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Electrochemistry at Very Positive Potentials in Liquid SO_2. Mononuclear Ru^{II} and Os^{II} Polypyridine Complexes

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Introduction

In the past few years Ru^{II} and Os^{II} polypyridine complexes containing bipyridine and dipyridylpyrazine as ligands have been widely studied from the photophysical and electrochemical points of view.[1] In fact, they can be used as building blocks to synthesize photochemical and photoelectrochemical supramolecular devices[2] capable of performing important functions, like information storage[3] and conversion of solar energy into electricity or fuels.[4]

To understand fully the properties of the more complex polynuclear species and to predict their electrochemical and photophysical behavior, it is of fundamental importance to study the corresponding properties of their subunits, i.e., the mononuclear complexes.

Herein we report the electrochemical behavior in liquid SO_2 of five mononuclear Ru^{II} and Os^{II} complexes of general formula $[M(bpy)_n(dpp)_{3-n}]^{2+}$ ($M = Ru^{II}, Os^{II}$; $n = 0, 2, 3$; bpy is 2,2′-bipyridine, and dpp is a dipyridylpyrazine ligand) and of the $[Ru(bpy)_2(2,3\text{-Medpp})]^{3+}$ complex (2,3-$Medpp^+$ = 2-[2-(1-methylpyridiumyl)]-3-(2-pyridyl)pyrazine). The structural formulas of the ligands are reported in Figure 1. Liquid SO_2 has been used, because this solvent, containing a suitable supporting electrolyte, such as $(TBA)AsF_6$, offers the widest known anodic range for electrochemical studies.[5]

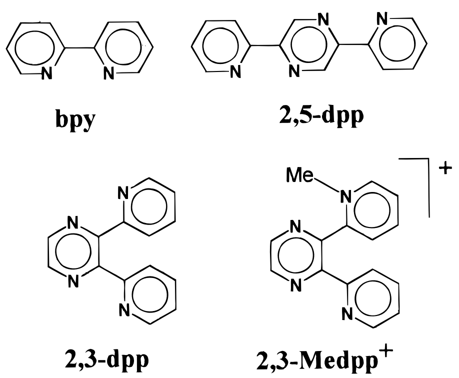

Figure 1. Structural formulas of the ligands 2,2′-bipyridine (bpy), 2,5- and 2,3-bis(2-pyridyl)pyrazine (2,5- and 2,3-dpp), and 2-[2-(1-methylpyridiumyl)]-3-(2-pyridyl)pyrazine (2,3-$Medpp^+$).

Experimental Section

The synthesis of all the investigated complexes has been previously reported.[1a,b,d,6] All of the experiments were carried out in liquid SO_2 at −70 °C. Procedures and apparatus have been described elsewhere.[5] The potentials reported are referred to SCE by measuring the AgQRE potential with respect to the 9,10-diphenylanthracene (DPA/DPA^+) couple.[5]

Digital simulations were performed as described elsewhere.[7]

Results and Discussion

Ru^{II} Complexes. The cyclic voltammogram (CV) of $[Ru(bpy)_2(2,3\text{-dpp})]^{2+}$ is shown in Figure 2A. Peaks I_a and II correspond to Nernstian and chemically reversible one-electron transfers, while III is a Nernstian one-electron oxidation with some degree of chemical irreversibility (Table 1). If the potential is scanned to more positive values (3.9 V) (Figure 2B), (i) an irreversible, greater than one-electron, oxidation occurs (IV); (ii) a new cathodic peak, I_c*, appears; (iii) I_a is no longer reversible ($i_{pc}(I_c)/i_{pa}(I_a) < 1$). The irreversibility of IV is ascribed to the occurrence of a chemical reaction, whose product gives rise to I_c*. The ratio $i_{pc}(I_c^*)/i_{pc}(I_c)$ is enhanced by increasing either scan rate (v) or reversal potential value. The anodic partner (I_a*) of I_c* is observed in a second scan performed without the renewal of the diffusion layer (Figure 2D). When the reversal potential ≥4.2 V, peaks I_c^*/I_a^* completely replace the original I_c/I_a and a substantial lowering of IV is observed.

