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# Separating Innocence and Non-Innocence of Ligands and Metals in Complexes $[(L)Ru(acac)_2]^n$ ($n = -1, 0, +1$; L = *o*-Iminoquinone or *o*-Iminothioquinone)

**Srikanta Patra,[†] Biprajit Sarkar,[‡] Shaikh M. Mobin,[†] Wolfgang Kaim,[*,‡] and Goutam Kumar Lahiri[*,†]**

*Department of Chemistry, Indian Institute of Technology-Bombay, Powai, Mumbai 400076, India,*
*and Institut für Anorganische Chemie, Universität Stuttgart, Pfaffenwaldring 55,*
*D-70550 Stuttgart, Germany*

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The diamagnetic title complexes were obtained from $Ru(acac)_2(CH_3CN)_2$ and 2-aminophenol or 2-aminothiophenol. X-ray structure analysis of $(L_1)Ru(acac)_2$ ($L_1$ = *o*-iminoquinone) revealed C–C intra-ring, C–O, and C–N distances which suggest a $Ru^{III}$-iminosemiquinone oxidation state distribution with antiparallel spin–spin coupling. One-electron oxidation and reduction of both title compounds to paramagnetic monocations $[(L)Ru(acac)_2]^+$ or monoanions $[(L)Ru(acac)_2]^-$ occurs reversibly at widely separated potentials ($\Delta E > 1.3$ V) and leads to low-energy shifted charge transfer bands. In comparison with clearly established $Ru^{II}$-semiquinone or $Ru^{III}$-catecholate systems the $g$ tensor components $2.23 > g_1 > 2.09$, $2.16 > g_2 > 2.07$, and $1.97 > g_3 > 1.88$ point to considerable metal contributions to the singly occupied MO, corresponding to $Ru^{III}$ complexes with either *o*-quinonoid (→ cations) or catecholate-type ligands (→ anions) and only minor inclusion of $Ru^{IV}$- or $Ru^{II}$-iminosemiquinone formulations, respectively. The preference for the $Ru^{III}$ oxidation state for all accessible species is partially attributed to the monoanionic 2,4-pentanedionate (acac) co-ligands which favor a higher metal oxidation state than, e.g., neutral 2,2′-bipyridine (bpy).

## Introduction

Following the recognition of chelating 1,2-dioxolenes[1] as “non-innocent” ligands[2] which can exist in the three oxidation states of *o*-quinone ($Q^o$), *o*-semiquinone ($Q^{\bullet -}$ or SQ), and catecholate ($Q^{2-}$ or Cat), many studies[1,3−17] have been aimed at establishing the interaction between redox-active transition metals and *o*-quinonoid $\pi$ systems. Such interactions may even have biochemical implications, e.g., in biocopper or bioiron chemistry.[9c,18−20] Partial or complete substitution of the O donor atoms by S, NH, or NR and other modifications were used to broaden the scope of this remarkable coordination chemistry.[11−17] Unusual phenomena such as redox isomerism (valence tautomerism) were observed[8−10] and it

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[*] Author to whom correspondence should be addressed. E-mail: kaim@iac.uni-stuttgard.de.

[†] Indian Institute of Technology-Bombay.

[‡] Universität Stuttgart.

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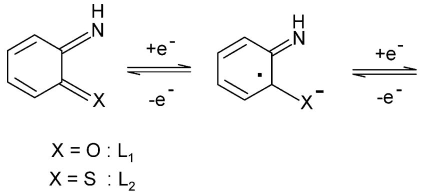
**Scheme 1**



was demonstrated that the eventual determination of oxidation states of metal and ligand may require an array of spectroscopic techniques.[16] In contrast to most 1,2-dioxolene complexes of the first row transition metals the 4d element ruthenium was early shown to exhibit less unambiguous oxidation state situations, in agreement with the notion of mixed ligand $\pi$/metal d orbitals.[4,11,12,14,15]

Herein we describe results obtained for two new conceptually simple systems. The complexes $[(L)Ru(acac)_2]^n$ with acac = 2,4-pentanedionato(1-), L = *o*-iminoquinone ($L_1$) or *o*-iminothioquinone ($L_2$) (Scheme 1), were isolated as neutral species, and, in the case of $L = L_1$, crystallographically characterized; the one-electron oxidized ($n = +1$) and reduced forms ($n = -1$) were investigated spectroelectrochemically and by EPR spectroscopy to establish the spin distribution and thus the appropriate oxidation state formulation.

