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Structural Systematics for *o*-C_6H_4XY Ligands with X,Y= O, NH, and S Donor Atoms. *o*-Iminoquinone and *o*-Iminothioquinone Complexes of Ruthenium and Osmium

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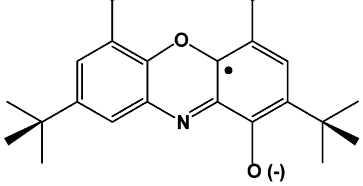
The structural features of quinone ligands are diagnostic of charge. The *o*-benzoquinone, radical semiquinonate, and catecholate electronic forms have C–O bond lengths and a pattern of ring C–C bond lengths that point to a specific mode of coordination. This correlation between ligand charge and structure has been extended to iminoquinone and iminothioquinone ligands, giving a charge-localized view of electronic structure for complexes of redox-active metal ions. The radical semiquinonate form of these ligands has been found to be a surprisingly common mode of coordination; however, the paramagnetic character of the radical ligand is often obscured in complexes containing paramagnetic metal ions. In this report, diamagnetic iminosemiquinonate (isq) and iminothiosemiquinonate (itsq) complexes of ls-d^5 Ru(III) with related complexes of osmium are reported. With osmium, the Os(IV)–amidophenolate (ap) redox isomer is formed. Electrochemical and spectral properties are described for $Ru(PPh_3)_2(isq)Cl_2$, $Ru(PPh_3)_2(itsq)Cl_2$, $Os(PPh_3)_2(ap)Br_2$, $Os(PPh_3)_2(atp)Br_2$, and $Os(PPh_3)_2(ap)H_2$. Crystallographic characterization of $Ru(PPh_3)_2(isq)Cl_2$, $Ru(PPh_3)_2(itsq)Cl_2$, and $Os(PPh_3)_2(ap)H_2$ was used to assign charge distributions.

Introduction

As the coordination chemistry of complexes containing quinone ligands has developed, the radical anion semiquinonate (SQ) electronic form has emerged as a surprisingly common mode of coordination.[1] In cases where the radical character is retained upon coordination, magnetic measurements and EPR spectroscopy provide useful information about ligand-based paramagnetism.[2] Quite commonly ligand spins couple with unpaired electrons on the metal or with other radical spins within the coordination sphere, obscuring the intrinsic SQ radical character of the ligand. In these cases, the structural features of quinone ligands have been found to provide insight into ligand charges and intramolecular charge distributions. Clear systematic differences in C−O and ring C−C bond lengths are diagnostic of ligand coordination in the form of either *o*-benzoquinone (BQ) or a radical semiquinonate (SQ) anion or as a catecholate (Cat) dianion.[1,3] Ligand C−O bond lengths increase from a value of 1.22 Å for BQ ligands to 1.34 Å for a chelated catecholate, a difference in bond length that is well within the significance level of current crystallographic methods of structure determination. Studies on complexes containing iminoquinone ligands have also been found to conform to specific charged forms with characteristic structural features. Complexes of the phenoxazinolate (PhenoxSQ) radical



PhenoxSQ

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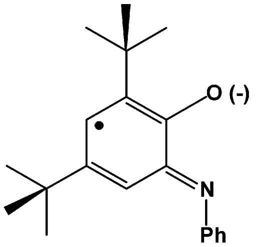
have been characterized magnetically, spectroscopically, and structurally,[4] and structural characterization of the free and complexed phenoxazin-1-one (PhenoxBQ) form of the ligand has provided structural features for the unreduced iminobenzoquinone (ibq).[4c,5] Wieghardt has investigated complexes containing the *N*-phenyl iminoquinone ligand coordinated as the radical iminosemiquinonate (isq)

