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Stable Binuclear *o*- and *p*-Semiquinone Complexes of $[Ru(bpy)_2]^{2+}$. Radical Ion versus Mixed Valence Dimer Formulation

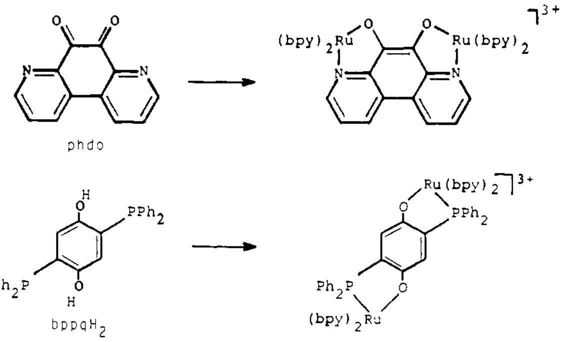
Sylvia Ernst,[1a,2a] Peter Hänel,[1a,2b] Jeanne Jordanov,[1b] Wolfgang Kaim,*,[1a] Volker Kasack,[1a] and Eberhard Roth[1a,b]

Contribution from the Institut für Anorganische Chemie, Universität Stuttgart, Pfaffenwaldring 55, D-7000 Stuttgart 80, Federal Republic of Germany, and the Département de Recherche Fondamentale, Service de Physique, Centre d'Etudes Nucléaires, 85X, F-38041 Grenoble, Cédex, France. *Received June 14, 1988*

Abstract: Paramagnetic binuclear complexes $\{[Ru(bpy)_2]_2(\mu\text{-}L)\}^{3+}$ with L being N,O;N′,O′-coordinating 4,7-phenanthroline-5,6-semidione and P,O;P′,O′-coordinating 2,5-bis(diphenylphosphino)-*p*-benzosemiquinone were obtained as redoxactive yet stable species. UV-vis/near infrared spectroscopic results have been analyzed for the three chemically and electrochemically available oxidation states (2+/3+/4+), and the EPR data of the (3+) intermediates show that these first binuclear semiquinone complexes are situated at the borderline between anion radical complexes and metal-centered mixed-valent dimers.

o- and *p*-semiquinones are important intermediates in chemical and biochemical redox reactions.[3-6] The chelating ability of *o*-semiquinones is responsible for a large number of mononuclear "ion pairs"[7-9] and complexes, including stable transition-metal compounds.[10-12] On the other hand, much less is known about transition-metal coordination compounds of *p*-semiquinones[13,14] although these too may play important roles in biological redox chains, as in the structurally characterized reaction center of bacterial photosynthesis.[15] The reason for this scarcity of stable metal complexes lies probably in the low basicity ($pK_{BH^+} < 5$)[16] and in the absence of a chelate coordination site in simple *p*-semiquinones.

Employing the substitutionally inert, yet electron transfer active[11,17-19] metal fragment $[Ru(bpy)_2]^{2+}$, we describe here the formation and electronic structure of stable binuclear complexes of the *o*-semiquinone phdo$^{\bullet-}$ and of the *p*-semiquinone bppq$^{\bullet-}$.



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4,7-Phenanthroline-5,6-dione (phdo, "Entobex") is a model compound[20] for the dehydrogenase and amine oxidase cofactor methoxatin (cofactor PQQ) which exhibits a stable and biochemically relevant semiquinone form[20-22] and shows response to metal coordination.[20b] Stable binuclear N,O;N′,O′-bonded copper(I)[23] and ruthenium(II)[24] complexes and an O,O′-coordinated mononuclear $[Ru(bpy)_2]$ complex[24] of the semiquinone phdo$^{\bullet-}$ have been reported. The 2,5-bis(diphenylphosphino)-*p*-semiquinone bppq$^{\bullet-}$ is distinguished by the σ donating but π accepting[25] R_2P cochelating substituents at the 2,5-positions. Whereas the free quinone form of that ligand has not yet been obtained, the hydroquinone is available via conventional synthetic procedures.[26] It is noteworthy that $(bpy)_2Ru(PR_3)$ fragments with the metal present in higher oxidation state were found to activate oxygen

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(1) (a) Universität Stuttgart. (b) C.E.N.G. Grenoble.

(2) (a) Present address: Beilstein-Institut, D-6000 Frankfurt, West Germany. (b) Present address: Metallgesellschaft (Chemetall), D-6000 Frankfurt, West Germany.