## Experimental Section

The starting complex $Ru(acac)_2(CH_3CN)_2$ was prepared according to the reported procedure.[21] 2-Aminophenol and 2-aminothiophenol were obtained from Fluka (Switzerland). Other chemicals and solvents were reagent grade and used as received. For spectroscopic and electrochemical studies HPLC grade solvents were used. Commercial tetraethylammonium bromide was converted into pure tetraethylammonium perchlorate by following an available procedure.[22]

**Instrumentation.** UV−visible spectra were recorded with 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. Magnetic susceptibility was checked with a PAR vibrating sample magnetometer. $^1H$ NMR spectra were obtained with a 300 MHz Varian FT spectrometer. The EPR measurements were made in a two-electrode capillary[23a] 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 $[NEt_4]ClO_4$ and the solute concentration was $\sim 10^{-3}$ M. The half-wave potential $E^0_{298}$ 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 were uncorrected for junction potentials. Spectroelectrochemical measurements were performed using an optically transparent thin-layer electrode (OTTLE) cell[23b] for UV−vis spectra. The elemental analyses were carried out with a Perkin-Elmer 240C elemental analyzer.

**Synthesis of Complexes.** The complexes $Ru(acac)_2$(iminosemiquinone) (**1**) and $Ru(acac)_2$(iminothiosemiquinone) (**2**) were prepared using a general procedure. Details are given for **1**.

The starting complex $Ru(acac)_2(CH_3CN)_2$ (100 mg, 0.26 mmol), the 2-aminophenol ligand ($L^1$, 43.6 mg, 0.40 mmol), and sodium acetate (32.8 mg, 0.40 mmol) were combined in 20 mL of ethanol, and the mixture was heated to reflux for 24 h under a dinitrogen atmosphere. The initial orange color of the solution gradually changed to purple. The volume of the solution was then reduced to 5 mL under reduced pressure and the concentrated solution was kept at −5 °C overnight. The solid product thus formed was filtered and thoroughly washed with cold ethanol. Yield for **1**: 64 mg (60%). Anal. Calcd for **1** ($C_{16}H_{19}NO_5Ru$, 406.4): C, 47.24; H, 4.67; N, 3.44%. Found: C, 46.87; H, 4.86; N, 3.65%. Yield for **2**: 60 mg (54.5%). Anal. Calcd for **2** ($C_{16}H_{19}NO_4RuS$, 422.46): C, 45.49; H, 4.53; N, 3.32%. Found: C, 45.18; H, 4.55; N, 3.34%. $^1H$ NMR ($CDCl_3$) **1**: $\delta = 7.15$ (d, 8.8 Hz, $H^1$), 7.43 (t, 8.0 Hz, 8.8 Hz, $H^2$), 6.77 (t, 8.0 Hz, 8.4 Hz $H^3$), 7.73 (d, 9.1 Hz, $H^4$), 13.42 (s, NH), 5.58, 5.41 (s, CH(acac)), 2,59, 2.33, 2.05, 1.99 (s, $CH_3$(acac)) ppm. $^1H$ NMR ($CDCl_3$) **2**: $\delta = 7.49$ (d, 8.8 Hz, $H^1$), 7.07 (t, 7.3 Hz, 7.7 Hz, $H^2$), 6.82 (t, 8.0 Hz, 7.3 Hz, $H^3$), 8.17 (d, 8.4 Hz, $H^4$), 12.74 (s, NH), 5.61, 5.43 (s, CH(acac)), 2.60, 2.42, 1.81, 1.75 (s, $CH_3$(acac)) ppm.

**Crystal Structure Determination.** Single crystals of **1** were grown by slow diffusion of a dichloromethane solution into *n*-hexane followed by slow evaporation. X-ray data of **1** were collected on a PC-controlled Enraf-Nonius CAD-4 (MACH-3) single-crystal X-ray diffractometer using Mo Kα radiation. Significant crystallographic parameters are listed in Table 1. The structure was solved and refined by full-matrix least-squares techniques on $F^2$ using SHELX-97 (SHELXTL program package).[24] A CIF file is available (see Supporting Information).

