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Syntheses, Structural Determination, and Electrochemistry of $Ru_2(Fap)_4Cl$ and $Ru_2(Fap)_4(NO)Cl$

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$Ru_2(Fap)_4Cl$ and $Ru_2(Fap)_4(NO)Cl$, where Fap is the 2-(2-fluoroanilino)pyridinate anion, were synthesized, and their structural, electrochemical, and spectroscopic properties were characterized. $Ru_2(Fap)_4Cl$, which was obtained by reaction between $Ru_2(O_2CCH_3)_4Cl$ and molten HFap, crystallizes in the monoclinic space group $P2_1/c$, with $a = 11.2365(4)$ Å, $b = 19.9298(8)$ Å, $c = 19.0368(7)$ Å, $\beta = 90.905(1)°$, and $Z = 4$. The presence of three unpaired electrons on the Ru_2^{5+} core and the 2.2862(3) Å Ru−Ru bond length for $Ru_2(Fap)_4Cl$ are consistent with the electronic configuration $(\sigma)^2(\pi)^4(\delta)^2(\pi^*)^2(\delta^*)^1$. The reaction between $Ru_2(Fap)_4Cl$ and NO gas yields $Ru_2(Fap)_4(NO)Cl$, which crystallizes in the orthorhombic space group *Pbca*, with $a = 10.0468(6)$ Å, $b = 18.8091(10)$ Å, $c = 41.7615(23)$ Å, and $Z = 8$. The Ru−Ru bond length of $Ru_2(Fap)_4(NO)Cl$ is 2.4203(8) Å, while its N−O bond length and Ru−N−O bond angle are 1.164(8) Å and 155.8(6)°, respectively. $Ru_2(Fap)_4(NO)Cl$ can be formulated as a formal $Ru_2^{II,II}(NO^+)$ complex with a linear Ru−N−O group, and the proposed electronic configuration for this compound is $(\sigma)^2(\pi)^4(\delta)^2(\pi^*)^3(\delta^*)^1$. The binding of NO to $Ru_2(Fap)_4Cl$ leads to some structural changes of the $Ru_2(Fap)_4$ framework and a stabilization of the lower oxidation states of the diruthenium unit. Also, IR spectroelectrochemical studies of $Ru_2(Fap)_4(NO)Cl$ show that NO remains bound to the complex upon reduction and that the first reduction involves the addition of an electron on the diruthenium core and not on the NO axial ligand.

Introduction

Nitric oxide is now known to play an important role in many biological functions;[1−5] therefore, the use of metallonitrosyl complexes as agents potentially capable of releasing or removing NO has become a very active area of research.[6,7]

Several mononuclear ruthenium nitrosyl complexes have been reported,[8−15] but the number of diruthenium nitrosyl complexes is rather scarce in the literature, and to our knowledge, $Ru_2(O_2CC_2H_5)_4(NO)_2$ and $Ru_2(O_2CCF_3)_4(NO)_2$ are the only two examples of diruthenium metal−metal bonded complexes with NO axial ligands that have been structurally characterized to date.[16] These compounds have been described as formal $Ru_2^{I,I}(NO^+)_2$ complexes, and it is of interest to examine whether the electronic distribution of the Ru_2−NO unit varies as a function of the basicity of the bridging ligand.

The present study reports the synthesis of $Ru_2(Fap)_4(NO)Cl$, where Fap is the 2-(2-fluoroanilino)pyridinate anion. This compound contains a more basic bridging ligand than that of the previously characterized diruthenium nitrosyl complexes and possesses one rather than two NO axial ligands. The newly synthesized compound is characterized in terms of its structural, electrochemical, and spectroscopic properties, and these data are compared to those of the parent compound, $Ru_2(Fap)_4Cl$, which is also structurally characterized in this paper.

Experimental Section

Chemicals. $Ru_2(O_2CCH_3)_4Cl$ was prepared according to a method previously published in the literature.[17] Tetra-*n*-butylammonium perchlorate (TBAP) was purchased from Fluka Chemika Co., recrystallized from ethyl alcohol, and dried under vacuum at 40 °C for at least 1 week prior to use. 2-Bromopyridine, 2-fluoroaniline, lithium chloride, and ruthenium chloride hydrate ($RuCl_3{\cdot}3H_2O$) were purchased from Aldrich and used as received. Silica gel (Merck, 230−400 mesh, 60 Å) and aluminum oxide (neutral, 150 mesh, 58 Å) were purchased from Aldrich and used for column chromatography. Ultrahigh-purity argon and nitric oxide were purchased from Matheson Trigas Co. Nitric oxide was first passed through anhydrous calcium sulfate and then through

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potassium hydroxide pellets and a cold trap (dry ice/acetone, −78 °C) to remove traces of water and higher nitrogen oxides. GC grade dichloromethane (CH_2Cl_2) was distilled over phosphorus pentoxide (P_2O_5) and stored over activated 3 Å molecular sieves before use. GC grade tetrahydrofuran (THF) was first distilled from calcium hydride (CaH_2) and then from sodium/benzophenone. Hexane (95% min, Aldrich), absolute ethanol (Mc Cormick, Inc.), acetone (GC grade, EM Science), ethanol (GC grade, EM Science), and acetic acid (GR, EM Science) were all used without purification.

