Contribution from the Department of Chemistry,
Wayne State University, Detroit, Michigan 48202

Osmium(VI)–Dioxo Complexes Derived from β-Diketone Schiff Bases and Their Reactivity with Arene- and Alkanethiols. Synthesis, Characterization, Structures, and Electrochemical Data

W. E. Lynch, R. L. Lintvedt,* and X. Q. Shui

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Novel *trans*-dioxoosmium(VI) complexes derived from dibasic tetradentate Schiff-base ligands obtained from the condensation of β-diketones and ethylenediamine have been synthesized. Reduction of these Os(VI) complexes with thiols yields Os(IV) products with trans thiolate ligands. The synthesis, characterization, and electrochemical properties of the Os(VI) oxo and Os(IV) thiolato complexes are described. Cyclic voltammetry was used to investigate the cathodic reduction and anodic oxidation potentials of the complexes. The substantial effect of the thiolate substituent on the reversible reduction potential ($E_{1/2}$) of the Os(IV)–Os(III) couple has been investigated. The reduction potential of the couple shifts anodically for more acidic thiols and cathodically for less acidic thiols. The trend in $E_{1/2}$ is correlated to the delocalization ability of the thiol ligand. A single-crystal X-ray structure determination has been completed for $Os^{VI}O_2[(BA)_2en]$ (**1**), recrystallized by slow diffusion from dichloromethane/diethyl ether. Crystal data: $P\bar{1}$, $a = 10.880$ (1) Å, $b = 12.634$ (2) Å, $c = 14.902$ (2) Å, $\alpha = 78.64$ (1)°, $\beta = 81.60$ (1)°, $\gamma = 72.559$ (9)°, $Z = 4$, $V = 2058.6$ (5) Å^3, $R = 0.0391$, $R_w = 0.0295$. A crystal structure of $Os^{IV}(SCH_2C_6H_5)_2[(BA)_2en]$ (**5**) was also completed. Single crystals were obtained from dichoromethane/diethyl ether. Crystal data: $P\bar{1}$, $a = 10.864$ (6) Å, $b = 17.903$ (3) Å, $c = 17.988$ (4) Å, $\alpha = 89.57$ (2)°, $\beta = 77.20$ (3)°, $\gamma = 84.67$ (3)°, $Z = 4$, $V = 3395$ (2) Å^3, $R = 0.0375$, $R_w = 0.0255$.

Introduction

The accessibility of several oxidation states of osmium has evoked a great deal of interest.[1-10] As a result, a variety of osmium compounds with oxidation states between +6 and +2 have been synthesized. The osmyl ion, *trans*-OsO_2^{2+}, is a particularly interesting source of Os(VI) compounds containing N_2O_2 tetradentate ligands.[11-14] It can be expected to bind four equatorial ligands atoms, giving rise to many normal coordination compounds. Reduction of osmyl compounds affords a convenient route to lower oxidation state compounds with the same equatorial ligands and different axial ligands.[11,14,15] This type of chemistry has not been heavily exploited until recently. Our interest in these systems stems largely from a desire to find synthetic pathways to high-oxidation-state binuclear osmium compounds in which the osmium atoms are approximately 3–3.5 Å apart. While the 1,3,5-triketones and their Schiff-base derivatives are potentially useful ligands to accomplish this purpose, there are synthetic difficulties to overcome. For this reason, we have undertaken a study of mononuclear osmyl complexes containing related but simpler ligands.

Quite surprisingly, the simplest mononuclear OsO_2^{2+} homologues of the 1,3,5-triketones, the bis(1,3-diketonato)OsO_2 complexes, have not been reported. There are apparently no literature references to any osmyl 1,3-diketonate-type complexes. Repeated attempts in our laboratory to prepare these simple compounds have failed. On the other hand, there are a few reports of Schiff-base type complexes of the osmyl ion.[15,16] This leads one to believe that whereas compounds with ligands containing all oxygen donors are difficult to prepare, compounds containing ligands with both nitrogen and oxygen donors are not. The results reported herein are consistent with this observation.

Table I. Elemental Analyses of Osmium Complexes[a]

complex	formula	% C	% H	% N	% S
$OsO_2[(BA)_2en]$ (**1**)	$OsC_{22}H_{22}N_2O_4$	46.2 (46.5)	3.7 (3.9)	4.7 (4.9)	
$OsO_2[(AA)_2en]$ (**2**)	$OsC_{12}H_{18}N_2O_4$	32.3 (32.4)	4.2 (4.1)	6.2 (6.3)	
$OsO_2[(iBu)_2en]$ (**3**)	$OsC_{18}H_{30}N_2O_4$	40.7 (40.9)	5.7 (5.7)	5.2 (5.3)	
$Os(SC_6H_5)_2[(BA)_2en]$ (**4**)	$OsC_{34}H_{32}N_2O_2S_2$	54.0 (54.1)	4.6 (4.3)	3.7 (3.7)	8.5 (8.5)
$Os(SCH_2C_6H_5)_2$-$[(BA)_2en]$ (**5**)[b]	$OsC_{36}H_{37}N_2O_{2.5}S_2$	54.9 (54.6)	4.6 (4.7)	3.4 (3.5)	8.3 (8.1)
$Os(SNp)_2[(BA)_2en]$ (**6**)	$OsC_{42}H_{36}N_2O_2S_2$	58.9 (59.0)	4.4 (4.2)	3.1 (3.3)	7.9 (7.5)
$Os(SC_6H_4CH_3)_2$-$[(BA)_2en]$ (**7**)	$OsC_{36}H_{36}N_2O_2S_2$	55.2 (55.2)	4.9 (4.6)	3.5 (3.6)	8.4 (8.2)
$Os(SC_6H_4F)_2[(BA)_2en]$ (**8**)[c]	$OsC_{34}H_{32}N_2O_3S_2F_2$	49.7 (50.5)	3.8 (4.0)	3.4 (3.5)	7.9 (7.9)
$Os(SEt)_2[(BA)_2en]$ (**9**)	$OsC_{26}H_{32}N_2O_2S_2$	47.6 (47.4)	5.0 (4.9)	4.2 (4.3)	9.3 (9.7)
$Os(SBu)_2[(BA)_2en]$ (**10**)	$OsC_{30}H_{40}N_2O_2S_2$	50.7 (50.4)	5.6 (5.6)	3.9 (3.9)	9.1 (9.0)
$Os(SC_6H_{11})_2[(BA)_2en]$ (**11**)	$OsC_{34}H_{44}N_2O_2S_2$	53.3 (53.4)	5.8 (5.9)	3.7 (3.7)	8.7 (8.2)

[a] Calculated values appear in parentheses. [b] Half a water molecule calculated in analysis from structural results. [c] One water molecule calculated in analysis.

