

Synthesis, characterization and photophysical properties of quinolin-8-olato chelated osmium(II) organometallics bearing a pendant imine-phenol motif and electrogeneration of trivalent analogue

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ABSTRACT

The reaction of $\text{Os}(\text{RL}^1)(\text{PPh}_3)_2(\text{CO})\text{Br}$, **1b**, with quinolin-8-ol (HQ), **2**, has furnished complexes of the type $[\text{Os}(\text{RL}^2)(\text{PPh}_3)_2(\text{CO})(\text{Q})]$, **3**, in excellent yield (RL^1 is $\text{C}_6\text{H}_2\text{O}-2\text{-CHNHC}_6\text{H}_4\text{R}(p)\text{-3-Me-5}$, RL^2 is $\text{C}_6\text{H}_2\text{OH}-2\text{-CHNC}_6\text{H}_4\text{R}(p)\text{-3-Me-5}$ and R is Me, OMe, Cl). In this process, quinolin-8-olato (Q) undergoes five-membered chelation, the iminium-phenolato function tautomerizing to the imine-phenol function. The trans geometry of the $\text{Os}(\text{PPh}_3)_2$ fragment is consistent with the occurrence of a single ^{31}P resonance near -6.0 ppm in **3**. In dichloromethane solution, **3** displays a quasireversible $3^+/3$ couple near 0.40 V vs. SCE (3^+ is the osmium (III) analogue of **3**). Coulometrically generated solutions of 3^+ displays a strong absorption near 340 nm, 415 nm and 500 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 2.44 , 2.20 , 1.83 . Distortion parameters using the observed g values have been computed. Solutions of **3** absorb near 420 nm and emit near 510 nm at 298 K and 580 nm at 77 K. The fluorescence is believed to originate from the $^3\text{MLCT}$ state.

Keywords: Osmium Organometallics; Quinolin-8-Olato Chelation; Emission Properties; Trivalent Osmium

1. INTRODUCTION

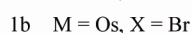
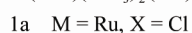
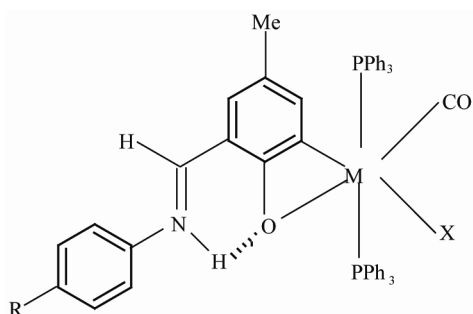
The chemistry of osmium has been receiving considerable attention largely because of the variety of reactivities and due to the fascinating electron transfer properties exhibited by complexes of this metal [1-9]. Variation of the coordination environment around osmium plays a key role in modulating the redox properties of its com-

plexes. In this article we studied the reactivity of an osmium system with 8-hydroxyquinoline because complexes incorporating quinoline moiety are important in the context of biological activity [10]. It was also reported in the literature that a series of compounds derived from 8-hydroxyquinoline showed that they could possess strong antifungal, antiasthmatic and antiplatelet activity [10-13]. In particular the chemistry of osmium compounds is of current interest in the context of synthesis, reactivity and photophysical properties [1,9,14-16].

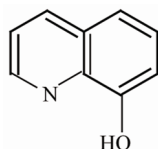
It was demonstrated that the decarbonylative metallation of 4-methyl-2,6-diformyl phenol by $\text{M}(\text{PPh}_3)_3\text{X}_2$ in the presence of primary aromatic amines ($\text{RC}_6\text{H}_4\text{NH}_2$) is known to furnish four-membered ruthenium/osmium organometallics of the type $\text{M}(\text{RL}^1)(\text{PPh}_3)_2(\text{CO})\text{X}$ (**1**) juxtaposed to a hydrogen bonded iminium-phenolato function [17-19]. We are scrutinizing the reactivity of these compounds. 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 [20-22] 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 [23, 24] while in case of osmium system isonitrile simply displaced bromide ligand furnishing the cationic complexes which are isolated as salts [25]. 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 [26]. We also explore the reactivity of **1** towards bidentate monoanionic donor reagents such as acetate [27], palmitate and terephthalate [28], nitrate and nitrite [29,30] xanthate [31], pyridine-2-thiolate [32] undergo four-membered chelation and we also reported

earlier that **1a** reacts with the electroneutral diimine ligands [33] such as bipyridine, phenanthroline and biimidazole [34] as well as 8-hydroxyquinoline [35] furnish five-membered ruthenium organometallics.

