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Inorganic Chemistry Article

Paramagnetism at Ambient Temperature, Diamagnetism at Low Temperature in a Ru_2^{6+} Core: Structural Evidence for Zero-Field Splitting

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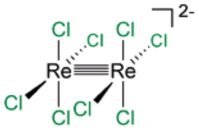
Variable temperature magnetic studies of the Ru_2^{6+} guanidinate compounds $Ru_2(hpp)_4Cl_2$ (**1**) and $Ru_2(hpp)_4(CF_3SO_3)_2$ (**2**) show that they are paramagnetic with two unpaired electrons at room temperature and that they appear essentially diamagnetic at 2 K. In neither compound do the Ru–Ru distances vary by more than 0.008(1) Å from 27 to 296 K. This argues strongly that the ground state electronic configuration remains constant over this temperature range and that the decrease in magnetism as the temperature is lowered must be attributable to zero-field splitting of the $^3A_{2g}$ ground state arising from the electronic configuration $\sigma^2\pi^4\delta^2\pi^{*2}$. The Ru-Ru distance in **1** is about 0.04–0.05 Å longer than that in **2** which indicates that the $Ru_2(hpp)_4^{2+}$ core is quite sensitive to the nature of the axial ligands. The electronic spectra show three absorption bands for each compound.

Introduction

Compounds having two roughly square-planar ML_4 units joined to each other by metal−metal multiple bonds have been known for four decades starting with the structural characterization of the $Re_2Cl_8^{2-}$ ion, **I**.[1] To date, a vast amount of information has been accumulated for such compounds as well as for those of the paddlewheel-type with bridging ligands, **II**.[2] This chemistry of compounds with metal−metal multiply bonded cores was extended to embrace the element ruthenium in the late 1960s when the first preparations were published.[3] The appearance of the first structure determination[4] and the first detailed studies of magnetism and electrochemistry provided[5] diruthenium chemistry with structural and physical foundations, and the field has expanded steadily ever since. Today, several hundred compounds are known, and structural data are available for about 200. Most of these compounds have paddlewheel structures, **II**, with a formal charge on the central Ru_2^{n+} unit which may be 4, 5, or 6.[6]



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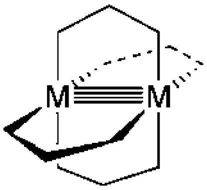

II

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Table 1. Possible Choices for the Electronic Configuration and Spin Degeneracies for Ru_2^{n+} Complexes Assuming That the δ^* and π^* Orbitals Are Nearly Degenerate

value of *n* in Ru_2^{n+} Core	electronic configuration[a]	symmetry label
5	$Q^8\delta^{*2}\pi^*$	^2E_g
5	$Q^8\delta^*\pi^{*2}$	$^2B_{1u}$
5	$Q^8\pi^{*3}$	^2E_g
4	$Q^8\delta^{*2}\pi^{*2}$	$^3A_{2g}$
4	$Q^8\delta^*\pi^{*3}$	^3E_u
4	$Q^8\pi^{*4}$	$^1A_{1g}$
6	$Q^8\delta^{*2}$	$^1A_{1g}$
6	$Q^8\delta^*\pi^*$	^3E_u
6	$Q^8\pi^{*2}$	$^3A_{2g}$

[a] $Q^8 = \sigma^2\pi^4\delta^2$.

Efforts to understand both the molecular and electronic structures of these compounds are nontrivial because of the uncertain order, and at times near degeneracy, of the δ^* and π^* orbitals.[7] The first class of Ru_2^{n+} compounds to be discovered and the most numerous are those with $n = 5$. Of the 11 electrons occupying the metal-based molecular orbitals of a Ru_2^{5+} core, eight are generally accounted for in the lower four MOs, namely as the partial configuration $\sigma^2\pi^4\delta^2$, which will be an invariant in the following discussion. Taken alone it would correspond to the formation of a quadruple bond, and it will be convenient to represent it compactly by Q^8. On the assumption that the δ^* and π^* orbitals may differ little in energy, three possible choices for the ground state electronic configurations, which may have different spin degeneracies, are possible as seen in Table 1. Such variability is also possible for Ru_2^{4+} and Ru_2^{6+} species, as also shown in Table 1.

