Inorganica Chimica Acta, *208* (1993) 231–237

Short Communication

Synthesis and characterization of bipyridylruthenium(II) complexes bound to the bridging ligand dipyrido(2,3-*a*;2′,3′-*h*)phenazine (dpop)

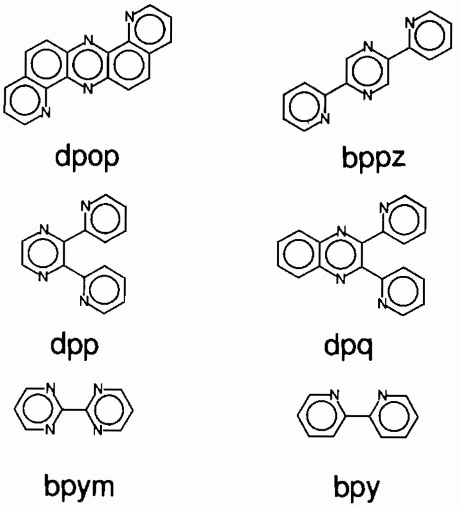
Jane E. B. Johnson and Ronald R. Ruminski*

Department of Chemistry, University of Colorado at Colorado Springs, Colorado Springs, CO 80933-7150 (USA)

(Received December 7, 1992; revised February 15, 1993)

Abstract

Mono- and bimetallic bis-bipyridylruthenium(II) complexes bound to the nitrogen aromatic heterocyclic ligand dipyrido(2,3-*a*;2′,3′-*h*)phenazine (dpop) have been prepared and their electronic absorption and emission and electrochemical properties studied. The monometallic $(bpy)_2Ru(dpop)^{2+}$ ion in CH_3CN has an intense 528 nm absorption attributed to a $Ru(d\pi) \rightarrow dpop(\pi^*)$ MLCT transition, with additional higher energy MLCT absorptions also present. The $(bpy)_2Ru(dpop)^{2+}$ ion undergoes emission at $\lambda = 768$ nm from the lowest lying triplet metal to ligand charge transfer state in room temperature CH_3CN solution. The bimetallic $((bpy)_2Ru)_2(dpop)^{4+}$ ion in CH_3CN displays an intense $Ru(d\pi) \rightarrow dpop(\pi^*)$ absorption at 661 nm, with higher energy MLCT absorptions, but does not emit within detection limits. Cyclic voltammetry results for the bimetallic ion give a $\Delta E = E_{1/2}(2) - E_{1/2}(1)$ value of 0.17 V. The comparison of these results with those for similar bis-bipyridylruthenium(II)(L_2) (L_2 = bidentate ligand) complexes, shows the $Ru(d\pi) \rightarrow L_2(\pi^*)$ MLCT absorption energy decreases in the order dpp > bpym > bppz > dpq > dpop. The comparative electrochemical results for the complexes indicate the ligand centered reduction values $E_{1/2}$ is less negative in the order dpop < dpq < bppz; bpym < dpp, while the $Ru^{2+/3+}$ centered oxidation couples become less positive in the order of coordinated ligand dpop > dpq; bpym > bppz > dpp. Overall results indicate that bis-bipyridylruthenium(II) coordination to the highly conjugated planar dpop ligand produces complexes that absorb and emit at lower energies than for complexes with similar ligands while retaining favorable electrochemical and photochemical properties for excited state energy transfer reactions.



Scheme 1.

Introduction

Nitrogen containing aromatic heterocyclic bridging ligands (BL) bound to tetraammineruthenium(II) or bis-bipyridylruthenium(II) centers typically produce a low spin d^6 electronic configuration, with intense MLCT electronic absorptions in the Vis–near-UV region of the spectrum. Mono- and bimetallic complexes have been prepared and studied for understanding of photoexcited-energy transfer, electrochemical and intervalence processes [1–13].** Rather than attaining a 'mature' state of development, the subject has cultivated a richness and complexity in the design of molecules within the last few years due, in part, to the preparation and study complexes bound to novel bridging ligands [5, 6]. Many of the new complexes utilize substituents on the bridging ligands, tridentate ligands or an extension of the conjugated ligand systems to modify metal to ligand electronic properties. Preparations and study of bimetallic and oligonuclear 'Supramolecular' (homo and hetero metallic) [14–20] complexes coupled through the BL system have been used to assess and optimize spectroscopic and electrochemical properties for photo-induced excited state energy transfer processes.

Many bis-bidentate bridging ligands such as bppz(2,5-dpp) [21–23], dpp(2,3-dpp) [12–14, 24] and dpq(2,3-dpq) [25] that are typically coordinated with Ru(II) contain pyridyl rings that are σ bonded to a central pyrazine or quinoxaline ring (Scheme 1). It has been shown that pyridyl ring rotation from Ru–BL–Ru planarity occurs for the $[((bpy)_2Ru)_2(dpp)](PF_6)_4$ complex

---

*Author to whom correspondence should be addressed.