The above importance of osmium complexes and the richness of this reaction chemistry have now prompted us to explore the reactivity of **1b** towards quinolin-8-ol, **2**, (HQ, H stands for the dissociable phenolic hydrogen) which is suited for five-membered N, O-chelation. A facile reaction is indeed observed furnishing the novel five-membered 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. It may be noted that the chemistry of osmium quinolin-8-olate appears to have relatively less attention [36-39] but to the best of my knowledge organoosmium compounds incorporating 8-hydroxyquinoline are unprecedented. Another point of special interest is that such species are potentially luminescent in the visible region and are electrochemically oxidizable to the trivalent analogue.



1



2

2. EXPERIMENTAL

2.1. Materials

The compounds $Os(PPh_3)_3Br_2$ [40] and $Os(RL)(PPh_3)_2(CO)Br$ [17] were prepared by reported methods. 8-hydroxyquinoline was obtained from Merck. The purification of dichloromethane and the preparation of tetraethyl ammonium perchlorate (TEAP) for electrochemical work were done as described in previous work [41]. All other

chemicals and solvents were of analytical grade and were used as received.

2.2. 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. 1H NMR spectra were obtained using a Bruker 300 MHz FT NMR spectrometer. The numbering scheme used for the 1H NMR is the same as shown in drawing **3**. Spin structures are abbreviated as: s, singlet; d, doublet; t, triplet; m, multiplet. ^{31}P NMR spectra were recorded with the help of a Varian 300 MHz spectrometer using H_3PO_4 as standard. 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. The supporting electrolyte was tetraethyl ammonium perchlorate and potentials are referenced to the saturated calomel electrode.

2.3. Synthesis of the Complexes [Os(RL²)(PPh₃)₂(CO)(Q)] (**3**)

[Os(RL²)(PPh₃)₂(CO)(Q)] (**3**) complexes were synthesized in excellent yield (~80%) by reacting $Os(RL^1)(PPh_3)_2(CO)Br$ (**1b**) in MeOH-CH₂Cl₂ (2:1) at room temperature with excess HQ. Details of a representative case are given below. The other compounds are prepared in an analogous manner.

2.3.1. [Os(MeL²)(PPh₃)₂(CO)(Q)], **3(Me)**

To a vigorously stirred violet solution of $Os(MeL^1)(PPh_3)_2(CO)Br$ (100 mg, 0.09 mmol) in a mixture of 50 ml methanol and 25 ml dichloromethane was added 65 mg (0.45 mmol) of HQ. The mixture was refluxed for 12 h when the colour of the solution changed from violet to yellow. The solvent was then removed under reduced pressure and the yellow solid thus obtained was washed with a little amount of methanol (removal of excess HQ). The residue was recrystallized from dichloromethane-hexane (1:3) mixture followed by drying in vacuo. Yield: 86 mg (81%).

Analysis: Calc. for $C_{61}H_{50}N_2O_3P_2Os$: C, 65.93; H, 4.53; N, 2.69%. Found C, 65.88; H, 4.51; N, 2.64%. 1H NMR (300 MHz, CDCl₃, ppm, 298 K): 12.56 (s, 1H, O-H,

disappeared upon shaking with D₂O), 7.80 (s, 1H, H7), 5.98 (s, 1H, H3), 1.92 (s, 3H, 4-Me), 2.32 (s, 3H, 13-Me), 8.01 (d, $J_{\text{HH}} = 6.2$ Hz, 1H, H16), 7.19 (d, $J_{\text{HH}} = 8.5$ Hz, 1H, H18), 6.11 (d, $J_{\text{HH}} = 7.6$ Hz, 1H, H19), 6.45 (d, $J_{\text{HH}} = 8.2$ Hz, 1H, H21), 6.33 - 6.38 (m, 2H, H17, H20). 6.65 - 7.05 (m, 35H, 2PPh₃, H5, H11, H12, H14, H15). ³¹P NMR (300 MHz, CDCl₃, ppm, 298 K): -6.196 (s, 2P). IR (KBr, cm⁻¹): 1893 (ν_{CO}), 1602 (ν_{C=N}).

