The synthesis, and UV–Vis, electrochemical, photochemical and intervalence characterization of tetraammine and tris chelated ruthenium(II) complexes bound to the bridging ligand dipyrido(2,3-a;2',3'-h)phenazine (dpop)

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Received by Editor 2 November 1993; received by Publisher 4 May 1994

Abstract

A series of ruthenium(II) complexes coordinated to the bridging ligand dipyrido(2,3-a;2',3'-h)phenazine (dpop) has been prepared and the spectroscopic, electrochemical, photochemical and intervalence properties studied. The mono and bimetallic $[((NH_3)_4Ru)_n(dpop)]^{2n+}$ ($n=1$, 2) ions display lowest energy MLCT transitions at 629 ($\epsilon=7.3\times10^3$ M^{-1} cm^{-1}) and 755 ($\epsilon=18\times10^3$ M^{-1} cm^{-1}) nm, respectively, in CH_3CN, with higher energy MLCT and IL transitions. The $Ru^{2+/3+}$ centered couples are more positive than those reported for similar bis-bipyridylruthenium(II) dpop complexes, and the bimetallic $[((NH_3)_4Ru)_2(dpop)]^{5+}$ mixed valence ion displays an IT absorption band at 1670 nm ($\epsilon=1250$ M^{-1} cm^{-1}) in D_2O. The $[(dpop)_3Ru]^{2+}$ ion has a lowest energy MLCT transition at 512 nm ($\epsilon=22\times10^3$ M^{-1} cm^{-1}) in CH_3CN, and displays an emission maximum at 710 nm with oxygen sensitive intensity. Irradiation of the $[(dpop)_3Ru]^{2+}$ ion at 546 nm in de-oxygenated CH_3CN produces the release of a dpop ligand with $\Phi=6\times10^{-4}$ mol/E.

Keywords: Electrochemistry; Photochemistry; Ruthenium complexes; Ammine complexes; Bidentate ligand complexes

1. Introduction

Previous studies in our laboratories have been directed at evaluating the effects of extended π delocalized μ-chelating aza-aromatic bridging ligands and of the non-bridging peripheral ligand on the spectroscopic and electrochemical properties of low spin d^6 metal complexes [1]. There is an interest in the design and study of ruthenium(II) polypyridyl complexes due, in part, to recent reports concerning the ability of similar compounds to 'harvest' light in wide areas of the visible spectrum or act as 'molecular light switches' for DNA [2]. In order to maximize light absorption, photostability and intramolecular energy transfer efficiency, numerous polypyridyl ruthenium(II) complexes with modified aza-aromatic ligands have been designed and studied [3].

In this paper we report the synthesis and characterization of $[(NH_3)_4Ru(dpop)](PF_6)_2$, $[((NH_3)_4Ru)_2(dpop)](PF_6)_4$ and $[(dpop)_3Ru](PF_6)_2$ complexes.
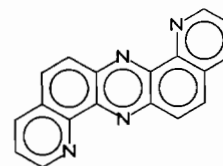
dipyrido(2,3-a;2',3'-h)phenazine (dpop)

A comparison of data with those previously reported for similar bis-bipyridylruthenium(II) dpop and other tris-bidentate polypyridylruthenium(II) complexes is used to evaluate the effects of (a) the replacement of the π competitive bpy peripheral ligands with the non-π bonding NH_3, and (b) the expanded π conjugated aza-aromatic bridging ligand, on electrochemical and spectroscopic properties.

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2. Experimental

2.1. Instrumentation

Vis–UV electronic absorption spectra were recorded on a Varian DMS 300 spectrophotometer and near-IR electronic absorption spectra were recorded on a Beckman 5240 spectrophotometer, with matching quartz cells. D_2O (99.8% D) was obtained from Aldrich Chemicals. Cyclic voltammograms were recorded on a Bio Analytical Systems CV-1B cyclic voltammograph with a Princeton Applied Research model 0074 X-Y recorder. Cyclic voltammograms were recorded in CH_3CN with 0.010 M tetrabutylammonium perchlorate as the supporting electrolyte. A Bio Analytical Systems Ag/AgCl (3 M KCl, nominally −0.04 V versus SCE) electrode was used as the reference electrode with a 1 mm diameter 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 with excitation and emission slits set at 3 nm and equipped 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 between 400 and 600 nm is corrected. Samples were deoxygenated by bubbling with Ar for 15 min 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 9.0×10^{-6} E/min at 546 nm and 1.2×10^{-6} E/min at 691 nm.

2.2. Materials

Reagent grade compounds were used for preparations described in this work. Elemental analyses were performed by Atlantic Microlab, Atlanta, GA.

2.3. Syntheses

The dpop ligand was prepared according to the literature [4] with minor modifications as previously described [5]. The $[(NH_3)_5Ru(H_2O)](CF_3SO_3)_3$ reactant was also prepared according to the literature [6].

