

of the interaction between copper(II) and nickel(II) within the Cu-Ni unit and show a doublet ground pair state whereas the EPR properties are those associated with the bis heterobinuclear entity (CuNi)₂. It is particularly unfortunate that we have not been able to grow single crystals of **5** suitable for an X-ray investigation in order to confirm the presence of such (CuNi)₂ species.

In this paper, we have shown that the magnetic properties of homo- and heterotrinnuclear species can be interpreted in a relatively accurate way. This is particularly true when the interacting metal centers have no first-order angular momentum and when the interaction between adjacent sites is important, as in **1** and **4**. In the near future, we intend to develop this aspect and to approach the study of the magnetic and EPR properties of molecular species with more than three magnetic centers.

Safety Notes. Perchlorate salts of metal complexes with organic ligands are potentially explosive. In general, when noncoordinating agents are required, every attempt should be made to substitute anions such as the fluoro sulfonates for the perchlorates. If a perchlorate must be used, only small amounts of material should be prepared and this should be handled with great caution. [Cf.: *J. Chem. Educ.* **1978**, *55*, A355. *Chem. Eng. News* **1983**, *61* (Dec 5), *4*; **1963**, *41* (July 8), *47*.]

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Supplementary Material Available: Listings of structure factor amplitudes, anisotropic thermal parameters for non-hydrogen atoms, and atomic coordinates for hydrogen atoms not refined in the least-squares refinement (12 pages). Ordering information is given on any current masthead page.

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Catechol-Quinone Redox Series Involving Bis(bipyridine)ruthenium(II) and Tetrakis(pyridine)ruthenium(II)

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A series of species belonging to the redox chain RuN₄(cat), [RuN₄(sq)]⁺, and [RuN₄(q)]²⁺ have been prepared and characterized by electronic, IR, and ESR spectroscopy and electrochemistry. The N₄ unit is bis(bipyridine) or tetrakis(pyridine), and the dioxolene ligands are catechol, 3,5-di-*tert*-butylcatechol, and tetrachlorocatechol and their one- and two-electron-oxidation products. Evidence is presented that oxidation of the dioxolene ligand to quinone occurs before oxidation of Ru(II) to Ru(III). Rich electronic spectra and electrochemistry are reported and assigned. The positions of the charge-transfer bands (metal to ligand, and ligand to ligand) are discussed in terms of the electrochemical potentials.

Introduction

There has been growing interest in catechol and its oxidation products (semiquinone and quinone) as ligands.²⁻³² Interest

centers mainly on the generation of redox chains, structural characterization, magnetic effects, the identification of effective oxidation levels, relationships with some natural biological catechol systems, and the quite complex electrochemistry that can arise through internal electron transfers and disproportionation. With the aim of developing polyelectron redox catalysts, we have studied complexes of the type RuN₄(0-0), where (0-0) is a variously substituted bidentate dioxolene ligand in the redox chain catechol-semiquinone-quinone and N₄ is two bipyridine (bpy) or four pyridine (py) units.

The dioxolenes are noninnocent ligands, which may coordinate in three different formal oxidation states. This can lead to ambiguity in assessing the oxidation state of the central ion. For example, in analogous dithiolene complexes considerable delocalization is thought to occur in the metal-ligand bond.³³ In dioxolene complexes, oxidation state assignments are generally

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more secure,² though in some cases the situation is unclear. Sofen et al.¹² reported the three-step oxidation of a $\text{Cr}^{\text{III}}(\text{DTBCat})_3$ species to give a species they regarded as closest to a $\text{Cr}(0)$ quinone derivative, while noting that the orbitals involved in the redox processes have both metal and ligand character. ESR studies⁷ of the same series of complexes indicate that the metal atom remains effectively $\text{Cr}(\text{III})$ and the redox processes occur at the ligands; i.e., $\text{Cr}^{\text{III}}(\text{DTBSq})_3$ is formed. In a second example, a series of four different tetraammineruthenium(III) catechols are oxidized to species best described as the corresponding tetraammineruthenium(II) quinones.²²

Our experimental data suggest that the ruthenium atom can be regarded as divalent in all the species under consideration here.

Experimental Section

Physical data were recorded on instrumentation as follows: conductivity, Wayne Kerr conductivity bridge; UV/vis/near-IR spectra, Hitachi Perkin-Elmer Model 340 microprocessor spectrophotometer; low-temperature electronic spectra, Cryosystems, Inc., closed circuit refrigerator; ESR, Varian E4 electron spin resonance spectrometer; NMR, Varian EM360 spectrometer; FTIR, Nicolet SX20 spectrometer. Electrochemical data were obtained by cyclic voltammetry and differential pulse voltammetry using Princeton Applied Research Models 173, 174, 175, and 179 instrumentation. The counter and working electrodes were platinum wires while a silver wire served as reference. The potentials were calibrated with respect to an internal ferrocenium/ferrocene couple.³⁴ Controlled-potential reductions were carried out inside a Vacuum Atmospheres drybox and solutions transferred therein to cuvettes or ESR tubes. CHN microanalyses were furnished by the Canadian Microanalytical Service, Vancouver.

Chemicals. *cis*- $\text{Ru}(\text{bpy})_2\text{Cl}_2$, and *trans*- $\text{Ru}(\text{py})_4\text{Cl}_2$ were prepared by using published procedures.^{35,36} 3,5-Di-*tert*-butylcatechol (DTBCatH_2 , Aldrich), was purified by recrystallization from benzene. Catechol (CatH_2) and 3,4,5,6-tetrachlorocatechol (TCICatH_2 , Aldrich) were used as supplied. Dichloroethane and acetonitrile (Aldrich, Spectrograde) were further purified by distillation over P_2O_5 . All other organic solvents were used without further purification. Tetrabutylammonium perchlorate (TBAP) was recrystallized from ethanol and vacuum-dried.

Preparation of Complexes. All the manipulations were carried out under a nitrogen atmosphere, unless otherwise stated, by using standard Schlenk techniques.

$\text{Ru}(\text{bpy})_2(\text{DTBCat})\cdot\text{H}_2\text{O}$. *cis*- $\text{Ru}(\text{bpy})_2\text{Cl}_2$ (0.6 g, 1.24 mmol) was suspended in methanol (60 mL) and heated for 1 h. DTBCatH_2 (0.28 g, 1.26 mmol), as a solid, and NaOH (0.1 g, 2.5 mmol) in methanol (20 mL), were added. The reaction mixture was refluxed for 4 h, during which time the initial violet solution turned green and a black precipitate was formed. This was filtered off and recrystallized from dichloromethane/diethyl ether. Yield: 78%. Anal. Calcd for bis(2,2'-bipyridine)(3,5-bis(1,1-dimethylethyl)-1,2-benzenediolato)ruthenium(II) monohydrate ($\text{Ru}(\text{bpy})_2(\text{DTBCat})\cdot\text{H}_2\text{O}$): C, 62.7; H, 5.9; N, 8.6. Found: C, 62.0; H, 5.8; N, 8.5.

