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Synthesis and Characterization of (Octaethylporphyrinato)ruthenium(II) and -ruthenium(III) Complexes with Thioether, Sulfoxide, and Benzoate Axial Ligands

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Complexes in the series $Ru(OEP)(RR'S)_2$ and $Ru(OEP)(RR'SO)_2$ (where OEP = the dianion of 2,3,7,8,12,13,17,18-octaethylporphyrin, R = methyl, ethyl, or decyl, and R′ = methyl or ethyl) were prepared by treatment of the dimer $[Ru(OEP)]_2$ with the appropriate thioether or sulfoxide ligands. Similarly, complexes of the type $[Ru(OEP)(RR'S)_2][BF_4]$ and $[Me_4N][Ru(OEP)(PhCOO)_2]$ were prepared by the addition of the appropriate thioether or $[Me_4N][PhCOO]$ to the dimer $[Ru(OEP)]_2[BF_4]_2$. All the complexes were characterized by use of ^1H-NMR, IR, and UV/vis spectroscopy, cyclic voltammetry (CV), and elemental analysis. IR data show that the $Ru(OEP)(RR'SO)_2$ complexes exist as the bis(S-bound) isomers in the solid state; CV data suggest that in solution rearrangement of S-bound to O-bound sulfoxide occurs after a metal-centered oxidation. The crystal structure of $[Ru(OEP)(decMS)_2][BF_4]$ (decMS = *n*-decyl methyl sulfide) was obtained; the crystals are triclinic, $P\bar{1}$, with $a = 10.995(4)$ Å, $b = 13.843(3)$ Å, $c = 10.305(4)$ Å, $\alpha = 101.60(2)°$, $\beta = 97.46(3)°$, $\gamma = 86.82(3)°$, and $Z = 1$. The structure was solved by the Patterson method and was refined by full-matrix least-squares procedures to $R = 0.050$ and $R_w = 0.040$ for 2948 reflections with $I \geq 3\sigma(I)$. The solid state geometry of $[Ru(OEP)(decMS)_2][BF_4]$ is not significantly different from that previously found for $Ru(OEP)(decMS)_2$.

Introduction

Interest in the use of metalloporphyrins for selective catalytic oxidations utilizing dioxygen as oxidant remains intense.[1] Much of this interest has been focused on the naturally occurring systems such as the mono- and dioxygenase type enzymes,[2] but some studies have also focused on the development of robust synthetic catalysts which could be used in industrial oxidation processes.[3]

Ruthenium porphyrins have been investigated both as models for the natural systems[2c,g] and as possible industrial catalysts.[3c] The sterically hindered *trans*-dioxo species $Ru(TMP)(O)_2$ and $Ru(OCP)(O)_2$[4] have attracted the most attention as dioxygenase-type catalysts;[1,2c,g,3c,5,6] other ruthenium porphyrin-based dioxygenase-type systems have also been reported but have received much less attention. For example, a previous paper from this group mentioned that $Ru(OEP)(PPh_3)_2$ can catalyze the O_2 oxidation of free phosphine to the corresponding phosphine oxide.[7a] Subsequent studies in our laboratories have shown that this reactivity can be extended to Ru(OEP)/dialkyl sulfide systems.[7b] In a series of papers, of which part 1 is presented here, we wish to describe a detailed mechanistic study of these thioether systems. This paper discusses the synthesis and characterization of several complexes which are proposed to be intermediates in the stoichiometric O_2 oxidation of $Ru(OEP)(RR'S)_2$ to $Ru(OEP)(RR'SO)_2$ in solutions containing benzoic acid (to be discussed in a second paper)[8] and in the $Ru(OEP)(RR'S)_2$-catalyzed O_2 oxidation of dialkyl sulfides to the corresponding sulfoxides under similar conditions (to be discussed in a third paper).[8]

Experimental Section

General Instrumentation. UV/vis or NMR spectra of air- or moisture-sensitive materials were carried out *in vacuo*.[9] UV/vis spectra were recorded at 20.0 °C on a Perkin-Elmer 552A spectrophotometer with the slit width adjusted to allow 2 nm resolution; typically the Soret bands were measured using a 0.1 cm cell, while for the visible bands a 1.0 cm cell was used. IR spectra were obtained on a Nicolet 5DX FT single beam spectrometer; samples were mulled in Nujol and sandwiched between KBr plates. Unless otherwise stated, ^1H NMR spectra were collected at 20.0 °C, using a Varian XL-300 FT instrument. ESR spectra were measured at liquid-N_2 temperature on a Bruker ESP 300 spectrometer (X-band); spectra for the three $[Ru(OEP)(RR'S)_2][BF_4]$ species were obtained at 10^{-3} M in CH_2Cl_2, while the spectrum

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(4) Abbreviations used: TMP, dianion of *meso*-tetramesitylporphyrin; OCP, dianion of *meso*-tetrakis(2,6-dichlorophenyl)porphyrin; OEP, dianion of 2,3,7,8,12,13,17,18-octaethylporphyrin; Por, a generic porphyrin; dms, dimethyl sulfide; dmso, dimethyl sulfoxide (*s* or *o* within an abbreviation for any sulfoxide ligand implies S- or O-bonded, respectively); decMS, *n*-decyl methyl sulfide; decMSO, *n*-decyl methyl sulfoxide; py, pyridine; Cp, cyclopentadienyl anion; R, methyl, ethyl, or decyl; R′, methyl or ethyl; CV, cyclic voltammetry.

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of $[Ru(OEP)(decMS)_2][BF_4]$ was also obtained at 10^{-2} M in toluene. The magnetic susceptibilities of paramagnetic compounds were determined using the Evans method;[10] the diamagnetic corrections for OEP and the thioether ligands were calculated from Pascal's constants.[11] Conductivity measurements were performed using a Model RCM 15B1 conductivity bridge (A. H. Thomas Co.), with a conductivity cell of constant 1.00 cm^{-1} (Yellow Springs Co.). CV measurements were carried out using an EG and G PAR Model 175 universal programmer to control the potential sweep; this unit was linked to a Model 173 PAR potentiostat equipped with a Model 176 current-to-voltage converter and a Model 178 electrometer probe. Voltammetric traces were recorded on a Hewlett-Packard Model 7005B X-Y recorder. Scan speed was 100 mV/s unless otherwise indicated. All electrochemical experiments were carried out in CH_2Cl_2, with 0.12 M $[n\text{-}Bu_4N][BF_4]$ acting as the supporting electrolyte. Potentials were measured, and were recorded, relative to a Ag/AgCl reference electrode; the $FeCp_2^+$/$FeCp_2$ couple occurred at $E^{\circ\prime} = 0.58$ V relative to this reference. The electrochemical cell, based on a design described by Van Duyne and Reilley,[12] was made by S. Rak of this department and was devised for use with minimal volumes of solution (2 mL) and to allow manipulation of highly air-sensitive samples.[8a] Elemental analyses were carried out by P. Borda of this department.

General Reagents, Gases, and Solvents. All nondeuterated solvents were obtained from BDH. Reagent grade hydrocarbon solvents were stored *in vacuo* over sodium benzophenone ketyl; other solvents (spectroscopic grade) were stored *in vacuo* over 3 Å molecular sieves. Deuterated solvents were obtained from MSD Isotopes or from CIL and were stored in the same way as the nondeuterated solvents.