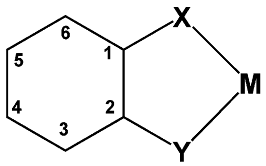


and as a fully reduced amidophenolate (ap) dianion.[6] Structural characterization of complexes of iminoquinone ligands in all three charged forms has shown a pattern in C−O, C−N, and ring C−C bond lengths consistent with the correlation between structure and ligand charge established for the quinone ligands. The results of these structure determinations show that the C−O bond lengths resemble those of BQ, SQ, and Cat ligands, but the range of C−N bond lengths is more narrow. The neutral PhenoxBQ ligand of $[Cu^{I}(PhenoxBQ)(\mu\text{-}Cl)]_2$ was found to have C−O and C−N bond lengths of 1.219(14) and 1.331(14) Å,[5] respectively, whereas the amidophenolate (ap) ligands of $Ir(PPh_3)_2(CO)Cl(L^{AP})$,[7] $V(L^{AP})(L^{AP}\text{-}H)_2$,[6c] $Mn(L^{ISQ})_2(L^{AP})$,[6e] and $Pd(bpy)(L^{AP})$[6f] have C−O and C−N bond lengths that average 1.35 and 1.39 Å, respectively.[6] Wieghardt has extended this analysis to complexes of iminothiosemiquinone (itsq) ligands.[8] Values for C−N and C−S bond lengths for itsq complexes are typically 1.35 and 1.72 Å, respectively, and the pattern of ring C−C bonds shows slight contraction at positions that would contain double bonds for a benzoquinone.[8] In contrast, complexes of fully reduced amidothiophenolate ligands have C−N and C−S bond lengths that average 1.38 and 1.76 Å, respectively. A list of diagnostic bond lengths for O, NR, and S donor ligands in the three electronic forms is given in Table 1. These values are based on a survey of structural data that included hundreds of independent structure determinations since 1985 that will appear later in the form of a review. Deviations from these values are approximately ±0.01 Å, with allowance for the esd of the measurement.

Table 1. Average Bond Lengths for Quinoid Ligands Containing Oxygen, Nitrogen, and Sulfur Donor Atoms

	C−X						
	X = O	X = NH	X = S	C1−C2[a]	C2−C3	C3−C4	C4−C5
BQ[b]	1.22	1.31	1.69	1.48	1.43	1.34	1.45
SQ	1.30	1.35	1.72	1.43	1.42	1.36	1.42
Cat	1.34	1.38	1.75	1.42	1.41	1.39	1.41

[a] Atoms of the ring follow the numbering scheme.



[b] The abbreviation BQ refers to the unreduced *o*-benzoquinone form of the ligand, SQ to the partially reduced radical *o*-semiquinonate electronic form, and Cat to the reduced dianionic catecholate form.

In this report, we explore this pattern further with unsubstituted iminoquinone and iminothioquinone complexes of Ru and Os. The complexes investigated contain the general $Ru(PPh_3)_2Cl_2$(iminoquinone) unit and can exist in one of three charge distributions, Ru^{II}−ibq, Ru^{III}−isq, or Ru^{IV}−ap, related by transfer of charge between metal and ligand-localized electronic levels. Structural characterization was used to assign ligand and metal charges.[9]

Experimental Section

Materials. Reagent-grade chemicals were used in all experiments, and solvents were purified using standard procedures. $Ru(PPh_3)_3Cl_2$ and $Os(PPh_3)_3Br_2$ were prepared using procedures described previously.[10,11] 2-Aminophenol and 2-aminothiophenol were purchased from Loba Chemie, Mumbai, India, and recrystallized before use.

Preparation of *trans*-$Ru(PPh_3)_2(isq)Cl_2$. $Ru(PPh_3)_3Cl_2$ (100 mg, 0.10 mmol) and 2-aminophenol (11 mg, 0.10 mmol) were dissolved in dichloromethane (30 mL), and the mixture was stirred for 6 h. During this time, the solution turned purple in color. Hexane was layered over the solution, producing purple crystals of $Ru(PPh_3)_2(isq)Cl_2$ in 75% yield.

Anal. Calcd for $C_{42}H_{35}NOP_2Cl_2Ru$: C, 62.7; H, 4.36; N, 1.74. Found: C, 62.4; H, 4.12; N, 1.52.

UV−vis (CH_2Cl_2): 556 nm (5.9×10^3 $M^{-1}cm^{-1}$), 466 (5.7×10^3), 348 (8.0×10^3), 288 (54.5×10^3), 232 (86.5×10^3).

CV [$E_{1/2}$, V vs SCE (ΔE_p, mV)]: −0.55 (E_{pc}), 0.66 (70).

Preparation of $Os(PPh_3)_2(ap)Br_2$. $Os(PPh_3)_3Br_2$ (114 mg, 0.10 mmol) and 2-aminophenol (11 mg, 0.10 mmol) were dissolved in dichloromethane (30 mL), and the mixture was stirred for 6 h. During this time, the solution turned red-violet in color. Hexane

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(9) Abbreviations for ligands: ibq, iminobenzoquinone; isq, iminosemiquinonate; ap, amidophenolate; itsq, iminothiosemiquinonate; atp, amidothiophenolate.

