Synthesis and Characterization of the Diruthenium(III) Complexes $Ru_2(F_4Oap)_2(F_5ap)_2$ and $Ru_2(F_4Oap)(F_4NCNap)(F_5ap)_2$ Where F_4Oap Is the 2-(3,4,5,6-Tetrafluoro-2-oxoanilino)pyridinate Anion, F_4NCNap Is the 2-(3,4,5,6-Tetrafluoro-2-cyanamidoanilino)pyridinate Anion, and F_5ap Is the 2-(2,3,4,5,6-Pentafluoroanilino)pyridinate Anion

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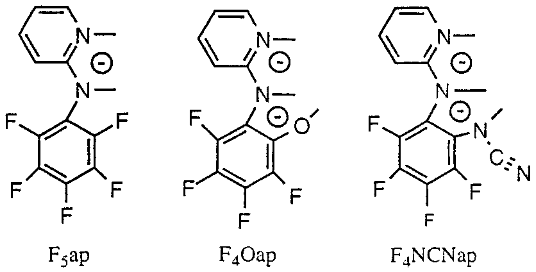
Introduction

The (4,0), (3,1), and (2,2) trans geometric isomers of $Ru_2(F_5ap)_4Cl$, **1**, defined according to the number of equivalent donor atoms on each ruthenium atom (anilino or pyridyl nitrogens), have previously been isolated from the reaction of $Ru_2(CH_3COO)_4Cl$ with 2,3,4,5,6-pentafluoro-2-anilinopyridine (HF_5ap) and characterized as to their spectral, chemical, and electrochemical properties.[1] The three isomers, all of which contain an Ru_2^{5+} core, have similar electrochemical behaviors, and all can be converted to their respective Ru_2^{4+} and Ru_2^{6+} oxidation states at potentials that vary according to the nature of the isomer.[1] However, the three isomers show different chemical reactivities,[2,3] which can be attributed to a combination of the structural and electronic features of the compounds.

It was earlier reported that the (3,1) isomer of **1** reacts with NaCN in THF to give three products which were isolated and structurally characterized as $Ru_2(F_5ap)_3[\mu\text{-}o\text{-}(NC)F_4ap](\mu\text{-}CN)$ and $Ru_2(F_5ap)_4(\mu\text{-}CN)_2$, the latter of which exists in two geometric forms.[3] The (3,1) isomer of **1** can also be converted to $Ru_2(F_4Oap)(F_5ap)_3Cl$, **2**, in THF which has been freshly distilled and left overnight prior to use. (see Chart 1 for a schematic representation of the ligands F_5ap, F_4Oap, and F_4NCNap).[2] The formation of **2** is believed to occur via a radical mechanism with the origin of the inserted oxygen atom being peroxide generated from dioxygen and the utilized THF solvent.[2,4]

Compound **2** was the first reported example of an Ru_2^{6+} derivative having a tridentate ligand bound to the two metal centers.[2] This particular geometry confers on the compound an interesting electrochemical behavior in that it undergoes not only metal-centered electrode reactions involving the Ru_2^{6+} core but also ligand-centered processes involving the electroactive quinone-type structure of the F_4Oap ligand.

Chart 1



Our laboratory has since pursued the synthesis of other diruthenium compounds having structures similar to that of **2**. To further explore the reactivity of the (3,1) isomer of **1**, the compound was reacted with disodium cyanamide (Na_2NCN) to determine whether other small molecules or atoms could be inserted into the original structure, thus replacing one or more fluorine atoms at the ortho positions of the anionic F_5ap ligand. The possibility of forming not only one but two quinone-type structures around the Ru_2^{6+} core was of interest, since compounds of this type might undergo several ligand-based redox processes without undergoing a cleavage of the Ru−Ru bond. This is indeed the case, as described in the present paper, which reports the syntheses, molecular structures, and electrochemical and spectroelectrochemical characterizations of $Ru_2(F_4Oap)_2(F_5ap)_2$, **3**, and $Ru_2(F_4Oap)(F_4NCNap)(F_5ap)_2$, **4**.

