

Isovalent and Mixed-Valent Diruthenium Complexes [(acac)₂Ru^{II}(μ -bpytz)Ru^{II}(acac)₂] and [(acac)₂Ru^{II}(μ -bpytz)Ru^{III}(acac)₂](ClO₄) (acac = Acetylacetonate and bpytz = 3,6-Bis(3,5-dimethylpyrazolyl)-1,2,4,5-tetrazine): Synthesis, Spectroelectrochemical, and EPR Investigation

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The title compounds involving the structurally characterized bridging ligand bpytz were characterized, showing very strong electrochemical stabilization of the mixed-valent Ru^{II}Ru^{III} state ($K_c = 10^{13.9}$) but no detectable ($\epsilon < 20 \text{ M}^{-1} \text{ cm}^{-1}$) intervalence charge-transfer band in the infrared region. In situ reduction of the neutral precursor produces a diruthenium(II) complex of the bpytz radical anion according to EPR spectroscopy, whereas oxidation of the mixed-valent form leads to a diruthenium(III) species.

Introduction

The design of polynuclear metal complexes exhibiting strong intermetallic electronic coupling in mixed-valent states via the mediation by suitably bridging functionalities has generated considerable research interest in recent years.¹ This has been primarily due to the relevance for biological processes,² molecular electronics,³ and theoretical studies of electron-transfer kinetics.⁴ The observation of exceptionally strong intermetallic electronic coupling in mixed-valent Ru^{II}-(tz)Ru^{III} complexes mediated by 3,6-substituted 1,2,4,5-tetrazine (tz) ligands has initiated continuous efforts in designing newer classes of tz-bridged diruthenium complexes.^{1a} Among the bridging ligands based on the tz unit, the bis-bidentate ligand 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine (bptz) has been extensively used in framing diruthenium complexes in combination with ancillary ligands of varying electronic aspects such as NH₃,⁵ 2,2'-bipyridine (bpy),⁶ acetylacetonate (acac),⁷ [9]aneS₃,⁸ and arenes.⁹ Considerable variation of comproportionation constant values (K_c) has been observed

in those complexes, on the basis of the electronic nature of ancillary ligands (K_c): 1×10^{15} (NH₃); 3×10^8 (bpy); 1×10^{13} (acac); 1.4×10^8 ([9]ane S₃). In addition, modified bis-bidentate forms of tetrazine ligands such as 3,6-bis-(3,5-dimethylpyrazolyl)-1,2,4,5-tetrazine (bpytz),¹⁰ 3,6-bis-(2-thienyl)-1,2,4,5-tetrazine (bttz),¹¹ 3,6-bis(4-methyl-2-pyridyl)-1,2,4,5-tetrazine (bmptz),¹¹ and 3,6-bis(dicarboxylic acid)-1,2,4,5-tetrazine (bctz)¹² have been utilized later on in developing diruthenium complexes [(bpy)₂Ru(tz)Ru(bpy)₂]ⁿ⁺ incorporating π -acidic bpy coligands.

The observed effect of the electron-rich acac coligands on the comproportionation constant value ($K_c = 1 \times 10^{13}$)⁷ of the bptz-bridged mixed-valent Ru^{II}Ru^{III} species in relation to that with the π -acidic bpy ligand ($K_c = 3 \times 10^8$)⁶ has prompted us to scrutinize the effect of the acac ancillary function in the bpytz-bridged diruthenium complex.

In this report, we describe the synthesis of isovalent [(acac)₂Ru^{II}(μ -bpytz)Ru^{II}(acac)₂] and mixed-valent [(acac)₂Ru^{II}(μ -bpytz)Ru^{III}(acac)₂](ClO₄) together with their spectroelectrochemical and EPR investigation.