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Table 2. Crystallographic Data for $Ru(PPh_3)_2(isq)Cl_2$, $Ru(PPh_3)_2(itsq)Cl_2$, and $Os(PPh_3)_2(ap)H_2$[a]

	$Ru(PPh_3)_2(isq)Cl_2$	$Ru(PPh_3)_2(itsq)Cl_2$	$Os(PPh_3)_2(ap)H_2$
fw	803.6	819.7	438.0
color	red	red	orange
cryst syst	monoclinic	orthorhombic	monoclinic
space group	$C2/c$	$Abm2$	$P2_1/n$
a (Å)	17.534(2)	9.6958(3)	9.2386(3)
b (Å)	10.675(2)	24.4220(6)	18.4140(6)
c (Å)	20.241(2)	15.6173(4)	20.3305(7)
β (deg)	103.77(1)	90.00	97.225(1)
V (Å^3)	3679.7(9)	3698.0(2)	3431.2(2)
T (K)	296	160	143
Z	4	4	4
D_{calcd} (g cm^{-3})	1.451	1.472	1.595
μ (mm^{-1})	0.683	0.743	3.845
T_{min}, T_{max}	0.805, 0.969	0.873, 0.950	0.634, 0.899
R, R_w[b]	0.030, 0.047	0.019, 0.045	0.043, 0.095

[a] Data for all three compounds were collected using Mo Kα radiation ($\lambda = 0.710\,73$ Å). [b] Discrepancy indices are defined as $R = \Sigma||F_o| - |F_c|/\Sigma|F_o|$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{1/2}$.

was layered over the solution, producing red-violet crystals of $Os(PPh_3)_2(ap)Br_2$ in 65% yield.

Anal. Calcd for $C_{42}H_{35}NOP_2Br_2Os$: C, 51.4; H, 3.57; N, 1.43. Found: C, 50.0; H, 3.81; N, 1.42.

UV−vis (CH_2Cl_2): 522 nm (5.6×10^3 M^{-1}cm^{-1}), 454 (8.1×10^3), 368 (7.1×10^3), 263 (46.1×10^3), 232 (82.0×10^3).

CV [$E_{1/2}$, V vs SCE (ΔE_p, mV)]: −0.74 (E_{pc}), 0.52 (80).

Preparation of *trans*-$Ru(PPh_3)_2(itsq)Cl_2$. $Ru(PPh_3)_3Cl_2$ (100 mg, 0.10 mmol) and 2-aminothiophenol (13 mg, 0.10 mmol) were dissolved in dichloromethane (30 mL), and the mixture was stirred for 4 h. During this time, the solution turned red in color. Hexane was layered over the solution, producing red crystals of $Ru(PPh_3)_2(itsq)Cl_2$ in 65% yield.

Anal. Calcd for $C_{42}H_{35}NSP_2Cl_2Ru$: C, 61.5; H, 4.27; N, 1.71. Found: C, 60.3; H, 4.22; N, 1.65.

UV−vis (CH_2Cl_2): 490 nm (6.6×10^3 M^{-1}cm^{-1}), 290 (45.1×10^3), 232 (91.6×10^3).

CV [$E_{1/2}$, V vs SCE (ΔE_p, mV)]: −0.53 (E_{pc}), 0.90 (80).

Preparation of $Os(PPh_3)_2(atp)Br_2$. $Os(PPh_3)_3Br_2$ (114 mg, 0.10 mmol) and 2-aminothiophenol (13 mg, 0.10 mmol) were dissolved in dichloromethane (30 mL), and the mixture was stirred for 6 h. During this time, the solution turned red in color. Hexane was layered over the solution, producing red crystals of $Os(PPh_3)_2(atp)Br_2$ in 60% yield.

Anal. Calcd for $C_{42}H_{35}NSP_2Br_2Os$: C, 50.6; H, 3.51; N, 1.40. Found: C, 50.1; H, 3.72; N, 1.43.

UV−vis (CH_2Cl_2): 488 nm (6.2×10^3 M^{-1}cm^{-1}), 444 (sh), 326 (6.6×10^3), 282 (85.3×10^3).

CV [$E_{1/2}$, V vs SCE (ΔE_p, mV)]: −0.72 (E_{pc}), 0.67 (60).

Preparation of $Os(PPh_3)_2(ap)H_2$. $Os(PPh_3)_3Br_2$ (114 mg, 0.10 mmol), 2-aminophenol (23 mg, 0.21 mmol), and triethylamine (21 mg, 0.21 mmol) were added to ethanol (40 mL), and the mixture was refluxed under N_2 for 4 h. Brownish-orange crystals of $Os(PPh_3)_2(ap)H_2$ separated from the solution during reflux. The crystals were collected by filtration and washed with ethanol to give $Os(PPh_3)_2(ap)H_2$ in 65% yield.

Anal. Calcd for $C_{42}H_{37}NOP_2Os$: C, 61.2; H, 4.49; N, 1.70. Found: C, 60.1; H, 4.52; N, 1.62.

UV−vis (CH_2Cl_2): 390 nm (8.8×10^3 M^{-1}cm^{-1}), 286 (7.9×10^3), 234 (26.0×10^3).

CV [$E_{1/2}$, V vs SCE (ΔE_p, mV)]: 0.45 (E_{pa}), 0.83 (E_{pa}).