Gases were supplied by Union Carbide of Canada Ltd. N_2 for the glovebox was prepurified grade; all others were USP grade. Unless otherwise specified, all gases were used without further purification. A gas could be dried by using 3 Å molecular sieves; for especially air-sensitive solutions, Ar was passed down a Ridox deoxygenation column prior to use.

The N_2 atmosphere for the glovebox was continuously recirculated through a Dri-Train HE-439 purification tower packed with 2.4 kg of 3 Å molecular sieves, 1.5 kg of 7 Å molecular sieves, and 2 kg of Ridox deoxygenation catalyst. This treatment kept the concentration of O_2 and H_2O below 1 ppm, as evidenced by the long lifetime of an exposed 25-W light bulb filament within the box.[13]

The dms, Et_2S (Aldrich), and decMS (Fairfield) were distilled prior to use, and their purity was checked by gas chromatography and ^1H-NMR spectroscopy. dmso was spectrograde from BDH, while dmso-d_6 was from MSD isotopes. Diethyl sulfoxide and decMSO were synthesized according to standard procedures.[14,15] Both dmso and Et_2SO were stored under Ar over 3 Å molecular sieves; solid decMSO required no special storage precautions.

PhCOOH (Aldrich), HBF_4 (MCB, 48% aqueous solution), $Me_4N(OH)$ (Anachemia, 25% aqueous solution), and $n\text{-}Bu_4N(OH)$ (BDH, 40% aqueous solution) were used as received. $AgBF_4$ (Aldrich) was stored in the glovebox.

Tetramethylammonium Benzoate, $[Me_4N][PhCOO]$. A 0.9 M solution of PhCOOH in EtOH (~14 mL) was added dropwise to 4 g of 25% aqueous $Me_4N(OH)$ until the resultant mixture was slightly acidic. The water and EtOH were removed, and the resultant solid was redissolved in EtOH (125 mL); the mixture was refluxed for ~15 min and then filtered to remove a grayish-white flaky precipitate. The filtrate volume was reduced to ~2 mL, and 40 mL of Et_2O was then added. The desired product was obtained as a white precipitate, which was filtered off and dried overnight at 80 °C. $[Me_4N][PhCOO]$ is extremely hygroscopic and had to be stored and handled in a glovebox; in solution, the salt was handled exclusively *in vacuo*. The benzoate is stable indefinitely in acetonitrile solution but slowly degrades in CH_2Cl_2. Yield: 95%. Anal. Calcd for $C_{11}H_{17}NO_2$: C, 67.66; H, 8.78; N, 7.17. Found: C, 67.76; H, 8.60; N, 6.99. NMR (δ; CD_3CN or CD_2Cl_2, 20 °C): 7.29 m ($H_{m,p}$), 7.96 m (H_o), 3.48 s (NCH_3).

Tetra-*n*-butylammonium Tetrafluoroborate, $[n\text{-}Bu_4N][BF_4]$. To 95 g (0.146 mol) of $n\text{-}Bu_4N(OH)$ solution was added enough HBF_4 solution to produce a pH-neutral mixture. The resulting white precipitate was filtered off, washed with three 50-mL aliquots of ice-cold water, and then dried *in vacuo* for 24 h. The dry powder was dissolved in 45 mL of ethyl acetate, the solution was passed through a filter paper, and then the solid crystallized out by adding ~ 25 mL of pentane and cooling at −5 °C for 1 h. After a second such procedure, the product was dried *in vacuo* at room temperature for 48 h and then showed no electrochemical activity in CV scans from −1.6 to +1.6 V in CH_2Cl_2. Molar conductivity (1 mM in CH_2Cl_2): $\Lambda = 22 \pm 2\ \Omega^{-1}\ cm^2\ mol^{-1}$.

Ruthenium Porphyrin Complexes. Ru was obtained on loan from Johnson, Matthey Ltd. or Colonial Metals Inc. as $RuCl_3{\cdot}3H_2O$ (~40% Ru). H_2OEP was kindly provided by Dr. D. Dolphin of this department.

Ru_3CO_{12},[16] $Ru(OEP)(CO)py$,[17] and $Ru(OEP)py_2$,[17] the necessary precursors to make $[Ru(OEP)]_2$[18] and $[Ru(OEP)]_2[BF_4]_2$,[19] were made by the literature procedures cited; for all these compounds the spectroscopic data (NMR, UV/vis, IR) were in excellent agreement with those reported previously, and elemental analyses for C, H, and N were within 0.3% of the theoretical values.

$[Ru(OEP)]_2$ was prepared by high-vacuum pyrolysis of $Ru(OEP)py_2$,[18] while $[Ru(OEP)]_2[BF_4]_2$ was prepared by adding 2 equiv of $AgBF_4$ to a benzene solution of $[Ru(OEP)]_2$.[19] Removal of metallic silver from the oxidized dimer required that a CH_2Cl_2 solution of the complex be filtered through Celite. Both dimers are extremely air-sensitive, both in solution and in the solid state. The solids were stored in the glovebox. In solution the dimers were handled using vacuum-transfer techniques where possible; when this was impractical, manipulations were carried out as fast as possible under dry, deoxygenated Ar, using a combination of Schlenk and syringe techniques.[9]

The synthesis and characterization of $Ru(OEP)(decMS)_2$ have been previously described.[7b]

$Ru(OEP)(dms)_2$. A 25 μL (0.34 mmol) volume of dms and 5 mL of CH_2Cl_2 were vacuum-transferred onto 0.108 g (0.085 mmol) of $[Ru(OEP)]_2$, which immediately gave a red solution. The volume was increased to about 15 mL with hexane and then slowly reduced until traces of precipitate appeared. The solution was filtered and the volume further decreased until considerable precipitation occurred. This concentrate was now heated to redissolve the complex and then allowed to cool slowly to 0 °C. The dark purple crystalline $Ru(OEP)(dms)_2$ was filtered off and dried *in vacuo* at 70 °C overnight. Yield: 80%. Anal. Calcd for $C_{40}H_{56}N_4S_2Ru$: C, 63.37; H, 7.45; N, 7.39. Found: C, 63.47; H, 7.48; N, 7.20. NMR (δ; CD_2Cl_2): OEP, 1.81 t (CH_3), 3.85 q (CH_2), 9.32 s (H_{meso}); dms, −2.66 s. UV/vis (0.0445 mM in C_6H_6 containing 68 mM dms) [λ_{max} (log ϵ)]: 407.5 (5.34), 498 (4.17), 525 (4.42) nm.

$Ru(OEP)(Et_2S)_2$. The procedure for the synthesis of $Ru(OEP)(Et_2S)_2$ was analogous to that for $Ru(OEP)(dms)_2$. Yield: 85%. Anal. Calcd for $C_{44}H_{64}N_4S_2Ru$: C, 64.91; H, 7.92, N, 6.88. Found: C, 64.73; H, 7.87; N, 6.68. NMR (δ; CD_2Cl_2): OEP, 1.78 t (CH_3), 3.96 q (CH_2), 9.25 s (H_{meso}); Et_2S, −1.32 t (CH_3), −2.47 q (CH_2). UV/vis (0.0340 mM in C_6H_6 containing 74 mM Et_2S) [λ_{max} (log ϵ)]: 409 (5.23), 499 (4.13), 525 (4.39) nm.

