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Contribution from the Departments of Chemistry, University of Southern California, Los Angeles, California 90089-1062,
and University of Victoria, Victoria, V8W 2Y2 Canada, and Chemistry Department,
Brookhaven National Laboratory, Upton, New York 11973

X-ray and Neutron Diffraction Studies of the Polyhydrido Complex $FeH_6Mg_4Br_{3.5}Cl_{0.5}(C_4H_8O)_8$: Discussion of Binary Transition-Metal Hydride Anions of the Type $[MH_x]^{n-}$

ROBERT BAU,*† MICHAEL Y. CHIANG,† DOUGLAS M. HO,† SIDNEY G. GIBBINS,*‡ THOMAS J. EMGE,§
and THOMAS F. KOETZLE*§

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The molecular structure of the polyhydrido complex $FeH_6Mg_4X_4(THF)_8$ ($X_4 \equiv Br_{3.5}Cl_{0.5}$) has been determined by single-crystal X-ray and neutron diffraction methods. The X-ray structure determination was carried out at room temperature, revealing an octahedral $[FeH_6]^{4-}$ core with $[MgBr(THF)_2]^+$ units situated over four of the eight faces of the octahedron. The $[FeH_6]^{4-}$ core exhibits crystallographic twofold symmetry, with an average Fe–H distance (as determined in the X-ray study) of 1.69 (9) Å. Neutron diffraction analysis of the title compound (carried out at 80 K at the Brookhaven High-Flux Beam Reactor on a crystal of volume 12 mm^3) fully confirmed this basic molecular geometry, yielding much more precise H positions. The Fe–H [1.609 (2) Å] and Mg–H [2.045 (18) Å] distances obtained from the neutron study support the idea that the Fe–H bond is largely "covalent" in nature while the Mg–H interaction is largely "ionic". A detailed discussion of available structural information for binary transition-metal hydride anions, $[MH_x]^{n-}$, is given in the text. Crystallographic details for the *X-ray* analysis of the title compound $C_{32}H_{70}Br_{3.5}Cl_{0.5}FeMg_4O_8$: space group $C2/c$ (monoclinic), a = 20.427 (4) Å, b = 11.623 (2) Å, c = 21.661 (7) Å, β = 109.39 (2)°, V = 4851 (2) Å^3, ρ(calcd) = 1.420 g cm^{-3} for Z = 4; $R(F)$ = 0.049 and $R_w(F)$ = 0.051 for 1476 reflections [$I > 3\sigma(I)$] collected at room temperature. Details for the *neutron* analysis (at 80 K): a = 20.808 (7) Å, b = 11.509 (3) Å, c = 21.009 (4) Å, β = 116.47 (2)°, V = 4504 (2) Å^3, ρ(calcd) = 1.524 g cm^{-3}; $R(F^2)$ = 0.117 and $R_w(F^2)$ = 0.091 for 5951 reflections (all data included).

Introduction

The reaction of ferric chloride with phenylmagnesium bromide and hydrogen gas, first investigated by Weichselfelder in 1926,[1] yielded a complex mixture of products ranging from tan precipitates to black tars. Over the years, various formulations have been suggested for these ill-defined solids, including FeH_3,[2,3] FeH_6,[2,4] and $Mg(FeH_4)_2$.[5] In 1977, it was discovered that a yellow crystalline material, formulated as $FeH_6Mg_4X_4(THF)_8$ ($X_4 \equiv Br_{3.5}Cl_{0.5}$), could be isolated from this system (in ~20% overall yield) upon extraction of the black tarry residue with tetrahydrofuran.[6] In this paper we report the X-ray and neutron structural investigations that confirm this assignment. A preliminary report of the X-ray analysis of this compound was published earlier.[7]

Experimental Section

The sample of $FeH_6Mg_4X_4(THF)_8$ used in this work was prepared and crystallized as described previously.[6] An NMR spectrum of this compound, recorded at room temperature in THF-d_8 solution, showed a broad proton signal at τ +30.3.[8]

X-ray Structural Analysis. A yellow, air-sensitive crystal of dimensions 0.55 × 0.25 × 0.15 mm was chosen for the analysis and sealed in a glass capillary in a nitrogen-filled glovebox. Unit cell parameters were derived from the angular settings of 15 well-centered reflections (9° < θ < 23°), measured at room temperature on a Nicolet/Syntex $P2_1$ diffractometer using graphite-monochromated Mo Kα radiation. The refined unit cell constants are presented in Table I along with other relevant crystal data. Two quadrants of data, ($+h,+k,\pm l$) and ($+h,-k,\pm l$), were collected in the θ–2θ scan mode with a variable scan speed ranging from 2.5 to 29.3°/min. The minimum and maximum 2θ limits employed were 3.5 and 45.0°, respectively. Three standard reflections were monitored at 50-reflection intervals throughout the data collection and showed no significant changes in their intensities. An analysis of the intensity values for an axial reflection ($\chi \sim 90°$) spindle angle ϕ revealed a 26% variation in intensity. Consequently, an empirical absorption correction was applied,[9] as well as corrections for Lorentz–polarization effects. A total of 5506 reflections was collected, of which 3099 were symmetry independent. After data reduction, 1476 reflections having F^2 values greater than $3\sigma(F^2)$ were used in the structure solution and refinement.

Table I. Crystal Data for $FeH_6Mg_4X_4(THF)_8$

	X-ray (room temp)	neutron (80 K)
crystal class	monoclinic	monoclinic
space group	$C2/c$ (No. 15)	$C2/c$ (No. 15)
unit cell parameters		
a, Å	20.427 (4)	20.808 (7)
b, Å	11.623 (2)	11.509 (3)
c, Å	21.661 (7)	21.009 (4)
β, deg	109.39 (2)	116.47 (2)
V, Å^3	4851 (2)	4504 (2)
Z	4	4
fw[a]	1033.4	1033.4
ρ(calcd), g cm^{-3}	1.420	1.524
abs coeff (μ), cm^{-1}	35.1[b]	2.777[c,d]

[a] Assuming $X_4 \equiv Br_{3.5}Cl_{0.5}$. [b] For Mo K$\alpha$ X-rays; λ = 0.71069 Å. [c] For λ = 1.16173 Å neutrons. [d] For the neutron analysis, the linear absorption coefficient (μ) was calculated from the formula $\mu = \rho[\Sigma(\mu/\rho)_i(\omega_i)]$, where ρ is the density of the crystal, ω_i is the weight fraction of the ith element in the molecule, and $(\mu/\rho)_i$ is the mass absorption coefficient for the ith element in the molecule. All values for $(\mu/\rho)_i$ were taken from: Bacon, G. E. "Neutron Diffraction", 3rd ed.; Clarendon Press: Oxford, England, 1975, pp 72–73. $(\mu/\rho)_H$ was calculated from the formula $(\mu/\rho)_H = \omega_H(10.055 + 14.117\lambda)$: Koetzle, T. F.; McMullan, R. K., private communication.

