

Figure 8. Apparatus for the sublimation of $\text{CH}_3\text{B}_2\text{H}_3 \cdot 2\text{P}(\text{CH}_3)_3$.

This sublimation process was continued for a period of 60 h or until no volatiles came out of the flask. Nitrogen gas was then admitted into the apparatus, and the flask was replaced with a cap. The apparatus was reevacuated, inverted around the joint J, and the sublimate in part B was washed into flask C with $\text{P}(\text{CH}_3)_3$ as solvent. After the removal of $\text{P}(\text{CH}_3)_3$ from flask C by pumping at 0°C , the solid sample was weighed and found to be 1.033 g (or 5.39 mmol, 100.7% yield assuming a pure sample of $\text{CH}_3\text{B}_2\text{H}_3 \cdot 2\text{P}(\text{CH}_3)_3$). In another preparation, where 3.45 mmol of $1\text{-CH}_3\text{B}_3\text{H}_8$ and 30.57 mmol of $\text{P}(\text{CH}_3)_3$ were employed, the sublimed

product weighed 0.680 g (or 3.55 mmol, 102.8% yield).

Reaction of $\text{CH}_3\text{B}_2\text{H}_3 \cdot 2\text{P}(\text{CH}_3)_3$ with HCl. A 0.485-mmol sample of $\text{CH}_3\text{B}_2\text{H}_3 \cdot 2\text{P}(\text{CH}_3)_3$ was dissolved in about 1.5 mL of CH_2Cl_2 in a 10-mm-o.d. Pyrex tube that was equipped with a stopcock. The solution was frozen at -197°C , and a 0.498-mmol sample of anhydrous HCl was condensed into the tube. The tube was placed in a -80°C bath, shaken to mix the reactants, and then allowed to warm slowly to room temperature. The solution remained clear, and only a trace of noncondensable gas was found in the tube. The ^{11}B spectrum of the reaction solution consisted of the signals of $\text{BH}_3 \cdot \text{P}(\text{CH}_3)_3$ and $\text{CH}_3\text{BHCl} \cdot \text{P}(\text{CH}_3)_3$ (-10.0 ppm, d of d, $J_{\text{BP}} = 80$ Hz, $J_{\text{BH}} = 110$ Hz) in an approximately 1:1 intensity ratio and the weak signal (ca. 7% of the total boron signal) of $\text{BH}_2\text{Cl} \cdot \text{P}(\text{CH}_3)_3$. No other signals were present in the spectrum.

Reaction of $\text{CH}_3\text{B}_2\text{H}_3 \cdot 2\text{P}(\text{CH}_3)_3$ with B_4H_{10} . A solution containing 0.490 mmol of $\text{CH}_3\text{B}_2\text{H}_3 \cdot 2\text{P}(\text{CH}_3)_3$ in 1.5 mL of CH_2Cl_2 was prepared in a 10-mm-o.d. Pyrex tube, and a 0.594-mmol sample of B_4H_{10} was condensed into the tube. The tube was shaken in a -80°C bath to mix the reactants and then placed in the probe of the XL-100 NMR spectrometer. The reaction began to occur slowly at -50°C and was completed in a period of 30 min at -40°C (see Figure 3a). The tube was then placed in a -35°C bath, and the volatile components were pumped out. The NMR spectrum of the distillate showed only the signals of B_4H_{10} . A fresh 1.5-mL portion of CH_2Cl_2 was condensed into the reaction tube to record the NMR spectrum of the residue (see Figure 3b).

Reaction of $\text{CH}_3\text{B}_2\text{H}_3 \cdot 2\text{P}(\text{CH}_3)_3$ with B_2H_6 . A solution containing 0.549 mmol of $\text{CH}_3\text{B}_2\text{H}_3 \cdot 2\text{P}(\text{CH}_3)_3$ in 1.5 mL of CH_2Cl_2 was prepared in a 10-mm-o.d. Pyrex tube, and a 0.548-mmol sample of B_2H_6 was condensed into the tube. The contents of the tube were mixed at -80°C , and the tube was placed in the probe of the XL-100 NMR spectrometer. In another run, a 0.557-mmol sample of $\text{CH}_3\text{B}_2\text{H}_3 \cdot 2\text{P}(\text{CH}_3)_3$ and 1.12 mmol of B_2H_6 were treated in the similar manner. The observed reaction progresses were described in the Results and Discussion section.