**The list of possible references is inexhaustible in the area. Several reviews are listed below. Specific relevant journal references are made pertinent to subject areas throughout this manuscript.

0020-1693/93/$6.00

which may disrupt the Ru(dπ)–BL(π^*)–Ru(dπ) interaction [24]. This result has lead some groups to prepare complexes bound with planar bridging ligands such as benzo[1,2-*b*:3,4-*b*:5,6-*b*″]tripyrazine (hat) [19, 26, 27].

An area of interest in our research group has been the preparation of Ru(II) complexes with different bridging ligands to compare the effects of the bis-bidentate bridging ligand on the electronic absorption, electrochemical and photochemical properties of the compounds [28–30]. The bis-bidentate bridging ligand dpop (Scheme 1) is a highly conjugated planar π system that eliminates metal to BL interactions with pyridyl rings not integrated within the π conjugated system.

We wish to report the synthesis and characterization of new [(bpy)$_2$Ru(dpop)](PF$_6$)$_2$ and [((bpy)$_2$Ru)$_2$(dpop)](PF$_6$)$_4$ complexes. The dpop ligand is the cyclized analog of bppz, and the preparation and characterization of the new complexes allows for comparison of electronic absorption and electrochemical results with the similar [((bpy)$_2$Ru)$_{1,2}$(bppz)](PF$_6$)$_{2,4}$ complexes to assess the effects of completely aromatic bridging ligands.

Experimental

Instrumentation

Electronic absorption spectra were recorded on a Varian DMS 300 spectrophotometer with matching quartz cells. Cyclic voltammograms were recorded on a Bioanalytical Systems CV-1B cyclic voltammograph with a Princeton Applied Research model 0074 X-Y recorder. Cyclic voltammograms were recorded in CH$_3$CN with 0.010 M tetrabutylammonium perchlorate as the supporting electrolyte. A Bioanalytical Systems Ag/AgCl (3 M KCl, nominally -0.04 V versus SCE) electrode was used as the reference electrode with a Pt working electrode. All potentials are reported versus SCE, and are uncorrected for junction potentials. The $E_{1/2}$ values reported for redox couples are obtained by averaging anodic and cathodic peak potentials. Emission experiments were conducted on a Hitachi model F-3210 fluorescence spectrophotometer, fitted with an extended range Hamamatsu R928 detector sensitive to 800 nm. This instrument cannot be corrected for emission wavelengths greater than 600 nm. The excitation spectrum 400–600 nm is corrected. Samples were degassed with Ar prior to data collection.

Deoxygenated samples were irradiated with a continuous beam photolysis apparatus consisting of an Ealing universal arc source lamp with a 200 W high pressure Hg lamp, a 1 inch diameter Oriel Hg line interference filter, and a thermostated cell compartment at 21 °C all mounted on an Ealing optical railing. Intensities of the apparatus measured by Reineckate actinometry were 1.2×10^{-5} E/min at 546 nm and 3×10^{-6} E/min at 691 nm.

Materials

Reagent grade compounds were used for preparations described in this work. Argon was deoxygenated by passing it through a chromous solution and then through a drying tube before use. Elemental analyses were performed by Atlantic Microlab Atlanta, GA.

Synthesis

The dpop ligand was prepared according to the literature [31] with minor modifications as previously described [32]. The (bpy)$_2$RuCl$_2\cdot$2H$_2$O reactant was also prepared according to the literature [33].

[((bpy)$_2$Ru)$_2$dpop](PF$_6$)$_4$

A 0.278 g (0.535 mmol) sample of (bpy)$_2$RuCl$_2\cdot$2H$_2$O and 0.050 g (0.177 mmol) dpop were dissolved in 0.10 dm^3 of 50% methanol/50% water and heated at reflux under argon for 12 h. The green solution which formed was rotary evaporated to remove the methanol, and filtered to remove any insoluble material. The crude product was eluted down a 15 cm (length)$\times$2 cm (diameter) alumina column using a solution of 1 g NaI/0.400 dm^3 H$_2$O. After removal of the red fraction that eluted first, the green fraction was collected, and an equal volume of aqueous NH$_4$PF$_6$ was added to induce precipitation. The green solid was collected by filtration, washed with a minimum volume of 0 °C H$_2$O$_{(l)}$ and dried. The solid was then dissolved in a minimum amount of CH$_3$CN and rotary evaporated to dryness. The dark green solid was again washed with a minimum volume of 0 °C H$_2$O$_{(l)}$ and dried. Yield 0.25 g (0.145 mmol), 82% based on dpop as the limiting reactant. *Anal.* Calc. for C$_{58}$H$_{42}$N$_{12}$P$_4$F$_{24}$Ru$_2\cdot$2H$_2$O mol mass 1725.0 a.m.u.: C, 40.36; H, 2.69; N, 9.74. Found: C 40.04; H, 2.64; N, 9.60%.