The structure was successfully refined in the monoclinic space group $C2/c$ (No. 15). The initial set of atomic positions was determined by direct methods,[10] which readily revealed the positions of the iron,

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† University of Southern California.
‡ University of Victoria.
§ Brookhaven National Laboratory.

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Table II. Atomic Parameters[a] for $FeH_6Mg_4X_4(OC_4H_8)_8$

atom	x	y	z
H(1)	0.00^b	0.3931 (4)	0.25^b
	0.00^b	0.362 (9)	0.25^b
H(2)	0.00^b	0.6732 (4)	0.25^b
	0.00^b	0.632 (9)	0.25^b
H(3)	0.0159 (2)	0.5335 (3)	0.3321 (2)
	0.017 (4)	0.500 (8)	0.342 (4)
H(4)	−0.0852 (2)	0.5308 (3)	0.2255 (2)
	−0.089 (5)	0.500 (8)	0.235 (4)
Fe	0.00^b	0.5329 (1)	0.25^b
	0.00^b	0.5048 (2)	0.25^b
Mg(1)	0.0867 (1)	0.4014 (2)	0.3433 (1)
	0.0826 (2)	0.3759 (3)	0.3312 (2)
Mg(2)	0.0669 (1)	0.6570 (2)	0.2023 (1)
	0.0639 (2)	0.6304 (3)	0.1964 (2)
Br(1)	0.0667 (1)	0.2766 (1)	0.4289 (1)
	0.0625 (1)	0.2594 (1)	0.4218 (1)
Br(2)	0.1667 (1)	0.7941 (1)	0.2697 (1)
	0.1619 (1)	0.7684 (1)	0.2520 (1)
O(1)	0.1321 (1)	0.2762 (2)	0.3024 (1)
	0.1259 (4)	0.2451 (7)	0.2910 (4)
O(2)	0.1865 (1)	0.4600 (2)	0.4167 (1)
	0.1808 (4)	0.4337 (8)	0.3849 (4)
O(3)	0.0023 (1)	0.7612 (2)	0.1180 (1)
	0.0037 (4)	0.7424 (6)	0.1262 (4)
O(4)	0.1135 (1)	0.5798 (2)	0.1442 (1)
	0.1112 (4)	0.5581 (6)	0.1339 (4)
C(11)	0.1236 (1)	0.1522 (1)	0.3079 (1)
	0.1140 (9)	0.1220 (14)	0.2992 (10)
C(12)	0.0881 (1)	0.1098 (2)	0.2318 (1)
	0.0969 (13)	0.0803 (16)	0.2283 (13)
C(13)	0.1256 (1)	0.1832 (2)	0.1978 (1)
	0.1343 (10)	0.1545 (21)	0.1963 (10)
C(14)	0.1365 (1)	0.2996 (2)	0.2360 (1)
	0.1401 (9)	0.2714 (14)	0.2303 (8)
C(21)	0.2473 (1)	0.3823 (2)	0.4488 (1)
	0.2370 (10)	0.3596 (14)	0.4253 (10)
C(22)	0.2977 (1)	0.4195 (2)	0.4177 (1)
	0.2978 (10)	0.4338 (21)	0.4460 (14)
C(23)	0.2769 (1)	0.5462 (2)	0.3955 (1)
	0.2773 (12)	0.5450 (22)	0.4262 (11)
C(24)	0.2171 (1)	0.5718 (2)	0.4164 (1)
	0.2051 (9)	0.5473 (16)	0.3832 (9)
C(31)	−0.0716 (1)	0.7862 (2)	0.1010 (1)
	−0.0608 (9)	0.7866 (20)	0.1304 (9)
C(32)	−0.0751 (1)	0.9173 (2)	0.0982 (1)
	−0.0835 (11)	0.8779 (18)	0.0846 (10)
C(33)	−0.0283 (1)	0.9462 (2)	0.0612 (1)
	−0.0297 (12)	0.8975 (16)	0.0552 (10)
C(34)	0.0292 (1)	0.8519 (1)	0.0873 (1)
	0.0305 (8)	0.8147 (14)	0.0853 (7)
C(41)	0.1885 (1)	0.5720 (2)	0.1594 (1)
	0.1854 (7)	0.5491 (16)	0.1444 (9)
C(42)	0.1887 (1)	0.5236 (2)	0.0921 (1)
	0.1890 (11)	0.4700 (20)	0.0913 (10)
C(43)	0.1202 (1)	0.4500 (2)	0.0605 (1)
	0.1176 (11)	0.4315 (18)	0.0535 (9)
C(44)	0.0689 (1)	0.5221 (2)	0.0775 (1)
	0.0678 (7)	0.5006 (14)	0.0744 (7)
H(11A)	0.0925 (2)	0.1412 (3)	0.3384 (2)
H(11B)	0.1767 (2)	0.1127 (4)	0.3372 (2)
H(12A)	0.0307 (2)	0.1302 (4)	0.2075 (2)
H(12B)	0.0957 (3)	0.0160 (4)	0.2289 (3)
H(13A)	0.1773 (2)	0.1448 (4)	0.2081 (3)
H(13B)	0.0928 (2)	0.1933 (4)	0.1407 (2)
H(14A)	0.0942 (2)	0.3616 (4)	0.2067 (4)
H(14B)	0.1891 (2)	0.3372 (4)	0.2499 (2)
H(21A)	0.2271 (2)	0.2935 (3)	0.4365 (2)
H(21B)	0.2723 (2)	0.3952 (4)	0.5066 (2)
H(22A)	0.2893 (3)	0.3671 (6)	0.3715 (3)
H(22B)	0.3536 (2)	0.4084 (4)	0.4571 (2)
H(23A)	0.2563 (3)	0.5557 (6)	0.3384 (3)
H(23B)	0.3217 (2)	0.6062 (5)	0.4207 (4)
H(24A)	0.2377 (2)	0.6079 (4)	0.4702 (2)
H(24B)	0.1743 (2)	0.6275 (3)	0.3788 (2)
H(31A)	−0.0828 (2)	0.7482 (4)	0.1426 (2)
H(31B)	−0.1067 (2)	0.7495 (4)	0.0492 (2)
H(32A)	−0.0508 (3)	0.9500 (4)	0.1531 (3)
H(32B)	−0.1299 (2)	0.9509 (4)	0.0697 (3)
H(33A)	−0.0598 (2)	0.9417 (5)	0.0041 (2)
H(33B)	−0.0054 (2)	1.0335 (4)	0.0737 (3)
H(34A)	0.0390 (2)	0.8131 (4)	0.0452 (2)
H(34B)	0.0798 (2)	0.8815 (4)	0.1295 (2)
H(41A)	0.2152 (2)	0.5117 (4)	0.2045 (2)
H(41B)	0.2119 (2)	0.6581 (4)	0.1746 (2)
H(42A)	0.1840 (2)	0.5931 (4)	0.0553 (2)
H(42B)	0.2367 (2)	0.4723 (4)	0.1036 (2)
H(43A)	0.1001 (2)	0.4359 (4)	0.0037 (2)
H(43B)	0.1297 (2)	0.3651 (3)	0.0874 (3)
H(44A)	0.0282 (2)	0.4718 (4)	0.0849 (2)
H(44B)	0.0432 (2)	0.5895 (3)	0.0372 (2)

