relative to SCN^-, the anion becomes less solvated on transfer from water to the new solvent; negative values show that the anion becomes more solvated, relative to the behavior of SCN^-, on transfer from water. The behavior shown in Table IX is in full agreement with our qualitative discussion of the effects of solvation on the chemistry of anions in protic and in dipolar aprotic solvents.[3,6–8] The numbers in Table IX put this discussion on a quantitative basis.

The range of P values is enormous; we show here values corresponding to a range of 23 kcal mole^{-1}, but even bigger differences are expected. The protic–dipolar aprotic solvent effects considered here could influence rates and equilibrium constants by 10^{18} upon solvent transfer. HMPT appears to exhibit the largest spread of P values, but salts are less soluble in this solvent so that DMF and DMAC are of greater practical value.

We are examining some extrathermodynamic methods[21,32,33] for the evaluation of log ${}^{W}\gamma_{Ag^+}^{S}$. It may be possible to estimate solvent activity coefficients for individual anions. This will give us numbers on which theories of protic–dipolar aprotic solvent effects can be based.

Acknowledgment. Helpful discussions with Professors R. T. Iwamoto and I. M. Kolthoff are gratefully acknowledged.

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The Structure of Iron(III) in Aqueous Solution

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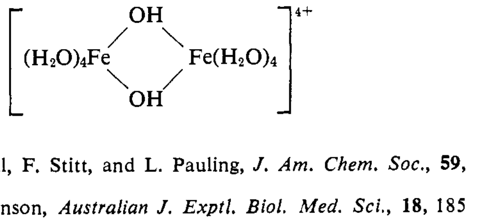
Abstract: [Fe^{III}HEDTA], the uncharged complex of ferric ion and the trianion of N-hydroxyethylethylenediaminetriacetic acid, reacts with equimolar amounts of NaOH to form a monomeric and dimeric species. The wine red dimer has two unpaired electrons. Magnetic and spectral data are used to describe the monomer–dimer equilibrium and possible structure of the dimer. Spin coupling *via* Fe–O–Fe bridging is proposed. The aquo dimer and polymer produced from the partial neutralization of ferric perchlorate solutions with bicarbonate were also investigated. Iron(III) in these materials is in an intermediate paramagnetic state, probably two unpaired spins per iron. Spin coupling *via* the bridging shown in structure B is proposed. Spin reduction in iron(III) pyrophosphate was also studied in a preliminary way. In a final section the possible role of dimeric structures in the spin reduction of iron(III) hemoproteins and porphyrin systems is discussed.

The structure of Fe(III) complexes in aqueous solution is a subject of considerable interest. One reason for the interest is the fact that many Fe(III) complexes with weak-field ligands exhibit solution magnetic moments significantly below the spin-only value of 5.92 BM expected for $S = {}^5/_2$ systems. For example, Pascal observed low moments for ammoniacal ferric pyrophosphate solutions;[2a] these moments increase on addition of HCl to the solutions. Later, Bose noted low magnetic moments for aqueous solutions of Fe(III) nitrate, chloride, and sulfate.[2b] Magnetic moments in the range expected for $S = {}^5/_2$ were obtained upon addition of the corresponding acids (nitric, hydrochloric, sulfuric). Bose suggested that the discrepancies were due to hydrolysis of the Fe(III) salts, but no specific analysis was given. A more comprehensive study yielded similar results.[3]

Coryell, Stitt, and Pauling found that the magnetic moment of ferrihemoglobin is pH dependent, decreasing to 4.47 BM on formation of ferrihemoglobin hydroxide.[4] This was interpreted as mononuclear Fe(III) with an intermediate spin of ${}^3/_2$, plus a large orbital contribution (the spin-only moment for $S = {}^3/_2$ is 3.88 BM). A similar study by Rawlinson showed that hematin in alkaline solution has $\mu_{eff} = 3.5$ BM.[5]

A relatively recent study is that of Mulay and Selwood, who observed that the magnetic susceptibilities of aqueous solutions of $Fe(ClO_4)_3 \cdot xH_2O$ decrease with increasing pH.[6] They attributed these results to the formation of a diamagnetic dimer of probable structure



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[1] (a) Columbia University. (b) California Institute of Technology. (c) Contribution No. 3441.

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A very promising system for the study of Fe(III) structure in aqueous solution is suggested from the work of Gustafson and Martell.[7] These workers have studied hydrolysis and dimerization in the Fe(III)–HEDTA system (HEDTA is N-hydroxyethylethylenediaminetriacetic acid). After 4 moles of NaOH is added to Fe(III) and HEDTA in equimolar concentration, their analysis indicates that a dimer is the predominant species in the Fe(III) concentration range studied (0.008 to 0.08 *M*). The reaction can be formulated as in eq 1–4B.

$$\mathrm{FeCl_3 + HEDTA + 3NaOH \longrightarrow \underset{monomer(0)}{[FeHEDTA]} + 3NaCl} \qquad (1)$$

$$\mathrm{[FeHEDTA] + NaOH \longrightarrow Na^+ + \underset{monomer}{[FeHEDTA]^-}} \qquad (2)$$

$$\mathrm{2[FeHEDTA]^- \rightleftarrows \underset{dimer}{[Fe_2HEDTA_2]^{2-}}} \qquad (3)$$

$$\mathrm{[FeHEDTA]^- + OH^- \longrightarrow \underset{monomer(-2)}{[FeHEDTA]^{2-}}} \qquad (4A)$$

$$\mathrm{[Fe_2HEDTA_2]^{2-} + 2OH^- \longrightarrow 2[FeHEDTA]^{2-}} \qquad (4B)$$

We have chosen to investigate the spectral and magnetic properties of the Fe(III)–HEDTA system in detail, with a view toward establishing a structural model for certain of the Fe(III) dimers in aqueous solution. In this paper are reported the results of magnetic susceptibility studies, potentiometric titration curves, nmr, and electronic spectral studies for the Fe(III)–HEDTA system in aqueous solution. The preparation and structural characterization of crystalline salts of dimeric complexes in the Fe(III)–HEDTA and Fe(III)–EDTA systems are presented. We also report results and suggest new structural interpretations for other related Fe(III) systems.

Experimental Procedures

Reagents. Chelate solutions were directly prepared from Fisher Certified Reagent $FeCl_3 \cdot 6H_2O$ (97.3% assay by iodometry), equivalent amounts of HEDTA (Matheson Coleman and Bell; 98.7 ± 0.3% assay by potentiometric titration with standard NaOH), and suitable amounts of standard NaOH ($\cong$0.2 *M*). High local concentrations of base must be avoided to prevent precipitation of ferric hydroxide. For certain studies, a stock solution of [FeHEDTA] was prepared by stirring a slurry of equivalent amounts of HEDTA and freshly prepared and carefully washed ferric hydroxide. A clear brown solution results after a few minutes stirring at 80–90°. Extended heating was required (and subsequent ligand oxidation occurred) if the ferric hydroxide was washed with hot water. An assay of Fe(III) in chelate solutions and isolated solids was determined by iodometry[8] using 0.100 *N* sodium thiosulfate (Fisher Certified Reagent) periodically checked against KIO_3 (99.9%, Baker Analyzed). Amend $K_4P_2O_7 \cdot 3H_2O$ was used as received.