Unfortunately, the discussion so far (while correct as far as it goes) is so superficial as to be completely insufficient to provide satisfactory interpretation of the experimental facts in many of the real cases. The following additional factors may come into play.

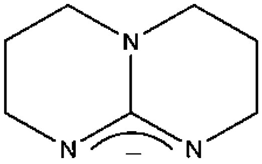
(1) Interaction of both filled and empty π orbitals on the paddlewheel ligands may vitiate the assumption of near degeneracy of the δ^* and π^* orbitals. The importance of this may change a great deal over a range of ligands from RCO_2^- at one extreme to guanidinate anions at the other.[8,9]

(2) The presence of strongly bound axial ligands may vitiate the assumption of an invariant Q^8 set of electrons.[10]

(3) Even if neither 1 nor 2 comes into play, two (or even three) states based on different configurations may be so close in energy that their populations will change significantly with temperature. This will make both structural and magnetic properties temperature dependent.

(4) For all triplet and quartet states, zero-field splitting (ZFS) due to spin−orbit coupling can cause the magnetic properties to be strongly temperature dependent. This is fairly prominent in the relatively few variable temperature (VT) magnetic studies of mainly Ru_2^{5+} species, where the magnetic moment at room temperature is generally about 4.0 μ_B (χT of 2.0 emu K mol^{-1}, if g is about 2.0) and can drop to about 3.0 μ_B (χT of 1.125 emu K mol^{-1}, if g is about 2.0) near 0 K.[11] Similar behavior is observed for carboxylates having Ru_2^{4+} units.[12]

It is clear from this introduction that a complete explanation of the properties of the entire range of Ru_2^{n+} paddlewheel compounds is still to be achieved and will result only from the accumulation of extensive experimental data combined with the application of appropriate (i.e., sufficiently sophisticated) theory. This report makes a modest but significant contribution which is concerned with compounds of the Ru_2^{6+} class with relatively weak axial ligation. We offer here some experimental results, including structural data of a type never presented before, for compounds so chosen that an entirely unambiguous interpretation is straightforwardly obtained. In a nutshell, the work described here proves unequivocally that, in both $Ru_2(hpp)_4Cl_2$, **1**, and $Ru_2(hpp)_4(CF_3SO_3)_2$, **2** (hpp = the anion of 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine, **III**), the electron configuration $Q^8\pi^{*2}$ ($S = 1$) persists from 2 to 300 K even though both compounds are essentially diamagnetic at 2 K.



III

Experimental Section

Materials and Methods. All reactions and manipulations were performed under a nitrogen atmosphere, using standard Schlenk line techniques. Commercial grade solvents were dried over appropriate drying agents, and deoxygenated by reflux for at least 24 h under an N_2 atmosphere. They were freshly distilled prior to use. Compound **1** was prepared as described in the literature.[13]

Mass spectrometry data (electrospray ionization) were recorded at the Laboratory for Biological Mass Spectrometry at Texas A&M University, using an MDS Series Qstar Pulsar with a spray voltage of 5 kV. Elemental analyses were performed by Robertson Microlit Laboratories, Inc., Madison, NJ. Infrared spectra were recorded in a Perkin-Elmer 16PC FT IR spectrophotometer as KBr pellets.

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(8) See for example: (a) Cotton, F. A.; Falvello, L. R.; Ren, T.; Vidyasagar, K. *Inorg. Chim. Acta* **1992**, *194*, 163. (b) Cotton, F. A.; Ren, T. *Inorg. Chem.* **1991**, *30*, 3675. (c) Cotton, F. A.; Yokochi, A. *Inorg. Chem.* **1997**, *36*, 567. (d) Cotton, F. A.; Yokochi, A. *Inorg. Chem.* **1998**, *37*, 2723.

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(10) See for example: Chen, W.-Z.; Ren T. *Inorg. Chem.* **2003**, *42*, 8847.

