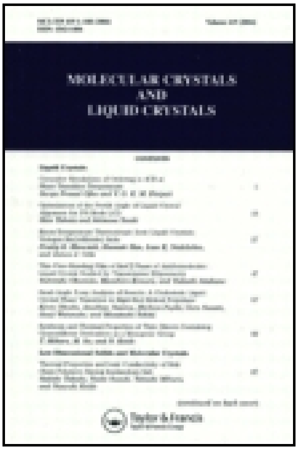

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^{57}Fe Mossbauer Spectroscopy Studies of New Examples of Fully Averaged Mixed Valence Diiron and Iron/Ruthenium Compounds

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^{57}Fe MOSSBAUER SPECTROSCOPY STUDIES OF NEW EXAMPLES OF FULLY AVERAGED MIXED VALENCE DIIRON AND IRON/RUTHENIUM COMPOUNDS

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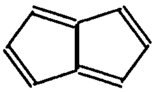
Abstract We report that the Fe(II/III) compounds $[(Cp^*Fe)_2L]^{\cdot+}$ (L = pentalene and symmetric indacene) appear to be fully averaged mixed valent binuclear species on a Mossbauer spectroscopy time scale (~100 ns) above 1.5K. This indicates essentially zero energy barrier to intramolecular electron transfer. In contrast, for L = asymmetric indacene trapped (discrete) Fe(II) and Fe(III) valence states are observed at ambient temperature. Finally the heterobinuclear complex $[Cp^*FeLCoCp^*]^n$ (L = pentalene) is similar to the homobinuclear Fe(II) analog for for n = 0, 1+ and similar to low spin FeIII) for the n = 2+ dication. The high degree of delocalization for the monocationic diiron and iron/ruthenium systems is attributed to the fused structure of the bridging ligands.

INTRODUCTION

Multidecker organometallic polymers based on metallocene units represent a unique class of compounds with potentially interesting magnetic properties. However, further understanding of electronic interaction between metal centers is paramount for the design and fabrication of high spin materials comprising extended organometallic polymer systems. In this regard mixed valent bimetallic complexes have been extensively investigated. Relatively few examples of $Fe^{II/III}$ mixed valent compounds that exhibit complete dynamic averaging of oxidation states below 4.2 K. An example from mineral chemistry is orthorhombic cubanite, $CuFe^{II}Fe^{III}S_3$.[1,2] An organometallic example is biferrocenylenium triiodide[3] whose ^{57}Fe Mossbauer spectrum at 4.2 K comprises a single quadrupole doublet of magnitude intermediate to the extremes found for classic ferrocene and ferrocenium iron.[4] The complexes of the present study are based on a rigid, fused bridging ligands: pentalene, **1**, and symmetric, **2**, and asymmetric, **3**, indacene. The bridging ligands with extensive delocalization suggests that there compounds may form a basis of a new class of anisotropic polymeric chain magnets composed of either homo- or heterobinuclear valence delocalized aggregates.



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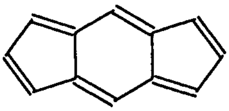

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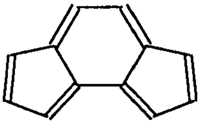

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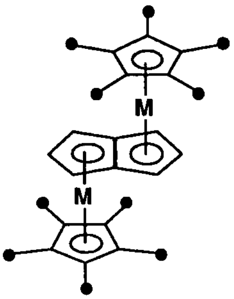
SYNTHESIS

A convenient procedure for the synthesis of bridged metallocenes employs $Cp^*M(acac)$ (Cp^* = pentamethylcyclopentadienyl; acac = acetylacetonate; M = Fe, Co, Ni).[5-7] The primary advantages of this method are its simplicity, the increased yields, and the lack of unwanted side reactions.

$$2\,Cp^*M(acac) \quad + \quad Li_2L \quad \Rightarrow \quad (Cp^*M)_2L \quad + \quad 2\,Li(acac)$$

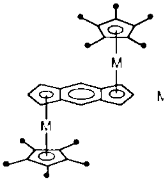
$$L = \mathbf{1}, \mathbf{2}, \text{or } \mathbf{3}$$

The synthesis and electrochemistry of neutral fused metallocene derivatives $(Cp^*M)_2\mathbf{1}$ (M = Fe, Co, Ni) as well as the molecular structure of and an extended Huckel MO calculations for $(Cp^*Fe)_2\mathbf{1}$ has recently been reported.[8] We have also prepared the mixed valent $[(Cp^*Fe)_2\mathbf{1}]^{\cdot+}$ and have determined that it is completely delocalized above 1.5K on the Mossbauer time scale (*vide infra*). Its molecular structure has also been determined.[8]

