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Synthesis and Characterization of (Bipyridine)(terpyridine)(chalcogenoether)ruthenium(II) Complexes. Kinetics and Mechanism of the Hydrogen Peroxide Oxidation of $[(bpy)(tpy)RuS(CH_3)_2]^{2+}$ to $[(bpy)(tpy)RuS(O)(CH_3)_2]^{2+}$. Kinetics of the Aquation of $[(bpy)(tpy)RuS(O)(CH_3)_2]^{2+}$[1]

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A series of chalcogenoether complexes of the general formula $[(bpy)(tpy)Ru^{II}L]^{2+}$ (bpy represents bipyridine; tpy represents terpyridine; L represents $S(CH_3)_2$, $Se(CH_3)_2$, $Te(CH_3)_2$, $S(CH_3)C_6H_5$, $CH_3SCH_2CH_2SCH_3$, 1,4-dithiacyclohexane, 1,5-dithiacyclooctane, phenothiazine, 10-methylphenothiazine, thianthrene) has been synthesized. Individual complexes have been characterized by elemental analyses, visible–UV spectrophotometry, and cyclic voltammetry. The chalcogenoether ligands stabilize the Ru(II) oxidation state relative to the Ru(III) state, presumably via π back-bonding, making the $[(bpy)(tpy)Ru^{III}L]^{3+}$ complexes reasonably strong oxidants. Hydrogen peroxide oxidation of $[(bpy)(tpy)Ru^{II}S(CH_3)_2]^{2+}$ cleanly yields the S-bonded dimethyl sulfoxide complex $[(bpy)(tpy)Ru^{II}S(O)(CH_3)_2]^{2+}$. The rate law for this process has the unusual acid dependence, rate = $[\text{complex}][H_2O_2]\{ab[H^+]/(1 + b[H^+])\}$, suggesting the participation of a bimolecular intermediate that can be reversibly protonated. The rate parameters and activation parameters governing this process are consistent with literature data on H_2O_2 oxidation of sulfur-containing nucleophiles, implying that the $[(bpy)(tpy)RuS(CH_3)_2]\cdot H_2O_2^{2+}$ reaction intermediate is generated via nucleophilic attack of the coordinated sulfur atom on the O–O bond of H_2O_2. The dimethyl sulfoxide product complex undergoes aquation at a specific rate of $(1.46 \pm 0.05) \times 10^{-5}\ s^{-1}$ at 50 °C ($I = 1.00$ M (LiCl)), independent of $[H^+]$. The parental thioether complex does not aquate at all under these conditions, reflecting the poorer ligating ability and increased steric requirements of the dimethyl sulfoxide ligand.

Introduction

The nucleophilicity of coordinated sulfur is essential in determining its reactivity toward numerous redox reagents and electrophiles. In this context the reactions of coordinated thiols (RS^-) with a wide variety of reagents have been studied in detail.[2-8] These reactions are related by a common mechanism, i.e. nucleophilic attack by the coordinated thiolate sulfur atom on the electrophilic substrate.[2] The reactivity of coordinated thioethers (RSR′) has been much less studied, presumably because of the inherent lower reactivity of these ligands, which results from greater steric hindrance at the sulfur atom and concomitant lower nucleophilicity. For example, the (thiolato)cobalt(III) complex $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ reacts with H_2O_2 at a specific rate of $3.20\ M^{-1}\ s^{-1}$ (25 °C, $\mu = [H^+] = 1.00$ M),[4] but the related thioether complex $[(en)_2Co(S(CH_3)CH_2CH_2NH_2)]^{3+}$ does not detectably react with H_2O_2 under these conditions.[9]

However, contrary to this characteristic unreactivity of coordinated thioethers, the sulfur atom of the ruthenium(II) thioether complex $[(bpy)(tpy)RuS(CH_3)_2]^{2+}$[10] is readily oxidized by reagents such as H_2O_2, IO_4^-, and $S_2O_8^{2-}$ (vide infra). The nucleophilicity of the coordinated sulfur atom is undoubtedly an important factor in determining the reactivity of the coordinated thioether ligand toward these oxidants. Thus, in order to understand more fully the influence of the central metal on the nucleophilicity of coordinated sulfur, we have synthesized a series of $[(bpy)(tpy)Ru(\text{chalcogenoether})]^{2+}$ complexes and have investigated the kinetics of the hydrogen peroxide oxidation of $[(bpy)(tpy)RuS(CH_3)_2]^{2+}$. The results of this study are reported herein, along with comparisons to the rates of H_2O_2 oxidation of other sulfur-containing nucleophiles. The spectrophotometric and electrochemical characterizations of the $[(bpy)(tpy)Ru(\text{chalcogenoether})]^{3+}$ complexes, as well as kinetic measurements on the aquation of $[(bpy)(tpy)RuS(O)(CH_3)_2]^{2+}$, are also reported.

Experimental Section

Materials. All common chemicals were reagent grade and were used as received unless otherwise noted. Acetone and dimethyl sulfoxide used in synthetic procedures were stored over 3- or 4-Å molecular sieves. Starting materials were obtained from several sources: dimethyl sulfide ($S(CH_3)_2$), thioanisole ($CH_3SC_6H_5$), 1,4-dithiane ($\overline{SCH_2CH_2SCH_2CH_2}$), 1,3-dimercaptopropane ($HSCH_2CH_2CH_2SH$), 2,2′-bipyridine, and $RuCl_3\cdot 3H_2O$ were from Aldrich Chemical Co.; dimethyl selenide ($Se(CH_3)_2$) and dimethyl telluride ($Te(CH_3)_2$) were from Alfa; 1,3-diiodopropane ($ICH_2CH_2CH_2I$) was from Eastman Chemical; 1,2-bis(methylthio)ethane ($CH_3SCH_2CH_2SCH_3$) was from Wateree Research; 2,2′:6,2″-terpyridine was obtained from both Alfa and Sigma.

Commercially available tank nitrogen or argon, used in synthetic and kinetic procedures, was deoxygenated and equilibrated with water by passing a stream through two chromous ion scrubbing towers containing ca. 250 mL of 0.1 M chromous ion in 1 M perchloric acid and then through distilled water. The chromium was kept in its reduced form with ca. 100 g of 2% amalgamated zinc. For nonaqueous preparations and electrochemical experiments, deoxygenated argon or nitrogen was passed through a scrubbing tower containing the same solvent used in the experiment, stored over 3-Å molecular sieves.

Sephadex SP C-25 strong-acid cation-exchange resin (sodium form) was prepared and stored as recommended by the manufacturer (Pharmacia). Activated alumina (Fisher) was dried at 110 °C for >24 h. Ammonium peroxydisulfate, $(NH_4)_2S_2O_8$, was recrystallized from water. Tetraethylammonium perchlorate (TEAP) used in electrochemical experiments was obtained from Eastman Chemical and was recrystallized twice from water and then dried at 110 °C for 24 h. Spectral grade acetonitrile was used for spectrophotometric and electrochemical measurements.

G. F. Smith doubly vacuum distilled 70–72% perchloric acid was used for kinetic experiments. Aqueous $LiClO_4$ solutions used in kinetic experiments were prepared by neutralization of Baker Ultrex lithium carbonate using doubly vacuum-distilled 70–72% $HClO_4$ as previously described.[11] Stock hydrochloric acid solutions were prepared from Baker Ultrex concentrated HCl by dilution with triply distilled water. Reagent grade lithium chloride was recrystallized from water and dried at 70 °C in vacuo. Aqueous hydrogen peroxide stock solutions were prepared from unstabilized 30% H_2O_2 (Fisher Scientific), stored in the dark at ca. 5 °C, and standardized just prior to use.

