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# Sensitive Oxidation State Ambivalence in Unsymmetrical Three-Center (M/Q/M) Systems $[(\mathrm{acac})_2\mathrm{Ru}(\mu\text{-Q})\mathrm{Ru}(\mathrm{acac})_2]^n$, Q = 1,10-Phenanthroline-5,6-dione or 1,10-Phenanthroline-5,6-diimine ($n$ = +, 0, −, 2−)

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The new redox systems $[(\mathrm{acac})_2\mathrm{Ru}(\mu\text{-Q}^1)\mathrm{Ru}(\mathrm{acac})_2]^n$ (**1**$^n$) and $[(\mathrm{acac})_2\mathrm{Ru}(\mu\text{-Q}^2)\mathrm{Ru}(\mathrm{acac})_2]^n$ (**2**$^n$) with $\mathrm{Q}^1$ = 1,10-phenanthroline-5,6-dione and $\mathrm{Q}^2$ = 1,10-phenanthroline-5,6-diimine were studied for $n$ = +, 0, –, and 2– using UV–Vis–NIR spectroelectrochemistry and, in part, EPR and susceptometry. The ligands can bind the first metal (left) through the phenanthroline nitrogen atoms and the second metal (right) at the *o*-quinonoid chelate site. The neutral compounds are already different: Compound **1** is formulated as a $\mathrm{Ru^{II}}(\mu\text{-Q}^1)^{\bullet-}\ \mathrm{Ru^{III}}$ species with partially coupled semiquinone and ruthenium(III) centers. In contrast, a $\mathrm{Ru^{III}}(\mu\text{-Q}^2)^{2-}\ \mathrm{Ru^{III}}$ structure is assigned to **2**, which shows a weak antiferromagnetic spin–spin interaction ($J$ = –1.14 cm$^{-1}$) and displays an intense half-field signal in the EPR spectrum. The one-electron reduced forms are also differently formulated as $\mathrm{Ru^{II}}(\mu\text{-Q}^1)^{2-}\ \mathrm{Ru^{III}}$ for **1**$^-$ with a $\mathrm{Ru^{III}}$-typical EPR response and as $\mathrm{Ru^{II}}(\mu\text{-Q}^2)^{\bullet-}\ \mathrm{Ru^{II}}$ for **2**$^-$ with a radical-type EPR signal at $g$ = 2.0020. In contrast, both **1**$^{2-}$ and **2**$^{2-}$ can only be described as $\mathrm{Ru^{II}}(\mu\text{-Q})^{2-}\mathrm{Ru^{II}}$ species. The monooxidized forms **1**$^+$ and **2**$^+$ show very similar spectroscopy, including a $\mathrm{Ru^{III}}$-type EPR signal. Although no unambiguous assignment was possible here for the alternatives $\mathrm{Ru^{II}}(\mu\text{-Q})^0\mathrm{Ru^{III}}$, $\mathrm{Ru^{III}}(\mu\text{-Q})^{2-}\mathrm{Ru^{IV}}$ or $\mathrm{Ru^{III}}(\mu\text{-Q})^{\bullet-}\mathrm{Ru^{III}}$, the last description is favored. The reasons for identical or different oxidation state combinations are discussed.

## Introduction

Ruthenium complexes of "non-innocent"[1] quinonoid ligands Q have been studied extensively[2−8] because they offer to combine a substitutionally inert but electron-transfer active transition metal with a redox-active chelate ligand with three viable oxidation states Q (quinone), $\mathrm{Q}^{\bullet-}$ (semiquinone radical), or $\mathrm{Q}^{2-}$ (catecholate or hydroquinone dianion). Mononuclear and dinuclear[3,4] paramagnetic states within such redox systems, ranging from clear radical complexes[3,5] via mixed systems[6] to predominantly metal-centered species,[7]

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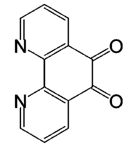
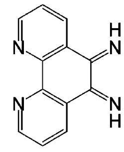
have been investigated mainly by spectroelectrochemistry and EPR.

