water molecules or the cations are close enough to the osmium(II) ion to be considered even as weakly co-ordinated. With five Br atoms, one NO ligand, and Os occupying a special position at a centre of inversion, the anion displays a nearly octahedral geometry; Os, Br(2), Br(3), Br(22) and Br(33) [Br(2), Br(22) and Br(3), Br(33) are centrosymmetrically related pairs] lie in a plane, involving disorder of the axial Br and NO. Comparison of the observed Os–N(1) (1.81 Å) and N(1)–O(1) (1.19 Å) distances and Os–N(1)–O(1) angle (172°) with the structural data available for linear mononuclear nitrosyl complexes[22] (Os–N and N–O ranging between 1.71 and 1.89 and 1.12 and 1.25 Å respectively) indicates that the nitrosyl ligand is linearly co-ordinated to the metal ion and best formulated as NO^+.[23] The Os–Br distances ranging from 2.478(7) to 2.540(2) Å are in agreement with those found in earlier work.[22,24,25] The observed shortening of the Os–Br distance, *trans* to the axial NO[Os–Br(3)], compared to Os–Br (*cis*) distances (Table 6) is typical for $\{M(NO)\}^6$ complexes where ν(NO) occurs[22a] above 1800 cm^{-1} (compare Table 1). Bond distances and angles in the cation have usual values.[26] The oxygen atom of the lattice water molecule is within hydrogen-bonding distance, 2.78 Å, of the N(2) atom of the cation.

Conclusion

Five-co-ordinate square-pyramidal species $[Os(NO)(C_2O_4)_2]^-$, generated by a single-pot, single-step reaction from OsO_4, $NH_2OH\cdot HCl$ and $C_2O_4{}^{2-}$ ions, reacts with strong HX forming the respective six-co-ordinate halogenonitrosylosmates(II), $[Os(NO)X_5]^{2-}$. However, it decomposes on boiling with strong alkali-metal hydroxides. Survival of the NO group in an atmosphere of H^+ and its destruction in an OH^- environment is chemical evidence in favour of NO existing as NO^+ in those complexes. The progressive increase of E°_{298} values of the electrochemical reaction $Os(NO)^{3+} \longrightarrow Os(NO)^{4+}$ as X changes from Cl^- to Br^- and I^-, is a beautiful exhibition of electron drainage from a formally osmium(II) centre *via* M→X π bonding which becomes more and more pronounced as we pass from Cl^- to stronger and stronger π acids, Br^- and I^-. Anionic complexes containing H_2phen^{2+} cations are rather more common than those of $Hphen^+$, though in the present case a complex with the latter cation as counter ion, $[Hphen]_2[Os(NO)Br_5]\cdot 2H_2O$, is formed with great ease and has been structurally characterised. The bond lengths described suggest that the single proton is firmly fixed on one of the two heterocyclic nitrogens in each phen, and enters into hydrogen-bonding with the oxygen atom of the lattice-held water. The structure of the octahedral anion shows that Os sits in a special position at a centre of inversion, four bromine atoms occupying the equatorial plane, and there is disorder of axial Br and NO. The mixed-alkali-metal salt of the corresponding fluoro complex does not show any structural disorder,[22a] but in a five-co-ordinate square-pyramidal complex $[Os(NO)Cl_4]^-$ the NO was found to be disordered between both the axial positions.[20] The type of conversion shown in reaction (3), in the

$$[Hphen]_2[Os(NO)Br_5] \longrightarrow [Os(NO)Br_3(phen)] + [H_2phen]Br_2 \quad (3)$$

solid state, is known in other cases containing H_2phen^{2+}

cations, where gaseous HBr is expelled instead of solid $[H_2phen]Br_2$ sublimed.

