Inorg. Chem. **2005**, *44*, 2843–2847

Inorganic Chemistry
Article

The Redox Series $[M(bpy)_2(Q)]^{n+}$, M = Ru or Os, Q = 3,5-Di-*tert*-butyl-N-phenyl-1,2-benzoquinonemonoimine. Isolation and a Complete X and W Band EPR Study of the Semiquinone States ($n = 1$)

Shengfa Ye,[†] Biprajit Sarkar,[†] Carole Duboc,[‡] Jan Fiedler,[§] and Wolfgang Kaim*[,†]

Institut für Anorganische Chemie, Universität Stuttgart, Pfaffenwaldring 55,
D-70550 Stuttgart, Germany, Grenoble High Magnetic Field Laboratory, MPI-CNRS,
25 Avenue des Martyrs, BP 166, F-38042 Grenoble Cedex 9, France, and J. Heyrovský Institute
of Physical Chemistry, Academy of Sciences of the Czech Republic, Dolejškova 3,
CZ-18223 Prague, Czech Republic

Received November 12, 2004

The complexes $[M(bpy)_2(Q)](PF_6)$ (bpy = 2,2′-bipyridyl; M = Ru, Os; Q = 3,5-di-*tert*-butyl-N-phenyl-1,2-benzoquinonemonoimine) were isolated and studied by X and W band EPR in a dichloromethane solution at ambient temperatures and at 4 K. For M = Ru, the ^{14}N hyperfine splitting confirms the Ru^{II}/semiquinone formulation, although at $a > 1$ mT, the $^{99,101}Ru$ satellite coupling is unusually high. W band EPR allowed us to determine the relatively small g anisotropy $\Delta g = g_1 - g_3 = 0.0665$ for the ruthenium complex. The osmium analogue exhibits a much higher difference $\Delta g = 0.370$, which is attributed not only to the larger spin–orbit coupling constant of Os versus that of Ru but also to a higher extent of metal contribution to the singly occupied molecular orbital. The difference ΔE between the oxidation and reduction potentials of the radical complexes is larger for the ruthenium compound ($\Delta E = 0.87$ V) than for the osmium analogue ($\Delta E = 0.72$), confirming the difference in metal/ligand interaction. The electrochemically generated states $[M(bpy)_2(Q)]^{n+}$, $n = 0$, 1, 2, and 3, were also characterized using UV–vis–near-infrared spectroelectrochemistry.

Ruthenium complexes of “non-innocent” [1] 1,2-dioxolene[2] ligands Q^n have long been studied[1b,2−9] because of the possibility to combine a redox active chelating ligand $Q/Q^{•-}/Q^{2-}$ with a substitutionally inert but electron-transfer active transition metal. Mononuclear[2−7] and dinuclear[8,9] paramagnetic species with quinonoid ligands ranging from clear radical complexes[3,5,8a] to predominantly metal-centered systems[7] have been investigated mainly by spectroelectrochem-

---

* To whom correspondence should be addressed. E-mail: kaim@iac.uni-stuttgart.de.

[†] Universität Stuttgart.

[‡] Grenoble High Magnetic Field Laboratory.

[§] Academy of Sciences of the Czech Republic.

(1) (a) Jørgensen, C. K. *Oxidation Numbers and Oxidation States*; Springer: Berlin, 1969; p 213. (b) Ward, M. D.; McCleverty, J. A. *J. Chem. Soc., Dalton Trans.* **2002**, 275. (c) Herebian, D.; Bothe, E.; Bill, E.; Weyhermüller, T.; Wieghardt, K. *J. Am. Chem. Soc.* **2001**, *123*, 10012.

(2) Pierpont, C. G. *Coord. Chem. Rev.* **2001**, *219−221*, 415.

