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Thioether, Thiolato, and 1,1-Dithioato Complexes of Bis(2,2'-bipyridine)ruthenium(II) and Bis(2,2'-bipyridine)osmium(II)¹

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A series of bis(2,2'-bipyridine)ruthenium(II) complexes containing sulfur-donating ligands has been prepared. In these complexes the two coordination sites not occupied by bipyridine are occupied by the following ligands or ligand combinations: CH₃SC-H₂CH₂SCH₃, CH₃CH₂SCH₂CH₂SCH₂CH₃, C₆H₅SCH₂CH₂SC₆H₅, 3,4-CH₃SC₆H₃(CH₃)SCH₃, *cis*-[S(CH₃)₂]₂, *trans*-[S(CH₃)₂]₂, CH₃SCH₂CH₂NH₂, C₆H₅CH₂SCH₂CH₂NH₂, C₆H₅SCH₂CH₂NH₂, CH₃S(O)CH₂CH₂NH₂, *cis*-[X,S(CH₂CH₃)₂] (X = Cl, Br), *cis*-[Cl,S(CH₃)C₆H₅]₂, *cis*-[P(C₆H₅)₃, S(CH₂CH₃)₂]₂, *cis*-[S(CH₃)₂]₂, *cis*-[S(CH₃)₂]₂, -S₂CN(CH₂CH₃)₂, -S₂CN(CH₂)₄, -S₂COCH₂CH₃. Related bis(2,2'-bipyridine)osmium(II) complexes have been prepared with the following thioether ligand combinations: *cis*-[S(CH₃)C₆H₅]₂, *cis*-[4-S(CH₃)C₆H₄C(CH₃)₃]₂, 3,4-CH₃SC₆H₃(CH₃)SCH₃. All complexes have been characterized by elemental analyses, cyclic voltammetry, and visible-UV spectrophotometry. Selected complexes have also been characterized by ¹H and ¹³C NMR spectroscopy, and emission spectra for the three Os(II) complexes have been obtained in acetonitrile solution. The redox and spectral properties of the sulfur-containing (bpy)₂M^{II} complexes can be rationalized in terms of the relative π-acid character of halogen-, nitrogen-, phosphorus-, and sulfur-containing ligands, within the tenet that π back-bonding is the salient feature of the chemistry of Ru(II) and Os(II) complexes. In general, the sulfur-containing (bpy)₂M^{II} complexes have properties intermediate between those of amine-containing and phosphine-containing analogues. Among the sulfur-Ru(II) complexes, the potential of the Ru(II)/Ru(III) couple increases with the increasing formal charge of the complex (thiolate < 1,1-dithioato < thioether), the range of observed potentials being greater than 1.7 V. The [(bpy)₂(thioether)₂Os]^{I,2+} complexes are more readily oxidized (by 0.3–0.4 V) than the corresponding Ru(II) complexes, consistent with established periodic trends.

Introduction

Our longstanding interest in the chemistry of coordinated sulfur has been manifested largely in the study of robust cobalt(III) and chromium(III) complexes.⁴ The first coordination spheres of these complexes were designed to contain a single sulfur atom and five blocking nitrogen or oxygen atoms, so that they could readily be applied to the explication of mechanistic and structural phenomena. Recent advances in this area, especially with regard to the diverse mechanisms available for the oxidation of coordinated sulfur,⁴ have indicated that complexes containing two sulfur atoms in a *cis* arrangement might undergo chemistry that would be both interesting and mechanistically informative. Of specific interest to us was the possibility of oxidizing two *cis* thiolato (RS⁻) ligands to generate the coordinated radical ion dimer RSSR⁻; this species has been proposed as a relatively stable reaction intermediate in the oxidation of both coordinated and noncoordinated thiols.⁴ It was felt that cobalt(III) and chromium(III) centers did not provide the synthetic flexibility necessary to generate the range of *cis*-sulfur-ligated complexes desired for mechanistic studies, and our attention was drawn to the fecund family of *cis*-disubstituted bis(2,2'-bipyridine)ruthenium(II) and bis(2,2'-bipyridine)osmium(II) complexes. Complexes in this family are already known with a variety of group 15⁷⁵ ligands (amines, phosphines, arsines, and stibines),^{5–12} with the halides of group 17,^{5,6,9,13,75} and recently with ligands donating the group 14⁷⁵ atom carbon.^{14–17} It seemed likely that (bpy)₂Ru^{II} and (bpy)₂Os^{II} (bpy = 2,2'-bipyridine) complexes containing sulfur-donating ligands could also be prepared in great variety, especially since other Ru and Os complexes containing thioether,^{4,18–25} thiolato,^{24–28} and 1,1-dithioato^{29,30} ligands are known.

The proposed *cis*-sulfur-ligated complexes are also of interest because of the potential use of (bpy)₂Ru^{II} and (bpy)₂Os^{II} complexes as photoredox catalysts. Variation in the sulfur-donating ligands should allow considerable fine tuning of the resulting redox and spectral properties of the complexes. In this paper we thus report the synthesis, electrochemical characterization, and spectrophotometric characterization of a variety of (bpy)₂Ru^{II} and (bpy)₂Os^{II} complexes containing *cis*-substituted thioether, thiolato, and 1,1-dithioato ligands. For comparison purposes, a *trans*-

substituted Ru(II) analogue is also prepared and similarly characterized.

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Experimental Section

Materials. All common chemicals were reagent grade and were used as received unless otherwise noted. Acetone used in synthetic procedures was stored over 3–4-Å molecular sieves.

Dimethyl sulfide ($S(CH_3)_2$), thioanisole ($CH_3SC_6H_5$), diethyl sulfide [$S(CH_2CH_3)_2$], thiophenol (HSC_6H_5), 4-*tert*-butylthiophenol [$HSC_6H_4C(CH_3)_3$], sodium dimethylthiocarbamate [$NaS_2CN(CH_3)_2$], ammonium pyrrolidinecarbodithioate [$NH_4S_2CN(CH_2)_4$], 2,2'-bipyridine, and $RuCl_3 \cdot 3H_2O$ were from Aldrich Chemical; 2-(phenylthio)-1-aminoethane ($C_6H_5SCH_2CH_2NH_2$) and $(NH_4)_2OsCl_6$ were from Alfa; 1,2-bis(methylthio)ethane ($CH_3SCH_2CH_2SCH_3$) was from Watere Research; 1,2-bis(ethylthio)ethane ($CH_3CH_2SCH_2CH_2SCH_2CH_3$) and 3,4-dimercaptotoluene [$3,4-HSC_6H_3(CH_3)SH$] were from Pfalz and Bauer; 1,2-bis(phenylthio)ethane ($C_6H_5SCH_2CH_2SC_6H_5$) was from Parish Chemical; triphenylphosphine [$P(C_6H_5)_3$] was from MCB. Potassium ethyl xanthate ($KS_2COCH_2CH_3$) (Eastman Chemical) was recrystallized from ethanol before use. 2-(Methylthio)-1-aminoethane ($CH_3SCH_2CH_2NH_2$),³¹ 2-(methylsulfinyl)-1-aminoethane [$CH_3S(O)C_2H_4NH_2$]³¹ and 2-(benzylthio)-1-aminoethane hydrochloride ($C_6H_5CH_2SCH_2CH_2NH_2 \cdot HCl$)³² were available from previous studies.

Commercially available tank nitrogen or argon was deoxygenated and equilibrated with water by passing the gas 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 finally passed through a scrubbing tower containing the same solvent used in the experiment, stored over 3-Å molecular sieves. Tetraethylammonium perchlorate (TEAP) used in electrochemical experiments was obtained from Eastman Chemical, recrystallized twice from water, and dried at 110 °C for 24 h.

Activated alumina was dried at 110 °C for >24 h.

3,4-Bis(methylthio)toluene [$CH_3SC_6H_3(CH_3)SCH_3$]. To 75 mL of deaerated absolute ethanol was added 3.4 g of KOH (0.06 mol). Upon dissolution, 4.7 g of 3,4-dimercaptotoluene (0.03 mol) was added and this mixture was allowed to stir for ca. 20 min. At this point 3.75 mL of CH_3I (0.06 mol) was added, and the reaction mixture was stirred for 90 min. The precipitated KI was removed, and the filtrate was evaporated to dryness under reduced pressure. The residue was taken up in 75 mL of diethyl ether and extracted with 25 mL of 10% K_2CO_3 . The aqueous layer was washed with two 75-mL portions of ether. The combined ether fractions were dried over anhydrous $MgSO_4$. After filtration by gravity, the ether was evaporated under reduced pressure until incipient precipitation and then the mixture was cooled to -20 °C overnight. The resulting white crystals were recovered by filtration and dried in vacuo. Anal. Calcd for $C_9H_{12}S_2$: C, 58.64; H, 6.58. Found: C, 58.90; H, 6.73. Mp (uncor): 36–38 °C. 1H NMR (60 MHz, CCl_4): δ 2.30, 2.34, 2.37 (3 s, 9 H, CH_3), 6.7–7.2 (m, 3 H, >CH). Mass spectrum (70 eV): m/e 184 (M^+).

***cis*-Dichlorobis(2,2'-bipyridine)ruthenium(II) Dihydrate** [*cis*-(bpy)₂RuCl₂·2H₂O]. This complex was prepared by a reported procedure.¹¹ Visible (CH_2Cl_2): λ_{max} 555, 378 nm.

Bis(2,2'-bipyridine)(sulfur ligand)ruthenium(II) Hexafluorophosphate [(bpy)₂RuL](PF₆)₂ [L = $CH_3SCH_2CH_2SCH_3$, $CH_3CH_2SCH_2CH_2SCH_3$, $C_6H_5SCH_2CH_2SCH_3$, 3,4- $CH_2SC_6H_3(CH_3)SCH_3$, *cis*-[S-(CH₃)₂]₂, $CH_3SCH_2CH_2NH_2$, $C_6H_5CH_2SCH_2CH_2NH_2$, $C_6H_5SCH_2CH_2NH_2$, $CH_3S(O)CH_2CH_2NH_2$]. These complexes were prepared by simple modification of the aqueous method previously described.¹¹ Typically, 0.260 g of (bpy)₂RuCl₂·2H₂O (0.50 mmol) and a 2–50-fold excess of a thioether (or the sulfoxide $CH_3S(O)CH_2CH_2NH_2$) were added to 50 mL of 50% aqueous ethanol, and the mixture was deaerated (for the $C_6H_5CH_2SCH_2CH_2NH_2$ complex the ligand was first converted to the free-base form in situ by addition of a stoichiometric amount of solid NaOH). The reaction mixture was heated at reflux with vigorous stirring for 1–4 h. The reaction solutions gradually turned a clear yellow or orange color during the reflux period. Excess ligand was removed by diethyl ether extraction. An excess of solid NH_4PF_6 was added to precipitate the product, and the resulting yellow or orange powder was collected by filtration, washed with water and ether, and air-dried. Perchlorate salts were prepared as above but were precipitated by addition of $LiClO_4$ or NH_4ClO_4 .

