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# NUCLEAR MAGNETIC RELAXATION DISPERSION MEASUREMENTS OF ETHYLENEDIAMINE-TETRAACETATOIRON(III) COMPLEXES AT HIGH pH AND IONIC STRENGTH

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Nuclear magnetic relaxation dispersion measurements are reported for aqueous solutions of iron(III)-EDTA complexes at high pH and high ionic strength where the dominant species is the  $\mu$ -oxo dimer. Formation of the dimeric species leaves only the outer coordination sphere contribution to the paramagnetic relaxation rate of the water protons in solution. The relaxation efficiency is further decreased by the decrease in the effective magnetic moment due to antiferromagnetic coupling. This result is in distinction to dimeric species that form with Gd(HEDTA) complexes at high pH in which antiferromagnetic coupling has not been observed to decrease the effective magnetic moment.

**Keywords:** Magnetic relaxation dispersion, iron(III), antiferromagnetic coupling,  $\mu$ -oxo-dimer, outer-sphere relaxation

## INTRODUCTION

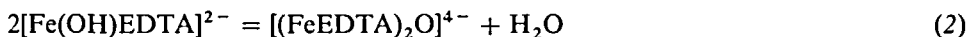
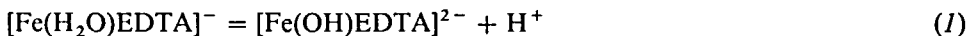
Paramagnetic metal complexes are of current interest as agents that may control nuclear spin relaxation in aqueous systems and by so doing control the information content of a magnetic image.<sup>1</sup> Many complexes studied to date provide a considerable diversity of relaxation efficiency that depends on the structural and dynamic features of the metal complex in complex ways.<sup>2,3</sup> A major difficulty associated with achieving maximal solvent relaxation rates is the contribution of the electron spin relaxation times to the effective correlation time for the electron-nuclear coupling between the metal centre and the solvent protons. If it is sufficiently short, it may dominate the whole relaxation process.<sup>4</sup>

Recent investigations of Gd(HEDTA) complexes have demonstrated approximately a factor of two gain in relaxation efficiency when a di- $\mu$ -dihydroxo dimer is made at high pH.<sup>5</sup> This increase presumably arises because each relaxing proton interacts with two metal centres simultaneously, rather than one.<sup>6,7,8</sup> This observation depends on the fact that, in the gadolinium complex, the electron relaxation properties of the individual metal centres do not change very much when the metals are brought close together in the dimer. Further significant antiferromagnetic coupling that compromises the magnitude of the effective electron moment is absent. We report here similar experiments on the well-characterized iron-EDTA system (a  $\mu$ -oxo dimer that has no first coordination sphere exchangeable protons). The

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magnetic relaxation in the solvent induced by this complex is outer-sphere; however, the relaxation efficiency is lost with dimer formation.

Dimeric metal complexes have been studied by several techniques including electron spin resonance, nuclear magnetic resonance, and magnetic susceptibility measurements in attempts to understand the details of magnetic coupling.<sup>6-9</sup> For the  $[\text{Fe}(\text{EDTA})]^-$  system, the important equilibria in water at pH values above 7 include (1) and (2).



At low ionic strength and pH values below 7, the aquo species dominates, and presumably has the 7-coordinate structure observed in the solid.<sup>10,11</sup> Reaction (1) is reported to have a pKa of 7.5,<sup>12,13</sup> thus making the hydroxo complex the dominant species at pH values greater than 8.<sup>14</sup> Dimerization of the hydroxo complex may be driven by high ionic strengths and the complex is readily identified spectrophotometrically because of a characteristic Fe-O-Fe stretch<sup>15</sup> at  $851.2 \text{ cm}^{-1}$  and electronic absorption that peaks at 475 nm with a molar extinction coefficient of  $180 \text{ M}^{-1} \text{ cm}^{-1}$ .<sup>16</sup>

## EXPERIMENTAL

$\text{Fe}(\text{NO}_3)_3$ ,  $\text{FeCl}_3$ , and  $\text{KNO}_3$  were obtained from the J. T. Baker Co., EDTA and TRIS acid and base from the Sigma Chemical Company, and  $\text{NaN}_3$  from the Aldrich Chemical Co. Stock solutions were prepared in 50 mM TRIS buffer.

