Table IV. Infrared Absorptions,[a] cm^{-1}

	BH	CO	Fingerprint (1300–900)
$(CH_3)_3NBH_2N(CH_3)_2(CH_2)_2CO_2C_2H_5^+PF_6^-$	2460 m, 2424 vw, 2380 vw, 2340 w	1720 s	1320 s, 1240 m, 1210 s, 1170 s multiplet, 1105 w, 1050 w, 1020 m, 1005 m, 970 m, 940–950 w doublet
$(CH_3)_3NBH_2N(CH_3)_2(CH_2)_3CO_2C_2H_5^+PF_6^-$	2460 m, 2380 vw, 2340 w	1720 s	1370 m, 1240 s, 1190 s, 1105 vw, 1070 vw, 1030 w, 1000 m, 980 m
$(CH_3)_3NBH_2O_2CCH_2N(CH_3)_3^+PF_6^-$	2410 m, 2300 vw	1690 s	1300 m, 1240 w, 1230 w, 1190 vw, 1170 s, 1125 w, 1110 vw, 1020 w, 985 m, 930 m
$(CH_3)_3NBH_2O_2C(CH_2)_2N(CH_3)_3^+PF_6^-$	2440 m, 2380 vw, 2310 vw	1675 s	1290 vw, 1265 w, 1255 m, 1195 s, 1175 m, 1125 vw, 1110 w, 995 m, 980 w, 950 vw, 930 m
$(CH_3)_3NBH_2O_2C(CH_2)_3N(CH_3)_3^+PF_6^-$	2380 m, 2290 w	1680 s	1320 s, 1250 m, 1225 w, 1190 m, 1160 s, 1140 w, 1120 vw, 1010 vw, 1020 vw doublet, 1005 w, 980 w, 965 w
$(CH_3)_3NBH_2O_2C(CH_2)_4N(CH_3)_3^+PF_6^-$	2410 m, 2300 w	1675 s	1285 w, 1240 w, 1195 w, 1160 s, 1120 vw, 1105 vw, 990 w, 970 w

[a] Run on a Perkin-Elmer 237B spectrophotometer neat or in mineral oil mulls. Abbreviations: s, strong; m, medium; w weak; vw, very weak.

Table V

ω-Dimethylamino acid ester	Starting material[a]	Bp, °C (pressure, mm)	Yield, %
$(CH_3)_2NCH_2CH_2CO_2C_2H_5$	$BrCH_2CH_2CO_2C_2H_5$	71 (21); lit.[5] 56–57 (12)	76
$(CH_3)_2N(CH_2)_3CO_2C_2H_5$	$Cl(CH_2)_3CO_2C_2H_5$	77–79 (14); lit.[6] 78–79 (18)	33
$(CH_3)_2N(CH_2)_4CO_2C_2H_5$	$Cl(CH_2)_4CO_2C_2H_5$	76–77 (6)	43

[a] Commercial material: Aldrich Chemical Co.

Betaine-Derived Cation, $(CH_3)_3NBH_2O_2C(CH_2)_2N(CH_3)_3^+PF_6^-$. A mixture of 327 mg (2.50 mmol) of betaine, $(CH_3)_3N(CH_2)_2CO_2$, and 20 ml of a chloroform solution of 2.59 mmol of $(CH_3)_3NBH_2I$ (from 3.31 mg of iodine added as a solid slowly to 188 mg of trimethylamine–borane in 20 ml of chloroform) was stirred 2 days. The insoluble iodide salt product (643 mg) was collected by filtration, dissolved in water, and metathesized to the title hexafluorophosphate salt with addition of excess solid ammonium hexafluorophosphate. The hexafluorophosphate salt was recrystallized from hot water before analysis. No more product was found in the chloroform reaction solution.

Other borane cations derived from betaines were soluble in chloroform as iodide salts. Workup involved solvent evaporation followed by dissolution in water and metathesis.

Amino Acid Ester Derived Cation, $(CH_3)_3NBH_2N(CH_3)_2(CH_2)_2CO_2C_2H_5^+PF_6^-$. A solution of 3.66 g (18.4 mmol) of $(CH_3)_3NBH_2I$ in 7 ml of methylene chloride was treated with 3.5 ml of ethyl ω-dimethylaminopropionate and allowed to stand overnight. Volatiles were removed under vacuum, and the resulting syrup was nearly crystalline on standing 1 day; it was dissolved in acidified water and metathesized to the title salt with ammonium hexafluorophosphate, giving a precipitate which slowly crystallized. The yield was 3.13 g (47%). A 1.0-g sample recrystallized from 100 ml of water (acidified with 4 drops of 6 M HCl) at 80 °C yielded 0.318 g of purified product. Salts of the higher acid esters did not crystallize from water, ethanol, methylene chloride, or acetonitrile and were purified by water washing and prolonged (8 h) drying under high vacuum.