[(bpy)$_2$Ru(dpop)](PF$_6$)$_2$

A 0.10 g (0.192 mmol) sample of (bpy)$_2$RuCl$_2\cdot$2H$_2$O and 0.084 g (0.298 mmol) dpop were dissolved in 0.10 dm^3 of 50% methanol/50% H$_2$O and heated at reflux under argon for 6 h. The red solution which was formed was rotary evaporated to remove the methanol, and the solution filtered to recover excess ligand. The crude product was eluted down an alumina column as previously described. The red monometallic fraction was collected and precipitated by addition of an equal volume of aqueous NH$_4$PF$_6$. The orange product was recrystallized from acetone with diethyl ether, washed with cold water and vacuum dried. Yield 0.14 g (0.142 mmol), 72% based on (bpy)$_2$RuCl$_2\cdot$2H$_2$O as limiting reactant. *Anal.* Calc. for C$_{38}$H$_{26}$N$_8$P$_2$F$_{12}$Ru, mol mass

985.63 a.m.u.: C, 46.30; H, 2.66; N, 11.36. Found: C, 45.83; H, 2.76; N, 11.09%.

Results and discussion

The syntheses of the mono- and bimetallic $((bpy)_2Ru)_{1,2}(dpop)^{2+,4+}$ complex ions are based on previously reported preparations of bis-bipyridylruthenium(II) complexes with similar nitrogen containing aromatic heterocyclic ligands such as bpym [17, 34, 35] or dpp [24], which prescribe heating the dpop ligand and $(bpy)_2RuCl_2 \cdot 2H_2O$ in an inert solvent under Ar. The mono- and bimetallic $((bpy)_2Ru)_{1,2}(dpop)^{2+,4+}$ ions were preferentially prepared by heating a 2 dpop (excess): 1 $(bpy)_2RuCl_2 \cdot 2H_2O$ or 1 dpop: 2.5 $(bpy)_2RuCl_2 \cdot 2H_2O$ (excess) mixture in deoxygenated solvent. After isolation, chromatography and washing, the products were identified as $[((bpy)_2Ru)_{1,2}(dpop)](PF_6)_{2,4}$ by percent C, H and N analyses, and by comparison of physical properties with similar compounds.

The monometallic $(bpy)_2Ru(dpop)^{2+}$ ion has the lowest energy absorption peak at 528 nm and higher energy absorptions at 430(sh), 413 and 360 nm (Fig. 1(a), Table 1) in CH_3CN. In previously reported $(bpy)_2Ru(BL)^{2+}$ mixed ligand complexes with π acceptor bridging ligands, the $Ru(d\pi) \rightarrow BL(\pi^*)$ has been measured at wavelengths longer than 450 nm, while the $Ru(d\pi) \rightarrow bpy(\pi^*)$ transition has been reported between 430 and 400 nm [12–14, 22, 24, 25]. Based on intensity, transition energy and electrochemical data for the $dpop^{0/1-}$ centered reduction, the 528 nm absorption for the $(bpy)_2Ru(dpop)^{2+}$ ion is attributed to a $Ru(d\pi) \rightarrow dpop(\pi^*)$ MLCT transition. The observed MLCT transition energies for $(bpy)_2Ru(BL)^{2+}$ complex ions decrease in BL order dpp > bpym > bppz > dpq > dpop. Comparison of previously reported absorption data for similar $(bpy)_2Ru(BL)^{2+}$ ions (Table 1) shows the $Ru(d\pi) \rightarrow BL(\pi^*)$ MLCT energies decrease as the number of BL π systems interacting with the metal increase. By rough analogy to energy solutions for the quantum mechanical particle in a box model [36], the MLCT transition energy between ground and excited $M(d\pi)$–$BL(\pi^*)$ molecular orbitals is inversely proportional to the number of BL π conjugated rings that interact with the metal [25, 37]. The observed MLCT transition energy for the $(bpy)_2Ru(dpop)^{2+}$ ion with five conjugated interactive rings is consistent with previous studies and explanations. The 430 nm absorbance for the $(bpy)_2Ru(dpop)^{2+}$ ion is lower in energy than previously reported for second $Ru(d\pi) \rightarrow BL(\pi^*)$ transitions, while the higher energy 413 nm absorbance is typically assigned to $Ru(d\pi) \rightarrow bpy(\pi^*)$ transitions in $(bpy)_2Ru(L_2)^{2+}$ (L_2 = dpq, dpp, bpm) ions [12–14, 27, 35]. Based on the results and assignments of previous mixed ligand ruthenium complexes and electrochemical results (later discussion), the lower energy absorption at 430 nm is tentatively assigned as a primarily $Ru(d\pi) \rightarrow dpop(\pi^*)$ transition while the 413 nm absorption is assigned as a primarily $Ru(d\pi) \rightarrow bpy(\pi^*)$ transition. The relative proximity of the transitions suggests some state overlapping occurs as noted for previously reported mixed ligand complexes. Resonance Raman data have previously been used to distinguish between closely lying $Ru(d\pi) \rightarrow dpp(\pi^*)$ and $Ru(d\pi) \rightarrow bpy(\pi^*)$ transitions for the $(bpy)_2Ru(dpp)^{2+}$ complex [24] and this type of data would be useful to confirm tentative assignments for the $(bpy)_2Ru(dpop)^{2+}$ complex.