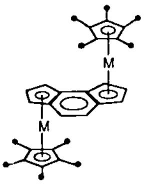


M = Fe, Co, Ni

In order to examine delocalized systems with larger metal-metal distances, the symmetric and asymmetric fused metallocene derivatives, $(Cp^*M)_2\mathbf{2}$ and $(Cp^*M)_2\mathbf{3}$ (M = Fe, Co, Ni) have been prepared.[9]



M = [Fe(2a)
Co(2b)
Ni(2c)]



M = [Fe(3a)
Co(3b)
Ni(3c)]

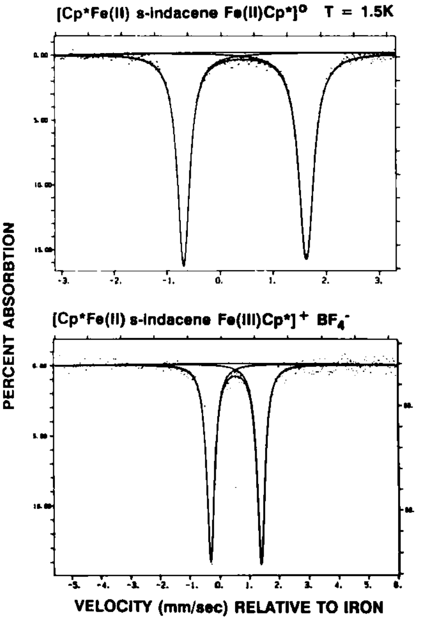
The Mossbauer spectra of $[(Cp^*Fe)_2\mathbf{2}]^{\cdot+}$ $Fe^{II/III}$ salt indicate completely averaged Fe sites at 1.5 K, while $[(Cp^*Fe)_2\mathbf{3}]^{\cdot+}$ is localized at room temperature.

MOSSBAUER SPECTRA

Homobinuclear System

Representative spectra of $(Cp^*Fe)_2\mathbf{2}$ and $(Cp^*Fe)_2\mathbf{3}$ are shown in Figures 1 and 2, respectively. The former exhibits the typical large quadrupole splitting effect characteristic of low spin Fe^{II} ferrocene, i. e., $\Delta E = 2.30$ mm/s at 1.5 K.[4] The spectrum of the mixed valent $[(Cp^*Fe)_2\mathbf{2}]^{\cdot+}$ monocation (bottom) is indicative of a unique average iron environment: $\Delta E = 1.68$ mm/s. The dicationic $[(Cp^*Fe)_2\mathbf{2}]^{2+}$ is not available for comparison. The delocalized nature of $[(Cp^*Fe)_2\mathbf{2}]^{+}$ is reminiscent of that of $[(Cp^*Fe)_2\mathbf{1}]^{\cdot+}$. The $[(Cp^*Fe)_2\mathbf{1}]^n$ (n = 0, 1+, 2+) complexes have been isolated {as $[BF_4]^-$ salts} and exhibit 1.5 K quadrupole splittings of 2.21, 1.34 and 0.80 mm/s, respectively. The observed value for $[(Cp^*Fe)_2\mathbf{1}]^{\cdot+}$ is close to the simple average (~1.50 mm/s) of those for $(Cp^*Fe)_2\mathbf{1}$ and $[(Cp^*Fe)_2\mathbf{1}]^{2+}$.

The Mossbauer spectrum of $[(Cp^*Fe)_2\mathbf{3}]^{\cdot+}$ at 4.7 K is shown in Figure 2 (bottom) and is typical of trapped Fe^{II} and Fe^{III} valences with $I_{Fe^{II}/Fe^{III}}$ ~ 1. Its spectrum at ambient temperature is relatively unchanged. However, the intensity of the central doublet has noticeably increased such that $I_{Fe^{II}/Fe^{III}}$ ~ 0.64. This suggests incipient detrapping and possibly complete averaging at even higher temperatures. Interestingly, the corresponding unmethylated analog $[(CpFe)_2\mathbf{3}]^{\cdot+}[I_3]^{-}\cdot 1/2I_2$ exhibits gradual detrapping and increased averaging over the temperature range of 100 to 300 K.[10] This was correlated with an activation energy (E_a) for electron hopping of ~ 0.04 eV (~325 cm^{-1}). The origin of the apparently higher value of E_a for the $[(Cp^*Fe)_2\mathbf{3}]^{\cdot+}$ is not clear. A better understanding of these systems may arise from a detailed study of [Cp*Fe3FeCp]·+.