Physical Measurements. Microanalyses (C, H, N) were performed using a Perkin-Elmer 240C elemental analyzer. Electronic spectra were recorded on a Jasco V-570 spectrophotometer. Magnetic susceptibility measurements were made using a PAR 155 vibrating sample magnetometer interfaced with a Walker L75FBAL magnet. ^{1}H NMR spectra were obtained on a Bruker Avance DRX300 spectrometer using TMS as the internal standard and are included as figures in the Supporting Information. Electrochemical measurements were made using CH Instruments 600A potentiostat. A platinum disk working electrode, a platinum wire auxiliary electrode, and an aqueous saturated calomel reference electrode (SCE) were used in a three-electrode configuration. All electrochemical measurements were recorded under an atmosphere of dry N_2 in a dichloromethane solution containing TBAP as the supporting electrolyte. The scan rate used was 50 mV/s, and $E_{1/2}$ [$E_{1/2} = 0.5(E_{pa} + E_{pc})$] was calculated from the anodic (E_{pa}) and cathodic (E_{pc}) peak potentials. All electrochemical data were recorded at 298 K and are uncorrected for the junction potential.

Crystallographic Structure Determinations. Crystals of $Ru(PPh_3)_2(isq)Cl_2$ and $Ru(PPh_3)_2(itsq)Cl_2$ were obtained by slow diffusion of hexane into a dichloromethane solution of the complex. Crystals of $Os(PPh_3)_2(ap)H_2$ were obtained directly from the reaction. Crystallographic information for all three molecules are given in Table 2. Data collection for $Ru(PPh_3)_2(isq)Cl_2$ was carried out using a Siemens P3/F diffractometer; data on $Ru(PPh_3)_2(itsq)Cl_2$ and $Os(PPh_3)_2(ap)H_2$ were collected on a Siemens Smart CCD diffractometer.

Tables containing positional and thermal parameters for atoms, bond lengths and angles, and hydrogen atom locations for $Ru(PPh_3)_2(isq)Cl_2$ and $Ru(PPh_3)_2(itsq)Cl_2$ are available in the Supporting Information. A CIF file for $Os(PPh_3)_2(ap)H_2$ is also available.

Results

Interest in the coordination chemistry of quinone ligands has turned to complexes of the iminoquinone ligands. Of particular interest in the context of metal-stabilized radical ligands are complexes containing the iminosemiquinone (isq) ligands. Identification of the radical ligand is generally uncomplicated in cases where it is the only paramagnetic center of the complex molecule. Characterization becomes more complicated for complexes containing multiple paramagnetic centers where spin coupling results in cooperative magnetic properties.[2] As with the quinone complexes, questions concerning charge distribution have become of interest for the iminoquinone complexes containing redox-active metal ions. The iminoquinone and iminothioquinone

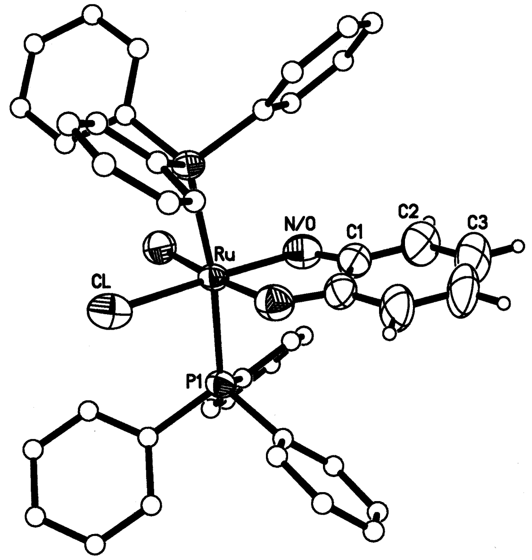

Figure 1. View of the $Ru(PPh_3)_2(isq)Cl_2$ complex molecule. The molecule is located along a crystallographic 2-fold axis that bisects the isq ligand, disordering the O and NH donor atoms.

Table 3. Selected Bond Lengths and Angles for $Ru(PPh_3)_2(isq)Cl_2$

bond lengths (Å)			
Ru−O(N)	2.003(2)	C1−C1′	1.431(7)
Ru−Cl	2.380(1)	C1−C2	1.415(5)
Ru−P	2.416(1)	C2−C3	1.358(6)
C1−O(N)	1.308(4)	C3−C3′	1.402(12)
angles (deg)			
O(N)−Ru−O(N)′	78.3(1)	O(N)−Ru−Cl	94.0(1)
Cl−Ru−Cl′	93.7(1)	P−Ru−Cl	83.7(1)
P−Ru−P′	171.7(1)	P−Ru−O(N)	91.4(1)

complexes of Ru and Os are of this type. Structural characterization of complexes containing the phenoxazinolate ligand in its iminobenzoquinone and iminosemiquinone electronic forms,[4,5] with recent studies from the Wieghardt group on complexes of *N*-phenyl iminosemiquinone and amidophenolate ligands,[6] have provided metrical features that can be used to assign ligand charges and, indirectly, the charge on the metal ion.