Results and Discussion

The bridging ligand 3,6-bis(3,5-dimethylpyrazolyl)-1,2,4,5-tetrazine (bpytz) was prepared according to the reported

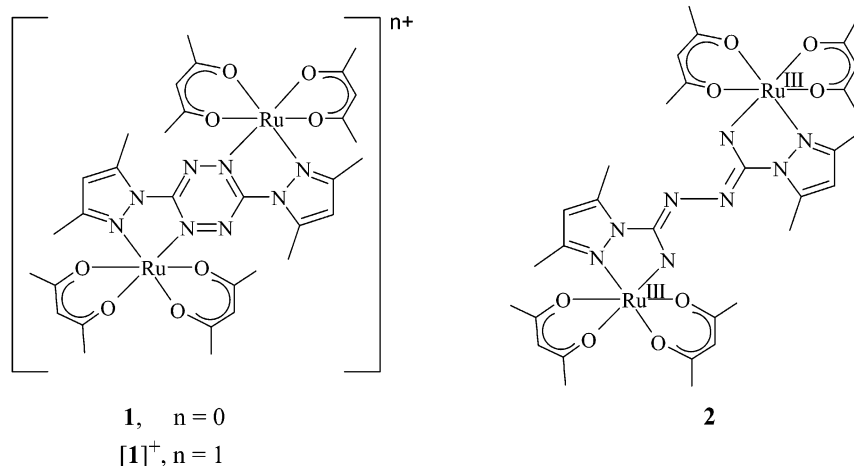
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Chart 1



procedure;¹³ its crystal structure[±] is shown in Figure 1. The bond distances and angles are in the expected range. The complexation reaction of bpytz was carried out with the precursor compound $\text{Ru}^{\text{II}}(\text{acac})_2(\text{CH}_3\text{CN})_2$ in a 1:2 molar ratio in EtOH under nitrogen, followed by chromatography, to yield purple and blue complexes corresponding to isova-

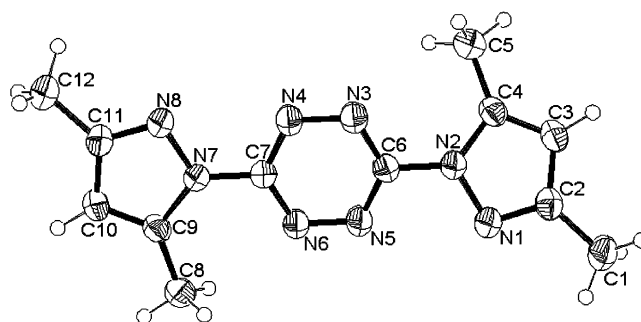


Figure 1. Crystal structure of bpytz.

lent $(\text{acac})_2\text{Ru}^{\text{II}}(\mu\text{-bpytz})\text{Ru}^{\text{II}}(\text{acac})_2$, **1**, and mixed-valent $[(\text{acac})_2\text{Ru}^{\text{II}}(\mu\text{-bpytz})\text{Ru}^{\text{III}}(\text{acac})_2](\text{ClO}_4)$, **[1]⁺**(ClO_4) (Chart 1). Alternatively, the chemical oxidation of **1** by an aqueous Ce^{IV} solution also resulted in **1⁺**. This mixed-valent complex can be reduced to the isovalent **1** by using reducing agents such as hydrazine hydrate. All attempts to synthesize a mononuclear derivative $(\text{acac})_2\text{Ru}^{\text{II}}(\text{bpytz})$ using a 1:1 molar ratio of $\{\text{Ru}(\text{acac})_2\}$ and bpytz have failed so far, confirming the propensity of such systems for charge-transfer-supported coordinative saturation.^{1a,5,6} On every occasion **1** and **1⁺** were obtained exclusively. The formation of the stable mixed-valent $\text{Ru}^{\text{II}}\text{Ru}^{\text{III}}$ species **[1]⁺** along with the isovalent $\text{Ru}^{\text{II}}\text{-Ru}^{\text{II}}$ state (**1**) can be explained in terms of the low $\text{Ru}^{\text{II}}\text{Ru}^{\text{III}} \rightleftharpoons \text{Ru}^{\text{II}}\text{Ru}^{\text{II}}$ redox potential (-0.15 V versus SCE) and the

