January, 1982] NOTES *Bull. Chem. Soc. Jpn.*, **55**, *327—328 (1982)*

A Voltammetric Study of the Reduction of Ruthenium(II) Complexes with Mixed Ligands

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(Received May 25, 1981)

Synopsis. Each cyclic voltammogram for the reduction of $[Ru(bpm)_3]^{2+}$ (bpm=2,2′-bipyrimidine) and $[Ru(bpm)L_2]^{2+}$ (L=2,2′-bipyridine and dimethyl derivatives) exhibits three reversible one-electron steps. The relation between the half-wave potentials of the complexes and those of ligands suggests that the lowest redox orbital of $[Ru(bpm)L_2]^{2+}$ should be localized on a single bpm molecule.

We have previously reported cyclic voltammograms for the reduction of complexes of the $[M(II)L_3]$ and $[M(II)L_2]$ forms with Fe and Ru as M and 2,2-bipyridine (bpy) and some other polypyridines as L.[1–4] The tris(or bis) complexes had one or two sets of three (or two) nearly neighbouring reduction steps. They were all reversible one-electron steps whose half-wave potentials ($E^{\mathrm{red}}_{1/2,\mathrm{C}}$) were related to the reversible half-wave potentials for the first reduction steps of the ligands ($E^{\mathrm{red}}_{1/2,\mathrm{L}}$) by the following equation:[1]

$$E^{\mathrm{red}}_{1/2,\mathrm{C}} = E^{\mathrm{red}}_{1/2,\mathrm{L}} + \mathrm{const.} \qquad (1)$$

This finding led us to the conclusion that the excess electrons over d^6 should be added to the ligand π^*-orbitals or, strictly speaking, that the redox orbitals should be molecular orbitals to which ligand π^*-orbitals make a predominant contribution. The characteristic patterns of the cyclic voltammograms suggested, furthermore, that the redox orbitals of the tris(or bis) complexes are probably three(or two)-fold degenerate. Molecular orbital calculations of the energies of the redox orbitals led to the same conclusion.[5] The present work is an extension of these works; it deals with mixed-ligand complexes.

The $[Fe(bpm)_3(PF_6)_2]$[6] (bpm=2,2′-bipyrimidine), $[Ru(bpm)_3(PF_6)_2]$[7,8] and $[Ru(bpm)(bpy)_2(PF_6)_2]$[7,9] complexes were prepared by the literature methods, while $[Ru(bpm)L_2(PF_6)_2]$ (L=4,4′-dimethyl-2,2′-bipyridine (4-dmbpy) and 5,5′-dimethyl-2,2′-bipyridine (5-dmbpy) were prepared by a method similar to that was used for $[Ru(bpm)(bpy)_2(PF_6)_2]$. The $[Ru(4\text{-}dmbpy)_3(ClO_4)_2]$ and $[Ru(5\text{-}dmbpy)_3(ClO_4)_2]$ complexes were described previously.[1] Cyclic voltammograms for the reduction of these complexes were obtained on a platinum working electrode with an acetonitrile base solution containing 0.1 M (1 M= 1 mol dm^{-3}) tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) at room temperature, unless otherwise noted. A $Ag/AgNO_3$(sat.) electrode was used as the reference electrode. The rate of potential sweep was 0.1 V s^{-1}.

The cyclic voltammogram of $[Ru(bpm)_3]^{2+}$ was similar to that of $[Ru(bpy)_3]^{2+}$ in exhibiting three nearly neighbouring steps. They were all reversible one-electron steps, judging from the well-defined anodic current peaks and from the separation between the cathodic peak potential and the anodic one (ΔE_p). The ratios of the anodic to the cathodic peak currents could not be determined, however, because of the proximity of the reduction steps. A similar pattern of voltammogram was obtained for $[Fe(bpm)_3]^{2+}$ at −40 °C, but at room temperature no reversible steps were observed besides the one for the liberated ligand molecules. The cyclic voltammograms for $[Ru(bpm)(bpy)_2]^{2+}$ and methyl derivatives were quite similar. They had one remote and two nearly neighbouring reversible one-electron steps. The reversible half-wave potentials and the peak separations thus obtained are listed in Table 1. The $E^{\mathrm{red}}_{1/2,\mathrm{L}}$ values for the first reduction steps of bpm, bpy, 4-dmbpy, and 5-dmbpy were, respectively, −2.33, −2.71, −2.77, and −2.82 V *vs.* $Ag/AgNO_3$(sat.).