$Ru(PPh_3)_2(isq)Cl_2$. The addition of 2-aminophenol to $Ru(PPh_3)_3Cl_2$ has been found to give $Ru(PPh_3)_2(isq)Cl_2$. Redox isomers for this product include, in order of increasing ligand charge, Ru^{II}(ibq), Ru^{III}(isq), and Ru^{IV}(ap) species. Electrochemical characterization shows a reversible couple at 0.66 V (vs SCE) and an irreversible reduction at −0.55 V. Uncoordinated iminoquinones show similar electrochemical processes, but shifted to more negative potentials, and we assign these as a ligand-based oxidation and reduction processes. This is in agreement with Lever's assignment for redox processes that appear at similar potentials for $[Ru(bpy)_2(isq)]^{2+}$.[13] The electronic spectrum of $Ru(PPh_3)_2(isq)Cl_2$ shows an absorption in the 550-nm region that is commonly found for complexes containing iminosemiquinonato ligands,[4,6] although low-intensity bands at lower energy that are also associated with isq ligands have not been observed.

Crystallographic characterization of $Ru(PPh_3)_2(isq)Cl_2$ (Figure 1) has shown that the molecule lies along a crystallographic two-fold axis of the monoclinic space group *C*2/*c*. The two halves of the isq ligand are related by symmetry, disordering the C−O and C−N bonds. Consequently, detailed features of the ligand that would provide insight into the charge distribution are imprecise. However, the C1−O(N) bond length of 1.308(4) Å (Table 3) is clearly too low for the Ru^{IV}(ap) charge distribution and too high for the average C═O and C═N double bonds of Ru^{II}(ibq). The assignment as $Ru(PPh_3)_2(isq)Cl_2$ with an iminosemiquinonate ligand is consistent with the charge distributions in $Ru(PPh_3)_2(PhenoxSQ)Cl_2$ and $Ru(PPh_3)_2(3,5\text{-}DBSQ)Cl_2$.[4c,14] As complexes of Ru(III), all three complex molecules consist of interacting paramagnetic centers at the metal and the radical ligand. Spins at both centers lie in codirectional orbitals of π symmetry, resulting in strong antiferromagnetic coupling.[2] Magnetic measurements show that the compounds are diamagnetic, and they all give sharp ^1H NMR spectra that show no effect from residual low-level paramagnetism. They all have spin singlet ground states with no evidence for thermal population of a triplet state at higher energy.

The closely related osmium complex $Os(PPh_3)_2(ap)Br_2$ has been prepared by treating $Os(PPh_3)_3Br_2$ with 2-aminophenol in dichloromethane. The similarity in CV electrochemical potential and in electronic spectrum with $Ru(PPh_3)_2(isq)Cl_2$ might point to a similar charge distribution. However, the solution spectra and redox potentials of $Os(PPh_3)_2(3,5\text{-}DBCat)Cl_2$ were observed to be similar to those of $Ru(PPh_3)_2(3,5\text{-}DBSQ)Cl_2$,[12,14] but the structural features of the quinone ligands in the solid state were consistent with different redox isomers. This observation was also consistent with differences in charge distribution for the neutral tris(quinone) complexes of Ru and Os, where structural and dynamic properties point to a $Os(3,5\text{-}DBCat)_3$ charge distribution and a lower oxidation state for the Ru center of $Ru(3,5\text{-}DBQ)_3$. Consequently, the Os(IV) redox isomer has been assumed for $Os^{IV}(PPh_3)_2(ap)Br_2$ with a reduced amidophenolate ligand, although a shift in charge distribution to the $Os^{III}(PPh_3)_2(isq)Br_2$ redox isomer might occur in solution.

