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Factors Affecting the Electrochemical and Spectroelectrochemical Properties of Diruthenium(III,II) Complexes Containing Four Identical Unsymmetrical Bridging Ligands

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Factors affecting the electrochemical and spectroelectrochemical properties of diruthenium(III,II) complexes containing four unsymmetrical bridging ligands are reported for seven related compounds which were isolated in one or two of the four possible isomeric forms. The investigated compounds are represented as $Ru_2(2\text{-}CH_3ap)_4Cl$, $Ru_2(2,5\text{-}F_2ap)_4Cl$, $Ru_2(2,6\text{-}F_2ap)_4Cl$, and $Ru_2(2,4,6\text{-}F_3ap)_4Cl$ where $2\text{-}CH_3ap$, $2,5\text{-}F_2ap$, $2,6\text{-}F_2ap$, and $2,4,6\text{-}F_3ap$ are, respectively, the 2-(2-methylanilino)pyridinate anion, the 2-(2,5-difluoroanilino)pyridinate anion, the 2-(2,6-difluoroanilino)pyridinate anion, and the 2-(2,4,6-trifluoroanilino)pyridinate anion. $Ru_2(2\text{-}CH_3ap)_4Cl$ and $Ru_2(2,5\text{-}F_2ap)_4Cl$ exist only in a (4,0) conformation while $Ru_2(2,4,6\text{-}F_3ap)_4Cl$ is present in both (3,1) and (4,0) isomeric forms. $Ru_2(2,6\text{-}F_2ap)_4Cl$ also exists in two isomeric forms, but only the (3,1) isomer was generated in sufficient quantities to be isolated and structurally characterized. This series of seven closely related metal–metal bonded complexes thus provides the first possibility to systematically examine how differences in position and number of the electron-donating or electron-withdrawing groups on the anionic bridging ligands might be related to the electronic properties and structural features of the compound as well as the type and number of geometric isomers which are formed. Each diruthenium derivative undergoes three one-electron transfers in CH_2Cl_2 containing 0.1 M tetra-*n*-butylammonium perchlorate (TBAP). The first reduction and first oxidation products were characterized by thin-layer UV–vis spectroelectrochemistry, and the spectroscopic data, along with $E_{1/2}$ values, were then related via linear free energy relationships to the type of isomer and/or position of the electron-donating or electron-withdrawing substituents on the anionic ap bridge. The electrogenerated Ru_2^{6+} and Ru_2^{4+} forms of the compounds were assigned on the basis of electrochemical and UV–vis spectroscopic data as having the electronic configuration $\sigma^2\pi^4\delta^2\pi^{*2}$ and $\sigma^2\pi^4\delta^2\pi^{*3}\delta^*$, respectively, and seemed to be independent of the isomer type ((3,1) or (4,0)). The spectral and electrochemical properties of the compounds both vary substantially as a function of the isomer type, but this is not reflected in the structural features of the compounds which are within the range of what is seen for other Ru_2^{5+} species described in the literature. The Ru–Ru bond lengths of the four structurally characterized (4,0) isomers of the ap complexes range from 2.275 to 2.296 Å while those of the three structurally characterized (3,1) isomers of ap derivatives fall in the range 2.284–2.286 Å and show no significant difference among the three compounds. The Ru–Cl bond lengths of the (3,1) isomers do not vary significantly with the bridging ligand and range from 2.458 to 2.471 Å whereas those of the (4,0) isomers range from 2.437 to 2.487 Å and show larger variations among the compounds. The Ru–Ru–Cl bond angle is virtually independent of the bridging ligand in the case of the (4,0) isomers but decreases with the electron-withdrawing effect of the substituent in the case of the (3,1) isomers.

Introduction

Dinuclear complexes with a metal–metal bond and a paddlewheel structure have been studied for several decades,[1–3] and some of their properties have made them attractive as inorganic liquid crystals,[4,5] one-dimensional polymers,[6–9] antitumor agents,[10] and/or possible candidates for molecules

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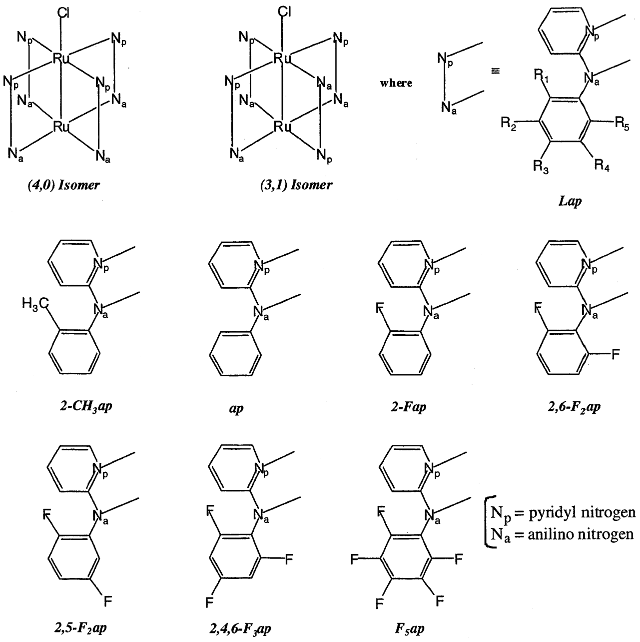
producing nonlinear optical effects.[11] The type of dinuclear compounds suitable for a particular application or a particular reactivity may be dictated in part by structural features and in part by the redox and spectroscopic properties of the metal−metal bonded compounds. These properties of the "paddlewheel complex" are in turn modulated by the electronic properties of the bridging ligands and/or the arrangement of the four equatorial ligands around the dinuclear core because both factors will, in most cases, affect the axial coordination of any incoming nucleophile. For instance, it has been shown that the electrophilicity of the metallo-carbenoid intermediate in carbene-transfer reactions catalyzed by dirhodium tetracarboxylate and their analogues can be substantially tuned by the electronic properties of the bridging ligands.[12]

Electrochemical and spectroscopic linear free energy relationships have been reported for compounds containing Mo_2, Cr_2, Ni_2, Ru_2, or Rh_2 dimetal units.[13,14] The dimetallic complexes investigated by Ren and co-workers[13] possessed four *identical* and *symmetrical* diarylformamidinate anions $((p\text{-}XC_6H_4)NCHN(p\text{-}XC_6H_4))$ as the bridging ligand, and these compounds showed dramatic changes in the redox properties with only small perturbation of the valence structure of the dinuclear cores. A similar result should also be observed for dinuclear complexes with a paddlewheel structure containing four *identical unsymmetrical* bridging ligands, although in this case, the magnitude of the electronic effect may also be a function of the isomeric form of the compounds which in theory can exist in up to four geometric forms labeled (4,0), (3,1), (2,2) trans, or (2,2) cis.[15−20]

Previously synthesized $Ru_2(L)_4Cl$ complexes, where L = ap, 2-Fap, and F_5ap, have be shown to possess different isomeric distributions.[15,16,21] This fact suggests that both electronic and steric effects of the bridging ligand may be responsible for the preferred conformation of these compounds. This point prompted us to synthesize a series of additional substituted ap derivatives. A schematic representation of the compounds investigated in this paper is described in Chart 1 where the bridging ligands differ in the number, position, and type of substituents on the phenyl group of the anilinopyridinate anion.

Chart 1



The Ru_2(III,II) derivatives obtained from the bridging ligands shown in Chart 1 are examined in the present study with respect to their structural, electrochemical, and spectroscopic properties and combined with earlier data in the literature on $Ru_2(ap)_4Cl$, $Ru_2(2\text{-}Fap)_4Cl$, and $Ru_2(F_5ap)_4Cl$ to better understand linear free energy relationships between the substituents on the bridging ligand and overall electrochemical and/or spectroscopic properties of the compounds. Three of the investigated complexes can be isolated in more than one isomeric form, and electrochemical and spectroscopic features of these compounds are also discussed in terms of the arrangement of the four bridging ligands, that is, (3,1) and (4,0).