Purification¹¹ of all complexes was effected by successively adsorbing a concentrated acetone or acetonitrile solution of the complex onto a 2 cm × 25 cm column containing activated alumina. The complexes were

separated by sequential elution using 1/3, 1/2, 5/7, and 1/1 $CH_3CN/C_6H_5CH_3$ solutions. The desired complex was the first band eluted, and it always comprised the major portion of the product. For perchlorate salts, more concentrated $CH_3CN/C_6H_5CH_3$ solutions were needed to effect elution. Purified complexes were reprecipitated from acetone/diethyl ether or CH_3CN /diethyl ether. Recovered yields were usually in the range of 50–70%. Relevant analytical, electrochemical, and spectrophotometric data are given in Tables I, II, and V, respectively.

***cis*-Dibromobis(2,2'-bipyridine)ruthenium(II)** [*cis*-(bpy)₂RuBr₂]. This complex was prepared from (bpy)₂RuCl₂·2H₂O as described.⁵ Visible (CH_2Cl_2): λ_{max} 548, 375 nm. Cyclic voltammetry (CH_3CN , 0.1 M TEAP, Pt vs. SSCE): $E_{1/2} = 0.37$ V.

***cis*-Bis(2,2'-bipyridine)(X)(thioether)ruthenium(II) hexafluorophosphate** [*cis*-(bpy)₂(X)RuL]PF₆ [L = $S(CH_2CH_3)_2$, X = Cl, Br; L = $S(CH_3)C_6H_5$, X = Cl]. These complexes were prepared from (bpy)₂RuCl₂ or (bpy)₂RuBr₂ and purified¹¹ by chromatography on alumina as described above. Relevant analytical, electrochemical, and spectrophotometric data are given in Tables I, II, and V, respectively.

***cis*-Chlorobis(2,2'-bipyridine)(triphenylphosphine)ruthenium(II) Hexafluorophosphate** [*cis*-(bpy)₂(Cl)RuP(C_6H_5)₃]PF₆. This complex was prepared by a modification of a literature procedure.¹¹ A 0.262-g sample of (bpy)₂RuCl₂·2H₂O (0.50 mmol) and 0.525 g of P(C_6H_5)₃ (2.0 mmol) were added to 40 mL of deaerated 80% aqueous ethanol and refluxed for 1 h. Excess P(C_6H_5)₃ and ethanol were extracted into a large excess of diethyl ether and the complex was precipitated by addition of excess solid NH_4PF_6 . The complex was purified by chromatography on alumina as described above and reprecipitated from acetone/ether. Visible (CH_3CN): λ_{max} 453 nm. Cyclic voltammetry (CH_3CN , 0.1 M TEAP, Pt vs. SSCE): $E_{1/2} = 0.92$ V.

***cis*-Bis(2,2'-bipyridine)(diethyl sulfide)(triphenylphosphine)ruthenium(II) Hexafluorophosphate** [*cis*-(bpy)₂(P(C_6H_5)₃)RuS(CH_2CH_3)₂](PF₆)₂. A 0.257-g sample of [(bpy)₂(Cl)RuP(C_6H_5)₃]PF₆ (0.30 mmol) and 0.063 g of $AgClO_4$ (0.30 mmol) were added to 30 mL of deaerated acetone, and the mixture was stirred at room temperature for ca. 3 h. A 0.065-mL sample of $S(CH_2CH_3)_2$ (0.60 mmol) was then added, and the reaction mixture was heated at gentle reflux for 1 h and then stirred under argon at room temperature for 12 h. The reaction solution was filtered, and the complex was isolated and purified by chromatography on alumina as described above. Relevant analytical, electrochemical, and spectrophotometric data are given in Tables I, II, and V, respectively.

(Carbonato)bis(2,2'-bipyridine)ruthenium(II) Dihydrate [(bpy)₂RuCO₃·2H₂O]. This complex was prepared by following a reported procedure³³ using (bpy)₂RuCl₂·2H₂O. Visible (CH_3CH_2OH): λ_{max} 545, 370 nm.

***trans*-Bis(2,2'-bipyridine)diaquoruthenium(II) Hexafluorophosphate** [*trans*-(bpy)₂Ru(OH₂)₂](PF₆)₂. This complex was prepared from (bpy)₂RuCO₃·2H₂O by slight modification of a literature preparation,³⁴ substituting HPF_6 for $HClO_4$.

***trans*-Bis(2,2'-bipyridine)bis(dimethyl sulfide)ruthenium(II) Hexafluorophosphate** [*trans*-(bpy)₂Ru(S(CH_3)₂)₂](PF₆)₂. This complex was prepared from *trans*-(bpy)₂Ru(OH₂)₂](PF₆)₂ by modification of a reported procedure.³⁵ To 20 mL of deaerated 50% aqueous ethanol were added 0.0965 g of *trans*-(bpy)₂Ru(OH₂)₂](PF₆)₂ (0.13 mmol) and 1 mL of $S(CH_3)_2$, and the resulting solution was refluxed for 22 h. The yellow precipitate was removed from the cooled reaction solution by filtration and dissolved in acetone, and the product was eluted from an alumina column with acetone and then 10/90 methanol/acetone. The desired product was precipitated with diethyl ether; yield 56% (based on Ru). Analytical, electrochemical, and spectrophotometric data are given in Tables I, II, and V, respectively.

***cis*-Bis(thiolato)bis(2,2'-bipyridine)ruthenium(II)** [*cis*-(bpy)₂RuL₂ (L = $-SC_6H_5$, $-SC_6F_5$)]. A 0.54-g sample of KOH (10 mmol) was dissolved in 50 mL of deaerated 50% aqueous methanol. To this solution was added 10 mmol of the appropriate thiol, and the solution was stirred for ca. 20 min. At this point, 0.262 g of (bpy)₂RuCl₂·2H₂O (0.50 mmol) was added and the reaction mixture was refluxed for 1 h. Dark purple crystals deposited on the walls of the reaction flask during reflux. The crystals were recovered by filtration, washed with water and diethyl ether, and air-dried. The (bpy)₂Ru(SC₆F₅)₂ complex was further purified by chromatography on alumina using $CH_3CN/C_6H_5CH_3$ eluents. Analytical and electrochemical data are given in Tables I and IV, respectively.

(1,1-Dithioato)bis(2,2'-bipyridine)ruthenium(II) Hexafluorophosphate [(bpy)₂RuL]PF₆ [L = $-S_2CN(CH_3)_2$, $-S_2CN(CH_2CH_3)_2$, $-S_2CN(CH_2)_4$,

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Table I. Elemental Analyses for Ruthenium(II) and Osmium(II) Chalcogen Complexes

