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Research paper

An insight into the redox activity of Ru and Os complexes of the N,N'-bis(2-pyridyl)benzene-1,2-diamine ligand: Structural, electrochemical and electronic structure analysis by density functional theory calculations

Rajesh Deka a,b,c, Peter C. Junk b,d, David R. Turner b,c, Glen B. Deacon b,c,* Harkesh B. Singh a,b,*

a Department of Chemistry, Indian Institute of Technology Bombay, Mumbai 400076, India
b IITB-Monash Research Academy, IIT Bombay, Powai, Mumbai 400076, India
c School of Chemistry, Monash University, Clayton, Victoria 3800, Australia
d College of Science & Engineering, James Cook University, Townsville 4811, QLD, Australia

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ABSTRACT

The synthesis of Ru and Os complexes of the ligand, N,N'-bis(2-pyridyl)benzene-1,2-diamine namely, [RuIII(acac)2(Py-bqdi)], (9), [RuIII(Ph-trpy)(Py-bqdi)Cl], (10) and [OsIII(bpy)2(Py-bqdi)](ClO4), ([11]ClO4) [where Py-bqdi = N,N'-dipyridyl-o-benzoquinonedimine, acac = 2,4-pentanedionate, Ph-trpy = 4'-phenyl-2,2'-6',2'-terpyridine, bpy = 2,2'-bipyridine] is reported. The molecular structures of complexes 9-11ClO4 are authenticated by single crystal X-ray diffraction studies. The electronic structural properties of the complexes, in particular, the accessible oxidized/reduced forms of the complexes, are examined by using an array of analytical techniques (magnetic resonance, UV–Vis-NIR spectroscopy and electrochemistry). Comprehensive Density Functional Theory (DFT) calculations have also been carried out to provide additional support to the experimental work.

1. Introduction

Over the last few decades, N,N'-disubstituted 1,2-diaminobenzenes have gained profound interest owing to their expedient applications in various aspects of chemistry, for example, as a building block for supramolecular arrays [1,2], in synthesizing N-heterocyclic carbenes [3,4] and their analogues such as N-heterocyclic phosphinoniums [5], germynes, stannylenes [6,7], boroles [8,9] and plumbylenes [10,11] species to name a few. Apart from these notable applications, N,N'-disubstituted 1,2-diaminobenzenes derivatives have been considered as one of the preferred choices of ligand frameworks for transition metal complexes [12]. The most intriguing feature of N,N'-disubstituted 1,2-diaminobenzenes as a ligand is their ‘redox non-innocent’ behavior, a term given by Jørgensen [13] to ligands that have variable, energetically accessible levels that can actively participate in redox processes, giving rise to an apparent ambiguity in oxidation states. Starting from mere academic curiosities, the redox non-innocence of a ligand is now considered to be a fascinating electronic phenomenon and has become a well-appreciated avenue in coordination chemistry [14]. Another interesting development of redox non-innocent ligands is their ability to function as an ‘electron reservoir’ for assisting multi-electron transformations in metals that have otherwise limited redox activity [14b,h,j,15]. As such, N,N'-disubstituted 1,2-diaminobenzenes can undergo two successive one-electron oxidations, thereby offering variable oxidation states to the bonded metal atom. The diaminonic ligand, L can undergo one electron oxidation to form the o-diminosemiquinone radical (L o) and the latter can further endure one electron oxidation, thereby resulting into a fully oxidized o-diminoquinone (L o) (Fig. 1).