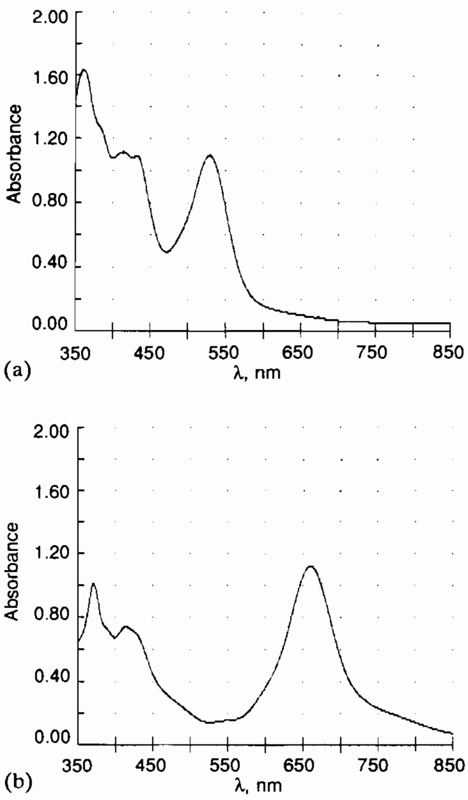


Fig. 1. Electronic absorption spectra of: (a) $(bpy)_2Ru(dpop)^{2+}$, (b) $((bpy)_2Ru)_2(dpop)^{4+}$ ions in acetonitrile.

Deoxygenated solutions of $(bpy)_2Ru(dpop)^{2+}$ in CH_3CN at room temperature, following excitation at 528 nm that involves a $Ru(d\pi) \rightarrow dpop(\pi^*)$ excitation, are found to be luminescent with $\lambda_{max} = 768$ nm. On this basis and in view of similar results for previously reported ruthenium(II) polypyridyl complexes [12–16, 22–27], we assign the emission as originating from the lowest energy triplet metal to ligand charge transfer state. A corrected excitation spectrum for $\lambda_{emission} = 768$ nm shows excitation maxima at 537 nm, and throughout the 430–410 nm region. This result indicates that regardless of the initial state populated, rapid efficient

TABLE 1. Electronic absorption and emission, and electrochemical data for some ruthenium(II) complexes

