Photophysical Properties, Electrochemistry and Crystal Structure of Nitridoosmium(VI) Complexes of 2,3-Diamino-2,3-dimethylbutane†

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The complex $[OsN(H_2L)_2Cl]Cl_2{\cdot}2H_2O$ **1** was prepared by the reaction of $[NBu_4][OsNCl_4]$ with 2,3-diamino-2,3-dimethylbutane (H_2L) in methanol. Treatment of **1** with CF_3SO_3H under argon gave $[OsN(H_2L)_2][CF_3SO_3]_3$ **2** which on prolonged standing in acetonitrile yielded $[OsN(HL)(H_2L)_2][CF_3SO_3]_2$ **3**. The crystal structures of **1** and **3** have been determined by X-ray crystallography: **1**, triclinic, space group, $P\bar{1}$ (no. 2), $a = 7.176(1)$, $b = 7.273(2)$, $c = 10.823(2)$ Å, $\alpha = 101.20(2)$, $\beta = 106.88(2)$, $\gamma = 97.96(2)°$, $Z = 1$; **3**, monoclinic, space group, $C2/c$ (no. 15), $a = 15.810(3)$, $b = 12.766(3)$, $c = 16.225(4)$ Å, $\beta = 110.25(2)°$, $Z = 4$. The emission spectrum of **1** at 77 K shows vibrational progression with spacing of 1050 cm^{-1} characteristic of the ground-state $\nu(Os{\equiv}N)$ stretch. In 0.1 mol dm^{-3} CF_3CO_2H the cyclic voltammogram of **2** displays a $3H^+$–$3e^-$ reduction wave at −0.34 V *vs.* saturated calomel electrode assignable to the reduction of $Os^{VI}{\equiv}N$ to Os^{III}–NH_3.

Osmium(VI) nitrido complexes have received considerable attention recently because of their intriguing photoluminescent and electrochemical properties.[1,2] These complexes usually possess long-lived $^3[(d_{xy})^1(d_{xz},d_{yz})^1]$ excited states, which can participate in bimolecular electron- and atom-transfer reactions.[1] Recently, Meyer and co-workers[2] showed that the electrochemistry of nitridoosmium(VI) systems such as $[OsN(terpy)Cl_2]^+$ (terpy = 2,2′:6′,2″-terpyridine) bears similarity to that of the corresponding oxo analogues in that proton-coupled multielectron redox couples are observed in aqueous solution. However, detailed electrochemical studies on $[OsN(terpy)Cl_2]^+$ are hampered because this complex undergoes rapid solvolysis in aqueous media.[2] In fact, few cationic nitridoosmium(VI) complexes have been reported.[3] Herein are described the photophysical and electrochemical properties of nitridoosmium(VI) complexes with the ligand 2,3-diamino-2,3-dimethylbutane (H_2L). This chelating diamine ligand was chosen because it forms stable complexes with transition-metal ions in high oxidation states.[4]

Experimental

Materials.—Osmium tetraoxide (> 99%) and 2,3-dimethyl-2,3-dinitrobutane were obtained from Aldrich Chemical Co. Deionized water for electrochemical experiments was purified by distillation over alkaline $KMnO_4$. All other chemicals were of analytical reagent grade used without further purification.

Preparations.—The salt $[NBu_4][OsNCl_4]$ was prepared according to literature procedures.[5]

Ligand H_2L. A mixture of 2,3-dimethyl-2,3-dinitrobutane (5 g) and granular tin (30 g) in concentrated hydrochloric acid (75 cm^3) was refluxed for 2 h. The suspension became a clear pale yellow solution. The excess of acid in the mixture was neutralized by slow addition of ice-cold 20% NaOH solution. The mixture was then steam distilled and the first 400 cm^3 were collected, cooled in an ice-bath and sodium hydroxide pellets (10 g) were added. The resulting solution was extracted with chloroform (3 x 100 cm^3), the chloroform extracts pooled, dried over anhydrous Na_2SO_4 and evaporated to dryness to give 2,3-diamino-2,3-dimethylbutane (H_2L) as a colourless solid (yield 80%). ^1H NMR (90 MHz) in $CDCl_3$: δ 1.12 (s, CH_3) and 1.31 (s, NH_2). The ligand was used in subsequent syntheses without further purification.