2.3.1. $[(NH_3)_4Ru(dpop)](PF_6)_2$

A 0.150 g (0.230 mmol) sample of $[(NH_3)_5Ru(H_2O)](CF_3SO_3)_3$ was added to 0.150 g (0.532 mmol) dpop and chunks of Zn/Hg in 100 ml of anhydrous ethanol and heated at reflux under argon for 1 h. After cooling to room temperature, the blue solid that formed during reflux was collected on a fine porosity filter funnel, and was washed with CH_2Cl_2 to remove excess unreacted dpop. The solid was then dissolved on the funnel in a minimum volume of H_2O (approx. 100 ml), and the blue solution suction filtered through the funnel. The blue solution was then suction filtered through a second fine porosity funnel, and 3.0 g of $NH_4PF_6(s)$ was added to form an immediate precipitate. The precipitate was collected by filtration and washed with ethanol, followed by diethyl ether, and vacuum dried. Yield 0.145 g (0.196 mmol), 85% based on $[(NH_3)_5Ru(H_2O)](CF_3SO_3)_3$ as limiting reactant. *Anal.* Calc. for $[(NH_3)_4Ru(dpop)](PF_6)_2$, mol. mass 741.4 a.m.u.: C, 29.2; H, 3.00; N, 15.1. Found: C, 29.4; H, 3.05; N, 14.9%.

2.3.2. $[((NH_3)_4Ru)_2dpop](PF_6)_4$

A 0.049 g (0.174 mmol) sample of dpop was placed in 100 ml of methanol in a 250 ml two neck round bottom flask that was fitted with a condenser (top closed with a septum and an Ar inlet needle) and a side arm addition flask. In the side arm flask, a sample of 0.324 g (0.497 mmol) of $[(NH_3)_5Ru(H_2O)](CF_3SO_3)_3$ was dissolved in methanol and reduced with Zn/Hg, then slowly added to the dpop solution in the two neck flask. The mixture was heated for 14 h and, after being cooled to room temperature, the solution was suction filtered through a fine porosity fritted disc funnel. The purple solution containing the crude product was eluted with methanol on a 15 cm (length) × 3 cm (diameter) Sephadex A-25 column. After the removal of some impurities on the column, the purple solution that eluted was collected and rotary evaporated to approx. 75 ml. The addition of 5 g of NH_4PF_6, then 200 ml of diethyl ether, induced precipitation. The solid was collected by filtration, washed with ethanol and air dried. The crude product was then dissolved in a minimum amount of CH_3CN, suction filtered, and 1 g of NH_4PF_6 was added. The solution was rotary evaporated to dryness, the solid collected and washed with several volumes of ethanol to remove excess $NH_4PF_6(s)$, and vacuum dried. Yield 0.0856 g (0.067 mmol), 39% based on dpop as the limiting reactant. *Anal.* Calc. for $[((NH_3)_4Ru)_2(dpop)](PF_6)_4 \cdot \frac{1}{2} CH_3CH_2OH$ mol. mass 1223.6 a.m.u.: C, 18.7; H, 3.05; N, 13.7. Found: C, 18.7; H, 3.06; N, 13.7%.

2.3.3. $[(dpop)_3Ru](PF_6)_2$

The tris-(dpop)ruthenium(II) hexafluorophosphate complex was prepared by the method previously described for other tris-chelated ruthenium complexes [7]. A mixture of 0.090 g (0.32 mmol) of dpop and 0.019

g (0.073 mmol) of $RuCl_3 \cdot 3H_2O$ was mixed and heated in 20 ml of ethylene glycol for 45 min. After cooling to room temperature, the volume was doubled with distilled water, and the red solution cooled in a refrigerator overnight. Excess ligand was removed by filtration and saturated aqueous NH_4PF_6 was added dropwise to induce precipitation. The red solid was collected by filtration and air dried. The crude product was dissolved in a minimum of CH_3CN, and eluted from an alumina column with CH_3CN. The red band was collected, rotary evaporated to dryness, and dried under vacuum overnight. The column retained a blue–black component that was neither collected nor characterized. No attempt was made to further separate the $[(dpop)_3Ru]^{2+}$ ion into the Δ, Λ, *fac* or *mer* isomers. Yield 0.039 g (0.030 mmol), 41% based on $RuCl_3 \cdot 3H_2O$ as the limiting reactant. *Anal.* Calc. for $[(dpop)_3Ru]$-$(PF_6)_2 \cdot 3H_2O$ mol. mass 1291.9 a.m.u.: C, 50.2; H, 2.81; N, 13.0. Found: C, 49.8; H, 2.76; N, 12.9%.