Complex ion	λ_{max} (nm)	$\epsilon \times 10^{-3}$ (M^{-1} cm^{-1})	Assignment	λ_{em} (nm)	Reference
$(bpy)_2Ru(dpop)^{2+}$	528	10.5	$Ru(d\pi) \rightarrow dpop(\pi^*)$	768	this work
	430	10.2	$Ru(d\pi) \rightarrow dpop(\pi^*)$		
	413	10.6	$Ru(d\pi) \rightarrow bpy(\pi^*)$		
	360	15.8	$Ru(d\pi) \rightarrow bpy(\pi^*)$		
$(bpy)_2Ru(bppz)^{2+}$	486	5.2	$Ru(d\pi) \rightarrow bppz(\pi^*)$	695	23
$(bpy)_2Ru(bpym)^{2+}$	480(sh)		$Ru(d\pi) \rightarrow bpym(\pi^*)$	690	14
	420	10.5	$Ru(d\pi) \rightarrow bpym(\pi^*)$		34
$(bpy)_2Ru(dpp)^{2+}$	470(sh)	11.5	$Ru(d\pi) \rightarrow dpp(\pi^*)$	691, 682	12–14, 23, 24
	430	12.0	$Ru(d\pi) \rightarrow bpy(\pi^*)$		
$(bpy)_2Ru(dpq)^{2+}$	515	8.1	$Ru(d\pi) \rightarrow dpq(\pi^*)$		25
	427(sh)		$Ru(d\pi) \rightarrow bpy(\pi^*)$		
$((bpy)_2Ru)_2(dpop)^{4+}$	775(sh)		$Ru(d\pi) \rightarrow dpop(\pi^*)$		this work
	661	29	$Ru(d\pi) \rightarrow dpop(\pi^*)$		
	475(sh)		$Ru(d\pi) \rightarrow dpop(\pi^*)$		
	425(sh)		$Ru(d\pi) \rightarrow bpy(\pi^*)$		
	413	18.2	$Ru(d\pi) \rightarrow bpy(\pi^*)$		
	390(sh)		$Ru(d\pi) \rightarrow bpy(\pi^*)$		
	370	25	$Ru(d\pi) \rightarrow bpy(\pi^*)$		
$((bpy)_2Ru)_2(bppz)^{4+}$	650(sh)		$Ru(d\pi) \rightarrow bppz(\pi^*)$	824	22, 23
	584	19.0	$Ru(d\pi) \rightarrow bppz(\pi^*)$		
	548(sh)		$Ru(d\pi) \rightarrow bppz(\pi^*)$		
	465				
	432	20	$Ru(d\pi) \rightarrow bpy(\pi^*)$		
$((bpy)_2Ru)_2(bpym)^{4+}$	592	7.9	$Ru(d\pi) \rightarrow bpym(\pi^*)$	790	14, 17, 22
	545(sh)		$Ru(d\pi) \rightarrow bpym(\pi^*)$		
	408	29.8	$Ru(d\pi) \rightarrow bpy(\pi^*)$		
$((bpy)_2Ru)_2(dpp)^{4+}$	525	21.0	$Ru(d\pi) \rightarrow dpp(\pi^*)$	802, 790	12–14, 23, 24
	425	17.0	$Ru(d\pi) \rightarrow bpy(\pi^*)$		
$((bpy)_2Ru)_2(dpq)^{4+}$	605	9.8	$Ru(d\pi) \rightarrow dpq(\pi^*)$		25
	423(sh)		$Ru(d\pi) \rightarrow bpy(\pi^*)$		
	399	12	$Ru(d\pi) \rightarrow bpy(\pi^*)$		

internal conversion processes occur that terminate in the lowest energy metal to ligand charge transfer state [13, 15].

The absorption spectrum of $((bpy)_2Ru)_2(dpop)^{4+}$ in CH_3CN displays several intense absorptions in the Vis–near-UV spectrum (Fig. 1(b)) and the results are summarized in Table 1. The lowest energy absorption maximum is 3800 cm^{-1} lower in energy for the bimetallic $((bpy)_2Ru)_2(dpop)^{4+}$ ion compared with the monometallic $(bpy)_2Ru(dpop)^{2+}$ ion. This result is consistent with the similar comparisons of mono- and bimetallic $((bpy)_2Ru)_{1,2}(BL)^{2+,4+}$ species, and is understood as being due to a stabilization of the dpop(π^*) LUMO when bonded to a second electropositive $(bpy)_2Ru^{2+}$ fragment (also verified electrochemically), which would result in a lower energy $Ru(d\pi) \rightarrow dpop(\pi^*)$(LUMO). The 775(sh), 661 and 474(sh) nm absorptions are therefore assigned to $Ru(d\pi) \rightarrow dpop(\pi^*)$ transitions. Higher energy absorptions are similar in energy to those found in the monometallic complex, and are assigned as being due to $Ru(d\pi) \rightarrow bpy(\pi^*)$ transitions. The lowest MLCT $Ru(d\pi) \rightarrow BL(\pi^*)$ energy of the bimetallic $((bpy)_2Ru)_2(dpop)^{4+}$ ion is less than that reported for similar $((bpy)_2Ru)_2(BL)^{4+}$ complexes (Table 1). This result is again consistent with the expanded π delocalized ligand, as the transition energy of the complex decreases in order of the BL dpp > bppz > bpym > dpq > dpop.

In the particular comparison of the lowest energy $Ru(d\pi) \rightarrow BL(\pi^*)$ transition for the $((bpy)_2Ru)_{1,2}(dpop)^{2+,4+}$ and $((bpy)_2Ru)_{1,2}(bppz)^{2+,4+}$ ions, where dpop is the cyclized analog of bppz, the lowest energy $Ru(d\pi) \rightarrow BL(\pi^*)$ transitions for the dpop mono- and bimetallic complexes are 1650 and 2000 cm^{-1} lower in energy than the bppz complexes, respectively. Room temperature excitation of $((bpy)_2Ru)_2(dpop)^{4+}$ in CH_3CN at 661 nm did not give detectable emission within the instrumental detection limit $\lambda < 800$ nm. Based on the difference in room temperature emission and absorption maxima for the bimetallic

$((bpy)_2Ru)_2(dpp)^{4+}$ [14], $((bpy)_2Ru)_2(bpym)^{4+}$ [14] and $((bpy)_2Ru)_2(bppz)^{4+}$ [23] ions, if room temperature emission from $((bpy)_2Ru)_2(dpop)^{4+}$ were to occur it would be estimated at 950–1160 nm, which is well beyond the detection limits of our instrumentation.