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ligands, especially in the series O/OH/OH_2;[27] these systems have recently been used by Takeuchi and co-workers as oxidation catalysts, e.g., for olefins.[28]

Our interest in preparing symmetrically *binuclear* complexes of semiquinones with the [Ru(bpy)$_2$] fragments[11] is based on the concept that two metal fragments induce a larger ligand perturbation than one,[19,29] an additional bonus being the possibility of ligand-mediated metal–metal interaction. The possible combination of metal–metal[30–33] *and* metal–ligand electron delocalization[34] in polynuclear complexes may, as a result, produce unusual electronic structures[34,35] related to that of the mixed-valent ($Ru^{II}Ru^{III}$) Creutz–Taube ion;[30–32] in fact, the work presented thereafter indicates that there is some degree of contribution from description (2B) in relation to the semiquinone (SQ) formulation (2A).

$$\underset{\mathrm{A}}{\mathrm{Ru^{II}(SQ)Ru^{II}}} \leftrightarrow \underset{\mathrm{B}}{\mathrm{Ru^{II}(Q^{2-})Ru^{III}}} \text{ or } \mathrm{Ru^{2.5}(Q^{2-})Ru^{2.5}} \qquad (2)$$

Q^{2-}: catecholate or
hydroquinone dianion

Electrochemical, UV–vis/near infrared, and EPR spectroscopic results obtained in aprotic media, i.e., in the absence of complicating acid–base equilibria and hydrogen bond interactions[31,36,37] are presented here in order to assess the contributions of resonance forms (2) to the stability and to the electronic structures of the compounds {(μ-phdo)[Ru(bpy)$_2$]$_2$}$^{3+}$ and {(μ-bppq)[Ru(bpy)$_2$]$_2$}$^{3+}$

Experimental Section

Instrumentation. EPR: Varian E 109, X band; UV–vis/near infrared: Shimadzu UV 160, Perkin-Elmer Lambda 9 and Cary 15; cyclic voltammetry: PAR potentiostat 363, Bank scan generator VG 72, glassy carbon working electrode, saturated calomel reference electrode (SCE). Elemental analyses were performed by Mikroanalytisches Laboratorium Malissa & Reuter, Gummersbach, Federal Republic of Germany, and at the facility at the University of Stuttgart.

Preparations and General Procedures. 4,7-Phenanthroline-5,6-dione (phdo) was a generous gift by Ciba-Geigy AG. 2,5-Bis(diphenylphosphino)hydroquinone (bppqH_2) has been obtained from 1,4-dimethoxybenzene via dibromination, bis-Grignard formation, diphenylphosphination with $ClPPh_2$ and ether cleavage with $AlCl_3$;[26] detailed procedures are available as Supplementary Material. Column chromatographic purification of the complexes was performed by using acidic alumina (Woelm A Super I, type W 200) as stationary phase; the eluents employed were acetone, acetonitrile, and *N,N*-dimethylformamide (in that order). Generation of the reduced (2+) and oxidized (4+) oxidation states of the binuclear complexes for absorption spectroscopy was accomplished with $NaBH_4$ in acetone as reductant and $AgBF_4$ in acetone as oxidant. Electrochemistry was performed with 0.1 M solutions of tetrabutylammonium perchlorate in dry acetonitrile as electrolyte. Concentration of complexes during measurement was about 10^{-3} M; the scan rate was 100 mV/s.

EPR spectra were taken in acetonitrile at room temperature and in frozen acetone solutions at 4 K. Samples were cooled in a stream of helium gas, the temperature of which was regulated by an Oxford Instruments ESR 900 cryostat. *g* factors were determined by simultaneously measuring the microwave frequency (EIP 548A frequency counter) and the magnetic field (Varian NMR gauss meter).

{(μ-phdo)[Ru(bpy)$_2$]$_2$}$^{3+}$. phdo (100 mg, 0.48 mmol) was heated to reflux for 15 min in argon-saturated ethanol/water (1:10) with 500 mg (0.96 mmol) of Ru(bpy)$_2$Cl$_2$·2H_2O. The green precipitate which formed after treating the cooled solution with NH_4PF_6 was column chromatographed. The last dark green fraction was collected and concentrated; addition of ether yielded 160 mg (23%) of the forest green product. Anal. Calcd for $C_{52}H_{38}F_{18}N_{10}O_2P_3Ru_2$ (1471.97): C, 42.42; H, 2.60; N, 9.52; P, 8.42; Ru, 13.73. Found: C, 42.60; H, 2.74; N, 9.52; P, 8.18; Ru, 13.80.

Table I. Redox Potentials and Stability Constants of Binuclear Complexes[a]

	(phdo)[Ru(bpy)$_2$]$_2$	(bppq)[Ru(bpy)$_2$]$_2$
$E(4+/3+)$	+0.64 (−0.50)[b]	+0.72
$E(3+/2+)$	+0.05 (−1.33)[b]	+0.14
log K_c (3+)	10.0 (14.1)[b]	9.8

[a] Midpoint potentials in V vs saturated calomel reference electrode for 1e reversible processes ($E^{pa} - E^{pc}$ = 60–80 mV) from cyclic voltammetry in acetonitrile solutions. [b] Data in brackets are for the (o/−/2−) forms of the phdo ligand from ref 20a.

{(μ-bppq)[Ru(bpy)$_2$]$_2$}$^{3+}$. bppqH_2[26] (60 mg, 0.13 mmol) and Ru(bpy)$_2$Cl$_2$·2H_2O (140 mg, 0.27 mmol) were heated under reflux in ethanol/water (1:10) for 3 h. The precipitate obtained after treating the cooled solution with NH_4PF_6 was purified through column chromatography; the brown fraction appearing with acetonitrile as eluent was concentrated, and the product was precipitated with diethylether as a mixed acetonitrile/ether solvate in 60 mg yield (19%). Anal. Calcd for $C_{76}H_{67}F_{18}N_9O_3P_5Ru_2$ (1894.26): C, 49.25; H, 3.64; N, 6.80. Found: C, 49.89; H, 3.83; N, 6.75.