[a] For each atom, the neutron diffraction result is given on the first line, and the X-ray diffraction result, if available, on the second.
[b] These parameters are required to be fixed by the space group symmetry.

magnesium, and bromine atoms. The remaining non-hydrogen atoms were located in subsequent difference-Fourier maps.[11] Full-matrix least-squares refinement with anisotropic thermal parameters for all atoms in this model resulted in agreement factors of $R(F) = 0.051$ and $R_w(F) = 0.053$.[12]

At this stage, a difference-Fourier synthesis based on low-angle reflections[13] (maximum $(\sin\theta)/\lambda = 0.36$ Å^{-1}) clearly revealed the hydride hydrogen positions. Of the seven largest peaks in the low-angle difference map, those having values of 0.37, 0.37, 0.24, and 0.30 e Å^{-3} were situated at the four sites of a regular octahedron with a twofold axis of symmetry at the central iron position. Hydrogen atoms H(1), H(2), H(3), and H(4) were placed at these sites in subsequent least-squares refinement cycles. The remaining three peaks in the difference map (0.29, 0.28, and 0.26 e Å^{-3}) were located at positions unreasonably close to the Br(1), Fe, and C(21) atoms, respectively, and were excluded.

The positional and isotropic temperature factors for the H atoms were added to the list of variables, and the refinement resumed in the following manner:[14] (a) all positional and thermal parameters were first refined with approximately 50% of the data (maximum $(\sin\theta)/\lambda = 0.36$ Å^{-1}, 731 reflections); (b) the coordinates and isotropic temperature factors of the H atoms were then fixed, and the positional and thermal parameters of all other atoms refined with the full set of 1476 reflections [$R(F) = 0.050$, $R_w(F) = 0.052$]; (c) all of the coordinates and temperature factors, as well as the populations of the halide atoms, were refined (again with the full data set), yielding the final agreement factors of $R(F) = 0.049$ and $R_w(F) = 0.051$.[12]

During the refinement, the halide ligands were treated as atoms with partial occupancies of two different form factors, bromine and chlorine, such that the sum of their fractional populations was equal to 1.00. The populations of the two independent halide sites refined to values of [Br(1) = 0.88 (1) Br + 0.12 (1) Cl] and [Br(2) = 0.89 (1) Br + 0.11 (1) Cl], as compared with [0.875 Br + 0.125 Cl] for

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(11) For the X-ray portion of this work, major computations were performed on the USC IBM 370-158 computer using CRYM, an amalgamated set of crystallographic programs developed by Dr. Richard Marsh's group at the California Institute of Technology. Scattering factors for the X-ray analysis were taken from: "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV. $\Delta f'$ corrections were applied to the form factors for Cl, Fe, and Br. For the neutron diffraction analysis, calculations were performed on CDC 6600 and 7600 computers using programs described by (or modifications thereof): Berman, H. M.; Bernstein, F. C.; Bernstein, H. J.; Koetzle, T. F.; Williams, G. J. B. Report 21714; Brookhaven National Laboratory: Upton, NY, 1976.

(12) $R(F) = \sum|F_o - |F_c||/\sum F_o$; $R_w(F) = [\sum w(F_o - |F_c|)^2/\sum wF_o^2]^{1/2}$; $R(F^2) = \sum|F_o^2 - F_c^2|/\sum|F_o^2|$; $R_w(F^2) = [\sum w(F_o^2 - F_c^2)^2/\sum w_o^4]^{1/2}$.

(13) (a) La Placa, S. J.; Ibers, J. A. *J. Am. Chem. Soc.* **1963**, *85*, 3501. (b) La Placa, S. J.; Ibers, J. A. *Acta. Crysallogr.* **1965**, *18*, 511.

(14) Kirtley, S. W.; Olsen, J. P.; Bau, R. *J. Am. Chem. Soc.* **1973**, *95*, 4532.

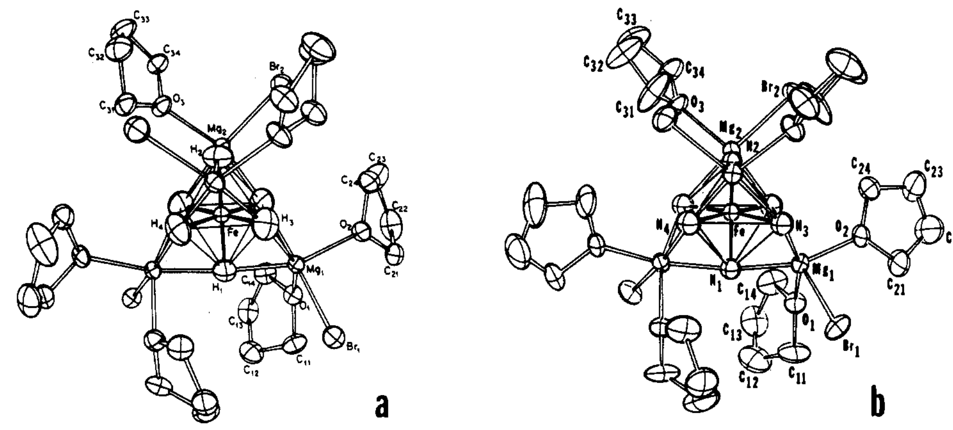

Figure 1. Molecular plots[52] of $FeH_6Mg_4X_4(THF)_8$: (a) neutron results (80 K); (b) X-ray results (room temperature). Two of the THF ligands have been removed for clarity.

the formulation $Br_{3.5}Cl_{0.5}$. Elemental analysis[6] indicated [0.85 Br + 0.15 Cl], or $Br_{3.4}Cl_{0.6}$.

