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Synthesis and Characterization of the Series of Compounds $Ru_2(O_2CMe)_x(admp)_{4-x}Cl$ (Hadmp = 2-Amino-4,6-dimethylpyridine, $x = 3, 2, 1, 0$)

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The reaction between $Ru_2(O_2CMe)_4Cl$ and Hadmp (Hadmp = 2-amino-4,6-dimethylpyridine) under different conditions has been investigated. By conducting the reaction in a methanol solution at room temperature the product obtained was $Ru_2(admp)(O_2CMe)_3Cl$ (**1**). In a melt reaction at 65 °C the product isolated is $Ru_2(admp)_2(O_2CMe)_2Cl$ (**2**); at 100 °C it is $Ru_2(admp)_3(O_2CMe)Cl$ (**3**); and at 140 °C it is $Ru_2(admp)_4Cl$ (**4**). The generality of these reactions was confirmed by the deliberate preparation of $Ru_2(chp)_3(O_2CMe)Cl$ (**5**) and $[Ru_2(DPhTA)_3(O_2CMe)(NCMe)_2][BF_4]$ (**6**). The structures of **1**, **2**, and **3** were determined by X-ray crystallography. The structure of **1** was determined from crystals of $\mathbf{1}\cdot 3CH_2Cl_2$ ($C_{16}H_{24}Cl_7N_2O_6Ru_2$), triclinic, $P\bar{1}$ (No. 2), with $a = 11.578(3)$ Å, $b = 12.5607(13)$ Å, $c = 20.903(3)$ Å, $\alpha = 99.927(14)°$, $\beta = 100.222(9)°$, $\gamma = 102.07(2)°$, $Z = 4$; that of **2**, from crystals of $\mathbf{2}\cdot 2.5CH_2Cl_2$ ($C_{21}H_{30}Cl_7N_4O_4Ru_2$), monoclinic, $P2_1/n$ (No. 14), with $a = 13.091(3)$ Å, $b = 19.098(4)$ Å, $c = 13.720(3)$ Å, $\beta = 105.51(3)°$; that of **3**, from crystals of $\mathbf{3}\cdot Hadmp\cdot C_6H_6$ ($C_{36}H_{46}ClN_8O_2Ru_2$), monoclinic, $P2_1/n$ (No. 14), with $a = 15.979(2)$ Å, $b = 14.9294(14)$ Å, $c = 17.131(4)$ Å, $\beta = 109.21(2)°$. The magnetic susceptibilities and electrochemistry of the four title compounds were also studied. It was observed that while compounds **1**, **2**, and **3** display magnetic moments compatible with the presence of three unpaired electrons and all yield stable one-electron oxidation products, **4** shows only one unpaired electron and the product of its one-electron oxidation decays sufficiently rapidly that no return wave is observed.

Introduction

Since the first complex containing the Ru_2^{5+} core, $Ru_2(O_2CMe)_4Cl$, was prepared over 30 years ago by Stephenson and Wilkinson,[1] many other molecules containing this core have been prepared by a variety of methods.[2] The two most common means by which the preparations have been accomplished are either the reaction between the diruthenium tetraacetate chloride and the anion of the intended ligand, in a suitable solvent, or the reaction between the same starting material and the neat ligand in either an appropriate solvent or in the molten ligand itself as the solvent.[2] While the first method described has consistently yielded the intended target product—that in which all four acetato ligands are replaced by the new ligand—on occasion, the reactions in which the nondeprotonated ligands are used lead to the formation of complexes of diruthenium containing a mixed ligand set, resulting from the incomplete substitution of the carboxylates. For example, when the melt reaction is performed using Hchp (Hchp = 2-chloro-6-hydroxypyridine) as the new ligand, the usual product is $Ru_2(chp)_4Cl$.[3a] However, when the reaction is carried out in methanol heated to reflux, $Ru_2(chp)_3(O_2CMe)Cl$ is the product isolated from this reaction.[3b] Likewise, while the reaction between the diruthenium tetracarboxylate chloride and Hap (Hap = 2-anilinopyridine) in a melt reaction results in the formation of $Ru_2(ap)_4Cl$,[3c] the same reaction performed in THF solution heated to reflux yields $Ru_2(ap)_2(O_2CMe)_2(Py\text{-}N(H)Ph)Cl$.[3b]

Complexes that retain some acetato ligands may be useful as intermediates, in which the acetates can then later be replaced by other ligands,[4] and are interesting for other reasons as well. We have investigated the reaction between $Ru_2(O_2CMe)_4Cl$ and Hadmp (Hadmp = 2-amino-4,6-dimethylpyridine) in an attempt to prepare the entire series of complexes, $Ru_2(admp)_x(O_2CMe)_{4-x}Cl$. This series of complexes offers the opportunity to study the effect of the π-basicity of the equatorial ligands on the relative ordering of the π^* and δ^* orbitals in Ru_2^{5+} complexes. It is known that the electronic ground state of Ru_2^{5+} molecules is greatly influenced by the nature of the bridging ligands because of the effect these ligands have on the gap between the π^* and δ^* orbitals. Changes in the energy gap occur because the ligands have filled orbitals of suitable symmetry to interact with the metal atom orbitals used to form the δ overlap, which leads to destabilization of both the δ and δ^* orbitals. When the $\pi^*-\delta^*$ gap is small, as it is in the great majority of Ru_2^{5+} compounds, the configuration of the 11 electrons populating the metal−metal bonding and antibonding orbital manifold is $\sigma^2\pi^4\delta^2\pi^{*2}\delta^{*1}$, which leads to molecules that, at room temperature, have three unpaired electrons and are designated as high-spin molecules. However, if the δ^* orbital moves well above the π^* orbitals, the configuration becomes $\sigma^2\pi^4\delta^2\pi^{*3}\delta^{*0}$, resulting in a low-spin molecule. We have studied the effect that the progressive raising of the δ^* orbital energy, caused by the addition of more of the $admp^-$ ligands

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to the coordination sphere of the Ru_2 unit, has on the potential at which the first oxidation of the Ru_2^{5+} unit occurs.