Preparation of Compounds. $[C_2N_2H_{10}][(FeHEDTA)_2O] \cdot 6H_2O$. A slurry of 0.30 mole each of N-hydroxyethylethylenediaminetriacetic acid and salt-free $Fe(OH)_3$ in 400 ml of water was stirred at 80–90° for several minutes. To the resulting brown solution of [FeHEDTA], sufficient ethylenediamine was added to raise the pH to 5.0. Although the desired material can be crystallized directly from aqueous solution, water–dimethylformamide (DMF) mixtures are easier to work with because of the large water solubility of $[C_2N_2H_{10}][(FeHEDTA)_2O] \cdot 6H_2O$. The red solid was recrystallized several times from water–DMF mixtures. Red, hexagonal-shaped crystals were obtained.

Anal. Calcd for $C_{22}H_{52}N_6O_{21}Fe_2$: C, 31.15; H, 6.18; N, 9.91; mol wt, 848. Found: C, 31.94; H, 6.36; N, 10.13; mol wt, 842 from unit cell volume and density, 850 by iodometry. Water loss (dried at 25° (3 mm) over Drierite for 3 days): Calcd: 12.7%. Found: 12.5%. Density: 1.584 g cm^{-3} by flotation method at 25°. Magnetic moment: 2.82 BM at 25°.

$Na_4[(FeEDTA)_2O] \cdot 12H_2O$. A slurry of salt-free $Fe(OH)_3$ (0.1 mole) in 400 ml of water was allowed to react with the disodium salt of ethylenediaminetetraacetic acid (0.1 mole) for several minutes at 80–90°. The resulting dark red solution had a pH of about 9.0. A crystalline red solid was readily obtained from water–DMF mixtures.

Anal. Calcd for $C_{20}H_{48}N_4O_{29}Fe_2Na_4$: C, 23.73; H, 4.78; N, 5.53; mol wt, 1012. Found: C, 23.70; H, 4.11; N, 5.46; mol wt, 1030 by iodometry. Water loss (dried at 100° (2 mm) over Drierite for 24 hr): Calcd: 21.4%. Found: 21.3%. Magnetic moment: 3.04 BM at 25°.

$K_4[(FeEDTA)_2O] \cdot 8H_2O$. This material was prepared as above, except that the dipotassium salt of EDTA was used.

Anal. Calcd for $C_{20}H_{40}N_4O_{25}Fe_2K_4$: C, 23.91; H, 4.01; N, 5.58; mol wt, 1005. Found C, 23.99; H, 3.90; N, 5.51; mol wt, 1008 by iodometry. Water loss (dried at 100° (2 mm) over Drierite for 24 hr): Calcd: 14.3%. Found: 16.7%. Magnetic moment: 2.87 BM at 25°.

Other Salts of $[(FeHEDTA)_2O]^{2-}$. A variety of salts of this dimeric anion were prepared by adding suitable bases to aqueous solutions of the [FeHEDTA] monomer until the pH was raised to 5–6. In this manner, the addition of CaO, $Ba(OH)_2$, and NaOH yielded the respective Ca^{2+}, Ba^{2+}, and Na^+ salts. These materials were obtained as glassy red solids. Attempts to prepare crystals were not successful.

Similarly, the $(n\text{-}Bu_4N)^+$ salt was obtained by neutralizing an aqueous solution of the [FeHEDTA] monomer with $(n\text{-}Bu_4N)OH$. On evaporation of the solvent, $(n\text{-}Bu_4N)[(FeHEDTA)_2O]$ was obtained as a red glassy solid.

Magnetic Measurements. Gouy Method. All samples were equilibrated with air that was scrubbed with dilute caustic to remove CO_2 and achieve water saturation. Measurements were made at 25°. Diamagnetic corrections were made by subtracting the weight change of a solution containing the ligand, a suitable amount of NaOH, and 3 equiv of chloride ion (except when the chloride-free [FeHEDTA] stock solution was used as a source of chelate). The susceptibilities do not vary significantly over a field strength of 3800–7500 gauss. The sample tubes were calibrated with $Cs_2[CoCl_4]$ solutions and $Hg[CoCl_4]$ for measurements on solution and solid samples, respectively, as described previously.[9]

Nmr Method. The procedure followed was essentially the one developed by Evans.[10] Susceptibilities were calculated from the difference between the resonance of the water in the 5-mm o.d. nmr tube containing chelate, etc., and the water in a 2.5-mm capillary containing everything but ferric ion (*e.g.*, the internal reference). Susceptibilities thus obtained agreed well with the Gouy determinations, *provided* the pH of the solutions in the nmr tube and reference capillary was not different.

Results and Discussion

Studies at a Single Fe(III) Concentration. Up to 2 moles of NaOH per mole of iron was included in aqueous solutions 0.03 *M* in both $FeCl_3$ and the trisodium salt of HEDTA. Here, the resulting solution was 0.03 *M* in chelate and 0.09 *M* in NaCl. Another set of measurements was made with added KCl (0.36 *M*). A plot of χ_m (the magnetic susceptibility per mole of iron with diamagnetic corrections) *vs.* pH is shown in Figure 1. With no added base (or one point not shown where an equimolar amount of HCl was added), χ_m is about 14.8×10^{-3} (equivalent to 6.0 BM), typical for ferric iron in its high spin state. However, χ_m falls linearly with added base. After reaching a minimum value of about 5.7×10^{-3} at 1 mole of base per mole of chelate, χ_m then rises linearly with additional base. The "normal" χ_m of about 14.8×10^{-3} is reached with another equivalent or base. The initial and final solutions are yellow; solutions with an intermediate amount of base are red.

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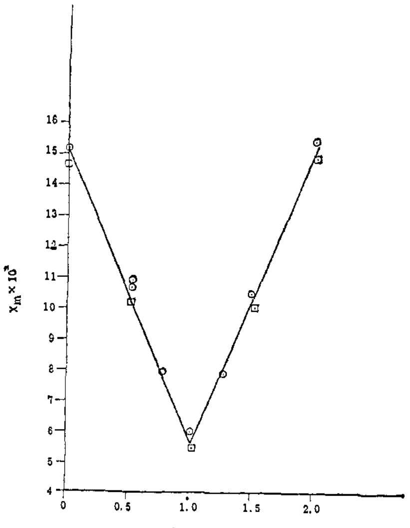

Figure 1. Dependence of $\chi_m \times 10^3$ (average molar susceptibility of Fe(III)) on the equivalents of added NaOH per mole of [FeHEDTA]: ⊙, [FeHEDTA] = 0.03 *M*, [NaCl] = 0.09 *M*; ⊡, same plus [KCl] = 0.36 *M*.

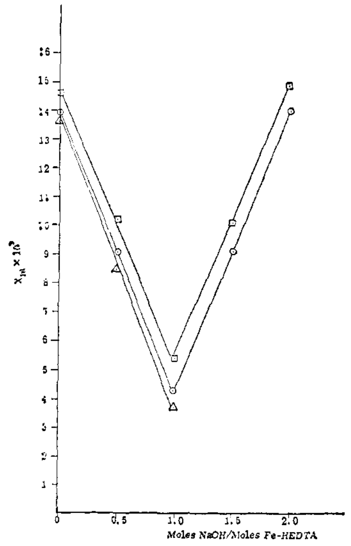

Figure 3. Concentration dependency of $\chi_m \times 10^3$ on equivalents of added NaOH per mole of [FeHEDTA]: ⊡, [FeHEDTA] = 0.03 *M*, [NaCl] = 0.09 *M*, [KCl] = 0.36 *M*; ⊙, [FeHEDTA] = 0.069 *M*; △, [FeHEDTA] = 0.138 *M*. Note: these runs are comparable since KCl has little effect at the chelate concentration range studied (Figure 1 and Table II).