(3) (a) Haga, M.; Dodsworth, E. S.; Lever, A. B. P. *Inorg. Chem.* **1986**, *25*, 447. (b) Masui, H.; Lever, A. B. P.; Auburn, P. *Inorg. Chem.* **1991**, *30*, 2402. (c) Ebadi, M.; Lever, A. B. P. *Inorg. Chem.* **1999**, *38*, 467. (d) Lever, A. B. P.; Auburn, P. R.; Dodsworth, E. S.; Haga, M.; Liu, W.; Melnik, M.; Nevin, W. A. *J. Am. Chem. Soc.* **1988**, *110*, 8076. (e) Auburn, P. R.; Dodsworth, E. S.; Haga, M.; Liu, W.; Nevin, W. A.; Lever, A. B. P. *Inorg. Chem.* **1991**, *30*, 3502. (f) Bag, N.; Pramanik, A.; Lahiri, G. K.; Chakravorty, A. *Inorg. Chem.* **1992**, *31*, 40. (g) Bag, N.; Lahiri, G. K.; Basu, P.; Chakravorty, A. *J. Chem. Soc., Dalton Trans.* **1992**, 113. (h) Okamura, R.; Wada, T.; Aikawa, K.; Nagata, T.; Tanaka, K. *Inorg. Chem.* **2004**, *43*, 7210. (i) Lever, A. B. P.; Gorelsky, S. L. *Struct. Bonding (Berlin)* **2004**, *107*, 77.

(4) (a) Bhattacharya, S.; Boone, S. R.; Fox, G. A.; Pierpont, C. G. *J. Am. Chem. Soc.* **1990**, *112*, 1088. (b) Bhattacharya, S.; Pierpont, C. G. *Inorg. Chem.* **1991**, *30*, 1511. (c) Haga, M.; Dodsworth, E. S.; Lever, A. B. P.; Boone, S. R.; Pierpont, C. G. *J. Am. Chem. Soc.* **1986**, *108*, 7413. (d) Boone, S. R.; Pierpont, C. G. *Inorg. Chem.* **1987**, *26*, 1769. (e) Bhattacharya, S.; Pierpont, C. G. *Inorg. Chem.* **1994**, *33*, 6038. (f) Cheng, H.-Y.; Lin, C.-C.; Tzeng, B.-C.; Peng, S.-M. *J. Chin. Chem. Soc.* **1994**, *41*, 775. (g) Mitra, K. N.; Majumdar, P.; Peng, S.-M.; Castiñeiras, A.; Goswami. S. *Chem. Commun.* **1997**, 1267. (h) Mitra, K. N.; Choudhury, S.; Castiñeiras, A.; Goswami, S. *J. Chem. Soc., Dalton Trans.* **1998**, 2901. (i) Das, C.; Kamar, K. K.; Ghosh, A. K.; Majumdar, P.; Hung, C.-H.; Goswami, S. *New J. Chem.* **2002**, *26*, 1409. (j) Connelly, N. G.; Manners, I.; Protheroe, J. R. C.; Whiteley, M. W. *J. Chem. Soc., Dalton Trans.* **1984**, 2713. (k) Bag, N.; Pramanik, A.; Lahiri, G. K.; Chakravorty, A. *Inorg. Chem.* **1992**, *31*, 40. (l) Kurihara, M.; Daniele, S.; Tsuge, K.; Sugimoto, H.; Tanaka, K. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 867. (m) Meacham, A. P.; Druce K. L.; Bell, Z. R.; Ward, M. D.; Keister, J. B.; Lever, A. B. P. *Inorg. Chem.* **2003**, *42*, 7887.

(5) Waldhör, E.; Schwederski, B.; Kaim, W. *J. Chem. Soc., Perkin Trans. 2* **1993**, 2109.

(6) Patra, S.; Sarkar, B.; Mobin, S. M.; Kaim, W.; Lahiri, G. K. *Inorg. Chem.* **2003**, *42*, 6469.

10.1021/ic048407i CCC: $30.25 © 2005 American Chemical Society
Published on Web 03/12/2005

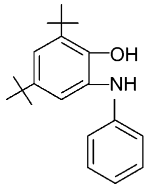
istry and electron paramagnetic resonance (EPR). However, the EPR information was frequently found unsatisfactory because of insufficient resolution, either for the hyperfine structure or for the g tensor anisotropy. In particular, those systems with a considerable metal contribution to the singly occupied molecular orbital (SOMO) did show g anisotropy in the X band (9.5 GHz) but no hyperfine splitting due to broad lines.[6,7,9] On the other hand, the small g anisotropies expected for complexes with a primarily ligand-based SOMO (anion radical complexes[10]) were often difficult to determine accurately in the X band.[3,5] Osmium analogues are less well-documented than the ruthenium complexes.[11] The EPR spectroscopy of osmium-containing compounds is typically affected by the high spin−orbit coupling constant of that 5d element[12,13] and by inherently rapid relaxation, leading to broadened lines or even "EPR silence". On the other hand, if the line width allows for detection, the conditions for metal hyperfine coupling are a little better for ^{189}Os ($I = {}^{3}/_{2}$, 16.1% natural abundance, $A_{\mathrm{iso}} = 471.0$ mT) than for the ruthenium isotopes ^{99}Ru ($I = {}^{5}/_{2}$, 12.7%, $A_{\mathrm{iso}} = 62.94$ mT) and ^{101}Ru ($I = {}^{5}/_{2}$, 17.0%, $A_{\mathrm{iso}} = 70.52$ mT).[13]