1,5-Dithiacyclooctane, $\overline{SCH_2CH_2CH_2SCH_2CH_2CH_2}$. This ligand was

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Table I. Elemental Analyses for (bpy)(tpy)Ru^{II} Chalcogenoether Complexes

complex		anal. % S	anal. % N	anal. % P	anal. % Cl
$[(bpy)(tpy)RuS(CH_3)_2](PF_6)_2$	calcd	3.81	8.31	7.35	
	found	3.78	8.29	6.98	
$[(bpy)(tpy)RuS(CH_3)C_6H_5](PF_6)_2$	calcd	3.54	7.74	6.85	
	found	3.40	7.77	6.47	
$[(bpy)(tpy)RuSe(CH_3)_2](PF_6)_2$	calcd		7.88	6.96	
	found		8.09	7.02	
$[(bpy)(tpy)RuTe(CH_3)_2](PF_6)_2$	calcd		7.47	6.60	
	found		7.86	6.67	
$[(bpy)(tpy)RuSCH_2CH_2SCH_2CH_2](ClO_4)_2$	calcd	7.92	8.65		8.76
	found	7.31	9.25		8.94
$[(bpy)(tpy)RuSCH_2CH_2CH_2SCH_2CH_2CH_2](PF_6)_2$	calcd	6.90	7.54	6.67	
	found	7.16	8.00	7.04	
$[(bpy)(tpy)Ru(thianthrene)](PF_6)_2$	calcd	6.43	7.03	6.21	
	found	6.24	7.00	6.07	
$[(bpy)(tpy)Ru(phenothiazine)](PF_6)_2$[a]	calcd	3.27	8.58	6.32	
	found	2.98	8.12	6.09	
$[(bpy)(tpy)Ru(10\text{-methylphenothiazine})](PF_6)_2$	calcd	3.23	8.46	6.23	
	found	3.52	8.32	5.97	

[a] Calcd: C, 45.36; H, 2.69. Found: C, 44.14; H, 2.96.

prepared by a modification of literature preparations.[12,13] To 500 mL of deaerated absolute ethanol was added 32.6 g of Cs_2CO_3 (0.10 mmol), and the mixture was stirred at 50 °C for 45 min under argon. A solution of 10.0 mL of 1,3-dimercaptopropane (0.10 mol) and 11.5 mL of 1,3-diiodopropane (0.10 mol) in 75 mL of absolute ethanol was added dropwise by means of a pressure-equalizing addition funnel over a period of 7 h under argon while the temperature was maintained at 50 °C. The reaction was stirred for an additional 1 h after the addition was complete and then allowed to cool to room temperature. The precipitated CsI was filtered by gravity, and the ethanol was removed in vacuo. The residue was taken up in diethyl ether, and the ether layer was shaken with three 25-mL portions of 10% K_2CO_3. The ether layer was then dried over anhydrous $MgSO_4$. Evaporation of the ether yielded a viscous white liquid. ^1H NMR (60 MHz, CCl_4): δ 2.3–1.7 (m, 4 H, $>CH_2$), 3.0–2.4 (m, 8 H, $-SCH_2-$). Mass spectrum (70 eV): *m/e* 148 (M^+).

Trichloro(2,2′:6′,2″-terpyridine)ruthenium(III), (tpy)$RuCl_3$. This complex was prepared as described.[14]

Chloro(2,2′-bipyridine)(2,2′:6′,2″-terpyridine)ruthenium(II) Hexafluorophosphate, [(bpy)(tpy)RuCl]PF_6. This complex was prepared from (tpy)$RuCl_3$ and 2,2′-bipyridine[15,16] and was purified by column chromatography (alumina, $CH_3CN/C_6H_5CH_3$ eluents) followed by precipitation from acetone/diethyl ether. Visible (CH_3CN): λ_{max} 504 nm. Cyclic voltammetry (CH_3CN, 0.10 M TEAP, Pt vs. SSCE): $E_{1/2} = 0.79$ V.

(2,2′-Bipyridine)(2,2′:6′,2″-terpyridine)(chalcogenoether)ruthenium(II) Hexafluorophosphate, [(bpy)(tpy)RuL]$(PF_6)_2$ (L = $S(CH_3)_2$, $CH_3SC_6H_5$, $Se(CH_3)_2$, $Te(CH_3)_2$, $CH_3SCH_2CH_2SCH_3$, $SCH_2CH_2SCH_2CH_2$, $SCH_2CH_2CH_2SCH_2CH_2CH_2$, Phenothiazine, 10-Methylphenothiazine, Thianthrene). Although initially the $S(CH_3)_2$, $CH_3SC_6H_5$, and $CH_3SCH_2CH_2SCH_3$ complexes were prepared by refluxing 0.200 g of [(bpy)(tpy)RuCl]PF_6 with a 50-fold excess of the appropriate ligand in 30 mL of deaerated 50% aqueous ethanol for >10 h, a more general procedure was used in subsequent syntheses. To 50 mL of deaerated acetone were added 0.200 g of [(bpy)(tpy)RuCl]PF_6 (0.30 mmol) and a slight molar excess of $AgClO_4$, and the resulting solution was heated with stirring at 55 °C for 2–3 h under argon. After the mixture was cooled to room temperature, a 10- to 40-fold excess of ligand was added, and the solution was stirred for 16–24 h under argon (an alternative method involves refluxing this solution for 3 h). The precipitated AgCl was removed by filtration, 10 mL of saturated aqueous NH_4PF_6 (or $NaClO_4$ for preparation of perchlorate salts) and ~300 mL of diethyl ether were added to the filtrate, and the resulting mixture was stirred for ca. 15 min. More H_2O was added, as needed, to effect separation of the aqueous and ether layers. The ether layer was removed by decantation and ~100 mL of H_2O was added to the aqueous layer that was then stirred for ca. 10 min. The orange precipitate was filtered, washed successively with a small amount of H_2O and then a copious amount of ether, and then air-dried. Each complex was purified by column chromatography (alumina, $CH_3CN/C_6H_5CH_3$ eluents) and reprecipitated from acetone solutions by dropwise addition to ~300 mL of stirring ether (the 1,5-dithiacyclooctane complex was reprecipitated by dropwise addition, in three portions, to ~300 mL of standing ether to avoid coagulation of the precipitate). Alternatively, the $S(CH_3)_2$ and $CH_3SC_6H_5$ complexes were also isolated from the filtered reaction solutions as the Cl^- salts by addition of excess solid tetrabutylammonium chloride. Purification of these salts was effected by elution from a Sephadex SP C-25 column using 0.1 M NaCl and then 0.15 M NaCl as eluents and finally precipitation of the PF_6^- salts by the addition of excess solid NH_4PF_6.

Table II. Electrochemical Parameters for Selected (bpy)(tpy)Ru^{II} Complexes As Measured by Cyclic Voltammetry[a,b]

complex	$E_{1/2}$, V oxidn	$E_{1/2}$, V redn	
$(bpy)(tpy)RuS(CH_3)_2{}^{2+}$	1.32	−1.24	−1.56
$(bpy)(tpy)RuS(CH_3)C_6H_5{}^{2+}$	1.36	−1.26	−1.55
$(bpy)(tpy)RuSe(CH_3)_2{}^{2+}$	1.30	−1.26	−1.55
$(bpy)(tpy)RuTe(CH_3)_2{}^{2+}$	1.26	−1.27	−1.54
$(bpy)(tpy)Ru(SCH_2CH_2SCH_2CH_2)^{2+}$	1.36	−1.22	−1.51
$(bpy)(tpy)RuCl^+$	0.79		
$(bpy)(tpy)RuNH_3{}^{2+}$[c]	1.02		

[a] Conditions: 0.1 M TEAP in CH_3CN vs. SSCE unless otherwise noted. [b] This work unless otherwise noted. [c] Conditions: 0.2 M $(CH_3CH_2CH_2CH_2)_4NPF_6$ in propylene carbonate (ref 65).

Chloride salts were prepared by adding a concentrated solution of tetrabutylammonium chloride in acetone to an acetone solution of the PF_6^- salts of the purified complexes.

Relevant analytical, electrochemical, and spectrophotometric data are given in Tables I–III, respectively.