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Comparative Studies on Charge Distribution for the Ruthenium and Osmium Quinone Complexes $[\text{M}(\text{bpy})_2(\text{quinone})]^n$ ($\text{M} = \text{Ru}, \text{Os}; n = 0, +1, +2$)

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The apparent shift in charge distribution that occurs for quinone complexes of metals of the iron triad has been investigated for members of the $\text{M}(\text{bpy})_2(\text{Q})^n$ ($\text{M} = \text{Ru}, \text{Os}$) redox series for values of n ranging from 0 to +2 and for complexes prepared with catechol (Cat), 3,5-di-*tert*-butylcatechol (DBCat), and tetrachlorocatechol (Cl_4Cat). The members of the series with $n = +1$ may have one of two localized charge distributions, $\text{M}(\text{II})\text{-SQ}$ or $\text{M}(\text{III})\text{-Cat}$, related by internal transfer of charge between the metal and the quinone ligand. Earlier characterization on $\text{Ru}(\text{bpy})_2(\text{DBSQ})^+$ indicated that the semiquinone form was most appropriate on the basis of the spectroscopy and structure of the complex cation. The osmium analogue, $[\text{Os}(\text{bpy})_2(\text{DBCat})](\text{ClO}_4)$, has been the subject of a crystallographic structure determination. Crystals of the complex form in the monoclinic space group $P2_1/c$ with $Z = 4$ in a unit cell of dimensions $a = 15.265$ (3) Å, $b = 24.153$ (6) Å, $c = 10.944$ (2) Å and $\beta = 102.89$ (2)°. Carbon–oxygen bond lengths of the structure indicate that the quinone ligand is catecholate and that the charge distribution for the complex is $\text{Os}(\text{III})\text{-DBCat}$. Spectroscopic characterization on the complex confirms the trivalent nature of the metal. It exhibits a rhombic EPR spectrum and low-energy transitions in the near-infrared region that are characteristic of $\text{Os}(\text{III})$. A comparative study on the electrochemical properties of the six complexes prepared with the two metals and three quinone ligands fails to show shifts in redox potentials that would be expected for species with metal- and ligand-localized electronic structures. This result, with earlier characterization on the Ru members of the series, points to significant metal–quinone charge delocalization for certain members of the series.

Introduction

The coordination chemistries of congeneric metals of the second and third transition series are generally regarded to be quite similar. Electron distribution in complexes containing semiquinone and catecholate ligands has been found to be sensitive to the orbital energy of metal valence electronic levels. Clear differences in

charge distribution have been noted for first-row metals relative to larger members of a group.² Specific examples exist for the Cr, Mo, and W triad, where chromium complexes are of the form $\text{Cr}^{\text{III}}(\text{SQ})_3$,³ while related complexes of the larger metals contain hexavalent metals bonded by catecholate ligands, $\text{M}^{\text{VI}}(\text{Cat})_3$ (M

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= Mo, W).⁴ Periodic trends are further evident across the second and third transition series as charge distribution shifts to favor semiquinone forms as d orbital energy decreases from Mo and W to Pd and Pt.⁵ The iron triad has been of particular interest as the metals of this group, particularly Ru and Os, have valence levels that are close in energy to the quinone π level.^{2,6} We recently presented evidence for a subtle difference in charge distribution for Ru(DBQ)₃ relative to Os(DBQ)₃, with the ruthenium complex closely resembling the corresponding iron complex as Ru^{III}(DBSQ)₃,⁷ while the osmium analogue appeared more like Re(DBCat)₃ as a complex of Os(VI), Os^{VI}(DBCat)₃. Other catecholate and semiquinone complexes of Ru and Os may show similar shifts in charge distribution, and in this context, the complexes containing a single quinone ligand are of interest. Cationic Ru(bpy)₂(DBQ)⁺ has been studied in detail.^{8,9} Two reasonable charge distributions exist for the complex Ru^{II}-(bpy)₂(DBSQ)⁺ or Ru^{III}(bpy)₂(DBCat)⁺, which contains either Ru(II) or Ru(III) with the paramagnetic center located on the semiquinone ligand in the first case and on the metal for the Ru(III) form. EPR spectra were interpreted to indicate that the Ru(II)-DBSQ charge distribution was most appropriate, but the assignment based upon EPR and structural properties was not unambiguous. We now report the results of characterization on the osmium analogue where these features are in more singular agreement about metal and ligand charge.

Experimental Section

Materials. *cis*-Os(bpy)₂Cl₂ was prepared by the literature method.¹⁰ 3,5-Di-*tert*-butylcatechol (H₂DBCat) and catechol (H₂Cat) were used as received. Tetrachlorocatechol (H₂Cl₄Cat) was synthesized by a published procedure.⁶ Dichloromethane and acetonitrile were dried over phosphorus pentoxide and further dried over CaH₂ before use in electrochemical experiments. All other reagents were used without further purification.

Preparation of Complexes. Os(bpy)₂(DBCat). Os(bpy)₂Cl₂ (0.3 g, 0.5 mmol) and H₂DBCat (0.12 g, 0.5 mmol) were combined in 40 mL of a 3:1 ethanol-water solution. The mixture was heated under nitrogen for 1 h, and then sodium hydroxide (0.04 g, 1.0 mmol) in 5 mL of water was added. The resulting mixture was refluxed for 70 h and cooled to room temperature. The complex was filtered from the solution under nitrogen as a black precipitate and dried in vacuo (66% yield). Anal. Calcd for C₃₄H₃₆N₄O₂Os·H₂O: C, 55.12; H, 5.17; N, 7.56. Found: C, 55.50; H, 4.97; N, 7.65.