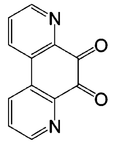
Because of symmetrically bis-chelating bridging ligands such as 4,7-phenanthroline-5,6-dione ($\mu$-Q$^3$)[3a] or 1,4,5,8-tetraoxonaphthalene,[4a] the dinuclear complexes investigated were usually symmetrical, leading to interesting alternatives Ru$^n$($\mu$-Q)$^m$Ru$^k$ for the oxidation state combinations.[4] In contrast, the isomeric form of Q$^3$, 1,10-phenanthroline-5,6-dione = Q$^1$, has become a popular, commercially available ligand[9−11] or precursor of ligands[11] that offers two distinctly *different* chelating sites, an *o*-quinone function and an α-diimine binding site. Calculations and experiments identify the *o*-quinone side as the location of primary electron uptake, α-diones being much better $\pi$ acceptors than aromatic α-diimines. Dinuclear complexes of Q$^1$ in different oxidation states have been reported;[9d−g] however, the coordination chemistry with the *o*-quinonediimine analogue 1,10-phenanthroline-5,6-diimine = Q$^2$ is much less developed.[12]



1,10-phenanthroline-5,6-dione (Q$^1$)



1,10-phenanthroline-5,6-diimine (Q$^2$)



4,7-phenanthroline-5,6-dione (Q$^3$)

In this paper, we describe the syntheses and, for some states, surprisingly different electrochemical, spectroscopic (UV−Vis−NIR, EPR), and magnetic properties of the dinuclear systems [(acac)$_2$Ru($\mu$-Q$^1$)Ru(acac)$_2$]$^n$ (**1**$^n$) and [(acac)$_2$Ru($\mu$-Q$^2$)Ru(acac)$_2$]$^n$ (**2**$^n$), $n = +, 0, -, 2-$; acac$^-$ = acetylacetonate = 2,4-pentanedionate(1−).

## Experimental Section

The starting complex Ru(acac)$_2$(CH$_3$CN)$_2$[13] and the ligands 1,10-phenanthroline-5,6-dione (Q$^1$)[14] and 5,6-diamino-1,10-phenanthroline (H$_2$Q$^2$)[15] 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 CH$_3$CN/0.1 M Bu$_4$NPF$_6$ at 298 K using an optically transparent thin layer electrode (OTTLE) cell[16] mounted in the sample compartment of a Bruins 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. $^1$H NMR spectra were obtained with a 300 MHz Varian FT spectrometer. The EPR measurements were made in a two-electrode capillary tube[17] with an 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 Et$_4$NClO$_4$, and the solute concentration was $\sim 10^{-3}$ M. The half-wave potential $E^\circ_{298}$ 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 experiments were carried out under a dinitrogen atmosphere, and no correction was made for junction potentials. The elemental analysis was carried out with a Perkin-Elmer 240C elemental analyzer. Electrospray mass spectra were recorded on a Micromass Q-ToF mass spectrometer. The magnetic susceptibility of the complexes **1** and **2** as a function of temperature was recorded from 1.8 to 300 K using a 0.1 T applied field on a Quantum Design MPMS XL7 SQUID magnetometer. The data were corrected for diamagnetic contributions to the magnetic susceptibility using Pascal's constants, for the diamagnetic contribution of the sample holder, and for temperature-independent paramagnetism (TIP).

**Synthesis of [(acac)$_2$Ru(Q$^1$)Ru(acac)$_2$] (1).** The starting complex Ru(acac)$_2$(CH$_3$CN)$_2$ (100 mg, 0.26 mmol) and the ligand Q$^1$ (27.5 mg, 0.13 mmol) were dissolved in 20 mL of ethanol, and the

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mixture was heated to reflux for 10 h under a dinitrogen atmosphere. The initial orange color of the solution gradually changed to brown. The solvent was removed under reduced pressure, and the residue was purified using a silica gel column. Initially, a red compound corresponding to Ru(acac)$_3$ was eluted by $CH_2Cl_2-CH_3CN$ (15:1), followed by a brown compound corresponding to **1**, which was eluted with $CH_2Cl_2-CH_3CN$ (1:5). Evaporation of the solvent mixture yielded the pure compound **1**. Yield: 53 mg (50%). Anal. Calcd (Found) for **1**: C, 47.52 (47.19); H, 4.24 (3.99); N, 3.46 (3.05). The positive ion electrospray mass spectrum of **1** in $CH_2Cl_2$ exhibited signals centered at *m*/*z* values of 810.13, 711.07, and 510.09 (Figure S1a, Supporting Information), corresponding to $\{\mathbf{1}\}^+$ (calculated molecular mass, 810.03), $\{\mathbf{1}\text{-acac}\}^+$ (calc. 710.98) and $\{\mathbf{1}\text{-Ru(acac)}_2\}^+$ (calc. 510.03), respectively.

