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Diruthenium Complex

# A Spin-Admixed Ruthenium Complex**

M. Carmen Barral, Santiago Herrero, Reyes Jiménez-Aparicio,* M. Rosario Torres, and Francisco A. Urbanos

Ruthenium complexes attract great attention because of their potential use in electronic and magnetic devices.[1] Multiply bonded diruthenium compounds, in particular, have been investigated as models or building blocks to construct magnets, wires, switches, and other molecular devices.[2] Among this type of compounds the diruthenium(II,III) complexes are the most widely studied owing to their unusual stability.[3,4] In general, they have three unpaired electrons in accordance with a ground state electronic configuration of $\sigma^2\pi^4\delta^2(\pi^*\delta^*)^3$ owing to close spacing of the $\pi^*$ and $\delta^*$ orbitals, as predicted by the theoretical studies of Norman et al.[5] This electronic configuration has been observed in all complexes containing the $[Ru_2(\mu\text{-L})_4]^+$ unit with L = carboxylate, amidate, hydroxypyridinate, or aminopyridinate.[3,4] When L is a triazenide or formamidinate ligand, the energy difference between the $\pi^*$ and $\delta^*$ levels is larger, and the electronic structure $\sigma^2\pi^4\delta^2\pi^{*3}$ is favored.[6] However, only a few examples of low-spin diruthenium(II,III) complexes with this

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[*] Dr. M. C. Barral, Dr. S. Herrero, Dr. R. Jiménez-Aparicio,
Dr. F. A. Urbanos
Departamento de Química Inorgánica
Universidad Complutense
Ciudad Universitaria, 28040 Madrid (Spain)
Fax: (+34) 91-394-4352
E-mail: qcmm@quim.ucm.es

Dr. M. R. Torres
Centro de Asistencia a la Investigación de Rayos X
Facultad de Ciencias Químicas
Universidad Complutense
Ciudad Universitaria, 28040 Madrid (Spain)

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electronic configuration are known.[6,7] Moreover, $[Ru_2Cl(\mu\text{-}O_2CMe)(\mu\text{-}DPhF)_3]$ (DPhF = *N*,*N*′-diphenylformamidinate)[8] has three unpaired electrons, whereas the derivative $[Ru_2(NCS)(\mu\text{-}O_2CMe)(\mu\text{-}DPhF)_3]$ is a low-spin complex with only one unpaired electron.[7] Chen and Ren also reported high- and low-spin diruthenium(III) complexes with the same core but different axial ligands.[9]

The high sensitivity of the magnetic moment to the nature of the axial ligand in this class of compounds challenged us to find the limit at which the difference in energy between the $\pi^*$ and $\delta^*$ levels becomes similar to the electron-pairing energy. The aim was to design compounds whose magnetic properties are very sensitive to small changes in the environment.

To facilitate the search for a suitable axial ligand we prepared in good yield an air-stable compound with a labile water molecule at the axial position, namely, $[Ru_2(\mu\text{-}O_2CMe)(\mu\text{-}DPhF)_3(H_2O)]BF_4{\cdot}0.5\,CH_2Cl_2$ (**1**). Crystals of **1** were used for all measurements, including an X-ray diffraction study.[10]

The crystal structure of **1** (Figure 1) shows an eclipsed paddle-wheel disposition of the equatorial acetate and diphenylformamidinate ligands with a torsion angle of less than 0.5°. The water molecule is coordinated to the axial positions of the diruthenium units with 50 % occupancy. The metal–metal bond (2.3503(9) Å) is longer than in the parent compounds $[Ru_2Cl(\mu\text{-}O_2CMe)(\mu\text{-}DPhF)_3]$ (2.3203(5) Å)[8] and $[Ru_2(NCS)(\mu\text{-}O_2CMe)(\mu\text{-}DPhF)_3]$ (2.3182(11) Å).[7]