Experimental Section

Chemicals and Reagents. Dichloromethane was obtained as HPLC grade from Fisher Scientific Co. and distilled over phosphorus pentoxide. Spectroscopic grade tetrahydrofuran (THF), purchased from Aldrich Chemical Co., was purified by distillation under Ar from sodium/benzophenone just prior to use. Analytical grade *n*-hexane (Mallinckrodt Chemical Co.) was used without further purification. Tetra-*n*-butylammonium perchlorate (TBAP), obtained from Fluka Chemical Co., was twice recrystallized from absolute ethanol and dried in an oven at 40 °C. Disodium cyanamide (Na_2NCN) was purchased from Aldrich Chemical Co. and was used as received.

Physical Measurements. Mass spectra were obtained on a high-resolution hybrid tandem VG Analytical model 70-SEQ (EEQQ geometry) mass spectrometer. A standard fast atom bombardment (FAB) source was used with *m*-nitrobenzyl alcohol (NBA) as the liquid matrix. Elemental Analyses were carried out by Galbraith Laboratories, Inc., Knoxville, TN.

Cyclic voltammograms were recorded on an IBM model EC 225 voltammetric analyzer using a conventional three-electrode electrochemical cell. The working electrode was a platinum button with a surface area of 0.19 mm^2, and the reference electrode was a homemade saturated calomel electrode (SCE) which was separated from the bulk solution with a fritted-glass bridge containing the solvent/supporting electrolyte mixture. A platinum wire was used as the counter electrode. Controlled-potential bulk electrolyses were carried out with a BAS model SP-2 potentiostat using an "H"-type cell. Two cylindrically shaped platinum gauge electrodes, separated by a fine-fritted disk, were used as working and counter electrodes, respectively. The reference electrode was a homemade SCE.

Thin-layer spectroelectrochemical measurements were carried out with an IBM model EC 225 voltammetric analyzer and a model 6500 Tracor Northern rapid-scan spectrometer coupled to an IBM PC-XT computer. The thin-layer cell utilized an optically transparent platinum gauze working electrode and had a design similar to that reported

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10.1021/ic991505x CCC: \$20.00

Table 1. Crystal Data and Data Collection and Processing Parameters for $Ru_2(F_4Oap)_2(F_5ap)_2$ (**3**) and $Ru_2(F_4Oap)(F_4NCNap)(F_5ap)_2$ (**4**)

	3	**4**
space group	$P\bar{1}$ (triclinic)	$P\bar{1}$ (triclinic)
a, Å	11.208(4)	11.235(7)
b, Å	15.945(4)	15.863(7)
c, Å	16.173(3)	16.278(6)
α, deg	63.72(1)	64.54(3)
β, deg	81.59(2)	82.80(4)
γ, deg	83.07(2)	84.20(4)
V, Å^3	2559	2595
empirical formula	$C_{44}H_{16}N_8O_2F_{18}Ru_2\cdot{}^1/_2CHCl_3\cdot{}^1/_2C_6H_{14}$	$C_{45}H_{16}N_{10}OF_{18}Ru_2\cdot 1/_2C_6H_{14}$
fw	1335.61	1299.95
Z	2	2
ρ, g/cm^3	1.73	1.66
μ, cm^{-1}	7.67	6.78
λ(Mo Kα), Å	0.710 73	0.710 73
collection range, deg	$4 \le 2\theta \le 48$	$4 \le 2\theta \le 47$
temp, °C	−50	−50
R^a ($I > 3\sigma(I)$)	0.038	0.037
$R_w{}^b$ ($I > 3\sigma(I)$)	0.042	0.041

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

in the literature.[5] ESR spectra were recorded with a Varian E-4 spectrometer.

