

unsaturated trimetallic compounds, the compound must be thermally more stable or sterically less hindered for the sixth coordination site. Realization of such conditions would be possible by changing or modifying the chelate and PR_3 ligands. The present work is the first demonstration of the possibility for photochemical ligand substitution reactions in sulfur-bridged trimetallic cluster compounds.

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Supplementary Material Available: Details of the X-ray data collections (Tables S1 and S2), anisotropic temperature factors (Tables S3 and S4), final positional and thermal parameters (Tables S7 and S8), bond lengths (Tables S9 and S10), and bond angles (Tables S11 and S12) (14 pages); observed and calculated structure factors (Tables S5 and S6) (31 pages). Ordering information is given on any current masthead page.

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Charge Distribution in Bis(quinone) Complexes of Ruthenium and Osmium. Structural, Spectral, and Electrochemical Properties of the $Os(bpy)(Cat)_2$ (Cat = Catecholate, 3,5-Di-*tert*-butylcatecholate, Tetrachlorocatecholate) Series

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The series of bis(catecholato)(bipyridine)osmium(IV) complexes have been prepared by treating $Os(bpy)Cl_3$ with either catechol, 3,5-di-*tert*-butylcatechol, or tetrachlorocatechol in the presence of base. Crystals of $Os(bpy)(Cl_4Cat)_2 \cdot 2C_6H_6$ form in the monoclinic crystal system, space group $P2_1/n$, in a unit cell of dimensions $a = 10.906$ (1) Å, $b = 19.395$ (5) Å, $c = 16.953$ (4) Å, $\beta = 91.23$ (1)°, and $V = 3585$ (1) Å³, for $Z = 4$. The complex molecule is octahedral with chelated *bpy* and Cl_4Cat ligands. Bond lengths to the metal and C-O lengths of the quinone ligands agree with the bis(catecholato)osmium(IV) charge distribution for the complex in solid state. Electrochemistry and UV-vis-near-IR spectra on the series suggest that in solution the charge distribution is similar to other members of the $M(bpy)(Q)_2$ and $M(PPh_3)_2(Q)_2$ series, with $M = Ru, Os$ and $Q = DBQ, Cl_4Q$. The five-membered redox series of these complexes show variations in potential with metal, counterligand, and quinone that permit assignment of couples as associated with metal, quinone, or metal-quinone delocalized electronic levels. Metal ion charge appears to remain relatively constant through the series $ML_2(Q)_2^n$, with n ranging from +2 to -2, to the final reduction step which corresponds to a M^{III}/M^{II} reduction. Extreme members of the redox series have well-defined charge distributions as $M^{II}L_2(Cat)_2^{2-}$ and $M^{III}L_2(BQ)(SQ)^{2+}$ species. Neutral forms of the complexes have variable charge distributions in the solid state but have similar properties in solution as delocalized $M^{III}L_2(SQ)(Cat)$ species.

Introduction

Prior to studies on complexes of ruthenium and osmium, the structural, spectral, and magnetic properties of quinone complexes appeared to indicate well-defined charge distributions with metal ions complexed by ligands in either the semiquinone or catecholate forms. This has included many situations where exchange between semiquinone radical ligands and paramagnetic metal ions has resulted in unusual magnetic behavior,¹ where complexes were found to contain mixed-charge semiquinone and catecholate ligands,² and cases where the unique bonding properties of these ligands stabilized metal ions in unusual oxidation states.³ In all cases, localized formal charges could be assigned to the metal ions and to the associated quinone ligands. The work of Lever and Haga has demonstrated that metal-quinone charge delocalization contributes significantly to the electronic structure of the bis(bipyridine)(quinone)ruthenium and -osmium redox series.^{4,5} Characterization on the tris(quinone)ruthenium and -osmium complexes has suggested that both metal-quinone delocalization and delocalization between quinone ligands contributes to the

electronic structure.⁶ In recent studies, we have been interested in the bis(quinone)ruthenium and -osmium complexes, as they offer the opportunity for investigation of both quinone ligand and counterligand effects.⁷⁻⁹ Counterligands used in these studies have been triphenylphosphine and bipyridine for their different bonding characteristics, quinones have included tetrachloro-1,2-quinone (Cl_4Q), and 3,5-di-*tert*-butyl-1,2-quinone (DBQ), representing ligands with redox potentials that differ by nearly 1 V.^{10,11} In the present report, we describe the properties of the $Os(bpy)(Q)_2^n$ redox series, where n varies from +2 to -2 over the five-membered redox series, for the complexes containing DBQ, Cl_4Q , and Q ligands. Results of this study are compared with the properties of the corresponding series of complexes containing either ruthenium or osmium and either PPh_3 or *bpy* counterligands.^{8,9,12}

Experimental Section

Materials. Catechol (H_2Cat), 3,5-di-*tert*-butylcatechol (H_2DBCat), triethylamine, 2,2'-bipyridine, and osmium trichloride hydrate were purchased from Aldrich. Tetrachlorocatechol (H_2Cl_4Cat) was prepared by a published procedure and sublimed before use.¹³

Complex Syntheses. $Os(bpy)Cl_3$. Bipyridine (60 mg, 0.38 mmol) was added to a solution containing 100 mg (0.34 mmol) of $OsCl_3$ in 50 mL of ethanol. A brown solid separated from solution almost immediately.