$[OsN(H_2L)_2Cl]Cl_2{\cdot}2H_2O$ **1**. A mixture of $[NBu_4][OsNCl_4]$ (0.2 g) and H_2L (0.1 g) in absolute methanol was stirred at room temperature for 0.5 h to give a pale yellow solution. Addition of diethyl ether gave a pale yellow precipitate which was collected, washed with absolute ethanol and recrystallized from 2 mol dm^{-3} HCl (yield 60%). IR data: $\nu(Os{\equiv}N)$ 1090; $\nu(NH_2)$ 3050, 3300 cm^{-1}.

$[OsN(H_2L)_2][CF_3SO_3]_3$ **2**. A mixture of complex **1** (0.1 g) in trifluoromethanesulfonic acid (3 cm^3) was stirred under a stream of argon gas for 0.5 h. Addition of diethyl ether to the resulting yellow solution gave $[OsN(H_2L)_2][CF_3SO_3]_3$ as a yellow solid. The product was collected, washed with diethyl ether and dried in vacuum (yield 90%) (Found: C, 20.3; H, 3.90; N, 7.70. Calc.: C, 20.4; H, 3.60; N, 7.90%). ^1H NMR (270 MHz) in CD_3CN: δ 1.47 (t, CH_3) and 1.94 (m, NH_2). Prolonged standing of $[OsN(H_2L)_2][CF_3SO_3]_3$ in acetonitrile in air gave a yellow crystalline solid with some white powder. The white powder was shown by NMR spectroscopy to be the free ligand H_2L. The yellow crystals obtained were shown by X-ray structure analysis to be $[OsN(HL)(H_2L)_2][CF_3SO_3]_2$ **3**. Recrystallization of $[OsN(H_2L)_2][CF_3SO_3]_3$ by diffusion of diethyl ether into acetonitrile gave $[OsN(HL)(H_2L)][CF_3SO_3]_2$ **4** (Found: C, 22.6; H, 4.40; N, 9.40. Calc.: C, 22.9; H, 4.25; N, 9.55%).

Measurements.—The UV/VIS absorption spectra were recorded on a Milton Roy Spectronic 3000 diode-array spectrophotometer, infrared spectra as Nujol mulls on a Nicolet 20FXC FT-IR spectrometer, solution ^1H NMR spectra on a

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Table 1 Atomic coordinates (× 10^4) for $[OsN(H_2L)_2Cl]Cl_2\cdot 2H_2O$

Atom	*x*	*y*	*z*
Os	0	0	0
Cl(1)	629(6)	3090(5)	−342(5)
Cl(2)	4046(4)	2194(4)	−2134(3)
N(1)	989(8)	−1154(8)	−1600(6)
N(2)	−2676(8)	−685(8)	−1604(6)
N(3)	−434(11)	−2353(11)	280(9)
C(1)	−707(9)	−2295(9)	−2844(7)
C(2)	−2441(9)	−1191(9)	−2972(7)
C(3)	−1281(10)	−4342(9)	−2750(8)
C(4)	125(10)	−2347(10)	−4019(7)
C(5)	−4388(10)	−2411(10)	−3958(8)
C(6)	−1981(10)	648(9)	−3403(7)
O(1)	4257(9)	6715(8)	8947(7)

The disordered atoms Cl(1) and N(3) have site-occupancy factors of 0.5.

Table 2 Atomic coordinates (× 10^4) for $[OsN(HL)(H_2L)_2][CF_3SO_3]_2$ **3**

Atom	*x*	*y*	*z*
Os	0	531(2)	2500
N(1)	0	−789(23)	2500
N(2)	1061(9)	694(18)	1959(9)
N(3)	1116(10)	709(17)	3687(12)
C(1)	1971(11)	853(21)	2633(12)
C(2)	2115(28)	2046(20)	2704(24)
C(3)	2719(31)	325(32)	2376(26)
C(4)	1945(14)	401(21)	3504(16)
C(5)	2027(30)	−802(20)	3497(24)
C(6)	2722(36)	860(35)	4283(13)
C(1′)	1989(13)	1040(26)	3608(19)
C(2′)	2175(13)	2211(25)	3525(31)
C(3′)	2765(29)	548(36)	4368(14)
C(4′)	1881(15)	468(28)	2740(14)
C(5′)	2038(35)	−716(26)	2921(28)
C(6′)	2571(40)	894(41)	2347(26)
N(4)	0	2291(20)	2500
C(7)	33(13)	3293(15)	2898(10)
C(8)	928(14)	3409(25)	3669(15)
C(9)	−762(15)	3446(29)	3228(20)
C(10)	−22(16)	4112(19)	2183(13)
C(11)	732(19)	3931(36)	1803(22)
C(12)	−942(17)	4051(27)	1437(16)
N(5)	0	5100(24)	2500
C(13)	−448(32)	2846(29)	5590(24)
F(1)	−1206(17)	3096(19)	4991(17)
F(2)	−642(16)	2779(16)	6317(15)
F(3)	131(18)	3611(20)	5670(18)
S(1)	−62(6)	1629(7)	5323(5)
O(1)	−785(15)	862(15)	5217(13)
O(2)	740(14)	1394(17)	6073(14)
O(3)	116(17)	1855(17)	4544(13)