In this report, we present a detailed EPR analysis of the isolated complexes $[\mathrm{M(bpy)_2(Q)}](\mathrm{PF_6})$ (bpy = 2,2′-bipyridyl) at X and W band frequencies (95 GHz) in a dichloromethane solution at ambient temperatures and at 4 K. We also report UV−vis−near-infrared (NIR) spectroelectrochemical results for the electrochemically generated states $[\mathrm{M(bpy)_2(Q)}]^{n+}$, $n = 0$, 1, 2, and 3.

Experimental Section

Instrumentation. X band EPR spectra were recorded on a Bruker System ESP 300 equipped with a Bruker ER035M gaussmeter and an HP 5350B microwave counter. W band EPR spectra were recorded using a multifrequency spectrometer.[14] A Gunn diode operating at 95 GHz was used as a radiation source. An InSb bolometer (QMC Instruments) was used for detection. The main magnetic field was provided by a superconducting magnet (Cryogenics Consultant), which generates fields up to 12 T. As a result of different field sweep conditions, the absolute values of the g components were obtained by calibrating the precisely measured g anisotropy data with the isotropic g value from X band measurements. Although this procedure does not account for the temperature dependence of g, the values extracted are identical with those obtained using an added standard. UV−vis−NIR absorption spectra were recorded on J & M Tidas Agilent 8453 and Bruins Instruments Omega 10 spectrophotometers. Cyclic voltammetry was carried out in 0.1 M $\mathrm{Bu_4NPF_6}$ solutions using a three-electrode configuration (glassy carbon electrode, Pt counter electrode, Ag/AgCl reference) and a PAR 273 potentiostat and function generator. The ferrocene/ferrocenium couple served as an internal reference. Spectroelectrochemical measurements were performed using an optically transparent thin-layer electrode (OTTLE) cell[15] for UV−vis−NIR absorption spectra.

Chart 1



Syntheses. The ligand 2-anilino-4,6-di-*tert*-butylphenol (Chart 1) was prepared according to a published procedure.[16]

$[\mathrm{Ru(bpy)_2(Q)}]\mathrm{PF_6}$ and $[\mathrm{Os(bpy)_2(Q)}]\mathrm{PF_6}$. The complexes were obtained in an analogous way. Solutions of 1.0 mmol of the ligand, 4 mL of 0.5 M $\mathrm{NaOCH_3}$, and 1.0 mmol of *cis*-$\mathrm{M(bpy)_2Cl_2{\cdot}2H_2O}$ (M = Ru, Os) were heated to reflux in the presence of air in 25 mL of acetonitrile for 4 h. After cooling, 1.0 mmol of $\mathrm{KPF_6}$ was added to precipitate the complexes at 4 °C. The precipitates were collected by filtration, and after washing with cold acetonitrile, dark microcrystalline materials were obtained in about 60% yield. Anal. Calcd for $\mathrm{C_{40}H_{41}F_6N_5ORuP}$: C, 56.27; H, 4.84; N, 8.20. Found: C, 56.57; H, 4.41; N, 8.34%. Anal. Calcd for $\mathrm{C_{40}H_{41}F_6N_5OOsP}$: C, 50.95; H, 4.38; N, 7.43. Found: C, 50.41; H, 4.06; N, 7.11%.