3. Results

The UV–Vis electronic absorption spectra of the $[(NH_3)_4Ru(dpop)]^{2+}$, $[((NH_3)_4Ru)_2(dpop)]^{4+}$ and $[(dpop)_3Ru]^{2+}$ ions in CH_3CN are dominated by intense absorptions (Table 1, Fig. 1) typical of monometallic [1c,6,8–11], bimetallic [1c,9–13] and tris-chelated Ru(II) [7,14–19] complexes bound to aza-aromatic ligands. The absorption spectrum of the $[(NH_3)_4Ru(dpop)]^{2+}$ ion (Fig. 1(a)) has a lowest energy absorption maximum at 629 nm ($\epsilon = 7.3 \times 10^3$ M^{-1} cm^{-1}), while the absorption spectrum of the $[((NH_3)_4Ru)_2(dpop)]^{4+}$ ion (Fig. 1(b)) shows distinctly lower energy absorption at 755 nm ($\epsilon = 18 \times 10^3$ M^{-1} cm^{-1}).

Deoxygenated room temperature solutions of $[(dpop)_3Ru]^{2+}$ in CH_3CN are found to be emissive with $\lambda_{max} = 710$ nm following excitation into the 512 nm absorption. The emission intensity at 710 nm is reduced to approximately 30% and 10% by bubbling with air and oxygen, respectively (Fig. 2(a)). A corrected ex-

Table 1
Electronic absorption data for some tetraammineruthenium(II) and tris-chelated ruthenium(II) complexes

Complex ion	λ_{max} (nm)	ϵ (M^{-1} cm^{-1}) $\times 10^{-3}$	Assignment	λ_{em} (nm)	Reference
$(dpop)_3Ru^{2+}$	512	22	$Ru(d\pi) \rightarrow dpop(\pi^*)$	710	this work
	460(sh)	9.8	$Ru(d\pi) \rightarrow dpop(\pi^*)$		
	413	15	MLCT/IL		
	352	42	$dpop(\pi) \rightarrow dpop(\pi^*)$		
$(dpp)_3Ru^{2+}$	455	16	$Ru(d\pi) \rightarrow dpp(\pi^*)$	621	[18a,b]
$(dpq)_3Ru^{2+}$	499	14	$Ru(d\pi) \rightarrow dpq(\pi^*)$	762	[7]
	470	sh	$Ru(d\pi) \rightarrow dpq(\pi^*)$		
	392	sh	$Ru(d\pi) \rightarrow dpq(\pi^*)$		
$(bpym)_3Ru^{2+}$	454	8.6	$Ru(d\pi) \rightarrow bpym(\pi^*)$	639	[17a]
	418	8.2	$Ru(d\pi) \rightarrow bpym(\pi^*)$		
$(NH_3)_4Ru(dpop)^{2+}$	629	7.3	$Ru(d\pi) \rightarrow dpop(\pi^*)$		this work
	483	3.9	$Ru(d\pi) \rightarrow dpop(\pi^*)$		
	391	8.7	MLCT/IL		
	372	12	MLCT/IL		
	355	13	$dpop(\pi) \rightarrow dpop(\pi^*)$		
$(NH_3)_4Ru(bpym)^{2+}$	567	2.0	$Ru(d\pi) \rightarrow bpym(\pi^*)$		[9]
	402	8.4	$Ru(d\pi) \rightarrow bpym(\pi^*)$		
$(NH_3)_4Ru(dpp)^{2+}$	545	4.5	$Ru(d\pi) \rightarrow dpp(\pi^*)$		[1b]
	454	4.8	$Ru(d\pi) \rightarrow dpp(\pi^*)$		
	368	5.0	$Ru(d\pi) \rightarrow dpp(\pi^*)$		
	307	17	$dpp(\pi) \rightarrow dpp(\pi^*)$		
$((NH_3)_4Ru)_2(dpop)^{4+}$	755	18	$Ru(d\pi) \rightarrow dpop(\pi^*)$		this work
	518	6.2	$Ru(d\pi) \rightarrow dpop(\pi^*)$		
	390	sh	MLCT/IL		
	375	sh	MLCT/IL		
	359	16	$dpop(\pi) \rightarrow dpop(\pi^*)$		
$((NH_3)_4Ru)_2(bpym)^{4+}$	697	4.0	$Ru(d\pi) \rightarrow bpym(\pi^*)$		[9]
	424	18	$Ru(d\pi) \rightarrow bpym(\pi^*)$		
$((NH_3)_4Ru)_2(dpp)^{4+}$	558	19	$Ru(d\pi) \rightarrow dpp(\pi^*)$		[1b]
	368	9.8	$Ru(d\pi) \rightarrow dpp(\pi^*)$		
	318	25	$dpp(\pi) \rightarrow dpp(\pi^*)$		