## Results and Discussion

The complexes $[(L)Ru(acac)_2]$ were obtained as stable species from the reactions of $Ru(acac)_2(CH_3CN)_2$ with the corresponding aminophenol. They could be well characterized through $^1H$ NMR spectroscopy because sharp NMR lines were observed, in agreement with the absence of any significant magnetic moment at room temperature. The compound with the N,O-donor ligand $L_1$ could be crystallized

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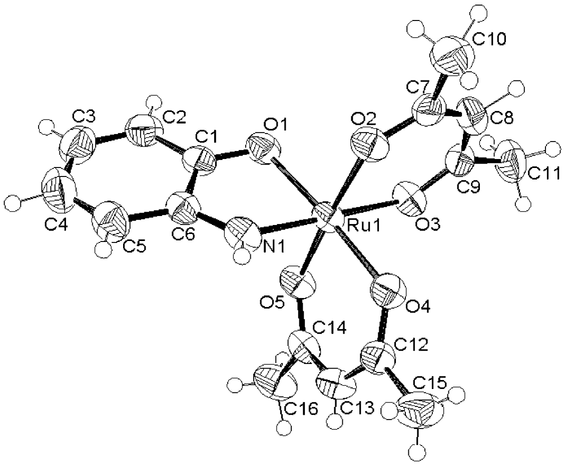

**Figure 1.** Molecular structure of Ru(acac)$_2$(iminosemiquinone) (**1**). Ellipsoids are drawn at 50% probability level.

**Table 1.** Crystallographic Data for **1**

| | |
|---|---|
| molecular formula | $C_{16}H_{19}NO_5Ru$ |
| fw | 406.39 |
| radiation | MoKα |
| temp./ K | 293(2) |
| crystal symmetry | monoclinic |
| space group | $P2_1/c$ |
| $a$/Å | 8.5450(5) |
| $b$/Å | 15.2710(13) |
| $c$/Å | 12.8160(10) |
| $\beta$/deg | 90.883(6) |
| $V$/Å$^3$ | 1672.2(2) |
| $Z$ | 4 |
| $\mu$/mm$^{-1}$ | 0.961 |
| $D_{calcd}$/g cm$^{-3}$ | 1.614 |
| $R$ | 0.0298 |
| $R_w$ | 0.0837 |

**Table 2.** Selected Bond Distances (Å) and Angles (deg) for **1**

| | | | |
|---|---|---|---|
| Ru1−N1 | 1.906(3) | O1−Ru1−N1 | 80.26(10) |
| Ru1−O1 | 2.045(2) | O1−Ru1−O2 | 95.12(9) |
| Ru1−O2 | 2.043(2) | O1−Ru1−O3 | 96.21(9) |
| Ru1−O3 | 2.060(2) | O1−Ru1−O4 | 174.75(9) |
| Ru1−O4 | 2.024(2) | O1−Ru1−O5 | 86.39(10) |
| Ru1−O5 | 1.996(2) | O2−Ru1−N1 | 93.99(10) |
| C1−O1 | 1.291(4) | O2−Ru1−O3 | 89.85(9) |
| C6−N1 | 1.340(4) | O2−Ru1−O4 | 85.35(10) |
| C1−C2 | 1.424(5) | O2−Ru1−O5 | 175.33(9) |
| C2−C3 | 1.363(6) | O3−Ru1−N1 | 174.99(10) |
| C3−C4 | 1.409(7) | O3−Ru1−O4 | 89.03(9) |
| C4−C5 | 1.345(6) | O3−Ru1−O5 | 85.59(9) |
| C5−C6 | 1.411(5) | O4−Ru1−N1 | 94.48(10) |
| C6−C1 | 1.439(4) | O4−Ru1−O5 | 93.56(10) |
| | | O5−Ru1−N1 | 90.62(10) |
| | | C6−N1 −Ru1 | 116.4(2) |
| | | C1−O1−Ru1 | 110.54(19) |

for X-ray diffraction. The crystallographic data are summarized in Table 1, and the relevant bond parameters of the molecule depicted in Figure 1 are listed in Table 2.