Experimental Section

General Procedures. All reactions were carried out under an atmosphere of dry N_2. $Ru_2(O_2CMe)_4Cl$ was prepared according to a published method.[5] Hadmp, HDPhTA (HDPhTA = 1,3-diphenyltriazene), and Hchp were purchased from the Aldrich Chemical Co. and purified by sublimation prior to use. $AgBF_4$ was also purchased from the Aldrich Chemical Co. and used as received. Solvents were dried and deoxygenated prior to use by distillation from an appropriate drying agent under an atmosphere of dry N_2. IR spectra were recorded from KBr pellets on a Perkin-Elmer 16-PC spectrophotometer.

Cyclic voltammograms (CV) were recorded on a BAS-100 electrochemical analyzer, from N_2-purged acetonitrile solutions that were 0.1 M in $[NBu_4][PF_6]$, using Pt working and auxiliary electrodes and using Ag/AgCl reference electrodes. In the system where the CV of **1**−**4** were recorded, the ferrocene/ferrocenium (Fc/Fc^+) couple appeared consistently at 625 mV and the difference between the anodic and cathodic waves (ΔE_p) was 62 mV. When the CV of **6** was recorded, a different Ag/AgCl electrode was used for which the Fc/Fc^+ couple appeared at 730 mV, while ΔE_p remained at 61 mV. In all cases the concentration of the sample used was approximately 1 mg/mL.

Magnetic susceptibilities were determined in a Johnson Matthey MSB-1 balance using a modified Gouy mechanism. Diamagnetic corrections, estimated from Pascal's constants,[6] were subtracted from the experimental susceptibilities to yield the molar paramagnetic susceptibilities from which magnetic moments were calculated. Since none of the compounds whose magnetic properties were investigated is harmed by exposure to air, the samples were handled in air.

Syntheses. $Ru_2(admp)(O_2CMe)_3Cl$ (1). In a Schlenk tube were placed 0.112 g of $Ru_2(O_2CMe)_4Cl$ and 1.0 g of Hadmp. After careful exclusion of air from the tube, 10 mL of freshly distilled methanol was added by means of a syringe. Immediately an orange solution formed that, over the course of a few hours, became green and then dark blue. The solvent was removed by evaporation at reduced pressure, and the dark residue was extracted with several portions of hot hexanes to remove unreacted Hadmp. The solid was then redissolved in CH_2Cl_2, the resulting solution was filtered, and hexanes were added to cause the formation of 0.120 g (95% yield) of a light blue solid.

Mass spectrometry (+ESI, mass, relative intensity): 1160 (10% $[2M]^+$); 1037 (15%, $[2M - Cl]^+$); 1002 (15%, $[2M - 2Cl]^+$); 499 (100%, $[M - Cl]^+$); 439 (65%, $[M - Cl - O_2CMe]^+$).

IR (cm^{-1}): 2960, s; 2925, s; 2854, m; 1620, s; 1506, m; 1450, s; 1352, m; 1301, m; 1262, s; 1094, s; 804, s; 690, s; 624, w.

Electrochemistry: $E_{1/2}$, 1106 mV; ΔE_p, 88 mV; $I_{p,a}/I_{p,c} = 0.92$. $E_{1/2}$, −439 mV; ΔE_p, 88 mV; $I_{p,a}/I_{p,c} = 0.94$.

$Ru_2(admp)_2(O_2CMe)_2Cl$ (2). Method A. This compound was prepared by a procedure similar to that used for $Ru_2(admp)(O_2CMe)_3Cl$ (**1**), except that 0.063 g of $Ru_2(O_2CMe)_4Cl$ was used and the resulting solution was heated to reflux. Yield: 0.073 g (92%).

Method B. $Ru_2(O_2CMe)_4Cl$ (0.052 g) was placed together with 0.25 g of Hadmp in a Schlenk tube equipped with a magnetic stirring bar and a finger condenser. Air was excluded by repeatedly evacuating and refilling with dry N_2. The mixture was then heated in a water bath to a temperature of 65 °C, barely above the melting point of the free Hadmp ligand. The mixture rapidly changed in appearance, from a clear liquid with a brown solid in suspension to a progressively darker green. The temperature was held for 2 h, the tube was allowed to cool, and any free acetic acid released by the reaction, evident as condensation on the finger condenser, was removed by evaporation at reduced pressure. The cycle of heating, cooling, and pumping was repeated once to ensure both completeness of reaction and that all acetic acid is removed from the mix. The mixture was then heated to 50 °C and a vacuum applied, resulting in the deposition of free Hadmp on the condenser and leaving behind a very dark residue. Finally, this residue was dissolved in 20 mL of CH_2Cl_2 and filtered, and the product was precipitated by addition of hexanes to the solution. The residue was washed with hot hexanes, and the remaining solid was redissolved in CH_2Cl_2 and precipitated with hexanes. Yield: 0.060 g (91%).

Mass spectrometry (+FAB, relative intensity): 600 (25%, M^+); 564 (75%, $[M - Cl]^+$).