In the present study, three Schiff-base ligands formed by condensing ethylenediamine and 1,3-diketones [3,3′-(1,2-ethanediylnitrilo)bis(1-R-1-butanonato)]; R = methyl, isobutyl, phenyl] were reacted with $K_2OsO_2(OH)_4$ to yield the osmyl Schiff-base complexes. These osmyl products were reacted with a variety of thiols, resulting in Os(IV) complexes with equatorial tetradentate Schiff-base ligands and axial thiolate ligands. The synthesis, characterization, structures, and electrochemical properties of these Os(VI) and Os(IV) compounds are reported.

Experimental Section

I. Synthesis. The syntheses of the β-diketone ethylenediamine–Schiff Base derivatives *N,N′*-bis(benzoylacetone) ethylenediimine, $H_2[(BA)_2en]$, *N,N′*-bis(acetylacetone) ethylenediimine, $H_2[(AA)_2en]$, and *N,N′*-bis(isobutyrylacetone) ethylenediimine, $H_2[(iBA)_2en]$, were carried out by modification of a previously described literature preparation.[17] Potas-

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sium tetrahydroxodioxoosmate(VI), $K_2OsO_2(OH)_4$, was prepared as described.[18] The thiol starting materials, (thiophenol, benzyl mercaptan, 2-naphthalenethiol, *m*-thiocresol, 4-fluorothiophenol, ethanethiol, 1-butanethiol, and cyclohexanethiol) were all used as supplied by Aldrich.

The syntheses for the three *trans*-dioxoosmium(VI)[11] and the *trans*-dithiolatoosmium(IV)[15] complexes are modifications of previously described methods. Elemental analyses are reported in Table I. Yields, although not maximized, are reported below.

Dioxo[3,3′-(1,2-ethanediyldinitrilo)bis(1-phenyl-1-butanonato)]osmium(VI), $OsO_2[(BA)_2en]$ (1). A methanolic solution of 0.25 g (0.68 mmol) of $K_2OsO_2(OH)_4$ was added to a suspension of the ligand $H_2[(BA)_2en]$ (0.28 g, 0.80 mmol) and benzoic acid[3] (0.166 g, 1.36 mmol) in 100 mL of methanol. This solution was allowed to stir for 1 h, at which time a brown-red precipitate formed upon standing. This solid was filtered off, washed with diethyl ether, and dried under vacuum. The product was then dissolved in dichloromethane, and X-ray-quality crystals were precipitated by slow diffusion of diethyl ether. Yield: 0.32 g (84%).

Dioxo[4,4′-(1,2-ethanediyldinitrilo)bis(2-pentanonato)]osmium(VI), $OsO_2[(AA)_2en]$ (2). The ligand $H_2[(AA)_2en]$ (0.20 g, 0.89 mmol), $K_2OsO_2(OH)_4$ (0.25 g, 0.68 mmol), and benzoic acid[3] (0.166 g, 1.36 mmol) were reacted as for **1**, except upon standing no precipitation was observed. The methanol was subsequently removed under vacuum. The resulting residue was dissolved in acetone, and the solution was filtered over a glass frit. The filtrate was collected and the solvent removed under vacuum. The residue then was dissovled in dichloromethane. The product was precipitated by slow diffusion of diethyl ether into the dichloromethane solution. Yield: 0.216 g (71%).

Dioxo[2,2′-(1,2-ethanediyldinitrilo)bis(6-methyl-4-heptanonato)]osmium(VI), $OsO_2[(iBA)_2en]$ (3). The compound was prepared in a manner similar to that for compound **2** except that equimolar quantities of $K_2OsO_2(OH)_4$ and ligand were used (0.68 mmol). The benzoic acid concentration was 1.36 mmol. Yield: 0.265 g (74%).

$Os(SR)_2[(BA)_2en]$ (4–11). Complex **1** (0.1 g, 0.176 mmol) was dissolved in 20 mL of degassed dichloromethane, and a 10-fold molar excess of the appropriate thiol was added dropwise or was added in one portion in the synthesis with the solid reactant 2-naphthalenethiol (**6**). This solution was refluxed under nitrogen for approximately 1 h. The color changed from dark red to blue-black during reflux. The solvent was subsequently removed under vacuum. The crude residue was purified on a silica gel column using pentane/acetone (95/5) to remove excess thiol and methanol as the eluent. Dark purple crystals of **5** were obtained by slow diffusion of diethyl ether into a dichloromethane solution of the crude product. Complexes **4** and **6–8** were also recrystallized by the same method. Complexes **9–11** were precipitated by addition of pentane to a dichloromethane solution of the crude product due to the higher solubility of the products. Yields for the arenethiol products (**4–8**) were nearly quantitative in the range 79%–92%, whereas those for the alkanethiol complexes (**9–11**) wer slightly lower, 59%–68%.

II. Physical and Chemical Measurements. Chemical analyses were performed by Galbraith Laboratories Inc., Knoxville, TN. The results of elemental analyses are reported in Table I. Infrared spectra were recorded as KBr pellets on a Nicolet 20DX Fourier transform spectrophotometer. Electronic absorption spectra in the visible and ultraviolet regions were recorded on a Perkin-Elmer Lambda3 spectrophotometer and a Hewlett Packard 8452A spectrophotometer in acetonitrile.

^1H and ^{19}F nuclear magnetic resonance spectra were recorded in the pulsed Fourier transform mode on General Electric QE-300 and GN-300 spectrometers, respectively. Proton chemical shifts were obtained relative to that of chloroform (7.26 ppm), whereas ^{19}F shifts were recorded with $CFCl_3$ as reference.

Electrochemical results were obtained with a Princeton Applied Research Model 173 potentiostat/galvanostat equipped with a PAR Model 179 digital coulometer and a Model 175 universal programmer. Data collection was accomplished with a Nicolet digital oscilloscope, Model 2090-3C with binary digital I/O, in conjunction with a Macintosh SE minicomputer. Computer programs for data transfer were designed in this laboratory. Electrochemical measurements were made in *N*,*N*-dimethylformamide (DMF). Solutions were deoxygenated with ultrahigh-purity N_2 that was passed through a pair of chromous–perchloric acid scrubbers and a $CaSO_4$ drying column.

