

# Synthesis, Molecular Structure, and Electrochemistry of a Paramagnetic Diruthenium(III) Complex. Characterization of $\text{Ru}_2(\text{hpp})_4\text{Cl}_2$ , Where hpp Is the 1,3,4,6,7,8-Hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidinate Ion

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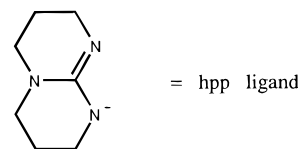
## Introduction

A number of diruthenium complexes containing different axial and equatorial ligands have been synthesized and characterized in the literature.<sup>1–15</sup> In general, the thermodynamically preferred oxidation state is  $\text{Ru}_2^{5+}$  for most complexes,<sup>1–7</sup> but several  $\text{Ru}_2^{4+}$  and  $\text{Ru}_2^{6+}$  complexes have also been isolated.<sup>8–15</sup> The electronic structures of these diruthenium compounds have provided interesting challenges to the development of metal–metal bonding theory. The orbitals that arise primarily from overlap of the metal d orbitals are  $\sigma$ ,  $\pi$  and  $\delta$  bonding ones (which follow that order of increasing energy) and their antibonding counterparts  $\sigma^*$ ,  $\pi^*$ , and  $\delta^*$ .<sup>1–4,8–11</sup> There is no doubt that the  $\sigma^*$  orbital is always well above the  $\pi^*$  and  $\delta^*$  orbitals for  $\text{Ru}_2^{6+}$ ,  $\text{Ru}_2^{5+}$ , and  $\text{Ru}_2^{4+}$  complexes, but the relative ordering and energy differences between the  $\pi^*$  and  $\delta^*$  orbitals will vary as a function of the diruthenium oxidation state, the type of bridging ligands and the type and number of axial ligands.

Three different energy level orderings are known for the  $\pi^*$  and  $\delta^*$  orbitals of  $\text{Ru}^{\text{II}}\text{Ru}^{\text{III}}$  and  $\text{Ru}^{\text{II}}_2$  derivatives.<sup>1–4,8–11</sup> These are as follows: (1)  $\pi^* \approx \delta^*$ , (2)  $\pi^* \ll \delta^*$ , and (3)  $\pi^* \gg \delta^*$ . The  $\pi^*$  and  $\delta^*$  orbitals of most diruthenium(II,III) complexes are nearly degenerate (case 1), and this gives an electronic configuration of  $(\sigma)^2(\pi)^4(\delta)^2(\delta^*\pi^*)^3$  with three unpaired electrons.<sup>1–4</sup> Some diamagnetic diruthenium(II,II) complexes have  $\pi^* \ll \delta^*$  (case 2) and a  $(\sigma)^2(\pi)^4(\delta)^2(\pi^*)^4$  configuration,<sup>8,9</sup> while others with strong metal–metal bonding interactions have an electronic configuration of  $(\sigma)^2(\pi)^4(\delta)^2(\delta^*)^2(\pi^*)^2$  with two unpaired electrons<sup>10,11</sup> and  $\pi^* \gg \delta^*$  (case 3).

Less is known about the electronic configuration of diruthenium(III) complexes since there are only four reported examples of  $\text{Ru}_2^{6+}$  species bridged by four equatorial ligands.<sup>12–16</sup> Three of these compounds,  $\text{Ru}_2(\text{dpf})_4(\text{C}\equiv\text{CC}_6\text{H}_5)_2$ ,<sup>12</sup> the 4,0 isomer of  $\text{Ru}_2(\text{pfap})_4(\text{C}\equiv\text{CC}_6\text{H}_5)_2$ ,<sup>13</sup> and  $\text{Ru}_2(\text{dpf})_4(\text{CN})_2$ <sup>14</sup> have monovalent bridging ligands<sup>17</sup> and are diamagnetic while the fourth,  $\text{K}_2[\text{Ru}_2(\text{SO}_4)_4(\text{H}_2\text{O})_2]$ ,<sup>15,16</sup> has divalent  $\text{SO}_4^{2-}$  bridging ligands and is paramagnetic with four unpaired electrons. The three diamagnetic complexes contain two axial ligands having  $\sigma$  donor and  $\pi$  acceptor properties. The exact electronic configuration of these species is not clear but they are unambiguously diamagnetic as determined by NMR spectroscopy and magnetic susceptibility measurements.<sup>12–14</sup> This contrasts with  $\text{K}_2[\text{Ru}_2(\text{SO}_4)_4(\text{H}_2\text{O})_2]$  which has the electronic configuration of  $(\sigma)^2(\pi)^4(\delta)^1(\pi^*)^2(\delta^*)^1$ , indicating that the  $\delta$ ,  $\pi^*$  and  $\delta^*$  orbitals are nearly degenerate.<sup>15,16</sup>