$Ru(OEP)(dm\textit{s}o)_2$ and the dmso-d_6 Analogue. $Ru(OEP)(dm\textit{s}o)_2$ was prepared by adding 16 μL (0.23 mmol) of dry, degassed dmso and 8 mL of CH_2Cl_2 to 0.072 g (0.057 mmol) of $[Ru(OEP)]_2$. To the deep red solution product was added 10 mL of hexane, and then the solvents were slowly removed until solid just appeared. The solution was filtered, and the volume was further reduced until considerable precipitation occurred. The microcrystalline product was filtered off

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and then dried *in vacuo* overnight at 70 °C. The dmso-perdeuterated analogue was prepared in an identical manner but using dmso-d_6 as the sulfoxide source. Yields were ~80% in each case. Anal. Calcd for $C_{40}H_{56}N_4O_2S_2Ru$: C, 60.81; H, 7.14; N, 7.09. Found: C, 60.39; H, 7.40; N, 6.78. NMR (δ; CD_2Cl_2): OEP, 1.87 t (CH_3), 3.98 q (CH_2), 9.78 s (H_{meso}); dmso, −2.18 s. IR (cm^{-1}, Nujol): ν_{SO}, 1105. UV/vis (0.0169 mM in C_6H_6 containing 22.6 mM dmso) [λ_{max} (log ϵ)]: 397.5 (5.44), 533 (4.04) nm.

Ru(OEP)(Et₂SO)₂. Ru(OEP)(Et_2SO)$_2$ was prepared in a manner analogous to that used for Ru(OEP)(dmso)$_2$. Yield: ~80%. Anal. Calcd for $C_{44}H_{64}N_4O_2S_2Ru$: C, 62.45; H, 7.62; N, 6.62. Found: C, 62.32; H, 7.58; N, 6.68. NMR (δ; CD_2Cl_2): OEP, 1.84 t (CH_3), 3.96 q (CH_2), 9.70 s (H_{meso}); Et_2SO, −1.55 br (CH_3), −2.12 br ($(CH_2)_a$), −2.74 br ($(CH_2)_b$). IR (cm^{-1}, Nujol): ν_{SO}, 1104. UV/vis (0.0390 mM in C_6H_6 containing 4.7 mM Et_2SO) [λ_{max} (log ϵ)]: 399.5 (5.49), 527 (4.10) nm.

Ru(OEP)(decMSO)₂. To 0.069 g (0.055 mmol) of [Ru(OEP)]$_2$ were added 0.050 g (0.25 mmol) of decMSO and 5 mL of benzene. The solution immediately became bright red. After 10 min the solvent was removed, the solid redissolved in 6 mL of pentane, and the resulting solution filtered to remove some brown solid. The filtrate was then cooled to −100 °C for 15 min to effect precipitation of Ru(OEP)(decMSO)$_2$, which was filtered off at −100 °C as a scarlet powder and dried *in vacuo* overnight. The complex is extremely lipophilic, and care had to be taken to avoid contamination with stopcock grease. Yield: ~80%. Anal. Calcd for $C_{58}H_{92}N_4O_2S_2Ru$: C, 66.82; H, 8.89; N, 5.37; S, 6.15. Found: C, 66.89; H, 8.89; N, 5.18; S, 5.95. NMR (δ; C_7D_8): OEP, 1.86 t (CH_3), 3.96 q (CH_2), 9.72 s (H_{meso}); decMSO, −2.34 s (SCH_3), −2.78 m ($^1CH_2$), −1.11 m ($^2CH_2$), −0.02 m ($^3CH_2$), 0.37 qn ($^4CH_2$), 0.73 qn ($^5CH_2$), 0.95 qn ($^6CH_2$), 1.0−1.25 m ($^{7-9}CH_2$), 0.839 t ($^{10}CH_3$). IR (cm^{-1}, Nujol): ν_{SO}, 1107. UV/vis (0.0101 mM in C_6H_6 containing 0.20 mM decMSO) [λ_{max} (log ϵ)]: 399 (5.59), 530 (4.15) nm.

[Ru(OEP)(dms)₂][BF₄]. To 0.053 g (0.037 mmol) of [Ru(OEP)]$_2$[BF_4]$_2$ were added 10.7 μL (0.147 mmol) of dms and 5 mL of CH_2Cl_2. The solution was stirred for 30 min, when it became a dark orange color. At this point 5 mL of hexane was added, and the total volume was reduced until precipitation just occurred. The solution was filtered, the volume was further reduced until most of the desired complex had precipitated, and the supernatant was very pale orange. The brownish-purple needles were filtered off, washed with pentane, and then dried *in vacuo* at 70 °C overnight. Yield: ~80%. Anal. Calcd for $C_{40}H_{56}N_4S_2RuBF_4$: C, 56.86; H, 6.68; N, 6.63. Found: C, 56.67; H, 6.70; N, 6.44. $\mu = 2.3\ \mu_B$. NMR (δ; CD_2Cl_2): OEP, 1.52 br (CH_3), 23.85 br (CH_2), 1.73 br (H_{meso}); dms, −0.174 br. UV/vis (0.111 mM in CH_2Cl_2) [λ_{max} (log ϵ)]: 394 (5.05) (Soret), 505 (4.05), 533 (4.03) nm. $\Lambda = 66\ \Omega^{-1}\ cm^2\ mol^{-1}$ (1.2 mM in CH_2Cl_2).

[Ru(OEP)(Et₂S)₂][BF₄]. The preparation of this complex was analogous to that described for [Ru(OEP)(dms)$_2$][BF_4]. Yield: ~80%. Anal. Calcd for $C_{44}H_{64}N_4S_2RuBF_4$: C, 58.66; H, 7.16; N, 6.22. Found: C, 58.39; H, 7.17; N, 6.15. $\mu = 2.4\ \mu_B$. NMR (δ; CD_2Cl_2): OEP, 1.31 br (CH_3), 23.09 br (CH_2), 1.61 br (H_{meso}); Et_2S, 3.57 br (CH_2), 7.82 br (CH_3). UV/vis (0.0838 mM in CH_2Cl_2) [λ_{max} (log ϵ)]: 394 (4.98), 505 (4.01), 533 (3.98) nm. $\Lambda = 72\ \Omega^{-1}\ cm^2\ mol^{-1}$ (0.93 mM in CH_2Cl_2).

[Ru(OEP)(decMS)₂][BF₄]. To 0.171 g (0.12 mmol) of [Ru(OEP)]$_2$[BF_4]$_2$ were added 110 μL (0.474 mmol) of decMS and 5 mL benzene. The purple, insoluble [Ru(OEP)]$_2$[BF_4]$_2$ was slowly converted to the orange, soluble [Ru(OEP)(decMS)$_2$][BF_4]. This product was recrystallized from benzene/heptane, in a manner analogous to that described for [Ru(OEP)(dms)$_2$][BF_4] where CH_2Cl_2/heptane was used. Crystals suitable for an X-ray structure determination were obtained by reducing the volume of a benzene/heptane solution until precipitation just occurred, heating to redissolve the precipitate, and then allowing the solution to cool slowly. Yield: ~80%. Anal. Calcd for $C_{68}H_{92}N_4S_2RuBF_4$: C, 63.48; H, 8.45; N, 5.11; S, 5.84. Found: C, 63.69; H, 8.62; N, 5.19; S, 5.66. $\mu = 2.4\ \mu_B$. NMR (δ; CD_2Cl_2): OEP, 1.44 br (CH_3), 23.13 br (CH_2), 1.83 br (H_{meso}); decMS, 0.50 br (SCH_3), 0.92 t ($^{10}CH_3$) {tentative: 9.06 br ($^1CH_2$), 4.39 br ($^2CH_2$), 2.22 br ($^3CH_2$), 1.96 br ($^4CH_2$), 1.60 br ($^5CH_2$), 1.55−1.30 br ($^{6-9}CH_2$); see text}. UV/vis (0.0921 mM in CH_2Cl_2) [λ_{max} (log ϵ)]: 394 (5.10), 505 (4.11), 533 (4.09) nm. $\Lambda = 68\ \Omega^{-1}\ cm^2\ mol^{-1}$ (1.0 mM in CH_2Cl_2).

