

Tuning of excited state reduction potentials via expanded π -systems. Synthesis and characterization of $[\text{Ru}(2,3\text{-di}(2'\text{-pyridyl})\text{benzo}(g)\text{quinoxaline})_3](\text{PF}_6)_2$

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Abstract

The synthesis of $[\text{Ru}(\text{dpb})_3](\text{PF}_6)_2$ ($\text{dpb} = 2,3\text{-di}(2'\text{-pyridyl})\text{(benzo}(g)\text{quinoxaline})$) is described. The electrochemical and spectral properties are examined and compared to related complexes. These properties follow the trends observed for homologous species, and indicate that the principal features controlling the electrochemical and spectral properties are the ligand reduction potential and the steric crowding around the metal center. The molecule shows an extremely low energy emission spectrum which is consistent with predictions based on the energy gap law.

Introduction

Recently, the preparations of variants of $\text{Ru}(\text{bpy})_3^{2+}$ ($\text{bpy} = 2,2'\text{-bipyridine}$) where the bpy ligand is replaced by polyaza derivatives have been described. Petersen and co-workers [1] synthesized the first of the tris chelated dpp -type complexes, $[\text{Ru}(\text{dpp})_3]^{2+}$ ($2,3\text{-di}(2'\text{-pyridyl})\text{pyrazine}$ (dpp ; see Fig. 1 for the ligand structures). Rillema *et al.* [2] have reported the preparation and properties of $[\text{Ru}(\text{bpy})_n(\text{dpq})_{3-n}]^{2+}$ ($2,3\text{-di}(2'\text{-pyridyl})\text{quinoxaline}$ (dpq ; $n = 0, 1$ or 2). The synthesis and properties of $[\text{Ru}(\text{bpy})_n(\text{LL})_{3-n}]^{2+}$ ($\text{LL} = 2,2'\text{-bipyrimidine}$ (bpm) [3, 4] or $2,2'\text{-bipyrazine}$ (bpz) [4–6]; $n = 0, 1$ or 2) have been reported and elaborated by several groups. The room temperature photophysical prop-

erties of the dpq [2], bpm [7] and bpz [7] complexes have been measured and are consistent with the decrease in the energy gap of these systems, as described by the 'energy gap' law [2, 7].

In an earlier report, the dpp ligand was shown to yield the first ligand bridged bimetallic complex with a reasonably long lived excited state ($[\text{Ru}(\text{bpy})_2]_2(\text{dpp})^{4+}$) [8, 9]. This success led to the preparation of $\{\text{Ru}[(\text{dpp})\text{Ru}(\text{bpy})_2]_3\}^{8+}$ utilizing $[\text{Ru}(\text{dpp})_3]^{2+}$ as the core [10]. This tetrametallic complex is luminescent at room temperature in fluid solution which is a unique observation for polymetallic complexes of this type.

Our interest in complexes containing dpp -type ligands has been due to the ease of the reduction of these ligands in metal complexes. Incorporation of additional aza linkages and conjugation decreases the reduction potential of these bridging bidentate ligands. Consistent with this, it has been shown for $\text{Re}(\text{dpq})(\text{CO})_3\text{Cl}$ [12a], $[\text{Re}(\text{CO})_3\text{Cl}]_2(\text{BL})$ ($\text{BL} = \text{dpp}, \text{dpq}$) [12a, b, c], $[\text{Ru}(\text{bpy})_2(\text{dpq})]^{2+}$ [13, 14] and $[\text{Ru}(\text{bpy})_2]_2(\text{dpq})^{4+}$ [13, 14] that the first and second reductions of these complexes both involve bridging ligand centered processes. The goal of developing additional Re complexes with two ligand-centered reductions led us to the synthesis of $\text{Re}(\text{dpb})(\text{CO})_3\text{Cl}$ and $[\text{Re}(\text{CO})_3\text{Cl}]_2(\text{dpb})$ ($\text{dpb} = 2,3\text{-di}(2'\text{-pyridyl})\text{benzo}(g)\text{quinoxaline}$) so as to further decrease the bridging ligand centered reduction potentials [12a]. Given the extensive information concerning the Ru complexes containing ligands of this

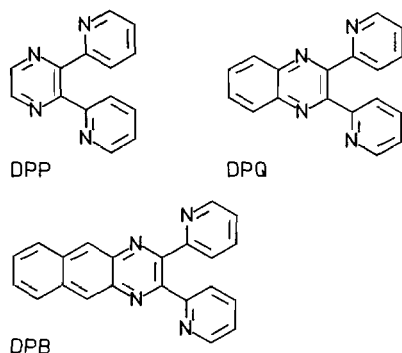


Fig. 1. Structures of the bridging ligands dpp , dpq and dpb .