Instrumentation. Cyclic voltammetry was carried out using an EG&G Princeton Applied Research (PAR) model 263 potentiostat/galvanostat. A conventional three-electrode cell was used and consisted of a glassy carbon working electrode (3.0 mm diameter), a platinum counter electrode, and a homemade saturated calomel reference electrode (SCE). The SCE was separated from the solution by a fritted glass bridge of low porosity that contained the solvent/supporting electrolyte mixture. An "H" type cell with two compartments separated by a fritted glass was used for controlled potential bulk electrolysis, and the working and counter electrodes were made from platinum gauze. Argon was used to deoxygenate the solutions for 5 min before carrying out any electrochemical experiments, and a positive argon pressure was maintained above the solution throughout the experiment. Potentials are reported vs the SCE, but measurements are also referenced to the ferrocene/ferrocenium (Fc/Fc^+) couple. The oxidation of ferrocene in CH_2Cl_2, 0.1 M TBAP was located at $E_{1/2} = 0.49$ V vs SCE under our experimental conditions.

UV−visible spectra were recorded on a Hewlett-Packard model 8453 diode array spectrophotometer. Thin-layer FTIR spectroelectrochemical measurements were carried out with a FTIR Nicolet 550 Magna IR spectrometer using a specially constructed light-transparent FTIR spectroelectrochemical cell.[18] ^1H and ^{13}C NMR measurements were recorded at room temperature on a General Electric QE-300 Plus spectrometer and were referenced to tetramethylsilane (TMS). ESR spectra were recorded on a Bruker ER 100E spectrometer. The g values were measured with respect to diphenylpicrylhydrazyl (DPPH: $g = 2.0036 \pm 0.0003$). Magnetic susceptibilities were measured according to the Evans method[19−22] on a General Electric QE-300 FT NMR spectrometer in CD_2Cl_2 with TMS as the internal reference compound. Mass spectra were recorded on a Finnigan TSQ 700 instrument at the University of Texas, Austin. A standard fast atom bombardment was used, and *m*-nitrobenzyl alcohol (NBA) was used as the liquid matrix. Elemental analysis was carried out by Atlantic Microlab, Inc., Norcross Georgia.

Synthesis of HFap. A mixture of 2-bromopyridine (20.53 g, 0.130 mol) and 2-fluoroaniline (29.02 g, 0.261 mol) was stirred under argon at 150 °C for 6 h in THF. During this time, the solution turned from colorless to light brown. After the solution was cooled to room temperature, a total of 100 mL of 10% NaOH was added and the unreacted starting materials were steam-distilled using water as an internal steam source. A light-yellow solid precipitated and was extracted with dichloromethane. The organic phase was dried over $MgSO_4$, and the solvent was evaporated under vacuum. The light-yellow residue was then twice recrystallized in hexane to give pure white crystals in an 83% yield; mp, 83−85 °C. Mass spectral data [*m*/*e*, (fragment)]: 188 $[HFap]^+$, 169 $[Hap]^+$. Elemental analysis ($C_{11}H_9N_2F$): C, 70.20; H, 4.82; N, 14.88. Found: C, 70.21; H, 4.80; N, 14.86. ^1H NMR (in CD_2Cl_2): δ 8.23 (dd, 1H), 8.11(td, 1H), 7.55-(td, 1H), 7.13(m, 2H), 6.99(m, 1H), 6.80(m, 3H) ppm. (Key: t, triplet; td, triplet of doublets; dd, doublet of doublets; m, multiplet). ^{13}C NMR (in CD_2Cl_2): δ 109.4, 115.0, 115.3, 115.4, 121.3, 122.4, 122.5, 124.3, 124.4, 129.0, 129.2, 137.6, 148.0, 152.1, 155.3, 155.6 ppm.

Synthesis of $Ru_2(Fap)_4Cl$. A mixture of $Ru_2(O_2CCH_3)_4Cl$ (0.85 g, 1.8 mmol) and HFap (4.90 g, 26.0 mmol) was heated and stirred under argon at 100 °C for 2 h in a sidearm flask equipped with a condenser. At this temperature, the HFap ligand was in the molten state. The dark-green solid that formed after cooling the flask to room temperature was dissolved in CH_2Cl_2 (10 mL), and the solution was filtered under vacuum to remove unreacted $Ru_2(O_2CCH_3)_4Cl$. The solvent was then evaporated under an air stream, and the excess ligand was sublimed under vacuum at 120 °C. The residue was purified by column chromatography on silica gel, eluting with acetone/hexane (4:6) to give $Ru_2(Fap)_4Cl$ as a dark-green solid (yield: 53%). Mass spectral data [*m*/*e*, (fragment)]: 987 $[Ru_2(Fap)_4Cl]^+$, 952 $[Ru_2(Fap)_4]^+$, 800 $[Ru_2(Fap)_3Cl]^+$, 765 $[Ru_2(Fap)_3]^+$. Elemental analysis ($C_{44}H_{32}N_8F_4Ru_2Cl$): C, 53.58; H, 3.27; N, 11.36. Found: C, 54.36; H, 3.44; N, 11.27. UV−vis spectrum in CH_2Cl_2 [λ, nm]: 428, 463, 750 (broad). Infrared spectrum (KBr pellet): 1603 (s), 1490 (s), 1467 (s), 1429 (s), 1356 (m), 1291 (m), 1253 (w), 1241 (m), 1197 (w), 1158 (w), 1117 (w), 1097 (m), 1033 (w), 1017 (w), 936 (w), 886 (m), 848 (m), 795 (w), 753 (s), 734 (m), 538 (w), 526 (w) cm^{-1} (s, strong; m, medium; w, weak).