The largest peak remaining in the final difference-Fourier map was a residual of the Br(1) atom. No attempt was made to locate the methylene hydrogen atoms of the THF molecules. The final positional parameters are given in Table II. Listings of the final thermal parameters and the observed and calculated structure factors from the X-ray analysis are available.[15]

Neutron Structural Analysis. A hexagonal platelike crystal (ca. 12 mm^3), with (100), (110), (001), ($\bar{2}$21) and their Friedel pairs as boundary planes, was mounted on a hollow aluminum pin approximately along the ($\bar{2}$21) direction and used in data collection. Due to its extreme sensitivity to air, the crystal was put into an indium-sealed aluminum can under a nitrogen atmosphere before being placed in a closed-cycle refrigerator.[16] Neutron diffraction data were collected at the Brookhaven National Laboratory High-Flux Beam Reactor using a four-cycle diffractometer. The incident neutron beam was monochromated by a Ge(220) crystal, and the wavelength of 1.161 73 (8) Å was calibrated by using a standard KBr crystal.[17]

The sample was cooled at 1 K/min to a temperature of 80 K, while the 006 reflection was monitored. During cooling, it was found that the angular settings of this reflection shifted drastically[18] in the region 195–165 K. In order to redetermine the orientation matrix, an autoindexing program was used on eight centered reflections to yield a new set of unit cell parameters, in which the β angle is 7° larger than at room temperature. A least-squares fit to the $\sin^2\theta$ values of 31 reflections gave the cell parameters at 80 K as listed in Table I. A sampling of 25 extinct reflections was performed to confirm the lattice type (monoclinic) and symmetry elements (*C* centering and *c* glide plane). A θ-2θ step-scan technique was used to collect the ($\pm h,+k,+l$) quadrant of data and 119 selected reflections in the ($\pm h,+k,-l$) quadrant. For low-angle data ($2\theta < 60°$), a fixed scan width of $\Delta(2\theta) = 3.0°$ was used; for high-angle data ($60° \leq 2\theta \leq 104.5°$), the formula $\Delta(2\theta) = 0.85\ (1 + 5.18 \tan\theta)°$ was used to define the variable scan width. Each scan consisted of about 70 steps (ca. 2 s/step), with the exact step time determined by monitoring the incident beam intensity. No appreciable change in the intensities of two monitor reflections was found throughout the data collection. The intensities of a total of 6465 reflections were measured. Background corrections were based on seven steps at either extremity of the scans. After averaging, 5951 unique observations were obtained. The observed intensities were corrected for Lorentz effects. An absorption correction was applied by numerical integration over a Gaussian grid of 256 points.[19]

An initial model consisting of the 13 independent non-carbon atoms, as determined from the earlier X-ray analysis, was used to phase the neutron data. The atomic coordinates of the THF rings at 80 K, which had shifted significantly from their room-temperature positions, were determined from a series of difference-Fourier maps and refined by differential synthesis.[20] Least-squares refinements were subsequently carried out minimizing $\sum[w(F_o^2 - F_c^2)^2]$, with $w = 1/[\sigma_{count}^2(F_o^2) + (0.02F_o^2)^2]$. Blocks of about 180 parameters were varied for each cycle of refinement. All 5951 unique reflections, including reflections with $F_o^2 < 0$, were used in the least-squares refinements to give final agreement factors[12] of $R(F^2) = 0.117$ and $R_w(F^2) = 0.091$ and goodness of fit $S = \sum w(F_o^2 - |F_c|^2)^2/(n_o - n_v) = 1.11$. The relatively high *R* values probably resulted from the fact that more than half of all the reflections used were weak reflections, for which $F_o^2 < 3\sigma(F_o^2)$. However, the bond lengths in the $[FeH_6]^{4-}$ core deviate from the mean by only ±0.005 Å. Neutron scattering lengths ($10^{-12}b$ cm) used in the refinements were $b_{Fe} = 0.954$, $b_{Mg} = 0.538$, $b_{Br} = 0.677$, $b_{Cl} = 0.957\,92$, $b_C = 0.6648$, $b_O = 0.5803$, and $b_H = -0.3741$.[21] The neutron scattering lengths for the mixed-halide atoms,[22] which were allowed to vary, refined to values of 0.750 (5) and 0.760 (5) for the two independent halide sites in the molecule. These gave an average Br:Cl ratio of 2.9:1.1, substantially different from the ratio of 3.5:0.5 obtained from the X-ray analysis. We have, at present, no satisfactory explanation for this discrepancy but tend to place more reliance on the X-ray results, because of the greater differentiation between X-ray scattering of Cl vs. Br atoms and also because of agreement with the chemical analysis result.[6] The final positional parameters are given in Table II. Listings of thermal parameters and the observed and calculated squared structure factors from the neutron analysis are available.[15]

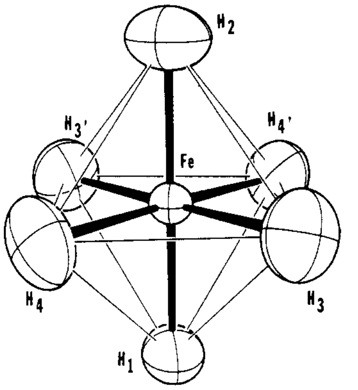

Figure 2. View of the $[FeH_6]^{4-}$ core structure of $FeH_6Mg_4X_4(THF)_8$ (neutron results).

Description of the Structure. The molecular geometry of $FeH_6Mg_4X_4(THF)_8$ is shown in Figures 1 and 2. Selected bond distances and angles, from both the X-ray and neutron structure determinations, are presented in Tables III and IV. The molecular

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(15) See paragraph at end of paper regarding supplementary material.

(16) Air Products and Chemicals Inc., DISPLEX Model CS-202.

(17) Lattice constant for KBr: $a_0 = 6.6000$ Å at 295 K.

(18) Shifts of the 006 reflection during the interval 195–165 K: $\Delta(2\theta) = 1.73°$, $\Delta\chi = 3.26°$, $\Delta\omega = 0.38°$.

(19) Coppens, P.; Leiserowitz, L.; Rabinovich, D. *Acta Crystallogr.* **1965**, *18*, 1035.

(20) The automatic refinement procedure utilized program DIFSYN: (McMullan, R. K., unpublished work).

(21) Koester, L. In "Neutron Physics"; Koester, L., Steyerl, A., Eds.; Springer-Verlag: Berlin, Heidelberg, New York, 1977; p 36.

(22) b_X, the neutron scattering length for mixed-halide atoms, is related to the Br/Cl occupancies via the expression $b_X = [(\%\ Br)(b_{Br}) + (\%\ Cl)(b_{Cl})]/100$.