[Cp*Fe(II) s-indacene Fe(II)Cp*]⁰ T = 1.5K

[Cp*Fe(II) s-indacene Fe(III)Cp*]+ BF_4^-

FIGURE 1. Mossbauer spectrum of $(Cp^*Fe)_2$**2** (top) and $[(Cp^*Fe)_2$**2**$]^{\cdot +}$ (bottom) at 1.5 K.

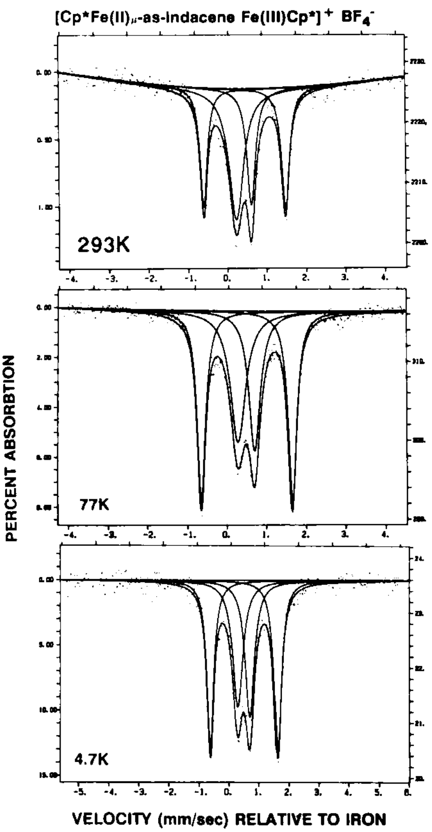

[Cp*Fe(II)$_\mu$-as-indacene Fe(III)Cp*]+ BF_4^-

FIGURE 2. Mossbauer spectra of $[(Cp^*M)_2$**3**$][BF_4]$ at 4.7, 77, and 293 K.

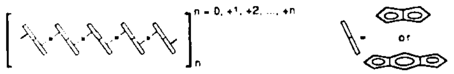
Heterobinuclear Systems

The Cp*Fe1NiCp* $[Cp^*Fe1M'Cp^*]^n$ (n = 0, 1+) (M' = Ru, Co) heterobinuclear systems have been isolated and characterized. The ^{57}Fe Mossbauer spectra indicate full delocalization and a unique iron environment for the monocationic Ru system over the entire range of 1.5 to 300 K. On the other hand, a transition from the trapped Fe(II), Ru(III) to Fe(III), Ru(II) is reported[11] as the temperature is increased from 78 K to ambient for the dimethylene bridged [1.1]-ferrocenylruthenocenophane(1+). It seems reasonable to assume that the primary reason for the different behaviors of these $(Fe/Ru)^{\cdot +}$ systems is the fused nature of the **1** bridge vs. coupling via $-CH_2$-groups.[11]

The ^{57}Fe Mossbauer spectra for $[Cp^*Fe1CoCp^*]^n$ (n = 0, 1+, 2+) attest to the inherent stability of low spin d^6 configurations with η^5-cyclopentadiene-like ligands and the expected redox behavior of the MCp^* fragments. That is, the Mossbauer spectra indicate that both the n = 0 and 1+ species contain essentially identical "ferrocene-like" Fe^{II}. Apparently, generation of the "mixed valent" n = 1+ complex involves loss of an electron for the more readily oxidized Co^{II} center, upon which the bimetallic complex achieves a d^6-d^6 configuration. The Mossbauer spectra confirm the expectation of ferrocenium (low spin Fe^{III}) for the n = 2+ dication. These assignments are supported by susceptibility data.

CONCLUSION

Magnetic susceptibility, X-ray crystallographic, electrochemical, and spectroscopic studies of intervalent charge transfer absorptions for the aforementioned compounds are currently in progress and will be published elsewhere along with the complete details of the Mossbauer spectra. Since one might expect that polymers derived from **1**, **2**, and **3**, might have novel electrical and magnetic properties and we plan on synthesizing and characterizing systems of the type shown below where M could be the same or different metals and where valence detrapping is still operating. Synthetic strategies are currently being devised and pursued in this context.



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