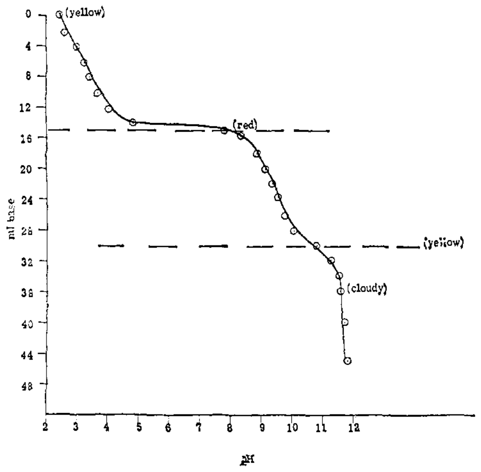

Figure 2. Potentiometric titration of 1.5 mmoles of [FeHEDTA] with 0.100 *N* NaOH.

The potentiometric titration curve for this system is shown in Figure 2. A marked pH inflection occurs as the number of moles of added base approaches the number of moles of chelate. Since the trisodium salt of the ligand was used, these results correspond to Gustafson and Martell's observations when 4 equiv of base was added to equimolar quantities of ferric ion and free HEDTA.[7]

In addition to the measurements described above, magnetic susceptibility measurements were obtained with excess ligand: 0.03 *M* in Fe(III) and 0.05 *M* in Na_3HEDTA. χ_m values with excess ligand have the same pH dependency as those obtained with equimolar Fe(III) and Na_3HEDTA.

The visible spectra for this system have also been studied. The yellow color of acidic Fe(III) solutions arises from end absorption at about 425 mμ. Typical molar extinction coefficients at this wavelength are 50 and 32 l. mole^{-1} cm^{-1} for $[FeEDTA]^-$ and $FeOH^{2+}$, respectively.[11] When 1 mole of base is added to [FeHEDTA], the red color corresponds to an absorption peak at about 480 mμ. When either 0.50 or 1.50 moles of NaOH is added per mole of chelate, the peak height at 480 mμ is one-half that for 1.0 mole of NaOH per mole of chelate. For both the optical and magnetic studies, the concentration of chelate was 0.03 *M*.

Effect of Concentration. The dimerization is described by Gustafson and Martell[7] as follows.

$$2(\text{monomer}) \underset{}{\overset{K}{\rightleftarrows}} \text{dimer} \qquad (5)$$

$$K = \frac{[\text{dimer}]}{(\text{total}[Fe^{+3}] - 2[\text{dimer}])^2} = 10^{2.38} \qquad (6)$$

Since the percentage dimerization obviously is concentration dependent, the effect of chelate concentration was studied next. The general type of behavior previously described holds for other concentrations, except for the important observation that the value of the minimum magnetic susceptibility decreases with increasing concentration of Fe(III). These results are shown in Figure 3. The variation of the minimum magnetic susceptibility with concentration is shown in Figure 4. At chelate concentrations below 0.01 *M*, the susceptibility rises sharply toward the value for high-spin Fe(III) (14.8 × 10^{-3}). Above 0.1 *M* the susceptibility per iron approaches that measured for the crystalline ethylenediammonium $(enH_2)^{2+}$ salt of $[(FeHEDTA)_2O]^{2-}$ (1.75 × 10^{-3}). Thus, the magnetic moment of the *dimeric species* in solution is approximately 2.9 BM, which suggests two unpaired electrons (*S* = 1). For comparison, the solid monomer (yellow powder) has a magnetic moment of 5.79 BM (χ_{monomer} = 14.3 × 10^{-3}), typical for high-spin Fe(III).

The magnetic susceptibility data and the equilibrium data of Gustafson and Martell are compatible. The curve in Figure 5 shows the concentration dependency of dimer formation calculated from the equilibrium data. The points represented by small squares were determined from the magnetic measurements by assign-

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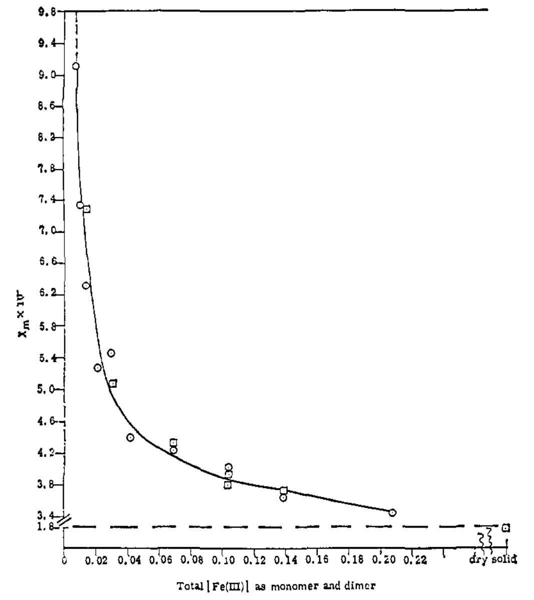


Figure 4. Dependency of minimum $\chi_m \times 10^3$ on total [Fe(III)] as monomer and dimer: ⊡, Gouy method; ⊙, nmr technique; pH 6 ± 1, [KCl] = 1.0 *M* (25°).

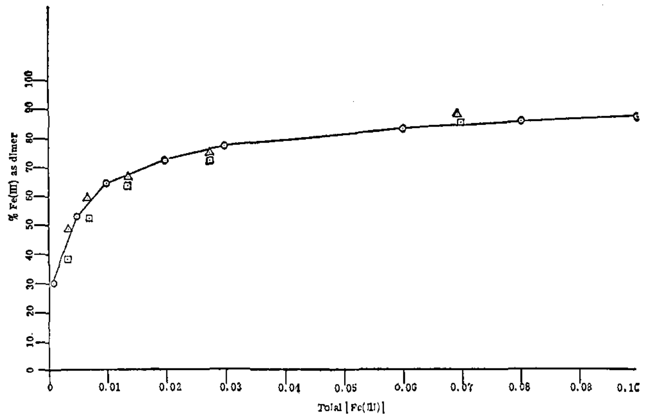


Figure 5. Percentage of Fe(III) as dimer against the total [Fe(III)], *M*, as monomer and dimer: ⊡, calculated from χ_m data; ⊙, calculated from *K*(equil) of Gustafson and Martell;[7] ⚠, spectrophotometric (25°, 1.0 *M* KCl).

ing the values $\chi_{\text{monomer}} = 14.3 \times 10^{-3}$ and $\chi_{\text{dimer}} = 3.50 \times 10^{-3}$. Optical measurements yield the same type of plot. A plot of the optical density at 540 mμ (monomer absorption zero here) *vs.* dimer concentration calculated from the equilibrium and susceptibility data is shown in Figure 6. Typical Beer's law behavior is evident. From this plot, the average slope leads to the relationship given in eq 7. Dimer concentrations

$$[\text{dimer}] = \frac{\text{optical density}}{121} \qquad (7)$$

determined in this manner yielded the triangular points in Figure 5. These points are consistent with the other measurements.