The CV of $[Ru(bpy)_2(2,5\text{-dpp})]^{2+}$ is almost identical to that of $[Ru(bpy)_2(2,3\text{-dpp})]^{2+}$ (Table 1). Peak IV is, however, significantly shifted to less positive potentials and corresponds to a one-electron transfer. Moreover at variance with $[Ru(bpy)_2(2,3\text{-dpp})]^{2+}$, inclusion of IV in the anodic scan does not give rise to the I_c^*/I_a^* couple. These are instead observed only if

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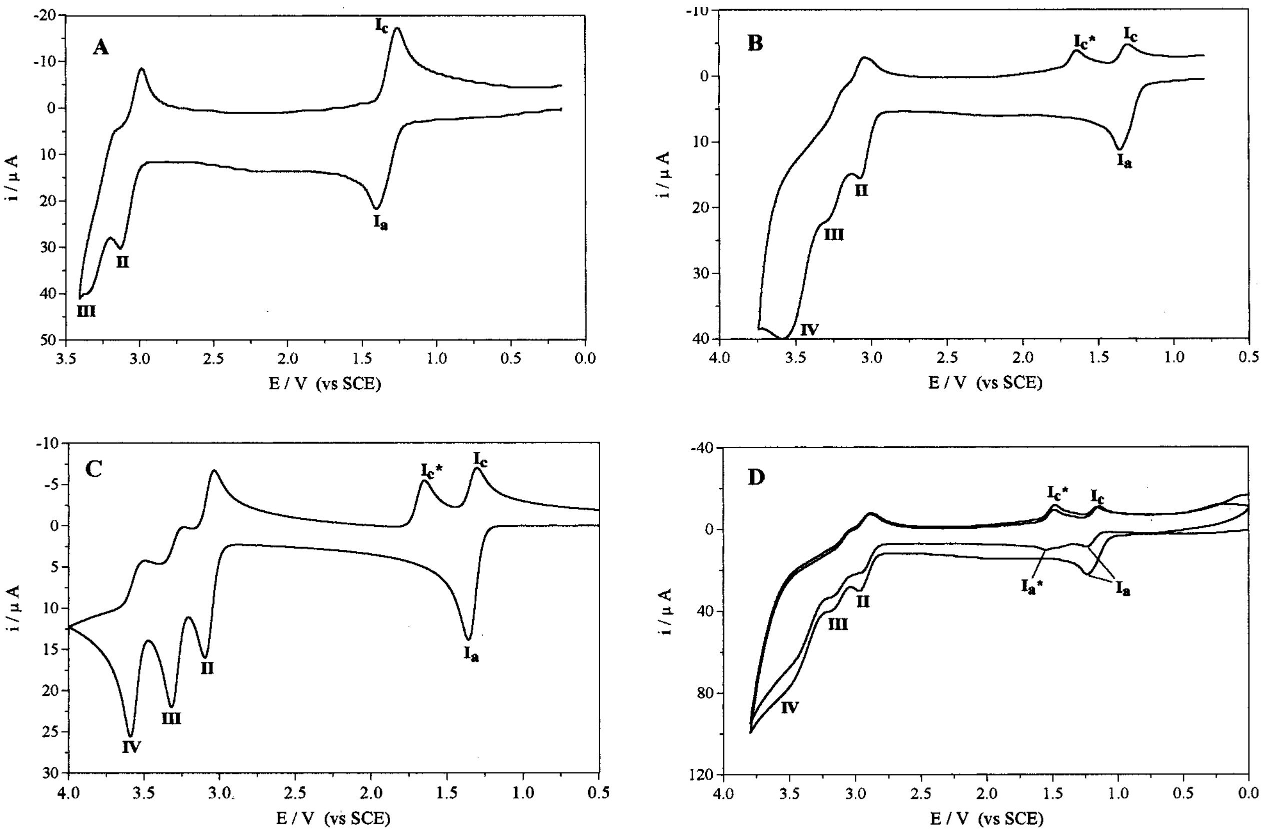


Figure 2. Cyclic voltammograms of 1 mM $[Ru(bpy)_2(2,3\text{-}dpp)](PF_6)_2$ in liquid SO_2/0.1 M $(TBA)AsF_6$ at −70 °C. Pt working electrode, $v = 2$ (A) and (D), 0.5 V/s (B). (D) The second cycle was performed without renewal of the diffusion layer. (C) Digital simulation for the system and conditions reported in B, see text.