2.3.2. [Os(MeOL¹)(PPh₃)₂(CO)(Q)], 3(OMe)

Os(MeOL¹)(PPh₃)₂(CO)Br (100 mg, 0.089 mmol) and HQ (64 mg, 0.441 mmol) were employed. Yield: 84 mg (79%). Analysis: Calc. for C₆₁H₅₀N₂O₄P₂Os: C, 65.00; H, 4.47; N, 2.48%. Found C, 65.05; H, 4.41; N, 2.50%. ¹H NMR (300 MHz, CDCl₃, ppm, 298 K): 12.61 (s, 1H, O-H, disappeared upon shaking with D₂O), 7.82 (s, 1H, H7), 6.01 (s, 1H, H3), 1.90 (s, 3H, 4-Me), 3.74 (s, 3H, 13-OMe). 8.02 (d, $J_{\text{HH}} = 6.5$ Hz, 1H, H16), 7.20 (d, $J_{\text{HH}} = 8.4$ Hz, 1H, H18), 6.13 (d, $J_{\text{HH}} = 7.5$ Hz, 1H, H19), 6.48 (d, $J_{\text{HH}} = 7.9$ Hz, 1H, H21), 6.32 - 6.39 (m, 2H, H17, H20), 6.63 - 7.04 (m, 35H, 2PPh₃, H5, H11, H12, H14, H15). ³¹P NMR (300 MHz, CDCl₃, ppm, 298 K): -6.270 (s, 2P). IR (KBr, cm⁻¹): 1896 (ν_{CO}), 1606 (ν_{C=N}).

2.3.3. [Os(CIL¹)(PPh₃)₂(CO)(Q)], 3(Cl)

Os(CIL¹)(PPh₃)₂(CO)Br (100 mg, 0.088 mmol) and HQ (64 mg, 0.441 mmol) were used. Yield: 83 mg (76%). Analysis: Calc. for C₆₀H₄₇N₂O₃P₂ClOs: C, 63.68; H, 4.19; N, 2.47%. Found C, 63.65; H, 4.23; N, 2.51%. ¹H NMR (300 MHz, CDCl₃, ppm, 298 K): 12.51 (s, 1H, O-H, disappeared upon shaking with D₂O), 7.79 (s, 1H, H7), 6.00 (s, 1H, H3), 1.92 (s, 3H, 4-Me). 7.99 (d, $J_{\text{HH}} = 6.3$ Hz, 1H, H16), 7.19 (d, $J_{\text{HH}} = 8.5$ Hz, 1H, H18), 6.12 (d, $J_{\text{HH}} = 7.3$ Hz, 1H, H19), 6.46 (d, $J_{\text{HH}} = 7.8$ Hz, 1H, H21), 6.33 - 6.40 (m, 2H, H17, H20), 6.62 - 7.02 (m, 35H, 2PPh₃, H5, H11, H12, H14, H15). ³¹P NMR (300 MHz, CDCl₃, ppm, 298 K): -6.345 (s, 2P). IR (KBr, cm⁻¹): 1892 (ν_{CO}), 1596 (ν_{C=N}).

2.4. Electrochemical Generation of 3⁺

The complexes of type 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 10 mg of 3(Me) in 25 ml dichloromethane solvent containing 35 mg of TEAP was oxidized coulometrically. The oxidation was performed at 0.75 V; $n^c = 1.108/1.086 = 1.02$, $n^c = Q/Q_1$, where Q₁ 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 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 electro-generated orange-red solution (10 ml) is used quickly for electronic spectral study. The oxidized complex 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 Ce⁴⁺. In this case the quantity of the byproducts was more than 25%. To date, we were not successful in isolating the trivalent osmium compound 3⁺ in its pure state. The trivalent complex 3(OMe)⁺ and 3(Cl)⁺ was generated in solution similarly as described above.