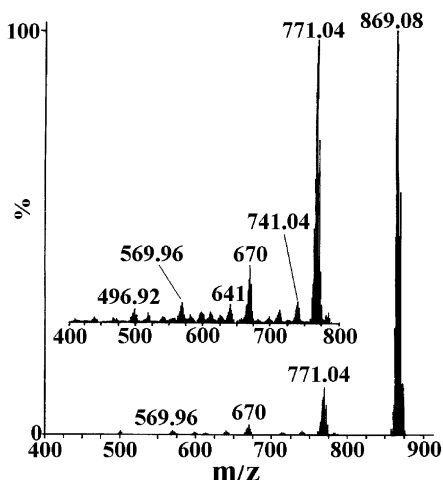
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Table 1. Redox Potentials and Comproportionation Constants (K_c) for Corresponding Diruthenium Complexes

compd	Ru ^{III} Ru ^{II} –Ru ^{II} Ru ^{II} couple E°_1/V	Ru ^{III} Ru ^{III} –Ru ^{III} Ru ^{II} couple E°_2/V	K_c	ref
(acac) ₂ Ru(bpytz)Ru(acac) ₂ (1) ^a	–0.15	0.67	10 ^{13.9}	present work
[(bpy) ₂ Ru(bpytz)Ru(bpy) ₂] ⁴⁺ ^a	1.25	1.70	10 ^{7.6}	10
(acac) ₂ Ru(bptz)Ru(acac) ₂ ^b	0.17	0.97	10 ^{13.6}	7
[(bpy) ₂ Ru(bptz)Ru(bpy) ₂] ⁴⁺ ^c	1.52	2.02	10 ^{8.5}	6, 14
[(NH ₃) ₂ Ru(bptz)Ru(NH ₃) ₂] ⁴⁺ ^d	0.69	1.58	10 ¹⁵	5

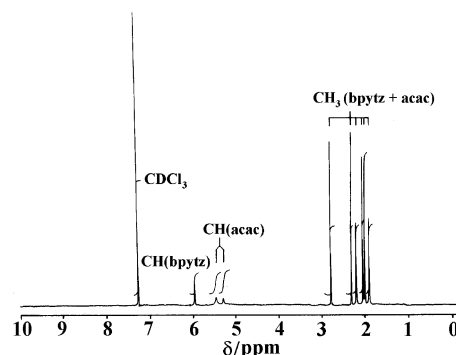
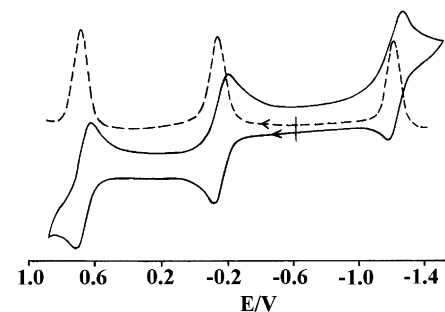
^a CH₃CN–(TEA)ClO₄, E/V versus SCE. ^b CH₂Cl₂–(TBA)BF₄, E/V versus Ag/AgCl. ^c CH₃CN–(TBA)ClO₄, E/V versus SCE. ^d CH₃CN–(TBA)ClO₄, E/V versus Ag/AgCl.

**Figure 2.** Electrospray mass spectrum of **1** in CH₃CN. The inset shows the expansion in the range $m/z = 800$ – 400 .

high comproportionation constant (K_c) value of 10^{13.9} in the mixed-valent state (see later). Earlier we have observed that the reaction of the precursor complex Ru(acac)₂(CH₃CN)₂ with the dihydrotetrazine form, i.e., 3,6-bis(3,5-dimethylpyrazolyl)-1,4-dihydro-1,2,4,5-tetrazine (H₂bpytz), unexpectedly led to the formation of a diruthenium(III) complex, (acac)₂Ru^{III}(μ -L²⁻)Ru^{III}(acac)₂ (**2**), where the preformed bridging ligand H₂bpytz underwent a tetrazine ring-opening process to a new class of dianionic bridging ligand, L²⁻.^{1m}

The complex **1** is diamagnetic and neutral whereas [**1**]-ClO₄ exhibits paramagnetism due to one unpaired electron and shows 1:1 conductivity. Both products yield satisfactory microanalyses (see Experimental Section). The formation of **1** and **1**⁺ was confirmed by their electrospray mass spectral data. Compound **1** exhibits signals centered at m/z values of 869.08, 771.04, 670, and 569.96 (Figure 2), corresponding to {**1**}⁺ (calculated molecular weight 868.87), {**1** – acac}⁺ (769.76), {**1** – 2acac}⁺ (670.66), and {**1** – 3acac}⁺ (571.55), respectively. Expectedly, [**1**]ClO₄ yielded a molecular mass at m/z , 869.07 corresponding to [**1**]⁺.

