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Synthesis and reactivity of osmium (VI) nitrido complexes containing pyridine-carboxylato ligands

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ABSTRACT

A series of osmium(VI) nitrido complexes containing pyridine-carboxylato ligands $Os^{VI}(N)(L)_2X$ (L = pyridine-2carboxylate (**1**), 2-quinaldinate (**2**) and X = Cl (**a**), Br (**1b** and **2c**) or CH_3O (**2b**)) and $[Os^{VI}(N)(L)X_3]^-$ (L = pyridine-2,6-dicarboxylate (**3**) and X = Cl (**a**) or Br (**b**)) have been synthesised. Complexes **1** and **2** are electrophilic and react readily with various nucleophiles such as phosphine, sulfide and azide. Reaction of $Os^{VI}(N)(L)_2X$ (**1** and **2**) with triphenylphosphine produces the osmium(IV) phosphiniminato complexes $Os^{VI}(NPPh_3)(L)_2X$ (**4** and **5**). The kinetics of nitrogen atom transfer from the complexes $Os^{VI}(N)(L)_2Br$ (**2c**) (L = 2-quinaldinate) with triphenylphosphine have been studied in CH_3CN at 25.0 °C by stopped-flow spectrophotometric method. The following rate law is obtained: $-d[Os(VI)]/dt = k_2[Os(VI)][PPh_3]$. $Os^{VI}(N)(L)_2Cl$ (L = 2-quinaldinate) (**2a**) reacts also with [PPN](N_3) to give an osmium(III) dichloro complex, *trans*-[PPN][$Os^{III}(L)_2Cl_2$] (**6**). Reaction of $Os^{VI}(N)(L)_2Cl$ (L = 2-quinaldinate) (**2a**) with lithium sulfide produces an osmium(II) thionitrosyl complex $Os^{II}(NS)(L)_2Cl$ (**7**). These complexes have been structurally characterised by X-ray crystallography.

1. Introduction

Osmium(VI) nitrido complexes are of interest due to their potential applications in nitrogen atom transfer reactions [1]. Notably complexes containing nitrogen-based ligands, such as *cis*- and *trans*-$[Os^{VI}(N)(tpy)Cl_2]^+$ (tpy = 2,2′:6′,2″-terpyridine), $[Os^{VI}(N)(tpm)Cl_2]^+$ (tpm = tris(1-pyrazolyl)methane), $[Os^{VI}(N)(Tp)Cl_2]$ (Tp = hydridotris(1-pyrazolyl)borate) and $[Os^{VI}(N)(bpy)Cl_3]$ (bpy = 2,2′-bipyridine) [1–13]; as well as also those containing N,O-ligands such as [Os(N)(salen)Cl] (salen = N–N′-Bis(salicylaldehyde)ethylenediamine) and $[Os(N)Q_2Cl]$ (Q = 8-quinolinolate); have been shown to exhibit electrophilic properties [14,15]. A variety of reagents, such as phosphines, amines, cyanide, azide, Grignard reagents, arylboranes, alkenes, chalcogenide and carbene have been reported to add to the nitrido ligand to produce various novel osmium products [1–15].

We report herein the synthesis of a series of new electrophilic osmium(VI) nitrido complexes containing pyridine-carboxylato ligands (Scheme 1). These are the first examples of high-valent osmium complexes containing this type of ligands. The reactivities of this new class of nitrido complexes towards various nucleophiles are also reported.

2. Experimental

2.1. Reagents and physical measurement

The complexes $[NBu^n_4][Os^{VI}(N)Cl_4]$, $[NBu^n_4][Os^{VI}(^{15}N)Cl_4]$, $[NBu^n_4][Os^{VI}(N)Br_4]$ and $[NBu^n_4][Os^{VI}(^{15}N)Br_4]$ were prepared by literature procedures [16,17]. Acetonitrile was first refluxed over calcium hydride and then distilled under argon. Triphenylphosphine (Aldrich) was recrystallized from *n*-hexane. Tetrabutylammonium hexafluorophosphate (Aldrich) was recrystallized three times from boiling ethanol and dried *in vacuo* at 120 °C for 1 day before use. Picolinic acid, quinaldic acid and pyridine-2,6-dicarboxylic acid were purchased from Aldrich and were used as received. All other chemicals were of reagent grade and used without further purification.

IR spectra were obtained from KBr discs using a Bomen MB-120 FTIR spectrophotometer. UV–Vis spectra were recorded on either a Perkin–Elmer Lamda 19 or a Shimadzu UV3100 spectrophotometer in 1 cm cuvettes. ^{1}H NMR spectra were recorded on a Varian (300 MHz) FT NMR spectrometer. The chemical shifts (δ ppm) were reported with reference to tetramethylsilane (TMS). Elemental analysis was done on an Elementar Vario EL Analyzer. Cyclic voltammograms were obtained from a PAR model 273 potentiostat. A glassy carbon disk working electrode and a $Ag/AgNO_3$ reference electrode were used. The supporting electrolyte was 0.1 M $[NBu^n_4]PF_6$ in

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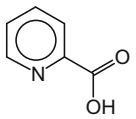
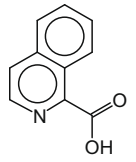
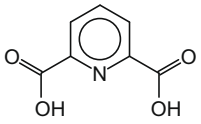


Picolinic acid (Hpic)



Quinaldic acid (Hquin)



Pyridine-2,6-dicarboxylic acid (H_2dipic)

Scheme 1. Pyridine-carboxylato ligands used.

CH_3CN. Kinetic studies were conducted with a Hi-Tech Scientific SF-61 stopped-flow spectrophotometer in acetonitrile.