Table 1. Data Collection and Processing Parameters for $Ru_2(Fap)_4Cl$ and $Ru_2(Fap)_4(NO)Cl$

	$Ru_2(Fap)_4Cl$	$Ru_2(Fap)_4(NO)Cl$
space group	$P2_1/c$ (monoclinic)	*Pbca* (orthorhombic)
a (Å)	11.2365(4)	10.0468(6)
b (Å)	19.9298(8)	18.8091(10)
c (Å)	19.0368(7)	41.7615(23)
β (deg)	90.905(1)	90.0
V (Å^3)	4262.6(3)	7891.7(8)
formula	$C_{44}H_{32}N_8F_4ClRu_2 \cdot CH_2Cl_2$	$C_{44}H_{32}N_9OF_4ClRu_2$
fw (g/mol)	1071.29	1016.38
Z	4	8
ρ (g/cm^3)	1.669	1.711
μ (cm^{-1})	9.59	9.02
λ (Mo Kα) (Å)	0.710 73	0.710 73
collection range (deg)	$3.0 \le 2\theta \le 50.0$	$2.0 \le 2\theta \le 46.6$
temp (°C)	−50(2)	50(2)
$R(F_o)^a$	0.0229	0.0456
$R_w(F_o)^b$	0.0587	0.1055

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

Synthesis of $Ru_2(Fap)_4(NO)Cl$. In a Schlenk flask, a stirred solution of $Ru_2(Fap)_4Cl$ (0.110 g, 0.11 mmol) in dichloromethane (20 mL) was saturated with argon for 15 min. Nitric oxide was passed through the solution for 10 min whereupon the color of the solution changed from green to dark red. Argon was then bubbled through the solution (during this time the solution turned from red to blue) to remove unreacted NO and to concentrate the compound in a total volume of approximately 1 mL, after which the compound was precipitated at −20 °C by addition of cold hexane (5 mL). The resulting dark-blue solid was washed twice with cold hexane (6 mL) and purified by column chromatography on alumina, eluting with dichloromethane/methanol (9:1) to give $Ru_2(Fap)_4(NO)Cl$ as a green-blue solid (yield, 48%). Mass spectral data [*m*/*e*, (fragment)]: 982 $[Ru_2(Fap)_4(NO)]^+$, 951 $[Ru_2(Fap)_4]^+$, 765 $[Ru_2(Fap)_3]^+$. UV−vis spectrum in CH_2Cl_2 [λ, nm]: 452, 687 (broad). Infrared spectrum (KBr pellet): 1740 (m), 1601 (s), 1487 (s), 1469 (s), 1426 (s), 1349 (w), 1289 (m), 1259 (w), 1237 (m), 1191 (m), 1162 (w), 1119 (w), 1099 (m), 1033 (w), 1017 (w), 939 (w), 883 (m), 847 (m), 794 (w), 758 (s), 731 (m) cm^{-1} (s, strong; m, medium; w, weak).

X-ray Crystallography of $Ru_2(Fap)_4Cl$ and $Ru_2(Fap)_4(NO)Cl$. Large crystalline blocks of $Ru_2(Fap)_4Cl$ and $Ru_2(Fap)_4(NO)Cl$ were obtained by very slow evaporation of a CH_2Cl_2/hexane (1:3) solution of the compound at ambient temperature. A single crystal of $Ru_2(Fap)_4Cl$ (a dark-green block with approximate dimensions of 0.28 mm × 0.24 mm × 0.24 mm) and a single crystal of $Ru_2(Fap)_4(NO)Cl$ (a green thin plate with approximate dimensions of 0.20 mm × 0.18 mm × 0.05 mm) were mounted in turn in a random orientation on a Nicolet R3m/V automatic diffractomer. The samples were 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 structure refinement of both crystals are listed in Table 1. The Laue symmetry was determined to be $2/m$ for $Ru_2(Fap)_4Cl$ and *mmm* for $Ru_2(Fap)_4(NO)Cl$. Investigation of the systematic absences unambigu-

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ously showed the space group to be $P2_1/c$ for Ru$_2$(Fap)$_4$Cl and $Pbca$ for Ru$_2$(Fap)$_4$(NO)Cl. 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 35 s/frame. The first 50 frames were remeasured 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 face plate. A Ψ-scan absorption correction based on the entire data set was applied. Redundant reflections were averaged. Final cell constants were refined using 7246 reflections having $I > 10\,\sigma$(I) for Ru$_2$(Fap)$_4$Cl and 6327 reflections having $I > 10\,\sigma(I)$ for Ru$_2$(Fap)$_4$(NO)Cl.

