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Synthesis, Structure, and Magnetic Properties of New Ru_2^{6+} Compounds

F. A. Cotton* and A. Yokochi

Department of Chemistry and Laboratory for Molecular Science and Bonding Texas A&M University, College Station, Texas 77843

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Three compounds containing the Ru_2^{6+} core have been prepared by clean and convenient synthetic routes: $[Ru_2(ap)_4(OH_2)][CF_3SO_3]_2$, $[Ru_2(ap)_4F][PF_6]$, and $[Ru_2(ap)_4Cl][FeCl_4]$ (ap = anilinopyridinate). The third one has been structurally characterized from a crystal of $[Ru_2(ap)_4Cl][FeCl_4]\cdot 2.5CH_2Cl_2$ and contains the Ru_2^{6+} core in a coordination environment identical to that of an Ru_2^{5+} compound. The compound crystallizes in the triclinic space group $P\bar{1}$, with $a = 9.660(2)$ Å, $b = 16.237(3)$ Å, $c = 17.724(4)$ Å, $\alpha = 86.34(3)°$, $\beta = 77.19(3)°$, $\gamma = 78.34(3)°$, and $Z = 2$. The Ru−Ru distance is 2.301(1) Å, and the magnetic moment indicates the presence of two unpaired electrons. A $\sigma^2\pi^4\delta^2\pi^{*2}$ electron configuration is inferred.

Introduction

While compounds of Ru_2^{n+} ($n = 4$, 5) are easily prepared and have been extensively studied,[1] their Ru_2^{6+} counterparts have proved elusive, with only five known in the current literature. The first bona fide series of Ru_2^{6+} compounds, containing the species $[Ru_2(SO_4)_4(H_2O)_2]^{2-}$, was reported in 1986 by Zhilyaev and co-workers,[2] and was shortly thereafter confirmed by this laboratory.[3] Recently, two new classes of compounds have been reported by Bear and co-workers.[4] One, of general formula $Ru_2(LL)_4(L_{ax})_2$, where (LL) is either diphenylformamidine or pentafluoroanilinopyridine and L_{ax} is $CCPh^-$ or CN^-, and a second class with its only representative $Ru_2(hpp)_4Cl_2$, where hpp is the 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidinate anion. The three classes of compounds have different magnetic properties: the first type has four unpaired electrons, those of the second type are diamagnetic, and the last one has two unpaired electrons. For some time we have been continuing to investigate the preparation of Ru_2^{6+} compounds and have synthesised three compounds of the third class. One of them has been studied by X-ray crystallography and contains the Ru_2^{6+} core in a coordination sphere similar to that of an Ru_2^{5+} homologue, $Ru_2(ap)_4Cl$ (ap = anilinopyridinate).[5] A discussion of the structural changes caused by the oxidation will be provided.

Experimental Section

All the work described here was carried out under an atmosphere of dry N_2 unless otherwise indicated. All solvents used were dried and deoxygenated prior to use and freshly distilled from an appropriate drying agent under an atmosphere of dry N_2. $Ru_2(ap)_4Cl$ was prepared according to published methods.[5] $Ag(CF_3SO_3)$ was purchased from Aldrich Chemical Co. and $Ag(PF_6)$ and $[FeCp_2][FeCl_4]$ were purchased from AESAR/Johnson Matthey and used as received. Elemental analyses were performed by Canadian Microanalytical Co. Infrared spectra were recorded on a Perkin Elmer FT-IR Model 1600 PC. Electronic absorption spectra were recorded on a Cary 17 spectrophotometer. Single-crystal X-ray diffraction data were collected on an Enraf Nonius FAST system. Mass spectrometry was carried out on a VG Analytical 70S high-resolution, double-focusing, sectored (EB) mass spectrometer. Bulk magnetic susceptibility was measured using a Johnson Matthey MSB-1 balance. In all cases the solids employed in the magnetic measurements and elemental analysis were dried under vacuum for several hours prior to use.

