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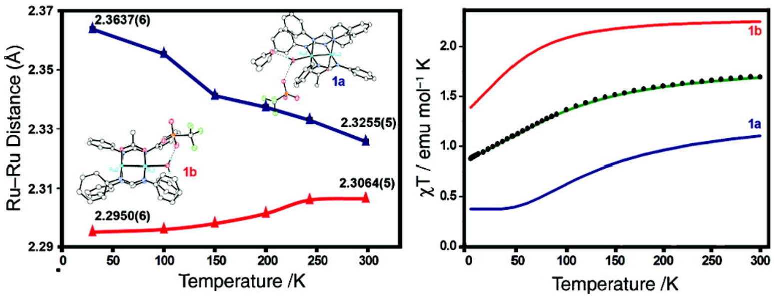

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# How Small Variations in Crystal Interactions Affect Macroscopic Properties

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Medium range intermolecular interactions are of great importance in chemistry and living organisms. A prominent example is hydrogen-bonding that helps shape the double helix in DNA and allows water to be a liquid under normal conditions while the heavier congener $H_2S$ is a gas.[1] Recently, there has been considerable excitement over the role that yet weaker interactions such as $\pi$-bonding in arenes may play in determining structure, stacking, and enantioselectivity.[2] However, well documented examples of how weak crystal interactions may unequivocally affect major macroscopic properties are infrequent. A rare example is that of $Co_3(dpa)_4Cl_2$, (dpa = 2,2′-dipyridylamine) a molecule that can be crystallized with one or two interstitial $CH_2Cl_2$ molecules.[3] Under most conditions the number of interstitial molecules may be considered irrelevant but in this case major structural differences were observed as the $Co_3^{2+}$ chain can be symmetrical or asymmetrical with Co−Co distances differing by ca. 0.17 Å. Because of the structural differences, the magnetic properties for each crystalline form also diverge.[3] Theoretical studies have shown the existence of a shallow energy minimum which appears to be responsible for the impact in macroscopic properties.[4]

In this report we explore the effect of weak interactions in two diruthenium molecules in a single crystal containing crystallographically independent solvation isomers. Generally $Ru_2$ compounds show a variety of electronic structures that give rise to remarkable magnetic properties[5,6] because of accidental degeneracy of the valence $\pi^*$ and $\delta^*$ orbitals.[7] Interest in these magnetic properties has led to the search and design of electronic and magnetic nanodevices[8] and the syntheses of supramolecular assemblies.[9]

The 11 electrons in the $Ru_2^{5+}$ core have been generally represented as $Q^8(\delta^*\pi^*)^3$ in which $Q^8$ denotes the eight electrons in the underlying $\sigma^2\pi^4\delta^2$ core. Three possible electronic configurations may arise when the $\pi^*$ and $\delta^*$ orbitals are close in energy: two doublets ((a) $Q^8\pi^{*1}\delta^{*2}$ and (b) $Q^8\pi^{*3}$) and one quartet state ((c) $Q^8\pi^{*2}\delta^{*1}$). Magnetic susceptibility measurements may distinguish between the doublet and quartet states but cannot distinguish between the two doublet states. However, variable temperature (VT) X-ray crystallography can differentiate between the doublet states, since the metal−metal bond distances of the two states should differ. This is because differences in orbital overlap of an electron in a $\delta^*$ orbital will have a lesser impact in elongating the Ru−Ru distance than an electron in a $\pi^*$ orbital. Indeed for $Ru_2(DAniF)_4Cl$ (DAniF = *N*,*N*′-di-*p*-anisylformamidinate),[10] VT X-ray crystallography provided unambiguous evidence for a spin transition from a $Q^8\pi^{*2}\delta^{*1}$ to a $Q\pi^{*3}$ state as the temperature descended from 298 to 27 K, and the Ru−Ru distances increased by ca. 0.05 Å.[10] It should be noted also that for $[Ru_2(OAc)(DPhF)_3(H_2O)]BF_4\cdot 1/2CH_2Cl_2$,[11] (DPhF = *N*,*N*′-diphenylformamidinate) VT magnetic susceptibility measurements showed a spin-admixed compound with intermediate spins between a doublet and a quartet state.