(2,2′-Bipyridine)(2,2′:6′,2″-terpyridine)(dimethyl sulfoxide-*S*)ruthenium(II) Hexafluorophosphate, [(bpy)(tpy)RuS(O)$(CH_3)_2$]$(PF_6)_2$. (1) Substitution Method: A 0.302-g sample of [(bpy)(tpy)RuCl]PF_6 (0.45 mmol) and 0.064 g of $AgPF_6$ (0.45 mmol) were added to 30 mL of deaerated dimethyl sulfoxide, and the mixture was heated with stirring at ca. 80 °C under argon for 2 days. The reaction solution was allowed to cool to room temperature, and the precipitated AgCl was removed by filtration. The filtrate was added dropwise to a large excess of stirring diethyl ether. The resulting yellow precipitate was purified and reprecipitated as described above for the chalcogenoether complexes. Anal. Calcd for $RuC_{27}H_{26}N_5OSP_2F_{12}$: N, 8.16; P, 7.21; S, 3.73. Found: N, 8.16; P, 6.75; S, 3.96. Visible–UV (CH_3CN) λ_{max}, nm (ϵ_{max}, M^{-1} cm^{-1}): 412 (7100), 330 (24 000), 314 sh (22 000), 294 sh (30 000), 282 (41 000), 272 sh (40 000), 240 (23 000). Cyclic voltammetry (CH_3CN, 0.10 M TEAP, glassy carbon vs. SSCE): $E_{p,a} = 1.63$ V, $E_{p,c} = 1.01$ V. IR (KBr, Cl^- salt): $\nu_{S=O} = 1100$ cm^{-1}. The ClO_4^- salt was prepared similarly but

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Table III. Visible and Ultraviolet Spectrophotometric Parameters for $(bpy)(tpy)Ru^{II}$ Chalcogen Complexes in Acetonitrile

complex	λ_{max}, nm ($10^{-3}\epsilon_{max}$, M^{-1} cm^{-1})
$(bpy)(tpy)RuS(CH_3)_2{}^{2+}$	454 (8.4), 330 sh (15), 305 (35), 285 (37), 274 sh (30), 254 (21), 241 (23), 230 sh (24), 207 sh (50)
$(bpy)(tpy)RuS(CH_3)C_6H_5{}^{2+}$	453 (8.8), 330 sh (16), 305 (35), 285 (39), 272 sh (30), 252 sh (26), 240 sh (30), 230 (32), 206 sh (60)
$(bpy)(tpy)RuSe(CH_3)_2{}^{2+}$	454 (9.1), 330 sh (13), 307 (36), 285 (41), 272 sh (30), 254 (21), 241 (24), 231 sh (24), 206 sh (50)
$(bpy)(tpy)RuTe(CH_3)_2{}^{2+}$	457 (9.5), 330 sh (15), 307 (40), 288 (39), 281 sh (37), 271 sh (32), 254 sh (21), 242 sh (26), 219 sh (44)
$(bpy)(tpy)RuS(O)(CH_3)_2{}^{2+}$	412 (7.1), 330 (24), 314 sh (22), 294 sh (30), 282 (41), 272 sh (40), 240 (23)
$(bpy)(tpy)RuS(CH_3)CH_2CH_2SCH_3{}^{2+}$	453 (8.3), 330 sh (15), 304 (36), 283 (39), 272 sh (31), 253 (22), 240 (25), 229 sh (25)
$(bpy)(tpy)Ru\overline{SCH_2CH_2SCH_2CH_2}{}^{2+}$	453 (9), 332 sh (15), 305 (38), 284 (42), 272 sh (30), 253 sh (23), 241 (28), 230 sh (28)
$(bpy)(tpy)Ru\overline{SCH_2CH_2CH_2SCH_2CH_2CH_2}{}^{2+}$	454 (8.8), 330 sh (15), 305 (35), 284 (39), 272 sh (30), 253 sh (20), 240 (24), 230 sh (25)
$(bpy)(tpy)Ru(phenothiazine)^{2+}$	452 (8.8), 430 sh (8.3), 331 sh (18), 303 (38), 285 (46), 272 sh (35), 254 sh (27), 240 sh (33), 215 sh (34)
$(bpy)(tpy)Ru(10\text{-}methylphenothiazine)^{2+}$	455 sh (7.5), 435 (7.7), 331 sh (19), 306 sh (34), 285 (46), 273 sh (36), 254 sh (27), 240 sh (37), 219 sh (29)
$(bpy)(tpy)Ru(thianthrene)^{2+}$	453 (8), 424 sh (7), 330 sh (14), 302 sh (36), 284 (44), 272 sh (36), 254 sh (31), 239 sh (41), 229 sh (44)

was precipitated by the addition of aqueous $NaClO_4$. Anal. Calcd for $RuC_{27}H_{26}N_5O_9SCl_2$: N, 9.13; Cl, 9.24; S, 4.18. Found: N, 9.21; Cl, 9.13; S, 4.09. Visible–UV (CH_3CN) λ_{max}, nm (ϵ_{max}, M^{-1} cm^{-1}): 410 (7300), 329 (24 000), 314 sh (22 000), 292 sh (40 000), 281 (42 000), 271 sh (40 000), 239 (23 000).

(2) Oxidation Method: A 0.30-g sample of $[(bpy)(tpy)RuS(CH_3)_2]Cl_2$ was dissolved in ca. 200 mL of H_2O, and to the resulting solution was added 2.3 g of $(NH_4)_2S_2O_8$ in several portions over 10 min. This reaction mixture was stirred for 4 h. A large excess of solid NH_4PF_6 was added, and the reaction mixture was stirred for ca. 5 min. The resulting yellow precipitate was removed by filtration and washed with a small amount of water and then with copious amounts of diethyl ether, and the solid was dried over $CaCl_2$ in vacuo. The product was reprecipitated from acetone by the addition of diethyl ether. Visible–UV (CH_3CN): ν_{max}, nm (ϵ_{max}, M^{-1} (cm^{-1})): 412 (7000), 330 (23 000), 314 sh (22 000), 294 sh (30 000), 282 (41 000), 272 sh (40 000), 240 (23 000). Cyclic voltammetry (CH_3CN, 0.1 M TEAP, glassy carbon vs. SSCE): $E_{p,a} = 1.63$ V, $E_{p,c} = 1.01$ V. IR (KBr, Cl^- salt): $\nu_{S=O} = 1100$ cm^{-1}.

The sulfoxide complexes from both of the above preparations were used interchangeably in subsequent studies.

(2,2′-Bipyridine)(2,2′:6′,2″-terpyridine)aquoruthenium(II) Perchlorate, $[(bpy)(tpy)RuOH_2](ClO_4)_2$. This complex was prepared by aquation of $[(bpy)(tpy)RuCl]PF_6$ on a Sephadex SP C-25 column (sodium form) according to the procedure reported for the preparation of the analogous $[(bpy)_2(py)RuOH_2](ClO_4)_2$ complex.[17] Visible (H_2O): $\lambda_{max} = 475$ nm. Cyclic voltammetry (propylene carbonate, 0.1 M TEAP, glassy carbon vs. SSCE): $E_{1/2} = 1.10$ V.

Equipment. All visible and ultraviolet spectra were obtained on a Cary 14 or Cary 210 recording spectrophotometer. Kinetic experiments were monitored on a Cary 118B recording spectrophotometer equipped with a thermostated cell compartment. Temperature within the cell compartment was monitored with a USC Model 581C digital thermometer (which had been calibrated against a NBS-certified mercury thermometer) and was maintained to ±0.1 °C, except at 65.0 °C where it was maintained to ±0.2 °C. For slower kinetic experiments an automatic sample changer was used to sequentially monitor up to five reaction solutions. Although for some experiments the raw data were recorded on the strip chart recorder of the Cary 118B spectrophotometer, most data were recorded in digital form with an interfaced Hewlett-Packard 5105A thermal printer. For most kinetic experiments, the digital OD_t–time data were also collected directly from the Cary 118B spectrophotometer and stored with the use of a UNC-UC microcomputer of local construction. The microcomputer conducted a preliminary linear least-squares analysis of ln ($OD_t - OD_\infty$) vs. time to yield initial estimates of k_{obsd} and the quantity ($OD_\infty - OD_0$). All other computer calculations were performed with an Amdahl 470/V6-II or 470/V7A computer located at the University of Cincinnati.

Infrared spectra were obtained using a Perkin-Elmer 599 IR spectrophotometer.

Aquation studies were conducted in a Haake FT constant-temperature bath maintained to ±0.1 °C.

Electrochemical measurements were conducted on a Bioanalytical Systems CV-1A or CV-1B sweep generator and potentiostat and were monitored with a Kiethley Model 178 digital multimeter and a Houston Instruments Model 100 X-Y recorder. A standard three-electrode electrochemical cell, consisting of working electrode, saturated sodium chloride calomel reference electrode, and platinum-wire auxiliary electrode, was used for cyclic voltammetry experiments.

Analyses. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN, or Guelph Chemical Laboratories, Ltd., Guelph, Ontario, Canada. Aqueous hydrogen peroxide stock solutions were standardized cerimetrically to a ferroin end point.

