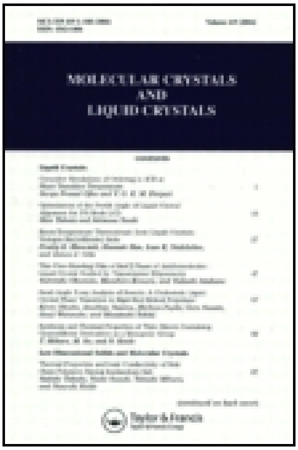

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Juan M. Manriquez [a] , Michael D. Ward [a] , Joseph C. Calabrese [a] , Paul J. Fagan [a] , Arthur J. Epstein [b] & Joel S. Miller [a]

[a] Central Research and Development Department, E.I. du Pont de Nemours & Co., P. O. Box 80328, Wilmington, DE, 19880-0328

[b] Department of Physics and Department of Chemistry, The Ohio State University, Columbus, OH, 43210-1106, U. S. A.

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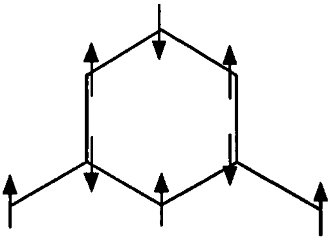
MAGNETIC COUPLING RELATIONSHIPS FOR BIS(METALLOCENE)-BENZENE COMPLEXES

JUAN M. MANRIQUEZ,[a] MICHAEL D. WARD,[a] JOSEPH C. CALABRESE,[a] PAUL J. FAGAN,[a] ARTHUR J. EPSTEIN,[b] AND JOEL S. MILLER[a]
[a] Contribution No. 5185 from the Central Research and Development Department E.I. du Pont de Nemours & Co., P. O. Box 80328, Wilmington, DE 19880-0328 and [b]Department of Physics and Department of Chemistry, The Ohio State University, Columbus, OH 43210-1106 U. S. A.

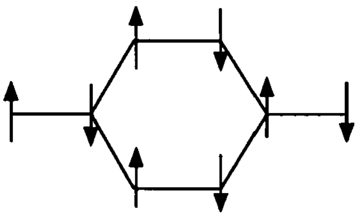
Abstract The synthesis and physical properties of meta- and para-bis(metallocene) benzene complexes with M = Fe, Co, Ni are reported. The electrochemical properties suggest greater electronic interaction between metal centers in the para-M complexes. In addition, the magnetic properties suggest different degrees of spin exchange for the meta and para complexes, with the latter exhibiting more pronounced antiferromagnetic coupling. These molecular complexes are considered prototypes for extended metallocene polymers.

INTRODUCTION

The magnetic behavior of molecular materials has been investigated intensively with particular emphasis on synthesizing compounds with high-spin ground states. For example, charge transfer salts of $(C_5Me_5)_2Fe$ with various polycyanoanion acceptors have been reported to exhibit ferromagnetic coupling at low temperature.[1] Recent reports[2] suggest that ferromagnetic coupling can exist in inorganic solids when spins are in close proximity so that Hund's rule is operative and when antiferromagnetic coupling can be suppressed by orthogonality of the magnetic orbitals. This behavior is also evidenced by the stability of triplet states in oxygen and carbenes. High spin ferromagnetic states have been reported for π-conjugated meta-substituted poly(phenylcarbenes),[3] in which the behavior was explained by favorable spin exchange interactions in meta-substituted compounds that is not present in para-substituted analogs, as illustrated below for bis(methylene)benzene.[4,5]