Results and Discussion

Preparation, Stability, and Electrochemistry. The binuclear *o*- and *p*-semiquinone complexes (1) have been obtained directly after chromatographic purification of reaction mixtures from *cis*-Ru(bpy)$_2$Cl$_2$ and the ligands phdo and bppqH_2; it is not uncommon that column chromatography at metal oxides in polar solvents causes redox reactions. The synthetic result is in agreement with the electrochemical data as presented in Table I.

Both paramagnetic (3+) species exist in a rather "normal" electrochemical potential region and enjoy a high degree of stability toward disproportionation (large log K_c).

$$\log K_c = \Delta E/0.059 \text{ V} \qquad (3)$$

A considerable anodic shift for the redox potentials of the ligands can be expected upon coordination of two dipositive ruthenium(II) fragments;[12,19,38] however, this argument implies completely ligand-centered redox processes (2A, 6A). In such a case, the ΔE should be about the same for the semiquinone ligand and for the anion radical complex;[12] the significant difference in the case of the phdo system (Table I) already indicates a deviation from purely ligand-centered redox processes. On the other hand, high electron densities at the coordinating centers favor the thermodynamic stability of mixed-valence metal dimers,[19] the oxygen centers in quinones would thus be well suited to effect such stabilization. Although the question of the contributions from resonance forms (2) can thus not be definitely answered from electrochemical experiments alone, it does already suggest some degree of metal participation at the redox transitions between the 2+/3+/4+ oxidation states.

While further oxidation of the 4+ species occurs irreversibly at high potentials (>+1.5 V vs SCE), cyclic voltammetry exhibits two additional reversible 2e$^-$ reduction processes at −1.5 V and −1.7 V vs SCE which are assigned to the total of four bpy ligands at the metal centers (→ bpy$^{\bullet-}$)[11,39] on the basis of previous studies of such dimers.[19] A third conceivable quinone-based reduction leading to a trianionic ligand could not be observed in either case. Owing to the π acceptor character of the diphenylphosphino group,[25] the potentials of the bppq complex are shifted positively relative to those of the phdo system.

Electronic Spectroscopy. Complexes of the Ru(bpy)$_2$ fragment are generally distinguished by a rich optical spectroscopy[11,18]

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Table II. Charge-Transfer Absorption Maxima ν (cm^{-1}) in the (2+/3+/4+) Oxidation States of Binuclear Complexes[a]

	$(phdo)[Ru(bpy)_2]_2$[b]	$(bppq)[Ru(bpy)_2]_2$[c]
	ν (MLCT) $d(Ru^{II}) \rightarrow \pi^*$ (bpy):	
(2+)	18700 (4.52)	21650 (4.08)
(3+)	21500 (4.31)	22500 (4.03)
(4+)	24500 (4.39)	25800 (4.00)
	ν (MLCT) $d(Ru^{II}) \rightarrow \pi^*$ (Q):	
(3+)	7100 sh	
	8500 (3.84)	7900 (3.38)
	9400 (3.82)	8500 sh
(4+)	9800 (4.54)	9200 (4.08)
	ν (LLCT) π(cat,SQ) $\rightarrow \pi^*$(bpy):	
(2+)	15100 sh	15600 sh
(3+)	*b*	not obsd

[a] log ϵ values in brackets. [b] In acetone solution. Additional bands and shoulders in the semiquinone form (Figure 1) are assigned to internal semiquinone transitions, cf. text. [c] In 1,2-dichloroethane solution.

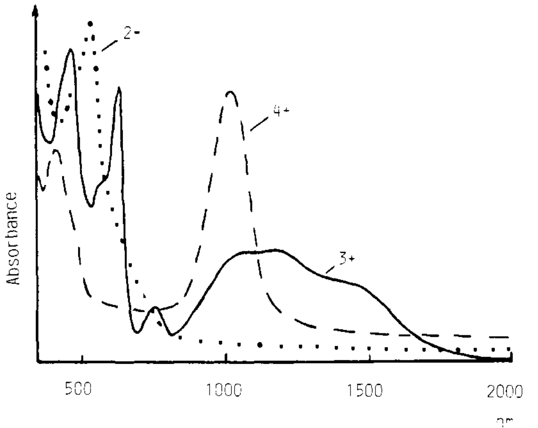

Figure 1. Absorption spectra of the (2+), (3+), and (4+) oxidation states of the binuclear system $(phdo)[Ru(bpy)_2]_2$ in acetone (absorbance scale different for each spectrum, for intensities see Table II).

