Studies on Transition-metal Nitrido- and Oxo-complexes. Part 6.[1] Nitrido-bridged Complexes of Osmium and Ruthenium

By **Jonathan P. Hall** and **William P. Griffith**,* Inorganic Chemistry Research Laboratories, Imperial College, London SW7

The new complexes $[Os_3N_2(NH_3)_8(OH_2)_6]Cl_6$, $[Os_3N_2(NH_3)_8(OH_2)_6]Cl_7$, and $[Ru_3N_2(NH_3)_8(OH)(OH_2)_5]Cl_5$ are reported. On the basis of the resonance Raman and i.r. spectra of normal, ^2H-, and ^{15}N-substituted forms of the complexes, structures analogous to that found in ' ruthenium red,' $[Ru_3O_2(NH_3)_{14}]Cl_6$, are proposed. Related structures are proposed for $[Os_3N_2(NH_3)_6(OH)_4(OH_2)_2]Cl_2$, $[Os_3N_2(NH_3)_4(OH)_8(OH_2)_2]$, $K_4[Os_3N_2(CN)_{10}(OH_2)_4]$, and $K_4[Os_3N_2(CN)_8(OH)_4(OH_2)_2]$. The possible application of $[Os_3N_2(NH_3)_8(OH_2)_6]Cl_6$ as a cell staining reagent is noted. All the complexes may be regarded as containing $M_3N_2^{6+}$, $M_3N_2^{7+}$, or $M_3N_2^{8+}$ ' cores.'

THE trimeric oxo-bridged complex ruthenium red, $[Ru_3O_2(NH_3)_{14}]Cl_6{\cdot}4H_2O$ has long been known,[2] although this formulation has only recently been established by chemical[3] and single-crystal *X*-ray[4] studies. The complex is widely used for specific staining of cell walls in optical and electron microscopy,[5] and will also specifically bind to those sites in tissue which normally attract calcium ions.[6] The present work arose from our attempts to prepare and characterise an osmium analogue of ruthenium red; since osmium has a greater electron-scattering power than ruthenium, such an analogue should be superior to ruthenium red as a cytological reagent for electron microscopy. We were, however, unable to prepare $[Os_3O_2(NH_3)_{14}]^{6+}$, but instead a series of related nitrido-bridged species were made, at least one of which, $[Os_3N_3(NH_3)_8(OH_2)_6]^{6+}$, does indeed have staining properties. We report here the preparation and likely structures of these osmium complexes, and also report a new nitrido-bridged complex of ruthenium.

RESULTS AND DISCUSSION

(*A*) *Nitrido-bridged Complexes of Osmium.*—Binuclear nitrido-bridged complexes of osmium(IV), *e.g.* $[Os_2NX_8(OH_2)_2]^{3-}$ (X = Cl or Br) and $[Os_2N(NH_3)_8X_2]^{n+}$ (X = Cl, Br, I, NCS, N_3, NO_3, or H_2O) are well established.[7,8] Trinuclear species have been little investigated, however. Reaction of the material known as ' Claus ' salt ' [made by reaction of osmium tetraoxide (OsO_4) and aqueous ammonia and formulated as ' $OsO_2{\cdot}2NH_3{\cdot}OH_2$ '] [9,10] with HX gives salts of $[Os_3N_2(NH_3)_3X_{11}]^{3-}$ (X = Cl or Br).[11] Reactions of OsO_4 with liquid ammonia gives an amorphous material $H_{21}N_7O_9Os_3$ [12] formulated as $Os_3N_2O_2(NH_3)_5(OH)_7$ [13] or $Os_3N_3(NH_3)_4(OH)_9$.[7] Recently, Gautier has reported an uncharacterised polynuclear material made from OsO_4 and aqueous ammonia which is effective at staining acid-hydrolysed DNA in tissue.[14]

(*i*) *Complexes containing the* $Os_3N_2^{6+}$ *core.* Ruthenium red can be made by aerial oxidation of a solution of hydrated ruthenium trichloride[3] or $[Ru(NH_3)_5Cl]^{2+}$ [15] in aqueous ammonia. We find that similar treatment of anhydrous $OsCl_3$ gave no reaction, but aeration of aqueous ammoniacal solutions of OsO_4, $[OsCl_6]^{2-}$, or $[Os(NH_3)_5Cl]Cl_2$ gives a deep violet species which by analogy with ruthenium red we call ' osmium violet '. The most convenient method of preparation is the anaerobic treatment of $Na_2[OsCl_6]$ with aqueous ammonia under pressure at 95 °C.