IR (cm^{-1}): 2924, s; 2854, s; 1622, s; 1507, s; 1429, s; 1350, s; 1301, m; 1266, s; 1095, s; 1022, s; 801, s; 693, s; 619, w.

Electrochemistry: $E_{1/2}$, 762 mV; ΔE_p, 115 mV; $I_{p,a}/I_{p,c} = 1.01$. $E_{1/2}$, −712 mV; ΔE_p, 101 mV; $I_{p,a}/I_{p,c} = 0.92$.

$Ru_2(admp)_3(O_2CMe)Cl$ (3). This complex was prepared using Method B described above for **2**, except that 0.054 g of $Ru_2(O_2CMe)_4Cl$ and 1.0 g of Hadmp were used and the mixture was heated to 100 °C. Yield: 0.066 g (88%).

Mass spectrometry (+FAB, relative intensity): 663 (25%, M^+); 625 (100% $[M - Cl]^+$).

IR (cm^{-1}): 2924, s; 2854, s; 1620, s; 1505, s; 1431, s; 1352, s; 1301, m; 1261, s; 1094, s; 1025, s; 804, s; 690, s; 624, w; 550, w.

Electrochemistry: $E_{1/2,ox}$, 477 mV; $\Delta E_{p,ox}$, 109 mV; $I_{p,a}/I_{p,c} = 0.90$. $E_{1/2,red}$, −1002 mV; $\Delta E_{p,red}$, 99 mV; $I_{p,a}/I_{p,c} = 0.97$.

$Ru_2(admp)_4Cl$ (4). This compound was prepared in the same manner as $Ru_2(admp)_2(O_2CMe)_2Cl$, except that 0.061 g of $Ru_2(O_2CMe)_4Cl$ was used and the mixture was heated to 140 °C in an oil bath. Yield: 0.075 g (80%).

Mass spectrometry (+ESI, relative intensity): 720 (50%, M^+); 785 (20% $[M - Cl]^+$); 598 (75% $[M - admp]^+$); 562 (20% $[M - admp - Cl]^+$).

IR (cm^{-1}): 1616, s; 1567, s; 1419, s; 1921, w; 1022, w; 668, m.

Electrochemistry: only an anodic current due to an oxidation was observed at $E_{p,a} = 1480$ mV.

$Ru_2(chp)_3(O_2CMe)Cl$ (5). This compound was prepared as was **2** above except that 0.043 g of $Ru_2(O_2CMe)_4Cl$ and 0.5 g of Hchp (Hchp = 2-chloro-6-hydroxypyridine) were used. After the air in the Schlenk flask was replaced with dry N_2, the mixture was heated to 128 °C (but not above) for 3 h. During this period the molten mixture rapidly became deep purple. After removal of excess Hchp by sublimation, the residue was redissolved in CH_2Cl_2 and precipitated by adding hexanes to this solution. Yield: 0.054 g (87%). Large block-shaped crystals were obtained from the diffusion of hexanes into a CH_2Cl_2 solution, and examination of these identified the product as $Ru_2(chp)_3(O_2CMe)Cl$.[7]

$[Ru_2(DPhTA)_3(O_2CMe)(NCMe)_2][BF_4]$ (6). This compound was prepared by a melt reaction, followed by the removal of the axial Cl^- by reaction with $AgBF_4$. In a Schlenk tube were placed 0.103 g of $Ru_2(O_2CMe)_4Cl$ and 0.5 g of HDPhTA. After moisture was removed by evacuation and the air was replaced with dry N_2, the mixture was heated to 120 °C for 3 h. During this period the molten mixture changed from a colorless liquid with the orange solid in suspension to a dark green mixture. After removal of excess free HDPhTA by sublimation, the dark residue was taken into CH_2Cl_2. The resulting solution was then cannulated into a second Schlenk flask containing 0.054 g of $AgBF_4$. The removal of the halide was rapid and efficient, with a fine white powder forming almost immediately. After the reaction had been allowed to proceed another 3 h the solution was filtered through Celite and 1 mL of freshly distilled acetonitrile added to this. A dark green solid (0.21 g) was obtained from the rapid

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(7) The compound was found in a different crystalline form than that reported in ref 3b. The crystals were found to be monoclinic with $a = 9.399(1)$ Å, $b = 15.890(3)$ Å, $c = 10.295(1)$ Å, $\beta = 115.02°$, and from the systematic absences observed the space group $P2_1/m$ (No. 11) was chosen. The unusual choice of space group for a molecular crystal was confirmed by successful refinement of the structure with R1 = 0.0907, wR2 = 0.1730, GooF = 1.214, Ru−Ru = 2.288(2) Å. The choice of space group is further rationalized by the contents of the asymmetric unit, where only one-half of the diruthenium complex is contained, the molecule being completed by a mirror plane defined by the four non-H atoms of the acetato ligand, the two ruthenium atoms, the axial chloride, and all the atoms of the chp^- ligand trans to the acetato ligand. One molecule of CH_2Cl_2 is also found in the asymmetric unit.

