

THE SYNTHESIS AND HYDROGEN-STORAGE CHEMISTRY OF
POLYHYDRIDOFERRATES

FINAL PROGRESS REPORT

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U.S. ARMY RESEARCH OFFICE

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13. ABSTRACT (Maximum 200 words) The reactions to prepare the complex hydride $[\text{FeH}_6]^{4-}$ have been surveyed and it has been determined that the high pressure sintering method is the most efficient. The complex hydride Mg_2FeH_6 has little tendency to release hydrogen under ordinary conditions. Electrophilic species were not successful in producing a "reversible" form of hydrogen-storage, <u>in situ</u> . Reactions of soluble complex species prepared by solution synthetic techniques have some fascinating properties. These species are formulated as $[\text{FeH}_6]\{\text{MgY}(\text{THF})_n\}_4$, Y = halide or alkoxide. The more important findings include: (1) The position of hydride in the spectrochemical series has been unambiguously determined for the first time; (2) The thermodynamic (i.e. equilibrium constant) and kinetic parameters for the ion pairing in these species, where X = halide, have been characterized; (3) Highly soluble species have been prepared, where Y = alkoxide, and their solvatochromism has been characterized; (4) Catalysis of hydrogen-transfer reactions in hydrocarbons has been observed in solutions of $[\text{FeH}_6]^{4-}$.				
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STATEMENT OF THE PROBLEM

The focus of the work was to investigate the synthesis of complexes of $[\text{FeH}_6]^{4-}$ and to determine whether such materials could serve as hydrogen-storage materials. The initial work at Stockholm University in Prof. Dag Nöregård's laboratory showed that solid state reactions of the elements with hydrogen were the most efficient means to produce these materials. The difficulty was that these complex hydrides were not convenient sources of hydrogen since they decompose only above 180 °C. Chemical activation using electrophilic reagents was also unsuccessful in preparing suitable forms of available hydrogen.

Recent efforts within the last 12 months have investigated the potential of soluble complexes of $[\text{FeH}_6]^{4-}$ to catalyze hydrogen transfer reactions such as in the dehydrogenation/hydrogenation in hydrocarbons. A stable reforming catalyst which operates at moderate temperatures would greatly benefit the efforts to solve the hydrogen-storage problem. Currently the best available catalysts operate above 150 °C and employ expensive phosphine ligands which resist destructive P-C bond cleavage. The homoleptic complexes such as $[\text{FeH}_6]^{4-}$ have the advantage that there is no phosphine ligand with which to have such concerns.

SUMMARY OF MOST IMPORTANT RESULTS

A collaboration developed in the course of this project with Prof. Sidney G. Gibbins (University of Victoria), who has synthesized an interesting complex hydride of iron which is soluble in THF to the extent of 5×10^{-3} mol/L. In the course of this collaboration it soon became evident that a good deal of scientific information on the homoleptic hydride complex, $[\text{FeH}_6]^{4-}$, could be gleaned by further study on this complex.

Any textbook of inorganic chemistry will record the spectrochemical series which measures the ability of a ligand to interact with d -electrons of a metal. $[\text{FeH}_6]^{4-}$ represents an unambiguous example of octahedral d^6 coordination to hydride. Consequently, it was possible to directly measure, for the first time, the ligand field stabilization parameter, Δ_o , for the hydride ligand.

Figure 1 shows the measured electronic spectrum of $[\text{FeH}_6]^{4-}$ and the assignments which were based on the energy level diagram and standard equations for low spin Fe^{2+} . These results show that hydride is at the high end of the spectrochemical series but below cyanide, CN^- . Thus hydride falls midway between the π -donor (low field) and the π -acceptor (high field) ligands. This would be expected since H^- is an exceptional σ -donor but it has no π -bonding capabilities.