The complex is only slightly soluble in water, but is more soluble in 0.1 mol dm^{-3} aqueous acetate or cacodylate solutions [the latter buffer, $AsMe_2O_2^-$, is commonly used in cytology] at pH 7—8 to give deep violet solutions. Because of the low solubility in water we were unable to obtain reliable conductivity or molecular weight data. Elemental analyses are in agreement with the formulation $[Os_3N_2(NH_3)_8(OH_2)_6]Cl_6$, and that the chlorine is ionic, as indicated by the fact that it is precipitated by $Ag[NO_3]$, and that chlorine-free thiosulphate and pyrophosphate salts may be obtained. Determination of the ammonia content by a modified Kjeldahl procedure[12,16] showed that only four-fifths of the total nitrogen is present as NH_3. Metal oxidation-state determinations [by oxidation of the osmium in the complex to osmium(VI) with VO_3^- [17,18]] gave a value of 4.2 ± 0.3. Oxidation with neutral potassium permanganate gave variable titration results: both OsO_4 and $[OsO_3N]^-$ are produced. *X*-Ray photoelectron spectroscopy (x.p.s.) gave Os $4f_{\frac{7}{2}}$ and $4f_{\frac{5}{2}}$ binding energies of 53.0 and 53.4 eV relative to C 1*s* of 285.0 eV (for $[Os^{IV}{}_2N(NH_3)_8Cl_2]Cl_3$ the $4f_{\frac{7}{2}}$ and $4f_{\frac{5}{2}}$ energies we find to be 53.1 and 55.4 eV, and for *trans*-$Na_2[Os^{VI}O_2(OH)_4]$ 56.0 and 58.1 eV respectively), again suggesting an oxidation state of +IV. The use of x.p.s. spectroscopy in assigning oxidation states in osmium complexes has recently been demonstrated.[19] Polarographic studies on the complex in 0.1 mol dm^{-3} sodium acetate showed no oxidation or reduction at the dropping mercury electrode (+0.3 to −1.8 V *versus* standard calomel electrode).

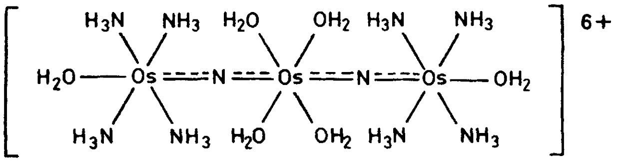
The i.r. spectrum of the complex (see Table) shows bands near 1 100 cm^{-1} which shift some 30 cm^{-1} to lower frequency on ^{15}N-substitution. We assign them to asymmetric vibrations of Os–N–Os–N–Os units; similar bands and isotopic shifts are observed in $[Os_2N(NH_3)_8X_2]^{3+}$ [7] and in $[Os_3N_2(NH_3)_3X_{11}]^{3-}$,[11] and the bands due to co-ordinated NH_3 are close to those observed in these complexes. No bands due to co-ordinated chloro-ligands were observed, nor bands due to co-ordinated NH or NH_2 ligands.[20] The intense purple colour of the complex arises from the strong electronic absorption at 590 nm (ε 13.95×10^3 dm^3 mol^{-1} cm^{-1}), and this prompted us to attempt to record resonance Raman spectra using excitation at 468.2, 520.8, 530.9, 568.2, and 647.1 nm from a krypton-ion laser. As with ruthenium red, which has a strong electronic absorption at 537 nm (ε 69.9 × 10^3 dm^3 mol^{-1} cm^{-1}),[15] a strong resonance Raman spectrum was observed. Excitation profiles for the observed bands show a maximum near 595 nm, suggesting that this is indeed the transition responsible for the resonance enhancement. In solution the strongest bands are polarised (ρ, the depolarisation ratio, is close to 0.3 suggesting [21] that these are symmetric axial modes). The main Raman bands are at 1 100, 792, 460, 287, and 222 cm^{-1}. On the assumption that these include essentially axial modes, those at 460 and 287 cm^{-1} may be assigned to symmetric ν[Os–N(NH$_3$)] and δ(N–Os–N) modes respectively (similar bands are observed in [Os(NH$_3$)$_6$]$^{3+}$ with similar isotopic shifts,[22] and bands in these regions are also seen in the i.r. spectrum of solid osmium violet and may be assigned to the corresponding asymmetric modes). The bands at 1 100 and 222 cm^{-1} may then be assigned to symmetric vibrations of the Os$_3$N$_2$ unit, the former involving mainly a motion of the nitrido-ligands so that there is a shift on ^{15}N-substitution; and the latter involving motion of the metal atoms, hence its immobility on isotopic substitution. The band at 790 cm^{-1} may involve some ammine rocking ρ(NH$_3$) character, though the small shift on ^{2}H-substitution is puzzling. The main features of the resonance Raman spectrum are similar to those of ruthenium red.[15, 23]

Infrared and Raman bands (cm^{-1}) of osmium and ruthenium nitrido-bridged complexes [a]