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- Abbreviations: BQ, SQ, and Cat have been used to refer to benzoquinone, semiquinone, and catecholate forms of the quinone ligands, Q has been used to refer to quinone ligands of unspecified charge, and DB- and Cl_4 - have been used as prefixes for the 3,5-di-*tert*-butyl- and tetrachloro-substituted quinone ligands.
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Table I. Crystallographic Data for $\text{Os}(\text{bpy})(\text{Cl}_4\text{Cat})_2 \cdot 2\text{C}_6\text{H}_6$

mol wt	994.3
color	purple
space group	$P2_1/n$
a , Å	10.906 (1)
b , Å	19.395 (5)
c , Å	16.953 (4)
β , deg	91.226 (15)
vol, Å ³	3584.9 (13)
Z	4
D_{calcd} , g cm ⁻³	1.842
D_{exptl} , g cm ⁻³	1.840
μ , mm ⁻¹	4.204
λ , Å	0.710 73 (Mo K α)
T , K	296
R , R_w (obsd data)	2.98%, 3.72%
GOF	0.86

The mixture was stirred for 2 h, and the solid was separated from solution by filtration. The solid was washed with ethanol and diethyl ether and dried in air. The yield was 90 mg (59%). A molecular ion was observed for the complex at m/e 452 in the mass spectrum.

$\text{Os}(\text{bpy})(\text{DBCat})_2$. H_2DBCat (100 mg, 0.45 mmol) and NEt_3 (0.3 mL) were added to a suspension of $\text{Os}(\text{bpy})\text{Cl}_3$ (90 mg, 0.20 mmol) in 50 mL of a warm 2:1 ethanol/water solution. The mixture was refluxed gently for 3 h with constant stirring. The color of the mixture gradually turned purple. Solvent was then removed under reduced pressure, and the resulting solid was redissolved in benzene. This solution was filtered, and the filtrate was chromatographed through an alumina column. With benzene as the eluant, a blue band appeared first, which was identified by electronic and IR spectra as $\text{Os}(\text{DBCat})_3$. Using a 1:1 benzene/acetonitrile solution as the eluant, a second purple band separated. This fraction was collected, and the solvent was evaporated to give $\text{Os}(\text{bpy})(\text{DBCat})_2$ (95 mg) in 61% yield.

$\text{Os}(\text{bpy})(\text{Cl}_4\text{Cat})_2$. The synthetic procedure was carried out as described above using $\text{H}_2\text{Cl}_4\text{Cat}$ instead of H_2DBCat . Chromatographic purification was carried out on a dichloromethane solution of reaction products using a 1:1 dichloromethane/acetonitrile solution as the eluant. One purple band was obtained, and the solvent was evaporated to give $\text{Os}(\text{bpy})(\text{Cl}_4\text{Cat})_2$ in 60% yield.

$\text{Os}(\text{bpy})(\text{Cat})_2$. The synthetic and purification procedure described for $\text{Os}(\text{bpy})(\text{Cl}_4\text{Cat})_2$ was used to synthesize this complex in 65% yield by substituting H_2Cat for $\text{H}_2\text{Cl}_4\text{Cat}$.

Physical Measurements. Electronic spectra were recorded on a Perkin-Elmer Lambda 9 spectrophotometer. Infrared spectra were obtained on an IBM IR/30 FTIR spectrometer with samples prepared as KBr pellets. ¹H NMR spectra were recorded on a Varian VXR 300S spectrometer. Cyclic voltammograms were obtained with a Cypress CYSY-1 computer-controlled electroanalysis system. A platinum-disk working electrode and a platinum-wire counter electrode were used. A Ag/Ag^+ reference electrode was used that consisted of a CH_3CN solution of AgPF_6 in contact with a silver wire placed in glass tubing with a Vycor frit at one end to allow ion transport. Tetrabutylammonium hexafluorophosphate (TBHP) was used as the supporting electrolyte, and the ferrocene/ferrocenium couple was used as an internal standard. With this experimental arrangement the Fc/Fc^+ couple appeared at 0.120 V (vs Ag/Ag^+) with ΔE_p of 95 mV.

