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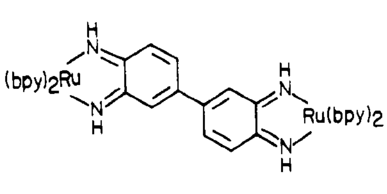
Synthesis and Spectroscopic Characterization of Bis[bis(bipyridine)ruthenium(II)] 3,3′,4,4′-Tetraimino-3,3′,4,4′-tetrahydrobiphenyl and Its Redox Products

Our recent studies with ruthenium dioxolene species[1-5] have emphasized the extensive mixing between the ruthenium d orbitals and the dioxolene ligand molecular orbitals, mixing which can be tuned by altering the oxidation state of the complex. We report ruthenium complexes of 3,3′,4,4′-tetraaminobiphenyl, forming dinuclear species, in a redox series, three members of which are described. The formation of conduction bands through polymeric versions of these complexes might allow for the construction of molecular wires, which could be switched by altering the oxidation state; this would alter the degree of conjugation in the pathway[6] and/or control the angle of twist at the biphenyl ligand.

Much is known of electron transfer between two metals of different oxidation states via a bridging ligand.[7-9] Less is known of electron transfer between ligands of different oxidation states.[10-12]

$\{[\mathrm{Ru^{II}(bpy)_2}]$(3,3′,4,4′-tetraimino-3,3′,4,4′-tetrahydrobiphenyl)$\}(\mathrm{PF_6})_4$ (bpy = 2,2′-bipyridine)[13,14] isolated in this bis(quinone diimine) oxidation level is abbreviated (RuQ,QRu). The labels Q, SQ, and CAT refer to the successively reduced quinone diimine fragment. A mononuclear $\{[\mathrm{Ru^{II}(bpy)_2}]$(3,4-diimino-3′,4′-diamino-3,4-dihydrobiphenyl)$\}(\mathrm{PF_6})_2$ species (RuQ,CAT) was also isolated.[15]



(RuQ, QRu)

On the basis of studies of related mononuclear ruthenium quinonoid[1-4] and quinone diimine[5] species, the electronic spectra (Figure 1) are assigned (Table I). Charge-transfer transitions occur from ruthenium to bipyridine and to the quinone diimine ligands in the spectra of both complexes (RuQ,QRu)[16] and (RuQ,CAT). The oscillator strength of the Ru(II) → π^* Q transition in the dinuclear species is almost twice that in the mononuclear species, but the Ru(II) → π^* transition is substantially more narrow in the (RuQ,QRu) complex. This narrowness is indicative of a smaller reorganization contribution and, hence, less charge-transfer character in the excited state of (RuQ,QRu) than in that of (RuQ,CAT). Evidently the excited electron is spread over both quinone diimine fragments in this symmetric, albeit not strictly coplanar, biphenyl ligand.[17] This species does not emit in fluid medium at room temperature, probably a consequence of internal redox quenching between the Ru → π^* bpy MLCT state and the quinone diimine fragment.

Voltammetry of (RuQ,QRu) in acetonitrile shows two oxidation processes at 1.39 and 1.51 V (vs AgCl/Ag in $\mathrm{CH_3CN}$) assigned to the formation of $(\mathrm{Ru^{III}(Q\cdots Q)Ru^{II}})$ and $(\mathrm{Ru^{III}(Q\cdots Q)Ru^{III}})$, respectively. There are four successive reductions of the biphenyl ligand (Figure 2) (−0.27, −0.49, −1.11, and −1.25 V vs AgCl/Ag), illustrating a series of mixed-valence products. Two more negative processes (−1.56 and −1.70 V) correspond with bipyridine reductions. The mononuclear species (RuQ,CAT) has two reduction processes generating (RuSQ,CAT) and (RuCAT,CAT) in acetonitrile at −0.485 and −1.12 V vs AgCl/Ag, respectively.