Complex		ν(M$_3$N$_2$)				ν(MN), ν(MO), ν(MC)					δ(NMN)		Other prominent bands
$[Os_3N_2(NH_3)_8(OH_2)_6]Cl_6$		1 075m			212vs		500w		466m	385m	267m		900m, 780vs
	b	1 100m			222s		511w		460m	380w	287m		835w, 792vs
		(0.25)			(0.25)		(0.31)		(0.26)		(0.32)		(0.33)
		1 078s	*1 040m*	*1 020m*		*555m*	*510w*	*475w*				*270m*	*865m*
$[Os_3N_2(N^2H_3)_8(O^2H_2)_6]Cl_6$		1 095m		1 015m	212vs				462w	380w	254s		900m, 785s, 580w
$[Os_3{}^{15}N_2({}^{15}NH_3)_8(OH_2)_6]Cl_6$		1 048m			212vs				468m	385w	262s		900m, 761m
		1 055s	*1 025s*			*558m*		*470w*				obsc.	*850m, 770m*
$[Os_3N_2(NH_3)_8(OH_2)_6]Cl_7$	*c*	1 091s	1 018m				475m		440w	335w	272s		793vs
	b, c	1 105m	1 025w		222m	510m	478m		444w	330m	282s		802s, 600m
		1 090s	*1 020m*					*470m*				*273s*	*965m, 833m, 550m*
$[Os_3N_2(N^2H_3)_8(O^2H_2)_6]Cl_7$	*c*	1 095s	1 020w		212vs		460m			328m	256s		790vs
		1 100m	*1 020m*				*450m*					*250m*	*863m, 790m, 550m*
$[Os_3{}^{15}N_2({}^{15}NH_3)_8(OH_2)_6]Cl_7$	*c*	1 064s	980w		obsc.	490m	445w						788s, 577m
			1 055s	*968m*			*470m*					*260m*	*845w, 750m, 525m*
$[Ru_3N_2(NH_3)_8(OH)(OH_2)_5]Cl_5$	*d*	1 060m			315s	470s		410s		351s	265s		795m, 665m
	b, d	1 060m			315s	480s		415s	390s	350s			760m, 690m
					(0.40)	(0.23)		(0.24)	(0.25)	(0.46)			(0.58), (0.35)
			1 040s				*475m*					*250s*	*810m, 540m*
$[Ru_3N_2(N^2H_3)_8(O^2H)(O^2H_2)_5]Cl_5$	*b, d*	1 050m			335s	470m		410s	373s				750s, 635m, 290m
$K_4[Os_3N_2(CN)_{10}(OH_2)_4]\cdot 4H_2O$	*e*			1 030m	228s	520m				465s			2 150s, 2 132s, 2 105m, 812s, 750m, 595w
	b, e			1 035m	234s	524m				460s			2 157 (p), 2 149w (p), 2 135w (dp), 840w, 800w, 350w, 120vs
		1 120s	*1 040vs*				*475m*						*2 130s, 2 105s, 2 085m, 2 047vs, 2 038w, 905w, 830w, 750m, 550m*
$K_4[Os_3N_2(CN)_8(OH)_4(OH_2)_2]$	*c*		1 080s	993s				467s					2 140, 2 110s, 2 078m, 2 065s, 2 040w, 2 020w, 755m, 608s, 420w, 370w
		1 170s	*1 070vs*	*960s*				*465s*					*2 122s, 2 042s, 785w, 555m*

[a] Data on solids for excitation at 568.2 nm unless otherwise stated. Infrared bands are italicised; all other data are Raman, depolarisation ratios (ρ) in parentheses below corresponding wavenumber. obsc. = obscured. [b] Data on aqueous solutions. [c] Excitation at 468.2 nm. [d] Excitation at 647.1 nm. [e] Excitation at 530.9 nm.

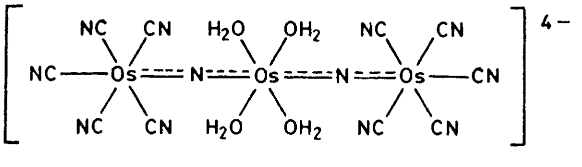
The vibrational spectra, oxidation state data, and composition of the complex lead us to suggest a trinuclear structure (I) involving osmium(IV), in accordance with the observed diamagnetism of the complex, and the fact that the complex can be prepared from $[Os^{IV}Cl_6]^{2-}$ and aqueous ammonia under anaerobic conditions. The sites of water and ammonia ligands can not be determined (all attempts to obtain crystals of the complex suitable for *X*-ray study have failed), but the known lability of the central four ammonia ligands relative to the ten terminal ligands in the related ruthenium red complex [24] leads us to suggest tentatively that water molecules may co-ordinate to the central osmium atom. Furthermore, the rarity of i.r.–Raman coincidences suggests a centro-symmetric structure such as (I). A weak Raman band at 385 cm^{-1} (unaffected by ^{15}N-substitution, but dropping to 380 cm^{-1} on ^{2}H-substitution) may well be a stretching ν(Os–O) vibration of *trans*-aquo ligands. Although formulation of the complex as a mixed oxidation-state species (*e.g.*, Os^{II}–Os^{VI}–Os^{II}) is possible, this seems unlikely since the x.p.s. $4f_{\frac{7}{2}}$ and $4f_{\frac{5}{2}}$ peaks are sharp and in positions expected for osmium(IV).



