

Highly soluble complexes of $[\text{FeH}_6]^{4-}$ and ion pairing interactions

Donald E. Linn Jr ^{a,*}, Sidney G. Gibbins ^b

^a Department of Chemistry, Indiana University–Purdue University at Fort Wayne, Fort Wayne IN 46805-1499, USA

^b Department of Chemistry, University of Victoria, Victoria V8W 2Y2, Canada

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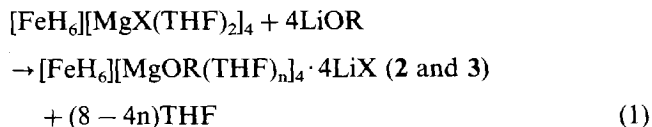
Abstract

The complex hydride, $[\text{FeH}_6][\text{MgX}(\text{THF})_2]_4$ (**1**), ($\text{X} = \text{Br}_{0.88}\text{Cl}_{0.12}$) serves as a model for the influences affecting the solubility of polyhydridic complex hydrides. (**1**) is converted to $[\text{FeH}_6][\text{MgOR}(\text{THF})_n]_4 \cdot 4\text{LiX}$ (**2**) and (**3**) ($\text{R} = \text{tBu}$ and Et , respectively) upon treatment with LiOR in benzene solution. The solubilities in THF are 6×10^{-3} and > 0.5 M for (**1**) and (**2**), respectively. ^1H NMR lineshape and electronic spectra suggests the presence of the ion pairing reaction: $[\text{FeH}_6][\text{MgY}(\text{THF})_2]_4 = [\text{FeH}_6][\text{MgY}(\text{THF})_2]_3^- + [\text{MgY}(\text{THF})_n]^+$ ($\text{Y} = \text{halide}$ and alkoxide). The species with alkoxides coordinated to magnesium show a ligand-to-metal charge transfer (LMCT) band which shows the corresponding hypsochromic shift with increasing solvent polarity. © 1998 Elsevier Science S.A. All rights reserved.

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Most homoleptic polyhydridic complexes are not molecular compounds [1,2]. Rather these solids retain a rigid network ionic to metallic lattice structure which does not permit dissolution in aprotic solvents. One rare exception to this is the molecular complex, $[\text{FeH}_6][\text{MgX}(\text{THF})_2]_4$, (**1**) [3]. The bonding within the $[\text{FeH}_6]^{4-}$ octahedron is clearly covalent as deduced from neutron diffraction, UV-visible and NMR spectroscopy [4]. If attention is called to the bonding between magnesium and $[\text{FeH}_6]^{4-}$ this can vary between strong network bonding as in Mg_2FeH_6 to that in (**1**). A unipositive magnesium complex cation apparently has the size and reduced charge required to render this species a soluble molecular complex hydride. Using this principle it has been possible to prepare other derivatives of (**1**) and examine their spectroscopic properties.

$[\text{FeH}_6][\text{MgX}(\text{THF})_2]_4$ reacted with four equivalents of LiOR ($\text{R} = \text{tBu}$ and Et , respectfully) in diethyl ether at room temperature to obtain the derivatives (**2**) and (**3**), respectively [5].



The ^1H NMR of (**2**) (Fig. 1) showed a broad split peak absorption at $\delta - 20.1$ ppm (fwhh = 500 Hz) which contrasts the double-humped peak at $\delta - 20.3$ (fwhh = 5 Hz) observed for (**1**). The hydride resonances gave line broadening with depends on temperature (narrowing above ambient) ([4]b). Metathetical displacement of LiX is deduced from the downfield shift in the Li^+ resonance and also by the upfield shift in the ^{35}Cl manifold in THF [6]. This is consistent with the formation of ion pairs yielding effective spin-spin relaxation times (T_2^*) dependent upon the position of the ion pair equilibrium and the rate constant for the reaction [7].