2.2. Synthesis of the complexes

2.2.1. $[Os^{VI}(N)(pic)_2Cl]$ (**1a**)

$[NBu^n_4][Os^{VI}(N)Cl_4]$ (80 mg, 0.136 mmol) was dissolved in methanol (10 mL) and picolinic acid (32 mg, 0.272 mmol) was added. The mixture was stirred and warmed to approx. 30 °C for 1 h. 2,6-Dimethylpyridine (0.5 mL) was then added dropwise and the mixture was stirred at 30 °C for another 2 h. The yellow solid formed was collected by filtration, washed with methanol and air-dried. Yield 40 mg (60%). *Anal. Calc.* for $C_{12}H_{10}N_3O_4ClOs$: C, 29.66; H, 2.07; N, 8.65. Found C, 30.13; H, 1.80; N, 8.51%. *UV-Vis (DMF)* λ_{max}, nm (ε, $M^{-1}\,cm^{-1}$) = 418 (170). IR (KBr, cm^{-1}): 1708 (vs), 1670 (vs), 1322 (s), 1293 (w), 1082 (w, $Os^{14}N$), 1048(w, $Os^{15}N$). ^1H NMR (300 MHz, dmso-d_6): δ = 9.33 (d, 1H), 9.72 (d, 1H), 8.48 (m, 2H), 8.28 (d, 1H), 8.25 (t, 1H), 8.15 (t, 1H), 8.05 (t, 1H).

2.2.2. $[Os^{VI}(N)(pic)_2Br]$ (**1b**)

The complex was synthesised as a yellow solid by a method similar to that for **1a** using $[NBu^n_4][Os^{VI}(N)Br_4]$ (104 mg, 0.136 mmol). Yield 45 mg (63%). *Anal.* Calc. for $C_{12}H_{12}N_3O_4BrOs$: C, 27.16; H, 1.88; N, 7.92. Found C, 27.45; H, 1.65; N, 8.02%. *UV-Vis (DMF)* λ_{max}, nm (ε, $M^{-1}\,cm^{-1}$) = 311 (4130), 411 (570). IR (KBr, cm^{-1}): 3079 (w), 1713 (vs), 1675 (vs), 1336 (s), 1314 (s), 1132 (w), 1082 (w, $Os^{14}N$), 1047 (w, $Os^{15}N$).

2.2.3. $[Os^{VI}(N)(quin)_2Cl]$ (**2a**)

$[NBu^n_4][Os^{VI}(N)Cl_4]$ (80 mg, 0.136 mmol) was dissolved in methanol (10 mL). Quinaldic acid (47 mg, 0.272 mmol) was added and the mixture was stirred for 15 min. 2,6-Dimethylpyridine (0.5 mL) was then added dropwise and the mixture was stirred for another hour. The orange solid formed was collected by filtration and washed with methanol. Yield 55 mg (69%). *Anal.* Calc. for $C_{20}H_{12}N_3O_4ClOs$: C, 41.12; H, 2.06; N, 7.20. Found C, 41.30; H, 2.10; N, 7.09%. *UV-Vis (DMF)* λ_{max}, nm (ε, $M^{-1}\,cm^{-1}$) = 326 (11910), 450 (710). IR (KBr, cm^{-1}) = 3078 (w), 1714 (vs), 1679 (vs), 1328 (s), 1313 (s), 1148 (w), 1076 (w, $Os^{14}N$), 1034 (w, $Os^{15}N$). ^1H NMR (300 MHz, dmso-d_6): δ = 7.07 (m, 1H), 7.42 (m, 1H), 7.78 (m, 1H), 8.15 (m, 2H), 8.44 (m, 4H), 9.10 (m, 3H).

2.2.4. $[Os^{VI}(N)(quin)_2(OMe)]$ (**2b**)

Evaporation of the filtrate in the above reaction produced yellow crystals. Yield 11 mg (14%). *Anal. Calc.* for $C_{21}H_{16}N_3OsO_5$: C, 43.73; H, 2.08; N, 7.29. Found C, 43.53; H, 2.47; N, 7.51%.

2.2.5. $[Os^{VI}(N)(quin)_2Br]$ (**2c**)

The complex was prepared by a method similar to that for **2a**, using $[NBu^n_4][Os^{VI}(N)Br_4]$ (104 mg, 0.136 mmol). Yield 54 mg (62%). *Anal.* Calc. for $C_{20}H_{12}N_3O_4BrOs$: C, 38.21; H, 1.91; N, 6.69. Found C, 38.53; H, 2.04; N, 6.96%. UV–Vis (DMF) λ_{max}, nm (ε, $M^{-1}\,cm^{-1}$) = 327 (17 540). IR (KBr, cm^{-1}): 3068 (w), 1723 (vs), 1677 (vs), 1329 (w), 1311 (w), 1140 (w), 1078 (w, $Os^{14}N$), 1045 (w, $Os^{15}N$).

2.2.6. $[NBu^n_4][Os^{VI}(N)(Hdipic)Cl_3]$ (**3a**)

Pyridine-2,6-dicarboxylic acid (H_2dipic; 23 mg, 0.136 mmol) was added to an acetone solution (15 mL) of $[NBu^n_4][Os^{VI}(N)Cl_4]$ (80 mg, 0.136 mmol). 2,6-Dimethylpyridine (0.5 mL) was then added dropwise and the reaction mixture was stirred for 1 h. A pink precipitate was formed, which was filtered and redissolved in H_2O (5 mL). Addition of tetrabutylammonium chloride (37.80 mg, 0.136 mmol) produced in a pink solid which was recrystallized from acetonitrile/ether. Yield 52 mg (53%). *Anal.* Calc. for $C_{24}H_{40}N_3O_4Cl_3Os$: C, 38.57; H, 5.58; N, 5.41. Found C, 38.38; H, 5.56; N, 5.34%. *UV–Vis (DMF)* λ_{max}, nm (ε, $M^{-1}\,cm^{-1}$) = 328 (850), 489 (120). IR (KBr, cm^{-1}): 2962 (s), 1675 (vs), 1315 (s), 1175 (w), 1086 (w), 1091 (w, $Os^{14}N$), 1059 (w, $Os^{15}N$).