JEOL 270 MHz Fourier-transform spectrometer using $SiMe_4$ as reference and emission spectra with a Spex Fluorolog-2 spectrofluorometer. Cyclic voltammetry was performed with a Princeton Applied Research (PAR) model 175 universal programmer, model 173 potentiostat and a Houston 2000 X-Y recorder. A conventional two-compartment cell was used. A saturated calomel electrode (SCE) was used as reference. The working electrodes were edge-plane pyrolytic graphite obtained from Union Carbide. A PAR 179 digital coulometer was used in conjunction with a PAR 173 potentiostat for coulometry experiments. Elemental analyses were performed by Butterworth Laboratory Ltd.

Table 3 Selected bond distances (Å) and angles (°) for $[OsN(H_2L)_2Cl]Cl_2\cdot 2H_2O$ **1**

Os–Cl(1)	2.352(5)	Os–N(1)	2.127(7)
Os–N(2)	2.100(5)	Os–N(3)	1.797(8)
N(1)–C(1)	1.522(7)	N(2)–C(2)	1.52(1)
C(1)–C(2)	1.56(1)	C(1)–C(3)	1.52(1)
C(1)–C(4)	1.55(1)	C(2)–C(5)	1.517(8)
C(2)–C(6)	1.53(1)		
Cl(1)–Os–N(1)	91.1(2)	Cl(1)–Os–N(2)	89.7(2)
N(1)–Os–N(2)	79.3(2)	Cl(1)–Os–N(3)	178.9(2)
N(1)–Os–N(3)	88.9(4)	N(2)–Os–N(3)	91.3(3)
Os(1)–N–C(1)	113.1(4)	Os–N(2)–C(2)	114.8(4)
N(1)–C(1)–C(2)	106.6(5)	N(1)–C(1)–C(3)	110.3(6)
C(2)–C(1)–C(3)	113.5(6)	N(1)–C(1)–C(4)	105.9(5)
C(2)–C(1)–C(4)	112.0(6)	C(3)–C(1)–C(4)	108.2(6)
N(2)–C(2)–C(1)	106.9(5)	N(2)–C(2)–C(5)	108.7(6)
C(1)–C(2)–C(5)	111.8(5)	N(2)–C(2)–C(6)	109.0(5)
C(1)–C(2)–C(6)	111.6(6)	C(5)–C(2)–C(6)	108.7(6)
Hydrogen bonding			
O(1) ··· Cl(2)	3.199(7)	O(1) ··· Cl(2b)	3.235(7)
N(1c) ··· O(1)	2.968(8)	N(2a) ··· O(1)	2.971(8)
Cl(2) ··· O(1) ··· Cl(2b)	108.6(4)	Cl(2) ··· O(1) ··· N(1c)	102.5(5)
Cl(2) ··· O(1) ··· N(2a)	99.7(5)	Cl(2b) ··· O(1) ··· N(2a)	128.2(5)
Cl(2b) ··· O(1) ··· N(2a)	114.9(5)	N(1c) ··· O(1) ··· N(2a)	98.9(6)

Symmetry transformations: a $-x, -y, 1-z$; b $1-x, 1-y, -z$; c $1-x, -y, -z$.

X-Ray Structure Determination.—*Crystal data for* $[OsN(H_2L)_2Cl]Cl_2\cdot 2H_2O$. M = 579.08, triclinic, space group $P\bar{1}$ (no. 2), a = 7.176(1), b = 7.273(2), c = 10.823(2) Å, α = 101.20(2), β = 106.88(2), γ = 97.96(2)°, U = 518.5(2) Å^3, D_c = 1.85 g cm^{-3}, Z = 1, $F(000)$ = 286, μ(Mo-Kα) = 65.56 cm^{-1}, crystal dimensions 0.04 × 0.2 × 0.22 mm.