Experimental Section

Chemicals and Reagents. Ultrahigh-purity argon (99.999% min) and high-purity nitrogen were purchased from Matheson-Trigas Co. Argon was passed through anhydrous calcium sulfate and potassium hydroxide pellets to remove traces of oxygen and water prior to use. Nitrogen was used as received. The solvents for synthesis were, in most cases, freshly distilled under nitrogen prior to use. Reagent grade dichloromethane (CH_2Cl_2) was distilled over phosphorus pentoxide (P_2O_5) and stored over activated 3 Å molecular sieves. Reagent grade tetrahydrofuran (THF) was first distilled from calcium hydride (CaH_2) and dried over sodium metal in benzophenone. The solvent was allowed to reflux and was distilled only after the blue color of the benzophenone ketyl radical anion

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remained, indicating a minimum content of water. Spectroscopic grade hexane (95% min. Aldrich), absolute ethanol (McCormick, Inc.), hexanes, and acetone (GR grade, EM Science) were used without purification. CD_2Cl_2 (99.8% atom in D) for NMR measurement was purchased from Aldrich Co. and was used as received. Tetra-*n*-butylammonium perchlorate (TBAP) was purchased from Fluka Chemical Co., twice recrystallized from ethyl alcohol and stored in a vacuum oven at 40 °C for at least one week prior to use. 2-Bromopyridine (C_5H_4NBr), 2-anilinopyridine ($C_6H_5NH_2$), 2,5-difluoroaniline ($C_6H_3F_2NH_2$), 2,6-difluoroaniline ($C_6H_3F_2NH_2$), 2,4,6-trifluoroaniline ($C_6H_2F_3NH_2$), *o*-toluidine ($CH_3C_6H_4NH_2$), lithium chloride (LiCl), and ruthenium chloride hydrate ($RuCl_3 \cdot 3H_2O$) were all purchased from Aldrich Co. and used as received. Silica gel (Merck 230−400 mesh 60 Å) used for column chromatography was also purchased from Aldrich Co.

Physical Measurements. Cyclic voltammetry was carried out with an EG&G model 173 potentiostat. A three-electrode system was used and consisted of a glassy carbon or platinum disk working electrode, a platinum wire counter electrode, and a homemade saturated calomel electrode (SCE) as the reference electrode. The SCE was separated from the bulk of the solution by a fritted-glass bridge of low porosity that contained the solvent/supporting electrolyte mixture. All potentials are referenced to the SCE, and all measurements were carried out at room temperature.

Spectroelectrochemical experiments were performed using an EG&G model 173 potentiostat and a thin-layer cell whose design has been described in the literature.[22] Time-resolved UV−vis spectra were recorded with a Hewlett-Packard model 8453 diode array spectrophotometer.

Magnetic moments were calculated using the Evans method,[23,24] and measurements were made in CD_2Cl_2 solution on a GE 300 spectrometer. TMS was used as indicator.

Elemental analysis was carried out by Atlantic microlab, Inc., Norcross Georgia. Mass spectra were recorded on a Finnigan TSQ 700 instrument at the University of Texas, Austin. Standard fast atom bombardment was used with *m*-nitrobenzyl alcohol (NBA) as the liquid matrix.

Synthesis of Bridging Ligands. All the ligands in this work were prepared using a method similar to the one described by Hisano et al.[25] A mixture of 2-bromopyridine and substituted aniline in a 1:2 molar ratio was heated at high temperature (>140 °C) under N_2 for at least 20 h. After cooling, the reaction mixture was treated with 10% NaOH aqueous solution (w/v) and steam-distilled. The mixture was then extracted with CH_2Cl_2 and the resulting organic layer dried over $MgSO_4$. After evaporation of the solvent, the residue was recrystallized to give a pure white crystalline material. In the case of H(2,5-F_2ap), the compound was also sublimed under vacuum at 100 °C to achieve better purity.

H(2-CH_3ap). Recrystallization solvent: hexanes. Yield: 65%. Mass spectral data [*m*/*e*,(fragment)]: 184 $[HCH_3ap]^+$; 169 $[Hap]^+$. Elemental analysis ($C_{12}H_{12}N_2$) Calcd: C, 78.22; H, 6.57; N, 15.21. Found: C, 78.29; H, 6.60; N, 15.24. ^1H NMR (in CD_2Cl_2): 8.23 (d, 1H), 7.49 (d, 1H), 7.44 (d, 1H), 7.25 (t, 1H), 7.21 (t, 1H), 7.07 (t, 1H), 6.70 (t, 1H), 6.65 (d, 1H), 5.96 (bs, 1H), 2.30 (s, 3H) ppm (key: s, singlet; bs, broad singlet; d, doublet; t, triplet; m, multiplet).

H(2,5-F_2ap). Recrystallization solvent: hexanes. Yield: 82%. Mass spectral data [*m*/*e*,(fragment)]: 206 $[HF_2ap]^+$, 187 $[HFap]^+$. ^1H NMR (in CD_2Cl_2): 8.33 (d, 1H), 8.29 (m, 1H), 7.58 (t, 1H), 7.06 (m, 1H), 6.86 (bs, 1H), 6.85 (t, 1H), 6.80 (d, 1H), 6.60 (m, 1H) ppm (key: d, doublet; t, triplet; m, multiplet; bs, broad singlet).

H(2,6-F_2ap). Recrystallization solvent: *n*-hexane/CH_2Cl_2 (v/v: 95/5). Yield: 91%. Mass spectral data [*m*/*e*,(fragment)]: 207 $[HF_2ap]^+$, 187 $[HFap]^+$, 167 $[Hap]^+$. ^1H NMR (in CD_2Cl_2): 8.15 (d, 1H), 7.55 (t, 1H), 7.02 (m, 2H), 7.18 (m, 1H), 6.79 (m, 1H), 6.54 (d, 1H), 6.28 (b, 1H) ppm (key: d, doublet; t, triplet; m, multiplet; b, broad).

H(2,4,6-F_3ap). Recrystallization solvent: *n*-hexane/CH_2Cl_2. Yield: 52%. ^1H NMR (in CD_2Cl_2): 8.14 (d, 1H), 7.52 (t, 1H), 6.80 (m, 3H), 6.51 (d, 1H), 6.15 (b, 1H) ppm (key: d, doublet; t, triplet; m, multiplet; b, broad).

Synthesis of Diruthenium Complexes. (4,0) $Ru_2(ap)_4Cl$. The compound was synthesized as described in the literature.[21]

(4,0) $Ru_2(2\text{-}CH_3ap)_4Cl$ (1). A mixture of diruthenium acetate, $Ru_2(O_2CCH_3)_4Cl$,[1,26] (0.35 g, 0.74 mmol) and H(2-CH_3ap) (2.18 g, 11.80 mmol) in a 1:16 ratio were stirred under argon overnight at 140 °C. The green solid formed upon cooling the solution was dissolved in CH_2Cl_2 and was filtered to remove any unreacted $Ru_2(O_2CCH_3)_4Cl$. The solvent was removed by rotary evaporation, and the residue was sublimed under vacuum at 120 °C to remove excess H(2-CH_3ap). The product was chromatographed on a silica gel column, using a mixture of acetone/hexane 3:7 as eluent. Mass spectral data [*m*/*e*, (fragment)]: 970 $[Ru_2(CH_3ap)_4Cl]^+$; 934 $[Ru_2(CH_3ap)_4]^+$; 788 $[Ru_2(CH_3ap)_3Cl]^+$; 752 $[Ru_2(CH_3ap)_3]^+$, 605 $[Ru_2(CH_3ap)_2]^+$. UV−vis spectrum in CH_2Cl_2 [λ_{max} nm ($10^{-3}\epsilon$, mol^{-1} L cm^{-1})]: 424 (4.3), 461 (4.7), 764 (7.3).

(4,0) $Ru_2(2,4,6\text{-}F_3ap)_4Cl$ (2) and (3,1) $Ru_2(2,4,6\text{-}F_3ap)_4Cl$ (3). A mixture of $Ru_2(O_2CCH_3)_4Cl$[1,26] (0.72 g, 1.51 mmol) and H(2,4,6-F_3ap) (3.26 g, 14.68 mmol) was placed in a 100 mL round-bottom flask equipped with a condenser, and the mixture was stirred under Ar for 4 h at 190 °C. During heating, the ligand was in a molten state, and to avoid subliming off the excess ligand, a sheet of aluminum foil was used to cover the condenser and the reaction flask right above the heating source. A black-greenish solid was formed upon cooling the flask to room temperature. The excess H(2,4,6-F_3ap) ligand was sublimed off under vacuum at 140 °C, and the unreacted $Ru_2(O_2CCH_3)_4Cl$ was separated by column chromatography on silica gel using 100% CH_2Cl_2 as the eluent. The remaining residue was again purified by column chromatography on silica gel, eluting with acetone/hexane (3:7) (v/v). There were two bands in the column, one yellow-green and the other green. These were collected as the (4,0) and (3,1) isomers of $Ru_2(2,4,6\text{-}F_3ap)_4Cl$, respectively. The yields were 43% for the (3,1) isomer and 10% for the (4,0) isomer. Elemental analysis ($C_{44}H_{24}N_8F_{12}Ru_2Cl$) of the (3,1) and (4,0) isomers follows. Calcd: C, 46.75; H, 2.14; N, 9.92. Found: C, 46.66; H, 2.14; N, 9.51. UV−vis spectrum in CH_2Cl_2 [λ_{max}, nm ($10^{-3}\epsilon$, mol^{-1} L cm^{-1})] (4,0) Isomer: 412 (2.2), 476 (2.6), 615 (0.7), 895 (2.7). (3,1) Isomer: 418 (4.5), 476 (4.7), 777 (4.5).