Table 1. Crystallographic Data

compound	[Ru(OEP)($CH_3S(CH_2)_9CH_3$)$_2$][BF_4]
formula	$C_{58}H_{92}BF_4N_4RuS_2$
fw	1097.39
cryst system	triclinic
space group	$P\bar{1}$
a, Å	10.995(4)
b, Å	13.843(3)
c, Å	10.305(4)
α, deg	101.60(2)
β, deg	97.46(3)
γ, deg	86.82(3)
V, Å^3	1522.7(9)
Z	1
ϱ_{calc}, g/cm^3	1.197
T, °C	21
radiation	Mo
λ, Å	0.710 69
μ, cm^{-1}	3.65
transm factors	0.88−1.00
$R(F)$	0.050
$R_w(F)$	0.040

The above three Ru(OEP)(RR′S)$_2^+$ complexes in frozen solution showed broad ESR signals (g = ~2.7, ~2.2, ~1.7).

[Me₄N][Ru(OEP)(PhCOO)₂]. To 0.104 g (0.0725 mmol) of [Ru(OEP)]$_2$[BF_4]$_2$ were added 0.063 g (0.322 mmol) of [Me_4N][PhCOO] and 10 mL of CH_2Cl_2. The color changed immediately from purple to a greenish-yellow, and then after about 1 h to a bright red. The solution was cooled to 0 °C, filtered to remove solid [Me_4N][BF_4], and then further cooled to −100 °C to precipitate the desired, crimson product. This was filtered off, washed with pentane, and then dried *in vacuo* overnight at room temperature. The compound is highly air-sensitive in solution, and the solid was stored in the glovebox. Yield: 75%. Anal. Calcd for $C_{54}H_{66}N_5O_4Ru$: C, 68.26; H, 7.00; N, 7.37. Found: C, 68.57; H, 7.16; N, 7.29. NMR (δ; CD_2Cl_2): OEP, −0.72 br (CH_3), 8.08 br (CH_2), 2.72 br (H_{meso}); PhCOO$^-$, 17.86 br (H_o), 10.74 br (H_m), 9.35 br (H_p); 5.64 br $N(CH)_3$. UV/vis (~0.1 mM in CH_2Cl_2) [λ_{max} (log ϵ)]: 401 (~5), 520 (~4) nm.

X-ray Crystallographic Analysis of [Ru(OEP)(decMS)₂][BF₄]. Crystallographic data appear in Table 1. The final unit-cell parameters were obtained by least-squares on the setting angles for 25 reflections with 2θ = 12.4−23.8°. The intensities of three standard reflections, measured every 200 reflections throughout the data collection, remained constant. The data were processed[20] and corrected for Lorentz and polarization effects and absorption (empirical, based on azimuthal scans for three reflections).

The structure analysis was initiated in the centrosymmetric space group $P\bar{1}$ on the basis of the E-statistics. The structure was solved by conventional heavy-atom methods, the coordinates of the Ru and S atoms being determined from the Patterson function and those of the remaining atoms from subsequent difference Fourier syntheses. The complex cation is situated at a center of symmetry, and the BF_4^- anion was found to be 1:1 disordered about a center of symmetry. The terminal carbon atoms of two of the four independent ethyl groups were also disordered. The disorder was modeled by split-atom refinement with site occupancy factors for the ethyl group components adjusted (as the refinement progressed) to give nearly equal thermal parameters. The n-decyl side chain displays substantial thermal motion and may be subject to minor disordering. No attempts to model this possible disorder were made. A parallel refinement of the structure in the noncentrosymmetric space group $P1$ failed to resolve any of the disorder described above. All non-hydrogen atoms except the low-occupancy carbon atoms C(12a) and C(16a) were refined with anisotropic thermal parameters. Hydrogen atoms were fixed in idealized positions with C−H = 0.98 Å and $B_H = 1.2B_{bonded\ atom}$. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from ref 21. Selected bond

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Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for Ru(OEP)(decMS)$_2$ and [Ru(OEP)(decMS)$_2$][BF$_4$][a]

	Ru(OEP)(decMS)$_2$[b]	[Ru(OEP)(decMS)$_2$][BF$_4$][c]
	Distances	
Ru−S	2.376(1)	2.377(2)
Ru−S*	2.361(1)	*c*
Ru−N(1)	2.044(3)	2.025(3)
Ru−N(2)	2.044(3)	2.047(3)
Ru−N(1)*	2.041(3)	*c*
Ru−N(2)*	2.056(3)	*c*
	Angles	
S−Ru−N(1)	86.9(1)	85.7(1)
S−Ru−N(2)	90.2(1)	90.1(1)
S−Ru−N(1)*	94.0(1)	94.3(1)
S−Ru−N(2)*	90.9(1)	89.9(1)
S*−Ru−N(1)	94.7(1)	*c*
S*−Ru−N(2)	90.7(1)	*c*
S*−Ru−N(1)*	84.5(1)	*c*
S*−Ru−N(2)*	88.3(1)	*c*
S−Ru−S*	178.27(3)	180.00

[a] Standard deviations in parentheses. [b] Data collected at −150 °C.[7b] [c] [Ru(OEP)(decMS)$_2$][BF$_4$] has a crystallographic inversion center; data collected at 21 °C.

lengths and bond angles appear in Table 2, along with the corresponding bond lengths and bond angles of the Ru^{II} analogue Ru(OEP)(decMS)$_2$, which we previously reported.[7b] Details of the data collection and reduction and the structure solution and refinement and complete tables of crystallographic data, atomic coordinates and equivalent isotropic thermal parameters, anisotropic thermal parameters, bond lengths and angles, torsion angles, intermolecular contacts, and least-squares planes are included as supplementary material.

Results and Discussion

Characterization of Ru(OEP)(RR'*S*O)$_2$ Complexes. A sulfoxide can bind to a metal center via either the sulfur or oxygen atom; experimentally, both types of complex have been observed, and theories have been proposed to explain the bonding in each case.[22] In the absence of structural data, IR and NMR have been used extensively to distinguish the two binding modes.[3c,22−25] In S-bound systems, the ν_{SO} stretching frequency in the IR is higher than in the free sulfoxide, whereas in O-bound systems it is lower.

The IR spectra of Ru(OEP)(dmso)$_2$, Ru(OEP)(Et$_2$SO)$_2$, and Ru(OEP)(decMSO)$_2$ all show a strong band, assigned to ν_{SO}, between 1104−1107 cm^{-1}, as compared with lower values for the free sulfoxides (1055 cm^{-1} for free dmso, 1001 cm^{-1} for Et$_2$SO, and 1030 cm^{-1} for decMSO); these data are consistent with S-bound complexes, at least in the solid state.