Experimental

Materials and Methods.—Osmium tetraoxide was obtained from Johnson and Mathey. All reagents required for compound preparation were of analytical grade. The analytical grade solvents used for physicochemical studies were further purified by the literature method[27] before use. Sodium perchlorate for electrochemical work was recrystallised from water and the supporting electrolyte, tetraethylammonium perchlorate, was prepared using the literature method.[28] Dinitrogen for electrochemical and thermoanalytical work was purified by bubbling it through an alkaline dithionite reducing solution. Infrared spectra of KBr/CsI pellets (4000–200 cm^{-1}) were recorded on a Perkin-Elmer model 597 spectrophotometer and those of polythene pellets (500–150 cm^{-1}) on an expanded scale with a model 130 instrument. Electronic spectra were recorded on a Pye-Unicam SP 8-150 UV–VIS or on a Hitachi 330 UV–VIS–NIR spectrophotometer. All the pH measurements were made with an E.C. (India) digital pH meter (model 5651). The solution conductances were measured with a Wayne Kerr B 331 Autobalance Precision Bridge. The magnetic susceptibilities were obtained by the Gouy method with the help of a PAR model 155 vibrating-sample magnetometer. Thermoanalyses were made on a Shimadzu thermoanalyser DT 30. Voltammetric measurements were done with the use of a PAR model 370-4 electrochemistry system, model 174A polarographic analyser, model 175 universal programmer, model RE 0074 XY recorder, model 175 potentiostat, model 179 digital coulometer and model 377 cell systems. All experiments have been made under a dinitrogen atmosphere in a three-electrode configuration using a planar Beckman model 39273 platinum-inlay working electrode, a platinum-wire auxiliary electrode and saturated calomel reference electrode (SCE). For coulometry a platinum-wire gauze working electrode was used. All results were collected at 298 K and the reported potentials were not corrected for junction contribution. Elemental analyses (C, H and N) were done on a Perkin-Elmer 240 C elemental analyser. Halogen contents were estimated as silver halides using literature methods.[29] The X-band EPR spectra were obtained using a Varian E-109C spectrometer fitted with a quartz Dewar for measurement at 77 K. The spectra were calibrated with the help of diphenylpicrylhydrazyl (dpph) ($g = 2.0037$).

Preparation of the Complexes.—*Solution A.* To a faintly yellow coloured solution of OsO_4 (0.1 g, 0.39 mmol) in water (10 cm^3) were added $NH_2OH{\cdot}HCl$ (0.3 g, 4.32 mmol) and $K_2C_2O_4{\cdot}H_2O$ (0.3 g, 1.90 mmol), and the resulting solution was stirred at 70–80 °C for 1 h when a clear deep red solution was obtained (pH *ca.* 2.5). This was cooled to 10 °C and the pH adjusted to 3.5 (solution A). Another solution, B, was prepared by exactly the same method but by using $NH_2OH{\cdot}HCl$ (0.4 g, 5.75 mmol) and $K_2C_2O_4{\cdot}H_2O$ (0.45 g, 2.44 mmol) and adjusting the pH to *ca.* 4.5.*

Potassium nitrosylbis(oxalato)osmate monohydrate **1a**. To solution A a cold (5–10 °C) mixture of propan-1-ol (25 cm^3) and propan-2-ol (25 cm^3) was added slowly until two distinct layers were obtained. The supernatant colourless layer was decanted off, and this addition of cold propanols and decantation of the supernatant layer was continued until an orange-red solid mass, mixed with white impurities, precipitated. The solid was filtered off, washed with propan-1-ol and diethyl ether and dried over P_4O_{10} *in vacuo*. The dry product was then extracted with dry, distilled dimethylformamide (dmf), and to the deep red extract diethyl ether was added to get a deep orange-red precipitate. The product was recrystallised from dmf–diethyl ether (1:3). Yield: 0.09 g (50%). The compound is slightly hygroscopic.

