Chemistry of a Family of Quinolin-8-thiolato Chelated Osmium (II) Organometallics and Electrogeneration of the EPR active Trivalent Analogue

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Abstract

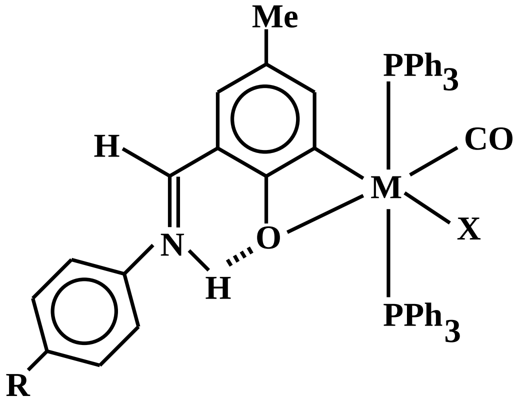
The reaction of $Os(RL^1)(PPh_3)_2(CO)Br$*,* ***1b****, with sodium salt of quinoline-8-thiol (HQ),* ***2****, has furnished complexes of the type* $[Os(RL^2)(PPh_3)_2(CO)(Q)]$*,* ***3****, in excellent yield (*RL^1 *is* C_6H_2O*-2-*$CHNHC_6H_4R$*(p)-3-Me-5,* RL^2 *is* C_6H_2OH*-2-*$CHNC_6H_4R$*(p)-3-Me-5 and R is Me, OMe, Cl). In this process, quinoline-8-thiolato (Q) undergoes five-membered chelation, the iminium-phenolato function tautomerizing to the imine-phenol function. The trans geometry of the* $Os(PPh_3)_2$ *fragment is consistent with the occurrence of a single* ^{31}P *resonance near –7.05 ppm in* ***3****. In dichloromethane solution,* ***3*** *displays a quasi-reversible* $\mathbf{3}^+/\mathbf{3}$ *couple near 0.75 V vs. SCE (*$\mathbf{3}^+$*is the osmium (III) analogue of* ***3****). Coulometrically generated solutions of* $\mathbf{3}^+$ *displays a strong absorption near 390 nm, 500 nm and 630 nm and are one-electron paramagnetic (low-spin* d^5*, S = 1/2) and show rhombic EPR spectra in 1 : 1 dichloromethane–toluene solution at 77 K with g values near 2.30, 2.03, 1.70. Distortion parameters using the observed g values have been computed. Solutions of* ***3*** *absorb near 475 nm and emit near 570 nm at 298 K and 650 nm at 77 K. The fluorescence is believed to originate from the* ^{3}*MLCT state.*

Keywords: Osmium aryls; Quinoline-8-thiolato Chelation; Photophysical Properties; Trivalent Osmium organometallics.

Introduction

The variation of the coordination environment around osmium plays a key role in modulating the redox properties of its complexes as well as the chemistry of osmium compounds is of current interest in the context of synthesis, reactivity and photophysical properties[1-3]. In this context it should be noted that authentic example of quinoline-8-thiolato chelated osmium (II) complexes are rare[4,5]

We are scrutinizing the reactivity of four-membered ruthenium/osmium organometallics of the type $M(RL^1)(PPh_3)_2(CO)X$ (**1**) juxtaposed to a hydrogen bonded iminium-phenolato function[6]. It has been found that different alkynes undergoes facile insertion into the Ru−C bond of the four-membered ruthenium metallacycles leading to two carbon expansion[7-8] whereas the osmium analogue remains unreactive. Upon treatment with isonitrile ruthenium system undergoes halide substitution as well as insertion into the Ru—O bond and the resultant product then exhibits aryl migration and C-C bond formation[9,10] while in case of osmium system isonitrile simply displaced bromide ligand furnishing the cationic complexes which are isolated as salts[11]. It is indeed found that ruthenium metallacycle is smoothly converted to the acyl system upon reaction with carbon monoxides under ambient conditions whereas the osmium analogue did not lead to insertion and afforded only an unreactive cis-dicarbonyl complex[12]. We also explore the reactivity of **1** towards bidentate monoanionic donor reagents such as acetate[13], palmitate and terephthalate[14], nitrate and nitrite[15,16] xanthate[17] undergo four-membered chelationand we also reported earlier that **1a** reacts with pyridine-2-thiolato[18] and the electroneutral diimine ligands such as bipyridine, phenanthroline[19], biimidazole[20] furnishing four and five-membered ruthenium organometallics respectively.