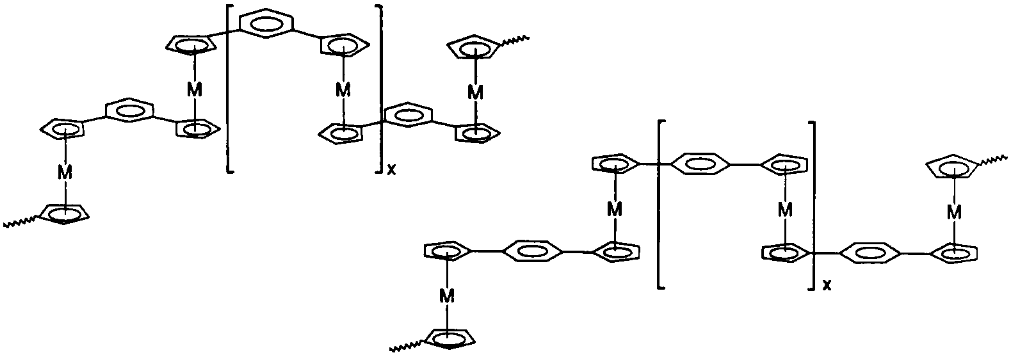


ferromagnetic coupling



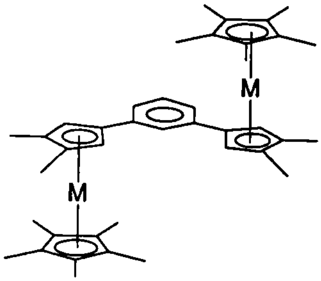
antiferromagnetic coupling

This coupling in bis(methylene)benzene has encouraged us to pursue high spin organometallic polymers shown below that are derived from benzene-metallocene fragments. If spin exchange between unpaired electrons in metal-based orbitals is mediated via the ligand system in a manner similar to that of bis(methylene)benzene, high spin states may be attained.

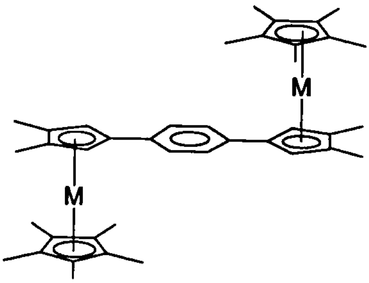


meta-polymer **para-polymer**

In order to explore the feasibility of this approach the bis(metallocene)-benzene complexes shown below were chosen as model systems for these polymers. Investigation of these complexes should establish whether spin exchange between metal centers can be mediated in a manner similar to that noted in bis(methylene)benzene. Our immediate goal was to elucidate the role of different positional substitution of the benzene ring in the electronic interaction between metal centers as well as the criteria for establishing favorable spin exchange.



meta-M_2^{n+}
(M = Fe, Co, Ni)
n = 0, 2

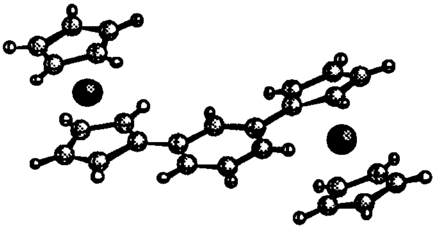


para-M_2^{n+}
(M = Fe, Co, Ni)
n = 0, 2

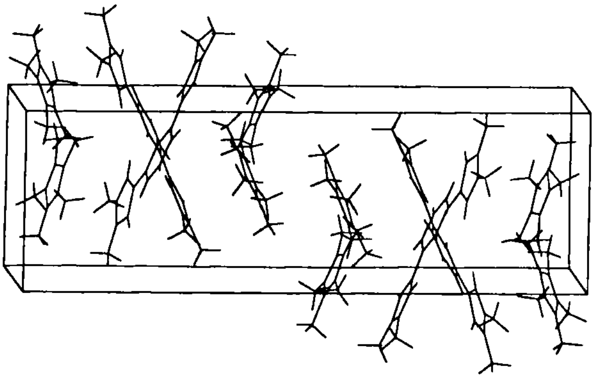
RESULTS

X-ray structure

The dimer complexes were synthesized by a procedure similar to that described previously.[6] Treatment of meta- or para-bis(cyclopentadienide)-benzene with (C_5Me_5)M(acetylacetonate) in THF affords the meta-M and para-M complexes depicted above. Subsequent chemical oxidations afford the mono- and dications, generally isolated as BF_4^- salts. Single crystal X-ray structural studies on the meta-M complexes indicate that the (C_5Me_5)M groups are oriented on opposite sides of a nearly planar meta-bis(cyclopentadienide)benzene ligand. The most significant solid state feature of the **meta-Ni_2** complex is similarity between the through-space intramolecular (8.24 Å) and intermolecular (8.74 and 8.78 Å) Ni-Ni distances. Therefore, intramolecular and intermolecular magnetic interactions should be considered when interpreting the electronic properties of these solids (vide infra).