Synthesis. Compounds **3** and **4** were synthesized by a reaction between the (3,1) isomer of **1** and disodium cyanamide. A mixture of 200 mg (0.15 mmol) of the (3,1) isomer of **1** and 20 mg (0.25 mmol) of Na_2NCN in 100 mL of deaerated THF was stirred at 45 °C for 30 min and cooled to room temperature prior to being stirred overnight. The solution, maintained under an Ar atmosphere for the entire period, was initially yellow-brown but became red overnight. It was then opened to the air and gradually turned blue. This color change may be associated with a redox process initiated by reaction with oxygen. The solvent was evaporated under vacuum and the reaction mixture separated on a silica gel column using CH_2Cl_2/hexane (9:1 v/v) as eluent. Two blue bands, which were in an approximate 1:1 ratio, were collected and corresponded to **3** and **4**, respectively. A third green band in a smaller amount than the two blue bands was also collected and corresponded to $Ru_2(F_5ap)_3[\mu\text{-}o\text{-}(NC)F_4ap](\mu\text{-}CN)$, which was described in an earlier publication.[3] The exact mechanism by which **1** is converted to **3** and **4** in the presence of Na_2NCN is unknown at the present time. The crude products were then twice purified on a silica gel column using the same mixture of solvents as used for the eluent. The yield of each blue compound varied between 30 and 35%. **3**: Mass spectral data for **3** (*m/e*, fragment): 1234, $[Ru_2(F_4Oap)_2(F_5ap)_2]^+$. Anal. Calcd for **3**, $C_{44}H_{16}N_8F_{18}O_2Ru_2$: C, 42.78; H, 1.30; N, 9.07; F, 27.71. Found: C, 42.61; H, 1.37; N, 8.79; F, 25.18. **4**: Mass spectral data for **4** (*m/e*, fragment): 1258, $[Ru_2(F_4Oap)(F_4NCNap)(F_5ap)_2]^+$. Anal. Calcd for **4**, $C_{45}H_{16}N_{10}F_{18}ORu_2$: C, 42.92; H, 1.27; N, 11.12; F, 27.18. Found: C, 42.84; H, 1.36; N, 10.65; F, 25.00.

X-ray Crystallography. Very dark blue-green parallelepipeds having approximate dimensions 0.44 × 0.20 × 0.18 mm^3 for **3** and 0.55 × 0.55 × 0.10 mm^3 for **4** were grown by diffusing *n*-hexane into the $CHCl_3$ solutions of **3** and **4**, respectively. The crystals were mounted in random orientations on a Nicolet R3m/V automatic diffractometer.[6] Data pertinent to the X-ray analyses are given in Table 1.

Hydrogen atoms were included in idealized positions, constrained to riding motion, and given a single isotropic temperature factor. During the refinements of both **3** and **4**, diffuse areas of residual electron density were observed. These were interpreted for **3** as a half-molecule each of *n*-hexane and chloroform and for **4** as a half-molecule of *n*-hexane. Satisfactory refinements of both crystal structures were attained when the latter were incorporated. The structures were solved by using the SHELTX direct method program, and all calculations were performed with the Nicolet SHELXTL PLUS (1987) series of crystallographic programs.