Procedures. Visible and UV spectra were obtained in spectral grade acetonitrile while electorchemical measurements were conducted in Burdick and Jackson spectral grade acetonitrile or propylene carbonate with 0.1 M TEAP as the supporting electrolyte. Cyclic voltammograms were recorded at ambient temperature at a glassy-carbon or platinum electrode (as noted) vs. a saturated sodium chloride calomel electrode (SSCE). Reported potentials are not corrected for junction potentials.

Oxidation Kinetics. Hydrogen peroxide oxidation was conducted in aqueous perchloric acid solutions maintained at a constant ionic strength of 1.00 ± 0.01 or 2.00 ± 0.02 M with $LiClO_4$, with a pseudo-first-order excess of H_2O_2. Reactions of $[(bpy)(tpy)RuS(CH_3)_2]^{2+}$ were usually monitored at the 454-nm absorption maximum of the thioether complex. In replicate kinetic experiments, no significant dependence was noted when the kinetics were monitored at the 400-nm absorption maximum of the product sulfoxide complex, $[(bpy)(tpy)RuS(O)(CH_3)_2]^{2+}$. Likewise, there was no significant difference in k_{obsd} values when the reaction solution was deaerated with argon prior to the start of the reaction, and so most reactions were conducted under aerobic conditions. The initial complex ion concentration was in the range 0.05–0.1 mM.

Reactions were initiated by syringe injection (through a platinum needle) of 0.02 mL of a (5–10) × 10^{-3} M $[(bpy)(tpy)RuS(CH_3)_2]Cl_2$ solution in water into a quartz spectrophotometric cell capped with a rubber septum cap. Each cell contained a 2.00-mL aliquot of an aqueous solution of H_2O_2, $HClO_4$, and $LiClO_4$ that had been temperature equilibrated in the thermostated cell compartment of the spectrophotometer.

In general, kinetic experiments were monitored for over 4 half-lives.

Aquation Kinetics. Aquation kinetic experiments were conducted in aqueous hydrochloric acid solutions maintained at a constant ionic strength of 1.00 ± 0.01 M with LiCl. Aquation reactions of $[(bpy)(tpy)RuS(O)(CH_3)_2]Cl_2$ were monitored at the 398-nm absorption maximum of the sulfoxide complex or at the 481-nm maximum of $[(bpy)(tpy)RuOH_2]^{2+}$ with no significant dependence on monitoring wavelength. Initial complex ion concentrations were in the range 0.05–0.10 mM.

Solutions of the sulfoxide comple were added to septum-capped test tubes and deaerated under a stream of argon. The reaction solutions were then placed in a constant-temperature bath at 50.0 ± 0.1 °C. Individual test tubes were removed periodically and rapidly cooled to room temperature, and values of OD_t were determined spectrophotometrically at ambient temperature against an appropriate blank.

Data Analyses. Values of k_{obsd} (and its associated standard deviation $\sigma_{k_{obsd}}$), OD_0, and OD_∞ that best fit the observed OD_t–t data within the first-order rate expression (eq 1) were calculated by using a standard

$$OD_t = OD_\infty - (OD_\infty - OD_0)e^{-k_{obsd}t} \qquad (1)$$

nonlinear least-squares analysis.[18] A minimum of 20 OD_t–t data points

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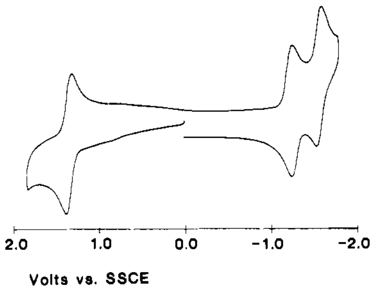


Figure 1. Cyclic voltammogram of $[(bpy)(tpy)RuS(CH_3)_2]^{2+}$. Conditions: 0.1 M TEAP in CH_3CN, glassy-carbon electrode vs. SSCE, ambient temperature, 200 mV s^{-1} scan rate.

were used in each calculation. Values of the second-order rate constant, k_2, and its associated standard deviation, σ_{k_2}, were calculated either by linear least-squares analysis of k_{obsd}–[reagent] data or, more usually, by averaging replicate values of k_{obsd}/[reagent]. In all calculations, each value of k_{obsd} was weighted by $(1/\sigma_{k_{obsd}}{}^2)$.

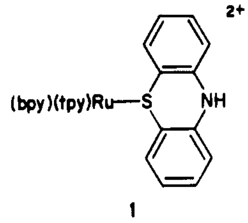
Activation parameters were calculated within the Eyring formalism by a nonlinear least-squares analysis.[18]

Results

Characterization. The ruthenium(II) complexes investigated in this work are characterized by (1) the methods of preparation, (2) satisfactory elemental analyses (see Experimental Section and Table I), (3) cyclic voltammetric parameters (see Experimental Section and Table II), and (4) visible–UV spectra (see Experimental Section and Table III).

Results from cyclic voltammetry experiments on various Ru(II) complexes are listed in Table II. Peak potential separations between anodic and cathodic waves, $E_{p,a} - E_{p,c}$, vary between 60 and 100 mV and are virtually independent of the scan rate. These peak separations are generally larger than the ideal Nernstian value of 59 mV but are commonly observed for complexes of this type[19,20] due to solution resistance.[20] Plots of peak current vs. the square root of the scan rate are linear, indicating that diffusion-controlled redox processes are occurring at the electrode. Where easily measured (i.e., where not complicated by other redox reactions), the ratios of cathodic to anodic peak currents, $i_{p,c}/i_{p,a}$, for the Ru(II)/Ru(III) redox couple range from 0.95 to 1.00. The cyclic voltammogram of $[(bpy)(tpy)RuS(CH_3)_2]^{2+}$ (Figure 1) is typical for the simple thioether complexes.

Absorption spectra of some Ru(II) complexes in CH_3CN are collected in Table III. The spectra of most of the complexes feature a single, broad maximum in the visible region and a series of UV peaks. The visible–UV spectra of $[(bpy)(tpy)Ru(phenothiazine)]^{2+}$ (**1**) and $[(bpy)(tpy)Ru(10\text{-methylphenothiazine})]^{2+}$ (**2**) are similar to that of $[(bpy)(tpy)Ru(thianthrene)]^{2+}$ (**3**) in which the ligating atom is unambiguously assigned as sulfur. Thus, the phenothiazine ligands are apparently coordinated through the sulfur atom rather than the nitrogen atom. Supporting this assignment, an attempt to prepare the the $[(bpy)(tpy)Ru(carbazole)]^{2+}$ complex (**4**) by the same method used for the thianthrene and phenothiazine complexes was unsuccessful.



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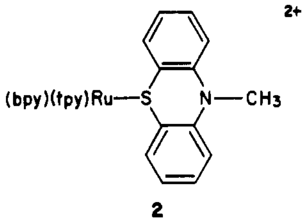

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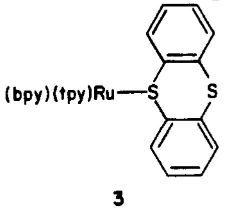

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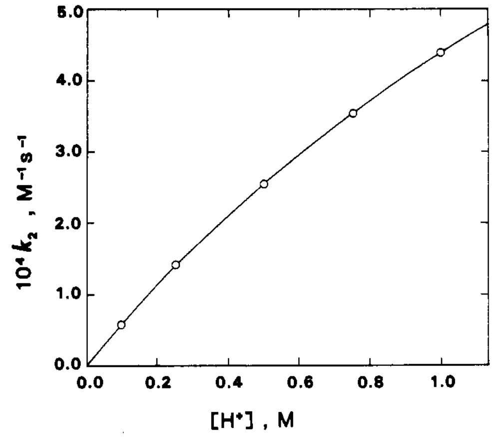
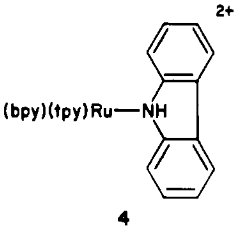


Figure 2. $[H^+]$ dependence of the reaction of $[(bpy)(tpy)RuS(CH_3)_2]^{2+}$ with H_2O_2.