Table 1. Half-Wave Potentials, Expressed in V ($E_{1/2}$ Values, Unless Otherwise Noted), for the Mononuclear Complexes Studied in Liquid SO_2 at −70 °C vs SCE[a]

complex	I	II	III	IV
$[Ru(bpy)_3]^{2+}$	1.26	3.12	3.50	≈4.4^c
$[Ru(bpy)_2(2,3\text{-}dpp)]^{2+}$	1.33 1.68^b	3.07	3.26	≈3.7^c
$[Ru(bpy)_2(2,3\text{-}Medpp)]^{3+}$	1.45 1.80^b	3.24	≈3.6^c	≈3.9^c
$[Ru(2,3\text{-}dpp)_3]^{2+}$	1.78	≈3.7^c		
$[Ru(bpy)_2(2,5\text{-}dpp)]^{2+}$	1.33 1.65^b	3.03	3.22	≈3.5^c
$[Os(bpy)_3]^{2+}$	0.83	2.47	3.57	≈4.0^c
$[Os(bpy)_2(2,3\text{-}dpp)]^{2+}$	0.94 1.37^b	2.56 2.74^b	≈3.6^c	≈4.0^c
$[Os(2,3\text{-}dpp)_3]^{2+}$	1.35	2.99	≈3.9^c	

[a] Roman numbers I−IV refer to the $E_{1/2}$ (except for the values indicated with c) of different redox steps. $E_{1/2}$ values are obtained either by averaging the cathodic and anodic peak potentials or by digital simulation. [b] Half-wave potential corresponding to the new species produced during the anodic scan to very positive values, see text. [c] Anodic peak potentials, E_{pa}.

the potential is scanned well beyond peak IV (≥4.0 V), where significant oxidation of supporting electrolyte (which is the anodic limiting process in liquid SO_2[5]) occurs.

The complex $[Ru(bpy)_2(2,3\text{-}Medpp)]^{3+}$ shows electrochemical properties very similar to those of $[Ru(bpy)_2(2,3\text{-}dpp)]^{2+}$, although all the oxidations are shifted toward more positive values (Figure 3 and Table 1). Also in this case, a peak, equivalent to I_c* in Figure 2B, appears if the potential is scanned to the fourth oxidation.

For $[Ru(2,3\text{-}dpp)_3]^{2+}$, the CV performed under the conditions of Figure 2B shows a first partially chemical irreversible oxidation, I_a, and an unresolved multielectronic irreversible peak (Table 1). Partial irreversibility of the first peak is also observed, although to a lesser extent, when the anodic scan is reversed just after I_a. In acetonitrile this process is fully reversible,[1d,e] thus indicating that the chemical reaction following I_a in $[Ru(2,3\text{-}dpp)_3]^{2+}$ involves SO_2.