Tetraphenylphosphonium nitrosylbis(oxalato)osmate monohydrate **1b**. An aqueous solution (10 cm^3) of PPh_4Cl (0.3 g, 0.72 mmol) was added to solution B with constant stirring at *ca.* 40 °C to yield a pink precipitate. The stirring was continued for 15 min, and the precipitate allowed to settle and then filtered off and washed thoroughly with water. The product was dried *in vacuo* over P_4O_{10}. The filtrate obtained was then concentrated on a water-bath to *ca.* 10 cm^3 when another crop of product was obtained which was washed and dried. The entire product was then crystallised twice from nitromethane–diethyl ether (1 : 3) when a pale pink microcrystalline product was obtained. Yield: 0.20 g (68%).

Tetraphenylarsonium nitrosylbis(oxalato)osmate monohydrate **1c**. The method for complex **1b** was followed, using $AsPh_4Cl{\cdot}H_2O$ (0.3 g, 0.69 mmol) instead of PPh_4Cl. A microcrystalline rose solid was obtained. Yield: 0.20 g (64%).

Reactions of $[Os(NO)(C_2O_4)_2]^-$ *with* HCl.—*Method* 1, in situ*: preparation of solution C.* To solution B was added concentrated HCl (12 mol dm^{-3}, 25 cm^3) and the resulting solution was boiled for 2–2.5 h. During boiling, further amounts of concentrated HCl were added, so as to keep the total volume of the solution at *ca.* 40–45 cm^3. The resulting deep red solution C was cooled to room temperature.

Bis(tetraphenylphosphonium) pentachloronitrosylosmate **2a**. A cold aqueous solution (50 cm^3) of PPh_4Cl (0.4 g, 0.96 mmol) was added dropwise to solution C with stirring at 60 °C, when a grey precipitate appeared. The mixture was then stirred magnetically for 15 min at 60 °C and the solid was filtered off, washed with water, 90% EtOH, and diethyl ether, and vacuum dried. The filtrate, before washing the precipitate, was collected and set aside. The dry product was crystallised from acetonitrile–diethyl ether (1:3), when deep grey crystals were obtained. Yield: 0.27 g (64%).

Bis(tetraphenylphosphonium) trichloronitrosyl(oxalato)-osmate **3**. The filtrate obtained above after filtering out **2a** was concentrated on a hot plate to *ca.* 15 cm^3. It was then cooled to 25 °C and allowed to stand for 6–8 h, when red crystals separated. The compound was filtered off, washed with water, cold 60% ethanol (twice), and diethyl ether and, dried *in vacuo* over P_4O_{10}. The solid was crystallised from chloroform–pentane (1:2). Yield: 0.08 g (20%). Crystal data: $a = 24.86$, $b = 7.64$, $c = 16.26$ Å, and $\beta = 96°$.

Trichloronitrosyl(1,10-phenanthroline)osmium **6a**. An aqueous solution of 1,10-phenanthroline (0.15 g, 0.76 mmol; dissolved in 10 cm^3 warm water) was added to solution C with constant stirring. The resulting solution was kept undisturbed for 5 d at room temperature (*ca.* 25 °C), when moss-green crystals appeared. These were filtered off, washed with water, 90% ethanol, and diethyl ether, and vacuum dried. The filtrate was kept for 3–4 d and a second crop of crystals was obtained, which was collected and washed as above. Yield: 0.06 g (30%). *Crystal data:* $a = 14.35$, $b = 7.77$, $c = 7.72$ Å, $\alpha = 87.2$, $\beta = 50.3$ and $\gamma = 81.0°$.