In this present paper, we report the first synthesis and characterization of a paramagnetic diruthenium(III) complex having two unpaired electrons. The investigated compound, represented by  $\text{Ru}_2(\text{hpp})_4\text{Cl}_2$ , where hpp = 1,3,4,6,7,8-hexahydro-



dro-2*H*-pyrimido[1,2-*a*]pyrimidinate ion, was characterized by X-ray single-crystal diffraction, electrochemistry, ESR, and UV–visible spectroscopy. Its unique paramagnetic feature is consistent with a ground-state electronic configuration of either  $(\sigma)^2(\pi)^4(\delta)^2(\pi^*)^2$  or  $(\sigma)^2(\pi)^4(\delta)^2(\pi^*)^1(\delta^*)^1$ .

## Experimental Section

**Chemicals and Reagents.**  $\text{CH}_2\text{Cl}_2$  was obtained as HPLC grade from Fisher Scientific Co. and distilled over phosphorus pentoxide ( $\text{P}_2\text{O}_5$ ). 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. Methanol and 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine (Hhpp), purchased from Aldrich Co., were used as received.

**Physical Measurements.** UV–visible spectra were measured on a Perkin-Elmer 330 spectrophotometer. Elemental analysis was carried out by Galbraith Laboratories, Inc., Knoxville, TN. Cyclic voltammograms were obtained with an IBM Model EC 225 voltammetric analyzer. The working electrode was a platinum button with a surface area of 0.19 mm<sup>2</sup>. The reference electrode was a homemade saturated calomel electrode (SCE). A platinum wire was used as a counter electrode. Magnetic moments were determined using a Johnson Matthey Model MSG-1 magnetic susceptibility balance.

**Synthesis of  $\text{Ru}_2(\text{hpp})_4\text{Cl}_2$ .** A 0.30 g (ca. 0.64 mmol) sample of  $\text{Ru}_2(\text{CH}_3\text{COO})_4\text{Cl}$  was mixed with 1.5 g (ca. 10.8 mmol) of Hhpp under an argon atmosphere. The mixture was first dried under vacuum for about 30 min and then heated to 150 °C under Ar for 10 h. Excess Hhpp ligand was sublimed under vacuum at 120 °C, and the residue, which was dark green, was purified on an alumina column using  $\text{CH}_3\text{OH}/\text{CH}_2\text{Cl}_2$  (1:9) as eluent. The green band was collected in a yield of 40%. The compound was found to be soluble in most common organic solvents with the exception of pure hexane or methanol. Single crystals suitable for X-ray analysis were obtained by slow diffusion of *n*-hexane into a  $\text{CH}_2\text{Cl}_2$  solution of  $\text{Ru}_2(\text{hpp})_4\text{Cl}_2$ . Anal. Calcd for  $\text{C}_{28}\text{H}_{48}\text{N}_{12}\text{Cl}_2\text{Ru}_2$ : C, 40.68; H, 5.81; N, 20.34; Cl, 8.60. Found: C,