(I)

(*ii*) *Other* $Os_3N_2^{6+}$ *species*. Preparation of the bromo-analogue of osmium violet using $[OsBr_6]^{2-}$ and ammonia gave $[Os_3N_2(NH_3)_8(OH)(OH_2)_5]Br_5$; its vibrational spectra are very similar to those of osmium violet. The species prepared by Cogliati and Gautier [14] is ill defined, but our analyses suggest $[Os_3N_2(NH_3)_6(OH)_4(OH_2)_2]Cl_2$ as a possible formula; again, this has a similar i.r. spectrum to the other ammine complexes. The compound is diamagnetic, as expected for the above formulation as an $Os_3N_2^{6+}$ core species.

Reaction of osmium violet $[Os_3N_2(NH_3)_8(OH_2)_6]Cl_6$ with hot concentrated potassium cyanide solution gives a brown-black salt $K_4[Os_3N_2(CN)_{10}(OH_2)_4]\cdot 4H_2O$, containing the cation (II). The i.r. spectrum shows bands in the CN stretching region (*ca.* 2 100 cm^{-1}), in addition to those near 1 100 cm^{-1} attributed to bridging nitride ligands, but no vibrations attributable to co-ordinated ammine ligands. The electronic spectrum has strong bands at 460, 510, and 640 nm and a resonance-enhanced Raman spectrum was observed for very dilute aqueous solutions (*ca.* 10^{-3} mol dm^{-3}; excitation at 468.2 and 530.9 nm). The Raman bands at 1 035 and 234 cm^{-1} are likely to be the counterparts of those at 1 100 and 222 cm^{-1} for osmium violet; they also have depolarisation ratios close to 0.3. Three bands are observed in the C≡N stretching region for the solutions, two being polarised and one depolarised. This, and the comparative rarity of coincidence of Raman and i.r. bands, suggests that a centrosymmetric structure is likely. We tentatively suggest the D_{4h} structure for which two polarised (a_{1g}) and two depolarised (b_{1g}, e_g) modes are expected. It has been noted that π-acceptor ligands such as CO and CN$^-$ will co-ordinate *trans* to bridging nitride ligands, as in *trans*-$[Ru_2NCl_8(CO)_2]^{3-}$ and $[Ru_2N(CN)_{10}]^{5-}$.[11]



(II)

(*iii*) *Complexes containing the* $Os_3N_2^{7+}$ *and* $Os_3N_2^{8+}$ *cores*. During the preparation of osmium violet, a brown material analysing as $[Os_3N_2(NH_3)_8(OH_2)_6]Cl_7$ was obtained; this again has similar vibrational spectra to $[Os_3N_2(NH_3)_8(OH_2)_6]Cl_6$, but is slightly paramagnetic ($\mu_{eff.}$ 0.87 B.M.* per trimer unit), and titrations with VO_3^- indicate an overall oxidation state of 4.4 ± 0.2. The x.p.s. spectrum gives Os $4f_{\frac{7}{2}}$ and $4f_{\frac{5}{2}}$ binding energies of 53.2 and 55.6 eV, both slightly higher than those for osmium violet and consistent with a slightly higher oxidation state than IV. It may thus be regarded as containing the $Os_3N_2^{7+}$ core.

The reaction of OsO_4 with aqueous ammonia gives the black 'Claus' salt',[9,10] a diamagnetic material.[11] The i.r. spectrum of this has features in common with the other amine complexes described here, and the analyses are consistent with a formulation $[Os_3N_2(NH_3)_4(OH)_8(OH_2)_2]$. The x.p.s. spectrum gives Os $4f_{\frac{7}{2}}$ and $4f_{\frac{5}{2}}$ binding energies of 54.4 and 56.2 eV, suggesting a somewhat higher overall oxidation state than +IV.

Reaction of 'Claus' salt' with hot aqueous K[CN] gives $K_4[Os_3N_2(CN)_8(OH)_4(OH_2)_2]$. This brown species gives only a very weak, non-resonance Raman spectrum. Both Claus' salt and this *cyano-complex* derived from it may be regarded as containing the OsN_2^{8+} core.

(*B*) *The* $Ru_3N_2^{6+}$ *Core Complex* $[Ru_3N_2(NH_3)_8(OH_2)_6]Cl_6$.—The binuclear species $[Ru_2NX_8(OH_2)_2]^{3-}$ and $[Ru_2N(NH_3)_5X_2]^{n+}$ (X = Cl, Br, I, NCS, N_3, or H_2O) are well established,[7] and the crystal structure of $K_3[Ru_2NCl_8(OH_2)_2]$ has been determined.[25] No trinuclear species of ruthenium have been reported, though a material $H_{33}N_{11}O_{12}Ru_4$ has been made from ruthenium tetraoxide (RuO_4) and liquid ammonia.[26]

During studies on the preparation and cytological properties of ruthenium red, Luft [27] noted the presence of an impurity which he named 'ruthenium violet', and which had staining properties similar to those of ruthenium red. We have prepared this complex and find it to analyse as $[Ru_3N_2(NH_3)_8(OH)(OH_2)_5]Cl_5$, so that it is closely related to osmium violet, $[Os_3N_2$-

---

* B.M. = Bohr magneton ≈ 0.927 × 10^{-23} A m^2.