Results and Discussion

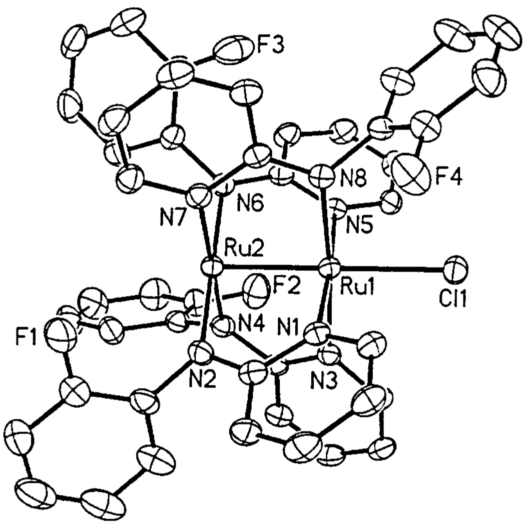
Synthesis. Ru$_2$(Fap)$_4$Cl was prepared by reacting Ru$_2$(O$_2$CCH$_3$)$_4$Cl with an excess of molten HFap ligand (14 equiv). A large excess of ligand is necessary to obtain a good yield because molten HFap plays the role of both solvent and starting material. This preparative route is particularly useful when the replaceable hydrogen is acidic enough to undergo an exchange with the acetate-bridging ligands of the starting material.[23−25]

Ru$_2$(Fap)$_4$(NO)Cl was prepared by passing NO gas through a solution of Ru$_2$(Fap)$_4$Cl. This method is the most widely used to synthesize nitrosyl complexes.[26] However, because NO is very reactive toward oxygen or water, even in trace amounts, the reaction must be carried out under strictly anaerobic and anhydrous conditions. The utilized glassware was therefore dried in an oven overnight at 120 °C, and any trace of air in the flask was replaced by ultrahigh purity argon using a Schlenk line.

Molecular Structures. Crystal structures of Ru$_2$(Fap)$_4$Cl and Ru$_2$(Fap)$_4$(NO)Cl are shown in Figure 1, and selected bond lengths, bond angles, and torsion angles are listed in Tables 2 and 3. The coordinations of Ru1 and Ru2 in Ru$_2$(Fap)$_4$Cl are essentially octahedral and square pyramidal, respectively, with four Fap nitrogen atoms forming the equatorial planes. One ruthenium atom, Ru1, is coordinated to the Cl$^-$ axial ligand and to three pyridyl and one anilino nitrogen atoms, while the other, Ru2, is coordinated to three anilino and one pyridyl nitrogen atoms. The compound therefore adopts a (3,1) isomeric conformation, which contrasts with the isomeric distributions of Ru$_2$(ap)$_4$Cl and Ru$_2$(F$_5$ap)$_4$Cl, where the ap derivative exists only in its (4,0) conformation,[23] and the F$_5$ap complex has been isolated in the (3,1), (4,0), and (2,2) trans configurations.[24]

The 2.2862(3) Å Ru−Ru bond length of Ru$_2$(Fap)$_4$Cl is slightly longer than the 2.275(3) Å Ru−Ru bond of Ru$_2$(ap)$_4$Cl[23] and is within the range of bond lengths expected for other diruthenium(II,III) complexes with this structural type.[24,25,27] The average 2.049(2) Å Ru−N$_a$ bond length of Ru$_2$(Fap)$_4$Cl (N$_a$ = anilino nitrogen, N2, N4, N6, and N8)) is shorter than the average 2.097(2) Å Ru−N$_p$ bond (N$_p$ = pyridyl nitrogen, N1, N3, N5, and N7). A similar trend between the average Ru−N$_a$ and Ru−N$_p$ bond lengths is also observed for Ru$_2$(Fap)$_4$(NO)Cl, and both results are consistent with the fact that the negative charge of the Fap$^-$ anionic ligands resides primarily on the amino nitrogen. Also, the average Ru(1)−N bond length of Ru$_2$(Fap)$_4$Cl is 0.05 Å larger than the average Ru(2)−N bond length, and this elongation can be related to the lack of an axial ligand on the Ru2 atom, which allows the four equatorial ligands to come closer to this Ru atom. In contrast, the average Ru(1)−N bond length of Ru$_2$(Fap)$_4$(NO)Cl is 0.03 Å shorter than the average Ru(2)−N bond.