The ¹H NMR spectrum of **1** in CDCl₃ showed only one set of signals (Figure 3), which implies the presence of either the C_s-symmetrical *meso* complex or a 1:1 mixture of C₂-symmetrical Δ,Δ and Λ,Λ enantiomers.^{6b,14} The observed three CH singlets (δ at 5.95 and 5.45 and 5.30 ppm corresponding to bpytz and acac, respectively) and six distinct CH₃ signals (δ/ppm : 2.78, 2.31, 2.20, 2.04, 2.00, 1.90; four from acac and two from bpytz) suggest that half of the molecule is essentially representative of **1** due to internal symmetry.

**Figure 3.** ¹H NMR spectrum of **1** in CDCl₃.**Figure 4.** Cyclic voltammograms (—) and differential pulse voltammograms (---) of **1** in CH₃CN. Scan rate = 50 mV sec⁻¹.

Compound **1** displays two quasi-reversible Ru^{II}/Ru^{III} processes in CH₃CN at $E^{\circ}_1 = -0.15$ V ($\Delta E_p = 80$ mV) and $E^{\circ}_2 = 0.67$ V ($\Delta E_p = 85$ mV) versus SCE (Figure 4; Table 1) which are assigned as successive Ru^{II}Ru^{III} \rightleftharpoons Ru^{II}Ru^{II} and Ru^{III}Ru^{III} \rightleftharpoons Ru^{II}Ru^{III} couples. The analogous bipyridine complex [(bpy)₂Ru^{II}(μ -bpytz)Ru^{II}(bpy)₂]⁴⁺ exhibited the same Ru^{II}/Ru^{III} based couples at a much higher potential¹⁰ (Table 1). This destabilization of the Ru^{II} state in **1** relative to the bpy derivative can account for the preferential formation of the mixed-valent Ru^{II}Ru^{III} species [**1**]⁺ along with **1**. A similar trend has also been observed in the bptz series for the acac and bpy complexes (Table 1).^{6,7,14} The observed 820 mV separation in the potentials between the successive Ru^{II}/Ru^{III} couples ($E^{\circ}_2 - E^{\circ}_1$) in **1** corresponds to a comproportionation constant (K_c) value of 10^{13.9} [calculated using the equation $RT \ln K_c = nF(\Delta E)^{15}$]. The observed high K_c value indicates strong electrochemical coupling, suggesting a delocalized mixed-valent Ru^{II}Ru^{III} state in **1**⁺. The K_c values of the corresponding other bpytz and bptz complexes are set in Table 1 which reveal a dramatic increase in the K_c value while changing from the combination bpy–tz to acac–tz. The lowering of the positive charge of the complex

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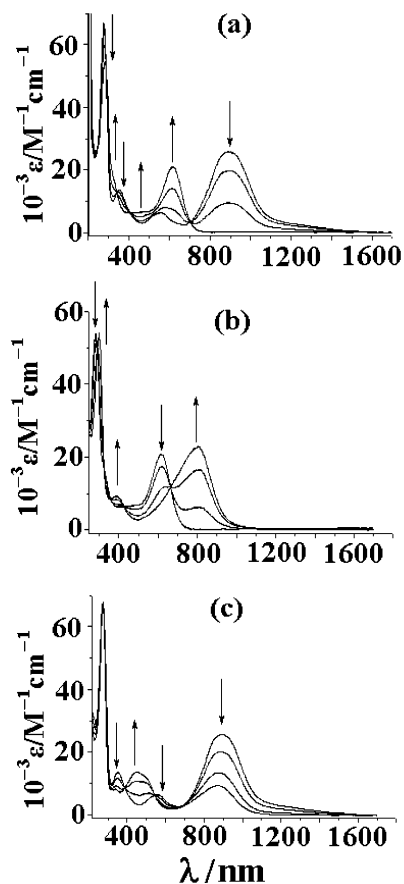


Figure 5. UV-vis-NIR spectroelectrochemistry of the conversions (a) $1 \rightarrow 1^+$, (b) $1^+ \rightarrow 1^{2+}$, and (c) $1 \rightarrow 1^-$ in $\text{CH}_2\text{Cl}_2/0.1 \text{ M Bu}_4\text{NPF}_6$.

