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Synthesis and Characterization of a New Structural Type of Diruthenium(III) Complex

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Introduction

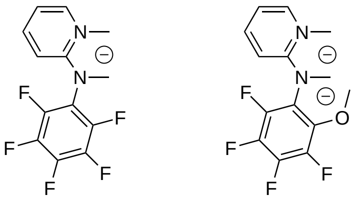
Four different diruthenium(III) complexes bridged by monovalent equatorial ligands have been reported in the literature.[1−3] The bridging ligands in these compounds are either *N,N'*-diphenylformamidinate (dpf),[1] 2-(2,3,4,5,6-pentafluoroanilino)pyridinate (F_5ap)[2] or 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidinate (hpp)[3] monoanions and the axial ligands are either $[C{\equiv}CC_6H_5]^-$, CN^-, or Cl^-. All of the Ru_2^{6+} complexes have two coordinated axial ligands. Those with $[C{\equiv}CC_6H_5]^-$ or CN^- are diamagnetic[1,2] and have a very long Ru−Ru bond distance while the compound with two Cl^- axial ligands, $Ru_2(hpp)_4Cl_2$,[3] is paramagnetic and has a short Ru−Ru bond distance. Each of the four Ru_2^{III} derivatives undergoes two or three, usually reversible, metal-centered redox processes corresponding to the generation of Ru_2^{4+}, Ru_2^{5+}, and Ru_2^{7+} species.[1−3]

It is known that diruthenium complexes bridged by four unsymmetrical ligands, such as in the case of F_5ap, have four geometric isomers designated as (4,0), (3,1), (2,2) trans, and (2,2) cis.[2,4] The (4,0) isomer of $Ru_2(F_5ap)_4(C{\equiv}CC_6H_5)_2$ was first described by our group in 1993,[2] and we were in the process of preparing the corresponding (3,1) isomer for characterization in a number of solvents when an unusual reaction was noted. This reaction occurred upon dissolving the (3,1) isomer of $Ru_2(F_5ap)_4Cl$[5] in THF which had been distilled and then left overnight prior to use. The distillation process removed the peroxide inhibitor that is present in commercial THF which then allowed the solvent to react with oxygen to give peroxide. This is the key point in the reaction which involves a cleavage of the ortho carbon−fluorine bond on the pentafluorophenyl ring followed by insertion of an oxygen to give $Ru_2(F_4Oap)(F_5ap)_3Cl$ where F_4Oap is the 2-(3,4,5,6-tetrafluoro-2-oxoanilino)pyridinate dianion (see Chart 1). The resulting Ru_2^{III} complex was purified on a silica gel chromatographic column using CH_2Cl_2/hexane (1:10) as eluent and was characterized by room temperature magnetic susceptibility, X-ray single-crystal diffraction, electrochemistry, and mass spectrometry.

Experimental Section

Chemicals and Reagents. CH_2Cl_2 was obtained as HPLC grade from Fisher Scientific Co. and distilled over phosphorus pentoxide (P_2O_5). Spectroscopic grade THF, purchased from Aldrich Chemical Co., was purified and the peroxide inhibitor removed by distillation under Ar from sodium/benzophenone. Tetra-*n*-butylammonium perchlorate (TBAP, Fluka Chemical Co.) was twice recrystallized from absolute ethanol and dried in the oven at 40 °C prior to use.

Chart 1



F_5ap F_4Oap

Synthesis of $Ru_2(F_4Oap)(F_5ap)_3Cl$. The Ru_2^{6+} compound was prepared by dissolving the (3,1) isomer of $Ru_2(F_5ap)_4Cl$[5] into a THF solution which was distilled over sodium and benzophenone and then allowed to stand overnight at room temperature prior to use. Anal. Calcd for ($C_{44}H_{16}N_8OF_{19}ClRu_2{\cdot}C_6H_{14}$): C, 44.17; H, 2.21; N, 8.24. Found: C, 44.21; H, 2.01; N, 8.07. Magnetic susceptibility (solid, 23 °C): 2.75 μ_B.

Physical Measurements. Mass spectra were obtained from a high-resolution hybrid tandem VG Analytical Model 70-SEQ (EEQQ geometry) mass spectrometer. A standard fast atom bombardment (FAB) source was used, and *m*-nitrobenzyl alcohol (NBA) was the liquid matrix. The elemental analysis was carried out by Galbrith Laboratories, Inc., Knoxville, TN.