Controlled-potential reduction of (RuQ,QRu) in propylene carbonate, just negative of the first and second reduction couples, yields respectively (RuQ,SQRu), which may also be generated chemically by triethylamine reduction of (RuQ,QRu) and is stable indefinitely, and (RuSQ,SQRu), which shows slow decomposition that could not be overcome regardless of solvent.

Species (RuQ,SQRu) shows a free-radical ESR spectrum ($g = 2.00$, $\Delta_{pp} = 19$ G, no hyperfine coupling to nitrogen, at 77 K),[7] while (RuSQ,SQRu) is ESR-silent, at least to liquid-nitrogen temperature. The electron in (RuQ,SQRu) is evidently ligand-localized and the electronic structure is clearly different from the analogous $(\mathrm{NH_3})_5\mathrm{Ru^{II}}$–(1,4-diimino-1,4-dihydrobenzene)–$\mathrm{Ru^{III}(NH_3)_5}$ species with a metal-localized ESR spectrum.[18]

(RuQ,SQRu) shows the Ru(II) → π^*(1) bpy electronic transition shifted to lower energy relative to (RuQ,QRu), since the overall positive charge on the ruthenium centers has been decreased. A Ru(II) → π^* Q transition appears at essentially the same energy as that of the monomeric (RuQ,CAT) species. The Ru(II) → π^* SQ transition, at 12 900 $\mathrm{cm^{-1}}$, is shifted to the red of that observed in monomeric (RuSQ,CAT) but is substantially broader and more intense (Figure 3) (Table I). The higher energy

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(1) Haga, M. A.; Dodsworth, E. S.; Lever, A. B. P. *Inorg. Chem.* **1986**, *25*, 447–53.

(2) Lever, A. B. P.; Auburn, P. R.; Dodsworth, E. S.; Haga, M. A.; Melnik, M.; Nevin, W. A. *J. Am. Chem. Soc.* **1988**, *110*, 8076–84.

(3) Haga, M. A.; Dodsworth, E. S.; Lever, A. B. P.; Boone, S. R.; Pierpont, C. G. *J. Am. Chem. Soc.* **1986**, *108*, 7413–4.

(4) Stufkens, D. J.; Snoeck, Th. L.; Lever, A. B. P. *Inorg. Chem.* **1988**, *27*, 953–6.

(5) Masui, H. M.; Lever, A. B. P. Paper in preparation.

(6) Woitellier, S.; Launay, J. P.; Joachim, C. *Chem. Phys.* **1989**, *131*, 481.

(7) Lever, A. B. P. *Inorganic Electronic Spectroscopy*, 2nd ed.; Elsevier: Amsterdam, 1984.

(8) Creutz, C. *Prog. Inorg. Chem.* **1983**, *30*, 1.

(9) Sullivan, B. P.; Curtis, J. C.; Kober, E. M.; Meyer, T. J. *Nouv. J. Chim.* **1980**, *4*, 643–50.

(10) Vogler, A. *Comments Inorg. Chem.*, in press.

(11) Penfield, K. W.; Miller, J. R.; Paddon-Row, M. N.; Cotsaris, E.; Oliver, A. M.; Hush, N. S. *J. Am. Chem. Soc.* **1987**, *109*, 5061–5.

(12) Warman, J. M.; De Haas, M. P.; Paddon-Row, M. N.; Cotsaris, E.; Hush, N. S.; Oevering, H.; Verhoeven, J. W. *Nature* **1986**, *320*, 615–6.

(13) $\{[\mathrm{Ru(bpy)_2}]_2$(3,3′,4,4′-tetraimino-3,3′,4,4′-tetrahydrobiphenyl)$\}(\mathrm{PF_6})_4$ (**1**) (bpy = 2,2′-bipyridine) (RuQ,QRu), was prepared by refluxing $\mathrm{Ru(bpy)_2Cl_2}$ (0.2 g) and 3,3′,4,4′-tetraaminobiphenyl (0.044 g, Aldrich) in degassed methanol (25 mL) for 6 h. After the mixture was cooled to ambient temperature, several drops of concentrated ammonia and a solution of ammonium hexafluorophosphate (0.2 g) in water (2 mL) were added. The blood red solution was oxygenated for 45 min to develop a rich purple color. After solvent removal and trituration with methylene dichloride to remove a red impurity, the product was recrystallized from acetone.