4

Sulfoxides are ambidentate ligands that may coordinate through either the oxygen or sulfur atoms. The IR spectrum of $[(bpy)(tpy)RuS(O)(CH_3)_2]Cl_2$ has a peak at 1100 cm^{-1} not observed in the spectrum of $[(bpy)(tpy)RuS(CH_3)_2]Cl_2$; this peak is thus assigned to a S=O stretching mode. This peak is situated between the ranges of S=O stretches usually observed for S-bonded and O-bonded sulfoxide ligands; values of $\nu_{S=O}$ for sulfur-bound dimethyl sulfoxide complexes are generally in the range 1120–1160 cm^{-1} while those for oxygen-bound sulfoxide complexes vary from 900 to 935 cm^{-1}.[21-23] However, the S=O stretching frequencies for S-bound sulfoxide ligands in various Ru(II) dimethyl sulfoxide complexes are somewhat lower than those reported for other S-bonded sulfoxide complexes,[21-23] ranging from 1045 cm^{-1} for $[(NH_3)_5RuS(O)(CH_3)_2]^{2+}$[24] to ca. 1100 cm^{-1} for some mixed chloride/dimethyl sulfoxide Ru(II) complexes[25-27] as well as $[Ru((CH_3)_2SO)_6]^{2+}$.[28] Single-crystal X-ray structure determinations of $[(NH_3)_5RuS(O)CH_3)_2]^{2+}$,[29] *fac*-$[RuCl_3(S(O)(CH_3)_2)_3]^-$,[25] $RuCl_2((CH_3)_2SO)_4$,[30] and $[Ru((CH_3)_2SO)_6]^{2+}$[28] demonstrate that Ru(II) bonds to sulfoxides preferentially through the sulfur atom, especially when the ligand trans to the sulfoxide ligand is "hard". Thus, the IR evidence and

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Table IV. Observed Pseudo-First-Order and Derived Second-Order Rate Constants for the Reaction of $[(bpy)(tpy)RuS(CH_3)_2]^{2+}$ with Hydrogen Peroxide as a Function of $[H_2O_2]$, $[H^+]$, Ionic Strength, and Temperature[a]

$[H^+]$, M	$[H_2O_2]$, M	10^4k_{obsd}, s^{-1}	10^4k_2, M^{-1} s^{-1}
		I = 1.00 M, T = 45 °C	
1.00	0.50	2.22 ± 0.02	4.44 ± 0.05
	0.75	3.31 ± 0.02	
	1.00	4.34 ± 0.06	
	1.50	6.34 ± 0.07	
	2.00	8.95 ± 0.07	
	2.00[b]	9.32 ± 0.12	
	2.00[b]	9.60 ± 0.12	
0.75	0.50	1.81 ± 0.01	3.56 ± 0.04
	1.00	3.40 ± 0.05	
	1.50	5.21 ± 0.04	
	2.00	7.12 ± 0.04	
0.50	0.50	1.31 ± 0.01	2.55 ± 0.02
	1.00	2.50 ± 0.02	
	1.50	3.72 ± 0.03	
	1.75	4.52 ± 0.05	
	2.00	5.06 ± 0.03	
	2.25	5.83 ± 0.03	
0.25	2.00	2.98 ± 0.01	1.46 ± 0.02
	2.00	2.96 ± 0.05	
	2.25	3.21 ± 0.01	
0.10	0.50	0.287 ± 0.005	0.585 ± 0.012
	1.00	0.547 ± 0.008	
	1.50	0.891 ± 0.009	
	2.00	1.27 ± 0.03	
		I = 2.00 M, T = 45 °C	
2.00	1.96	25.4 ± 0.3	12.8 ± 0.1
	1.96	25.0 ± 0.4	
1.50	1.75	17.5 ± 0.1	10.1 ± 0.1
	1.75	17.7 ± 0.1	
1.00	1.77	13.2 ± 0.1	7.44 ± 0.01
	1.77	13.2 ± 0.1	
0.75	1.58	9.13 ± 0.06	5.73 ± 0.03
	1.58	9.02 ± 0.04	
0.50	1.02	4.14 ± 0.02	4.11 ± 0.05
	1.02	4.25 ± 0.18	
		I = 1.00 M, 55 °C	
1.00	0.50	4.92 ± 0.06	9.31 ± 0.21
	1.00	8.86 ± 0.11	
	1.50	13.2 ± 0.2	
	2.00	18.9 ± 0.1	
0.75	1.00	7.42 ± 0.7	7.34 ± 0.13
	1.50	10.9 ± 0.1	
	2.00	14.3 ± 0.1	
	2.25	17.6 ± 0.2	
0.50	1.00	5.39 ± 0.04	5.29 ± 0.03
	1.50	7.83 ± 0.06	
	2.00	10.5 ± 0.1	
	2.25	11.9 ± 0.1	
0.25	1.75	5.07 ± 0.02	2.90 ± 0.01
	2.00	5.80 ± 0.05	
	2.25	6.74 ± 0.12	
0.10	2.00	2.33 ± 0.03	1.29 ± 0.04
	2.25	2.85 ± 0.02	
	2.25	2.97 ± 0.02	
		I = 1.00 M, T = 65 °C	
1.00	0.50	10.8 ± 0.2	18.3 ± 0.8
	1.00	18.3 ± 0.2	
	1.50	27.3 ± 0.3	
	2.00	30.0 ± 0.8	
0.50	1.00	9.41 ± 0.22	10.1 ± 0.1
	1.50	15.3 ± 0.1	
	1.50	15.0 ± 0.1	
	2.00	20.6 ± 0.2	
0.25	1.50	7.54 ± 0.14	5.36 ± 0.10
	2.00	10.5 ± 0.1	
	2.25	12.4 ± 0.1	
0.10	2.01	4.42 ± 0.07	2.17 ± 0.05
	2.01	4.59 ± 0.09	
	2.01	4.18 ± 0.10	

[a] λ = 454 nm, ionic strength held constant with $LiClO_4$. [b] λ = 400 nm.

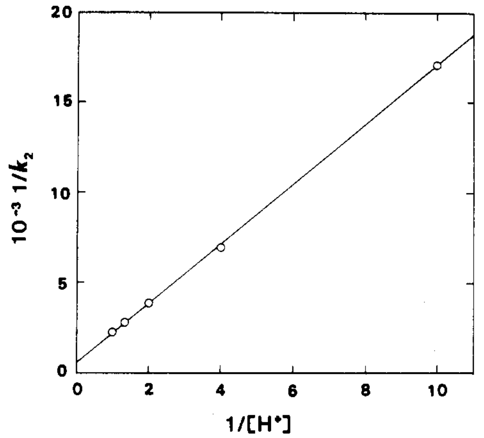


Figure 3. Plot of $10^{-3}/k_2$ vs. $1/[H^+]$ for the reaction of $[(bpy)(tpy)RuS(CH_3)_2]^{2+}$ with H_2O_2.

Table V. Rate Parameters Describing the Acid Dependence of the Reaction of $[(bpy)(tpy)RuS(CH_3)_2]^{2+}$ with H_2O_2 as a Function of Temperature and Ionic Strength[a]

	$k_2 = ab[H^+]/(1 + b[H^+])$	
T, °C	10^3a, M^{-1} s^{-1}	b, M^{-1}
45	1.53 ± 0.15	0.404 ± 0.049
45[b]	4.15 ± 0.50	0.218 ± 0.032
55	3.12 ± 0.22	0.410 ± 0.033
65	10.6 ± 1.2	0.211 ± 0.026

[a] Conditions: I = 1.00 M ($LiClO_4$), $[H^+]$ = 1.00–0.10 M. [b] Conditions: I = 2.00 M ($LiClO_4$), $[H^+]$ = 2.00–0.50 M.

general chemistry of Ru(II) sulfoxide complexes lead to the conclusion that $[(bpy)(typ)RuS(O)(CH_3)_2]^{2+}$ contains S-bonded sulfoxide. Presumably, the values of $\nu_{S—O}$ for the Ru(II) complexes occur at lower energies than those of other S-bonded sulfoxide complexes[21-23] because of Ru(II)-to-sulfoxide π back-bonding that lowers the S—O bond order and decreases the frequency of the S═O stretch.