Cyclic voltammograms were obtained by using a three-electrode glass cell with a saturated NaCl calomel reference electrode, a Pt-wire counter electrode, and a Pt-bead working electrode that was designed in this laboratory. The reference electrode was separated from the sample chamber by two salt bridges. The bridge adjacent to the reference electrode contained a 0.13 M tetraethylammonium perchlorate (TEAP) aqueous solution, and the one adjacent to the sample chamber contained a 0.1 M TEAP solvent solution. Under the experimental conditions, the ferrocenium–ferrocene couple was located at +0.32 V.

Table II. Experimental Crystallographic Data

	1	5
formula	$OsO_2[(BA)_2en]$	$Os(SCH_2C_6H_5)_2[(BA)_2en]\cdot {}^1/_2H_2O$
empirical formula	$OsC_{22}H_{22}N_2O_4$	$OsC_{36}H_{37}N_2O_{2.5}S_2$
fw	568.6	792.1
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a, Å	10.880 (1)	10.864 (6)
b, Å	12.634 (2)	17.903 (3)
c, Å	14.902 (2)	17.988 (4)
α, deg	78.64 (1)	89.57 (2)
β, deg	81.60 (1)	77.20 (3)
γ, deg	72.559 (9)	84.67 (3)
V, Å^3	2058.6 (5)	3395 (2)
Z	4	4
ρ_{calcd}, g cm^{-3}	1.833	1.531
λ(Mo Kα_1), Å	0.71069	0.71073
T, °C	23	23
μ, cm^{-1}	65.54	41.3
transm coeff	0.158–0.302	0.493–0.694
$R(F_o)$	0.0391	0.0375
$R_w(F_o)$	0.0295	0.0255

III. Crystallographic and Structure Determination. $OsO_2[(BA)_2en]$ (1). A red cubic crystal of **1** was placed on the end of a glass fiber and then sealed with Cole Parmer epoxy 8778. Preliminary examination of the crystal and the data collection were performed on a Nicolet R3 automated diffractometer using Mo Kα radiation from a graphite monochromator at room temperature. All information concerning crystallographic data collection and results are summarized in Table II. Absorption corrections were made by empirical methods and yielded transmission coefficients of 0.158–0.302. The structure was solved by heavy-atom methods and refined as blocked matrices in least-squares calculations.[19] Hydrogen atom positions were calculated, and their isotropic temperature factors were all assigned to a single variable (0.06 Å^2). All non-hydrogen atoms were refined anisotropically except for N2′. In the final cycle of least-squares refinement, the maximum shift was $<0.01\sigma$. No correction for secondary extinction was made; however, six reflections that were affected, (020), (130), (022), (1$\bar{5}$3), (2$\bar{4}$3), and (3$\bar{6}$5), were removed. The highest peak in the difference map was 1.36 e Å^{-3} in the vicinity of Os1. The number of observations was 5638, and the number of variable parameters was 516. Other crystallographic details are listed in Table II. Table III contains the positional coordinates, while Table IV contains the bond distances and angles obtained from the experiment.

$Os(SCH_2C_6H_5)_2[(BA)_2en]$ (5). Compound **5** crystallizes as dark purple, nearly black rectangular rods. A single crystal was placed on the end of a glass fiber and sealed with Cole Parmer epoxy 8778. Preliminary examination and data collection were performed on a Nicolet R3 automated diffractometer equipped with Mo Kα radiation and a graphite monochromator. Other details concerning collection of data and results are listed in Table II. Absorption corrections were performed by empirical methods and produced transmission coefficients of 0.493–0.694. The structure was solved by heavy-atom methods and refined as blocked matrices in least-squares calculations.[19] Hydrogen atoms were placed in calculated positions and held invariant. Isotropic temperature factors for the hydrogen atoms were all tied to a single variable (0.06 Å^2). Two phenyl rings containing the atoms C5–C10 and C31–C36 were treated as rigid bodies. All other non-hydrogen atoms were refined anisotropically. In a final cycle of least-squares refinement, the maximum shift was $<0.03\sigma$. No correction for secondary extinction was made. The highest peak in the difference map was 1.07 e Å^{-3} near Os1′. The number of observations was 5507, and the number of variable parameters was 758. Other details of the crystallographic experiment are given in Table II. Positional coordinates are given in Table V, and bond distances and angles are given in Table VI.

Results

I. X-ray Crystallography. 1. Description of the Structure of $OsO_2[(BA)_2en]$ (1). Tabular data for compound **1** are presented

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Table III. Selected Atomic Positional Parameters for $OsO_2[(BA)_2en]$ (**1**)

atom	*x*	*y*	*z*
	Molecule 1		
Os1	0.25312 (3)	0.75604 (3)	0.46984 (2)
O1	0.2772 (5)	0.8721 (4)	0.4054 (3)
O2	0.2219 (5)	0.6375 (4)	0.5207 (4)
O3	0.0746 (5)	0.7954 (4)	0.4163 (4)
O4	0.3380 (6)	0.6849 (5)	0.3546 (4)
N1	0.1818 (8)	0.8250 (6)	0.5827 (4)
N2	0.4211 (6)	0.7153 (5)	0.5283 (4)
C1	0.6439 (8)	0.6116 (7)	0.5544 (6)
C2	0.5265 (8)	0.6468 (7)	0.4988 (5)
C3	0.5416 (8)	0.6030 (6)	0.4189 (6)
C4	0.4564 (8)	0.6272 (6)	0.3508 (6)
C5	0.5022 (8)	0.5869 (7)	0.2618 (5)
C11	0.0139 (8)	0.9263 (6)	0.6849 (5)
C12	0.0561 (9)	0.8759 (6)	0.5988 (5)
C13	−0.0398 (8)	0.8855 (6)	0.5408 (5)
C14	−0.0304 (9)	0.8450 (7)	0.4619 (6)
C15	−0.1532 (8)	0.8488 (6)	0.4244 (5)
C21	0.2782 (9)	0.8007 (8)	0.6515 (6)
C22	0.4127 (9)	0.7695 (8)	0.6072 (6)
	Molecule 2		
Os1′	0.10615 (3)	0.78385 (3)	0.96746 (2)
O1′	0.1856 (5)	0.6615 (4)	1.0217 (4)
O2′	0.0402 (5)	0.9025 (4)	0.8993 (3)
O3′	0.0666 (5)	0.7071 (4)	0.8728 (3)
O4′	0.2799 (5)	0.7849 (4)	0.8878 (4)
N1′	−0.0625 (7)	0.7874 (5)	1.0457 (4)
N2′	0.1417 (6)	0.8572 (5)	1.0622 (4)
C1′	0.2580 (9)	0.9383 (8)	1.1386 (6)
C2′	0.2401 (9)	0.8894 (6)	1.0621 (5)
C3′	0.3391 (8)	0.8838 (7)	0.9850 (5)
C4′	0.3536 (8)	0.8329 (6)	0.8449 (5)
C5′	0.4760 (8)	0.8286 (7)	0.8449 (5)
C11′	−0.280 (1)	0.7679 (9)	1.0826 (7)
C12′	−0.1490 (9)	0.7496 (7)	1.0264 (6)
C13′	−0.1322 (9)	0.6870 (8)	0.9580 (6)
C14′	−0.0294 (9)	0.6698 (7)	0.8882 (5)
C15′	−0.0354 (8)	0.6012 (7)	0.8210 (6)
C21′	0.0487 (9)	0.8495 (7)	1.1479 (5)
C22′	−0.0860 (8)	0.8565 (7)	1.1158 (6)