Thermodynamics of the Dimerization. The temperature dependence of the dimerization was measured by an optical technique. Absorption curves of a 0.00345 *M* Na[FeHEDTA] solution (1.0 *M* in KCl) in a 10-cm jacketed cell are shown in Figure 7 for 20, 30, 40, and 50 ± 0.1°. From the optical density at 540 mμ and the relationship to dimer concentration derived from Figure 6, a log *K* *vs.* 1/*T* plot was constructed (Figure 8). The values of the slope and intercept yield $\Delta H° = -7.1$ kcal mole^{-1} and $\Delta S° = -13.0$ eu. These values may be compared with the thermodynamic parameters for the analogous cyclohexanediaminetetraacetic acid (CDTA) and ethylenediaminetetraacetic acid (EDTA) systems studied by Gustafson and Martell[7] (see Table I).

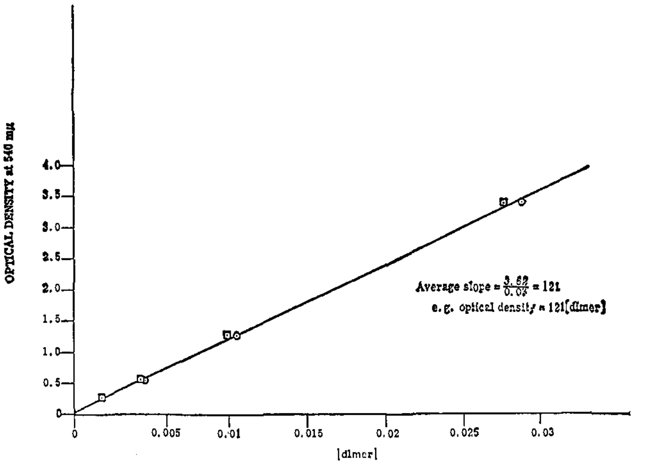


Figure 6. Optical density at 540 mμ *vs.* dimer concentration (*M*): ⊙, [dimer] calculated from data of Gustafson and Martell;[7] ⊡, calculated from χ_m data; all measurements normalized for a 1.0-cm cell.

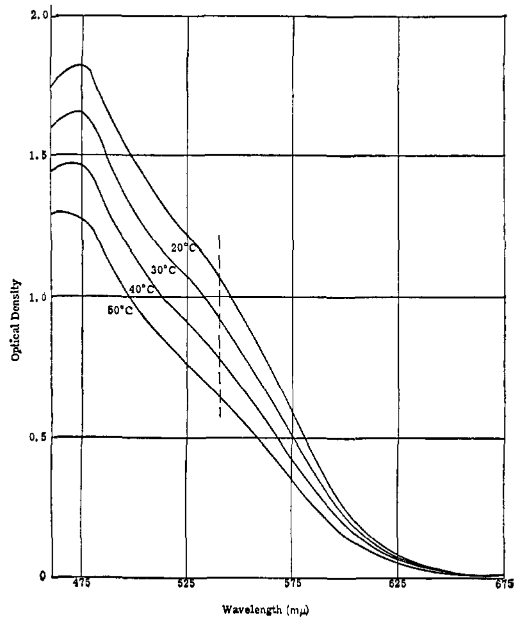


Figure 7. Temperature dependence of absorption curve: 0.00345 *M* Na[FeHEDTA], 1.0 *M* KCl (10-cm cell).

Table I. Thermodynamic Parameters for the Dimerization of Fe$^{\text{III}}$L Complexes[a]

Ligand	$\Delta H°$, kcal mole^{-1}	$\Delta S°$, eu
EDTA	-15^a	-36^a
HEDTA	-7.1	-13.0
CDTA	-3.9^a	-9^a

[a] From ref 7.

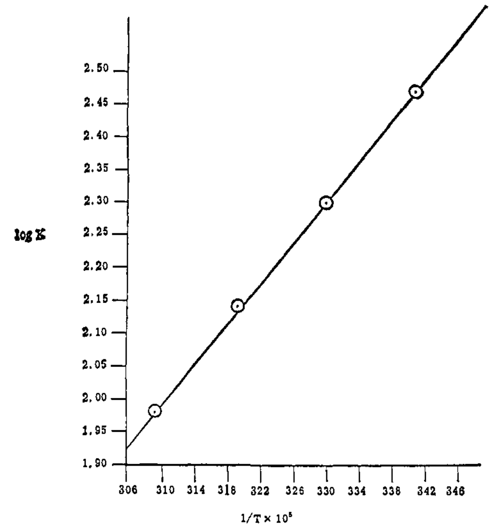


Figure 8. *K vs.* $1/T$ plot for 0.00345 *M* Na[FeHEDTA] in 1.0 *M* KCl; slope = 1660; intercept = −3.05.

Dependency of Dimerization on Ionic Strength. Solutions of the sodium salt of $[FeHEDTA]^-$ with and without KCl (1.0 *M*) were prepared. From the data set out in Table II, it is apparent that the dimerization is not significantly assisted by added KCl when the chelate concentration is greater than about 0.05 *M*. This dimerization is much less sensitive to ionic strength variations than the aquo dimer of Fe(III) studied by Milburn and Vosburgh.[12] This is not unexpected in view of the larger charge (4+) on the aquo dimer.

Table II. Effect of Added KCl on the Dimerization

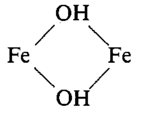
Na[FeHEDTA], *M*	No KCl		1.0 *M* KCl	
	χ (perFe)	% Fe as dimer	χ (perFe)	% Fe as dimer
0.069	4.25×10^{-3}	80.4	4.2×10^{-3}	80.2
0.0276	...	...	5.32×10^{-3}	71.6
0.0138	7.3×10^{-3}	55.7	6.33×10^{-3}	63.5
0.0069	9.16×10^{-3}	40.9	7.74×10^{-3}	52.3
0.00345	11.1×10^{-3}	25.5	9.60×10^{-3}	37.5

A related subject is the solvent dependency of the dimerization. The alkali metal salts of the dimeric dianion are not significantly soluble in nonaqueous solvents. However, the tetra-*n*-butylammonium salt is quite soluble in methanol, DMSO, acetonitrile, etc. Originally, it was hoped that infrared spectra in nonaqueous solvents might shed light on the structure of the dimer. Surprisingly, solutions of $[n\text{-}Bu_4N]_2[Fe_2HEDTA_2]$ in polar organic solvents all show the characteristic color of the high-spin *monomer*. However, when water is added to these solutions, the red color of the low-spin dimer reappears, but at an intensity lower than the theoretical level for total conversion. The molar susceptibility χ_m is 11.4×10^{-3} for a 0.03 *M* solution of the quaternary ammonium salt in anhydrous MeOH. Only 29% of the Fe(III) is dimeric (assuming the same equilibrium species exist in nonaqueous systems). However, it is interesting that the characteristic red color of the dimer is absent.