- (1) Stephenson, T. A.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1966**, *28*, 2285.
- (2) Cotton, F. A.; Ren, T. *Inorg. Chem.* **1995**, *34*, 3190.
- (3) Charkravarty, A. R.; Cotton, F. A.; Tocher, D. A. *Inorg. Chem.* **1985**, *24*, 172.
- (4) Charkravarty, A. R.; Cotton, F. A. *Inorg. Chim. Acta.* **1986**, *113*, 19.
- (5) Cotton, F. A.; Pedersen, E. *Inorg. Chem.* **1975**, *14*, 388.
- (6) Malinski, T.; Chang, D.; Feldmann, F. N.; Bear, J. L.; Kadish, K. M. *Inorg. Chem.* **1983**, *22*, 3225.
- (7) Chavan, M. Y.; Feldmann, F. N.; Lin, X. Q.; Bear, J. L.; Kadish, K. M. *Inorg. Chem.* **1984**, *23*, 2373.
- (8) Cotton, F. A.; Ren, T. *Inorg. Chem.* **1991**, *30*, 3675.
- (9) Cotton, F. A.; Matusz, M. *J. Am. Chem. Soc.* **1988**, *110*, 5761.
- (10) Cotton, F. A.; Ren, T.; Eglin, J. L. *Inorg. Chem.* **1991**, *30*, 2552.
- (11) Cotton, F. A.; Ren, T.; Eglin, J. L. *J. Am. Chem. Soc.* **1990**, *112*, 3439.
- (12) Bear, J. L.; Han, B. C.; Huang, S. R. *J. Am. Chem. Soc.* **1993**, *115*, 1175.
- (13) Li, Y. L.; Han, B. C.; Bear, J. L.; Kadish, K. M. *Inorg. Chem.* **1993**, *32*, 4175.
- (14) Bear, J. L.; Han, B. C.; Huang, S. R.; Van Caemelbecke, E.; Kadish, K. M. *Inorg. Chem.*, in press.
- (15) Kuz'menko, I. V.; Zhilyaev, A. N.; Fomina, T. A.; Porai-Koshits, M. A.; Baranovskii, I. B. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1989**, *34*, 1457.

- (16) Cotton, F. A.; Datta, T.; Labella, L.; Shang, M. Y. *Inorg. Chim. Acta* **1993**, *203*, 55.
- (17) dpf = *N,N'*-diphenylformamidinate and pfap = 2,3,4,5,6-pentafluoro-2-anilino-pyridinate.

**Table 1.** X-ray Data Collection and Processing Parameters for Ru<sub>2</sub>(hpp)<sub>4</sub>Cl<sub>2</sub>

space group	<i>I4/m</i> (tetragonal)
cell const	
<i>a</i> , Å	9.984(1)
<i>c</i> , Å	15.947(3)
<i>V</i> , Å <sup>3</sup>	1590
mol formula	C <sub>28</sub> H <sub>48</sub> N <sub>12</sub> Cl <sub>2</sub> Ru <sub>2</sub>
fw	825.92
<i>Z</i>	2
$\rho$ , g/cm <sup>3</sup>	1.73
$\mu$ , cm <sup>-1</sup>	11.42
$\lambda$ , (Mo K $\alpha$ ), Å	0.710 73
collen range, deg	4 $\leq$ 2 $\theta$ $\leq$ 60
temp, °C	-50
<i>R</i> <sup>a</sup>	0.033
<i>R</i> <sub>w</sub> <sup>b</sup>	0.038

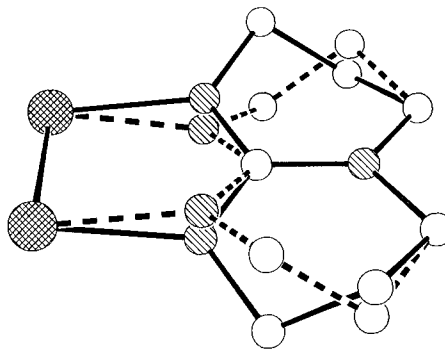
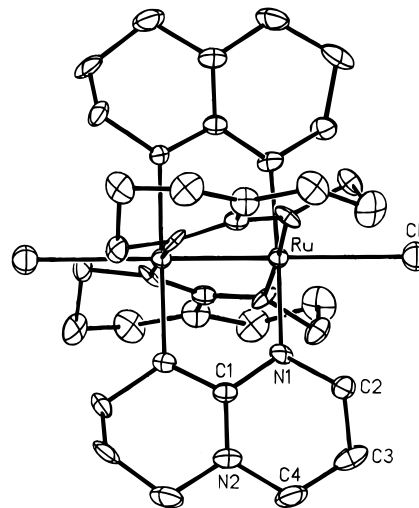
$$^a R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, \quad ^b R_w = \frac{[\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}}{}$$

40.86; H, 5.94; N, 18.57; Cl, 9.57. UV-visible data in CH<sub>2</sub>Cl<sub>2</sub> [ $\lambda$ , nm]: 430, 610, and 770.

**X-ray Crystallography.** A very dark green octahedron having approximate dimensions 0.25  $\times$  0.25  $\times$  0.30 mm was mounted in a random orientation on a Nicolet R3m/V automatic diffractometer. Since the crystals were potentially air-sensitive, the sample was placed in a stream of dry nitrogen gas at -50 °C. The radiation used was Mo K $\alpha$  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 4/*m*, and from the systematic absences noted the space group was shown to be *I4*, *I* $\bar{4}$ , or *I4/m*. Intensities were measured using the  $\omega$  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, as well as a semiempirical absorption correction based on  $\psi$  scans of 10 reflections having  $\chi$  values between 70 and 90 °C.