**Synthesis of [(acac)$_2$Ru(Q$^2$)Ru(acac)$_2$] (2).** The starting complex Ru(acac)$_2$($CH_3CN$)$_2$ (100 mg, 0.26 mmol), the ligand $H_2Q^2$ (27.3 mg, 0.13 mmol), and sodium acetate (21 mg, 0.26 mmol) were dissolved in 20 mL of ethanol, and the mixture was heated to reflux for 10 h. The purple solution thus formed was purified using a silica gel column. Initially, a red compound corresponding to Ru(acac)$_3$ was eluted with $CH_2Cl_2-CH_3CN$ (15:1). With $CH_3CN-MeOH$ (1:20), a red compound corresponding to **2** was eluted. Evaporation of the solvent mixture yielded the pure complex **2**. Yield: 58 mg (55%). Anal. Calcd (Found) for **2**: C, 47.64 (47.09); H, 4.50 (4.84); N, 6.94 (7.08). The positive ion electrospray mass spectrum in dichloromethane of **2** exhibited signals centered at *m*/*z* values of 807.08 and 708.03 (Figure S1b, Supporting Information), corresponding to $\{\mathbf{2}\}^+$ (calculated molecular mass, 808.06) and $\{\mathbf{2}\text{-acac}\}^+$ (calc. 709.02), respectively.

## Results and Discussion

The neutral complexes [(acac)$_2$Ru($\mu$-Q)Ru(acac)$_2$] were obtained by reacting the ruthenium(II) precursor compound Ru(acac)$_2$($CH_3CN$)$_2$ with either Q$^1$ or $H_2Q^2$. Obviously, the latter reaction involved an oxidative deprotonation step, facilitated by the coordination of two imine-affine ruthenium atoms. The compounds **1** and **2** were identified by analysis and electrospray mass spectroscopy (Figure S1, Supporting Information); they were further investigated using SQUID susceptometry, EPR, cyclic voltammetry (Figure 1, Table 1), and absorption spectroscopy in various oxidation states (UV−Vis−NIR spectroelectrochemistry, Figure 2, Table 2).

The absence of conventional $^1$H NMR spectra for the neutral reaction products indicated the presence of oxidation states different than the diamagnetic Ru$^{II}$($\mu$-Q)$^0$Ru$^{II}$ configuration.

Complex **1** exhibits a weak, broad EPR signal in the $g = 2$ region and a small, temperature-independent $\chi T$ value (Figure S2, Supporting Information), corresponding to about 0.6 unpaired electron equivalents per molecule. Absorption bands at 780, 497, and 405 nm are observed (see Figure 2 and Table 2), in agreement with the presence of the anion radical of Q$^1$ ($\lambda_{max} = 747$sh, 566, 404 nm[11]). The results suggest a Ru$^{II}$($\mu$-Q$^1$)$^{\bullet-}$ Ru$^{III}$ formulation for **1** with partially coupled spins at the Ru$^{III}$/semiquinone coordination site. Such Ru$^{III}$/*o*-semiquinone antiferromagnetic spin−spin coupling has been observed before,[6] the oxidation state assignment being supported by structural data. The situation is more complicated for **1** which formally involves a Ru$^{II}$Ru$^{III}$ mixed-valent arrangement bridged by an anion radical; the origin of the residual paramagnetism will require more detailed investigations. Alternative formulations such as Ru$^{III}$($\mu$-Q$^1$)$^{\bullet-}$-Ru$^{II}$ (Ru$^{III}$ at the α-diimine site), Ru$^{II}$($\mu$-Q$^1$)$^0$Ru$^{II}$, or Ru$^{III}$-($\mu$-Q$^1$)$^{2-}$Ru$^{III}$ can be ruled out, considering the magnetic and spectroscopic results. The range between the one-electron oxidation and reduction potentials of **1** is rather small at only about 350 mV (Figure 1, Table 1).