Structure of the $[Fe_2HEDTA_2]^{2-}$ Dimer. Iron complexes (and those of other metals) commonly are thought to dimerize *via* oxo or hydroxo bridging, *e.g.*

Fe–O–Fe

A



B

Demonstration of dimerization is usually provided by the potentiometric titration technique of Sillén.[13] Unfortunately, this method cannot differentiate between dimers of structures A and B. For the specific case of $[FeHEDTA]^-$, the data only indicate that (a) each chelate parts with a proton and forms a polymerization product and (b) the polymerization does not significantly proceed beyond a dimeric structure. A further complication is that either or both of the ligand hydroxyethyl groups can in principle participate in structure B. The structural issue was partially resolved by reference to the infrared properties of oxo bridges, as described by Cotton and Wing[14] and by Hewkin and Griffith.[15] Although comprehensive data are not available yet, the antisymmetric stretching mode of the M–O–M systems seems to give a characteristic strong absorption at about 850 cm^{-1}. X-Ray studies have shown that $[Cl_5Ru\text{–}O\text{–}RuCl_5]^{4-}$ and $[Cl_5Re\text{–}O\text{–}ReCl_5]^{4-}$ have the structural feature A. These compounds absorb at 888 and 855 cm^{-1}, respectively. Related to these complexes are $[Br_5Ru\text{–}O\text{–}RuBr_5]^{4-}$ and $[Cl_5Os\text{–}O\text{–}OsCl_5]^{4-}$, which absorb at 860 and 840 cm^{-1}, respectively. In the molybdenum series, Cotton and co-workers[16] have assigned the 860-cm^{-1} band to the linear Mo–O–Mo bridge. Also, Cousins and Green have reported an infrared band at 850 cm^{-1} for μ-oxo-bis(dioxo)cyclopentadienylmolybdenum(VI).[17] In the iron series, Earnshaw and Lewis assigned an oxo bridge to the iron–phenanthroline dimer $[(phen)_2Fe\text{–}O\text{–}Fe(phen)_2]Cl_3$ which absorbs at 850 cm^{-1}.[18] Similar phenanthroline- and bipyridyliron dimers studied by Anderegg were assigned a structural unit A on the basis of an infrared band at 850 cm^{-1}.[19]

We have prepared a number of solid samples from solutions containing the $[Fe_2HEDTA_2]^{2-}$ dimeric complex, as salts of the cations Na^+, Ba^{2+}, Ca^{2+}, and $(enH_2)^{+2}$. The first three materials are glassy, red solids but the $(enH_2)^{2+}$ salt can be obtained as red crystals. Infrared spectra in KBr pellets show that a strong peak at about 830 cm^{-1} is present in all four samples. The relative intensity of this peak is not diminished after the salts are exchanged with D_2O. Neither the chelating agent nor the monomer(0) absorbs strongly in this region. Therefore, a structural unit A and formula $[(FeHEDTA)_2O]^{2-}$ is proposed

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(18) A. Earnshaw and J. Lewis, *ibid.*, 396 (1961).

(19) G. Anderegg, *Helv. Chim. Acta*, **45**, 1643 (1962).

for the dimeric anion in the solid materials.[20] The optical properties of the crystalline $(enH_2)[(FeHEDTA)_2O]\cdot 6H_2O$ complex closely parallel those of aqueous solutions containing the dimeric anion; thus we suggest that $[(FeHEDTA)_2O]^{2-}$ is *also* the correct structural formulation for the solution species.

The infrared spectra are consistent with but do not rigorously prove the absence of uncoordinated carboxylate anion in the dimer. The relevant observation is that the antisymmetric CO_2^- stretching band at about 1630 cm^{-1} is fairly sharp.[21] Therefore, our best formulation of the structure of the dimer includes five coordination positions of each Fe(III) occupied by HEDTA, with the sixth position functioning in the Fe–O–Fe bridge unit.

We have also obtained red, crystalline materials from alkaline, aqueous Fe(III)–EDTA solutions.[22] On the basis of analytical and molecular weight results and the presence of an infrared band at 830 cm^{-1} assignable to the Fe–O–Fe structural unit, these materials are formulated as $Na_4[(FeEDTA)_2O]\cdot 12H_2O$ and $K_4[(FeEDTA)_2O]\cdot 8H_2O$. As polycrystalline samples at 25°, $(enH_2)[(FeHEDTA)_2O]\cdot 8H_2O$ and the EDTA dimers all have magnetic moments in the 2.8–3.0-BM range. The observed near-invariance of the magnetic moments with Na^+, K^+, and $(enH_2)^{2+}$ variously as cations suggests that both $[(FeHEDTA)_2O]^{2-}$ and $[(FeEDTA)_2O]^{4-}$ have true $S = 1$ ground states.[23] Further information on this point should come from studies now in progress of the temperature dependence of the magnetic susceptibilities.

Aquo Dimer of Fe(III). Mulay and Selwood have studied[6] the hydrolytic polymerization of 0.04 *M* ferric perchlorate solutions which contain 3 *M* $NaClO_4$. As the pH is increased from about 0.5 to 2.5 with $NaHCO_3$, the μ_{eff} per Fe drops from 5.9 to about 3.8 BM. The decreasing magnetic moments were attributed to increasing amounts of a *diamagnetic* dimer.

It is not reasonable to expect all ten d electrons to be paired in an Fe(III) dimer involving only weak-field ligands. If an Fe–O–Fe unit is involved, we would expect an $S = 1$ dimer from our work on the Fe(III)–HEDTA system. If the bridge is that shown in structure **B**, an even higher spin state could result.[15]

We suggest that Selwood and Mulay's magnetic data[6] are more compatible with the equilibrium shown in eq 8. The most detailed investigation of equilibrium 8 is that of Milburn and Vosburgh.[12] Taking their value of *K*, we have plotted two μ_{eff} *vs.* pH curves, one assuming $S = 0$ for the dimer and the other assuming $S = 2$. These two calculated curves are compared with the Mulay and Selwood magnetic moment *vs.* pH experimental data in Figure 9. It is clear that the experimental data are more compatible with the calculated curve for a paramagnetic dimer.

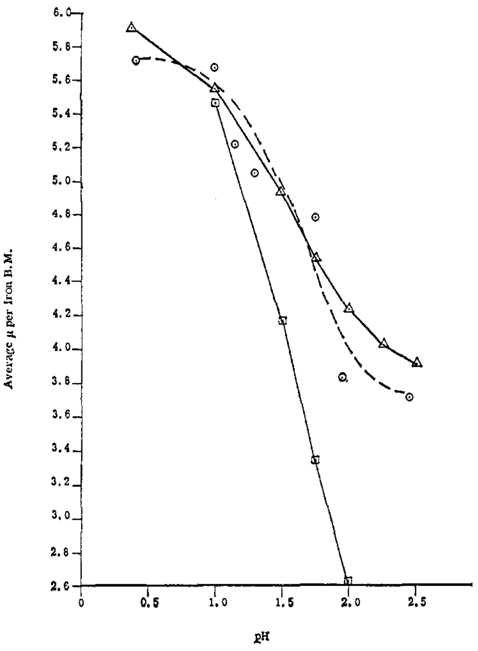
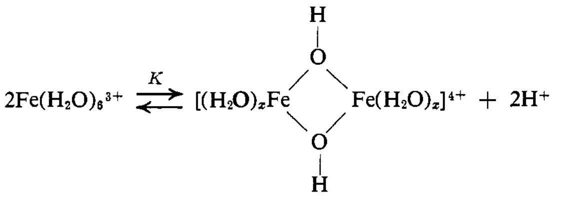