3. RESULTS AND DISCUSSION

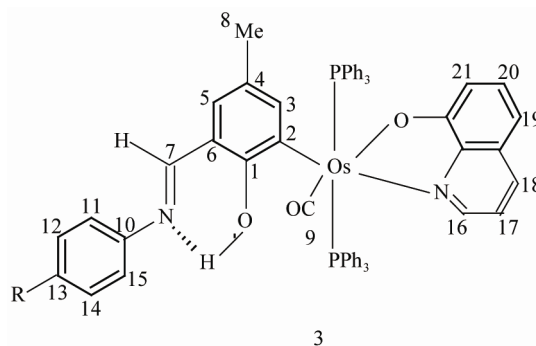
3.1. Coordination with Quinolin-8-olato

In methanol-dichloromethane solution, Os(RL¹)(PPh₃)₂(CO)Br (1) reacts smoothly with five fold excess of HQ upon stirring at room temperature, according to, Equation (1), the colour of the



solution changes from violet to yellow, from which [Os(RL²)(PPh₃)₂(CO)(Q)] (3) is obtained in excellent yield. 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(MeL²)(PPh₃)₂(CO)(Q)]. The complex 3 has been isolated in pure form in ~ 80% yield. An isomer (because quinolin-8-ol is unsymmetrical) of 3 is possible in principle but it has never been observed. Careful examination of ¹H NMR 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}(quinolin-8-olato) complexes [38,39] and also by comparing with acetate, thioxanthate, pyridine-2-thiolato chelated ruthenium/osmium organometallics [27,31,32].

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



3

tautomeric form **4**. Chelation of quinolin-8-olato 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.

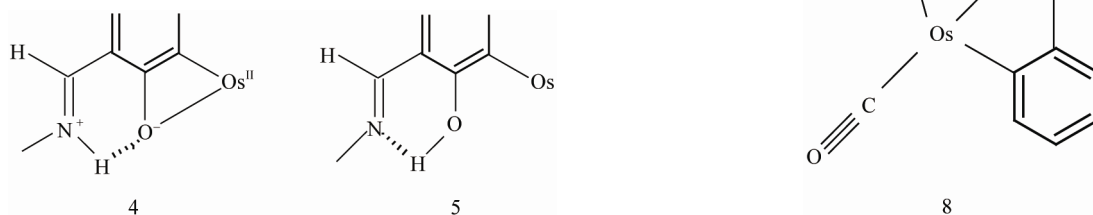
Thus the C=N stretching frequency in **3** is significantly lower ($\sim 1600\text{ cm}^{-1}$) than that in **1** ($\sim 1620\text{ cm}^{-1}$) as expected [42]. Also the aldimine CH signal in $^1\text{H NMR}$ in **3** (**Figure 1**) occurs at lower field viz. 7.8 ppm as compared to ~ 7.5 ppm in **1** [17]. The O-H resonance in **3** is a relatively sharp signal near 12.5 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 [17]. The prototropic transformation between **1** and **3** has certain similarities with the imine-iminium tautomerization in rhodopsins [42].

A plausible mechanism [31,32,35] 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**.

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 [32,33]. Thus the Schiff base fragment rotates by $\sim 180^\circ$ around the metal-carbon bond in course of the reaction of equation 1 due to steric repulsion between the phenolic and the quinolin-8-olato function as highlighted in the hypothetical anti configuration **8** for Os(CO)(Q) fragment.