because the bpy coligands alone provide low-lying unoccupied molecular orbitals[24,40] which are therefore available for charge-transfer interactions. Furthermore, the rigid chelate situation around the ruthenium center allows only small Franck–Condon contributions, so that correlations between redox potential differences and optical transition energies become very useful.[17]

Electron spectroscopic data (Table II) for the three oxidation states (2+/3+/4+) of the binuclear complexes (1) can be analyzed in terms of the assignments made earlier for mononuclear *o*-quinone complexes by Lever and co-workers.[11]

Starting with the phdo system (Figure 1), the reduced form (2+) shows one intense band in the visible region, corresponding to a Ru(II) → bpy ($d \rightarrow \pi^*$) metal-to-ligand charge-transfer transition (MLCT). This band is at rather low energies because the strongly basic catecholate ligand $phdo^{2-}$ destabilizes occupied metal d levels.[10,11] A long wavelength shoulder of this band may be attributed to a ligand-to-ligand charge transfer (LLCT): π(catecholate) → π^* (bpy); a simplified molecular orbital situation giving rise to this assignment is shown in Figure 2A.

The semiquinone complex (3+) has the Ru(II) → bpy MLCT transition shifted to higher energies because the semiquinone is a weaker base than the catecholate.[11] Additional band systems are related to the creation of a singly occupied molecular orbital (SOMO):[12] A sharp band in the visible (630 nm, log ϵ = 4.23) may be attributed either to a transition π(SOMO) → π^*(bpy) (LLCT) or to an internal $\pi \rightarrow \pi^*$ (ILCT) transition of the polynuclear *o*-semiquinone,[41] intensity and shape being more

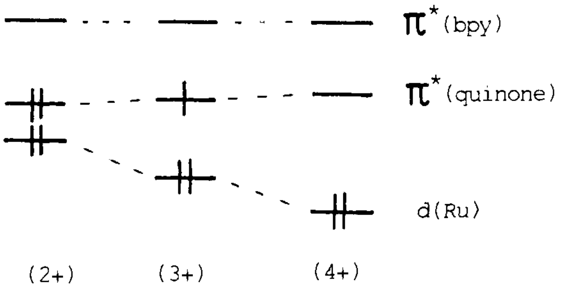

Figure 2. Simplified orbital diagrams for three different oxidation states of system $(phdo)[Ru(bpy)_2]_2$ as deduced from major charge-transfer absorption bands.

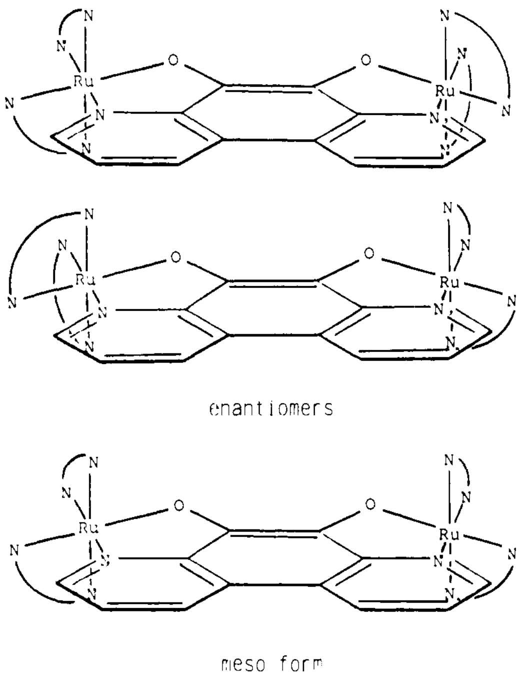

Figure 3. Meso form (bottom) and pairs of enantiomers (top) of the binuclear phdo complex with $[Ru(bpy)_2]$ fragments.

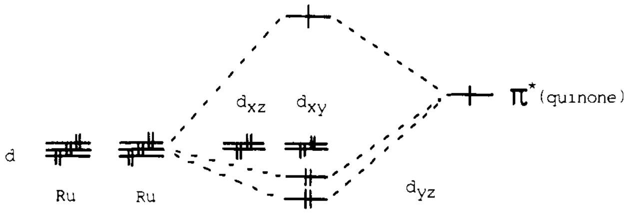

Figure 4. Orbital diagram for the interaction of two equivalent low spin d^6 metal centers with a semiquinone ligand.

compatible with the latter alternative. The band system in the near infrared region exhibits three distinguishable humps (Figure 1) which are assigned as MLCT transitions: d(Ru) → π(SOMO). A splitting is not uncommon for MLCT bands originating from low spin d^6 metal centers,[42,43] including Ru^{II};[44] it is traced back to different transitions from the d_{yz} and d_{xy} orbitals of the t_{2g} subset.[44] The splitting into *three* discernible bands is unusual; however, one possible explanation could be the presence of two diastereoisomers (Figure 3) with slightly different spectral features in that region. We have recently drawn attention to the fact that there are two equivalent chiral metal centers present in such