| complex | | analysis | | | | |
|--|-------|----------|-------|-------|------|--------------------|
| | | % Ru | % S | % N | % P | % Cl |
| [(bpy) ₂ Ru(S(CH ₃)CH ₂ CH ₂ SCH ₃)](PF ₆) ₂ | calcd | 12.24 | 7.77 | 6.79 | 7.50 | |
| | found | 12.09 | 7.51 | 6.76 | 7.34 | |
| [(bpy) ₂ Ru(S(CH ₂ CH ₃)CH ₂ CH ₂ SCH ₂ CH ₃)](PF ₆) ₂ | calcd | 11.84 | 7.51 | 6.56 | 7.26 | |
| | found | 12.08 | 7.80 | 6.68 | 7.25 | |
| [(bpy) ₂ Ru(S(C ₆ H ₅)CH ₂ CH ₂ SC ₆ H ₅)](PF ₆) ₂ | calcd | | 5.96 | 6.75 | 5.90 | |
| | found | | 5.80 | 6.79 | 5.80 | |
| [(bpy) ₂ Ru(3,4-S(CH ₃)C ₆ H ₃ (CH ₃)SCH ₃)](PF ₆) ₂ | calcd | | 7.22 | 6.31 | 6.98 | |
| | found | | 7.21 | 6.21 | 6.55 | |
| [(bpy) ₂ Ru(S(CH ₃)CH ₂ CH ₂ NH ₂)](PF ₆) ₂ | calcd | 12.72 | 4.03 | 8.82 | 7.80 | |
| | found | 13.11 | 4.06 | 9.12 | 7.64 | |
| [(bpy) ₂ Ru(S(CH ₂ C ₆ H ₅)CH ₂ CH ₂ NH ₂)](PF ₆) ₂ | calcd | 11.61 | 3.68 | 8.05 | 7.11 | |
| | found | 10.88 | 3.75 | 7.76 | 6.57 | |
| [(bpy) ₂ Ru(S(C ₆ H ₅)CH ₂ CH ₂ NH ₂)](PF ₆) ₂ | calcd | | 3.74 | 8.18 | 7.23 | |
| | found | | 3.55 | 8.33 | 6.82 | |
| [(bpy) ₂ Ru(S(O)(CH ₃)CH ₂ CH ₂ NH ₂)](PF ₆) ₂ | calcd | | 3.96 | 8.64 | 7.64 | |
| | found | | 4.10 | 8.59 | 7.42 | |
| <i>cis</i> -[(bpy) ₂ Ru(S(CH ₃) ₂)](PF ₆) ₂ | calcd | 12.21 | 7.75 | 6.77 | 7.48 | |
| | found | 12.52 | 7.04 | 7.13 | 7.15 | |
| <i>trans</i> -[(bpy) ₂ Ru(S(CH ₃) ₂)](PF ₆) ₂ | calcd | | 7.75 | 6.77 | 7.48 | |
| | found | | 7.95 | 6.74 | 7.38 | |
| <i>cis</i> -[(bpy) ₂ (Cl)RuS(CH ₂ CH ₃) ₂]PF ₆ | calcd | | 4.69 | 8.19 | 4.53 | 5.18 |
| | found | | 4.41 | 8.19 | 4.48 | 5.40 |
| <i>cis</i> -[(bpy) ₂ (Cl)RuS(CH ₃)C ₆ H ₅]PF ₆ | calcd | | 4.46 | 7.80 | 4.31 | 4.94 |
| | found | | 4.38 | 7.88 | 4.21 | 5.02 |
| <i>cis</i> -[(bpy) ₂ (Br)RuS(CH ₂ CH ₃) ₂]PF ₆ | calcd | | 4.40 | 7.69 | 4.25 | 10.97 ^a |
| | found | | 4.96 | 7.60 | 4.10 | 10.83 ^a |
| <i>cis</i> -[(bpy) ₂ (P(C ₆ H ₅) ₃)RuS(CH ₂ CH ₃) ₂](PF ₆) ₂ | calcd | | 3.04 | 5.31 | 8.80 | |
| | found | | 3.40 | 5.98 | 8.71 | |
| <i>cis</i> -[(bpy) ₂ Os(S(CH ₃)C ₆ H ₅) ₂](PF ₆) ₂ | calcd | | 6.16 | 5.38 | 5.95 | |
| | found | | 6.52 | 5.44 | 5.50 | |
| <i>cis</i> -[(bpy) ₂ Os(S(CH ₃)C ₆ H ₄ C(CH ₃) ₃) ₂](PF ₆) ₂ | calcd | | 5.56 | 4.86 | 5.37 | |
| | found | | 5.96 | 4.86 | 5.46 | |
| [(bpy) ₂ Os(3,4-S(CH ₃)C ₆ H ₃ (CH ₃)SCH ₃)](PF ₆) ₂ | calcd | | 6.56 | 5.74 | 6.34 | |
| | found | | 6.83 | 5.58 | 6.74 | |
| [(bpy) ₂ RuS ₂ CN(CH ₃) ₂]PF ₆ | calcd | | 9.45 | 10.32 | 4.56 | |
| | found | | 9.71 | 10.09 | 4.17 | |
| [(bpy) ₂ RuS ₂ CN(CH ₂ CH ₃) ₂]PF ₆ | calcd | | 9.07 | 9.91 | 4.38 | |
| | found | | 9.27 | 9.78 | 4.16 | |
| [(bpy) ₂ RuS ₂ CN(CH ₂) ₄]PF ₆ | calcd | | 9.10 | 9.96 | 4.40 | |
| | found | | 9.58 | 9.84 | 4.09 | |
| [(bpy) ₂ RuS ₂ COCH ₂ CH ₃]PF ₆ | calcd | | 9.43 | 8.25 | 4.56 | |
| | found | | 9.73 | 8.10 | 4.20 | |
| (bpy) ₂ Ru(SC ₆ H ₅) ₂ ^b | calcd | 16.00 | 10.15 | 8.87 | | |
| | found | 17.39 | 10.38 | 8.98 | | |
| <i>cis</i> -(bpy) ₂ Ru(SC ₆ F ₅) ₂ ^c | calcd | | 7.90 | 6.90 | | |
| | found | | 9.18 | 6.25 | | |

^a% Br. ^bCalcd: C, 60.83; H, 4.16. Found: C, 60.67; H, 4.46. ^cCalcd: F, 23.41. Found: F, 23.40.

-S₂COCH₂CH₃)). These complexes were prepared in the same manner as the analogous complexes containing chelated thioether ligands (vide supra). Relevant analytical, electrochemical, and spectrophotometric data are given in Tables I, IV, and VII, respectively.

***cis*-Dichlorobis(2,2'-bipyridine)osmium(II) Hydrate** [*cis*-(bpy)₂OsCl₂·H₂O]. This complex was prepared from (NH₄)₂OsCl₆ and 2,2'-bipyridine by a published method.⁹ Visible (CH₂Cl₂): λ_{max} 560, 465, 382.

***cis*-Bis(2,2'-bipyridine)bis(thioether)osmium(II) Hexafluorophosphate** [*cis*-(bpy)₂OsL₂](PF₆)₂ [L = S(CH₃)C₆H₅, 4-S(CH₃)C₆H₄C(CH₃)₃, 1/2 3,4-S(CH₃)C₆H₃(CH₃)SCH₃)]. These complexes were prepared by methylation of the corresponding thiolato complex.³⁶ In a typical preparation, 0.10 g of *cis*-[(bpy)₂OsCl₂]·H₂O (0.17 mmol) was refluxed for 4–6 h with 3.6 mmol each of thiol and NaOH in 10 mL of deaerated 50% aqueous ethanol. Dark crystals of the thiolato complex deposited during reflux. After reduction of the solution volume by ca. one-third, the crystals were recovered by filtration, washed with water and diethyl ether, and air-dried; yield 0.10 g. This isolated product (0.10 g) was dissolved in 10 mL of DMF, 1–2 mL of CH₃I was added, and the resulting solution was stirred for 1–3 h. To the reaction solution were added 10 mL of saturated aqueous NH₄PF₆ and 300 mL of diethyl ether, and the mixture was stirred for ca. 15 min. The ether layer was removed, 100 mL of H₂O was added, and the mixture was stirred for ca. 10 min. The resulting

orange-brown precipitate was recovered by filtration, washed with water and ether, and air-dried. The complexes were purified by chromatography on alumina with CH₃CN/C₆H₅CH₃ eluents and reprecipitated from acetone/ether. Relevant analytical, electrochemical, and spectrophotometric data are given in Tables I, III, and VI, respectively.

Equipment. All visible and ultraviolet spectra were obtained on a Cary 14 or Cary 210 recording spectrophotometer. Luminescence spectra were recorded on a Perkin-Elmer 650-10S fluorescence spectrophotometer equipped with a Hewlett-Packard 7015A X-Y recorder. Infrared spectra were obtained with a Perkin-Elmer 599 IR spectrophotometer. Electrochemical measurements were made by using 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 a working electrode, a saturated sodium chloride calomel reference electrode, and a platinum-wire auxiliary electrode, was used for cyclic voltammetric experiments. ¹H NMR spectra were obtained on a Varian T-60 spectrometer or a Nicolet 300 MHz FT-NMR spectrometer; the latter instrument was used to obtain all ¹³C NMR spectra.

Analyses. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN, or Guelph Chemical Laboratories, Ltd., Guelph, Ontario, Canada.

Procedures. Visible and UV spectra were obtained in spectral grade acetonitrile while electrochemical measurements were made in Burdick and Jackson spectral grade acetonitrile or propylene carbonate with 0.10 M TEAP as the electrolyte. Cyclic voltammograms were recorded at

(36) Elder, R. C.; Kennard, G. J.; Payne, M. D.; Deutsch, E. *Inorg. Chem.* **1978**, *17*, 1296–1303.

Table II. Electrochemical Parameters for Selected (bpy)₂Ru^{II} Complexes As Measured by Cyclic Voltammetry^a

| complex | $E_{1/2}^{\text{ox}}, \text{V}$ | | $E_{1/2}^{\text{red}}, \text{V}$ | |
|---|---------------------------------|--------------------|----------------------------------|-------|
| Thioether (and Sulfoxide) Complexes ^b | | | | |
| [(bpy) ₂ Ru(S(CH ₃)CH ₂ CH ₂ SCH ₃)] ²⁺ | 1.43 | | -1.28 | -1.49 |
| [(bpy) ₂ Ru(S(CH ₂ CH ₃)CH ₂ CH ₂ SCH ₂ CH ₃)] ²⁺ | 1.41 | | -1.28 | -1.48 |
| [(bpy) ₂ Ru(S(C ₆ H ₅)CH ₂ CH ₂ SC ₆ H ₅)] ²⁺ | 1.50 | | -1.28 | -1.46 |
| [(bpy) ₂ Ru(3,4-S(CH ₃)C ₆ H ₃ (CH ₃)SCH ₃)] ²⁺ | 1.54 | | -1.25 | -1.45 |
| [(bpy) ₂ Ru(S(CH ₃)CH ₂ CH ₂ NH ₂)] ²⁺ | | | -1.36 | -1.57 |
| [(bpy) ₂ Ru(S(CH ₂ C ₆ H ₅)CH ₂ CH ₂ NH ₂)] ²⁺ | | | -1.34 | -1.55 |
| [(bpy) ₂ Ru(S(C ₆ H ₅)CH ₂ CH ₂ NH ₂)] ²⁺ | | | -1.38 | -1.59 |
| [(bpy) ₂ Ru(S(CH ₃)C ₆ H ₆ N)] ²⁺ | 1.38 | | -1.28 | -1.48 |
| [(bpy) ₂ Ru(S(O)(CH ₃)CH ₂ CH ₂ NH ₂)] ²⁺ | | | -1.25 | -1.45 |
| <i>cis</i> -[(bpy) ₂ Ru(S(CH ₃) ₂)] ²⁺ ^c | 1.42 | | -1.31 | -1.52 |
| <i>trans</i> -[(bpy) ₂ Ru(S(CH ₃) ₂)] ²⁺ ^c | 1.37 | | | |
| <i>cis</i> -[(bpy) ₂ (Cl)Ru(S(CH ₂ CH ₃) ₂)] ⁺ | 0.88 | -1.32 ^d | -1.49 | -1.71 |
| <i>cis</i> -[(bpy) ₂ (Cl)Ru(S(CH ₃)C ₆ H ₅)] ⁺ | 0.88 | -1.33 ^d | -1.50 | -1.71 |
| <i>cis</i> -[(bpy) ₂ (Br)Ru(S(CH ₂ CH ₃) ₂)] ⁺ | 0.92 | -1.29 ^d | -1.47 | -1.65 |
| <i>cis</i> -[(bpy) ₂ (P(C ₆ H ₅) ₃)Ru(S(CH ₂ CH ₃) ₂)] ²⁺ | 1.55 | | -1.28 | -1.47 |
| Phosphine Complexes ^{e,f} | | | | |
| [(bpy) ₂ Ru((C ₆ H ₅) ₂ PCH ₂ P(C ₆ H ₅) ₂)] ²⁺ | 1.63 | | -1.29 | -1.54 |
| [(bpy) ₂ Ru((C ₆ H ₅) ₂ PCH ₂ CH ₂ CH ₂ P(C ₆ H ₅) ₂)] ²⁺ | 1.62 | | -1.30 | -1.50 |
| [(bpy) ₂ Ru((C ₆ H ₅) ₂ PCH=CHP(C ₆ H ₅) ₂)] ²⁺ | 1.75 | | -1.28 | -1.51 |
| <i>cis</i> -[(bpy) ₂ (Cl)Ru(P(CH ₂ CH ₂ CH ₂ CH ₃) ₃)] ⁺ | 0.81 | -1.32 ^d | -1.51 | -1.76 |
| <i>cis</i> -[(bpy) ₂ (Cl)Ru(P(CH ₃)(C ₆ H ₅) ₂)] ⁺ | 0.91 | -1.33 ^d | -1.59 | -1.71 |
| <i>cis</i> -[(bpy) ₂ (Cl)Ru(P(C ₆ H ₅) ₃)] ⁺ | 0.94 | -1.29 ^d | -1.47 | -1.67 |

^a Conditions: 0.1 M TEAP in CH₃CN vs. SSCE unless otherwise noted. ^b This work, unless otherwise noted. ^c In propylene carbonate with 0.1 M TEAP. ^d Irreversible anodic peak. ^e Reference 11. ^f 0.1 M (CH₃CH₂CH₂CH₂)₄NPF₆. ^g Complex of 8-(methylthio)quinoline. Reference 74.

