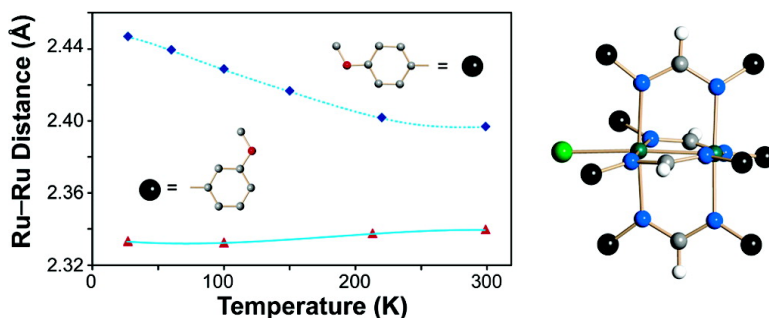


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Structural and Magnetic Evidence Concerning Spin Crossover in Formamidinate Compounds with Ru₂⁵⁺ Cores

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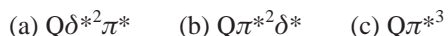
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Since the first Ru₂⁵⁺ compound, Ru₂(O₂CC₃H₇)₄Cl,¹ was prepared and the structure (which refuted the assumption¹ that the paramagnetism ruled out Ru–Ru bonding) was reported,² the chemistry of compounds with Ru₂⁴⁺, Ru₂⁵⁺, and Ru₂⁶⁺ cores has flourished. There are now more than 500 such compounds known, of which at least 235 have been structurally characterized.^{3a} These compounds are being widely investigated for possible uses in electronic and magnetic devices.⁴

The electronic structures of Ru₂ⁿ⁺ compounds were first rigorously treated by Norman, Renzoni, and Case,⁵ who showed that the highest filled orbitals, π^* and δ^* , were likely to be close in energy (even accidentally degenerate). From this, it can be inferred that for the Ru₂⁵⁺ compounds the three configurations, $Q\pi^{*2}\delta^*$, $Q\pi^{*3}$, and $Q\delta^*\pi^*$ (where Q represents the underlying $\sigma^2\pi^4\delta^2$ arrangement), are all a priori likely. The practice of simply writing $(\pi^*\delta^*)^3$ has become common in the literature when authors wish to avoid choosing a specific configuration or proposing an energy ordering of the π^* and δ^* orbitals.⁶

The earliest magnetic study aimed at elucidating the electronic structures of Ru₂⁵⁺ complexes was that of Cotton and Pedersen,⁷ who showed that Ru₂(O₂CC₃H₇)₄Cl is in a spin quartet state from 60 to 300 K and also in methanol solution at about 300 K. Low-temperature deviation from the Curie law was attributed to a combination of antiferromagnetic coupling (the Ru₂⁵⁺ units are linked into chains by μ -Cl ions) and zero-field splitting (ZFS), although the latter was not quantitated. Later, Telser and Drago⁸ were able to show that ZFS (110 K) was the dominant factor; in their fitting of the data they confirmed that $g_{\perp} = 2.20$, but revised g_{\parallel} down from 2.03 to 1.945.

In recent years, many paddlewheel compounds of Ru₂⁵⁺ with ligands more basic than carboxylates have been made.³ Some of the most interesting of these have four bridging *N,N'*-diaryl-formamidinate ligands (DArF), which allow the electronic structures to be tuned by changing the substituents on the aryl rings. In these, the Ru₂(DArF)₄Cl molecules are not linked, and thus the magnetic properties should be almost completely dictated by the inherent electronic structure of the Ru₂⁵⁺ core. As noted earlier, there are three possibilities:



For (a) and (c), the magnetism should follow the Curie law for one unpaired electron, with $\chi T = 0.36^9$ plus or minus any constant orbital contribution. For (b), there should be three unpaired electrons at all temperatures, but because of zero-field splitting the magnitude of χT should vary from about 1.87, if $g_{av} \approx 2.0$, at room temperature to values approaching zero as *T* goes to 0 K. This is case I of temperature dependence of χT .