Difficulties in distinguishing ν_{SO} (particularly of O-bonded sulfoxide) from the ϱ_{CH_3} signals of, for example, dmso by IR may be overcome by comparing data for the dmso complex with those for the dmso-d_6 analogue.[22,23] The ϱ_{CH_3} modes are isotopically shifted when the perdeuterated analogue is used, whereas the ν_{SO} signals remain unchanged. In the case of Ru(OEP)(dm*s*o)$_2$ and Ru(OEP)(dm*s*o-d_6)$_2$, the IR spectra obtained are essentially identical in the region from 500 to 1500 cm^{-1}. Presumably the C−H and C−D rocking modes in these complexes are buried under signals attributable to Ru(OEP). When the IR spectra of Ru(OEP)(dm*s*o)$_2$ and the perdeuterated analogue are compared with that of Ru(OEP)(dms)$_2$, the only significant difference in the region mentioned is that the spectrum of the thioether complex lacks the strong 1105 cm^{-1} band; the spectra of all three species are otherwise virtually identical. This confirms the assignment of the ν_{SO} band, and similarly the ν_{SO} signals of Ru(OEP)(Et$_2$*S*O)$_2$ and Ru(OEP)(decM*S*O)$_2$ were assigned by comparing their IR spectra with those of the corresponding dialkyl sulfide complexes.

In the solid state, the Ru(II) thioether and sulfoxide complexes are air-stable, but in solution they can undergo aerial oxidation, depending on conditions.[8] Addition of excess thioether/sulfoxide retards the oxidation rates, which thus likely proceed via a dissociative mechanism, well documented in Ru^{II}(Por) chemistry, in which dissociation of an axial ligand is followed by coordination of O$_2$ at the vacant axial site.[7,8] The UV/vis data were conveniently measured in the presence of excess thioether/sulfoxide.

The peak positions of all the Ru(OEP)(RR'SO)$_2$ (and Ru(OEP)(RR'S)$_2$) ^{1}H-NMR signals are typical of those observed for other related Ru^{II}(OEP) species; the most complex spectrum, that of Ru(OEP)(decMSO)$_2$, was assigned by direct analogy with the previously reported spectrum of Ru(OEP)(decMS)$_2$, in which the alkyl protons of the decyl chain are nicely resolved.[7b] The dominant factor which determines the peak positions of such diamagnetic porphyrin species is the ring current generated by the porphyrin π electrons,[26,27] and this is specifically discussed for Ru(OEP)(decMS)$_2$ in ref 7b. The extent to which the peak positions of the axial ligand protons shift upon coordination can be considerable; for example, δ_{CH_3} = 2.3 ppm for free dmso, as compared to −2.18 ppm for the coordinated ligand.

The Ru(OEP)(RR'SO)$_2$ ^{1}H-NMR spectra show no evidence that these species undergo linkage isomerization in solution; in particular, each spectrum shows one sharp H$_{meso}$ signal, which is good evidence for the presence of only one species. On the basis of the solid-state IR evidence, it is almost certain that the solution species is Ru(OEP)(RR'*S*O)$_2$ in each case. This assignment is further supported by previous studies carried out in our laboratories on Ru(TMP)(Et$_2$SO)$_2$, which showed that although Ru(TMP)(Et$_2$S*O*)$_2$ can be generated *in situ* by treatment of *trans*-Ru(TMP)O$_2$ with Et$_2$S, this species with O-bonded Et$_2$SO is gradually converted to the thermodynamically more stable Ru(TMP)(Et$_2$*S*O)$_2$.[3c,28]

The Ru(OEP)(dmso)$_2$ complex has been made previously by irradiation of Ru(OEP)(CO) in dmso; however, no spectroscopic data were presented, and the C analysis was 1.55% low.[29]

Characterization of Ru^{III}(OEP) Complexes. Oxidation of metalloporphyrins can occur either at the metal center or at the porphyrin ring, generating a π-cation radical.[30] In the present work, all the formally Ru(III) complexes isolated were synthesized from the Ru(III) precursor [Ru(OEP)]$_2$[BF$_4$]$_2$, and to our knowledge all Ru^{II}(por$^{+\bullet}$) π-cation radical species observed to date contain an axial π-acceptor CO ligand, which stabilizes the Ru(II) oxidation state.[31−33] The complexes within either

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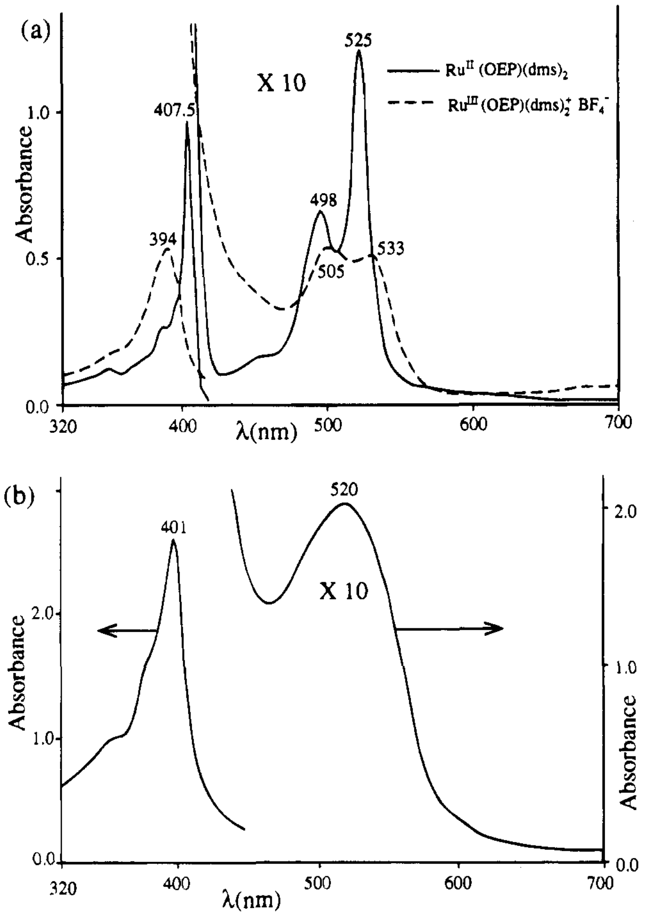

Figure 1. UV/vis spectra in CH$_2$Cl$_2$ of (a) Ru(OEP)(dms)$_2$ and [Ru(OEP)(dms)$_2$][BF$_4$] and (b) [Me$_4$N][Ru(OEP)(PhCOO)$_2$].