Cyclic voltammograms were obtained with an IBM Model EC 225 voltammetric analyzer by utilizing a three-electrode electrochemical cell. The working electrode was a platinum button with a surface area of 0.19 mm^2. The reference electrode was a homemade saturated calomel electrode (SCE). A platinum wire was used as a counter electrode.

X-ray Crystallography. Dark blue single crystals of $Ru_2(F_4Oap)(F_5ap)_3Cl$ suitable for X-ray analysis were obtained by slow diffusion of hexane into a CH_2Cl_2 solution of the compound after which a multifaceted block having approximate dimensions 0.50 × 0.50 × 0.45 mm was mounted in a random orientation on a Nicolet R3m/V automatic diffractometer. Since the crystals were known to decompose outside the mother liquor, 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. Final cell constants, as well as other information pertinent to data collection and refinement, are listed in Table 1. The Laue symmetry was determined to be $\bar{1}$ and the space group was shown to be either $P1$ or $P\bar{1}$. 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 every 100 data collected, and these showed no significant variation. During data reduction, Lorentz and polarization corrections were applied. However, no correction for absorption was made due to the low absorption coefficient.

Since the unitary structure factors displayed centric statistics, space group $P\bar{1}$ was assumed from the outset. The structure was solved by the SHELXTL direct methods program, which revealed the positions of most of the non-hydrogen atoms in the molecule. Remaining atoms were located in subsequent difference Fourier syntheses. The usual sequence of isotropic and anisotropic refinement was followed after which all hydrogens were entered in ideal calculated positions and constrained to riding motion, with a single variable isotropic temperature factor for all of them. Heavily disordered solvent molecules were also located at two different sites. One site in a general position was positively identified as methylene chloride, and this was modeled by using ideal rigid bodies in three slightly different orientations, each with a population factor of 33%. Another disordered site, located about an inversion center, could not be positively identified, nor could any rigid body be introduced with satisfactory results. Eventually six unconstrained individual carbon atoms were refined here, each with 35 to 50% occupancy. This is presumed to be heavily disordered hexane, but THF and methylene chloride cannot be ruled out. After all shift/esd ratios were less than 0.2, convergence was reached at the agreement factors listed in Table 1. No unusually high correlations

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Table 1. X-ray Data Collection and Processing Parameters for $Ru_2(F_4Oap)(F_5ap)_3Cl$

space group	$P\bar{1}$ (triclinic)
cell const	$a = 12.861(3)$Å
	$b = 16.412(5)$
	$c = 13.385(3)$
	$\alpha = 90.58(2)°$
	$\beta = 114.51(2)$
	$\gamma = 95.94(2)$
	$V = 2552$Å^3
mol formula	$C_{44}H_{16}N_8OF_{19}ClRu_2{\cdot}CH_2Cl_2{\cdot}{}^1/_2C_6H_{14}$
fw	1399.30
formula units per cell	$Z = 2$
density	$\rho = 1.82$ g cm^{-3}
abs coeff	$\mu = 8.52$ cm^{-1}
temp	$T = -50$ °C
radiation (Mo Kα)	$\lambda = 0.71073$Å
collcn range	$4° < 2\theta < 45°$
scan width	$\Delta\theta = 1.25 + (K\alpha2\text{-}K\alpha1)°$
scan speed range	2.0−15.0° min^{-1}
tot. no. of data collcd	6574
no. of independent data	5774
tot. no. of variables	725
R^a	0.030
$R_w{}^b$	0.035
weights	$w = \sigma(F)^{-2}$

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

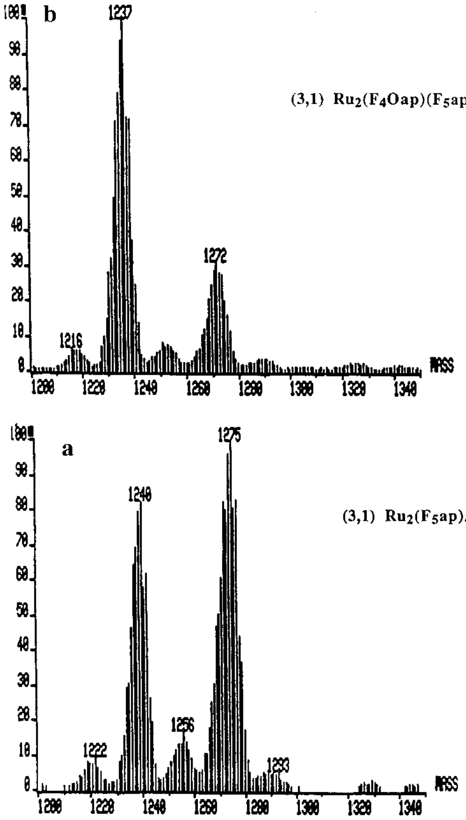

Figure 1. Mass spectra of (a) (3,1) $Ru_2(F_5ap)_4Cl$ and (b) (3,1) $Ru_2(F_4Oap)(F_5ap)_3Cl$.

were noted between any of the variables in the last cycle of full-matrix least-squares refinement, and the final difference density map showed a maximum peak of about 0.6 e/Å^3. All calculations were made using Nicolet's SHELXTL PLUS (1987) series of crystallographic programs.