Figure 9. Average magnetic moment per Fe(III) *vs.* pH; 0.04 *M* $Fe(ClO_4)_3$ with pH adjusted with HCO_3^-: ⊙, experimental data of Mulay and Selwood; △, calculated from equilibrium data of Milburn and Vosburgh[12] for μ = 3.7 BM; ⊡, same for μ = 0.0 BM.



$$2\mathrm{Fe(H_2O)_6}^{3+} \overset{K}{\rightleftarrows} \left[(\mathrm{H_2O})_x\mathrm{Fe}\begin{matrix}\mathrm{H}\\ |\\ \mathrm{O}\\ \diagup\quad\diagdown\\ \diagdown\quad\diagup\\ \mathrm{O}\\ |\\ \mathrm{H}\end{matrix}\mathrm{Fe(H_2O)}_x\right]^{4+} + 2\mathrm{H}^+ \qquad (8)$$

$S = {}^5/_2$ monomer paramagnetic dimer

In view of the possible complications due to high polymer formation,[24] it is difficult to assign an exact spin value to the paramagnetic aquo dimer. There is strong evidence from recent work,[25] however, that the aquo dimer is in a spin state higher than the $S = 1$ observed for $[(FeHEDTA)_2O]^{2-}$. We take this as evidence that a different bridging unit, leading to less spin coupling, is present in the aquo dimer. Specifically, the data suggest two hydroxo bridges (structural unit B) for the aquo dimer. Consistent with this view, our infrared studies on various solid materials obtained from the aquo dimer solutions and reprecipitated from D_2O show no absorption of the type (850-cm^{-1} region) assignable to an Fe–O–Fe bridge.

Broersma has studied[26] the nmr relaxation in ferric perchlorate systems at various pH's. He observed that the unhydrolyzed Fe^{3+} and monomeric $(FeOH)^{2+}$

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[20] Equilibrium mixtures in which 70 and >90% of the iron is present as dimer were allowed to react with excess KF (moles of KF/mole of Fe ≅ 5) at room temperature for several hours. The invariance of pH indicates the absence of labile hydroxyl groups. A single crystal X-ray analysis of $(enH_2)[(FeHEDTA)_2O]\cdot 6H_2O$ is presently being performed in collaboration with S. J. Lippard. Preliminary results indicate an approximately linear Fe–O–Fe bridging unit and two pentadentate HEDTA ligands.

[21] M. L. Morris and D. H. Busch, *J. Am. Chem. Soc.*, **78**, 5178 (1956).

[22] Kachanova and Purmal have studied the Fe(III)–EDTA system in acidic and alkaline media.[11] The end absorption which gives rise to a yellow solution is replaced by a peak at 480 mμ in alkaline media. Also, the spin–lattice relaxation time of the solvent (H_2O) protons is pH dependent. However, the authors were not aware that the chelate dimerizes and the magnetic susceptibility is pH dependent. (We have observed that μ_{eff} per iron varies with pH in the Fe(III)–CDTA and Fe(III)–EDTA systems.) Therefore, their structural assignments are based on incorrect interpretations of the titration and nmr data.

[23] Mössbauer spectra of samples containing $[(FeHEDTA)_2O]^{2-}$ and $[(FeEDTA)_2O]^{4-}$ at 300 and 77°K are identical. This supports the interpretation that the low moments represent authentic $S = 1$ states. We thank Professor R. H. Herber of Rutgers University for these measurements.

[24] T. G. Spiro, S. E. Allerton, J. Renner, A. Terzis, R. Bils, and P. Saltman, *J. Am. Chem. Soc.*, **88**, 2717 (1966).

[25] T. G. Spiro, private communication.

[26] S. Broersma, *J. Chem. Phys.*, **26**, 1405 (1957).

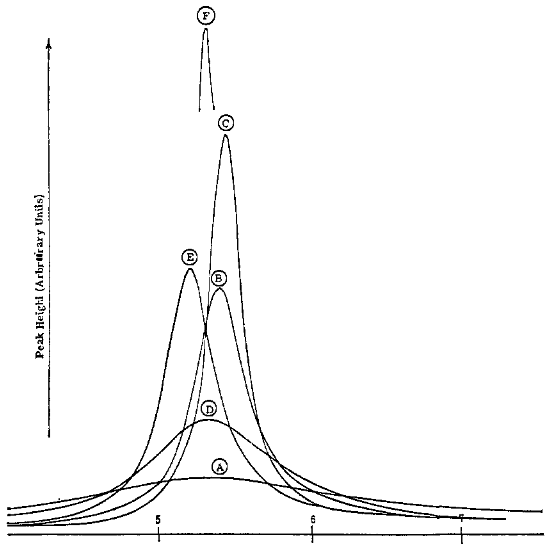


Figure 10. Dependency of H_2O resonance on $[FeCl_3]$ and added HCO_3^- (molar concentrations): (A) $[FeCl_3] = 0.03$, $[HCl] = 0.004$; (B) $[FeCl_3] = 0.03$, $[HCO_3^-] = 0.06$; (C) $[FeCl_3] = 0.03$, $[HCO_3^-] = 0.075$; (D) $[FeCl_3] = 0.0075$, $[HCl] = 0.001$; (E) $[FeCl_3] = 0.003$, $[HCl = 0.0004]$; (F) $[FeCl_3] = 0.0015$, $[HCl] = 0.0002$; all runs with 1.0 *M* KCl (25°).

hydrolyzed species in a ferric perchlorate solution theoretically account for the *entire* observed nmr relaxation rate. On this basis, he supported the concept of a diamagnetic dimer advanced by Mulay and Selwood.[6] The relative population of the various species was calculated from the equilibria measured by Milburn and Vosburgh[12] and Mulay and Selwood.[6]

Broersma's studies may also be interpreted in terms of a paramagnetic dimer that does not efficiently contribute to spin-lattice relaxation of the water protons.[27] When the relaxation time of the electron spin is short with respect to the time for diffusion past the nucleus to be relaxed (in this case the water protons), that nucleus is not efficiently relaxed. For example, the actual moments of Fe(II), Co(II), and Ni(II) are two and one-half to six times larger than the effective moments measured by nmr relaxation, whereas those for Fe(III), Cr(III), and Mn(II) show no such discrepancy.

We have made independent nmr studies of hydrolytic polymerization in a $FeCl_3$–KCl system. The line broadening of the water resonance is systematically dependent upon the concentration of Fe(III), as shown in Figure 10. Curves A, D, E, and F illustrate the effect on the water resonance as the concentration of Fe(III) is decreased respectively to 25, 10, and 5% of the original value of 0.03 *M*. For all runs, the KCl concentration was kept at 1.0 *M*. Assuming that a diamagnetic compound forms when the pH is increased, 42% of the high-spin Fe(III) (5.9 BM) must be present when μ_{eff} falls from 5.9 to about 3.8 BM. Curves B and C result when the original Fe(III) solution is made 0.06 and 0.075 *M* in $NaHCO_3$. By inspection, the broadening of the water resonance corresponds to respective Fe(III) levels only about 10–15 and 6–8% of the initial Fe(III) concentration. The effective magnetic moments per iron in these two solutions are 4.16 and 3.84 BM, respectively. Clearly, a diamagnetic dimer requires more Fe(III) of $S = {}^5/_2$ than appears to be present. Since in the Fe(III)–HEDTA system the dimer causes considerably less broadening of the H_2O resonance, the above results are qualitatively consistent with approximately 90% of the iron as dimeric ($\mu \cong 3.4$ BM per iron) and about 10% as the monomer ($\mu \cong 5.9$ BM).