Method 2. The compound $[PPh_4][Os(NO)(C_2O_4)_2]{\cdot}H_2O$ **1b**, was treated with concentrated HCl (12 mol dm^{-3}, 10 cm^3) and the suspension was gently boiled on a hot plate for 30 min. An orange-red solution was obtained. It was cooled to *ca.* 25 °C, when a mixture of grey and red crystals separated. The products were filtered off, washed with water, cold 40% ethanol, and diethyl ether, and dried *in vacuo*. The filtrate, on concentration, yielded another crop of the product mixture, which was washed and dried as above. The entire product was extracted with dichloromethane leaving a grey product. The CH_2Cl_2 extract

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* The preparation of solutions A and B is particularly important in order to get pure products **1a**–**1c** with higher yields. For the preparation of **1a**, solution A is employed, where an optimum amount of reactants is used to avoid contamination by excess of unconverted reactants. On the other hand, the greater amount of reactants employed in preparing solution B helps to increase the yields of **1b** and **1c**.

on evaporation gave red crystals. Yield: 0.02 g (14%). This red compound was found to be identical with compound **3**. On the other hand the grey product was found to be identical with compound **2a**. Yield: 0.025 g (17%).

Reactions with HBr.—*Method* 1, in situ. To solution B was added concentrated HBr (47%, 30 cm^3) and the resulting solution was boiled for 1.5 h with addition of the acid so as to keep the total volume around 40 cm^3. The deep maroon-red solution D was cooled to room temperature.

Bis(tetraphenylphosphonium) pentabromonitrosylosmate **2b**. Solution D was added to an aqueous solution (10 cm^3) of PPh_4Cl (0.4 g, 0.96 mmol) and then stirred for 15 min. The brownish grey precipitate formed was filtered off, washed with water, 80% ethanol, and diethyl ether, and vacuum dried. The filtrate on concentration (*ca.* 15 cm^3) yielded another crop of crystalline product which was washed and dried as above. The crops were combined and recrystallised from $MeCN-Et_2O$ (1:3) when deep brown crystals were obtained. Yield: 0.36 g (70%).

Tetraphenylphosphonium aquatetrabromonitrosylosmate hemihydrate **4a**. Solution D was diluted to *ca.* 120 cm^3 in water (80 cm^3). An aqueous solution (20 cm^3) of PPh_4Cl (0.4 g, 0.96 mmol) was added with stirring at room temperature. Stirring was continued for 45 min. The solid which separated was filtered off, washed thoroughly with warm (60 °C) water, and dried *in vacuo.* The filtrate was set aside and the solid was extracted with absolute ethanol when a grey solid, **2b**, was obtained. The red ethanol extract was evaporated under reduced pressure to a small volume when pink crystals were obtained, these were washed with diethyl ether and dried *in vacuo.* Yield of **4a**: 0.12 g (35%). The filtrate on concentration yielded deep brown crystals of compound **2b**. Combined yield of compound **2b**: 0.2 g (40%).

Tetraphenylphosphonium tetrabromonitrosylosmate hemihydrate **4b**. In an attempt to crystallise compound **4a** (0.2 g) from $MeCN-Et_2O$ or $MeNO_2-Et_2O$ the compound **4b** was obtained. This snuff-brown compound could also be obtained when the MeCN or $MeNO_2$ extract of compound **4a** was evaporated. Yield: 0.18 g (90%) (based on compound **4a**).

1,10-*Phenanthrolinedium pentabromonitrosylosmate* **5a**. Solution D was treated with a hot (70 °C) aqueous (15 cm^3) solution of phen (0.2 g, 0.10 mmol). The resulting solution was stirred for 45 min at room temperature (25 °C) when shiny golden-brown crystals separated. These were filtered off and dried under vacuum. The product was then thoroughly washed with benzene, dried again under P_4O_{10} *in vacuo* (0.01 mmHg) for 24 h, and stored in a vacuum desiccator. Yield: 0.26 g (83%).

Bis(1,10-*phenanthrolinium) pentabromonitrosylosmate monohydrate* **5b** *and dihydrogen pentabromonitrosylosmate* **5d**. Compound **5a** (0.25 g) was taken in a sintered glass crucible and washed with water under mild suction. Thus **5a** is converted into **5b** giving a red filtrate (pH 2.0), which on concentration yielded red-brown crystals of $H_2[Os(NO)Br_5]$ **5d**. Yield: 0.06 g (30%). The residue, **5b**, was thoroughly washed with water, 90% ethanol, and diethyl ether, and dried *in vacuo.* This was further purified by crystallising from dmf–diethyl ether (1 : 4). Yield: 0.19 g (66%).