Table 1. Crystal Data and Structure Refinement Parameters

empirical formula	$C_{16}H_{24}Cl_7N_2O_6Ru_2$ (**1**)	$C_{21}H_{30}Cl_7N_4O_4Ru_2$ (**2**)	$C_{36}H_{46}ClN_8O_2Ru_2$ (**3**)
fw	790.7	852.78	860.40
a, Å	11.578(3)	13.091(3)	15.979(2)
b, Å	12.5607(13)	19.098(4)	14.9294(14)
c, Å	20.903(3)	13.720(3)	17.131(4)
α, deg	99.927(14)		
β, deg	100.222(9)	105.51(3)	109.21(2)
γ, deg	102.07(2)		
V, Å^3	2855.3(9)	3305.1(11)	3859.0(12)
Z	4	4	4
space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$
D_c, g/cm^3	1.846	1.714	1.481
μ, mm^{-1}	1.746	1.512	0.894
λ, Å	0.710 73	0.710 73	0.710 73
T, K	213(2)	213(2)	213(2)
final *R* indices^a [$I > 2s(I)$]	R1 = 0.048, wR2 = 0.117	R1 = 0.047, wR2 = 0.107	R1 = 0.068, wR2 = 0.150
R indices (all data)	R1 = 0.057, wR2 = 0.126	R1 = 0.066, wR2 = 0.115	R1 = 0.091, wR2 = 0.162

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = \{\sum[w(F_o^2 - F_c^2)/\sum[w(F_o^2)^2]\}^{1/2}$.

diffusion of hexanes into this solution (84% yield). Bands for the CN stretch of the NCMe molecules appeared as very weak absorptions, observable only in extremely concentrated and thick KBr pellets. The complex was also obtained as single crystals suitable for single-crystal X-ray diffractometry from the slow diffusion of hexanes into a solution of the complex in THF, to which a drop of acetonitrile had been added.[8]

IR (cm^{-1}): 2925, w; 2308, vw; 2280, vw; 1629, m; 1592, m; 1486, m; 1439, w; 1310, m; 1123, m; 1084, s; 1032, m; 913, w; 758, m; 693, m; 534, m; 470, w.

Electrochemistry: $E_{1/2,ox}$, 1606 mV; $\Delta E_{p,ox}$, 94 mV; $I_{p,a}/I_{p,c} = 1.40$. $E_{1/2,red}$, 428 mV; $\Delta E_{p,red}$, 61 mV; $I_{p,a}/I_{p,c} = 0.93$. $E_{1/2,red}$, -755 mV; $\Delta E_{p,red}$, 76 mV; $I_{p,a}/I_{p,c} = 0.91$.

Magnetic Measurements. From the bulk susceptibility measurements, at ca. 20 °C, the following magnetic moments, in μ_B, were calculated: **1**, 3.93; **2**,4.00; **3**, 3.94; **4**, 1.53; **6**, 1.54.

X-ray Crystallography. General Procedures. Crystals were mounted on quartz fibers with the aid of hydrocarbon grease and rapidly placed in the cold stream (−60 °C) of the cryostat of a Nonius FAST area detector diffractometer. Procedures for crystal indexing, data collection, and data reduction for this instrument have been described elsewhere.[9] Corrections for the effects of absorption anisotropy were done using a locally modified version of the program SORTAV.[10] Structure solutions were obtained using direct methods as programmed in SHELXS-86,[11] and structure refinement was done using SHELXL-93.[12] Crystallographic parameters for the structures discussed are given in Table 1. Listings of selected bond lengths and angles are in Tables 2−4.

$Ru_2(admp)(O_2CMe)_3Cl{\cdot}3CH_2Cl_2$ (1). Crystals of this compound were obtained from the diffusion of hexanes into a CH_2Cl_2 solution of the compound. The crystals lose solvent very rapidly once removed from the mother liquor, and they had to be kept cold. Two molecules of the diruthenium compound and six molecules of dichloromethane form the asymmetric unit. The two molecules of the diruthenium compound dimerize by forming a weak bond between the oxygen atom of one of the acetato ligands in one of the molecules and the axial position of the other.

$Ru_2(admp)_2(O_2CMe)_2Cl{\cdot}2.5CH_2Cl_2$ (2). Crystals of this compound were obtained from the diffusion of hexanes into a CH_2Cl_2 solution of the compound. One molecule of the diruthenium compound and three molecules of dichloromethane are found in the asymmetric unit.

$Ru_2(admp)_3(O_2CMe)Cl{\cdot}Hadmp{\cdot}C_6H_6$ (3). Crystals of sufficient quality for structural characterization were obtained from the slow diffusion of hexanes into a benzene solution of the compound. One molecule of the diruthenium compound, one molecule of the neutral form of the ligand, and one molecule of benzene form the asymmetric unit. The benzene molecule is disordered over two positions but is well defined.

Results and Discussion

Synthesis. The complexes in the title series were prepared by reaction of $Ru_2(O_2CMe)_4Cl$ with the neutral ligand, either in a solvent or in the melted ligand. While $Ru_2(admp)(O_2CMe)_3Cl$ (**1**) was obtained by reaction in methanol at room temperature, when the same reaction was carried out in THF heated to reflux, $Ru_2(admp)_2(O_2CMe)_2Cl$ (**2**) was obtained. From the melt reaction, when the mixture was heated barely to the melting point of the free ligand, $Ru_2(admp)_2(O_2CMe)_2Cl$ (**2**) was again isolated, whereas at 100 °C $Ru_2(admp)_3(O_2CMe)Cl$ (**3**) was obtained, and at 140 °C $Ru_2(admp)_4Cl$ (**4**) was formed. To show the generality of this approach, compounds containing other ligands of this type, $Ru_2(chp)_3(O_2CMe)Cl$ (**5**) (Hchp = 2-chloro-6-hydroxypyridine) and $[Ru_2(DPhTA)_3(O_2CMe)(NCMe)_2][BF_4]$ (**6**) (HDPhTA = diphenyltriazene), were deliberately prepared using the melt reaction technique but never raising the temperature beyond 130 °C.