Ru$_2$(Fap)$_4$Cl



Ru$_2$(Fap)$_4$(NO)Cl

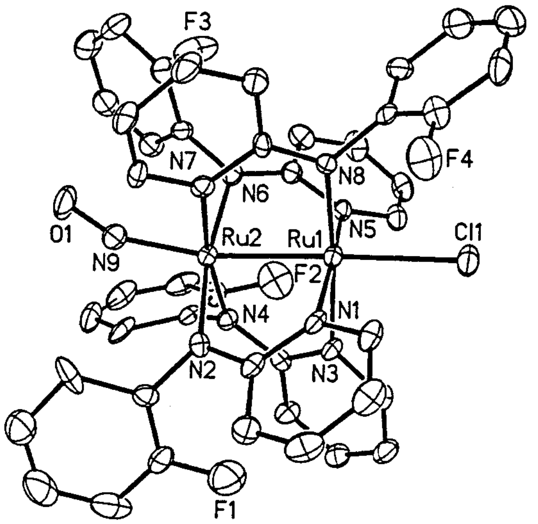


Figure 1. Thermal ellipsoid plot (40% equiprobability envelopes) of Ru$_2$(Fap)$_4$Cl and Ru$_2$(Fap)$_4$(NO)Cl. H atoms have been omitted for clarity.

Table 2. Selected Bond Lengths (Å) of Ru$_2$(Fap)$_4$Cl and Ru$_2$(Fap)$_4$(NO)Cl

Ru$_2$(Fap)$_4$Cl		Ru$_2$(Fap)$_4$(NO)Cl	
Ru(1)−Ru(2)	2.2862(3)	Ru(1)−Ru(2)	2.4203(8)
Ru(1)−Cl(1)	2.4611(7)	Ru(1)−Cl(1)	2.5882(19)
Ru(1)−N(8)	2.073(2)[a]	Ru(1)−N(8)	1.975(6)[a]
Ru(1)−N(1)	2.100(2)	Ru(1)−N(1)	2.075(6)
Ru(1)−N(5)	2.102(2)	Ru(1)−N(5)	2.051(6)
Ru(1)−N(3)	2.120(2)	Ru(1)−N(3)	2.096(6)
Ru(2)−N(4)	2.031(2)[a]	Ru(2)−N(4)	2.052(6)[a]
Ru(2)−N(2)	2.046(2)[a]	Ru(2)−N(2)	2.050(6)[a]
Ru(2)−N(6)	2.046(2)[a]	Ru(2)−N(6)	2.094(6)[a]
Ru(2)−N(7)	2.064(2)	Ru(2)−N(7)	2.108(6)
		Ru(2)−NO	1.869(6)
		O(1)−N(9)	1.164(8)

[a] Ru−N$_a$ (anilino nitrogen) bond lengths.

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Table 3. Selected Bond Angles (deg) and Torsion Angles (deg) of $Ru_2(Fap)_4Cl$ and $Ru_2(Fap)_4(NO)Cl$

$Ru_2(Fap)_4Cl$		$Ru_2(Fap)_4(NO)Cl$	
Bond Angles			
Ru(2)−Ru(1)−Cl(1)	179.62(2)	Ru(2)−Ru(1)−Cl(1)	178.37(5)
N(6)−Ru(2)−Ru(1)	90.33(6)	N(6)−Ru(2)−Ru(1)	83.92(16)
N(4)−Ru(2)−Ru(1)	90.88(6)	N(4)−Ru(2)−Ru(1)	87.40(16)
N(2)−Ru(2)−Ru(1)	89.47(6)	N(2)−Ru(2)−Ru(1)	86.89(16)
N(7)−Ru(2)−Ru(1)	90.19(6)	N(7)−Ru(2)−Ru(1)	83.44(16)
N(8)−Ru(1)−Ru(2)	88.46(6)	N(8)−Ru(1)−Ru(2)	89.94(16)
N(1)−Ru(1)−Ru(2)	88.92(6)	N(1)−Ru(1)−Ru(2)	87.68(16)
N(5)−Ru(1)−Ru(2)	87.89(6)	N(5)−Ru(1)−Ru(2)	88.39(16)
N(3)−Ru(1)−Ru(2)	87.11(6)	N(3)−Ru(1)−Ru(2)	85.99(16)
		O(1)−N(9)−Ru(2)	155.8(6)
		N(9)−Ru(2)−Ru(1)	169.49(19)
Torsion Angles			
N(1)−Ru(1)−Ru(2)−N(2)	17.58(8)	N(1)−Ru(1)−Ru(2)−N(2)	18.8(2)
N(3)−Ru(1)−Ru(2)−N(4)	18.63(8)	N(3)−Ru(1)−Ru(2)−N(4)	21.7(2)
N(5)−Ru(1)−Ru(2)−N(6)	18.47(8)	N(5)−Ru(1)−Ru(2)−N(6)	24.5(2)
N(8)−Ru(1)−Ru(2)−N(7)	15.86(8)	N(8)−Ru(1)−Ru(2)−N(7)	22.6(2)

The coordination of each ruthenium atom in $Ru_2(Fap)_4(NO)Cl$ is essentially octahedral with four Fap nitrogen atoms forming the equatorial planes. The 2.4203(8) Å Ru−Ru bond length in $Ru_2(Fap)_4(NO)Cl$ is longer than the 2.2862(3) Å Ru−Ru bond of $Ru_2(Fap)_4Cl$, thus suggesting that the bond order decreases upon going from $Ru_2(Fap)_4Cl$ to $Ru_2(Fap)_4(NO)Cl$. An elongation of the Ru−Ru bond is also observed upon addition of NO to the previously investigated diruthenium(II,II) complexes $Ru_2(O_2CR)_4$ (R = C_2H_5 or CF_3),[16] where the Ru−Ru bonds of both $Ru_2(O_2CR)_4(NO)_2$ complexes (R = C_2H_5 or CF_3) are approximately 0.25 Å longer than those of the related $Ru_2(O_2CR)_4$ parent complexes. One might therefore expect to see an increase of about 0.125 Å in the Ru−Ru bond for each nitrosyl group bound to the diruthenium core, and this is consistent with the structural data of $Ru_2(Fap)_4(NO)Cl$ and $Ru_2(Fap)_4Cl$ where the Ru−Ru distance in the NO derivative is 0.134 Å longer than that of its parent compound.