Acknowledgment. Support of this research by a grant (GP 14902) from the National Science Foundation is gratefully acknowledged.

Registry No. $C_2H_5O_2C(CH_2)_2N(CH_3)_2BH_2N(CH_3)_3^+PF_6^-$, 58815-52-4; $C_2H_5O_2C(CH_2)_3N(CH_3)_2BH_2N(CH_3)_3^+PF_6^-$, 58815-54-6; $C_2H_5O_2C(CH_2)_4N(CH_3)_2BH_2N(CH_3)_3^+PF_6^-$, 58815-56-8; $(CH_3)_3NCH_2CO_2BH_2N(CH_3)_3^+PF_6^-$, 58815-59-1; $(CH_3)_3N(CH_2)_2CO_2BH_2N(CH_3)_3^+PF_6^-$, 58815-62-6; $(CH_3)_3N(CH_2)_3CO_2BH_2N(CH_3)_3^+PF_6^-$, 58815-65-9; $(CH_3)_3N(CH_2)_4CO_2BH_2N(CH_3)_3^+PF_6^-$, 58815-68-2; $(CH_3)_2NCH_2CH_2CO_2C_2H_5$, 20120-21-2; $(CH_3)_2N(CH_2)_3CO_2C_2H_5$, 22041-23-2; $(CH_3)_2N(CH_2)_4CO_2C_2H_5$, 58735-52-7; betaine, 6458-06-6; $(CH_3)_3NBH_2I$, 25741-81-5.

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Spectroscopic and Magnetic Studies of a Mixed-Valence Iron Fluoride, $Fe_2F_5 \cdot 7H_2O$[1a]

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In 1958 Brauer and Eichner[2] reported that the reaction of metallic iron with hot, concentrated hydrofluoric acid produced a yellow mixed-valence iron fluoride, $Fe_2F_5 \cdot 7H_2O$, and that this material could be dehydrated to a red trihydrate and a blue-gray anhydrous complex. Since the color changes observed upon dehydration suggest variation in the extent of iron–iron interactions, these systems may prove to be valuable probes for studying interactions in mixed-valence complexes. Although the dehydration of this material has been shown to be much more complex than originally proposed,[1,3,4] the existence of the heptahydrate has been repeatedly confirmed. In this note we report a variety of physical evidence bearing on the structure of the heptahydrate.

Experimental Section

The complex was prepared as described by Brauer and Eichner[2] and crystallized from solutions of iron in concentrated HF upon standing at room temperature. Anal. Calcd for $Fe_2F_5(H_2O)_7$: Fe, 33.56; F, 28.59; H_2O, 37.88. Found: Fe, 33.56; F, 28.54; H_2O, 37.89.

Magnetic susceptibilities were measured by the Faraday method. The balance was calibrated using $HgCo(NCS)_4$.[5] Mössbauer spectra

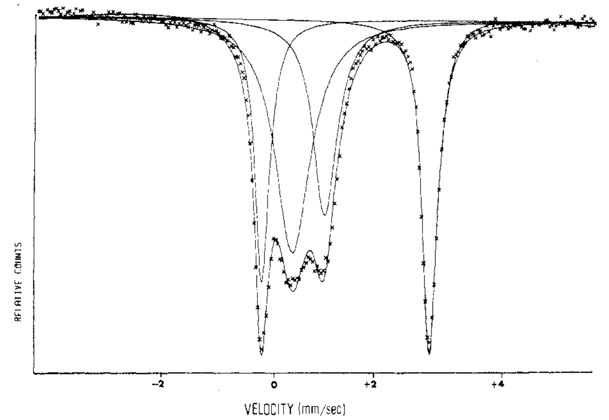

Figure 1. Room-temperature Mössbauer spectrum of $Fe_2F_5 \cdot 7H_2O$.

were obtained on a spectrometer which has previously been described,[6] using a 10-mCi $^{57}Co/Pt$ source obtained from New England Nuclear Corp. Isomer shifts are, in all cases, reported relative to sodium nitroprusside. For both systems, variable temperatures, from 20 K to room temperature, were attained using an Air Products Co. Displex CS-202 closed-cycle helium refrigerator. Analyses were performed by Dornis u. Kolbe, Mulheim, West Germany.