It is apparent that modification of the donor atoms or the substituent R in N,N'-disubstituted 1,2-diaminobenzenes can significantly alter the electronic structures of the resulting metal complexes. For example, when 2-aminothiophenol, where one of the donor atom was replaced with sulfur, was reacted with CpRuCl(PPh3)2, the sulfur atom was found to take part in the redox activity of the resulting complex ([PPh3]2RuCl(L)Cl (where, L = 6-iminocyclohexa-2,4-dienethione) (Chart 1, compound 1) [16]. Contrastingly, in case of complexes 2 and 3, where the flanking arms in o-phenylenediamine contain neutral sulfur donor atoms, the redox reactivity was solely localized on the o-phenylenediamine backbone and the sulfur being a neutral donor did not take part in the electron transfer processes [16,17]. Interesting redox behavior was also manifested when o-phenylenediamine was flanked with phenolate groups. For example, when tetra-dentate ligand,
N,N′-bis(3,5-di-tert-butyl-2-hydroxy-phenyl)-1,2-phenylenediamine, was reacted with [Cu(NCCH3)](ClO4) or Zn(BF4)2·2H2O, it was observed that the resulting complexes, 4 (M = Cu) and 5 (M = Zn) showed redox activity localized on both at the o-phenylenediamine backbone as well as on the flanking phenolate groups [18]. Similar results were also observed when the redox behavior of the Mo or Zr complexes of the same ligand were examined [19,20]. However, in case of complex 6, where the the flanking arms in o-phenylenediamine was changed to aniline groups the redox activity was only restricted to the pyridine (pap) in aniline incorporation of an acceptor group to the Ru and Os precursors. We anticipated that π-acceptor co-ligands such as 2,2′-bipyridine (bpy) in 7 and 2-(phenylazo)pyridine (pap) in 8 can extend their role to redox activity of the complexes in addition to their typical spectator role [12].

In the present work, we have incorporated two pyridine rings as flanking arms to o-phenylenediamine and have explored the redox innocent properties of the new ligand, namely N,N′-bis(2-pyridyl)benzene-1,2-diamine, H2L, with Ru and Os precursors. We anticipated that incorporation of a π-acceptor group to the flanking arms would significantly modulate the redox properties of the resulting complexes. It was further envisaged to compare the electronic structural properties of the synthesized complexes with similar reported complexes wherein different substituents were present in the flanking arms of o-phenylenediamine. It is worth mentioning that, although the synthesis of H2L was reported earlier [22], however, its ligation properties, to our knowledge, have not been explored yet. Thus, the synthesized complexes, 9-[11]ClO4 are of considerable interest with respect to their general coordination chemistry as well as the non-innocent behavior of the ligand.

### 2. Results and discussion

Ligand H2L was prepared by following the reported procedure wherein o-phenylenediamine was reacted with 2-bromopyridine at 195°C for 1 h [22]. The metal precursors cis-[Ru9(acac)2(2,4-pentanedionate)] [23], [Ru9(bpy)2Cl2] [24] and cis-[Os9(bpy)2Cl2] [25] (cis configuration with respect to chloride, pyridine and nitrogen atoms) [acac = 2,4-pentanedionato, Ph-trpy = 2′-phenyl-2,2′-6′,2″-terpyridine, bpy = 2,2′-bipyridine] were reported as the mononuclear complexes [Ru9(acac)2(Py-bqdi)], (9), [Ru9(Ph-trpy)(Py-bqdi)Cl] (10) and [Os9(bpy)2(Py-bqdi)](ClO4)1/2 (11)[ClO4], where Py-bqdi = N,N′-diphenyl-o-benzoxquinonediamine were synthesized in a single step reaction between the ligand (H2L) and the respective metal precursors; cis-[Ru9(acac)2(CH2CN)2], [Ru9(Ph-trpy)(Cl)3] and cis-[Os (bpy)2Cl2] respectively in the presence ofEt3N in polar protic solvent medium (e.g. ethanol or methanol) at elevated temperature (Scheme 1). All the synthesized complexes were purified by alumina column chromatography by a gradient elution with a dichloromethane/acetone/titrile mixture.

The identity of the complexes was validated using various analytical techniques like mass spectrometry (ESI-MS), conductivity, NMR and UV–Vis-NIR spectroscopy, which substantiate the structure of the complexes in their respective electronic states. The molar conductivities show 9 and 10 are non-electrolytes and [11]ClO4 is a 1:1 electrolyte. In the 1H NMR spectrum complex 9 exhibits aromatic proton resonances corresponding to the ligand (H2L) in the region of 6–8 ppm. A single resonance at 5.08 ppm can be ascribed to the methine proton at the acetylacetone backbone, while the methyl groups of the acetylacetone display singlet resonances at 1.86 ppm and 1.85 ppm respectively. On the other hand, complex [11]ClO4 exhibits overlapping proton resonances corresponding to bipyrindine and the ligand respectively in the range 6.5–8.3 ppm. The N–H resonance was not observed in the 1H NMR spectrum, however, s(N–H) is evident in the IR spectrum.