NMR in CDCl_3 showed two signals due to the *tert*-butyl group at 0.4 and 1.67 ppm referenced to Me_4Si .

$\text{Ru}(\text{bpy})_2(\text{Cat})\cdot 1.5\text{H}_2\text{O}$. This complex was similarly synthesized by using a solution of catechol in methanol. Yield: 72%. Anal. Calcd for bis(2,2'-bipyridine)(1,2-benzenediolato)ruthenium(II) sesquihydrate ($\text{Ru}(\text{bpy})_2(\text{Cat})\cdot 1.5\text{H}_2\text{O}$): C, 56.9; H, 4.2; N, 10.2. Found: C, 56.8; H, 3.75; N, 10.4.

$\text{Ru}(\text{bpy})_2(\text{TCICat})$. This was prepared in a similar fashion from 3,4,5,6-tetrachlorocatechol. Yield: 56%. Anal. Calcd for bis(2,2'-bipyridine)(3,4,5,6-tetrachloro-1,2-benzenediolato)ruthenium(II) hemihydrate ($\text{Ru}(\text{bpy})_2(\text{TCICat})\cdot 0.5\text{H}_2\text{O}$): C, 46.7; H, 2.6; N, 8.4. Found: C, 46.8; H, 2.3; N, 8.4.

$\text{Ru}(\text{py})_4(\text{DTBCat})\cdot\text{H}_2\text{O}$. A suspension of $\text{Ru}(\text{py})_4\text{Cl}_2$ (0.5 g, 1 mmol) and DTBCatH_2 (0.23 g, 1 mmol) was refluxed in methanol (60 mL) for 1 h. To the resulting solution was added NaOH (0.9 g, 2.2 mmol), and the mixture was refluxed for a further 10 h. The suspension slowly dissolved, and the solution color changed from orange to brown. After filtration, the solution was cooled in a refrigerator. A brown precipitate was dried in vacuo. Yield: 60%. Anal. Calcd for (3,5-bis(1,1-dimethylethyl)-1,2-benzenediolato)tetrakis(pyridine)ruthenium(II) monohydrate ($\text{Ru}(\text{py})_4(\text{DTBCat})\cdot\text{H}_2\text{O}$): C, 62.3; H, 6.45; N, 8.5. Found: C, 62.4; H, 6.3; N, 8.4.

$\text{Ru}(\text{py})_4(\text{TCICat})$. This species was prepared in a manner similar to that of the DTBCat analogue. Brown crystals were obtained. Anal. Calcd for (3,4,5,6-tetrachloro-1,2-benzenediolato)tetrakis(pyridine)ruthenium(II), $\text{Ru}(\text{Py})_4(\text{TCICat})$: C, 47.1; H, 3.05; N, 8.45. Found: C, 47.0; H, 3.1; N, 8.2.

$[\text{Ru}(\text{bpy})_2(\text{DTBSq})]\text{ClO}_4\cdot\text{Et}_2\text{O}$. A methanol-dichloromethane (1:1 v/v, 40 mL) solution of $\text{Ru}(\text{bpy})_2(\text{DTBCat})$ (0.36 g, 0.6 mmol) was added to TBAP (0.2 g) and stirred at room temperature, in air, until the color changed to brown (about 7 h). The resulting solution was concentrated under reduced pressure and ether added to induce precipitation. Yield: 76%. Anal. Calcd for bis(2,2'-bipyridine)(3,5-bis(1,1-dimethylethyl)-3,5-cyclohexadiene-1,2-dionato(radical(1-)))ruthenium(II) perchlorate diethyl ether solvate ($[\text{Ru}(\text{bpy})_2(\text{DTBSq})\text{ClO}_4\cdot\text{Et}_2\text{O}]$): C, 56.5; H, 5.7; N, 6.9. Found: C, 57.2; H, 5.2; N, 7.0. Conductivity 140 mho $\text{cm}^2 \text{mol}^{-1}$ in acetonitrile ($6.2 \times 10^{-4} \text{ mol L}^{-1}$ (1:1 electrolyte³⁷)).

$[\text{Ru}(\text{bpy})_2(\text{DTBSq})]\text{PF}_6$ was similarly prepared by using tetraethylammonium hexafluorophosphate in lieu of TBAP. Anal. Calcd for bis(2,2'-bipyridine)(3,5-bis(1,1-dimethylethyl)-3,5-cyclohexadiene-1,2-dionato(radical(1-)))ruthenium(II) hexafluorophosphate ($[\text{Ru}(\text{bpy})_2(\text{DTBSq})\text{PF}_6]$): C, 52.4; H, 4.7; N, 7.2. Found: C, 52.0; H, 4.6; N, 7.15.

The species bis(2,2'-bipyridine)(3,4,5,6-tetrachloro-3,5-cyclohexadiene-1,2-dionato(radical(1-)))ruthenium(II) cation ($[\text{Ru}(\text{bpy})_2(\text{TCISq})]^+$), (3,5-bis(1,1-dimethylethyl)-3,5-cyclohexadiene-1,2-dionato(radical(1-)))tetrakis(pyridine)ruthenium(II) cation ($[\text{Ru}(\text{py})_4(\text{DTBSq})]^+$), (3,4,5,6-tetrachloro-3,5-cyclohexadiene-1,2-dionato(radical(1-)))tetrakis(pyridine)ruthenium(II) cation ($[\text{Ru}(\text{py})_4(\text{TCISq})]^+$), bis(2,2'-bipyridine)(3,5-bis(1,1-dimethylethyl)-3,5-cyclohexadiene-1,2-dione)ruthenium(II) cation ($[\text{Ru}(\text{bpy})_2(\text{DTBQ})]^{2+}$), bis(2,2'-bipyridine)(3,4,5,6-tetrachloro-3,5-cyclohexadiene-1,2-dione)ruthenium(II) cation ($[\text{Ru}(\text{bpy})_2(\text{TCIQ})]^{2+}$), (3,5-bis(1,1-dimethylethyl)-3,5-cyclohexadiene-1,2-dione)tetrakis(pyridine)ruthenium(II) cation ($[\text{Ru}(\text{py})_4(\text{DTBQ})]^{2+}$), and (3,4,5,6-tetrachloro-3,5-cyclohexadiene-1,2-dione)tetrakis(pyridine)ruthenium(II) cation ($[\text{Ru}(\text{py})_4(\text{TCIQ})]^{2+}$) were prepared by controlled-potential oxidation of the precursor catechol or semiquinone at a platinum electrode but were not isolated in the solid state. Coulometry confirmed the one-electron nature of these oxidations. Bis(2,2'-bipyridine)(3,5-cyclohexadiene-1,2-dionato(radical(1-)))ruthenium(II) cation ($[\text{Ru}(\text{bpy})_2(\text{Sq})]^+$) was prepared in solution by bromine oxidation of the catechol derivative. Solution colors in 1,2-dichloroethane are as follows: $\text{Ru}(\text{bpy})_2(\text{cat})$, green (DTBCat , Cat , TCICat); $\text{RuPy}_4(\text{cat})$, brown (DTBCat), orange (TCICat); $[\text{Ru}(\text{bpy})_2(\text{sq})]^+$, pink-brown (DTBSq , Sq), yellow (TCISq); $[\text{Ru}(\text{py})_4(\text{sq})]^+$, green (DTBSq , TCISq). The quinone species all gave blue solutions.

