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Article

An Unusual Dinuclear Ruthenium(III) Complex with a Conjugated Bridging Ligand Derived from Cleavage of a 1,4-Dihydro-1,2,4,5-Tetrazine Ring. Synthesis, Structure, and UV–Vis–NIR Spectroelectrochemical Characterization of a Five-Membered Redox Chain Incorporating Two Mixed-Valence States

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Reaction of [Ru(acac)$_2$(CH$_3$CN)$_2$] with 3,6-bis(3,5-dimethylpyrazol-1-yl)-1,4-dihydro-1,2,4,5-tetrazine (H$_2$L) results in formation of an unexpected dinuclear complex [(acac)$_2$Ru^{III}(L^1)Ru^{III}(acac)$_2$] (**1**) in which the bridging ligand [L^1]$^{2-}$ contains an $^-$HN—C═N—N═C—NH$^-$ unit arising from two-electron reduction of the 1,4-dihydro-1,2,4,5-tetrazine component of H$_2$L. The crystal structure of complex **1** confirms the oxidation assignment of the metal ions as Ru(III) and clearly shows the consequent arrangement of double and single bonds in the bridging ligand, which acts as a bis-bidentate chelate having two pyrazolyl/amido chelating sites. Cyclic voltammetry of the complex shows the presence of four reversible one-electron redox couples, assigned as two Ru(III)/Ru(IV) couples (oxidations with respect to the starting material) and two Ru(II)/Ru(III) couples (reductions with respect to the starting material). The separation between the two Ru(III)/Ru(IV) couples ($\Delta E_{1/2} = 700$ mV) is much larger than that between the two Ru(II)/Ru(III) couples ($\Delta E_{1/2} = 350$ mV) across the same bridging pathway, because of the better ability of the dianionic bridging ligand to delocalize an added hole (in the oxidized mixed-valence state) than an added electron (in the reduced mixed-valence state), implying some ligand-centered character for the oxidations. UV–vis–NIR spectroelectrochemical measurements were performed in all five oxidation states; the Ru(II)–Ru(III) mixed-valence state of [**1**]$^-$ has a strong IVCT transition at 2360 nm whose parameters give an electronic coupling constant of $V_{ab} \approx 1100$ cm^{-1}, characteristic of a strongly interacting but localized (class II) mixed-valence state. In the Ru(III)–Ru(IV) mixed-valence state [**1**]$^+$, no low-energy IVCT could be detected despite the strong electronic interaction, possibly because it is in the visible region and obscured by LMCT bands.

Introduction

The selective transformation of stable organic molecules via the participation of a metal fragment is of considerable significance, as it facilitates the formation of unusual new products which would be difficult or even impossible to synthesize following conventional synthetic routes.[1] In such processes, the metal fragment acts as a suitable reactive center which mediates the transformation process. The present article describes one such unusual example where a 1,4-dihydro-1,2,4,5-tetrazine ring, the central component of the preformed molecule 3,6-bis(3,5-dimethylpyrazol-1-yl)-1,4-dihydro-1,2,4,5-tetrazine (H$_2$L), is transformed on reaction with [Ru(acac)$_2$(CH$_3$CN)$_2$] to a new symmetric, dianionic, dinucleating bridging ligand [L^1]$^{2-}$, which contains an open chain $^-$NH—C(R)═N—N═C(R)—NH$^-$ central fragment (Scheme 1). The result is the neutral diruthenium(III) complex [(acac)$_2$Ru^{III}(L^1)Ru^{III}(acac)$_2$] (**1**) which has interesting redox and spectroscopic properties.

The crystal structure of H$_2$L and its ability to function as a dinucleating bridging ligand were recently described by us.[2] Despite the stability of the free ligand both in the solid

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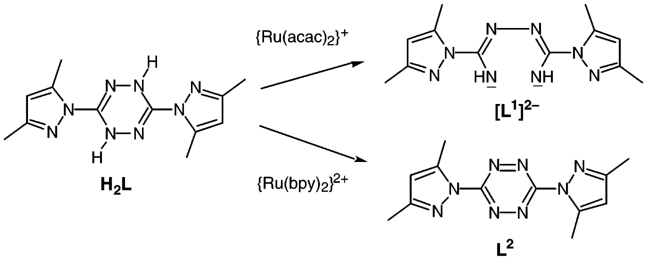
Scheme 1



state and in solution, it underwent spontaneous oxidative dehydrogenation on complexation to $\{Ru(bpy)_2\}^{2+}$ units, giving the complex $[(bpy)_2Ru(\mu\text{-}L^2)Ru(bpy)_2]^{4+}$ (**2**).[2] Therefore, a remarkable difference in the reactivity of H_2L has been observed on moving from π-acidic (bipyridine) to σ-donating (acetylacetonate) peripheral ligands on the metal fragments, even though the oxidation state of the metal reagent used in the reaction is unchanged.