(3,1) $Ru_2(2,6\text{-}F_2ap)_4Cl$ (4). This compound was synthesized by a method similar to that used for the synthesis of $Ru_2(2,4,6\text{-}F_3ap)_4Cl$. There were two bands in the column (yellow-green and green) as in the case of the F_3ap derivative. The yellow-green band gave too little product to be isolated, and only the green band was collected in a pure form. This band yielded the (3,1) isomer of $Ru_2(2,6\text{-}F_2ap)_4Cl$ which was isolated and structurally characterized. Mass spectral data [*m*/*e*, (fragment)]: 1059 $[Ru_2(F_2ap)_4Cl]^+$; 1023 $[Ru_2(F_2ap)_4]^+$; 854 $[Ru_2(F_2ap)_3Cl]^+$. UV−vis spectrum in CH_2Cl_2 [λ_{max}, nm ($10^{-3}\epsilon$, mol^{-1} L cm^{-1})]: 422 (4.2), 475 (4.0), 788 (3.9). The yellow-green band has UV−vis characteristics of the (4,0)

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Table 1. Crystal Data and Data Collection and Processing Parameters for the Characterized Compounds

	(4,0) isomer			(3,1) isomer	
	$Ru_2(2\text{-}CH_3ap)_4Cl$ (**1**)	$Ru_2(2,5\text{-}F_2ap)_4Cl$ (**5**)	$Ru_2(2,4,6\text{-}F_3ap)_4Cl$ (**2**)	$Ru_2(2,6\text{-}F_2ap)_4Cl$ (**4**)	$Ru_2(2,4,6\text{-}F_3ap)_4Cl$ (**3**)
space group	*C*2/*c* monoclinic	$P\bar{1}$ triclinic	$P2_1/n$ monoclinic	$P2_1/n$ monoclinic	*C*2/*c* monoclinic
cell const *a* (Å)	19.2054(11)	10.9425 (5)	11.8672 (5)	12.8353 (6)	22.9789 (12)
b (Å)	15.3926(9)	12.7472 (6)	34.2648 (15)	23.5414 (11)	9.7169 (5)
c (Å)	17.6305(10)	17.3791 (6)	11.9028 (5)	15.3047 (7)	38.3705 (21)
α (deg)		99.471 (1)			
β (deg)	108.855(1)	91.858 (1)	90.825 (1)	93.743 (1)	103.666 (1)
γ (deg)		93.460 (1)			
V (Å^3)	4932.3(5)	2384.53 (19)	4839.5 (4)	4614.6 (1)	8325.0 (8)
mol formula	$C_{48}H_{44}N_8ClRu_2\cdot 2CH_2Cl_2$	$C_{44}H_{28}N_8F_8ClRu_2\cdot 2CH_2Cl_2$	$C_{44}H_{24}N_8ClF_{12}Ru_2\cdot 2C_3H_6O$	$C_{44}H_{28}N_8ClF_8Ru_2\cdot 1.33CH_2Cl_2\cdot 1.33C_6H_{14}$	$C_{44}H_{24}N_8ClF_{12}Ru_2$
fw (g/mol)	1140.35	1228.19	1246.46	1200.31	1130.30
Z	4	2	4	4	8
ρ_{calcd} (g/cm^3)	1.536	1.711	1.711	1.728	1.804
μ (cm^{-1})	0.927	0.989	0.777	0.945	0.889
λ (Mo Kα) (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
temp (K)	223	223	223	223	223
$R(F_o)^a$	0.0302	0.0362	0.0229	0.0283	0.0261
$R_w(F_o)^b$	0.0813	0.0995	0.0129	0.0120	0.0142

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

isomer along with overlapping bands of the isolated (3,1) isomer of the compounds (see Figure S1 in Supporting Information). All attempts to obtain the (4,0) isomer in pure form have so far been unsuccessful.[27]

(4,0) $Ru_2(2,5\text{-}F_2ap)_4Cl$ (5). A mixture of $Ru_2(O_2CCH_3)_4Cl$ and $H(2,5\text{-}F_2ap)$ in a 1:20 ratio was heated at 120 °C for 8 h under N_2. A green solid precipitate was obtained upon cooling the flask. It was then dissolved in CH_2Cl_2 and filtered to remove the insoluble $Ru_2(O_2CCH_3)_4Cl$. The compound was sublimed at 120 °C under vacuum to remove excess ligand and then subjected to column chromatography on a silica gel column with a mixture of acetone/hexane 3:7 (v/v) as eluent. Mass spectral data [*m*/*e*, (fragment)]: 1058 $[Ru_2(F_2ap)_4Cl]^+$; 1023 $[Ru_2(F_2ap)_4]^+$; 1004 $[Ru_2(F_2ap)_3(Fap)]^+$; 854 $[Ru_2(F_2ap)_3Cl]^+$; 817 $[Ru_2(F_2ap)_3]^+$. UV−vis spectrum in CH_2Cl_2 [λ_{max}, nm ($10^{-3}\epsilon$, mol^{-1} L cm^{-1})]: 422 (4.8), 466 (5.3), 774 (5.8).

Magnetic Moment. All the investigated compounds possess three unpaired electrons, with μ_{eff} ranging from 3.84 μ_B to 3.95 μ_B at ca. 15 °C. These data are consistent with the $\sigma^2\pi^4\delta^2\pi^{*2}\delta^*$ electronic ground state proposed for this type of compound.

X-ray Crystallography of Compounds 1−5. Single-crystal X-ray crystallographic studies were performed at the University of Houston X-ray Crystallographic Center. Each sample was placed in a steam of dry nitrogen gas at −50 °C in a random position. The radiation used was Mo Kα monochromatized by a highly ordered graphite crystal. Final cell constants as well as other information pertinent to data collection and structure refinement are listed in Table 1.

All measurements were made with a Siemens SMART platform diffractometer equipped with a 1K CCD area detector. A hemisphere of data 1271 frames at 5 cm detector distance was collected using a narrow-frame method with scan widths of 0.30° in *ω* and an exposure time of 20 s/frame. The first 50 frames were measured again at the end of data collection to monitor instrument and crystal stability, and the maximum correction on *I* was <1%. The data were integrated using the Siemens SAINT program, with the intensities corrected for Lorentz factor, polarization, air absorption, and absorption due to variation in the path length through the detector faceplate. A Ψ-scan absorption correction was applied based on the entire data set. Redundant reflections were averaged. Final cell constants were refined using 4966 reflections for **1**, 7802 reflections for **2**, 6316 reflections for **3**, 6703 reflections for **4,** and 6522 reflections for **5** having $I > 10\sigma(I)$. The Laue symmetries were determined to be 2/*m* for compounds **1**−**4** and −1 for **5**, and from the systematic absences noted, the space groups were shown to be $P2_1/n$ for **2** and **4**, either *Cc* or *C*2/*c* for **1** and **3**, and *P*1 or $P\bar{1}$ for **5**.

Results and Discussion

Five diruthenium complexes with ap-type bridging ligands were synthesized according to eq 1 and characterized with respect to their electrochemical, spectroscopic, and structural properties.

$$Ru_2(O_2CCH_3)_4Cl + 4HL \rightarrow Ru_2(L)_4Cl + 4CH_3CO_2H \quad (1)$$

As described in the Experimental Section, the synthesis of $Ru_2(L)_4Cl$ was carried out in the melt with the reaction being allowed to proceed for times ranging between 4 and 15 h. The excess ligand was removed by sublimation, and the product purified by column chromatography was obtained in yields ranging from 50% to 70%. The yield and isomeric distribution seem not to depend on the time the reaction mixture was heated because similar results were obtained whether the mixture was left to react for 4 h or overnight.

As shown by their X-ray crystal structure (see following section of this paper), complexes with the bridging ligands $2\text{-}CH_3ap$ and $2,5\text{-}F_2ap$ exist only in a (4,0) isomeric form while both the (3,1) and (4,0) isomers are obtained for $Ru_2(2,4,6\text{-}F_3ap)_4Cl$.