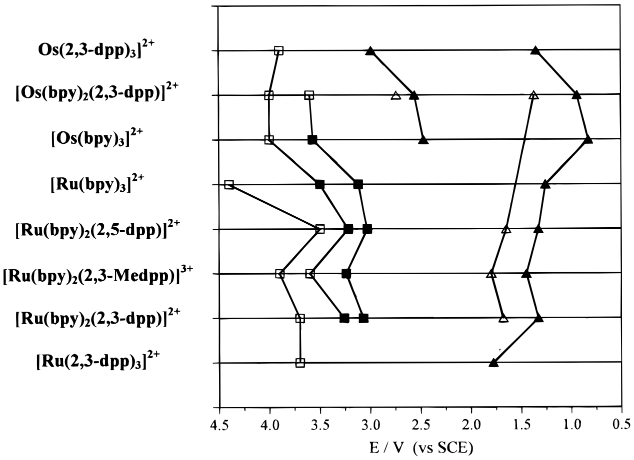
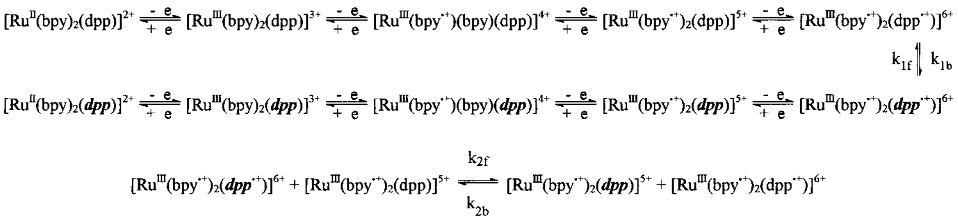


Figure 3. Comparison of the redox potentials for the mononuclear complexes studied in 0.1 M $(TBA)AsF_6/SO_2$ (T = −70 °C). (▲) $E_{1/2}$ values for normal metal oxidations. (△) New, metal-centered, electrochemical processes following oxidation at very positive potentials, see text. (■) Ligand oxidations. (□) E_{pa} values for ligands oxidations at very positive potentials.

Redox Site Locations. In discussing the electrochemical properties of these complexes a localized valence description of Ru^{II} and Os^{II} polypyridine complexes is considered,[2] i.e., redox processes can be classified as metal- or as ligand-centered.

The first oxidation process of the ruthenium complexes is attributed to Ru^{II}/Ru^{III} oxidation, as already reported for [Ru-

Scheme 1



$$[\mathrm{Ru^{II}(bpy)_2(dpp)}]^{2+} \xrightleftharpoons[+\,e]{-\,e} [\mathrm{Ru^{III}(bpy)_2(dpp)}]^{3+} \xrightleftharpoons[+\,e]{-\,e} [\mathrm{Ru^{III}(bpy^{\bullet+})(bpy)(dpp)}]^{4+} \xrightleftharpoons[+\,e]{-\,e} [\mathrm{Ru^{III}(bpy^{\bullet+})_2(dpp)}]^{5+} \xrightleftharpoons[+\,e]{-\,e} [\mathrm{Ru^{III}(bpy^{\bullet+})_2(dpp^{\bullet+})}]^{6+}$$

$$k_{1f} \; \big\| \; k_{1b}$$

$$[\mathrm{Ru^{II}(bpy)_2(}\boldsymbol{dpp}\mathrm{)}]^{2+} \xrightleftharpoons[+\,e]{-\,e} [\mathrm{Ru^{III}(bpy)_2(}\boldsymbol{dpp}\mathrm{)}]^{3+} \xrightleftharpoons[+\,e]{-\,e} [\mathrm{Ru^{III}(bpy^{\bullet+})(bpy)(}\boldsymbol{dpp}\mathrm{)}]^{4+} \xrightleftharpoons[+\,e]{-\,e} [\mathrm{Ru^{III}(bpy^{\bullet+})_2(}\boldsymbol{dpp}\mathrm{)}]^{5+} \xrightleftharpoons[+\,e]{-\,e} [\mathrm{Ru^{III}(bpy^{\bullet+})_2(}\boldsymbol{dpp}^{\bullet+}\mathrm{)}]^{6+}$$

$$[\mathrm{Ru^{III}(bpy^{\bullet+})_2(}\boldsymbol{dpp}^{\bullet+}\mathrm{)}]^{6+} + [\mathrm{Ru^{III}(bpy^{\bullet+})_2(dpp)}]^{5+} \xrightleftharpoons[k_{2b}]{k_{2f}} [\mathrm{Ru^{III}(bpy^{\bullet+})_2(}\boldsymbol{dpp}\mathrm{)}]^{5+} + [\mathrm{Ru^{III}(bpy^{\bullet+})_2(dpp^{\bullet+})}]^{6+}$$