Results and Discussion

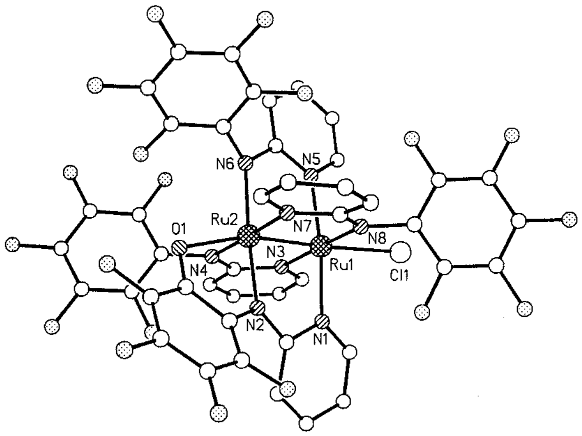

Figure 2. View of the $Ru_2(F_4Oap)(F_5ap)_3Cl$ molecule showing the atom numbering scheme for the core atoms, with hydrogens omitted.

Mass spectra of $Ru_2(F_5ap)_4Cl$ and $Ru_2(F_4Oap)(F_5ap)_3Cl$ are shown in Figure 1. $Ru_2(F_5ap)_4Cl$ has an *m/e* of 1275 while the $Ru_2{}^{III}$ product of the THF reaction, $Ru_2(F_4Oap)(F_5ap)_3Cl$, has an *m/e* of 1272 consistent with a substitution of oxygen for a fluorine atom at the ortho position of the pentafluorophenyl ring as shown in Chart 1.

The formation of $Ru_2(F_4Oap)(F_5ap)_3Cl$ is believed to occur via a radical mechanism with the origin of the inserted oxygen atom being peroxide generated from oxygen and the utilized THF solvent.[6,7] Evidence for a reaction involving peroxide comes from the fact that the (3,1) isomer of $Ru_2(F_5ap)_4Cl$ does not react with freshly distilled or commercially available THF even under an O_2 atmosphere. It also does not react with distilled THF to which 2,6-di-*tert*-butyl-4-methylphenol, a known radical inhibitor, has been added prior to letting the solution stand overnight. In contrast, $Ru_2(F_4Oap)(F_5ap)_3Cl$ could be readily generated by addition of *tert*-butyl peroxide to freshly distilled THF or toluene solutions containing the (3,1) isomer of $Ru_2(F_5ap)_4Cl$. All of the experiments therefore support that peroxide is involved in the reaction.

As seen in Figure 2, $Ru_2(F_4Oap)(F_5ap)_3Cl$ contains four bridging ligands, one of which is dianionic and is both axially and equatorially bound to one of the two Ru atoms. Room temperature magnetic moment measurements indicate that there are two unpaired electrons in the compound. The Ru−Ru distance of 2.336 Å is similar to 2.321 Å for $Ru_2(hpp)_4Cl_2$[3] and 2.343 Å for $K_2[Ru_2(SO_4)_4(H_2O)_2]$.[8,9] Both of the latter species are paramagnetic and contain 2 and 4 unpaired electrons, respectively. The value of 2.336 Å for $Ru_2(F_4Oap)(F_5ap)_3Cl$ is, however, much shorter than Ru−Ru distances in the diamagnetic complexes of $Ru_2(dpf)_4(C{\equiv}CC_6H_5)_2$ (2.556 Å),[1] $Ru_2(dpf)_4(CN)_2$ (2.539 Å),[1b] and the (4,0) isomer of $Ru_2(F_5ap)_4(C{\equiv}CC_6H_5)_2$ (2.451Å).[2] On the other hand, the Ru−Cl bond length of 2.568 Å for $Ru_2(F_4Oap)(F_5ap)_3Cl$ is significantly shorter than the Ru−Cl distance of 2.705 Å in $Ru_2(hpp)_4Cl_2$ (which also contains a $Ru_2{}^{6+}$ core[3]) and is slightly larger than the Ru−Cl bond lengths of most Ru$_2$(II,III) complexes containing a single Cl^- ligand which fall in the range of 2.412 to 2.556 Å .[1,10,11]