### 2.1. Structural elucidation

The identity of complex 9 was further validated by single crystal X-ray diffraction study. The single crystals of 9 were obtained from the slow evaporation of a solution of 9 in n-hexane/chloromethane mixture. An ORTEP view of complex 9 is shown in Fig. 2 and crystallographic data and structure refinement parameters are given in Table S1 (Supporting Information). The spatial arrangement of the Ru(III) ion is distorted octahedral and is defined by a N2O4 donor set. Of particular interest are the C1-N1 and C2-N2 distances, which are of 1.335(6) Å and 1.342(5) Å respectively. These bond distances are in good agreement with those observed [1.336(3) Å and 1.346(3) Å in [Ru9(acac)2(Pb-bqdi)] where Pb-bqdi = N,N′-diphenyl-o-benzoxquinonediamine [12]]. While comparing the C–N and C–C intra-ring bond distances in 9 with the literature values [12c,26,27], it can be inferred that in complex 9, the ligand is in the semiquinone state (L−). The Ru1-N1 [1.981(4) Å] and Ru1-N2 [1.991(4) Å] bond distances and N1-Ru1-N2 bite angle [79.19(18)°] in 9 are comparable to those observed in [Ru9(acac)2(Pb-bqdi)] [Ru1-N1 = 1.963(2) Å, Ru1-N2 = 1.982(19) Å and 2N1-Ru1-N2 = 80.10(9)°] [12]. The Ru-O(acac) bond lengths and associated angles are in good agreement with the data observed in related complexes [28].

An ORTEP view of complex 10 is shown in Fig. 3. Single crystals of compound 10 were obtained by slow evaporation of a n-hexane/dichloromethane solution. The geometry around Ru(II) ion is distorted octahedral wherein its coordination environment is completed by a N2Cl donor set. The chloride ligand is trans to the N2 atom with a trans angle of 172.9(3)°. The C1-N1 bond distance is 1.37(1) Å, which is on the longer side of the C–N double bond values and resembles more that of a C–N distance observed in the fully reduced diatomic catecholate form [27]. On the other hand, the C2-N2 distance of 1.368(1) Å corresponds to a typical C–N double bond. Again, the C1-N1 distance in 10 is considerably longer than the C–N distances [1.317(9) Å and 1.316(9) Å] observed in [Ru(trpy)(Cl)2(bqdi)]ClO4 [bqdi = o-benzoxquinonediamine; trpy = 2, 2′6′,2″-terpyridine] [29a]. Again, the C1-C6 bond length of 1.42 (1) Å is shorter than normal C–C single bonds. Hence, from these observations, it can be inferred that like in complex 9, the ligand in 10 is also in semiquinone state (L−). The Ru1-N1 and Ru1-N2 bond distances are 2.007(8) Å and 1.991 (7) Å respectively, which are in agreement with that of complex 9 [1.980(4) Å and 1.991 (4) Å] and [Ru(trpy)(Cl)2(bqdi)]ClO4 [1.985(6) Å and 1.991 (7) Å] [29a]. The N1-Ru2-N2 bite angle of 78.13(3)° is smaller than that observed in 9 [79.19(18)°]. The Ru1-C11 distance [2.404(2) Å] and Ru1-N1-Ru1 distance [2.456 (4) Å] of 10 are in good agreement with the data reported for related molecules [29].

The molecular structure of complex [11]ClO4 is shown in Fig. 4. Single crystals of complex [11]ClO4 were obtained by slow evaporation of its n-hexene/dichloromethane solution. The geometry of the Os(II) ion is distorted octahedral and is coordinated to one nitrogen atom (N1) of the o-phenylenediamine core, one nitrogen atom (N3) from the flanking pyridine group and two bipyridyl ancillary ligands. The remaining positive charge on the Os ion is balanced by a perchlorate.

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Fig. 1. Redox transformations of N,N′-disubstituted 1,2-diaminobenzenes.