(bpy)$_2$(2,3-dpp)]$^{2+}$ and [Ru(bpy)$_2$(2,5-dpp)]$^{2+}$ in acetonitrile.[1a,d,e] The positive shift with respect to [Ru(bpy)$_3$]$^{2+}$ (Table 1, Figure 3) derives from the stronger electron withdrawing character of dpp compared to bpy.[1b] The oxidation of coordinated bpy or dpp is expected to occur at much more positive potentials. In fact, the chemical irreversible oxidation of uncoordinated bpy in SO$_2$ is at 2.0 V (E_{pa})[8] and that of 2,3-dpp at about 2.1 V (E_{pa}); a positive shift for this process is expected upon metal coordination, as already observed for bpy.[8] Analogously to [Ru(bpy)$_3$]$^{2+}$, the further oxidation of metal would not be observed and peaks II and III of the heteroleptic complexes are rather attributed to the successive one-electron oxidation of bpy's and IV to that of dpp. In fact, both 2,3- and 2,5-dpp are more difficult to oxidize because their π orbitals lie lower in energy than in bpy (in 2,3-Medpp^{+} such orbitals are further stabilized by the positive charge). In line with the above attributions: (i) peaks II and III coincide for the [Ru(bpy)$_2$(dpp)]$^{2+}$ complexes and they are located in the same potential region of the corresponding processes in [Ru(bpy)$_3$]$^{2+}$; (ii) the first ligand-centered oxidation in [Ru(2,3-dpp)$_3$]$^{2+}$ is shifted positive with respect to bpy-containing complexes. Oxidation of dpp is found to occur at less positive potentials in [Ru(bpy)$_2$(2,5-dpp)]$^{2+}$ than in [Ru(bpy)$_2$(2,3-dpp)]$^{2+}$ (Table 1, Figure 3). Although caution has to be exerted in considering potential shifts relative to (chemically) irreversible redox processes, a possible explanation resides in the distortion of 2,3-dpp geometry, tilting the uncoordinated pyridine ring out of the plane containing the pyrazine and the coordinated pyridine.[1a] Such distortion makes its π orbitals less extended than in 2,5-dpp: 2,3-dpp would therefore turn out to be less capable of stabilizing the positive charge and therefore more difficult to oxidize than 2,5-dpp.

Chemical Reaction Following dpp Oxidation. The 2,3- or 2,5-dpp ligands are involved in this mechanism. Indeed, I$_c$* and I$_a$* are observed only when the potential is scanned to or beyond dpp oxidation, and [Ru(bpy)$_3$]$^{2+}$ does not show this peak.[9] The experimental observations that the I$_c$*/I$_a$* redox couple ($E_{1/2} = 1.68$ V in [Ru(bpy)$_2$(2,3-dpp)]$^{2+}$) is close to the I$_c$/I$_a$ couple ($E_{1/2} = 1.33$ V) and the corresponding peaks have related heights support the hypothesis that I$_c$*/I$_a$* corresponds to a Ru^{II}/Ru^{III} couple in a modified ligand environment. Since the oxidation of 2,3- or 2,5-dpp weakens the metal−N bond, a possible chemical reaction following the dpp oxidation could be the complete loss of the dpp ligand or the breaking of only one Ru−N bond. The first hypothesis can be discarded because in Figure 2D the second cycle shows the 2,3-dpp oxidation peak (IV) unchanged in comparison to the first cycle, while the oxidation process involving free 2,3-dpp would be at about 2.1 V. The second hypothesis seems to be the most likely, also considering that breaking of a Ru−N bond in chelating polypyridine Ru complexes often occurs photochemically.[10] Any attempt to characterize the product of the hypothesized reaction further, performing a controlled potential electrolysis, failed.