Molecular Structures. Selected average bond lengths and average bond angles for compounds **1**−**5** are summarized in Table 2 while their ORTEP diagrams are illustrated in Figure 1 for three structurally characterized (4,0) isomers and Figure 2 for two structurally characterized (3,1) isomers

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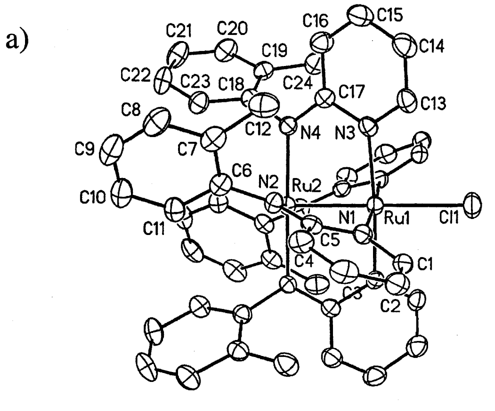
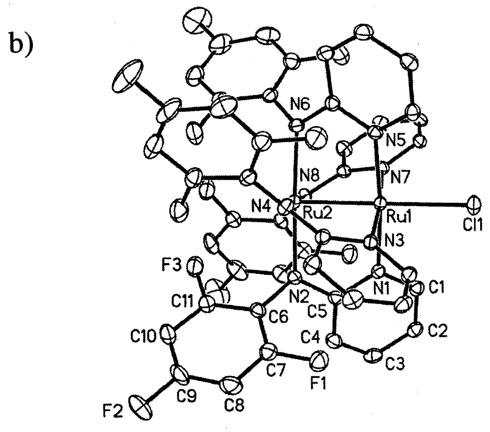
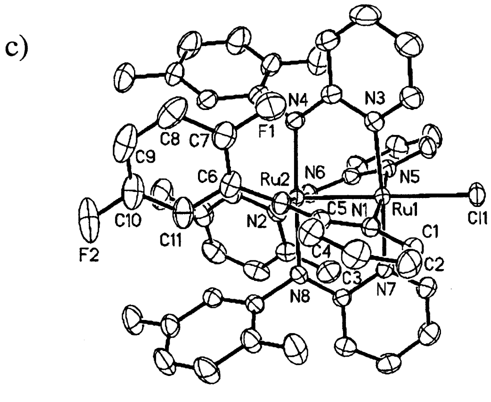
(27) The UV−vis spectrum of the yellow-green band displays three bands at 425, 480, and 863 nm. On the basis of the similarity of the UV−vis data obtained from the (4,0) and (3,1) isomer of $Ru_2(2,4,6\text{-}F_3ap)_4Cl$, both of which were structurally characterized, the yellow-green band was assigned as being a (4,0) isomer.



(4,0) $Ru_2(2\text{-}CH_3ap)_4Cl$ (**1**)



(4,0) $Ru_2(2,4,6\text{-}F_3ap)_4Cl$ (**2**)



(4,0) $Ru_2(2,5\text{-}F_2ap)_4Cl$ (**5**)

Figure 1. Molecular structures of the (4,0) isomers of (a) $Ru_2(2\text{-}CH_3\text{-}ap)_4Cl$ (**1**), (b) $Ru_2(2,4,6\text{-}F_3ap)_4Cl$ (**2**), and (c) $Ru_2(2,5\text{-}F_2ap)_4Cl$ (**5**). The H atoms have been omitted for clarity.

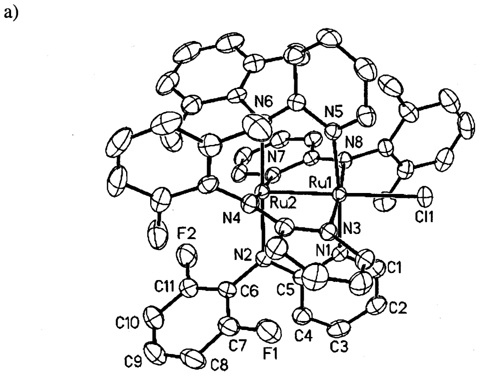
of $Ru_2(L)_4Cl$. All intramolecular bond lengths and angles as well as other structural data of the five compounds are given in the Supporting Information.

The coordination of Ru1 and Ru2 in compounds **1**−**5** is essentially octahedral and square pyramidal, respectively, with four "substituted ap" bridging ligands forming the equatorial plane. For **1**, **2**, and **5**, Ru1 is coordinated to the chloride axial ligand and to four pyridyl nitrogen atoms while Ru2 is coordinated to four anilino nitrogen atoms. For **3** and **4**, Ru1 is coordinated to the axial chloride and to three pyridyl nitrogen atoms and one anilino nitrogen atom while Ru2 is coordinated to three anilino nitrogen atoms and one pyridyl nitrogen atom.

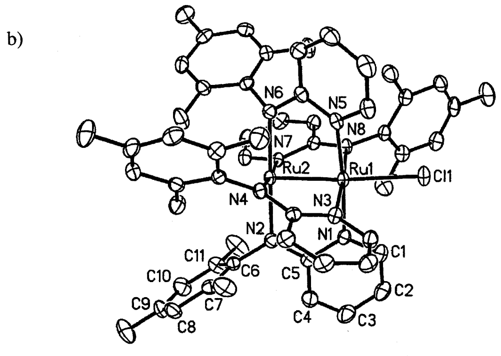
Table 2. Selected Average Bond Lengths (Å) and Bond Angles (deg) of the (4,0) and (3,1) Isomers of $Ru_2(L)_4Cl$, where L = 2-CH_3ap, ap,[21] 2,5-F_2ap, or 2,4,6-F_3ap for the (4,0) Isomer and L = 2-Fap,[16] 2,6-F_3ap, or 2,4,6-F_3ap for the (3,1) Isomer

	(4,0)				(3,1)		
	2-CH_3ap	ap	2,5-F_2ap	2,4,6-F_3ap	2-Fap	2,6-F_2ap	2,4,6-F_3ap
	Bond Lengths (Å)						
Ru−Ru	2.279	2.275	2.284	2.296	2.286	2.286	2.284
Ru−N_a[a]	2.053	2.026	2.044	2.047	2.047	2.048	2.045
Ru−N_p[b]	2.101	2.104	2.102	2.100	2.099	2.094	2.098
Ru−Cl	2.487	2.437	2.460	2.473	2.461	2.471	2.458
	Bond Angles (deg)						
Ru−Ru−Cl	180.0	180.0	179.7	179.9	179.6	178.9	176.0
Ru−Ru−N_a[a]	89.5	89.0	89.9	89.0	89.8	89.3	89.1
Ru−Ru−N_p[b]	87.8	87.9	88.2	87.4	88.5	88.3	89.0
N−Ru−Ru−N	21.6	22.7	18.6	24.0	18.2	19.7	17.0

[a] N_a: anilino nitrogen (see Chart 1). [b] N_p: pyridyl nitrogen (see Chart 1).



(3,1) $Ru_2(2,6\text{-}F_2ap)_4Cl$ (**4**)



(3,1) $Ru_2(2,4,6\text{-}F_3ap)_4Cl$ (**3**)

Figure 2. Molecular structures of the (3,1) isomers of (a) $Ru_2(2,6\text{-}F_2\text{-}ap)_4Cl$ (**4**) and (b) $Ru_2(2,4,6\text{-}F_3ap)_4Cl$ (**3**).

The Ru−Ru bond lengths of **1**−**5** range from 2.279 to 2.296 Å, and these values are within the expected range of Ru−Ru bond distances of other Ru_2(III,II) complexes with this structural type.[15,20,21,25] The Ru−Ru bond lengths of the (4,0) isomers range from 2.275 to 2.296 Å while those of the (3,1) isomers fall in the range 2.284−2.286 Å and show no significant difference between the three compounds. As shown in Table 2, the Ru−Ru bond distance slightly increases from 2.284 to 2.296 Å upon going from the (3,1) to the (4,0) isomer of $Ru_2(2,4,6\text{-}F_3ap)_4Cl$.

The Ru−Cl bond lengths of **1**−**5** range from 2.458 to 2.487 Å and are comparable with the Ru−Cl bond distances of Ru$_2$(ap)$_4$Cl (2.44 Å)[21] and Ru$_2$(dpf)$_4$Cl (2.41 Å)[28] but are smaller than the Ru−Cl bond distance of 2.577 Å found in Ru$_2$(O$_2$CCH$_3$)$_4$Cl.[29] The Ru−Cl bond lengths of the (3,1) isomers fall in the range 2.458−2.471 Å and do not vary significantly with the bridging ligand while those of the (4,0) isomers range from 2.437 to 2.487 Å and show more variations among the four compounds (see Table 2). For instance, the Ru−Cl bond distance of the ap complex is shorter than those of the other three (4,0) isomers.