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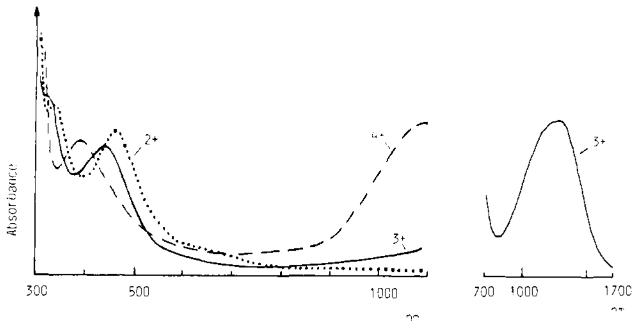

Figure 5. Absorption spectra of the (2+), (3+), and (4+) oxidation states of the binuclear system (bppq)[Ru(bpy)$_2$]$_2$ in 1,2-dichloroethane; the near infrared band of the (3+) form is shown separately on the right. Absorbance scale different for each spectrum; for intensities see Table II.

symmetrically binuclear Ru tris-chelate complexes and presented NMR evidence for the formation of both diastereoisomers in one favorable case.[19]

The possibility of discernible spectral differences between such isomers seems unlikely, however; even fac and mer isomers of one recently reported tris(chelate)ruthenium(II) complex showed no detectable electrochemical or spectral differences.[45] Therefore, another explanation for the occurrence of three bands in the near infrared spectrum of the (3+) form (Figure 1) involves the metal–metal interaction in the dimer. Such an interaction would create, simply speaking, two split d_{yz} levels from which fully allowed transitions to the singly occupied MO (probably still mainly of semiquinone π character) can occur; in conjunction with the less allowed[44] transition from the d_{xy} levels this situation should result in three near infrared bands of comparable intensity as observed experimentally (Figure 1). Figure 4 illustrates the MO situation resulting from the interaction of a π acceptor ligand with *two* equivalent low-spin d^6 metal centers; note that transitions from the d_{xz} orbitals to the π level are forbidden.[44]

While the above rationale (Figures 2 and 4) helps to assign the major ($\epsilon > 5000$ M^{-1} cm^{-1}) bands, there are a number of additional weak bands and shoulders in the spectrum of the (3+) form (Figure 3). These features are attributed to transitions to the second lowest unoccupied MO (SLUMO) of the phdo π system, the related phenanthrosemiquinone exhibits such transitions as free anion radical or in the form of alkali metal ion pairs.[41] Hückel MO calculations[46] using Coulomb integral parameters $h_O = h_N = 0.5$ and an overlap integral parameter $k_{C=O} = 1.3$ show that the LUMO (b_1, $\epsilon_j = -0.31\,\beta$) of phdo has *o*-semiquinone character with high electron density at the oxygen atoms ($c_O^2 = 0.234$, $c_N^2 = 0.027$) and an electron distribution similar to that of phenanthroquinone; the relatively low-lying SLUMO (b_1, $\epsilon_j = -0.70\,\beta$), on the other hand, has virtually no electron density at the oxygen centers ($c_O^2 = 0.005$) but some contribution from the nitrogen atoms ($c_N^2 = 0.096$). The smaller overall electron density at the coordinating centers in the SLUMO would be in agreement with the low intensities of the transitions to that orbital.[46]

The oxidized form (4+) of the binuclear phdo complex displays two major long wavelength absorptions, the Ru(II) → π*(bpy) MLCT absorption maximum at still higher energy than in the semiquinone complex and an intense band in the near infrared which may be attributed to a Ru(II) → π*(*o*-quinone) MLCT transition (Figure 2C). The intensity of the band ($\epsilon = 34\,800$ M^{-1} cm^{-1}) and the absence of shoulders suggest that the metal–metal interaction (Figure 4) is smaller with the less basic quinone as bridging ligand. Considerable mixing of metal and ligand orbitals as described by the three resonance forms (4A–C) may leave a localized MLCT formulation as only partly valid. Similarly intense charge-transfer bands in the near infrared region have been observed recently for tetranuclear TCNE and TCNQ complexes of manganese;[34] they may be a general feature of highly delocalized multimetal complexes of strongly interacting (= efficient orbital overlap) redoxactive ligands.

Table III. *g* Factors of Paramagnetic (3+) Binuclear Complexes from EPR Spectroscopy in Frozen Acetone Solution

	{(phdo)[Ru(bpy)$_2$]$_2$}$^{3+\,a}$	{(bppq)[Ru(bpy)$_2$]$_2$}$^{3+}$
g_1	2.051 (2.021)	2.032
g_2	2.026 (1.998)	2.032
g_3	1.981 (1.985)	1.996
$\langle g \rangle_{calcd}$	2.019 (2.0015)	2.020
$\langle g \rangle_{obsd}$^{b}	2.0112 (2.0014)	2.025

^{a}Values for the O,O′-coordinated mononuclear semiquinone complex (phdo)[Ru(bpy)$_2$]$^+$ in brackets. ^{b}Isotropic *g* from room temperature spectra in acetonitrile solution.