In a recent report Bhattacharya, Pierpont, and co-workers have listed the typical C−C intra-ring, C−O, and C−N bond lengths pertaining to the individual oxidation states of *o*-quinonoid molecules, based on hundreds of structure determinations since 1985. A comparison of corresponding data for [(L$_1$)Ru(acac)$_2$] from Table 2 with that list clearly identifies the coordinated ligand as the semiquinone $L_1^{\bullet -}$, leaving a +III oxidation state for the metal. Strong antiparallel spin−spin pairing must thus be invoked for this compound and for the analogous diamagnetic [(L$_2$)Ru(acac)$_2$]; a similar interpretation was given on the basis of experimental and DFT calculations for the compounds (bpy$^{\bullet -}$)M$^{II}$(C$_5$R$_5$), M = Rh or Ir.[25] The neutral complexes are thus best described by the central formulation in Scheme 2.

**Scheme 2**

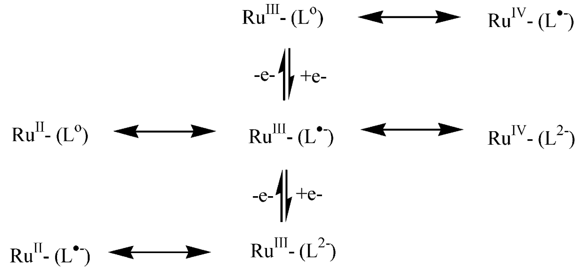

**Table 3.** UV-vis Data of Complexes from Spectroelectrochemistry[a]

| compound | $\lambda_{max}$ ($\epsilon$)[b] |
|---|---|
| **1**$^+$ | 590 (6500), 400sh |
| **1** | 531 (8050), 420sh, 350sh |
| **1**$^-$ | 715 (5350), 415 (6670), 375 (7220) |
| **2**$^+$ | 580 (4010), 355 (7500) |
| **2** | 533 (10850), 370sh |
| **2**$^-$ | 700 (4800), 430 (5450), 360 (6850) |

[a] In CH$_3$CN/0.1 M Bu$_4$NPF$_6$. [b] Absorption wavelengths in nm, extinction coefficients in M$^{-1}$ cm$^{-1}$.

Both neutral complexes [(L)Ru(acac)$_2$] are oxidized and reduced reversibly ($\Delta E$ = 60−75 mV) at conventional scan rates of 100 mV/s in acetonitrile/0.1 M Et$_4$NClO$_4$ with half-wave potentials of 0.37 V and −0.96 V (L$_1$ complex) or 0.72 and −0.59 V (L$_2$ complex) (cf. Figure S1 in Supporting Information). The very large redox potential differences of $\Delta E > 1.3$ V between the one-electron steps translate to comproportionation constants of $K_c = 10^{\Delta E/0.059\text{V}} > 10^{22}$, in agreement with the stability of the neutral compounds. The generally higher potentials for [(L$_2$)Ru(acac)$_2$] illustrate the better acceptor capacity of C=S vs C=O. In agreement with the very similar redox potential differences, the maxima of the intense and relatively narrow charge transfer[4,12,15] absorptions ($\epsilon > 8000$ M$^{-1}$ cm$^{-1}$) in the visible range are virtually identical at about 535 nm in acetonitrile solution (Table 3).

A spectroelectrochemical study of the complexes (Figure 2) revealed bathochromic shifts and intensity reduction of the long-wavelength charge-transfer bands (Table 2). This result suggests that the dioxolene ligand $\pi^*$/metal d$\pi$ interaction and orbital mixing is strongest for the (diamagnetic) neutral forms, whereas the cations and anions exhibit more localized electronic structures. Considering the dominant metal contributions to the singly occupied MOs of both the cations and the anions as evident from EPR (vide infra, Scheme 2) the long-wavelength bands are assigned to metal-to-iminequinone ligand charge transfer (MLCT) transitions for the cations and “catecholate” ligand-to-metal charge transfer (LMCT) transitions for the anionic species.