Table 2. UV-Vis-NIR Data for 1^{n+} ($n = 2, 1, 0, -1$) from Spectroelectrochemistry^a

compd	$\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1} \text{cm}^{-1}$)
1^{2+}	808 (22 950), 390 (9360), 300 (54 100)
1^+	617 (21 000), 455 (br sh), 320 (sh), 285 (54 800)
1	895 (25 900), 557 (6400), 353 (13 680), 277 (67 500)
1^-	872 (9860), 450 (13 800), 340 (sh), 275 (68 100)

^a In $\text{CH}_2\text{Cl}_2/0.1 \text{ M Bu}_4\text{NPF}_6$.

molecule from +4 to 0 essentially facilitates the intermetallic electrochemical coupling process to a large extent in the mixed-valent state.

The tetrazine-based one-electron reduction was observed at $E^\circ = -1.21 \text{ V}$ ($\Delta E_p = 80 \text{ mV}$) versus SCE in CH_3CN . For the corresponding bpy-bpytz complex this process appeared at -0.13 V .¹⁰ Therefore, the introduction of the acac function in **1** in place of bpy effects substantial destabilization of both the metal-based highest occupied molecular orbitals and of the tetrazine-based LUMO.

UV-vis-NIR spectroelectrochemical studies of $[1]^{n+}$ ($n = 2, 1, 0, -1$) were performed in dichloromethane at 298 K using an OTTLE setup.¹⁶ The spectra are shown in Figure 5, and the data are listed in Table 2. The presence of distinct isosbestic points during the oxidation and reduction processes (Figure 5) and the electrochemical regeneration without significant degradation support the reversibility of the

electron-transfer transformations during spectroelectrochemical experiments.

The starting $\text{Ru}^{\text{II}}\text{Ru}^{\text{II}}$ complex **1** exhibits two intense transitions in the visible region at 895 nm ($\epsilon = 25\,900 \text{ M}^{-1} \text{cm}^{-1}$) and 557 nm ($\epsilon = 6400 \text{ M}^{-1} \text{cm}^{-1}$). Ligand-based strong transitions are observed in the UV region. The long-wavelength bands at 895 and 557 nm are assigned as $\text{Ru}^{\text{II}} \rightarrow \text{bpytz}$ and $\text{Ru}^{\text{II}} \rightarrow \text{acac}$ based MLCT transitions, respectively.¹⁰ This is consistent with the observation that the tetrazine function in the bridging ligands (bptz, bpytz) undergoes facile reduction.^{1a,7,10} The energy of the bpytz-based MLCT transition of **1** can be estimated with the help of eqs 1 and 2.¹⁷

$$\nu(\text{MLCT}) = 8065(\Delta E_{1/2}) + 3000 \text{ cm}^{-1} \quad (1)$$

$$\Delta E_{1/2} = E_{1/2}(\text{Ru}^{\text{III}}-\text{Ru}^{\text{II}}) - E_{1/2}(\text{ligand}) \quad (2)$$

where $E_{1/2}(\text{Ru}^{\text{III}}-\text{Ru}^{\text{II}})$ is the formal potential in V of the reversible first $\text{Ru}^{\text{III}}\text{Ru}^{\text{II}}$ couple, $E_{1/2}$ is the potential of the bpytz-based reduction, and $\nu(\text{MLCT})$ is the predicted wave-number of the charge-transfer band in cm^{-1} ; $8065 \text{ cm}^{-1}/\text{V}$ is the conversion factor, and the term 3000 cm^{-1} is of empirical origin. Considering the value of 1.06 V for $\Delta E_{1/2}$, the calculated MLCT energy is $11\,549 \text{ cm}^{-1}$, well comparable to the observed lowest energy MLCT transition of $11\,173 \text{ cm}^{-1}$.