Results and Discussion

For purposes of comparison of electrochemical and optical data, we have prepared various series of complexes $\text{RuN}_4(0-0)$, where N_4 is $(\text{bpy})_2$ or $(\text{py})_4$, and the series may originate from DTBCatH_2 , CatH_2 , or TCICatH_2 (though only a selection of the possible combinations are reported here). The one- and two-electron oxidation products of the catechol complexes have been prepared, yielding compounds in the redox chain



where the lower case symbols cat, sq, and q are used to designate a general rather than a specific member of a chain.

The reaction of RuN_4Cl_2 with a catechol, in the presence of base, readily generates brown or black crystals of $\text{Ru}^{\text{II}}\text{N}_4(\text{cat})$, containing a deprotonated catecholate dianion. These complexes are soluble in a range of organic solvents but are insoluble in water. They are electrically neutral and nonconductors in solution.

Oxidation yields the $[\text{Ru}^{\text{II}}(\text{bpy})_2(\text{sq})]^+$ cations, where sq is a monoanionic, deprotonated semiquinone species obtained through one-electron oxidation of a catecholate dianion. The sensitivity to oxidation increases in the order $\text{TCICat} < \text{Cat} < \text{DTBCat}$, with the DTBCat species rapidly oxidized by aerial oxygen and the TCICat only being oxidized slowly in air in the presence of TBAP but easily oxidized by chemical oxidants such as bromine. The sq species may be reduced back to the cat species with reductants such as ascorbic acid.

$[\text{Ru}(\text{bpy})_2(\text{DTBSq})]\text{ClO}_4$ shows a room-temperature ESR spectrum consisting of a broadened free-radical signal centered at $g = 2.003$ with peak to peak separation of about 30 G in 1,2-dichloroethane (solvent dependent), indicating oxidation of

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Table I. Electrochemical Potentials (V) of RuN₄(O-O) Complexes

species ^a	Ru(III)/Ru(II)	q/sq	sq/cat	bpy/bpy ⁻
couple	IV	III	II	I
Ru(bpy) ₂ (DTBCat)	1.25 ^b	0.15	-0.75	-1.99
Ru(bpy) ₂ (Cat)	1.40 ^b	0.31	-0.57	-1.96
Ru(bpy) ₂ (TClCat)	1.44 ^b	0.64	-0.22	-1.93 ^c
Ru(py) ₄ (DTBCat)	1.55 ^b	0.16	-0.84	
Ru(py) ₄ (TClCat)		0.70	-0.33	

^a Bulk solution. ^b Irreversible. ^c (bpy)₂⁻/(bpy)₂²⁻ couple observed at -2.24 V. All potentials are reported with respect to SCE in dichloroethane containing 0.1 or 0.2 M TBAP, assuming the ferrocenium/ferrocene couple lies at 0.40 V vs. NHE, or 0.16 V vs. SCE.³⁴ The potentials are the average anodic and cathodic peak potentials in a cyclic voltammogram recorded at 100 mV/s. Differential-pulse data provided essentially identical potentials.

the ligand rather than the metal. No hyperfine structure was observed even at temperatures down to 77 K. However, at low temperature, in polar solvents such as DMF or CH₃CN, an apparently axial spectrum is obtained, with $g_{\perp} = 1.985$ and $g_{\parallel} = 2.067$ (in DMF). The difference between g_{\perp} and g_{\parallel} is smaller than normally observed for a Ru(III) species, e.g. [Ru^{III}(NH₃)₄cat]⁺,²² but the apparent axial symmetry leads to the conclusion that the MO containing the unpaired electron is partially localized on the metal; i.e., the true description of the ground state contains some Ru(III). Similar conclusions have been drawn^{20,29,30,32} for other semiquinone complexes of Ru(II) and Rh(III). Investigation of the low-temperature ESR spectra continues.

The X-ray structure of this complex has been briefly described.³⁸ The bond distances are generally consistent with a semiquinone coordinated to Ru(II), but there is some distortion of the dioxolene ligand toward the catechol structure, consistent with partial Ru(III) character. Thus considering the Ru—O—C=C—O ring at the semiquinone ligand, Ru—O₁ = 203.0 pm, O₁—C₁ = 128.9 pm, C₁—C₂ = 144.5 pm, O₂—C₂ = 132.7 pm, and Ru—O₂ = 205.0 pm. Within the error limits ($R = 5\%$), there are real differences between the two C—O distances. In particular O₂—C₂ is clearly a semiquinone distance, but O₁—C₁ is much closer to a catechol distance.

FTIR spectra were collected for some typical catechol and semiquinone complexes. Coordinated catechols^{3,13,15,16} show two characteristic intense bands, near 1480 (ring stretching involving the C—C bond between the two oxygen atoms) and 1250 cm⁻¹ (C—O stretching). These are present in the free catechol and gain intensity in the coordinated species. In the DTBCat complexes, two strong bands are seen near 1250–1275 cm⁻¹, while the TClCat species show only one near 1250 cm⁻¹. A strong band is also observed near 1440 cm⁻¹ in these catechol complexes but this region of the spectrum is complicated by bpy and py vibrations.

Coordinated semiquinones should show the C—O vibration in the crowded region near 1400–1500 cm⁻¹.³ Bands in the 1250-cm⁻¹ region are much weaker than those in the catecholates, as expected. Thus the strong bands near 1250 cm⁻¹ can be used as a marker for the presence of the catechol rather than semiquinone ligand; their absence in the first oxidation product provides further evidence that ligand oxidation has occurred (see Table V in the supplementary material).

Electrochemistry. The bpy complexes show four redox couples in the region studied (Figure 1, Table I). Essentially the same voltammogram is observed irrespective of whether the bulk solution is in the catechol, semiquinone, or quinone oxidation level. The most negative couple, observed near -1.9 V (couple I), has a potential almost independent of the specific catechol species involved, is absent from the tetrapyridine series, and is therefore associated with the bpy/bpy⁻ redox process.

The next two couples, II and III, have potentials depending strongly upon the substituents in the catechol and are reasonably associated thereby with the sq/cat and q/sq processes. The po-

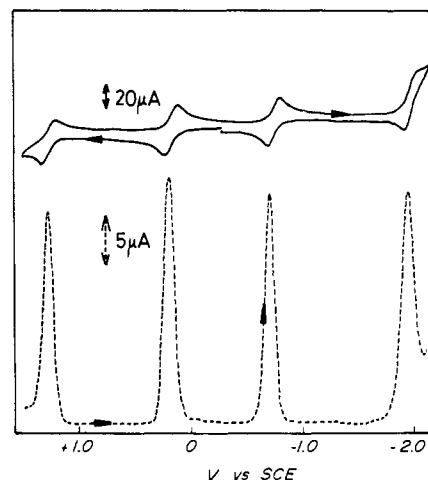


Figure 1. Electrochemistry of Ru(bpy)₂(DTBCat) in 1,2-dichloroethane: (—) cyclic voltammogram, scan rate 200 mV s⁻¹; (---) differential-pulse voltammogram, scan rate 5 mV s⁻¹.