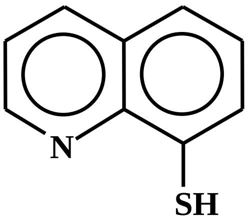


$M(RL^1)(PPh_3)_2(CO)X$

1a M = Ru, X = Cl

1b M = Os, X = Br

1



HQ

2

The richness of this reaction chemistry have now prompted us to explore the reactivity of **1b** towards quinoline-8-thiol, **2**, (HQ, H stands for the dissociable thiol hydrogen) which is suited for five-membered S, N-chelation. A facile reaction is indeed observed furnishing the novel five-membered S, N-chelated osmium organometallics for the first time via displacement of Os−O and Os−Br bonds. Changes in the coordination mode and tautomeric state of the Schiff base ligand accompany the synthetic reaction. Another point of special interest is that such species are potentially luminescent in the visible region and are electrochemically oxidizable to the trivalent analogue which is EPR active.

Experimental details

Materials

The compounds $Os(PPh_3)_3Br_2$[21] and $Os(RL^1)(PPh_3)_2(CO)Br$[6] were prepared by reported methods. Quinoline-8-thiol was obtained from Aldrich (USA). The purification of dichloromethane and the preparation of tetraethyl ammonium perchlorate (TEAP) for electrochemical work were done according to the reported method[22]. All other chemicals and solvents were of analytical grade and were used as received.

Physical Measurements

Electronic, IR and fluorescence spectra were recorded with a Shimadzu UV-1601 PC spectrophotometer, Nicolet Magna IR series II spectrometer and Perkin–Elmer model LS 55 luminescence spectrometer respectively. ^{1}H NMR spectra were obtained using a Bruker 300 MHz FT NMR spectrometer. The numbering scheme used for the ^{1}H NMR is the same as shown in drawing **3**. Microanalyses (C, H,N) were done by using a Perkin–Elmer 240C elemental analyzer. The magnetic behavior of the complexes was examined by a PAR 155 vibrating sample magnetometer. EPR spectra were recorded on a Varian E-109C X-band spectrometer fitted with a quartz dewar. Solution electrical conductivity was measured in acetone with a Phillips PR 9500 bridge using a platinized electrode (cell constant of 1.05). Electrochemical measurements were performed in a nitrogen atmosphere in dichloromethane solution using a CHI model 620A electrochemical analyzer.

Preparation of NaQ

NaOH (0.864 g, 21.6 mmol) was taken in a beaker. Then 60 mL of distilled water was added to it. The solution was then stirred and to this stirred solution 3.5 gm (19.1 mmol) of quinolin-8-thiol was added slowly. The mixture was then stirred for 30 minutes and then evaporated to deposit the salt. It was then filtered and dried in vacuo. Yield: 69%.

Synthesis of the Complexes [Os(RL^2)(PPh$_3$)$_2$(CO)(Q)] (3)

[Os(RL^2)(PPh$_3$)$_2$(CO)(Q)] (**3**) complexes were synthesized in excellent yield (~ 85%) by reacting Os(RL^1)(PPh$_3$)$_2$(CO)Br (**1b**) in MeOH-CH$_2$Cl$_2$ (1 : 1)at room temperature with excess (1:10) NaQ. Details of a representative case are given below. The other compounds are prepared in an analogous manner.

[Os(MeL^2)(PPh$_3$)$_2$(CO)(Q)], 3 (Me)

To a vigorously stirred violet solution of Os(MeL^1)(PPh$_3$)$_2$(CO)Br (100 mg, 0.096 mmol) in a mixture of 50 ml methanol and 50 ml dichloromethane was added 176 mg (0.96 mmol) of NaQ. The mixture was refluxed for 24 h when the colour of the solution changed from violet to orange. The solvent was then removed under reduced pressure and the orange solid thus obtained was washed repeatedly with a little amount of methanol (removal of excess NaQ). The residue was recrystallized from dichloromethane–hexane(1 : 3) mixture followed by drying in vacuo. Yield: 94 mg (87%).
Analysis: Calc. for $C_{61}H_{50}N_2O_2P_2SOs$: C, 64.99; H,4.47; N, 2.48%. Found C, 64.93; H, 4.49; N, 2.49%.^{1}H NMR (300 MHz, CDCl$_3$, ppm, 298 K): 12.61(s, 1H, O–H, disappeared upon shaking with D$_2$O),7.82 (s, 1H, H7), 5.89 (s, 1H, H3), 1.94 (s, 3H, 4-Me), 2.31 (s, 3H, 13-Me), 7.98 (d, J_{HH} = 6.8 Hz, 1H,H16), 7.21 (d, J_{HH} = 8.2 Hz, 1H, H18), 6.11 (d,J_{HH} = 7.4 Hz, 1H, H19), 6.45 (d, J_{HH} = 8.1 Hz, 1H,H21), 6.33-6.38 (m, 2H, H17, H20), 6.65–7.05 (m,35H, 2PPh$_3$, H5, H11, H12, H14, H15).^{31}P NMR (300 MHz, CDCl$_3$, ppm, 298 K) : -7.084 (s, 2P). IR (KBr, cm^{-1}): 1933 (ν_{CO}), 1590 ($\nu_{C=N}$).