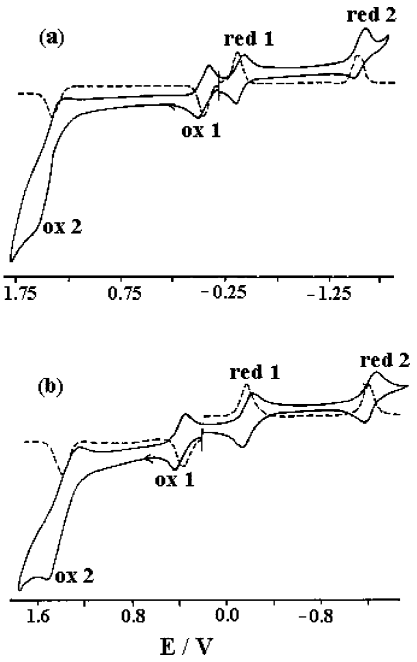


**Figure 1.** Cyclic voltammograms (—) and differential pulse voltammograms (- - -) of (a) **1** and (b) **2** in $CH_3CN$/0.1 M $Et_4NClO_4$.

**Table 1.** Redox Potentials[a] for Compounds **1** and **2**

| | $E°/V(\Delta E_p/mV)$ | | | |
|---|---|---|---|---|
| compound | ox 2 | ox 1 | red 1 | red 2 |
| **1** | 1.44 (190) | −0.02 (90) | −0.37 (90) | −1.51 (100) |
| **2** | 1.43 (150) | 0.41 (80) | −0.17 (90) | −1.21 (90) |

[a] In $CH_3CN$/0.1 M $Et_4NClO_4$, potentials vs SCE.

In contrast, the difference between oxidation and reduction potentials amounts to 580 mV for **2** (Figure 1, Table 1). This compound exhibits a temperature-dependent magnetic behavior between 1.8 and 300 K (Figure S3, Supporting Information), which can be reproduced assuming two antiferromagnetically coupled spins ($J = -1.14 \pm 0.02$ cm$^{-1}$).

Compound **2** also displays a very strong Ru$^{III}$-type EPR spectrum with $g_1 = 2.36$, $g_2 = 2.21$, and $g_3 = 1.82$, complemented by an intense half-field signal at $g = 4.28$ (Figure 3). The absorption spectrum shows major long-wavelength bands at 615 and 418 nm (Figure S4, Supporting Information, Table 2).

We associate these very different results for **2** in contrast to **1** with an oxidation state situation Ru$^{III}$($\mu$-Q$^2$)$^{2-}$Ru$^{III}$, assigning the half-field transition in the EPR with the triplet state available for a diruthenium(III) complex (estimated Ru···Ru distance at about 8 Å[9f,g]). The absorption bands are then attributed to ligand-to-metal charge transfer (LMCT) transitions and to intraligand charge-transfer transitions between the occupied quinone-centered MO (b$_1$) and the

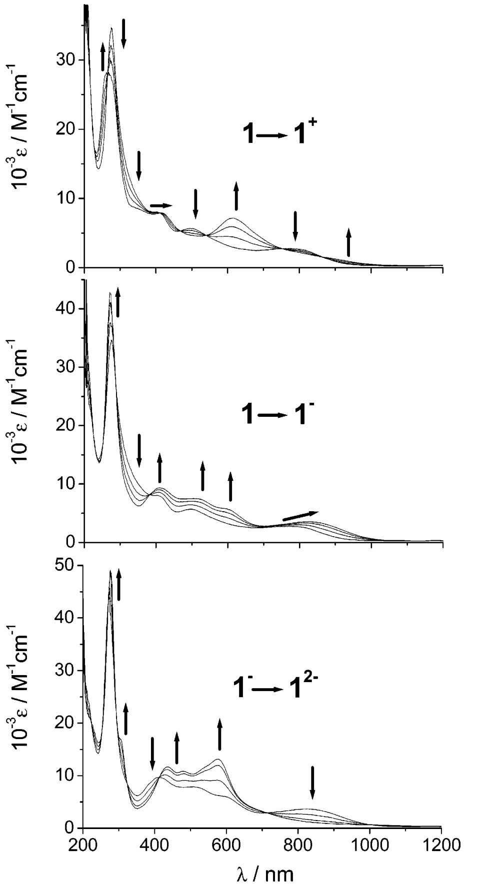
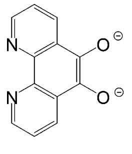
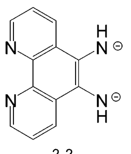