Both $Ru_2(Fap)_4(NO)Cl$ and $Ru_2(Fap)_4Cl$ have linear Ru−Ru−Cl angles (178.4° and 179.6°, respectively), but the Ru−Cl bond of $Ru_2(Fap)_4(NO)Cl$ is 0.127 Å longer than that of $Ru_2(Fap)_4Cl$. An elongation of the Ru−Cl bond is predicted when a second axial ligand binds trans to the Cl^- anion, and an abnormally long Ru−Cl bond distance of 2.705(2) Å has also been reported for $Ru_2(hpp)_4Cl_2$.[28]

The Ru−N−O and Ru−Ru−N(O) angles in $Ru_2(Fap)_4(NO)Cl$ are 155.8° and 169.5°, respectively. The Ru(2)−N(6) and Ru(2)−N(7) bonds in $Ru_2(Fap)_4(NO)Cl$ are on the average 0.05 Å longer than the Ru(2)−N(4) and Ru(2)−N(2) bonds, while the N(6)−Ru(2)−Ru(1) and N(7)−Ru(2)−Ru(1) bond angles are on the average 3.5° smaller than the N(2)−Ru(2)−Ru(1) and N(4)−Ru(2)−Ru(1) bond angles. These structural differences are not observed for $Ru_2(Fap)_4Cl$ maybe because the NO group bends toward the nitrogen atoms N7 and N6, most likely to avoid some steric hindrance with the other anilino groups. The binding of NO to $Ru_2(Fap)_4Cl$ also leads to structural changes of the $Ru_2(Fap)_4$ framework. The average Ru(2)−N bond distance in $Ru_2(Fap)_4(NO)Cl$ is 0.03 Å larger than the average Ru(2)−N bond distances in $Ru_2(Fap)_4Cl$, while the average Ru(1)−N bond distance in $Ru_2(Fap)_4(NO)Cl$ is 0.05 Å shorter than the average Ru(1)−N bond distance in $Ru_2(Fap)_4Cl$.

In addition, as shown in Table 3, the arrangement of the four equatorial ligands in $Ru_2(Fap)_4(NO)Cl$ leads to large torsion angles about the Ru−Ru bond; the N(5)−Ru(1)−Ru(2)−N(6) and N(8)−Ru(1)−Ru(2)−N(7) torsion angles average 23.6°, whereas the N(1)−Ru(1)−Ru(2)−N(2) and N(3)−Ru(1)−Ru(2)−N(4) angles average 20.3°. These values are on average 4.3° larger than similar torsion angles in $Ru_2(Fap)_4Cl$ and is most likely due to some steric hindrance between the NO axial ligand and the $Ru_2(Fap)_4$ framework.

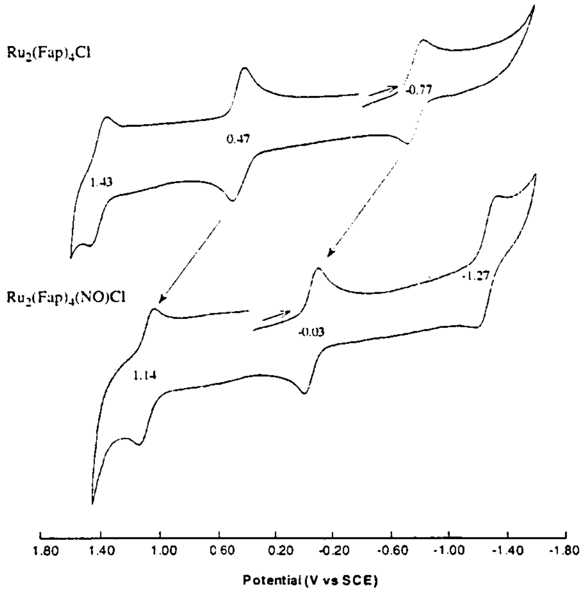

Figure 2. Cyclic voltammograms of $Ru_2(Fap)_4Cl$ and $Ru_2(Fap)_4(NO)Cl$ in CH_2Cl_2, 0.1 M TBAP. Scan rate is 0.1 V/s.