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counter anion. Interestingly, the second N–H hydrogen of the o-phenylenediamine did not undergo deprotonation during the reaction and eventually did not take part in coordination to the metal center. The N1 atom and the pyridyl nitrogen (N3) make a four-membered chelating ring with the Os center with a N1-Os1-N3 bite angle of 62.0(1)°. It is worth noting that complex [11]ClO₄ is the first example of an osmium complex of any benzoquinonedimine ligand, which contains a four-membered chelating ring. Being part of the four-membered chelating ring, this bite angle is significantly smaller than the N1-Os1-N3 angle observed in Os(H₂)(HNC₆H₄NMe)(ΠPr₃)₂ [76.2(2)°] [26] and Os(H₂)(HNC₆H₄NH)(ΠPr₃)₂ [76.35(15)°] [30a], where the nitrogen atoms are part of five-membered chelating rings. The Os1-N1 and Os1-N3 bond distances are 2.146(3) and 2.090(3) Å respectively. The C1-N1 bond distance is 1.411(5) Å. While comparing with the related literature values [26–28], it can be inferred that this value clearly approaches that of a single bond, and hence the best description of [11]ClO₄ is [OsII(bpy)₂(LH⁻)Cl](ClO₄), where the negative charge is localized on the N1 atom. The Os-N (bpy) bond lengths and associated angles are in good agreement with the data observed in related Os(II) complexes [30].

2.2. Electrochemistry

Electrochemical techniques like cyclic voltammetry and differential pulse voltammetry provide a better perception about accessible redox states within the molecule. Compounds 9, 10 and [11] − demonstrate one oxidation (O1) and one (R1) or two successive reductions (R2 and R3) waves in the potential range 0.12–1.21 V and −0.43 to −1.71 V versus SCE in CH₃CN. The respective electrochemical parameters are represented in Fig. 5 and Table 1. Appreciable differences in the
potentials between the first oxidation (O1) and reduction process (R2), \(-E = 1.29 \text{ V}, 1.64 \text{ V} \) and \(1.56 \text{ V}, \) respectively for 9, 10 and 11, translate to a high value of the comproportionation constant \( (K_c) \) (\(10^{23}, 10^{27} \) and \(10^{26}\)), thereby indicating high stability of the native states. Depending on the nature of the donor/acceptor co-ligands, a considerable shift in potentials could be observed for the accessible charged states. In particular, the strong electron donating nature of the acac co-ligands in 9 makes the first oxidation easier and the first reduction

Fig. 2. Molecular structure of 9; thermal ellipsoids are set at the 50% probability level.

Fig. 3. Molecular structure of 10; thermal ellipsoids are set at the 50% probability level.

Fig. 4. Molecular structure of [11]ClO₄; thermal ellipsoids are set at the 50% probability level.

Fig. 5. Cyclic (black) and differential pulse (red) voltammograms of (a) 9 (b) 10 and (c) [11]ClO₄ in CH₃CN/0.1 M Et₄NClO₄. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
more difficult to access as compared to 10 owing to the π-accepting nature of the terpyridine co-ligand. Moreover, the oxidation potential in the pyridine containing benzoquinonediimine complex (9) shifts to a positive value as compared to the analogous phenyl containing benzoquinonediimine (Ph-bqdi) complex, [Ru(acac)2(Ph-bqdi)] [12i], while the reduction potentials shift to less negative values, an outcome which is attributed to the electron withdrawing nature of the pyridine ring.

In complex 10, the irreversible wave corresponding to the RuII/RuIII oxidation indicates that the oxidized species (10/10+) is not stable on the cyclic voltammetric scale. This is quite similar to the oxidation profile of the previously reported complex [Ru(trpy)(bqdi)] [29a]. The effect of the electron accepting nature of the pyridine ring of the pendant arm is evident from the change in electronic potentials as compared to corresponding trim/trpy [tpm = tris(pyrazolyl)methane, trpy = 2,2′:6,2′′-terpyridine] containing derivatives of benzoquinone-diimine [29a,31a]. The first reduction (R1; 10/10−) could be associated with the ligand backbone, while the successive reduction (R2; 10−/10−) takes place on trpy based orbitals. These assignments are validated by Mulliken spin density calculations (vide infra) and in agreement with that of the similar reported complexes [29a,31]. The difference in π-donation capability of osmium and bipyridine could be held accountable for the change in electronic potentials in complex 11. The negative charge derived from the anionic nitrogen atom is primarily responsible for the very low oxidation potential of complex 11+ resulting in the formation of a ligand centered radical, while successive reduction processes could be attributed to the presence of low-lying π*-acceptor orbitals of bipyridine. More precise assignment of oxidation states is discussed with the help of EPR spectroscopy in combination with theoretically computed Mulliken spin density values (vide infra).