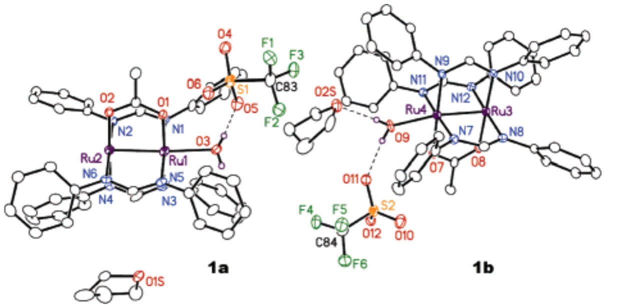

***Figure 1.*** Thermal ellipsoid plot at the 40% probability level of the two crystallographically independent molecules of **1** in the asymmetric unit. At 30 K the distances are 2.3637(6) Å for Ru(1)−Ru(2) and 2.2950(6) Å for Ru(3)−Ru(4). The corresponding distances are 2.3255(5) and 2.3064(5) Å at room temperature. Donor···acceptor distances in Å for hydrogen bonding interactions at 30 K (and at room temperature): O3−O5, 2.787(6), (2.760(5)); O9−O11, 2.780(6), (2.786(5)); O9−O2S, 2.631(1), (2.67(2)).

Here we present a unique situation involving a crystal with two crystallographically independent species which have the same chemical formula but very different behavior. The $Ru_2^{5+}$ compound $[Ru_2(OAc)(DPhF)_3(H_2O)](SO_3CF_3)\cdot THF$, **1**, prepared similarly to the $BF_4^-$ analogue,[11] has been characterized by both VT X-ray crystallography (Figure 1) and magnetic susceptibility measurements. Although the molecules possess the same core structure, each of the two Ru−Ru bond distances is significantly different. One $Ru_2$ unit (**1a**) has a longer Ru−Ru bond at 30 K (2.3637(6) Å) than that for the other unit (**1b**) (2.2950(6) Å). It should be noted that each independent molecule has an axially coordinated water molecule that displays a hydrogen-bonding interaction to the corresponding triflate counteranion. In **1b**, a THF molecule is also hydrogen bonded to the axially coordinated aqua ligand. The other diruthenium species, **1a**, also has an axially coordinated water molecule, but the corresponding interaction to the interstitial THF moiety is absent. The additional hydrogen bond to the THF molecule in **1b** is the *only* significant chemical difference between these two independent $Ru_2$ units. At 30 K, the $Ru_2$ unit that has the longer Ru−Ru bond, **1a**, has a long $Ru-OH_2$ axial interaction (2.247(4) Å), and **1b** with the short Ru−Ru bond, has a short $Ru-OH_2$ axial interaction (2.176(3) Å).

The general variation in Ru−Ru (triangles) and $Ru-OH_2$ (squares) distances for both crystallographically independent $Ru_2$ units from 30 to 298 K is shown in Figure 2. For **1a** (blue), as the temperature decreases the Ru−Ru distance increases by 0.03 Å,[12] consistent with a population increase of the $Q^8\pi^{*3}$ electronic state at low-temperature due to a spin transition that decreases the

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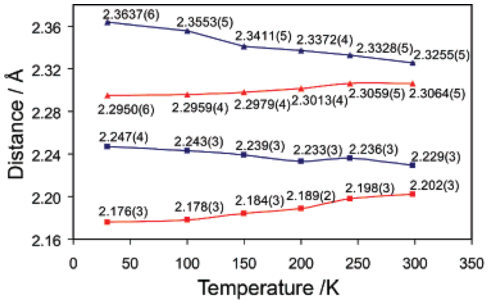

***Figure 2.*** Change in Ru−Ru distances of the two crystallographically independent molecules of **1** (triangles) and change in the Ru−$OH_2$ distances (squares): **1a** (blue), **1b** (red). Note that the average standard deviation in Ru−Ru distances for **1a** of ca. 0.0005 Å is significantly smaller than the change in such distances over the range of 30 to 298 K (ca. 0.04 Å).