The development of new classes of polynuclear metal complexes incorporating bridging ligands which can lead to the formation of stable mixed-valence states is an area of continuous current research interest.[1c,2,3] This is primarily due to the relevance of such complexes to the study of electron-transfer kinetics,[4] biological processes,[5] and the designing of molecular electronic devices.[6] The new diruthenium(III) complex (**1**) incorporating the in-situ generated bridging ligand $[L^1]^{2-}$ provides an interesting system with respect to study of redox and spectroelectrochemical properties, because it contains two stable mixed-valence states.

Herein we report the synthesis of **1**, its crystal structure, and the results of redox and spectroelectrochemical properties. To the best of our knowledge, the present work demonstrates the first example of ruthenium-ion mediated transformation of a tetrazine ring via a ring-opening process, although hydrolysis of tetrazine-based ligands by other metal ions has been reported recently.[7]

Results and Discussion

The reaction of 3,6-bis(3,5-dimethylpyrazol-1-yl)-1,4-dihydro-1,2,4,5-tetrazine (H_2L) with the ruthenium precursor complex $[Ru(acac)_2(CH_3CN)_2]$ (acac = acetylacetonate) in ethanol solvent under an air atmosphere afforded, after chromatographic purification, a dark green complex whose formulation was initially unclear. The material was identified as the neutral diruthenium(III) complex $[(acac)_2Ru(\mu\text{-}L^1)\text{-}Ru(acac)_2]$ (**1**) by X-ray crystallography (Figure 1, Tables 1 and 2). The centrosymmetric molecule consists of two $\{Ru(acac)_2\}$ units which are linked by an almost planar bridging unit which has obviously derived from opening of the central tetrazine ring (the maximum deviation from planarity is 0.09 Å), and which acts as an *N*,*N*′-bidentate donor to each metal center, forming two five-membered chelate rings. Each ruthenium ion shows a distorted octahedral environment formed by four oxygen atoms of the two acac ligands and two nitrogen atoms of the bridging ligand.

From the structural determination, the oxidation states of metal and bridging ligand components are not initially obvious. The two possible formulations are shown in

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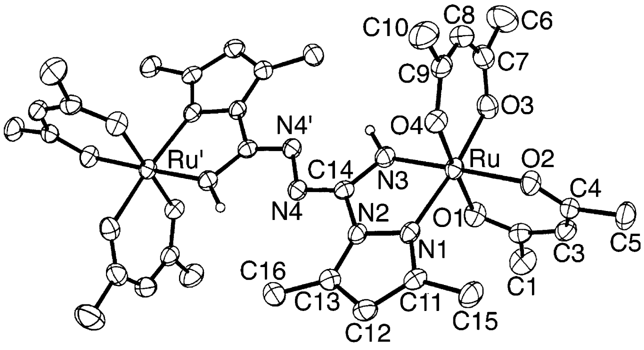


Figure 1. Molecular structure of $[\{(acac)_2Ru\}_2(\mu\text{-}L^1)]$ (**1**). Ellipsoids are drawn at 30% probability level. Hydrogen atoms (with the exception of the N−H) and the CH_2Cl_2 solvent molecule have been omitted for clarity. Atoms marked by primes are generated by the symmetry operation −*x*, −*y*, −*z*.

Table 1. Crystallographic Data for $\mathbf{1}\cdot 2(CH_2Cl_2)$

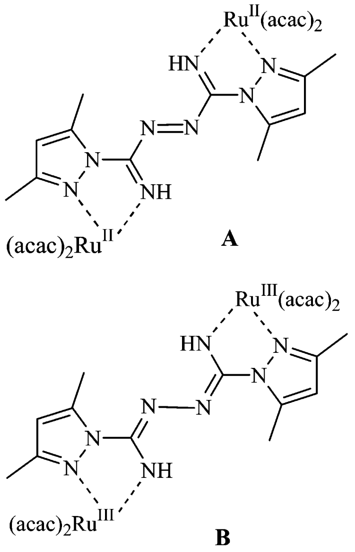
molecular formula	$C_{34}H_{48}Cl_4N_8O_8Ru_2$
fw	1040.74
radiation	Mo Kα
temp/K	293(2)
cryst symmetry	triclinic
space group	$P\bar{1}$
a/Å	7.83980(20)
b/Å	11.57980(29)
c/Å	13.12910(29)
α/deg	76.7230(11)
β/deg	80.9431(11)
γ/deg	74.0127(11)
V/Å^3	1109.516(48)
Z	1
μ/mm^{-1}	0.976
D_{calcd}/g cm^{-3}	1.558
R	0.0528
R_w	0.1289