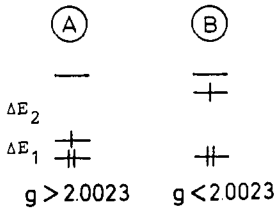

Figure 6. Two different frontier orbital situations in an $S = 1/2$ system.

$$\underset{A}{\mathrm{Ru^{II}(Q)Ru^{II}}} \leftrightarrow \underset{B}{\mathrm{Ru^{II}(SQ)Ru^{III}}} \leftrightarrow \underset{C}{\mathrm{Ru^{III}(Q^{2-})Ru^{III}}} \qquad (4)$$

Q: quinone; SQ: semiquinone;

Q^{2-}: catecholate or hydroquinone dianion

The three oxidation states of the binuclear complex involving the *p*-semiquinone (bppq) system also display Ru(II) → bpy MLCT transitions (Figure 5, Table II). The somewhat higher energies suggest that bppq is a weaker base than phdo in all three oxidation states. The transitions involving the SOMO are more different between both systems; the broad MLCT band of the bppq (3+) complex in the near IR is hardly split (Figure 5), and intraligand charge-transfer (ILCT) bands for the semiquinone complex are absent in the visible. The much smaller π system (eight π centers vs 16 for phdo) and the higher symmetry (inversion center in the meso form)[19] of the *p*-semiquinone complex are probably responsible for this result.

In the (4+) state, the bppq complex shows an MLCT band at 9200 cm^{-1}; provided the quinone formulation (4A) is valid, this would be the lowest energy yet reported for a d[Ru(bpy)$_2$] → π* transition.[18,38] Whereas an assessment of the contributions of resonance forms (4A–C) to the (4+) states is not easy in view of the even-electron nature of the tetracation, the contributions of forms (2A,B) in the odd-electron (3+) intermediates (1) may be estimated by using EPR spectroscopy.[47]

EPR Spectroscopy. Paramagnetic complexes of the [Ru(bpy)$_2$] fragment rarely show hyperfine structures even in those cases where the unpaired electron must clearly reside on the ligand.[40,48] Inhomogeneous line broadening due to numerous overlapping hyperfine lines and the presence of a metal with large spin orbit coupling factor ($\zeta = 700$–1000 cm^{-1})[49] are responsible for this unfortunate absence of valuable information.[40] In the present situation, the hyperfine couplings from nuclei ^{1}H, ^{14}N, and ^{31}P are already small (<0.3 mT) in the pure ligand semiquinones[26,50] so that no hyperfine splitting could be expected. Despite this drawback, our previous studies[12,24,43] on transition-metal complexes have shown that the remaining spectral parameter, the *g* factor, may provide valuable information on the relative ordering of frontier orbitals; measured data are summarized in Table III.

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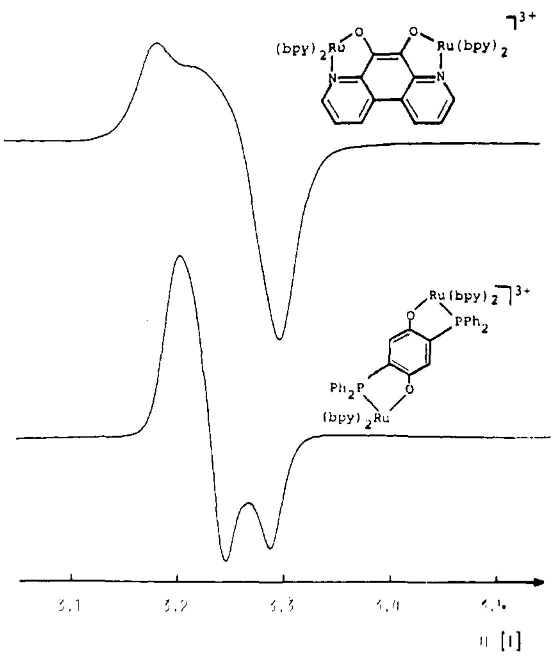


Figure 7. EPR spectra of the binuclear phdo (top) and bppq semiquinone complex (bottom) at 4 K in glassy acetone matrix (microwave frequency, 9.22277 GHz; microwave power, 0.01 mW; modulation amplitude, 1.25 mT).

Typical ligand-centered radical complexes of the $[Ru(bpy)_2]^{2+}$ fragment have $\langle g\rangle$(radical complex) < $\langle g\rangle$(ligand radical)[24,40,48] because there are low-lying π^* levels of the bpy ligands available,[24,40] leading to a situation (Figure 6B) which results in a small isotropic g value according to the approximation (5).[40]

$$g - g(\text{electron}) = g - 2.0023 = k\cdot\zeta(1/\Delta E_1 - 1/\Delta E_2) \quad (5)$$

ζ: spin orbit coupling constant

Lowering of the SOMO level within the d(Ru)/π^* framework should bring about an increase in $\langle g\rangle$(radical complex) above $\langle g\rangle$(ligand radical) according to (Figure 6A), a result which is apparently observed for both semiquinone complexes discussed here (Table III). However, the isotropic $\langle g\rangle = 2.025$ of the bppq complex would be unusually high if attributed to a ligand-centered radical;[12,51] both ligands have $\langle g\rangle = 2.0050$,[26] and there is obviously significant participation of the metal centers with their large spin orbit coupling constant ζ (Ru)[49,52] to the SOMO.