Since the unitary structure factors displayed acentric statistics, space group *I4/m* was initially ruled out, and space group *I4* was randomly chosen from the remaining two possibilities. 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 found 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. It was noted that, although the four ligands all seemed to have the same chirality, the anisotropic thermal parameters of several of the atoms (including both N1 types) were extremely large, as if some type of disorder were present. Most of the chemically equivalent bond lengths showed quite large differences, and the N-Ru-Ru-N torsion angle of 0° did not make sense for this type of molecule, reinforcing the possibility that the N1 type atoms were really "average" positions. Therefore, the model was shifted and the space group converted to *I* $\bar{4}$  to see if the disorder could be removed. This refinement led to a similar *R* value and somewhat better agreement between equivalent bonds. However the obvious disorder of the ligands remained. Attempts at ab initio structure solution in this space group produced no change whatsoever. Since the noncentrosymmetric space groups were giving less than desirable geometries (albeit great *R* values), it was decided to try refinement in *I4/m*. This refinement clarified the nature of the disorder substantially, gave similar *R* values, and dramatically improved the agreement between the chemically equivalent bonds. It was still necessary to apply mild distance constraints to some of the disordered atoms however, and the heavily disordered hydrogens had to be omitted. The asymmetric unit in this case consists of 1/8 molecule situation about a 4/*m* site, and the N1, C2, and C3 atoms were refined with 50% occupancy at two different locations. A view of the disordered model used is shown in Figure 1.

Thus, after exhaustive refinement in all three possible space groups, the *R* values were virtually the same and the disorder could not be

**Figure 1.** View of one ligand showing the disordered model used.**Figure 2.** View of the molecule showing the atom labeling scheme. Thermal ellipsoids are 30% equiprobability envelopes, and hydrogens are omitted. Only one orientation of each disordered ligand is shown.**Table 2.** Selected Bond Lengths (Å) and Angles (deg) for Ru<sub>2</sub>(hpp)<sub>4</sub>Cl<sub>2</sub><sup>a</sup>

Bond Lengths			
Ru-Cl	2.705(2)	Ru-RuA	2.321(1)
Ru-N1	2.045(5)	Ru-N1'	2.063(5)
N1-C1	1.332(6)	N1-C2	1.475(9)
N1'-C1	1.352(5)	N1'-C2'	1.493(9)
N2-C1	1.363(7)	N2-C4	1.468(6)
C2-C3	1.516(18)	C3-C4	1.500(14)
C2'-C3'	1.516(14)	C3'-C4	1.500(12)
Bond Angles			
C1-Ru-N1	91.6(1)	C1-RuN1'	90.2(1)
C1-Ru-RuA	180.0	N1-Ru-RuA	88.4(1)
N1'-Ru-RuA	89.8(1)	N1-Ru-N1B	176.9(3)
N1-Ru-N1C	90.0(1)	N1'-Ru-N1'B	179.5(2)
N1'-Ru-N1'C	90.0(1)	Ru-N1-C1	121.2(4)
Ru-N1-C2	124.2(4)	C1-N1-C2	114.6(5)
Ru-N1'-C1	118.8(4)	Ru-N1'-C2'	121.9(4)
C1-N1'-C2'	119.2(5)	C1-N2-C4	122.7(2)
C4-N2-C4A	114.5(5)	N1-C1-N2	121.7(3)
N1'-C1-N2	119.8(5)	N1'-C1-N1'A	116.9(5)
N1-C1-N1A	112.1(6)	N1-C2-C3	111.4(8)
C2-C3-C4	104.6(8)	N1'-C2'-C3'	106.7(6)
N2-C3-C3'	111.7(5)	N2-C4-C3	112.7(7)

<sup>a</sup> The disordered sites for atoms N1, C2, and C3 are indicated by primed and unprimed atom numbers.

removed. Since the *I4/m* refinement produced the best anisotropic thermal parameters and the fewest high correlations in the least squares (namely zero), in the end this space group was selected. After all shift/esd ratios were less than 0.1 convergence was reached at the agreement factors listed in Table 1. No unusually high correlations 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