2.2.7. $[NBu^n_4][Os^{VI}(N)(Hdipic)Br_3]$ (**3b**)

The complex was prepared by a similar procedure for **3a** using $[NBu^n_4][Os^{VI}(N)Br_4]$ (104 mg, 0.136 mmol). Yield 73 mg (63%). Crystals suitable for X-ray crystallography were grown from acetonitrile/ether. *Anal.* Calc. for $C_{24}H_{40}N_3O_4Br_3Os$: C, 32.38; H, 4.69; N, 4.93. Found C, 32.24; H, 4.57; N, 4.89%.

2.2.8. $[Os^{IV}(NPPh_3)(pic)_2Cl]$ (**4**)

$[Os^{VI}(N)(pic)_2Cl]$ (80 mg, 0.165 mmol) was suspended in acetonitrile (12 mL) and triphenylphosphine (43 mg, 0.165 mmol) was added. The mixture was stirred for 1 h under argon. The yellow solid gradually dissolved and an orange solid was formed, which was filtered, washed with acetonitrile and air-dried. Yield 91 mg (74%). *Anal.* Calc. for $C_{35}H_{25}N_3O_4ClPOs$: C, 48.28; H, 3.08; N, 5.63. Found C, 47.98; H, 3.20; N, 5.45%. *UV–Vis (DMF)* λ_{max}, nm (ε, $M^{-1}\,cm^{-1}$): 373 (13 440). IR (KBr, cm^{-1}): 1684 (vs), 1324 (w), 1288 (w), 1108 (w, NP), 1071 (w), 856 (w), 759 (w).

2.2.9. $[Os^{IV}(NPPh_3)(quin)_2Cl]$ (**5a**)

$[Os^{VI}(N)(quin)_2Cl]$ (80 mg, 0.137 mmol) was suspended in acetonitrile (12 mL) and triphenylphosphine (36 mg, 0.137 mmol) was added. The mixture was stirred for 1 h under argon. The yellow solid gradually dissolved to give a dark brown solution, and then a dark brown crystalline solid was formed, which was filtered, washed with acetonitrile and then air-dried. Yield 84 mg (72%). *Anal.* Calc. for $C_{38}H_{27}N_3O_4ClOsP$: C, 53.92; H, 3.19; N, 4.97. Found C, 53.80; H, 3.47; N, 5.21%. Recrystallization from acetonitrile/ether affords dark brown single crystals suitable for X-ray crystallography. *UV–Vis (DMF)* λ_{max}, nm (ε, $M^{-1}\,cm^{-1}$): 293 (14 850). IR (KBr, cm^{-1}): 3057 (w), 1677 (vs), 1320 (w), 1162 (w), 1108 (w, NP), 1064 (s).

2.2.10. $[Os^{IV}(NPPh_3)(quin)_2Br]$ (**5b**)

The complex was prepared by a similar procedure for **4a**, using **2c**. The product was recrystallized from acetonitrile. Yield 51 mg (45%). *Anal.* Calc. for $C_{38}H_{27}N_3O_4BrOsP$: C, 51.24; H, 3.03; N, 4.72. Found C, 51.13; H, 3.17; N, 4.94%. *UV–Vis (CH_2Cl_2)* λ_{max}, nm (ε, $M^{-1}\,cm^{-1}$): 243 (63 900), 300 (17 000), 638 (3080). IR(KBr, cm^{-1}): 3057 (w), 1677 (vs), 1107 (w, NP).

2.2.11. trans-$[PPN][Os^{III}(quin)_2Cl_2]$ (**6**)

[PPN](N_3) (80 mg, 0.137 mmol) (PPN = Bis(triphenylphosphoranylidene)ammonium) was added to a suspension of $[Os^{VI}(N)$

$(quin)_2Cl]$ (80 mg, 0.137 mmol) in dichloromethane (15 mL) under argon, and the mixture was stirred for 24 h to give a blue solution. The solution was chromatographed on a silica gel column. The blue band eluted with dichloromethane/acetone (5:1) was collected and the volatile was removed under reduced pressure to give a blue solid. Yield 49 mg (31%). Single crystals suitable for X-ray crystallography were obtained by recrystallization from acetone/diethyl ether. *Anal. Calc.* for $C_{56}H_{42}N_3O_4OsCl_2P_2$: C, 58.79; H, 3.67; N, 3.67. Found C, 59.13; H, 3.64; N, 3.49%. *UV–Vis* (CH_2Cl_2) λ_{max}, nm (ε, $M^{-1}\,cm^{-1}$): 289 (26 500), 501 (6380), 595 (4600). IR (KBr, cm^{-1}):3058 (w), 2964 (w), 1659 (vs, CO), 1332 (w), 1266 (w), 1114 (w).