### 2.3. EPR spectroscopy, spin density analysis and redox series

EPR spectroscopy serves as an indispensable tool for assessing contributions of metal or ligand or mixed metal–ligand of the singly occupied molecular orbitals of paramagnetic states. Hence, precise assignments of oxidation state can be done unambiguously with the help of EPR spectroscopy in combination with calculated spin densities. Quite expectedly, due to larger values of the spin–orbit coupling constant for the Ru/Os atom as compared to the C, H or N atoms, the g-values deviate significantly from the ideal value of 2.0023. The EPR spectra of electrochemically oxidized or reduced states have been recorded in a frozen solution of the samples in CH3CN at 77 K. Representative EPR spectra of paramagnetic states are illustrated in Fig. 6 and the values of the respective parameters have been summarized in Table 2. The theoretically calculated spin density diagram and respective values are given in Fig. 7 and Table 3 respectively.

Compound 9, designated as RuII/Pybq−, failed to display any EPR spectrum which might be attributed to the antiferromagnetic coupling between the low-spin Ru(III) (S = ½) and the ligand based radical (S = ½). This is clearly reflected in the DFT calculated [Broken symmetry (BS) analysis, Supporting Information] Mulliken spin density distributions of Ru: 0.216/0.939, Pybq(L): −0.203/1.012 in singlet/triplet energy states respectively. A preferential stabilization of the

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Table 1

<table>
<thead>
<tr>
<th>Complex</th>
<th>$E_{200}(V)$</th>
<th>$\Delta E_p$ (mV)</th>
<th>O2</th>
<th>O1</th>
<th>R1</th>
<th>R2</th>
<th>R3</th>
<th>$K_{c1}$</th>
<th>$K_{c3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>0.48(90)</td>
<td>-0.81(1 0 0)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>7.3 × 1021</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>1.21(90)</td>
<td>-0.43(90)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>6.2 × 1027</td>
<td>2.0 × 109</td>
</tr>
<tr>
<td>11[ClO4]</td>
<td>0.12(70)</td>
<td>-1.44 (80)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.7 × 1026</td>
<td>3.7 × 104</td>
</tr>
<tr>
<td>[Ru(acac)2(Ph-bqdi)]′</td>
<td>0.36(60)</td>
<td>-1.05(70)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>7.9 × 1023</td>
<td>-</td>
</tr>
<tr>
<td>[Ru(acac)2(bqdi)]′</td>
<td>0.53</td>
<td>-0.96</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.7 × 1025</td>
<td>-</td>
</tr>
<tr>
<td>[Ru(trpy)(bqdi)]′</td>
<td>1.32(90)</td>
<td>-0.54(70)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.27 (140)</td>
<td>-</td>
</tr>
<tr>
<td>[Ru(tpm)(bqdi)]′</td>
<td>0.82(80)</td>
<td>-0.79(80)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 2

<table>
<thead>
<tr>
<th>Complex</th>
<th>g</th>
<th>$g_1$</th>
<th>$g_2$</th>
<th>$g_3$</th>
<th>$&lt; g &gt; \pm 1$</th>
<th>$\Delta g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>-</td>
<td>2.369</td>
<td>2.136</td>
<td>1.828</td>
<td>2.122</td>
<td>0.541</td>
</tr>
<tr>
<td>10</td>
<td>2.003</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>112-</td>
<td>2.005</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

---
singlet state \([\text{BS}(1,1) \, S = 0]\) over the triplet state \((S = 1)\) could be attributed to significant energy difference between the two states. This is further evident by diamagnetic nature of the \(^1\)H NMR spectrum of 9 (vide supra). Upon oxidation, it exhibits the characteristic metal-based rhombic EPR signal corresponding to the Ru\(^{III}\) (d\(^5\)) state as confirmed from the <\(g\)> value of 2.122 and a large anisotropic parameter of 0.542. Moreover, the 80% contribution (as indicated by Mulliken spin density calculation) of metal spin in the oxidized state \(9^+\) adds further validation to the ligand-based transformation of \({\text{Pybq}}^+ \rightarrow \text{Pybq}^0\) leaving metal center as the sole contributor towards the overall spin.