Os(bpy)₂(L) (L = Cl₄Cat, Cat). These complexes were prepared by using the procedure described above by substituting the appropriate catechol (L) for H₂DBCat. L = Cl₄Cat, 71% yield. Anal. Calcd for C₂₆H₂₀N₄O₂Cl₄Os: C, 41.50; H, 2.68; N, 7.44. Found: C, 41.35, H, 2.33; N, 7.48. L = Cat, 58% yield. Anal. Calcd for C₂₆H₂₀N₄O₂Os·H₂O: C, 49.67; H, 3.53; N, 8.91. Found: C, 50.17; H, 3.39; N, 8.96.

[Os(bpy)₂(DBCat)](ClO₄). A 1:1 dichloromethane-methanol solution (50 mL) containing Os(bpy)₂(DBCat) (0.17 g, 0.23 mmol) and tetrabutylammonium perchlorate (0.15 g, 0.44 mmol) was stirred in air at room temperature for 24 h. During this time the solution turned dark brown. The solution was reduced to half-volume and cooled in a refrigerator to give black crystals of the complex in 90% yield. Anal. Calcd for C₃₄H₃₆N₄O₆ClOs: C, 49.66; H, 4.41; N, 6.81. Found: C, 49.66; H, 4.46; N, 6.82.

Physical Measurements. Electronic spectra were obtained on a Shimadzu UV-210A double-beam spectrophotometer from 200 to 850 nm and a Hitachi U-3400 spectrophotometer from 800 to 2600 nm. Infrared spectra were recorded on a Shimadzu IR-420 grating infrared spectrometer as Nujol mulls (4000–400 cm⁻¹).

Electrochemical measurements (cyclic voltammetry and differential-pulse voltammetry) were performed with a Yanagimoto P-1100 polaro-

Table I. Crystal Data for [Os(bpy)₂(DBCat)](ClO₄)

empirical formula	OsC ₃₄ H ₃₆ N ₄ O ₆ Cl	Z	4
fw	822.34	<i>D</i> (calcd), g/cm ³	1.39
cryst syst	monoclinic	<i>D</i> (exptl), g/cm ³	1.41 (2)
<i>a</i> , Å	15.265 (3)	μ , mm ⁻¹	3.35
<i>b</i> , Å	24.153 (4)	<i>T</i> _{max} ; <i>T</i> _{min}	0.927; 0.859
<i>c</i> , Å	10.944 (2)	radiation (λ , Å)	Mo K α (0.710 73)
β , deg	102.89 (2)	temp, K	294–297
<i>V</i> , Å ³	3933 (1)	<i>R</i> ; <i>R</i> _w	0.032; 0.040
space group	<i>P</i> ₂ ₁ / <i>c</i>	GOF	0.87

Table II. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^4$) for [Os(DBCat)(bpy)₂](ClO₄)

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> (eq) ^a
Os1	2366 (1)	451 (1)	614 (1)	32 (1)
O1	1496 (3)	1048 (2)	931 (4)	38 (2)
O2	2857 (3)	1108 (2)	-131 (4)	36 (2)
C1	1579 (4)	1518 (3)	310 (6)	36 (2)
C2	2310 (4)	1552 (3)	-257 (6)	33 (2)
C3	2450 (4)	2031 (3)	-927 (6)	37 (2)
C4	1839 (5)	2459 (3)	-952 (7)	43 (3)
C5	1130 (5)	2442 (3)	-359 (7)	41 (2)
C6	1008 (4)	1959 (3)	288 (6)	39 (2)
N1	3283 (4)	575 (2)	2274 (5)	39 (2)
N2	3385 (4)	-65 (2)	413 (5)	41 (2)
C15	4075 (5)	304 (3)	2398 (7)	46 (3)
C16	4760 (6)	393 (4)	3449 (8)	66 (3)
C17	4604 (7)	722 (5)	4373 (9)	82 (4)
C18	3805 (7)	979 (4)	4272 (8)	70 (4)
C19	3136 (5)	890 (3)	3206 (7)	54 (3)
C20	4124 (5)	-73 (3)	1377 (7)	50 (3)
C21	4859 (6)	-403 (4)	1327 (9)	67 (3)
C22	4825 (7)	-736 (4)	308 (10)	78 (4)
C23	4069 (6)	-740 (4)	-639 (9)	67 (4)
C24	3376 (5)	-400 (3)	-566 (7)	52 (3)
N3	1743 (3)	-219 (2)	1179 (5)	34 (2)
N4	1438 (3)	245 (2)	-1002 (5)	36 (2)
C25	1053 (4)	-448 (3)	315 (6)	36 (2)
C26	587 (5)	-898 (3)	580 (7)	47 (3)
C27	829 (6)	-1145 (3)	1755 (7)	55 (3)
C28	1514 (5)	-914 (3)	2624 (8)	56 (3)
C29	1959 (5)	-459 (3)	2309 (6)	43 (2)
C30	865 (4)	-169 (3)	-914 (6)	36 (2)
C31	179 (5)	-317 (3)	-1915 (7)	45 (3)
C32	85 (5)	-35 (3)	-3020 (7)	51 (3)
C33	659 (5)	380 (3)	-3119 (7)	52 (3)
C34	1336 (5)	520 (3)	-2107 (6)	43 (2)