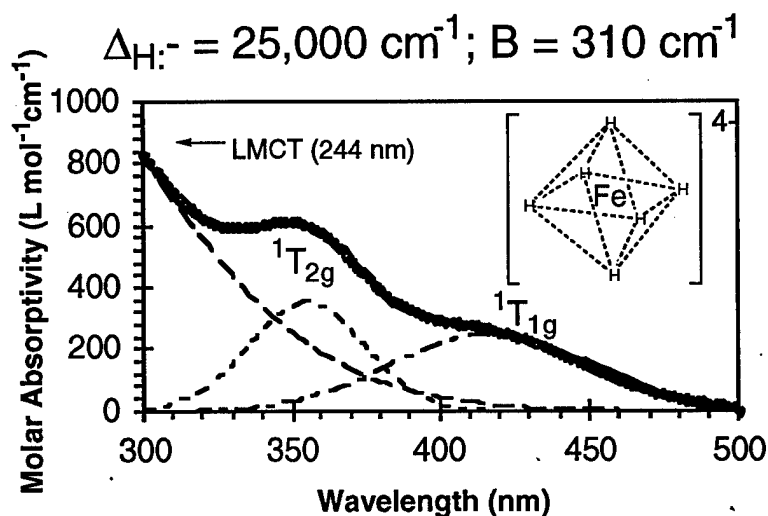
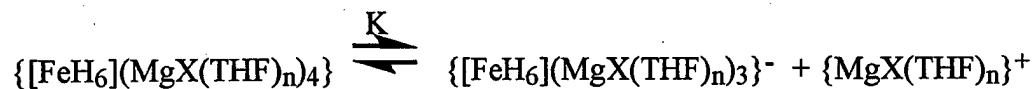


Figure 1. Assignments in the Electronic Spectrum of $[\text{FeH}_6]^{4-}$ in THF (assuming that $C/B = 4$)

Investigation of the solution spectroscopic properties of $[\text{FeH}_6]^{4-}$ has also given more information on the unique bonding properties present in the *soluble* complexes of

$[\text{FeH}_6]^{4-}$. The hypsochromic shift which is evident upon titrating solutions of $[\text{FeH}_6]^{4-}$ with $[\text{MgCl}_2]$ has suggested an ion pairing equilibrium:



This equilibrium constant ($K = 3 \times 10^{-3}$) has been obtained by spectroscopic titration. The rate of the complexation of the complex anion $\{[\text{FeH}_6](\text{MgX}(\text{THF})_n)_3\}^-$ with $\{\text{MgX}(\text{THF})_n\}^+$ is independent of $[\text{MgX}_2]$ ($k = 55 \text{ s}^{-1}$, $27 \text{ }^\circ\text{C}$). All these data suggest a highly dynamic species in solution, whereas the constancy of the ligand field absorptions requires that the octahedral, $[\text{FeH}_6]^{4-}$, remains intact.

The intriguing picture of the ion pairing phenomenon prompted synthesis and characterization of some more highly soluble complexes of $[\text{FeH}_6]^{4-}$. **Figure 2** illustrates the molecular models of two such complexes, $[\text{FeH}_6]\{\text{MgOR}(\text{THF})_n\}_4$ where $\text{R} = \text{}^t\text{Bu}$ and 1-adamantyl. The highly soluble nature of these species is due the presence of the

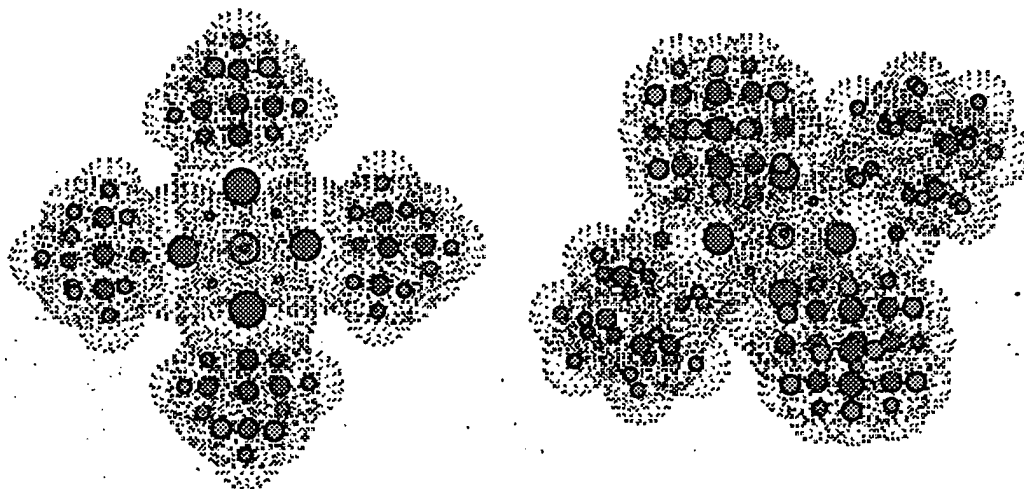


Figure 2. Molecular Structures of Highly Soluble Complexes $[\text{FeH}_6]\{\text{MgOR}(\text{THF})_n\}_4$ (from left: $\text{R} = \text{}^t\text{Bu}$ and 1-adamantyl)

large lipophilic side-chains which are oriented in a tetrahedral manner around $[\text{FeH}_6]^{4-}$.