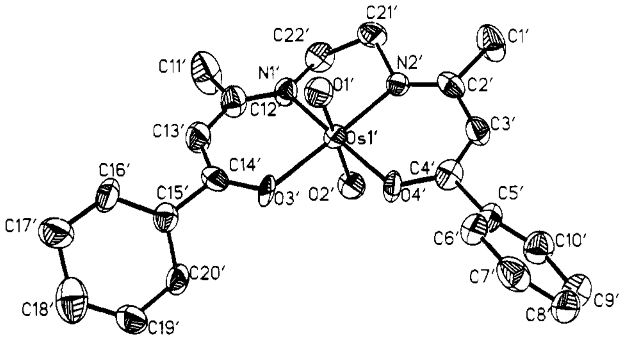

Figure 1. Perspective view of $OsO_2[(BA)_2en]$ (**1**). Thermal ellipsoids are drawn at the 50% probability level.

in Tables III and IV and include atomic coordinates, bond lengths, and bond angles. Atomic labeling for molecule II is given in Figure 1, with the second crystallographically independent molecule using the corresponding number scheme designated without a "prime".

The two crystallographically independent molecules, I and II, are essentially equivalent. The metal atom is bonded to two axial oxygens and to the N_2O_2 donor atoms of the ligand. The osmium atoms are located within 0.01 Å (I) and 0.004 Å (II) in the mean planes of N_2O_2, whereas the methylene carbons of the ethylenediamine bridge are staggered above and below the plane approximately 0.2 and 0.3 Å for molecules I and II, respectively. The trans osmyl Os–O bond lengths of 1.753 (7) and 1.753 (7) Å (I) and 1.730 (7) and 1.742 (7) Å (II) are normal with respect to the average Os–O distance reported in *trans*-[OsO_2(3-*t*-Bu-saltmen)] of 1.741 Å.[16] The bond angle of the trans osmyl moiety for molecules I and II are 172.2 (3)° (I) and 172.0 (3)° (II), respectively. Both are significantly bent compared to the value reported in the previously mentioned compound, in which the O–Os–O bond angle is 176.6°.[16] The average equatorial Os–O(keto) bond lengths of 2.092 Å (I) and 2.078 Å (II) are slightly longer than those reported previously for the M–O distances in Cu[$(BA)_2$en] (1.907 Å)[20] and Ni[$(BA)_2$en] (1.854 Å).[21] The Os–N(imine) bond distances of 2.023 Å (I) and 2.020 Å (II) are also longer than those of the corresponding copper (1.928 Å)[20] and nickel (1.855 Å)[21] complexes. Both of these bond types (Os–O and Os–N) correspond well with distances reported for [OsO_2(3-*t*-Bu-saltmen)].[16] The Schiff-base bond lengths and angles are normal for this ligand system.[20,21]

Table IV. Selected Bond Lengths (Å) and Bond Angles (deg) for $OsO_2[(BA)_2en]$ (**1**)

	molecule 1	molecule 2
Os1–O1	1.753 (7)	1.730 (7)
Os1–O2	1.753 (7)	1.742 (7)
Os1–O3	2.087 (6)	2.073 (7)
Os1–O4	2.097 (7)	2.083 (6)
Os1–N1	2.029 (9)	2.018 (7)
Os1–N2	2.018 (7)	2.022 (8)
O3–C14	1.31 (1)	1.27 (1)
O4–C4	1.29 (1)	1.29 (1)
N1–C12	1.34 (1)	1.29 (1)
N1–C21	1.50 (1)	1.49 (1)
N2–C2	1.32 (1)	1.27 (1)
N2–C22	1.49 (2)	1.52 (1)
C21–C22	1.49 (1)	1.58 (1)
O1–Os1–O2	172.2 (3)	172.0 (3)
O1–Os1–O3	88.1 (3)	86.1 (3)
O1–Os1–O4	87.3 (3)	87.2 (3)
O1–Os1–N1	91.7 (4)	94.0 (3)
O1–Os1–N2	94.2 (3)	93.4 (3)
O2–Os1–O3	86.4 (3)	89.4 (3)
O2–Os1–O4	87.0 (3)	86.1 (3)
O2–Os1–N1	94.3 (4)	92.9 (3)
O2–Os1–N2	91.5 (3)	91.2 (3)
O3–Os1–O4	88.4 (3)	87.6 (2)
O3–Os1–N1	94.8 (3)	93.9 (3)
O3–Os1–N2	176.9 (3)	178.6 (3)
O4–Os1–N1	176.6 (3)	178.1 (3)
O4–Os1–N2	93.7 (3)	93.7 (3)
N1–Os1–N2	83.0 (3)	84.8 (3)

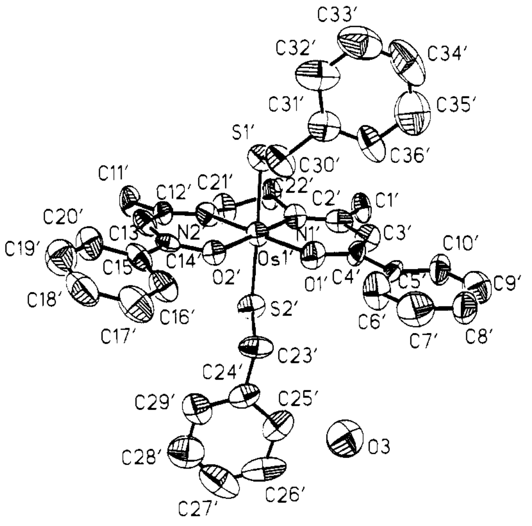

Figure 2. Perspective view of $Os(SCH_2C_6H_5)_2[(BA)_2en]$ (**5**). Thermal ellipsoids are drawn at the 50% probability level.