Table III. Bond Distances (Å) for $FeH_6Mg_4X_4(THF)_8$[a]

	X-ray	neutron		X-ray	neutron
		Iron-Hydrogen			
Fe-H(1)	1.67 (11)	1.608 (5)	Fe-H(4)	1.74 (10)	1.610 (3)
Fe-H(2)	1.47 (11)	1.615 (5)	average		1.609 (2)
Fe-H(3)	1.90 (8)	1.604 (3)			
		Magnesium-Hydrogen			
Mg(1)-H(1)	2.00 (9)	1.988 (2)	Mg(2)-H(3′)	2.19 (9)	2.097 (4)
Mg(1)-H(3)	2.03 (9)	2.057 (4)	Mg(2)-H(4′)	2.06 (9)	2.010 (4)
Mg(1)-H(4′)	2.07 (9)	2.065 (4)	average		2.045 (18)
Mg(2)-H(2)	2.02 (9)	2.054 (2)			
		Magnesium-Bromine			
Mg(1)-Br(1)	2.526 (4)	2.479 (2)	average		2.483 (4)
Mg(2)-Br(2)	2.535 (4)	2.487 (2)			
		Magnesium-Oxygen			
Mg(1)-O(1)	2.090 (9)	2.104 (3)	Mg(2)-O(4)	2.083 (9)	2.067 (3)
Mg(1)-O(2)	2.068 (9)	2.071 (3)	average		2.077 (9)
Mg(2)-O(3)	2.068 (8)	2.064 (3)			
		THF Molecules			
O(1)-C(14)	1.47 (2)	1.463 (3)	O(3)-C(34)	1.44 (2)	1.463 (2)
O(1)-C(11)	1.47 (2)	1.449 (3)	O(3)-C(31)	1.46 (2)	1.445 (2)
C(11)-C(12)	1.54 (3)	1.513 (3)	C(31)-C(32)	1.42 (3)	1.510 (3)
C(12)-C(13)	1.47 (3)	1.525 (3)	C(32)-C(33)	1.46 (3)	1.529 (3)
C(13)-C(14)	1.53 (3)	1.525 (3)	C(33)-C(34)	1.53 (3)	1.524 (2)
O(2)-C(24)	1.47 (2)	1.436 (3)	O(4)-C(44)	1.46 (2)	1.452 (2)
O(2)-C(21)	1.42 (2)	1.447 (3)	O(4)-C(41)	1.46 (2)	1.448 (2)
C(21)-C(22)	1.46 (3)	1.523 (3)	C(41)-C(42)	1.50 (3)	1.522 (2)
C(22)-C(23)	1.39 (4)	1.533 (3)	C(42)-C(43)	1.49 (3)	1.531 (3)
C(23)-C(24)	1.46 (3)	1.522 (3)	C(43)-C(44)	1.48 (3)	1.514 (2)

[a] Primed atoms are those related by the crystallographic twofold axis.

structure consists of an octahedral $[FeH_6]^{4-}$ anion capped on four of the eight triangular faces by $[MgX(THF)_2]^+$ units. A crystallographic C_2 axis passes through Fe, H(1), and H(2). The Fe–H distances show considerable self-consistency, ranging from 1.604 (3) to 1.615 (5) Å. These neutron-derived bond lengths are, of course, much more precise than the X-ray values, which show a scatter from 1.47 (11) to 1.90 (8) Å. Nevertheless, it is noteworthy that the *average* Fe–H distance as determined by the X-ray analysis [1.69 (9) Å] is, within experimental error, equivalent to that determined by neutron diffraction [1.609 (2) Å].

Although it is difficult to tell, from the structural results alone, whether the Mg···H interactions are ionic or covalent, it is our feeling that they are largely ionic, since the average Mg–H distance in the title compound [2.045 (18) Å] is significantly longer than that in MgH_2 (1.95 Å).[23] In contrast, the Fe–H interaction [1.609 (2) Å] is clearly covalent, comparing favorably with the terminal Mn–H bond in the covalent molecule $HMn(CO)_5$ [1.601 (16) Å].[24] In addition, the ^1H NMR chemical shift mentioned earlier (τ +30.3) is more consistent with a covalent Fe–H interaction than a Mg–H interaction (which would have a ^1H chemical shift in the region τ +4.5 to +6.5).

Aside from the obvious difference in precision, the main difference between the neutron (80 K) and X-ray (room temperature) results in the fact that the orientation of one set of THF ligands (those labeled O_2, C_{21}, etc., in Figure 1) has changed abruptly upon cooling. This is most likely responsible for the shift in the β angle (~7°) from the room-temperature to the low-temperature forms. Also noticeable is the fact that, at low temperature, the THF rings show the familiar puckered conformation. In contrast, at room temperature they appear to be somewhat planar (see ring labeled O_3 in Figure 1b), indicating a disordered superposition of two or more nonplanar conformers.

Discussion

Soluble $[MH_x]^{n-}$ Systems. To our knowledge, soluble binary transition-metal hydrido anions have been reported only for the elements rhenium, technetium, iron, and copper. Prior to our own study on the $FeH_6Mg_4X_4(THF)_8$ aggregate reported here, the only example of a single-crystal investigation of a binary transition-metal hydrido anion was that of $[ReH_9]^{2-}$.[25,26] The history of the latter complex is a classic one spanning some 27 years of research. Since the initial studies of Lundell and Knowles,[27] a variety of formulations (Re^-,[27,28] $[ReH_4]^-$,[29] $[ReH_8]^{2-}$ [30]) were suggested for the "rhenide" species before a single-crystal neutron diffraction analysis finally established the complex as the tricapped-trigonal-prismatic $[ReH_9]^{2-}$ anion. As shown in the present report, we have now confirmed the existence of the isoelectronic $[FeH_6]^{4-}$ anion, an unusual octahedral hydridic species with a history strikingly similar to that of $[ReH_9]^{2-}$, having been formulated as FeH_6,[1,4] FeH_3,[2] $[FeH_4]^-$,[5] $[FeH_3]^{2-}$,[31] and finally $[FeH_6]^{4-}$ over a period of 55 years. With the exception of $[TcH_9]^{2-}$,[32] the only other soluble binary metal hydrido anions reported to date are the copper complexes $[CuH_2]^-$, $[CuH_4]^{3-}$, and $[CuH_5]^{4-}$, which are formally 14-, 18-, and 20-electron species, respectively.[33] The latter intriguing molecules have not yet been confirmed structurally and are known to decompose to some extent upon exposure to X-rays. However, powder or single-crystal neutron diffraction methods might prove applicable and are deserving of future consideration.