**Figure 2.** Spectroelectrochemical (OTTLE) response of a 3.5 mM solution of compound $\mathbf{1}^n$ in $CH_3CN$/0.1 M $Bu_4NPF_6$ during potentiostatic scans within one oxidation and two reduction peaks.

unoccupied phenanthroline-based MOs $b_1(\psi)$ and $a_2(\chi)$ (Scheme 1).[9,11]

Although there is a well-established stronger preference of quinone molecules for the reduced state relative to corresponding quinoneimines, the differences between the dinuclear complexes **1** and **2** point into the opposite direction, reflecting the strong coordination between the $Ru^{III}$ centers and the more basic diamido ligand $(Q^2)^{2-}$ in contrast to $(Q^1)^{2-}$. This effect, attributed to enhanced covalent bonding contributions, is confirmed by the ca. 0.3 V positive shift for the redox potentials of **2** (Table 1).


$(Q^1)^{2-}$


$(Q^2)^{2-}$

One-electron reduction of **1** produces a species $\mathbf{1}^-$ with a $Ru^{III}$-type EPR response ($g_1 = 2.39$, $g_2 = 2.11$, $g_3 = 1.95$) and long-wavelength LMCT and IVCT absorptions at 830, 600, 517, and 410 nm (Figure 2, Table 2). These results are compatible with a $Ru^{II}(\mu\text{-}Q^1)^{2-}$ $Ru^{III}$ formulation, involving a reduction of the bridging ligand and a metal−metal mixed-valent situation in a rather unsymmetrical setting (α-diimine bonded $Ru^{II}$). The strong asymmetry is responsible for high-energy IVCT transitions. Again, the formally analogous $\mathbf{2}^-$ differs considerably: It exhibits a narrow ($\Delta H_{pp} = 0.8$ mT) unresolved radical-type EPR signal at $g_{iso} = 2.0020$ (Figure 3), and the absorptions are also quite different at 640(sh), 552, 440, and 415 nm. On the basis of the EPR evidence we formulate $\mathbf{2}^-$ as a $Ru^{II}(\mu\text{-}Q^2)^{\bullet-}$ $Ru^{II}$ species.[3a] The absorption bands would thus be assigned to MLCT and internal semiquinone transitions.

Whereas the transition from **1** to $\mathbf{1}^-$ would thus only involve a ligand reduction from the semiquinone to the catecholate form, the conversion of **2** to $\mathbf{2}^-$ as elucidated here implies the oxidation of the ligand to the semiquinone form, set off by double metal reduction. Such seemingly paradoxical redox rearrangements were observed previously by Pierpont and co-workers for dioxolene compounds of vanadium where the reduction of $V^{III}(Q^{\bullet-})_3$ led to an oxidation of the metal in $V^{V}(Q^{2-})_3$.[18] The reason for the unusual triple oxidation state change observed for $\mathbf{2} \rightarrow \mathbf{2}^-$ lies in the strong affinity between ruthenium(II) and imine nitrogen centers.[19]

Simple one-electron reduction from either $\mathbf{1}^-$ or $\mathbf{2}^-$ leads to the fully reduced EPR-silent dianionic species which can only be formulated as $Ru^{II}(\mu\text{-}Q)^{2-}$ $Ru^{II}$. Protonation of the reduced forms at the metal-coordinated amido function is unlikely because rigorously dried solvent and electrolyte were used. In addition, the full reversibility of the reduction steps both in cyclic voltammetry and during the OTTLE reduction/reoxidation cycles suggests that no chemical complication is involved. Nevertheless, the differences between the catecholate and the much more electron-rich 1,2-diamidoarene ligand are evident from the distinct spectral variations as summarized in Table 2, possibly signifying energetically different intraligand charge transfer transitions between the now fully occupied quinone-centered MO ($b_1$) and the unoccupied phenanthroline-based MOs $b_1(\psi)$ and $a_2(\chi)$ (Scheme 1).[11]