Each ruthenium ion in $Ru_2(F_4Oap)(F_5ap)_3Cl$ has a distorted octahedral coordination, with four nitrogens forming the equatorial plane. The Ru−Ru−Cl bond angle is nearly linear (174.4°)

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Table 2. Selected Bond Lengths (Å) and Angles (deg) of $Ru_2(F_4Oap)(F_5ap)_3Cl$

Bond Lengths			
Ru(1)–Ru(2)	2.336(1)	Ru(1)–Cl(1)	2.568(2)
Ru(1)–N(5)	2.096(5)	Ru(1)–N(8)	2.089(3)
Ru(1)–N(1)	2.085(5)	Ru(1)–N(3)	2.082(3)
Ru(2)–O(1)	2.168(4)	Ru(2)–N(2)	2.014(5)
Ru(2)–N(4)	2.048(3)	Ru(2)–N(6)	2.019(5)
Ru(2)–N(7)	2.075(3)	O(1)–C(7)	1.301(7)
Bond Angles			
Ru(2)–Ru(1)–Cl(1)	174.4(1)	Ru(2)–Ru(1)–N(1)	90.6(1)
Cl(1)–Ru(1)–N(1)	91.2(1)	Ru(2)–Ru(1)–N(3)	91.3(1)
Cl(1)–Ru(1)–N(3)	94.2(1)	N(1)–Ru(1)–N(3)	84.7(2)
Ru(2)–Ru(1)–N(5)	87.3(1)	Cl(1)–Ru(1)–N(5)	91.7(1)
N(1)–Ru(1)–N(5)	170.8(1)	N(3)–Ru(1)–N(5)	86.5(2)
Ru(2)–Ru(1)–N(8)	86.2(1)	Cl(1)–Ru(1)–N(8)	88.4(1)
N(1)–Ru(1)–N(8)	93.1(2)	N(3)–Ru(1)–N(8)	176.7(2)
N(5)–Ru(1)–N(8)	95.6(2)	Ru(1)–Ru(2)–O(1)	164.8(1)
Ru(1)–Ru(2)–N(2)	87.6(1)	O(1)–Ru(2)–N(2)	77.4(2)
Ru(1)–Ru(2)–N(4)	88.2(1)	O(1)–Ru(2)–N(4)	90.5(1)
N(2)–Ru(2)–N(4)	94.9(2)	Ru(1)–Ru(2)–N(6)	92.0(1)
O(1)–Ru(2)–N(6)	103.2(2)	N(2)–Ru(2)–N(6)	172.2(1)
N(4)–Ru(2)–N(6)	92.9(2)	Ru(1)–Ru(2)–N(7)	93.0(1)
O(1)–Ru(2)–N(7)	88.5(1)	N(2)–Ru(2)–N(7)	85.8(2)
N(4)–Ru(2)–N(7)	178.7(2)	N(6)–Ru(2)–N(7)	86.5(2)
Ru(2)–O(1)–C(7)	109.1(3)		

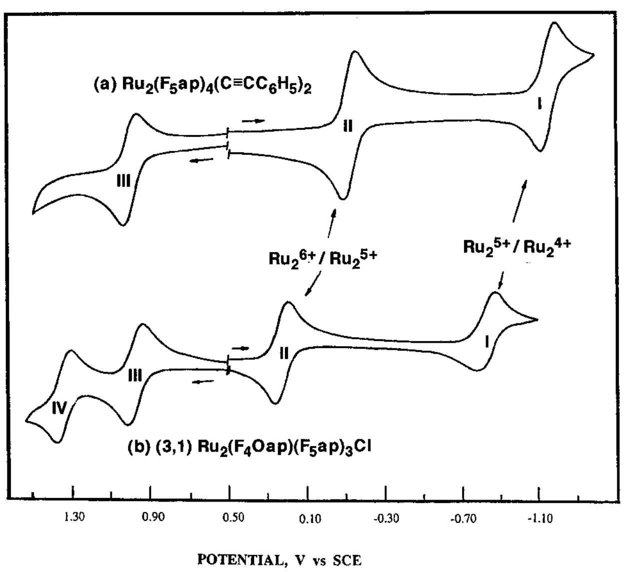

Figure 3. Cyclic voltammograms of (a) $Ru_2(F_4Oap)(F_5ap)_3Cl$ and (b) the (3,1) isomer of $Ru_2(F_5ap)_4(C{\equiv}CC_6H_5)_2$ in CH_2Cl_2 containing 0.1 M TBAP. Scan rate = 0.1 V/s.