[Os(MeOL^2)(PPh$_3$)$_2$(CO)(Q)], 3(OMe)

Os(MeOL^1)(PPh$_3$)$_2$(CO)Br (100 mg, 0.094 mmol) and NaQ (172 mg, 0.94 mmol) were employed. Yield: 96 mg (89%).Analysis: Calc. for $C_{61}H_{50}N_2O_3P_2SOs$: C, 64.08; H,4.41; N, 2.45%. Found C, 64.13; H, 4.43; N, 2.41%.^{1}H NMR (300 MHz, CDCl$_3$, ppm, 298 K): 12.57 (s, 1H, O–H, disappeared upon shaking with D$_2$O), 7.84 (s, 1H, H7), 5.96 (s, 1H, H3), 1.98 (s, 3H, 4-Me), 3.28 (s, 3H, 13-OMe), 8.01 (d, J_{HH} = 7.4 Hz, 1H, H16), 7.23 (d, J_{HH} = 8.5 Hz, 1H, H18), 6.15 (d,J_{HH} = 8.0 Hz, 1H, H19), 6.51 (d, J_{HH} = 8.2 Hz, 1H, H21), 6.35-6.41 (m, 2H, H17, H20), 6.60–7.10 (m,35H, 2PPh$_3$, H5, H11, H12, H14, H15).^{31}P

NMR (300 MHz, $CDCl_3$, ppm, 298 K) : -7.052 (s, 2P). IR (KBr, cm^{-1}): 1930 (ν_{CO}), 1595 ($\nu_{C=N}$).

$[Os(ClL^2)(PPh_3)_2(CO)(Q)]$, 3 (Cl)

$Os(ClL^1)(PPh_3)_2(CO)Br$ (100 mg, 0.094 mmol) and NaQ (172 mg, 0.94 mmol) were used. Yield: 91 mg (85%). Analysis: Calc. for $C_{60}H_{47}N_2O_2P_2SClOs$: C, 62.79; H,4.13; N, 2.44%. Found C, 62.75; H, 4.17; N, 2.41%.^{1}H NMR (300 MHz, $CDCl_3$, ppm, 298 K): 12.56 (s, 1H, O–H, disappeared upon shaking with D_2O), 7.85 (s, 1H, H7), 5.96 (s, 1H, H3), 1.99 (s, 3H, 4-Me), 8.03 (d, J_{HH} = 7.5 Hz, 1H, H16), 7.25 (d, J_{HH} = 8.4 Hz, 1H, H18), 6.16 (d,J_{HH} = 8.1 Hz, 1H, H19), 6.50 (d, J_{HH} = 8.0 Hz, 1H, H21), 6.34-6.40 (m, 2H, H17, H20), 6.65–7.10 (m, 35H, $2PPh_3$, H5, H11, H12, H14, H15).^{31}P NMR (300 MHz, $CDCl_3$, ppm, 298 K) : -7.045 (s, 2P). IR (KBr, cm^{-1}): 1925 (ν_{CO}), 1587 ($\nu_{C=N}$).

Electrochemical Generation of 3^+

The complexes of type $\mathbf{3}^+$ were generated in solution by constant potential coulometric oxidation of solutions of type **3**. Details of a representative example are noted below.

A solution of 30 mg of **3(Me)** in 30 ml dichloromethane solvent containing 40 mg of TEAP was oxidized coulometrically. The oxidation was performed at 0.95 V; n^e = 1.112/1.079 = 1.03, $n^e = Q/Q_1$, where Q_1 is the calculated coulomb count for one electron transfer and Q is the coulomb count found after exhaustive electrolysis. A part of the electrogenerated solution (5 ml) of $\mathbf{3(Me)}^+$ was mixed with an equal volume of toluene and the mixture was quickly frozen at 77 K, and then used for an EPR measurement. Another part of this electrogenerated orange-red solution (10 ml) is used quickly for electronic spectral study. The oxidized complex $\mathbf{3(Me)}^+$ was stable in solution at room temperature for few minutes only. Most of it (>90%) underwent reduction to produce **3**, associated with some insoluble material of unknown composition. The oxidation of **3** also may be performed chemically using an aqueous solution of Ce^{4+}. In this case the quantity of the byproducts was more than 25%. To date, we were not successful in isolating the trivalent osmium compound $\mathbf{3}^+$ in its pure state. The trivalent complex $\mathbf{3(OMe)}^+$ and $\mathbf{3(Cl)}^+$ was generated in solution similarly as described above.