The $\text{Ru}^{\text{II}} \rightarrow \pi^*(\text{tetrazine})$ transition in the corresponding bipyridine complex $[(\text{bpy})_2\text{Ru}^{\text{II}}(\mu\text{-bpytz})\text{Ru}^{\text{II}}(\text{bpy})_2]^{4+}$ appeared at 757 nm.¹⁰ The red-shift of 138 nm for the $\text{Ru}^{\text{II}} \rightarrow \pi^*(\text{tetrazine})$ transition on moving from bpy to acac ancillary ligands implies substantial destabilization of the Ru^{II} state in **1** relative to the bpy derivative, as confirmed by their metal redox potentials stated above. A less pronounced red-shift of the $\text{Ru}^{\text{II}} \rightarrow \pi^*(\text{tetrazine})$ transition has been reported in the bptz series, going from $[(\text{bpy})_2\text{Ru}^{\text{II}}(\mu\text{-bptz})\text{Ru}^{\text{II}}(\text{bpy})_2]^{4+}$ (683 nm)^{14,18} to $[(\text{acac})_2\text{Ru}^{\text{II}}(\mu\text{-bptz})\text{Ru}^{\text{II}}(\text{acac})_2]$ (707 nm).⁷

On one-electron oxidation to the mixed-valent $\text{Ru}^{\text{II}}\text{Ru}^{\text{III}}$ species $[1]^+$, the $\text{Ru}^{\text{II}} \rightarrow \pi^*(\text{tetrazine})$ transition is blue-shifted to 617 nm with appreciable reduction in intensity ($\epsilon = 21\,000 \text{ M}^{-1} \text{cm}^{-1}$), in accord with a decrease in the number of Ru^{II} centers in $[1]^+$. The mixed-valent state $[1]^+$ did not exhibit a detectable IVCT band in the near- or mid-IR region. The whole spectral range of the near- and even mid-IR was explored in the search for the IVCT band, using UV-vis-NIR and FTIR instruments. In contrast, the corresponding $[(\text{bpy})_2\text{Ru}^{\text{II}}(\mu\text{-bpytz})\text{Ru}^{\text{III}}(\text{bpy})_2]^{5+}$ showed one narrow IVCT band at 1534 nm ($\epsilon = 1800 \text{ M}^{-1} \text{cm}^{-1}$) with the characteristics of class III mixed-valent species.¹⁰

In view of the very large K_c value of $10^{13.9}$, the absence of the typically expected IVCT transition in $[1]^+$ appears puzzling at first. However, a look at bptz-bridged diruthenium(II,III) complexes reveals that the intensity of the IVCT

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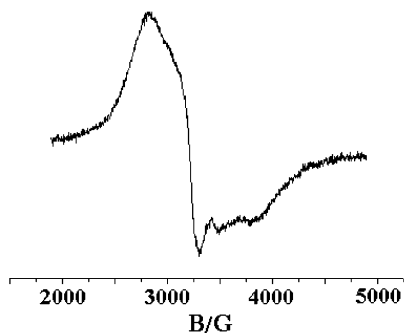


Figure 6. EPR spectrum of 1^+ in CH_2Cl_2 at 4 K.