3.2. 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 con-

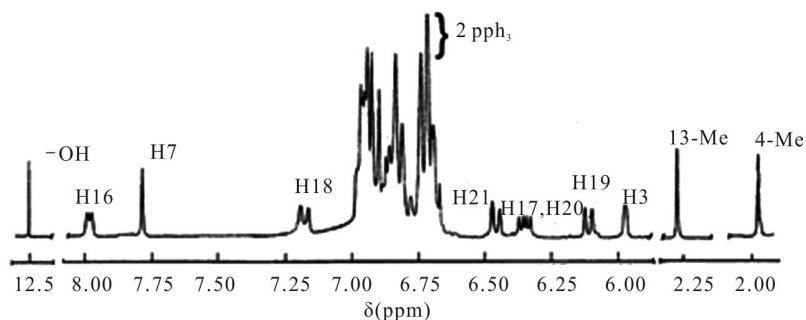
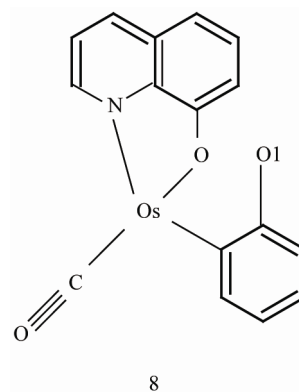
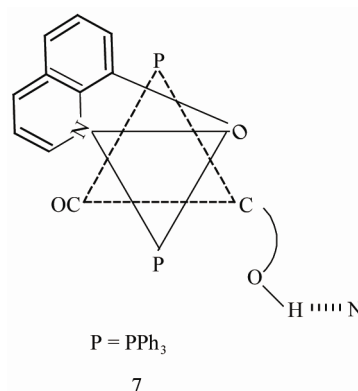
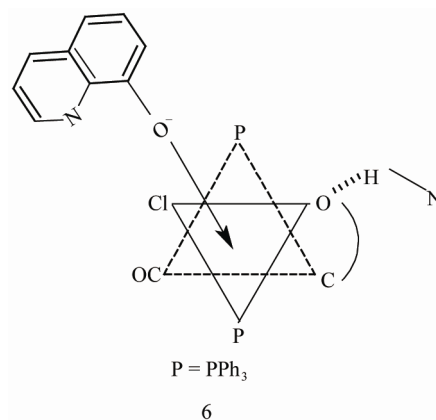


Figure 1. $^1\text{H NMR}$ spectrum of **3(Me)** in CDCl_3 solution.

figuration. In IR, the CO stretch is seen as a sharp band near 1890 cm^{-1} , the stretch is at slightly lower frequency due to the superior back bonding ability of bivalent osmium. In $^1\text{H NMR}$ (**Figure 1**) the 3-H proton of the metallated ring occur as sharp singlets near 6.0 ppm, while the C(4)-Me protons resonate near 1.9 ppm. These protons are subject to shielding by phosphine phenyl rings [17,27,43]. The PPh_3 , Schiff base ($\text{C}_6\text{H}_4\text{R}$) aromatic protons form a complex multiplet in the region 6.60 - 7.05 ppm and the quinolin-8-olate aromatic protons appear in the 6.00 - 8.05 ppm region.

Detailed assignments of the ligand protons are given in the experimental section. In the previous section the chemical shifts of the imine-phenol protons were considered. The complexes uniformly display a single ^{31}P signal for the two phosphine ligands implicating *trans*- $\text{Os}(\text{PPh}_3)_2$ configuration. The resonance occurs near -6.0 ppm, exact data are given in the experimental section. A representative spectrum is shown in **Figure 2**. The redox and photophysical properties of the complexes are examined in later sections.

3.3. Redox Properties and EPR Spectra

In dichloromethane solution **3** displays a quasireversible one-electron cyclic voltammetric response near 0.40 V (peak-to-peak separation is ~ 100 mV) vs. SCE corresponding to the



couple where $\mathbf{3}^+$ represents the osmium(III) analogue of **3**. 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 ($\text{OMe} < \text{Me} < \text{Cl}$), see **Table 1**. The reduction potentials are systematically lower than those of the type **1** precursors [17] by ~ 200 mV, indicating better stabilization of the trivalent state in **3** compared with that in **1**. 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 0.75 V affords a coulomb count corresponding

to one-electron transfer (**Table 1**).

Low potentials for the $\text{Os}^{\text{II}}/\text{Os}^{\text{III}}$ couple in the complexes of type **3** persuaded us to try and isolate the corresponding osmium(III) complexes $\mathbf{3}^+$ in their pure states. Accordingly, we tried to oxidize them both chemically and electrochemically. Unfortunately, the oxidized com-

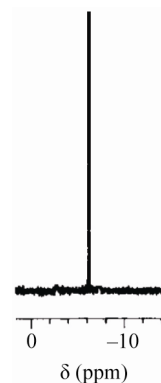


Figure 2. ^{31}P NMR spectrum of **3(OMe)** in CDCl_3 .