2.2.12. $[Os^{II}(NS)(quin)_2Cl]$ (**7**)

$[Os^{VI}(N)(quin)_2Cl]$ (80 mg, 0.137 mmol) was suspended in methanol (12 mL). A solution of Li_2S (6.3 mg, 0.137 mmol in 3 mL methanol) was added drop wise and the solution turned blue gradually. After 3 h, the yellow crystalline solid was filtered, washed with methanol and air-dried. Yield 64 mg (76%). *Anal. Calc.* for $C_{20}ClH_{12}N_3O_4OsS$: C, 38.98; H, 1.95; N, 6.82. Found C, 39.06; H, 1.83; N, 6.98%. *UV–Vis* (*DMF*) λ_{max}, nm (ε, $M^{-1}\,cm^{-1}$): 288 (21 500), 420 (2750), 535 (470). IR (KBr, cm^{-1}): 3065 (w), 2901 (w), 2787 (w), 1694 (vs), 1317 (s), 1250 (s, ^{14}NS), 1219 (s, ^{15}NS). ^{1}H NMR (300 MHz, dmso-d_6): δ = 6.63 (d, 1H), 7.29(t, 1H), 7.72 (t, 1H), 8.01 (d, 1H), 8.15 (t, 1H), 8.30 (m, 2H), 8.48 (t, 2H), 8.62 (t, 1H), 8.87 (d, 1H), 9.10 (d, 1H).

2.3. Kinetics

The kinetics of the reaction of **2c** with PPh_3 were studied by using a Hi-Tech SF-61 stopped-flow spectrophotometer. The concentrations of PPh_3 were at least 10-fold excess of that of Os^{VI}. The reaction progress was monitored by observing the absorbance change at 380 nm. Pseudo-first-order rate constant, k_{obs} was obtained by nonlinear least-square fits of A_t versus t according to the equation $A_t = A_\infty + (A_0 - A_\infty)\exp(-k_{obs}t)$, where A_0 and A_∞ are the initial and final absorbance, respectively. Kinetics carried out in air and under argon were found to give the same rate constants.

2.4. X-ray crystallography

All measurements were made with a Bruker SMART CCD (**1–3b**, **5a** and **6**) diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71069 Å). The data were collected at 25 ± 1 °C (**1–3b** and **6**) or 28 ± 1 °C (**5a**) using the ω-scan technique (MAR). Details of the intensity data collection and crystal data are given in Table 1. Selected bond lengths and angles are given in Tables 2–6. The data were corrected for Lorentz and polarisation effects. All non-H atoms were refined anisotropically. Most hydrogen atoms on the organic moieties were observable from difference Fourier map but were generated in their ideal positions (C–H, 0.93 Å). All calculations were performed using the programme package TEXSAN [18] on a Silicon-Graphic computer. The structures for compounds **1–3b**, **5a** and **6** were solved by direct methods

Table 2
Selected bond lengths (Å) and bond angles (°) of $[Os^{VI}N(pic)Br]$ (**1b**).

O(1)–Os(1)	1.995(6)
O(3)–Os(1)	2.134(5)
N(1)–Os(1)	1.655(7)
N(2)–Os(1)	2.106(6)
N(3)–Os(1)	2.113(7)
Br(1)–Os(1)	2.490(1)
O(1)–C(1)	1.32(1)
O(2)–C(1)	1.222(10)
O(3)–C(7)	1.26(1)
O(4)–C(7)	1.243(10)
N(1)–Os(1)–O(3)	165.1(3)
N(2)–Os(1)–Br(1)	161.3(2)
N(3)–Os(1)–O(1)	165.1(3)
N(2)–Os(1)–O(1)	80.4(2)
N(3)–Os(1)–O(3)	79.5(2)

Table 3
Selected bond lengths (Å) and bond angles (°) of $[Os^{VI}N(quin)_2(OCH_3)]$ (**2b**).

O(1)–Os(1)	2.150(2)
O(3)–Os(1)	1.997(2)
O(5)–Os(1)	1.944(2)
N(1)–Os(1)	2.123(2)
N(2)–Os(1)	2.148(3)
N(3)–Os(1)	1.654(3)
O(1)–C(1)	1.290(4)
O(2)–C(2)	1.209(4)
O(3)–C(11)	1.331(4)
O(4)–C(11)	1.207(4)
N(3)–Os(1)–O(1)	162.2(1)
N(1)–Os(1)–O(3)	157.6(1)
N(2)–Os(1)–O(5)	165.3(1)
N(1)–Os(1)–O(1)	75.60(9)
N(2)–Os(1)–O(3)	79.61(10)
Os(1)–O(5)–C(21)	118.9(2)

Table 1
Crystal data of compounds **1b**, **2c**, **3b**, **5a** and **6**.

	1b	2b	3b	5a	6
Empirical formula	$OsBrN_3O_4H_8C_{12}$	$OsN_3O_5C_{21}H_{15}$	$OsN_3O_4C_{23}H_{40}Br_3$	$C_{38}H_{27}ClN_3O_4OsP$	$C_{56}H_{42}Cl_2N_3O_4OsP_2$
Formula Weight	*528.32*	*579.56*	*852.50*	846.28	1143.97
Space group	$P2_1/n$(#14)	$P2_1/n$(#14)	$C2/c$ (#15)	$P2_1/c$(#14)	$P2_1/c$
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
a (Å)	9.835(1)	9.486(1)	20.3090	17.808(3)	8.8753(3)
b (Å)	14.016(2)	14.610(2)	8.6210	11.482(2)	17.8352(7)
c (Å)	10.304(1)	13.739(2)	35.2800	18.442(3)	15.9487(6)
α (°)	90	90	90	90	90
β (°)	96.08(1)	101.26(1)	102.3500	112.41(2)	100.1621(7)
γ (°)	90	90	90	90	90
V ($Å^3$)	1412.4(3)	1867.4(4)	6034.0195	3466(1)	2484.96(16)
Z value	*4*	*4*	*8*	4	2
D_{calc} (g cm^{-3})	2.484	2.065	1.877	1.621	1.529
F_{000}	976.00	1116.00	3296.00	1664.00	1142
μ (Mo Kα) (cm^{-1})	118.79	68.66	82.40	38.44	
R	0.038	0.019	0.050	0.031	
R_w	0.058	0.020	0.050	0.035	
Goodness-of-fit	1.70	1.11	1.18	1.03	1.006

Table 4
Selected bond angles and bond lengths of [N Bu^n_4][Os^{VI}(N)(Hdipic)Br_3] (**3b**).