Oxidation Kinetics. Observed pseudo-first-order and derived second-order rate constants for the H_2O_2 oxidation of $[(bpy)(tpy)RuS(CH_3)_2]^{2+}$ as a function of $[H_2O_2]$, $[H^+]$, ionic strength, and temperature are listed in Table IV. Sequential scans of the visible–UV spectrum show a constant isosbestic point. Plots of k_{obsd} vs. $[H_2O_2]$ are linear with no significant intercept term, and thus the oxidation reaction is first order in each reactant (eq 2).

$$-d[\text{complex}]/dt = k_2[\text{complex}][H_2O_2] \quad (2)$$

Plots of k_2 vs. $[H^+]$ are *not* linear (Figure 2), whereas linearity is commonly observed for H_2O_2 oxidations. However, plots of $1/k_2$ vs. $1/[H^+]$ are linear (Figure 3), giving a rate law of the form

$$k_2 = ab[H^+]/(1 + b[H^+]) \quad (3)$$

Inclusion of a hydrogen ion independent term in the numerator (eq 4) leads to a value of c that is indistinguishable from zero.

$$k_2 = (c + ab[H^+])/(1 + b[H^+]) \quad (4)$$

An attempt to fit the data to a rate law of the form in eq 5 also led to a negligible value of c.

$$k_2 = c[H^+] + ab[H^+]/(1 + b[H^+]) \quad (5)$$

Values for a and b derived within eq 3 at various temperatures are given in Table V.

Aquation Kinetics. The aquation of $[(bpy)(tpy)RuS(O)(CH_3)_2]^{2+}$ (eq 6) was briefly studied at 50.0 ± 0.1 °C with I = 1.00 M (LiCl). There is no significant dependence of k_{obsd} on

$$(bpy)(tpy)RuS(O)(CH_3)_2^{2+} \xrightarrow{k_{aq}} (bpy)(tpy)RuOH_2^{2+} + (CH_3)_2S{=}O \quad (6)$$

the monitoring wavelength or on the hydrogen ion concentration over the range $[H^+] = 0.10$–1.00 *M*. The value of k_{aq} at 50 °C is $(1.46 \pm 0.04) \times 10^{-5}$ s^{-1}.

The product aquo complex $[(bpy)(tpy)RuOH_2]^{2+}$ is identified spectrophotometrically by its visible maximum at 480 nm in 1 M HCl.[17,31] This product is further identified by adjusting the fully reacted solution to pH 12 with 3 M NaOH, yielding the characteristic visible spectrum of $[(bpy)(tpy)RuOH]^+$: $\lambda_{max} = 509$ nm; $\lambda_{sh} = 360$ nm.[17,31]

The parent thioether complex $[(bpy)(tpy)RuS(CH_3)_2]^{2+}$ does not aquate within the time scale of these experiments; there is no significant change in the visible spectrum of this complex over 4 days at 50 °C in 1.0 M HCl.

Discussion

Synthesis and Reactivity. For thioether, selenoether, and telluroether complexes of the type $[(bpy)(tpy)RuL]^{2+}$, the most general preparation involves Ag(I) abstraction of chloride from $[(bpy)(tpy)RuCl]^+$ in acetone:

$$(bpy)(tpy)RuCl^+ + Ag^+ \xrightarrow{\text{acetone}} (bpy)(tpy)Ru(acetone)^{2+} + AgCl \quad (7)$$

Introduction of an appropriate ligand leads to the desired complex:

$$(bpy)(tpy)Ru(acetone)^{2+} + L \rightarrow (bpy)(tpy)RuL^{2+} \quad (8)$$

In addition to this substitution method (eq 9), the dimethyl

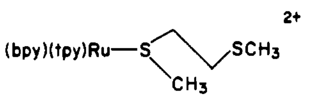
$$(bpy)(tpy)RuCl^+ + Ag^+ \xrightarrow{(CH_3)_2S{=}O} (bpy)(tpy)RuS(O)(CH_3)_2{}^{2+} + AgCl \quad (9)$$

sulfoxide complex $[(bpy)(tpy)RuS(O)(CH_3)_2]^{2+}$ was also prepared via a redox pathway involving oxidation of the parent thioether complex (e.g., eq 10) by oxidants such as H_2O_2, IO_4^- (but not

$$(bpy)(tpy)RuS(CH_3)_2{}^{2+} + H_2O_2 \rightarrow (bpy)(tpy)RuS(O)(CH_3)_2{}^{2+} + H_2O \quad (10)$$

IO_3^-), $S_2O_8{}^{2-}$, and $Ce_{aq}{}^{4+}$. Other examples of oxidation of coordinated thioethers to coordinated sulfoxides are scarce.[32,33] Specifically, the Co(III) thioether complex $[(en)_2Co(S(CH_3)CH_2CH_2NH_2)]^{3+}$ is not oxidized to the sulfoxide complex by the strong oxidants H_2O_2, Cl_2, or *N*-bromosuccinimide.[9]

A. Electrochemical Characterization. Cyclic voltammograms of the simple $[(bpy)(tpy)RuL]^{2+}$ chalcogenoether complexes feature a single, reversible redox wave at positive potentials due to the Ru(II)/Ru(III) redox couple and two reversible waves between −1.2 and −1.6 V attributed to reduction of the coordinated bipyridine and terpyridine ligands.[19,34–36] For the complexes containing pendant thioether groups, **5–7**, more complex redox behavior is observed at positive potentials, apparently reflecting oxidation of the noncoordinated sulfur atom.[37,38]



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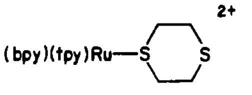

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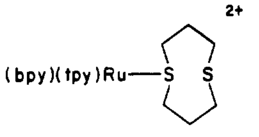

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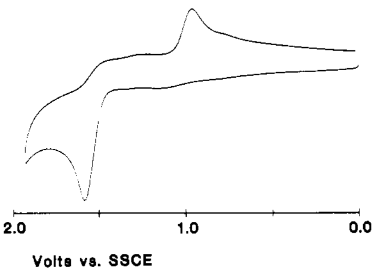

Figure 4. Cyclic voltammogram of $[(bpy)(tpy)RuS(O)(CH_3)_2]^{2+}$. Conditions are as in Figure 1.

The Ru(II)/Ru(III) $E_{1/2}$ values of Table II show that all the $[(bpy)(tpy)Ru^{III}(chalcogenoether)]^{3+}$ complexes are stronger oxidants than are the corresponding $[(bpy)(tpy)Ru^{III}Cl]^{2+}$ and $[(bpy)(tpy)Ru^{III}NH_3]^{3+}$ species. This effect clearly results from greater stabilization of the "softer" Ru(II) oxidation state by the "soft" chalcogenoether ligands. This same stabilization of a lower oxidation state by a soft ligand makes *trans*-$[(dppe)_2Tc^{III}Br_2]^+$ a stronger 1-equiv oxidant than the chloro congener *trans*-$[(dppe)_2Tc^{III}Cl_2]^+$ (dppe = 1,2-bis(diphenylphosphino)ethane).[39] Among the $[(bpy)(tpy)Ru^{III}(chalcogenoether)]^{3+}$ complexes themselves, the range of observed Ru(II)/Ru(III) $E_{1/2}$ values is only 0.10 V and thus the trends in these values are less readily explained: (1) The aromatic ligand $CH_3SC_6H_5$ is a stronger π acid than CH_3SCH_3 and therefore is expected to better stabilize the Ru(II) state and lead to $[(bpy)(tpy)Ru^{III}S(CH_3)C_6H_5]^{3+}$ being a stronger oxidant than $[(bpy)(tpy)Ru^{III}S(CH_3)_2]^{3+}$. The data of Table II do indeed bear out this expectation. (2) However, for the three analogous, S, Se, and Te complexes, the softness argument presented above would predict the Te complex to be the strongest oxidant, but in reality it is the weakest. This implies that in these three complexes π back-bonding from Ru to the chalcogen becomes less efficient for the larger Se and Te ligands. Further data will be required to establish whether or not this hypothesis is valid.