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Table 2. Crystallographic Data for $Ru_2(hpp)_4Cl_2$ (**1**) and $Ru_2(hpp)_4(O_3SCF_3)_2$ (**2**) at Selected Temperatures[a]

	1		**2**		
formula	$C_{28}H_{48}Cl_2N_{12}Ru_2$		$C_{30}H_{48}F_6N_{12}O_6Ru_2S_2$		
fw	825.82		1053.06		
T (K)	27	296	27	100	296
space group	$I4/m$ (No. 87)	$I4/m$ (No. 87)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)
a (Å)	9.8910(9)	10.060(3)	15.4770(9)	15.5202(9)	9.4194(8)
b (Å)	9.8910(9)	10.060(3)	15.4839(9)	15.4928(9)	15.515(1)
c (Å)	15.845(1)	16.021(4)	17.003(1)	17.030(1)	13.613(1)
α (deg)	90	90	90	90	90
β (deg)	90	90	110.4650(10)	110.4930(10)	95.326(2)
γ (deg)	90	90	90	90	90
V (Å^3)	1550.1(2)	1621.3(7)	3817.5(4)	3835.6(4)	1980.8(3)
Z	2	2	4	4	2
d_{calcd} (g/cm^3)	1.769	1.692	1.832	1.824	1.766
μ (mm^{-1})	1.190	1.138	0.991	0.986	0.955
radiation			Mo Kα (λ = 0.71073 Å)		
R1,[b] wR2[c]	0.031, 0.067	0.027, 0.070	0.068, 0.154	0.068,0.154	0.049, 0.128

[a] For data at other temperatures, see Supporting Information. [b] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = [\max(0 \text{ or } F_o^2) + 2(F_c^2)]/3$.

Electronic spectra was recorded on a Shimadzu UV-2501 PC spectrophotometer. Variable temperature magnetic susceptibility measurements were obtained with the use of a Quantum Design SQUID magnetometer MPMS-XL at 1000 G, from 300 to 2 K, and the data were corrected for diamagnetism. Cyclic voltammograms (see Supporting Information) were recorded using a BAS 100 electrochemical analyzer with a 2 mm Pt disk working electrode, Ag/AgCl reference electrode, and Pt wire auxiliary electrode using dichloromethane solutions that were 1 mM in analyte and 0.1 M in Bu_4NPF_6 supporting electrolyte.

Synthesis of $Ru_2(hpp)_4(O_3SCF_3)_2$, 2. A solution of **1** (0.100 g, 0.121 mmol) in 20 mL of CH_2Cl_2 was transferred to a Schlenk flask containing silver triflate (0.055 g, 0.242 mmol). The dark green solution turned deep blue, and a colorless precipitate was observed. The mixture was stirred for 1 h and then filtered through Celite into a Schlenk tube and layered with hexanes. Crystals of **2** as deep blue needles were harvested after 10 days. Yield: 0.079 g (66%). IR (KBr, cm^{-1}): 3323 (m), 3246 (m), 2961 (m), 2883 (m), 1635 (s), 1534 (s), 1468 (m), 1444 (m), 1425 (m), 1382 (m), 1324 (m), 1261 (s), 1227 (s), 1156 (s), 1097 (m), 1065 (m), 1029 (s), 901 (w), 877 (w), 801 (m), 758 (w), 638 (s), 575 (w), 519 (w), 460 (w). Elemental analysis. Calcd for $C_{30}H_{48}F_6N_{12}O_6Ru_2S_2$: C, 34.21; H, 4.59; N, 15.96. Found: C, 34.06; H, 3.94; N, 15.78. Mass spectrum (ESI$^+$): 1054.1 $(M + H^+)^+$, 904.2 $((M - [O_3SCF_3^-])^+$, main peak). UV−Vis (CH_2Cl_2) λ_{MAX}, nm (ϵ_M, L·mol^{-1}·cm^{-1}): 730 (11000), 586 (sh), 389 (4900). Cyclic voltammetry (potential vs Ag/AgCl): 0.869 V ($E_{p,a}$, Ru^{6+}/Ru^{7+}), −0.262 V ($E_{1/2}$, Ru^{5+}/Ru^{6+}).