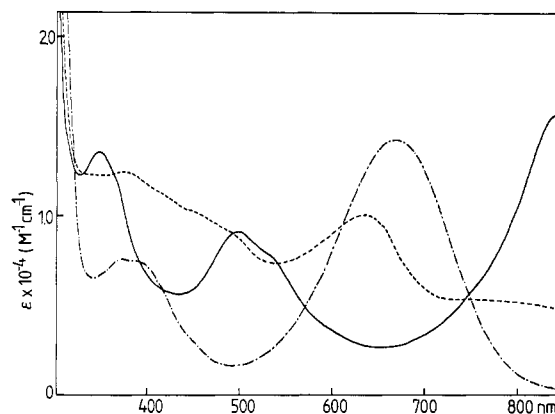


Figure 2. Electronic spectra of Ru(bpy)₂(DTBCat) and its one- and two-electron-oxidation products, prepared by controlled-potential electrolysis in 1,2-dichloroethane: (---) catechol; (—) semiquinone; (-·-) quinone.

tentials vary linearly with the Hammett σ constant of the substituent. There is an approximate 0.5-V difference between the couples involving DTBCat and TClCat, the latter lying at more positive potentials, similar to the spread observed in the free ligands.¹⁴ The differences between the two couples in each complex also correspond to those of the free ligand. Binding to the ruthenium(II) causes a significant shift, in both couples, of approximately 0.5 V, to more positive potentials, compared with the free ligands.

The most positive couple, observed near 1.4 V (couple IV), shows a smaller but significant dependence upon the bound catechol and is reasonably associated with the Ru(III)/Ru(II) couple. Thus oxidation to Ru(III) does not occur until the dioxolene ligand is oxidized to the quinone level. This provides electrochemical evidence for the divalency of ruthenium in all the complexes discussed here. Couple IV is quasi-reversible in ClC—H₂CH₂Cl and irreversible in CH₃CN, preventing preparation and study of a Ru(III)—quinone complex, at least at room temperature. Spectroelectrochemical data reported below reveal the existence of a paramagnetic ruthenium complex beyond couple IV, but the irreversibility of the reaction precludes ready identification.

Waves I–III are reversible one-electron couples with $i_c/i_a = 1$, $i \propto v^{1/2}$ (v = scan rate), and peak to peak separations not highly dependent upon scan rate and approaching 60 mV at slow scan rates.³⁹

Optical Spectra. The visible and near-IR spectra of these complexes are dominated by charge-transfer transitions (Figures

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Table II. Electronic Spectra in 1,2-Dichloroethane and Assignments^a

species	DTB	f^b	unsubst	TCI	assignt
Ru(bpy) ₂ (cat)	13 000 (3.82)	0.15	13 700 br (3.60)	14 700 br (3.59)	3b ₁ (cat) → π*(1) ^c
	15 650 (4.00)	0.10	16 200 (3.93)	16 900 (3.88)	Ru(II) → π*(1)
	20 000–25 000		20 850–24 650	21 750–25 000	{ 3b ₁ (cat) → Ru(II)σ*, π*(2)
	26 300 (4.10)		26 300 (3.96)	27 300 (4.03)	{ Ru(II) → π*(2)
			30 050 (3.97)		internal cat?
Ru(py) ₄ (cat)	17 250 (3.67)	0.05			3b ₁ (cat) → π*(1)Py
	20 650 (4.13)	0.21		22 400 (4.32)	Ru(II) → π*(1)Py
	24 400 (4.09)	0.24		25 750 (4.19)	Ru(II) → π*(1)Py
	29 050 (3.90)	0.20		29 600 (3.94)	{ Ru(II) → π*(2)Py?
					{ 3b ₁ (cat) → Ru(II)σ*
[Ru(bpy) ₂ (sq)] ⁺	8 350 sh (2.87)				
	11 850 (4.19)	0.12	11 250 (4.13)	10 650 (4.20)	Ru(II) → 3b ₁ (sq)
	16 650 sh		17 250 sh	19 250 sh	{ 3b ₁ (sq) → π*(1), Ru(II)dσ*
	19 050 sh		19 400 sh		{ Ru(II) → π*(1)
	20 250 (3.96)	0.19 ^d	20 300 (3.40)	22 200 br (3.74)	{ Ru(II) → π*(1)
	28 750 (4.13)	0.42 ^e	29 050 (3.95)	29 750 sh	{ Ru(II) → π*(2)
					internal sq
[Ru(py) ₄ (sq)] ⁺	8 700 sh (2.87)				
	10 800 (4.06)	0.09		10 250 (4.03)	Ru(II) → 3b ₁ (sq)
	26 750 (4.15)	0.42		30 600 (4.23)	{ Ru(II) → π*(1)Py
	31 250 sh (3.89)				{ internal sq?
[Ru(bpy) ₂ (q)] ²⁺	14 950 (4.15)	0.21		15 650 (4.05)	Ru(II) → 3b ₁ (q)
	25 000 sh (3.86)			26 250 (3.73)	Ru(II) → π*(1)
	26 850 (3.88)	0.22 ^d			internal q?
[Ru(py) ₄ (q)] ²⁺	14 850 (4.02)	0.19		16 050 (4.06)	Ru(II) → 3b ₁ (q)
	26 300 sh (3.49)			24 750 br (3.52)	{ internal q?
	27 800 sh (3.66)				{ Ru → py?

^a In cm⁻¹; log ε in parentheses. Some transitions show a small solvent dependence, generally less than 500 cm⁻¹. ^b Oscillator strength. ^c The π*(1) and π*(2) orbitals are the lowest lying empty orbitals on the bipyridine ligand. ^d Oscillator strength of combined transition. ^e Includes some contribution to the oscillator strength from the UV tail.

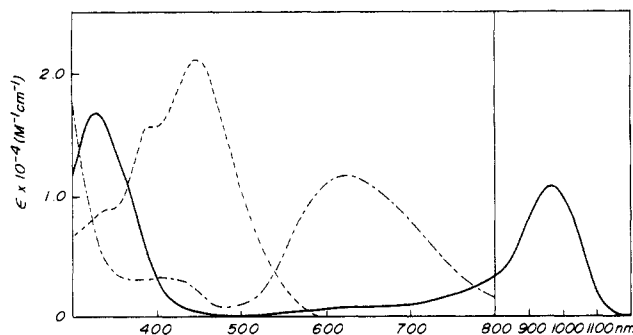


Figure 3. Electronic spectra of Ru(py)₄(TClCat) and its one- and two-electron-oxidation products, prepared by controlled-potential electrolysis in 1,2-dichloroethane: (---) catechol; (—) semiquinone; (-·-) quinone.