^aEquivalent isotropic *U* defined as one-third of the trace of the orthogonalized *U*_{ij} tensor.

graphic analyzer connected to a Watanabe WX 4401 x-y recorder. The working electrodes were either platinum disk or glassy-carbon disk electrodes. A platinum-plate auxiliary electrode was used, and a silver wire was used as a quasi-reference electrode. Potentials were calibrated according to the ferrocene/ferrocenium (Fc/Fc⁺) couple, which lies at +0.16 V vs SCE.¹¹ Coulometry was performed at a platinum-gauze working electrode by using a Hokuto Denko HA-301 potentiostat-galvanostat and a Hokuto Denko HF-201 coulomb/ampere hour meter. Spectroelectrochemistry was performed by using a platinum-minigrid (80-mesh) working electrode in a thin-layer cell with an optical path length of 0.05 cm, designed by Lexa et al.¹² The cell was located directly in the spectrophotometer, and the absorption change was monitored during the electrolysis.

Crystallographic Structure Determination on [Os(bpy)₂(DBCat)](ClO₄). Crystals of the complex form as dark brown parallelepipeds. Axial photographs indicated monoclinic symmetry, and the centered settings of 25 reflections in the 2θ range between 24.4 and 30.3° gave the unit cell dimensions listed in Table I. The unit cell dimensions and the pattern of reflection intensities indicated that the complex was approximately isostructural with the ruthenium analogue studied earlier.⁹ Atomic coordinates from this structure determination were used successfully in initial cycles of refinement on [Os(bpy)₂(DBCat)](ClO₄).

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

Distances (Å)			
Os1-O1	2.040 (5)	C2-O2	1.345 (8)
Os1-O2	2.004 (5)	C1-C2	1.394 (10)
Os1-N1	2.053 (5)	C2-C3	1.411 (10)
Os1-N2	2.042 (6)	C3-C4	1.390 (10)
Os1-N3	2.041 (6)	C4-C5	1.381 (11)
Os1-N4	2.066 (5)	C5-C6	1.400 (10)
C1-O1	1.344 (8)	C1-C6	1.373 (9)

Angles (deg)			
O1-Os1-O2	80.1 (2)	O1-Os1-N1	95.0 (2)
O2-Os1-N1	90.1 (2)	O1-Os1-N2	171.5 (2)
O2-Os1-N2	94.4 (2)	N1-Os1-N2	78.4 (2)
O1-Os1-N3	98.2 (2)	O2-Os1-N3	173.0 (2)
N1-Os1-N3	96.8 (2)	N2-Os1-N3	88.1 (2)
O1-Os1-N4	88.1 (2)	O2-Os1-N4	95.1 (2)
N1-Os1-N4	174.3 (2)	N2-Os1-N4	98.8 (2)
N3-Os1-N4	78.0 (2)		

Final cycles of full anisotropic refinement including fixed contributions for hydrogen atoms converged with $R = 0.034$ and $R_w = 0.035$. The methyl carbon atoms of one *tert*-butyl group (C12-C14) were found to suffer from 2-fold disorder and were refined in two sets of locations with half-occupancy factors. Hydrogen atoms of these methyl groups were not included in the refinement. Final positional and derived isotropic thermal parameters for all nonhydrogen atoms of the structure determination are given in Table II. Tables containing anisotropic thermal parameters and hydrogen atom locations are available as supplementary material.