X-ray Crystallography. Single crystals of **1** and **2** were mounted on a glass fiber with cyanoacrylate glue ("super glue") and transferred to a goniometer head. Data were collected for **1** and **2** at 27, 50, 100, and 296 K. For each compound, one crystal was used in data collection at all temperatures, except for the room temperature data collection of **2**.[14] A BRUKER SMART 1000 X-ray three-circle diffractometer equipped with an Oxford Helix cooling system for low-temperature measurements was employed for crystal screening, unit cell determination, and data collection. The goniometer was controlled using the SMART software suite.[15] For comparison, data were also collected at 213 K for **2** using a second BRUKER SMART 1000 diffractometer. No significant differences were observed upon solution of the structures. Integrated intensity information for each reflection was obtained by reduction of the data frames with the program SAINT.[16] The absorption correction program SADABS[17] was employed to correct the data for absorption effects.

A phase transition was observed for **2** at temperatures below 213 K. The unit cell at low temperature is related to that at higher temperatures by the transformation matrix (101, 0 −10, 10 −1). As a result, the unit cell volume is doubled at lower temperature, and the space group, determined from systematic reflection conditions and statistical tests, is $P2_1/c$ for the data sets collected between 27 and 100 K and $P2_1/n$ for the sets collected at 213 K and room temperature. Determination of the space group for **1**, $I4/m$, has been discussed previously.[13] The structures were solved readily in their respective space group choices by Patterson map interpretation. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms bound to carbon atoms were placed in idealized positions. The structures were refined (weighted least squares refinement on F^2) to convergence.[18] The carbon atoms in the periphery of the bicyclic ring system as well as the nitrogen atoms bonded to ruthenium in **1** were disordered (50/50) over two positions and were modeled with distance restraints. For **2**, the carbon atoms on the periphery of the bicyclic ring system appear to be disordered (50/50) over two positions and were modeled accordingly. Selected structure parameters at different temperatures for **1** and **2** are given in Table 2.

Results and Discussion

Magnetism. Because of the paucity of variable temperature magnetic studies and the possibility of various ground state electronic configurations of Ru_2^{6+} complexes, the VT study of the magnetic properties of $Ru_2(hpp)_4Cl_2$ and $Ru_2(hpp)_4(CF_3SO_3)_2$ was undertaken. The results, presented in Figure 1, show χT values at room temperature of about 1.1 emu K mol^{-1}, which correspond to 2 unpaired electrons. This is consistent with the room temperature measurement of the magnetic susceptibility of **1** reported earlier. However,

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(14) Use of a second crystal of **2** was necessary because some decomposition was observed at room temperature while collecting data on the crystal used for the low temperature data collections.

(15) *SMART* V5.625, *Program for Data Collection on Area Detectors*; Bruker AXS Inc.: Madison, WI.

(16) *SAINT* V6.45, *Program for Reduction of Area Detector Data*, Bruker AXS Inc.: Madison, WI.

(17) *SADABS*, V2.05, *Program for Absorption Correction of Area Detector Frames*; Bruker AXS Inc.: Madison, WI.

(18) Sheldrick, G. *SHELXL-97 Program for Crystal Structure Refinement*; Institüt für Anorganische Chemie der Universität: Göttingen, Germany, 1997.

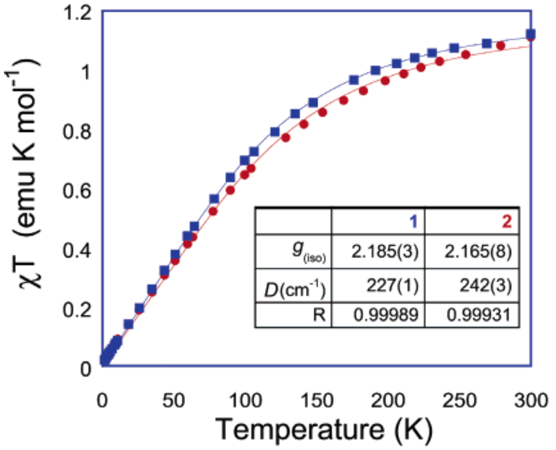

Figure 1. Variation of the magnetic susceptibilities of **1** (blue) and **2** (red) as a function of temperature showing the presence of two unpaired electrons at room temperature and a steady decrease in magnetism as the temperature is lowered to 2 K.

as Figure 1 shows, χT decreases steadily as the temperature is lowered to values of essentially zero at 2 K which make the compounds essentially diamagnetic at that temperature. Variable temperature magnetic data for the more common Ru_2^{5+} species have shown that a lowering of the χT values with decreasing temperature is often found but such values never approach zero.[19,20] Such decreases have always been attributed to zero-field splitting, the essence of which lies in weak interaction of the spins mediated by spin−orbit coupling.