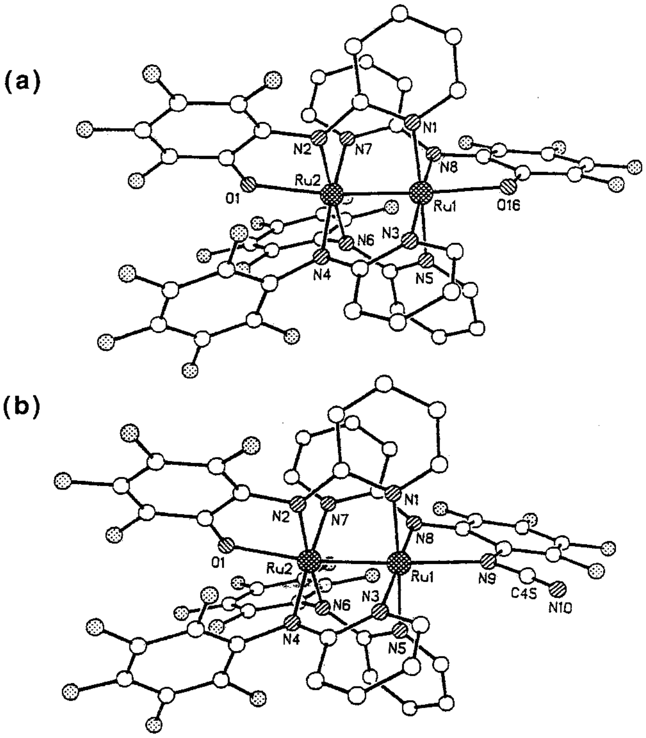

Figure 1. Molecular structures of (a) $Ru_2(F_4Oap)_2(F_5ap)_2$ (**3**) and (b) $Ru_2(F_4Oap)(F_4NCNap)(F_5ap)_2$ (**4**).

Table 2. Selected Bond Lengths (Å)^a for $Ru_2(F_4Oap)_2(F_5ap)_2$ (**3**) and $Ru_2(F_4Oap)(F_4NCNap)(F_5ap)_2$ (**4**)

	Compound **3**		
Ru(1)−Ru(2)	2.308(1)	Ru(1)−O(16)	2.139(5)
Ru(1)−N(1)	2.073(4)	Ru(1)−N(3)	2.059(6)
Ru(1)−N(5)	2.102(4)	Ru(1)−N(8)	2.034(6)
Ru(2)−O(1)	2.131(5)	Ru(2)−N(2)	2.061(4)
Ru(2)−N(4)	2.105(6)	Ru(2)−N(6)	2.040(4)
Ru(2)−N(7)	2.080(6)	O(1)−C(7)	1.305(7)
O(16)−C(40)	1.303(9)		
	Compound **4**		
Ru(1)−Ru(2)	2.332(1)	Ru(1)−N(9)	2.198(5)
Ru(1)−N(3)	2.085(5)	Ru(2)−N(2)	2.063(4)
Ru(1)−N(8)	2.037(5)	Ru(2)−N(6)	2.019(4)
Ru(2)−O(1)	2.111(4)	O(1)−C(7)	1.299(6)
Ru(2)−N(4)	2.090(5)	Ru(1)−N(1)	2.061(4)
Ru(2)−N(7)	2.068(5)	N(10)−C(45)	1.153(7)
Ru(1)−N(5)	2.116(4)	N(9)−C(45)	1.332(7)

^{a} Individual values.

Results and Discussion

Molecular Structures. **3** and **4** were characterized by X-ray crystallography, and their structures are shown in Figure 1. Selected bond lengths for both compounds are given in Table 2. As was seen for compound **2**, the two newly investigated compounds show a (3,1) arrangement of the F_5ap equatorial ligands; i.e., Ru(1) is bound to three nitrogen atoms belonging to a pyridyl group and a single nitrogen atom belonging to a pentafluoroanilino group. At least one ortho fluorine of the F_5ap ligand is also replaced by one oxygen in each structure. Both Ru atoms of each diruthenium complex have octahedral coordination, with four nitrogens forming the equatorial plane.

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(6) Single-crystal X-ray crystallographic studies were performed at the University of Houston X-ray Crystallographic Center. Since the materials were subject to rapid decomposition, the samples were placed in a stream of dry nitrogen gas at −50 °C. Additional pertinent data are provided in the Supporting Information.