$(NH_3)_8(OH_2)_6]Cl_6$, and like the latter, it is diamagnetic. The complex is sufficiently soluble to permit conductivity measurements: the conductance at infinite dilution, 780 Ω^{-1} cm^2 mol^{-1} in water at 25 °C, is comparable with that of other 5 : 1 electrolytes (*e.g.* $[Ru_2N(NH_3)_8(OH_2)_2]^{5+}$, 801 Ω^{-1} cm^2 mol^{-1}). The vibrational spectra of normal and ^{2}H-substituted ruthenium violet are listed in the Table; again, resonance enhancement of the Raman spectrum at 530.9, 568.2 and 647.1 nm is observed by virtue of the electronic transition at 620 nm (ε 1.29 $\times$ 10^4 dm^3 mol^{-1} cm^{-1}) and the main bands may be assigned in a similar fashion to the other nitrido-complexes already described.

(*C*) *Cytological Properties of Osmium Violet.**—Staining of barley leaf and root cells by osmium violet is comparable with that found for ruthenium red; membranes, chromatin, nucleoli, and ribosomes gained intensity relative to other cell constituents. In the absence of additional staining the intensity of the osmium images appeared somewhat greater than that of the ruthenium image.

EXPERIMENTAL

Octa-amminehexa-aquodi-μ-nitrido-triosmium(IV) *Hexachloride*, $[Os_3N_2(NH_3)_8(OH_2)_6]Cl_6$, *'Osmium Violet'*.—*Method* 1. A saturated solution of $Na_2[OsCl_6]\cdot nH_2O$ (2.0 g, 3.6 mmol) was added to combined solutions of ammonium chloride (6.6 g, 0.12 mol) and sodium hydroxide (4.0 g, 0.1 mol) in 40 cm^3 of water. The mixture was heated in a closed pressure bottle on a steam bath for six hours, the black solid filtered from the cooled solution and washed with water, ethanol, and ether. Yield 47%.

Method 2. A solution of $Na_2[OsCl_6]\cdot nH_2O$ (5 g, 9 mmol) in hydrochloric acid (0.25 mol dm^{-3}, 75 cm^3) and ethanol (15 cm^3) was refluxed for three hours, and the brown solution treated with concentrated ammonia solution (0.880, 100 cm^3) with stirring at 75 °C in air for 4 h. Sufficient ammonia was added to offset losses. Yield of product 15%.

Method 3. The complex $[Os(NH_3)_5Cl]Cl_2$ (prepared as previously described [28]) (1.0 g, 3.2 mmol) was stirred in air with aqueous ammonia (0.880, 50 cm^3) and warmed to 75 °C for three hours. Ammonia was added to offset losses. Yield 35%.

Method 4. Osmium tetraoxide (5.0 g, 20 mmol) was warmed with concentrated hydrochloric acid (15 cm^3), water (25 cm^3), and ethanol (10 cm^3) for 40 h. The resulting dark green solution was evaporated to half-volume and excess ammonia solution (0.880, 100 cm^3) added and the mixture stirred at 60 °C for 5 h with further addition of ammonia to offset losses. Total yield of product, 25% (Found: H, 3.2; Cl, 18.9; N, 14.0; O, 9.7; Os, 54.1. $H_{36}Cl_6N_{10}O_6Os_3$ requires H, 3.4; Cl, 20.2; N, 13.3; O, 9.1; Os, 54.1%).

Ammonia was analysed by a Kjeldahl procedure by boiling the sample with 45% sodium hydroxide solution and collecting the NH_3 in saturated boric acid solution [12,16] (Found: NH_3, 13.9%. $[Os_3N_2(NH_3)_8(OH_2)_6]Cl_6$ requires NH_3, 12.9%).

The ^{2}H and ^{15}N forms of the salt were made by method 1 using $[N^2H_4]Cl$, $Na[O^2H]$, and ^2H_2O, or $[^{15}NH_4]Cl$ (98.6% ^{15}N) respectively.