while the Ru–Ru–O angle is bent (164.8°). There is a 50:50 mixture of left-handed and right-handed torsion angles in the crystal with respect to N–Ru–Ru–N. However, within any given molecule, the four individual torsion angles are widely different from each other. Two of the angles are close to 0°, while the other two, having the largest magnitudes, are actually opposite in sign. A disparity of this type is quite rare for diruthenium complexes and must result from the unusual axial binding of an oxygen atom to the Ru_2^{6+} unit. Finally, the two Ru atoms of $Ru_2(F_4Oap)(F_5ap)_3Cl$ have distinctly different Ru–N bond lengths. The Ru(1)–N distances are all about equal, averaging 2.088 Å. Three of the four Ru(2)–N bonds are shorter, averaging 2.027 Å, but one, Ru(2)–N(7), is longer (2.075 Å).

Cyclic voltammograms of $Ru_2(F_4Oap)(F_5ap)_3Cl$ and the (3,1) isomer of $Ru_2(F_5ap)_4(C{\equiv}CC_6H_5)_2$[5] in CH_2Cl_2 containing 0.1 M TBAP are illustrated in Figure 3. $Ru_2(F_4Oap)(F_5ap)_3Cl$ differs from all previously investigated Ru_2^{6+} derivatives[1–3] in that it undergoes four, rather than three, reversible one-electron transfer reactions. Two are oxidations, at $E_{1/2} = 1.35$ and 0.98 V and two are reductions at $E_{1/2} = +0.22$ and -0.82, as confirmed by rotating disk voltammetry.

Under the same experimental conditions $Ru_2(F_5ap)_4(C{\equiv}CC_6H_5)_2$ undergoes two reversible one-electron reductions located at $E_{1/2} = -0.13$ and -1.15 V and one reversible one-electron oxidation at $E_{1/2} = 1.00$ V under the same solution conditions (see Figure 3). Each process is metal-centered, corresponding to the formation of Ru_2^{5+}, Ru_2^{4+}, and Ru_2^{7+} complexes. Thus, one remarkable feature in the electrochemistry of $Ru_2(F_4Oap)(F_5ap)_3Cl$ is that it has two oxidation processes while $Ru_2(F_5ap)_4(C{\equiv}CC_6H_5)_2$ undergoes only one oxidation, even when the potential is scanned anodically to +1.80 V. On the basis of comparisons between the two diruthenium(III) derivatives, the reductions of $Ru_2(F_4Oap)(F_5ap)_3Cl$ at +0.22 and -0.82 V are assigned as being metal-centered while one of the two oxidations, at $E_{1/2} = 1.35$ or 0.98 V, is assigned as being ligand-centered and the other as a metal-centered reaction. The oxidation of an equatorial ligand on diruthenium complexes is presumably due to the electroactive quinone type structure of the F_4Oap dianionic ligand.[12]

As mentioned above, $Ru_2(F_4Oap)(F_5ap)_3Cl$ has two unpaired electrons as does $Ru_2(hpp)_4Cl_2$,[3] and this suggests the electronic configuration of $(\sigma)^2(\pi)^4(\delta)^2(\pi^*\delta^*)^2$ or $(\sigma)^2(\pi)^4(\delta)^2(\pi^*)^2$. ESR spectra could not be observed for the neutral compound nor are signals seen for the singly reduced or singly oxidized form of the complex. This was also the case for $[Ru_2(hpp)_4Cl_2]^n$ where $n = 0$, +1 or -1.[3]

In summary, a new type of diruthenium(III) complex, $Ru_2(F_4Oap)(F_5ap)_3Cl$, has been synthesized from an unexpected reaction involving the (3,1) isomer of $Ru_2(F_5ap)_4Cl$ and trace peroxide in THF. The resulting compound is the first example of a diruthenium(III) derivative having a tridentate ligand bound to the two metal centers. Attempts to synthesize other compounds with this unusual structural type are now underway.

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Supporting Information Available: Tables of data collection parameters, atomic coordinates, anisotropic displacement parameters, and all molecular bond lengths and angles and views of the molecule and a molecular packing diagram (13 pages). Ordering information is given on any current masthead page.

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