Intensities were measured on a Nicolet R3m four-circle diffractometer with Mo-Kα radiation (λ = 0.710 73 Å) using the ω–2θ scan (3.01–15.63° min^{-1}) technique in the bisecting mode up to 2θ_{max} = 50°. Raw intensities were processed with the profile-fitting procedure of Diamond[6] and corrected for absorption using ψ-scan data. Of the 2306 unique data measured, 2303 observed data with $|F_o| \geqslant 6\sigma(|F_o|)$ were used in structure analysis. The weighting scheme $w = (\sigma^2|F_o| + 0.002|F_o|^2)^{-1}$ was used giving R_F = 0.055, R' = 0.074 and S = 1.490. The osmium atom was located from a Patterson map, and the remaining non-hydrogen atoms in subsequent Fourier difference maps. The disordered Cl(1) and N(3) atoms were assigned the same site-occupancy factor of 0.5. All non-hydrogen atoms except N(3) were subjected to anisotropic refinement, and the hydrogen atoms were generated geometrically (C–H 0.96 Å) and assigned appropriate isotropic thermal parameters. The residual peaks in the final difference map are all in the neighbourhood of the osmium atom, caused by the series-termination effect.

Crystal data for $[OsN(HL)(H_2L)_2][CF_3SO_3]_2$. M = 849.97, monoclinic, space group $C2/c$ (no. 15), a = 15.810(3), b = 12.766(3), c = 16.225(4) Å, β = 110.25(2)°, U = 3072(1) Å^3, D_c = 1.837 g cm^{-3}, Z = 4, $F(000)$ = 1704, μ(Mo-Kα) = 4.36 cm^{-1}, crystal dimensions 0.18 × 0.22 × 0.26 mm.

Intensities were measured with graphite-monochromatized Mo-Kα radiation (λ = 0.710 73 Å) using the ω–2θ scan mode (4.0° min^{-1}) up to 2θ_{max} = 48°. Absorption corrections were applied using ψ-scan data. Of the 2322 unique data measured, 1492 observed with $|F_o| \geqslant 3\sigma(|F_o|)$ were used in structure analysis. The weighting scheme $w = (\sigma^2|F_o| + 0.002|F_o|^2)$ was used giving R_F = 0.084, R' = 0.072 and S = 1.90.

All computations were performed using the SHELXTL-PLUS program package[7] on a DEC MicroVax II computer. Tables 1 and 2 list the atomic coordinates of non-hydrogen atoms. Selected bond distances and angles are given in Tables 3 and 4.

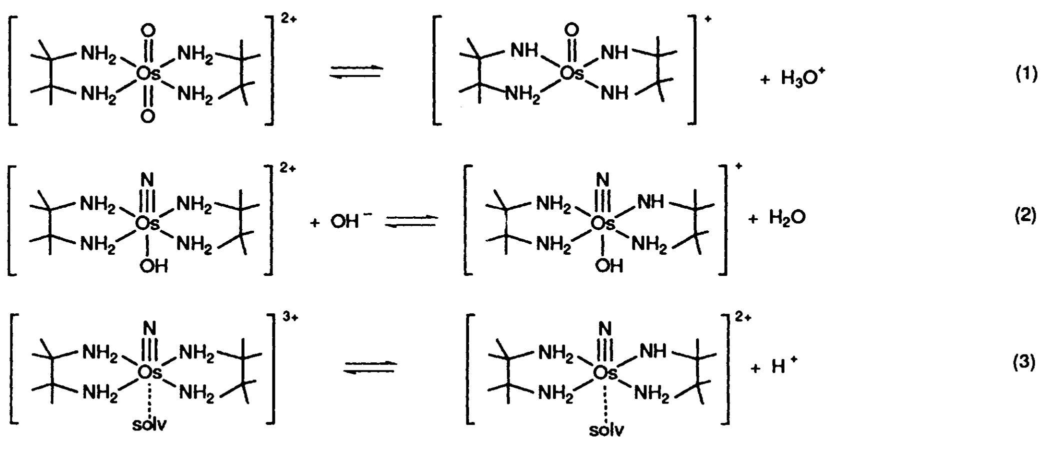


Table 4 Selected bond distances (Å) and angles (°) for $[OsN(HL)(H_2L)_2][CF_3SO_3]_2$ **3**