(14) ^{1}H NMR: δ 12.08 (s, 2 H, imine), 11.98 (s, 2 H, imine), 8.50 (m, 8 H), 8.14 (m, 8 H), 7.62 (m, 8 H), 7.5 (m, 10 H), 7.38 (d, 2 H), 7.27 (d, 2 H). Anal. Calcd for $\mathrm{C_{52}H_{42}F_{24}N_{12}P_4Ru_2}$: C, 38.7; H, 2.6; N, 10.4. Found: C, 39.2; H, 3.2; N, 9.9.

(15) $\{[\mathrm{Ru(bpy)_2}]$(3,4-diamino-3′,4′-diimino-3′,4′-dihydrobiphenyl)$\}(\mathrm{PF_6})_2$ (RuQ,CAT) (bpy = 2,2′-bipyridine): $\mathrm{Ru(bpy)_2Cl_2}$ (0.1 g) and 3,3′-diaminobenzidine (0.088 g) were refluxed in degassed methanol (25 mL) for 24 h. The red-orange solution was exposed to air and filtered. The addition of several drops of concentrated ammonia changed the color to deep blue-purple. This solution was oxygenated for 6 h and then reduced in volume to 5 mL. Dropwise addition of an aqueous saturated solution of $\mathrm{NH_4PF_6}$ provided blue microcrystals (0.15 g, 80%). Anal. C, H. N. ^{1}H NMR: δ 13.12 (s, 1 H, imine), 12.54 (s, 1 H, imine), 8.83 (m, 4 H), 8.25 (m, 4 H), 7.80 (m, 2 H), 7.43 (d, $J = 9.44$ Hz, 1 H), 7.26 (m, 4 H), 7.13 (m, 2 H), 7.05 (m, 1 H), 6.91 (m, 2 H), 6.59 (d, $J = 8.25$ Hz, 1 H), 6.52 (d, $J = 6.5$ Hz, 1 H), 5.23 (br s, 2 H, amine); 4.74 (br s, 2 H, amine).

(16) Resonance Raman data are available in support of the assignments of the (RuQ,QRu) complex spectrum: Stufkens, D. J.; Lever, A. B. P. To be published.

(17) Almlof, J. *Chem. Phys.* **1974**, *6*, 135–9.

(18) Joss, S.; Reust, H.; Ludi, A. *J. Am. Chem. Soc.* **1981**, *103*, 982–4.

0020-1669/90/1329-2551\$02.50/0

Table I. Electronic Spectra and Assignments[a]

	energy (log ϵ)	$\Delta_{1/2}$	f	assgnt
(RuQ,QRu)[b]	23 050 (4.07)			Ru(II) d → $\pi^*(1)$ bpy
	17 100 (4.78)	1800	0.5	Ru(II) d → π^* Q
(RuQ,CAT)[c]	23 000 (3.78)			Ru(II) d → $\pi^*(1)$ bpy
	19 700 sh			
	17 000 (4.29)	3930	<0.35[d]	Ru(II) d → π^* Q
(RuQ,SQRu)[b]	29 400 (4.38)			Ru(II) d → $\pi^*(2)$ bpy (?)
	21 500 sh			Ru(II) d → $\pi^*(1)$ bpy
	18 800 (4.33)			Ru(II) d → π^* Q
	14 800 (4.23)			
	12 900 (4.28)	2600[c]	0.23[c]	Ru(II) d → π^* SQ
	7 750 (4.02)	2050	0.1	SQ → Q LLCT
(RuSQ,CAT)[c]	23 000 (3.94)			
	20 050 (4.02)			Ru(II) d → $\pi^*(1)$ bpy
	15 300 (4.12)	1820	0.11	Ru(II) d → π^* SQ
(RuSQ,SQRu)[b]	25 400 sh			Ru(II) d → $\pi^*(2)$ bpy
	18 600 (4.23)			Ru(II) d → $\pi^*(1)$ bpy
	14 600			
	12 800 (4.24)			Ru(II) d → π^* SQ
	8 500 (4.37)	1650	0.18	internal ligand (RuSQ,SQRu)