meta-Ni (neutral)



Unit cell of meta-Ni$_2$^{0}

Electrochemistry

The degree of electronic interaction in bimetallic dimers is commonly estimated from the separation between potentials associated with electrochemical redox events as observed in cyclic voltammetry.[7] All the complexes exhibit reversible electrochemical oxidations to the dications (removal of two electrons). With the exception of the cobalt complexes, cyclic voltammetry reveals larger separations between the first two 1e$^-$ events for the para complexes, consistent with a greater degree of electronic interaction between metal centers compared to the meta dimers (Figure 1). This is especially evident for the nickel complexes; **meta-Ni$_2$** exhibits a single 2e$^-$ wave to form **para-Ni$_2$$^{2+}$**, whereas **para-Ni$_2$** exhibits two clearly separated 1e$^-$ waves. The separation in the **para-Fe$_2$** is less significant. This behavior clearly indicates that the electronic coupling is dependent upon the symmetry of the substituted benzene ring, and is in accord with expectations for greater electronic coupling between para substituents. The cobalt complex exhibits a single 2e$^-$ wave for both isomers, in apparent contradiction to the other complexes. This apparent discrepancy, is presently under investigation. The predominance of single 2e$^-$ oxidations has prevented the syntheses of single oxidized **meta-M$_2$$^+$** and **para-M$_2$$^+$** cations, as these compounds are not stable towards disproportionation. The more significant separation between single electron events observed in **para-Ni$_2$$^+$** suggests that **para-Ni$_2$$^+$** is attainable, but attempts to prepare this salt have not yet been successful. Electrochemical generation of **meta-Ni$_2$$^{4+}$** and **para-Ni$_2$$^{4+}$** at higher potentials can also be observed by cyclic voltammetry; both complexes form insoluble blue films at the electrode surface as evidenced by the large surface wave upon reduction.

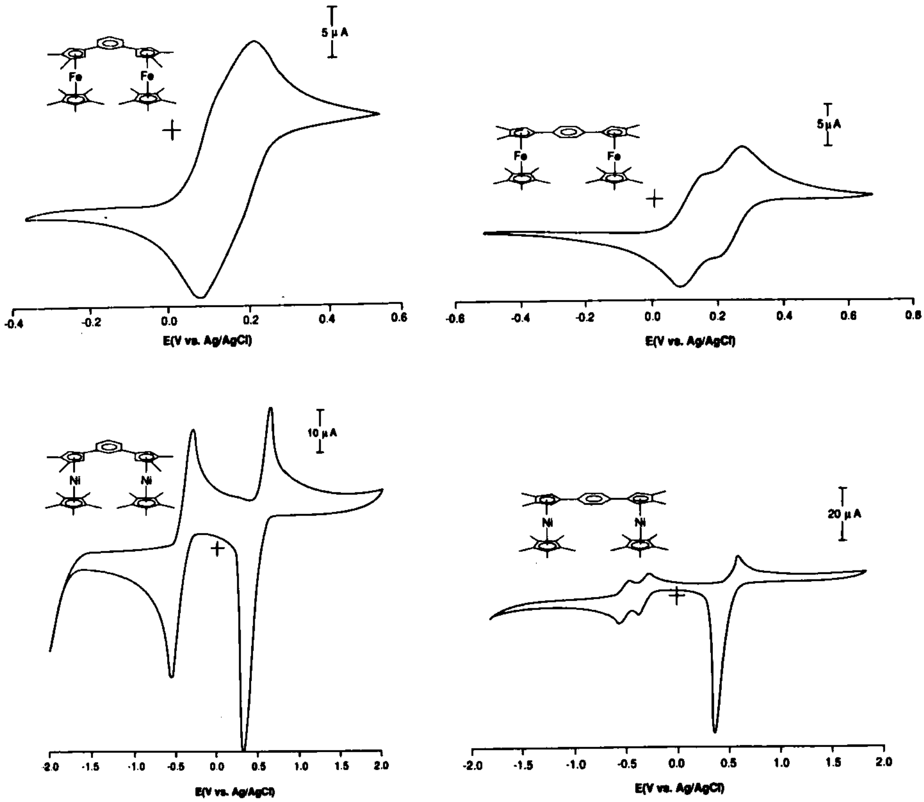


FIGURE 1. Cyclic voltammograms for meta-M_2 and para-M_2 (M = Fe, Ni) complexes.