Complex 10 exhibits a broad isotropic signal with a \(g_{\text{iso}}\) value of 2.003, which points towards the formation of a radical anion in the native state \((\text{Ru}^{III}(\text{Pybq}^\cdot))\). The irreversible nature of the oxidation process in the case of complex 10, precludes observation of any EPR spectrum upon oxidation. Upon reduction (R1), no signal was observed quite expectedly due to the doubly reduced dianionic ligand indicating a ligand-based first reduction \((\text{Pybq}^\cdot \rightarrow \text{Pybq}^{2\cdot})\). While, the successive reduction (R2; \(10^-/10^{2-}\)) takes place on trpy based orbitals, which is substantiated by Mulliken spin density calculations (Table S3, Supporting Information) and are in agreement with that of the similar reported complexes \([29a,31]\). The native state of compound \(11^+\) is EPR silent due to the diamagnetic nature of the ground state. The oxidized species, \(11^{2+}\) displays an isotropic EPR signal with a \(g\) value of 2.005 along with 71% ligand contribution to overall spin density indicating a ligand-based oxidation process. No EPR signals were observed upon reduction which is expected to be composed of bipyridine \((\text{bpy}^\cdot)\) based spin.

Based on these observations obtained by the combined studies of electrochemistry, theoretically formulated Mulliken spin density and EPR spectroscopy, the best possible representations of the redox formulation across the series of complexes \([9, 10, \text{and } 11^+]\) are depicted in Scheme 2. The native forms are marked in pink.

**Table 3**

DFT calculated Mulliken spin densities for paramagnetic forms of 9\(^n\), 10\(^n\) and 11\(^n\) (\(n = -1 \text{ to } +2\)).

<table>
<thead>
<tr>
<th>complexes</th>
<th>Ru/Os</th>
<th>Q(L)</th>
<th>bpy</th>
<th>trpy</th>
<th>acac</th>
</tr>
</thead>
<tbody>
<tr>
<td>(9^+(S = 1/2))</td>
<td>0.807</td>
<td>0.120</td>
<td>–</td>
<td>0.073</td>
<td></td>
</tr>
<tr>
<td>(9^-(S = 1/2))</td>
<td>0.408</td>
<td>0.578</td>
<td>–</td>
<td>0.014</td>
<td></td>
</tr>
<tr>
<td>(10(S = 1/2))</td>
<td>0.126</td>
<td>0.715</td>
<td>0.159</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>(11^{2+}(S = 1/2))</td>
<td>0.244</td>
<td>0.715</td>
<td>0.041</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>(11(S = 1/2))</td>
<td>0.260</td>
<td>–0.150</td>
<td>0.890</td>
<td>–</td>
<td></td>
</tr>
</tbody>
</table>

**Fig. 7.** DFT calculated Mulliken spin density plots of (a) \(9^+(S = 1/2)\) (b) \(9^-(S = 1/2)\) (c) \(10(S = 1/2)\), (d) \(11^{2+}(S = 1/2)\) and (e) \(11(S = 1/2)\).

**Scheme 2.** Assignments of oxidation states across the redox series of \(9^+, 10^\text{n}\) and \(11^\text{n}\) (native forms are marked in pink, the free radicals are depicted on red).
oxidation in CH₃CN/0.1 M Bu₄NClO₄. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 4

<table>
<thead>
<tr>
<th>Complex</th>
<th>λ, [nm] (ε [M⁻¹cm⁻¹])</th>
</tr>
</thead>
<tbody>
<tr>
<td>9⁺</td>
<td>270(17050), 319(9060), 529(10790)</td>
</tr>
<tr>
<td>9⁻</td>
<td>257(17740), 455(6860), 556(9350)</td>
</tr>
<tr>
<td>10⁺</td>
<td>284(6920), 317(4770), 521(3760)</td>
</tr>
<tr>
<td>[11]⁺</td>
<td>295(34940), 350(19330), 528(8290), 778(1900)</td>
</tr>
<tr>
<td>[11]⁺ˣ⁻</td>
<td>394(8600), 481(4300), 56(1730)</td>
</tr>
</tbody>
</table>

2.4. UV–Vis-NIR spectroscopy

The electronically accessible paramagnetic states of the complexes 9, 10 and 11 could be analyzed by controlled potential coulometry in association with UV–vis-NIR spectroscopy (Fig. 8). Multiple transitions observed in the region are summarized in Table 4, while the nature of the transitions could be assigned on the basis of the TD-DFT calculations (ESI). Compound 9 displays a moderately intense transition at 529 nm which can be described as ligand-to-metal charge transfer (LMCT) involving π-orbitals of the partially reduced ligand to dₓ orbitals of metals. While one electronic oxidation species 9⁺ exhibits Ru (dπ) → L(π⁻) MLCT band at 556 nm which further validates a ligand based oxidation process as stated before (vide supra). Quite obviously presence of the pyridine ring results in a hypsochromic shift of the band position by ~10 nm as compared to the phenyl substituted analogous compound [Ru(acac)₂(Ph-bqdi)] [12].