To probe the mechanism of this reaction lineshapes were measured as depicted in Table 1. Measurements were performed on (**1**) in the 'near fast exchange' region [8]. For THF-d_8 solutions containing $[\text{I}]_{\text{total}} = 2.0 \times 10^{-3}$ M and $[\text{MgCl}_2]_{\text{total}}$ encompassing 0.0125–0.200

* Corresponding author. Tel.: +1 219 4816813; fax: +1 219 4816880; e-mail: linn@ipfw.edu

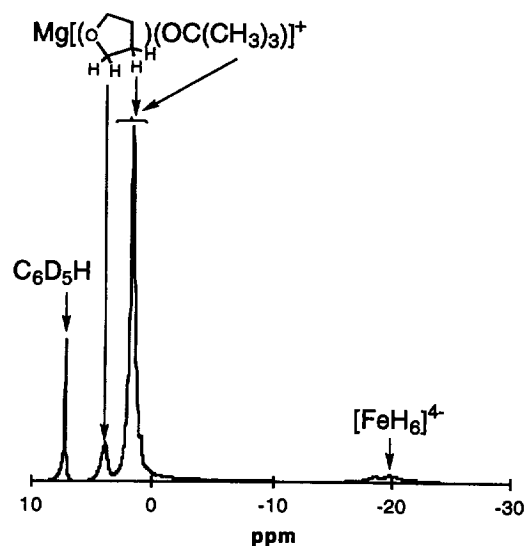
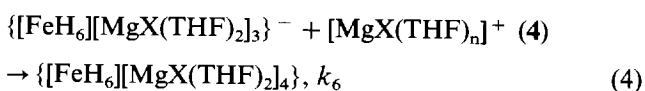
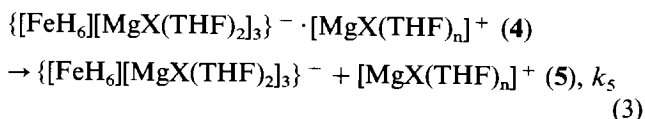
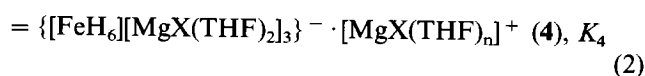
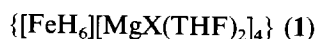


Fig. 1. NMR (200 MHz) of $[\text{FeH}_6][\text{MgO}^t\text{Bu}]_4 \cdot 4\text{LiX} \cdot 3\text{THF}$ at 23°C in C_6D_6 .

M, the $(\tau_1)^{-1}$ were independent of $[\text{MgCl}_2]_{\text{total}}$. A plausible mechanism for the reaction can be described as involving contact ion pairs and separated ion pairs, (4) and (5), respectively:



Here the mode of reaction involves the Lewis acidic $[\text{MgX}(\text{THF})_n]^+$ units attacking the triangular faces of the $[\text{FeH}_6]^{4-}$ octahedron. Applying the steady state approximation to (5) ($k_6[\text{MgX}(\text{THF})_n]^+ \gg K_4 k_5$) pertaining to the ion pair formation and trapping reactions (2)–(4), thus yields:

Table 1
Kinetic data for the reaction of $[\text{FeH}_6][\text{MgX}(\text{THF})_2]$ and $[\text{MgCl}_2]$ in THF- D_8 at 23–65°C

$[\text{MgCl}_2]_{\text{Total}}$	T (°C)	$\nu_{1/2}$ (Hz)	$\Delta\nu$ (Hz)	x_1	$(\tau_1)^{-1}$ (s^{-1})	$[(\tau_1)^{-1}]_{\text{calc}}$
0.020	23	60	30	0.125	60	52 ± 8
0.065	23	44	14	0.0421	50	52 ± 8
0.12	23	38	8.3	0.0233	49	52 ± 8
0.20	23	34	4.9	0.0141	51	52 ± 8
0.020	33	46	17	0.125	105	96
0.020	43	44	15	0.125	125	140
0.020	43	41	12	0.125	160	140
0.020	55	39	10	0.125	190	205
0.020	65	36	7.0	0.125	290	280