The molecules are stacked in centrosymmetric pairs by van der Waals forces. The relatively close contact in the range 3.6–4.3

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Table V. Selected Atomic Positional Parameters for $Os(SCH_2C_6H_5)_2[(BA)_2en]\cdot{}^1/_2H_2O$ (**5**)

atom	*x*	*y*	*z*
		Molecule 1	
Os1	0.65254 (4)	0.57821 (2)	0.29125 (2)
S1	0.7477 (3)	0.4710 (2)	0.3333 (2)
S2	0.5537 (3)	0.6867 (2)	0.2515 (2)
O1	0.6829 (6)	0.5363 (3)	0.1825 (4)
N1	0.8129 (8)	0.6243 (4)	0.2731 (5)
O2	0.4851 (6)	0.5342 (3)	0.3123 (4)
N2	0.6286 (8)	0.6224 (4)	0.3960 (4)
C1	1.016 (1)	0.6664 (7)	0.1986 (6)
C2	0.893 (1)	0.6275 (6)	0.2063 (7)
C3	0.870 (1)	0.5983 (6)	0.1375 (6)
C4	0.775 (1)	0.5556 (6)	0.1274 (6)
C5	0.7651 (8)	0.5254 (5)	0.0525 (4)
C11	0.517 (1)	0.6522 (5)	0.5299 (5)
C12	0.527 (1)	0.6149 (5)	0.4514 (6)
C13	0.4271 (9)	0.5731 (6)	0.4446 (6)
C14	0.4107 (9)	0.5385 (5)	0.3792 (7)
C15	0.289 (1)	0.5012 (5)	0.3832 (7)
C21	0.7263 (9)	0.6747 (6)	0.4017 (6)
C22	0.849 (1)	0.6488 (6)	0.3442 (6)
C23	0.4500 (9)	0.6499 (6)	0.1953 (6)
C24	0.430 (1)	0.7080 (6)	0.1336 (7)
C30	0.714 (1)	0.3910 (5)	0.2797 (6)
C31	0.835 (1)	0.3408 (7)	0.2567 (5)
		Molecule 2	
Os1′	0.22595 (4)	0.03558 (2)	0.78955 (3)
S1′	0.2777 (3)	−0.0663 (2)	0.8597 (2)
S2′	0.1686 (3)	0.1393 (2)	0.7220 (2)
N1′	0.3931 (8)	0.0724 (4)	0.7830 (5)
N2′	0.1771 (9)	0.0990 (4)	0.8852 (5)
O1′	0.2826 (7)	−0.0247 (3)	0.6910 (3)
O2′	0.0513 (6)	−0.0005 (3)	0.7987 (4)
C1′	0.6176 (9)	0.0912 (6)	0.7275 (6)
C2′	0.493 (1)	0.0572 (6)	0.7264 (7)
C3′	0.494 (1)	0.0101 (6)	0.6635 (6)
C4′	0.398 (1)	−0.0277 (6)	0.6484 (6)
C5′	0.413 (1)	−0.0765 (5)	0.5795 (6)
C11′	0.033 (1)	0.1558 (6)	1.0015 (6)
C12′	0.062 (1)	0.1009 (6)	0.9329 (6)
C13′	−0.0349 (9)	0.0569 (6)	0.9231 (6)
C14′	−0.040 (1)	0.0135 (6)	0.8607 (7)
C15′	−0.158 (1)	−0.0226 (6)	0.8580 (7)
C21′	0.276 (1)	0.1501 (6)	0.8901 (6)
C22′	0.405 (1)	0.1147 (6)	0.8514 (6)
C23′	0.083 (1)	0.1019 (6)	0.6566 (6)
C24′	0.020 (1)	0.1663 (6)	0.6181 (7)
C30′	0.242 (1)	−0.1519 (6)	0.8117 (6)
C31′	0.359 (1)	−0.2083 (6)	0.7991 (8)
O3	0.0950 (8)	0.0182 (4)	0.4439 (4)

Table VI. Selected Bond Lengths (Å) and Bond Angles (deg) for $Os(SCH_2C_6H_5)_2[(BA)_2en]\cdot{}^1/_2H_2O$ (**5**)

	molecule 1	molecule 2
Os1–S1	2.298 (3)	2.308 (3)
Os1–S2	2.315 (3)	2.323 (3)
Os1–O1	2.047 (8)	2.027 (8)
Os1–O2	2.008 (6)	2.032 (6)
Os1–N1	1.958 (8)	1.967 (8)
Os1–N2	2.00 (1)	2.01 (1)
S1–C30	1.84 (1)	1.88 (1)
S2–C23	1.84 (1)	1.82 (1)
O1–C4	1.31 (1)	1.32 (1)
N1–C2	1.32 (2)	1.32 (2)
N1–C22	1.50 (2)	1.49 (2)
O2–C14	1.29 (1)	1.32 (1)
N2–C12	1.33 (1)	1.35 (1)
N2–C21	1.50 (1)	1.49 (1)
C21–C22	1.53 (2)	1.50 (1)
C23–C24	1.55 (2)	1.53 (2)
C30–C31	1.50 (2)	1.52 (2)
S1–Os1–S2	178.7 (1)	178.2 (1)
S1–Os1–O1	92.4 (2)	91.5 (2)
S1–Os1–N1	90.5 (3)	91.3 (3)
S1–Os1–O2	90.7 (2)	88.9 (2)
S1–Os1–N2	88.5 (3)	89.9 (3)
S2–Os1–O1	88.7 (2)	90.0 (2)
S2–Os1–N1	90.1 (3)	89.6 (3)
S2–Os1–O2	88.7 (2)	90.2 (2)
S2–Os1–N2	90.5 (3)	88.7 (3)
O1–Os1–N1	94.2 (4)	93.8 (4)
O1–Os1–O2	87.5 (3)	87.7 (3)
O1–Os1–N2	177.4 (3)	176.9 (3)
O2–Os1–N2	94.9 (3)	95.1 (3)
N1–Os1–O2	177.9 (3)	178.5 (4)
N1–Os1–N2	83.4 (4)	83.4 (4)
Os1–S1–C30	107.8 (4)	106.8 (4)
Os1–S2–C23	102.5 (4)	104.3 (4)
S1–C30–C31	107.5 (8)	108.5 (8)
S2–C23–C24	108.7 (8)	109.8 (8)