The effect of the bridging ligand on the Ru−Ru−Cl bond angle is not the same for the (3,1) and (4,0) isomers. For instance, the three (4,0) isomers in Table 2 are characterized by a Ru−Ru−Cl bond angle of 179.7−180.0° independent of the electronic properties of the bridging ligand. In contrast, the Ru−Ru−Cl bond angles of the (3,1) isomers range from 179.6° to 176.0° and decrease with an increase in the electron-withdrawing effect of the substituent on the bridging ligand.

The averaged Ru−N$_a$ bond length (N$_a$ = anilino nitrogen) is smaller than the averaged Ru−N$_p$ bond length (N$_p$ = pyridyl nitrogen) in both (4,0) and (3,1) isomers. These structural features have also been observed in the case of Ru$_2$(2-Fap)$_4$Cl,[16] and the results are consistent with the fact that the negative charge of the Xap$^-$ anionic ligands resides primarily on the anilino nitrogen. In each (3,1) isomer, the Ru1−N$_a$ bond length is the longest among all the four Ru−N$_a$ bond distances, and the Ru2−N$_p$ bond length is the shortest among all the four Ru−N$_p$ bond lengths. This result may be the consequence of a steric hindrance between the anilino ring and the chloride axial ligand. Also, as shown in Table 2, the (4,0) isomers exhibit larger averaged N−Ru−Ru−N torsion angles than the (3,1) isomers, with the exception of Ru$_2$(2,5-F$_2$ap)$_4$Cl whose value falls in the range of N−Ru−Ru−N torsion angles found for the (3,1) isomers. This trend was also observed for the (3,1) and (4,0) isomers of Ru$_2$(F$_5$ap)(C$_2$C$_6$H$_5$)$_2$.[15]

Cotton and co-workers[21] have proposed that the (4,0) isomeric configuration adopted by Ru$_2$(ap)$_4$Cl was the result of a steric hindrance between the chloride and the anilino groups, because the four anilino nitrogen atoms in this type of compound are coordinated to the Ru without the chloride axial ligand. This argument could explain why Ru$_2$(2-CH$_3$-ap)$_4$Cl and Ru$_2$(2,5-F$_2$ap)$_4$Cl exist only in the (4,0) isomeric form but does not account for the existence of the (3,1) and (2,2) trans isomers of Ru$_2$(F$_5$ap)$_4$Cl nor does it explain why the (3,1) arrangement can be found in the isomeric distribution of Ru$_2$(2-Fap)$_4$Cl,[16] Ru$_2$(2,6-F$_2$ap)$_4$Cl, and Ru$_2$(2,4,6-F$_3$-ap)$_4$Cl.

The isomeric distibution and yields of each isomer of Ru$_2$(L)$_4$Cl (L is one of the seven bridging ligands shown in Chart 1) are given in Table 3. Four of the seven compounds in this table have been isolated exclusively in a (4,0) or (3,1) isomeric form but not both. One compound, Ru$_2$(2,6-F$_2$-ap)$_4$Cl, exists almost exclusively as the (3,1) isomer (see Experimental Section) while another, Ru$_2$(2,4,6-F$_3$ap)$_4$Cl, forms both (3,1) and (4,0) isomers with the (3,1) isomer being preferred. The last compound, Ru$_2$(F$_5$ap)$_4$Cl, was examined in a previous study[15] and is known to exist as a (2,2) trans isomer in addition to the (4,0) and (3,1) isomers.

Table 3. Isomeric Distribution of Ru$_2$(L)$_4$Cl Complexes, Where L = 2-CH$_3$ap, ap, 2-Fap, 2,6-F$_2$ap, 2,5-F$_2$ap or 2,4,6-F$_3$ap

cmpd	(4,0) isomer	(3,1) isomer	ref
Ru$_2$(2-CH$_3$ap)$_4$Cl (**1**)	73%	0%	tw[a]
Ru$_2$(ap)$_4$Cl	72%	0%	21
Ru$_2$(2-Fap)$_4$Cl	0%	53%	16
Ru$_2$(2,6-F$_2$ap)$_4$Cl (**4**)	trace[b]	40%[c]	tw
Ru$_2$(2,4,6-F$_3$ap)$_4$Cl (**2**), (**3**)	10%	43%	tw
Ru$_2$(2,5-F$_2$ap)$_4$Cl (**5**)	64%	0%	tw

[a] tw = this work. [b] The second isomer for this compound has not been fully characterized yet (see Experimental Section). [c] Yield given within a 5% margin error.

Table 4. Half-Wave Potentials (V vs SCE) of the (4,0) and (3,1) Isomers of Ru$_2$(L)$_4$Cl, Where L = 2-CH$_3$ap, ap, 2-Fap, 2,6-F$_2$ap, 2,5-F$_2$ap, 2,4,6-F$_3$ap, and F$_5$ap in CH$_2$Cl$_2$ Containing 0.1 M TBAP under N$_2$

ligand		oxidations		reduction
$\Sigma\sigma$	cmpd	Ru$_2^{7+}$/Ru$_2^{6+}$	Ru$_2^{6+}$/Ru$_2^{5+}$	Ru$_2^{5+}$/Ru$_2^{4+}$
		(4,0)		
−0.17	Ru$_2$(2-CH$_3$ap)$_4$Cl (**1**)	1.44	0.41	−0.89
0.00	Ru$_2$(ap)$_4$Cl	∼1.33	0.37	−0.86
+0.54	Ru$_2$(2,4,6-F$_3$ap)$_4$Cl (**2**)	1.59	0.69	−0.67
+0.58	Ru$_2$(2,5-F$_2$ap)$_4$Cl (**5**)		0.65	−0.63
+1.22	Ru$_2$(F$_5$ap)$_4$Cl	1.68	0.95	−0.35
		(3,1)		
+0.24	Ru$_2$(2-Fap)$_4$Cl	1.43	0.47	−0.77
+0.48	Ru$_2$(2,6-F$_2$ap)$_4$Cl (**4**)	1.51	0.56	−0.72
+0.54	Ru$_2$(2,4,6-F$_3$ap)$_4$Cl (**3**)	1.55	0.62	−0.65
+1.22	Ru$_2$(F$_5$ap)$_4$Cl	1.61	0.78	−0.35

Thus, the known Ru$_2^{5+}$ derivatives with substituted ap ligands can be divided into three categories. The first adopts only a (4,0) geometric conformation and includes Ru$_2$(L)$_4$-Cl derivatives where L = 2-CH$_3$ap, ap, and 2,5-F$_2$ap. The second category consists of diruthenium complexes that are isolated in only the (3,1) isomeric form with Ru$_2$(2-Fap)$_4$Cl being the only compound in this category. The third group involves derivatives that are isolated in more than one isomeric form, that is, (3,1) and (4,0) or (3,1), (4,0) and (2,2) trans, with examples of this group being given for L = 2,6-F$_2$ap, 2,4,6-F$_3$ap, and F$_5$ap.

The yields for the (3,1) and (4,0) isomers of compounds in the last category also vary with the type of bridging ligand. In some cases, the (4,0) isomer is the major product while in others it is the (3,1) isomer. The type and number of isomers might be governed by the size of the bridging ligand, but one must also consider the ligand basicity which differs substantially among the investigated compounds (see range of $\Sigma\sigma$ values in Table 4). Interestingly, as seen in Table 3, those compounds which possess two substituents at the ortho positions of the phenyl ring on the ap ligand (see Chart 1) such as Ru$_2$(2,6-F$_2$ap)$_4$Cl, Ru$_2$(2,4,6-F$_3$ap)$_4$Cl, and Ru$_2$(F$_5$-ap)$_4$Cl are the only ones existing in more than one isomeric form.

Electrochemistry. The redox behavior of compounds **1**−**5** was investigated by cyclic voltammetry in the noncoordinating solvent CH$_2$Cl$_2$ containing 0.1 M TBAP, and the data

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(28) Bear, J. L.; Han, B.; Huang, S.; Kadish, K. M. *Inorg. Chem.* **1996**, *35*, 3012.

(29) Martin, D. S.; Newman, R. A.; Vlasnik, L. M. *Inorg. Chem.* **1980**, *19*, 3404.