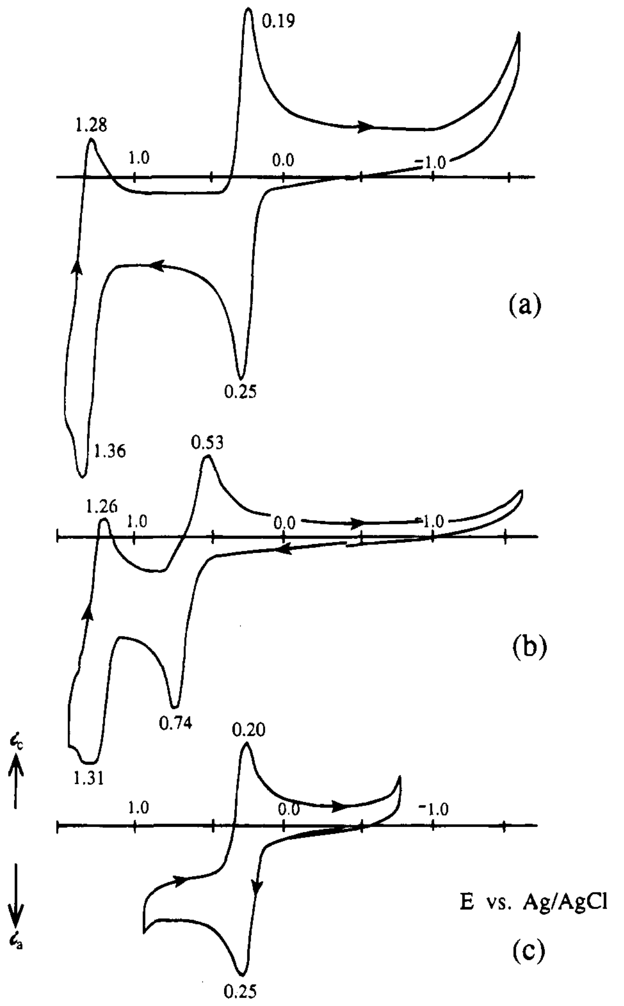

Figure 2. Cyclic voltammograms in CH$_2$Cl$_2$/[*n*-Bu$_4$N][BF$_4$] for (a) Ru(OEP)(dms)$_2$, (b) Ru(OEP)(dmso)$_2$, and (c) [Me$_4$N][Ru(OEP)(PhCOO)$_2$]. The cyclic voltammograms of the other dialkyl sulfide and sulfoxide complexes are virtually indistinguishable from those of the dms and dmso complexes illustrated. Also, a CV identical to (a) was obtained for [Ru(OEP)(dms)$_2$][BF$_4$].

formulation are low-spin d^5 ($S = {}^1/_2$), as demonstrated here by the magnetic susceptibilities, while direct evidence that the Ru(OEP)(RR′S)$_2^+$ complexes are Ru(III) species is given by the broad signals seen in the ESR spectra of frozen solution samples; these are typical of axially symmetric Ru(III) species,[34] and the $g = 2.0$ signal expected for the cation radical[31,32] is not seen. The structural data for [Ru(OEP)(decMS)$_2$][BF$_4$] (see below) are also consistent with the Ru(III) formulation.

The UV/vis spectra of Ru(OEP)(dms)$_2$ and [Ru(OEP)(dms)$_2$][BF$_4$] (Figure 1) are quite similar in the 500 nm region, and this also qualitatively supports just differences in the oxidation state of the metal; π-cation radicals typically show much broader spectra in the 500–700 nm region.[19,35] The spectra of the other [Ru(OEP)(RR′S)$_2$][BF$_4$] complexes were essentially identical to that of the dms one; the spectrum of [Me$_4$N][Ru(OEP)(PhCOO)$_2$] (Figure 1b) could not be compared to that of the corresponding, unknown, dianionic Ru(II) analogue, but the fairly localized absorption maximum at 520 nm, with no significant absorption above 600 nm, is consistent with a Ru(III) formulation.

Dialkyl sulfide ligands do not show significant π-acceptor properties,[7b] and this, together with CV studies in this work (Figure 2a), further supports the presence of the Ru(III) oxidation state; the standard reduction potentials of all three [Ru(OEP)(RR′S)$_2$][BF$_4$] complexes are 0.22 ± 0.02 V. Such values are comparable to those obtained for systems such as Ru(OEP)py$_2^+$/Ru(OEP)py$_2$, which are known to undergo oxidation at the metal[31] but are well below the corresponding potentials of the Ru(OEP$^{+\bullet}$)(CO)L/Ru(OEP)(CO)L systems (L = py or a vacant site), which are typically 0.65–0.70 V.[31,32a]

We attempted to synthesize sulfoxide complexes of Ru(III) via treatment of the Ru(II)–sulfoxide species with AgBF$_4$, and via reaction of [Ru(OEP)]$_2$[BF$_4$]$_2$ with sulfoxide, but have been unable to isolate pure complexes, although they undoubtedly exist. An *in situ* redox titration of Ru(OEP)(Et$_2$SO)$_2$ with AgBF$_4$ gave a final UV/vis spectrum (Figure 3a) very similar to those of the [Ru(OEP)(RR′S)$_2$][BF$_4$] complexes (cf. Figure 1a), suggesting formation of a Ru^{III} derivative. Figure 3b shows the ^{1}H-NMR spectrum of an *in situ* 1:8 mixture of [Ru(OEP)]$_2$[BF$_4$]$_2$ and dmso, in CD$_2$Cl$_2$ at 20 °C; this spectrum has several features similar to those seen in the corresponding [Ru(OEP)(dms)$_2$][BF$_4$] spectrum (see Experimental Section). However, the presence of two signals for the OEP methylenes now indicates that the complex is no longer symmetrical about the porphyrin plane. There are also several small signals, some of which can probably be assigned to another minor Ru(OEP) paramagnetic product. The presence of these extra signals complicates the assignment of any signals due to coordinated dmso; however, the signals at $\delta = 0.02$ and 10.20 each have

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the correct integration for one sulfoxide coordinated to the major Ru(III)−OEP species present. Furthermore, when the experiment was repeated using dmso-d_6, both these signals were absent from the resulting spectrum. On the basis of the ^{1}H-NMR evidence, the major species present is almost certainly [Ru^{III}(OEP)(dm*s*o)(dms*o*)][BF$_4$]; the signal at $\delta = 0.02$ is assigned to the S-bound dmso by comparison with the [Ru(OEP)(dms)$_2$][BF$_4$] system, while the signal at $\delta = 10.2$ is thus assigned to the O-bound dmso.

The cyclic voltammograms for the Ru(OEP)(RR'*S*O)$_2$ complexes (Figure 2b) also show evidence of a change in coordination on changing the metal oxidation state between II and III; the oxidation wave has a maximum current at 0.74 V, while the reduction maximum occurs at 0.53 V. The large peak to peak separation indicates that the complex being reduced is not the same one that was oxidized, but the shape of the CV does not change regardless of how many times the scan is repeated, which suggests that upon reduction the original complex is recovered intact. The data are consistent with the following plausible processes, exemplified for the dmso system:

$$\mathrm{Ru^{II}(OEP)(dm\textit{s}o)_2} \rightleftharpoons \mathrm{Ru^{III}(OEP)(dm\textit{s}o)_2^{+}} + e^- \quad (1)$$

$$\mathrm{Ru^{III}(OEP)(dm\textit{s}o)_2^{+}} \rightleftharpoons \mathrm{Ru^{III}(OEP)(dm\textit{s}o)(dms\textit{o})^{+}} \quad (2)$$

$$\mathrm{Ru^{III}(OEP)(dm\textit{s}o)(dms\textit{o})^{+}} + e^- \rightleftharpoons \mathrm{Ru^{II}(OEP)(dm\textit{s}o)(dms\textit{o})} \quad (3)$$

$$\mathrm{Ru^{II}(OEP)(dm\textit{s}o)(dms\textit{o})} \rightleftharpoons \mathrm{Ru^{II}(OEP)(dm\textit{s}o)_2} \quad (4)$$