Because of the reversibility of one-electron oxidation and reduction, the odd-electron cations and anions could be

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**Table 4.** EPR Data of Paramagnetic Ruthenium Complexes

| complex | $g_1$ | $g_2$ | $g_3$ | $\Delta g$[a] | $\langle g\rangle$[b] | best description[c] |
|---|---|---|---|---|---|---|
| $[(L_1)Ru(acac)_2]^+$ | 2.2278 | 2.1468 | 1.9232 | 0.3046 | 2.103 | $Ru^{III}$-$L^{O}$ ($Ru^{IV}$-$L^{\bullet-}$) |
| $[(L_1)Ru(acac)_2]^-$ | 2.0922 | 2.0922 | 1.8870 | 0.2052 | 2.026 | $Ru^{III}$-$L^{2-}$($Ru^{II}$ − $L^{\bullet-}$) |
| $[(L_2)Ru(acac)_2]^+$ | 2.156 | 2.156 | 1.9645 | 0.1915 | 2.094 | $Ru^{III}$-$L^{O}$ ($Ru^{IV}$- $L^{\bullet-}$) |
| $[(L_2)Ru(acac)_2]^-$ | 2.111 | 2.0735 | 1.8895 | 0.2215 | 2.027 | $Ru^{III}$-$L^{2-}$ ($Ru^{II}$- $L^{\bullet-}$) |
| **I** (ref 3) | 2.722 | 2.722 | 1.889 | 0.833 | 2.476 | $Ru^{III}$-$L^{2-}$ |
| **II** (ref 4) | 2.067 | 1.985 | 1.985 | 0.082 | 2.013 | $Ru^{II}$- $L^{\bullet-}$ ($Ru^{III}$-$L^{2-}$) |
| **III** (ref 5) | 2.0053 | 2.0053 | 1.997 | 0.0083 | 2.0025 | $Ru^{II}$- $L^{\bullet-}$ |
| **IV** (ref 11b) | 2.021 | 1.998 | 1.985 | 0.036 | 2.0014 | $Ru^{II}$- $L^{\bullet-}$ |
| **V** (ref 11b) | 2.051 | 2.026 | 1.981 | 0.070 | 2.019 | $Ru^{II}_2$- $L^{\bullet-}$, ($Ru^{III}$-$L^{2-}$-$Ru^{II}$) |
| **VI** (ref 14) | 2.107 | 2.030 | 1.981 | 0.126 | 2.040 | $Ru^{II}_2$- $L^{\bullet-}$, ($Ru^{III}$-$L^{2-}$-$Ru^{II}$) |
| **VII** (ref 14) | 2.364 | 1.982 | 1.853 | 0.511 | 2.078 | $Ru^{III}$-$L^{2-}$-$Ru^{II}$ ($Ru^{II}_2$- $L^{\bullet-}$) |

[a] $\Delta g = g_1 - g_3$. [b] $<g> = [(g_1^2 + g_2^2 + g_3^2)/3]^{1/2}$. [c] Minority contribution in parentheses.

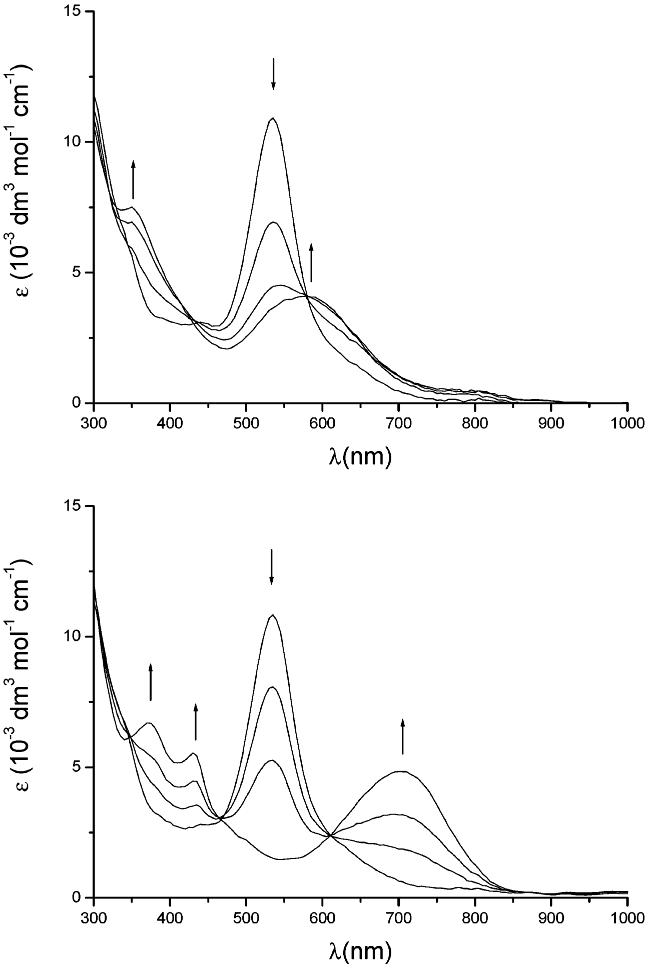

**Figure 2.** Spectral changes of compound **2** on oxidation (top) and reduction (bottom) from OTTLE spectroelectrochemistry in $CH_3CN$/0.1 M $Bu_4NPF_6$.