band in the near-infrared decreases considerably by replacing π -accepting ancillary ligands in $[(\text{bpy})_2\text{Ru}(\mu\text{-bptz})\text{Ru}(\text{bpy})_2]^{5+}$ ($\epsilon = 2800 \text{ M}^{-1} \text{ cm}^{-1}$)¹⁸ with an “innocent” neutral ammine in $[(\text{H}_3\text{N})_5\text{Ru}(\mu\text{-bptz})\text{Ru}(\text{NH}_3)_5]^{5+}$ ($\epsilon = 500 \text{ M}^{-1} \text{ cm}^{-1}$)⁵ and further with anionic acac^- in $[(\text{acac})_2\text{Ru}(\mu\text{-bptz})\text{Ru}(\text{acac})_2]^+$ ($\epsilon = 20 \text{ M}^{-1} \text{ cm}^{-1}$).⁷ Starting from a lower ϵ of $1800 \text{ M}^{-1} \text{ cm}^{-1}$ for the $\text{bpy}/\text{bpytz}/\text{bpy}$ combination,¹⁰ perhaps due to less favorable chelate arrangements involving the five-membered heterocycles, the absence of a detectable IVCT band for 1^+ ($\epsilon < 20 \text{ M}^{-1} \text{ cm}^{-1}$) is thus not completely unexpected. It seems unreasonable to assume what would be an enormous high-energy shift of the IVCT transition to about 620 nm where the first long-wavelength band is observed. At this point we cannot offer a simple explanation of this substantial band intensity effect which occurs for well-delocalized species according to the very large K_c values; however, it should be noted that very weak to undetectable IVCT bands despite reasonably large K_c values have been reported previously for a number of diruthenium and triruthenium mixed-valent systems.^{1e,k,5,19a,b} We, therefore conclude that large K_c values are really independent of the IVCT band intensity.

On further oxidation to the $\text{Ru}^{\text{II}}\text{Ru}^{\text{III}}$ species, 1^{2+} , a new intense transition appeared at 808 nm ($\epsilon = 22\,950 \text{ M}^{-1} \text{ cm}^{-1}$) which is assigned to a ligand $\rightarrow \text{Ru}^{\text{III}}$ LMCT transition involving the bridging ligand bpytz and/or the terminal acac ligands.²⁰

On one-electron reduction to 1^- , the $\text{Ru}^{\text{II}} \rightarrow \text{bpytz}$ MLCT transition was found to be slightly blue-shifted from 895 nm ($\epsilon = 25\,900 \text{ M}^{-1} \text{ cm}^{-1}$) to 872 nm ($\epsilon = 9860 \text{ M}^{-1} \text{ cm}^{-1}$) with a substantial drop in intensity. This is a consequence of placing an electron in the LUMO (which thus becomes a singly occupied MO, SOMO).²¹ On the other hand, the transition ascribed to a $\text{Ru}^{\text{II}} \rightarrow \text{acac}$ MLCT is appreciably blue-shifted from 557 nm ($\epsilon = 6400 \text{ M}^{-1} \text{ cm}^{-1}$) to 450 nm ($\epsilon = 13\,800 \text{ M}^{-1} \text{ cm}^{-1}$) with a reasonable enhancement in intensity.

The isolated mixed-valent $\text{Ru}^{\text{II}}\text{Ru}^{\text{III}}$ species 1^+ displays a rhombic EPR spectrum in CH_2Cl_2 glass at 4 K with $g_1 = 2.442$, $g_2 = 2.146$, and $g_3 = 1.818$ (Figure 6). The calculated

isotropic g value of 2.15 agrees with $g = 2.17$ reported for the bptz -bridged analogue.⁷ That spectral profile clearly indicates a distorted octahedral arrangement around the ruthenium center(s) in 1^+ with negligible ligand contribution and a valence-averaged situation.^{1c,d,22,23} The one-electron-reduced species 1^- exhibited an unstructured EPR signal in CH_2Cl_2 at 4 K with $g = 2.0058$. The obviously small g anisotropy as well as the value close to g (electron) = 2.0023 confirms that the additional electron in the reduced state 1^- is largely localized on the bridging ligand bpytz .