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sort, it would be useful to compare the properties of the dpb [15] ligand to similar ruthenium based systems. With this goal in mind, we would like to report the preparation and characterization of $[\text{Ru}(\text{dpb})_3]^{2+}$.

Experimental

Materials

The acetonitrile (Burdick and Jackson) used in the electrochemical measurements was spectro-quality, and was stored over activated 4 Å molecular sieves (Davidson). The tetrabutylammonium hexafluorophosphate (TBAH) used as the supporting electrolyte was prepared from tetrabutylammonium bromide (Fluka) and hexafluorophosphoric acid (Aldrich) followed by several recrystallizations from ethanol and overnight storage in a vacuum oven at 100 °C. The $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (Johnson Matthey), 2,2'-pyridyl (Aldrich), *o*-phenylenediamine (Aldrich) 2,3-diaminonaphthalene (Lancaster), and 2,3-di(2'-pyridyl)pyrazine (dpp) (Aldrich) were used as supplied. All other solvents were reagent grade.

Syntheses

The 2,3-di(2'-pyridyl)quinoxaline (dpq) [16], $[\text{Ru}(\text{dpp})_3](\text{PF}_6)_2$ [1] and $[\text{Ru}(\text{dpq})_3](\text{PF}_6)_2$ [2] were prepared by literature methods.

2,3-Di(2'-pyridyl)benzo(g)quinoxaline (dpb)

This ligand was prepared via a slight modification of literature methods [12a, 15, 17]. Equimolar amounts of 2,2'-pyridyl and 2,3-diaminonaphthalene were slurried in ethanol and refluxed for *c.* 5 h. The resulting brown crystalline solid was recrystallized once from ethanol, reprecipitated from methylene chloride and pentane, then recrystallized several times from ethanol, yielding yellow crystals.

$[\text{Ru}(\text{dpb})_3](\text{PF}_6)_2$

A slurry of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (0.014 g, 0.05 mmol) and dpb (0.116 g, 0.35 mmol) was prepared in a 3:1 ethanol/water solution and refluxed under nitrogen for 20 h. The reaction mixture was allowed to cool and then filtered. The ethanol was removed by rotary-evaporation and the hexafluorophosphate salt was precipitated by addition of saturated aqueous KPF_6 . The complex was chromatographed on an alumina column with an acetonitrile/toluene eluent. The purple band was collected and the solvent was removed by rotary-evaporation. The resulting solid was dissolved in acetone and reprecipitated by addition to stirring diethyl ether (yield 0.022 g (30%)). *Anal.* Calc. for $\text{C}_{66}\text{H}_{42}\text{N}_{12}\text{F}_{12}\text{Ru} \cdot 2\text{H}_2\text{O}$: C, 55.43; H, 3.24; N, 11.75. Found: C, 55.50; H, 3.06; N, 11.73%.

Instrumentation

Absorption spectra were recorded on a Hewlett-Packard 8425A photodiode array spectrophotometer controlled by an AT & T 6300 microcomputer. Emission spectra were recorded on a Spex F222A spectrofluorimeter. Measurements at 77 K were recorded in quartz tubes using ethanol freshly distilled from $\text{Mg}(\text{OCH}_2\text{CH}_3)_2$ as the solvent.

Cyclic voltammetry measurements were made using a Bioanalytical Systems BAS-100 on samples dissolved in acetonitrile that was 0.1 M TBAH as the supporting electrolyte. All measurements were made using a 100 mV/s scan rate (except as noted) and the results reported versus a saturated sodium chloride calomel (SSCE; 0.236 V versus NHE) reference electrode. The reduction potentials reported were obtained from the cyclic voltammograms by averaging the peak oxidative and reductive potentials.

Results and discussion

Electrochemistry

Figure 2A displays the cyclic voltammogram of dpb in the positive and negative potential regions. The free ligand shows one reversible reduction and two irreversible oxidations in the 2.00 to -2.00 potential region. The complex ion $[\text{Ru}(\text{dpb})_3]^{2+}$ shows three reversible reductions between -0.48 and -0.88 and an irreversible oxidation centered at 1.7 V (Fig. 2B). The oxidation remains irreversible even at scan rates as high as 5 V/s. Table 1 lists the reduction potentials for $[\text{Ru}(\text{dpb})_3]^{2+}$, dpb and some homologous complexes.