Electrochemistry. Cyclic voltammograms of $Ru_2(Fap)_4Cl$ and $Ru_2(Fap)_4(NO)Cl$ in CH_2Cl_2 containing 0.1 M TBAP are shown in Figure 2. $Ru_2(Fap)_4Cl$ exhibits a single reversible one-electron reduction and two reversible one-electron oxidations, while $Ru_2(Fap)_4(NO)Cl$ is characterized by two reversible one-electron reductions and a single reversible one-electron oxidation within the potential limit of the solvent. The nitrosyl complex is harder to oxidize by 670 mV and easier to reduce by 740 mV than the parent compound $Ru_2(Fap)_4Cl$. Similar shifts in potentials have been reported between oxidation or reduction of $Ru_2(O_2CR)_4(NO)_2$ and $Ru_2(O_2CR)_4$ (R = C_2H_5 or CF_3),[27] and this can be accounted for by the ability of the NO ligand to accept delocalized π electron density onto its π^* orbital. This back-donation will shift electron density away from the diruthenium core, thus stabilizing the lower oxidation states of the compound.[29]

Infrared Spectroelectrochemistry. The infrared spectrum of $Ru_2(Fap)_4(NO)Cl$ in CH_2Cl_2, 0.1 M TBAP exhibits a ν_{NO} band at 1740 cm^{-1}, while the diruthenium species produced after controlled-potential reduction at −0.45 V in a thin-layer cell is characterized by a ν_{NO} band at 1669 cm^{-1} (see Figure 3). The spectral changes upon reduction are reversible, and the IR spectrum of $Ru_2(Fap)_4(NO)Cl$ can be regenerated upon controlled-potential oxidation at 0.20 V in the thin-layer cell. This result indicates that the electroreduced form of $Ru_2(Fap)_4(NO)Cl$ is stable on the experimental time scale and that the NO group remains bound to the complex after reduction.

When $Ru_2(Fap)_4(NO)Cl$ is reduced by one electron, the increased electron density on the ruthenium core leads to an increased back-donation from the π(Ru) to the π^*(NO) orbital, thus resulting in a smaller value of ν_{NO}. The shift of 71 cm^{-1}

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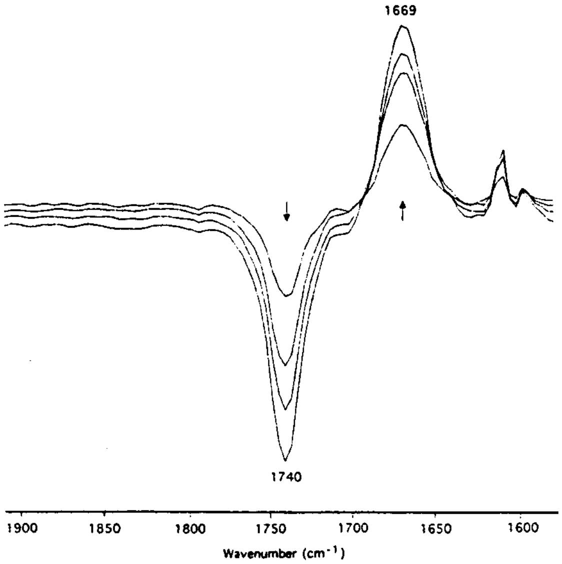

Figure 3. Thin-layer FTIR spectra obtained during electrolysis of $Ru_2(Fap)_4(NO)Cl$ at an applied potential of −0.45 V in CH_2Cl_2, 0.1 M TBAP. The background is the IR spectrum of the compound when no potential is applied to the thin-layer cell.

in ν_{NO} upon going from the neutral to the singly reduced form of $Ru_2(Fap)_4(NO)Cl$ is consistent with a reduction of the diruthenium core because a larger shift of approximately 300 cm^{-1} would be expected if the addition of the electron occurred on the NO axial ligand.[30]

Electronic Configuration. The magnetic moment of $Ru_2(Fap)_4Cl$, measured by the Evans method, is 3.91 μ_B, which corresponds to three unpaired electrons in the compound. This result is consistent with a ground-state electronic configuration of $(\sigma)^2(\pi)^4(\delta)^2(\pi^*\delta^*)^3$ for the Ru_2^{5+} core. The relative ordering and energy difference between the π^* and δ^* orbitals of diruthenium complexes will depend on several parameters, including the diruthenium oxidation state, the type of bridging ligands, and the type and number of axial ligands. Indeed, the δ and δ^* orbitals can both be destabilized via interaction with the filled orbitals of the bridging ligands that are of suitable symmetry. $Ru_2(O_2CR_4)Cl$, where R is an alkyl group, is known[31] to have the electronic configuration $(\sigma)^2(\pi)^4(\delta)^2(\pi^*)^2(\delta^*)^1$. In addition, structural and spectroscopic studies of $Ru_2(admp)_4Cl$, where admp is the 2-amino-4,6-dimethylpyridinate anion, have shown that a stepwise substitution of each acetato ligand in $Ru_2(O_2CR)_4Cl$ by the nitrogen-donor anionic admp ligand results in a destabilization of the δ^* orbital.[32] Therefore, one would expect the energy gap between the δ^* and π^* orbitals to increase upon going from $Ru_2(O_2CCH_3)_4Cl$ to $Ru_2(Fap)_4Cl$. Thus, $Ru_2(Fap)_4Cl$ has the electronic configuration $(\sigma)^2(\pi)^4(\delta)^2(\pi^*)^2(\delta^*)^1$, or $(\sigma)^2(\pi)^4(\delta)^2(\pi^*)^3$ if the $\pi^*-\delta^*$ gap becomes very large. The fact that $Ru_2(Fap)_4Cl$ contains three unpaired electrons is not consistent with the electronic configuration $(\sigma)^2(\pi)^4(\delta)^2(\pi^*)^3$, and therefore, $Ru_2(Fap)_4Cl$ has the electronic configuration $(\sigma)^2(\pi)^4(\delta)^2(\pi^*)^2(\delta^*)^1$ with a bond order of 2.5 for the diruthenium unit.