$[Ru_2(ap_4)(OH_2)][O_3SCF_3]_2$. In a Schlenk flask equipped with a magnetic stirring bar were placed 0.10 g $Ru_2(ap)_4Cl$ (0.11 mmol) and 0.06 g $Ag(O_3SCF_3)$ (0.23 mmol). The flask was sealed with a rubber septum and all air excluded by repeatedly evacuating and refilling with dry N_2. CH_2Cl_2 (20 mL) was then syringed into the flask through the rubber septum. A deep green solution formed initially which changed to dark red overnight. The solution was stirred for 12 h and then filtered through a fine glass frit to leave behind a dark gray solid—possibly a mixture of excess $Ag(O_3SCF_3)$, AgCl, and metallic silver. A dark red solid was obtained by removing the solvent at reduced pressure. Yield: 0.115 g (96%). Crystals of this compound were obtained by layering a CH_2Cl_2 solution with hexanes, but due to extensive disorder, observed as disorder streaks in axial photographs, the structure has not been refined satisfactorily. Anal. Calcd for $Ru_2N_8C_{46}H_{38}O_7S_2F_6$: C, 46.23; H, 3.20; N, 9.38; O, 9.37. Found: C, 46.02; H, 3.20; N, 9.02; O, 10.53. IR (KBr, cm^{-1}): 3505 w, 2924 m, 1597 s, 1462 s, 1429 s, 1341 m, 1287 s, 1256 s, 1210 s, 1158 s, 1031 s, 924 m, 870 s, 802 w, 763 s, 735 w, 698 s, 636 s, 573 w, 517 w, 498 w. Vis−near-IR (CH_2Cl_2, nm): 395, 490, 940 (broad).

$[Ru_2(ap_4)F][PF_6]$. In a Schlenk flask equipped with a magnetic stirring bar were placed 0.10 g $Ru_2(ap)_4Cl$ (0.11 mmol) and 0.07 g $Ag(PF_6)$ (0.28 mmol). The flask was sealed with a rubber septum and all air excluded by repeatedly evacuating and refilling with dry N_2. CH_2Cl_2 (20 mL) was then syringed into the flask through the rubber septum. A deep green solution formed initially which rapidly changed to dark red. The solution was stirred for 12 h and then filtered through a fine glass frit to leave behind a dark gray solid. To the resulting solution was then added 5 mL of freshly distilled acetonitrile and the resulting solution layered with 10 mL of hexanes to afford small clusters of thin plate-shaped crystals. Yield: 0.094 g (90%). The compound was structurally characterized,[6] but due to extensive disorder of the PF_6^- counterion, the structure has not been refined to a satisfactory conclusion at this moment, and may be reported elsewhere. Anal. Calcd for $Ru_2N_8C_{44}H_{36}PF_7$: C, 50.67; H, 3.48; N, 10.74. Found: C, 49.57; H, 3.78; N, 10.08. IR (KBr, cm^{-1}): 3058 w, 2924 m, 1598 s, 1463 s, 1429 s, 1339 m, 1287 m, 1259 w, 1209 s, 1161 w, 1113 w, 1072 w,

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Table 1. Crystal Data and Structure Refinement for $[Ru_2(ap)_4Cl][FeCl_4]\cdot 2.5CH_2Cl_2$

empirical formula: $C_{46.50}H_{41}Cl_{10}FeN_8Ru_2$
fw = 1324.41
space group: $P\bar{1}$
unit cell dimens: $a = 9.660(2)$ Å, $b = 16.237(3)$ Å, $c = 17.724(9)$ Å, $\alpha = 86.34(3)°$, $\beta = 77.19(3)°$, $\gamma = 78.34(3)°$
$V = 2654.4(9)$ Å^3
$Z = 2$
$d(\text{calcd}) = 1.657$ g/cm^3
abs coeff 1.376 mm^{-1}
wavelength = 0.71073 Å
temp = 213(2) K
refinement method: full-matrix least-squares on F^2
final R indices [$I > 2\sigma(I)$]: $R_1{}^a = 0.073$; $wR2^b = 0.161$
R indices (all data): $R_1{}^a = 0.103$; $wR2^b = 0.179$

^{a} $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $wR2 = |\sum[w(F_o{}^2 - F_c{}^2)^2]/\sum[w(F_o{}^2)^2]]^{0.5}$.