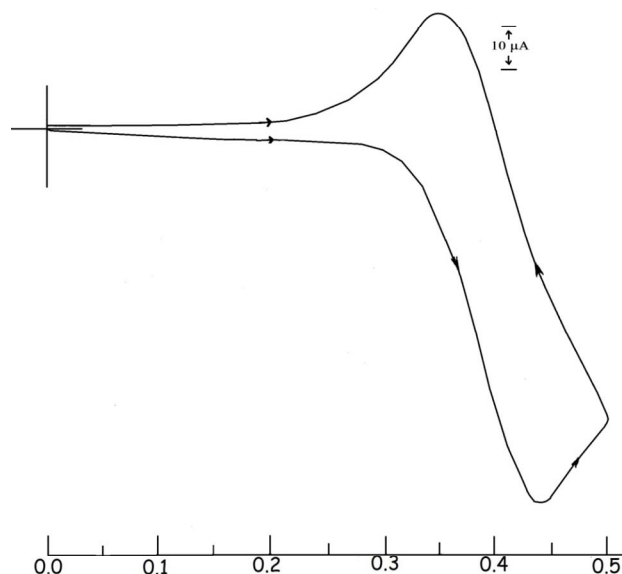


Figure 3. Cyclic voltammogram of **3(OMe)** in dichloromethane solution.

Table 1. Absorption, emission spectral and electrochemical data of **3**.

Complexes	UV-Vis data ^a λ_{max} , nm (ϵ^b , $\text{M}^{-1}\cdot\text{cm}^{-1}$)		Emission data λ_{max} , nm (Φ_r) ^{b,c}		Electrochemical data	
			298 K	77 K	$E_{1/2}$, V (ΔE_p , mV) ^d	n^e
3(Me)	346 (18690)	425 (9850)	515 (2.06×10^{-3})	573	0.43 (160)	1.02
3(OMe)	354 (20755)	421 (9930)	514 (1.64×10^{-3})	588	0.41 (124)	1.08
3(Cl)	349 (16375)	414 (9520)	509 (1.34×10^{-3})	582	0.46 (142)	0.97

^aSolvent: dichloromethane; ^bmolar absorption coefficient; ^cexcitation at the higher wavelength absorption peak; ^dsolvent: dichloromethane; ΔE_p is peak-to-peak separation; $n^e = Q/Q_1$ where Q is the observed coulomb count and Q_1 is the calculated coulomb count for one-electron transfer.

plexes 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 superimposable 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 340 nm, 410 nm and 500 nm. A representative spectrum is shown in **Figure 4** and spectral data are given in **Table 2**. Electron paramagnetic resonance (EPR) spectra of the 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 5** 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, O-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 and e) and rhombic distortion (V , which splits e). The splitting pattern is illustrated in **Figure 5**. Spin-orbit coupling causes further changes in the energy gaps. Thus two electronic transitions (transition energies ΔE_1 and ΔE_2 ; $\Delta E_1 < \Delta E_2$) are possible in principle within these three levels. All these energy parameters have been computed (**Table 2**) using the 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 [44,45]. 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 [27] and xanthate [31] 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 [31] but for

quinolin-8-olato chelated osmium complexes we are able to generate the osmium(III) analogue in solution this is probably due to the five-membered chelation instead of four-membered chelation for the former.

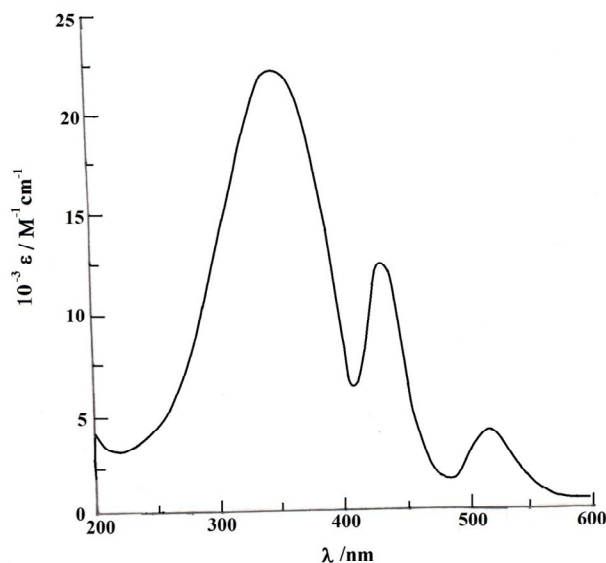


Figure 4. Electronic spectrum of $3(\text{Cl})^+$ in CH_2Cl_2 solution.