(The reduction potentials for the couples shown in eqs 1 and 3 are ~0.74 and 0.53 V, respectively). Such a rearrangement of S-bound sulfoxide to the O-bound isomer in Ru(dmso) complexes after metal-centered oxidation has been observed previously by Scott and Taube for Ru^{II}(NH$_3$)$_5$(dm*s*o)$^{2+}$ in aqueous solutions.[36] The harder O-donor (*vs* S) is expected to favor Ru(III) relative to Ru(II). Of note, the reduction potential of 0.74 V for eq 1 is actually higher than the corresponding value reported for the Ru(OEP$^{+\bullet}$)(CO)/Ru(OEP)(CO) couple.[31,32a] It is possible that two S-bonded dmso ligands have sufficient π-acceptor character[7b,22,23] to stabilize Ru(II) sufficiently so that ring oxidation does occur initially and that internal electron transfer takes place after one of the sulfoxides rearranges to yield the O-bound isomer; i.e. the product of eq 1 and the reactant of eq 2 is Ru(OEP$^{+\bullet}$)(dm*s*o)$_2$. Such electron transfer upon modification of the coordination sphere (involving reversible addition and loss of CO) has been previously documented for ruthenium porphyrins.[32]

Both the Ru(OEP)L$_2$ complexes (L = dialkyl sulfide or sulfoxide) exhibit a second redox couple at around 1.3 V (Figure 2a,b). This was not further investigated, but previous studies in our laboratories have yielded evidence that the second oxidation of complexes such as Ru(OEP)(P^{n}Bu$_3$)$_2$ occurred at the ring at around 1.2 V, to yield the Ru^{III} π-cation radical.[32a] Figure 2c shows the CV for [Me$_4$N][Ru(OEP)(PhCOO)$_2$] with a redox couple of 0.23 V. As expected, the presence of two anionic ligands renders the complex much more easily oxidizable; in fact, oxidation of the bis(benzoato)ruthenium(III) species is as easy as the one-electron oxidation of the Ru^{II}(OEP)(RR'S)$_2$ complexes. This point is of significance in the O$_2$-oxidation work,[8a] which will be presented in future publications. Presumably, given the ease of oxidation, electron abstraction from Ru(OEP)(PhCOO)$_2^-$ takes place at the metal to generate Ru(IV) species. Corresponding reduction potentials for the related Ru(OEP)X$_2$ species (X = Cl, Br) occur at 0.40 and 0.42 V, respectively;[37] the 0.2 V difference relative to Ru(OEP)(PhCOO)$_2$ can be attributed to the stronger σ-basicity of benzoate relative to that of Cl$^-$ and Br$^-$.

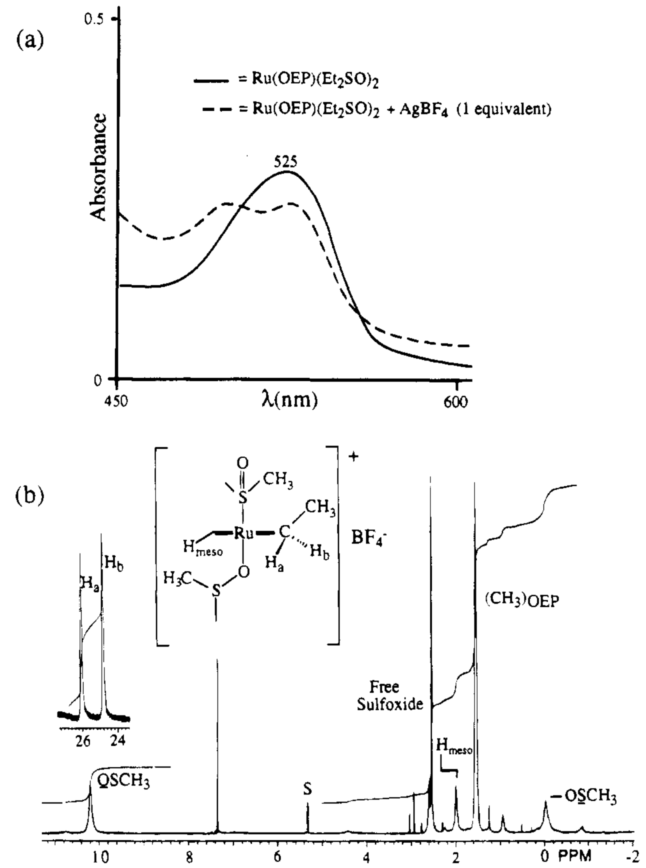

Figure 3. (a) Visible spectrum of a 1:1 mixture of Ru(OEP)(Et$_2$SO)$_2$ and AgBF$_4$ in CH$_2$Cl$_2$. (b) ^{1}H-NMR spectrum of a CD$_2$Cl$_2$ solution initially containing [Ru(OEP)]$_2$[BF$_4$]$_2$ and free dmso in approximately 1:8 ratio (S = solvent, T = 20 °C).

The signals in the paramagnetic ^{1}H-NMR spectra of [Ru(OEP)(RR'S)$_2$][BF$_4$] and [Me$_4$N][Ru(OEP)(PhCOO)$_2$] are shifted considerably from their characteristic diamagnetic positions. The magnitudes and directions of the observed paramagnetic shifts (from 0 to 20 ppm, with the methylene proton signals shifting downfield and the meso proton signals shifting upfield) are typical of those seen for Ru^{III}(OEP) low-spin complexes.[38-41] The magnetic susceptibilities of the complexes are comparable to those previously reported for other Ru^{III}(Por) complexes.[38-41]

The ^{1}H-NMR spectra of the Ru(III) complexes were generally assigned primarily based on the relative intensities of all the signals; however, the spectrum for [Ru(OEP)(decMS)$_2$][BF$_4$] (Figure 4) was more difficult to interpret. The porphyrin signals and the SCH$_3$ signals are assigned by analogy to the simpler systems, while the signal due to the thioether ^{10}CH$_3$ is unshifted relative to either that of the free ligand or of Ru(OEP)(decMS)$_2$.[7b] A peak at $\delta = 9.06$ is tentatively assigned to