1024 w, 922 w, 868 s, 839 s, 766 m, 738 w, 697 m, 557 m, 501 w. Vis−near-IR (CH_2Cl_2, nm): 395, 490, 940 (broad).

$[Ru_2(ap_4)Cl][FeCl_4]$. In a Schlenk flask equipped with a magnetic stirring bar were placed 0.10 g $Ru_2(ap)_4Cl$ (0.11 mmol) and 0.05 g $[FeCp_2][FeCl_4]$ (0.13 mmol). The flask was sealed with a rubber septum and all air excluded by repeatedly evacuating and refilling with dry N_2. CH_2Cl_2 (20 mL) was then syringed into the flask through the rubber septum. A deep green solution formed initially, but the color immediately changed to dark red. The solution was stirred for 1 h and the solvent removed by evaporation at reduced pressure. The resulting solid was washed with several 5 mL portions of freshly distilled hexanes until no yellow color attributable to dissolved ferrocene could be detected by eye. Yield: 0.107 g (96%). The solid was then redissolved in CH_2Cl_2 and layered with 30 mL of hexanes. Over the course of several days, very small, thin crystals formed. Anal. Calcd for $Ru_2N_8C_{44}H_{36}FeCl_5\cdot CH_2Cl_2$: C, 45.15; H, 3.20; N, 9.36; Cl, 20.73. Found: C, 46.14; H, 3.21; N, 8.99; Cl, 21.15. In the NMR spectrum of the same solid used for elemental analysis dissolved in $CDCl_3$ a signal at 5.302 ppm is clearly visible, confirming the presence of CH_2Cl_2. MS (FAB$^+$, *m/z* (relative intensity)): 914 (M$^+$, 100%, 880 ($[M - Cl]^+$, 37%), 746 ($[M - ap]^+$, 24%), 540 ($[M - 2ap - Cl]^+$, 37%). IR (KBr, cm^{-1}): 3057 w, 2924 w, 1596 s, 1540 w, 1478 m, 1460 s, 1428 s, 1336 m, 1289 m, 1254 m, 1210 s, 1160 m, 1073 w, 1017 m, 923 m, 871 s, 762 m, 734 w, 697 s, 648 w, 498 m. Vis−near-IR (CH_2Cl_2, nm): 430, 505, 975.

Magnetic Susceptibility Measurements. Magnetic measurements were carried out only on $[Ru_2(ap)_4F][PF_6]$ and $[Ru_2(ap)_4(OH_2)][SO_3CF_3]_2$, since the counterion in $[Ru_2(ap)_4Cl][FeCl_4]$ is strongly paramagnetic.

Method a: Measurement on the Bulk Solid Using a Modified Gouy Technique. In a carefully calibrated tube were placed, in air, 0.023 g of finely ground $[Ru_2(ap)_4F][PF_6]$. The measurement was carried out several times. From the susceptibility, and after correction for diamagnetic contributions from the ligands, counterion, and displaced air, a magnetic moment, μ_{eff}, of 2.75 μ_B was calculated.

Method b: Measurement in Solution by the Evans Method.[7] A solution consisting of 0.0119 g of $[Ru_2(ap)_4F][PF_6]$ in 1.3738 g of CH_2Cl_2 (0.0115 g/mL) was placed, in air, in an NMR tube equipped with an internal reference of neat CH_2Cl_2. Measurement of the ^1H NMR spectrum revealed two broad lines with a separation of 20.2 Hz. For this measurement, and after correcting for diamagnetic contributions, a magnetic moment of 2.90 μ_B was calculated.

In a similar fashion, a solution of $Ru_2(ap)_4(OH_2)(SO_3CF_3)_2$ in CH_2Cl_2 with a concentration of 0.0417g/mL was placed, in air, in the insert of an externally referenced NMR tube. The reference, in this case, consisted of a 5% CH_2Cl_2 solution in $CDCl_3$. The NMR spectrum revealed a sharp line due to unshifted CH_2Cl_2, and a broad line shifted 48.6 Hz from this. From calculations corrected for diamagnetic contributions a value for the magnetic moment of 2.81 μ_B was calculated.