A solution containing 70% dimer,  $[(\text{FeEDTA})_2\text{O}]^{4-}$ , was obtained in equilibrium with the monomer,  $[\text{Fe}(\text{OH})\text{EDTA}]^{2-}$ , at pH 10 and high ionic strength using 1.0 M potassium nitrate as the supporting electrolyte. The dimer was identified by its electronic absorption at 475. The azido complex was made by the addition of azide ion to the  $[\text{FeEDTA}]^-$  complex and identified by the absorption peak at 409 nm which is absent in the  $[\text{Fe}(\text{H}_2\text{O})\text{EDTA}]^-$  complex.<sup>17</sup> The proton nuclear magnetic relaxation rate,  $1/T_1$ , was measured over a range of magnetic field strengths corresponding to proton Larmor frequencies between 0.01 and 30 MHz at 287K in a field cycling spectrometer described elsewhere.<sup>5</sup>

## RESULTS AND DISCUSSION

Figure 1 (curve A) shows the relaxation dispersion profile of the iron EDTA complex over the range of proton Larmor frequencies from 0.01 to 30 MHz at pH 4.4. These data are consistent with the earlier reports to within the differences in temperature<sup>14</sup> and are consistent with a significant contribution from the first coordination sphere water molecule. The solid line through the data was computed including an outer sphere contribution as well as a first coordination sphere contribution. An independent means for determining the magnitude of the outer sphere contribution to the relaxation is to make the azido complex and displace the remaining water. The optical spectrum reflects the change in the ligand set on the iron,<sup>17</sup> and absorbance obtained using a 1 mm optical cell is shown as a function of azide concentration in Figure 2. The water proton relaxation profile is shown as curve B in Figure 1. It is