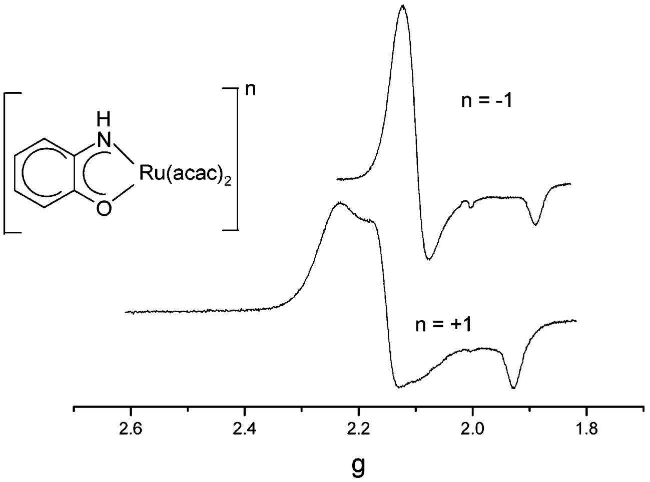

**Figure 3.** EPR spectra of in situ generated $[(L_1)Ru(acac)_2]^n$ in $CH_3CN$/0.1 M $Bu_4NPF_6$ at 110 K: $n = -1$ (top) and $n = +1$ (bottom).

conveniently generated by in situ electrolysis for EPR spectroscopy (Figure 3).

Scheme 2 summarizes the alternative formulations for the oxidized and reduced states of complexes $[(L)Ru(acac)_2]$. EPR spectroscopy of glassy frozen solutions of these paramagnetic species is especially suitable to evaluate the amount of spin on the heavy metal center because this will be reflected through spin−orbit coupling (i) by the anisotropy of the $g$ tensor as quantified by $\Delta g = g_1 - g_3$ and (ii) by the deviation of the isotropic $g$ factor $<g>$ from the value of 2.0023 for the free electron (see eq 1) or from typical values of about 2.005 for free semiquinone anion radicals.[11,26] Table 4 contains the pertinent data, including also those of relevant paramagnetic ruthenium complexes with quinonoid ligands.

Two complex ions, $[(L_1)Ru(acac)_2]^-$ and $[(L_2)Ru(acac)_2]^+$, exhibit an axial $g$ pattern, whereas the other two exhibit some degree of splitting of the $g_\perp$ component. In any case, two $g$ components lie distinctly above 2 whereas $g_3 < 2$. This behavior is typical for $Ru^{III}$ (low-spin $d^5$) as exemplified by the catecholatoruthenium(III) complex **I** (Scheme 3).[3] The total $g$ anisotropy values of $0.19 < \Delta g < 0.31$ for the complexes described here are smaller than the $\Delta g = 0.833$ of **I**, signifying some amount of ligand participation at the singly occupied MO (SOMO). However, all $\Delta g$ values observed here are significantly larger than the $\Delta g < 0.082$ reported for genuine semiquinoneruthenium(II) complexes **II**−**V**.[4,5,11b] The apparent mixing of metal and ligand $\pi$ orbitals in $[(L)Ru(acac)_2]^{+/-}$ has a precedent in a series of dinuclear complexes **VI**, **VII**,[14] and related such species[6] with quinonoid bridging ligands. The results of Table 4 indicate that both the ruthenium(III) and the semiquinone formulations from Scheme 2 contribute to the proper description of $[(L)Ru(acac)_2]^{+/-}$, with the dominating effect from the $Ru^{III}$ formulation. This result may be attributed in part to the 2,4-pentanedionato co-ligands which, other than $\pi$ accepting neutral 2,2′-bipyridine (bpy), favor rather higher metal oxidation states. As an example, the oxidation potential of