Magnetic data: χ -2.9×10^{-9} m^3 kg^{-1} at 294 K, giving $\mu_{\text{eff.}}$ 0.64 B.M. per trimer unit. Electronic spectra (recorded in 0.1 mol dm^{-3} sodium acetate solution measured from 250—850 nm): maxima at 330 (ε 6.9 $\times$ 10^3); 590 (ε 14.0 $\times$ 10^3); 710 nm (ε 12.5 $\times$ 10^3 dm^3 mol^{-1} cm^{-1}). Infrared spectra (ammine modes): 3 360s, 3 110vs ν(NH), 1 603vs $\delta_{\text{asym}}(NH_3)$, 1 322s $\delta_{\text{sym}}(NH_3)$, 740 $\rho(NH_3)$; in deuteriate 2 360s, 2 290vs, 1 240m, 1 000s, 700ms cm^{-1}.

Octa-amminepenta-aquohydroxodi-μ-nitrido-triosmium(IV) *Pentabromide*, $[Os_3N_2(NH_3)_8(OH)(OH_2)_5]Br_5$.—This complex was made from $[NH_4]_2[OsBr_6]$ (3.0 g, 4.3 mmol), ammonium bromide (12.5 g, 0.13 mol), and sodium hydroxide (4.2 g, 0.1 mol) by method 1 above. Yield of black material, 40% (Found: H, 2.7; Br, 28.4; N, 11.3; Os, 46.9. $H_{35}Br_5N_{10}O_6Os_3$ requires H, 2.2; Br, 32.2; N, 11.3; Os, 46.0%). Infrared spectrum (solid state): 3 400 ν(OH), 3 220s, 3 150s ν(NH), 1 610s $\delta_{\text{asym}}(NH_3)$, 1 310s $\delta_{\text{sym}}(NH_3)$, 1 105s, 1 020m $\nu(Os_3N_2)$, 835m $\rho(NH_3)$ cm^{-1}.

Octa-amminehexa-aquodi-μ-nitrido-triosmium Heptachloride, $[Os_3N_2(NH_3)_8(OH_2)_6]Cl_7$.—This was extracted, following evaporation to low volume, from the solutions remaining from the above methods 1—4 after precipitation of osmium violet; method 2 gives the best yield, 1.5 g of product from 5.0 g of $Na_2[OsCl_6]\cdot nH_2O$.

It can also be made by the reaction of $Na_2[OsCl_6]\cdot nH_2O$ (1.5 g, 2.7 mmol) and ammonia solution (0.880, 25 cm^3), warmed in a sealed pressure bottle on a steam bath for 6 h. The brown-black solid was filtered off, washed with ammonia solution, and dried *in vacuo*. Yield 10% (Found: H, 2.9; Cl, 21.7; N, 12.6; O, 9.4; Os, 52.1. $H_{36}Cl_7N_{10}O_6Os_3$ requires H, 3.2; Cl, 22.8; N, 12.9; O, 8.8; Os, 52.3%). Ammonia (by Kjeldahl procedure as above) (Found: NH_3, 13.1. $[Os_3N_2(NH_3)_8(OH_2)_6]Cl_7$ requires NH_3, 12.5%). The isotopically enriched ^{2}H and ^{15}N forms were made from $K_2[OsCl_6]$ and N^2H_3 in ^2H_2O, and from $Na_2[OsCl_6]\cdot nH_2O$ and $^{15}NH_3$ respectively.

Magnetic data: χ -2.0×10^{-9} m^3 kg^{-1} at 294 K gives $\mu_{\text{eff.}}$ 0.84 B.M. per trinuclear unit. Electronic spectrum (recorded in 0.1 mol dm^{-3} sodium acetate solution, 250—850 nm): maxima at 320 (ε 5.3 $\times$ 10^3) and 380 nm (ε 6.4 $\times$ 10^3 dm^3 mol^{-1} cm^{-1}). Infrared spectra (ammine modes): 3 400vs ν(OH), 3 240vs, 3 170vs $\nu(NH_3)$, 1 615s, $\delta_{\text{asym}}(NH_3)$, 1 345s, 1 310s $\delta_{\text{sym}}(NH_3)$, 833m $\rho(NH_3)$; in deuteriate: 2 340s, 2 260s, 1 250m, 863m, 790m, 550 cm^{-1}.

Tetra-amminediaquo-octahydroxodi-μ-nitrido-triosmium $[Os_3N_2(NH_3)_4(OH)_8(OH_2)_2]$ ('*Claus' salt*').—Concentrated aqueous ammonia (0.880, 150 cm^3) was added to OsO_4 (3.6 g, 1.4 mmol in 100 cm^3 of water) and the mixture refluxed for 2 d. The black precipitate was filtered off and dried *in vacuo*. Yield 90% (Found: H, 2.4; N, 10.0. $H_{24}N_6O_{10}Os_3$ requires H, 2.9; N, 10.0%). Infrared spectrum: 3 380s, 3 160s, 1 620m, 1 335m, 1 090s, 965vs, 530s cm^{-1}.