Cyclic voltammograms of the $[(bpy)(tpy)RuS(O)(CH_3)_2]^{2+}$ complex indicate several complicated redox reactions at both positive (Figure 4) and negative potentials. An irreversible anodic wave and an irreversible cathodic wave are observed at positive potentials for scan rates up to 5 V s^{-1}. These may result from a process similar to that reported by Taube and co-workers[33] for $[(NH_3)_5RuS(O)(CH_3)_2]^{2+}$. Upon oxidation of this material to the corresponding Ru(III) complex, sulfur-to-oxygen linkage isomerization occurs with a specific rate constant of 7.0×10^{-2} s^{-1}. Upon rereduction to Ru(II), the oxygen-bound sulfoxide rearranges to the sulfur-bound isomer. The Ru(II)/Ru(III) $E_{1/2}$ values for the $(NH_3)_5Ru^{II}$ S-bound and O-bound sulfoxide complexes are 1.0 and 0.1 V, respectively (conditions: H_2O, $I = 0.1$ M, $[H^+] = 0.01$ M). The two irreversible peaks for $[(bpy)(tpy)RuS(O)(CH_3)_2]^{2+}$ in CH_3CN occur at 1.63 V for the anodic wave and at 1.01 V for the cathodic wave. These results may be understood if sulfur-to-oxygen linkage isomerization also occurs upon oxidation of this complex and if the rate of this reaction is fast on the time scale of the cyclic voltammetry experiment ($k > 25$ s^{-1}). Thus, the anodic wave could represent the oxidation of $[(bpy)(tpy)Ru^{II}S(O)(CH_3)_2]^{2+}$ to the corresponding Ru(III) complex that would rapidly isomerize; the cathodic wave could represent the reduction of $[(bpy)(tpy)Ru^{III}O{=}S(CH_3)_2]^{3+}$ to the corresponding Ru(II) complex that would also rapidly isomerize.

For the complexes that contain ligands such as phenothiazine, 10-methylphenothiazine, and thianthrene, the cyclic voltammograms are rather complicated at positive potentials (e.g., see Figure 5) compared to those of the simple thioether complexes (e.g., see Figure 1). This evidently results from oxidation of the coordinated phenothiazine or thianthrene ligand and perhaps subsequent re-

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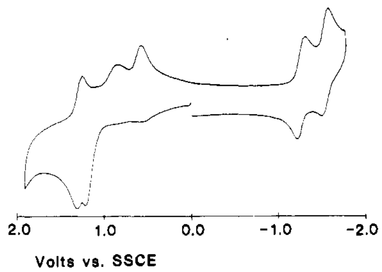
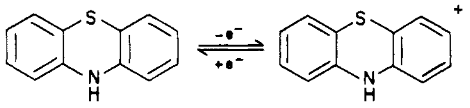


Figure 5. Cyclic voltammogram of $[(bpy)(tpy)Ru(phenothiazine)]^{2+}$. Conditions are as in Figure 1 except scan rate is 300 mV s^{-1}.

actions of these oxidation products. A cyclic voltammogram of phenothiazine (CH_3CN, 0.1 M TEAP, Pt vs. SSCE) shows two quasi-reversible redox waves at 0.65 and 0.96 V, while for thianthrene these waves occur at 1.23 and 1.73 V under similar conditions (CH_3CN, 0.2 M $(CH_3CH_2CH_2CH_2)_4NBF_4$, Pt vs. SCE).[40] The free ligands form relatively stable radical cations upon 1-equiv oxidation[41–43]



and it has been shown that the coordinated ligands can also do so.[44]

B. Spectrophotometric Characterization. The visible spectra of the $[(bpy)(tpy)Ru(chalcogenoether)]^{2+}$ complexes (Table III) generally exhibit a single absorption maximum. Comparison of this peak to similar peaks of analogous complexes[19,45,46] indicates that this band arises from a Ru ($4d\pi$) to bpy (or tpy) π^* metal-to-ligand charge-transfer transition (MLCT). A similar assignment is made for the shoulder observed at ca. 330 nm.[47–50] UV peaks occurring between 310 and 280 nm are assigned to bipyridine and terpyridine intraligand $\pi \rightarrow \pi^*$ transitions. Other UV peaks of higher energies may also be reasonably assigned to similar intraligand transitions.

The $(bpy)(tpy)Ru^{II}$ phenothiazine and thianthrene complexes also exhibit broad visible bands that apparently result from overlapping $Ru(4d\pi) \rightarrow$ phenothiazine (or thianthrene) π^* bands.

Oxidation Kinetics and Mechanism. When H_2O_2 acts as a 2-equiv oxidant toward nucleophilic substrates, it is generally accepted that oxidation proceeds through nucleophilic attack at the O–O bond.[51–54] The acid dependences of H_2O_2 oxidations of nucleophilic substrates, including $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ and $[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+}$, are almost exclusively described by eq 11.[4,5,51,53] However, for H_2O_2 oxidation of

$$k_2 = a + b[H^+] \tag{11}$$

$[(bpy)(tpy)RuS(CH_3)_2]^{2+}$ the acid dependence over the range 2.00 $\geq [H^+] \geq 0.10$ M (Table IV) is expressed by eq 3. For the oxidations of S-containing substrates, this more complicated rate law appears to be unique to this Ru(II) substrate. At least two plausible mechanistic schemes can be proposed to account for this rate law. In Scheme I a steady-state intermediate is formed from the reaction of H_2O_2 with $[(bpy)(tpy)RuS(CH_3)_2]^{2+}$. This intermediate may take the form of a sulfur–H_2O_2 adduct **8**, which may conceivably be stabilized through hydrogen bonding between a peroxide hydrogen atom and a filled Ru $4d\pi$ orbital. Formation of an intermediate wherein H_2O_2 initially bonds to the Ru(II) metal ion center itself cannot be ruled out, and indeed this pathway has been proposed for the H_2O_2 oxidation of $[(NH_3)_5RuL]^{2+}$ (L = NH_3, OH_2, 1-methylimidazole) complexes.[55,56] However, in the $[(bpy)(tpy)RuS(CH_3)_2]^{2+}$ system, intermediate **8** is preferred because of the established nucleophilicity of coordinated sulfur. Consonant with this view is the observation that the H_2O_2 oxidation of $[(bpy)(tpy)RuS(CH_3)C_6H_5]^{2+}$ is slower than oxidation of the corresponding $S(CH_3)_2$ complex due to both electronic effects and steric constraints. Similarly, on the basis of very limited data, the initial stages of the H_2O_2 reduction of Pu(VI) is speculated to proceed through an intermediate in which H_2O_2 is bonded to an oxygen atom of PuO_2^{2+}.[57] Also, it has been reported that a sulfinyl oxide, $R_2S{=}O{-}O$, intermediate is formed during the H_2O_2 oxidation of alkoxy sulfuranes.[58] For either of the intermediates (S bonded or Ru bonded), protonation of the peroxide oxygen atom then catalyzes the formation of the sulfoxide complex since H_2O is a better leaving group than is OH^-. Scheme I leads to the rate law shown in eq 12, where, from eq 3, $a = k_1$ and $b = k_2K_1/k_{-1}$.

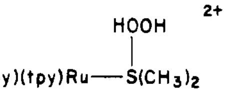
$$k_2 = \frac{(k_1k_2K_1/k_{-1})[H^+]}{1 + (k_2K_1/k_{-1})[H^+]} \tag{12}$$

Scheme I

$$(bpy)(tpy)RuS(CH_3)_2^{2+} + H_2O_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} I^{2+}$$

$$I^{2+} + H^+ \overset{K_1}{\rightleftharpoons} IH^{3+}$$

$$IH^{3+} \xrightarrow{k_2} (bpy)(tpy)RuS(O)(CH_3)_2^{2+} + H_3O^+$$



$$\overset{\displaystyle HOOH\quad ^{2+}}{(bpy)(tpy)Ru{-}S(CH_3)_2}$$

8

In Scheme II, a preequilibrium between the thioether complex and H^+ is established. The product of the equilibrium in this scheme may possibly be protonated either on the sulfur atom or directly on the Ru(II) metal center. Acid-catalyzed aquation of $[Ru(NH_3)_6]^{2+}$ has been proposed to proceed via protonation of the filled $d\pi$ metal orbitals.[59] Reaction of the protonated intermediate with H_2O_2 could then lead to the sulfoxide product

Scheme II

$$(bpy)(tpy)RuS(CH_3)_2^{2+} + H^+ \overset{K_2}{\rightleftharpoons} (bpy)(tpy)RuS(CH_3)_2^{2+}, H^+$$

$$(bpy)(tpy)RuS(CH_3)_2^{2+}, H^+ + H_2O_2 \xrightarrow{k_3} (bpy)(tpy)RuS(O)(CH_3)_2^{2+} + H_3O^+$$