Os–N(1)	1.68(3)	Os–N(2)	2.15(2)
Os–N(3)	2.13(1)	Os–N(4)	2.25(3)
Os–N(2a)	2.15(2)	Os–N(3a)	2.13(1)
N(1)–Os–N(2)	95.6(6)	N(1)–Os–N(3)	96.2(6)
N(2)–Os–N(3)	80.6(6)	N(1)–Os–N(4)	180.0(1)
N(2)–Os–N(4)	84.4(6)	N(3)–Os–N(4)	83.8(6)
N(1)–Os–N(2a)	95.6(6)	N(2)–Os–N(2a)	169(1)
N(3)–Os–N(2a)	98.2(6)	N(4)–Os–N(2a)	84.4(6)
N(1)–Os–N(3a)	96.2(6)	N(2)–Os–N(3a)	98.2(6)
N(3)–Os–N(3a)	168(1)	N(4)–Os–N(3a)	83.8(6)
N(2a)–Os–N(3a)	80.6(6)		
Os–N(2)–C(1)	114(1)	Os–N(3)–C(4)	108(1)
Os–N(4)–C(7)	153.8(8)	Os–N(4)–C(7a)	153.8(8)

Symmetry transformation: a $-x, y, \frac{1}{2} - z$.

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

Results and Discussion

The synthesis of five- and six-co-ordinated oxoosmium(VI) complexes of H_2L has previously been communicated.[4a] Both H_2L and its deprotonated form HL can act as bidentate chelating ligands and reaction (1) has been reported previously.

In this work, H_2L reacts rapidly with $[OsNCl_4]^-$ leading to the formation of $[OsN(H_2L)_2Cl]^{2+}$ isolated as a chloride salt **1**. The co-ordinated chloride is labile in water since the ε_{max} of this complex at 258 nm varies with the pH of the solution (pH 2, $\varepsilon_{max} = 2.48 \times 10^3$; pH 5, $\varepsilon_{max} = 1.74 \times 10^3$ dm^3 mol^{-1} cm^{-1}). Both the co-ordinated and non-co-ordinated chlorides in **1** are readily removed by heating in neat CF_3SO_3H. The complex $[OsN(H_2L)_2][CF_3SO_3]_3$ **2** was characterized by elemental analysis. Because $CF_3SO_3^-$ is a non-co-ordinating ligand an aqueous solution of **2** would give either $[OsN(H_2L)_2(OH_2)]^{3+}$ or $[OsN(H_2L)_2(OH)]^{2+}$ depending on the pH. Since both the λ_{max} and ε_{max} of **2** remain constant throughout the range pH 1.5–5, the major species present in solution in this range is $[OsN(H_2L)_2(OH)]^{2+}$ (see also electrochemical results discussed later). For a tripositive $[Os^{VI}(OH_2)]^{3+}$ complex cation such as $[OsN(H_2L)_2(OH_2)]^{3+}$ a low pK_a value is expected for the co-ordinated H_2O. Not surprisingly, the UV/VIS absorption spectrum of **2** in solution at pH < 6 resembles to that of **1** in aqueous acidic media. The spectrum starts to change at pH $\geqslant 7$. At pH 8, two peaks at 241 and 271 nm with similar intensities are found. When the pH is $\geqslant 9$ the absorption spectrum is dominated by a single intense band at ≈ 230 nm. This spectrum is similar to that of an acetonitrile solution of **2**. We suggest reaction (2) takes place in solutions at pH $\geqslant 7$.

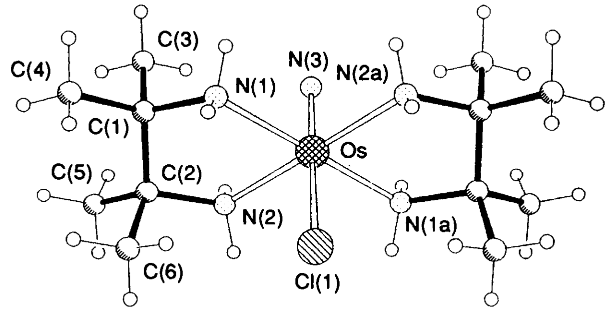


Fig. 1 A perspective view of plot of $[OsN(H_2L)_2Cl]^{2+}$

Our previous work[4a] on oxoosmium(VI) complexes of H_2L showed that deprotonation of the ligand readily occurs in acetonitrile *via* equation (1). Thus it is not unreasonable to expect a similar reaction (3) (solv = solvent) in an acetonitrile solution of complex **2**. We have attempted to trap the complex cation $[OsN(HL)(H_2L)]^{2+}$. Prolonged standing of **2** in acetonitrile gave a yellow crystal the structure of which has been determined to be $[OsN(HL)(H_2L)_2][CF_3SO_3]_2$ **3**. The chemical formulation of **3** is also in accord with its molar conductivity of ≈ 210 Ω cm^2 mol^{-1} in acetonitrile, characteristic of a 1:2 electrolyte.