Modeling of the magnetic data by employing the equation previously used for a dimetal system with a $^3A_{2g}$ ground state[7a] indicates that for these two compounds a satisfactory fitting is obtained with isotropic g values of 2.185(3) and 2.165(8) for **1** and **2**, respectively. The equation employed is

$$\chi = \frac{N\beta^2 g^2}{3kT}\cdot\frac{8\cdot\left(e^{-D/kT} + \left(\frac{2kT}{D}\right)\left(1 - e^{-D/kT}\right)\right)}{\left(1 + 2e^{-D/kT}\right)}$$

where D is the ZFS parameter,[21] k is the Boltzmann constant, N is Avogadro's number, and β is the Bohr magneton. The resulting g values are within the range found in other Ru_2 species.[5,8a,22] The values for the ZFS parameter D of 227(1) and 242(3) cm^{-1} for **1** and **2**, respectively, are similar to those in $Ru_2(O_2CCH_3)_4$,[23] which has a D value of 244(10) cm^{-1}, but they are much larger than those previously reported in Ru_2^{5+} species,[20] or for that matter in most transition metal complexes.[24]

It should be kept in mind that even though compounds with 10 core electrons and an Ru_2^{6+} unit are the smallest group of diruthenium paddlewheel species, they offer a remarkable variety and range of behavior. The Ru−Ru distances have been reported to vary from the unusual and very short unsupported bond of 2.166(1) Å in a corrole homodimer, $Ru_2(hedmc)_2$ where hedmc is the trianion of 2,3,8,12,17,18-hexaethyl-7,13-dimethylcorrole,[25] to distances as large as about 2.5 Å in a growing number of complexes of the type $Ru_2(amidinate)_4X_2$, where the groups X are $-C\equiv N$ or $-C\equiv CR$.[22,26] The number of unpaired electrons in Ru_2^{6+} species has been documented to vary from 0 to 2 to 4. Diamagnetic complexes are those with either extremely long or extremely short metal−metal distances, e.g., $Ru_2(hedmc)_2$ and $Ru_2(amidinate)_4X_2$, X = acetylides. The diamagnetism in the former can be straightforwardly explained by assigning ground state electronic configurations of $Q^8\delta^{*2}$. The electronic configuration of the latter is still subject to debate, but a proposed configuration of the type $\sigma^0\pi^4\delta^2\delta^{*0}\pi^{*4}$ is consistent with the long Ru−Ru distances and diamagnetism.[10] For Ru_2^{6+} complexes with 2 unpaired electrons, such as those of the type $Ru_2(Yap)_4X_2$, where Yap is a substituted aminopyridinate group, or $Ru_2(amidinate)_4X_2$, and X is a weak π donor group, it has been suggested that the ground state electronic configuration is $Q^8\pi^{*2}$.[10] These compounds generally have Ru−Ru distances slightly above 2.3 Å. The compound $K_2[Ru_2(SO_4)_4(H_2O)_2]$, with a Ru−Ru distance of 2.3052(4) Å, has 4 unpaired electrons,[27] and a $\sigma^2\pi^4\delta\pi^{*2}\delta^*$ configuration has been proposed to account for this.

Two explanations for the magnetic behavior of **1** and **2** can be considered. The first is that the ground state derives from a $Q^8\delta^{*2}$ configuration but that there is a thermally accessible triplet state derived from a $Q^8\delta^*\pi^*$ configuration. Were this the case, the Ru−Ru distance should be temperature-dependent, increasing by roughly 0.05 Å from 0 to 296

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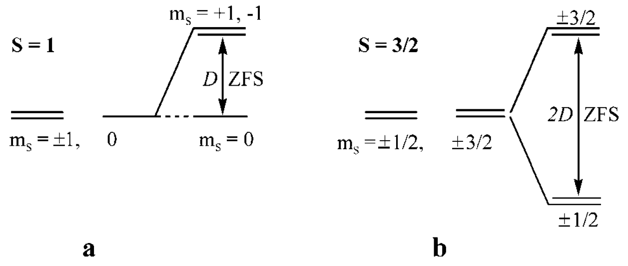
(19) Note that a χT value of 0 is not possible for a system with $S = {}^3/_2$, because the splitting due to ZFS results in Kramer doublets with m_S values of $\pm{}^1/_2$ and $\pm{}^3/_2$.