Crystallographic Structure Determination on $\text{Os}(\text{bpy})(\text{Cl}_4\text{Cat})_2 \cdot 2\text{C}_6\text{H}_6$. Dark purple crystals of $\text{Os}(\text{bpy})(\text{Cl}_4\text{Cat})_2$ were obtained as needles from a 1:1 dichloromethane/benzene solution. Axial photographs indicated monoclinic symmetry, and the centered settings of 25 reflections in the 2θ range between 21.5 and 35.1° gave the unit cell dimensions listed in Table I. Data were collected by θ - 2θ scans within the angular range 3.0–45.0°. Locations of the Os atom and many of the smaller atoms were determined by direct methods. Final cycles of least-squares refinement converged with discrepancy indices of $R = 0.030$ and $R_w = 0.037$. Final positional parameters for atoms of the complex molecule are listed in Table II. Tables containing a full listing of atom positions, anisotropic displacement parameters, and hydrogen atom locations are available as supplementary material.

Results

The neutral $\text{Os}(\text{bpy})(\text{Cat})_2$ complexes with unsubstituted catechol, 3,5-di-*tert*-butylcatechol, and tetrachlorocatechol ligands have been prepared by treating $\text{Os}(\text{bpy})\text{Cl}_3$ with the corresponding catechol in the presence of base. An ethanol/water mixture was used as the reaction medium. The water is an important component in this system, as reactions carried out in ethanol alone gave significantly lower yields of product. Infrared

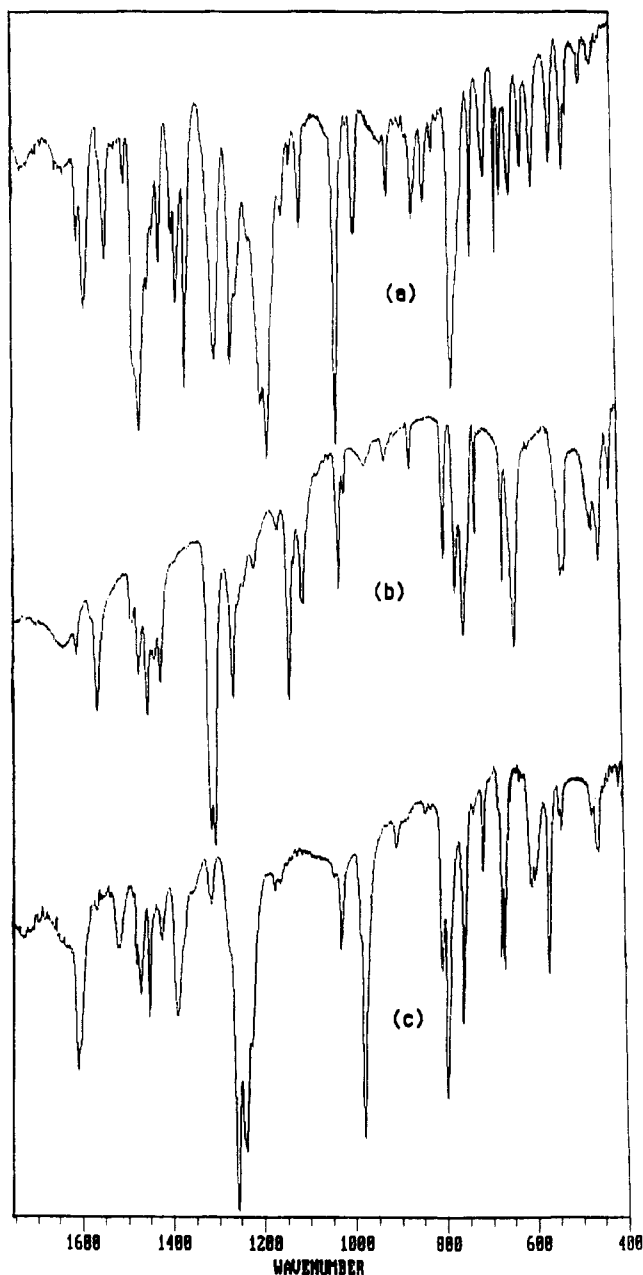


Figure 1. Infrared spectra for (a) $\text{Os}(\text{bpy})(\text{DBCat})_2$, (b) $\text{Os}(\text{bpy})(\text{Cat})_2$, and (c) $\text{Os}(\text{bpy})(\text{Cl}_4\text{Cat})_2$.