Structures of Complexes **1** *and* **3**.—Fig. 1 shows the molecular structure of the $[OsN(H_2L)_2Cl]^{2+}$ cation with the atom numbering. The osmium atom occupies a centrosymmetric site so that both nitrido and chloro ligands are two-fold disordered. The osmium is six-co-ordinated, by five nitrogen and one chlorine atom. The Os–N(1) and Os–N(2) distances of 2.127(7) and 2.100(5) Å are normal. The Os–N(3) distance of 1.797(8) Å is an unusual feature. It is longer than those found in other nitridoosmium complexes such as that of 1.647(7) Å in $[OsN(CN)_5]^-$,[1b] 1.663(5) Å in $[OsN(terpy)Cl_2]^+$,[2] 1.608(7) Å in $[OsN(O_2CCH_2CH_2S)_2]^-$[8] and 1.63(1) Å in $[OsN\{O_2CCH(NHCOMe)CH_2S\}_2]^-$.[8] However, such a long Os≡N distance may be due to incomplete separation of the disordered nitrido and chloro ligands. The unusually long Os–Cl(1) distance of 2.352(5) Å is attributed to the structural *trans* effect of the nitrido group. The chloride ions and water molecules form hydrogen-bonded $(Cl \cdots H_2O)_2$ rings, which are linked to the complex cations by N–H $\cdots$ O hydrogen bonds to give layers corresponding to the (010) set of planes.

A perspective view of the $[OsN(HL)(H_2L)_2]^{2+}$ cation is

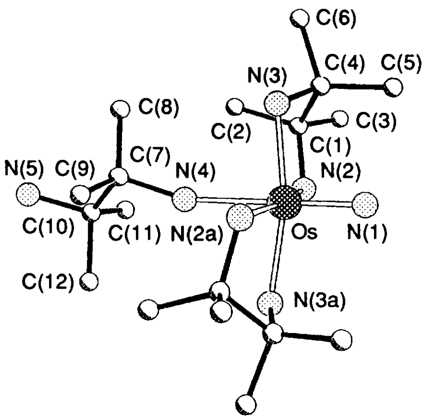


Fig. 2 A perspective view of plot of $[OsN(HL)(H_2L)_2]^{2+}$

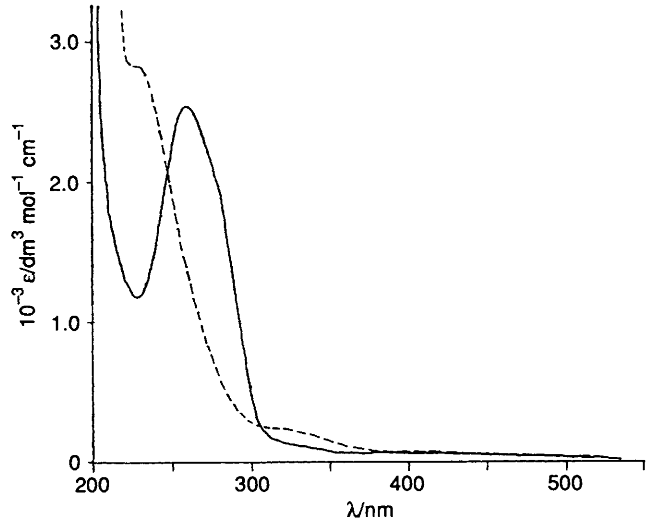


Fig. 3 The UV/VIS spectra of $[OsN(H_2L)_2Cl]^{2+}$ in 0.1 mol dm^{-3} HCl (——) and in 0.1 mol dm^{-3} NaOH (- - - -)

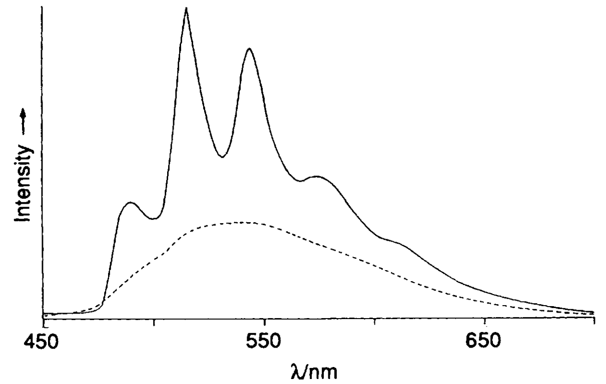


Fig. 4 Emission spectra of a solid sample of $[OsN(H_2L)_2Cl]Cl_2$ at 298 K (- - - -) and 77 K (——). Excitation wavelength: 350 nm