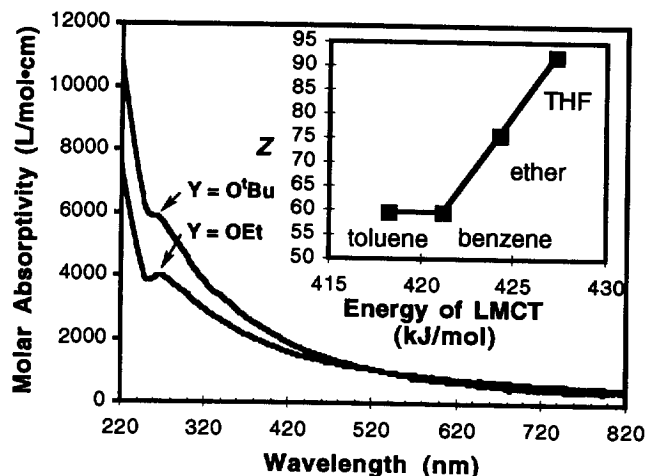


Fig. 2. Electronic spectra of $[\text{FeH}_6][\text{MgY}(\text{THF})_n]_4$ ($Y = \text{O}^t\text{Bu}$ or OEt) in diethyl ether. Inset: Dependence of the LMCT band in $[\text{FeH}_6][\text{MgO}^t\text{Bu}(\text{THF})_n]$ in solvents of differing polarities.

$$\text{Rate constant for exchange} = (\tau_1)^{-1} = K_4 k_5 \quad (5)$$

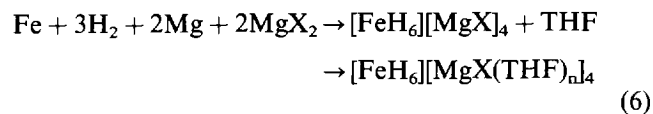
Hence $K_4 k_5 = 52 \pm 8 \text{ s}^{-1}$ at 23°C (Table 1) [9].

In the complex hydrides (1)–(3) which contain $[\text{FeH}_6]^{4-}$ there exists H^- ligands which are both octahedrally coordinated to iron and weakly coordinated to magnesium through ion pair contacts. Ion pair structures in the metal carbonylates have been characterized in which the contact ion pairs are less reactive than the separated ion pairs [10]. For this reason it is deduced that the ion pair reaction between $[\text{MgX}(\text{THF})_n]^+$ and the octahedral faces of $[\text{FeH}_6]^{4-}$ is most likely a separated, (5), or symmetrically solvated ion pair due to the zero-order dependence on $[\text{MgCl}_2]$.

UV-visible spectroscopy is also an useful technique to observe ion pairing by measuring the HOMO–LUMO energy gap. Fig. 2 displays the spectra of the hydrocarbon-soluble complexes (2) and (3) in ether. Both have an assigned ligand-to-metal charge transfer (LMCT) band at 268 nm similar to that observed previously in THF ([4]b). Further, the LMCT band of complex (2) is sensitive to solvent polarity in a manner reminiscent of pyridinium iodides. Fig. 2 also shows the dependence

on the energy of the LMCT band with different solvents. A good correlation exists between the solvent effect of this band and the spectroscopic Z parameter of pyridinium iodides [11]. The explanation for this follows from the fact that this absorption measures simultaneously both the lowering of the ground state energy and the raising of the energy of the excited state upon solvation. The promotion of an electron into an e_g^* orbital of $[\text{FeH}_6]^{4-}$ arising from the d orbitals creates a dipole of lesser magnitude and orthogonal to that in the ground state structure. The latter has a filled t_{2g} orbital. The Frank–Condon principle predicts that since solvent reorganization is much slower than the time scale for the measurement, the relative positions of the ground states and excited states move to higher energies versus the gas phase. These results illustrate that the ‘solvating power’ of the hydrocarbon solvents are similar to the gas phase ($Z = 60$) and correspondingly that diethyl ether is a more potent solvent than THF.

