A Novel Diamagnetic Diruthenium(III) Complex Bridged by Four *Unsymmetrical* Carboxylate-Type Ligands. Synthesis, Molecular Structure, Electrochemistry, and Spectroelectrochemistry of $Ru_2(pfap)_4(C{\equiv}CC_6H_5)_2$, Where pfap Is 2,3,4,5,6-Pentafluoro-2-anilinopyridinate

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Numerous spectral and electrochemical studies have been published on diruthenium complexes bridged by carboxylate-type ligands. Most of the species investigated contain a Ru_2^{5+} core,[1–5] but several diruthenium(II) complexes with Ru_2^{4+} cores have also been isolated and characterized.[6–9] Diruthenium(III) complexes with several bridging configurations as well as with highly charged bridging ligands are also known,[10–12] but until recently,[13] all attempts to isolate or spectrally characterize diruthenium(III) or diruthenium(III,IV) derivatives with four three-atom singly charged anionic bridging ligands have proven to be unsuccessful.[5,14–16] Thus, the methodology to make or to characterize these desirable complexes is much needed.

The synthesis of $Ru_2(dpf)_4(C{\equiv}CC_6H_5)_2$ (dpf = diphenylformamidinate) was recently reported by our group.[13] This compound has the Ru_2^{6+} unit complexed by four *symmetrical* dpf bridging ligands, and this prompted us to attempt the synthesis of other diruthenium(III) complexes, particularly those with four *unsymmetrical* bridging ligands. This has now been successful, and in this communication we report the X-ray crystal structure, electrochemistry, and spectroelectrochemistry of the first such compound, $Ru_2(pfap)_4(C{\equiv}CC_6H_5)_2$, where pfap = 2,3,4,5,6-pentafluoro-2-anilinopyridinate.[17]

We initially tried to make a compound analogous to $Ru_2(ap)_4(C{\equiv}CC_6H_5)$ (ap = 2-anilinopyridinate), which was reported by Charkravarty and Cotton.[5] The reaction of $Ru_2(pfap)_4Cl$ with $LiC{\equiv}CC_6H_5$ in THF under Ar (23 °C, 8 h) generates both a red and a blue compound upon purification on a silica gel column using CH_2Cl_2 as eluent. The red compound (yield: 60%), which turns out to be $Ru_2(pfap)_4(C{\equiv}CC_6H_5)$, has a magnetic moment of 3.93 μ_B (22 °C), as does $Ru_2(pfap)_4Cl$ (3.92 μ_B, 22 °C) and $Ru_2(ap)_4(C{\equiv}CC_6H_5)$ (3.92 μ_B, 35 °C).[5] In contrast, the blue compound (yield: 40%) is diamagnetic, as determined by its ^1H and ^{19}F NMR spectra.[17] This is also the case for $Ru_2(dpf)_4(C{\equiv}CC_6H_5)_2$, which contains four *symmetrical* dpf bridging ligands.[13]

The formation of $Ru_2(pfap)_4(C{\equiv}CC_6H_5)_2$ is unusual and quite fascinating since the metal ion of diruthenium and dirhodium units which is coordinated by four anilino nitrogen atoms has long been suggested to be "blocked" by the four phenyl groups due to steric hindrance.[5,18] A pentafluoro rather than a regular phenyl ring is present in the title compound, and this should lead to an even greater steric hindrance. This experimental fact therefore suggests that axial coordination of a second $C{\equiv}CC_6H_5$ ligand will depend upon the nature and reactivity of the two central metal atoms rather than being determined solely by steric hindrance. To provide further evidence for this hypothesis, we reinvestigated the work of Charkravarty and Cotton[5] and were able to isolate both $Ru_2(ap)_4(C{\equiv}CC_6H_5)_2$ and $Ru_2(ap)_4(C{\equiv}CC_6H_5)$ using their reported procedure for synthesis of the $C{\equiv}CC_6H_5$ monoadduct.[19]

The structure of $Ru_2(pfap)_4(C{\equiv}CC_6H_5)_2$, shown in Figure 1,[20] has the following noteworthy features: (i) a totally polar arrangement of ligands known previously as a 4,0 isomer is obtained; (ii) both Ru1 and Ru2 are essentially octahedral with four nitrogens forming the equatorial plane and each Ru metal having an axially bound phenylacetylide; (iii) the bond distances of Ru1–C45 and Ru2–C53 are 1.955(12) and 1.951(11) Å, respectively, and are not significantly different from each other, which is unusual for a 4,0 arrangement; (iv) the Ru–Ru bond distance is 2.441(1) Å, which is shorter than that of $Ru_2(dpf)_4(C{\equiv}CC_6H_5)_2$[13] but still much longer than expected; (v) the average Ru–Ru–C angle is 171.4°, which is nearly linear compared to the same angle of $Ru_2(dpf)_4(C{\equiv}CC_6H_5)_2$ (159.8°); (vi) the rotation of the pentafluorophenyl ring is restricted; (vii) the Ru–N bond distances are different from each other with two long and two short ones. In all cases, there is a direct correlation among the Ru–N bond length, the Ru–Ru–N angle, and the