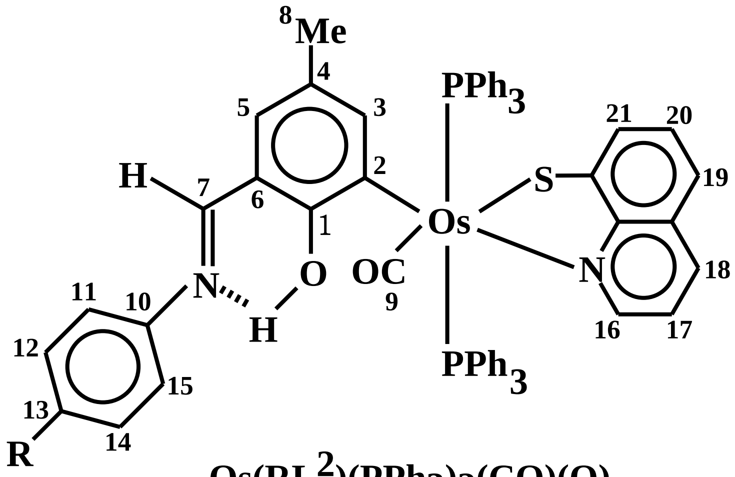
Results and discussion

Coordination with Quinoline-8-thiolato

In methanol–dichloromethane solution, $Os(RL^1)(PPh_3)_2(CO)Br$ (**1**) reacts smoothly with seven fold excess of NaQ upon stirring at room temperature, according to, equation 1, the colour of the solution changes from violet to orange, from which $[Os(RL^2)(PPh_3)_2(CO)(Q)]$ (**3**) is obtained in excellent yield.

$$\mathbf{1} + NaQ \rightarrow \mathbf{3} + NaBr \qquad (1)$$

The R groups utilized in the present work are Me, OMe and Cl. Specific compounds are identified by putting R in parentheses: thus **3**(Me) stands for $[Os(MeL^2)(PPh_3)_2(CO)(Q)]$. The complex **3** has been isolated in pure form in ~ 85% yield. An isomer (because quinolin-8-thiol is unsymmetrical) of **3** is possible in principle but it has never been observed. Careful examination of ^{1}HNMR spectra of crude sample (before recrystallization) did not reveal the presence of any extra signals apart from those characterizing **3**. We assign structure **3** to it in analogy with the stereochemistry of other Os^{II}(quinoline-8-thiolato) complexes[4,5] and also by comparing with acetate, thioxanthate, chelated ruthenium/osmiumorganometallics[13,17].



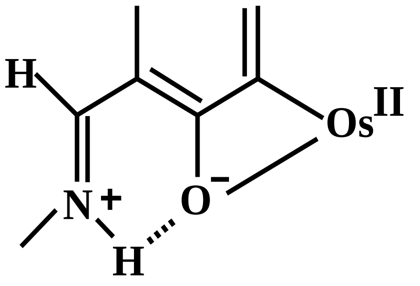
$Os(RL^2)(PPh_3)_2(CO)(Q)$

R = Me, OMe and Cl

3

The conversions **1**→**3** is attended with a prototropic shift within the salicyaldimine function. In **1** the metal is coordinated to phenolato oxygen and the Schiff base function occurs in the zwitterionic iminium–phenolato tautomeric form **4**. Chelation ofquinoline-8-thiolato is attended with the cleavage of the Os–O bond and the Schiff base function becomes an imine-phenol **5**. This is fully consistent with the spectroscopic data.

Thus the C=N stretching frequency in **3** is significantly lower (~ 1590 cm^{-1}) than that in **1** (~ 1620 cm^{-1}) as expected[23]. Also the aldimine CH signal in ^{1}HNMR in **3** (**Figure 1**) occurs at lower field viz.7.85 ppm as compared to ~ 7.5 ppm in **1**[6]. The O–H resonance in **3** is a relatively sharp signal near 12.6 ppm having half-height width of ~ 30 Hz. In contrast, the iminium N–H resonance in **1** is broad(width, ~ 150 Hz) evidently due to the quadrupole moment of the nitrogen atom[6]. The prototropic transformation between **1** and **3** has certain similarities with the imine–iminium tautomerization in rhodopsins[23].