spectra for the neutral complexes in the solid state are shown in Figure 1. The spectra are complicated, and individual band assignments have not been made, but comparison with the published spectra of two analogous ruthenium complexes prepared with Cat and DBCat ligands shows significant differences that may be related to differences in charge distribution.¹² All three complexes are diamagnetic, and $\text{Os}(\text{bpy})(\text{DBCat})_2$ shows a sharp ¹H NMR spectrum. Asymmetry of the catechol ligands results in three possible isomers for the complex, two of C_2 symmetry and a third asymmetric isomer. If all three isomers were present in solution, eight *tert*-butyl resonances would be observed. Samples of the complex actually show only six resonances at 0.989, 1.004, 1.265, 1.279, 1.320, and 1.367 ppm. Either only one of the C_2 isomers is formed or two resonances of the three-isomer mixture are overlapped. The latter case seems most likely, since the ruthenium analogue showed only seven resonances for the mixture due to overlap.¹² Electronic spectra for the three neutral complexes are shown in Figure 2, and band positions are listed in Table III. There is remarkable similarity between the three spectra, given the electronic differences between catechol ligands. The general pattern of two high-intensity bands with lower intensity bands at

Table II. Selected Atomic Coordinates for Os(bpy)(Cl₄Cat)₂

	x/a	y/b	z/c
Os	2096 (1)	5089 (1)	6079 (1)
Cl1	-1293 (2)	6768 (1)	5625 (2)
Cl ₂	-350 (3)	8285 (1)	5682 (2)
Cl3	2430 (3)	8576 (1)	6035 (2)
Cl4	4245 (2)	7337 (1)	6286 (2)
Cl5	-816 (2)	3154 (1)	6230 (2)
Cl6	-2011 (2)	3052 (1)	7903 (2)
Cl7	-1248 (3)	4113 (2)	9201 (2)
Cl8	757 (3)	5212 (2)	8863 (2)
O1	3033 (5)	5971 (3)	6052 (3)
O2	721 (5)	5724 (3)	5788 (3)
O3	1698 (5)	5131 (3)	7223 (3)
O4	1054 (5)	4251 (3)	6146 (3)
N1	2554 (6)	4844 (3)	4949 (4)
N2	3668 (6)	4528 (3)	6253 (4)
C1	2311 (7)	6523 (4)	6014 (5)
C2	1058 (7)	6394 (4)	5857 (5)
C3	238 (7)	6937 (4)	5763 (5)
C4	665 (8)	7611 (4)	5803 (5)
C5	1914 (8)	7740 (4)	5951 (5)
C6	2711 (8)	7196 (4)	6061 (5)
C7	822 (8)	4684 (4)	7408 (5)
C8	475 (7)	4212 (4)	6828 (5)
C9	-414 (8)	3710 (4)	6983 (5)
C10	-944 (8)	3684 (4)	7703 (6)
C11	-584 (9)	4158 (5)	8286 (6)
C12	301 (9)	4664 (5)	8145 (5)
C13	1871 (7)	5008 (4)	4301 (5)
C14	2219 (9)	4822 (5)	3567 (6)
C15	3278 (8)	4460 (5)	3461 (6)
C16	3972 (8)	4275 (4)	4126 (5)
C17	3596 (8)	4457 (4)	4867 (5)
C18	4227 (8)	4289 (4)	5601 (5)
C19	5293 (8)	3901 (4)	5674 (6)
C20	5813 (9)	3765 (5)	6397 (7)
C21	5224 (9)	4008 (5)	7044 (6)
C22	4157 (9)	4389 (4)	6980 (6)

Table III. Selected Bond Distances and Angles for Os(bpy)(Cl₄Cat)₂

Distances, Å			
Os-N1	2.047 (7)	Os-N2	2.048 (7)
Os-O1	1.994 (5)	Os-O3	1.998 (6)
Os-O2	1.994 (5)	Os-O4	1.988 (5)
C1-O1	1.329 (9)	C7-O3	1.332 (10)
C2-O2	1.355 (9)	C8-O4	1.332 (10)
C1-C2	1.409 (11)	C7-C8	1.391 (12)
C2-C3	1.388 (11)	C8-C9	1.401 (11)
C3-C4	1.388 (11)	C9-C10	1.364 (13)
C4-C5	1.402 (13)	C10-C11	1.400 (13)
C5-C6	1.377 (11)	C11-C12	1.399 (14)
C6-C1	1.378 (11)	C12-C7	1.384 (13)