**Table 3.** Selected Properties of Diruthenium(III) Compounds

compound	unpaired electrons	Ru–Ru dist, Å	Ru–Ru–L angle, deg	half-wave potentials, V vs SCE <sup>a</sup>			ref <sup>b</sup>
				Ru <sub>2</sub> <sup>7+</sup> /Ru <sub>2</sub> <sup>6+</sup>	Ru <sub>2</sub> <sup>6+</sup> /Ru <sub>2</sub> <sup>5+</sup>	Ru <sub>2</sub> <sup>5+</sup> /Ru <sub>2</sub> <sup>4+</sup>	
Ru <sub>2</sub> (hpp) <sub>4</sub> Cl <sub>2</sub>	2	2.321(1)	180.0	0.55	–0.60		tw
Ru <sub>2</sub> (pfap) <sub>4</sub> (C≡CC <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	0	2.441(1)	171.4	0.90	–0.05	–1.18	13
Ru <sub>2</sub> (dpf) <sub>4</sub> (CN) <sub>2</sub>	0	2.539(1)	160.3		–0.25	–1.34 <sup>c</sup>	14
Ru <sub>2</sub> (dpf) <sub>4</sub> (C≡CC <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	0	2.556(1)	159.8	0.73	–0.61	–1.54	12

<sup>a</sup> All potentials were measured in CH<sub>2</sub>Cl<sub>2</sub> containing 0.1 M TMAP. <sup>b</sup> tw = this work. <sup>c</sup> Cathodic peak potential,  $E_{pc}$ , at a scan rate of 100 mV/s.

peak of about 0.6 e/Å<sup>3</sup>. All calculations were made using Nicolet's SHELXTL PLUS (1987) series of crystallographic programs.

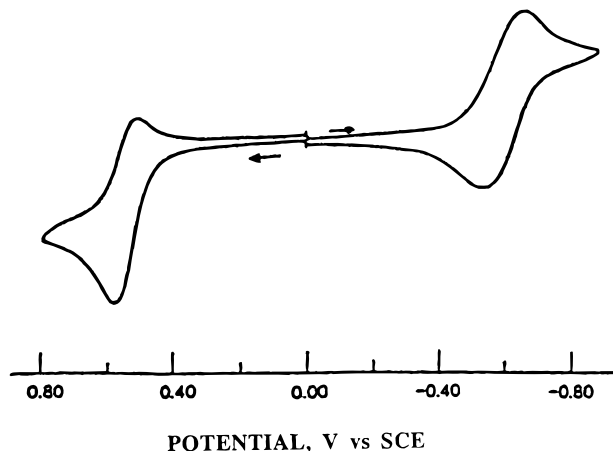
## Results and Discussion

The structure of Ru<sub>2</sub>(hpp)<sub>4</sub>Cl<sub>2</sub> is given in Figure 2, and selected bond lengths and angles of this compound are summarized in Table 2. The coordination about each Ru atom is essentially octahedral with four hpp nitrogens (average Ru–N = 2.054 Å) forming the equatorial plane. The Ru–Ru bond distance of 2.321(1) Å is quite short compared to diamagnetic diruthenium(III) complexes whose distances range from 2.451 to 2.556 Å (see Table 3) but it is of comparable length to the 2.343 Å found in K<sub>2</sub>[Ru<sub>2</sub>(SO<sub>4</sub>)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>],<sup>15,16</sup> a compound with four unpaired electrons. The Ru–Cl distance of 2.705(2) Å in Ru<sub>2</sub>(hpp)<sub>4</sub>Cl<sub>2</sub> is extraordinarily long compared to diruthenium complexes containing a single Cl<sup>–</sup> axial ligand (2.412–2.558 Å)<sup>2,3,14</sup> and this may be due to a significant trans influence in Ru<sub>2</sub>(hpp)<sub>4</sub>Cl<sub>2</sub> which results in weak Ru–Cl interactions. No other diruthenium(III) complexes with two axial chloride ligands have ever been reported and therefore comparisons of Ru–Cl distances can only be made with diruthenium(II,III) compounds containing a single Cl<sup>–</sup> axial ligand, such as in the case of Ru<sub>2</sub>(dpf)<sub>4</sub>Cl which has a Ru–Cl bond distance of 2.414(2) Å.<sup>14</sup>