(20) See for example: (a) Jiménez-Aparicio, R.; Urbanos, F. A.; Arrieta, J. M. *Inorg. Chem.* **2001**, *40*, 613. (b) Barral M. C.; de la Fuente, I.; Jiménez-Aparicio, R.; Priego, J. L.; Torres, M. R.; Urbanos, F. A. *Polyhedron* **2001**, *20*, 2537.

(21) For a system with an $S = 1$, the D parameter is defined as shown in part a, while that of an $S = {}^3/_2$ is given in part b as $2D$. Thus, Ru_2^{5+} systems with $S = 3/2$ are usually fitted with an equation which has a D parameter which is half of that used in this equation.



(22) See also: (a) Bear, J. L.; Han, B.; Huang, S. *J. Am. Chem. Soc.* **1993**, *115*, 1175. (b) Bear, J. L.; Han, B.; Huang, S.; Kadish, K. M. *Inorg. Chem.* **1996**, *35*, 3012.

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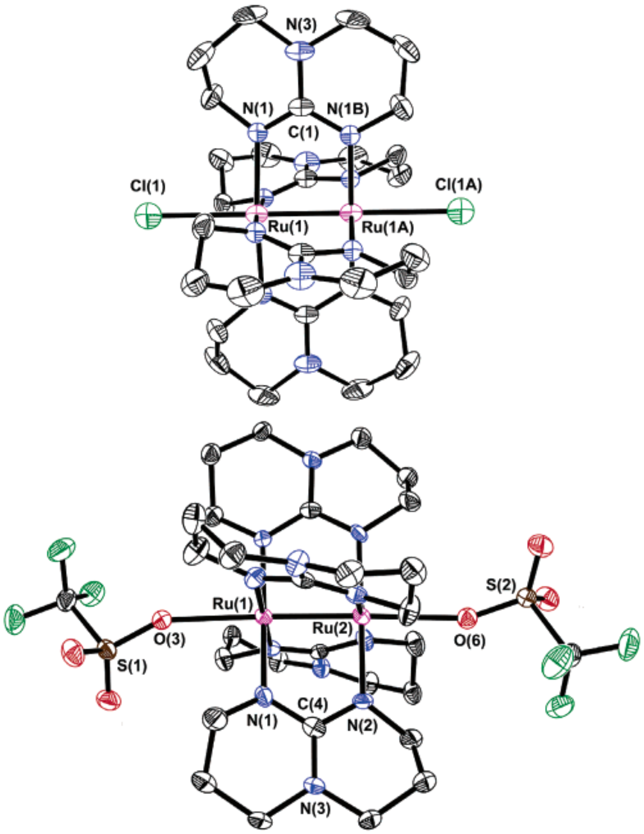

Figure 2. The structures of **1** (top) and **2** (bottom), at 100 K, with displacement ellipsoids at the 50% probability level.

Table 3. Selected Distances for **1** and **2** at Various Temperatures[a]

$Ru_2(hpp)_4Cl_2$ (**1**)

T/K	Ru(1)−Ru(1A)	Ru(1)−Cl(1)	Ru(1)−N_{av}
27	2.3233(9)	2.679(2)	2.046[3]
50	2.3250(9)	2.680(2)	2.05[2]
100	2.3238(9)	2.682(2)	2.05[2]
213[b]	2.3167(6)	2.705(1)	2.04[2]
296	2.3242(9)	2.697(2)	2.05[1]

$Ru_2(hpp)_4(O_3SCF_3)_2$ (**2**)