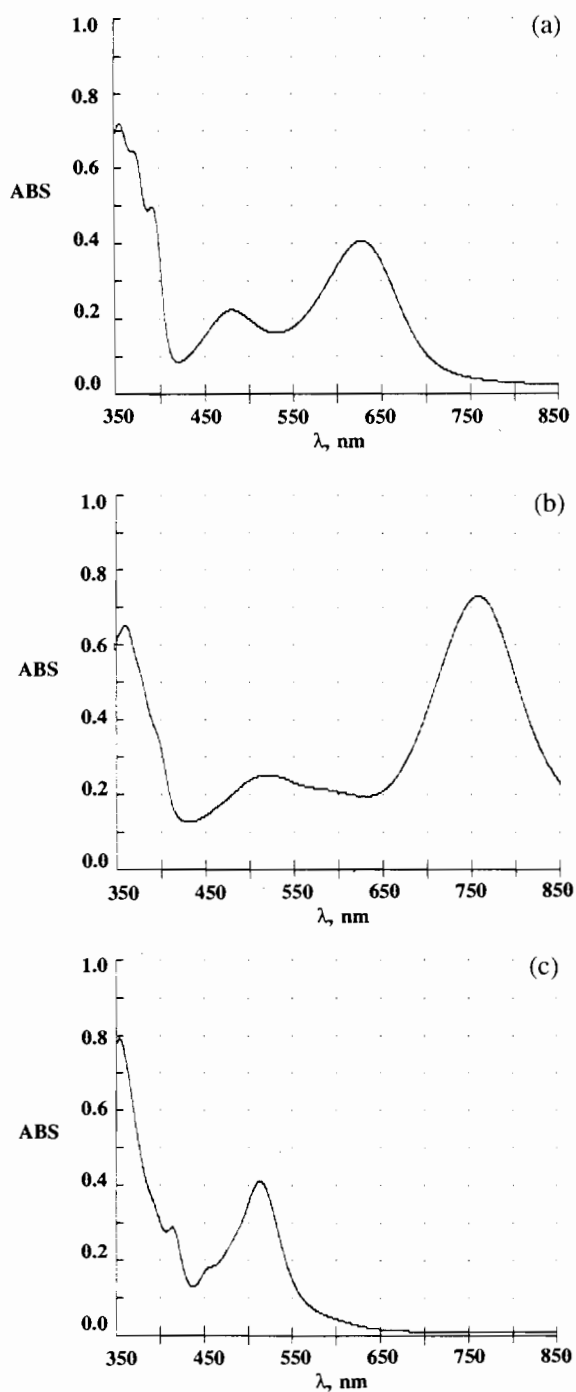2,2′-bipyrimidine = bpym; 2,3-bis(2-pyridyl)pyrazine = dpp; 2,3-bis(2-pyridyl)quinoxaline = dpq.

Fig. 1. Electronic absorption spectra of: (a) $[(NH_3)_4Ru(dpop)]^{2+}$, (b) $[((NH_3)_4Ru)_2(dpop)]^{4+}$, (c) $[(dpop)_3Ru]^{2+}$ ions in acetonitrile.

Fig. 2. (a) Emission spectra of $[(dpop)_3Ru]^{2+}$ in room temperature de-oxygenated (top); air saturated (middle) and O_2 saturated (bottom) acetonitrile solution. (b) Excitation spectrum of $[(dpop)_3Ru]^{2+}$ in room temperature de-oxygenated acetonitrile with $\lambda_{em} = 710$ nm.

$[((NH_3)_4Ru)_2(dpop)]^{4+}$ ion shows reversible $Ru^{2+/3+}$ oxidation waves at $E_{1/2}(1) = +0.73$ and $E_{1/2}(2) = +1.24$ V, and $dpop^{0/-1/-2}$ centered reduction waves at $E_{1/2} = -0.70$ and -1.36 V. Application of positive potential to the $[(dpop)_3Ru]^{2+}$ ion gives an oxidation shoulder and subsequent reduction peak which is estimated (due to the onset of the solvent window) at $E = +1.81 \pm 0.05$. The $[(dpop)_3Ru]^{2+}$ ion gives three reversible $dpop^{0/-1}$ reduction waves at $E_{1/2} = -0.48$, -0.62 and -0.85 V versus SCE.

The bimetallic $[((NH_3)_4Ru)_2(dpop)]^{4+}$ ion in D_2O was oxidized chemically with $Ce(NH_4)_2(NO_3)_6$, and the electronic absorption spectrum recorded between 350 and 1800 nm (Fig. 3). Throughout oxidation of the bimetallic ion, the lowest energy MLCT absorption maximum shifted from 733 to 690 nm, while an absorption at 1670 nm ($\epsilon = 1250$ M^{-1} cm^{-1}; $\nu_{1/2} = 1900$ cm^{-1}) appeared and increased in intensity. Isosbestic points were observed at 370, 480, 600, 715 and 1050 nm throughout the oxidation. Additional amounts of Ce^{4+} caused a decrease in the absorption maxima at both 690 and 1670 nm and loss of the isosbestic points.