Table III. Electrochemical Parameters for Selected (bpy)₂Os^{II} Complexes As Measured by Cyclic Voltammetry^a

| complex | $E_{1/2}^{\text{ox}}, \text{V}$ | $E_{1/2}^{\text{red}}, \text{V}$ | |
|---|---------------------------------|----------------------------------|-------|
| Thioether Complexes ^b | | | |
| [(bpy) ₂ Os(S(CH ₃)C ₆ H ₅) ₂] ²⁺ | 1.12 | -1.24 | -1.48 |
| [(bpy) ₂ Os(4-S(CH ₃)C ₆ H ₄ C(CH ₃) ₃) ₂] ²⁺ | 1.11 | -1.23 | -1.48 |
| [(bpy) ₂ Os(3,4-S(CH ₃)C ₆ H ₃ (CH ₃)SCH ₃)] ²⁺ | 1.18 | -1.17 | -1.39 |
| Phosphine Complexes ^c | | | |
| [(bpy) ₂ Os((C ₆ H ₅) ₂ PCH ₂ P(C ₆ H ₅) ₂)] ²⁺ | 1.27 | -1.26 | |
| [(bpy) ₂ Os((C ₆ H ₅) ₂ PCH=CHP(C ₆ H ₅) ₂)] ²⁺ | 1.40 | -1.26 | |

^a Conditions: 0.1 M TEAP in CH₃CN vs. SSCE unless otherwise noted. ^b This work. ^c 0.1 M (CH₃CH₂CH₂CH₂)₄NPF₆. Reference 12.

Table IV. Electrochemical Parameters for (bpy)₂Ru^{II} 1,1-Dithioato and Thiolato Complexes As Measured by Cyclic Voltammetry^a

| complex | $E_{1/2}^{\text{ox}}, \text{V}$ | $E_{1/2}^{\text{red}}, \text{V}$ | |
|---|---------------------------------|----------------------------------|-------|
| [(bpy) ₂ RuS ₂ CN(CH ₃) ₂] ⁺ | 0.54 | -1.53 | -1.78 |
| [(bpy) ₂ RuS ₂ CN(CH ₂ CH ₃) ₂] ⁺ | 0.55 | -1.52 | -1.78 |
| [(bpy) ₂ RuS ₂ CN(CH ₂) ₄] ⁺ | 0.54 | -1.53 | -1.78 |
| [(bpy) ₂ RuS ₂ COCH ₂ CH ₃] ⁺ | 0.74 | -0.15 ^b | -1.48 |
| [(bpy) ₂ Ru(SC ₆ H ₆ N)] ⁺ ^c | 0.30 | -1.49 | -1.74 |
| (bpy) ₂ Ru(SC ₆ H ₅) ₂ | -0.28 | | |
| (bpy) ₂ Ru(SC ₆ F ₅) ₂ | 0.12 | | |

^a Conditions: 0.1 M TEAP in CH₃CN vs. SSCE. ^b Irreversible anodic peak. ^c Complex of 8-mercaptoquinoline. Reference 74.

ambient temperatures at a glassy-carbon electrode vs. a saturated sodium chloride calomel electrode (SSCE) and are uncorrected for junction potentials. All $E_{1/2}$ values are given as oxidation potentials with an estimated error of ± 0.01 V. ¹H and ¹³C NMR spectra were obtained in organic solvents with (CH₃)₄Si as an internal standard.

Results

The ruthenium(II) and osmium(II) complexes prepared for this study are characterized by (1) the methods of preparation, (2) satisfactory elemental analyses (Table I), (3) cyclic voltammetric parameters (Tables II–IV), (4) visible and ultraviolet spectra (Tables V–VII), and (5) ¹H and ¹³C NMR spectra of representative complexes (Table IX).

Results from cyclic voltammetry experiments for various Ru(II) and Os(II) complexes are listed in Tables II–IV. Peak potential

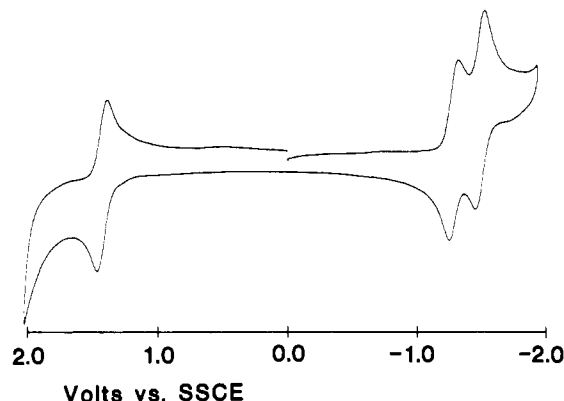


Figure 1. Cyclic voltammograms of [(bpy)₂Ru(S(CH₃)CH₂CH₂SCH₃)]²⁺. Conditions: 0.1 M TEAP in CH₃CN, glassy-carbon electrode vs. SSCE, ambient temperature, 100 mV s⁻¹ scan rate.

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,^{11,37} apparently due to uncompensated solution resistance.³⁷ Plots of peak currents 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. 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) and Os(II)/Os(III) redox couples generally range from 0.95 to 1.00; this ratio is somewhat lower for the complexes containing a halide atom. The cyclic voltammogram of [(bpy)₂Ru(S(CH₃)CH₂CH₂SCH₃)]²⁺ (Figure 1) is typical for the simple thioether complexes.

Spectrophotometric parameters obtained in CH₃CN are collected in Tables V–VII. The spectra of the dicationic thioether complexes feature a single, broad maximum in the visible region plus a series of UV peaks. However, the monocationic thioether complexes containing a halide atom, as well as the thiolato and 1,1-dithioato complexes, exhibit other visible peaks (or shoulders).

(37) Callahan, R. W.; Keene, F. R.; Meyer, T. J.; Salmon, D. J. *J. Am. Chem. Soc.* **1977**, *99*, 1064–1073.

Table V. Visible and Ultraviolet Spectrophotometric Parameters for Selected (bpy)₂Ru^{II} Complexes in Acetonitrile