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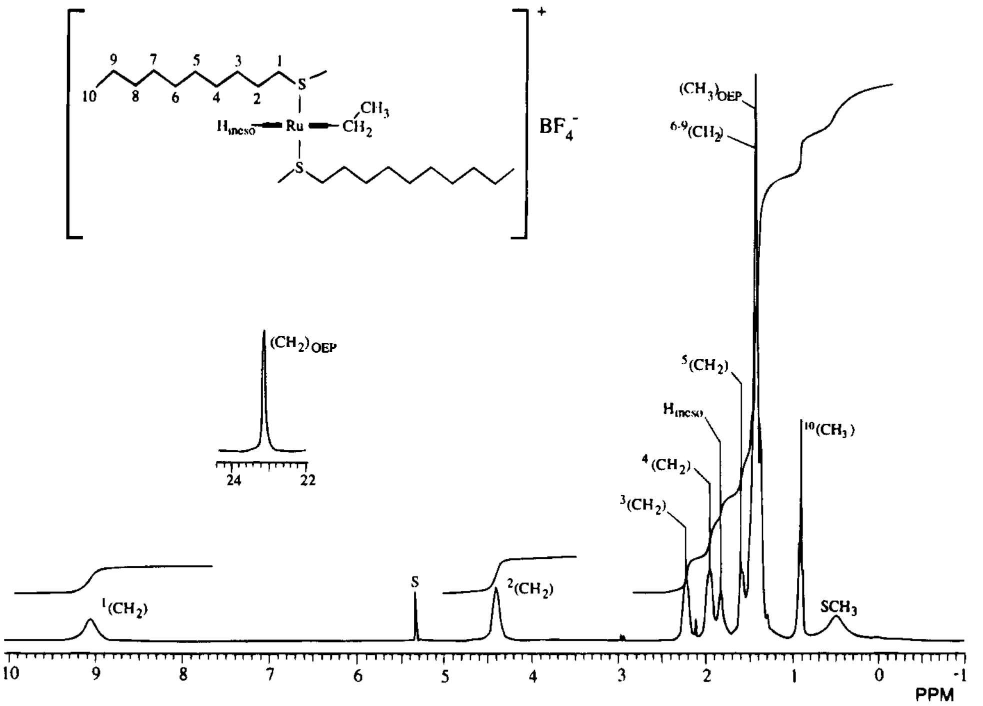

Figure 4. ^{1}H-NMR spectrum of [Ru(OEP)(decMS)$_2$][BF$_4$] in CD$_2$Cl$_2$, taken at 20.0 °C (S = solvent).

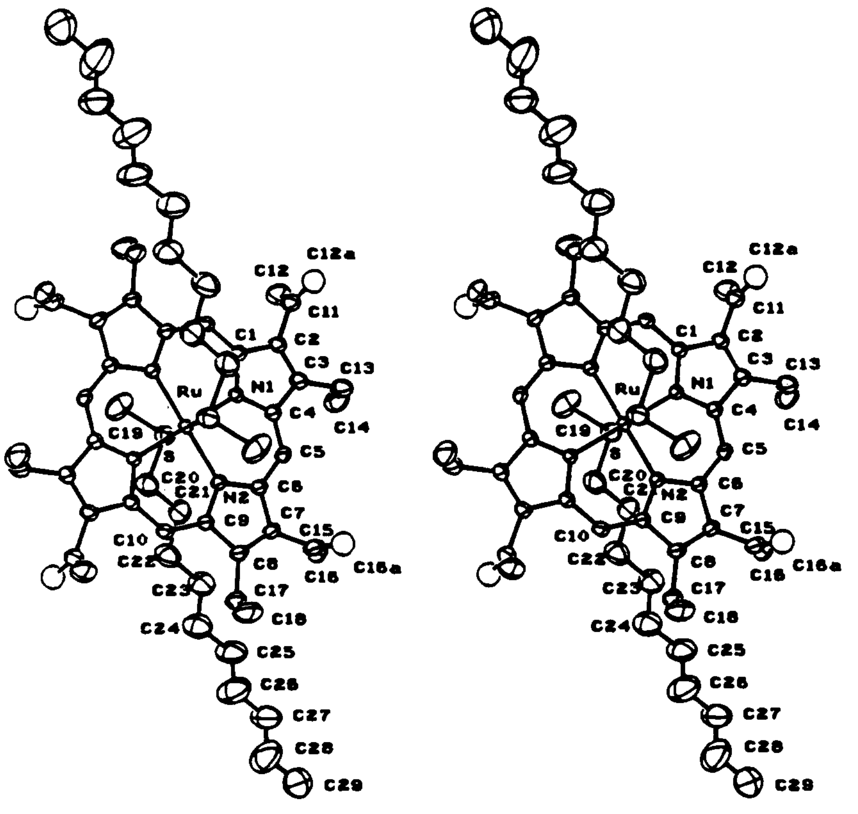

Figure 5. Molecular structure of [Ru(OEP)(decMS)$_2$][BF$_4$]. Thermal ellipsoids are drawn at the 20% probability level.

(^{1}CH$_2$), on the basis of its integration and the fact that it is the broadest of the unassigned signals. A series of progressively sharper signals at δ = 4.39, 2.22, 1.96, and 1.60 are assigned to (^{2}CH$_2$)−(^{5}CH$_2$); the last two actually show some fine structure. Finally, the signals for ($^{6-9}$CH$_2$) are buried beneath the porphyrin methyl signal, although a broad multiplet is just discernible at δ = 1.38.

Solid-State Structure of [Ru(OEP)(decMS)$_2$][BF$_4$]. The crystal structure of [Ru(OEP)(decMS)$_2$][BF$_4$] is shown in Figure 5, while Table 2 compares selected bond lengths and angles of the Ru^{III} complex with those of Ru(OEP)(decMS)$_2$.[7b] The differences in corresponding bond lengths between the two species are within about 0.020 Å, while the corresponding bond angles are within 2° of each other; the differences are not significant, especially since the structures were done at diverse temperatures. Our report on the structure of Ru(OEP)(decMS)$_2$ included a survey of crystal structures of Ru^{II}(OEP) complexes and of other complexes containing Ru−S bonds.[7b] It is clear that the change in oxidation state of the metal does not significantly affect the geometry of the Ru(OEP)(decMS)$_2$

moiety. Stynes and Ibers have reported that the Ru−N bond length in $Ru(NH_3)_6^{2+}$ is ~0.04 Å longer than the corresponding bond length in $Ru(NH_3)_6^{3+}$ and attributed the difference to increased electrostatic attraction between the metal and the ligands in the latter.[42] Both species are low-spin, and the oxidation involves removal of an electron from a nonbonding metal t_{2g} orbital. The two $Ru(OEP)(decMS)_2$ complexes have approximately D_{4h} symmetry, and the oxidation state change probably involves removal of an electron from a metal e_g orbital.[17] The metal e_g orbitals of ruthenium porphyrins are capable of some bonding interaction with e_g* orbitals in the porphyrin[17] and probably also interact to some degree with empty d orbitals on the axial ligand. Thus for ruthenium porphyrins, removal of an electron from a metal e_g orbital would tend to weaken any back-bonding interaction between the metal and the ligand, and this would tend to counter the increased electrostatic attraction in the higher oxidation state.

Summary

This paper described the synthesis and characterization of several Ru^{II} and Ru^{III} complexes. The $Ru^{III}(OEP)(RR'S)_2$ complexes are postulated intermediates in the stoichiometric O_2 oxidation of $Ru(OEP)(RR'S)_2$ complexes in benzene, toluene, or CH_2Cl_2 solutions containing benzoic acid, while the $Ru(OEP)(RR'SO)_2$ complexes are the final products of this oxidation.[8] These species also form part of a catalytic cycle in which free dialkyl sulfides are oxidized by O_2 to the corresponding sulfoxides.[8] While $[Me_4N][Ru(OEP)(PhCOO)_2]$ is probably not involved in the oxidations, its reactivity provides valuable insights into the oxidation reactions.[8]

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for financial support and Johnson Matthey Ltd. and Colonial Metals Inc. for the loan of Ru; Dr. A. Raitsimring, at the University of Arizona, kindly did the ESR measurements for us.

Supplementary Material Available: Tables of crystallographic data collection procedures and parameters, complete atomic coordinates and thermal parameters, bond distances and angles, torsion angles, and least-squares planes (23 pages). Ordering information is given on any current masthead page.

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