Results and Discussion

Synthesis and Electrochemistry. The radical complexes $[\mathrm{M(bpy)_2(Q)}](\mathrm{PF_6})$ were obtained from reactions between the *cis*-$\mathrm{M(bpy)_2Cl_2}$ precursors and 2-anilino-4,6-di-*tert*-butylphenol. The oxidation equivalents required to obtain the semioxidized complexes are believed to come from traces of $\mathrm{O_2}$, which, in the reduced form, also acts as proton acceptor. Identification of the isolated complexes by elemental analysis, EPR, and cyclic voltammetry in $\mathrm{CH_2Cl_2}$/0.1 M $\mathrm{Bu_4NPF_6}$ showed that the isolated paramagnetic compounds are intermediates with not too closely spaced one-electron reduction and oxidation waves (Figure 1; Table 1). After the first oxidation to $[\mathrm{M(bpy)_2(Q)}]^{2+}$ at about −0.5 V, a second oxidation to $[\mathrm{M(bpy)_2(Q)}]^{3+}$ was observed in both cases at rather high potentials; bpy-centered reduction processes cannot be observed before the negative potential limit of the $\mathrm{CH_2Cl_2}$ solvent.

The second oxidation waves are associated with $\mathrm{M^{II}} \rightarrow \mathrm{M^{III}}$ processes,[3] characteristically[11,17] with a significantly lower value for the osmium analogue. The difference ΔE between the oxidation and reduction potentials of the complexes $[\mathrm{M(bpy)_2(Q)}](\mathrm{PF_6})$ is slightly higher for the ruthenium analogue (0.87 V vs 0.72 V), a phenomenon familiar from related systems that signifies less metal/ligand orbital mixing.[11,17]

---

(7) Salmonsen, R. B.; Abelleira, A.; Clarke, M. J. *Inorg. Chem.* **1984**, *23*, 387.

(8) (a) Ernst, S.; Hänel, P.; Jordanov, J.; Kaim, W.; Kasack, V.; Roth, E. *J. Am. Chem. Soc.* **1989**, *111*, 1733. (b) Ernst, S.; Kasack, V.; Bessenbacher, C.; Kaim, W. *Z. Naturforsch.* **1987**, *42b*, 425.

(9) (a) Dei, A.; Gatteschi, D.; Pardi, L. *Inorg. Chem.* **1990**, *29*, 1443. (b) Kasack, V.; Kaim, W.; Binder, H.; Jordanov, J.; Roth, E. *Inorg. Chem.* **1995**, *34*, 1924. (c) Knödler, A.; Fiedler, J.; Kaim, W. *Polyhedron* **2004**, *23*, 701. (d) Patra, S.; Sarkar, B:, Ghumaan, S.; Fiedler, J.; Zalis, S.; Kaim, W.; Lahiri, G. K. *J. Chem. Soc., Dalton. Trans.* **2004**, 750.

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

(11) (a) Haga, M.; Isobe, K.; Boone, S. R.; Pierpont, C. G. *Inorg. Chem.* **1990**, *29*, 3795. (b) Mitra, K. N.; Goswami, S. *Inorg. Chem.* **1997**, *36*, 1322.

(12) Kober, E. M.; Meyer. T. J. *Inorg. Chem.* **1984**, *23*, 3877.

(13) Weil, J. A.; Bolton, J. R.; Wertz, J. E. *Electron Paramagnetic Resonance*; Wiley: New York, 1994.

(14) Barra, A.-L.; Brunel, L.-C.; Robert, J.-B. *Chem. Phys. Lett.* **1990**, *165*, 107.

(15) Krejcik, M.; Danek, M.; Hartl, F. *J. Electroanal. Chem.* **1991**, *317*, 179.

(16) Chaudhuri, P.; Verani, C. N.; Bill, E.; Bothe, E.; Weyhermüller, T.; Wieghardt, K. *J. Am. Chem. Soc.* **2001**, *123*, 2213.

(17) Kaim, W.; Kasack, V. *Inorg. Chem.* **1990**, *29*, 4696.

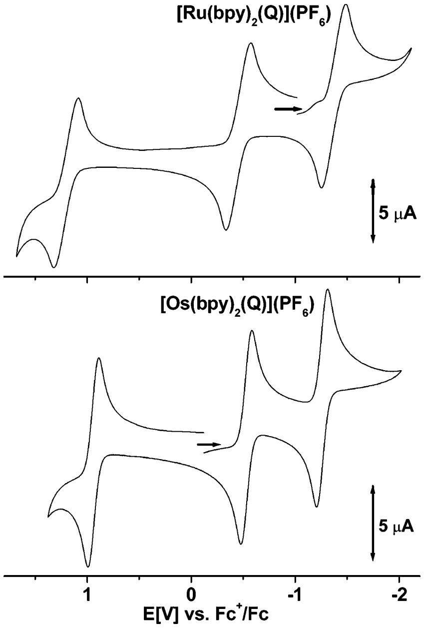


Figure 1. Cyclic voltammograms of compounds $[M(bpy)_2(Q)](PF_6)$ in dichloromethane/0.1 M Bu_4NPF_6 at 100 mV/s scan rate: M = Ru (top), M = Os (bottom, preoxidized to $[Os(bpy)_2(Q)]^{2+}$).