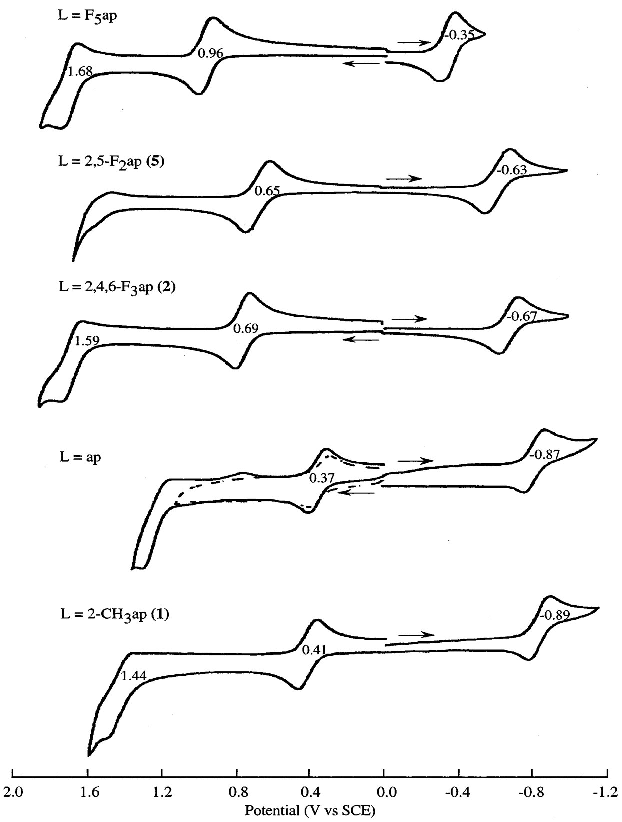

Figure 3. Cyclic voltammograms of the (4,0) isomers of $Ru_2(L)_4Cl$ in CH_2Cl_2 containing 0.1 M TBAP under N_2. Scan rate at 0.1 V/s.

are compared to those of $Ru_2(ap)_4Cl$, $Ru_2(2\text{-}Fap)_4Cl$,[16] and $Ru_2(F_5ap)_4Cl$.[15]

Cyclic voltammograms of compounds **1**, **2**, and **5** are shown in Figure 3 along with those of the other (4,0) isomers (L = ap and F_5ap) while cyclic voltammograms of compounds **3** and **4** are illustrated in Figure 4 along with those of other (3,1) isomers (L = 2-Fap and F_5ap). Half-wave potentials for the redox reactions of compounds **1**−**5** are listed in Table 4 along with half-wave potentials for the redox processes of $Ru_2(ap)_4Cl$, $Ru_2(F_5ap)_4Cl$, and $Ru_2(2\text{-}Fap)_4Cl$ for comparison purposes.

Eight of the nine electrochemically examined diruthenium complexes undergo three one-electron metal-centered processes, while $Ru_2(2,5\text{-}F_2ap)_4Cl$ shows only two well-defined metal-centered processes, one of which is an oxidation and the other is a reduction. A stepwise conversion between compounds with Ru_2^{7+}, Ru_2^{6+}, Ru_2^{5+}, or Ru_2^{4+} cores can therefore be electrochemically accomplished as shown by eqs 2−4 where L is an anionic bridging ligand.

$$(L)_4Ru_2^{5+} + e^- \rightleftarrows (L)_4Ru_2^{4+} \qquad (2)$$

$$(L)_4Ru_2^{5+} \rightleftarrows (L)_4Ru_2^{6+} + e^- \qquad (3)$$

$$(L)_4Ru_2^{6+} \rightleftarrows (L)_4Ru_2^{7+} + e^- \qquad (4)$$

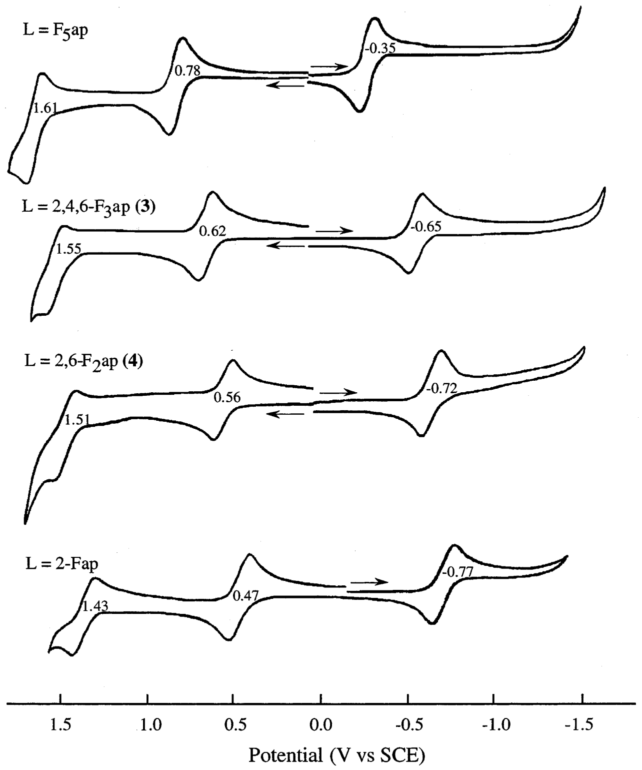

Figure 4. Cyclic voltammograms of the (3,1) isomers of $Ru_2(L)_4Cl$ in CH_2Cl_2 containing 0.1 M TBAP under N_2. Scan rate at 0.1 V/s.

We have shown previously that the $E_{1/2}$ for a given electrode reaction of $Ru_2(F_5ap)_4Cl$ was dependent upon the type of geometric isomer.[15] The $E_{1/2}$ for the first oxidation of this complex, that is, the Ru_2^{6+}/Ru_2^{5+} process, was shifted cathodically by 170 mV upon going from the (4,0) to the (3,1) isomer, but no shift at all was observed between the first reduction potentials of these two isomers. A similar trend is also seen in Table 4 for the case of the (4,0) and (3,1) isomers of $Ru_2(2,4,6\text{-}F_3ap)_4Cl$, although in this case there is less difference in $E_{1/2}$ between the oxidations of the two compounds. This is explained by the fact that the electronic perturbation upon going from the (4,0) to the (3,1) isomer is smaller in the case of $Ru_2(2,4,6\text{-}F_3ap)_4Cl$ than in the case of $Ru_2(F_5ap)_4Cl$; that is, the anilino group of the ap ligand has three fluorines in the case of $Ru_2(2,4,6\text{-}F_3ap)_4Cl$ and five in the case of $Ru_2(F_5ap)_4Cl$.

Plots of $E_{1/2}$ versus the sum of substituent constants $(\Sigma\sigma)$[30] for the three redox reactions of both (4,0) and (3,1) isomers of $Ru_2(L)_4Cl$ (L is $2\text{-}CH_3ap$, ap, 2-Fap, $2,5\text{-}F_2ap$, $2,6\text{-}F_2ap$, $2,4,6\text{-}F_3ap$, or F_5ap) are shown in Figure 5. The dependence of $E_{1/2}$ on the electronic effect of the substituents can be quantified by linear least-squares fit of the data to the Hammett relationship shown in eq 5:[31,32]

$$\Delta E_{1/2} = E_{1/2}(X) - E_{1/2}(H) = 4\Sigma\sigma\rho \qquad (5)$$

where ρ is the reactivity constant. Because there are four equivalent bridging ligands on each investigated diruthenium complex, $4\Sigma\sigma$ is used in eq 5. The reactivity constants (ρ) and the correlation coefficients (R) for the plots in Figure 5 are listed in Table 5. As shown in this table, ρ ranges from

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(30) Zuman, P. *Substituent Effects in Organic Polarography*; Plenum Press: New York, 1967.

(31) Zuman, P. *The Elucidation of Organic Electrode Process*; Academic Press: London, 1967.