X-ray Crystallography. A needle-shaped crystal of approximate dimensions 0.1 × 0.05 × 0.02 mm^3 was mounted on a quartz fiber by using a dab of hydrocarbon stopcock grease and rapidly transferred to the cold stream of the diffractometer. A detailed description of the procedures employed for this instrument is given elsewhere[8] but can be summarized as follows: After optical centering of the crystal in the X-ray beam, 500 reflections were found by automated procedures. The first 50 of these were used to index the crystal, and revealed a triclinic lattice. The structural parameters were then refined from the 250 strongest reflections in the range $10 < \theta < 20$. Axial rotation images confirmed the observed axial lengths as well as the absence of higher symmetry. Data were collected by integration of 0.2 degree oscillation images around the ω axis in four different crystal orientations, to measure a total of 12 449 reflections of which 6274 were unique ($R_{\text{merge}} = 7.4\%$). The space group $P\bar{1}$ was selected since intensity statistics suggested a centrosymmetric space group.

The positions of the metal atoms and their first coordination sphere were determined by direct methods as programmed in SHELXS-86,[9] and this solution was refined by using the program SHELXL-93.[10] All non-hydrogen atoms were found by successive iterations of least-squares refinements followed by Fourier synthesis and, during the final cycles, refined anisotropically. Hydrogen atoms were placed in idealized positions, and a common thermal parameter was refined. Prior to completion of the refinement, the data were corrected for absorption effects using a local modification of the program SORTAV.[11]

Relevant crystal constants, details of data collection, and structure refinement parameters are given in Table 1. Selected bond lengths and angles are in Table 2, and fractional coordinates for the atoms defining the Ru_2N_8Cl core in Table 3.

Discussion

Synthesis. While the compounds containing the $[Ru_2(SO_4)_4(H_2O)_2]^{2-}$ anion were prepared by deliberately oxidizing an $Ru_2{}^{5+}$ compound, all the others prepared since have been the result of intended or unintended oxidation by air or the ligand. The current work was prompted by the observation that with appropriate ligands supporting the $Ru_2{}^{5+}$ unit it should be relatively easy to obtain $Ru_2{}^{6+}$ species by simple oxidation of $Ru_2{}^{5+}$ compounds.[12] The products obtained from the action of such well known oxidizing agents[13] as Ag^+ or Cp_2Fe^+ on the starting $Ru_2{}^{5+}$ compound confirm this. As an additional observation we have found that not only are the diruthenium(5+) tetracarboxylates impervious to such oxidation, but so also are some compounds which are structurally similar to $Ru_2(ap)_4Cl$, such as chlorotetrakis(6-chloro-2-hydroxypyridinato)diruthenium(5+). The reasons for this are not known with certainty, but perhaps the basicity of the ligands is so important that the lower basicity of the hydroxypyridinato ligand in comparison with the aminopyridinato ligand makes it unable to stabilize the $Ru_2{}^{6+}$ entity.

Structure. A thermal ellipsoid plot of the structure of the cation containing the $Ru_2{}^{6+}$ moiety is shown in Figure 1. Upon

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(6) The compound crystallyzed in the triclinic space group $P\bar{1}$ with $a = 12.811(2)$ Å, $b = 16.451(1)$Å, $c = 12.801(1)$Å, $\alpha = 101.44(3)°$, $\beta = 113.61(5)°$, and $\gamma = 79.10(5)°$. A total of 11 809 data, of which 6943 are unique ($R_{\text{int}} = 0.0731$) and of those 5557 have intensities greater than $2\sigma(I)$, were collected. These have been used to refine 617 parameters resulting in residuals of $R = 0.0868$, $wR2 = 0.2279$ and $G_{\text{oof}} = 1.026$. The relevant structural parameters are Ru−Ru = 2.296(1) Å, the average Ru−pyridine-N = 2.070(5) Å, Ru−amine-N = 2.009(5) Å, Ru−F = 2.104(2) Å.