T/K	Ru(1)−Ru(2)	Ru(1)−O(3)	Ru(2)−O(6)	Ru(1)−N_{av}	Ru(2)−N_{av}
27	2.2831(5)	2.371(3)	2.454(3)	2.05[1]	2.04[2]
50	2.2824(5)	2.374(3)	2.454(3)	2.05[1]	2.04[2]
100	2.2805(5)	2.382(3)	2.455(3)	2.04[1]	2.04[2]
213[c]	2.2804(7)	2.434(3)		2.05[1]	
296	2.2763(6)	2.453(3)		2.03[1]	

[a] Except for the data at 213 K, all data were collected on a BRUKER SMART 1000 diffractometer equipped with an Oxford Helix cooling system. [b] See ref 13a. [c] Data collected on a different SMART diffractometer.

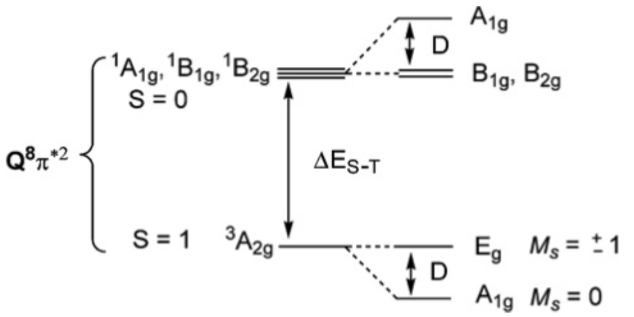

Figure 3. Diagram of the states arising from a $\sigma^2\pi^4\delta^2\pi^{*2}$ ($Q^8\pi^{*2}$) configuration and the splitting of the ground state, $^3A_{2g}$.

K.[28] A second explanation is that a $Q^8\pi^{*2}$ configuration prevails over the entire temperature range, with the changing magnetic susceptibility attributable to ZFS of $D > 0$ causing a nonmagnetic state to lie below a state with two unpaired electrons. In this second case, the structure should be essentially independent of temperature even though χT is changing a great deal. To bring this decisive structural criterion into play, we have determined the structures of **1** and **2** from 27 K (the lowest temperature attainable with our helium cryostat) to 296 K.

Structures at Various Temperatures. Structures of **1** and **2** (Figure 2) were determined at 27, 50, 100, 213, and 296 K, and a selected number of data are provided in Table 3. The Ru−Ru distances are essentially invariant at all measured temperatures for both **1** and **2**, and the maximum variation is less than 0.008(1) Å. Such small variations can be accounted for by the expected changes in thermal motion as the temperature drops.[29] A change in the ground state electronic configuration would have led to significant changes in Ru−Ru distances (vide supra). The invariance of the metal−metal distances indicates unambiguously that the electronic configuration does not change and supports an electronic configuration of $Q^8\pi^{*2}$ that persists from 2 to 300 K. Therefore, the drop in magnetism as the temperature decreases must be attributed to ZFS in a way described in Figure 3, which shows that the degeneracy of the $^3A_{2g}$ ground state is partially removed by splitting into A_{1g} and E_g terms. These arise from the microstates $M_S = 0$ and $M_S = \pm1$ derived from the $S = 1$ state. The splitting pattern is similar to that in $Ru_2(O_2CCH_3)_4$, an Ru_2^{4+} species which also has a $^3A_{2g}$ ground state.[23]

There are also minor changes in the weak Ru−Cl_{ax} bond in **1** for which the distances are in the range 2.679(2)−2.705(1) Å. For **2**, the crystal undergoes a phase transition (see Experimental Section) somewhere between 100 and 213 K which modifies the bonding to the axial triflate ligand. In the high temperature range, the two triflate anions are crystallographically equivalent, but they are inequivalent in the low temperature range (Table 3).

Even though the Ru−Ru distances do not change significantly with temperature for either compound, there are important differences in those distances from one compound to the other. The Ru−Ru distance in **1** is about 0.045 Å longer than that in **2**. This provides an excellent example of the fact that even when axial interactions are relatively weak, the metal−metal distance is quite sensitive to changes of the axial ligand. However, in the $Ru_2(hpp)_4^{2+}$ core the Ru−N distances are the same within the error of the measurement in both **1** and **2** (Table 3). Similar behavior has been observed before in $Ru_2(DMBA)_4X_2$ compounds, $X^- = BF_4$, NO_3, N_3,

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(28) Changes in metal−metal distances of about 0.03−0.05 Å are commonly observed by removal of electrons from δ or δ^* orbitals, whereas a larger increase, 0.05−0.08 Å, would be expected by populating π^* orbitals. See for example: Cotton, F. A.; Daniels, L. M.; Murillo, C. A.; Timmons, D. J.; Wilkinson, C. C. *J. Am. Chem. Soc.* **2002**, *124*, 9249.