The previous discussion assumed for the sake of convenience that the hydrolysis of iron salts leads to dimers, *i.e.*, the degree of polymerization is two. It should be noted that the arguments against the existence of diamagnetic species are independent of the degree of polymerization. Namely, the inferences from magnetic susceptibility data, from line broadening of the H_2O resonance by paramagnetic ions, and from the presence of only weak field ligands stand by themselves.

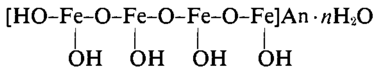
A different approach to the hydrolysis of ferric salts has suggested the formation of a tetramer. Zvyagintsev and Lopatto have partially hydrolyzed ferric nitrate solutions with Na_2CO_3.[28] A reddish brown powder was precipitated with organic solvents from the resulting brown solutions. Analysis indicates the molar ratio of iron to nitrogen is 4:1. The molecular weight determined by cryoscopy (and consistent with the composition data) is 485.

The following stoichiometry was suggested.

$$8Fe(NO_3)_3 + 11NaCO_3 + 5H_2O \longrightarrow 2\,[Fe_4O_3(OH)_5]NO_3 + 22NaNO_3 + 11CO_2 \quad (9)$$

However, the possibility of high polymers as observed by Spiro and co-workers[24] makes the cryoscopy data dubious.

Addition of NaF and subsequent titration with HCl demonstrated the production of 5 moles of NaOH per mole of tetramer. This was interpreted as evidence that the tetramer contained five hydroxyl groups in the coordination sphere. The tetramer was represented as



$$[\underset{\displaystyle OH}{HO\text{–}\underset{|}{Fe}}\text{–}O\text{–}\underset{\underset{\displaystyle OH}{|}}{Fe}\text{–}O\text{–}\underset{\underset{\displaystyle OH}{|}}{Fe}\text{–}O\text{–}\underset{\underset{\displaystyle OH}{|}}{Fe}]An\cdot nH_2O$$

where An = monoanion.

Aqueous solutions where An = NO_3^-, ClO_4^-, etc., give a pH of 2.8, approximately the same as that for the aquo dimer of Mulay and Selwood (~2.0).[6] These results are difficult to interpret since neither were magnetic susceptibility data taken nor was ionic strength specified. Milburn and Vosburgh found that the "dimerization constant" is very sensitive to the ionic strength.[12]

The most recent study of the hydrolytic polymerization of ferric ion was conducted by Spiro and co-workers.[24] These investigators have isolated a discrete polymer (mol wt = 1.4×10^5) by gel filtration. For 0.3 *M* ferric nitrate solutions, polymer formation was observed after 0.50 to 0.75 equiv of bicarbonate was added per mole of iron. Polymer formation was monitored by measuring Schlieren patterns after ultracentrifugation. These results are compatible with the magnetic susceptibility measurements of hydrolyzed solutions 3.0 *M* in $NaClO_4$ and originally 0.197 *M* in $Fe(ClO_4)_3$ (Figure 11). The susceptibility per mole of iron is normal for high-spin ferric ion when excess $HClO_4$ is present. When the excess $HClO_4$ is neutral-

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[27] J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p 209.

[28] O. E. Zvyagintsev and Yu. S. Lopatto, *Russ. J. Inorg. Chem.*, **6**, 439 (1961).

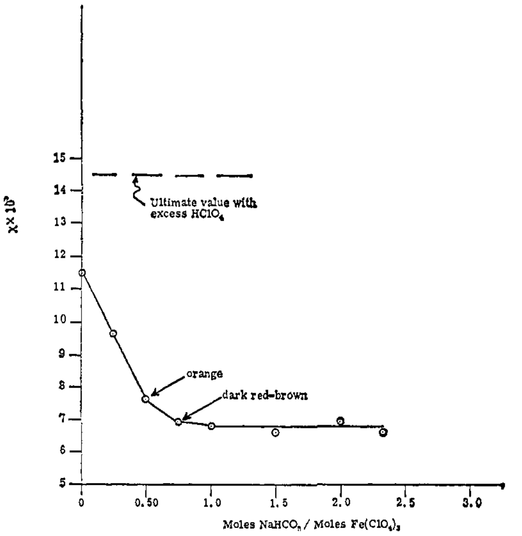

Figure 11. Dependency of $\chi_m \times 10^3$ on the molar ratio of added HCO_3^- to initial $Fe(ClO_4)_3$: $[Fe(ClO_4)_3] = 0.197$ *M*, $[NaClO_4] = 3.0$ *M* (25°).

ized the susceptibility is considerably lower (this parallels the behavior of the nitrate, sulfate, and chloride previously investigated by Bose[2b]). After 0.50 to 0.75 equiv of bicarbonate has been added, the color changes from yellow-orange to deep red-brown and the susceptibility levels out at about 6.9×10^{-3} (about 3.9 BM per iron). Further addition of bicarbonate (up to 2.5 equiv) results in a more intense color, but no further change in susceptibility. Measurements were made on clear solutions, although precipitation was observed in the dark solutions after a dew days.

It is probable that a paramagnetic dimer or perhaps a higher aggregate forms before polymerization occurs. It is also likely that structural feature B, which causes some spin pairing, is incorporated into the polymer. Since the moment per iron in hydrous ferric oxide is about 3.5 BM,[29] presumably the B structural unit remains intact when the water-soluble polymer is converted into water-insoluble ferric hydroxide.

Aasa, Malmström, Saltman, and Vänngård have studied the pH dependency of the magnetic and related properties of Fe(III)–fructose complexes.[30] At pH ≅7, the susceptibility, nmr broadening of the solvent (H_2O) protons, and esr amplitude (77°K) all go through minima. This behavior parallels that of the aquo dimer and Fe(III)–HEDTA systems, except for the esr behavior which was not determined at low temperatures for the latter two systems. The fact that the esr amplitude actually goes to zero suggests that high-spin Fe(III) is not present at that pH. At higher pH values, the above measurable quantities increase as in the Fe(III)–HEDTA system. Of course, in the absence of suitable complexing agents, the formation of ferric hydroxide makes such measurements impossible. The graphical results in the Fe(III)–fructose system show the minimum magnetic moment to be in the 3.5–4.0-BM (per iron) range. Aasa and co-workers stated that it is "tempting to suggest that all iron is converted into a dimer with somewhat other magnetic properties than those of the dimer formed in the absence of fructose" (the latter referring to the diamagnetic aquo dimer postulated by Mulay and Selwood).