Oxidation of **1** to $\mathbf{1}^+$ (or of **2** to $\mathbf{2}^+$) produces rather similar results, viz., the appearance of $Ru^{III}$-type EPR signals at $g_1 = 2.354$ (2.356), $g_2 = 2.212$ (2.204), and $g_3 = 1.832$ (1.831), respectively (Figure 3). The absorption spectra are dominated in both cases by an intense band around 600 nm (Figure 2, Table 2); we thus assume a very similar electronic configuration for $\mathbf{1}^+$ and $\mathbf{2}^+$. However, all three reasonable oxidation state combinations $Ru^{II}(\mu\text{-}Q)^0Ru^{III}$, $Ru^{III}(\mu\text{-}Q)^{\bullet-}$ $Ru^{III}$, and $Ru^{III}(\mu\text{-}Q)^{2-}$ $Ru^{IV}$ would be compatible with a $Ru^{III}$-type EPR signal. On the basis of the above argument about strongly different intraligand transitions of $(Q^1)^{2-}$ and $(Q^2)^{2-}$ we disfavor the third alternative, and a bridging quinone in the presence of $(acac)_2Ru^{II}$ seems unlikely. We therefore consider the three-spin situation $Ru^{III}(\mu\text{-}Q)^{\bullet-}$ $Ru^{III}$ with coupled spins at the $Ru^{III}$/semiquinone coordination site[6] (as for **1**), an assignment that is supported by similar absorption maxima of $\mathbf{1}^+$ (920sh, 615, 418 nm), $(Q^1)^{\bullet-}$ (747sh, 566, 404 nm),[11] and **1** (780, 497, 405 nm). In contrast to **1**, the

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[18] (a) Pierpont, C. G.; Lange, C. W. *Prog. Inorg. Chem.* **1994**, *41*, 331. (b) Pierpont, C. G. *Coord. Chem. Rev.* **2001**, *219*−*221*, 415.

[19] (a) Taube, H. *Angew. Chem.* **1984**, *96*, 315; Taube, H. *Angew. Chem. Int. Ed.* **1984**, *23*, 329. (b) Evans, I. P.; Everett, G. W.; Sargeson, A. M. *J. Am. Chem. Soc.* **1976**, *98*, 8041.

**Table 2.** UV−VIS−NIR Absorption Data[a] for Complexes $[(acac)_2Ru(\mu\text{-}Q)Ru(acac)_2]^n$ from Spectroelectrochemistry[b]

| | $\mathbf{1}^n$ | $\mathbf{2}^n$ |
|---|---|---|
| $n = +1$ | 920sh, 615 (7200), 418 (7930) | 650sh, 573 (8680) |
| $n = 0$ | 780 (2800), 497 (5690), 405 (8110) | 554 (7950), 530sh, 455 (9780), 398sh |
| $n = -1$ | 830 (3700), 600 (5820), 517 (7580), 410 (9470) | 640sh, 552 (10230), 440sh, 415 (8250) |
| $n = -2$ | 576 (13220), 480sh, 435 (11780) | 780 (5830), 585sh, 508 (11100), 423sh |

[a] Absorption maxima in nanometers, molar extinction coefficients in $M^{-1}$ $cm^{-1}$ (in parentheses). [b] In $CH_3CN/0.1$ M $Bu_4NPF_6$.