$Os(PPh_3)_2(ap)H_2$. The reaction between $Os(PPh_3)_3Br_2$ and 2-aminophenol carried out in ethanol gives the dihydrido complex $Os(PPh_3)_2(ap)H_2$. Decomposition occurs slowly in solution, but electrochemical characterization shows two irreversible oxidations, and the electronic spectrum fails to show the intense low-energy transitions that appear characteristically for the iminosemiquinonate ligand. Crystallographic characterization has provided insight into the charge distribution (Figure 2). Using the C−O and C−N bond lengths as a measure of ligand charge, values of 1.337(9) and 1.371(9) Å, respectively, (Table 4) point to an amidophenolate electronic structure for the ligand. Further, the bond lengths between carbon atoms of the ring reflect an aromatic structure rather than the contracted lengths at the C2−C3 and C4−C5 bonds that are generally seen for semiquinonate and iminosemiquinonate ligands. The phos-

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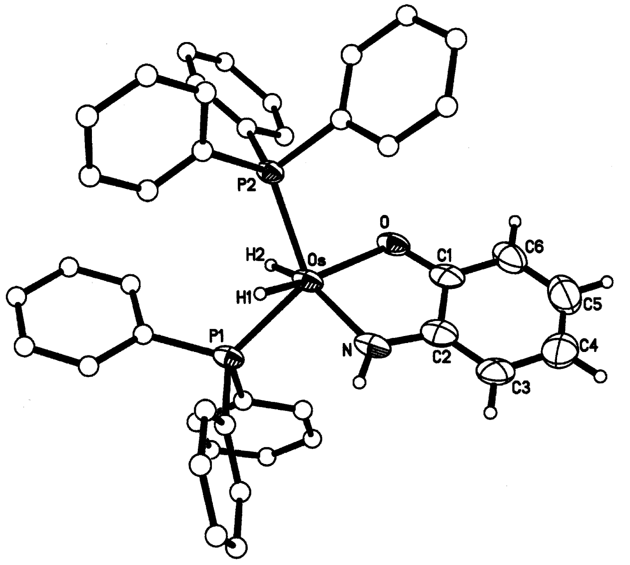

Figure 2. View of $Os(PPh_3)_2(ap)H_2$. Hydride ligands are shown in their refined locations.

Table 4. Selected Bond Lengths and Angles for $Ru(PPh_3)_2(itsq)Cl_2$ and $Os(PPh_3)_2(ap)H_2$

	$Ru(PPh_3)_2(itsq)Cl_2$	$Os(PPh_3)_2(ap)H_2$
	bond lengths (Å)	
M−N	1.946(2)	1.972(6)
M−O(S)	2.2967(5)	2.037(4)
M−X1	2.4072(5)	1.49(2)
M−X2	2.4560(6)	1.52(2)
M−P1	2.3851(3)	2.264(2)
M−P2	–	2.308(2)
C1−O(S)	1.706(2)	1.337(9)
C2−N	1.326(3)	1.371(9)
C1−C2	1.432(3)	1.409(10)
C2−C3	1.430(3)	1.391(10)
C3−C4	1.354(3)	1.402(11)
C4−C5	1.430(4)	1.370(12)
C5−C6	1.372(4)	1.393(12)
C6−C1	1.415(3)	1.400(10)
	angles (deg)	
N−M−O(S)	81.79(5)	78.8(2)
P1−M−P2	170.09(2)	115.13(7)
P1−M−O(S)	92.633(8)	146.25(13)
P2−M−O(S)	–	88.58(14)
P1−M−N	94.527(10)	94.13(16)
P2−M−N	–	140.88(16)
X1−M−X2	95.79(2)	110.7(5)

phine ligands are bent toward the *cis*-dihydrido ligands, away from the amidophenolate ring. The P1−Os−P2 bond angle is 115.13(7)°, and the dihedral angle between the Os−P1−P2 plane and the plane of the ap ligand is twisted with a value of 136.4°. Both hydrido ligands of the molecule were refined to give Os−H bond lengths of 1.49(3) and 1.52(3) Å and a H1−Os−H2 bond angle of 110.7°. The amidophenolate ring is twisted out of the Os−H1−H2 plane with a dihedral angle of 40.7°.

The difference in charge distribution between $Ru^{III}(PPh_3)_2(isq)Cl_2$ and $Os^{IV}(PPh_3)_2(ap)H_2$ might be associated with the distortion of the phosphine ligands from axial coordination sites to positions where they would interact strongly with the partially filled octahedral dπ orbital. Ligand field destabilization could induce electron transfer from the osmium to the iminoquinone ligand, resulting in the Os(IV)−ap electronic structure. However, it is more likely that the Os^{IV}(ap) charge distribution results from the difference in d-orbital energy for the two metals and that the structural distortion of $Os^{IV}(PPh_3)_2(ap)H_2$ is mainly a consequence of the higher oxidation state of the metal, together with the smaller radii of the hydride ligands.