Insoluble Ternary Hydrides. While $[ReH_9]^{2-}$ and $[FeH_6]^{4-}$ are presently the only two soluble binary transition-metal hydrido anions that have been structurally characterized, X-ray and neutron diffraction studies on insoluble ternary metal hydrido systems have also been reported. Both stoichiometric

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Table IV. Bond Angles (deg) for $FeH_6Mg_4X_4(THF)_8$[a]

	X-ray	neutron		X-ray	neutron
		At Iron			
H(1)-Fe-H(3)	88 (4)	90.2 (1)	H(3)-Fe-H(3')	176 (4)	179.5 (3)
H(1)-Fe-H(4)	88 (4)	89.2 (1)	H(3)-Fe-H(4)	90 (4)	90.8 (2)
H(2)-Fe-H(3)	92 (4)	89.8 (1)	H(3)-Fe-H(4')	90 (4)	89.2 (2)
H(2)-Fe-H(4)	92 (4)	90.8 (1)	H(4)-Fe-H(4')	176 (4)	178.3 (3)
		At Magnesium			
H(1)-Mg(1)-H(3)	76 (4)	68.5 (2)	H(2)-Mg(2)-H(3')	71 (4)	66.3 (1)
H(1)-Mg(1)-H(4')	71 (4)	67.7 (1)	H(2)-Mg(2)-H(4')	69 (4)	68.8 (1)
H(3)-Mg(1)-H(4')	78 (4)	66.4 (1)	H(3')-Mg(2)-H(4')	75 (3)	67.7 (1)
Br(1)-Mg(1)-H(1)	109 (3)	108.4 (1)	Br(2)-Mg(2)-H(2)	106 (3)	103.9 (1)
Br(1)-Mg(1)-H(3)	90 (2)	99.6 (1)	Br(2)-Mg(2)-H(3')	174 (2)	167.1 (1)
Br(1)-Mg(1)-H(4')	168 (3)	166.0 (1)	Br(2)-Mg(2)-H(4')	99 (3)	101.5 (1)
Br(1)-Mg(1)-O(1)	97.7 (3)	98.7 (1)	Br(2)-Mg(2)-O(3)	97.7 (3)	100.3 (1)
Br(1)-Mg(1)-O(2)	96.6 (3)	94.9 (1)	Br(2)-Mg(2)-O(4)	95.8 (3)	96.7 (1)
O(1)-Mg(1)-O(2)	90.3 (4)	92.5 (1)	O(3)-Mg(2)-O(4)	93.9 (3)	92.4 (1)
O(1)-Mg(1)-H(1)	86 (3)	86.6 (1)	O(3)-Mg(2)-H(2)	94 (3)	92.4 (1)
O(1)-Mg(1)-H(3)	162 (2)	152.7 (1)	O(3)-Mg(2)-H(3')	88 (2)	88.8 (1)
O(1)-Mg(1)-H(4')	95 (3)	94.5 (1)	O(3)-Mg(2)-H(4')	159 (3)	154.1 (1)
O(2)-Mg(1)-H(1)	154 (3)	156.6 (1)	O(4)-Mg(2)-H(2)	155 (3)	157.7 (2)
O(2)-Mg(1)-H(3)	105 (2)	105.9 (1)	O(4)-Mg(2)-H(3')	86 (2)	92.0 (1)
O(2)-Mg(1)-H(4')	84 (3)	89.1 (1)	O(4)-Mg(2)-H(4')	96 (3)	98.9 (1)
		At Oxygen			
Mg(1)-O(1)-C(11)	123.1 (9)	123.3 (1)	Mg(2)-O(3)-C(31)	120.7 (9)	122.8 (1)
Mg(1)-O(1)-C(14)	117.3 (8)	119.5 (1)	Mg(2)-O(3)-C(34)	124.0 (8)	124.2 (1)
Mg(1)-O(2)-C(21)	124.4 (9)	121.5 (1)	Mg(2)-O(4)-C(41)	127.5 (9)	129.7 (1)
Mg(1)-O(2)-C(24)	124.9 (10)	126.0 (1)	Mg(2)-O(4)-C(44)	118.8 (8)	120.0 (1)
		At Hydrogen			
Fe-H(1)-Mg(1)	85 (4)	87.3 (1)	Mg(1')-H(1)-Mg(1)	170 (6)	174.5 (3)
Fe-H(2)-Mg(2)	90 (5)	84.8 (1)	Mg(2')-H(2)-Mg(2)	179 (6)	169.5 (3)
Fe-H(3)-Mg(1)	78 (3)	85.1 (2)	Mg(2')-H(3)-Mg(1)	153 (4)	167.7 (2)
Fe-H(3)-Mg(2')	74 (3)	83.6 (2)	Mg(2')-H(4)-Mg(1')	162 (5)	171.0 (2)
Fe-H(4)-Mg(1')	81 (4)	84.6 (2)			
Fe-H(4)-Mg(2')	81 (4)	86.4 (2)			
		In THF Molecules			
C(14)-O(1)-C(11)	114 (1)	108.6 (2)	C(34)-O(3)-C(31)	112 (1)	108.9 (1)
O(1)-C(11)-C(12)	100 (1)	104.6 (2)	O(3)-C(31)-C(32)	108 (2)	103.6 (1)
C(11)-C(12)-C(13)	108 (2)	101.8 (1)	C(31)-C(32)-C(33)	108 (2)	102.0 (1)
C(12)-C(13)-C(14)	105 (2)	103.1 (1)	C(32)-C(33)-C(34)	109 (2)	103.7 (1)
C(13)-C(14)-O(1)	104 (1)	106.4 (1)	C(33)-C(34)-O(3)	102 (1)	105.9 (1)
C(24)-O(2)-C(21)	110 (1)	105.0 (1)	C(44)-O(4)-C(41)	114 (1)	110.3 (1)
O(2)-C(21)-C(22)	105 (1)	104.6 (1)	O(4)-C(41)-C(42)	104 (1)	105.5 (1)
C(21)-C(22)-C(23)	109 (2)	104.1 (1)	C(41)-C(42)-C(43)	109 (2)	102.6 (1)
C(22)-C(23)-C(24)	110 (2)	104.6 (1)	C(42)-C(43)-C(44)	109 (2)	102.2 (1)
C(23)-C(24)-O(2)	105 (2)	104.4 (2)	C(43)-C(44)-O(4)	104 (1)	105.3 (1)

(e.g., Mg_2NiH_4) and nonstoichiometric (e.g., $FeTiH_x$ where $x = 0.10$, 1.04, 1.20, 1.40, 1.60, and 1.95) ternary hydrides are known, with solid-state structures having been described in terms of extended arrays of metal atoms with interstitial hydrogens occupying either tetrahedral or octahedral holes.[34] For stoichiometric species such as Mg_2NiH_4, however, descriptions based on discrete binary transition-metal hydrido anions (e.g., $[NiH_4]^{4-}$) present themselves as attractive alternatives to the previously mentioned hole-filling model. Indeed, certain members of the latter group of stoichiometric ternary hydrides and $FeH_6Mg_4X_4(THF)_8$ appear to share a number of common structural features. Consequently, for comparative purposes, we attempt to summarize below the available structural information on the stoichiometric ternary hydrides that appear most clearly related to $FeH_6Mg_4X_4(THF)_8$.