Results

Description of Os(bpy)₂(DBCat)⁺. Carbon-oxygen and oxygen-metal bond lengths often provide information on the charge distribution for complexes containing quinone ligands. Semiquinone and catecholate C-O bond lengths each have been found to fall into a narrow range of values,¹³ and catecholate ligands bonded to high-oxidation-state metals generally have short M-O lengths.^{2,14} The most widely characterized group of complexes that deviate from this pattern have been prepared with ruthenium. These include the neutral bis(quinone) complexes Ru(N-N)(Q)₂ and the cationic complex containing a single quinone ligand Ru(bpy)₂(DBQ)⁺.^{9,15} Oxidation or reduction of the bis(quinone) molecules gives species with more clearly defined charge distributions, Ru^{III}(N-N)(SQ)₂⁺ and Ru^{III}(N-N)(Cat)₂⁻, and the apparently delocalized electronic structure of the neutral complex results from interacting quinone and metal levels that are close in energy.^{6,15} Neutral Ru(bpy)₂(DBCat) appears to be a localized Ru(II)-catecholate complex.⁸ However, the singly oxidized form of the complex shows evidence for delocalization. Localized Ru(II)-DBSQ and Ru(III)-DBCat forms are possible, and mainly on the basis of the EPR spectrum of the complex, the Ru(II) charge distribution was assigned for Ru(bpy)₂(DBSQ)⁺. Structural features of the cation proved to be ambiguous, however. Ruthenium-nitrogen bond lengths fall into the same range for Ru(II) and Ru(III), and lengths to the metal in this structure provided no information on charge distribution. Carbon-oxygen lengths within the DBQ ligand were similarly uninformative, with one at a semiquinone value of 1.29 (1) Å and the second nearer to the catecholate value at 1.33 (1) Å. The average is similar to the delocalized values of 1.321 (5) Å found for Ru(DBQ)₃, Ru-(4-*t*-Bupy)₂(DBQ)₂, and Ru(bpy)(Q)₂.^{2,9,15}

The transition from ruthenium to osmium in the M(DBQ)₃ series appeared to result in greater catecholate character for the quinone ligands and a more highly oxidized metal center.² Structural features that were in accord with this trend included an average Os-O (1.958 (7) Å) length that was shorter than the Ru-O length (1.976 (4) Å) and an increase in the average ligand C-O length. Differences are small, however, and it would be useful

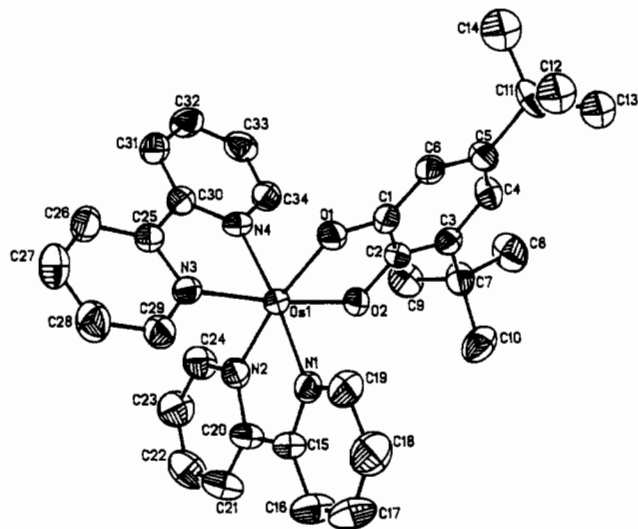


Figure 1. View showing the Os(bpy)₂(DBCat)⁺ cation and the atomic numbering scheme.

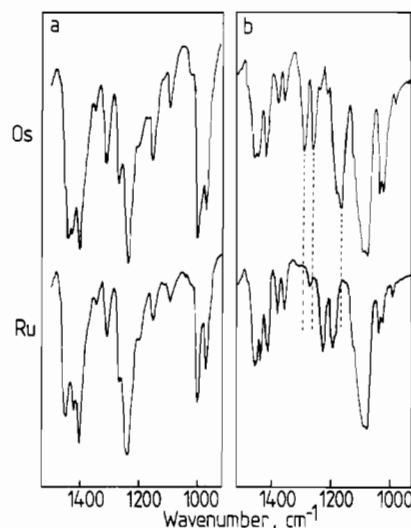


Figure 2. Comparison of infrared spectra (KBr disk) of the Os complexes with those of Ru analogues: (a) [M(bpy)₂(DBCat)]⁺; (b) [M(bpy)₂(DBQ)]⁺.

to see if a pattern existed that more clearly demonstrated the subtle difference in charge distribution for the Os complexes relative to their Ru analogues. The structural features of Os(bpy)₂(DBCat)⁺ are shown in Figure 1, and bond distances and angles for the cation are given in Table III. There is essentially no change in the average M-O and M-N lengths between the Ru and Os cations despite a slight increase in radius for Os.¹⁶ Average values of 2.021 (4) and 2.052 (5) Å are found for these lengths in Os-(bpy)₂(DBCat)⁺; in Ru(bpy)₂(DBQ)⁺ these values were 2.020 (8) and 2.054 (10) Å.⁹ The ambiguity in C-O lengths encountered in the Ru structure determination does not appear in the Os analogue. Both values are 1.346 (7) Å for Os(bpy)₂(DBCat)⁺, typical of a catecholate ligand.¹³