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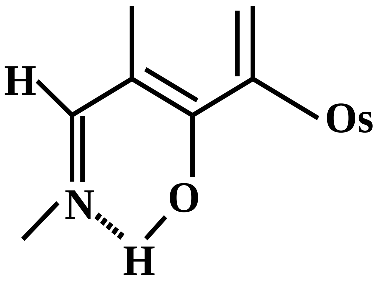

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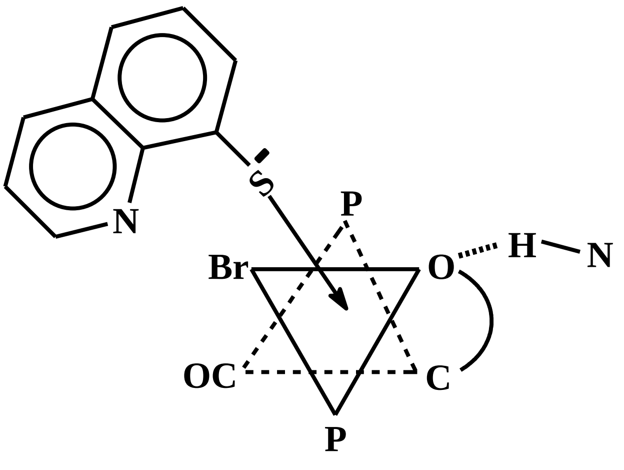
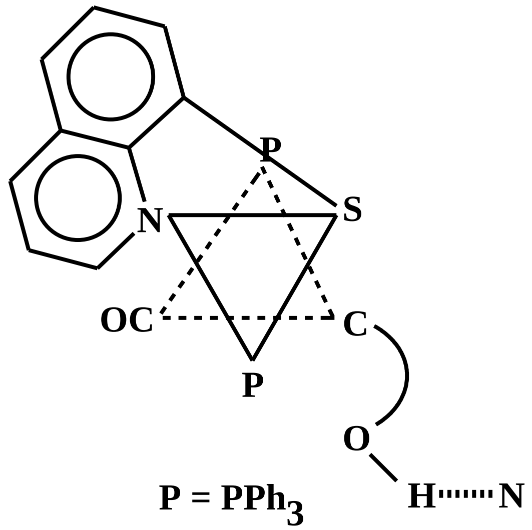
A plausible mechanism[17,18] for the displacement of bromide in **1** consists of *cis* attack by Q$^-$is shown in **6**. The anchored ligand displaces the phenolato oxygen and halide atoms achieving Q$^-$ chelation with concomitant prototropic shift and conformational reorganization as in **7**.



P = PPh$_3$

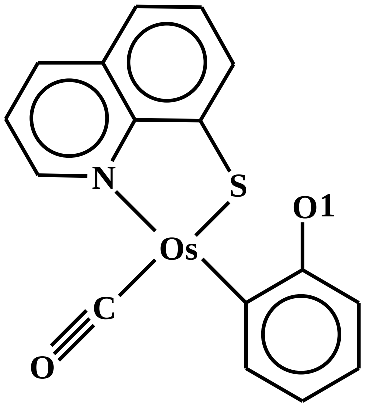
6



P = PPh$_3$

7

In both **1** and **3**, the carbon monoxide ligand lies cis to the metallated carbon atom. It is however, located cis and trans to the phenolato oxygen in **3** and **1**, respectively which is revealed by our previous study also[17,18]. Thus the Schiff base fragment rotates by ~ 180° around the metal-carbon bond in course of the reaction of equation 1 due to steric repulsion between the phenolic and the quinolin-8-thiolato function as highlighted in the hypothetical anti configuration **8** for Os(CO)(Q) fragment.



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Characterization

Osmium organometallics of type **3** are non-electrolytic in solution and are diamagnetic, consistent with a metal oxidation state of + 2 having idealized t_{2g}^{6} electronic configuration. In IR, the CO stretch is seen as a sharp band near 1930 cm^{-1}, the stretch is at slightly lower frequency due to the superior back bonding ability of bivalent osmium. In ^{1}H NMR (**Figure 1**) the 3-Hoccurs in the region 5.9 ppm and 5-H proton of the metallated ring occurs in the region 6.60-7.10 while the C(4)-Me protons resonate near 1.95 ppm. These protons are subject to shielding by phosphine phenyl rings[6,13].