Table 2. Important Bond Distances (Å) and Angles (deg) for $\mathbf{1}\cdot 2(CH_2Cl_2)$

Ru−O1	2.015(3)	O1−Ru−O2	90.110(13)
Ru−O2	2.052(3)	O1−Ru−O3	87.540(15)
Ru−O3	2.028(4)	O1−Ru−O4	176.51(13)
Ru−O4	2.011(3)	O1−Ru−N1	90.630(15)
Ru−N1	2.048(4)	O1−Ru−N3	90.180(15)
Ru−N3	1.943(4)	O2−Ru−O3	88.580(14)
O1−C2	1.280(6)	O2−Ru−O4	86.660(12)
O2−C4	1.265(5)	O2−Ru−N1	99.660(14)
O3−C7	1.281(7)	O2−Ru−N3	178.54(15)
O4−C9	1.294(6)	O3−Ru−O4	93.700(14)
N1−C11	1.327(6)	O3−Ru−N1	171.56(14)
N1−N2	1.387(5)	O3−Ru−N3	92.860(15)
N2−C13	1.352(6)	O4−Ru−N1	88.610(14)
N2−C14	1.424(5)	O4−Ru−N3	93.020(15)
N3−C14	1.348(6)	N1−Ru−N3	78.910(15)
N3−H3	0.960(5)		
N4−C14	1.288(6)		
N4−N4′	1.396(7)		
C11−C12	1.402(7)		
C12−C13	1.368(7)		

Scheme 2. In the first case (**A**), the metal ions would be in the Ru(II) oxidation state, in which case the bridging ligand would necessarily be neutral with pyrazolyl and imine units constituting each bidentate chelating site. The alternating pattern of double bonds would require the central N═N linkage [N(4)−N(4′)] to be a double bond, and the adjacent bond N(4)−C(14) (and the symmetry equivalent) to be single. In this arrangement, neither the bridging unit nor the metal ions have undergone any change in oxidation state compared to H_2L and $[Ru(acac)_2(CH_3CN)_2]$. Alternatively (structure **B**), the metal ions could be in the Ru(III) oxidation state, in which case the bridging ligand would be dianionic with one anionic $R{-}NH^-$ donor at each bidentate chelating site; compared to the starting materials, the bridging ligand has undergone a two-electron reduction, and each metal center has undergone a one-electron oxidation.

Scheme 2



The alternating pattern of single and double bonds would require the central N−N linkage [N(4)−N(4′)] to be a single bond, and the adjacent bond N(4)−C(14) (and the symmetry equivalent) to be double. Close inspection of the metrical parameters shows quite clearly that the second formulation (**B**) is correct. Specifically, the N(4)−N(4′) separation is 1.387(5) Å, characteristic of a single bond, and the N(4)−C(14) separation is 1.288(4) Å, characteristic of a double bond. In addition, the Ru(1)−N(3) separation of 1.943(4) Å is much too short to be a Ru(II)−(neutral imine) bond; its shortness is however consistent with the strong interaction between Ru(III) (with a smaller ionic radius) and an anionic ligand and may be contrasted with the Ru(1)−N(1) separation of 2.048(4) Å which involves a neutral N-donor. The Ru−O bond lengths of 2.011(3)−2.052(3) Å (average 2.027 Å) are in the normal range of Ru(III)−acetylacetonates.[8] The N−N, C═N, and C−N distances in the central HN−C═N−N═C−NH fragment of the azine bridging ligand may be compared with the corresponding parameters in the related ligands *N*,*N*′-bis(picolinamide)azine (1.425, 1.287, 1.342 Å),[9] bis(2-methylphthalazino)azine (1.392, 1.310, 1.405 Å),[10] and 5-(methoxycarbonyl)methylene-4-oxo-3-(*n*-propyl)imidazolidin-2-one-azine (1.418, 1.277, 1.383 Å).[11] The complex was further characterized by elemental analysis, which was consistent with the formulation determined from the crystal structure. In the IR spectrum, the NH vibration of the bridging ligand appears at 3355 cm^{-1}.