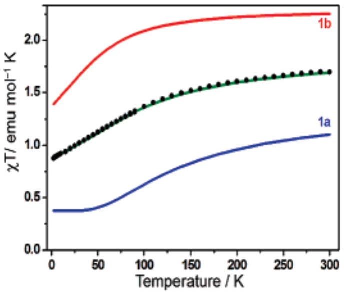

***Figure 3.*** Magnetic susceptibility of **1** between 3 and 300 K. The blue (bottom) and red (top) curves represent the components of **1a** and **1b**, respectively, obtained from the fitted data (green), as explained in the text. Note that **1b** is mainly in a quartet $Q^8\pi^{*2}\delta^{*1}$ electronic configuration at all measured temperatures but **1a** is best represented by a mixture of $Q^8\pi^{*2}\delta^{*1}$ and $Q^8\pi^{*3}$ electronic states.

population of species in the quartet state ($Q^8\pi^{*2}\delta^{*1}$). However, for **1b** (red) the Ru−Ru bond distance increases only slightly (ca. 0.01 Å) as the temperature increases. This behavior is consistent with a $Q^8\pi^{*2}\delta^{*1}$ electronic configuration at all measured temperatures.[13]

A natural question is whether this assignment is consistent with the magnetism. The variation of $\chi T$ with respect to temperature for **1** is shown by the black dots in Figure 3. Near room temperature, $\chi T$ is about 1.7,[14] which is slightly less than the spin-only value for $S = {}^3/_2$ (1.87). The $\chi T$ value slowly decreases as the temperature is lowered reaching a minimum of 0.87 at 2 K, a value that is significantly higher than that for one unpaired electron (0.375). When this curve was fitted using the model suggested by the structural data, namely one having equal amounts of a mixture of two different systems, one that shows a spin-transition from a doublet ground-state at low-temperatures to a low-lying quartet state accessible at higher temperatures, and another that is a quartet at all temperatures, a very good agreement is obtained as seen by the solid green line in Figure 3. Furthermore, deconvolution of the magnetic data into these two components for **1a** and **1b** afford the red and blue curves in Figure 3 whose shapes and relative values are in very good agreement with similar $Ru_2$ compounds having such states.[10] Importantly, data fitting indicates that the energy separation between the doublet and quartet state for **1a** is very small, only 153 $cm^{-1}$ (about 0.4 kcal/mol). Furthermore the $D$ values of 55−64 $cm^{-1}$ are also in the common range for $Ru_2^{5+}$ compounds (see Supporting Information).

These data raise the important question: Why do these seemingly akin $Ru_2^{5+}$ units that differ only in the weak interactions of the axial water molecules behave so differently? This is undoubtedly due to the fact that in this crystal the energies of the two $Ru_2^{5+}$-units are so similar that even minor changes in the environment significantly affect the relative orbital energies. This is consistent with a possible existence of a shallow energy minimum in which there are little energy changes with changes in Ru−Ru and Ru−$OH_2$ distances.[15]

In conclusion these results show two crystallographically independent $Ru_2$ molecules in one asymmetric unit that behave drastically different and demonstrate unequivocally that a very small change in packing forces due to weak interactions may have an effect far more reaching than what may have been anticipated. The differences of ca. 0.07 Å in Ru−Ru distances at 30 K (0.02 Å at 298 K) are dramatic as are the differences in Ru−$OH_2$ distances of 0.07 Å at 30 K (ca. 0.03 at 298 K).

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**Supporting Information Available:** X-ray crystallographic data in CIF format for **1** at 30, 100, 150, 200, 243, and 298 K; details on the synthesis, magnetic data fit, crystallographic data, and a table of hydrogen bonding interactions. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) As shown in squares in Figure 2, the Ru−$OH_2$ distances also change as the temperature is varied. As the temperature is increased, the Ru−$OH_2$ distance in **1a** (blue) decreases and the opposite effect occurs in **1b** (red) where the Ru−$OH_2$ distance increases as temperature increases. As indicated in the caption to Figure 1 and Figure S1, the donor···acceptor distances for the hydrogen bonding interactions for O3···O5 and O9···O11 remain essentially constant with temperature. However, those for O9···O2S change significantly.

(13) It should be noted that an electronic configuration $Q^8\delta^{*1}\pi^2$ may also be possible.

(14) Units for $\chi T$ values are emu·mol$^{-1}$·K.

(15) To understand the interplay between Ru−Ru and Ru−$OH_2$ distances DFT calculations, structural work using neutron studies and variable pressure as well as measurements using VT high-field EPR appear to be necessary. These will be done in due time. However, it should be pointed out that our intention in this paper is to call attention as to how small variations in crystal interactions may have large effects in physical properties.

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