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(17) Anal. Calcd for $C_{60}H_{26}N_8F_{20}Ru_2$: C, 50.07; H, 1.93; N, 7.63; F, 26.31. Found: C, 50.00; H, 1.81; N, 7.78; F, 26.39. ^1H NMR (CD_2Cl_2): δ 9.85 (d, 4H), 8.18 (d,d, 4H), 8.10 (t, 2H), 8.03 (t, 2H), 5.92 (d, 2H), 5.66 (t, 1H), 5.12 (t, 1H), 4.85 (d, 2H), 4.54 (d, 4H), 4.11 (t, 4H). ^{19}F NMR (CD_2Cl_2): δ −133.99 (d, 1F), −143.26 (d, 1F), −153.82 (t, 1F), −158.30 (t, 1F), −158.46 (t, 1F).

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(20) A very dark blue-green flat plate having approximate dimensions 0.56 × 0.40 × 0.14 mm was mounted in a random orientation on a Nicolet R3m/V automatic diffractomer. The sample was placed in a stream of dry nitrogen gas at −50 °C. The radiation used was Mo Kα monochromatized by a highly ordered graphite crystal. The structures were solved by the SHELXTL direct methods program. Final cell constants, as well as other information pertinent to data collection and refinement, are as follows: $C_{60}H_{26}N_8F_{20}Ru_2$; space group $P2_1/c$ (monoclinic); a = 23.436(6) Å, b = 20.640(6) Å, c = 23.504(6) Å, β = 105.82(2)°; Z = 8; absorption coefficient, μ = 6.55 cm^{-1}; radiation (Mo Kα), λ = 0.710 73 Å; collection range, $4° \leq 2\theta \leq 37°$; total data collected, 8712; independent data, $I > 3\sigma(I)$, 5887; R = 0.039, R_w = 0.036. All calculations were made using Nicolet's SHELXTL PLUS (1987) series of crystallographic programs. The laue symmetry was determined to be $2/m$, and from the systematic absences noted the space group was shown unambiguously to be $P2_1/c$. The cell almost transforms to a C-centered orthorhombic lattice having a' = 28.31, b' = 37.44, and c' = 20.64 Å (γ' = 89.83°). However, axial photographs on a' and b' are not symmetrical, thus ruling out *mmm* Laue symmetry. Intensities were measured using the ω-scan technique, with the scan rate depending on the count obtained in rapid prescans of each reflection. Two standard reflections were monitored after every 2 h or 100 data collected, and these showed no significant change. During data reduction, Lorentz and polarization corrections were applied, but no correction was made for absorption due to the small absorption coefficient.

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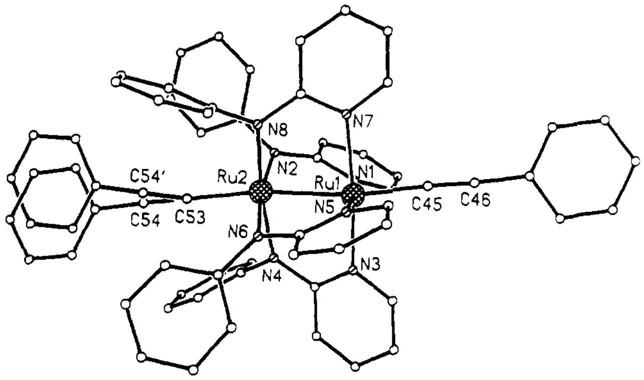

Figure 1. View of $Ru_2(pfap)_4(C\equiv CC_6H_5)_2$ with the H and F atoms omitted. Both orientations of the disordered ligand are shown.

C-Ru-N angle, with the long bonds having small Ru-Ru-N and C-Ru-N angles. The effect is the same on both the anilino and pyridino ends of the molecule, and this seems to be affected little by the obvious difference in steric bulk between the two ends of the pfap ligand.