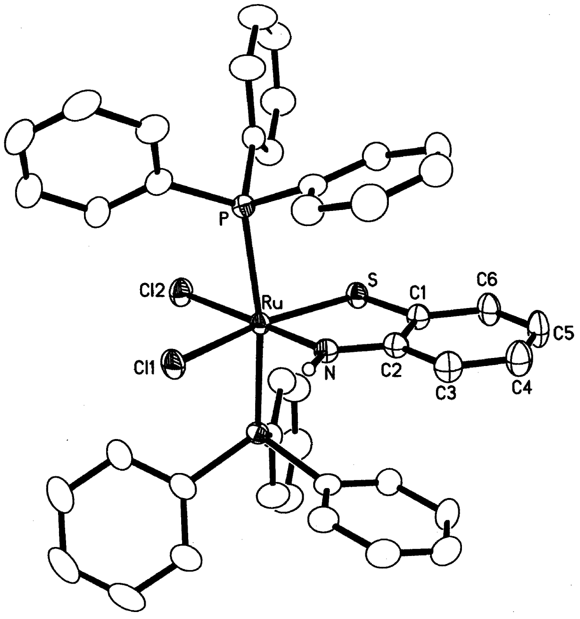

Figure 3. View of the $Ru(PPh_3)_2(itsq)Cl_2$ complex molecule. The ruthenium atom, the chloride ligands, and the itsq ligand lie on a crystallographic mirror plane.

$Ru(PPh_3)_2(itsq)Cl_2$. The iminothioquinone ligands have the potential to coordinate with transition metals as either a neutral iminothiobenzoquinone (itbq), an iminothiosemiquinonate (itsq) radical anion, or the amidothiophenolate (atp) dianion. In a recent survey of complexes containing iminothioquinone ligands, Wieghardt concluded from ligand metrical values that, in many cases, the ligand coordinated in the radical itsq form.[8] This analysis was based on C−S bond lengths that were found to be close to a value of 1.724 Å, C−N bond lengths of 1.356 Å, and a pattern of C−C bond lengths for the ring that shows slight contraction at the bonds that would be double bonds in the benzoquinone structure. Strong M−itsq and/or intramolecular itsq−itsq spin coupling often results in magnetic properties that obscure the radical character of the ligands. However, the difference in structural features relative to more oxidized or reduced forms of the ligand is clear (Table 1).

The addition of *o*-aminothiophenol to $Ru(PPh_3)_3Cl_2$ has been found to give $Ru(PPh_3)_2(itsq)Cl_2$ (Figure 3). Electrochemical potentials for the complex are similar to those of $Ru(PPh_3)_2(isq)Cl_2$, but with a slight positive shift for the reversible oxidation at 0.90 V. Structural characterization revealed features that are similar to those of $Ru(PPh_3)_2(isq)Cl_2$, but free of the disorder resulting from crystallographically imposed two-fold symmetry. However, in the centered orthorhombic space group *Abm*2, the complex molecule is located on a crystallographic mirror plane that relates the two triphenylphosphine ligands. Features of the iminothioquinone ligand were resolved with high precision (Table 4).

The C−S and C−N bond lengths of 1.706(2) and 1.326(3) Å, respectively, fall among the shorter values noted by Wieghardt for radical iminothiosemiquinonate ligands.[7] Carbon−carbon bond lengths within the ring show the short/long pattern associated with semiquinonate and iminosemiquinonate ligands. Contracted C−C bond lengths of 1.354(3) and 1.372(4) Å at positions that would have double bond values for a benzoquinone are significantly smaller than other ring C−C bond lengths. Features point clearly to the Ru^{III}−itsq charge distribution, further illustrating the utility of structural data in analysis of charge distribution for cases where magnetic and spectroscopic properties provide little insight. $Ru(PPh_3)_2(itsq)Cl_2$ is diamagnetic at all temperatures and gives a clearly resolved ^1H NMR spectrum in the region for aromatic proton resonances.

The reaction between *o*-aminothiophenol and $Os(PPh_3)_3Br_2$ gives the *o*-iminothiophenolate complex $Os(PPh_3)_2(atp)Br_2$. The electrochemistry and solution electronic spectrum for the complex are quite similar to those of $Os(PPh_3)_2(ap)Br_2$, but a distinction between the $Os^{III}(PPh_3)_2(itsq)Br_2$ and $Os^{IV}(PPh_3)_2(atp)Br_2$ redox isomers in the solid state will require further crystallographic characterization.

Structural Features of Quinoid Ligands with Oxygen, Nitrogen, and Sulfur Donor Atoms. Structural reports have appeared for complexes containing chelated quinoid ligands that contain information on bond lengths for oxygen, nitrogen, and sulfur donor atoms. These studies include early reports on aromatic dithiolate/dithiolene complexes,[16] benzene−1,2-diimine complexes,[17] catecholate/semiquinonate complexes,[1] as well as complexes containing mixed-donor ligands. Many of the structures are, for various reasons, imprecise or disordered, and an unambiguous structural distinction between ligands of different charge is unclear. However, the view of ligand coordination that emerges from an analysis of precisely determined structures is one of localized charge; quinoid ligands bound with defined BQ, SQ, or Cat electronic structures to metal ions of well-defined charge.