Os(1)–N(1)	1.599(8)
Os(1)–N(2)	2.168(5)
Os(1)–O(1)	2.168(5)
Os(1)–Br(1)	2.4951(9)
Os(1)–Br(2)	2.4649(9)
Os(1)–Br(3)	2.4982(9)
O(1)–C(6)	1.261(12)
O(2)–C(6)	1.23(1)
O(3)–C(7)	1.306(10)
O(4)–C(7)	1.190(11)
N(1)–Os(1)–O(1)	170.2(3)
N(2)–Os(1)–Br(2)	165.1(2)
Br(1)–Os(1)–Br(3)	165.71(4)
N(2)–Os(1)–O(1)	74.9(2)

Table 5
Selected bond lengths (Å) and bond angles (°) of [Os^{IV}($NPPh_3$)$(quin)_2$Cl] (**5a**).

O(1)–Os(1)	2.027(3)
O(3)–Os(1)	2.068(3)
N(1)–Os(1)	2.097(4)
N(2)–Os(1)	2.102(4)
N(3)–Os(1)	1.895(4)
Cl(1)–Os(1)	2.359(1)
P(1)–N(3)	1.595(4)
O(1)–C(1)	1.304(6)
O(2)–C(1)	1.213(6)
O(3)–C(11)	1.283(6)
O(4)–C(11)	1.221(6)
O(1)–Os(1)–N(1)	79.5(1)
O(3)–Os(1)–N(2)	78.3(1)
Os(1)–N(3)–P(1)	141.3(2)
N(3)–Os(1)–O(3)	174.9(1)
N(1)–Os(1)–Cl(1)	168.9(1)
N(2)–Os(1)–O(1)	165.7(1)

Table 6
Selected bond lengths (Å) and bond angles (°) of [Os^{III}(quin)Cl_2]$^-$ anion (**6**).

Os–O(1)	2.0358(15)
Os–O(1A)	2.0358(15)
Os–N(1)	2.1036(18)
Os–N(1A)	2.1036(18)
Os–Cl(1)	2.3613(6)
Os–Cl(1A)	2.3613(6)
C(1)–O(1)	1.303(3)
C(1)–O(2)	1.218(3)
O(1)–Os–O(1A)	180.00(8)
N(1)–Os–N(1A)	180.00(1)
N(1)–Os–O(1)	77.99(7)
N(1A)–Os–O(1A)	77.99(7)
Cl(1)–Os–Cl(1A)	180.0

(SHELXS86, SHELX97 or SIR92) [19–21] and expanded using Fourier techniques (DIRDIF94)[22].

3. Results and discussion

3.1. Synthesis of [Os^{VI}(N)$(L)_2$X] (L = pic or quin; X = Cl, Br or OMe)

Reaction of [NBu^n_4][Os^{VI}(N)Cl_4] with 2 mol equiv. of picolinic acid (Hpic) in methanol in the presence of 2,6-dimethylpyridine produced [Os^{VI}(N)$(pic)_2$Cl] (**1a**). The ^{15}N-labelled complex was prepared by the same method using [NBu^n_4][$Os^{VI}(^{15}N)Cl_4$]. In the IR spectrum of **1a** the peak at 1082 cm^{-1} is assigned as ν(Os≡^{14}N), which is shifted to 1048 cm^{-1} upon ^{15}N-labelling. The ν(Os≡N) is comparable with those of [Os^{VI}(N){N($SPPh_2$)$_2$}$_2$($OCOCF_3$)] (1082 cm^{-1}) [23,24] and [Os^{VI}(N)(4,4′-Me_2bpy)Cl_3] (1084 cm^{-1}) (4,4′-Me_2bpy = 4,4′-dimethyl-2,2′-bipyridine) [25]. In the UV–Vis spectrum of [Os^{VI}(N)$(pic)_2$Cl] in DMF, a weak absorption is observed at 418 nm.

The bromo substituted derivative [Os^{VI}(N)$(pic)_2$Br] (**1b**) was prepared by a similar reaction of [NBu^n_4][Os^{VI}(N)Br_4] with picolinic acid. The weak absorption in the IR spectrum of **1b** at 1082 cm^{-1} is assigned as ν(Os≡^{14}N); the peak is shifted to the expected position of 1047 cm^{-1} upon ^{15}N-labelling. Apparently, changing the equatorial ligands from Cl to Br has no effect on the ν(Os≡N).

Reaction of [NBu^n_4][Os^{VI}(N)Cl_4] with 2 mol equiv. of quinaldic acid (Hquin) in methanol in the presence of 2,6-dimethylpyridine produced a mixture of orange [Os^{VI}(N)$(quin)_2$Cl] (**2a**) and yellow [Os^{VI}(N)$(quin)_2$(OMe)] (**2b**). In the IR spectrum of compound **2a** the medium absorption at 1076 cm^{-1} is assigned to ν(Os≡^{14}N) and this assignment is supported by ^{15}N-labelling (1034 cm^{-1}). The ν(Os≡N) is comparable with that of **1a**. In the IR spectrum of [Os^{VI}(N)$(quin)_2$Br] (**2c**) the weak peak at 1078 cm^{-1} is assigned as ν(Os≡^{14}N), which is shifted to 1045 cm^{-1} upon ^{15}N-labelling. The ν(Os≡N) of [Os^{VI}(N)$(quin)_2$X] is also insensitive to the substituent Cl or Br.