[a] Energy is given in wavenumbers. $\Delta_{1/2}$ is the half-bandwidth in wavenumbers; f is the oscillator strength. [b] In propylene carbonate. [c] In acetonitrile. [d] Estimated and likely slightly high due to overlapping bands.

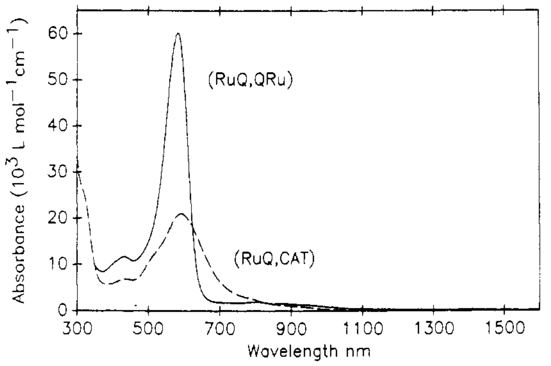

Figure 1. Electronic spectrum of dinuclear (RuQ,QRu) in propylene carbonate with the spectrum of mononuclear (RuQ,CAT) in acetonitrile for comparison.

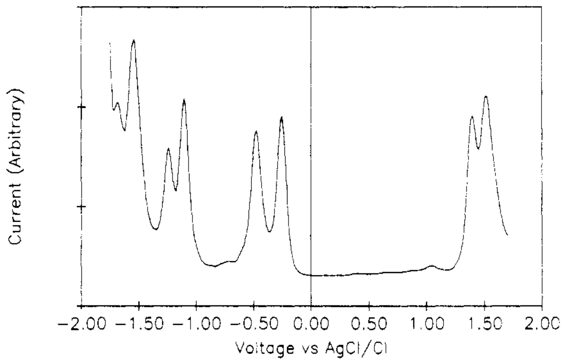

Figure 2. Differential pulse voltammetry of (RuQ,QRu) in acetonitrile containing tetrabutylammonium hexafluorophosphate as supporting electrolyte. Scan rate = 2 mV/s; amplitude = 5 mV.

shoulder on this band may arise through splitting in the t_{2g} manifold or is perhaps an internal ligand transition. It lies fortuitously at almost the same energy as the Ru → π^* SQ transition in mononuclear (RuSQ,CAT). However the possibility that this mononuclear species is an impurity in the dinuclear (RuQ,SQRu) is eliminated by NMR spectroscopy. An additional broad transition at 7750 cm^{-1} in (RuQ,SQRu) is absent from the spectrum of the mononuclear (RuSQ,CAT) and lies at too low an energy[1] to be regarded as an MLCT Ru(II) → SQ type transition.

(RuQ,SQRu) may exist in two extreme forms: **1a**, where the two ligating termini are electronically and structurally equivalent existing midway between Q and SQ, and **1b**, where the SQ and Q termini are distinct, differing electronically and structurally, likely caused by twisting at the central C–C bond.[17]