Infrared Spectra. Changes in charge distribution often result in changes in infrared spectrum. The spectrum of Fe(DBSQ)₃ is typical of di-*tert*-butylsemiquinone complexes, Re(DBCat)₃ shows a spectrum that is similar to those for other di-*tert*-butylcatecholate complexes, and the delocalized complexes Ru-(DBQ)₃ and Os(DBQ)₃ have spectra that differ from those of either of the charge-localized forms.² Infrared spectra recorded on Os(bpy)₂(DBCat), [Os(bpy)₂(DBCat)](ClO₄), and the analogous ruthenium complexes are shown in Figure 2. While the spectra of Ru(bpy)₂(DBCat) and Os(bpy)₂(DBCat) are quite

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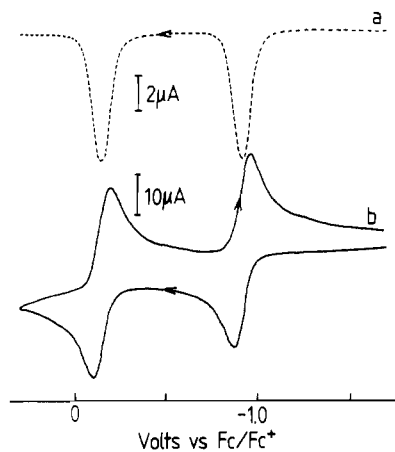


Figure 3. Differential-pulse voltammogram (a) and cyclic voltammogram (b) of $\text{Os}(\text{bpy})_2(\text{DBCat})$ in 1,2-dichloroethane (0.1 M TBAP).

Table IV. Electrochemical Data for the $[\text{M}(\text{bpy})_2(\text{L})]$ Complexes^a

M	L	$E_{1/2}$, V vs Fc/Fc^+ (ΔE , mV)			
		Ox_{III}	Ox_{II}	Ox_{I}	Red
Os	DBCat	+1.07 ^b	-0.120 (89)	-0.88 (88)	-2.25 (145)
Ru	DBCat ^c	+1.09	-0.01	-0.91	-2.15
Os	Cat	+1.20 ^b	+0.02 (99)	-0.77 (97)	-2.16 (116)
Ru	Cat ^c	+1.24	+0.15	-0.73	-2.12
Os	Cl_4Cat	<i>d</i>	+0.37 (86)	-0.55 (95)	-2.09 (95)
Ru	Cl_4Cat^c	+1.28	+0.48	-0.38	-2.09

^a In 1,2-dichloroethane (0.1 M TBAP) at 20 °C. $E_{1/2}$ = half-wave potential; ΔE = peak separation between anodic and cathodic peaks of CV. ^b Irreversible. ^c Reference 8. ^d Not well-defined.

similar, there are marked differences between the spectra of $[\text{Ru}(\text{bpy})_2(\text{DBSQ})](\text{ClO}_4)$ and $[\text{Os}(\text{bpy})_2(\text{DBCat})](\text{ClO}_4)$. Moreover, the spectrum of $[\text{Os}(\text{bpy})_2(\text{DBCat})](\text{ClO}_4)$ is not simply a superposition of the spectrum of $\text{Os}(\text{bpy})_2(\text{DBCat})$ with that of perchlorate. Oxidation of the neutral complex has apparently been accompanied by a change in ligand bonding, and the spectral difference between the complex cations of Ru and Os is more consistent with the difference in charge distribution.

Electrochemistry. The cyclic voltammogram and the differential-pulse voltammogram of neutral $\text{Os}(\text{bpy})_2(\text{DBCat})$ in dichloromethane show three oxidation processes and one reduction process.⁷ Figure 3 shows the typical voltammograms for the first and second oxidation processes. Both oxidations are reversible as is the reduction process. The third oxidation is irreversible. Similar studies have been carried out on related complexes prepared with the tetrachlorocatecholate and unsubstituted catecholate ligands, and these results are summarized in Table IV. The first and second oxidation potentials for the ruthenium and osmium complexes of the three catecholates ligands follow a linear relationship indicating that, for all three complexes of the two metals, the sites of oxidation are related.

Both the metals and ligands of the Os and Ru complexes are potentially redox-active sites. Reduction of the bpy ligands would occur at potentials that are more negative than -1.0 V, and the process near -2.0 V may be related to bpy reduction. Redox processes that occur for second- and third-row metal ions within a group are generally shifted to more negative potentials for the third-row metal. This is observed for some of the couples of the first and second oxidations given in Table IV, but the shifts are relatively small, on the order of 0.1–0.2 V, relative to the shifts of 0.2–0.5 V noted for the $\text{M}(\text{bpy})_3^{2+}$, $\text{M}(\text{bpy})_2\text{Cl}_2$, and $\text{M}(8\text{-quin})_3^+$ complexes.^{17–19} Catecholate ligand oxidations reflect the redox character of the parent catecholate or quinone. Oxidation of Cat and DBCat ligands is generally observed to occur at po-

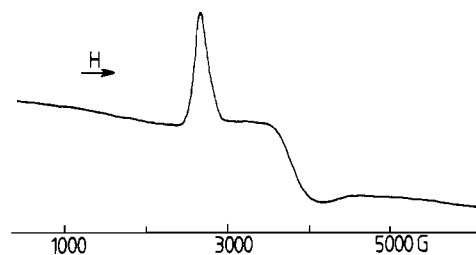


Figure 4. EPR spectrum of $[\text{Os}(\text{bpy})_2(\text{DBCat})](\text{ClO}_4)$ in $\text{CH}_2\text{Cl}_2\text{-CH}_3\text{CN}$ (3:1 v/v) at 77 K.