Magnetic and Redox Properties. The magnetic and redox properties of compounds **1**−**4** are listed in Table 5. While **1**−**3** display magnetic moments consistent with the presence of three unpaired electrons, from which a high-spin electronic ground state can be inferred, the magnetic moment of **4** shows the presence of only one unpaired electron, and **4** is therefore a low-spin molecule. This is because the π system of the admp$^-$ ligands interacts significantly with those d orbitals on the metal atoms used to form the δ overlap, as has been shown for other ligands.[13] The replacement of the acetates with a progressively larger number of admp$^-$ ligands causes a steady rise in the energy of the δ^* orbital, eventually creating a gap between the π^* and δ^* orbitals large enough to result in the reorganization of the electronic ground state from high-spin to low-spin.

This change in the electronic ground state is also reflected in the electrochemistry of these molecules, particularly in the facility with which the molecules are oxidized. The cyclic voltammograms (CV) of **1**−**4** and **6** were recorded. Those for **1**−**3** are very similar, except for the potential at which the redox processes occur. The same is true for those of **4** and **6**. For this reason only those for **1** and **6** are shown in Figure 1a and b, respectively.

The CV of the three high-spin molecules, **1**−**3**, show progressively easier, quasireversible, one-electron oxidations, from Ru_2^{5+} to Ru_2^{6+}, as well as increasingly harder one-electron reductions, from Ru_2^{5+} to Ru_2^{4+}. This observation is consistent with a stepwise destabilization of the δ^* orbital by each new admp$^-$ moiety placed in the ligand sphere of the Ru_2 unit. This is because both oxidation and reduction of a high-spin Ru_2^{5+}

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(8) This complex crystallizes in the triclinic space group $P\bar{1}$ (No. 2) with $a = 12.775(2)$ Å, $b = 13.435(2)$ Å, $c = 17.142(3)$ Å, α = 84.63(4)°, $\beta = 74, 42(2)$°, $\gamma = 69.41(2)$°. The complete molecule is found in the asymmetric unit, along with a BF_4^- counterion and two molecules of THF of crystallization. However, large peaks (ca. 2.5 e$^-$/Å^3) remained in the final difference Fourier map, in positions close to the two metal atoms (i.e., within 0.5 Å). Refinement yielded the following values: R1 = 0.0754, wR2 = 0.1390, Goof = 1.120, Ru−Ru distance = 2.3822(8) Å.

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for $Ru_2(admp)(O_2CMe)_3Cl$ (**1**)

Ru(11)−N(11)	1.966(6)	Ru(21)−N(21)	1.943(7)
Ru(11)−O(131)	2.027(4)	Ru(21)−O(231)	2.038(5)
Ru(11)−O(111)	2.044(4)	Ru(21)−O(211)	2.039(5)
Ru(11)−O(121)	2.068(5)	Ru(21)−O(221)	2.063(6)
Ru(11)−Ru(12)	2.2767(8)	Ru(21)−Ru(22)	2.2768(9)
Ru(11)−Cl(1)	2.477(2)	Ru(21)−Cl(2)	2.469(2)
Ru(12)−O(132)	2.027(4)	Ru(22)−O(212)	2.039(4)
Ru(12)−N(12)	2.047(6)	Ru(22)−N(22)	2.040(6)
Ru(12)−O(122)	2.049(5)	Ru(22)−O(232)	2.049(4)
Ru(12)−O(112)	2.063(4)	Ru(22)−O(222)	2.063(5)
N(11)−Ru(11)−O(131)	91.2(2)	N(11)−Ru(11)−O(111)	90.9(2)
O(131)−Ru(11)−O(111)	177.1(2)	N(11)−Ru(11)−O(121)	179.2(2)
O(131)−Ru(11)−O(121)	88.9(2)	O(111)−Ru(11)−O(121)	89.0(2)
N(11)−Ru(11)−Ru(12)	89.1(2)	O(131)−Ru(11)−Ru(12)	88.40(13)
O(111)−Ru(11)−Ru(12)	89.55(12)	O(121)−Ru(11)−Ru(12)	90.10(13)
N(11)−Ru(11)−Cl(1)	92.6(2)	O(131)−Ru(11)−Cl(1)	91.34(14)
O(111)−Ru(11)−Cl(1)	90.64(13)	O(121)−Ru(11)−Cl(1)	88.29(14)
Ru(12)−Ru(11)−Cl(1)	178.37(5)	O(132)−Ru(12)−N(12)	87.6(2)
O(132)−Ru(12)−O(122)	89.4(2)	N(12)−Ru(12)−O(122)	177.0(2)
O(132)−Ru(12)−O(112)	178.6(2)	N(12)−Ru(12)−O(112)	91.4(2)
O(122)−Ru(12)−O(112)	91.6(2)	O(132)−Ru(12)−Ru(11)	90.30(13)
N(12)−Ru(12)−Ru(11)	91.4(2)	O(122)−Ru(12)−Ru(11)	88.43(13)
O(112)−Ru(12)−Ru(11)	88.78(12)	N(21)−Ru(21)−O(231)	91.9(2)
N(21)−Ru(21)−O(211)	90.7(2)	O(231)−Ru(21)−O(211)	176.4(2)
N(21)−Ru(21)−O(221)	179.7(2)	O(231)−Ru(21)−O(221)	87.7(2)
O(211)−Ru(21)−O(221)	89.7(2)	N(21)−Ru(21)−Ru(22)	89.3(2)
O(231)−Ru(21)−Ru(22)	89.2(2)	O(211)−Ru(21)−Ru(22)	88.39(14)
O(221)−Ru(21)−Ru(22)	90.57(14)	N(21)−Ru(21)−Cl(2)	92.2(2)
O(231)−Ru(21)−Cl(2)	90.4(2)	O(211)−Ru(21)−Cl(2)	91.9(2)
O(221)−Ru(21)−Cl(2)	87.9(2)	Ru(22)−Ru(21)−Cl(2)	178.45(6)
O(212)−Ru(22)−N(22)	89.3(2)	O(212)−Ru(22)−O(232)	179.7(2)
N(22)−Ru(22)−O(232)	90.9(2)	O(212)−Ru(22)−O(222)	88.6(2)
N(22)−Ru(22)−O(222)	177.6(2)	O(232)−Ru(22)−O(222)	91.2(2)
O(212)−Ru(22)−Ru(21)	90.23(14)	N(22)−Ru(22)−Ru(21)	91.0(2)
O(232)−Ru(22)−Ru(21)	89.52(14)	O(222)−Ru(22)−Ru(21)	87.97(14)