| complex | λ_{\max} , nm (ϵ_{\max} , M ⁻¹ cm ⁻¹) |
|---|---|
| Thioether (and Sulfoxide) Complexes ^a | |
| [(bpy) ₂ Ru(S(CH ₃)CH ₂ CH ₂ SCH ₃)] ²⁺ | 416 (7200), 282 (50 000), 252 sh (17 000), 242 (20 000), 234 sh (18 000), 204 sh (50 000) |
| [(bpy) ₂ Ru(S(CH ₂ CH ₃)CH ₂ CH ₂ SCH ₂ CH ₃)] ²⁺ | 422 (7600), 283 (55 000), 252 sh (17 000), 242 (20 000), 234 sh (18 000), 205 sh (50 000) |
| [(bpy) ₂ Ru(S(C ₆ H ₅)CH ₂ CH ₂ SC ₆ H ₅)] ²⁺ | 404 (6600), 284 (40 000), 254 sh (20 000), 237 (40 000), 204 sh (65 000) |
| [(bpy) ₂ Ru(3,4-S(CH ₃)C ₆ H ₃ (CH ₃)SCH ₃)] ²⁺ | 397 (6200), 282 (46 000), 252 sh (24 000), 240 sh (30 000), 208 sh (53 000) |
| [(bpy) ₂ Ru(S(CH ₃)CH ₂ CH ₂ NH ₂)] ²⁺ | 447 (8300), 332 sh (7000), 286 (58 000), 254 sh (15 000), 243 (20 000) |
| [(bpy) ₂ Ru(S(CH ₂ C ₆ H ₅)CH ₂ CH ₂ NH ₂)] ²⁺ | 446 (7900), 330 sh (7000), 288 (55 000), 254 sh (19 000), 237 (29 000) |
| [(bpy) ₂ Ru(S(C ₆ H ₅)CH ₂ CH ₂ NH ₂)] ²⁺ | 444 (8000), 330 sh (7000), 287 (51 000), 254 sh (17 000), 238 (26 000) |
| [(bpy) ₂ Ru(S(O)(CH ₃)CH ₂ CH ₂ NH ₂)] ²⁺ | 390 (6300), 320 sh (17 000), 277 (78 000), 247 (33 000) |
| [(bpy) ₂ Ru(S(CH ₃)C ₉ H ₉ N)] ²⁺ ^b | 422 (5800), 283 (51 000), 253 sh (22 000), 234 (35 000), 204 sh (70 000) |
| <i>cis</i> -[(bpy) ₂ Ru(S(CH ₃) ₂)] ²⁺ | 431 (7200), 283 (54 000), 252 sh (17 000), 241 (21 000), 205 sh (53 000) |
| <i>trans</i> -[(bpy) ₂ Ru(S(CH ₃) ₂)] ²⁺ | 429 (8000), 283 (54 000), 253 sh (16 000), 242 (19 000), 205 sh (50 000) |
| <i>cis</i> -[(bpy) ₂ (Cl)Ru(S(CH ₂ CH ₃) ₂)] ⁺ | 482 (8300), 343 (7700), 291 (55 000), 255 sh (15 000), 238 (23 000), 207 sh (40 000) |
| <i>cis</i> -[(bpy) ₂ (Cl)Ru(S(CH ₃)C ₆ H ₅)] ⁺ | 481 (8400), 342 (7700), 291 (56 000), 254 sh (24 000), 240 (29 000), 205 sh (50 000) |
| <i>cis</i> -[(bpy) ₂ (Br)Ru(S(CH ₂ CH ₃) ₂)] ⁺ | 484 (8800), 344 (7300), 292 (52 000), 241 (30 000) |
| <i>cis</i> -[(bpy) ₂ ((C ₆ H ₅) ₃ P)Ru(S(CH ₂ CH ₃) ₂)] ²⁺ | 406 (7300), 284 (39 000), 232 sh (40 000) |
| Phosphine Complexes ^c | |
| [(bpy) ₂ Ru((C ₆ H ₅) ₂ PCH ₂ P(C ₆ H ₅) ₂)] ²⁺ | 384 (5800), 319 sh (9300), 280 (27 000), 277 (50 000), <215 (>10 000) |
| [(bpy) ₂ Ru((C ₆ H ₅) ₂ PCH ₂ CH ₂ CH ₂ P(C ₆ H ₅) ₂)] ²⁺ | 394 (5400), 321 sh (8100), 289 (23 000), 232 (41 000), <210 (>10 000) |
| [(bpy) ₂ Ru((C ₆ H ₅) ₂ PCH=CHP(C ₆ H ₅) ₂)] ²⁺ | 373 (8700), 317 sh (16 000), 293 sh (18 000), 276 (35 000), 268 sh (33 000), 223 (76 000), <202 (>10 000) |
| <i>cis</i> -[(bpy) ₂ (Cl)Ru(P(CH ₂ CH ₂ CH ₂ CH ₃) ₃)] ⁺ | 485 (7100), 347 (6500), 295 (43 000), 244 (18 000), <200 (>10 000) |
| <i>cis</i> -[(bpy) ₂ (Cl)Ru(P(CH ₃)(C ₆ H ₅) ₂)] ⁺ | 464 (6200), 333 (6000), 293 (50 000) |
| <i>cis</i> -[(bpy) ₂ (Cl)Ru(P(C ₆ H ₅) ₃)] ⁺ | 454 (6200), 328 (7100), 292 (40 000), 231 (40 000), <207 (>10 000) |
| Amine Complexes ^d | |
| [(bpy) ₂ Ru(NH ₂ CH ₂ CH ₂ NH ₂)] ²⁺ | 485 (9900), 344 (7600), 291 (60 000), 243 (21 000) |
| [(bpy) ₂ Ru(NH ₂ C(CH ₃) ₂ CH ₂ NH ₂)] ²⁺ | 487 (10 000), 345 (7600), 292 (58 000), 244 (21 000) |
| [(bpy) ₂ Ru(NH ₂ CH ₂ CH ₂ CH ₂ NH ₂)] ²⁺ | 492 (8500), 348 (6600), 292 (52 000), 244 (18 000) |
| [(bpy) ₂ Ru(NH ₂ CH ₂ C ₆ H ₄ N)] ²⁺ | 471 (10 000), 422 sh (6300), 339 (11 000), 298 (55 000), 244 (23 000) |

^aThis work. ^bComplex of 8-(methylthio)quinoline. Reference 74. ^cReference 11. ^dReference 8.

Table VI. Visible and Ultraviolet Spectrophotometric Parameters for Selected (bpy)₂Os^{II} Complexes in Acetonitrile

| complex | λ_{\max} , nm (ϵ_{\max} , M ⁻¹ cm ⁻¹) |
|---|---|
| Thioether Complexes ^a | |
| [(bpy) ₂ Os(S(CH ₃)C ₆ H ₅)] ²⁺ | 535 (2500), 443 (6200), 406 sh (5700), 289 (46 000), 246 sh (24 000), 219 (50 000) |
| [(bpy) ₂ Os(4-S(CH ₃)C ₆ H ₄ C(CH ₃) ₃)] ²⁺ | 536 (2500), 445 (6200), 408 sh (5700), 290 (46 000), 228 (50 000) |
| [(bpy) ₂ Os(3,4-S(CH ₃)C ₆ H ₃ (CH ₃)SCH ₃)] ²⁺ | 526 (1900), 387 (8200), 360 sh (7600), 283 (48 000), 254 sh (20 000), 239 (26 000), 212 (56 000) |
| Phosphine Complexes ^b | |
| [(bpy) ₂ Os((C ₆ H ₅) ₂ PCH ₂ P(C ₆ H ₅) ₂)] ²⁺ | 475 |
| [(bpy) ₂ Os((C ₆ H ₅) ₂ PCH=CHP(C ₆ H ₅) ₂)] ²⁺ | 466 |
| Amine Complexes ^c | |
| [(bpy) ₂ Os(NH ₂ CH ₂ CH ₂ NH ₂)] ²⁺ | 718 (3040), 670 sh, 510 (10 150), 480 sh, 425 (23 530), 380 sh, 359 (8250), 295 (56 500), 245 |
| [Os(bpy) ₃] ²⁺ | 579 (3270), 478 (11 100), 447 sh, 436 (10 660), 385 sh (9020), 368 (9550), 290 (77 300), 254 sh, 244 (27 400) |

^aThis work. ^bReference 12. ^cReference 6; in CH₃OH.

Table VII. Visible and Ultraviolet Spectrophotometric Parameters for (bpy)₂Ru^{II} 1,1-Dithioato and Thiolato Complexes in Acetonitrile

| complex | λ_{\max} , nm (ϵ_{\max} , M ⁻¹ s ⁻¹) |
|---|---|
| [(bpy) ₂ RuS ₂ CN(CH ₃) ₂] ⁺ | 518 (9300), 457 sh (6100), 349 (12 000), 294 (55 000), 242 (36 000) |
| [(bpy) ₂ RuS ₂ CN(CH ₂ CH ₃) ₂] ⁺ | 520 (9200), 460 sh (6300), 351 (12 000), 294 (55 000), 244 (37 000) |
| [(bpy) ₂ RuS ₂ CN(CH ₂) ₄] ⁺ | 521 (9300), 460 sh (6300), 348 (12 000), 294 (54 000), 243 (37 000) |
| [(bpy) ₂ RuS ₂ COCH ₂ CH ₃] ⁺ | 492 (8900), 447 sh (7000), 357 (8800), 292 (56 000), 255 sh (20 000), 245 (24 000) |
| [(bpy) ₂ Ru(SC ₉ H ₆ N)] ⁺ ^a | 501 (9700), 457 (9200), 420 sh (7300), 371 sh (7200), 345 (7800), 331 sh (7600), 293 (45 000), 277 sh (31 000), 249 (32 000), 205 sh (65 000) |

^aComplex of 8-mercaptoquinoline. Reference 74.

Room-temperature emission maxima of some (bpy)₂Os^{II} dithioether (and related) complexes in CH₃CN, as well as calculated excited-state redox potentials, are given in Table VIII. In this study the concentration of the osmium-thioether complex is 2 × 10⁻⁶ M. In a cursory examination of a solution of 1 × 10⁻⁶ M [(bpy)₂Ru(3,4-S(CH₃)C₆H₃(CH₃)SCH₃)]²⁺ in CH₃CN, no emission maximum was observed.

The IR spectrum of [(bpy)₂Ru(S(O)(CH₃)CH₂CH₂NH₂)]-(PF₆)₂ has a peak at 1070 cm⁻¹, which is absent from the IR spectrum of [(bpy)₂Ru(S(CH₃)CH₂CH₂NH₂)]Cl₂ and which is assigned to a S=O stretching mode. Values of $\nu_{S=O}$ for sul-

fur-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.^{38–40} The values of $\nu_{S=O}$ for various Ru(II) S-bonded sulfoxide complexes^{41–45} occur at somewhat lower

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(39) Wayland, B. B.; Schramm, R. F. *J. Chem. Soc., Chem. Commun.* **1968**, 1465–1466; *Inorg. Chem.* **1969**, *8*, 971–976.

(40) Kitching, W.; Moore, C. J.; Doddrell, D. *Inorg. Chem.* **1970**, *9*, 541–545.

Table VIII. Emission Maxima and Calculated Excited-State Electrochemical Parameters of Selected (bpy)₂Os^{II} Complexes in Acetonitrile

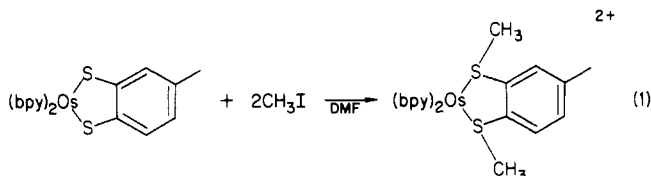
| complex | λ_{em} , nm | $E_{1/2}^{1*},^{a,b}$, V | $E_{1/2}^{2*},^{a,c}$, V |
|---|---------------------|---------------------------|---------------------------|
| [(bpy) ₂ Os(S(CH ₃)C ₆ H ₅) ₂] ^{2+ d,g} | 632 | -0.94 | 0.82 |
| [(bpy) ₂ Os(4-S(CH ₃)C ₆ H ₄ C(CH ₃) ₃) ₂] ^{2+ e,g} | 635 | -0.94 | 0.82 |
| [(bpy) ₂ Os(3,4-S(CH ₃)C ₆ H ₃ (CH ₃)-S(CH ₃))] ^{2+ f,g} | 627 | -0.90 | 0.91 |
| [(bpy) ₃ Os] ^{2+ h} | 723 | -0.98 | 0.50 |
| [(bpy) ₂ Os(NCCH ₃) ₂] ^{2+ h} | 673 | -1.03 | 0.59 |
| [(bpy) ₂ Os((C ₆ H ₅) ₂ PCH ₂ P(C ₆ H ₅) ₂)] ^{2+ h} | 622 | -0.82 | 0.83 |
| [(bpy) ₂ Os((C ₆ H ₅) ₂ PCH=CHP(C ₆ H ₅) ₂)] ^{2+ h} | 609 | -0.74 | 0.88 |

^a Estimated as outlined in ref 12 and 71. ^b [(bpy)₂OsL]³⁺ → [(bpy)₂OsL]^{2+*}. ^c [(bpy)₂OsL]^{2+*} → [(bpy)(bpy⁻)OsL]⁺. ^d λ_{irr} = 535 nm. ^e λ_{irr} = 536 nm. ^f λ_{irr} = 526 nm. ^g This work. ^h Reference 12.

energies than for other S-bonded sulfoxide complexes, presumably because of Ru(II) to sulfoxide back-bonding. Thus, the sulfoxide ligand of [(bpy)₂Ru(S(O)(CH₃)CH₂CH₂NH₂)]²⁺ is assigned as being bonded through the sulfur and nitrogen atoms.