Conversion of H_2L to $[L^1]^{2-}$ involves a two-electron reduction of the starting dihydro-1,2,4,5-tetrazine unit and

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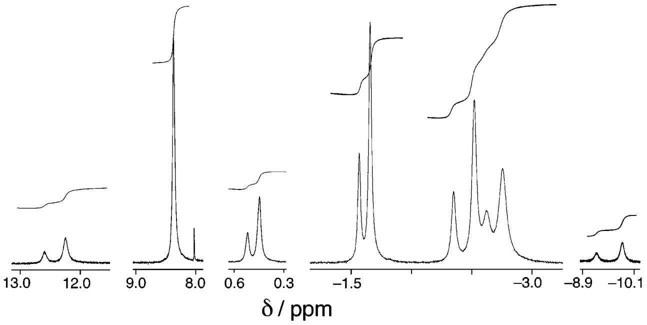

Figure 2. ^{1}H NMR spectrum of **1** in CD_2Cl_2 (400 MHz).

concomitant cleavage of one N−N bond; in the absence of any identifiable intermediates the mechanism is not clear. However, it has been reported recently that the central tetrazine unit of the well-known potentially binucleating bridging ligand 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine (BPTZ) undergoes transformations to give 2,5-bis(2-pyridyl)-1,3,4-oxodiazole and *N*,*N′*-bis(α-hydroxyl-2-pyridyl)ketazine units via copper(II)-assisted selective hydrolysis of BPTZ leading to a variety of products.[7]

The bis-Ru(III) formulation of **1** was further established by the ^{1}H NMR spectrum, which is paramagnetically shifted with signals appearing in the range −10 to +13 ppm (Figure 2). Given the twofold symmetry of the complex, we expect to see six signals of relative intensity 3H each from methyl groups (two from each of the acac ligands and two from the dimethylpyrazolyl group), and four signals of relative intensity 1H each (one from the central CH of each acac ligand, one pyrazolyl H^4 proton, and the NH proton). Of these we can clearly see four CH_3 signals (at 8.4, −1.6 ppm and two overlapping at ca. −2.4 and −2.7 ppm), and three single proton signals (at 12.4, 0.5, and −9.5 ppm) with the correct relative integrals. All of these signals are split into two closely spaced components with an approximate 2:1 ratio. This doubling-up of signals indicates that the complex is actually a mixture of diastereoisomers, to be expected since there are two chiral tris-chelate centers in the complex, of which one has crystallized preferentially to give the X-ray quality crystals. We could not see in the NMR spectrum the remaining one methyl or one single proton signals, and we assume that these arise from the groups closest to the metal center and are broadened to the point of nondetectability. While not fully characterizing the complex, the ^{1}H NMR spectrum is consistent with the formulation provided by the X-ray crystal structure and confirms unequivocally that resonance structure **B** in Scheme 2 is correct.

In dichloromethane solution, **1** exhibits four chemically reversible one-electron redox processes, constituting two oxidations and two reductions with respect to the starting redox state of **1**. The potentials [E°_{298}, V (ΔE_P, mV)] are the following: couple A, −0.25 (85); couple B, +0.45 (80); couple C, −1.40 (85); and couple D, −1.75 (100), all referenced versus the ferrocene/ferrocenium couple (Figure 3).[12a,b] Given the dianionic nature of the bridging ligand, it is unlikely that it could be reduced further, and accordingly, the two reductions are assigned as metal-centered Ru(II)/Ru(III) couples, with a mixed-valence Ru(II)−Ru(III) species $[\mathbf{1}]^-$ being generated following the first reduction (the potential window between couples C and D). Assignment of the first reduction (couple C) as a Ru(II)/Ru(III) process is also in reasonable agreement with the prediction of Lever's electrochemical parameters for the effects of different ligands on Ru(II)/Ru(III) redox potentials.[13] The separation of 350 mV between the successive Ru(II)/Ru(III) couples implies a comproportionation constant K_c of 1.1×10^6 for the Ru(II)−Ru(III) mixed-valence state, indicating a reasonably strong electronic interaction between the metals mediated via the six-atom conjugated pathway through the bridging ligand (the K_c value was calculated using eq 1).[3g,12]

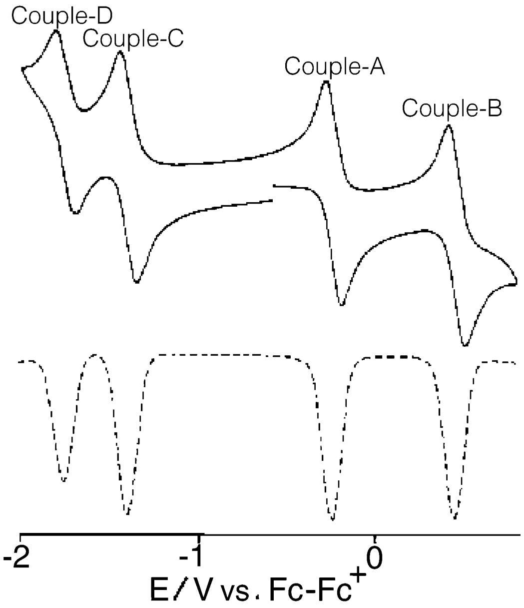

Figure 3. Cyclic (—) and square-wave (- - -) voltammograms of **1** in dichloromethane solvent at 298 K at a Pt-bead electrode (scan rate 0.2 V s^{-1}).