Bis(1,10-*phenanthrolinium) pentabromonitrosylosmate dihydrate* **5c**. Compound **5b** was dissolved in dimethyl sulphoxide and water (three times the volume of dmso) was added. Deep brown crystals of compound **5c** were obtained on keeping the mixture for 4 d at 10 °C. The crystals were collected by filtration, washed with water, and dried *in vacuo* (0.01 mmHg) for 12 h over P_4O_{10}.

Method 2. The compound $[PPh_4][Os(NO)(C_2O_4)_2]\cdot H_2O$ **1b**, was treated with concentrated HBr (10 cm^3, 47%) and the suspension was gently boiled on a hot plate for 20 min. A deep orange solution was obtained, with a reduced volume (2 cm^3). It was cooled to 25 °C when a dark grey-brown product separated. This was filtered off and the filtrate collected. The grey-brown precipitate was washed with water, 90% EtOH, and Et_2O, and vacuum dried. It was characterised as compound **2b**. Yield: 0.03 g (18%). The filtrate and first washing with water were combined and concentrated by evaporation. A deep red solid was obtained which was extracted with dry ethanol. The ethanol extract on evaporation produced a pink-red crystalline compound which was subsequently characterised as **4a**. Yield: 0.02 g (20%). The deep red residue left after extracting the red solid with ethanol was found to be $H[Os(NO)Br_4(H_2O)]$ **4c**. Yield: 0.02 g (28%). This compound is hygroscopic. Addition of PPh_4Cl to an aqueous solution of this compound produced **4a** quantitatively.

Tribromonitrosyl(1,10-*phenanthroline)osmium* **6c**. Compound **5a** or **5b** (0.1 g) in an aluminium boat was placed in a long Pyrex glass tube under a dinitrogen atmosphere and heated in a tube furnace at 300–320 °C. A greenish brown compound, which was subsequently crystallised from dmf–Et_2O to yield deep greenish brown microcrystals, was obtained as a residue in the hot portion of the tube. Yield: 0.06 g (69% with respect to **5a**) or 0.05 g (78% with respect to **5b**). A pink-red compound deposited at the cooler part of the glass tube and was identified as $[H_2phen]Br_2$.

Tribromonitrosylbis(pyridine)osmium dihydrate **7**. The compound $[Hphen]_2[Os(NO)Br_5]\cdot H_2O$ **5b** (0.12 g, 0.12 mmol), was suspended in MeOH (25 cm^3) and the suspension was treated with pyridine (2 cm^3) in MeOH (10 cm^3). The mixture was stirred at 60–70 °C for 30 min when a clear red-brown solution was obtained. Stirring was continued at 25 °C for 15 min. Finally the solution was cooled and kept at 0 °C for 30 min. The solution (*ca.* 10 cm^3) was filtered and to the filtrate was added diethyl ether (40 cm^3), when orange microcrystals were obtained, these were filtered off, washed with diethyl ether, and dried *in vacuo.* Yield: 0.05 g (70%).

Preparation of Solution E: Reactions with HI.—Solution B was warmed (60–65 °C) with freshly distilled * concentrated HI on a steam-bath for 10 min when a deep red solution was obtained. This was then cooled to room temperature (solution E).

Bis(tetraphenylphosphonium) pentaiodonitrosylosmate **2c**. Solution E was added to an aqueous (20 cm^3) solution of PPh_4Cl (0.4 g, 0.96 mmol) with stirring at 25 °C when a brownish yellow solid separated. It was filtered off, washed thoroughly with water, 60% ethanol (thrice), carbon tetrachloride, and diethyl ether, and dried over P_4O_{10} at reduced pressure. The compound was then crystallised from acetonitrile–diethyl ether (1:4) as saffron crystals. Yield: 0.24 g (40%).