Further insights into the oxidation mechanism for the heteroleptic Ru complexes were obtained by performing the digital simulations of the CV curves according to Scheme 1, where ***dpp*** is the dpp ligand involved in the chemical reaction. The homogeneous electron-transfer reaction between [Ru^{III}(bpy$^{\bullet+}$)$_2$(***dpp***$^{\bullet+}$)]$^{6+}$ and [Ru^{III}(bpy$^{\bullet+}$)$_2$(dpp)]$^{5+}$ was introduced in the mechanism to reproduce correctly the experimental ratio of i_{pc}(I$_c$*)/i_{pc}(I$_c$). The enhancement of this ratio on increasing v demonstrates that the two forms of Ru^{III} complexes are in equilibrium. This ratio also gradually increases if the reversal potential is made more and more positive beyond IV: I$_c$ eventually disappears, and only I$_c$* is observed (with a height comparable to I$_a$). Furthermore, IV is greatly decreased during the second scan probably because of an irreversible reaction between the oxidized dpp ligand and a product of oxidation of the supporting electrolyte. This reaction would lower the rate of interconversion between the two forms of Ru^{III} complexes. In the simulation, the partial chemical irreversibility associated with the reduction of the ligands (in particular, peaks III and IV), not shown in Scheme 1, was also taken into account.

The relevant parameters used in the simulations for [Ru(bpy)$_2$(2,3-dpp)]$^{2+}$ (Figure 2C) were $k_{1f} = 10^5$ s^{-1}, $k_{1b} = 10$ s^{-1}, $k_{2f} = 5 \times 10^3$ M^{-1} s^{-1}, $k_{2b} = 10$ M^{-1} s^{-1}, and $E_{1/2}$ values reported in Table 1. The agreement between the simulated and the experimental curves can be considered satisfactory[11] for all the peaks except IV. A better fit for the height of the last peak can be obtained by considering the contribution of the supporting electrolyte oxidation and a catalytic mechanism, probably involving the solvent, as proposed for [Ru(bpy)$_3$]$^{2+}$.[5]

Os^{II} Complexes. A typical CV for [Os(bpy)$_2$(2,3-dpp)]$^{2+}$ is shown in Figure 4A. The two reversible peaks I and II are Nernstian one-electron transfers. If the potential is scanned to 4 V, the CV (Figure 4B) shows a further multielectronic and partially irreversible peak (III). At the same time, in the reverse scan, two new cathodic peaks appear (II$_c$* and I$_c$*) reminiscent of the behavior observed in the CV of the Ru analogue.

The CV of [Os (2,3-dpp)$_3$]$^{2+}$ shows two not completely reversible peaks upon scanning the potential to 3 V. When the potential is scanned to more positive values (4 V), an irreversible

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(9) [Ru(2,3-dpp)$_3$]$^{2+}$ does not show any peak equivalent to I$_c$* in Figure 2B when the potential to the ligand oxidations is scanned. However, this complex is not very stable in SO$_2$, likely because of the reactivity introduced by the presence of three 2,3-dpp ligands.

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(11) After the first anodic peak, the current remains significantly higher than expected for a diffusion-controlled process. This behavior is characteristic of all the complexes studied in liquid SO$_2$ and is unobserved in acetonitrile, for example. The simulation suggests two possible explanations: (i) the presence of a very slow catalytic mechanism involving the oxidized complex and a species in great concentration, such as the solvent or the supporting electrolyte, and (ii) an inadequate applicability of the theory of semi-infinite linear diffusion to the actual situation of a finite diffusion layer of approximately 50 μm thickness in SO$_2$. This result is in agreement with the low viscosity of liquid SO$_2$ compared to acetonitrile. For sake of simplicity, such effects were not included in the simulation reported in this work.