$$RT \ln K_c = nF(\Delta E) \qquad (1)$$

Assignment of the oxidations is not so obvious: they could plausibly be assigned to either the metal ions or the bridging ligand. If metal-based, they would be Ru(III)/Ru(IV) couples; if ligand-based, they would result in eventual oxidation of the bridging ligand to the neutral form shown in Scheme 2, with three double bonds including two imine units. The doubly oxidized complex could therefore be formulated as $Ru^{IV}\{(L^1)^{2-}\}Ru^{IV}$ or $Ru^{III}(L^1)Ru^{III}$, respectively. However, on the basis that numerous mononuclear Ru(III) complexes with comparable donor sets undergo reversible Ru(III)/Ru(IV) couples at comparable potentials,[14] we assign couples A and B as having predominantly metal-based character (but see the following discussion).

The redox separation between couples A and B is very large at 700 mV, which gives a K_c value of ca. 10^{12} for the

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Ru(III)−Ru(IV) mixed-valence state $[\mathbf{1}]^{+}$; this value is much larger than that obtained for the reduced mixed-valence state $[\mathbf{1}]^{-}$. This indicates more extensive delocalization of the hole in $[\mathbf{1}]^{+}$ than of the odd electron in $[\mathbf{1}]^{-}$, due to better matching of the metal and bridging ligand orbitals in the former case. We have observed similar behavior before in a variety of dinuclear complexes,[3m,15] and the reasons have been discussed in a recent review.[16] In complex **1**, the dianionic bridging ligand will have relatively high-energy orbitals, such that the HOMO is not far below the metal d(π) frontier orbitals in energy, but the LUMO is much higher. The mixed-valence state generated by oxidation of one metal center (addition of a hole) has a facile delocalization route via hole-transfer through the bridging ligand HOMO, viz. $M^{+}{-}L{-}M \rightarrow M{-}L^{+}{-}M \rightarrow M{-}L{-}M^{+}$, because $M^{+}{-}L{-}M$ and $M{-}L^{+}{-}M$ are similar in energy. In contrast, the extra electron of the reduced mixed-valence state must use the high-energy LUMO to delocalize $[M^{-}{-}L{-}M \rightarrow M{-}L^{-}{-}M \rightarrow M{-}L{-}M^{-}]$, a more energetically difficult process since $M{-}L^{-}{-}M$ has a much higher energy than $M^{-}{-}L{-}M$. This is exactly analogous to the behavior shown by numerous dinuclear Mo(V) complexes connected by a bis-phenolate bridging ligand, in which the two Mo(V)/Mo(VI) redox couples were split to a much greater extent than the Mo(IV)/Mo(V) couples, because of the greater ability of the dianionic bis-phenolate to accommodate a hole than an additional electron.[15,16] Similar behavior has been also observed in a dinuclear Ru(III) complex in which two {Ru(acac)$_3$} fragments were connected by a diacetylene bridge, although the magnitude of the electrochemical interactions was less.[12a]

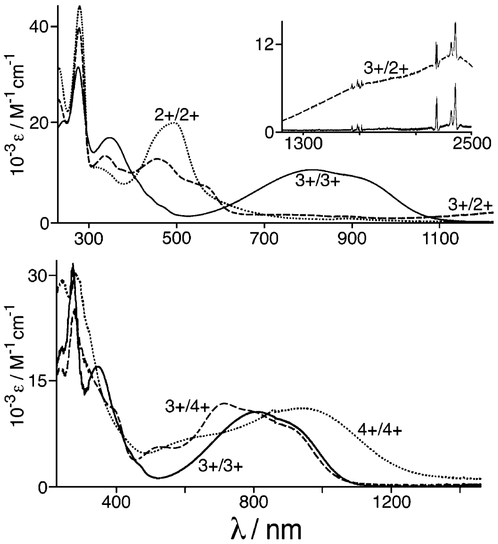

Figure 4. Electronic spectra of **1** in all five oxidation states. Top: **1** [Ru(III)−Ru(III), —], $[\mathbf{1}]^{-}$ [Ru(III)−Ru(II), - - -], and $[\mathbf{1}]^{2-}$ [Ru(II)−Ru(II), · · ·]. Bottom: [Ru(III)−Ru(III), —], $[\mathbf{1}]^{+}$ [Ru(III)−Ru(IV), - - -], and $[\mathbf{1}]^{2+}$ [Ru(IV)−Ru(IV), · · ·]. All spectra are from an OTTLE experiment in CH$_2$Cl$_2$ at 243 K. Note that the very weak d−d transitions of **1** are not apparent at this concentration.