Results and Discussion

The pale yellow color observed for the heptahydrate suggests that it is probably a class I mixed-valence complex,[7] and our experimental data are, we believe, sufficient to identify the structure as consisting of discrete $Fe(H_2O)_6^{2+}$ and $FeF_5(H_2O)^{2-}$ ions. First, over the entire temperature range the susceptibility exhibits Curie–Weiss law behavior, with a molar susceptibility, corrected for diamagnetism,[8] given by

$$\chi_M = \frac{7.94 \pm 0.01}{T + 5.0 \pm 0.3}\ \text{cgsu}$$

Both the near-zero value of the Weiss constant and the magnitude of the susceptibility itself suggest that there is no interaction of Fe^{2+} and Fe^{3+}, consistent with class I behavior. In a material containing two distinct paramagnetic ions, susceptibilities should be additive in the absence of cooperative effects. Thus, for a species AB, the magnetic moment, μ_{AB}, should be given by

$$\mu_{AB} = (\mu_A{}^2 + \mu_B{}^2)^{1/2}$$

The magnetic moment expected for $Fe_2F_5 \cdot 7H_2O$ may then be predicted from the moments of appropriate model compounds. Bearing in mind the proposed structure, suitable model compounds for which (room-temperature) data are available are $FeSO_4 \cdot 7H_2O$, with $\mu_{eff} = 5.22\ \mu_B$,[9] and $(NH_4)_2FeCl_5(H_2O)$, with $\mu_{eff} = 5.94\ \mu_B$.[9] The expected magnetic moment for $Fe_2F_5 \cdot 7H_2O$ is then 7.91 μ_B, in good agreement with the experimental value of 7.97 μ_B. This result may be contrasted to a somewhat similar material, $LiFe_2F_6$, in which exchange interactions are known to occur[10] and which has a room-temperature moment of 6.19 μ_B.

The most compelling evidence for the proposed structure comes from Mössbauer spectra, which have the form shown in Figure 1. The outer peaks are assigned to high-spin Fe^{2+}, with $\delta = 1.51$ mm/s and $\Delta E = 3.31$ mm/s. The inner peaks are assigned to high-spin Fe^{3+}, with $\delta = 0.70$ mm/s and $\Delta E = 0.59$ mm/s.[11] The observation of quadrupole splitting for Fe^{3+} is consistent with our proposed formulation. Moreover, the observed parameters are nearly identical with those reported for model compounds; viz., for $[Fe(H_2O)_6]SO_4 \cdot H_2O$; $\delta = 1.52$ mm/s and $\Delta E = 3.22$ mm/s;[12] for $K_2[FeF_5(H_2O)]$; $\delta = 0.68$ mm/s and $\Delta E = 0.60$ mm/s.[13]

Electronic spectra further confirm that $Fe_2F_5 \cdot 7H_2O$ contains the $Fe(H_2O)_6^{2+}$ ion. The diffuse-reflectance spectrum of $Fe_2F_5 \cdot 7H_2O$ (Figure 2) is virtually identical with that of the $Fe(H_2O)_6^{2+}$ ion in ferrous ammonium sulfate, obtained under identical conditions. (The Fe^{3+} ligand field absorptions are presumably too weak to be seen.) The absence of further absorptions in the visible region, in contrast to the class II dihydrate, supports the class I formulation. If fluoride were coordinated to Fe^{2+} in the heptahydrate, the spectrum would be expected to be red-shifted, as is indeed observed in $Fe_2F_5 \cdot 2H_2O$.