2 and 3). Since the metal is present as Ru(II), transitions of the metal to ligand charge-transfer (MLCT) type are expected.⁴⁰ Metal to bpy (or py) transitions are readily identified in each of the complexes (Table II) by comparison with other bis(bipyridine) and *cis*-tetrakis(pyridine) systems in the literature⁴⁰ and by direct comparison of bpy with the analogous *cis*-tetrakis(pyridine) species.

The MO treatment of Gordon and Fenske⁶ (GF) provides a basis for understanding the optical spectra of the metal-bound catechol, semiquinone, and quinone complexes. The dioxolene 3b₁ (HOMO in cat) is expected to lie between the filled Ru(II) "t_{2g}" (stabilized by the π-acceptor bpy) and the (bpy)π* levels. As the complex is oxidized, the Ru levels will be stabilized, as will the bpy levels but to a lesser extent. However, according to GF,⁶ the 3b₁ orbital increases in energy in the sequence cat < sq < q. This is probably due to increasing C=O π* antibonding character in that sequence.

Using the labels for C_{2v} symmetry, (C₂ axis bisects the dioxolene ligand), d_{xz}, d_{xy}, and d_{yz} span a nonbonding orbital of a₁ symmetry

(in the dioxolene plane), and two, lower energy, π-bonding orbitals of a₂ and b₁ symmetry. Transitions from all three orbitals to the (bpy)π* orbitals are allowed, but only transitions from the latter two orbitals are permitted to the dioxolene 3b₁ orbital, the former (d(a₁) → 3b₁) yielding, in the first approximation, a zero-intensity transition due to overlap orthogonality.

(a) Ru^{II}(bpy)₂(cat) Series. The Ru → (bpy)π* transitions are readily identified through comparison with those of the pyridine analogues (Table II). They increase in energy by about 1300 cm⁻¹ from DTBCat to TClCat.

The spectrum of Ru(bpy)₂(TClCat) dissolved in an EtOH-DMF (3:1) glass at around 20 K shows a broad Ru(II) → (bpy)π* CT band resolved into two components at 17 850 and 15 400 cm⁻¹, attributed to splitting of the d(a₁), d(a₂, b₁) manifold. The splitting of 2450 cm⁻¹ is greater than that calculated for the (bpy)π* manifold in [Ru(bpy)₃]²⁺.⁴¹

The complexes show a broad, but well-defined transition centered near 12 800 cm⁻¹ in the DTBCat complex (Figure 2) absent from this energy region in the pyridine series. It must therefore involve bipyridine. A broad shoulder appears in the Ru(py)₄-(DTBCat) spectrum shifted by approximately the same amount to higher energy as the MLCT transitions. The band shifts to higher energy when the cat is changed from DTBCat to the more oxidizing TClCat; the shift is about twice as great as the shift in the Ru → bpy MLCT transition. This feature is believed to be the expected 3b₁(cat) → (bpy)π*(1) interligand transition (LLCT). This type of transition is not well documented; most previous reports of interligand transitions have involved square-planar complexes. LLCT bands have been tentatively assigned in mixed-valence complexes containing both catechol and semiquinone ligands, e.g. [Co^{III}(bpy)(cat)(sq)]²⁷ and [Fe(bpy)-(Phencat)(Phensq)]³ (Phencat = 1,2-phenanthrodiol). Interligand transitions involving bipyridine have been observed in Pt^{II}(bpy)(tdt)⁴² (tdt = 3,4-toluenedithiolate) and Zn(bpy)(tdt).⁴³

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Weak intervalence ($\text{bpy}^- \rightarrow \text{bpy}$) bands are observed in the near-IR spectra of the first and second reduction products of $[\text{Ru}(\text{bpy})_3]^{2+}$.⁴⁴

Bipyridine complexes usually exhibit a second MLCT transition, involving a higher $\pi^*(2)$ level, 7000–9000 cm^{-1} above the first. The broad absorption seen in this series of complexes from about 20 000 to 25 000 cm^{-1} encompasses the $\text{Ru}(\text{II}) \rightarrow \pi^*(2)$ and catechol $\rightarrow \pi^*(2)$ transitions analogous to those discussed above.

The crystal field transitions in these species cannot be positively identified, but the transitions to components of the lowest state, $^1T_{1g}$ in O_h , lie in this region. The d–d splitting can be estimated, from consideration of regular RuN_4O_2 low-spin species, to be about 24 000 cm^{-1} ($10Dq - C$).⁴⁰ This corresponds to an acceptor level potential of about 3.0 eV, lying, therefore, about 8500 cm^{-1} above the $\pi^*(1)$ bipyridine level. Hence the broad absorption in the 20 000–25 000- cm^{-1} region may also contain a catechol to $\text{Ru}(\text{II})\sigma^*$ LMCT transition. An internal catechol transition is also expected to occur in this region; this lies at 32 000 cm^{-1} in the DTBCat anion.¹⁴

(b) $\text{Ru}^{\text{II}}(\text{py})_4(\text{cat})$. Fewer transitions are expected in the visible region than in the bipyridine complex, therefore explaining its higher resolution; three transitions are observed in the 20 000–30 000- cm^{-1} region (Figure 3). In addition there is a shoulder near 17 250 cm^{-1} assigned above to $3b_1(\text{DTBCat}) \rightarrow (\text{Py})\pi^*(1)$. The MLCT transitions in $\text{Ru}(\text{bpy})_2(\text{NCS})_2$ and $\text{Ru}(\text{py})_4(\text{NCS})_2$ differ by 0.86 eV,⁴⁵ while the pairs $\text{W}(\text{CO})_4(\text{bpy})-\text{W}(\text{CO})_4(\text{Py})_2$ and $\text{ClRe}(\text{CO})_3(\text{phen})-\text{ClRe}(\text{CO})_3(\text{Py})_2$ differ by 0.77 and 0.9 eV, respectively^{40,46} (phen = phenanthroline, energetically similar to bipyridine). Thus the $\text{Ru}(\text{II}) \rightarrow (\text{py})\pi^*(1)$ transition should lie about 0.7–1 eV above the corresponding bpy transition. A *cis*-tetrakis(pyridine) complex should exhibit two $\text{Ru} \rightarrow (\text{py})\pi^*$ transitions,⁴⁰ and the two lower lying bands of the triple-band system are assigned to these transitions. They are comparable in energy with two intense bands in the spectrum of *cis*- $\text{Ru}(\text{py})_4\text{Cl}_2$ at 20 650 and 22 600 cm^{-1} assigned as d–d transitions⁴⁷ but which are the likely the $\text{Ru} \rightarrow (\text{py})\pi^*$ MLCT transitions. In the TClCat derivative these transitions are shifted to slightly higher energy, consistent with the ruthenium being more difficult to oxidize and with the fact that these transitions do not involve the dioxolene ligand directly.

In general the $\text{Ru} \rightarrow (\text{py})\pi^*$ transitions in the dioxolene complexes are stronger than the corresponding transitions to bipyridine. This may arise because the pyridine rings are free to rotate into the optimum overlap configuration.