TABLE 1. Electrochemical redox potentials determined from cyclic voltammetry (in V vs. Ag/AgCl).

Compound	E^o_1 (n e^-)	E^o_2 (n e^-)	E^o_3 (n e^-)	$E^o(2^+/1^+)$ - $E^o(1^+/0)$
Meta-Fe_2[a]	0.11 (1 e^-)	0.17 (1 e^-)		0.06
Para-Fe_2[a]	0.12 (1 e^-)	0.23 (1 e^-)		0.11
Meta-Co_2[b]		-1.00 (2 e^-)		0
Para-Co_2[c]		-0.15 (2 e^-)	1.52 (2 e^-)	0
Meta-Ni_2[c]		-0.42 (2 e^-)	0.51 (2 e^-)	0
Para-Ni_2[c]	-0.48 (1 e^-)	-0.27 (1 e^-)	0.52 (2 e^-)	0.21

[a] 0.1 *M* *n*-$Bu_4N^+ClO_4^-$ /CH_3CN; [b] 0.1 *M* *n*-$Bu_4N^+ClO_4^-$ /THF; [c] 0.1 *M* *n*-$Bu_4N^+ClO_4^-$ /CH_2Cl_2; platinum electrode

Magnetic properties

The ability to prepare stable meta-M_2 and para-M_2 complexes as neutral, monocationic or dicationic species, and therefore with different d-electron counts, is particularly advantageous for investigating the magnetic properties of these complexes. The **meta-Fe_2** and **para-Fe_2** complexes are not described in detail here due to difficulties in interpretation of the data that result from their anisotropic g-factors. Complexes with d^6-d^6 configurations (**meta-Fe_2^o**, **para-Fe_2^o**, **meta-Co_2^{2+}** and **para-Co_2^{2+}**) were diamagnetic as expected. However, **meta-Co_2^o**, **para-Co_2^o**, **meta-Ni_2^{2+}**, **para-Ni_2^{2+}**, **meta-Ni_2^o** and **para-Ni_2^o** exhibited high magnetic moments at room temperature and antiferromagnetic ground states. Isoelectronic d^7-d^7 pairs (**meta-Co_2^o/meta-Ni_2^{2+}** and **para-Co_2^o/para-Ni_2^{2+}**) exhibited essentially identical behavior. The moments for **meta-Co_2^o** and **meta-Ni_2^{2+}** at room temperature [$\mu_{eff}(300\ K) = 2.49\ \mu_B$] were larger than those for the para analogs [$\mu_{eff}(300\ K) = 2.15\ \mu_B$] and the transition toward the antiferromagnetic ground state occurred at lower temperatures for the meta complexes (Figure 2). These observations are consistent with either a pair of independent $S = 1/2$ spins [$\mu_{eff} = 2.44\ \mu_B$] or a $S = 1$ triplet excited state and a antiferromagnetic ground state, with a lesser degree of antiferromagnetic spin exchange in the meta isomers. For the d^8-d^8 **meta-Ni_2^o** and **para-Ni_2^o** stronger exchange is evident for the para isomer as well, with the room temperature moments (**meta-Ni_2^o** = 3.92 μ_B; **para-Ni_2^o** = 3.60 μ_B) approaching that expected for a quintet state (i. e., 4.0 μ_B).