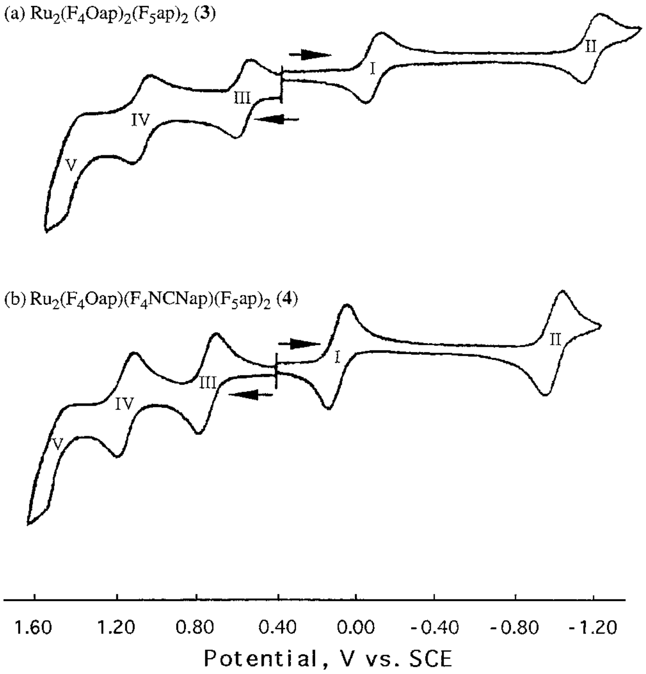

Figure 2. Cyclic voltammograms of (a) $Ru_2(F_4Oap)_2(F_5ap)_2$ (**3**) and (b) $Ru_2(F_4Oap)(F_4NCNap)(F_5ap)_2$ (**4**) in CH_2Cl_2/0.1 M TBAP. Scan rate = 0.1 V/s.

The 2.308(1) Å Ru−Ru bond length of **3** is shorter than the Ru−Ru bond length of **2** (2.336(1) Å)[2] or **4** (2.332(1) Å) but is within the range of distances (2.238−2.556 Å) observed for metal−metal bonds of diruthenium complexes which are derived from the parent tetracarboxylates.[1,7−10] The shortening of the Ru−Ru bond length may be explained in terms of the number of oxygen atoms coordinated to the diruthenium core of the three compounds as discussed in the following paragraph.

The oxygen−carbon bond lengths of 1.299(6)−1.305(7) Å in the three diruthenium complexes are similar to values reported for chelated π complexes of (*o*-benzoquinone)ruthenium which possess carbon−oxygen double bonds.[11] Consequently, the oxygen p_{π^*} orbitals should interact more effectively with the π^* orbitals of the diruthenium core and lead to a shift of electron density from the Ru_2 π^* to the p_{π^*} orbitals of oxygen, thus decreasing the Ru−Ru bond length. The $Ru-O_{ax}$ bond distances decrease from 2.168(4) Å in **2** to an average of 2.135(5) Å in **3** and to 2.111(4) Å in **4** (see Table 2) and are all longer than averages of 1.98−2.09 Å[9,10,12−15] reported for the $Ru-O_{eq}$ bond lengths of diruthenium complexes with tetracarboxylate-type structures.

Electrochemistry. The electrochemistry of **3** and **4** was examined in CH_2Cl_2 containing 0.1 M TBAP. Cyclic voltammograms of the two compounds are shown in Figure 2. Both compounds undergo well-defined one-electron redox processes which are labeled in the figure as processes I and II on reduction and processes III−V on oxidation.