Hexa-amminediaquotetrahydroxodi-μ-nitrido-triosmium(IV), $[Os_3N_2(NH_3)_6(OH)_4(OH_2)_2]Cl_2$.—This was made from OsO_4 as described previously [14] (Found: H, 2.9; Cl, 6.3; N, 12.6. $H_{26}Cl_2N_4O_6Os_3$ requires H, 3.0; Cl, 8.1; N, 12.8%). Determination of NH_3 by the modified Kjeldahl procedure (Found: NH_3, 10.6. $[Os_3N_2(NH_3)_6(OH)_4(OH_2)_2]Cl_2$ requires NH_3, 11.6%). Magnetic data: χ -3.5×10^{-9} m^3 kg^{-1} at 294 K giving $\mu_{\text{eff.}}$ 0.38 B.M. per trinuclear unit. Infrared spectrum: 3 360s ν(OH), 3 100vs ν(NH), 1 580s

---

* Tests carried out by Dr. C. Sargent, Imperial College.

$\delta_{asym}(NH_3)$, 1 320vs $\delta_{sym}(NH_3)$, 1 010s, 970m $\nu(Os_3N_2)$, 715m $\rho(NH_3)$.

Tetrapotassium Tetra-aquodecacyanodi-μ-nitrido-triosmate(IV) *Tetrahydrate*, $K_4[Os_3N_2(CN)_{10}(OH_2)_4]\cdot 4H_2O$.—The complex $[Os_3N_2(NH_3)_8(OH_2)_6]Cl_6$ ('osmium violet') (0.35 g, 0.33 mmol) was dissolved in potassium cyanide solution (2 g, in 5 cm³ water), and the mixture stirred and heated under reflux for 7 h. The brown solution was added when cold to methanol (20 cm³), the brown precipitate filtered off, and washed with methanol followed by diethyl ether. It was recrystallised by dissolving in water (20 cm³) and adding methanol (*ca.* 10 cm³) until the solution was turbid on cooling. Yield of black product, 20% (Found: C, 9.7; H, 1.4; K, 12.7; N, 14.6; O, 11.2. $C_{10}H_{16}K_4N_{12}O_8Os_3$ requires C, 10.4; H, 1.4; K, 13.5; N, 14.5; O, 11.0%). Electronic absorption spectrum (in water): 370 (ε 4.3 × 10³), 510 (ε 6 × 10³), 640 nm (4.1 × 10³ dm³ mol⁻¹ cm⁻¹).

Tetrapotassium Diaquo-octacyanotetrahydroxodi-μ-nitrido-triosmate, $K_4[Os_3N_2(CN)_8(OH)_4(OH_2)_2]$.—The complex $[Os_3N_2(NH_3)_4(OH)_8(OH_2)_2]$ ('Claus' salt') (1 g, 1.2 mmol) was dissolved in potassium cyanide solution (2.5 g, in 75 cm³ water), and the mixture heated under reflux for 7 h. The brown solution was added when cold to methanol (150 cm³), the brown precipitate filtered off, and washed with methanol followed by diethyl ether. The product was recrystallised from water–methanol. Yield of dark brown product, 60% (Found: C, 8.9; H, 1.0; K, 13.9; N, 13.7. $C_8H_8K_4N_{10}O_6Os_3$ requires C, 9.0; H, 0.8; K, 14.7; N, 13.1%).

Octa-amminepenta-aquohydroxodi-μ-nitrido-triruthenium(IV), $[Ru_3N_2(NH_3)_8(OH)(OH_2)_5]Cl_5$, '*Ruthenium Violet*'.—Hydrated ruthenium trichloride (2 g, 8 mmol) was refluxed with HCl (0.25 mol dm⁻³, 40 cm³) and ethanol (10 cm³) for 3 h and left to cool. It was then treated with concentrated ammonia (0.880, 100 cm³) and the mixture kept at room temperature in air for 1 d. More ammonia (100 cm³) was added and the mixture allowed to stand overnight. Yield of blue-black product, 20% (Found: H, 4.4; Cl, 25.5; N, 18.2; O, 12.3. $H_{35}Cl_5N_{10}O_6Ru_3$ requires H, 4.7; Cl, 23.6; N, 18.6; O, 12.8%). Isotopically enriched (^{2}H) ruthenium violet was made by evaporating to dryness *in vacuo* a solution in ^2H_2O.

Magnetic Data: χ −2.02 × 10⁻⁹ m³ kg⁻¹ at 296 K, giving $\mu_{eff.}$ 0.80 B.M. per trinuclear unit. Electronic absorption spectrum: 385 (ε 7 × 10³), 495 (ε 9.1 × 10³), 620 (ε 12.9 × 10³), 750 nm (ε 19.9 × 10³ dm³ mol⁻¹ cm⁻¹). Conductivities: measurements over the concentration range 4 × 10⁻⁵ to 6 × 10⁻⁶ mol dm⁻³ gave the limiting conductance Λ^0 780 Ω⁻¹ cm² mol⁻¹ in water at 25 °C. Values of Λ^0 for comparable ions are 801 Ω⁻¹ cm² mol⁻¹ for $[Ru_2N(NH_3)_8(OH_2)_2]^{5+}\cdot 5(Cl^-)$ and 1 030 Ω⁻¹ cm² mol⁻¹ for $[Ru_3O_2(NH_3)_{14}]^{6+}\cdot 6(Cl^-)$.

