How magnetic interaction between two distant paramagnetic metals is influenced by central diamagnetic cyanidometal?

Magnetism is an ancient and classic physical phenomenon and will be forever interesting topics. Molecule-based magnetic materials, in which the structural building blocks are molecular in nature, are of increasing interest because they provide fundamental insight into magnetic phenomena and are potential in applications such as molecular switches, high-density information storage and quantum computation and so on. As important molecule-based magnetic materials, cyanide-bridged complexes have been obtained extensive attention due to their variable molecular structures and interesting magnetic coupling between paramagnetic metal centers through the cyanide bridge, such as photomagnetic materials, high T_c magnets, single-molecule magnets, single-chain magnets, and spin crossover materials.

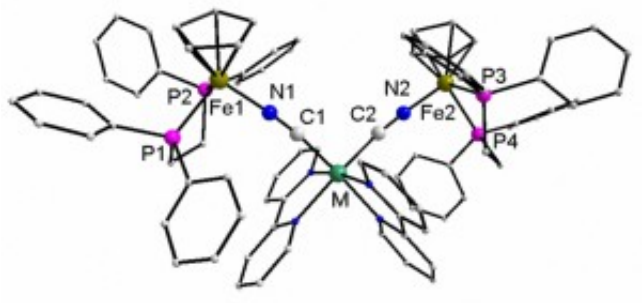

Fig. 1. The molecular structure of compounds 1-3 (M = Ru 1, Os 2 and Fe 3).

Generally, magnetic coupling between two paramagnetic metal centers directly bridged by the CN^- ions, namely M_p-C?N-M_p (M_p = paramagnetic metal ion), is strong. In contrast, cyanide-bridged complexes in which paramagnetic metal centers are separated by a diamagnetic cyanidometal bridge, namely M_p-N?C-M_d-C?N-M_p (M_d = diamagnetic metal ion, M_p = paramagnetic metal ion), exhibit only very weak and even disappeared magnetic coupling. Therefore, the preparation of such compounds with a strong magnetic coupling is still a great challenge in this field. We are interested in investigating the distant magnetic coupling across a diamagnetic cyanidometal bridge, because we believe that spin delocalization along M_p-N?C-M_d-C?N-M_p may increase magnetic coupling. Recently, we have synthesized a series of cyanide-bridged complexes with diamagnetic building blocks, some of which exhibit strong magnetic coupling. For example, the magnetic exchange constant *J* of the two distant Fe^{III} centers in compound $[Cp(dppe)Fe^{III}(NC)M^{II}(bpy)_2(CN)Fe^{III}(dppe)Cp][PF_6]_4$ 1 (bpy = 2, 2'- bipyridine, dppe = bis(diphenylphosphino)ethane, Cp = cyclopentadienide anion) is high up to -13.6 cm^{-1} even though separated by the diamagnetic cyanidometal NC-Ru^{II}-CN bridge. It should be mentioned that *J* is positive for ferromagnetic coupling and negative for antiferromagnetic coupling. And, the stronger the magnetic coupling is, the greater the?*J*?value is. The theoretical investigation has shown that

the spin delocalization mechanism should be responsible for the strong magnetic coupling. Furthermore, one would like to know how the magnetic coupling between the distant Fe^{III} ions is influenced by the central diamagnetic cyanidometal bridge. To understand this, the isostructural compounds $[Cp(dppe)Fe^{III}(NC)M^{II}(bpy)_2(CN)Fe^{III}(dppe)Cp][PF_6]_4$ (M = Os 2, Fe 3) have been synthesized and characterized, their magnetic properties have also been investigated. The molecular structures of compounds 1-3 are shown in Figure 1.

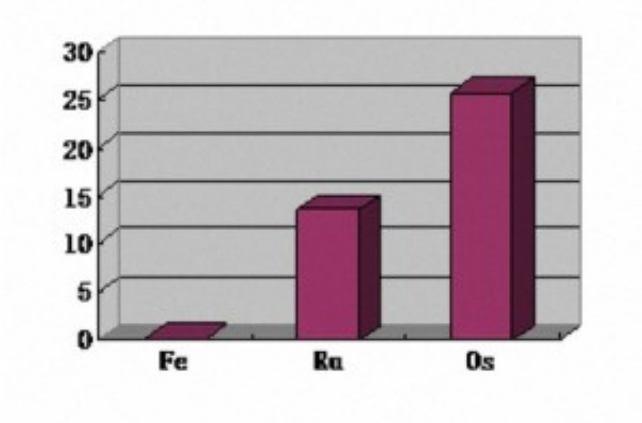

Fig. 2. Relationship between?J?(cm^{-1}) and the central diamagnetic metal.

The experimental results show that compound **2** exhibit a strong antiferromagnetic coupling between the two distant Fe^{III} ions although separated by the diamagnetic cyanidometal NC-$Os^{II}(bpy)_2$-CN bridge (J = -25.8 cm^{-1}). To the best of our knowledge, this is the strongest magnetic coupling between the distant paramagnetic metal ions across a diamagnetic cyanidometal bridge reported by far. For compound 3 with the diamagnetic cyanidometal NC-$Fe^{II}(bpy)_2$-CN bridge, however, the distant two Fe^{III} ions posses only very weak antiferromagnetic coupling (J = -0.15 cm^{-1}). The magnetic susceptibilities studies indicate the magnetic coupling strength between the distant paramagnetic Fe^{III} ions across diamagnetic cyanidometal NC-M^{II}-CN (M = Fe, Ru, Os) bridge increases with the central metal in the order of Fe

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