3.1.1. Structure of [Os^{VI}(N)$(pic)_2$Br]

The structure of the **1b** was determined by X-ray crystallography (Fig. 1 and Table 2). The osmium (VI) centre has a distorted octahedral geometry and the two picolinates are *cis* to one another. The three nitrogen atoms N(1), N(2) and N(3) are in a *facial* arrangement and an O(pic) is *trans* to the nitrido ligand, as in Os^{IV}(N)Q_2Cl [15]. The Os≡N bond distance is 1.655(7) Å and is within the reported range (1.52–1.70 Å) commonly found for other osmium nitrido complexes [4,16,17]. The Os(1)–O(1) and Os(1)–O(3) distances are 1.995(6) and 2.134(5) Å, respectively. The significant difference between the two Os–O(pic) distances suggests a rather strong *trans* influence of the Os≡N bond.

3.1.2. Structure of [Os^{VI}(N)$(quin)_2$(OMe)]

The structure of [Os^{VI}(N)$(quin)_2$(OMe)] (**2b**) has also been determined by X-ray crystallography (Fig. 2 and Table 3). The osmium (VI) centre adopts a distorted octahedral geometry and the two quin ligands are *cis* to each others. The structure is similar to that of **2a,** with the Cl being replaced by CH_3O. The Os≡N bond distance 1.654(3) Å is within reported range (1.50–1.70 Å) for Os(VI) nitride species [4,16,17]. The O(quin)–Os distances are 2.150(2) and 1.997(2) Å and are comparable to the O(pic)–Os distance in **1b**. The Os–N(quin) distances are 2.123(2) and 2.148(3) Å and are also similar to the Os-N(pic) distances in **1b**. The Os–O(5) distance of 1.944(2) Å is much shorter than the Os^{VI}–O(methanol) distance of 2.346(7) Å in [Os^{VI}(N)(salophen)(CH_3OH)]ClO_4 (H_2salophen = N,N′-bis(salicylidene)ethylenediamine) [14] and is consistent with the stronger σ-donating property of the methoxide.

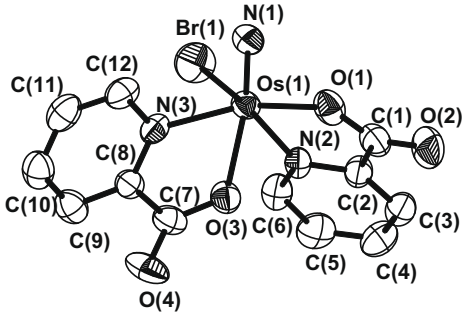


Fig. 1. ORTEP diagram of **1b**, thermal ellipsoids are drawn at the 50% probability (hydrogen atoms omitted for clarity).

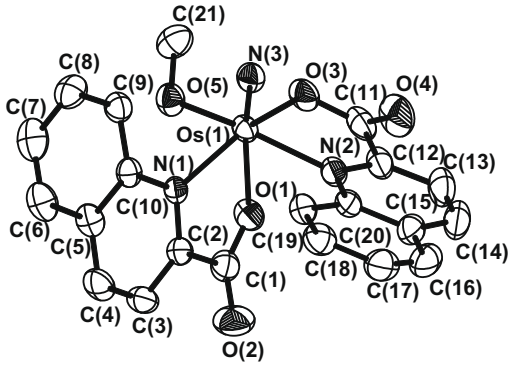


Fig. 2. ORTEP diagram of **2b**, thermal ellipsoids are drawn at the 50% probability (hydrogen atoms omitted for clarity).

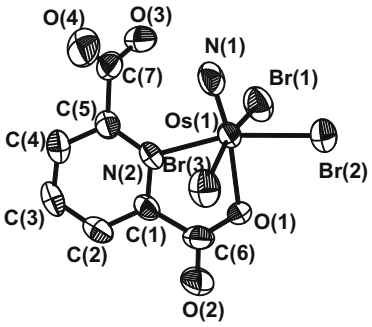


Fig. 3. ORTEP diagram of the anion of **3b**, thermal ellipsoids are drawn at the 50% probability (hydrogen atoms omitted for clarity).

3.2. Synthesis and characterisation of $[NBu^n_4][Os^{VI}(N)(Hdipic)X_3]$ (X^- = Cl and Br)

Reaction of $[NBu^n_4][Os^{VI}(N)X_4]$ (X = Cl and Br) and pyridine-2,6-dicarboxylic acids (H_2dipic) in acetone in the presence of 2,6-dimethylpyridine produces $[NBu^n_4][Os^{VI}(N)(Hdipic)X_3]$ (X = Cl for **3a** and Br for **3b**). The H_2dipic is singly deprotonated and acts as a bidentate ligand. In the IR spectrum, the weak band at 1091 cm^{-1} is assigned as $\nu(Os{\equiv}{}^{14}N)$, which is supported by ^{15}N-labelling (1059 cm^{-1}).

3.2.1. Structure of $[NBu^n_4][Os^{VI}(N)(Hdipic)Br_3]$

The bromo analogue (**3b**) is synthesised by a similar procedure using $[NBu^n_4][Os^{VI}(N)Br_4]$. Complex **3b** is structurally determined by X-ray diffraction and the ORTEP diagram is shown in Fig. 3. The Os(VI) centre has a distorted octahedral geometry with one singly deprotonated pyridine-2,6-dicarboxylate and three bromo ligands. An O (Hdipic) is *trans* to the nitrido ligand as in the case of **1b** and **2b**. The Os≡N distance is 1.599 (8) Å (Table 4). The relatively short Os≡N distance is similar to those in $[AsPh_4][[Os^{VI}(N)Cl_4]$ (1.583(15) Å) and $[Os^{VI}(N)(L_{Oet})Cl_2]$ (1.58(1) Å) [26,27]. The Os(1)–Br distances (2.4649(9)–2.4982(9) Å) are comparable to that in **1b**.