Table 3. Summary of Electronic Spectral Data from the Spectroelectrochemistry experiment (CH$_2$Cl$_2$, 243 K)

species	λ_{max}/nm ($10^{-3}\epsilon$/M^{-1} cm^{-1})
$[\mathbf{1}]^{2+}$	923 (11.3), 608 (sh), 270 (30.6), 238 (29.4)
$[\mathbf{1}]^{+}$	902 (sh), 786 (sh), 718 (12.0), 539 (5.8), 389 (sh), 279 (25.4)
1	2300 (0.2), 1400 (sh), 901 (sh), 808 (10.9), 347 (17.4), 275 (31.7)
$[\mathbf{1}]^{-}$	2360 (11.3), 1723 (sh), 560 (sh), 456 (13.0), 335 (13.7), 276 (39.7)
$[\mathbf{1}]^{2-}$	492 (20.4), 309 (11.3), 277 (44.2)

UV−vis−NIR spectroelectrochemical experiments were performed in CH$_2$Cl$_2$ at 243 K using an OTTLE cell; the resultant spectra of the redox chain $[\mathbf{1}]^{n+}$ ($n = -2, -1, 0, 1, 2$) are shown in Figure 4, and the peaks are listed in Table 3. Starting with neutral **1**, the spectrum is dominated by an intense transition at 808 nm which has a low-energy shoulder at ca. 900 nm; given the presence of an anionic π-donor bridging ligand, and a hole in the metal d(π) orbital set, we assign this to a $[L^1]^{2-} \rightarrow$ Ru(III) LMCT process. Also worthy of note are two very weak transitions in the near-IR region (1400 and 2300 nm) characteristic of low-spin Ru(III) centers in a distorted octahedral coordination geometry; these arise from d−d transitions within the partially occupied d(π) whose three members are not degenerate as a consequence of the irregular ligand field.[14a]

On one-electron reduction to the Ru(II)−Ru(III) species $[\mathbf{1}]^{-}$, this LMCT transition completely disappears, and an intense, broad near-IR transition appears with a maximum at ca. 2360 nm. The position, intensity, and width of this peak are all exactly consistent with it being a Ru(II) → Ru(III) IVCT transition, and from the Hush equation (eq 2)

$$V_{ab} = \{[2.05 \times 10^{-2}(\epsilon_{max}\bar{\nu}_{max}\Delta\bar{\nu}_{1/2})^{1/2}]/R\} \qquad (2)$$

(where ϵ_{max}, $\bar{\nu}_{max}$, and $\Delta\bar{\nu}_{1/2}$ are the molar extinction coefficient, the absorption maximum in wavenumbers, and the bandwidth at half-maximum height in wavenumbers, respectively; R is the metal−metal distance in Å),[3g,17] we find $V_{ab} = 1100$ cm^{-1}, a typical value for a strongly coupled class II mixed-valence complex.[3] Also, in the Ru(II)−Ru(III) state two new transitions appear at 456 nm and ca. 560 nm (the latter being a shoulder); the growth of these as one metal center is reduced implies MLCT character, possibly involving the π-accepting pyrazolyl unit. On further reduction to the Ru(II)−Ru(II) state $[\mathbf{1}]^{2-}$ (couple D) the IVCT transition disappears, and the MLCT absorption associated with Ru(II) (now at 492 nm) is further increased in intensity as there are now two Ru(II) centers.

The electronic spectra of the oxidized forms of the complex are not so easy to assign. On one-electron oxidation of **1** to $[\mathbf{1}]^{+}$ (couple A), the LMCT transition of **1** at 808 nm is blue-shifted to 718 nm but does not change significantly in shape or intensity. Metal-centered oxidation of Ru(III) to Ru(IV) would be expected to result in the LMCT transition being red-shifted as the metal orbitals are lowered in energy, but this is clearly not happening here. A likely explanation is that a substantial degree of metal−ligand orbital mixing is occurring (cf. the electrochemical results) such that

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designation of the transition as "LMCT", implying localized ligand and metal orbitals, is inappropriate.