(c) $[\text{Ru}^{\text{II}}(\text{bpy})_2(\text{sq})]^+$. The splitting of 1200 cm^{-1} , increasing to 1300 cm^{-1} at liquid-nitrogen temperature, evident in the $\text{Ru} \rightarrow (\text{bpy})\pi^*(1)$ transition center near 20 000 cm^{-1} , arises as a consequence of the d orbital splitting mentioned above. The shifts in the $\text{Ru} \rightarrow (\text{bpy})\pi^*(1)$ transition with changing dioxolene parallel those in the catechol series. The higher energy band near 28 800 cm^{-1} contains $\text{Ru}(\text{II}) \rightarrow (\text{bpy})\pi^*(2)$ and internal semiquinone transition expected¹⁴ near 26 500 and 29 000 cm^{-1} .

The strong feature near 11 000 cm^{-1} may be attributed to the split $\text{Ru}(\text{II})(a_1^2b_1^2a_2^2) \rightarrow \text{sq}(3b_1)$ MLCT transitions, since it is present in both the pyridine and bipyridine systems (Figure 4) and shifts to lower energy as the semiquinone involved becomes a stronger acceptor. Free DTBSq radical anion possesses a weak transition in the visible region,¹⁴ which, from the GF⁶ analysis, is assigned to the internal $n \rightarrow \pi^*$ transition ($9a_1 \rightarrow 3b_1$). The $9a_1$ orbital will be stabilized by metal coordination such that this $n \rightarrow \pi^*$ transition should blue-shift. Moreover the $n \rightarrow \pi^*$ transition probability is small and even in the real low symmetry of the molecule is unlikely to generate such an intense band.

The $\text{sq} \rightarrow (\text{bpy})\pi^*(1)$ transition may tentatively be associated with a weak shoulder near 16 500 cm^{-1} in the DTBSq complex, shifting as expected to higher energy in the TClSq derivative.

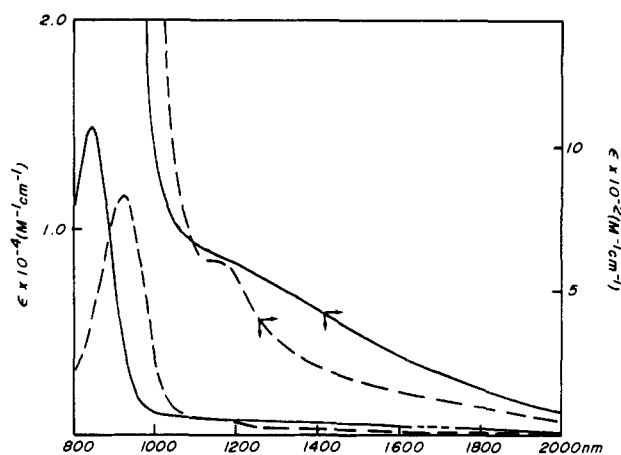


Figure 4. Near-infrared electronic spectra of semiquinone species in 1,2-dichloroethane; comparison of bpy and py species: (—) $[\text{Ru}(\text{bpy})_2(\text{DTBSq})]^+$; (---) $[\text{Ru}(\text{py})_4(\text{DTBSq})]^+$.

Transitions from $3b_1(\text{sq})$ to both $\text{Ru}(\text{II})d\sigma^*$ and $(\text{bpy})\pi^*(1)$ are calculated to lie at about the same energy as the double band assigned as a split $\text{Ru} \rightarrow (\text{bpy})\pi^*$ transition. On the basis of the bpy $\pi \rightarrow \pi^*$ energy and the sq/cat redox potential (vide infra), the LLCT $(\text{bpy})\pi \rightarrow 3b_1(\text{sq})$ transition is calculated to lie around 26 000 cm^{-1} .

(d) $[\text{Ru}^{\text{II}}(\text{py})_4(\text{sq})]^+$. The assignments in Table II follow from the discussion above. The $\text{Ru} \rightarrow (\text{Py})\pi^*$ transition occurs at a higher energy than in the catechol derivative. The second such transition is hidden under the rising UV absorption, which also contains an internal sq transition.

(e) $[\text{Ru}^{\text{II}}(\text{bpy})_2(\text{q})]^{2+}$. As the dioxolene becomes more electronegative, the $\text{Ru}(\text{II}) \rightarrow (\text{bpy})\pi^*(1)$ transition shifts to even higher energies and is associated with the band at 25 000 cm^{-1} (DTBQ). This is clearly absent in the corresponding tetrakis(pyridine) species.

The quinone complexes show a strong band near 15 000 cm^{-1} , also present in the tetrakis(pyridine) derivatives, which can only reasonably be associated with the expected $\text{Ru} \rightarrow \text{q}$ MLCT transition. There are no lower lying transitions (above 7000 cm^{-1}) that might be so-assigned. The absorption band is broad and shifts slightly to higher energy in the sequence DTBQ to TClQ, the reverse of the shift expected for an MLCT transition⁴⁰ (see below). In the analogous $[\text{Ru}(\text{NH}_3)_4(o\text{-benzoquinone})]^{2+}$ species, a strong band, which can also only reasonably be assigned to $\text{Ru} \rightarrow \text{q}$ MLCT, occurs at even higher energy, 19 550 cm^{-1} ,²² contrary to what might be expected when bipyridine is replaced by ammonia.

Resonance Raman excitation into this 15 000- cm^{-1} band⁴⁸ provides resonant enhancement of M–L(quinone) and internal quinone deformation modes, primarily in the 400–600 cm^{-1} region, consistent with the assignment and with considerable distortion in the excited-state quinone molecule.

The possibility that these complexes are better regarded as $\text{Ru}(\text{III})$ species, i.e. $[\text{Ru}^{\text{III}}(\text{bpy})_2(\text{sq})]^{2+}$, has previously been argued strongly against²² in the case of the $[\text{Ru}(\text{NH}_3)_4(o\text{-benzoquinone})]^{2+}$ species, on the bases of electrochemical potentials and ESR and IR spectroscopy. Further, the assignment of the 25 000- cm^{-1} band to $\pi(\text{bpy}) \rightarrow \text{Ru}(\text{III})$ would follow from the reassignment of oxidation states, but it appears to be too high in energy.^{40,49} The $\text{Ru}(\text{II})$ hypothesis is also supported by the anticipated stabilization of this oxidation state by the π -acceptor quinone.

Oxidation of the blue $[\text{Ru}^{\text{II}}(\text{bpy})_2(\text{DTBQ})]^{2+}$ species, in DCE, some 200 mV positive of couple IV, yields a yellow solution with peaks at 383 and 471 nm, with no lower lying electronic transitions. The ESR spectrum of this solution shows a broad (ca. 300 G) structured peak suggestive of a $\text{Ru}(\text{III})$ species with some delocalization onto the ligand. However rereduction of this solution

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Table III. Calculated Redox Potentials for $[\text{Ru}(\text{bpy})_2(\text{O}-\text{O})]^{n+}$ ^a

Ru(III)/Ru(II) couple	DTB	unsubst	TCl
cat	-0.09	0.01	0.15
sq	0.79	0.80	1.16 ^b
q	1.69		1.93

^aCalculated from eq 4. Standard deviation 0.10 eV. ^bThe Ru \rightarrow (bpy) $\pi^*(1)$ transition is part of a very broad band; this potential is probably overestimated.

does not regenerate the blue Ru(II)-quinone species, and the complex has not been identified.