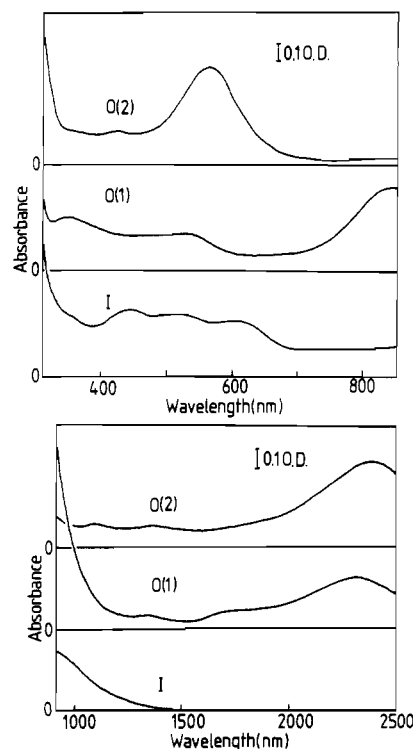


Figure 5. Spectroelectrochemical UV and near-IR absorption spectra for $\text{Os}(\text{bpy})_2(\text{DBCat})$ (I) and the first and second oxidation products, O(1) and O(2). UV spectra (top) were recorded in CH_2Cl_2 (7.17×10^{-4} M); near-IR spectra (bottom) were recorded in dichloroethane (3.00×10^{-3} M). The optical path length of the cell used for both sets of spectra was 0.05 cm.

tentials that are approximately 0.5 V more negative than that for the corresponding oxidation of a tetrachlorocatecholate ligand.²⁰ While the shifts are not quite of this magnitude a clear trend toward positive potential appears for the complexes containing Cl_4Cat ligands.

EPR Spectra. Complexes containing semiquinone ligands that are not magnetically coupled with other paramagnetic centers in the molecule generally show EPR spectra that have g values close to the free electron value and weak coupling to other associated nuclei.²¹ Spectra recorded on $[\text{Ru}(\text{bpy})_2(\text{DBQ})](\text{ClO}_4)$ were observed to be isotropic, narrow compared with normal Ru^{3+} spectra, and centered about a g value of 2.003.⁸ This led to the assignment of charge distribution as $\text{Ru}^{\text{II}}(\text{bpy})_2(\text{DBSQ})^+$. At low temperature in polar solvents (DMF, CH_3CN), an axial spectrum was obtained with $g_1 = 1.985$ and $g_2 = 2.067$, which resulted from the metal contribution to the delocalized ground state. Figure 4 shows the EPR spectrum of $[\text{Os}(\text{bpy})_2(\text{DBCat})](\text{ClO}_4)$ in a dichloromethane/acetonitrile glass at 77 K. It consists of two components at $g_1 = 2.448$ and $g_2 = 1.71$ and displays the characteristic rhombic structure associated with low-spin d^5 Os(III)

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in a distorted octahedral environment.¹⁹ The third component of rhombic Os(III) spectra occurs at high field and is often unobserved. This supports the Os(III)–DBCat charge distribution and further illustrates the difference between Ru and Os in these complexes.

Spectroelectrochemistry. Spectroelectrochemical experiments were performed on Os(bpy)₂(DBCat) in acetonitrile for the reversible first and second oxidation processes. Spectra are shown in Figure 5. Upon one-electron oxidation of the neutral complex, MLCT bands at 604, 510, and 442 nm disappear and new bands at 2300, 873, and 536 nm appear for the complex cation. Further one-electron oxidation results in the appearance of a new band at 558 nm and an increase in intensity for the band at 2360 nm.

The near-infrared absorption at 2300 nm observed for both [Os(bpy)₂(DBCat)]⁺ and [Os(bpy)₂(DBSQ)]²⁺ is tentatively assigned as a dπ–dπ transition between levels that arise from the effects of spin–orbit coupling for Os(III).¹⁹ Other absorptions bands of [Os(bpy)₂(DBCat)]⁺ that appear at 536 and 873 nm may be assigned as π(bpy) → Os(III) and π(DBCat) → Os(III) LMCT bands, respectively. The band at 873 nm moves to higher energy when DBCat is replaced by Cl₄Cat, which is in accord with the positive shift in oxidation potential for the catecholate. The band at 558 nm for [Os(bpy)₂(DBSQ)]²⁺ is tentatively assigned as a π(DBSQ) → Os(III) LMCT transition. Studies are in progress to provide further information on spectral assignments.