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $Ru_2(admp)_2(O_2CMe)_2Cl$ (**2**)

Ru(1)−N(13)	2.008(4)	Ru(1)−Cl	2.4633(14)
Ru(1)−N(14)	2.020(4)	Ru(2)−O(21)	2.029(4)
Ru(1)−O(12)	2.046(4)	Ru(2)−O(22)	2.030(4)
Ru(1)−O(11)	2.051(4)	Ru(2)−N(23)	2.063(5)
Ru(1)−Ru(2)	2.2736(7)	Ru(2)−N(24)	2.076(4)
N(13)−Ru(1)−N(14)	179.3(2)	N(13)−Ru(1)−O(12)	89.8(2)
N(14)−Ru(1)−O(12)	90.6(2)	N(13)−Ru(1)−O(11)	90.2(2)
N(14)−Ru(1)−O(11)	89.3(2)	O(12)−Ru(1)−O(11)	177.3(2)
N(13)−Ru(1)−Ru(2)	89.68(13)	N(14)−Ru(1)−Ru(2)	89.76(13)
O(12)−Ru(1)−Ru(2)	88.97(11)	O(11)−Ru(1)−Ru(2)	88.33(11)
N(13)−Ru(1)−Cl	91.86(13)	N(14)−Ru(1)−Cl	88.69(14)
O(12)−Ru(1)−Cl	92.03(12)	O(11)−Ru(1)−Cl	90.66(11)
Ru(2)−Ru(1)−Cl	178.16(4)	O(21)−Ru(2)−O(22)	179.4(2)
O(21)−Ru(2)−N(23)	90.3(2)	O(22)−Ru(2)−N(23)	89.2(2)
O(21)−Ru(2)−N(24)	88.2(2)	O(22)−Ru(2)−N(24)	92.3(2)
N(23)−Ru(2)−N(24)	177.6(2)	O(21)−Ru(2)−Ru(1)	90.39(11)
O(22)−Ru(2)−Ru(1)	89.83(12)	N(23)−Ru(2)−Ru(1)	91.11(13)
N(24)−Ru(2)−Ru(1)	90.75(13)		

Table 4. Selected Bond Lengths (Å) and Angles (deg) for $Ru_2(admp)_3(O_2CMe)Cl$ (**3**)

Ru(1)−N(14)	1.967(9)	Ru(1)−Cl(1)	2.455(3)
Ru(1)−N(11)	2.013(8)	Ru(2)−O(22)	2.068(7)
Ru(1)−N(13)	2.026(8)	Ru(2)−N(21)	2.080(8)
Ru(1)−O(12)	2.123(8)	Ru(2)−N(24)	2.096(9)
Ru(1)−Ru(2)	2.2833(12)	Ru(2)−N(23)	2.108(8)
N(14)−Ru(1)−N(11)	92.8(4)	N(14)−Ru(1)−N(13)	89.2(4)
N(11)−Ru(1)−N(13)	177.2(3)	N(14)−Ru(1)−O(12)	177.0(3)
N(11)−Ru(1)−O(12)	89.7(3)	N(13)−Ru(1)−O(12)	88.2(3)
N(14)−Ru(1)−Ru(2)	91.1(3)	N(11)−Ru(1)−Ru(2)	88.1(2)
N(13)−Ru(1)−Ru(2)	89.9(3)	O(12)−Ru(1)−Ru(2)	87.3(2)
N(14)−Ru(1)−Cl(1)	91.5(3)	N(11)−Ru(1)−Cl(1)	90.5(3)
N(13)−Ru(1)−Cl(1)	91.4(3)	O(12)−Ru(1)−Cl(1)	90.1(2)
Ru(2)−Ru(1)−Cl(1)	177.10(9)	O(22)−Ru(2)−N(21)	87.9(3)
O(22)−Ru(2)−N(24)	179.4(3)	N(21)−Ru(2)−N(24)	92.7(3)
O(22)−Ru(2)−N(23)	84.9(3)	N(21)−Ru(2)−N(23)	172.5(3)
N(24)−Ru(2)−N(23)	94.5(3)	O(22)−Ru(2)−Ru(1)	91.1(2)
N(21)−Ru(2)−Ru(1)	92.2(2)	N(24)−Ru(2)−Ru(1)	89.1(2)
N(23)−Ru(2)−Ru(1)	90.0(2)		

molecule normally involve the addition or abstraction of a δ^* electron,[14] and therefore we can expect both the oxidation and reduction potentials to be affected by the nature of the equatorial ligands.