Correlation of Optical Spectra and Electrochemistry. We have discussed correlation of electronic charge-transfer energies with electrochemical potentials.⁵⁰⁻⁵³ The energy of an MLCT transition such as



is estimated by taking the difference between two electrochemical potentials

$$E_{\text{op}}(\text{MLCT}) = E[\text{M}^{\text{III}}\text{L}/\text{M}^{\text{III}}\text{L}] - E[\text{M}^{\text{III}}\text{L}/\text{M}^{\text{III}}\text{L}^-] + \chi_i + \chi_o \quad (2)$$

where M and L represent metal and ligand in a complex, the $\text{M}^{\text{III}}\text{L}^-$ species in the second potential is in the singlet state, and χ_i and χ_o are the inner (vibrational) and outer (solvation) reorganization energies.

The required L/L⁻ reduction potential, for ligand bound to Ru(III) in this case, is not available experimentally, the corresponding value for ligand bound to Ru(II) being observed. The required "Ru(III)" potential is expected to be more positive than the observed "Ru(II)" potential by, e.g., y V. Thus if the optical transition is approximated by

$$E_{\text{op}}(\text{MLCT}) = E[\text{M}^{\text{III}}\text{L}/\text{M}^{\text{III}}\text{L}] - E[\text{M}^{\text{II}}\text{L}/\text{M}^{\text{II}}\text{L}^-] \quad (3)$$

the error in the calculated transition energy will be $(\chi_i + \chi_o - y)$, where χ_i , χ_o , and y are all positive.

The utility of eq 3 has been tested⁵¹ for a series of $[\text{Ru}(\text{bpy})_2\text{LL}']^{n+}$ complexes for which metal oxidation, bipyridine reduction, and charge-transfer data are available in the literature. The predicted Ru(II) \rightarrow (bpy) π^* CT energies from eq 3 are underestimated, on average, by 0.21 eV with a standard deviation of 0.11 eV; i.e., the average value of $(\chi_i + \chi_o - y)$ is 0.21 eV. Ghosh and Chakravorty have recently reported a similar observation.⁵⁴

In order to use eq 3, the Ru(III)/Ru(II) potentials are required for species containing catecholate and semiquinone, the measured Ru(III)/Ru(II) potential referring to a species containing bound quinone. The value for this couple when bound to catecholate (or semiquinone) cannot be observed experimentally since the catecholate dianion (or semiquinone) oxidizes before the ruthenium(II). Numerical values for these potentials can be estimated by using the Ru \rightarrow (bpy) π^* MLCT transitions as probes, in the various dioxolene complexes, in the following manner.

There are examples in the literature⁵⁵⁻⁵⁷ where the CT energy, E_{op} (in eV), of a RuL species is linearly dependent upon the Ru(III)/Ru(II) potential, $E(\text{III}/\text{II})$. Correlations involving redox potential differences, such as in (3), are also possible, as are

Table IV. Calculated Transition Energies (cm^{-1}) Involving the Dioxolene Ligand^a

transition	DTB	unsubst	TCl
$\text{Ru}^{\text{II}}(\text{bpy})_2(\text{cat})$			
$3b_1(\text{cat}) \rightarrow (\text{bpy})\pi^*(1)$	10 000	11 200	13 800
$3b_1(\text{cat}) \rightarrow \text{Ru}(\text{II})d\sigma^*$	18 850	19 500	21 200
$[\text{Ru}^{\text{II}}(\text{bpy})_2(\text{sq})]^+$			
$\text{Ru}(\text{II}) \rightarrow 3b_1(\text{sq})$	12 400	11 150	11 150 ^b
$3b_1(\text{sq}) \rightarrow \text{Ru}(\text{II})d\sigma^*$	19 000	20 150	20 000 ^b
$[\text{Ru}^{\text{II}}(\text{bpy})_2(\text{q})]^{2+}$			
$\text{Ru}(\text{II}) \rightarrow 3b_1(\text{q})$	12 400		10 400

^aTransition energies are calculated from eq 3 and data in Tables I and III. The $d\sigma^*\text{Ru}(\text{II})$ level is assumed to lie 3.0 eV above the Ru(II)(t_{2g}) manifold. The predictions are underestimated by $(\chi_i + \chi_o - y)$, all of which depend upon the complex concerned (see text). ^bBased upon a very broad band for Ru \rightarrow bpy; see Table III.

correlations with $E(\text{bpy}/\text{bpy}^-)$;⁵⁸ these are discussed elsewhere.⁵¹ We have recently⁵¹ demonstrated the validity of eq 4 for variously

$$E_{\text{op}} = 0.65E[\text{Ru}(\text{III})/\text{Ru}(\text{II})] + 2.00 \quad [86 \text{ pts}] \quad (4)$$

$$R = 0.93$$

charged $[\text{Ru}(\text{bpy})_2\text{LL}']^{n+}$ ($n = 0-2$) species, where R is the regression coefficient. From eq 4, optical CT energies may be predicted from the electrochemical potential with a standard deviation of 0.1 eV. This is a good fit given that several variables including reorganization energies are expected to vary. Thus, assuming good behavior, the Ru(III)/Ru(II) redox potentials for the dioxolene series may be derived directly from the observed Ru \rightarrow (bpy) π^* MLCT energy (Table III). The potentials for the quinone complexes are, as expected, rather higher than the measured irreversible potentials. The potentials increase significantly as the dioxolene ligand is oxidized and also increase, in each series, as the dioxolene ligand becomes a better acceptor.

From the potentials in Table III and eq 3, the Ru \rightarrow (dioxolene) π^* and related LLCT and LMCT transition energies may be estimated from the observed electrochemical potentials (Table IV). These results can be compared with the observed spectra, as assigned in Table II. Differences between observed and calculated spectra are due to the term $(\chi_i + \chi_o - y)$ and possibly to d-orbital splitting. The calculated Ru(III)/Ru(II) potentials refer to the average d orbital energy in the cat and q species where the band maximum is used. In the sq species, the $d(a_{2g}, b_{1g})$ energy is calculated.

Studies of the spectra of these species in solvents of varying polarity reveal little solvent dependence in any of the transitions.⁵³ Thus χ_o is expected to be small (ca 1400 cm^{-1} , 0.17 eV) and not to vary much between transitions.⁵³

Any electron-transfer transition involving the dioxolene ligand will change its oxidation state. The equilibrium geometric configurations of the catechol, semiquinone, and quinone are markedly different. For example, the C-O distances in typical complexed catechol, semiquinone, and quinone species lie near 135, 128, and 123 pm, respectively.³¹ Consequently, the Franck-Condon (CT) excited states involving the dioxolene ligands will be highly vibrationally excited. Thus these transitions may contain significant contributions from χ_i , and could be broadened because of the vibrational distortion involved.