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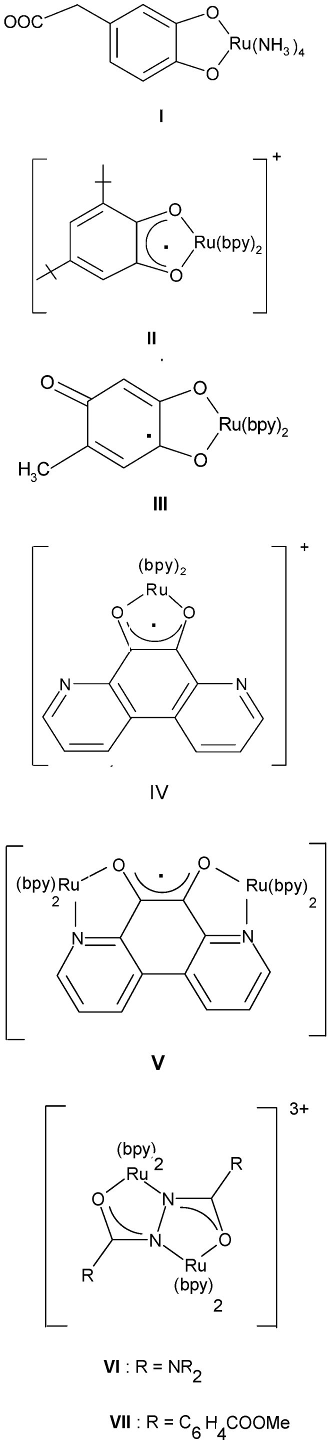
(26) Kaim, W. *Coord. Chem. Rev.* **1987**, *76*, 187.

**Scheme 3**



$\{(\mu\text{-bptz})[Ru(acac)_2]_2\}$ is 0.17 V[27] vs Ag/AgCl in comparison to 1.52 V for $\{(\mu\text{-bptz})[Ru(bpy)_2]_2\}^{4+}$ (bptz = 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine).[28]

According to the $\Delta g$ criterion the highest contribution from a $Ru^{III}$ formulation is observed for $[(L_1)Ru(acac)_2]^+$ which can be explained by the reluctance for oxidation to the alternative ruthenium(IV) state. With the $L_2$ ligand this effect may be attenuated through more covalent S−Ru bonding. The calculated isotropic $<g>$ values from Table 4 show higher values for the cations than for the anions. In agreement with approximation (1) and established concepts[25] for the deviation of $g$ this result confirms closer occupied ($d_{Ru}$) orbitals to the SOMO in the case of the cations.

$$g = g_e - \frac{2}{3}\sum_i\sum_n\sum_{kj}\frac{\langle\psi_0|\xi_k\mathbf{L}\delta_k|\psi_n\rangle\langle\psi_n|\mathbf{L}_{ij}\delta_j|\psi_0\rangle}{E_n - E_0} = g_e + \Delta g \qquad (1)$$

where $\xi$ is the spin−orbit coupling constant, L is the angular momentum operator, and $E_0$ is energy of singly occupied molecular orbital (SOMO).

An exact quantitative assessment of the amount of spin residing on individual atoms will have to await comparative high-level calculations incorporating spin−orbit coupling interactions and the involvement of excited states.[29]

Concluding, we have established through structure determination the validity of an oxidation state formulation $[(L_1)^{-I}Ru^{III}(acac)_2]$ with $(L_1)^{-I}$ = *o*-iminosemiquinone, while the EPR results for $[(L)Ru(acac)_2]^n$, $n = -1$ or $+1$, also indicate dominant contributions from ruthenium(III) forms with either *o*-quinonoid (→ cations) or catecholate-type ligands L (→ anions). Although some metal/ligand orbital mixing is evident from the EPR data it is apparently not the 4d transition metal in its relatively invariant $Ru^{III}$ state but mainly the ligands L which are undergoing the redox transitions in this case. As a consequence, the low-energy charge-transfer transitions involving $Ru^{III}$ have to be assigned differently than the transitions for ruthenium(II) containing complexes of dioxolenes in their different oxidation states.[4,12,15] The propensity of such systems for facile intramolecular transfer makes them useful for optical applications[30] and as substrates for unusual intermediates.[31]

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**Supporting Information Available:** Cyclic voltammograms of complexes **1** and **2** (PDF) and an X-ray crystallographic file in CIF format for $[(L_1)Ru(acac)_2]$. This material is available free of charge via the Internet at http://pubs.acs.org.

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