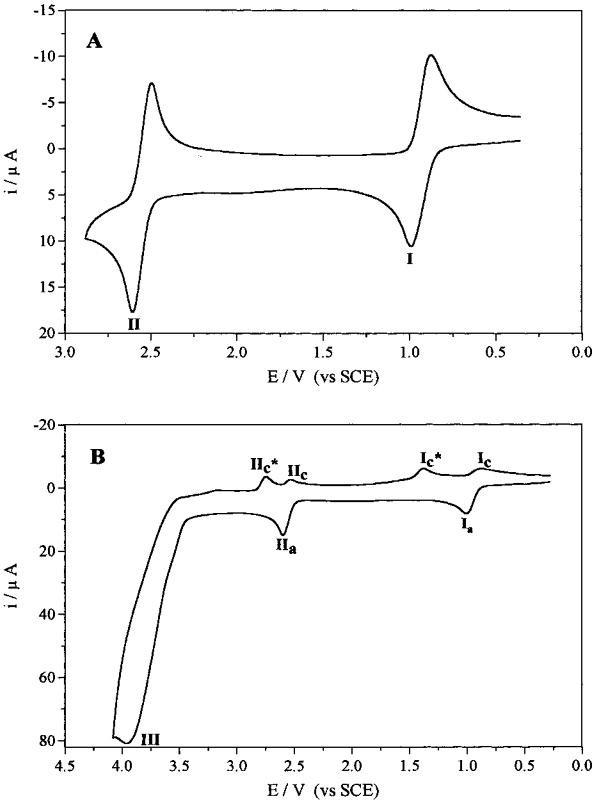

Figure 4. Cyclic voltammograms of 1 mM $[Os(bpy)_2(2,3\text{-}dpp)](PF_6)_2$ in liquid SO_2/0.1 M (TBA)AsF_6 at −70 °C. Pt working electrode, v = 0.5 V/s.

peak with an i_{pa} value about three times larger than the first one appears and the degree of chemical irreversibility of the first and second peak increases.

On the basis of the reported behavior of $[Os(bpy)_3]^{2+}$,[5] we assign the first two oxidations to the Os ion (Os^{II}/Os^{III} and Os^{III}/Os^{IV}) and the following ones to the ligands. Analogous to the corresponding Ru^{II} complexes, a positive shift in the metal oxidations is observed upon substitution of bpy with 2,3-dpp ligands (Figure 3).

For the Os complexes the ligand oxidations occur at more positive potentials and are less resolved than in the corresponding Ru^{II} complexes, so it is difficult to distinguish between bpy and 2,3-dpp oxidation, but a similar behavior is assumed. In particular, for $[Os(bpy)_2(2,3\text{-}dpp)]^{2+}$, III may involve successive one-electron oxidations of the two bpy's (the first corresponding to the barely visible shoulder at 3.6 V) and of the 2,3-dpp, although for $[Os(bpy)_3]^{2+}$ only two bpy oxidations were observed.[5] In fact, the appearance of I_c* and II_c* for $[Os(bpy)_2(2,3\text{-}dpp)]^{2+}$, scanning the potential to the end of III, proves that the oxidation of the 2,3-dpp ligand takes place, analogous to the corresponding Ru^{II} complex.[12]

To rationalize I_c* and II_c* for $[Os(bpy)_2(2,3\text{-}dpp)]^{2+}$ (Figure 4B), we note that they are near (slightly more positive than) the normal Os reductions, as already pointed out for the corresponding Ru complex. The hypothesis that they correspond to reductions of the metal ion in a modified ligand environment is also supported by the equality of the number of these new peaks (1 for Ru complexes and 2 for Os ones) and that of the usual metal oxidations. Therefore, a mechanism analogous to that for $[Ru(bpy)_2(2,3\text{-}dpp)]^{2+}$, but with two successive reductions of the product, can be used to simulate this behavior.

Conclusions

The heteroleptic Ru^{II} mononuclear complexes studied show a metal-centered followed by three ligand-centered oxidations, while for the Os^{II} analogues two metal oxidations are followed by less resolved ligand-centered processes.

The replacement of bpy ligands with dpp's displaces the metal-centered oxidations toward more positive potentials because of the higher electron-withdrawing character of dpp with respect to bpy. Moreover, for all the compounds of general formula $[M(bpy)_2(dpp)]^{2+}$, if the potential is scanned to very positive values (4 V), the last dpp-centered oxidation starts a chemical reaction, whose product displays metal-centered reductions (one in the Ru complexes and two in the Os ones) at more positive potentials than the initial species.

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(12) In line with this hypothesis, upon increasing v, peak III current function does not tend to the value expected for a two-electron-transfer process, in contrast to the reported behavior of $[Os(bpy)_3]^{2+}$.[5]