Table 1. Redox Potentials[a] for Complexes $[M(bpy)_2(Q)]^n$

	E[a]	
n	M = Ru	M = Os
3+/2+	1.22	0.95
2+/+	−0.42	−0.51
+/0	−1.29	−1.23

[a] From cyclic voltammetry at 100 mV/s scan rate in CH_2Cl_2/0.1 M Bu_4NPF_6. Potentials in V vs that of $[Fe(C_5H_5)_2]^{+/0}$.

Table 2. Electronic Spectra of Complexes[a]

	λ_{max} (10^3 ϵ)[b]
$[Ru(bpy)_2(Q)]^{3+}$	309(26.1), 437(8.1), 504(8.1), 591(sh)
$[Ru(bpy)_2(Q)]^{2+}$	281(31.1), 411(5.8), 595(13.4)
$[Ru(bpy)_2(Q)]^{+}$	294(36.0), 350(9.5), 376(sh), 496(6.3), 686(7.4)
$[Ru(bpy)_2(Q)]^{0}$	295(35.6), 374(9.8), 423(sh), 531(7.0), 607(sh)
$[Os(bpy)_2(Q)]^{3+}$	286(17.0), 501(6.6)
$[Os(bpy)_2(Q)]^{2+}$	287(22.1), 512(7.6)
$[Os(bpy)_2(Q)]^{+}$	292(27.1), 390(6.9), 465(sh), 534(5.5), 688(5.9)
$[Os(bpy)_2(Q)]^{0}$	295(29.9), 385(8.6), 542(6.8), 805(sh)

[a] From spectroelectrochemistry in CH_2Cl_2/0.1 M Bu_4NPF_6. [b] Wavelengths in nm, molar extinction coefficients in M^{-1} cm^{-1}.

Spectroelectrochemistry. The results from OTTLE spectroelectrochemistry are listed in Table 2 and illustrated for the ruthenium complex in Figure 2.

A one-electron reduction to $[M(bpy)_2(Q)]$ and two one-electron oxidation processes to $[M(bpy)_2(Q)]^{2+}$ and $[M(bpy)_2(Q)]^{3+}$ could be observed. Although more bands could have been expected for the osmium analogue as a result of the effect of higher spin−orbit coupling allowing observable triplet absorption features,[11] both the osmium and the ruthenium redox systems $[M(bpy)_2(Q)]^n$ exhibit bands very similar to those reported for the N-unsubstituted ruthenium complex.[3b,i] This overall agreement justifies the adoption of the reasonable assignments made by Masui, Lever, and Auburn for the main long-wavelength transitions, that is, ligand-to-ligand charge transfer (LLCT; $Q^{2-} \rightarrow bpy$) and π^*(bpy)-targeted metal-to-ligand charge transfer (MLCT) bands at about 530 and 370 nm for $[M(bpy)_2(Q)]^0$, semiquinone- and bpy-targeted MLCT bands at about 690 and 500 nm for $[M(bpy)_2(Q)]^+$, and quinone- and bpy-targeted MLCT bands at about 590 and 410 nm for $[Ru(bpy)_2(Q)]^{2+}$.[3b,i] The bands of the $[M(bpy)_2(Q)]^{3+}$ species at ca. 500 nm are assigned to intraquinone ligand transitions.[16]