Figure 2a shows a cyclic voltammogram of $Ru_2(pfap)_4(C\equiv CC_6H_5)_2$ in CH_2Cl_2 containing 0.1 M TBAP. A single reversible one-electron oxidation ($E_{1/2}$ = 0.90 V) and two reversible one-electron reductions ($E_{1/2}$ = -0.05, -1.18 V) are observed. Each process is believed to be metal centered, and this would correspond to the electrogeneration of complexes with Ru_2^{7+}, Ru_2^{5+}, and Ru_2^{4+} units. The second reduction is irreversible on the spectroelectrochemical time scale (1 mV/s) while the two other electrode reactions remain quite reversible under these experimental conditions. This reversibility makes it possible to spectroscopically monitor the electrogeneration of both the Ru_2^{7+} and Ru_2^{5+} complexes, the former of which is novel.

Figure 2b shows the spectral changes that occur upon the first one-electron oxidation of $Ru_2(pfap)_4(C\equiv CC_6H_5)_2$. The neutral species has absorption bands at 441, 582 (sh), 647, 720 (sh), and 803 nm while the UV-visible spectrum of the singly oxidized species has bands at 516, 705, and 913 nm. The presence of four isosbestic points clearly indicates the absence of spectrally-detectable intermediates. To our knowledge, this is the first UV-visible spectrum of a diruthenium(III,IV) complex which is bridged by four carboxylate-type ligands. An assignment of the bands in this spectrum would definitively require a thorough MO calculation on this system.

The UV-visible spectrum of electrogenerated $[Ru_2(pfap)_4(C\equiv CC_6H_5)_2]^-$ is illustrated in Figure 2c. This spectrum has absorptions at 534 and 847 nm and is similar to the spectrum reported for $Ru_2(ap)_4(C\equiv CC_6H_5)$.[5] There is, however, a marked difference between the magnetic properties of $[Ru_2(pfap)_4(C\equiv CC_6H_5)_2]^-$ and $Ru_2(ap)_4(C\equiv CC_6H_5)$, despite the fact that both compounds contain a Ru_2^{5+} core. The pfap derivative has only a single unpaired electron, and its ESR spectrum is characterized by a sharp, well-resolved rhombic signal. In contrast, the complex with four ap bridging ligands has three unpaired electrons with μ = 3.92 μ_B (35 °C) and no ESR signal can be detected.[5]

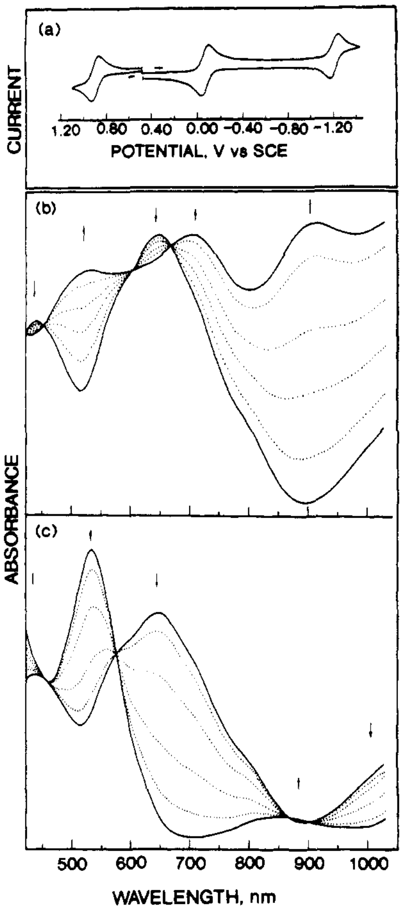

Figure 2. (a) Cyclic voltammogram of $Ru_2(pfap)_4(C\equiv CC_6H_5)_2$ in CH_2Cl_2 containing 0.1 M TBAP (scan rate = 0.1 V/s) and spectral changes associated with the electrode reactions of $Ru_2(pfap)_4(C\equiv CC_6H_5)_2$ in CH_2Cl_2, 0.1 M TBAP upon switching the potential (b) from +0.50 to +1.10 V (first oxidation) and (c) from +0.50 to -0.30 V (first reduction).

There remain many unanswered questions regarding relationships between the molecular orbitals and spectral interpretation of the title compound as compared to other related diruthenium complexes. Studies of these complexes are still in their infancy and invite further work. Systematic investigations in this area are now underway.

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Supplementary Material Available: Text giving a detailed description of the X-ray diffraction experiment and some crystallographically interesting features, tables listing data collection and processing parameters, atomic coordinates and equivalent isotropic displacement parameters, bond lengths, bond angles, anisotropic displacement parameters, H atom coordinates and isotropic displacement parameters, and torsion angles, and figures showing the structure, space filling, and packing of the molecule in the unit cell (29 pages). Ordering information is given on any current masthead page.