There is a second possible case (II) where χT would be temperature-dependent: if the π^* orbital is a little more stable than the δ^* orbital (or for more subtle reasons), there might be a

Boltzmann distribution between a more stable π^{*3} configuration and a less stable $\pi^{*2}\delta^*$ configuration, so that χT would have a high-temperature limit well below 1.87 and then drop to a value of 0.36 (again plus or minus an increment due to spin-orbit coupling) as *T* approaches 0 K. A third case (III) is also possible, where the δ^* orbital is more stable than the π^* orbital, and where a Boltzmann distribution occurs between the ground-state configuration $Q\delta^*\pi^*$ and a slightly less stable $Q\delta^*\pi^{*2}$. The χT behavior of case III should be similar to that of case II.

The question we have addressed is: How can we choose among case I, case II, and case III? The answer we present here is that there are two complementary ways to do it. One entails the obvious approach of measuring and trying to interpret the temperature dependence of χT . The other entails determining the temperature dependence of the structure. The basis of the second way is that δ^* and π^* electrons, while both antibonding with respect to the Ru–Ru linkage, differ in the magnitudes of their effect on the metal–metal distances.^{3b} A π^* electron has 2–3 times the effect of a δ^* electron, the approximate changes upon addition of one or the other being 0.05–0.07 Å and 0.02–0.03 Å, respectively.

Thus in case I, where the electron configuration does not change with temperature, the Ru–Ru distance will not change (significantly) with temperature. In case II, however, where the configuration changes from predominantly $Q\pi^{*2}\delta^*$ to exclusively $Q\pi^{*3}$, from 300 to ~0 K, the Ru–Ru distance should increase by 0.02–0.05 Å. With the same logic, in case III, where the changes in configuration occur from $Q\delta^*\pi^{*2}$ to $Q\delta^*\pi^*$, the Ru–Ru distance should decrease by ~0.03 Å when the temperature changes from 300 to ~0 K. Since Ru–Ru distances can be determined to about ± 0.0005 Å, unambiguous results should be obtained.

We have examined two Ru₂(DArF)₄Cl compounds, one with Ar = *p*-C₆H₄OMe and the other with Ar = *m*-C₆H₄OMe. These differ considerably in their Hammett σ constants, which are –0.27 and +0.12, respectively.¹⁰ These two compounds, which we shall refer to simply as the meta (**1**) and para (**2**) isomers, show very different behavior both magnetically and structurally. More quantitative details of the magnetic properties will be presented elsewhere. The features shown in Figure 1 are sufficient for our own purposes here.

The χT for the para isomer reaches a value of only 1.6 at 300 K and with decreasing temperature declines to a value of 0.5 at 2 K, following a sigmoidal curve. This is exactly the behavior expected for case II as described above. For case II, the Ru–Ru distance would be expected to increase by 0.02 to 0.05 Å as the temperature drops from 300 to 2 K. As seen in Figure 2, the measured change from 300 to 27 K is 0.0503(9) Å. Thus, the conclusion we draw from the magnetic behavior is fully supported by the structural behavior, and that conclusion is: the para isomer has a spin doublet ground-state derived from a $Q\pi^{*3}$ configuration with a quartet state derived from a $Q\pi^{*2}\delta^*$ configuration lying only 100–200 K above it in energy.

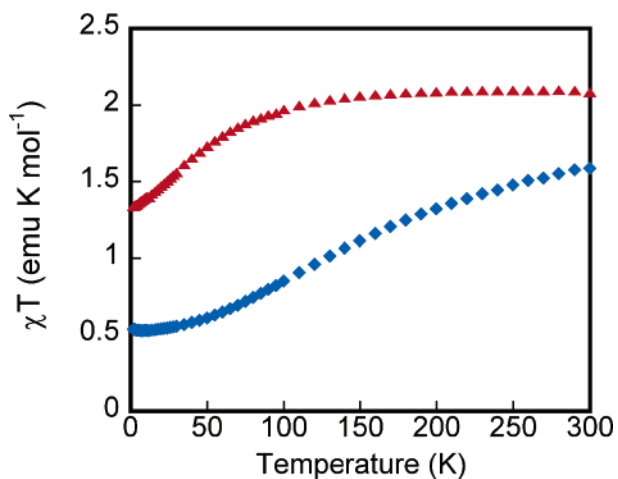


Figure 1. Magnetic susceptibility vs temperature of the meta (red \blacktriangle) and para (blue \blacklozenge) isomers of $Ru_2(DArF)_4Cl$.