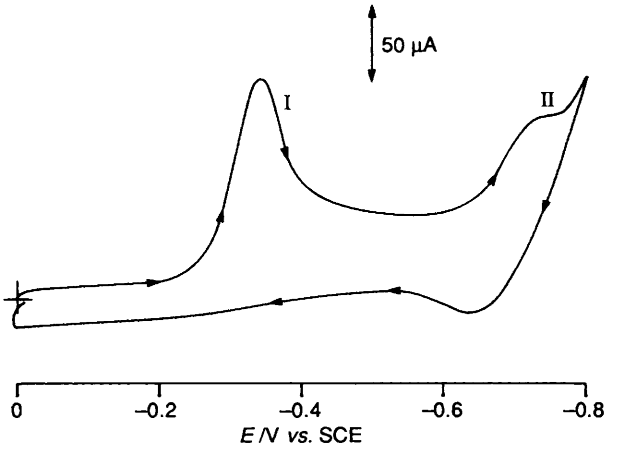


Fig. 5 Cyclic voltammogram of $[OsN(H_2L)_2][CF_3SO_3]_3$ **2** in 0.1 mol dm^{-1} CF_3CO_2H. Working electrode: edge-plane pyrolytic graphite. Scan rate: 50 mV s^{-1}

shown in Fig. 2. The Os≡N bond length of 1.68(3) Å is comparable to values found in other nitrodoosmium complexes.[1b,2,8] The structure indicates that the complex which exists in acetonitrile has one of the equatorial ligands deprotonated, consistent with equation (3). The weakly bound ligand H_2L which is *trans* to the Os≡N unit probably comes from some degraded complexes during recrystallization.

Spectroscopic Properties.—The infrared spectrum of $[OsN(H_2L)_2Cl]Cl_2$ shows a band at 1090 cm^{-1} assignable to ν(Os≡N). In the ^1H NMR spectrum of $[OsN(H_2L)_2][CF_3SO_3]_3$ in CD_3CN there is no evidence in the spectrum for paramagnetic broadening indicating that the complex is diamagnetic.

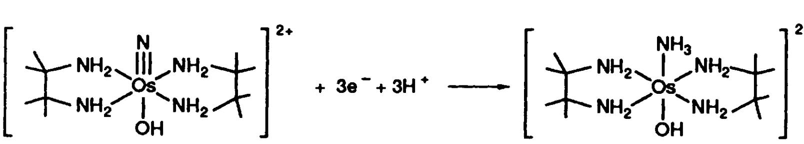
The UV/VIS absorption spectrum of $[OsN(H_2L)_2Cl]^{2+}$ in 0.1 mol dm^{-3} HCl is shown in Fig. 3. Two bands are observed: a weak one centred at ≈400 nm with $\varepsilon = 70$ dm^3 mol^{-1} cm^{-1} and an intense one at 258 nm ($\varepsilon = 2.5 \times 10^3$ dm^3 mol^{-1} cm^{-1}). The weak band is probably due to the spin-forbidden $(d_{xy})^2 \longrightarrow (d_{xy})^1(d_{\pi^*})^1$ transition where ($d_{\pi^*} = d_{xz},d_{yz}$). The higher-energy band at 258 nm which is also found for **2** is assigned to the $p_\pi(N^{3-}) \longrightarrow (d_{\pi^*})$ transition.

Excitation of a solid sample of $[OsN(H_2L)_2Cl]Cl_2$ at 350 nm results in photoluminescence with an emission maximum at ≈550 nm ($\tau = 5.0 \pm 0.5$ μs) at 298 K. Cooling the sample to 77 K led to an increase in the emission intensity. The low-temperature emission spectrum shows well resolved vibrational progression with a spacing of 1050 cm^{-1} characteristic of the ν(Os≡N) stretch in the ground state (Fig. 4). The large difference in emission and lowest-allowed absorption energies and the long emission lifetime indicate that the emission is phosphorescence. With reference to previous work on other Os^{VI}≡N complexes,[1d,9] the ^3E state of $^3[(d_{xy})^1(d_{\pi^*})^1]$ is most likely to be the emitting state.

Complex **4** shows an emission at ≈560 nm in acetonitrile at room temperature. At concentrations of 1.8×10^{-4}–3.0×10^{-4} mol dm^{-3}, the lifetime and quantum yield of the emission are 2.0 μs and 9.2×10^{-3} respectively.