M'_xMH_6 Systems. The ternary hydrides M_2RuH_6 (M = Ca, Sr, Eu, Yb)[35-37] are particularly relevant to the present study. Powder X-ray and neutron diffraction studies on the deuterated strontium derivative Sr_2RuD_6,[35] for example, reveal a remarkably similar "local" structure to that observed in $FeH_6Mg_4X_4(THF)_8$, i.e., consisting of octahedral $[RuD_6]^{4-}$ units (Ru–D = 1.69 Å) with each face of the octahedron of deuterium atoms capped by a strontium ion. (Recall that, for $FeH_6Mg_4X_4(THF)_8$, the magnesium ions are situated over four of the eight faces of the $[FeH_6]^{4-}$ octahedron). The calcium, europium, and ytterbium derivatives are suggested to be isostructural with Sr_2RuH_6 on the basis of their X-ray powder patterns. The analogous Mg_2FeH_6 has very recently been reported,[38] with a Fe–D distance of 1.556 (5) Å from a powder neutron diffraction study. It would be interesting to see whether the related Mg_2RuH_6 compound might also be prepared, as well as $RuH_6Mg_4X_4(THF)_8$.

The osmium derivatives are also presently not known but are worthy of future consideration. Subsequent to the dis-

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covery of the binary transition-metal hydrido anion $[ReH_9]^{2-}$, it was suggested that the isoelectronic $[OsH_9]^-$ anion might also prove to be isolable.[39] On the basis of our own study on $FeH_6Mg_4X_4(THF)_8$ and the work of Moyer et al. on the M_2RuH_6 system, the possibility of a stable $[OsH_6]^{4-}$ species cannot be excluded.

Interestingly, it has been noted that ternary hydridic products (e.g., Li_4FeH_6, Li_4RuH_6, and Li_4OsH_6) could not be obtained by reaction of LiH with Fe, Ru, or Os under a hydrogen atmosphere.[40] It was suggested that steric hindrance might have been a deciding factor, at least for the first-row derivative Li_4FeH_6, in that it might not have been possible to position the required number of H ligands about the rather small central Fe atom. The structural confirmation of $[FeH_6]^{4-}$ presented here suggests that this steric argument is not valid. In fact, it is conceivable that even ligands as bulky as phenyl groups might be accommodated around a central iron atom in an octahedral arrangement, as was suggested in one of our earlier papers[6] ($[FePh_6]^{4-}$ was mentioned as a possible intermediate in the formation of $[FeH_6]^{4-}$).

In addition to the above examples, reference should be made to reports of three other hexahydrido ternary complexes, i.e., the pale yellow Li_3IrH_6,[40] the grayish black Li_4IrH_6,[41] and the colorless Li_5CuH_6.[33] Further characterization of these materials is clearly desirable. Should they indeed contain $[MH_6]^{n-}$ anionic units, it would be most interesting to see what structural changes might accompany the presence of excess electrons in the latter two substances, $[IrH_6]^{4-}$ and $[CuH_6]^{5-}$ being formally 19- and 22-electron species, respectively. The synthesis of Th_2PdH_6 has also been reported.[42]

M_xMH_5 Systems. Pentahydrido ternary complexes that are relevant to the present study include Li_4RhH_5, Ca_2RhH_5, Sr_2RhH_5, Ca_2IrH_5, Sr_2IrH_5,[35,43] and Eu_2IrH_5.[44] A single-crystal X-ray investigation of Li_4RhH_5 was attempted by Lundberg, Cromer, and Magee in 1972, but close examination of the samples eventually revealed that they were all twinned.[43] The intensity data were not good enough to locate either lithium or hydrogen atoms. More definitive results have, however, been obtained from two powder neutron diffraction studies on Sr_2IrD_5, which has very recently been shown to undergo a temperature-dependent phase transition.[35,45] The room-temperature cubic phase (space group *Fm*3*m*) is found to contain the same antifluorite structure characteristic of Sr_2RuD_6,[35] with each iridium atom exhibiting octahedral coordination symmetry (the five deuterium atoms being disordered over the six vertices of each octahedron), while in the low-temperature tetragonal phase (space group *I*4/*mmm*) a lowering in symmetry is observed, resulting in the octahedron of deuterium atoms being significantly elongated in the *c* direction. Hence, the crystal structure of Sr_2IrD_5 may be viewed as containing square-pyramidal $[IrD_5]^{4-}$ anionic units that are sixfold disordered in the high-temperature phase and twofold disordered in the low-temperature modification.[45] As in $FeH_6Mg_4X_4(THF)_8$ and Sr_2RuD_6, the alkaline-earth atoms in Sr_2IrD_5 are located over the triangular faces of each octahedron of deuterium atoms. Eu_2IrH_5 is isostructural with Sr_2IrH_5,[44] but powder neutron diffraction studies of Eu_2IrD_5 indicate no deuterium-ordering transition down to a temperature of 9 K.[46]

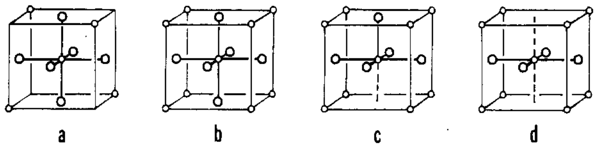

Figure 3. Immediate environment about the $[FeH_6]^{4-}$ anion, and related MH_x (x = 4–6) units in ternary metal hydrides: (a) $FeH_6Mg_4X_4(THF)_8$; (b) Sr_2RuH_6; (c) Sr_2IrH_5; (d) Mg_2NiH_4. Large circles represent H atoms, while transition-metal atoms are indicated by small circles at the center of each cube. Remaining small circles represent alkaline-earth atoms.

M_xMH_4 Systems. Finally, we mention also the tetrahydrido complexes Li_4RhH_4, $ThCoH_4$, Sr_2PdH_4, and Mg_2NiH_4. Considerable difficulties were encounteed in the single-crystal X-ray analysis of Li_4RhH_4.[43] The Rh···H distance was constrained to be 1.90 Å, and the isotropic temperature factor of the H atom was found to refine to the physically unreasonable value of -0.58 Å^2. Nevertheless, the crystal structure would seem to contain square-planar RhH_4 units. The rather long Rh···H distance of 1.90 Å [vs. the known terminal Rh–H bond length of 1.57 (8) Å],[47] as well as other structural and chemical similarities to LiH, however, led to a proposed structure involving ionic bonding between hydrogen and both the lithium and rhodium atoms. A reexamination of this system, preferably with neutrons, to more accurately define the Rh···H distance would be most useful in determining whether or not covalent interactions are in fact present. The ternary hydride $ThCoH_4$ might be suspected to contain square-planar CoH_4 units in analogy to Li_4RhH_4, but unfortunately the structure of $ThCoH_4$ (and also Sr_2PdH_4)[48] has not yet been determined.[49]