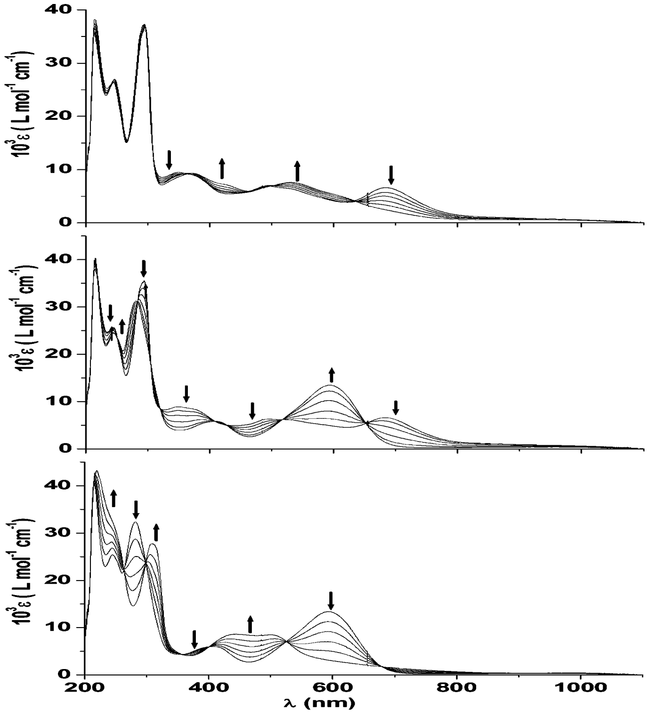


Figure 2. UV−vis-spectroelectrochemical response of $[Ru(bpy)_2(Q)](PF_6)$ in dichloromethane/0.1 M Bu_4NPF_6 on one-electron reduction (top) and on first (center) and second oxidations (bottom).

EPR Spectroscopy. Both $[M(bpy)_2(Q)](PF_6)$ complexes exhibit EPR signals in the dichloromethane solution at room temperature. This result alone is evidence for a predominantly ligand-based spin, as has been mentioned before.[6] Significant amounts of metal-centered spin would be expected to lead to rapid relaxation and to large *g* anisotropy with concomitant line broadening.[8,10]

Semiquinone complexes of ruthenium(II) were often found to show only partially useful EPR spectra because of unresolved hyperfine structure or detailed *g* tensor anisotropy information in the X band.[3] Osmium analogues are less well-documented than the ruthenium complexes.[11]

Whereas $[Os(bpy)_2(Q)](PF_6)$ exhibits only a broad unresolved line (ΔH_{pp} = 9 mT) at g_{iso} = 1.982 in the X band EPR experiment at room temperature, the ruthenium analogue $[Ru(bpy)_2(Q)](PF_6)$ gives a spectrum at g_{iso} = 2.0049 (Figure 3, Table 3), a typical value for free semiquinone radicals.[18,19] Fortunately, the spectrum is sufficiently resolved to determine the ^{14}N and $^{99,101}Ru$ hyperfine couplings.

At 0.78 mT, the magnitude of a(^{14}N) is typical for *o*-semiquinonemonoimine complexes.[18] Remarkably, how-

---

(18) Stegmann, H. B.; Ulmschneider, K. B.; Hieke, K.; Scheffler, K. *J. Organomet. Chem.* **1976**, *118*, 259.

(19) Burghaus, O.; Plato, M.; Rohrer, M.; Möbius, K.; MacMillan, F.; Lubitz, W. *J. Phys. Chem.* **1993**, *97*, 7639.

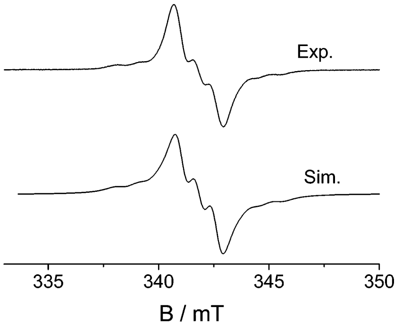


Figure 3. X band EPR spectrum of $[Ru(bpy)_2(Q)](PF_6)$ in dichloromethane at 298 K: experimental (top) and simulated spectra (bottom).

Table 3. EPR Data of Complexes $[M(bpy)_2(Q)](PF_6)^a$

	M = Ru	M = Os
	298 K	
g_{iso}	2.0049^b	1.982^c
	5 K	
g_1	2.0393^d	2.160
g_2	2.0022^d	1.913
g_3	1.9728^d	1.790
$\Delta g = g_1 - g_3$	0.0665	0.370
g_{av}	2.0048	1.960

[a] In CH_2Cl_2. [b] a(^{14}N) = 0.78 mT; a(^{99}Ru) = 1.01 mT; a(^{101}Ru) = 1.13 mT. [c] ΔH_{pp} = 9 mT. [d] From the W band spectrum.