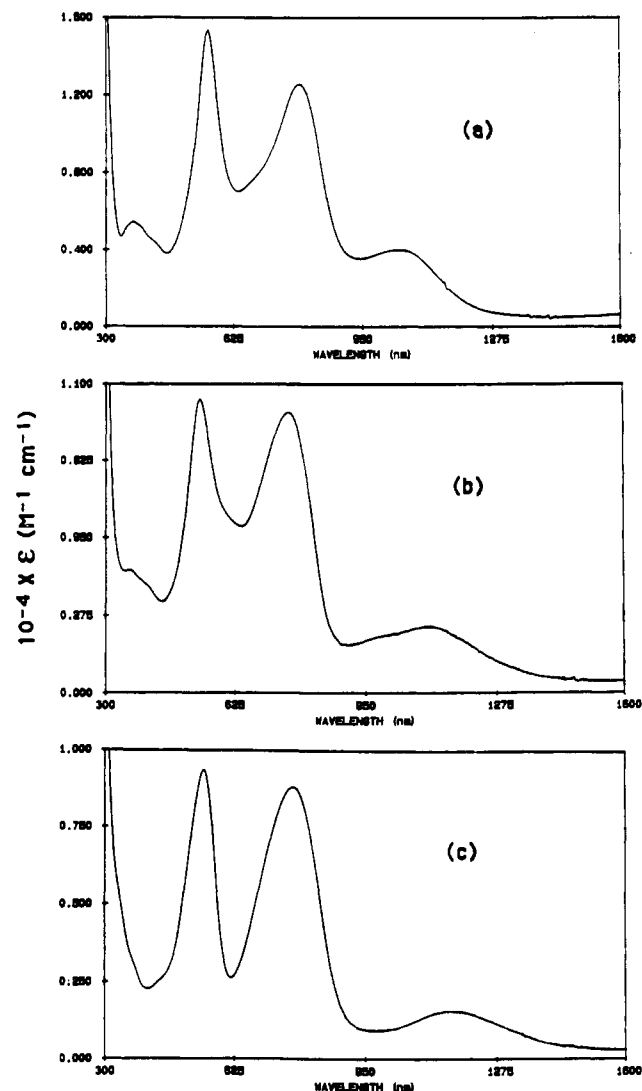
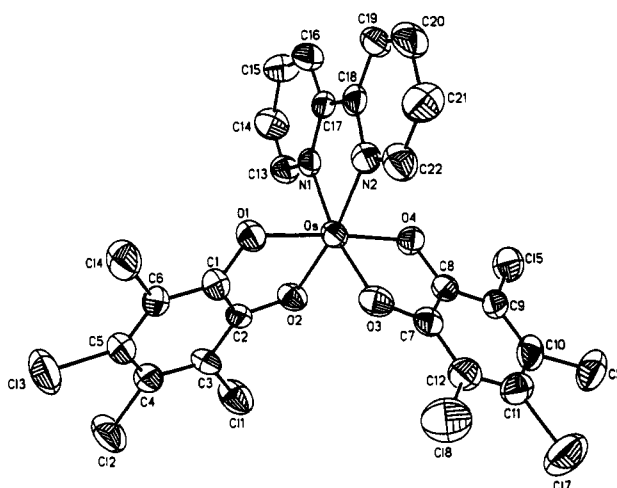
Angles (deg)			
O1-Os-O2	81.3 (2)	O1-Os-O3	96.3 (2)
O2-Os-O3	92.1 (2)	O1-Os-O4	175.5 (2)
O2-Os-O4	95.2 (2)	O3-Os-O4	80.9 (2)
O1-Os-N1	92.4 (2)	O2-Os-N1	96.3 (2)
O3-Os-N1	168.7 (2)	O4-Os-N1	90.8 (2)
O1-Os-N2	91.8 (2)	O2-Os-N2	170.8 (2)
O3-Os-N2	94.6 (3)	O4-Os-N2	92.0 (2)
N1-Os-N2	77.9 (3)		

Table IV. Electronic Spectral Data Recorded in Dichloromethane Solution

compd	λ, nm (ε, M ⁻¹ , cm ⁻¹)
Os(bpy)(DBCat) ₂	1043 (4000), 792 (12 600), 562 (15 300), 369 (5500), 426 ^a (4400), 294 (26 600)
Os(bpy)(Cat) ₂	1104 (2400), 759 (10 000), 538 (10 400), 405 ^a (3800), 360 ^a (4400), 290 (22 600)
Os(bpy)(Cl ₄ Cat) ₂	1160 (1600), 772 (8800), 550 (9300), 374 ^a (3000), 296 (19 200)

^a Shoulder.

either side appears to be a general feature of the bis(quinone) complexes of Ru and Os, having been found for the series con-

**Figure 2.** Visible and near-IR spectra for (a) Os(bpy)(DBCat)₂, (b) Os(bpy)(Cat)₂, and (c) Os(bpy)(Cl₄Cat)₂ recorded in dichloromethane solution.**Figure 3.** View of the Os(bpy)(Cl₄Cat)₂ molecule.

taining PPh₃ and bpy counterligands with both DBQ and Cl₄Q quinone ligands.^{8,9,12}

Structural Features of Os(bpy)(Cl₄Cat)₂. The structure of Os(bpy)(Cl₄Cat)₂ has been determined crystallographically. A view of the complex molecule is given in Figure 3; selected bond distances and angles are listed in Table IV. Information concerning charge distribution between the metal and quinone ligands