The short Ru–Ru bond distance of 2.321(1) Å in Ru<sub>2</sub>(hpp)<sub>4</sub>Cl<sub>2</sub> is not unusual if one considers that the theoretically predicted bond orders for Ru<sub>2</sub><sup>4+</sup>, Ru<sub>2</sub><sup>5+</sup>, and Ru<sub>2</sub><sup>6+</sup> complexes are 2, 2.5, and 3, respectively.<sup>18</sup> Thus, it is the diamagnetic rather than the paramagnetic complexes of Ru<sub>2</sub><sup>6+</sup> which show unusual Ru–Ru bond distances. In addition, the distortion in octahedral symmetry observed for diamagnetic Ru<sub>2</sub><sup>6+</sup> complexes is not present in Ru<sub>2</sub>(hpp)<sub>4</sub>Cl<sub>2</sub> where the Ru–Ru–Cl bond angle is 180.0° as opposed to 159.8–168.5° for the other derivatives (see Table 3). It thus appears that the metal–metal bond distances and the Ru–Ru–ligand bond angles of diruthenium(III) complexes will both vary widely depending on the nature of the equatorial and axial ligands.

The room temperature magnetic susceptibility of Ru<sub>2</sub>(hpp)<sub>4</sub>Cl<sub>2</sub> in the solid state is 2.78 μ<sub>B</sub>, consistent with two unpaired electrons. This implies a significant energy difference between the δ orbital and the π\*, δ\* orbitals with the latter two being higher in energy. Under this condition, the electronic configuration should be either (σ)<sup>2</sup>(π)<sup>4</sup>(δ)<sup>2</sup>(π\*)<sup>2</sup> or (σ)<sup>2</sup>(π)<sup>4</sup>(δ)<sup>2</sup>(π\*)<sup>1</sup>(δ\*)<sup>1</sup>. A related dioxmium complex, Os<sub>2</sub>(DFM)<sub>4</sub>Cl<sub>2</sub> (where DFM = di-*p*-tolylformamidinate), has been suggested to have the electronic configuration (σ)<sup>2</sup>(π)<sup>4</sup>(δ)<sup>2</sup>(π\*)<sup>2</sup> with two unpaired electrons in the π\* orbitals<sup>19</sup> while a ground state electronic configuration of (σ)<sup>2</sup>(π)<sup>4</sup>(δ)<sup>1</sup>(π\*)<sup>2</sup>(δ\*)<sup>1</sup> has been proposed for the related paramagnetic diruthenium(III) complex, K<sub>2</sub>[Ru<sub>2</sub>(SO<sub>4</sub>)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>].<sup>15,16</sup>

The electronic structures of Ru<sub>2</sub>(dpf)<sub>4</sub>(C≡CC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>, Ru<sub>2</sub>(dpf)<sub>4</sub>(CN)<sub>2</sub>, and the (4,0) isomer of Ru<sub>2</sub>(pfap)<sub>4</sub>(C≡CC<sub>6</sub>H<sub>5</sub>)<sub>2</sub> are not clear. The Ru–Ru bond distances in these diamagnetic complexes (see Table 3) are more consistent with a single bond



**Figure 3.** Cyclic voltammogram of Ru<sub>2</sub>(hpp)<sub>4</sub>Cl<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub> containing 0.1 M TBAP. Scan rate = 0.1 V/s.

than with the expected triple bond<sup>18</sup> and the ESR spectra of their electrogenerated radical anions<sup>12–14</sup> (singly reduced forms) strongly suggest a SOMO of δ\* symmetry.<sup>20</sup> The structural and ESR data of these species are consistent with two electronic configurations, either (σ)<sup>2</sup>(π)<sup>4</sup>(π\*)<sup>4</sup> or (π)<sup>4</sup>(δ)<sup>2</sup>(π\*)<sup>4</sup>. A number of factors could be responsible for the different electronic configurations among the Ru<sub>2</sub><sup>6+</sup> complexes. The most probable is that the diamagnetic complexes contain axial ligands with both σ donor and π acceptor properties on each ruthenium atom<sup>12–14</sup> whereas the axial ligands of the paramagnetic complexes are only weak σ donors.