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Table 2. Selected Bond Lengths (Å), Angles (deg), and Torsion Angles (deg) for $[Ru_2(ap)_4Cl][FeCl_4]\cdot 2.5CH_2Cl_2$

Ru(1)−Ru(2)	2.301(1)	Ru(1)−Cl	2.419(2)
Ru(1)−N(11)	2.083(7)	Ru(1)−N(12)	2.098(7)
Ru(1)−N(13)	2.089.7	Ru(1)−N(14)	2.079(7)
Ru(2)−N(21)	2.012(7)	Ru(2)−N(22)	2.002(7)
Ru(2)−N(23)	2.000(7)	Ru(2)−N(24)	2.010(7)
Ru(2)−Ru(1)−Cl	179.84(6)		
N(11)−Ru(1)−Ru(2)	87.4(2)	N(12)−Ru(1)−Ru(2)	87.1(2)
N(13)−Ru(1)−Ru(2)	87.4(2)	N(14)−Ru(1)−Ru(2)	86.7(2)
N(21)−Ru(2)−Ru(1)	89.0(2)	N(22)−Ru(2)−Ru(1)	89.4(2)
N(23)−Ru(2)−Ru(1)	89.1(2)	N(24)−Ru(2)−Ru(1)	90.0(2)
N(11)−Ru(1)−Cl	92.7(2)	N(12)−Ru(1)−Cl	93.0(2)
N(13)−Ru(1)−Cl	92.4(2)	N(14)−Ru(1)−Cl	93.3(2)
N(11)−Ru(1)−N(12)	90.2(3)	N(11)−Ru(1)−N(13)	174.9(3)
N(11)−Ru(1)−N(14)	89.7(3)	N(12)−Ru(1)−N(13)	89.6(3)
N(12)−Ru(1)−N(14)	173.8(3)	N(13)−Ru(1)−Nu(14)	89.9(3)
N(21)−Ru(2)−N(22)	90.5(3)	N(21)−Ru(2)−N(23)	178.2(3)
N(21)−Ru(2)−N(24)	89.8(3)	N(22)−Ru(2)−N(23)	89.6(3)
N(22)−Ru(2)−N(24)	179.2(3)	N(23)−Ru(2)−N(24)	90.1(3)
N(11)−Ru(1)−Ru(2)−N(21)	−21.3(3)	N(12)−Ru(1)−Ru(2)−N(22)	−21.2(3)
N(13)−Ru(1)−Ru(2)−N(23)	−21.3(3)	N(14)−Ru(1)−Ru(2)−N(24)	−21.3(3)
av torsion angle	−21.3		

Table 3. Atomic Coordinates ($\times 10^{-4}$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for the Unique Atoms Defining the Ru_2N_8Cl Core[a]

	x	*y*	*z*	*U*(eq)
Ru(1)	3195(1)	6924(1)	−2640(1)	19(1)
Ru(2)	818(1)	6915(1)	−2643(1)	17(1)
Cl	5697(2)	6930(2)	−2639(1)	30(1)
N(11)	2454(8)	8026(5)	−2011(4)	21(2)
N(21)	211(7)	7660(5)	−1716(4)	21(2)
N(12)	3263(8)	7628(5)	−3678(4)	23(2)
N(22)	777(8)	7926(5)	−3351(4)	24(2)
N(13)	3745(7)	5817(4)	−3269(4)	18(2)
N(23)	1487(7)	6173(5)	−3564(4)	21(2)
N(14)	2896(7)	6222(5)	−1614(4)	21(2)
N(24)	886(7)	5895(4)	−1937(4)	20(2)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