An instructive analogy is provided by the mononuclear redox pair $[Ru(bpy)_2(sq)]^+$ and $[Ru(bpy)_2(q)]^{2+}$ (sq = 1,2-benzosemiquinone radical anion; q = 1,2-benzoquinone) which are linked by a ligand-centered sq/q redox couple.[18] In $[Ru(bpy)_2(sq)]^+$, there is a strong Ru(II) → sq MLCT transition at 890 nm. On oxidation of the ligand from the "sq" to the "q" state, it would simplistically be expected that reduction in energy of the ligand π-acceptor orbitals would result in this MLCT transition being red-shifted. In fact, it moves to higher energy (640 nm); as the ligand orbitals descend in energy closer to the metal orbitals, a greater degree of mixing between them occurs to give two new orbitals of mixed character that are even further apart. We suggest that similar behavior is occurring here, with the expected red-shift of the $[L^1]^{2-} \rightarrow$ Ru(IV) transition being compensated for by greater mixing as the metal orbitals are lowered in energy and become closer to the ligand orbitals. Accordingly, the second oxidation (couple B) also does not result in a substantial change in this transition; it is red-shifted to 923 nm, this time in accordance with expectations, but its intensity is unchanged. A long low-energy "tail" is apparent on this transition.

A surprising feature of these spectra is that we can find no evidence for a low-energy IVCT transition in the Ru(III)−Ru(IV) species $[\mathbf{1}]^+$, despite the obviously strong electronic interaction which is apparent from the electrochemical data. Whether the mixed-valence state is class II or class III, a strong transition in the near-IR region, broad for class II and narrower for class III, is usually expected, cf. $[\mathbf{1}]^-$.[3] We can only assume that the transition is at unusually high energy and contributes to the strong region of absorption between 550 and 1000 nm which also includes LMCT transitions. Equation 2 suggests that, for a fixed metal−metal separation and peak width, an increased electronic coupling requires the IVCT transition to either increase in intensity or move to higher energy and, given the stronger coupling in $[\mathbf{1}]^+$ compared to $[\mathbf{1}]^-$, a high-energy IVCT is quite plausible.

An EPR spectroelectrochemistry experiment was also performed. Complex **1** in frozen CH_2Cl_2 at 100 K shows a broad, weak signal centered at $g = 2.16$ whose lack of fine structure may be attributed to exchange broadening arising from coupling between the two Ru(III) centers. One-electron reduction of **1** to $[\mathbf{1}]^-$ in CH_2Cl_2 was performed inside an EPR tube at 243 K, and the resulting solution was then frozen (100 K). The Ru(II)−Ru(III) species $[\mathbf{1}]^-$ exhibits a rhombic EPR spectrum [$g_1 = 2.139$, $g_2 = 2.010$, and $g_3 = 1.895$] (Figure 5) entirely characteristic of a low-spin, mononuclear Ru(III) ion in a distorted octahedral environment.[19] This provides additional confirmation of both the Ru(III)−Ru(III) formulation of neutral **1** (Scheme 2) and of the metal-centered nature of couples C and D. The spectrum of the oxidized species $[\mathbf{1}]^+$ is expected, like the spectrum of **1**, to be very broad due to exchange coupling and to provide no significant structural information, and it was therefore not measured.

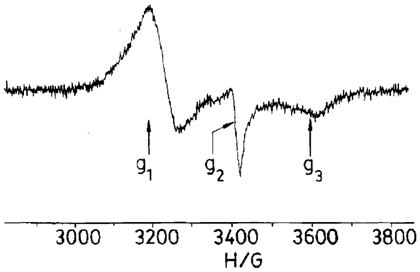

Figure 5. EPR spectrum of $[\mathbf{1}]^-$ in frozen CH_2Cl_2 at 100 K.

Conclusion

We have observed the formation of diruthenium(III)−acetylacetonate complex **1** incorporating an unusual conjugated bridging ligand containing a diazine fragment, which formed via the ruthenium ion mediated cleavage of the 1,4-dihydro-1,2,4,5-tetrazine ring of the starting material 3,6-bis(3,5-dimethylpyrazol-1-yl)-1,4-dihydro-1,2,4,5-tetrazine (H_2L). The unexpected formation of **1** from the starting materials $[Ru^{II}(acac)_2(CH_3CN)_2]$ and H_2L involves one-electron oxidation of each $\{Ru^{II}(acac)_2\}$ moiety and two-electron reduction of the bridging unit H_2L. Complex **1** exhibits a five-membered redox chain $[\mathbf{1}]^{n+}$ ($n = +2, +1, 0, -1, -2$) linking the (formal) oxidation states Ru(IV)−Ru(IV), Ru(IV)−Ru(III), Ru(III)−Ru(III), Ru(III)−Ru(II), and Ru(II)−Ru(II), with a much greater redox separation between the successive Ru(III)/Ru(IV) couples than between the Ru(II)/Ru(III) couples, indicating that the "Ru(III)/Ru(IV)" couples are not purely metal-localized but have some bridging ligand character. The Ru(III)−Ru(II) mixed-valence state $[\mathbf{1}]^-$ exhibits a strong IVCT transition at 2360 nm corresponding to an electronic coupling constant $V_{ab} \approx 1100$ cm^{-1}, characteristic of a strongly interacting but localized (class II) mixed-valence state; $[\mathbf{1}]^-$ displays a rhombic EPR spectrum characteristic of a low-spin Ru(III) ion in a distorted octahedral environment. In the Ru(IV)−Ru(III) mixed-valence state $[\mathbf{1}]^+$, no low-energy IVCT band could be detected despite the presence of strong electronic coupling ($K_c = 1.1 \times 10^{12}$) observed from electrochemical data; possibly, it is at relatively high energy (consistent with the strong electronic interactions) and obscured by intense LMCT bands.