Extended irradiation of the bimetallic $[((NH_3)_4Ru)_2(dpop)]^{4+}$ ion at 691 nm in deoxygenated CH_3CN produced negligible spectral change and the upper limit for reactant loss was $\Phi < 1 \times 10^{-4}$ mol/E. Irradiation of the $[(dpop)_3Ru]^{2+}$ ion at 546 nm into the lowest energy MLCT transition, produced a shift to higher energy and lower absorbance of the lowest energy MLCT absorption maximum, and the growth of a peak at 397 nm (Fig. 4). Photolysis was continued until the spectrum remained constant over a 1 h interval, and the upper limit for reactant loss, based on spectra of up to 25% reaction, was $\Phi = 6 \times 10^{-4}$ mol/E. After completion of the photolysis reaction, the 5.0 ml solution was eluted from a Sephadex C-25 cation column with CH_3CN.

citation spectrum shows emission also occurs following excitation into the absorptions at 460 and 413 nm (Fig. 2(b)). Neither of the tetraammineruthenium(II)(dpop) ions was observed to be luminescent in room temperature deoxygenated CH_3CN solutions.

The cyclic voltammogram for the $[(NH_3)_4Ru(dpop)]^{2+}$ ion shows a reversible $Ru^{2+/3+}$ couple at $E_{1/2} = +0.83$ V and reversible $dpop^{0/-1}$ reduction at $E_{1/2} = -0.89$ versus SCE. The bimetallic
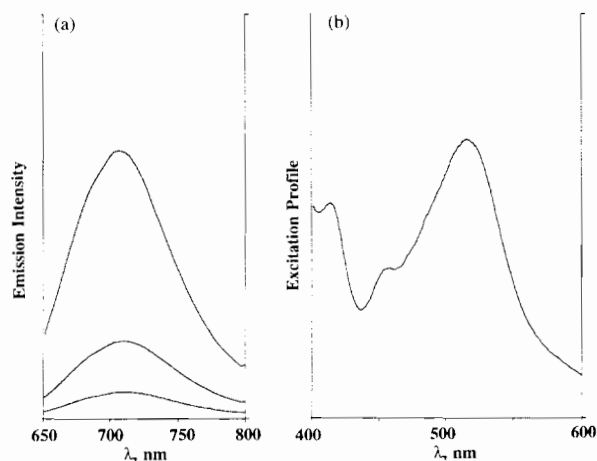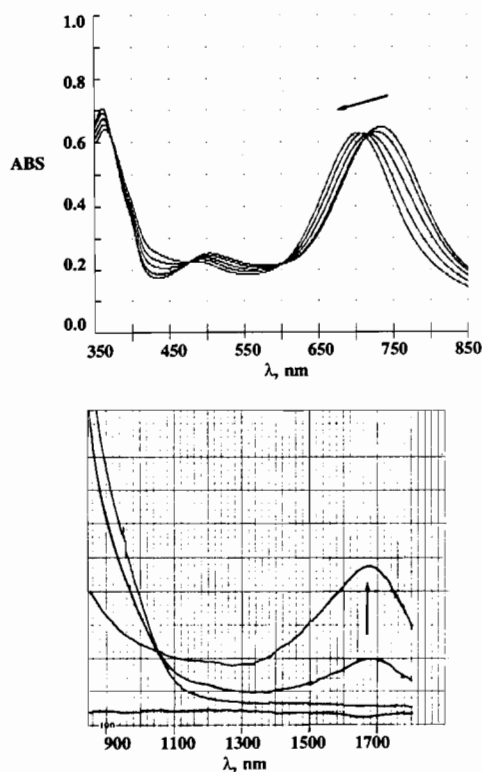
Fig. 3. Visible near-IR absorption spectra of [((NH$_3$)$_4$Ru)$_2$-(dpop)]$^{4+/5+}$ throughout Ce^{4+} additions up to 1.0 equiv.
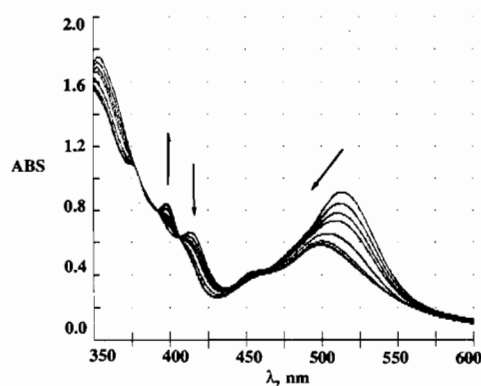

Fig. 4. Absorption spectra of [(dpop)$_3$Ru]$^{2+}$ during 546 nm irradiation recorded at t=0, 10, 20, 30, 60, 120, 180 and 240 min.