It should be pointed out that spin pairing is also observed for diruthenium(II,III) compounds which contain two axial π acid ligands.<sup>14</sup> For example, Ru<sub>2</sub>(dpf)<sub>4</sub>Cl contains a Ru<sub>2</sub><sup>5+</sup> core and is paramagnetic with three unpaired electrons ( $S = 3/2$ ).<sup>14</sup> Three unpaired electrons are also observed for Ru<sub>2</sub>(dpf)<sub>4</sub>(C≡CC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>.<sup>14</sup> However, the binding of a second axial phenylacetylide ligand leads to [Ru<sub>2</sub>(dpf)<sub>4</sub>(C≡CC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sup>–</sup> which has one unpaired electron ( $S = 1/2$ ).<sup>12–14</sup> We also attempted to synthesize Ru<sub>2</sub>(hpp)<sub>4</sub>(C≡CC<sub>6</sub>H<sub>5</sub>)<sub>2</sub> for comparison with Ru<sub>2</sub>(hpp)<sub>4</sub>Cl<sub>2</sub>. However, only decomposition products were obtained upon addition of LiC≡CC<sub>6</sub>H<sub>5</sub> to Ru<sub>2</sub>(hpp)<sub>4</sub>Cl<sub>2</sub>. It is likely that the [C≡CC<sub>6</sub>H<sub>5</sub>]<sup>–</sup> anion replaces not only the axial Cl<sup>–</sup> ligand but also one or more of the bridging equatorial hpp ligands.<sup>21</sup>

The cyclic voltammogram of Ru<sub>2</sub>(hpp)<sub>4</sub>Cl<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub> containing 0.1 M TBAP is shown in Figure 3. A reversible reduction is seen at  $E_{1/2} = -0.60$  V and there is also a reversible oxidation at  $E_{1/2} = 0.55$  V. Both processes involve a one-electron transfer which appears to be metal-centered, thus generating a Ru<sub>2</sub><sup>5+</sup> complex upon reduction and a Ru<sub>2</sub><sup>7+</sup> complex upon oxidation. A similar cyclic voltammogram has been reported for Os<sub>2</sub>(DFM)<sub>4</sub>Cl<sub>2</sub>.<sup>19</sup> Table 3 summarizes half-wave potentials for oxidation and reduction of the known

(18) Norman, Jr. J. G.; Renzoni, G. E.; Case, D. A. *J. Am. Chem. Soc.* **1979**, *101*, 5256.

(19) Cotton, F. A.; Ren, T.; Eglin, J. L. *Inorg. Chem.* **1991**, *30*, 2559.

(20) Yao, C. L.; Park, K. H.; Khokhar, A. R.; Jun, M. J.; Bear, J. L. *Inorg. Chem.* **1990**, *29*, 4033.

(21) Tooze, R. P.; Wilkinson, G.; Motevalli, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton. Trans.* **1986**, 2711.

diruthenium(III) compounds having four monovalent bridging ligands. The dpf and hpp ligands are more basic than the pfap ligand and this is seen in the ordering of  $E_{1/2}$  for the  $\text{Ru}_2^{6+}/\text{Ru}_2^{5+}$  process where the pfap derivative is easier to reduce.

Finally, as mentioned earlier,  $\text{Ru}_2(\text{hpp})_4\text{Cl}_2$  contains two unpaired electrons and has the configuration of  $(\sigma)^2(\pi)^4(\delta)^2(\pi^*)^2$  or  $(\sigma)^2(\pi)^4(\delta)^2(\pi^*)^1(\delta^*)^1$ . No ESR signals could be obtained for this  $\text{Ru}_2^{6+}$  derivative at room or low temperature due presumably to the zero-field splitting.<sup>22</sup> In addition, all attempts to record ESR signals of the singly oxidized species,  $[\text{Ru}_2(\text{hpp})_4\text{Cl}_2]^+$ , have to date been unsuccessful and only decomposition products with complicated cyclic voltammograms were been obtained. On the other hand,  $[\text{Ru}_2(\text{hpp})_4\text{Cl}_2]^-$  could

be generated electrochemically by reduction at a controlled potential of  $-0.80$  V. The monoanion is stable in solution but ESR silent, as is the case for  $\text{Ru}_2(\text{dpf})_4\text{Cl}$  and  $\text{Ru}_2(\text{dpf})_4(\text{C}\equiv\text{CC}_6\text{H}_5)$ ,<sup>14</sup> and its electronic configuration is consistent with  $\sigma^2\pi^4\delta^2(\pi^*\delta^*)^3$  and three unpaired electrons.

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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 a molecular packing diagram (6 pages). Ordering information is given on any current masthead page.

IC950956O

(22) Smith, K. M. *Porphyryns and Metalloporphyryns*; Elsevier Scientific Publishing Co: New York, 1975; p 582.