Triiodonitrosyl(1,10-*phenanthroline)osmium* **6b**. A hot (70–80 °C) aqueous solution (20 cm^3) of phen (0.15 g, 0.76 mmol) was added to solution E with constant stirring at room temperature (25 °C) and the stirring was continued for 20 min. The product was filtered off, washed with water, 60% ethanol, carbon tetrachloride, and diethyl ether, and dried *in vacuo.* The solid was crystallised from acetonitrile–diethyl ether (1:6) as shiny deep greenish brown crystals. Yield: 0.14 g (45%).

For the preparation of both compounds **2c** and **6b** it was observed that there was a remarkable improvement in the yield if the entire reaction was carried out only in diffused light. The greater the intensity of light the higher was the tendency to form a non-nitrosyl iodo complex.

Preparation of Otherwise Known Compounds.—Dipotassium pentachloro- or pentabromo-nitrosylosmate. To solution C or D was added an aqueous (10 cm^3) solution of KCl or KBr. The resulting solution was concentrated to 15 cm^3 and kept in a refrigerator (5 °C) for 24 h, when a red or red-brown compound, respectively, separated. This was filtered off, washed once with a small quantity (5 cm^3) of cold water, ethanol, and dried *in vacuo.* Further concentration of the filtrate

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* The hydroiodic acid must be freshly distilled (before distillation it was decolourised with H_3PO_2) and should be colourless.

yielded another crop of product. Yield: 0.08 (43) for X = Cl and 0.14 g (52%) for X = Br.

Dicaesium pentachloro- or pentabromo-nitrosylosmate. The procedure applied above was followed except that CsCl or CsBr was used instead of KCl or KBr, when a red-brown or chocolate brown compound, respectively, was obtained. Yield: 0.16 (60) for X = Cl and 0.23 g (66%) for X = Br.

X-Ray Structure Analysis of $[\text{Hphen}]_2[\text{Os(NO)Br}_5]\cdot 2H_2O$ **5c**.—Deep brown crystals were grown from a dmso–water mixture.

Crystal data. $C_{24}H_{22}Br_5N_5O_3Os$, $M = 1018.2$, monoclinic, space group $P2_1/c$, $a = 7.371(1)$, $b = 13.646(1)$, $c = 14.001(2)$ Å, $\beta = 99.88(1)°$, $U = 1426.9$ Å^3 (by least-squares refinement of diffractometer angles for 25 automatically centred reflections, $\lambda = 0.710\,69$ Å), $Z = 2$, $D_c = 2.39$ g cm^{-3}, crystal dimensions $0.25 \times 0.2 \times 0.1$ mm, μ(Mo-Kα) = 111.8 cm^{-1}, maximum and minimum transmission factors 0.67 and 0.48.

Data collection and processing. Hilger-Watt diffractometer, ω–2θ mode, 293 K, graphite-monochromated Mo-Kα radiation; 2354 unique reflections ($1 < \theta < 25°$; $\pm h, k, l$) giving 1221 with $I > 3\sigma(I)$. No significant decay of intensity controls during data collection. Absorption correction according to ref. 30.

Structure analysis and refinement. Heavy-atom method. Block-diagonal least-squares refinement with all non-hydrogen atoms anisotropic [NO group refined with constraints on Os–N(1) and N(1)–O(1) distances 1.81 and 1.19 Å respectively and fixed $U_{\text{iso}} = 0.06$ Å^2; independent refinement for this part gave unrealistic distances* due to prevailing disorder] and hydrogens in geometrically calculated positions. The weighting scheme $w = 1/[\sigma^2(F_o) + 0.001|F_o|^2]$, with $\sigma(F_o)$ from counting statistics. Final R and R' values were 0.052 and 0.055. Largest parameter shift/e.s.d. 0.35. Maximum and minimum peak heights in final difference Fourier map: +2.3 and −0.8 e Å^{-3} (extreme values associated with the positions of the Os atom). Sources of scattering factor data (Os and Br atoms treated as anomalous scatterers) and programs, used (Vax computer, University of York) are given in refs. 31 and 32.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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* Distances Os–N(1) and N(1)–O(1) in that case were 2.00(3) and 0.85(5) Å respectively; the R value, however, remaining practically the same.