Experimental Section

The starting complex $\text{Ru}(\text{acac})_2(\text{CH}_3\text{CN})_2$ ²⁴ and L^{13} were prepared according to the reported procedures. Other chemicals and solvents were reagent grade and used as received. For spectroscopic and electrochemical studies HPLC grade solvents were used. UV–vis–NIR spectroelectrochemical studies were performed in $\text{CH}_2\text{Cl}_2/0.1 \text{ M}^{-1} \text{ cm}^{-1} \text{ Bu}_4\text{NPF}_6$ at 298 K using an optically transparent thin layer electrode (OTTLE) cell¹⁶ mounted in the sample compartment of a Bruin Instruments Omega 10 spectrophotometer. FT-IR spectra were taken on a Nicolet spectrophotometer with samples prepared as KBr pellets. Solution electrical conductivity was checked using a Systronic 305 conductivity bridge. Magnetic susceptibility was checked with CAHN electrobalance 7550. ^1H NMR spectra were obtained with a 300 MHz Varian FT spectrometer. The EPR measurements were made in a two-electrode capillary tube²⁵ with a X-band Bruker system ESP300, equipped with a Bruker ER035M gaussmeter and a HP 5350B microwave counter. Cyclic voltammetric, differential pulse voltammetric, and coulometric measurements were carried out using a PAR model 273A electrochemistry system. Platinum wire working and auxiliary electrodes and an aqueous saturated calomel reference electrode (SCE) were used in a three-electrode configuration. The supporting electrolyte was $[\text{NEt}_4]\text{ClO}_4$, and the solute concentration was $\sim 10^{-3} \text{ M}$. The half-wave potential $E_{0.298}^o$ was set equal to $0.5(E_{\text{pa}} + E_{\text{pc}})$, where E_{pa} and E_{pc} are anodic and cathodic cyclic voltammetric peak potentials, respectively. A platinum wire-gauze working electrode was used in coulometric experiments. All experiments were carried out under a dinitrogen atmosphere. The elemental analysis was carried out with a Perkin-Elmer 240C elemental analyzer. Electrospray mass spectra were recorded on a Micromass O-ToF mass spectrometer.

Synthesis of 1 and $1(\text{ClO}_4)$. The starting complex $\text{Ru}(\text{acac})_2(\text{CH}_3\text{CN})_2$ (100 mg, 0.26 mmol), and the ligand L (36 mg, 0.13 mmol) were added to 20 mL of ethanol, and the mixture was heated to reflux for 12 h under a dinitrogen atmosphere. The initial orange color of the solution gradually changed to dark blue. The solvent of the reaction mixture was reduced to 5 mL and kept in deep freeze overnight. It was then filtered, and the violet solid mass thus obtained was washed thoroughly with cold ethanol. The blue filtrate was then evaporated to dryness under reduced pressure. The violet precipitate was dissolved in minimum volume of CH_2Cl_2 and purified by using a silica gel column. Initially, a red compound corresponding to $\text{Ru}(\text{acac})_3$ was eluted with $\text{CH}_2\text{Cl}_2\text{--CH}_3\text{CN}$ (20:1). With $\text{CH}_2\text{Cl}_2\text{--CH}_3\text{CN}$ (3:1), a violet compound corresponding

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to **1** was separated later on. Evaporation of solvent under reduced pressure yielded complex **1** in the pure state. Yield: 40 mg (35%). Anal. Calcd (found) for **1**: C, 44.24 (44.13); H, 4.87 (4.20); N, 12.90 (11.99).

The blue mass obtained from the filtrate as stated above was dissolved in minimum volume of CH₃CN. To this an excess aqueous NaClO₄ solution was added and the mixture kept in deep freeze overnight. It was then filtered and the solid mass washed with ice-cold water followed by cold ethanol and dried under vacuum. It was then purified using a neutral alumina column. Initially a small amount (<3–5%) of the violet compound **1** was eluted with CH₂Cl₂–CH₃CN (30:1), followed by a blue compound corresponding to [1](ClO₄), which was separated with CH₂Cl₂–CH₃CN (8:1). Evaporation of the solvent under reduced pressure resulted in pure [1](ClO₄). Yield: 38 mg (30%). Anal. Calcd (found) for [1](ClO₄): C, 39.69 (39.24); H, 4.37 (4.44); N, 11.57 (10.62). Λ_M (Ω^{-1} cm² M⁻¹) in CH₃CN at 298 K: 115. IR data [ν (ClO₄⁻), cm⁻¹]: 1098 and 629.

Crystal Structure Determination. Single crystals of bpytz were grown by slow diffusion of a dichloromethane solution of it in hexane followed by slow evaporation. X-ray data of bpytz were collected on a PC-controlled Enraf-Nonius CAD-4 (MACH-3) single-crystal X-ray diffractometer using Mo K α radiation. The

structure was solved and refined by full-matrix least-squares on F^2 using SHELX-97 (SHELXTL).²⁶ Hydrogen atoms were included in the refinement process as per the riding model.

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Supporting Information Available: X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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