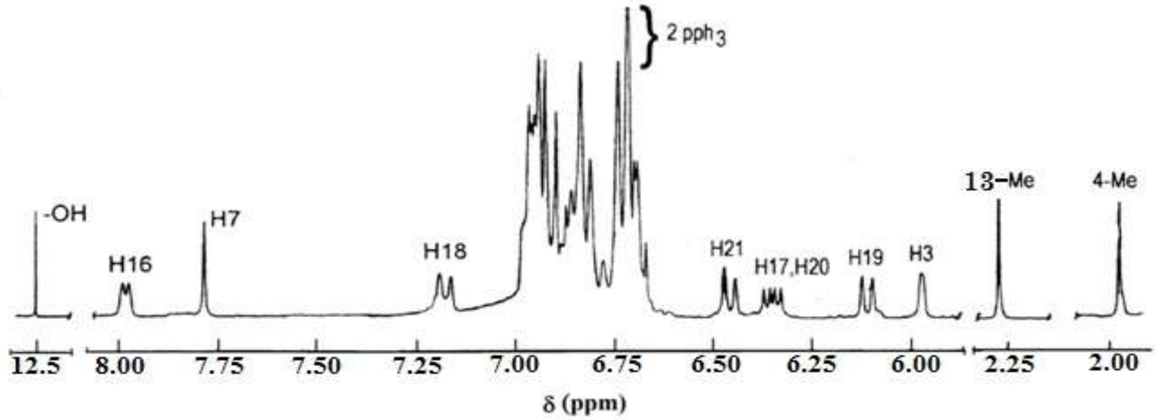

Fig.1:^{1}H NMR spectrum of 3(Me) in $CDCl_3$ solution

The six protons of quinolin-8-thiolato occur as well-resolved doublets and multiplets in the region 6.10-8.03 ppm. The PPh_3 and Schiff base aromatic protons form a complex multiplet in the region 6.60-7.10 ppm and the azomethine singlet occurs near 7.85 ppm. The phenolic O−H proton in **3** occur near 12.6 ppm consistent with imine-phenol description, *vide infra*.

Detailed assignments of the ligand protons are given in the experimental section. The complexes uniformly display a single ^{31}P signal for the two phosphine ligands implicating *trans*-$Os(PPh_3)_2$ configuration. The resonance occurs near –7.05 ppm, exact data are given in the experimental section. A representative spectrum is shown in **Figure 2**.

Fig.2: ^{31}P NMR spectrum of 3(Cl) in $CDCl_3$

$Os(RL^2)(PPh_3)_2(CO)(Q)$, **3**, complexes uniformly display two allowed bands in the region 470-480 nm and 395-410 nm and spectral data are collected in **Table 1**. The precursor species of type **1** incorporating a metal-chelated iminium-phenolato ring is characterized by an MLCT band near 510 nm[6]. In contrast the imine-phenol ligand is mono-coordinated in **3** and the band near 510 nm is also absent.

Redox Properties and EPR spectra

In dichloromethane solution **3** displays a quasi-reversible one-electron cyclic voltammetric response near 0.75 V (peak-to-peak separation is ~ 150 mV) vs.SCE corresponding to the couple where $\mathbf{3}^+$ represents the osmium(III) analogue of **3**.

$$\mathbf{3}^+ + e \rightarrow \mathbf{3} \qquad (2)$$

A representative cyclic voltammogram is shown in **Figure 3**. As *R* is varied, the $E_{1/2}$ values become more positive as the electron withdrawing power of the R group increases (OMe < Me < Cl), see **Table 1**.

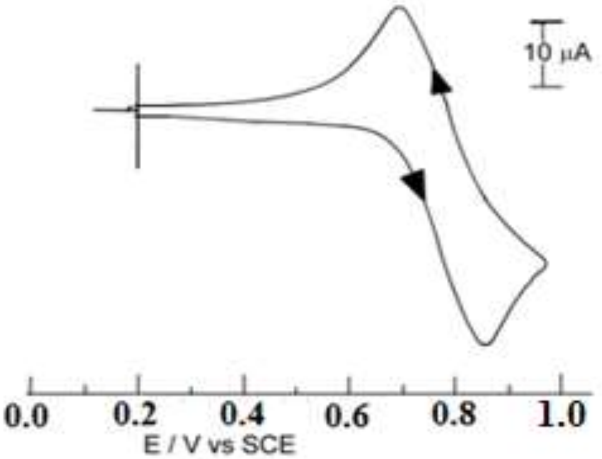

Fig.3: Cyclic vo3ltammogram of 3(OMe) in dichloromethane solution.