The colorless liquid that eluted before the pink metal photoproduct reached the bottom of the column, was collected and the UV–Vis spectrum had peaks at 398, 376 and 360 nm. An unphotolyzed sample, chromatographed and diluted in the identical manner, showed no absorptions between 320 and 400 nm.

4. Discussion

The intense absorptions in the visible spectrum for the [(NH$_3$)$_4$Ru(dpop)]$^{2+}$ ion are similar to those previously reported for other monometallic tetraammineruthenium(II) complexes bound to aza-aromatic ligands,

and these results are summarized in Table 1. On the basis of intensity and energy, the 629 and 483 nm absorptions are assigned to Ru(dπ)→dpop(π^*) transitions. The absorptions at 391 and 372 nm are similar in shape and energy to the absorptions of the uncomplexed dpop ligand [4,5], and thus could be due to a combination of MLCT and dpop intraligand transitions in the [(NH$_3$)$_4$Ru(dpop)]$^{2+}$ ion. The data in Table 1 show that the ruthenium(II) dpop complexes consistently exhibit an intense absorption maximum between 350 and 360 nm, and therefore the 355 nm absorption in the [(NH$_3$)$_4$Ru(dpop)]$^{2+}$ ion is attributed to an intraligand dpop transition. The absorption spectrum of the bimetallic [((NH$_3$)$_4$Ru)$_2$(dpop)]$^{4+}$ ion is similar to those previously reported for other bimetallic tetraammineruthenium(II) complexes bound to aza-aromatic ligands, and these results are summarized in Table 1. By analogy to those complexes, the 755 and 518 nm absorptions for the [((NH$_3$)$_4$Ru)$_2$(dpop)]$^{4+}$ ion are assigned to Ru(dπ)→dpop(π^*) MLCT transitions. Shoulders observed near 390 and 375 nm could again be due to a combination of MLCT and dpop intraligand transitions, while the 359 nm absorption maximum is assigned to a dpop intraligand transition. The Ru(dπ) →dpop(π^*) MLCT transitions for the mono- and bimetallic tetraammineruthenium(II)(dpop) ions are at lower energy than those for bis-bipyridylruthenium(II)(dpop) ions. This is explained by bpy (π^*) LUMO participation in backbonding with, and therefore stabilization of, the ruthenium(II) dπ orbitals. As a result, in the tetraammineruthenium(II) complex with σ only coordinating NH$_3$ ligands, the Ru (dπ) orbitals are relatively de-stabilized and the Ru(dπ)→dpop(π^*) MLCT transition occurs at longer wavelength.

The lowest energy MLCT transition for the bimetallic [((NH$_3$)$_4$Ru)$_2$(dpop)]$^{4+}$ ion is 2650 cm^{-1} lower in energy than for the monometallic [(NH$_3$)$_4$Ru(dpop)]$^{2+}$ ion. The shift of the Ru(dπ)→BL(π^*) MLCT transition to lower energy for bimetallic complexes has been reported for numerous aza-aromatic bridging ligands (BL) including pyrazine (pz) [10,11], 2,2'-bipyrimidine (bpym) [9,16,20], 2,3-bis(2-pyridyl)pyrazine (dpp) [1b,21,22] and 2,3-bis(2-pyridyl)quinoxaline (dpq) [23]. The decrease in MLCT transition energy is attributed to the coordination of the second electropositive ruthenium center on the BL causing a stabilization of the BL(π^*) LUMO. The Ru(dπ)→dpop(π^*) energy stabilization of 2650 cm^{-1} due to coordination of the second tetraammineruthenium(II) center is less than the 3810 cm^{-1} stabilization caused by coordination of the second bis-bipyridylruthenium(II) metal center [1a]. This result supports the assertion the bis-bipyridylruthenium(II) fragment is more π acidic than the tetraammineruthenium(II) fragment, and that the π competitive peripheral bpy ligand influences the Ru(dπ)–dpop spectroscopic properties.

The absorption spectrum of the $[(dpop)_3Ru]^{2+}$ ion consists of several intense transitions that are similar in energy and intensity, as previously reported for other $[(BL)_3Ru]^{2+}$ complexes [14–23]. Despite the unsymmetric structure of the dpop ligand and splitting of the $Ru(d\pi)$ orbitals by the reduction of symmetry of the $[(dpop)_3Ru]^{2+}$ ion, no obvious splitting of the lowest energy MLCT absorption in solution is observed. The 512, 460(sh) and 413 nm absorptions are assigned as $Ru(d\pi) \rightarrow dpop(\pi^*)$ transitions, while the 352 nm absorption is assigned as a dpop intraligand transition. The comparison of transition energies for several $[(BL)_3Ru]^{2+}$ complexes shows that the $Ru(d\pi) \rightarrow BL(\pi^*)$ transition is lower in energy for BL = dpop than for BL = dpp, dpq and bpym.