Experimental Section

The starting complex $[Ru(acac)_2(CH_3CN)_2]$ was prepared according to the reported procedure.[20] The ligand 3,6-bis(3,5-dimethylpyrazol-1-yl)-1,4-dihydro-1,2,4,5-tetrazine (H_2L) was prepared by following the reported method.[21] All chemicals and solvents were reagent grade and used as received. For spectroscopic and electrochemical studies, HPLC grade solvents were used.

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Commercial tetraethylammonium bromide was converted into pure tetraethylammonium perchlorate by following an available procedure.[1a]

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. The ^{1}H NMR spectrum of **1** was obtained with a JEOL Eclipse 400 MHz NMR spectrometer using CD_2Cl_2 as solvent. Cyclic voltammetric, differential pulse voltammetric, and coulometric measurements were carried out using a PAR model 273A electrochemistry system. The supporting electrolyte was $[NEt_4]ClO_4$, and the solute concentration was $\sim 10^{-3}$ M. The half-wave potential E°_{298} was set equal to $0.5(E_{pa} + E_{pc})$, 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 electrochemical experiments were carried out under a dinitrogen atmosphere and were uncorrected for junction potentials. UV−vis−NIR spectroelectrochemical studies were performed in CH_2Cl_2 at 243 K using an optically transparent thin layer electrode (OTTLE) cell mounted in the sample compartment of a Perkin-Elmer Lambda 19 spectrophotometer; the cell design and the method used have been described previously.[22] The elemental analyses were carried out with a Perkin-Elmer 240C elemental analyzer. The EPR measurements were made with an X-band Bruker system ESP300, equipped with a Bruker ER035M gaussmeter and an HP 5350B microwave counter.

Synthesis of $[\{(acac)_2Ru\}_2(\mu\text{-}L^1)]$ (1). The starting complex $[Ru(acac)_2(CH_3CN)_2]$ (100 mg, 0.26 mmol) and 3,6-bis(3,5-dimethylpyrazol-1-yl)-1,4-dihydro-1,2,4,5-tetrazine (H_2L) ligand (35.69 mg, 0.13 mmol) were taken in 20 mL of ethanol, and the mixture was heated at reflux for 12 h. The initial orange color of the solution gradually changed to dark. The solvent was then removed under reduced pressure. The solid mass thus obtained was purified by using a silica column. Initially, a red solution corresponding to $Ru(acac)_3$ was eluted by C_6H_6/CH_2Cl_2 (2:1). With CH_2Cl_2/CH_3CN (16:1), a green solution corresponding to **1** was separated later on. Evaporation of solvent under reduced pressure afforded complex **1**. Yield: 34 mg (30%). Anal. Calcd (Found) for **1**: C, 44.09 (43.28); H, 4.82 (4.83); N, 12.86 (12.37).

Crystal Structure Determination. Single crystals of **1** were grown by slow evaporation of a dichloromethane solution of it. Intensity data were collected at 298 K using a Nonius κ-CCD diffractometer. Selected data collection parameters and other crystallographic data are summarized in Table 1. Calculations were carried out with SHELXTL PC 5.03[23] and SHELXL-97[24] program systems installed on local personal computers. The phase problem was solved by direct methods, and the structure was refined on F_o^2 by full-matrix least-squares refinement. A numerical absorption correction using the program X-SHAPE[25] was applied. Anisotropic thermal parameters were refined for all non-hydrogen atoms. Hydrogen atoms were placed in the idealized positions and refined in a riding model approximations, including free rotation for methyl groups. For most hydrogen atoms, the assigned U_{iso} was allowed to refine. Isotropic displacement parameters being larger than 0.15 were constrained to either $1.2U_{eq}$ (CH, CH_2) or $1.5U_{eq}$ (CH_3) of the parent atom. The position and the thermal parameter of the N-bonded hydrogen atom was allowed to refine freely. Final R values are listed in Table 1.

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Supporting Information Available: X-ray crystallographic data for **1** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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