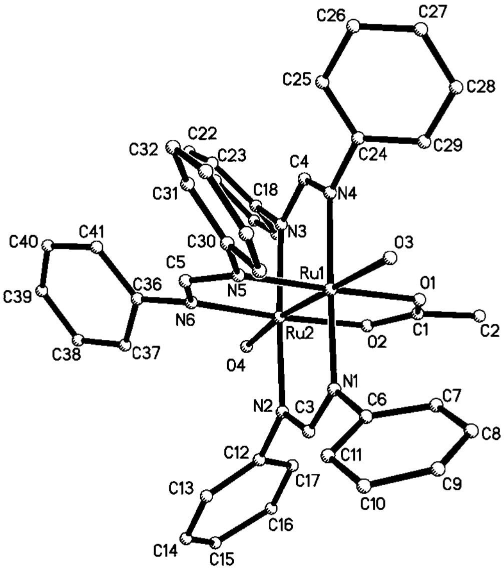

***Figure 1.*** PLUTO view of the cationic unit $[Ru_2(\mu\text{-}O_2CMe)(\mu\text{-}DPhF)_3(H_2O)]^+$ in **1**. Hydrogen atoms are omitted for clarity.

Complex **1** shows exceptional magnetic behavior (Figure 2), intermediate between those observed for the chloro and the isothiocyanato derivatives. The $\mu_{\text{eff}}$ value at room temperature corresponds to the presence of two unpaired electrons (3.09 $\mu_B$). Similar values for the magnetic moment (between $S = 1/2$ and $S = 3/2$) were also found at room temperature for diosmium(II,III) complexes such as $[Cp_2Co][Os_2Cl_2(\mu\text{-}O_2CPr)_4]$[11] and $[Os_2Cl(\mu\text{-}chp)_4]$ (chp = 6-chloro-2-hydroxypyridinate)[12]: 2.73 and 2.90 $\mu_B$, respectively. However, $[Os_2Cl(\mu\text{-}fhp)_4]$ (fhp = 6-fluoro-2-hydroxypyridinate) has a magnetic moment of 3.70 $\mu_B$.[13] at room temperature. These intermediate values were ascribed to some important contributions of the $S = 1/2$ and $S = 3/2$ spin states.[11–14] Unfortunately, the absence of magnetic data for a wide temperature range prevented the authors from providing a more satisfactory explanation.

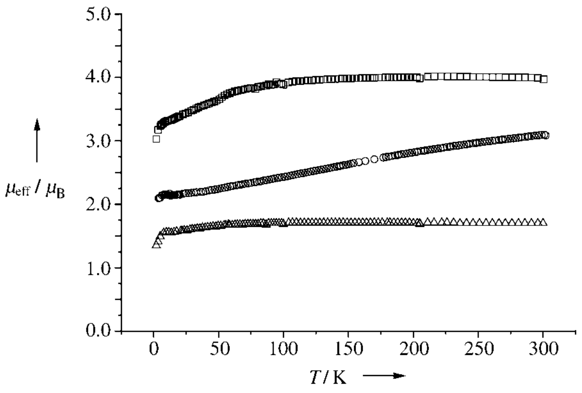

***Figure 2.*** Magnetic moment curves versus temperature for $[Ru_2Cl(\mu\text{-}O_2CMe)(\mu\text{-}DPhF)_3]$ (□), $[Ru_2(NCS)(\mu\text{-}O_2CMe)(\mu\text{-}DPhF)_3]$ (△), and $[Ru_2(\mu\text{-}O_2CMe)(\mu\text{-}DPhF)_3(H_2O)]BF_4{\cdot}0.5\,CH_2Cl_2$ (**1**; ○).

Our attempts to simulate the experimental curve of $\mu_{\text{eff}}$ versus $T$ for **1** as a thermal spin equilibrium (spin crossover) between the $S = 1/2$ and $S = 3/2$ spin states or as a physical spin mixture were unsuccessful. However, this magnetic behavior can be explained by considering a quantum mechanical spin admixture which generates a new discrete spin state by mixing of the $S = 1/2$ and $S = 3/2$ spin states. This mixing of states takes place through spin–orbit coupling[15] when both spin configurations are close in energy (with a difference comparable to or less than the spin–orbit coupling constant).

Such spin admixtures have been observed in several first-row transition-metal complexes, mainly for low-symmetry iron compounds in which high, low, and intermediate spin states are possible.[15] To our knowledge, there is no example of complexes of metals of the second and third transition series that show this type of magnetic behavior. This is not surprising given the usually large energy gap between the different spin states for these type of compounds. However, in complexes with a $[Ru_2(\mu\text{-}O_2CMe)(\mu\text{-}DPhF)_3]^+$ core, the $S = 1/2$ and $S = 3/2$ spin states are sufficiently close in energy that either can be obtained by variation of the axial ligand. Furthermore, ruthenium is a second-row transition metal, for which significant spin–orbit interactions can be expected. Indeed, in compounds of this kind with three unpaired electrons, the drop in magnetic moment at low temperatures indicates the presence of zero-field splitting, the magnitude of which is related to the strength of the spin–orbit coupling. Therefore, these diruthenium compounds could form spin-admixed ground states with an appropriate axial ligand, as observed in complex **1**. This finding and the potential of compound **1** to be used as a building block open the door to designing supramolecular materials with special magnetic properties.