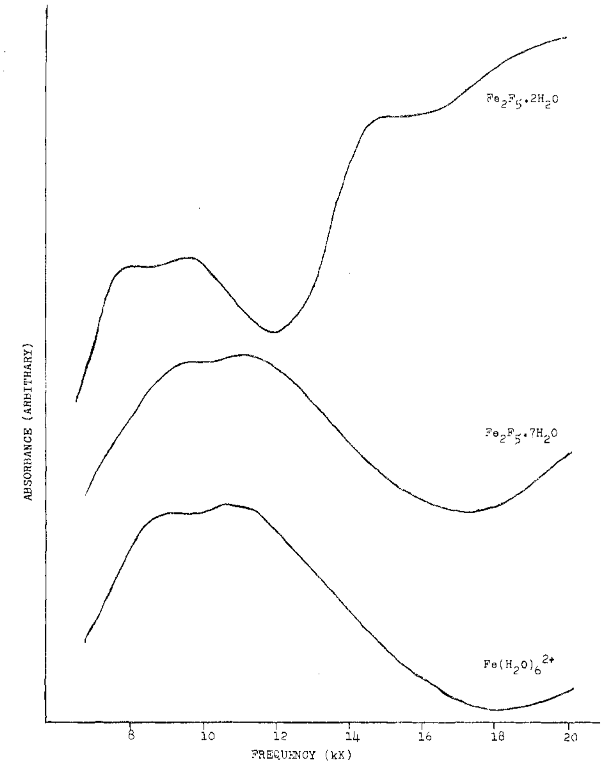

Figure 2. Diffuse-reflectance spectra of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$, $Fe_2F_5 \cdot 7H_2O$, and $Fe_2F_5 \cdot 2H_2O$.

This evidence all supports the formulation of the heptahydrate as a class I mixed-valence system and as containing the hexaaquoiron(II) and pentafluoroaquoferrate(III) ions. The thermal behavior of this material and the more complex nature of the dehydration products will be communicated at a later date.

Note Added in Proof. Sakai and Tominaga[14] have arrived at the same conclusion regarding the structure of this material using ^{19}F broad-line NMR and x-ray powder patterns of this and related complexes.

Acknowledgment. We thank the Office of Naval Research for support of this work. Funds for the construction of the Faraday balance were provided by the Research Corp.

Registry No. $Fe_2F_5 \cdot 7H_2O$, 57033-88-2; $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$, 59034-06-9; $Fe_2F_5 \cdot 2H_2O$, 56941-11-8.

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Stereodynamics of $L_2CuB_3H_8$. Rate of $B_3H_8^-$ Rearrangement as a Function of L

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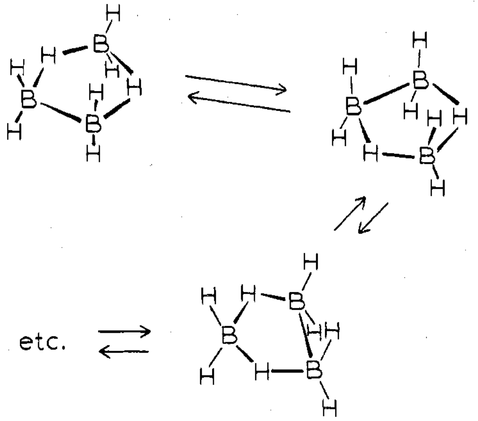
In previous papers, we reported changes in the ^1H DNMR spectra of various triborohydride ion ($B_3H_8^-$) derivatives which may be attributed to two fundamentally different rate processes.[2,3] One phenomenon involves quadrupole-induced ^{10}B and ^{11}B spin relaxation which becomes more efficient with increasing solution viscosity and/or decreasing temperature and leads to eventual decoupling of ^{10}B and ^{11}B from ^1H and a *simplification* of the ^1H DNMR spectra.[2,3] The other phenomenon involves a slowing of $B_3H_8^-$ "pseudorotation" or rearrangement on the DNMR time scale and a separation of the ^1H DNMR spectrum into several signals corresponding to protons in different environments in an essentially static $B_3H_8^-$ system.[2,3] For example, the ^1H DNMR spectra of TlB_3H_8 and $(CH_3)_4NB_3H_8$ show a typical ten-line multiplet for the $B_3H_8^-$ protons at 33 °C which collapses to a relatively sharp *singlet* at −137 °C consistent with efficient quadrupole-induced boron spin relaxation. The observation of a singlet resonance at −137 °C reveals all $B_3H_8^-$ protons to be equivalent due most likely to *rapid* $B_3H_8^-$ rearrangement on the DNMR time scale (eq 1). In contrast, the $B_3H_8^-$ proton resonance of $[(C_6H_5)_3P]_2CuB_3H_8$ shows spectral sharpening from room temperature to about −40 °C (i.e., quadrupole-induced boron spin relaxation) but at lower temperatures (−40 to −90 °C) broadens and separates into several ^1H resonances consistent with slowing $B_3H_8^-$ rearrangement on the DNMR time scale [eq 2; L = $(C_6H_5)_3P$].



