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

Bikash Kumar Panda

Department of Chemistry, Jangipur College, Murshidabad, India
Email: panda_bikas@rediffmail.com, bikash.panda66@yahoo.com

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ABSTRACT

The reaction of Os(RL_1)(PPh_3)_2(CO)Br, 1b, with quinolin-8-ol (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, quinolin-8-olato (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 ^3P 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 ^3MLCT 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 complexes. 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 M(PPh_3)_2X_2 in the presence of primary aromatic amines (RC_6H_4NH_2) is known to furnish 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 [17-19]. We are scrutinizing the reactivity of these compounds. It has been found that different alkynes undergo 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 organooosmium 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.

2. EXPERIMENTAL

2.1. Materials

The compounds Os(PPh₃)₃Br₂ [40] and Os(RL₁)(PPh₃)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. ³¹P NMR spectra were recorded with the help of a Varian 300 MHz spectrometer using H₃PO₄ 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(RL₁)(PPh₃)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(MeL₁)(PPh₃)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 C₆₁H₅₀N₂O₃P₂Os: 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, JHH = 6.2 Hz, 1H, H16), 7.19 (d, JHH = 8.5 Hz, 1H, H18), 6.11 (d, JHH = 7.6 Hz, 1H, H19), 6.45 (d, JHH = 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): –6.270 (s, 2P); IR (KBr, cm–1): 1896 (υC=N).

2.3.2. [Os(MeOL1)(PPh3)2(CO)(Q)]3(Cl)+ 3P NMR (300 MHz, CDCl3, ppm, 298 K): –6.196 (s, 2P); IR (KBr, cm–1): 1892 (υC=N).

2.3.3. [Os(CIL1)(PPh3)2(CO)(Q)]3(OMe)+ 3P NMR (300 MHz, CDCl3, ppm, 298 K): –6.270 (s, 2P); IR (KBr, cm–1): 1893 (υC=O), 1602 (υC=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° = 1.108/1.086 = 1.02, n° = Q/Q1, 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

1 + HQ → 3 + HBr (1)

solution changes from violet to yellow, from which [Os(RL1)(PPh3)2(CO)(Q)]3+ (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(MeL1)(PPh3)2(CO)(Q)]3+. The complex 3 has been isolated in pure form in ~ 80% yield. An isomer (because quinol-8-ol is unsymmetrical) of 3 is possible in principle but it has never been observed. Careful examination of 13C NMR spectra of crude sample (before recrystallization) did not reveal the presence of any extra signals apart from those characteristic of 3. We assign structure 3 to it in analogy with the stereochemistry of other Os(III) and Os(IV) complexes [38,39] and also by comparing with acetate, thiocyanate, 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...
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 (~1600 cm\(^{-1}\)) than that in 1 (~1620 cm\(^{-1}\)) as expected [42]. Also the aldime 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 ~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-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\(_{2g}\) electronic con-
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 \(^1\)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 (C\(_6\)H\(_4\)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-Os(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

\[
3^+ + e^{-} \rightarrow 3
\]

couple where 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 (OMe < Me < 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 Os\(^{III}\)/Os\(^{II}\) 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 com-

<table>
<thead>
<tr>
<th>Complexes</th>
<th>UV-Vis data (\lambda_{max}, \text{nm} (\varepsilon, \text{M}^{-1} \text{cm}^{-1}))</th>
<th>Emission data (\lambda_{max}, \text{nm} (\Phi_r))</th>
<th>Electrochemical data (E_{1/2}, \text{V} (\Delta E_p, \text{mV}))</th>
<th>(n^e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3(Me)</td>
<td>346 (18690) 425 (9850)</td>
<td>298 K 515 (2.06 \times 10^{-3})</td>
<td>0.43 (160) 1.02</td>
<td></td>
</tr>
<tr>
<td>3(OMe)</td>
<td>354 (20755) 421 (9930)</td>
<td>298 K 514 (1.64 \times 10^{-3})</td>
<td>0.41 (124) 1.08</td>
<td></td>
</tr>
<tr>
<td>3(Cl)</td>
<td>349 (16375) 414 (9520)</td>
<td>298 K 509 (1.34 \times 10^{-3})</td>
<td>0.46 (142) 0.97</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)Solvent: dichloromethane; \(^b\)molar absorption coefficient; \(^c\)excitation at the higher wavelength absorption peak; \(^d\)solvent: dichloromethane; \(\Delta E_p\) 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 ($\Delta$, 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 $\Delta E_1$ and $\Delta E_2$; $\Delta E_1 < \Delta E_2$) are possible in principle within these three levels. All these energy parameters have been computed (Table 2) using the 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](image1.png)

**Figure 4.** Electronic spectrum of $3(\text{Cl})^+$ in CH$_2$Cl$_2$ solution.

![Figure 5](image2.png)

**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-picyrylhydrazyl.

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

<table>
<thead>
<tr>
<th>Complexes</th>
<th>UV-Vis data$^a$</th>
<th>EPR g values$^e$ and derived parameters$^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$3(\text{Me})^+$</td>
<td>$\lambda_{\text{max}}$, nm ($\epsilon$, M$^{-1}$ cm$^{-1}$)</td>
<td>$g_1$</td>
</tr>
<tr>
<td>$3(\text{OMe})^+$</td>
<td>339 (23513)</td>
<td>409 (12748)</td>
</tr>
<tr>
<td>$3(\text{Cl})^+$</td>
<td>344 (24580)</td>
<td>414 (13544)</td>
</tr>
<tr>
<td>$3(\text{Me})^+$</td>
<td>341 (22331)</td>
<td>419 (12418)</td>
</tr>
</tbody>
</table>

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and is believed to have significant and 410 - 425 nm. The latter band is weaker two allowed absorption bands in the regions 345 - 355 type. We also note that the parent organometallics of band has MLCT character as suggested above, the possibility of the 3MLCT state [15,16,33] incorporating Φtumum yield (...), quantum yields are calculated using Equation (3) as described previously [46,47] where Φstd 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, 

\[ \Phi_r = \Phi_{\text{std}} \left( \frac{\Lambda_{\text{std}}}{\Lambda_r} \right) \left( \frac{I_r}{I_{\text{std}}} \right) \left( \frac{\eta^2_r}{\eta^2_{\text{std}}} \right). \] (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 3MLCT state [15,16,33] incorporating π*(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 tautomerization. OsIII/OsII 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 [Ru(bpy)3]2+ standard.

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