Based on these findings it should be possible to obtain the soluble complex hydrides formulated as $[\text{FeH}_6][\text{MgX}(\text{THF})_n]_4$ ($X = \text{halide}$) by a more direct synthesis:



These syntheses, however, are complicated by the high temperature and pressure required. Nevertheless, reactions at pressures exceeding 800°C and 1500 bar hydrogen have been demonstrated as feasible only recently [12].

Acknowledgements

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- [5] Preparation of $[\text{FeH}_6][\text{MgO}^i\text{Bu}]_4 \cdot 4\text{LiX} \cdot n\text{THF}$ (2). In an inert atmosphere glove box a 50 ml Schlenk flask was charged with 0.200 g (0.195 mmol) of (1). To this flask was added 5 ml of benzene and 0.062 g (0.78 mmol) of LiO^iBu with stirring at room temperature. Dissolution occurred within 1 h and the mixture was stirred 4 h. The resulting yellow brown solution was filtered, evaporated to dryness and the resulting tannish solid was triturated with hexane. Yield (2, $n = 3$): 0.17 g, 64%. Results: 33.8% C (33.4% found); 6.71% H (6.42% found); 5.6% Fe (5.1% found); $^1\text{H NMR}$ (C_6D_6): δ 3.75 (m, 12 H), 1.34 (br s, 48H), -20.1 (br s, 6H); $^6\text{Li NMR}$ (THF): δ 0.78. A $^1\text{H COSY}$ spectrum of the region between 4.5 and 1.2 δ showed cross peaks corresponding to the two methylene units in the bound THF. Complex (3) was prepared using the same procedure.
- [6] The chemical shifts measured for Li^+ in THF at 0.35 M are 0.04 and 0.38 ppm for LiO^iBu and LiBr , respectively. This reflects the normal halide ion versus oxygen anion behavior. See J.W. Akitt, in: J. Mason (Ed.), *Multinuclear NMR*, Plenum, New York, 1987, p. 203. An upfield shift in the $^{35}\text{Cl NMR}$ for ‘free Cl^- ’ has been seen previously (see reference 4b).
- [7] Lineshape data were used to obtain rate constants for exchange according to the expression for moderately fast exchange: $(\tau_1)^{-1} = 4\pi(1 - x_1)^2(x_1)(\Delta\nu)(\Delta\nu_{1/2})^{-1}$. Here τ_1 is the lifetime of MgCl_2 in the outer coordination sphere of (1), x_1 is the mole fraction of (1), $\Delta\nu$ is the chemical shift difference between (1) and (4) and $\Delta\nu_{1/2}$ ($\nu_{1/2} = 1/\pi T_2^*$) is the difference in line width at half-height between the line width in the presence and absence of exchange. $K_4 \approx 3 \pm 1 \times 10^{-3}$ (22°C) was estimated previously by spectrophotometric titration assuming dissociation of $[\text{MgCl}_2]$ (see reference 4b).
- [8] The line-widths at half-heights in the ‘very fast exchange’ limit were deduced from plots of $\Delta\nu_{1/2}$ versus x_1 at various temperatures. The limiting value was determined by extrapolation to $x_1 = 0$ (see S.S. Zumdahl, R.S.J. Drago, *Am. Chem. Soc.* 89 (1967) 4319 and references therein).
- [9] Assuming the equilibrium constant, K_4 , for exchange is relatively constant over the range of temperatures 22–65°C, yields activation parameters $\Delta H = 29 \pm 2 \text{ kJ mol}^{-1}$ and $\Delta S = -130 \pm 120 \text{ J mol}^{-1} \text{ deg}^{-1}$ (calculated at the University of Victoria).
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