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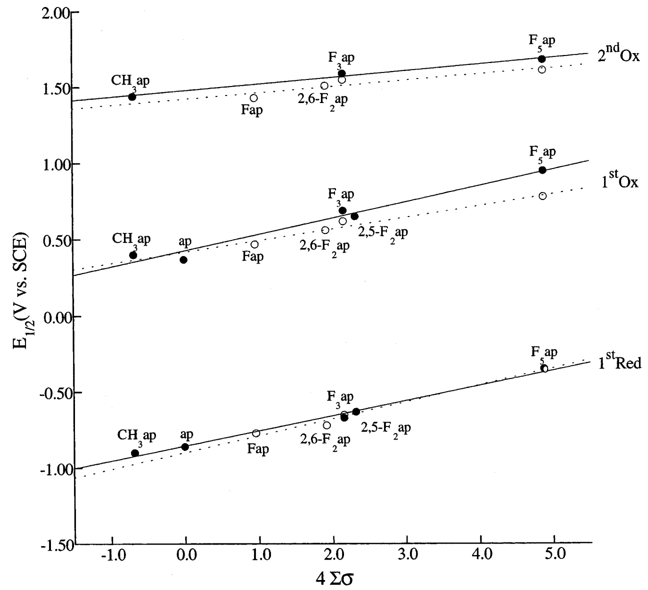

Figure 5. Linear free energy relationship for the redox reactions of the (4,0) isomers (●, —) and (3,1) isomers (O, - - -) of $Ru_2(L)_4Cl$, where L = 2-CH_3ap, ap, 2-Fap, 2,6-F_2ap, 2,5-F_2ap, 2,4,6-F_3ap, or F_5ap.

Table 5. ρ Values (in mV) for (4,0) and (3,1) Isomers of $Ru_2(L)_4Cl$, Where L = 2-CH_3ap, ap, 2-Fap, 2,6-F_2ap, 2,5-F_2ap, 2,4,6-F_3ap, and F_5ap in CH_2Cl_2, with *R* Values of Linear Least-Square Fit

	ρ (*R*)		
isomer	1st red.	1st ox.	2nd ox.
(4,0)	100 (0.995)	107 (0.984)	43 (0.991)
(3,1)	111 (0.992)	76 (0.981)	41 (0.916)

41 to 111 mV, but its exact value depends on both the nature of the redox reaction and the type of geometric isomer. The magnitude of ρ is larger for the first reduction and first oxidation than for the second oxidation and also depends on the isomer type. For example, the first reduction and the second oxidation are both insensitive to the isomer type because the ρ values of these reactions are similar for (3,1) and (4,0) isomers. This is not the case for the first oxidation where the (4,0) isomer exhibits a larger value of ρ than the (3,1) isomer. Table 5 also reveals that the first reduction and the first oxidation have similar values of ρ in the (4,0) series of compounds but not in the (3,1) series where ρ for the first reduction is larger than ρ for the first oxidation.

The electronic ground state $\sigma^2\pi^4\delta^2\pi^{*2}\delta^*$ of these compounds suggests that the oxidation involves a removal of an electron from the δ^* orbital and the reduction the addition of an electron in the π^* orbital. This assumption is also confirmed by the fact that the UV−vis spectra of most singly oxidized (3,1) and (4,0) isomers exhibit similar features (see next section of this paper), all of which are consistent with the removal of an electron from the δ^* orbital upon going from Ru_2^{5+} to Ru_2^{6+}. As discussed already, only the first oxidation of the compounds differs in the ρ values upon going from (3,1) to (4,0) isomers, thus suggesting that the δ^* orbital is more sensitive to the isomer type than the π^* orbital.

UV−Vis Absorption Spectra. The UV−vis absorption features of the investigated compounds are summarized in Table 6. This table also includes the spectral data for the singly reduced Ru_2^{4+} and singly oxidized Ru_2^{6+} forms of the complexes. Most of the compounds in a Ru_2^{5+} oxidation state exhibit three absorption bands labeled as bands I, II, and III in Table 6 and two of these five derivatives (**2** and the (4,0) isomer of $Ru_2(F_5ap)_4Cl$) possess an additional band labeled as band III in Table 6. Both the (3,1) and (4,0) isomers exhibit little effect of substituent on the λ_{max} of bands I, II, and III. The (3,1) isomers of $Ru_2(L)_4Cl$ also show little effect of the substituent on the λ_{max} of band IV, but this is not the case for the (4,0) isomers where λ_{max} of band IV ranges from 764 nm for L = 2-CH_3ap and ap to 910 nm for L = F_5ap.

Table 6. UV−Vis Spectra Data of the (4,0) and (3,1) Isomers of $Ru_2(L)_4Cl$, Where L Is 2-CH_3ap, ap, 2-Fap, 2,5-F_2ap, 2,4,6-F_3ap, 2,6-F_2ap, and F_5ap, in CH_2Cl_2 Containing 0.2 M TBAP

oxidation state	ligand	λ_{max}, nm ($\epsilon \times 10^{-3}$, M^{-1} cm^{-1}) band I	band II	band III	band IV
		(4,0) Isomer			
Ru_2^{6+}	CH_3ap (**1**)	443 (6.9)	530 (6.5)		990 (15.9)
	2,4,6- F_3ap (**2**)	432 (2.9)	522 (3.9)	842 (sh)	1033 (3.8)
	2,5-F_2ap (**5**)	413 (5.5)	504 (5.5)		975 (11.2)
	F_5ap		520 (6.4)	900 (sh)	>1050
Ru_2^{5+}	CH_3ap (**1**)	424 (4.3)	461 (4.7)		764 (7.3)
	ap	421 (5.8)	452 (5.7)		778 (7.0)
	2,4,6-F_3ap (**2**)	412 (2.2)	476 (2.6)	615 (0.7)	895 (2.7)
	2,5-F_2ap (**5**)	422 (4.8)	466 (5.3)		774 (5.8)
	F_5ap		482 (5.8)	598 (1.1)	910 (5.0)
Ru_2^{4+}	CH_3ap (**1**)		534 (3.6)		
	2,4,6-F_3ap (**2**)		507 (1.4)		
	2,5-F_2ap (**5**)		515 (4.1)		
	F_5ap		518 (3.2)		
		(3,1) Isomer			
Ru_2^{6+}	2-Fap	431 (4.1)	494 (3.9)		960 (5.2)
	2,4,6-F_3ap (**3**)	487 (5.7)	670 (4.4)		965 (9.5)
	F_5ap	428	524		904
Ru_2^{5+}	2-Fap	428 (3.6)	463 (3.6)		750 (3.9)
	2,6-F_2ap (**4**)	422 (4.2)	475 (4.0)		788 (3.9)
	2,4,6-F_3ap (**3**)	418 (4.5)	476 (4.7)		777 (4.5)
	F_5ap		480		770
Ru_2^{4+}	2-Fap		482 (sh)		
	2,4,6-F_3ap (**3**)		476 (sh)		
	F_5ap		486 (sh)		

Table 6 and Figure 6 also show that the higher energy transitions (bands I and II) of the (3,1) and (4,0) isomers of the F_3ap derivative have similar absorption maxima, but this is not the case for the lower energy transitions (band IV) which are located at 777 and 895 nm for the (3,1) and (4,0) isomers, respectively. This trend is also observed for band IV of the (3,1) and (4,0) isomers of the F_5ap derivative which occurs at 770 and 990 nm, respectively (see Table 6), thus suggesting that if a diruthenium complex with a substituted ap bridging ligand exists in two isomeric forms (most likely (3,1) and (4,0)), one can then differentiate the (3,1) from the (4,0) isomer on the basis of their UV−vis spectra.

The singly reduced and singly oxidized forms of the (3,1) and (4,0) isomers of $Ru_2(L)_4Cl$ where L = 2-CH_3ap, 2-Fap, 2,4,6-F_3ap, or F_5ap were in situ generated in a spectroelectrochemical thin-layer cell. The absorption maxima of the Ru_2^{5+}, Ru_2^{4+}, and Ru_2^{6+} forms of each isomer are summarized in Table 6, and examples of UV−vis spectra for the two isomers of $Ru_2(2,4,6\text{-}F_3ap)_4Cl$ are illustrated in Figure 7.

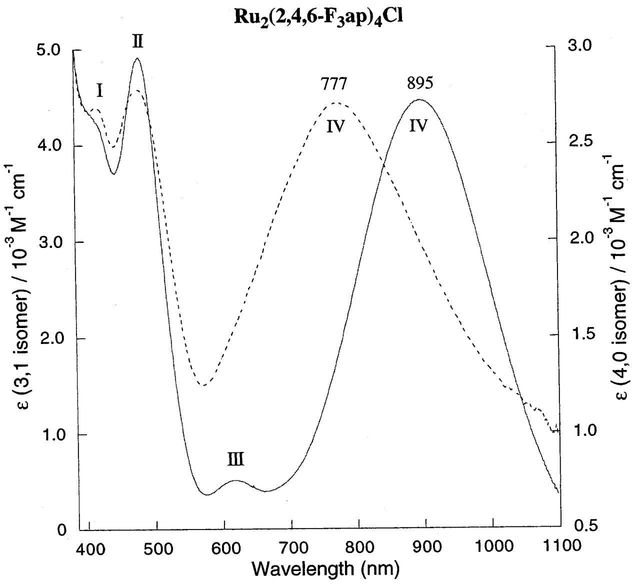

Figure 6. UV−vis spectra of 2.7 × 10^{-4} M (3,1) Ru$_2$(2,4,6-F$_3$ap)$_4$Cl (− − −) and 4.5 × 10^{-4} M (4,0) Ru$_2$(2,4,6-F$_3$ap)$_4$Cl (—) in CH$_2$Cl$_2$.