(29) (a) Cruickshank, D. W. J. *Acta Crystallogr.* **1956**, *9*, 1005. (b) Bürgi, H. B.; Capelli, S. C. *Acta Crystallogr.* **2000**, *A56*, 403. (c) Capelli, S. C.; Förtsch, M.; Bürgi, H. B. *Acta Crystallogr.* **2000**, *A56*, 413.

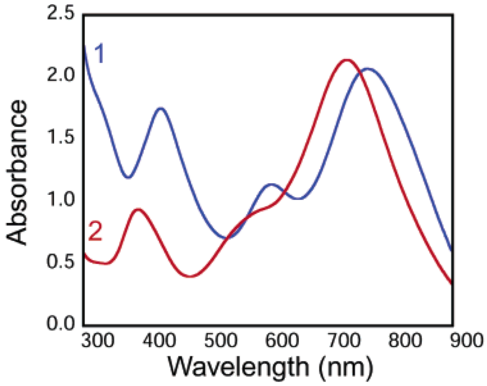

Figure 4. Electronic spectra showing 3 absorption bands in the visible region of 460 μM and 190 μM CH_2Cl_2 solutions of **1** (blue) and **2** (red), respectively.

$N(CN)_2$, I, Cl, and DMBA = *N*,*N*′-dimethylbenzamidinate,[10,26d] and also in other compounds with substituted aminopyridinate anions.[30]

Electronic Spectra. Little effort has been devoted to the electronic spectra of Ru_2^{6+} compounds. As shown in Figure 4, each compound shows three absorptions, in CH_2Cl_2 solutions, in the visible region. For **1**, these are at 427, 607, and 763 nm,[31] and for **2**, they appear at 389, 586(sh), and 730 nm. Bear, Kadish, and co-workers have reported the appearance of the same number of bands in compounds of the type $Ru_2(Yap)_4^{2+}$ which have the same electronic configuration as **1** and **2**. These compounds were generated using electrochemical means from $Ru_2(Yap)_4Cl$ precursors.[32] The positions of the bands in such compounds is very sensitive to the nature of the solvent.

On the contrary, other Ru_2^{6+} compounds with other electronic configurations exhibit very different electronic spectra. For example, the product of oxidation of $K_2[Ru_2(HPO_4)_3(PO_4)(H_2O)_2]$ which yields an analogue of $K_2[Ru_2(SO_4)_4(H_2O)_2]$ with 4 unpaired electrons gives a spectrum with only one peak at 490 nm,[27] while those diamagnetic compounds with long Ru−Ru bonds of the type $Ru_2(amidinate)_4X_2$ show a peak at around 500−550 nm and what appears to be a charge transfer band with the onset at around 800 nm.[33,26a] The diamagnetic species $Ru_2(corrole)_2$ with a short Ru−Ru bond has a band at 336 nm with a shoulder at 393 nm and no major bands in the visible region.[34] Thus, the limited data available for Ru_2^{6+} compounds show significant differences in the electronic spectra which is consistent with variations in electronic configuration.

Summary Remark

It has been shown that the drop in magnetism as the temperature is lowered in $Ru_2(hpp)_4Cl_2$ and $Ru_2(hpp)_4(CF_3SO_3)_2$ that makes them essentially diamagnetic at 2 K is not due to a change in electronic configuration but is due to zero-field splitting.

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Supporting Information Available: Crystallographic data in CIF format for compounds **1** and **2** at 27, 50, 100, and 296 K, and at 213 K for **2**. Cyclic voltammogram of **2** in PDF. This material is available free of charge via the Internet at http://pubs.acs.org.

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(31) This values are similar to those reported earlier. See ref 13b.

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