Table V. Structural Features of the $ML_2(Q)_2$ Complexes of Ru and Os

complex	M-O, Å	M-L, Å	C-O, Å	ref
<i>trans</i> -Ru(3-Cl-py) ₂ (DBSQ) ₂ ⁺	2.010 (3)	2.085 (2)	1.293 (4)	7
<i>cis</i> -Ru(PPh ₃) ₂ (Cl ₄ SQ) ₂	2.025 (7)	2.365 (3)	1.296 (8)	8
<i>trans</i> -Ru(4-Bu-py) ₂ (DBQ) ₂	1.993 (3)	2.079 (3)	1.321 (5)	16
Ru(bpy)(Q) ₂	1.989 (3)	2.048 (4)	1.321 (5)	7
<i>cis</i> -Os(PPh ₃) ₂ (DBQ) ₂	2.018 (4)	2.353 (2)	1.330 (7)	9
Os(bpy)(Cl ₄ Cat) ₂	1.933 (5)	2.048 (7)	1.337 (9)	a

^aThis work.

in the solid state can be obtained from a comparative analysis of bond lengths to the metal and the C-O lengths of the quinone ligands. Both the average Os-N and Os-O lengths of Os(bpy)(Cl₄Cat)₂, listed in Table V, are shorter than values of 2.021 (4) and 2.052 (5) Å found for Os(bpy)₂(DBCat)⁺, a complex of Os(III).⁵ The average C-O length of the quinone ligands of Os(bpy)(Cl₄Cat)₂ is 1.337 (9) Å, a value typical of catechololate ligands, and the C-C lengths of the ligand rings fail to show the bonding pattern observed for benzoquinone and semiquinone ligands.^{14,15} Therefore, the structural features of Os(bpy)(Cl₄Cat)₂ point clearly to a bis(catecholato)osmium(IV) charge distribution in the solid state.

It is of interest to compare this result with the features of other bis(quinone) complexes of Os and Ru with bpy and PPh₃ counterligands. Features of four complexes of this series are listed in Table V. Within this group, M-N and M-P lengths show little variation from Ru to Os. M-O lengths are longer for complexes containing the phosphine ligands, but within pairs of PPh₃ and bpy complexes, there is little difference between M-O lengths for Ru and Os. Average values for quinone ligand C-O lengths tend to be longer for osmium complexes than for corresponding Ru complexes. This result was also apparent for the neutral tris(quinone) complexes and for the M(bpy)₂(DBQ)⁺ and M(PPh₃)₂Cl₂(DBQ) complexes of Ru and Os containing a single quinone ligand.^{8,9,16} Additionally, the complexes containing bpy ligands have longer C-O lengths than the PPh₃ complexes, a pattern that follows the expected nucleophilic character of the metal resulting from the different bonding properties of the nitrogen and phosphorus donor ligands. While variations in C-O lengths follow predictable patterns, variations in length within a single structure determination are often 0.02 Å, much larger than the standard deviations of individual lengths. This may be random or the result of solid-state environmental effects, but it limits the statistical significance of such bond length comparisons. Nevertheless, a large number of structure determinations have been carried out on complexes containing semiquinone and catechololate ligands, and charge distribution assignments based on average values for C-O lengths have been consistent with information obtained from other physical properties of the complex. The complexes of Ru and Os have been particularly difficult to analyze, since there are no other spectral or magnetic probes to use in the assignment of charge distribution, and they seem to show charge delocalization in a way that is unique among other complexes of quinone ligands.

Electrochemistry of the Os(bpy)(Cat)₂ Series. Members of the bis(quinone) series of complexes containing Ru or Os typically show five-membered redox series. Redox couples associated with metal-based electronic levels would be expected to show a shift to negative potentials for the osmium complexes relative to their ruthenium analogues, and complexes containing phosphine ligands should show corresponding couples shifted toward positive potentials relative to their bipyridine analogues. Quinone ligand based redox couples should reflect substituent effects, with potentials for tetrachloroquinone ligands being approximately 0.5 V more positive than corresponding potentials of the di-*tert*-butylquinone ligands. From these general trends, it is possible to