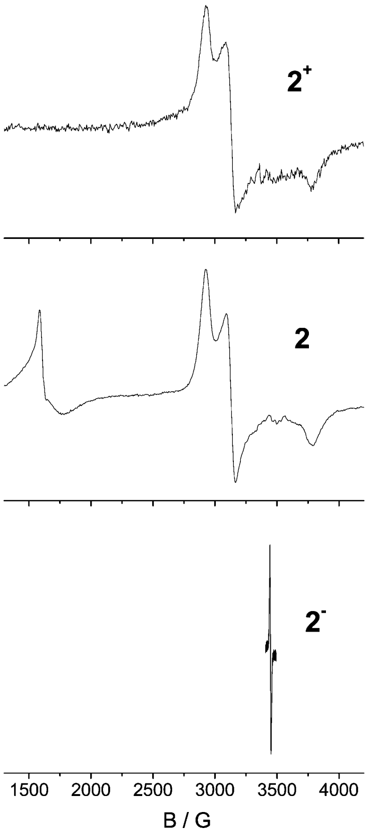
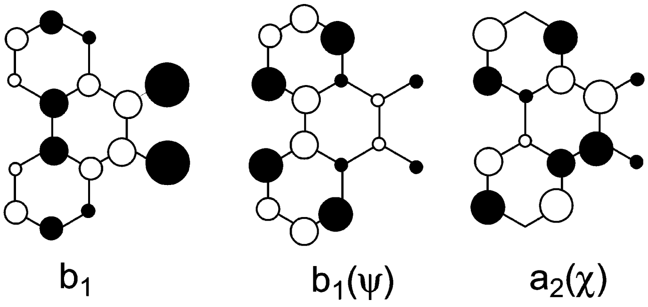
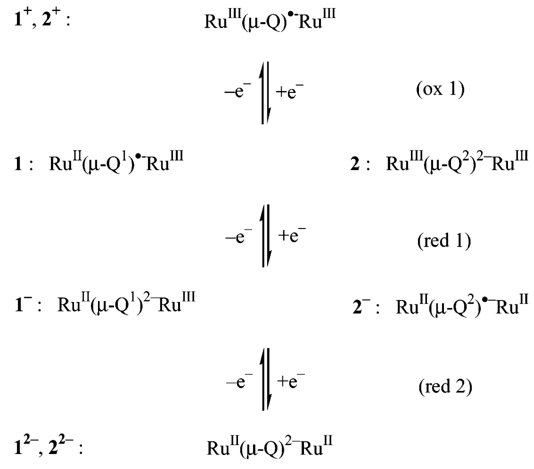


**Figure 3.** EPR spectra of redox system $\mathbf{2}^n$ in $CH_2Cl_2/0.1$ M $Bu_4NPF_6$ at 4 K.

**Scheme 1**



**Scheme 2**



left Ru : $[Ru(acac)_2]^n$ bound to $N^1$, $N^{10}$

right Ru : $[Ru(acac)_2]^n$ bound to $O^5$, $O^6$ or $N^5$, $N^6$

presence of a second oxidized metal center ($Ru^{III}$) in $\mathbf{1}^+$ allows for a more intense LMCT band in the visible range at 615 nm. It has to be reiterated here that the notorious strong orbital mixing between ruthenium and *o*-quinonoid ligands[2−8] can lead to a high degree of covalent bonding that may render conventional oxidation state assignments difficult. However, we have shown in this report how combinations of spectroscopic methods can in favorable cases serve to ascertain the oxidation state distribution even within an asymmetric metal/ligand/metal system with three redox active components (Scheme 2):

Starting from the unequivocal $Ru^{II}(\mu\text{-}Q)^{2-}Ru^{II}$ formulation for both $\mathbf{1}^{2-}$ and $\mathbf{2}^{2-}$, the stepwise oxidation proceeds straightforwardly for $\mathbf{1}^n$ via the O,O-bonded ruthenium ion and the bridging ligand to the N,N-coordinated metal center. For system $\mathbf{2}^n$, however, the first oxidation of the dianionic form involves the bridging ligand. As outlined above, the step from $\mathbf{2}^-$ to $\mathbf{2}$ implies an unusual triple oxidation state change, an oxidation of both metal ions offset by the one-electron reduction of the bridge. Conversion to $\mathbf{2}^+$ involves again ligand-based oxidation. Both the lower coordination asymmetry (all N donor atoms) and the more covalent metal-donor bonding for the quinonediimine bridging system $(Q^2)^k$ vs $(Q^1)^k$ are responsible for these remarkably different electron pathways.

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**Supporting Information Available:** Electrospray mass spectra of **1** and **2** (Figure S1), $\chi T$ vs $T$ diagrams for **1** (Figure S2) and **2** (Figure S3) and spectroelectrochemical response of compound **2** (Figure S4). This material is available free of charge via the Internet at http://pubs.acs.org.

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