Comparison of the data in Tables II and IV shows good agreement between observed and calculated Ru \rightarrow sq; i.e., the $(\chi_i + \chi_o - y)$ term is very small. The narrow bandwidth of these transitions requires little vibrational distortion of the excited state. Given the ESR and X-ray data reported above, we conclude that the ground state should be described as $a\psi(\text{Ru}^{\text{II}}(\text{sq})) + b\psi(\text{Ru}^{\text{III}}(\text{cat}))$. Since the excited state would also be described as a mixture of these two configurations, the reorganization energy (χ_i) would be small.

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This conclusion is also a natural consequence of the extensive mixing of the 2B_1 ground state with the low-lying 2B_1 MLCT state ($Ru(db_1) \rightarrow sq(3b_1)$, vide supra) whose equilibrium configuration is $Ru^{III}(cat)(3b_1)^2$.

In contrast, the calculated $Ru \rightarrow q$ transition energies are significantly less than those observed, the difference being larger in the TClQ complex. The observed energies are also higher than the $Ru \rightarrow sq$ energy. The bands are also very broad, with half-bandwidths of 1990 and 1420 cm^{-1} for the TClQ and DTBQ complexes, respectively, indicating that the excited state is highly distorted;⁴⁰ i.e., the reorganization energy is large and is consistent with the resonance Raman data cited above. The unexpected result that the MLCT transition to the quinone lies at a higher energy than that to the semiquinone, when the former is the better acceptor, is thus related to the much greater inner reorganization energy contribution to the former transition. Thus the extent of mixing of ground and excited states is much less in the quinone complexes than in the semiquinones.

The quinone acceptor orbital is mainly $C=O \pi^*$ in nature.⁶ The electron-withdrawing nature of the Cl substituents in TClQ will increase the $C=O$ bond order relative to DTBQ and thus increase the reorganizational energy. This may explain the increase in transition energy and bandwidth from DTBQ to TClQ.

The $3b_1(cat) \rightarrow (bpy)\pi^*(1)$ transition in the cat derivatives is also broad and has an observed energy greater than the calculated energy, indicative of a significant contribution from reorganization energy. The catecholate derivatives must therefore also have a relatively pure ground-state configuration, as expected in the absence of any low-lying CT states to mix into the ground state.

Conclusions. Assuming that these complexes contain ruthenium(II), there is essential agreement between the observed electronic spectra both as a function of oxidation state and dioxolene ligand substituent and the predictions based on the electrochemical potentials and the GF analysis.⁶ Combined analysis involving both electrochemistry and optical spectroscopy provides a more complete understanding of the nature of the ground and excited states in these molecules. This is the most detailed assignment of dioxolene complexes that has yet been attempted. Low-temperature (liquid He) data should provide further data concerning the electronic structure of this interesting series of complexes, and such an investigation, in concert with ESR studies, is in hand.

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Registry No. $Ru(bpy)_2(DTBCat)$, 99687-84-0; $Ru(bpy)_2(Cat)$, 99687-85-1; $Ru(bpy)_2(TClCat)$, 99687-86-2; $Ru(py)_4(DTBCat)$, 99687-87-3; $Ru(py)_4(TClCat)$, 99687-88-4; $[Ru(bpy)_2(DTBCat)]^+$, 99687-89-5; $[Ru(bpy)_2(Cat)]^+$, 99687-90-8; $[Ru(bpy)_2(TClCat)]^+$, 99687-91-9; $[Ru(py)_4(DTBCat)]^+$, 99748-27-3; $[Ru(bpy)_2(DTBQ)]^{2+}$, 99705-94-9; $[Ru(bpy)_2(Q)]^{2+}$, 99687-92-0; $[Ru(bpy)_2(TClQ)]^{2+}$, 99687-93-1; $[Ru(py)_4(DTBQ)]^{2+}$, 99687-94-2; $[Ru(py)_4(TClQ)]^{2+}$, 99687-95-3; $[Ru(py)_4(TClSq)]^+$, 99687-96-4; $[Ru(bpy)_2(DTBCat)]^{2-}$, 99687-97-5; $[Ru(bpy)_2(Cat)]^{2-}$, 99687-98-6; $[Ru(bpy)_2(TClCat)]^{4-}$, 99687-99-7; *cis*- $Ru(bpy)_2Cl_2$, 19542-80-4; $Ru(py)_4Cl_2$, 16997-43-6.

Supplementary Material Available: Table V, FTIR data (2 pages). Ordering information is given on any current masthead page.

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Copper Complexes of a Flexible Binucleating Ligand. Syntheses and Spectroscopic, Thermodynamic, and Kinetic Studies

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The synthesis of the macrocyclic "earmuff" ligand 1,4-bis((1-oxa-4,10-dithia-7-azacyclododec-7-yl)methyl)benzene, L, and its mononucleating analogue L' is reported. L and L' react with copper(I) to form the dinuclear and mononuclear complexes $[Cu_2L]X_2$, $[Cu_2L']X_2$, and $[CuL']X$ ($X = BF_4, ClO_4, PF_6, OTf$). Binding of the donor groups has been investigated by NMR spectroscopy in a donor solvent (acetonitrile, dimethyl sulfoxide). The accessibility of the copper(II) centers to reaction is demonstrated by the formation of a stable bis(triphenylphosphine) adduct $[Cu_2L(PPh_3)_2]X_2$ as well as the reversible addition of carbon monoxide in propylene carbonate to $[Cu_2L]X_2$. The synthesis of the binuclear copper(II) complexes $[Cu_2L]X_4$ and $[Cu_2(\mu-OH)L]X_3$ and of the mononuclear species $[CuL']X_2$ as well as their characterization by spectroscopic methods is also reported. Finally the complexation of Cu(II) by L and L' has been investigated by potentiometric and spectrophotometric means. Our results show the very high stability in water of $[Cu_2(\mu-OH)L]^{3+}$, which can be rapidly protonated under the appropriate conditions to form $[Cu_2L]^{4+}$, thereby demonstrating the conformational flexibility of L.

Introduction

Binuclear copper complexes in which the two copper sites are in close proximity are of considerable interest. Much of this interest stems from the proposed existence of such bimetallic sites in several copper enzymes, particularly those concerned with oxygen transport, storage, and reactivity, e.g. hemocyanin and tyrosinase. The detailed mechanism of action of such sites of this type on model systems may help cast light on the nature of the interactions involved between the binuclear site, oxygen, and substrate. In the construction of such a model, an evident paradox

presents itself. The less that is known of the structure and action of the enzyme, the more useful the model but the more difficult its construction. However, as the details of the natural structure become better defined, the model is easier to construct yet, in part, loses progressively its *raison d'être*.

When this work was started several years ago, little was known about the ligand environment about the two copper centers in hemocyanin. On the basis of UV/visible spectroscopy, imidazole¹ and sulfhydryl² groups were suggested as possible ligands. In the

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