Table VII. Pertinent IR Bands (cm^{-1})

complex	$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{O})$	$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{C})$	ν(O–Os–O)
1	1588	1511	843
2	1560	1508	838
3	1576	1507	844
4	1554	1484	
5	1560	1480	
6	1553	1484	
7	1554	1484	
8	1552	1483	
9	1559	1485	
10	1560	1482	
11	1559	1483	

Å between C22 and the ring C5′–C10′ may give rise to the uncommon tilt of this ring toward the OsN_2O_2 (II) plane (53.97°).

2. Description of the Structure of $Os(SCH_2C_6H_5)_2[(BA)_2en]\cdot{}^1/_2H_2O$ (5). Final atomic coordinates, bond lengths, and bond angles for **5** are given in Tables V and VI. The atomic labeling scheme is shown in Figure 2, for molecule II. The second independent molecule is designated accordingly without the "prime" labeling scheme.

The two independent molecules, I and II, are equivalent except for the orientation of select phenyl rings and a water molecule. The water molecule is essentially sandwiched between a benzene ring of the equatorial Schiff-base ligand and a phenyl ring of an apical benzyl mercaptan ligand of molecule II. This positioning increases the angle between these phenyl planes by approximately 25° when compared with the angle between the corresponding planes in molecule I.

The osmium metal atom is bonded axially to two sulfur atoms, while being bonded to equatorial N_2O_2 donor atoms of the Schiff-base backbone. The osmium atoms are located 0.0184 Å (I) and 0.140 Å (II) within the mean N_2O_2 planes, whereas the methylene carbons of the ethylenediamine Schiff-base bridge are staggered approximately 0.25 Å above and below the plane. The trans Os–S bond lengths of 2.298 (3) and 2.315 (3) Å (I) and 2.323 (3) and 2.308 (3) Å (II) are roughly equivalent to those observed in $Os(SPh)_2(salen)_2$, namely 2.298 (2) and 2.343 (2) Å.[15] The S–Os–S bond angles of 178.7 (1) and 178.2 (1)° are significant larger than the angle reported in a similar osmium compound os 171.7 (1)°.[15] The average equatorial bond lengths Os–O(keto) (2.027 Å (I) and 2.029 Å (II) and Os–N(imine) (1.979 Å (I) and 1.988 Å (II)) are slightly shorter than those reported for $OsO_2[(BA)_2en]$ (see above).

The close contacts to the thiolate ring are 4.09, 4.012, and 3.649 Å, while the contacts to the Schiff-base rings are 4.100 and 4.073 Å. The molecules are also stacked in pairs centrosymmetrically, and these contact distances may give rise to the difference in planar angles in the two independent molecules.

II. Spectral Data. 1. Infrared Spectra. The prominent IR bands of the complexes are listed in Table VII. The two most important features of the spectra are (a) the lower energy shifts of the strong $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{O})$ and $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{C})$ bands from the fully enolated ligand spectrum to that of the complexes[22,23] and (b) the O–Os–O

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Table VIII. ^{1}H NMR Chemical Shifts (δ, ppm) in CDCl$_3$

	Schiff base					axial thiolate		
complex	ethylene bridge $-CH_2CH_2-$	methyl $-CH_3$	phenyl (R) Ar H	isobutyl (R) $-CH_2CH(CH_3)_2$	methyl (R) $-CH_3$	phenyl Ar H	methylene CH_2R'	methyl $-CH_3$
1	4.11 (4 H, s)	2.46 (6 H, s)	8.13–7.27 (10 H, m)					
2	3.99 (4 H, s)	2.41 (6 H, s)			2.29 (6 H, s)			
3	3.94 (4 H, s)	2.28 (6 H, s)		0.98 (12 H, d) 2.16 (2 H, m) 2.44 (4 H, d)				
4	3.87 (4 H, s)	3.77 (6 H, s)	7.91–7.20 (10 H, m)			7.20–6.25 (10 H, m)		
5	3.78 (4 H, s)	3.81 (6 H, s)	8.26–7.25 (10 H, m)			7.20–6.70 (10 H, m)	5.30 (4 H, s)	
6	4.03 (4 H, s)	3.83 (6 H, s)	7.94–7.42 (10 H, m)			7.35–6.69 (14 H, m)		
7	3.95 (4 H, s)	3.81 (6 H, s)	8.01–7.32 (10 H, m)			7.00–6.15 (8 H, m)		1.88 (6 H, s)
8	4.10 (4 H, s)	3.84 (6 H, s)	7.92–7.23 (10 H, m)			6.83–6.38 (8 H, m)		
9	3.80 (4 H, s)	3.88 (6 H, s)	8.17–7.32 (10 H, m)				5.34 (4 H, q)	0.96 (6 H, t)
10	3.77 (4 H, s)	3.86 (6 H, s)	8.16–7.30 (10 H, m)				5.28 (4 H, t) 1.14 (4 H, m) 1.04 (4 H, m)	0.54 (6 H, t)
11	3.71 (4 H, s)	3.92 (6 H, s)	8.16–7.28 (10 H, m)				3.20 (2 H, m) 1.57 (8 H, m) 0.88 (8 H, m) 0.70 (4 H, m)	