Discussion

Synthesis. The ruthenium(II) chalcogen complexes described herein were prepared by modifications of methods used to prepare similar (bpy)₂Ru^{II} complexes containing amine,^{5,6} phosphine,¹¹ and other^{5,6} ligands. For [(bpy)₂RuL]²⁺ complexes containing chelating thioether (or sulfoxide) ligands, (bpy)₂RuCl₂ was simply refluxed with the appropriate bidentate ligand. However, attempts to prepare analogous (bpy)₂Os^{II} thioether complexes by this direct substitution method^{9,12} were unsuccessful. These complexes are readily prepared via alkylation of the corresponding thiolato complexes³⁶ (eq 1).



Electrochemistry. Thioether–Ru(II) Complexes. Cyclic voltammograms of the thioether (and sulfoxide) complexes listed in Table II are qualitatively very similar to those observed for the corresponding phosphine complexes,¹¹ all being dominated by a single reversible redox wave at positive potentials due to the Ru(II)/Ru(III) couple. The effects of various parameters on the potential of this Ru(II)/Ru(III) couple can be summarized as follows:

(1) The Ru(II)/Ru(III) couple occurs at a potential ca. 0.4–0.5 V lower for the monocationic complexes (containing one halide and one thioether ligand) than for the dicationic complexes (containing two thioether ligands), at least in part because of their lower formal charge. This effect is larger in the phosphine complexes, the dicationic species being 0.8–0.9 V more difficult to oxidize than the monocationic species. The effect of formal charge also contributes to making the thioether complex [(bpy)₂Ru(S(CH₃)C₉H₆N)]²⁺ ca. 1.0 V more difficult to oxidize than the thiolato analogue [(bpy)₂Ru(SC₉H₆N)]⁺ (Tables II and IV).

It should be noted that redox potential differences are expected between M^{2+/3+} and M^{1+/2+} couples simply because the different charge types lead to different changes in solvation energy for the

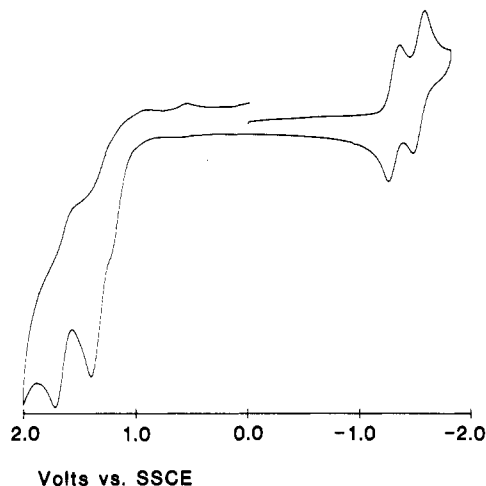


Figure 2. Cyclic voltammogram of [(bpy)₂Ru(S(CH₃)CH₂CH₂NH₂)]²⁺. Conditions are as in Figure 1.

redox processes. In the following discussion it is assumed that, as a first approximation, the solvation energy difference for a redox couple is dependent only on the charge type (M^{2+/3+} or M^{1+/2+}) and not on the nature of the ligands comprising the complexes of the couple. Thus, complexes of the same charge type are compared even though the sizes of the ligands comprising these complexes may be quite disparate.

(2) The complex containing one thioether and one phosphine ligand, *cis*-[(bpy)₂Ru(P(C₆H₅)₃)(S(CH₂CH₃)₂)]²⁺, is ca. 0.13 V more difficult to oxidize from Ru(II) to Ru(III) than is the analogous dithioether complex *cis*-[(bpy)₂Ru(S(CH₃)₂)₂]²⁺, presumably because the phosphine ligand better stabilizes Ru(II) than does the thioether ligand. As expected, the diphosphine complexes are even more difficult to oxidize from Ru(II) to Ru(III). Interestingly, the presence of one halide ligand in the coordination sphere significantly reduces the effect on the Ru(II)/Ru(III) couple of changing a thioether ligand to a phosphine ligand.

(3) Within all series of thioether and phosphine complexes, replacement of a pendant (to S or P) alkyl group by a pendant aryl group stabilizes Ru(II) and increases the $E_{1/2}$ value of the Ru(II)/Ru(III) couple. Thus, within the [(bpy)₂Ru(dithioether)]²⁺ complexes, the potential of the Ru(II)/Ru(III) couple increases in the order CH₃CH₂SCH₂CH₂SCH₂CH₃ ~ CH₃SC-H₂CH₂SCH₃ < C₆H₅SCH₂CH₂SC₆H₅ < 3,4-CH₃SC₆H₃(CH₃)SCH₃. This ordering parallels the expected increase in π -electron-accepting ability of the thioether ligands and thus the expected stabilization of Ru(II) relative to Ru(III).

(4) The bromo complex *cis*-[(bpy)₂Ru(Br)(S(CH₂CH₃)₂)]⁺ is more difficult to oxidize than the chloro analogue, demonstrating that the softer halogen better stabilizes the Ru(II) oxidation state.

(5) As observed for other *cis*- and *trans*-(bpy)₂Ru^{II} complexes,³⁵ the potential of the Ru(II)/Ru(III) couple of *cis*-[(bpy)₂Ru(S(CH₃)₂)₂]²⁺ is greater than that of the *trans* isomer. This implies that the *cis* configuration stabilizes Ru(II), relative to Ru(III), more than does the *trans* configuration, presumably through more efficient π back-bonding within the *cis* arrangement. Such a result is reasonable since two *trans*-situated π acids compete with each other for limited t_{2g} electron density more than do two *cis*-situated π acids.⁴⁶

Oxidation waves are also observed for the complexes [(bpy)₂Ru(3,4-S(CH₃)C₆H₃(CH₃)S(CH₃))]²⁺ and [(bpy)₂Ru(S(C₆H₅)CH₂CH₂SC₆H₅)]²⁺ (at faster scan rates) at potentials slightly higher than those of the Ru(II)/Ru(III) couples, presumably resulting from oxidation of the aromatic moieties. This presumption is supported by the cyclic voltammograms of non-coordinated 3,4-CH₃SC₆H₃(CH₃)SCH₃, which exhibits two ir-

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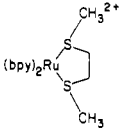
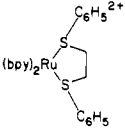
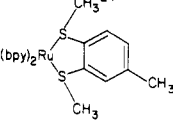
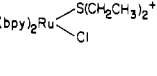
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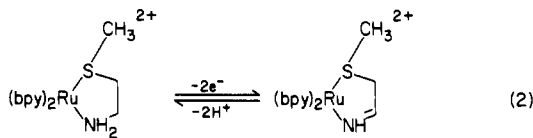
Table IX. 300-MHz ¹H and ¹³C NMR Spectral Data of Representative (bpy)₂Ru^{II} Thioether Complexes^a

| complex | ¹ H | | | ¹³ C | | |
|---|-------------------------|------------------------------|-------------------|-----------------|--------------|-----------------|
| | δ | character | assgnt | δ | no. of peaks | assgnt |
|  | 1.51 | singlet | CH ₃ | 15.5 | 1 | CH ₃ |
| | 2.86 (<i>J</i> = 9 Hz) | doublet | CH ₂ | | | |
| | 3.51 (<i>J</i> = 9 Hz) | doublet | CH ₂ | 36.6 | 1 | CH ₂ |
| | 7.53 | triplet | bpy H | | | |
| | 7.99 | multiplet | | 125.3–158.7 | 10 | bpy C |
| | 8.18 | triplet | | | | |
| | 8.43 | triplet | | | | |
| | 8.74 | doublet | | | | |
| | 8.84 | doublet | | | | |
| 9.48 | doublet | | | | | |
|  | 3.43 (<i>J</i> = 8 Hz) | doublet | CH ₂ | 32.2 | 1 | CH ₂ |
| | 4.08 (<i>J</i> = 8 Hz) | doublet | CH ₂ | | | |
| | 6.6–9.8 | complex series of multiplets | aromatic H | 125.0–158.0 | 16 | aromatic C |
|  | 1.89 | doublet | SCH ₃ | 20.6–21.4 | 3 | CH ₃ |
| | 2.47 | singlet | >CCH ₃ | | | |
| | 7.5–9.2 | complex series of multiplets | aromatic H | 125.5–158.6 | 16 | aromatic C |
|  | 1.05 (<i>J</i> = 7 Hz) | triplet | CH ₃ | | | |
| | 1.95 | multiplet | CH ₂ | | | |
| | 2.54 | multiplet | CH ₂ | | | |
| | 7.3–10.0 | complex series of multiplets | aromatic H | | | |

^a In acetone-*d*₆ vs. Me₄Si.

reversible anodic waves at 1.3 and 1.8 V (CH₃CN, 0.1 M TEAP, Pt vs. SSCE, 200 mV s⁻¹).