Table 1. Reversible half-wave potentials for the reduction of iron(II) and ruthenium(II) complexes in acetonitrile containing 0.1 Bu_4NPF_6 at room temperature

Complex	$[-E^{\mathrm{red}}_{1/2,\mathrm{C}}$ *vs.* $(Ag/AgNO_3)]/V$ $(\Delta E_p/mV)$		
	1st	2nd	3rd
$[Fe(bpm)_3]^{2+}$	1.41(45)[a]	1.57(48)[a]	1.75(50)[a]
$[Ru(bpm)_3]^{2+}$	1.40(60)	1.55(60)	1.75(63)
$[Ru(bpy)_3]^{2+}$	1.81(60)	2.01(65)	2.25(60)
$[Ru(4\text{-}dmbpy)_3]^{2+}$	1.94(60)	2.13(65)	2.37(64)
$[Ru(5\text{-}dmbpy)_3]^{2+}$	1.98(62)	2.19(62)	2.44(65)
$[Ru(bpm)(bpy)_2]^{2+}$	1.51(61)	1.95(65)	2.14(70)
$[Ru(bpm)\text{-}(4\text{-}dmbpy)_2]^{2+}$	1.52(60)	2.05(65)	2.26(68)
$[Ru(bpm)\text{-}(5\text{-}dmbpy)_2]^{2+}$	1.53(60)	2.12(65)	2.36(65)

a) At −40 °C, the $E^{\mathrm{red}}_{1/2,\mathrm{C}}$ values are almost unaffected by the temperature.

The $E^{\mathrm{red}}_{1/2,\mathrm{C}}$ values for the (a) first, (b) second, and (c) third reduction steps of the unmixed-ligand complexes, $[Ru(bpm)_3]^{2+}$, $[Ru(bpy)_3]^{2+}$, $[Ru(4\text{-}dmbpy)_3]^{2+}$, and $[Ru(5\text{-}dmbpy)_3]^{2+}$, are plotted in Fig. 1 against the $E^{\mathrm{red}}_{1/2,\mathrm{L}}$ values. The experimental points for each step obey Eq. 1 approximately. Consequently, we may conclude that the redox orbitals of $[Ru(bpm)_3]^{2+}$ are also three-fold degenerate ligand π^*-orbitals.

Figure 2 shows similar plots for the mixed-ligand complexes, $[Ru(bpm)(bpy)_2]^{2+}$, $[Ru(bpm)(4\text{-}dmbpy)_2]^{2+}$, and $[Ru(bpm)(5\text{-}dmbpy)_2]^{2+}$. A striking feature is that the $E^{\mathrm{red}}_{1/2,\mathrm{C}}$ values for the first steps are almost independent of the ligands. All the experimental points for the second and the third steps lie on straight lines. Their slopes are inconsistent with Eq. 1, but this is not surprising because only two of the three ligands are changed in this case.