Table IX. UV–Vis Spectral Data for the Osmium Complexes in Acetonitrile (nm)

complex	λ_{max} (log ϵ)
1	384 (3.78), 338 (4.06), 272 (4.01)
2	376 (3.47), 318 (4.04), 250 (3.78)
3	378 (3.52), 318 (4.06), 252 (3.77)
4	686 (4.20), 580 (4.00), 380 (4.15), 246 (4.55)
5	548 (3.94), 368 (3.87), 240 (4.34)
6	731 (3.95), 605 (3.78), 378 (4.00), 283 (4.42), 251 (4.69)
7	721 (3.94), 599 (3.82), 373 (4.03), 280 (4.55), 247 (4.77)
8	678 (3.87), 582 (3.85), 364 (4.05), 274 (4.32), 244 (4.45)
9	550 (3.76), 366 (3.85), 268 (4.22)
10	550 (4.06), 375 (4.10), 265 (4.34)
11	551 (4.14), 374 (4.15), 270 (4.72)

stretches in the three *trans*-dioxo compounds. In the ligand spectra, the two bands $\nu(\mathrm{C{\cdots}O})$ and $\nu(\mathrm{C{\cdots}C})$ are located approximately at 1612 and 1543 cm^{-1}, respectively. Upon complexation, these bands are shifted approximately 40–50 cm^{-1} to lower energy, as outlined in Table VII. In the three *trans*-dioxo compounds, the intense ν(Os=O) stretch is located at approximately 840 cm^{-1}, which is normal for these compounds.

2. **^{1}H NMR Spectra.** The proton magnetic resonance spectra of the complexes were examined in CDCl$_3$ relative to chloroform (7.26 ppm), and the data are presented in Table VIII. The features the 11 compounds have in common are the ligand's ethylene bridge and the terminal methyl protons. The protons of the ethylene bridge, observed as a singlet and located between δ 3.78 and 4.11 (4 H), are shifted downfield from that of the free ligand (δ 3.55). The methyl group on the ligand backbone is observed as a singlet at approximately 2.4 and 3.8 ppm in the Os(VI) *trans*-dioxo complexes and Os(IV) thiolate complexes, respectively.

3. **^{19}F NMR Spectra.** ^{19}F NMR spectra were recorded for complex **8**, $Os(SC_6H_4F)_2[(BA)_2en]$ (ppm relative to CFCl$_3$). In the Os(IV) thiolate complex the resonance is located at δ −113.5. Another reaction product, with a resonance observed at δ −112.2, can be assigned to the disulfide (p-$FC_6H_4S)_2$.[24] The starting material, 4-fluorothiophenol, was recorded at δ −115.6.

4. **Absorption Spectra.** Spectral results and extinction coefficients obtained in acetonitrile are summarized in Table IX. Complexes **1**–**3** exhibit strong absorbances between 318 and 338 nm that show minimal dependence on the ligand substituent. The band can likely be assigned the ligand Schiff-base to metal charge transfer. This absorption is located between 366 and 380 nm in the thiolate complexes and is approximately equal in intensity to the *trans*-$Os^{VI}O_2$ species. Other bands, observed only in the thiolato compounds and located between 550 and 700 nm, are assigned as sulfur to osmium charge transfers.

Table X. Electrochemical Redox Potentials (V)[a]

	redn		oxidn
complex	E_{pc}(VI/V)	$E_{1/2}$(IV/III)	E_{pa}(IV/V)
1	−1.19		
2	−1.27		
3	−1.23		
4		−0.59	+0.69
5		−0.75	+0.74
6		−0.58	+0.75
7		−0.58	+0.74
8		−0.60	+0.73
9		−0.84	+0.65
10		−0.86	+0.65
11		−0.86	+0.65

[a] Solution composition is 0.5 mM complex in DMF with 0.1 M TEAP as supporting electrolyte; scan rate is 500 mV/s; working electrode is a platinum bead.

III. **Electrochemistry.** The cyclic voltammetric measurements for the reported compounds recorded in DMF at 500 mV s^{-1} are summarized in Table X. The experimental potential ranges were all between −2.0 V and +1.2 V vs SSCE.

In all three *trans*-dioxoosmiu(VI) compounds an irreversible Os(VI/V) reduction is observed at approximately −1.2 V. Compounds **2** and **3** (R = methyl, isobutyl) also produce a second reduction wave, which likely corresponds to the Os(V/IV) reduction. These irreversible reductions are observed at approximately −1.85 V. The reversibility of the redox couples was not improved significantly over the scan rate range of 0.02–5.0 V s^{-1}.

The thiolate–osmium(IV) complexes yield significantly more interesting electrochemistry than that observed in the *trans*-dioxoosmium(VI) complexes. In all eight complexes, a very nearly reversible Os(IV/III) wave is observed. The range of the redox couple spans from the most positive $E_{1/2}$ of −0.576 V in the naphthyl complex (**6**) to the most negative half-wave potental of −0.862 V in the cyclohexyl derivative (**10**). These values correspond to data taken at a scan rate of 500 mV s^{-1}. The current ratios are all in the range of 1.01 ± 0.10 in the scan range of 50 mV s^{-1} except that for **10**. The cyclohexyl complex has an i_{pa}/i_{pc} ratio of 1.08 ± 0.06 over the range 0.100–5.00 V s^{-1}. An irreversible oxidation corresponding to the Os(IV/V) couple is observed from about +0.65 V for all three alkyl complexes (ethyl, *n*-butyl, and cyclohexyl) to +0.75 V in the naphthyl complex. The reversibility of the oxidation did not improve significantly over the scan range of 0.02–5.0 V s^{-1}. In the phenyl complex (**4**), an oxidation is also observed at +1.05 V at 500 mV s^{-1}, which likely corresponds to the Os(V/VI) couple. These results are summarized in Table X.

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Discussion

$K_2OsO_2(OH)_4$ has recently been shown to be a useful starting material for synthesizing osmyl complexes containing anionic chelating ligands.[11-16] The resulting *trans*-dioxoosmium(VI) chelates have been reacted with a variety of reducing ligands, including alcohols, thiols, and phosphines, to yield stable lower oxidation state osmium complexes.[11-15] Virtually all of the osmyl chelates containing anionic ligands reported to date contain nitrogen donor atoms and are tri- or tetradentate. Conspicuously absent are any literature reports of osmyl chelates containing simple oxygen donor ligands such as the ubiquitous 1,3-diketonates. It was not known whether this represents a simple omission or real synthetic difficulties in the preparation of the bis(1,3-diketonato)OsO_2 complexes. Since our principal synthetic goal in osmyl chemistry is to prepare binuclear osmyl-containing molecules by using ligands such as the 1,3,5-triketones and their Schiff-base derivatives, learning to synthesize the simpler mononuclear homologues is an important step toward achieving this goal. Repeated attempts to isolate pure compounds from reactions of $K_2OsO_2(OH)_4$ with 1,3-diketones under a variety of conditions have failed. This work will continue and may eventually produce the desired compounds, but it is clear that the synthesis is not entirely straightforward as might be expected. On the other hand, the tetradentate Schiff-base ligands formed by condensing ethylenediamine and 1,3-diketones do straightforwardly react with $K_2OsO_2(OH)_4$ to yield the expected osmyl complexes. Three such compounds have been prepared and characterized that contain different 1,3-diketonate moieties. The procedure appears generally applicable to a variety of related ligands.