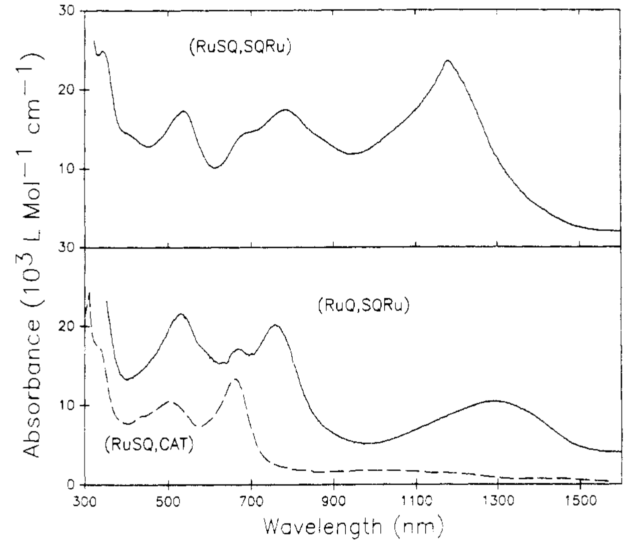

Figure 3. Electronic spectra of (RuSQ,SQRu) (upper) and (RuQ,SQRu) (lower) in propylene carbonate. The spectrum of mononuclear (RuSQ,CAT) (lower) in acetonitrile is included for comparison.

The electronic spectra appear to support **1b**, albeit with some electronic coupling between the two ends of the molecule. The band at 7750 cm^{-1} is then regarded as an intervalence LLCT (ligand-to-ligand charge-transfer state, though in this case more an intramolecular LLCT) transition. This intervalence band is broad (half-bandwidth ca. 2050 cm^{-1}) as a consequence of a significant reorganization contribution. The delocalization coefficient[9] $\alpha^2 = 1.1/R^2 = 0.05$, if the interligand distance, R, is assumed to be that between the centers of the two benzene rings, ca. 4.5 Å. The appropriate value of R to use is, however, uncertain. The electron-coupling integral is estimated[9,19] to lie in the range 0.2–0.35 eV (using eq 25 or 28 in ref 19), substantially larger than in the Creutz–Taube mixed-valence (metal-to-metal) systems[10,19] but comparable to the values observed in the shortest M_2N-4-DCV organic systems (dimethoxynaphthalene–dicyanovinyl) discussed by Penfield et al.[11] Thermal electron transfer in this extreme model will then be extremely fast. This transition is solvent dependent showing a linear dependence upon $[(1/D_{op}) - (1/D_s)]$[9,11] with slope 1060 cm^{-1} and intercept 7200 cm^{-1} ($R = 0.996$, five solvents).[20]

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(19) Hush, N. S. *Coord. Chem. Rev.* **1985**, *64*, 135–57.

(20) This transition shows some structure in certain solvents. These solvents are not included in this analysis.

The Ru(II) → π^* SQ transition is broader in (RuQ,SQRu) than in (RuSQ,CAT), an observation inconsistent with model **1a**, but consistent with **1b**, especially if the twist angle of the excited-state differs significantly from that of the ground state. Thus (RuQ,SQRu) is a class II[21] delocalized complex in which the $(bpy)_2Ru^{II}Q\cdot\cdot$ and $(bpy)_2Ru^{II}SQ\cdot\cdot$ chromophores can separately be identified spectroscopically but are significantly coupled.

The second reduced species (RuSQ,SQRu) shows a further red shift in the Ru(II) → $\pi^*(1)$ bpy and Ru(II) → $\pi^*(2)$ bpy transitions relative to (RuQ,SQRu). The Ru(II) → π^* SQ transition does not shift significantly, relative to (RuQ,SQRu), but it does become weaker and broader; its oscillator strength is probably little changed (Figure 3). A near-IR band is still observed, shifted to the blue, narrower and more intense than that observed in the spectrum of (RuQ,SQRu).

The decrease in molar intensity for the Ru(II) → π^* SQ MLCT transition is especially informative. If the halves of the molecule were independent and uncoupled, the oscillator strength of this transition might double relative to the (RuQ,SQRu) species, since the transition probability doubles.