The CV of the two low-spin molecules prepared, **4** and **6**, show three distinct redox processes. For example, that for $[Ru_2(DPhTA)_3(O_2CMe)]^+$ (**6**), shown in Figure 1b), shows an oxidation at 1606 mV, from Ru_2^{5+} to Ru_2^{6+}, a reduction at 428 mV, from Ru_2^{5+} to Ru_2^{4+}, and a second reduction at −755 mV, from Ru_2^{4+} to Ru_2^{3+}. These observations are also consistent with the discussion provided above as follows. The reorganization of the orbital manifold brought about by the transition from high-spin to low-spin causes the ground state of the Ru_2^{5+} molecule to be $\sigma^2\pi^4\delta^2\pi^{*3}\delta^{*0}$, as stated in the Introduction. Reduction of this species involves the addition of a π^* electron and leads to a molecule with a ground state described as $\sigma^2\pi^4\delta^2\pi^{*4}\delta^{*0}$.[15] However, further reduction of this species must now involve the addition of a δ^* electron, which, due to the π-basicity of the equatorial ligands, now lies rather high in energy and causes the process to become more difficult. This is further supported by the fact that the CV of $Ru_2(DTolTA)_4$ also shows a similar set of three redox processes and that the

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[14] (a) Cotton, F. A.; Yokochi, A. *Inorg. Chem.* **1997**, *36*, 567. (b) Cotton, F. A.; Miskowski, V. M.; Zhong, B. J. *J. Am. Chem. Soc.* **1989**, *111*, 6177. (c) Maldivi, P.; Giroud-Godquin, A.; Marchon, J.; Guillon, D.; Skoulios, A. *Chem. Phys. Lett.* **1989**, *157*, 552.

[15] Cotton, F. A.; Matusz, M. *J. Am. Chem. Soc.* **1988**, *110*, 5761.

Table 5. Magnetic and Redox Properties for Compounds **1**−**4**[a]

	magnetic susceptibility (μ_B)	oxidation			reduction		
		$E_{1/2}$ (mV)	ΔE_p (mV)	$I_{p,a}/I_{p,c}$	$E_{1/2}$ (mV)	ΔE_p (mV)	$I_{p,a}/I_{p,c}$
1	3.93	1106	88	0.92	−439	88	0.94
2	4.00	762	115	1.01	−712	101	0.92
3	3.94	477	109	0.90	−1002	99	0.97
4	1.53	1480					

[a] Under the conditions the electrochemical measurements were made, the Fc/Fc^+ couple ($E_{1/2}$) appears at 625 mV and the separation between anodic and cathodic waves (ΔE_p) is 61 mV.

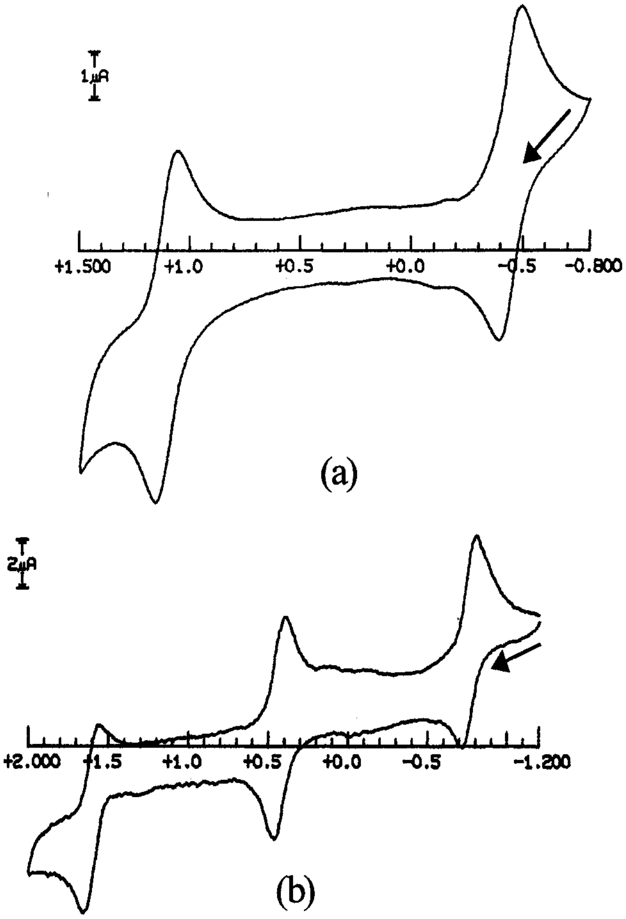

Figure 1. Cyclic voltammogram of $Ru_2(admp)(O_2CMe)_3Cl$ (**1**) in CH_2Cl_2 (a) and $[Ru_2(DPhTA)_3(O_2CMe)(NCMe)_2]^+$ (**6**) in acetonitrile (b). The solutions used for these measurements were 0.1 M in $[n\text{-}Bu_4N][PF_6]$ and contained 1 mg/mL of the analyte. A scan rate of 100 mV/s was used.

process corresponding to the Ru_2^{4+} to Ru_2^{3+} reduction now occurs at −1100 mV.[15] This large shift of the position of this reduction toward a more negative potential corresponds to a further destabilization of the δ^* orbital by the addition of another highly π-basic ligand to the molecule.

Structures. The structures of these compounds, which offer no surprises, are shown as thermal ellipsoid plots in Figures 2−4. As with other diruthenium compounds containing one axial ligand, the incoming ligands enter regiospecifically, with the methyl groups all directed to the end of the molecule that is away from the axial ligand. Since **1** has only one $admp^-$ ligand in its coordination sphere, the presence of the lone methyl group is not sufficient to block access to the second axial position of the Ru_2 unit, and the molecules dimerize in the manner shown in Figure 5. Other Ru_2 complexes, as for example $[1,3\text{-}Ru_2(chp)_4]_2$,[16] behave similarly.