Extended irradiation in CH_3CN of $(bpy)_2Ru(dpop)^{2+}$ at 546 nm and of $((bpy)_2Ru)_2(dpop)^{4+}$ at 691 nm into the respective lowest energy $Ru(d\pi) \rightarrow dpop(\pi^*)$ MLCT transition produced no detectable loss ($\Phi < 10^{-3}$) of reactant as estimated by monitoring the 528 and 661 nm absorption maxima of the mono- and bimetallic ions. While these wavelengths specifically monitor the loss of the $Ru(d\pi) \rightarrow dpop(\pi^*)$ transition, lack of change in the overall absorption (850–350 nm) indicates no bpy loss as well.

Cyclic voltammograms of the uncomplexed dpop ligand and of the $((bpy)_2Ru)_{1,2}(dpop)^{2+,4+}$ ions (Fig. 2) were recorded in CH_3CN/0.01 M TBAP between +1.8 and −1.5 V versus SCE, and show reversible $Ru^{2+/3+}$ oxidation and $dpop^{0/1-/2-}$ reduction couples (Table 2).

The $dpop^{0/1-}$ reduction couple measured at −1.27 V is less negative (more easily reduced) than for $bppz^{0/1-}$ at −1.6 V [38]. The obvious effect of cyclization of the bppz ring to give dpop is to shift in a positive direction the ligand reduction couple, or increase the π acidity of the BL.

The monometallic $(bpy)_2Ru(dpop)^{2+}$ ion exhibits a reversible $Ru^{2+/3+}$ couple at +1.44 V, and reduction couples at −0.63 and −1.34 V versus SCE. Previous studies have shown the $bpy^{0/1-}$ reduction couples in mixed ligand $(bpy)_2Ru(BL)^{2+}$ complexes more negative than −1.5 V [23], thus the first two reduction couples are attributed to $dpop^{0/1-/2-}$ centered processes. With respect to earlier absorption assignments, the tentative assignment of the two lowest energy transitions as $Ru(d\pi) \rightarrow dpop(\pi^*)$ is based in part on the fact that the first two reduction couples are localized on the dpop ligand. An additional wave at −1.46 V is also observed which could be due to $bpy^{0/1-}$ reduction.

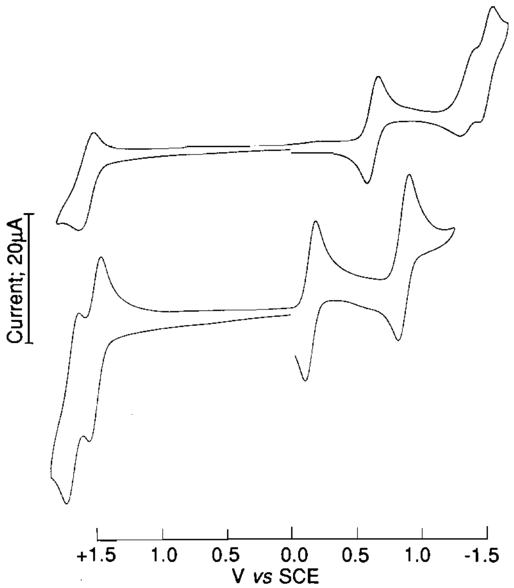


Fig. 2. Cyclic voltammograms for successive ruthenium oxidations and dpop reduction couples of $(bpy)_2Ru(dpop)^{2+}$ (top) and $((bpy)_2Ru)_2(dpop)^{4+}$ ions in deoxygenated acetonitrile 0.01 M TBAP solutions.

The difference between the metal oxidation couple and the first BL reduction, defined as $E_{ox/red}$ measures the electrochemical energy difference between the $Ru(d\pi)$ HOMO and the dpop (π^*) LUMO. The $E_{ox/red}$ value for $(bpy)_2Ru(dpop)^{2+}$ of 2.07 V is less than that for previously reported bis-bipyridylruthenium(II) (BL) complexes (Table 2), and is consistent with the lowest energy spectroscopic MLCT measurement, $E_{op} = 2.35$ V of comparative complexes.

The bimetallic $((bpy)_2Ru)_2(dpop)^{4+}$ ion shows two reversible $Ru^{2+/3+}$ oxidation couples at +1.66 and +1.47 V, and $dpop^{0/1-/2-}$ dpop centered reduction couples at −0.18 and −0.90 V. The $E_{ox/red}$ value of 1.67 V is again lower than for the analogous bppz bridged ion (Table 2). The positive shift of the $dpop^{0/1-}$ centered reduction couple by 0.61 V upon formation of the monometallic ion, and by an additional 0.45 V for the bimetallic ion, is consistent with the expectation upon coordination of one and two electropositive $(bpy)_2Ru^{2+}$ fragments on the dpop BL.