The difference in carbon−oxygen bond lengths for ligands in the three charged states represents the greatest variation for the series (Table 1). Precise structure determinations have been reported for complexes containing *o*-benzoquinone, *o*-semiquinonate, and catecholate ligands chelated with transition metal ions. Systematic differences in C−O and ring C−C bond lengths had been noted much earlier and used as a diagnostic of ligand charge.[1,18] In many cases, magnetic and spectroscopic properties supported the charge distribution between ligand and metal inferred from ligand structure. Structural features of the iminoquinone ligands in the three charged forms given in Table 1 are based on reports on complexes of the phenoxazinylate radical (an iminosemiquinonate);[4,5] on investigations of the SQ−N−SQ and Cat−N−SQ ligands;[19] and, most recenty, on comprehensive studies on iminosemiquinonate and amidophenolate complexes by the Wieghardt group.[6] The variation in the C−N bond length with the reduced state of the imino- or diiminoquinone ligands is smaller than the range of C−O bond lengths. A similar pattern appears for quinoid ligands with sulfur in place of the oxygen donors. Precise structural data are available for complexes containing both iminothiosemiquinonate (itsq) and amidothiophenolate (atp) ligands.[8] The structural difference between these ligands is clear, as seen for the $[Tc^{V}Cl_4(atp)]^-$ anion (C−S 1.751, C−N 1.45, C3−C4 1.40)[20] relative to $Ni^{II}(itsq)_2$ (C−S 1.724, C−N 1.348, C3−C4 1.364)[8] and $Ru^{III}(PPh_3)_2(itsq)Cl_2$.

Conflicting views of ligand charge for the 1,2-dithiolate/1,2-dithiolene complexes become clear for complexes prepared with the 1,2-benzenedithiolate ligands upon recognition of the potential for coordination as a 1,2-dithiosemiquinonate ligand. For example, the ligands of $Ni(S_2{-}dtbsq)_2$ have dithiosemiquinonate features (C−S 1.72, C3−C4 1.36), whereas the ligands of the dianion $[Ni(S_2\text{-}dtcat)_2]^{2-}$ (C−S 1.76, C3−C4 1.40) are clearly dithiocatecholate.[21] In both complexes, the metal is Ni(II), and the redox process relating members of the redox series is ligand-based. The benzenedithiolate ligands of $[W(bdt)_3]^{2-}$ (C−S 1.752, C3−C4 1.387) are clearly dithiocatecholate in charge,[22] whereas the ligands of $Mo(bdt)_3$ (C−S 1.727, C3−C4 1.359)[23] are dithiosemiquinonate with strong spin coupling, resulting in diamagnetism for the complex of Mo(III).

Electronic Coupling Between Mixed-Charge Quinone Ligands. Electronic coupling between ligands of SQ−M−Cat complexes can be viewed as resembling coupling in ligand-bridged bimetallic mixed-valence (M−L−M′) complexes. The strength of exchange in bimetallic systems is commonly referenced to the Robin−Day classification scheme, where type 2 refers to weakly coupled systems that appear charge-localized on some observable time scale and type 3 systems are delocalized. Differences in ligand structure place members of the Co^{III}(N−N)(SQ)(Cat) series in the type 2 classification,[24] for example, and the absence of a difference between ligands in the Ru^{III}(N−N)(SQ)(Cat) series might place these complexes in the type 3 classification.[1a,4d] Members of the Co^{III}(N−N)(SQ)(Cat) series have intense Cat → SQ LL′IT bands in the 2500-nm region of the IR spectrum, whereas the Ru^{III}(N−N)(SQ)(Cat) complexes fail to show electronic transitions that can be assigned as intervalence transitions between charge-localized SQ and Cat ligands. This distinction is relevant to the assignment of

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ligand charge based on structural features. Members of the $\mathrm{Ru^{III}(N{-}N)(SQ)(Cat)}$ series typically have C−O bond lengths that are intermediate between the localized SQ and Cat values. The members of this series and a few other complexes of platinum-group metals that contain two or three quinone ligands stand as unique exceptions to the structural pattern that associates features with localized ligand charge and a defined formal charge for the coordinated metal ion.[1b]

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Supporting Information Available: ^{1}H NMR spectra for the five complexes described in the Experimental Section. Complete tables of crystallographic data, final atomic coordinates, bond lengths and angles, and hydrogen atom coordinates for $\mathrm{Ru(PPh_3)_2(isq)Cl_2}$ and $\mathrm{Ru(PPh_3)_2(itsq)Cl_2}$ are available as Supporting Information. A CIF file for $\mathrm{Os(PPh_3)_2(ap)H_2}$ has been deposited. This material is available free of charge via the Internet at http://pubs.acs.org.

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