ever, the metal hyperfine coupling is large enough to be clearly detectable at the wings of the main signal. The values of a(^{99}Ru) = 1.01 mT and a(^{101}Ru) = 1.13 mT are larger than those observed for $[Ru(bpy)_2(abpy)]^+$ (0.77/0.86 mT; abpy = 2,2′-azobispyridine),[20] $[Ru(bpy)_2(abcp)]^+$ [0.72 mT; abcp = 2,2′-azobis(5-chloropyrimidine)],[21] $[Ru(bpy)_2(PQQ)]^+$ (0.50 mT; PQQ = pyrroloquinolinequinone),[22] $[Ru(bpz)(CN)_4]^{3-}$ (0.514/0.458 mT; bpz = 2,2′-bipyrazine),[23] $[Ru(mpz)(CN)_5]^{3-}$ (0.39/0.437 mT; mpz$^+$ = methylpyrazinium),[24] $[Ru(mpz)(NH_3)_5]^{2+}$ (0.58/0.65 mT),[25] or $[Ru(bpy)_2(Q')]$ (0.225 mT; Q′ = 5-methyl-2-oxido-1,4-benzosemiquinone).[5] Even for $[Ru(NO)(CN)_5]^{3-}$, the calculated isotropic value for a (^{101}Ru) was below 1 mT.[26] We attribute this large metal hyperfine coupling to an efficient spin transfer (spin polarization) from the *o*-semiquinoneimine ligand to the metal in a chelate situation, this enhanced orbital overlap being additionally favored by the well-established strength of the $Ru^{II}-N$ bond.[27]

Although the hyperfine coupling of ^{189}Os should be better detectable than the ruthenium values,[28] it was not observed here for $[Os(bpy)_2(Q)](PF_6)$ because of the large line width. Conversely, however, the *g* components could be detected in frozen dichloromethane solution in the X band (Figure 4; Table 3), confirmed also through W band measurements.

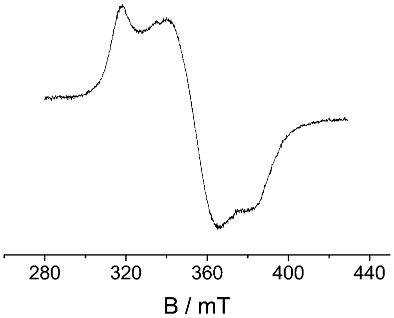


Figure 4. X band EPR spectrum of $[Os(bpy)_2(Q)](PF_6)$ in dichloromethane at 4 K.

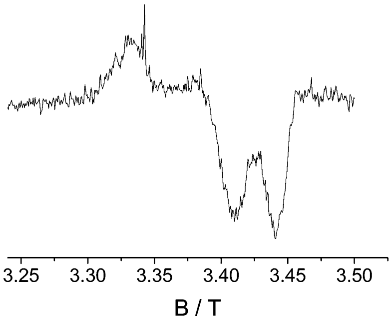


Figure 5. W band EPR spectrum of $[Ru(bpy)_2(Q)](PF_6)$ in dichloromethane/toluene (4:1) at 5 K.

For the analogous $[Ru(bpy)_2(Q)](PF_6)$, the W band studies were essential to determine the *g* anisotropy (Figure 5; Table 3) because of the much smaller difference $\Delta g = g_1 - g_3 = 0.0665$ in comparison to $\Delta g = 0.370$ for the osmium complex.

In relation to typical catecholatoruthenium(III) species ($\Delta g \approx 0.8$)[7] or extensively metal−ligand mixed systems ($\Delta g \approx 0.25$),[6] the *g* anisotropy of $[Ru(bpy)_2(Q)](PF_6)$ is so small as to allow its labeling as a ruthenium(II)−semiquinoneimine complex $[Ru^{II}(bpy)_2(Q^{\bullet -})]^+$. However, the isotropic *g* value of 2.0049 showing almost no difference to a metal-free semiquinone is deceptive; the Δg value of 0.0665 is still much larger than the corresponding *g* anisotropies of about 0.006 for typical free semiquinones.[19] Recently reported high-field EPR studies[29] of Ru^{II}−radical complexes have shown Δg values between 0.01 and 0.04, that is, clearly lower than the 0.0665 observed for $[Ru(bpy)_2(Q)]^+$. Thus, both the *g* anisotropy as determined from W band EPR and the ^{99,101}Ru hyperfine coupling from high-resolution X band EPR suggest a nonnegligible contribution from the metal to the SOMO.