References

1 Part 15, R. G. Bhattacharyya, N. Ghosh and G. P. Bhattacharjee, *J. Chem. Soc., Dalton Trans.*, 1989, 1963.
2 J. H. Enemark and R. D. Feltham, *Proc. Natl. Acad. Sci. USA*, 1972, **60**, 3534.
3 K. K. Pandey, *Coord. Chem. Rev.*, 1983, **51**, 69.
4 E. A. Zuech, W. B. Hughes, D. H. Kubicek and E. T. Kittleman, *J. Am. Chem. Soc.*, 1970, **92**, 528; S. T. Wilson and J. A. Osborn, *J. Am. Chem. Soc.*, 1971, **93**, 3068.
5 F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Wiley-Interscience, New York, 1972.
6 (*a*) S. Sarkar and A. Muller, *Z. Naturforsch., Teil B*, 1978, **38**, 1953; (*b*) R. G. Bhattacharyya and A. M. Saha, *J. Chem. Soc., Dalton Trans.*, 1984, 2085; (*c*) R. G. Bhattacharyya and A. M. Saha, *Inorg. Chim. Acta*, 1983, **77**, L81.
7 (*a*) R. G. Bhattacharyya, G. P. Bhattacharjee and P. S. Roy, *Inorg. Chim. Acta*, 1981, **54**, L263; (*b*) R. G. Bhattacharyya and G. P. Bhattacharjee, *J. Chem. Soc., Dalton Trans.*, 1983, 1593; *Polyhedron*, 1983, **2**, 1221; (*c*) R. G. Bhattacharyya, G. P. Bhattacharjee and N. Ghosh, *Polyhedron*, p. 543; (*d*) R. G. Bhattacharyya, G. P. Bhattacharjee and A. M. Saha, *Transition Met. Chem.*, 1983, **8**, 255; (*e*) R. G. Bhattacharyya, P. S. Roy and A. K. Dasmahapatra, *J. Organomet. Chem.*, 1984, **267**, 293; (*f*) A. Muller, S. Sarkar, N. Mohan and R. G. Bhattacharyya, *Inorg. Chim. Acta*, 1980, **45**, L245; (*g*) K. Wieghardt, U. Quilitzch, B. Nuber and J. Weiss, *Angew. Chem., Int. Ed. Engl.*, 1978, **90**, 381; (*h*) K. Wieghardt, W. Holzhach and J. Weiss, *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 548; (*i*) K. Wieghardt, G. B. Dahman, W. Swiridoff and W. Weiss, *Inorg. Chem.*, 1983, **22**, 1221.
8 F. Bottomley and E. M. R. Kiremire, *J. Chem. Soc., Dalton Trans.*, 1977, 1125 and refs. therein.
9 S. Glasstone, *Text book of Physical Chemistry*, Macmillan, London, 1972; W. J. Geary, *Coord. Chem. Rev.*, 1971, **7**, 81.
10 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley-Interscience, 1986.
11 J. H. Enemark and R. D. Feltham, *Coord. Chem. Rev.*, 1974, **13**, 339.
12 O. E. Zxyagintsev and A. Kubanov, *J. Inorg. Chem. (USSR), Engl. Transl.*, 1958, **3**, 108.
13 (*a*) W. P. Griffith, in *The Chemistry of the Rarer Platinum Metals*, Wiley-Interscience, New York, 1967; (*b*) J. Lewis, R. J. Irving and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 1958, **7**, 32.
14 R. Charronat, *Ann. Chim. (Paris)*, 1931, **16**, 123, 168, 188.
15 R. G. Bhattacharyya and P. S. Roy, *J. Coord. Chem.*, 1982, **12**, 129; *Transition Met. Chem.*, 1982, **7**, 285.