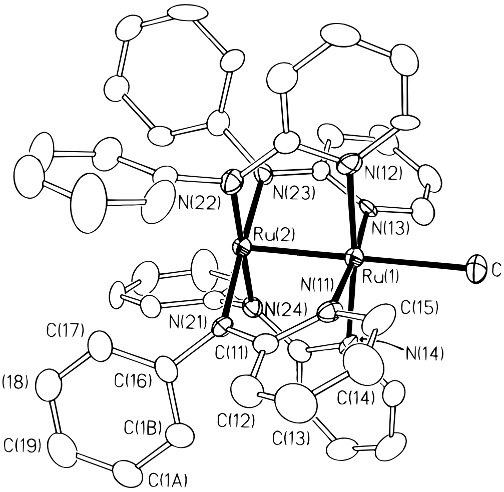
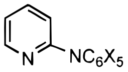


Figure 1. Thermal ellipsoid drawing of the cation in $[Ru_2(ap)_4Cl]$-$[FeCl_4]\cdot 2.5CH_2Cl_2$.

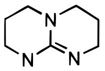
Table 4. Three Classes of Ru_2^{6+} Complexes

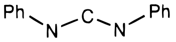
no. of unpaired electrons	complex	Ru−Ru (Å)	most probable electron confign
4	$[Ru_2(SO_4)_4(H_2O)_2]^{2-}$	2.343	$\sigma^2\pi^4\delta\pi^{*2}\delta^*$
0	$Ru_2(pfap)_4(CCPh)_2$	2.441	$\pi^4\delta^2\pi^{*4}$
	$Ru_2(DPhF)_4(CCPh)_2$	2.556	
	$Ru_2(DPhF)_4(CN)_2$	2.539	
2	$Ru_2(hpp)_4Cl_2$	2.321	$\sigma^2\pi^4\delta^2\pi^{*2}$
	$[Ru_2(ap)_4Cl]^+$	2.301	
3	$Ru_2(ap)_4Cl$	2.275	$\sigma^2\pi^4\delta^2\pi^{*2}\delta^*$

Ligand abbreviations: ap⁻ =


X = H

pfap⁻ = Same as ap⁻ with X = F

hpp⁻ =


DPhF⁻ =


oxidation only minor changes in the geometry of the Ru_2N_8Cl core are observed. The Ru−Ru distance increases to 2.301(1) Å, a 0.026 Å increase from its Ru_2^{5+} analogue, while the Ru−Cl distance decreases to 2.419(2) Å, a 0.018 Å decrease. The slight increase is entirely reasonable, since any tendency to decrease the metal−metal distance by the removal of a weakly antibonding electron is compensated by the increased electrostatic repulsion between the metal atoms. This increased electrostatic charge also causes the observed shortening of the Ru−Cl bond to yield one of the shortest such bonds observed to date.[5,12] Since most of the negative charge on the bridging ligands is expected to lie primarily on the amine-N it would be expected that the Ru−amine-N bonds should be shorter than the Ru−pyridine-N bonds, and, indeed, this is so. The Ru−amine-N bonds average 2.006(3) Å, and the Ru−pyridine-N bonds average 2.087(4) Å. Both of these are shorter than in the Ru_2^{5+} analogue, the difference being 0.017 Å for the Ru−pyridine-N bonds and 0.020 Å for the Ru−amine-N bonds. These differences are on the order of 3 times the standard uncertainty associated with the measurements. Finally, the N−Ru−Ru−N torsion angles in this molecule, averaging 21.3°, are approximately the same as those in its Ru_2^{5+} analogue, with an average of 22.7°.

Magnetic Properties. The magnetic properties, as well as the Ru−Ru bond distances, for various Ru_2^{6+} complexes fall into three different groups, i.e., those with 4, 2, or 0 unpaired electrons (Table 4). For comparison, the 11-electron analog of $[Ru_2(ap)_4Cl]^+$ is also included in Table 4.

As previously discussed[2,3] the sulfato-bridged anion has four unpaired electrons because of the near degeneracy of the δ, π^*, and δ^* orbitals. The resulting electron configuration, $\sigma^2\pi^4\delta\pi^{*2}\delta^*$, means that there is a δ bond order of zero and a π bond order of one. The resulting distance is 2.34 Å. Although, as will be seen, this distance is consistent with the electronic structure for this species as well as with the data for the remaining complexes in Table 4, we can hardly use this complex as a bench mark because it is so different from the others. It also seems unlikely that there will be many (or any) more examples of this unusual electron configuration.