Significant metal contribution is also evident from low-temperature EPR work on glassy solutions of the complexes which shows a fairly wide spread of g components. Semiquinones alone show only little anisotropy ($g_\perp - g_\parallel \approx 0.004$),[5,53] and also the radical complex $[Ru^{II}(bpy^{\bullet-})(bpy)_2]^+$ did not exhibit a splitting into g components in frozen glassy solution.[48] Lever and coworkers reported $g_\perp = 1.985$ and $g_\parallel = 2.067$ for a mononuclear o-semiquinone complex of $[Ru(bpy)_2]$; our results (Figure 7, Table III) similarly suggest considerable contribution of Ru^{III}-containing forms (2B) to the electronic ground state of the binuclear complexes.

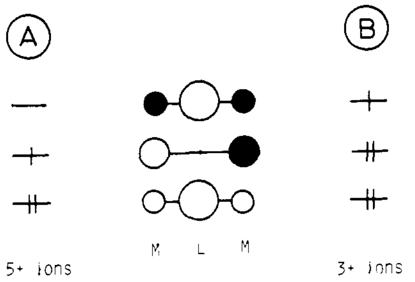
The EPR data show a wide spread of g components for the binuclear o-semiquinone complex (Table III) which is twice as large as the anisotropy found for the O,O′-coordinated mononuclear system:[24] $g_1 = 2.021$, $g_2 = 1.998$, $g_3 = 1.985$. There is also a striking difference between the two semiquinone complexes concerning the symmetry of g. The $g_\parallel < g_\perp$ result for the potentially inversion-symmetrical p-semiquinone system corresponds to the typical high symmetry d^5 (l.s.) situation as found, e.g., for $Ru(acac)_3$[54] and for the Creutz–Taube ion,[55] albeit the latter display a larger g anisotropy due to the *predominant* Ru^{III} character. The rhombic signal found for the o-semiquinone dimer reflects the lower symmetry of that complex (Figure 3); indeed, in contrast to the bppq system, the binuclear phdo complex cannot possess an inversion center. Also, the presence of rather differently behaving meso and DL-diastereomers cannot be totally excluded for the phdo complex (Figure 3), as pointed out before, and may be responsible for the peculiar EPR line shape (Figure 7); the excellent elemental analysis of the material after column chromatographic purification should rule out the presence of a major impurity.

Concluding Remarks

The spectroscopic data for the two paramagnetic complexes described in this paper suggest that these systems are situated right at the borderline between binuclear anion radical complexes[12] with the unpaired electron being mainly ligand-centered and d^5/d^6 mixed-valence dimers[30-32] with the spin residing chiefly on the metal centers.[33,52,55] In the absence of more direct information from EPR coupling constants of metal or ligand nuclei[47] the definition of that borderline is not easy; both the anisotropy and the isotropic values of g for the two semiquinone complexes are larger than usually found for anion radical complexes of transition metals.[12] Because of the approximative character of (5) and the very different spin-orbit coupling constants of the heavy metal[49,52] and the light atoms C, N, O making up the ligand, there is no simple linear relationship between g and the amount of metal/ligand delocalization. The problem of metal–metal (de)localization *within* resonance form (2B) has not been addressed here although it is believed that the strong contribution from the semiquinoid ligands favors a completely delocalized situation (6).

$$Ru^{II+\delta}(L^{-1-2\delta})Ru^{II+\delta} \quad (6)$$

Adopting the three-center model proposed by Ondrechen et al.[52] which suggests an allyl *radical* type situation (7A) for the Creutz–Taube (5+) ion, a (3+) $Ru^{II}Ru^{III}$ dimer should then exhibit much more spin density in the bridging π ligand according to the allyl *dianion radical* situation (7B).



(7)

While EPR spectroscopy has helped to assess the situation of the ground state of the paramagnetic (3+) states, the problem of contribution from resonance forms (4A–C) to the ground state of the (4+) systems requires a different, preferably structural approach. The very intense charge-transfer transitions of delocalized polymetallic complexes of π ligands in the interesting near infrared region[34] warrants further synthetic and spectroscopic studies of such materials.

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Registry No. $\{(\mu\text{-phdo})[\mathrm{Ru(bpy)_2}]_2\}(\mathrm{PF_6})_3$, 118494-61-4; $\mathrm{Ru(bpy)_2Cl_2}$, 19542-80-4; $\{(\mu\text{-bppq})[\mathrm{Ru(bpy)_2}]_2\}(\mathrm{PF_6})_3$, 118513-70-5; $\{(\mu\text{-phdo})[\mathrm{Ru(bpy)_2}]_2\}^{2+}$, 118494-62-5; $\{(\mu\text{-phdo})[\mathrm{Ru(bpy)_2}]_2\}^{4+}$, 109998-78-9; $\{(\mu\text{-bppq})[\mathrm{Ru(bpy)_2}]_2\}^{2+}$, 118494-63-6; $\{(\mu\text{-bppq})[\mathrm{Ru(bpy)_2}]_2\}^{4+}$, 118494-64-7.