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Table VI. Selected Kinetic Data for the Hydrogen Peroxide Oxidation of Sulfur-Containing Nucleophiles[a, b]

	a, $M^{-1}\ s^{-1}$	ΔH_a^*, kcal mol^{-1}	ΔS_a^*, eu
SCN^- [c]	5.2×10^{-4}	15	−25
$(HOCH_2CH_2)_2S$[c]	2.2×10^{-3}		
$O(CH_2CH_2)_2S$[c]	2.6×10^{-3}	13	−27
$(NH_2)_2C{=}S$[c]	7.0×10^{-2}	15	−14
$(NHCH_3)_2C{=}S$[c]	9.4×10^{-2}	13	−17
$(NH_2CH_2CH_3)_2C{=}S$[c]	8.6×10^{-2}	13	−19
$(en)_2Co(NO_2)(NCS)^+$ [c]	4.6×10^{-5}		
$(NH_3)_5CoNCS^{2+}$ [c]	5.3×10^{-5}	17	−17
$(en)_2Co(S(O)CH_2CH_2NH_2)^{2+}$ [d]	3.4×10^{-4}	15	−26
$(bpy)(tpy)RuS(CH_3)_2^{2+}$ [e]	1.5×10^{-4}	19 ± 2	−13 ± 8

[a] Conditions: H_2O solvent, variable ionic strength, 25 °C. [b] $k_2 = a + b[H^+]$. [c] Reference 66. [d] Reference 5. [e] This work. $k_2 = ab[H^+]/(1 + b[H^+])$; a is extrapolated to 25 °C.

complex. Scheme II yields the rate law shown in eq 13, where from eq 3 $a = k_3$ and $b = K_2$.

$$k_2 = k_3K_2[H^+]/(1 + K_2[H^+]) \tag{13}$$

These two mechanisms are kinetically indistinguishable as long as [Ru] << [H^+], which is true under all conditions used in this study. However, Scheme II is discounted on the basis that there is no observable difference in the visible spectrum of $[(bpy)(tpy)RuS(CH_3)_2]^{2+}$ in H_2O, 1.0 M HCl, 2.0 M HCl, or 4.0 M HCl. A spectral change would be anticipated if protonation of the complex occurred at either the sulfur or ruthenium atoms. Extrapolated to 25 °C, the kinetically determined value of K_2 would be 0.95 M^{-1}, and thus the complex would be expected to be 49% protonated in 1 M H^+ at 25 °C. Further, the $d\pi$ orbitals of $[(bpy)(tpy)RuS(CH_3)_2]^{2+}$ are not anticipated to be as basic as those of $[Ru(NH_3)_6]^{2+}$ because of the presence of the π-electron-accepting polypyridyl[60] and thioether ligands.

Assuming Scheme I is operative, the a rate term represents reaction of $[(bpy)(tpy)RuS(CH_3)_2]^{2+}$ with H_2O_2 (k_1). Comparing the value of a, extrapolated to 25 °C, with those of other sulfur-containing nucleophiles (Table VI) shows that it is in the range observed for Co(III) complexes as well as those observed for noncoordinated thioethers and noncoordinated SCN^-. The data of Table VII are also consistent with H_2O_2 oxidation of $[(bpy)(tpy)RuS(CH_3)_2]^{2+}$ proceeding by the classical nucleophilic attack mechanism. For each transition-metal complex, the values of the observed activation entropies fall within a narrow range. The disparate rates are controlled largely by the activation enthalpies, consistent with nucleophilic cleavage of H_2O_2. There is an increase in ΔH_2^* (and concomitant decrease in k_2) with increasing steric constraints about the sulfur atom. For two-coordinate sulfur, $\Delta H_2^* \sim 10$ kcal/mol while for three-coordinate sulfur, $\Delta H_2^* \sim 14.5$ kcal/mol.

In sum, it is concluded that H_2O_2 oxidation of $[(bpy)(tpy)RuS(CH_3)_2]^{2+}$ proceeds by the usual nucleophilic attack on H_2O_2 but that the Ru(II) center is capable of stabilizing a bimolecular reaction intermediate that can be reversibly protonated.

The data in Table IV at [H^+] = 1.00, 0.75, and 0.50 M at 45 °C show that there is a positive salt effect upon changing the reaction medium from 1.00 to 2.00 M ClO_4^-. For the reaction of an uncharged molecule with a charged species, as described by k_1, the modified Debye–Huckel equation (eq 14) reduces to eq 15.[61,62]

Table VII. Selected Second-Order Rate Constants and Activation Parameters Describing the Reaction of H_2O_2 with Chalcogen Complexes of Cobalt(III), Chromium(III), and Ruthenium(II)[a]

complex	k_2, $M^{-1}\ s^{-1}$	ΔH_2^*, kcal mol^{-1}	ΔS_2^*, eu
$(bpy)(tpy)RuS(CH_3)_2^{2+}$ [b]	8.4×10^{-5}	14.6	−28
$(en)_2Co(SCH_2CH_2NH_2)^{2+}$	3.20	7.3	−32
$(en)_2Co(SCH_2COO)^+$	2.54	10.2	−22
$(en)_2Co(SCH(CH_3)COO)^+$	2.20	9.7	−25
$(en)_2Co(SC(CH_3)_2COO)^+$	0.52	9.2	−29
$(en)_2Co(S(O)CH_2CH_2NH_2)^{2+}$ [c]	8.0×10^{-4}	14.4	−25
$(en)_2Cr(SCH_2CH_2NH_2)^{2+}$	1.13	9.7	−26
$(en)_2Cr(SCH_2COO)^+$	1.13	9.3	−27
$(en)_2Cr(SCH_2CH_2COO)^+$	1.19	10.0	−25
$(en)_2Cr(SC(CH_3)_2COO)^+$	0.16	10.6	−27
$(H_2O)_5CrSCH_2CH_2NH_3^{3+}$	0.176	10.6	−26
$(H_2O)_5CrSC_6H_4NH_3^{3+}$	0.045	10.8	−28
$(H_2O)_4Cr(SCH_2COO)^+$	0.445	10.4	−26

[a] Rate = k_2[complex][H_2O_2]. Conditions: I = [$HClO_4$] = 1.00 M, $T \simeq 25$ °C. Data taken from ref 4 unless otherwise noted. [b] This work. k_2 extrapolated to 25 °C. [c] Calculated from the data given in ref 5.

$$\log k_1 = \log k_0 + \frac{Az_1z_2I}{1 + BI} + CI \tag{14}$$

$$\log k_1 = \log k_0 + CI \tag{15}$$

Using the a parameters ($=k_1$) for the reaction of $[(bpy)(tpy)RuS(CH_3)_2]^{2+}$ with H_2O_2 at 45 °C, c is calculated to be 0.43 M^{-1}, which is of the order of magnitude of C values observed in other systems.[61,62]

Aquation Kinetics. Aquation of $[(bpy)(tpy)RuS(O)(CH_3)_2]^{2+}$ to $[(bpy)(tpy)RuOH_2]^{2+}$ occurs rather slowly. At T = 50 °C and I = 1.0 M ((H/Li)Cl), $k_{aq} = (1.46 \pm 0.04) \times 10^{-5}\ s^{-1}$. Under similar conditions, the parent thioether complex $[(bpy)(tpy)RuS(CH_3)_2]^{2+}$ does not form detectable amounts of the aquo complex. These results reflect the greater ligating ability of S(−II) relative to S(0) as well as the greater steric requirements of four-coordinate sulfur relative to three-coordinate sulfur.

The aquation reactions of $[(bpy)(tpy)RuX]^+$ complexes (X = Cl, Br, I) are rapid and virtually complete upon dissolution.[63] Although halides are good σ-electron donors they are poor π-electron acceptors, thus again underscoring the importance of back-bonding from the Ru(II) metal ion center. The $[(bpy)(tpy)Ru(thiourea)]^{2+}$ complex also aquates very slowly.[63]

In contrast to $[(bpy)(tpy)RuS(O)(CH_3)_2]^{2+}$, aquation of $[(NH_3)_5RuS(O)(CH_3)_2]^{2+}$ apparently involves loss of coordinated ammonia,[33] which is also observed for the $(NH_3)_5Ru^{II}(chalcogenoether)^{2+}$ complexes.[64] A similar mechanism is precluded for the $(bpy)(tpy)Ru^{II}$ complexes because of the more securely bound, chelated bipyridine and terpyridine ligands.

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