The reduction potentials are close to the type **1** precursor[6]. The one-electron nature of these responses has been confirmed by comparing their current heights with the standard ferrocene/ferrocenium couple under identical experimental conditions. The exhaustive coulometric oxidation at 0.95 V affords a Coulomb count corresponding to one-electron transfer (**Table 1**).

Table 1: Absorption, emission Spectral and electrochemical data of 3

			Emission data λ_{max}, **nm** (Φ_r)[a,c]		**Electrochemical data**	
Complexes	**UV-Vis data**[a] λ_{max}, **nm** (ε^b, $M^{-1}cm^{-1}$)		**298 K**	**77 K**	$E_{1/2}$, **V** (ΔE_p, **mV**)[d]	**n**[e]
3(Me)	404(14885)	472(3950)	570 (1.76×10^{-3})	641	0.78(130)	1.03
3(OMe)	411(13280)	476(3670)	563 (1.64×10^{-3})	650	0.75 (150)	1.04
3(Cl)	395(15650)	474(4170)	568 (1.72×10^{-3})	644	0.79 (160)	1.08

[a]Solvent: dichloromethane; [b]molar absorption coefficient; [c]excitation at the higher wavelength absorption peak; [d]solvent: dichloromethane.

Low potentials for the Os^{II}/Os^{III} couple in the complexes of type **3** persuaded us to try and isolate the corresponding osmium(III) complexes **3**$^+$ in their pure states. Accordingly, we tried to oxidize them both chemically and electrochemically. Unfortunately, the oxidized complexes were not stable enough for their isolation, as they revert to the parent bivalent complexes rapidly. However, we were able to generate the cationic complexes, **3**$^+$, in solution by the controlled potential bulk electrolysis of **3**.

Trivalent organometallics **3**$^+$, generated coulometrically, have been examined in solution. Their cyclic voltammograms (initial scan cathodic) are virtually superimposible on those of **3** (initial scan anodic), showing that **3**$^+$ retains the gross structure of **3**. Orange-red solutions of **3**$^+$ are characterized by an intense band near 390 nm, 500 nm and 630 nm. Spectral data are given in **Table 2**.

Table 2: Electronic and EPR spectral data of 3^+

				EPR g values[c] and derived parameters[d]						
Complexes	**UV-Vis data[a]** **λ_{max}, nm (ε^b, $M^{-1}cm^{-1}$)**			**g_1**	**g_2**	**g_3**	**Δ**	***V***	**ΔE_1**	**ΔE_2**
3(Me)$^+$	392 (19201)	505 (13422)	631 (7201)	2.318	2.029	1.714	18403	9102	12709	22505
3(OMe)$^+$	385 (19413)	501 (13504)	625 (7444)	2.302	2.035	1.709	18392	9089	12811	22485
3(Cl)$^+$	389 (19111)	507 (13344)	620 (7346)	2.285	2.037	1.711	18330	9052	12754	22431

[a]Solvent: dichloromethane; [b]molar absorption coefficient; [c] In 1 : 1 dichloromethane–toluene solution at 77 K;[d] Taking the value of the spin-orbit coupling constant (λ) for low-spin osmium(III) as equal to 3000 cm^{-1}.

Electron paramagnetic resonance (EPR) spectra of the $\mathbf{3}^+$ complexes, recorded in 1 : 1 dichloromethane–toluene solution at 77 K, show rhombic spectra with three distinct signals (g_1, g_2 and g_3,in decreasing order of magnitude). A representative spectrum is shown in **Figure 4** and the spectral data are presented in **Table 2**. The observed rhombicity of the EPR spectra is understandable in terms of the gross molecular symmetry of these complexes, containing the three non-equivalent P–Os–P, S–Os–C and N–Os–C axes. The rhombic distortion can be thought of as a combination of axial distortion (*Δ*, which splits t_2 into a ande) and rhombic distortion (*V*, which splits e). The splitting pattern is illustrated in **Figure 4.** Spin–orbit coupling causes further changes in the energy gaps.

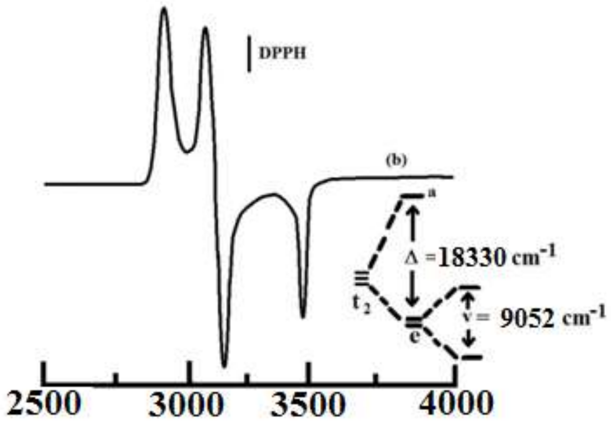

Fig. 4: EPR spectra of 3(Cl)$^+$ in frozen 1 : 1 dichloromethane–toluene solution at 77 K, showing the computed splitting of the t_2 orbitals. DPPH = diphenyl-picrylhydrazyl.