The oxygen sensitive emission observed following excitation at 512 nm into the lowest energy MLCT absorption, as well as throughout the 400–512 nm region, indicates that regardless of the initial state populated, rapid efficient internal relaxation processes occur that terminate in the lowest energy triplet metal to ligand charge transfer state. The emission is therefore attributed to a ^{3}MLCT to ground state relaxation process.

The electrochemical results for the monometallic $[(NH_3)_4Ru(dpop)]^{2+}$ ion show that the reversible $Ru^{2+/3+}$ oxidation couple is 0.61 V less positive than for the $[(bpy)_2Ru(dpop)]^{2+}$ ion [1a]. This is interpreted as indicating greater $Ru(d\pi)$ electron density, or radial extension on the tetraammineruthenium(II) ion due to the absence of π backdonation to peripheral bpy ligands. Comparative values (Table 2) for the bimetallic tetraammine and bis-bipyridylruthenium(II) ions follow

a similar trend for the same rational. Comparison of the metal centered oxidation results for $[(BL)_3Ru]^{2+}$ ions shows the $[(dpop)_3Ru]^{2+}$ ion to be more positive than for similar ions which is interpreted as indicating the dpop ligand exerting more π electron-withdrawing influence upon the ruthenium(II) than similar nitrogen containing aromatic heterocyclic bridging ligands. The series of three reversible one-electron reductions for the $[(dpop)_3Ru]^{2+}$ ion is found to be less negative than for similar $[(BL)_3Ru]^{2+}$ ions, which is consistent with dpop as a more π withdrawing bridging ligand.

As previously noted by other research groups, when the electrochemical metal centered oxidation and BL centered reduction involve the same $Ru(d\pi)$ HOMO and $BL(\pi^*)$ LUMO as the MLCT transition, a comparison may be made between the electrochemical (E_{ox-red}) and lowest energy MLCT spectroscopic (E_{op}) energies [15,17,24]. Since the $Ru(d\pi) \rightarrow BL(\pi^*)$ optical transition occurs more quickly than molecular rearrangement, while the electrochemical process is much slower, E_{op} is found to be larger than E_{ox-red}. A plot of E_{op} (eV) versus ΔE_{ox-red} is expected to be linear when the same metal and ligand orbitals are involved in both the optical and electrochemical processes. Data for the $[(NH_3)_4Ru(dpop)]^{2+}$, $[((NH_3)_4Ru)_2(dpop)]^{4+}$ and $[(dpop)_3Ru]^{2+}$ ions give a linear least-squares fit of

$$E_{op} = 0.899\Delta E_{ox-red} + 0.422 \qquad r = 0.995$$

and supports the optical transition as being an MLCT process for the three complexes involving the same $d\pi$ HOMO and dpop π^* LUMO.

Table 2
Electrochemical data for some ruthenium(II) ammine, bipyridyl and tris-chelated ions, and calculated parameters

	$E_{1/2}(2)$	$E_{1/2}(1)$	$\Delta E(2-1)$	$E_{1/2}^{0/1-}$	$E_{1/2}^{1-/2-}$	E_{op}	E_{ox-red}	Reference
Monometallic complexes								
$(NH_3)_4Ru(dpop)^{2+}$		0.83		−0.89	−1.69(ir)	1.97	1.72	this work
$(bpy)_2Ru(dpop)^{2+}$		1.44		−0.63	−1.45	2.35	2.07	[1a]
$(NH_3)_4Ru(dpp)^{2+}$		0.77						[1b]
$(NH_3)_4Ru(bpym)^{2+}$		0.52[a]						[9]
Bimetallic complexes								
$((NH_3)_4Ru)_2(dpop)^{4+}$	1.24	0.73	0.51	−0.70	−1.24	1.64	1.43	this work
$((bpy)_2Ru)_2(dpop)^{4+}$	1.66	1.49	0.17	−0.18	−0.90	1.88	1.67	this work
$((NH_3)_4Ru)_2(dpp)^{4+}$	1.05	0.66						[1b]
$((NH_3)_4Ru)_2(bpym)^{4+}$	0.78	0.59[a]	0.19					[9]
	$E_{1/2}$		$E_{1/2}^{0/1-}$	$E_{1/2}^{1-/2-}$	$E_{1/2}^{2-/3-}$	E_{op}	E_{ox-red}	
Tris-complexes								
$(dpop)_3Ru^{2+}$	1.81 ± 0.5		−0.48	−0.62	−0.85	2.42	2.29	this work
$(dpp)_3Ru^{2+}$	1.68		−0.95	−1.12	−1.39			[18a,b]
$(bpy)_3Ru^{2+}$	1.27		−1.31	−1.50	−1.77			[17a,b]
$(bpym)_3Ru^{2+}$	1.69		−0.91	−1.08	−1.28			[17a,b]
$(dpq)_3Ru^{2+}$	1.70		−0.60	−0.78	−1.04			[7]