The amino thioether complexes (as well as the corresponding sulfoxide complex) undergo a series of irreversible oxidations at positive potentials (Figure 2). These oxidations can also be accomplished with Ce(IV) in H₂SO₄, the products resulting from 2-equiv oxidation of [(bpy)₂Ru(S(CH₃)CH₂CH₂NH₂)₂]²⁺ and [(bpy)₂RuS(C₆H₅)CH₂CH₂NH₂]²⁺ exhibiting absorption maxima at 436 and 432 nm, respectively. Addition of excess NaBH₄ to solutions of the oxidized complexes regenerates the visible spectra of the parent complexes. Comparative IR spectra show that these oxidized products do *not* contain a S=O moiety, and are thus likely to result from oxidation of the coordinated amine to a coordinated imine (eq 2). This type of reaction has been previously reported for a variety of amine complexes of (bpy)₂Ru^{II}.^{8,47}



Two reversible reduction waves between -1.2 and -1.6 V for the dicationic thioether complexes are each attributed to reduction of coordinated bipyridine ligands.^{11,48–50} For the monocationic thioether complexes, the reversible (or quasireversible) reduction waves occur between -1.5 and -1.7 V, reflecting the greater difficulty of reducing complexes of lower formal charge. An irreversible anodic wave is observed at ca. -1.3 V for these complexes, as is true for the analogous phosphine complexes.¹¹ This wave is related to a product (or products) formed from the second reduction wave. The coordinated bipyridine reduction waves for the amino thioether complexes occur at more negative potentials

than do those for the corresponding dithioether complexes because the amine nitrogen atom is a better σ -electron donor than is a thioether sulfur atom. However, the reduction of [(bpy)₂Ru(S(CH₃)C₉H₆N)]²⁺ occurs more easily than the reduction of the amino thioether complexes, reflecting the π -electron-accepting properties of the aromatic nitrogen terminus of the 8-(methylthio)quinoline ligand; also, relative to an aliphatic N atom, this aromatic N atom is a poorer σ -electron donor. Other waves are also observed for [(bpy)₂Ru(S(C₆H₅)CH₂CH₂SC₆H₅)]²⁺ and [(bpy)₂Ru(S(C₆H₅)CH₂CH₂NH₂)]²⁺ at more negative potentials; these waves may result from reduction of the pendant phenyl groups.

Thioether-Os(II) Complexes. Cyclic voltammograms of the thioether complexes listed in Table III are dominated by a single reversible redox wave at positive potentials due to the Os(II)/Os(III) couple. Comparison of the data in Tables II and III shows that the (bpy)₂Os^{II} complexes are more readily oxidized (by ca. 0.3–0.4 V) than are the corresponding Ru(II) complexes and that this is true for both the thioether and phosphine derivatives. The direction and magnitude of this effect are exactly as expected from established periodic trends,⁵¹ the heavier congener of second- and third-row elements always being much more stable in the higher oxidation state. For example, the difference in M(III)/M(II) couples for *trans*-[M(diars)₂Cl₂]⁺⁰ (where diars represents *o*-phenylenebis(dimethylarsine)) is 0.32 V for both the Ru/Os pair⁵¹ and the Tc/Re pair.⁵²

As is true for the Ru complexes, phosphine ligands stabilize Os(II) to a greater extent than do thioether ligands. The magnitude of this effect is approximately the same in both the Ru and Os series of complexes.

Thiolato and 1,1-Dithioato Ru Complexes. The data of Tables II and IV show that the potential of the Ru(II)/Ru(III) couple increases in the order thiolate < 1,1-dithioate < thioether. This order parallels the increase in formal charge of the (bpy)₂Ru(II) complexes, reflecting the increasing difficulty in oxidizing more positive charged centers. The following summarizes the effects

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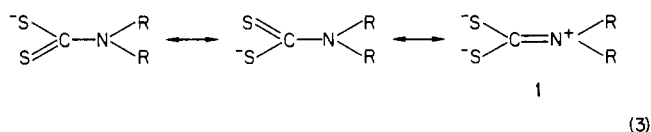
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of various parameters on the potentials of the Ru(II)/Ru(III) couples of these complexes:

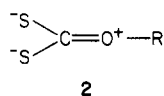
(1) The potential of the Ru(II)/Ru(III) couple is greater for $(\text{bpy})_2\text{Ru}(\text{SC}_6\text{F}_5)_2$ than for $(\text{bpy})_2\text{Ru}(\text{SC}_6\text{H}_5)_2$ due to the presence of the electron-withdrawing fluorine atoms. A complicated series of irreversible redox waves are observed at more positive potentials for both complexes, most likely due to thiolate oxidation processes.

(2) The xanthate complex exhibits an irreversible anodic wave at -0.15 V. This wave is derived from products generated in the second reduction process. At more positive potentials, irreversible waves resulting from oxidation of the coordinated dithioate ligand are observed.

(3) The dithiocarbamate complexes are more easily oxidized than the xanthate complex (by ca. 0.2 V), presumably due to the importance of resonance form 1.^{29,53} This resonance form localizes



formal negative charges on each of the coordinated sulfur atoms, thereby lowering the oxidation potential of the Ru(II) metal ion center. For the xanthate complex the analogous resonance form 2 is less likely to contribute significantly,²⁹ making the rutheni-



um(II) xanthate complex more difficult to oxidize than the ruthenium(II) dithiocarbamate complexes.

Electronic Absorption Spectra. The visible-UV spectra of the $(\text{bpy})_2\text{Ru}^{\text{II}}$, $(\text{bpy})_2(\text{X})\text{Ru}^{\text{II}}$, and $(\text{bpy})_2\text{Os}^{\text{II}}$ thioether complexes (Tables V and VI) are similar to those of the analogous phosphine complexes^{11,12} and are rather typical for complexes of this type.^{6,13} Peak assignments for the thioether complexes follow those for similar complexes.^{11,13,54-56}

The visible spectra of $(\text{bpy})_2\text{Ru}^{\text{II}}$ and $(\text{bpy})_2(\text{X})\text{Ru}^{\text{II}}$ ($\text{X} = \text{Cl}, \text{Br}$) thioether complexes feature a single absorption maximum. From comparisons of λ_{max} and ϵ_{max} values for this transition to similar parameters for analogous complexes,^{6,11,13} this peak is assigned as a Ru $4d_{\pi} \rightarrow \text{bpy} \pi^*$ metal-to-ligand charge-transfer transition (MLCT). For the monocationic thioether complexes, an absorption maximum at ca. 340 nm is observed with nearly the same intensity as the lower energy maximum. This peak is assigned as a second Ru $4d_{\pi} \rightarrow \text{bpy} \pi^*$ transition. A similar peak has been noted for the corresponding phosphine complexes, but because it occurs at higher energies, it appears as a shoulder on an intense peak at ~ 280 nm (wide infra). The shoulder at ca. 330 nm in the spectra of the amino thioether complexes and the amino sulfoxide complex may also be reasonably assigned to this second MLCT band. In the spectra of the dithioether complexes, this second MLCT band is apparently completely obscured by higher energy absorptions. The bipyridine π^* -acceptor orbitals involved in the $d_{\pi} \rightarrow \pi^*$ MLCT transitions may be characterized as symmetric (χ) or antisymmetric (ψ) with respect to the C_2 axis of the ligand.^{55,57-59} The two MLCT bands observed in the spectra of the monocationic and amino thioether complexes thus may be assigned to (in increasing energy) $4d_{\pi} \rightarrow \pi^*(\psi)$ and $4d_{\pi} \rightarrow \pi^*(\chi)$ transitions. The peak occurring between 280 and 290 nm is assigned to a bipyridine intraligand $\pi \rightarrow \pi^*$ transition.^{6,11,13} Other

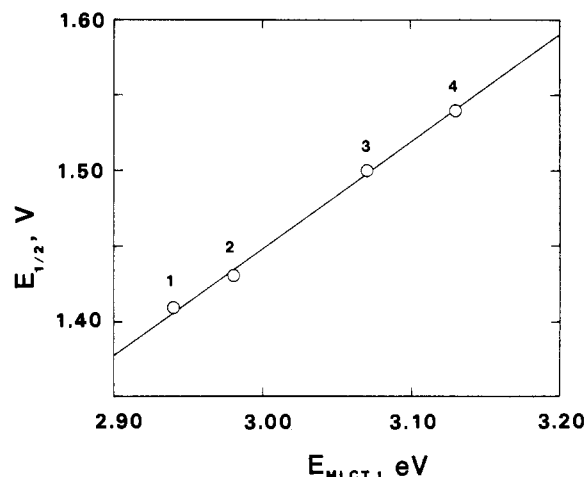


Figure 3. Plot of Ru(II)/Ru(III) $E_{1/2}$ value vs. the energy of the metal-to-ligand charge transition (E_{MLCT}) for selected $[(\text{bpy})_2\text{Ru}(\text{thioether})]^{2+}$ complexes. Thioether ligands: 1, $\text{CH}_3\text{CH}_2\text{SCH}_2\text{CH}_2\text{SCH}_2\text{C}_6\text{H}_5$; 2, $\text{CH}_3\text{SCH}_2\text{CH}_2\text{SCH}_3$; 3, $\text{C}_6\text{H}_5\text{SCH}_2\text{CH}_2\text{SC}_6\text{H}_5$; 4, $3,4\text{-CH}_2\text{SC}_6\text{H}_3(\text{CH}_3)\text{SCH}_3$.

peaks at higher energies are also likely to be due to bipyridine (or phenyl, where applicable) $\pi \rightarrow \pi^*$ transitions (or $n \rightarrow \pi^*$ for phenyl groups).

The visible absorption maxima for the dithioether complexes occur at lower energies than do those of the corresponding diphosphine complexes but appear at higher energies than do those of the amine complexes (Table V), consonant with the electron-donor and -acceptor properties of these ligand types. In addition, the energies of the visible MLCT peaks for the "mixed" thioether-amine and thioether-phosphine complexes are intermediate between those of the dithioether and diamine, and those of the dithioether and diphosphine complexes, respectively.

The positive $E_{1/2}$ values for the Ru(II)/Ru(III) couple of the dithioether complexes, representing the electrochemical oxidation of Ru(II), and the energies of the visible MLCT transitions, representing the photochemical oxidation of Ru(II), are linearly related as seen in Figure 3. Relationships of this type have been previously noted.^{10,60,61}

Although the visible MLCT bands for *cis*- $(\text{bpy})_2\text{Ru}^{\text{II}}$ complexes are usually observed at lower wavelengths than those for the *trans* isomers,³⁵ the spectra of *cis*- and *trans*- $[(\text{bpy})_2\text{Ru}(\text{S}(\text{CH}_3)_2)_2]^{2+}$ have visible peaks at nearly the same wavelength.