The first reduction and two oxidations of the (3,1) isomer of $Ru_2(F_5ap)_4(C{\equiv}CC_6H_5)_2$ involve metal-centered electrode reactions,[1] and as shown by UV−visible spectroelectrochemistry (next section), this is also the case for processes I and III of the two newly investigated diruthenium complexes. The two reductions of **3** and **4** are reversible on the cyclic voltammetry time scale (see Figure 2), while **2** has a reversible first reduction and an irreversible second reduction.[2]

The two reductions of compounds **2**−**4** are shifted anodically in potential with respect to the same two reductions of the (3,1) isomer of $Ru_2(F_5ap)_4(C{\equiv}CC_6H_5)_2$ ($E_{1/2} = -0.14$ and -1.20 V),[1] thus suggesting that the axial O atom or NCN group which has been inserted between Ru and the anilinopyridine ligand has a lower donor ability than the two $C{\equiv}CC_6H_5$ groups. Compounds **3** and **4** are easier to oxidize than the (3,1) isomer of $Ru_2(F_5ap)_4(C{\equiv}CC_6H_5)_2$ ($E_{1/2} = 1.00$ V),[1] and **3** is the easiest to oxidize owing to the presence of the second inserted oxygen atom.

Bulk controlled-potential electrolyses of **3** and **4** were carried out at potentials slightly more negative than that of process I, after which ESR measurements were performed to determine whether the singly reduced species contained one or more than one unpaired electron. The cyclic voltammograms obtained before and after electrolysis were identical in each case, implying that the two singly reduced complexes were both stable on the bulk electrolysis time scale. No ESR signal was observed after the first reduction of either compound, suggesting that each diruthenium complex with a paramagnetic Ru_2^{5+} core contains more than one unpaired electron. Indeed, diruthenium complexes with an Ru_2^{5+} core that contain one unpaired electron generally exhibit a sharp and well-resolved rhombic signal, while those with three unpaired electrons show either no signal at all or an ill-resolved ESR spectrum.[1,2,8,16−19]

Attempts were also made to characterize by ESR spectroscopy the singly oxidized products of **3** and **4**. Bulk controlled-potential electrolysis of each compound was carried out at a potential slightly more positive that that of process III, but in both cases, the cyclic voltammograms obtained after electrolysis were significantly different from those recorded prior to electrolysis, indicating that the electrogenerated oxidation products were unstable on the longer bulk electrolysis time scale needed to carry out the ESR experiments.

Compound **2** has previously been shown to exhibit two one-electron oxidations, one of which was assigned as ligand-centered and proposed to involve the electroactive quinone-type structure of the F_4Oap dianionic ligand.[2] The electrochemical data for the newly investigated compounds (Figure 2) are also consistent with this type of assignment. Compounds **2**−**4** all possess quinone-type structures, and each complex undergoes more than a single oxidation. As discussed above, process III for each compound involves the conversion of an Ru_2^{6+} to an Ru_2^{7+} core, suggesting that one of the two quinone-type structures is oxidized during process IV. This result is further supported by the fact that the first oxidations of **3** and **4** differ in $E_{1/2}$ by 140 mV while the second oxidations of the same two compounds differ in $E_{1/2}$ by only 30 mV. The oxidation of

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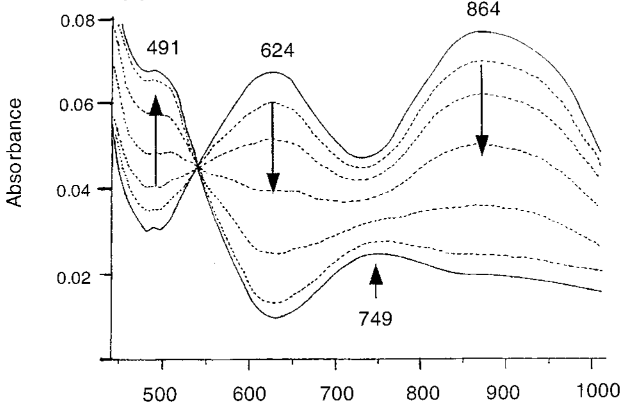
Table 3. UV−Visible Spectral Data of $Ru_2(F_4Oap)_2(F_5ap)_2$ (**3**), $Ru_2(F_4NCNap)(F_4Oap)(F_5ap)_2$ (**4**), and $Ru_2(F_4Oap)(F_5ap)_3Cl$ (**2**) in Three Different Oxidation States