The presence of a linear Ru−N−O group on $Ru_2(Fap)_4(NO)Cl$ would result in a formal one-electron reduction of the diruthenium core,[33] thus leading to a $Ru_2^{II,II}(NO^+)$ complex with the electronic configuration $(\sigma)^2(\pi)^4(\delta)^2(\pi^*)^3(\delta^*)^1$, while the presence of a bent Ru−N−O group would result in a formal one-electron oxidation of the diruthenium core and a $Ru_2^{III,III}(NO^-)$ complex with the electronic configuration $(\sigma)^2(\pi)^4(\delta)^2(\pi^*)^2$. The NO stretching frequency at 1740 cm^{-1} may be interpreted in terms of either a linear or a bent Ru−N−O group. However, the X-ray structural data show an elongation of the Ru−Ru bond upon going from $Ru_2(Fap)_4Cl$ (2.2862(3) Å) to $Ru_2(Fap)_4(NO)Cl$ (2.4203(8) Å), and this result is consistent with the electronic configuration $(\sigma)^2(\pi)^4(\delta)^2(\pi^*)^3(\delta^*)^1$ and a decreased bond order from 2.5 to 2 upon the addition of NO to $Ru_2(Fap)_4Cl$.

No ESR signal is observed for $Ru_2(Fap)_4(NO)Cl$, but the electroreduced form of $Ru_2(Fap)_4(NO)Cl$ exhibits a signal at 123 K characterized by $g_1 = 2.167$ and $g_2 = 1.901$. This ESR spectrum is well-defined and characteristic of a species containing one rather than three unpaired electrons because in the latter case either no signal at all or a broad and ill-resolved ESR spectrum is usually observed.[34,35] Furthermore, the signal resembles the ESR spectra[23,24] of $[Ru_2(Fap)_4(C{\equiv}CC_6H_5)_2]^-$ and $[Ru_2(dpf)_4(C{\equiv}CC_6H_5)_2]^-$, two compounds whose electronic ground states have been proposed as $(\pi)^4(\delta)^2(\pi^*)^4(\delta^*)^1$. No ^{14}N hyperfine splitting is seen in the ESR spectrum of singly reduced $Ru_2(Fap)_4(NO)Cl$, thus suggesting that the reduction of $Ru_2(Fap)_4(NO)Cl$ occurs on the diruthenium core and not on the NO ligand.[36] A similar result based on IR spectroelectrochemical measurements is also proposed. Overall, the ESR spectrum of the product obtained after reduction of $Ru_2(Fap)_4(NO)Cl$ by one electron is thus consistent with the electronic configuration $(\sigma)^2(\pi)^4(\delta)^2(\pi^*)^4(\delta^*)^1$, which also agrees with the electronic configuration $(\sigma)^2(\pi)^4(\delta)^2(\pi^*)^3(\delta^*)^1$ proposed for $Ru_2(Fap)_4(NO)Cl$. Thus, despite a Ru−N−O bond angle of 155.8°, $Ru_2(Fap)_4(NO)Cl$ may be formulated as a $Ru_2^{II,II}(NO^+)$ complex with a linear Ru−N−O group. $Ru_2(O_2CR)_4(NO)_2$ ($R = C_2H_5$ or CF_3) compounds have also been proposed to contain linear Ru−N−O groups,[16] and these two compounds have Ru−N−O angles about 3.2° smaller than that of $Ru_2(Fap)_4(NO)Cl$. The present study shows that $Ru_2(Fap)_4(NO)Cl$ still adopts a linear Ru−N−O group despite the fact that Fap is more basic than O_2CR ($R = C_2H_5$ or CF_3).

Summary

$Ru_2(Fap)_4(NO)Cl$ was synthesized by reaction between the (3,1) isomer of $Ru_2(Fap)_4Cl$ and NO. The binding of an axial NO ligand on $Ru_2(Fap)_4Cl$ results in an increase in the Ru−Ru distance along with some structural changes of the $Ru_2(Fap)_4$ framework. $Ru_2(Fap)_4(NO)Cl$ can be formally described as a diruthenium(II,II) complex with a linear Ru−N−O group. The NO ligand on $Ru_2(Fap)_4(NO)Cl$ stabilizes the lower oxidation states of the diruthenium unit, thus leading to additional reductions as compared to the parent $Ru_2(Fap)_4Cl$ complex.

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Supporting Information Available: X-ray crystallographic files in CIF format and figures for the structure determination of $Ru_2(Fap)_4Cl$ and $Ru_2(Fap)_4(NO)Cl$. This material is available free of charge via the Internet at http://pubs.acs.org.

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