Electrochemistry.—The cyclic voltammogram of $[OsN(H_2L)_2][CF_3SO_3]_3$ in 0.1 mol dm^{-3} CF_3CO_2H displays an irreversible reduction wave (I) with peak potential (E_{pc}) −0.34 V *vs.* SCE followed by a quasi-reversible couple (II) with $E_{\frac{1}{2}}$ at −0.69 V (Fig. 5). Constant-potential coulometry at −0.50 V *vs.* SCE gave $n = 3.0$ indicating that wave I is a $3e^-$ reduction process. From the size of the peak current, II is estimated to be a $1e^-$ couple. The E_{pc} of wave I was found to shift by 60 mV per pH unit from pH 1 to 7.5. The $E_{\frac{1}{2}}$ of couple II also shifts cathodically by 60 mV per pH unit as the pH of the medium is raised. These observations are consistent with the following electrode reactions (4) for I and (5) for II. The Pourbaix diagram is shown in Fig. 6. At pH > 7.5 the slope for wave I becomes ≈90 mV per pH unit suggesting a four-proton three-electron process (6). Couple II becomes very broad at pH > 8 and its $E_{\frac{1}{2}}$ was difficult to estimate.

A comparison of the electrochemistry of complex **2** with that of $[OsN(terpy)Cl_2]^+$ shows that both undergo proton-coupled reduction of Os^{VI}≡N to Os^{III}–NH_3 in aqueous media. In the $[OsN(terpy)Cl_2]^+$ system[2] a study of the pH dependence of the formal potential was prohibited by rapid solvolysis of co-



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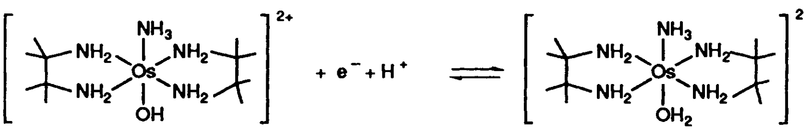

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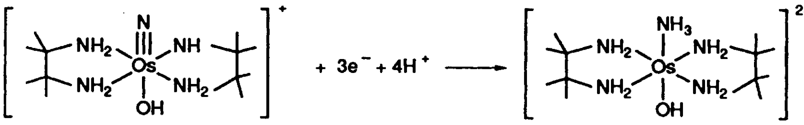

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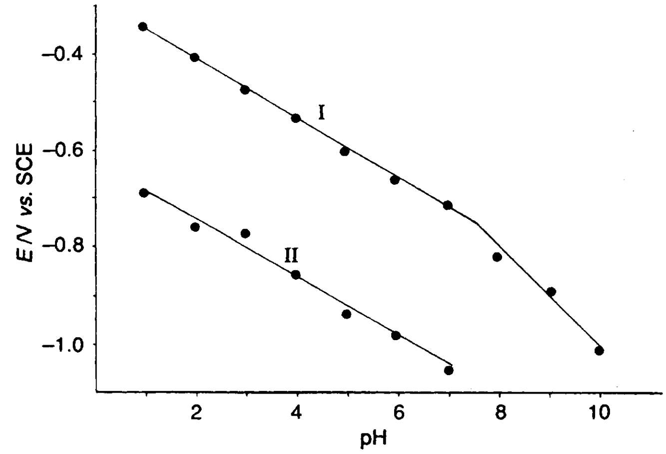

Fig. 6 Pourbaix diagram for $[OsN(H_2L)_2][CF_3SO_3]_3$ **2**. $E = E_{pc}$ for wave I and $E_{\frac{1}{2}}$ for couple II

ordinated chloride in aqueous solution. In this work we have been able to obtain a nice Pourbaix diagram for the reduction of $Os^{VI}{\equiv}N$ to $Os^{III}{-}NH_3$. In general, the formal potential for the redox couples of **2** are less positive than those of $[OsN(terpy)Cl_2]^+$, which is not surprising in view of the higher σ-donor strength of H_2L. For $[OsN(terpy)Cl_2]^+$ a four-electron reduction of $Os^{VI}{\equiv}N$ to $Os^{II}{-}NH_3$ was observed at pH 1.2. This is because the $E°(Os^{III}{-}Os^{II})$ for this complex is more positive than the $E°(Os^{VI}{-}Os^{III})$ in acidic media. Indeed at pH > 5.5 the $Os^{VI}{-}Os^{III}$ wave becomes well separated from the $Os^{III}{-}Os^{II}$ wave. For both complexes, electrode kinetic effects appear to play an important role in giving less well defined electrochemical responses at higher pH.

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