16 K. A. Bol'shakov, N. M. Sinitsyn, V. F. Travkin and Z. B. Itkina, *Dokl. Acad. Nauk. SSSR*, 1972, **206**, 98; *Dokl. Chem. Proc. Acad. Sci. (USSR)*, 1972, **206**, 688; N. M. Sinitsyn, V. G. Travkin, A. A. Svetlov and Z. B. Itkina, *Koord. Chim.*, 1975, **1**, 103; *Sov. J. Coord. Chem.*, 1975, **1**, 82; M. J. Cleare and W. P. Griffith, *J. Chem. Soc. A*, 1969, 372.
17 P. Gans, A. Sabatini and L. Sacconi, *Inorg. Chem.*, 1966, **5**, 1877.
18 S. Sarkar and A. Müller, *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 183.
19 K. Dehnicke and R. Lössberg, *Chem. Z.*, 1981, **105**, 305.
20 B. Czeska, K. Dehnicke and D. Fenske, *Z. Naturforsch., Teil B*, 1983, **38**, 1031.
21 (*a*) B. A. Goodman and J. B. Raynor, *Adv. Inorg. Chem. Radiochem.*, 1970, **13**, 135; (*b*) R. G. Bhattacharyya, P. S. Roy and A. K. Dasmahapatra, *J. Chem. Soc., Dalton Trans.*, 1988, 793.
22 (*a*) W. P. Griffith, in *Comprehensive Coordination Chemistry*, eds. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon, Oxford, 1987, vol. 4, p. 519 and refs. therein; (*b*) B. F. G. Johnson, B. L. Haymore and J. R. Dilworth, *Comprehensive Coordination Chemistry*, eds. G. Wilkinson, R. D. Gillard and J. H. McCleverty, Pergamon, Oxford, 1987, vol. 2, p. 99 and refs. therein; (*c*) G. R. Clark, K. R. Grundy, W. W. Roper, J. M. Waters and K. R. Whittle, *J. Chem. Soc., Chem. Commun.*, 1972, 119; (*d*) J. M. Waters and K. R. Whittle, *Chem. Commun.*, 1971, 518; (*e*) G. R. Clark, J. M. Waters and K. R. Whittle, *J. Chem. Soc., Dalton Trans.*, 1975, 463.
23 D. M. P. Mingos and J. A. Ibers, *Inorg. Chem.*, 1971, **10**, 1479.
24 F. Bottomley, I. J. B. Lin and P. S. White, *J. Chem. Soc., Dalton Trans.*, 1978, 1726.
25 D. Collison, C. D. Garner, F. E. Mabbs, J. A. Salthouse and T. J. Kind, *J. Chem. Soc., Dalton Trans.*, 1981, 1812.
26 S. Nishigaki, H. Yoshioka and K. Nakatsu, *Acta Crystallogr., Sect. B*, 1978, **34**, 875.
27 D. D. Perrin, W. L. F. Armerogo and D. R. Perrin, *Purification of Laboratory Chemicals*, Pergamon, New York, 1966.
28 S. Goswami, A. R. Chakravarty and A. Chakravorty, *Inorg. Chem.*, 1982, **21**, 2737.
29 A. I. Vogel, *A Text Book of Quantitative Inorganic Analysis*, The

English Language Book Society and Longmans, London, 1968.

30 A. C. T. North, D. C. Phillips and F. S. Mathews, *Acta Crystallogr., Sect. A*, 1968, **24**, 351.

31 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4.

32 G. M. Sheldrick, SHELX 76, Program for Crystal Structure Determination, University of Cambridge, 1976.

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