The $[Ru_2(ap)_4Cl]^+$ ion is the first example of an Ru_2^{6+} unit bridged by $N-C-N^-$ type ligands with only one axial ligand. The recently reported[4c] $Ru_2(hpp)_4Cl_2$ is the only other example of an Ru_2^{6+} core bridged by $N-C-N^-$ type ligands but in this case there are two axial ligands. In these two the Ru−Ru distances, 2.32 and 2.30 Å, are very similar and consistent with the electron configuration $\sigma^2\pi^4\delta^2\pi^{*2}$. This consistency can be established by using the properties of the previously reported $Ru_2(ap)_4Cl$ (Ru−Ru = 2.28 Å) as a point of departure. The electron configuration of this molecule is unequivocally $\sigma^2\pi^4\delta^2\pi^{*2}\delta^*$ because it has three unpaired electrons, and no other configuration can account for that.

In going from $Ru_2(ap)_4Cl$[5] to the cation, $[Ru_2(ap)_4Cl]^+$, we do not change the ligand set at all, we merely remove an electron and raise the charge on the Ru_2 core by one unit, from +5 to +6. The increase in positive charge alone would tend to increase the Ru−Ru distance by *ca.* 0.02−0.03 Å, while the loss of a δ^* or a π^* electron would cause a contraction of either *ca.* 0.01−0.02 or *ca.* 0.08 Å, respectively. Clearly the net result of losing a δ^* electron would be a slight (0.01−0.02 Å) increase to *ca.* 2.29 Å. Conversely, loss of a π^* electron would cause a net 0.05−0.06 Å contraction to *ca.* 2.23 Å. From the actual result, a 0.02−0.03 Å increase, it is clear that a δ^* electron is lost. The electron configuration $\sigma^2\pi^4\delta^2\pi^{*2}$ must be correct for the $[Ru_2(ap)_4Cl]^+$ cation. The same configuration seems correct for the $Ru_2(hpp)_4Cl_2$ molecule,[4c] where the slightly greater Ru−Ru distance (by 0.02 Å) may be due to the presence of two axial Cl^- ligands.

This analysis is also consistent with having Ru−Ru distances of *ca.* 2.42−2.47 Å in $Ru_2(N-C-N)_4$ and $Ru_2(N-N-N)_4$ molecules[1] because of the combined effect of lowering the oxidation state from Ru_2^{6+} to Ru_2^{4+} and adding two π^* electrons to give a $\sigma^2\pi^4\delta^2\pi^{*4}\delta^{*0}$ $(-0.02 - 0.02 + 0.08 + 0.08 = +0.12)$ should take the Ru−Ru distance in an Ru_2^{6+} unit, *ca.* 2.32 Å, to about 2.44 Å in the corresponding Ru_2^{4+} unit.

Finally, we turn to the three Ru_2^{6+} species[4a,b] that have strongly bound $PhC{\equiv}C^-$ or $N{\equiv}C^-$ axial ligands, no unpaired electrons and very long Ru−Ru distances, 2.44, 2.54, and 2.56 Å. Simply removing two antibonding electrons from a $\sigma^2\pi^4\delta^2\pi^{*4}$ or $\sigma^2\pi^4\delta^2\pi^{*2}\delta^{*2}$ configuration could not possibly lengthen the Ru−Ru distance from ca. 2.30 Å to something in the range of 2.44−2.56 Å. So, how can we account for the experimental observations? We can do this only by removing the Ru−Ru σ bond, which frees the d_{z^2} orbitals to form very strong Ru−C bonds and gives a $\pi^4\delta^2\pi^{*4}$ configuration. Since this has only a net δ bond, the Ru−Ru distance will be very long.

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Supporting Information Available: Tables of fractional atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen atom coordinates are avaliable as an X-ray crystallographic file in CIF format. Access information is avaliable on any current masthead page.

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