The most definitive evidence for the existence of square-planar MH_4 units is that provided by recent powder neutron diffraction experments on the high-temperature (cubic, *Fm*3*m*) phase of Mg_2NiD_4.[50] An antifluorite metal structure was found in which the four deuterium atoms were disordered over the six vertices of an octahedron centered on each nickel atom with Ni–D = 1.52 Å, in good agreement with the known terminal Ni–H bond length of 1.45 (9) Å.[47] The observed Mg···D distance of 2.30 Å clearly indicates a nonbonding interaction (Mg–H = 1.95 Å in MgH_2[23]), suggesting that Mg_2NiD_4 is probably best viewed as consisting of Mg^{2+} cations and discrete covalent $[NiD_4]^{4-}$ anions. A low-temperature powder neutron diffraction study on Mg_2NiD_4 is being pursued by Norëus and Werner.[51]

Summary. The THF-soluble product $FeH_6Mg_4X_4(THF)_8$ obtained from the reaction of PhMgBr, $FeCl_3$, and H_2 has been analyzed by single-crystal X-ray and neutron diffraction methods and established as the magnesium salt of the binary metal hydrido anion $[FeH_6]^{4-}$. In the solid state, discrete octahedral $[FeH_6]^{4-}$ units are observed with Mg^{2+} ions situated over four of the eight faces of each octahedron (resulting in a local structure quite similar to that found in a number of insoluble ternary metal hydrido systems (Figure 3). However, a direct correspendence between the binary hydrido anions and the ternary hydrides has yet to be established. It would be

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interesting to see whether $[FeH_6]^{4-}$ and other binary hydrido anions might prove useful as precursor species for the synthesis of ternary or intermetallic hydrides under mild conditions. We note, for example, that the preparation of the latter ternary hydrides currently employs a high-temperature process, while the former binary hydrido anions can, in contrast, be obtained under ambient temperatures.

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Supplementary Material Available: Listings of thermal parameters and the observed and calculated structure factors for both the X-ray and neutron analysis of $FeH_6Mg_4X_4(THF)_8$ (44 pages). Ordering information is given on any current masthead page.

Contribution from the Istituto di Chimica Generale ed Inorganica, Università di Venezia, 30100 Venice, Italy, and Christopher Ingold and Ralph Forster Laboratories, Chemistry Department, University College, London WC1H OAJ, England

Displacement of Ammonia from *cis*-Diamminebis(dimethyl sulfide)platinum(II) Perchlorate in Basic Aqueous Solution. First- and Second-Order Dependences of Rate on Hydroxide Concentration

GIULIANO ANNIBALE,[†] MASSIMILIANO BONIVENTO,[†] LUCIO CATTALINI,*[†] GIANNI MICHELON,[†] and MARTIN L. TOBE[‡]

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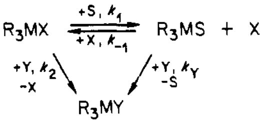
In basic aqueous solution, the ammonias in *cis*-$[Pt(Me_2S)_2(NH_3)_2]^{2+}$ are displaced by hydroxide in two consecutive stages. The first follows the rate law $-d \ln [\text{complex}]/dt = k_1° + k_a[OH^-] + k_b[OH^-]^2$, with $k_1° = 6.5 \times 10^{-5}$ s^{-1}, $k_a = 4.4 \times 10^{-3}$ M^{-1} s^{-1}, and $k_b = 4.6 \times 10^{-3}$ M^{-2} s^{-1}, all at 25.0 °C and $\mu = 0.1$. The displacement of the second ammonia follows the simpler rate law $-d \ln [\text{complex}]/dt = k_1°' + k_a'[OH^-]$, with $k_1°' = 3.6 \times 10^{-6}$ s^{-1} and $k_a' = 7.8 \times 10^{-4}$ M^{-1} s^{-1} at 50.0 °C and $\mu = 0.1$. The nature of the $[OH^-]$ dependence is discussed, and it is suggested that direct nucleophilic substitution and/or ion association provides a better explanation of the observations than base catalysis resulting from the deprotonation of the ammonia.

Introduction

The rate law for ligand-substitution reactions in four-coordinate planar d^8 metal complexes carried out under pseudo-first-order conditions (a sufficient excess of entering and leaving groups) takes the form $k_{obsd} = k_1k_Y(k_{-1}[X] + k_Y[Y])^{-1} + k_2[Y]$, which reduces to the usual form, $k_{obsd} = k_1 + k_2[Y]$ when $k_Y[Y] \gg k_{-1}[X]$. This is consistent with the mechanism in which associative displacement of S by Y in the reaction $R_3MX + Y = R_3MY + X$ is paralleled by associative solvolysis and competition for the solvento intermediate, R_3MS, which must be labile and only present in very low concentration if the relationship is to hold.[1]



Frequently, the contribution from the solvolytic path is small, and studies of the reaction with relatively low concentrations of weak nucleophiles in order to obtain precise values for k_1 may be complicated by the reversibility of the solvolytic pathway (i.e., $k_Y[Y] \gg k_{-1}[X]$).[2] A common way of avoiding this problem is to study the solvolytic reaction alone, but this is generally reversible. When the leaving group, Y, is basic, it might be possible to force the solvolysis to completion by adding an acid, care being taken to ensure that the solvolytic process was not subject to acid catalysis.[3] If the solvent is protonic, use can be made of the fact that a lyate ion (deprotonated neutral ligand) generally forms much stronger complexes than the ligand itself. A much used system is the aquo–hydroxo acid–base pair in aqueous solution (or methanol–methoxide in methanol). Coupled with the fact that hydroxide and methoxide have been shown, in the past, to be poor nucleophiles,[4] it has frequently been a practice to add excess hydroxide to an aqueous or methanolic solution in order to obtain a precise measurement of k_1.

As part of our studies of the ways in which the charge of the substrate affected its reactivity and nucleophilic discrimination properties, we recently examined the reactions of *cis*-$[Pt(Me_2S)_2(NH_3)_2]^{2+}$ with anionic nucleophiles.[5] The reactions occurred in two stages, stopping at the neutral product. The first step was always the displacement of ammonia while the second depended upon the nature (mainly the trans effect) of the entering group. With NH_3 as the leaving group it was convenient to determine k_1 in the presence of perchloric acid, but as a cross-check, we also looked at the solvolysis in the presence of excess hydroxide. Thus

$$cis\text{-}[Pt(Me_2S)_2(NH_3)_2]^{2+} + H_2O \rightarrow cis\text{-}[Pt(Me_2S)_2(NH_3)(H_2O)]^{2+} + NH_3$$

$$cis\text{-}[Pt(Me_2S)_2(NH_3)(H_2O)]^{2+} + NH_3 \xrightarrow{+H^+,\ \text{fast}}$$

$$cis\text{-}[Pt(Me_2S)_2(NH_3)(H_2O)]^{2+} + NH_4^+ \xrightarrow{+OH^-,\ \text{fast}} cis\text{-}[Pt(Me_2S)_2(NH_3)(OH)]^{+} + NH_3 + H_2O$$

The values of k_1 obtained with excess acid or with low concentrations (<0.001 M) of hydroxide were in good agreement,

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[†] Università di Venezia.
[‡] University College, London.

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