Consider however that the two π^* orbitals on each SQ terminus couple to yield a lower energy orbital of odd parity that is filled and an upper empty orbital of even parity. The Ru(II) → π^* MLCT transitions terminate on this upper orbital. Coupling of the pairs of ruthenium *xz*, *xy*, and *yz* orbitals yields three pairs of orbitals of even and of odd parities. Transitions from the odd-parity combinations to the empty ligand orbital generate three possible transitions, one strongly allowed, one weakly allowed, and one forbidden. There is threrefore one strongly allowed transition per (strongly coupled, delocalized) dinuclear molecule, rather than the two expected in a localized dinuclear molecule; thus the transition probability may not increase relative to (RuQ,SQRu), as observed.

The near-infrared absorption has a quite different shape in (RuSQ,SQRu), being narrower (half-bandwidth ca. 1500 cm^{-1}), indicative of a smaller difference between the equilibrium ground- and excited-state potential surfaces than for (RuQ,SQRu). This is also consistent with a delocalized species, with this transition being internal to the (RuSQ,SQRu) framework with little charge-transfer character. It is possibly a transition between the pair of SQ terminus molecular orbitals defined in the previous paragraph. Solvent dependence data are not yet available.

Further studies on this system are planned to probe the twist angles in both the ground and excited states and the variation in coupling between the two termini of the ligand as a function of oxidation state.

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(21) Robin, M. B.; Day, P. *Adv. Inorg. Chem. Radiochem.* **1967**, *10*, 247-422.

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Alkane Functionalization by Non-Porphyrin Iron Complexes: Mechanistic Insights

Biological catalysts capable of functionalizing alkanes include cytochrome P-450[1] (which contains a heme active site), methane monooxygenase[2] (which has a diiron active site), and prolyl hydroxylase[3] (which requires mononuclear iron and α-ketoglutarate). While an oxo(porphyrin cation radical)iron(IV) complex is strongly implicated as the active species in the cytochrome P-450 mechanism,[4] less is known of corresponding species in the non-heme iron systems. We have thus initiated an effort to uncover alkane functionalization chemistry by non-porphyrin complexes of iron. Previous work toward this goal has included $Fe(ClO_4)_{2\text{ or }3}/H_2O_2/CH_3CN$,[5] $Fe_3O(OAc)_7/HOAc/pyridine/O_2$,[6] and $Fe_2O(OAc)_2(bpy)_2Cl_2/t\text{-}BuOOH/CH_3CN$[7] systems. But mechanistic insights from these systems into the nature of the oxidizing species have not been forthcoming. On the basis of our work on modeling the reactivity of the catechol dioxygenases,[8] we have initiated an investigation of the reactivity of iron complexes with tripodal ligands in the presence of oxygen atom donors to gain insight into how non-heme iron centers may affect such chemistry. Tripodal ligands were selected for this study since they offer the important advantage of control over the ligand environment at a labile iron center.

In a typical reaction, a 0.77 M solution of cyclohexane was reacted with 0.10 M TBHP[9] in acetonitrile in the presence of 0.70 mM $[Fe^{III}(TPA)Cl_2](ClO_4)$[10] (**1**) at 25 °C under 1 atm of oxygen-free argon. A turnover number of 56 is observed after 2 h for the TBHP oxidation of cyclohexane catalyzed by **1**, resulting in the formation of cyclohexanol, cyclohexanone, chlorocyclohexane, and (*tert*-butylperoxy)cyclohexane (Table I). Similar products were obtained by using $[Fe^{III}(TPA)Br_2](ClO_4)$ (**2**), except that bromocyclohexane formed in lieu of chlorocyclohexane. Replacement of TBHP with MCPBA in the **1**-catalyzed reaction afforded the same products, but no ROOR′. All of the oxidation products of cyclohexane were accounted for in these reactions, as mass balance of substrate was observed in each case. The cyclohexanone formed may at least partially result from the oxidation of cyclohexanol produced in this system, since the **1**-catalyzed TBHP oxidation of cyclohexanol (in the absence of cyclohexane) resulted in the formation of 33 catalyst turnovers of cyclohexanone. The fate of **1** was followed by ^1H NMR spectroscopy during the TBHP/cyclohexane oxidation, and the appearance of the (μ-oxo)diiron(III) species $[Fe_2(TPA)_2O(Cl)_2]^{2+}$ was observed. In an independent reaction this species was found to be catalytically inactive under the conditions of the experiment.