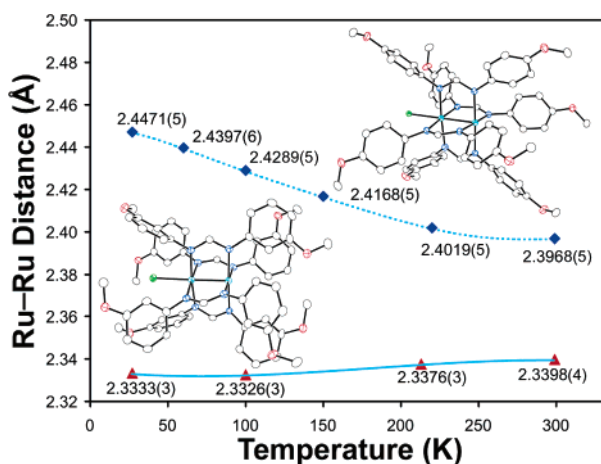


Figure 2. Temperature dependence of the Ru–Ru bond distance of the meta (red \blacktriangle) and para (blue \blacklozenge) isomers of $Ru_2(DArF)_4Cl$.

For the meta isomer, the magnetic behavior is quite different and conforms to expectation for a $\pi^*2\delta^*$ configuration at all temperatures, with the drop in χT being due to ZFS for a $4B_{2u}$ state. This is the typical behavior observed in the literature for Ru_2^{5+} compounds.^{8,11} This interpretation is supported by the structural behavior shown in Figure 2, where the Ru–Ru distance is essentially constant within the limits of error ($3\sigma = 0.001 \text{ \AA}$) over the entire temperature range of 300–27 K. The slight decrease of 0.007(1) \AA is attributable to the expected damping of vibrational amplitudes.¹²

The results reported here have two features of principal interest: (1) The sensitivity of the electronic structure of the Ru_2^{5+} core to seemingly conservative changes in the isomeric bridging ligands has been clearly delineated. There has not previously been any data bearing directly on this,¹³ although electrochemical data has demonstrated a relationship of the first oxidation potential to changes in the arene Hammett constants.^{10,14} (2) It is shown that in each of the two cases, by following structural change down to very low temperature (27 K), unequivocal support for the postulated explanations for the magnetic behavior can be obtained. We have previously done this for two Ru_2^{6+} compounds¹⁵ with different axial ligands, but in that case both compounds behaved the same way magnetically and both showed temperature-independent Ru–Ru

distances. In the present work, we have been able to show that when magnetic properties change the structural behavior changes accordingly and that when changes are expected they stand out clearly because the experimental uncertainty is relatively small.

On the basis of the success of the work reported here, interesting possibilities for further work may be foreseen. For one thing, the use of the structural criterion for determining whether there is a temperature dependence of the electron configuration (for which we know of no precedent in any type of compound) should be applicable in other cases. Those that come readily to mind are $Ru_2(DArF)_4Cl$ compounds with Ar groups covering a still wider range of Hammett σ values (i.e., in the range 0.2–0.7), $Ru_2(DArF)_4X$ compounds with a selection of axial ligands other than Cl, $Ru_2(DArF)_4$ compounds, Ru_2^{n+} compounds with bridging ligands other than formamidates, and a number of Os_2^{n+} compounds that show temperature dependence of χT . Now that the validity of the structure versus temperature technique is established, much new insight should become available for the compounds just listed, as well as for others.

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Supporting Information Available: X-ray crystallographic data in CIF format for **1** at 27, 100, 213, and 299 K and **2**·0.5CH₂Cl₂ at 27, 60, 100, 150, 220, and 299 K, and displacement ellipsoid plots of **1** and **2** and data collection information in PDF. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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