Dilution experiments performed by cocrystallization of the paramagnetic complexes in a host of the isomorphous Fe complexes gave clear indications of a significant intermolecular spin exchange. For example, dilutions of <3% of **meta-Ni_2^o** in an isomorphous **meta-Fe_2^o** host gave significantly higher moments (when normalized for concentration) at low temperatures. Similar results were obtained for **para-Ni_2^o** in an **para-Fe_2^o** host, although isomorphism is presumed here as X-ray structural information is lacking. These results suggest that statistically fewer intermolecular exchange interactions results in less intermolecular exchange associated with Ni-Ni contacts. As noted above, the crystal structure of **meta-Ni^o** reveals nearly equivalent intermolecular and intramolecular Ni-Ni distances. Therefore, through-space intermolecular spin exchange interactions are also an important consideration in the design of high spin systems based on the complexes. It is noted that the magnitude of the through space exchange is reminiscent of that observed for $[(C_5Me_5)_2Fe]$[tetracyanoethylene]. More detailed investigations of the properties of these dimer complexes, which are currently in progress, are required before attempting to synthesize polymers based on this concept.

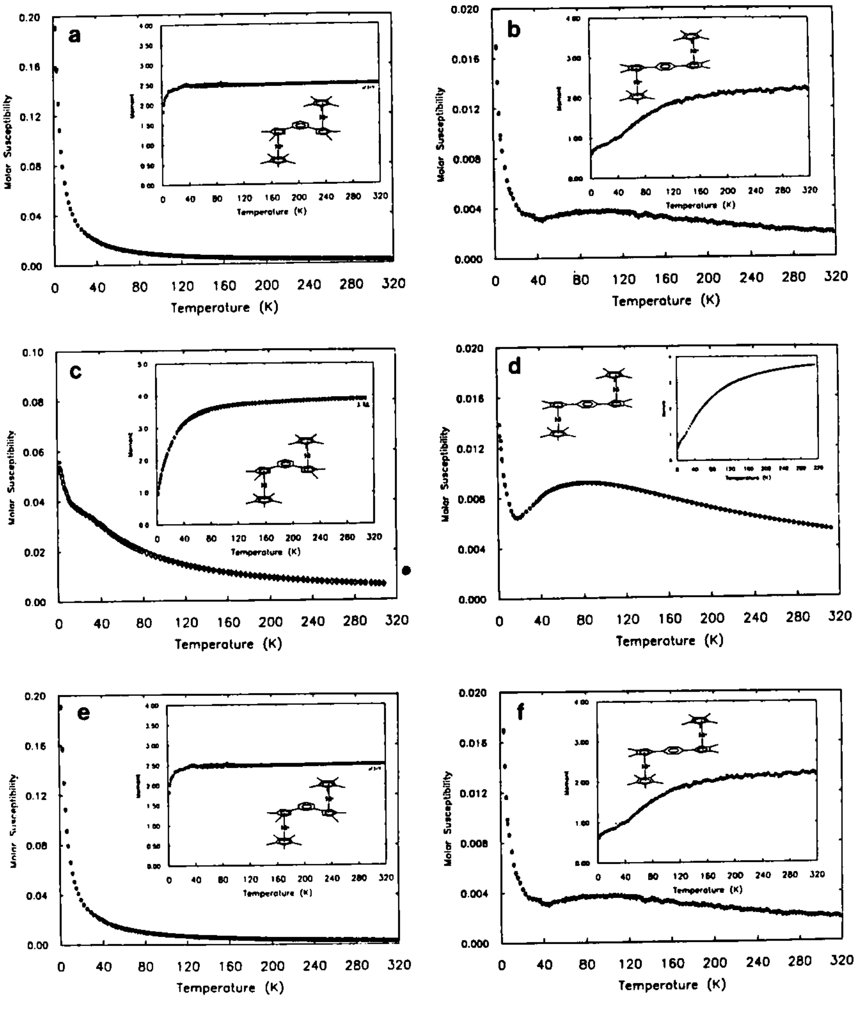


FIGURE 2. Magnetic susceptibilities and moment (inset) plots for meta-M_2^{n+} and para-M_2^{n+} complexes (a) meta-Co_2^0 (b) para-Co_2^0 (c) meta-Co_2^{2+} (d) para-Co_2^{2+} (e) meta-Ni_2^0 (f) para-Ni_2^0.

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