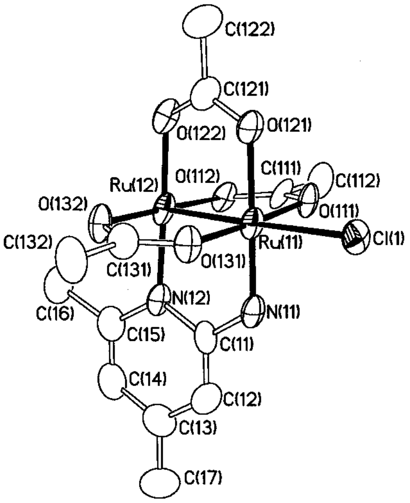

Figure 2. Thermal ellipsoid plot (50% probability ellipsoids) of $Ru_2(admp)(O_2CMe)_3Cl$ (**1**).

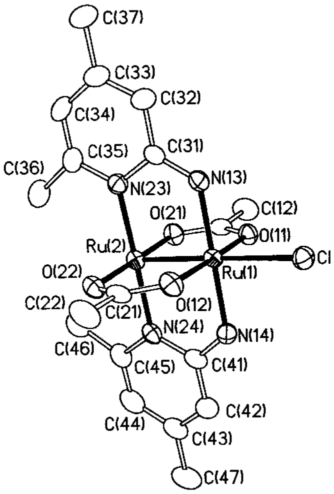

Figure 3. Thermal ellipsoid plot (50% probability ellipsoids) of $Ru_2(admp)_2(O_2CMe)_2Cl$ (**2**).

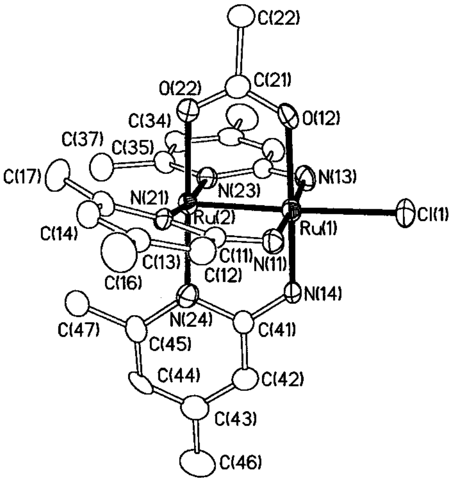

Figure 4. Thermal ellipsoid plot (50% probability ellipsoids) of $Ru_2(admp)_3(O_2CMe)Cl$ (**3**).

The Ru−Ru bond lengths for **1**−**3** are all well within the range expected for high-spin Ru_2^{5+} compounds. A clear trend for the changes in Ru−Ru distance does not appear to exist, since the bond stays relatively unchanged between **1** and **2** but

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[16] Cotton, F. A.; Ren, T.; Eglin, J. *J. Am. Chem. Soc.* **1990**, *112*, 3439.

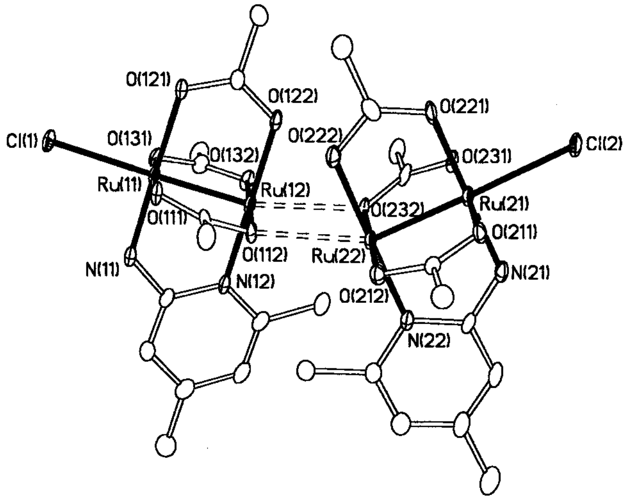

Figure 5. Thermal ellipsoid plot (50% probability ellipsoids) of the complete dimer of $Ru_2(admp)(O_2CMe)_3Cl$ (**1**) in the asymmetric unit.

is significantly lengthened between **2** and **3**. However, it is possible that in **1** the interaction between the axial position of each Ru_2 unit and the acetato oxygen atom of the neighboring molecule causes the Ru−Ru bond to lengthen to such an extent that the trend is obscured.

Unfortunately, compound **4** could not be obtained as single crystals suitable for a structural determination. The mass spectrum of the compound unequivocally shows **4** to be $Ru_2(admp)_4Cl$, and, due to the presence of the four pendant 6-methyl groups, only one structure seems possible, viz., the 0,4− regioisomer. Furthermore, since this is a low-spin molecule we can predict that the Ru−Ru bond length must be ca. 2.45 Å.

Conclusions

The synthetic portion of this study shows clearly that in the reaction between $Ru_2(O_2CMe)_4Cl$ and Hadmp, the temperature at which the reaction is carried out can be used to control the product obtained, whether the reaction is done as a melt or in solution. This was also demonstrated to be true for the similar ligands, Hchp and HDPhTA. Magnetic measurements revealed that when a sufficient number of strongly π-basic ligands are placed around the Ru_2 unit a reorganization of the ground electronic state occurs, in which the molecule goes from a high-spin state to a low-spin one.

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Supporting Information Available: Three X-ray crystallographic files, in CIF format, are available. Access information is given on any current masthead page.

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