3.3. Reaction of osmium(VI) nitrido complexes with various nucleophiles

3.3.1. Reaction of $[Os^{VI}(N)(L)_2X]$ (L = pic or quin and X = Cl or Br) with PPh_3

Complex **1a** is found to be electrophilic and reacts readily with PPh_3 in acetonitrile to give the orange osmium(IV) phosphiniminato complex $[Os^{IV}(NPPh_3)(pic)_2Cl]$ (**4**). ^1H NMR study shows a temperature-dependent, strongly paramagnetically shifted spectrum which is consistent with the formula of **1a** as paramagnetic, d^4 Os(IV) complex [1]. In the IR spectrum of the **1a**, the peak at 1108 cm^{-1} is tentatively assigned as ν(P=N). The ν(P=N) of *trans*-$[Os^{IV}(NPPh_3)(tpy)Cl_2]PF_6$ [1,28] and $[Os^{VI}(NPPh_3)$(salophen)Cl] [14] has been assigned at 1112 and 1089 cm^{-1}[14], respectively.

The cyclic voltammogram of **4** exhibits two reversible couples at 0.31 and −1.03 V versus Fc^+/Fc, which are assigned as $Os^{V/IV}$ and $Os^{IV/III}$ couples, respectively. Similar reversible $Os^{V/IV}$ and $Os^{IV/III}$ couples are also observed for $[Os^{IV}(NPPh_3)(tpy)Cl_2]PF_6$ (0.577 and −0.613 V versus Fc^+/Fc) and $[Os^{IV}(NPPh_3)$(salophen)Cl]) (0.14 and −0.21 V versus Fc^+/Fc) [1,14,28]. These data indicate that picolinate stabilizes the osmium (IV) centre more than salophen and tpy and that **5** is stable over a broader range of potentials.

$[Os^{VI}(N)(quin)_2Cl]$ (**2a**) reacts similarly with triphenylphosphine in acetonitrile to give the dark brown $[Os^{IV}(NPPh_3)(quin)_2Cl]$ (**5a**). Compound **5a** also exhibits a temperature-dependent, strongly paramagnetically shifted ^1H NMR spectrum. In the IR spectrum, the peak at 1108 cm^{-1} is tentatively assigned as ν(P=N). The cyclic voltammogram of complex **5a** shows reversible couples at 0.50, −0.83 and −1.03 versus Fc^+/Fc, which are assigned as $Os^{V/IV}$, $Os^{IV/III}$ and $Os^{III/II}$ couples, respectively. Similar reversible $Os^{III/II}$ couple is less common in other osmium(IV) phosphiniminato complex and is only observed for *trans*-$[Os^{IV}(NPPh_3)(tpy)Cl_2]PF_6$ (−1.70 V) [1].

A similar reaction of $Os^{VI}(N)(quin)_2Br$ (**2c**) with PPh_3 produced $[Os^{IV}(NPPh_3)(quin)_2Br]$ (**5b**). The kinetics of this reaction has been followed by stopped-flow spectrophotometry in acetonitrile at 380 nm at $[Os^{VI}] = 1.60 \times 10^{-4}$–$4 \times 10^{-4}$ M and $[PPh_3] = 1.6 \times 10^{-3}$–$1.6 \times 10^{-2}$ M. In the presence of at least 10-fold excess of PPh_3, clean pseudo-first order kinetics were observed. The pseudo-first-order rate constant k_{obs} depends linearly on $[PPh_3]$ (Fig. 4), indicating the rate law is rate = $k_{obs}[Os^{VI}] = k_2[Os^{VI}][PPh_3]$. At 298 K $k_2 = (4.09 \pm 0.09 \times 10^3\ M^{-1}\ s^{-1})$.

3.3.1.1. Structure of $[Os^{IV}(NPPh_3)(quin)_2Cl]$. The structure of $[Os^{IV}(NPPh_3)(quin)_2Cl]$ (**5a**) has been determined by X-ray crystallography (Fig. 5). The osmium(IV) centre has a distorted octahedral geometry, and the relative arrangement of the Cl and the two quin ligands is the same as that of the parent nitrido complex, i.e. there is no change in geometry upon addition of PPh_3. The P–N distance is 1.595(4) Å (Table 5), which lies within the reported range (1.59–1.66 Å) for P–N bond lengths in other phosphiniminato complexes

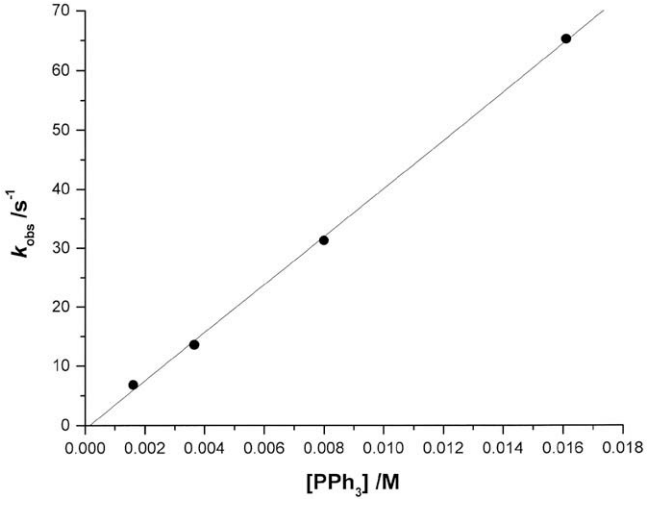


Fig. 4. Plot of k_{obs} vs $[PPh_3]$ for the reaction of $[Os(N)(quin)_2Br]$ (**2b**) with PPh_3 in acetonitrile at 298 K