The spectroscopic measure of the energy difference between the $Ru(d\pi)$HOMO and the $dpop(\pi^*)$LUMO, defined as E_{op}, is larger than the $E_{ox/red}$ electrochemical measure. This is due to the fact that electronic promotions occur without time for the molecular geometry to rearrange. Therefore the difference between optical and electrochemical energies yields solvation and vibrational re-organizational information by the relationship $\chi = E_{op} - E_{ox/red}$ [39]. The measured values for the $((bpy)_2Ru)_{1,2}(dpop)^{2+,4+}$ ions are similar to those for previously reported bis-bipyridylruthenium(II)(BL) ions and indicate relatively small geometrical changes in the MLCT state.

Metal–metal interaction in symmetric bimetallic complexes has previously been estimated by the $\Delta E = E_{1/2}(2) - E_{1/2}(1)$ value [21, 23, 40]. The measured $\Delta E_{1/2}$ value for the $((bpy)_2Ru)_2(dpop)^{4+/5+/6+}$ metal oxidation couples of 0.16 V is smaller by 0.03 V than the ΔE value for the $((bpy)_2Ru)_2(bppz)^{4+/5+/6+}$ metal oxidation couples, and suggests that metal–metal interaction is not enhanced, but in fact diminished, by the more delocalized dpop BL. This result supports the previously reported work which demonstrated that the comproportionation constant $K_c = 750$ as calculated [40] from $\exp(\Delta E/25.69)$, is not directly related to the number

TABLE 2. Electrochemical data for some $((bpy)_2Ru)_{1,2}(BL)^{2+,4+}$ ions, and calculated parameters

Complex	$E_{1/2}(2)$	$E_{1/2}(1)$	$\Delta E(2\text{-}1)$	$E_{1/2}(0/1-)$	$E_{1/2}(1-/2-)$	$\Delta E_{ox/red}$	E_{op}	χ	Reference
$(bpy)_2Ru(dpq)^{2+}$		1.41		−0.78	−1.41	2.19	2.41	0.22	25
$(bpy)_2Ru(dpp)^{2+}$		1.31		−1.06		2.37	2.61	0.25	23
$(bpy)_2Ru(bpym)^{2+}$		1.40		−1.02	−1.45	2.42	2.58	0.16	22
$(bpy)_2Ru(dpop)^{2+}$		1.44		−0.63	−1.34	2.07	2.35	0.28	this work
$(bpy)_2Ru(bppz)^{2+}$		1.33		−1.03		2.36	2.55	0.19	23
$((bpy)_2Ru)_2(dpq)^{4+}$	1.62	1.47	0.15	−0.37	−1.10	1.84	2.05	0.21	25
$((bpy)_2Ru)_2(dpp)^{4+}$	1.55	1.38	0.17	−0.67	−1.17	2.05	2.35	0.30	23
$((bpy)_2Ru)_2(bpym)^{4+}$	1.69	1.53	0.16	−0.41	−1.08	1.94	2.09	0.15	22
$((bpy)_2Ru)_2(bppz)^{4+}$	1.58	1.39	0.19	−0.55	−1.09	1.94	2.12	0.18	22
$((bpy)_2Ru)_2dpop)^{4+}$	1.66	1.49	0.17	−0.18	−0.90	1.67	1.88	0.21	this work

of π mediating centers, but to electron density at the coordination centers of the bridging ligand LUMO [21].

Conclusions

The complexation of bis-bipyridylruthenium(II) to the highly delocalized dpop bridging ligand gives comparative information concerning the role of the BL on spectroscopic and electrochemical properties. The mono- and bimetallic $[((bpy)_2Ru)_{1,2}(dpop)](PF_6)_{2,4}$ complexes in solution show lower energy $Ru(d\pi) \rightarrow BL(\pi^*)$ MLCT transitions than for similar bis-bipyridylruthenium complexes with less highly conjugated α-diimine bridging ligands. This further shifts the photon capture ability of chromophoric molecules into the Vis–near-UV region of the solar spectrum. Despite the increased delocalization of the planar dpop BL, electrochemical metal–metal interaction is not enhanced when compared with bridging ligands such as bppz that contain coordinating σ-pyridyl rings. This suggests the comproportionation constant is not a function of the number of conjugated rings in the BL system.