compound	Ru oxidation state	λ, nm ($10^{-3}\,\epsilon$, $cm^{-1}\,M^{-1}$)			
$Ru_2(F_4Oap)_2(F_5ap)_2$ (**3**)	III, III		624 (0.48)		864 (0.49)
$Ru_2(F_4Oap)(F_4NCNap)(F_5ap)_2$ (**4**)	III, III		634 (0.96)		896 (0.97)
$Ru_2(F_4Oap)(F_5ap)_3Cl$ (**2**)	III, III	486 (0.51)	623 (0.55)	706 (0.63)	880 (0.71)
$[Ru_2(F_4Oap)_2(F_5ap)_2]^-$	II, III	491 (0.46)	749 (0.28)		
$[Ru_2(F_4Oap)(F_4NCNap)(F_5ap)_2]^-$	II, III	513 (0.78)	781 (0.40)		
$Ru_2(F_4Oap)(F_5ap)_3$	II, III	492 (0.55)	730 (0.21)	952 (0.24)	
$[Ru_2(F_4Oap)_2(F_5ap)_2]^+$	III, IV	523 (0.41)	666 (0.58)	837 (0.65)	
$[Ru_2(F_4Oap)(F_4NCNap)(F_5ap)_2]^+$	III, IV	514 (0.68)	654 (0.90)	873 (1.11)	
$[Ru_2(F_4Oap)(F_5ap)_3Cl]^+$	III, IV	507 (0.76)	686 (0.60)	950	

(a) Reduction



(b) Oxidation

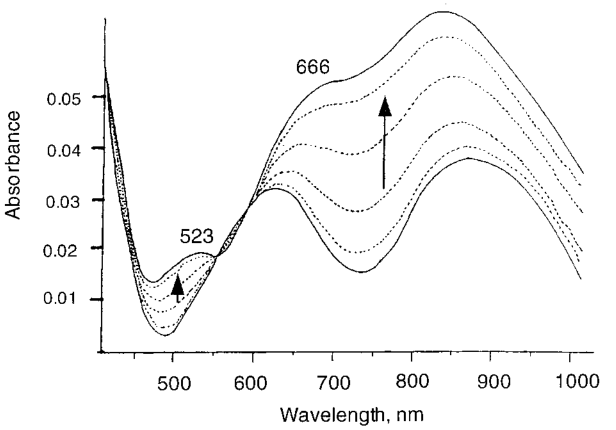


Figure 3. Thin-layer UV−visible spectral changes upon (a) reduction and (b) oxidation of $Ru_2(F_4Oap)_2(F_5ap)_2$ (**3**) in CH_2Cl_2/0.2 M TBAP.

hydroquinone occurs at 0.70 V in water,[20] and the fact that process IV of **3** and **4** is shifted positively by 500−650 mV with respect to this potential (see Figure 2) can be accounted for by the strong electron-withdrawing ability of the pentafluoroanilino ring. Process V could involve the oxidation of the second quinone-type structure in **3** and **4**, or it might involve conversion of the diruthenium core from an Ru_2^{7+} to an Ru_2^{8+} oxidation state.

UV−Visible Spectroelectrochemistry. The first reduction and first oxidation of **3** and **4** in CH_2Cl_2/0.2 M TBAP are reversible on the thin-layer electrochemical time scale, and the singly reduced and singly oxidized products could therefore be characterized by UV−visible spectroelectrochemistry. Examples of the resulting spectra for **3** are shown in Figure 3a (reduction) and Figure 3b (oxidation), and a summary of the spectal data obtained before and after each redox process is given in Table 3, which also includes, for comparison purposes, data for **2**.[2]