2,2'-bipyrimidine = bpym; 2,3-bis(2-pyridyl)pyrazine = dpp; 2,3-bis(2pyridyl)quinoxaline = dpq.
[a]Recorded in aqueous solution.

The observed photostability of the bimetallic $[((NH_3)_4Ru)_2(dpop)]^{4+}$ ion is consistent with previous results for low spin d^6 ruthenium(II) ammine complexes [8] in which the lowest energy MLCT transition lies lower in energy than the LF transition. The detection of uncomplexed dpop following photolysis of $[(dpop)_3Ru]^{2+}$ indicates that photosolvation of the tris-complex occurs. The quantum yield of $\Phi = 6 \times 10^{-4}$ is lower than those reported for $[(bpy)_3Ru]^{2+}$ and $[(dpq)_3Ru]^{2+}$ of 2.1×10^{-3} and 2.9×10^{-2}, respectively [7].

The electrochemical metal–metal interaction in the bimetallic $[((NH_3)_4Ru)_2(dpop)]^{4+}$ ion measured as $\Delta E = E_{1/2}(2) - E_{1/2}(1)$ is 0.51 V and is larger than the ΔE value of 0.17 V previously reported for the $[((bpy)_2Ru)_2(dpop)]^{4+}$ ion [1a]. This is consistent with π electron density being drawn towards the non-bridging ligand and away from the $Ru(d\pi)$–$dpop(\pi^*)$–$Ru(d\pi)$ interaction in bis-bipyridyl complexes. The ΔE value of 0.51 V for the bimetallic $[((NH_3)_4Ru)_2(dpop)]^{4+}$ ion is larger than the 0.39 V previously reported for the Creutz–Taube $[((NH_3)_5Ru)_2(pz)]^{4+}$ ion [10], suggesting substantial ruthenium–ruthenium interaction through the dpop bridging ligand. The distinctly separable $E_{1/2}(2)$ and $E_{1/2}(1)$ values allow calculation of the comproportionation constant K_c, for the reaction

$$[((NH_3)_4Ru)_2(dpop)]^{4+} + [((NH_3)_4Ru)_2(dpop)]^{6+} \longrightarrow$$
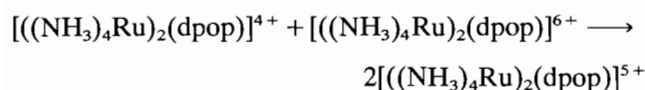
$$2[((NH_3)_4Ru)_2(dpop)]^{5+}$$

from the formula $\exp(\Delta E/25.69)$, as 4.2×10^8 [25]. The absorption at 1670 nm in D_2O of the chemically generated mixed valence $[((NH_3)_4Ru)_2(dpop)]^{5+}$ species is attributed to an intervalence (IT) transition on the basis of absorption increase and subsequent decrease throughout Ce^{4+} additions, and similarity in energy with that of other mixed valence ruthenium bimetallic complexes [11,26,27]. Due to the large comproportionation constant value, the extinction coefficient is measured and calculated without statistical correction as 1250 M^{-1} cm^{-1}. The observed value of $\Delta\nu_{1/2}$ (bandwidth at half height) of 1900 cm^{-1} is significantly different than that calculated from the Hush theory [28] by the equation $\Delta\nu_{1/2} = (2310\nu)^{1/2}$ of 3700 cm^{-1}, and suggests that the mixed valence complex is a more delocalized system (Class II/III) to which the Hush model is no longer valid.

5. Conclusions

Results indicate the replacement of π competitive peripheral ligands such as bpy with the σ coordinating NH_3 ligand shifts $Ru(d\pi) \rightarrow dpop(\pi^*)$ MLCT transitions to lower energy, as well as shifting $Ru^{2+/3+}$ and $dpop^{0/-1}$ electrochemical potentials towards less positive

potential. The $\Delta E(2-1)$ value of 510 mV for the tetraammineruthenium(II) dpop complex indicates substantially greater metal–metal interaction is found than in the analogous bis-bipyridylruthenium(II) dpop complex due to greater π density localized between the metal centers. The larger number of π conjugated rings directly coordinated to the Ru(II) center results in lower energy MLCT transitions than for similar tetraammineruthenium(II) BL complexes.

Acknowledgements

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