On the other hand compounds 10 and 11⁺ exhibit absorption bands with high intensity at 521 nm and 528 nm respectively corresponding to the characteristic metal to ligand charge transfer transitions (MLCT), while the appearance of several higher energy peaks can be assigned to ligand-to-ligand charge transfer (LLCT) transitions [12]. Complex 11⁺²⁻ displays a broad band corresponding to the Os(dπ) → L(π⁻) MLCT transition arising out of the generation of a possible radical at the ligand center.

It is worth mentioning that a slight disparity in position of the spectral bands on moving from 9 to 10 to [11]ClO₄ is mainly due to the variation in σ-donating (acac) and π-acceptor (trpy and bpy) capabilities of ancillary ligands.

3. Conclusion

A series of Ru and Os complexes has been synthesized by using the bidentate ligand N,N′-bis(2-pyridyl)benzene-1,2-diamine. The experimental information in combination with theoretical investigations point out the intricate details about the electronic structure formulation of benzoquinonediimine in the presence of π-acceptor pyridyl groups attached to NH arms. Although the exact valence structure formulation of the aforesaid benzoquinonediimine ligand has remained a point of debate in the literature, herein we have highlighted the possible redox states of the metals as well as the ligands in all three complexes. It is observed that due to the incorporation of the π-acceptor pyridyl group, a minor variation in the electronic properties of [Ru(acac)₂(Py-bqdi)] has been observed in comparison to that of the similar reported complexes [12–j,29a,31]. However, due to the combined effect of a π-acceptor ‘ph-trpy’ co-ligand as well as pyridyl side arms, the effects were more pronounced in [Ru(Ph-trpy)(Py-bqdi)]. The osmium complex, [Os(bpy)₂(Py-bqdi)]ClO₄ also shows interesting electronic behaviour, wherein it makes use of the negative charge of the mono deprotonated ligand in the native form. Here, the electrochemically induced oxidations are found to be ligand based (71%), while the reductions are purely bpy based (89%). Complex [Os(bpy)₂(Py-bqdi)]ClO₄ is found to be interesting from the structural point of view, as it involves the formation of a four-membered chelate ring of the ligand with Os metal. It is noteworthy that the formation of a four-membered chelation ring with Os metal center is the first of its kind for any benzoquinonediimine ligand.

4. Experimental section

All the reactions were performed under nitrogen atmosphere by using standard Schlenk techniques and were occasionally monitored by using thin layer chromatography (TLC). The starting materials and solvents were purchased from commercial sources. Solvents were purified by standard techniques.¹H (400 MHz and 500 MHz) NMR spectra were recorded on Bruker AV 400 MHz and Bruker AV 500 MHz spectrometers at 25 °C. Chemical shifts are cited with respect to Me₄Si as an internal standard for ¹H NMR. Electron spray mass spectra (ESI-MS) were carried out using a Q-tof micro (YA-105) mass spectrometer. The electrical conductivities were measured by an autoranging conductivity meter (Toshcon Industries, India). The EPR spectra were recorded on a Bruker EMX Plus instrument. A PAR model 273A electrochemistry system was used to carry out the cyclic voltammetric and differential pulse voltammetric measurements of the complexes. Platinum wire working and auxiliary electrode and an aqueous saturated calomel reference electrode (SCE) were used in a three-electrode configuration. Tetraethylammonium perchlorate (TEAP) was used as the supporting electrolyte (substrate concentration = 10⁻³ M; standard scan rate 100 mVs⁻¹). The half-wave potential E½ was set to equal 0.5(Epa + Epc), in which Epa and Epc are anodic and cathodic cyclic voltammetry peak potentials, respectively. A platinum wire-gauze working electrode was used for the constant potential coulometry experiments.