Compounds **3** and **4** exhibit two absorption bands of similar intensities between 450 and 900 nm, consistent with other diruthenium(III) complexes containing four unsymmetrical carboxylate-type bridging ligands.[17,21] In contrast, **2** exhibits four absorption bands of different molar absorptivities. Compound **2** has been shown to contain two unpaired electrons, and its electronic configuration[2] was suggested to be either $(\sigma)^2(\pi)^4(\delta)^2(\pi^*\delta^*)^2$ or $(\sigma)^2(\pi)^4(\delta)^2(\pi^*)^2$. The magnetic data[22] for the two newly synthesized compounds suggest that they also contain two unpaired electrons, and the fact that all three compounds differ in their UV−visible spectra may be attributed to differences in the types of axial ligands. Hence, one can propose an electronic structure of $(\sigma)^2(\pi)^4(\delta)^2(\pi^*)^2$ for both **3** and **4**. The addition of one electron to either compound **3** or compound **4** will yield a complex with three unpaired electrons and an electronic configuration of $(\sigma)^2(\pi)^4(\delta)^2(\pi^*)^2\delta^*$. As already discussed, this result is consistent with the fact that no ESR signal is observed for the reduction products of either **3** or **4**.

Compounds **3** and **4** in their neutral forms have similar UV−visible spectra, and similar spectral changes are also seen after the addition of one electron to give an $Ru^{II}Ru^{III}$ product. The singly reduced species is characterized by a major absorption band at 491−513 nm and another band of reduced intensity is seen at 749−781 nm (see Table 3). Both sets of spectra show an isosbestic point at 525−550 nm. The product of the one-electron reduction of **2** has three absorption bands,[2] two of which are located at wavelengths similar to those for the diruthenium(II,III) complexes generated from **3** and **4**. Each reduced form of the complexes in Table 3 has a UV−visible spectrum similar to those for diruthenium(II,III) species with a tetracarboxylate-type structure,[4,7,9] thus further indicating that **2**−**4** are all converted to their Ru_2^{5+} forms upon the first one-electron reduction.

The one-electron oxidation product of **3** exhibits three absorption bands at 523, 666, and 837 nm (see Figure 3b), and a similar spectral pattern is also observed for the one-electron oxidation of compounds **2** and **4** (see Table 3). The only known UV−visible spectrum for a mixed diruthenium(III,IV) species bridged by four carboxylate-type ligands is that of $[Ru_2(F_5ap)_4(C{\equiv}CC_6H_5)_2]^+$, which was obtained by the one-electron oxidation of $Ru_2(F_5ap)_4(C{\equiv}CC_6H_5)_2$.[16] This compound is characterized by absorption bands at 516, 705, and 913 nm and has UV−visible spectral features similar to those of singly oxidized **3** and **4** (see Table 3).

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(20) Harris, D. C. *Quantitative Chemical Analysis*, 4th ed.; W. H. Freeman and Co.: New York, 1995; p AP 33.

(21) Huang, S. Ph.D. Dissertation, University of Houston, 1994.

(22) Magnetic moments of **3** and **4**, calculated using the Evans method are 2.60 and 2.93 μ_B, respectively.[23] The data imply that each compound possesses two unpaired electrons.

(23) Evans, D. F. *J. Chem. Soc.* **1959**, 2003.

Summary. The present study reports the syntheses and spectroscopic and electrochemical characterizations of two never before reported diruthenium(III) complexes possessing a quinone-type structure. These two compounds are isolated as products from the reaction between the (3,1) isomer of $Ru_2(F_5ap)_4Cl$ and Na_2NCN. Both diruthenium core- and ligand-centered electrode reactions are observed upon oxidation or reduction, and this result is attributed to the electroactive quinone-type structure of the bridging ligands. Visible−NIR absorption bands of the two compounds are used as diagnostic criteria for assigning the dimetal oxidation states.

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Supporting Information Available: Space-filling and unit cell packing diagrams, listings of detailed crystallographic data, atomic positional and thermal parameters, and bond lengths and angles, and a table of $E_{1/2}$ values. This material is available free of charge via the Internet at http://pubs.acs.org.

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