The nature of the C–H bond cleavage step was probed for these reactions. Significant kinetic isotope effects observed in a competitive oxidation of cyclohexane and cyclohexane-d_{12} indicate that C–H bond breaking is at least partially rate determining.[11] When

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(1) (a) Ortiz de Montellano, P. R., Ed. *Cytochrome P-450: Structure, Mechanism, and Biochemistry*; Plenum: New York, 1985. (b) Sato, R.; Omura, T., Eds.; *Cytochrome P-450*; Academic: New York, 1978.

(2) (a) Fox, B. G.; Froland, W. A.; Dege, J. E.; Lipscomb, J. D. *J. Biol. Chem.* **1989**, *264*, 10023-10033. (b) Woodland, M. P.; Patil, D. S.; Cammack, R.; Dalton, H. *Biochim. Biophys. Acta* **1986**, *873*, 237-242.

(3) Udenfriend, S.; Cardinale, G. *Oxygenases and Oxygen Metabolism*; Academic: New York, 1982; p 99.

(4) Groves, J. T. *J. Chem. Educ.* **1985**, *62*, 928-931.

(5) (a) Groves, J. T.; Van Der Puy, M. *J. Am. Chem. Soc.* **1976**, *98*, 5290-5297. (b) Sugimoto, H.; Sawyer, D. T. *J. Org. Chem.* **1985**, *50*, 1784-1786.

(6) Barton, D. H. R.; Boivin, J.; Gastiger, M. J.; Morzycki, J.; Hay-Motherwell, R. S.; Motherwell, W. B.; Ozbalik, N.; Schwartzentruber, K. M. *J. Chem. Soc., Perkin Trans. 1* **1986**, 947.

(7) Vincent, J. B.; Huffman, J. C.; Christou, G.; Li, Q.; Nanny, M. A.; Hendrickson, D. N.; Fong, R. H.; Fish, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 6898-6900.

(8) (a) Que, L., Jr.; Kolanczyk, R. C.; White, L. S. *J. Am. Chem. Soc.* **1987**, *109*, 5373-5380. (b) Cox, D. D.; Que, L., Jr. *J. Am. Chem. Soc.* **1988**, *110*, 8085-8092.

(9) Abbreviations used: BPG = *N,N*-bis(2-pyridylmethyl)glycine; NTB = tris(2-benzimidazolylmethyl)amine; TPA = tris(2-pyridylmethyl)amine; OAc = acetate; TBHP = *tert*-butyl hydroperoxide; MCPBA = *m*-chloroperbenzoic acid; salen = *N,N′*-ethylenebis(salicylideneamine).

(10) The synthesis of $[Fe^{III}(TPA)Cl_2](ClO_4)$ (**1**) proceeded as follows: a 135-mg sample of $Fe^{III}Cl_3{\cdot}6H_2O$ was added to a warm methanolic solution of $TPA{\cdot}3HClO_4$ (295 mg in 75 mL of MeOH), which upon 2-3 days of standing yielded yellow crystals of $[Fe^{III}(TPA)Cl_2](ClO_4)$ (35% yield). A similar scheme, but with $Fe(ClO_4)_3/NaBr$ replacing $FeCl_3$, was utilized for the preparation of **2**. *Caution!* In the solid state, perchlorate salts of metal complexes with organic ligands are potentially explosive; care should be exercised in handling these complexes. See: (a) Wolsey, W. C. *J. Chem. Educ.* **1973**, *50*, A335-A337. (b) Raymond, K. *Chem. Eng. News* **1983**, *61*, (Dec 5), 4.

0020-1669/90/1329-2553$02.50/0