Raman spectra (60—1 200 cm⁻¹) were run on a Spex Ramalog 5 instrument with a krypton-ion laser, using solids as pressed KBr discs or aqueous solutions, both being spun in the beam to avoid thermal decomposition. Infrared spectra (200—4 000 cm⁻¹) were measured as liquid paraffin mulls between caesium iodide plates on a Perkin-Elmer 597 instrument. Conductivity measurements were made on a Wayne–Kerr A.C. Bridge. Electronic spectra (250—800 nm) were measured on a Perkin-Elmer 402 instrument. *X*-Ray photoelectron spectra were measured on a Vacuum Generators ESCA 3 instrument.

We thank Dr. C. Sargent for staining tests using osmium violet, ruthenium violet, and ruthenium red, and Mr. S. Bean of Johnson, Matthey Ltd. for x.p.s. measurements. We acknowledge the loan of osmium and ruthenium from Johnson, Matthey Ltd., and the S.R.C. for a research studentship (to J. P. H.).

[0/295 *Received*, 20*th February*, 1980]

REFERENCES

[1] Part 5, A. J. Nielson, M. Schröder, and W. P. Griffith, *J.C.S. Dalton*, 1979, 1607.

[2] A. Joly, *Compt. rend. Acad. Sci.*, 1892, **114**, 291.

[3] J. M. Fletcher, B. F. Greenfield, C. J. Hardy, D. Scargill, and J. L. Woodhead, *J. Chem. Soc.*, 1961, 2000.

[4] M. A. A. F. de C. T. Carrondo, W. P. Griffith, J. P. Hall, and A. C. Skapski, *Biochim. Biophys. Acta*, 1980, **627**, 332.

[5] P. R. Blanquet, *Histochemistry*, 1976, **47**, 63.

[6] K. C. Reed and F. L. Bygrave, *Biochem. J.*, 1974, **140**, 143.

[7] M. J. Cleare and W. P. Griffith, *J. Chem. Soc.* (*A*), 1970, 1117.

[8] M. J. Cleare, F. M. Lever, and W. P. Griffith, *Adv. Chem. Ser.*, 1971, **98**, 54.

[9] C. Claus, *Bull. Acad. Petersburg*, 1863, **6**, (3), 175.

[10] J. J. Berzelius, *Pogg. Ann.*, 1829, **15**, 215.

[11] W. P. Griffith and D. Pawson, *J.C.S. Dalton*, 1973, 1315.

[12] G. W. Watt and E. M. Potrafke, *J. Inorg. Nuclear Chem.*, 1961, **17**, 248.

[13] G. W. Watt and W. C. McCordie, *J. Inorg. Nuclear Chem.*, 1965, **27**, 2013.

[14] R. Cogliati and A. Gautier, *Compt. rend. Acad. Sci.*, 1973, **D276**, 3041.

[15] J. R. Campbell, R. J. H. Clark, W. P. Griffith, and J. P. Hall, *J.C.S. Dalton*, 1980, 2228.

[16] L. Winkler, *Z. angew. Chem.*, 1914, **27**, 630.

[17] R. V. Casciani and E. J. Behrman, *Inorg. Chim. Acta*, 1978, **28**, 69.

[18] V. S. Syrokomskii, *Doklady Akad. Nauk S.S.S.R.*, 1945, **46**, 305.

[19] D. L. White, S. B. Andrews, J. W. Faller, and R. J. Barrnett, *Biochim. Biophys. Acta*, 1976, **436**, 577.

[20] D. J. Hewkin and W. P. Griffith, *J. Chem. Soc.* (*A*), 1966, 472.

[21] J. san Filippo, P. J. Fagan, and E. J. DiSalvo, *Inorg. Chem.*, 1977, **16**, 1016.

[22] W. P. Griffith, *J. Chem. Soc.* (*A*), 1966, 899.

[23] J. M. Friedman, D. L. Rousseau, G. Navon, S. Rosenfeld, P. Glynn, and K. B. Lyons, *Arch. Biochem. Biphys.*, 1979, **193**, 14.

[24] P. M. Smith, T. Fealey, J. E. Earley, and J. V. Silverton, *Inorg. Chem.*, 1971, **10**, 1943.

[25] M. Ciechanowicz and A. C. Skapski, *J. Chem. Soc.* (*A*), 1971, 1792.

[26] G. Watt and W. C. McCordie, *J. Inorg. Nuclear Chem.*, 1965, **27**, 262.

[27] J. H. Luft, *Anat. Rec.*, 1971, **171**, 347.

[28] A. D. Allen and J. R. Stevens, *Canad. J. Chem.*, 1972, **50**, 3093; 1973, **51**, 92.