Discussion

The structural and spectroscopic properties of [Ru(bpy)₂(DBSQ)]⁺ and [Os(bpy)₂(DBCat)]⁺ indicate a subtle change in

charge distribution for the complexes of second- and third-row metals. Carbon–oxygen bond lengths of the quinone ligand of the osmium complex indicate that it is a reduced catecholate, and the near-infrared transitions and rhombic EPR spectrum are indicative of Os(III). The properties of the ruthenium complex indicate that its electronic structure is best described as a mix of Ru(II)–DBSQ and Ru(III)–DBCat localized-charge forms. The comparative electrochemical properties of the Ru and Os complexes prepared with all three quinone ligands fail to show shifts in potential that would indicate that redox processes are either metal or ligand localized. The conclusion from this analysis is that the ground-state electronic structures of both the Ru and Os complexes contain weighted contributions of both quinone ligand and metal, but that the ligand orbital contribution is significantly less for osmium than ruthenium.

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Supplementary Material Available: Tables giving electronic spectral data, crystal data and details of the structure determination, bond distances and angles, atom coordinates, anisotropic thermal parameters, and hydrogen atom parameters for [Os(bpy)₂(DBCat)](ClO₄) (9 pages); a table of structure factors for [Os(bpy)₂(DBCat)](ClO₄) (17 pages). Ordering information is given on any current masthead page.

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Spectroscopic and Kinetic Investigation of Bis(*N*-alkylsalicylaldiminato)copper(II) Complexes: A Study on the Existence of Planar ⇌ Tetrahedral Configuration Equilibria

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For several bis(*N*-alkylsalicylaldiminato)copper(II) complexes Cu(R-sal)₂ with R = methyl (I), ethyl (II), *n*-propyl (III), isopropyl (IV), neopentyl (V), 2,4-dimethylpentyl (VI), and *tert*-butyl (VII), a spectroscopic and kinetic study on the existence of configurational equilibria of the type planar ⇌ tetrahedral was carried out. It follows from the analysis of the EPR and ligand field spectra taken for the solid state, frozen solutions, and acetone solutions that, depending on the structural properties of the organic group R, the N₂O₂ coordination geometry around the copper ranges from planar to close to tetrahedral. The main conclusions derived from the spectroscopic results are as follows: (i) neither for the solid state nor for acetone solutions is an indication of a fluxional behavior in the sense of an equilibrium planar ⇌ tetrahedral found; (ii) in the solid state the angle O–Cu–O (obtained from structural data) follows the sequence I, V (180°) > VI (163°) > II (155°) > VII (142°) > IV (138°); (iii) in acetone solution the sequence is I, II, V, VI (≈155°) > IV (≈150°) > VII (≈140°); (iv) the degree of α- and/or β-branching in the alkyl group R controls the degree of nonfluxional distortion found. Visible spectrophotometry was used to study the reaction Cu(R-sal)₂ + H₂salen → Cu(salen) + 2R-salH in acetone at 298 K under pseudo-first-order conditions ([H₂salen]₀ ≫ [Cu(R-sal)₂]₀; H₂salen = *N,N'*-disalicylideneethylenediamine). The kinetic data follow a two-term rate law, rate = (k_S + k_L[H₂salen])[complex], with k_S ranging from 3.8 × 10⁻³ (I) to 0.18 × 10⁻³ s⁻¹ (V) and k_L ranging from 17 × 10⁻² (I) to 0.095 × 10⁻² M⁻¹ s⁻¹ (V). The size of second-order rate constant k_L, which can be interpreted as describing an associatively controlled ligand substitution, reflects the steric accessibility of the copper in Cu(R-sal)₂ rather than the degree of distortion of the CuN₂O₂ polyhedron. The kinetic results are in line with the spectroscopic findings in the sense that there is no indication of a dynamic equilibrium planar ⇌ tetrahedral for complexes Cu(R-sal)₂.

Introduction

The stereochemical variability and flexibility of bis(*N*-alkylsalicylaldiminato)metal(II) complexes M(R-sal)₂ have been the subject of numerous investigations.^{2,3} Complexes Zn(R-sal)₂^{3,4}

and Co(R-sal)₂³ prefer tetrahedral N₂O₂ coordination, whereas the coordination geometry of complexes Ni(R-sal)₂ and Cu(R-sal)₂ is basically of the planar *trans*-N₂O₂ type, as long as the steric demands of the organic group R are small enough.³ Bulky groups (such as R = *tert*-butyl), however, enforce more or less strong tetrahedral distortion.

A very interesting property of the nickel complexes Ni(R-sal)₂ is their fast configurational isomerism in solution according to

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