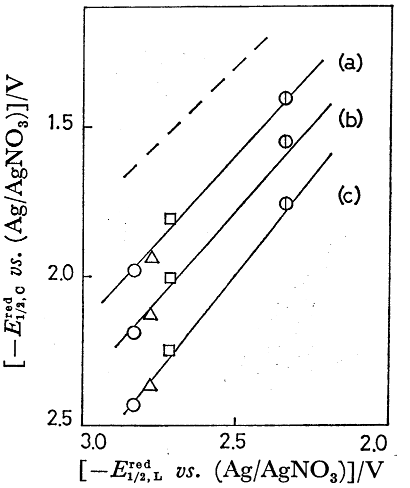

Fig. 1. Plots of $E^{1/2,\rm C}_{\rm red}$ for (a) $[{\rm RuL_3}]^{2+}$, (b) $[{\rm RuL_3}]^+$, and (c) $[{\rm RuL_3}]$ vs. $E^{\rm red}_{1/2,\rm L}$ for L. L=(⦶) bpm, (□) bpy, (△) 4-dmbpy and (○) 5-dmbpy. The broken line shows the slope given by Eq. 1.

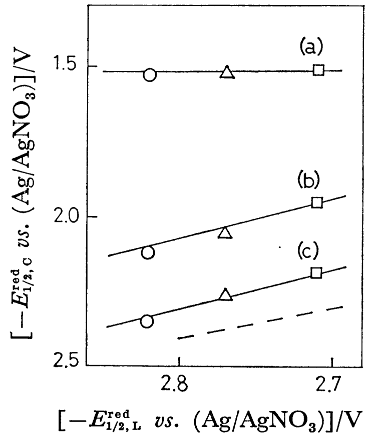

Fig. 2. Plots of $E^{1/2,\rm C}_{\rm red}$ for (a) $[{\rm Ru(bpm)L_2}]^{2+}$, (b) $[{\rm Ru(bpm)L_2}]^+$, and (c) $[{\rm Ru(bpm)L_2}]$ vs. $E^{\rm red}_{1/2,\rm L}$ for L. L=(□) bpy, (△) 4-dmbpy and (○) 5-dmbpy. The broken line shows the slope given by Eq. 1.

The feature of Fig. 2 can be explained as follows. When we construct the MO of a $[{\rm Ru(bpm)L_2}]^{2+}$ complex by the configuration interaction of the d_π atomic orbitals of the central metal and the LUMO's (lowest unoccupied molecular orbitals) of bpm and two L's, the metal orbitals are not taken into consideration.[5] Since the LUMO of bpm is lower than the LUMO's of L's by about 0.4 to 0.5 eV, it does not mix with the latter, which form two-fold degenerate orbitals. In $[{\rm Ru(bpm)_3}]^{2+}$, three LUMO's of bpm can mix with each other and form three-fold degenerate orbitals, which are probably lower than the unmixed bpm orbital. This orbital order is consistent with the experimental finding that $[{\rm Ru(bpm)_3}]^{2+}$ is reducible at a more positive potential than $[{\rm Ru(bpm)L_2}]^{2+}$ (Table 1). When three electrons are added to $[{\rm Ru(bpm)L_2}]^{2+}$, they may occupy these redox orbitals with parallel spins, because the energy of repulsion between a pair of electrons on the same MO may be much greater than the promotion energy between the lowest and the second lowest orbitals. Since the lowest orbital of $[{\rm Ru(bpm)L_2}]^{2+}$ should be insensible to the small perturbation of methyl substitution applied to bpy, the $E^{\rm red}_{1/2,\rm C}$ values for the first steps should be invariable among the three $[{\rm Ru(bpm)L_2}]^{2+}$ complexes.

In conclusion, the LUMO of $[{\rm Ru(bpm)L_2}]^{2+}$ is actually localized on a single ligand bpm and is not delocalized over three ligand molecules. On the basis of the emission spectra of the mixed-ligand complexes of Rh(III) with bpy and 1,10-phenanthroline, Halper and DeArmond[10] have concluded that π^*-orbitals are localized on each ligand molecule, even when the $E^{\rm red}_{1/2,\rm L}$ values are almost identical. If their conclusion is right, though we are not in a position to comment on it now, it should be quite natural to get our present result.

We wish to thank Dr. Eiichi Ichikawa for his guidance in the synthesis of 2,2′-bipyrimidine.

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