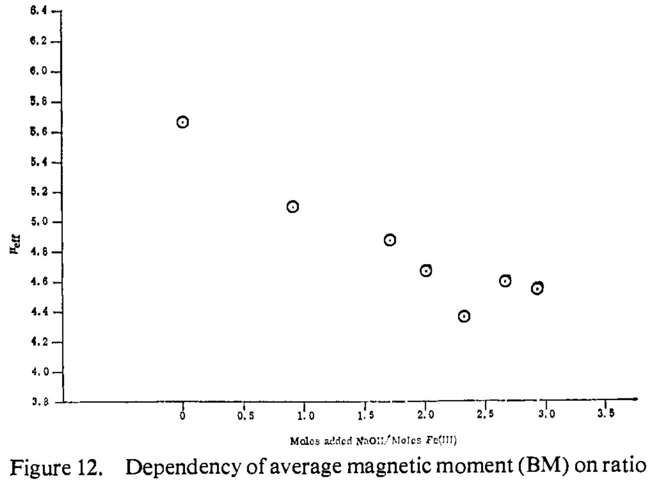

Figure 12. Dependency of average magnetic moment (BM) on ratio of added NaOH to initial Fe(III): $[FeCl_3] = 0.03$ *M*, $[K_4P_2O_7] = 0.06$ *M* (25°).

Fe(III)–Pyrophosphate System. Werbel, Dibeler, and Vosburgh noted that ferric pyrophoshate solutions show less than the theoretical moment per Fe(III) (5.6 *vs.* 5.92 BM).[3] Although pH values were not reported, their data clearly indicate that the magnetic susceptibility decreases with increasing pH. Their method consisted of adding varying amounts of $Na_4P_2O_7$ and $HClO_4$ to a fixed amount of $Fe(ClO_4)_3$. We have added varying amounts of NaOH to a fixed ratio of $FeCl_3$ and $K_4P_2O_7$. Solutions were 0.03 *M* in $FeCl_3$ and 0.06 *M* in $K_4P_2O_7$. The resulting complex is $Fe(P_2O_7)_2^{5-}$.[31] Addition of base generates a red-brown solution. Coloration is due to "end absorption" in the visible, and no new absorption band was observed. The results are summarized in Figure 12. The effective magnetic moment per Fe(III) as a function of pH is different from that observed in the Fe(III)–HEDTA system. Although spin pairing is clearly indicated, the behavior is probably complicated by overlapping equilibria.[32]

Holroyd, Jameson, Odell, and Salmon have measured the magnetic susceptibility of aqueous solutions containing varying ratios of orthophosphate ion to ferric ion.[33] A minimum μ_{eff} per Fe(III) of < 5.3 BM results when PO_4^{3-}/Fe(III) is about 0.5. Following the precedent established by Mulay and Selwood,[6] diamagnetic dimers were invoked of general formula

$$[Fe_2(OH)(HPO_4)(H_2O)_x]^{3+} \text{ or } [Fe_2(OH)(PO_4)(H_2O)_x]^{2+}$$

These are structurally analogous to the aquo dimer $[Fe_2(OH)_2]^{4+}$. While each case must be decided from its own particular properties, we propose here that participation of paramagnetic Fe(III) dimers seems more

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(29) L. N. Mulay and M. C. Naylor in "Advances in the Chemistry of Coordination Compounds," S. Kirschner, Ed., The Macmillan Co., New York, N. Y., 1961, p 520.

(30) R. Aasa, B. Malmström, P. Saltman, and T. Vänngård, *Biochem. Biophys. Acta*, **88**, 430 (1964).

(31) S. Banerjee and S. K. Mitra, *Sci. Cultures* (Calcutta), **16**, 530 (1951); *Chem. Abstr.*, **46**, 8562*h* (1940).

(32) A solution for which μ_{eff} per iron is the smallest (4.36 BM) was stripped of water with a rotary evaporator. Infrared analysis of the resulting red-brown solid (KBr pellet) revealed no absorption in the 850-cm^{-1} region. The spectrum was very similar to that of potassium pyrophosphate. Thus, spin pairing probably takes place across hydroxo bridges which link dimers or higher polymers. By analogy to the ferric perchlorate system, a spin state higher than one spin per iron is suggested.

(33) A. Holroyd, R. F. Jameson, A. L. Odell, and J. E. Salmon, *J. Chem. Soc.*, 3239 (1957).

plausible than diamagnetic Fe(III) species in the presence of weak-field ligands.

Iron(III) in Biological Systems. A variety of biological substances or derived substances contain Fe(III) with a reduced magnetic moment. The hypothesis that structural features in these systems may be similar to the ones described in this report is currently being investigated in these laboratories.

The reduced magnetic moment of ferrihemoglobin hydroxide[4] was described in the introduction. Rawlinson and Scutt[34] have made a detailed study of the magnetic properties of hemin itself (the ferriporphyrin unit of ferrihemoglobin). In aqueous base, magnetic moments of 2.85–3.55 BM per iron were observed. Among the structures envisioned which would permit iron–iron interaction is one which incorporates hydroxo bridging analogous to that postulated for the Fe(III) aquo dimer. Previously, Michaelis and coworkers[35] observed a magnetic moment per iron of 3.81 BM in ferritin, the iron-storage protein. It is interesting, although perhaps coincidental, that the ferric hydroxide which they derived from ferritin had the same μ_{eff}.

Recently, Jordan and Bednarski[36] have shown *via* polarographic techniques that hemin in base undergoes a reversible *two-electron reduction*. This was interpreted as conclusive evidence that the ferriporphyrin is *dimeric*. However, no analysis of the structure of the dimer was offered.

George, Beetlestone, and Griffith have recently reviewed the subject of ferrihemoprotein hydroxides and their low magnetic moments.[37] The view that the "low" magnetic moments arise from thermal mixtures of high- and low-spin forms was proposed from a correlation of magnetic and spectral data. However, the nature of the low-spin forms is still vague. For hemin, the simple porphyrin itself, a dimeric structure does not appear unreasonable.[38] For a similar mechanism to be operable for spin pairing of Fe(III) in metmyoglobin, methemoglobin, peroxidase, etc., unwinding and perhaps formal separation of the protein chain from the porphyrin presumably must occur. Such a process would be consistent with the observed relatively rapid exchange of free heme with the heme in ferrihemoglobin.[39] It is also interesting that in addition to diminishing in magnetic susceptibility above pH 7, ferrihemoglobin also can be oxidized to a compound which behaves in its redox properties like "Fe(IV)."[40] This may simply indicate that the $S = 1$ *unit* $[\text{Fe–O–Fe}]^{4+}$, in comparison with monomeric Fe(III), is relatively easily oxidized.

Acknowledgments. The authors have benefited greatly from stimulating discussions with Dr. Thomas G. Spiro. The work described in this paper was supported in part by National Science Foundation grants.

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[34] W. A. Rawlinson and P. B. Scutt, *Australian J. Sci. Res.*, **A5**, 173 (1952); *Chem. Abstr.*, **46**, 7147*c* (1940).

[35] L. Michaelis, C. D. Coryell, and S. Granick, *J. Biol. Chem.*, **148**, 463 (1943).

[36] J. Jordan and T. M. Bednarski, *J. Am. Chem. Soc.*, **86**, 5690 (1964).

[37] P. George, J. Beetlestone, and J. S. Griffith, *Rev. Mod. Phys.*, **36** (1), 441 (1964).

[38] Of relevance is the recent structural determination of a diamagnetic phthalocyanotomanganese(III) dimer containing an essentially linear Mn–O–Mn bridge: L. H. Vogt, A. Zalkin, and D. H. Templeton, *Science*, **151**, 569 (1966).

[39] H. F. Bunn and J. H. Jandl, *Proc. Natl. Acad. Sci. U. S.*, **56**, 974 (1966).

[40] P. George and D. H. Irvine, *J. Chem. Soc.*, 587 (1954).