Figure 3 shows the ^1H NMR in C_6D_6 of one such highly soluble complex of $[\text{FeH}_6]^{4-}$. The broad lines are an indication that there is some paramagnetism present, mostly likely due to admixture of paramagnetic excited states and the ground state, or temperature independent paramagnetism. This phenomenon is also seen in ^{13}C NMR (Figure 4). The broadening of the carbon lines follows their proximity to the iron center. The attempt to observe the ^{57}Fe signal was not possible due to this paramagnetism.

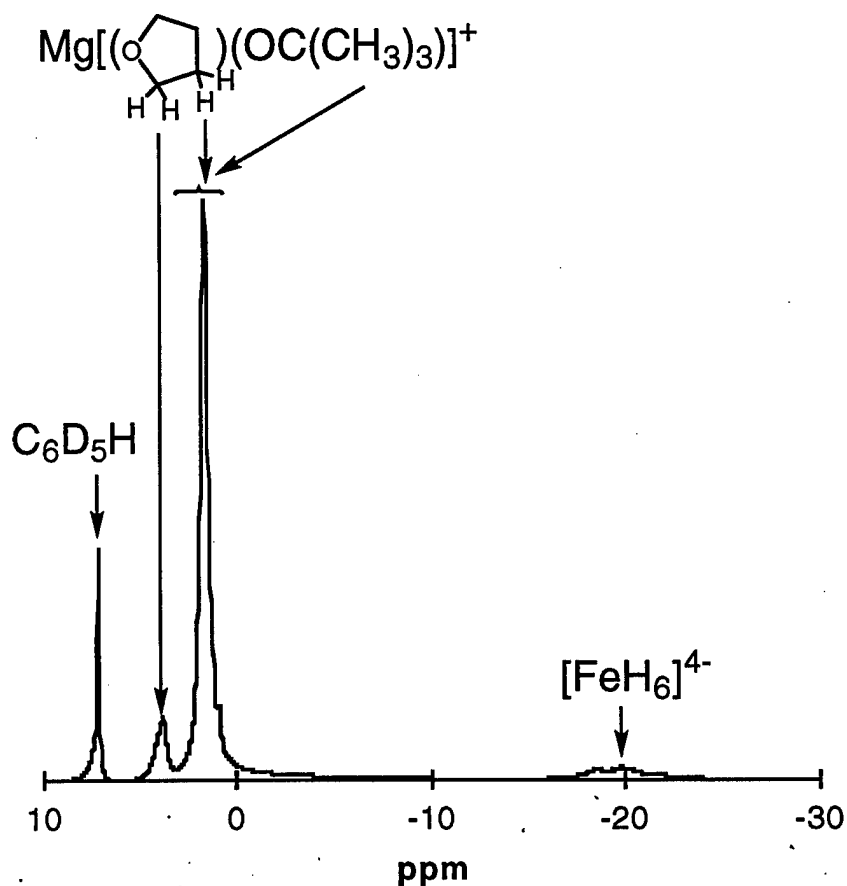


Figure 3. ^1H NMR Spectrum of $[\text{FeH}_6]\{\text{MgO}^t\text{Bu}(\text{THF})_{0.75}\}_4$ in C_6D_6