Acknowledgements

Acknowledgement is made to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

References

1 V. Balzani (ed.), *Supramolecular Photochemistry*, NATO ASI Series C214, Reidel, Dordrecht, Netherlands, 1987.
2 M. A. Fox and M. Chanon (eds.), *Photoinduced Electron Transfer*, Elsevier, New York, 1988.
3 T. J. Meyer, *Acc. Chem. Res., 22* (1989) 163.
4 A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser and A. von Zelewsky, *Coord. Chem. Rev., 84* (1988) 85.
5 R. Hage, J. G. Haasnoot, J. Reedijk and J. G. Vos, *Chemtracts-Inorg. Chem., 4* (1992) 75.
6 P. J. Steel, *Coord. Chem. Rev., 106* (1990) 227.
7 E. Krausz and J. Ferguson, *Prog. Inorg. Chem., 37* (1989) 293.
8 V. Balzani, F. Barigelletti and L. De Cola, *Top. Curr. Chem., 158* (1990) 31.
9 B. D. MacQueen and J. D. Petersen, *Coord. Chem. Rev., 97* (1990) 249.
10 T. J. Meyer, *Pure Appl. Chem., 58* (1986) 1193.
11 K. Kalyanasundaram, M. Gratzel and E. Pelizzetti, *Coord. Chem. Rev., 69* (1986) 57.
12 Y. Fuchs, S. Lofters, T. Dieter, W. Shi, R. Morgan, T. C. Strekas, H. D. Gafney and A. D. Baker, *J. Am. Chem. Soc., 109* (1987) 2691.
13 R. M. Berger, *Inorg. Chem., 29* (1990) 1920.
14 K. Kalyanasundaram and Md. K. Nazeeruddin, *Inorg. Chem., 29* (1990) 1888.
15 G. Denti, S. Campagna, S. Serroni, M. Ciano and V. Balzani, *J. Am. Chem. Soc., 114* (1992) 2944.
16 W. R. Murphy, Jr., K. J. Brewer, G. Gettliffe and J. D. Petersen, *Inorg. Chem., 28* (1989) 81.
17 M. Hunziker and A. Ludi, *J. Am. Chem. Soc., 99* (1977) 7370.
18 W. F. Wacholtz, R. A. Auerbach and R. H. Schmehl, *Inorg. Chem., 26* (1987) 2989.
19 R. Sahai, D. P. Rillema, S. Shaver, S. Van Wallendael, D. C. Jackman and M. Boldaji, *Inorg. Chem., 28* (1989) 1022.
20 A. Vogler and J. Kisslinger, *Inorg. Chim. Acta, 115* (1986) 193.
21 S. Ernst, V. Kasack and W. Kaim, *Inorg. Chem., 27* (1988) 1146.
22 S. Ernst and W. Kaim, *Inorg. Chem., 28* (1989) 1520.
23 G. Denti, S. Campagna, L. Sabatino, S. Serroni, M. Ciano and V. Balzani, *Inorg. Chem., 29* (1990) 4750.
24 C. H. Braunstein, A. D. Baker, T. C. Strekas and H. D. Gafney, *Inorg. Chem., 23* (1984) 857.
25 D. P. Rillema and K. B. Mack, *Inorg. Chem., 21* (1982) 3849.
26 A. Masschelein, Kirsch-DeMesmaeker, C. Verhoeven and R. Nasielski-Hinkens, *Inorg. Chim. Acta, 129* (1987) L13.
27 R. Sahai, L. Morgan and D. P. Rillema, *Inorg. Chem., 27* (1988) 3495.
28 R. R. Ruminski, T. Cockroft and M. Shoup, *Inorg. Chem., 27* (1988) 4026.
29 R. R. Ruminski, J. Kiplinger, T. Cockroft and C. Chase, *Inorg. Chem., 28* (1989) 370.

30 J. E. B. Johnson, C. DeGroff and R. R. Ruminski, *Inorg. Chim. Acta, 187* (1991) 73.

31 F. R. Pfeiffer and F. H. Case, *J. Org. Chem., 31* (1966) 3384.

32 R. R. Ruminski, C. DeGroff and S. J. Smith, *Inorg. Chem., 31* (1992) 3325.

33 B. P. Sullivan, D. J. Salmon and T. J. Meyer, *Inorg. Chem., 71* (1978) 3334.

34 E. V. Dose and L. J. Wilson, *Inorg. Chem., 17* (1978) 2660.

35 D. P. Rillema, G. Allen, T. J. Meyer and D. Conrad, *Inorg. Chem., 22* (1983) 1617.

36 M. Karplus and R. N. Porter, *Atoms and Molecules,* W. A. Benjamin, Menlo Park, CA, 1970.

37 J. A. Baiano, D. L. Carlson, G. M. Wolosh, D. E. DeJesus, C. F. Knowles, E. G. Szabo and W. R. Murphy, Jr., *Inorg. Chem., 29* (1990) 2327.

38 W. Kaim and S. Kohlmann, *Inorg. Chem., 26* (1987) 68.

39 E. Dodsworth and A. B. P. Lever, *Chem. Phys. Lett., 119* (1985) 61.

40 D. E. Richardson and H. Taube, *Inorg. Chem., 20* (1981) 1278.