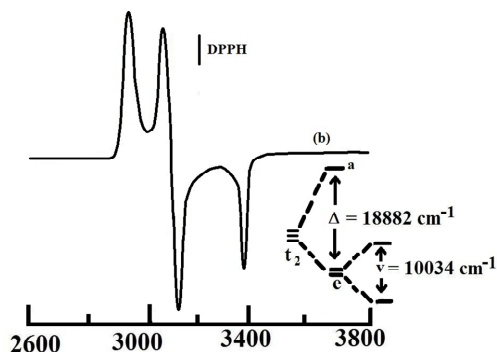


Figure 5. EPR spectra of $3(\text{OMe})^+$ in frozen 1:1 dichloromethane-toluene solution at 77 K, showing the computed splitting of the t_2 orbitals. DPPH = diphenyl-picrylhydrazyl.

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

Complexes	UV-Vis data ^a λ_{max} , nm (ϵ^b , $\text{M}^{-1}\cdot\text{cm}^{-1}$)			EPR g values ^c and derived parameters ^d						
				g_1	g_2	g_3	Δ	V	ΔE_1	ΔE_2
$3(\text{Me})^+$	339 (23513)	409 (12748)	503 (4052)	2.469	2.161	1.815	18902	10045	14168	24498
$3(\text{OMe})^+$	344 (24580)	414 (13544)	495 (4175)	2.443	2.185	1.843	18882	10034	14125	24455
$3(\text{Cl})^+$	341 (22331)	419 (12418)	509 (3932)	2.442	2.264	1.832	18745	10022	14043	24322

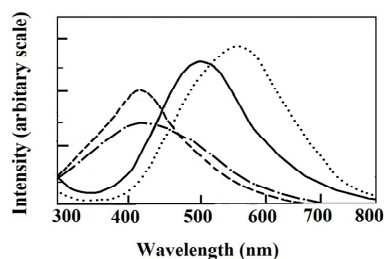


Figure 6. Absorption (---), excitation (—•—), and fluorescence spectra at 298 K (—) and at 77 K (•••) of **3(CI)** in dichloromethane solution.

3.4. Emission Properties

In dichloromethane solution complexes of type **3** display two allowed absorption bands in the regions 345 - 355 and 410 - 425 nm. The latter band is weaker in intensity and is believed to have significant $d\pi(\text{Os}) - \pi^*(\text{Q})$ 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 505 - 515 and 570 - 590 nm at 298 K and 77 K respectively (**Figure 6**, **Table 1**) makes **3** fluorescent in the visible region. 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 $[\text{Ru}(\text{bpy})_3]^{2+}$ standard [46,47] (**Table 1**). Quantum yields are calculated using Equation (3) as described previously [46,47] where Φ_{std} is 0.042 at 298 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,

$$\Phi_r = \Phi_{\text{std}} \left(\frac{A_{\text{std}}}{A_r} \right) \left(\frac{I_r}{I_{\text{std}}} \right) \left(\frac{\eta_r^2}{\eta_{\text{std}}^2} \right). \quad (3)$$

Excitation spectral studies show that fluorescence is associated with the absorption band near 420 nm. A representative case is shown in **Figure 6**. Assuming that the band has MLCT character as suggested above, the possible involvement of the $^3\text{MLCT}$ state [15,16,33] incorporating $\pi^*(\text{Q})$ contribution is implicated in the emission process. We also note that the parent organometallics of type **1** do not display any fluorescence in the visible region.

4. CONCLUSION

It is demonstrated that the metallacycles of type **1** react smoothly with HQ furnishing aryl osmium organometallics of type **3**. The conversion **1**→**3** is attended with cleavage of Os-O and Os-Br bonds, (N, O) chelation of quinolin-8-olate, iminium-phenolato→imine-phenol tau-

merization. $\text{Os}^{\text{III}}/\text{Os}^{\text{II}}$ reduction potentials are systematically lower than those 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 $[\text{Ru}(\text{bpy})_3]^{2+}$ standard.

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