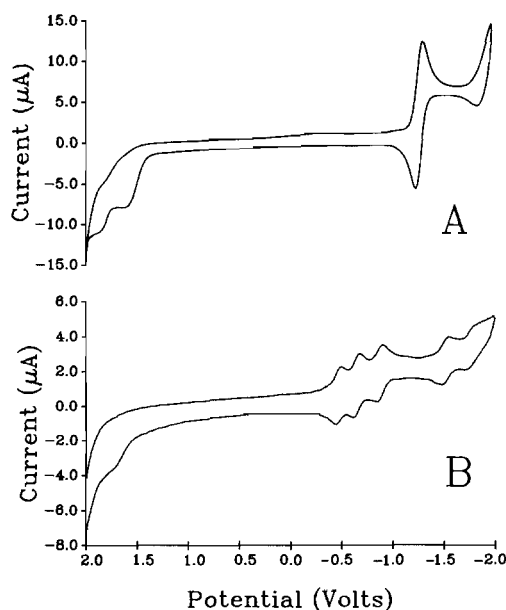


Fig. 2. Cyclic voltammograms of dpb (A) and $[\text{Ru}(\text{dpb})_3]^{2+}$ (B) in acetonitrile with 0.1 M TBAH.

TABLE 1. Electrochemical and electronic spectral data in acetonitrile for $[\text{Ru}(\text{dpb})_3]^{2+}$ and some related complexes. $E_{1/2}^{\text{ox}}$, $E_{1/2}(1)$, $E_{1/2}(2)$ and $E_{1/2}(3)$ are the first metal oxidation and first, second and third ligand-localized reductions, respectively

Complex	$E_{1/2}^{\text{ox}}$	$E_{1/2}(1)$	$E_{1/2}(2)$	$E_{1/2}(3)$	λ_{Abs}	ϵ ($\text{M}^{-1} \text{cm}^{-1}$)	λ_{Em}
$[\text{Ru}(\text{bpy})_3]^{2+}$	1.26	-1.35	-1.54	-1.77	452	1.4×10^4	630
$[\text{Ru}(\text{dpp})_3]^{2+}$	1.68	-0.95	-1.13	-1.40	455	1.6×10^4	636
$[\text{Ru}(\text{dpq})_3]^{2+}$	1.65	-0.63	-0.82	-1.08	499	1.4×10^4	724
$[\text{Ru}(\text{dpb})_3]^{2+}$	1.67	-0.48	-0.65	-0.88	540	1.2×10^4	810
$[\text{Ru}(\text{bpy})_2(\text{dpb})]^{2+}$	1.43	-0.63	-1.29	-1.61	550	8.2×10^3	810
dpb	1.7	-1.29					

Absorbance data on $[\text{Ru}(\text{bpy})_3]^{2+}$ from ref. 2 and $[\text{Ru}(\text{dpq})_3]^{2+}$ from ref. 1. Data on $[\text{Ru}(\text{bpy})_2(\text{dpb})]^{2+}$ from ref. 18. Absorption maxima in acetonitrile.

The three reversible reductions for $[\text{Ru}(\text{dpb})_3]^{2+}$ are assigned to the addition of an electron to each of the dpb ligands. This pattern is typical of complexes of this type [19–21]. It should be noted that the orbital energies of this and similar ligands control their ability to act as multiple electron reservoirs, as noted by Vleck [22].

The anodic shift of the ligand-centered reductions in the series of complexes $[\text{Ru}(\text{dpp})_3]^{2+} < [\text{Ru}(\text{dpq})_3]^{2+} < [\text{Ru}(\text{dpb})_3]^{2+}$ is consistent with the increasing conjugation of the ligand. This is rationalized in terms of the “particle in a box model”, where the energy of the particle is inversely proportional to the length of the box. The increase in conjugation of the polyaza ligand increases the length of the π^* -orbital or “box” that the electrons are occupying [13, 14, 23]. This trend of positive shifts in ligand reduction energy illustrates the ability to synthetically control the energy of the lowest unoccupied orbital on the ligand acting as the electron reservoir.

The irreversible oxidation wave at 1.7 V has been assigned to a ligand-centered process as well, due to the observation of a similar wave at 1.5 V in the free ligand. The inhibition of a metal centered oxidation or the preferential reaction of an exposed ligand group has been observed in other tris-chelated ruthenium systems [24, 25]. Binding the metal to the ligand removes electron density from the ligand, which is commonly manifested as the anodic shift of the ligand centered reduction relative to the reduction of the free ligand. A ligand-centered oxidation would also be shifted positively relative to the free ligand. In liquid SO_2 , free bpy oxidizes at 2.1 V, while for $[\text{Ru}(\text{bpy})_3]^{3+}$, the bpy oxidation is found at 2.76 V [26]. In this case, Ru(III) is causing a 0.66 V anodic shift of the ligand oxidation. A ligand-centered oxidative process involving Ru(II) would be expected to shift anodically less than this, which is the case for $[\text{Ru}(\text{dpb})_3]^{2+}$. The oxidation