Peak assignments in the visible region for the $(\text{bpy})_2\text{Os}^{\text{II}}$ complexes (Table VI) are complicated by the intricacy of the spectra, possibly due to larger spin-orbit coupling or greater delocalization of Os(II) metal orbitals toward the ligands.^{55,62} The broad, low-energy, low-intensity band is tentatively assigned as an Os $5d_{\pi} \rightarrow \text{bpy} \pi^*$ MLCT transition.^{6,54,63} The energy of this band has the same ligand dependency as does the analogous Ru(II) MLCT peak. The higher energy visible bands exhibit similar properties and may also be tentatively assigned to $d_{\pi} \rightarrow \pi^*$ transitions.^{6,54,63} The UV peaks are assigned to various intraligand transitions, as for the analogous Ru(II) complexes.

The spectra of the $(\text{bpy})_2\text{Ru}^{\text{II}}$ 1,1-dithioate complexes are more complicated than those of the thioether complexes (Table VII). The peaks at 490-520 and 340-360 nm may be assigned to Ru $4d_{\pi} \rightarrow \text{bpy} \pi^*$ MLCT transitions. Other bands, generally appearing as shoulders on MLCT peaks, may be due to 1,1-dithioate intraligand $n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$, and $n \rightarrow \sigma^*$ transitions.^{53,64-66} or

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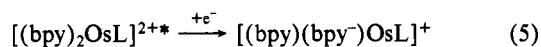
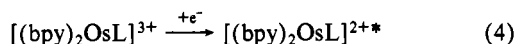
(64) Janssen, M. J. *Recl. Trav. Chim. Pays-Bas* **1960**, *79*, 454-463, 1066-1075.

MLCT transitions to the dithioato ligands.²⁹ The UV peaks are again assigned as bipyridine intraligand transitions.

An important feature of sulfur-containing (en)₂Co^{III} complexes is the sulfur $\sigma \rightarrow$ cobalt $d\sigma^*$ LMCT band at ca. 280 nm.^{36,67-70} An analogous transition for the (bpy)₂Ru^{II} complexes was not observed and either appears at a wavelength <200 nm or is masked by other intense UV absorptions in the spectra of these complexes.

Emission Spectra. Lowest energy emission maxima occurring at a wavelength <710 nm for the three (bpy)₂Os^{II} dithioether complexes are given in Table VIII. Each complex was irradiated at its lowest energy absorption maximum. Although the differences are small, the energy of the emission maxima increase in the order [(bpy)₂Os(S(CH₃)C₆H₄C(CH₃)₃)₂]²⁺ < [(bpy)₂Os(S(CH₃)C₆H₅)₂]²⁺ < [(bpy)₂Os(3,4-S(CH₃)C₆H₃(CH₃)SCH₃)]²⁺ (as do the energies of the lowest energy absorption maximum) paralleling the increase in π -electron-accepting abilities of the thioether ligands. The emission maxima (Table VIII) for the thioether complexes are intermediate between those of (bpy)₂Os^{II} complexes with nitrogen and phosphine donor ligands, a trend observed in the corresponding absorption maxima.

Also listed in Table VIII are calculated excited-state redox potentials, $E_{1/2}^{1*}$ (eq 4) and $E_{1/2}^{2*}$ (eq 5). The values of $E_{1/2}^{1*}$



and $E_{1/2}^{2*}$ were estimated by using eq 6 and 7.⁷¹ The spectro-

$$E_{1/2}^{1*} = E_{1/2}^{Os(II/III)} - E_{00} \quad (6)$$

$$E_{1/2}^{2*} = E_{1/2}^{bpy/bpy} + E_{00} \quad (7)$$

scopic zero-zero energy, E_{00} , was estimated as the energy of the emission maximum (in eV) plus 0.1 eV, as described.¹² In general, values of $E_{1/2}^{1*}$ and $E_{1/2}^{2*}$ for the thioether complexes are intermediate between values for the phosphine (more positive) and N-donor ligand (more negative) complexes.

¹H and ¹³C NMR Spectra. Both ¹H and ¹³C NMR spectra were obtained for representative (bpy)₂Ru(II) thioether complexes (Table IX). The ¹H NMR spectrum of [(bpy)₂Ru(S(CH₃)CH₂CH₂SCH₃)]²⁺ exhibits a singlet at δ 1.51 due to the methyl protons of the thioether ligand. Two doublets appear at δ 2.86 and 3.51. These resonances are assigned to the methylene protons

of the thioether ligand, which are thus described by a AA'BB' type pattern, similar to the patterns observed at low temperature for Cl₂Pt(S(CH₃)CH₂CH₂SCH₃).⁷² A comparison of these two systems indicate that inversion at the sulfur atoms of the Ru(II) complex is slow on the NMR time scale. The peaks and splitting patterns of the bpy proton resonances are similar to those observed for [(bpy)₂Ru(en)]²⁺.⁷³

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Registry No. [(bpy)₂Ru(S(CH₃)CH₂CH₂SCH₃)](PF₆)₂, 97278-92-7; [(bpy)₂Ru(S(CH₃)CH₂CH₂SCH₃)]³⁺, 97279-31-7; [(bpy)₂Ru(S(CH₃)CH₂CH₂SCH₂CH₃)](PF₆)₂, 97278-94-9; [(bpy)₂Ru(S(CH₂CH₃)CH₂CH₂SCH₂CH₃)]³⁺, 97279-32-8; [(bpy)₂Ru(S(C₆H₅)CH₂CH₂SC₆H₅)](PF₆)₂, 97278-96-1; [(bpy)₂Ru(S(C₆H₅)CH₂CH₂SC₆H₃)]³⁺, 97279-33-9; [(bpy)₂Ru(3,4-S(CH₃)C₆H₃(CH₃)SCH₃)](PF₆)₂, 97278-98-3; [(bpy)₂Ru(3,4-S(CH₃)C₆H₃(CH₃)SCH₃)]³⁺, 97279-34-0; [(bpy)₂Ru(S(CH₃)CH₂CH₂NH₂)](PF₆)₂, 97279-00-0; [(bpy)₂Ru(S(CH₂C₆H₅)CH₂CH₂NH₂)](PF₆)₂, 97279-02-2; [(bpy)₂Ru(S(C₆H₅)CH₂CH₂NH₂)](PF₆)₂, 97279-04-4; [(bpy)₂Ru(S(O)(CH₃)CH₂CH₂NH₂)](PF₆)₂, 97293-72-6; *cis*-[(bpy)₂Ru(S(CH₃)₂)](PF₆)₂, 97279-06-6; *cis*-[(bpy)₂Ru(S(CH₃)₂)]³⁺, 97279-35-1; *trans*-[(bpy)₂Ru(S(CH₃)₂)](PF₆)₂, 97335-17-6; *trans*-[(bpy)₂Ru(S(CH₃)₂)]³⁺, 97335-18-7; *cis*-[(bpy)₂(Cl)RuS(CH₂CH₃)₂]PF₆, 97279-08-8; *cis*-[(bpy)₂(Cl)RuS(CH₂CH₃)₂]²⁺, 97279-36-2; *cis*-[(bpy)₂(Cl)RuS(CH₂CH₃)₂]PF₆, 97279-10-2; *cis*-[(bpy)₂(Cl)RuS(CH₃)C₆H₅]²⁺, 97279-37-3; *cis*-[(bpy)₂(Br)RuS(CH₂CH₃)₂](PF₆)₂, 97279-12-4; *cis*-[(bpy)₂(Br)RuS(CH₂CH₃)₂]²⁺, 97279-38-4; *cis*-[(bpy)₂(P(C₆H₅)₃)RuS(CH₂CH₃)₂](PF₆)₂, 97293-74-8; *cis*-[(bpy)₂(P(C₆H₅)₃)RuS(CH₂CH₃)₂]³⁺, 97293-77-1; *cis*-[(bpy)₂Os(S(CH₃)C₆H₅)₂](PF₆)₂, 97293-76-0; *cis*-[(bpy)₂Os(S(CH₃)C₆H₅)₂]³⁺, 97293-78-2; *cis*-[(bpy)₂Os(S(CH₃)C₆H₄C(CH₃)₂)](PF₆)₂, 97279-14-6; *cis*-[(bpy)₂Os(S(CH₃)C₆H₄C(CH₃)₂)]³⁺, 97279-39-5; [(bpy)₂Os(3,4-S(CH₃)C₆H₃(CH₃)SCH₃)](PF₆)₂, 97279-16-8; [(bpy)₂Os(3,4-S(CH₃)C₆H₃(CH₃)SCH₃)]³⁺, 97293-79-3; [(bpy)₂RuS₂CN(CH₃)₂]PF₆, 97279-18-0; [(bpy)₂RuS₂CN(CH₃)₂]²⁺, 97279-40-8; [(bpy)₂RuS₂CN(CH₂CH₃)₂]PF₆, 97279-20-4; [(bpy)₂RuS₂CN(CH₂CH₃)₂]²⁺, 97279-41-9; [(bpy)₂RuS₂CN(CH₂)₄]PF₆, 97279-22-6; [(bpy)₂RuS₂CN(CH₂)₄]²⁺, 97279-42-0; [(bpy)₂RuS₂COCH₂CH₃]PF₆, 97279-24-8; [(bpy)₂RuS₂COCH₂CH₃]²⁺, 97279-43-1; (bpy)₂Ru(SC₆H₅)₂, 97279-25-9; [(bpy)₂Ru(SC₆H₅)₂]⁺, 97279-44-2; *cis*-(bpy)₂Ru(SC₆F₅)₂, 97279-26-0; *cis*-[(bpy)₂Ru(SC₆F₅)₂]⁺, 97279-45-3; (bpy)₂RuCl₂, 15746-57-3; (bpy)₂RuBr₂, 15868-15-2; *cis*-[(bpy)₂(Cl)RuP(C₆H₅)₃]PF₆, 67710-99-0; [(bpy)₂Ru(OH₂)₂](PF₆)₂, 72203-26-0; *cis*-[(bpy)₂OsCl₂], 79982-56-2; [(bpy)₂RuS(CH₃)CH₂CHNH](PF₆)₂, 97279-28-2; [(bpy)₂RuS(Ph)CH₂CHNH](PF₆)₂, 97279-30-6; 3,4-S(CH₃)C₆H₃(CH₃)SCH₃, 29690-14-0; CH₃I, 74-88-4; 3,4-dimercaptotoluene, 496-74-2.

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 (75) In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III \rightarrow 3 and 13.)