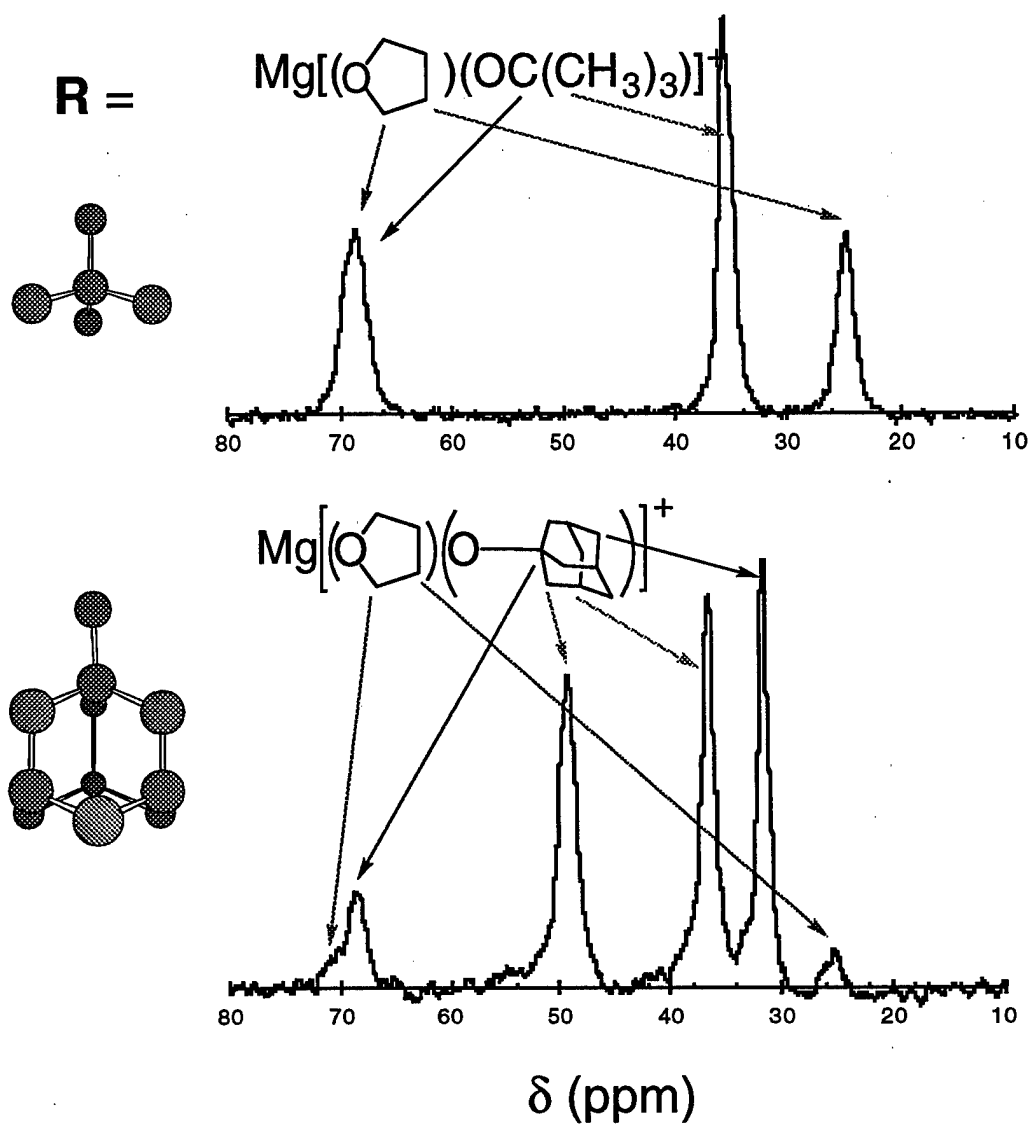


Figure 4. $^{13}\text{C}\{^1\text{H}\}$ NMR Spectra of the Complexes $[\text{FeH}_6]\{\text{MgOR}(\text{THF})_n\}_4$ in C_6D_6 ($\text{R} = \text{tBu}$ and 1-adamantyl)

From these highly soluble species a solvatochromic effect is clearly observed for the ligand to metal (LMCT) band. Here the molecular dipole moment in the excited state is orthogonal to that in the ground electronic state. In solvents such as benzene and toluene the band is red shifted *ca.* 20 nm versus a more polar solvent, THF.

A hydrogen-transfer reaction catalyzed by solutions $[\text{FeH}_6]^{4-}$ was characterized.

In Figure 5 the results of reactions between THF and benzene are illustrated.