4.1. Synthesis of [Ru(acac)₂(Ph-bqdi)], 9

A mixture comprising H₂L [22] (0.038 g, 0.144 mmol) and NET₃ (0.031 g, 0.306 mmol) in 25 mL EtOH was stirred at room temperature for 15 min under a nitrogen atmosphere. The metal precursor, cis-[Ru (acac)₂(CH₃CN)₂] [23] (0.055 g, 0.144 mmol) in 15 mL EtOH was added to the reaction mixture which was refluxed for 6 h. After completion of the reaction, solvents were removed under vacuum to get the crude product. The purification was done on a neutral alumina column and the pink colored compound corresponding to 9 was obtained by
using a CH$_2$Cl$_2$/CH$_3$CN (20:1) solvent mixture as eluent. 

Yield: 0.068 g (84%). m. p. 157–159 °C. MS (ESI+, CH$_3$CN): m/z ([M + H]$^+$) = 561.12; Found: 561.12. H NMR in CDCl$_3$ (δ/ppm (J/Hz)) = 8.46 (dd, J = 4.9, 1.2 Hz, 2H), 7.73 (td, J = 7.8, 1.9 Hz, 2H), 7.69–7.57 (m, 2H), 7.44 (d, J = 8.0 Hz, 2H), 7.30–7.22 (m, 2H), 6.78–6.75 (m, 2H), 5.08 (s, 2H), 1.87 (d, J = 3.9 Hz, 6H), 1.85 (s, 6H). 

Molar conductivity ($\Lambda_m$ (Ω$^{-1}$ cm$^{-2}$ mol$^{-1}$)), CH$_3$CN: 8. Anal. Calc. for C$_{36}$H$_{29}$ClN$_8$O$_4$Os: C, 50.08; H, 3.39; N, 12.98. 

4.2. Synthesis of [Ru(Ph-trpy)(Ph-bqdi)(Cl)], 10 

A methanolic solution (15 mL) of H$_2$L [22] (0.056 g, 0.213 mmol) and Et$_3$N (0.045 g, 0.448 mmol) was stirred at room temperature for 15 min. The precursor complex, [Ru(Ph-trpy)Cl$_2$] [24] (0.110 g, 0.213 mmol) in 10 mL CH$_2$OH was added followed by a heating at 55–60 °C for 4 h. The resulting purple colored solution was then evaporated under reduced pressure to obtain a dark colored solid which was then subjected to a neutral alumina column. The desired brown color band was eluted by a subsequent addition of metal precursor, [Os(bpy)$_2$Cl$_2$] [25] (0.050 g, 0.190 mmol) in 10 mL CH$_3$OH was added followed by a heating at 100 °C for 2 h. The solution turned brown to deep brown. After completion of the reaction, the solution was evaporated and the crude reaction mixture was subjected to a neutral alumina column. The desired brown complex 10 was obtained by using a CH$_2$Cl$_2$/CH$_3$CN (5:1) solvent mixture as eluent. 

Yield: 0.093 g (62%). m. p. 184 °C. MS (ESI+, CH$_3$CN): m/z ([M + H]$^+$) = 714.16; Found: 714.16. 


A mixture containing H$_2$L [22] (0.050 g, 0.190 mmol) and Et$_3$N (0.040 g, 0.400 mmol) was stirred for 15 min followed by a subsequent addition of metal precursor, [Os(bpy)$_2$Cl$_2$] [25] (0.109 g, 0.190 mmol). The resulting mixture was then refluxed overnight. The color of the solution gradually changes from reddish-brown to deep brown. After completion of the reaction, the solution was evaporated and the crude reaction mixture was subjected to a neutral alumina column. The desired brown color band was eluted by a CH$_2$Cl$_2$/CH$_3$CN (4:1) solvent mixture and evaporated to obtain the pure complex [11]ClO$_4$. 

Yield: 0.114 mg (69%). m. p. 197 °C. MS (ESI+, CH$_2$Cl$_2$): 114. Anal. Calc. for C$_{37}$H$_{27}$ClN$_7$Ru: C, 62.93; H, 3.85; N, 12.77. 

References 

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Appendix A. Supplementary data 

CCDC 1941891-1941893 (Compounds 9-[11]ClO$_4$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre. 

Computational details, NMR spectra, ESI-MS spectra and single X-ray structural parameters are given as Supporting Information. 

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ica.2019.111913.