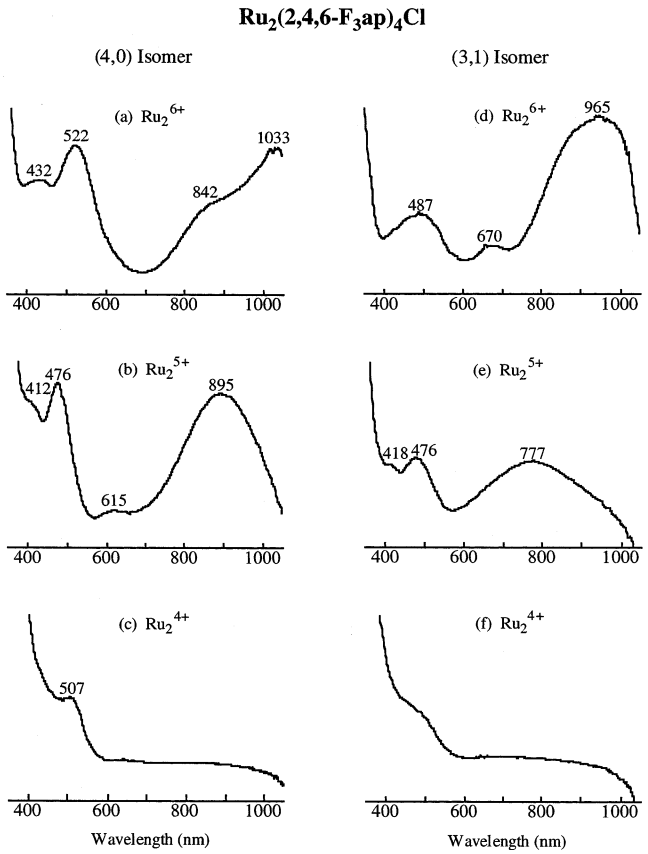

Figure 7. Neutral and electrogenerated forms of (4,0) and (3,1) isomers of Ru$_2$(2,4,6-F$_3$ap)$_4$Cl.

Most of the electrogenerated Ru$_2$$^{6+}$ complexes exhibit three absorption bands between 400 and 1100 nm (**2** and the (4,0) isomer of Ru$_2$(F$_5$ap)$_4$Cl also display an additional shoulder at 842−900 nm) and this is similar to the spectral features of the Ru$_2$$^{6+}$ complex, [Ru$_2$(ap)$_4$Cl](FeCl$_4$)[33] (λ_{max} = 430, 505 and 975 nm), whose electronic structure has been proposed as $\sigma^2\pi^4\delta^2\pi^{*2}$. This orbital assignment implies that an electron is invariably removed from the δ^* orbital upon going from Ru$_2$$^{5+}$ to Ru$_2$$^{6+}$ for each compound in Table 6. The data also suggests that the same electron-transfer mechanism occurs upon oxidation of each compound, a result consistent with the linear free energy relationship between $E_{1/2}$ and $4\Sigma\sigma$ for the first oxidation (see Figure 5).

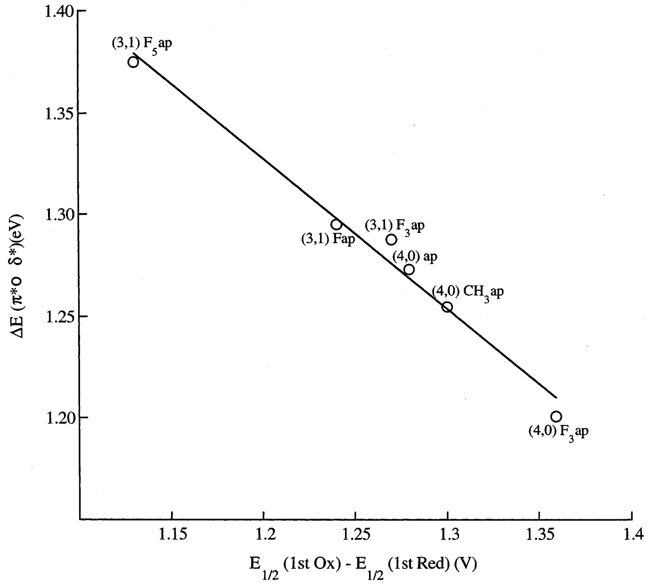

Figure 8. Correlation Between λ_{max} ($\pi^* \rightarrow \delta^*$) for band IV in Ru$_2$$^{6+}$ and the HOMO−LUMO gap (See Table 6 for details). HOMO corresponds to $E_{1/2}$ for first oxidation. LUMO corresponds to $E_{1/2}$ for first reduction. Correlation for the slope was 0.992.

All Ru$_2$$^{6+}$ forms of the compounds display a near-IR band that ranges from 900 to 1100 nm (see Table 6), and the energy of this transition correlates well (R = 0.992) with the electrochemical HOMO−LUMO gap, that is, the potential difference between the first oxidation and the first reduction (Figure 8). The oxidation of each compound is proposed to involve a removal of an electron from the δ^*, and the reduction most likely involves the addition of an electron to the π^* orbital, thus suggesting that the near-IR band between 900 and 1100 nm can be assigned as a $\pi^* \rightarrow \delta^*$ transition. A similar electronic transition has been proposed for the 907 nm absorption band of Ru$_2$[(*p*-tol)-NCHN(*p*-tol)]$_4$,[34] a compound which possesses an empty δ^* orbital as is the case for the Ru$_2$$^{6+}$ species examined in the present study.

As shown in Table 6, the UV−vis spectra of the Ru$_2$$^{4+}$ forms of the (3,1) and (4,0) isomers show similar patterns. In both series of compounds, there are no distinctive features in the visible region except for a small absorption band between 476 and 534 nm for the two series of isomers. The spectral data and the electrochemical results of the same compounds are therefore self-consistent, and both suggest that each Ru$_2$$^{4+}$ species in Table 6 has the electronic configuration $\sigma^2\pi^4\delta^2\pi^{*3}\delta^*$.

Summary

In the present study, we have examined the structural, electrochemical, and spectral properties of a series of

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[33] Cotton, F. A.; Yokochi, A. *Inorg. Chem.* **1997**, *36*, 567.

[34] Cotton, F. A.; Ren, T. *Inorg. Chem.* **1991**, *30*, 3675.

diruthenium complexes bridged by four anilinopyridinate anions with electron-withdrawing and/or electron-donating groups at the ortho, meta, or para positions of the phenyl ring. Both the type and number of geometric isomers are affected by the nature of the bridging ligand, and among the compounds investigated, only those with two substituents at the ortho positions of the phenyl ring exist in more than one isomeric form.

Virtually all compounds undergo two one-electron oxidations and a single one-electron reduction in CH_2Cl_2, 0.1 M TBAP, and each electrode process follows linear free energy relationships when the $E_{1/2}$ values are plotted as a function of the Hammett parameters of the substituent on the bridging ligand. The first reduction and the second oxidation are insensitive to the isomer type, but this is not the case for the first oxidation where the (4,0) isomers exhibit a larger substituent effect than the (3,1) isomers. The UV−vis spectra of virtually all neutral (3,1) and (4,0) diruthenium complexes consist of three absorption maxima between 400 and 1100 nm with the higher energy transition being the only one affected by the isomer type. Although the optical and electrochemical properties of the compounds vary substantially with the arrangement of the bridging ligands around the dimetal core, those changes are reflected neither in the structural features of the compounds nor in the electronic configuration of their reduced or oxidized state.

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Supporting Information Available: X-ray crystallographic files in CIF format, figures for the structural determination of Ru_2(2-CH_3ap)$_4$Cl, Ru_2(2,5-F_2ap)$_4$Cl, Ru_2(2,6-F_2ap)Cl, and the (3,1) and (4,0) isomers of Ru_2(2,4,6-F_3ap)$_4$Cl as well as UV−vis spectra for (3,1) Ru_2(2,6-F_2ap)$_4$Cl and for a mixture of (3,1) and (4,0) Ru_2(2,6-F_2ap)$_4$Cl. This material is available free of charge via the Internet at http://pubs.acs.org.

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