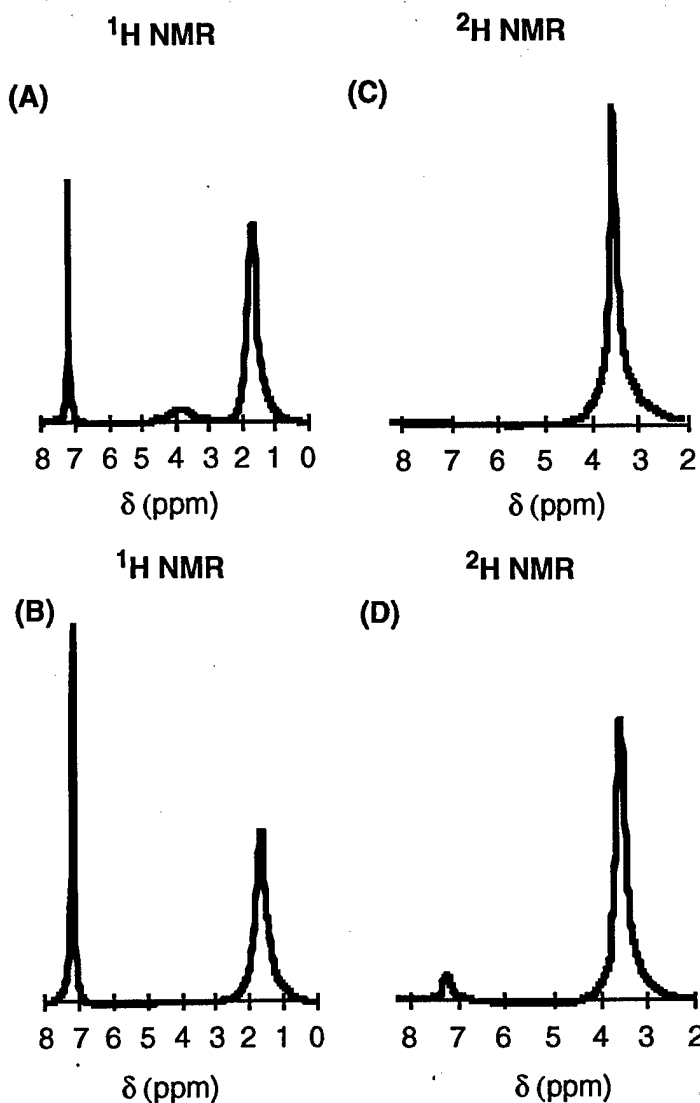


Figure 5. NMR Spectra Demonstrating Hydrogen-Deuterium Exchange Between THF and Benzene Catalyzed by $[\text{FeH}_6]^{4-}$ (A) Initial ^1H NMR (200 MHz) spectrum of 0.030 M $[\text{FeH}_6]^{4-}$ where $[\text{THF}]_0 = 0.060 M$ in C_6D_6 ; (B) ^1H NMR spectrum after heating 20 h at 60°C ; (C) Initial ^2H NMR (30.7 MHz) spectrum of 0.41 M THF- d_8 and 0.080 M (3) in C_6H_6 ; (D) ^2H NMR spectrum after 9 h at 80°C (the amount of H(D) exchange corresponds to 9 and 4 mol H(D) exchanged per mol $[\text{FeH}_6]^{4-}$, respectively).

Here it is seen from the ^1H NMR that hydrogen in THF is transferred to the deuterated solvent to produce a much larger C_6HD_5 peak. In an analogous manner the ^2H NMR shows that deuterium in THF- d_8 is transferred to benzene to yield a $\text{C}_6\text{H}_5\text{D}$. Both of these reactions occur at 65°C overnight. The most important outcome of this experiment has been to show that it is possible now to begin to focus on catalysts for hydrogen-transfer as a way to perform hydrogen-storage.

These $[\text{FeH}_6]^{4-}$ catalyst solutions show comparable initial rates to the best currently available phosphine-containing noble metal catalysts.¹ Further study is required to delineate the factors influencing the activity of the catalyst.

The use of higher pressure and high temperature sintering methods is a favorable development in this area.² The opportunity now exists for exploring new conditions for preparing soluble homoleptic hydrides for metals in Groups 8-10.

LIST OF ALL PUBLICATIONS

- Linn, Donald E., Jr.; Gibbins, S. G. "Solution Spectroscopic and Chemical Properties of $[\text{FeH}_6]^{4-}$ ", *Inorganic Chemistry*, **1997**, *37*, 3461-3466.
- Linn, Donald E., Jr.; Sidney G. Gibbins "Highly Soluble Complexes of $[\text{FeH}_6]^{4-}$ and Ion Pairing Interactions", *Journal of Organometallic Chemistry* **1998**, 000, 0000-0000.
- Linn, Donald E, Jr. " $[\text{FeH}_6]^{4-}$ and Homogeneous Hydrogen Transfer Catalysis", invited article in "Topical Volume on Iron Chemistry" *Inorganica Chimica Acta*, in preparation.

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