Supplementary Material Available: A detailed description of the synthesis of the hydroquinone derivative bppqH_2 (1 page). Ordering information is given on any current masthead page.

Pressure-Induced Spin-State Interconversion of $[\mathrm{Fe(6\text{-}Me\text{-}py)_3tren}](\mathrm{ClO_4})_2$ in Solution

William S. Hammack,[1,2] Andrew J. Conti,[1] David N. Hendrickson,*[,1] and Harry G. Drickamer*[,1,2]

Contribution from the School of Chemical Sciences, Department of Physics, and Materials Research Laboratory, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801.

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Abstract: The series of pseudooctahedral $\mathrm{Fe^{II}}$ spin-crossover complexes $[\mathrm{Fe(6\text{-}Me\text{-}py)_3tren}](\mathrm{ClO_4})_2$ (**4**), $[\mathrm{Fe(6\text{-}Me\text{-}py)_2pytren}](\mathrm{ClO_4})_2$ (**3**), and $[\mathrm{Fe(6\text{-}Me\text{-}py)py_2tren}](\mathrm{ClO_4})_2$ (**2**) exhibit varying degrees of high- and low-spin population in solution. Specifically complex **4** is mostly high spin, while complexes **2** and **3** are of an intermediate spin state. The principal result of this paper is that with pressure the spin state of complex **4** changes from high spin ($^5T_2$) to low spin ($^1A_1$). This change is monitored by following the changes with pressure in the metal-to-ligand charge-transfer bands of the complex which are at higher energy and lower intensity for a high-spin as compared to a low-spin complex. The effect of pressure on the metal-to-ligand charge-transfer (CT) bands of complexes **2**, **3**, and **4** has been studied in acetone and dichloromethane solutions. The pressure range studied is from 0.001 kbar to 10.0 kbar (1.0 kbar = 986.92 atm = 0.1 GPa). The predominant effect of pressure, in both media for all three complexes, is a shift to lower energy and an increase in intensity of the CT bands. The difference in magnitude for these spectral changes with pressure indicate that the predominantly high-spin complex **4** is converted to a low-spin complex in solution upon the application of pressure.

Octahedral complexes of metal ions with a d^6 configuration may exist in either a high- or a low-spin electronic configuration, depending on the relative magnitude of the ligand field, 10 Dq, and the 3d-electron mean-pairing energy, P. If $|P - 10\ \mathrm{Dq}| \cong kT$, then both the high- ($^5T_2$) and low-spin ($^1A_1$) states of the complex may be thermally populated. A spin equilibrium, $^1A_1 \rightleftarrows {}^5T_2$, arises in this case.[3-7] A compound which exhibits this phenomenon is often called a spin-crossover complex. In the solid state a number of spin-crossover complexes convert from high to low spin with decreasing temperature[3,5] or increasing pressure.[8,9] In solution spin-state interconversion has been observed with a change of temperature. The principal result presented in this paper is that the spin state of a $\mathrm{Fe^{II}}$ spin-crossover complex changes from high to low spin in solution with increasing pressure. This change is monitored by following the changes with pressure of the metal-to-ligand charge-transfer bands of the complex. Previously Ewald et. al[10] presented magnetic susceptibility measurements on the one compound $[\mathrm{Fe(S_2CN(Bu^n{}_2)_3}]$ in chloroform which showed measurable spin pairing over a range of 3 kilobars. From the pressure derivative of the equilibrium constant, they extracted from their results a high-spin to low-spin volume change of −3.6 to −4.0 cc/mol.

The complexes studied in this paper are the perchlorate salts of composition $[\mathrm{Fe(6\text{-}Me\text{-}py)}_n\mathrm{py}_{3-n}\mathrm{tren}](\mathrm{ClO_4})_2$, where the number of methyl-substituted pyridine arms of the ligand is changed to give the following complexes:

complex **1**: $n = 0$

complex **2**: $n = 1$

complex **3**: $n = 2$

complex **4**: $n = 3$

Hoselton et al.[11] have shown that the PF_6^- salts of the cations of complexes **2** and **3** exhibit spin-crossover behavior in acetone and $\mathrm{Me_2SO}$ solutions. Steric interactions between the methyl groups on adjacent pyridine rings cause compound **4** to be mostly high spin in the same solvents. In addition, they have estimated the difference $|P - 10\ \mathrm{Dq}|$ to be ~200 $\mathrm{cm^1}$ for complexes **2** and **3** in solution.[12]

The laser-flash photolysis technique was employed by Xie and Hendrickson[13] to determine the $^5T_2 \rightarrow {}^1A_1$ relaxation rate of complex **3** doped in polystyrene sulfonate from 300 to 4.2 K. The temperature independence of this relaxation rate below ~100 K definitively showed that complex **3** tunnels from the $^5T_2$ to the $^1A_1$ state. In a separate study it was found[14] that the apparent

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(2) Department of Physics and Materials Research Laboratory.

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