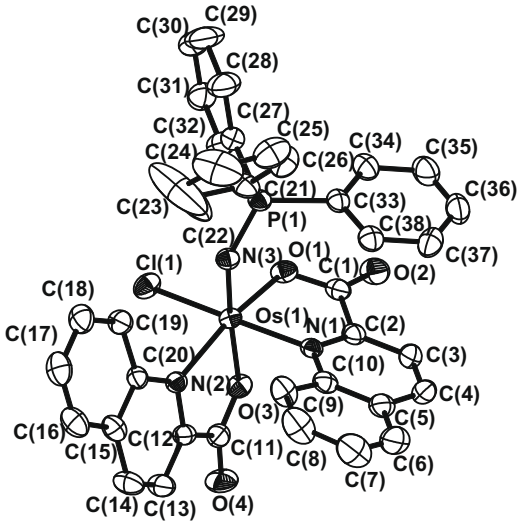


Fig. 5. ORTEP diagram of **5a**, thermal ellipsoids are drawn at the 50% probability (hydrogen atoms omitted for clarity).

[27,28]. The Os–N(PPh_3) distance of 1.895(4) Å is comparable with those in [Os^{IV}($NPPh_3$)(salophen)Cl] (1.92(1) Å) and [TpO-s^{IV}($NPPh_3$)Cl_2] (1.908(4) Å) [14,29,30] and is indicative of a bond order of close to 1. The rather acute Os(1)–N(3)–P(1) angle (141.4(2)°) also suggests that there is no significant multiple-bond character in the Os–N(PPh_3) bond. The two Os–O(quin) bonds have similar lengths (2.027(3) and 2.068(3) Å), reflecting that the *trans* influence of the phosphiniminato ligand is negligible.

3.3.2. Reaction of [Os^{VI}(N)(quin)$_2$Cl] with azide

Reaction of [Os^{VI}(N)(quin)$_2$Cl] with [PPN](N_3) in CH_2Cl_2 produces *trans*-[PPN][Os^{III}(quin)$_2Cl_2$] (**6**). Gas bubbles were observed during the reaction, presumably it is N_2. An Os–N_4 intermediate was probably formed during the reaction, as proposed in the reaction of [OsN(tpy)Cl_3] with [PPN](N_3), which then decomposed to give *trans*-[PPN][Os^{III}(quin)$_2Cl_2$] [6]. ^{1}H NMR study shows temperature-dependent, strongly paramagnetically shifted spectrum consistent with a paramagnetic d^5 Os (III) complex.

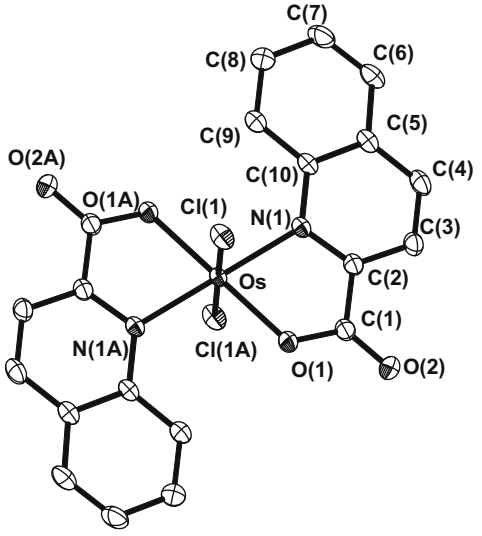


Fig. 6. ORTEP diagram of **6**, thermal ellipsoids are drawn at the 50% probability (hydrogen atoms omitted for clarity).

3.3.2.1. Structure of [Os^{III}(quin)$_2Cl_2$]$^-$ Anion. The structure of **6** was determined by X-ray crystallography (Fig. 6). Selected bond lengths and bond angle are shown in Table 6. The osmium (III) centre adopts an octahedral geometry with both the quin and chloro ligands in *trans* configuration. The Os(1)–O(quin), Os(1)–N(quin) and Os(1)–Cl distances are 2.0358(15), 2.1036(18) and 2.3613(6) Å, respectively.

3.3.3. Reaction of [Os^{VI}(N)(quin)$_2$Cl] with Li_2S

Reaction of [Os^{VI}(N)(quin)$_2$Cl] with Li_2S in methanol affords the yellow osmium(II) thionitrosyl complex, [Os^{II}(NS)(quin)$_2$Cl] (**7**). In the IR spectrum, the strong peak at 1250 cm^{-1} is assigned as ν(N≡S), which shifts to the expected position of 1218 cm^{-1} upon ^{15}N-labelling. The ν(N≡S) of another neutral osmium(II) thionitrosyl complex, [TpOs^{II}(NS)Cl_2], occurs at 1284 cm^{-1}; while that of the cationic osmium(II) thionitrosyl complex [(tpm)Os^{II}(NS)-$(Cl)_2$]PF_6 occurs at a higher frequency (1316 cm^{-1}), as a result of the weaker electron donating property of the neutral tpm ligand [10,11,31].

The ^{1}H NMR shows two sets of aromatic protons for the two 2-quinaldinato ligands, suggesting the two 2-quinaldinates are *cis* to each others and the geometry and spatial arrangement of the ligands in the parent nitrido complex **2a** is conserved.

4. Conclusion

A series of stable osmium(VI) nitrido complexes containing pyridine-carboxylato ligands have been synthesised and characterised. These nitrido complexes are electrophilic and they react readily with various nucleophiles, including phosphine, sulfide and azide.

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Appendix A. Supplementary material

CCDC 710753, 710736, 710737, 710738 and 710739 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2009.04.002.

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