Since osmyl complexes are useful starting materials for the preparation of lower oxidation state complexes, there is good reason to investigate the electrochemical behavior of these molecules. The cyclic voltammograms of all three *trans*-dioxo Os(VI) complexes of these Schiff-base ligands exhibit an irreversible reduction wave at about −1.2 V vs SCE. There is no anodic current for this process, which is assigned to Os(VI) → Os(V). The reduction peak potential is virtually independent of scan rate and the substituent group on the diketone moiety. The irreversibility is almost certainly due to the instability of the OsO_2^+ product. Presumably, the Os(V) loses one or both of the oxygens extremely rapidly. This is in sharp contrast to the electrochemical behavior of UO_2^{2+} complexes, which also contain a divalent *trans*-dioxo cation. In the same nonaqueous electrochemical media used in this study, uranyl complexes exhibit cyclic voltammetric waves characteristic of a highly reversible UO_2^{2+}/UO_2^+ couple.[25,26] Under these conditions the UO_2^+ ion appears quite stable. On the other hand, the instability of the OsO_2^+ ion probably accounts for the relative ease with which lower oxidation state complexes are prepared from osmyl precursors by using reducing ligands such as alcohols, thiols, and phosphines.[11-15]

Reaction of OsO_2[(1,3-diketonato)$_2$en] complexes with excess thiol proceeds smoothly to yield the analogous Os(IV) complex with trans thiolato ligands. A similar reaction involving cis molybdenum dioxo complexes has been investigated by Holm.[24] The products of that reaction shown in eq 1 are quite different

$$MoO_2(L) + 2RSH \rightarrow MoO(L)(solvent) + RSSR + H_2O \quad (1)$$

from the OsO_2^{2+} case, most likely due to the greater stability of the MoO^{2+} species versus the OsO^{2+} analogue. The reaction (eq 2) for the Os(VI) → Os(VI) reduction by various thiols has been

$$OsO_2(L) + 4RSH \rightarrow Os(SR)_2(L) + RSSR + 2H_2O \quad (2)$$

quantitatively established from the following evidence. The existence of the *trans*-$Os(SR)_2^{2+}$ moiety as well as the production of water as a side product has been proven crystallographically. ^{19}F NMR was used to confirm the presence of the disulfide (p-$FC_6H_4S)_2$, which is analogous to the case of the molybdenum reaction.[24]

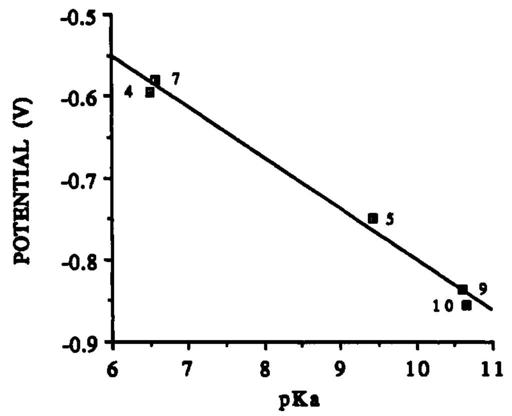

Figure 3. Plot of $E_{1/2}$ vs pK_a (correlation 0.99, slope −0.062) illustrating the dependence of redox properties on the pK_a of the thiol substituent. Substituent pK_a values: (**4**) 6.50; (**5**) 9.43; (**7**) 6.58; (**9**) 10.60; (**10**) 10.65.[27]

It is interesting to compare the equatorial bond distances in OsO_2[(BA)$_2$en] and $Os(SR)_2$[(BA)$_2$en]. Although the oxidation number of the Os is reduced from VI to IV in going from the dioxo to the dithiolato complex, the equatorial Os–O and Os–N bond lengths actually decrease slightly (ca. 0.05 Å). One may conclude from this observation that the positive charge of the central metal in the equatorial plane is very slightly greater in the Os(IV) product than in the Os(VI) starting material. It is clear from these structural studies that the only significant changes that take place upon reduction are in the axial positions. The bonding in the equatorial plane is only slightly affected. This fact together with the instability of the OsO_2^+ ion (and the OsO^{2+} ion as well) may account for the relative ease of producing the trans Os(IV) complexes with reducing agents that function as good axial ligands. The constancy of the equatorial bond distances and angles make it easy to imagine that the tetradentate ligand acts as a template for the axially oriented electron transfer/ligand substitution reactions.

Access to Os complexes in oxidation states lower than IV is also of general interest. The cyclic voltammetric properties of the $Os(SR)_2$[(BA)$_2$en] complexes (**4**–**11**) were investigated as a preliminary means of determining the value of the thiolate complexes as precursors to lower oxidation state compounds. Each member of the $Os(SR)_2$[(BA)$_2$en] series exhibits reversible one-electron transfer, as evidenced by the cyclic voltammetric results.

The series of thiolate complexes with the same Schiff-base ligand were synthesized to examine the effect of the thiolate substituent group on the redox potential of $Os(SR)_2$[(BA)$_2$en]. The observed trend in the potentials for this series correlates very well with the acidities of the parent thiols. The plot of thiol pK_a[27] versus the $E_{1/2}$ values for $Os(SR)_2$[(BA)$_2$en] complexes yields a straight line, as shown in Figure 3.

Acknowledgment. We are grateful to the National Science Foundation (Grant CHE 86-10808) for financial support of this research.

Supplementary Material Available: For the crystal structures of **1** and **5**, full listings of crystallographic data, atomic positional parameters, bond lengths and angles, thermal parameters, and hydrogen atomic parameters (15 pages); tables of observed and calculated structure factors (80 pages). Ordering information is given on any current masthead page.

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