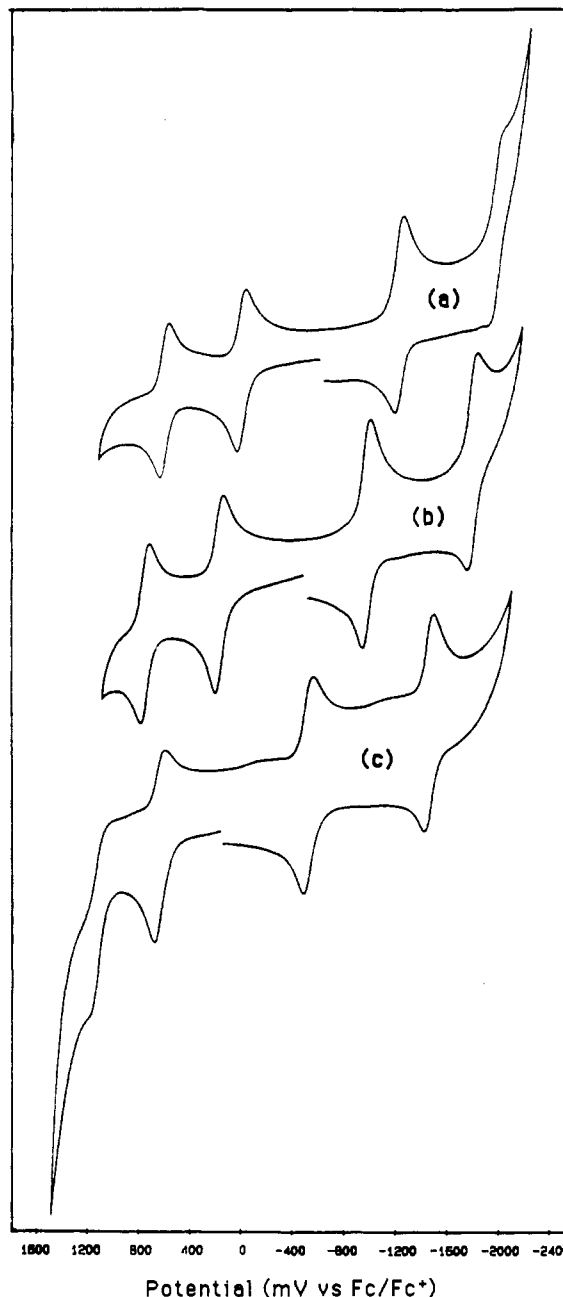


Figure 4. Cyclic voltammograms of (a) Os(bpy)(DBCat)₂, (b) Os(bpy)(Cat)₂, and (c) Os(bpy)(Cl₄Cat)₂ recorded in dichloromethane at a scan rate of 100 mV/s.

make tentative assignments, ligand or metal, for couples of the redox series.

The three bis(quinone)(bipyridine)osmium complexes prepared with the unsubstituted quinone, 3,5-di-*tert*-butylquinone, and tetrachloroquinone ligands all show five-membered redox series. CV's for the complexes are shown in Figure 4. Potentials for Os(bpy)(Cat)₂ reductions are -1.003 (72) and -1.831 (92) V (vs Fc/Fc⁺); oxidations occur at 0.148 (62) and 0.731 (69) V. Corresponding potentials for the related complex containing the tetrachloroquinone ligand are shifted positively, and the di-*tert*-butylquinone ligand potentials occur at more negative values. Both sets of potentials are listed in Table VI along with values for corresponding couples for related complexes of Ru and Os.

Potentials of the two oxidation steps for the complexes listed in Table VI show a strong dependence upon the form of the quinone ligand and little dependence on the metal, Ru or Os, or on counterligand, bpy or PPh₃. The conclusion from this observation is that both oxidations occur at the two quinone ligands. The first reduction also shows a strong dependence upon the

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Table VI. Potentials ($E_{1/2}$, V vs Fc/Fc⁺ (ΔE_p , mV)) for Steps in the Five-Membered Redox Series of the $ML_2(Q)_2^+$ Complexes of Ru and Os Recorded in Dichloromethane Solution

complex	Ox(II)	Ox(I)	Red(I)	Red(II)	ref
Ru(bpy)(DBQ) ₂	0.58	-0.11	-1.13	-1.84	12
Os(bpy)(DBQ) ₂	0.580 (72)	-0.034 (72)	-1.265 (74)	-2.023 (106)	a
Ru(PPh ₃) ₂ (DBQ) ₂	0.438 (126)	-0.220 (86)	-1.330 (118)	-1.791 (92) ^b	8
Os(PPh ₃) ₂ (DBQ) ₂	0.505 (112)	-0.114 (98)	-1.335 (120)		9
Ru(PPh ₃) ₂ (DBQ)(Cl ₄ Q)	0.739 (100)	0.155 (84)	-0.876 (110)	-1.437 (108) ^b	8
Os(PPh ₃) ₂ (DBQ)(Cl ₄ Q)	0.799 (103)	0.177 (87)	-0.943 (92)		9
Ru(bpy)(Cl ₄ Q) ₂	0.94	0.57	-0.31	-1.26	12
Os(bpy)(Cl ₄ Q) ₂	1.114 (100)	0.630 (78)	-0.533 (72)	-1.469 (80)	a
Ru(PPh ₃) ₂ (Cl ₄ Q) ₂	0.943 (87)	0.440 (82)	-0.383 (80)	-1.147 (108)	8
Os(PPh ₃) ₂ (Cl ₄ Q) ₂	0.707 (103)	0.463 (90)	-0.494 (116)	-1.380 (144)	9

^aThis work. ^bPotential measured in acetonitrile solution.