(1)

Thus, it appears that the upper limit to the barrier to $B_3H_8^-$ scrambling in the "free" $B_3H_8^-$ anion [i.e., TlB_3H_8 and $(CH_3)_4NB_3H_8$] is below 6.5 kcal/mol consistent with recent theoretical calculations.[4] It is also apparent that complexation of $B_3H_8^-$ in $[(C_6H_5)_3P]_2CuB_3H_8$ provides an effective "brake" on $B_3H_8^-$ scrambling and this rate process slows significantly relative to TlB_3H_8 and $(CH_3)_4NB_3H_8$.[2] In contrast to these systems, the ^{11}B NMR spectrum of the $(OC)_4MB_3H_8^-$ ion (M = Cr, Mo, W) reveals a *static* B_3H_8 moiety at room temperature.[5]

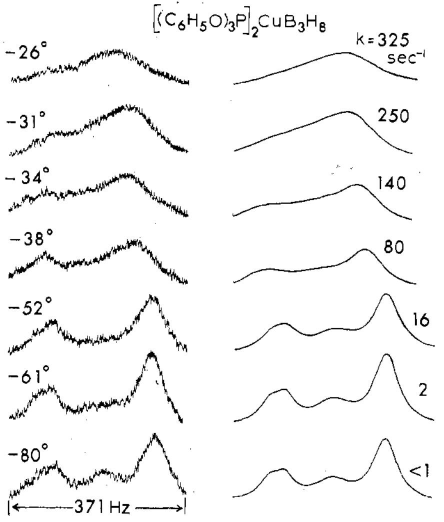
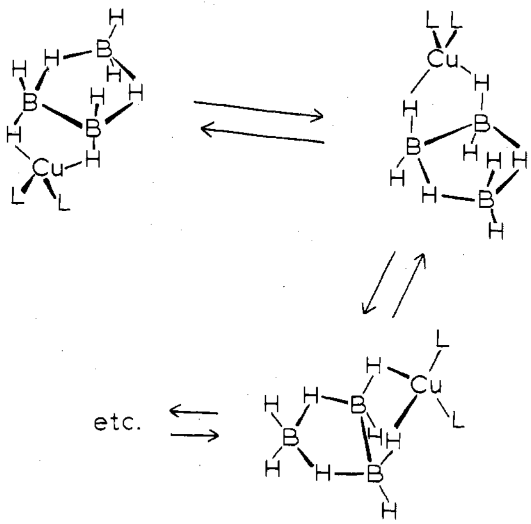


Figure 1. The ^1H DNMR spectra (60 MHz) of $[(C_6H_5O)_3P]_2CuB_3H_8$ in 50% $CDCl_3$/50% CD_2Cl_2 (v/v) and theoretical spectra calculated as a function of the rate of $B_3H_8^-$ scrambling (*k* is the first-order rate constant for disappearance of a proton from any site on the $B_3H_8^-$ moiety).



(2)

In light of these observations, it was intriguing to consider what effect variation of the electron-donating properties of L (eq 2) would have on the rate of $B_3H_8^-$ rearrangement in $L_2CuB_3H_8$.

Examination of the ^1H DNMR spectrum (60 MHz) of the $B_3H_8^-$ protons of $[(C_6H_5O)_3P]_2CuB_3H_8$ in 50% $CDCl_3$/50% CD_2Cl_2 (v/v) at room temperature showed a broad resonance which first sharpened at lower temperatures followed by asymmetric broadening and separation into several resonances by −80 °C (Figure 1). The spectrum of $[(C_6H_5O)_3P]_2CuB_3H_8$ at −80 °C (Figure 1) is consistent with slow $B_3H_8^-$ rearrangement [eq 2; L = $(C_6H_5O)_3P$] on the DNMR time scale. A complete ^1H DNMR line shape analysis for the $B_3H_8^-$ group of $[(C_6H_5O)_3P]_2CuB_3H_8$ was performed in exactly the same manner as reported previously for $[(C_6H_5)_3P]_2CuB_3H_8$.[2] Chemical shift values, widths at half-height, and relative peak areas are compiled in Table I. The kinetic model used to simulate the exchange-broadened spectra, e.g., −26 to −61 °C, is the random exchange system employed previously for