process probably involves the exposed naphthalene moiety of dpb, and is irreversible on the time scale of the cyclic voltammetry experiment. It is likely that having three dpb ligands around the metal favors oxidation of the ligand due to the remoteness of the metal from the electrode. Preliminary results on $[\text{Ru}(\text{bpy})_2(\text{dpb})]^{2+}$ and $[\text{Ru}(\text{bpy})_2(\text{dpb})]^{4+}$ [18] show that the metal-centered oxidations are reversible and in the expected potential region, which suggests that the bpy ligands permit close approach to the electrode. Furthermore, the metal center is expected to be easier to oxidize in $[\text{Ru}(\text{bpy})_2(\text{dpb})]^{2+}$ than in $[\text{Ru}(\text{dpb})_3]^{2+}$, since bpy is less electron-withdrawing than dpb.

Electronic spectroscopy

Figure 3 shows the absorption spectrum of $[\text{Ru}(\text{dpb})_3]^{2+}$, $[\text{Ru}(\text{dpp})_3]^{2+}$ and $[\text{Ru}(\text{dpq})_3]^{2+}$ in acetonitrile. Table 1 lists the lowest energy absorption maximum these and some related complexes in acetonitrile. The spectrum of $[\text{Ru}(\text{dpb})_3]^{2+}$ displays a high energy band at 318 nm and a structured band with peaks at 390 and 410 nm, assignable to $\text{p}\pi \rightarrow \text{p}\pi^*$ transitions. This latter band shifts to 424 nm in toluene,

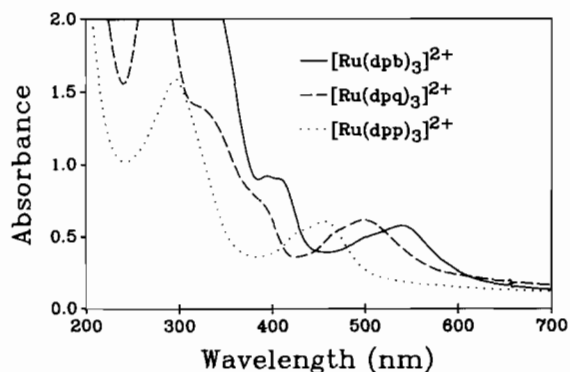


Fig. 3. Electronic absorption spectra of $[\text{Ru}(\text{dpp})_3]^{2+}$, $[\text{Ru}(\text{dpq})_3]^{2+}$ and $[\text{Ru}(\text{dpb})_3]^{2+}$ dissolved in acetonitrile.

and corresponds to a similar transition in the free ligand [12a]. The low energy band at 540 nm is assigned to the $d\pi(\text{Ru}^{\text{II}}) \rightarrow p\pi^*(\text{dpb})$ charge transfer process, based on the solvent sensitivity of the maximum (i.e. shifting to 570 nm in toluene) and by analogy with homologous complexes [1, 2, 8, 13, 27, 28].

The room temperature emission spectrum of $[\text{Ru}(\text{dpb})_3]^{2+}$ shows a weak band at 810 nm (the emission profile is distorted in this energy region due to the non-linear response of our PMT). The emission intensity increases at 77 K, but no vibrational progressions are resolved. We were unable to measure the emission lifetime at room temperature due to the low emission intensity.

It has been generally observed that complexes like $[\text{Ru}(\text{dpb})_3]^{2+}$ obey the energy gap law [2, 7] which predicts that k_{nr} and Φ_{nr} increase as the energy gap decreases, competing with radiative deactivation. Given the low energy of the emission observed for $[\text{Ru}(\text{dpb})_3]^{2+}$, it is therefore not surprising that the emission intensity for this complex is so small. Another factor that appears in the energy gap law is the number of vibrational modes that act as acceptor modes for the excitation energy. An X-ray structure determination of $[\text{Ru}(\text{dpq})_3]^{2+}$ shows a 24° angle between the pyrazine and the bound pyridine, and a torsional angle of the chelate ring of 16° [2]. This can be compared to $[\text{Ru}(\text{bpy})_3]^{2+}$, which shows essentially a regular octahedron and planar bpy ligands [29]. This suggests that the non-planarity of dpq and (presumably) dpb increases the number of ligand normal modes available for coupling the ground and excited states, thereby increasing the non-radiative relaxation [30, 31]. The 3,3'-annelated 2,2'-bipyridines systems studied by Thummel and co-workers [31, 32] and Gafney and co-workers [31], where the 3,3'-annelation progressively increases the dihedral angle between the two pyridine rings, is consistent with this.

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