Thus two electronic transitions (transition energies Δ*E***1** and Δ*E***2**; Δ*E***1** < Δ*E***2**) are possible in principle within these three levels. All these energy parameters have been computed (**Table 2**) using the observed *g*-values, the *g*-tensor theory of low-spin d^5 complexes and a reported method[24]. The axial distortion is observed to be much stronger than the rhombic. The EPR data analysis thus shows that the **3**$^+$ complexes are significantly distorted from ideal octahedral geometry which is observed previously in the crystal structure of acetate[13] and xanthate[17] derivatives. In this connection it should be pointed out that for thioxanthate chelated osmium organometallics we indicate the better stabilization of the trivalent state but isolation of osmium (III) species via electrooxidation has not been succeeded[17] but for quinoline-8-thiolato chelated osmium complexes we are able to generate the osmium(III) analogue in solution this is probably due to the much more stability of the five-membered ring than the former.

Emission Properties

In dichloromethane solution complexes of type **3** display two allowed absorption bands in the regions 395–410 and 470–480 nm. The latter band is weaker in intensity and is believed to have significant *dπ*(Os)-*π**(Q) MLCT character. Selected UV–Vis spectral data are given in **Table 1**. The solutions are fluorescent at room temperature, and also at low temperature (77 K). The peaks lying in the region 560–570 and 640–650 nm at 298 K and 77 K respectively (**Figure 5**, **Table 1**) makes **3** fluorescent in the visible region.

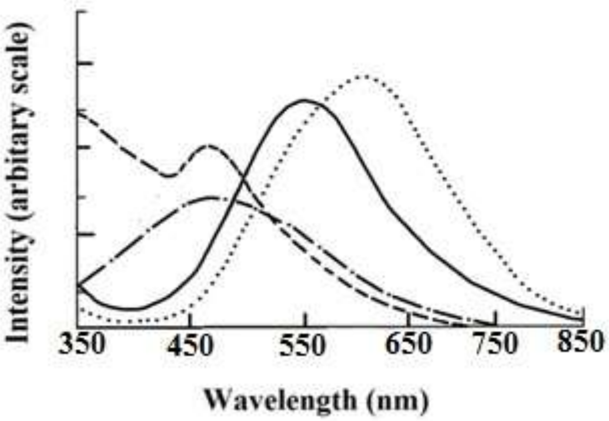

Fig. 5: Absorption (− − −), excitation (— •—), and fluorescence spectra at 298 K (——) and at 77 K (• • •) of 3(OMe) in dichloromethane solution.

Low-temperature emission spectra are red-shifted from room temperature ones. The complexes are weak emitters, as noted from their quantum yield (Φ_r) values which are one order of magnitude lower than that of the $[Ru(bpy)_3]^{2+}$ standard[25] (**Table 1**). Quantum yields are calculated using equation (3) as described previously[25] where Φ_{std} is 0.042 at298 K, *A* is the solution absorbance at the excitation wave length, *I* is the relative emission intensity, *η* are the refractive index values of the solvent for the sample (subscript *r*) and the standard reference (subscript std) respectively,

$$\Phi_r = \Phi_{std}\ (A_{std}/A_r)(I_r/I_{std})\ (\eta_r^2/\eta_{std}^2\ ). \qquad (3)$$

Excitation spectral studies show that fluorescence is associated with the absorption band near 475 nm. Assuming that the band has MLCT character as suggested above, the possible involvement of the ^{3}MLCTstate[13,17] incorporating *π** (Q) contribution is implicated in the emission process.

Conclusions

It is demonstrated that the metallacycles of type **1** react smoothly with NaQ furnishing aryl osmium organometallics of type **3**. The conversion **1**→**3** is attended with cleavage of Os–O and Os–Br bonds,(N,S) chelation of quinolin-8-thiolato, iminium-phenolato→imine-phenol tautomerization. Os^{III}/Os^{II} reduction potentials are close to that of **1** and **3** is electrooxidizable to the osmium(III) analogue

3^+ characterized by rhombic EPR spectra. The Os → Q MLCT absorption in the visible region makes **3** fluorescent with quantum yields one order of magnitude less than that of the $[Ru(bpy)_3]^{2+}$ standard.

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