## Experimental Section

**1** was prepared by adding $AgBF_4$ (0.118 g, 0.606 mmol) to a suspension of $[Ru_2Cl(\mu\text{-}O_2CMe)(\mu\text{-}DPhF)_3]$[8] (0.526 g, 0.596 mmol) in 10 mL of THF. The mixture was protected from light and stirred for 1 day. The bluish solution was filtered though Celite, and the solvent was removed by evaporation. The residue was dissolved in 10 mL of dichloromethane (hydrous), and the resulting solution was layered with 80 mL of hexane. When the diffusion was complete, the crystals were collected. Yield: 81 %. Elemental analysis (%) calcd for **1**: C 50.14, H 3.95, N 8.45; found: C 50.16, H 4.03, N 8.44; IR (KBr): $\tilde{\nu} =$ 3058, 3036, 2959, 1626, 1592, 1531, 1488, 1439, 1316, 1216, 1083, 1057, 1027, 1001, 940, 842, 777, 739, 696, 659, 619, 519 $cm^{-1}$; UV/Vis (MeOH): $\lambda_{max}$ $(\varepsilon) = 495$ (5900), 564 nm ($6000\,M^{-1}cm^{-1}$); $\Lambda = 118.6\,\Omega^{-1}cm^2mol^{-1}$; ESI-MS ($CHCl_3$): $m/z$: 848 $[M^+-H_2O]$.

Magnetic susceptibility was measured on a Quantum Design MPMSXL SQUID susceptometer and corrected for diamagnetic contributions. The differences in the magnetic behavior for samples prepared directly from crystals to those prepared by crushing the crystals to form disks under pressure are insignificant.

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[10] Crystal data for **1**: $BC_{41.5}ClF_4H_{39}N_6O_3Ru_2$, $M_r = 994.209$, thin violet plate ($0.04 \times 0.30 \times 0.38$ mm), triclinic, space group $P\bar{1}$, $a = 11.8028(8)$, $b = 12.1149(9)$, $c = 16.5002(12)$ Å, $\alpha = 100.1500(10)$, $\beta = 99.0910(10)$, $\gamma = 109.4040(10)°$, $V = 2130.1(3)$ Å$^3$, $Z = 2$, $\rho_{calcd} = 1.481\,g\,cm^{-3}$, $\mu = 0.770\,mm^{-1}$, $2\theta_{max} = 57.7°$, $\lambda(Mo_{K\alpha}) = 0.71073$ Å, $T = 293(2)$ K, 9653 unique reflections ($R(int) = 0.0342$), $R1 = 0.0821$, $wR2 = 0.2572$ $[I > 2\sigma(I)]$, $R1 = 0.1370$, $wR2 = 0.2966$ (all data), GOF $(F^2) = 0.956$, $N_0/N_v = 9653/494$, highest residual electron density $3.571\,e^-$ Å$^{-3}$. X-ray diffraction data were measured on a Bruker Smart CCD diffractometer. The structure was solved by direct methods and refined by full-matrix least-squares techniques using the SHELX system of programs: G. M. Sheldrick, SHELXS-97, program for the solution of crystal structures, University of Göttingen, Göttingen, **1997**. All non-hydrogen atoms were refined anisotropically except for those of the anion and the dichloromethane of crystallization. The presence of this solvent was confirmed by elemental analysis and NMR and IR spectroscopy. In the crystal structure, dichloromethane is severely disordered about an inversion center, and no coordinates were retained. The $BF_4^-$ ion was refined with geometrical constraints (B–F fixed at 1.43 Å). The hydrogen atoms attached to carbon atoms in the complex were generated and assigned isotropic thermal parameters, riding on their parent carbon atoms. CCDC-245747 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk). The powder diffractogram of **1** was registered on a Philips X'Pert diffractometer to be sure that the samples contained only one phase. All reflections were indexed with the cell parameters obtained from the single-crystal X-ray study on **1**.

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