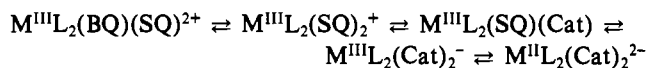
quinone ligand but also shows the expected shift to negative potentials for Os complexes relative to the Ru analogues. However, this shift is not as large as might be expected for a metal-based couple, and the first reduction appears to occur at an orbital that has both metal and quinone ligand character. Potentials for this reduction for the mixed quinone ligand complexes, $M(PPh_3)_2(DBQ)(Cl_4Q)$ ($M = Ru, Os$), are an approximate average of the values for individual $M(PPh_3)_2(DBQ)_2$ and $M(PPh_3)_2(Cl_4Q)_2$ complexes, suggesting significant interligand delocalization. The second reduction shows the most pronounced negative shift for the Os complexes and also shows a consistent positive shift for the PPh_3 complexes relative to their bpy analogues. This couple appears to be mainly metal-based, corresponding to the M^{3+}/M^{2+} reduction step.

Discussion

The complexes of Ru and Os have been of particular interest in the investigation of periodic trends in charge distribution within quinone complexes of the transition metals.⁶ Metals to the left tend to form complexes containing high-oxidation-state metals chelated by reduced catecholate ligands. Metals to the right of Ru and Os are more difficult to oxidize and tend to form complexes of semiquinone ligands with lower valent metals. Quinone and metal orbital energies appear to be quite close for the Ru and Os complexes. As a consequence, delocalization contributes more strongly to the electronic structures of complexes containing these metals. Studies on the bis(quinone) complexes of Ru and Os have concentrated on the effects of counterligand bonding, quinone substituent, and overall complex charge on electronic structure. Extreme members of the five-membered redox series, complexes with charges of +2 and -2, are best formulated as $Ru^{III}L_2(SQ)(BQ)^{2+}$ and $Ru^{II}L_2(Cat)_2^{2-}$, respectively. The most negative reduction is best assigned as reduction of Ru^{3+} to Ru^{2+} , and the most positive oxidation appears to be a SQ^-/BQ couple. The neutral species at the center of the redox series may have several possible charge distributions. Structural characterization on the four members of the series listed in Table V has shown that forms ranging from $Ru^{II}(SQ)_2$ to $Os^{IV}(Cat)_2$ may exist in the solid state, with degrees of metal and quinone orbital mixing. Spectral and electrochemical data recorded in solution point to a more consistent charge distribution for the neutral complexes. For example, the complexes in Table V that show the most extreme differences in charge distribution, $Ru(PPh_3)_2(Cl_4SQ)_2$ and $Os(bpy)(Cl_4Cat)_2$, show rather similar electronic spectra and show only slight shifts

in their respective first oxidation and reduction potentials. We assign the $Ru^{III}L_2(Cat)(SQ)$ charge distribution to the neutral members of the series in solution with significant charge delocalization between quinone ligands. The properties of the mixed-ligand complexes $M(PPh_3)_2(DBQ)(Cl_4Q)$ show the effects of interligand delocalization in a particularly clear way. Oxidation of the neutral complexes occurs at the quinone ligands giving a species of form $M^{III}L_2(SQ)_2^{+}$.⁷ This is evident from the trend in potentials given in Table VI and from the results of structural characterization on $Ru(3-Cl-py)_2(DBSQ)_2^+$. Reduction of the neutral complexes occurs at an orbital that is a mix of metal and quinone ligand contributions. However, it must be largely quinone ligand in composition, since effects showing dependence upon metal and counterligand are small and it is unlikely that the second reduction, which is more strongly metal based, reduces the metal beyond the +2 charge.

The conclusion from this extensive analysis of bis(quinone) complexes of Ru and Os is that members of the redox series are best described in solution as



Charge distribution assignments are in essential agreement with conclusions reached by Lever and co-workers based on analysis of members of the $Ru(bpy)(Q)_2$ and $trans-Ru(py)_2(Q)_2$ redox series.^{12,17} Species at either end of the series appear to have localized electronic structures, while the neutral complexes show evidence of greatest delocalization. Metal charge remains relatively constant through the series in solution; however, the solid-state structures of the neutral complexes show greater charge variability.

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Supplementary Material Available: For $Os(bpy)(Cl_4Cat)_2$, tables giving crystal data and details of the structure determination, atom coordinates, bond lengths, bond angles, anisotropic thermal parameters, and hydrogen atom locations (12 pages); a listing of observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

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