The metal participation at the SOMO is obviously still higher for $[Os(bpy)_2(Q)](PF_6)$. Although the spin−orbit coupling constants of osmium centers are only about 2−3 times higher than those of ruthenium analogues,[12,13] the *g* anisotropy of the osmium complex is more than 5 times as large as that for $[Ru(bpy)_2(Q)](PF_6)$. This disproportionate

---

(20) Krejcik, M.; Zalis, S.; Klima, J.; Sykora, D.; Matheis, W.; Klein, A.; Kaim, W. *Inorg. Chem.* **1993**, *32*, 3362.

(21) Kaim, W.; Doslik, N.; Frantz, S.; Sixt, T.; Wanner, M.; Baumann, F.; Denninger, G.; Kümmerer, H.-J.; Duboc-Toia, C.; Fiedler, J.; Zalis, S. *J. Mol. Struct.* **2003**, *656*, 183.

(22) Schwederski, B.; Kasack, V.; Kaim, W.; Roth, E.; Jordanov, J. *Angew. Chem.* **1990**, *102*, 74; *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 78.

(23) Waldhör, E.; Poppe, J.; Kaim, W.; Cutin, E.; Garcia Posse, M.; Katz, N. E. *Inorg. Chem.* **1995**, *34*, 3093.

(24) Waldhör, E.; Kaim, W.; Olabe, J. A.; Slep, L. D.; Fiedler, J. *Inorg. Chem.* **1997**, *36*, 2969.

(25) Poppe, J.; Kaim, W.; Ben Altabef, A.; Katz, N. E. *J. Chem. Soc., Perkin Trans. 2* **1993**, 2105.

(26) Frantz, S.; Sarkar, B.; Sieger, M.; Kaim, W.; Roncaroli, F.; Olabe, J. A.; Zalis, S. *Eur. J. Inorg. Chem.* **2004**, 2902.

(27) Taube, H. *Angew. Chem.* **1984**, *96*, 315; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 329.

(28) Kaim, W.; Reinhardt, R.; Sieger, M. *Inorg. Chem.* **1994**, *33*, 4453.

(29) (a) Sarkar, B.; Frantz, S.; Kaim, W.; Duboc, C. *J. Chem. Soc., Dalton Trans.* **2004**, 3727. (b) Sarkar, B.; Kaim, W.; Fiedler, J.; Duboc, C. *J. Am. Chem. Soc.* **2004**, *126*, 14706.

increase suggests a stronger contribution from formulations such as $[Os^{III}(bpy)_2(Q^{2-})]^+$, the higher oxidation state being more stable for the 5d element system. The shifts of g_{iso}, g_2, and g_3 to lower values < 2 indicate the presence of close-lying excited states with nonzero angular orbital momentum to the doublet ground state.[10] However, such states cannot yet be identified with certainty; high-level calculations based on structural data will be necessary for such assessments. It is remarkable that the formally related species $[Fe(cyclam)(Q)]^+$ was reported to exhibit a catecholate (*o*-imidophenolate) ligand state with coordinated high-spin iron(III).[30] Apparently, the preference for the low-spin d^6 metal configuration with the semiquinoneimine state of the ligand is most pronounced for the ruthenium system, whereas the heavier homologue (Os) tends toward higher metal oxidation states, and the first row transition metal analogue (Fe) readily adopts odd d-electron and even high-spin configurations.

In summary, this report on redox systems $[M(bpy)_2(Q)]^{n+}$ (M = Ru, Os) has not only confirmed the UV−vis spectroelectrochemical results obtained by Lever and co-workers for the N-unsubstituted quinoneimine ligand form (M = Ru),[3i] it also describes the facile isolation of both radical states and their comprehensive EPR analysis at two very different frequencies with the result of a remarkably large $^{99,101}Ru$ hyperfine coupling and an unusually pronounced *g* anisotropy difference between the ruthenium and osmium analogues.

Acknowledgment. We thank the DFG (Graduate College “Magnetic Resonance”), the Fonds der Chemischen Industrie, and the European Community (Access to Research Infrastructure Action of the Improving Human Potential Program) for continued support. J.F. acknowledges grants from the Grant Agency of the Czech Republic (Grant 203/03/082) and the Ministry of Education of the Czech Republic (Grant COST OC D15.10).

IC048407I

---

(30) Chun, H.; Bill, E.; Bothe, E.; Weyhermüller, T.; Wieghardt, K. *Inorg. Chem.* **2002**, *41*, 5091.