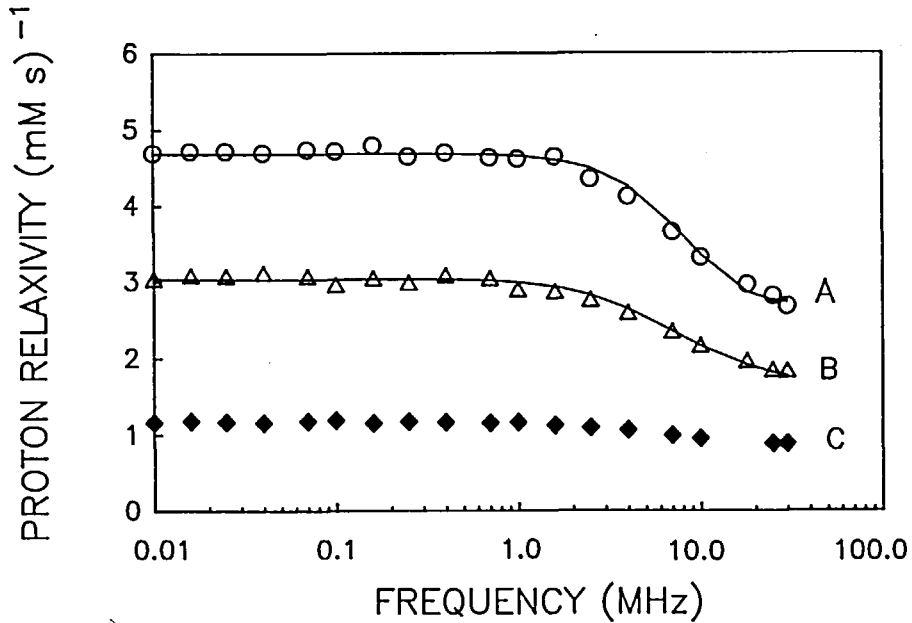


FIGURE 1 The water proton nuclear spin-lattice relaxation rate as a function of magnetic field strength plotted as the proton Larmor frequency for A:  $[\text{FeEDTA}]^-$  ion at pH 4.4; B:  $[\text{Fe}(\text{N}_3)(\text{EDTA})]^{2-}$  ion; C: solution containing 70% of the  $\mu$ -oxo dimer at pH 10 and 1.00 M potassium nitrate at 287K. The solid lines through the data points are calculated based on the Solomon-Bloembergen and Morgan Equations<sup>19,20,21</sup> for the inner coordination sphere contribution to the relaxation and Freed's<sup>22</sup> formulation for the outer sphere contribution.

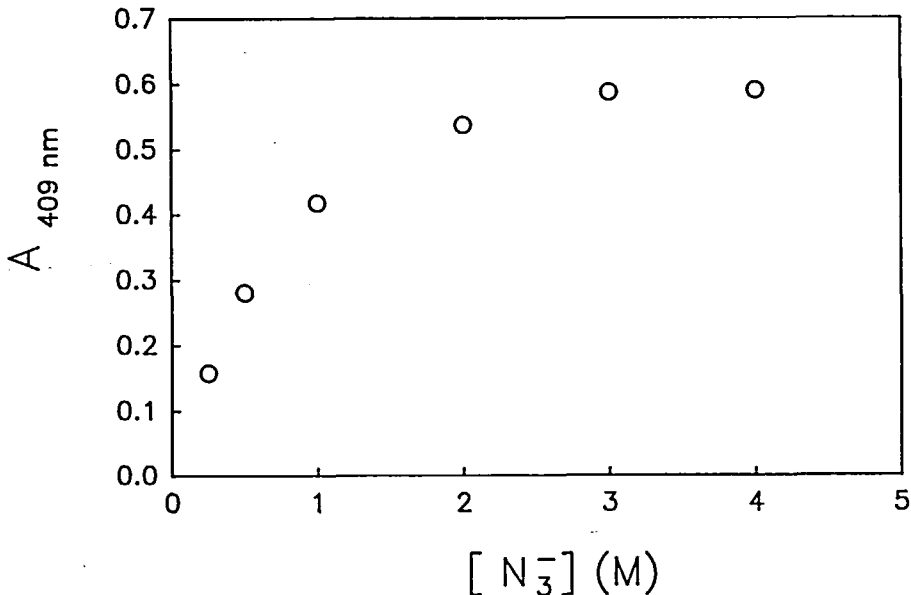


FIGURE 2 The absorbance of iron-EDTA solutions at 409 nm for 2 mM iron(III)ion and 5 mM EDTA in 50 mM tris buffer as a function of the sodium azide concentration.

clear that the outer sphere contribution is comparable in magnitude with the first coordination sphere contribution to the water proton relaxivity.

Data obtained for a solution containing 70% of the dimer in equilibrium with the monomer complex are shown in Figure 1 as the curve D. The relaxation efficiency clearly drops considerably, as is consistent with the loss of the exchangeable protons in the first coordination sphere and a reduction of the magnetic moment from 5.9 BM<sup>18</sup> to 1.9 BM because of antiferromagnetic coupling. The relaxation observed at high ionic strength may be almost completely accounted for by the remaining monomeric hydroxo complex. That is, the relaxation rate at low field for the monomer is estimated as the outer sphere contribution measured by the azido complex plus half the contribution from the first coordination sphere aquo complex or 3.8 s<sup>-1</sup> mM<sup>-1</sup>. 30% of this rate is 1.1 s<sup>-1</sup> mM<sup>-1</sup>, which accounts for all of the relaxation rate observed for the high ionic strength solution. Though the temperatures are somewhat different, these estimates are approximately consistent with the data reported by Bloch and Navon<sup>14</sup> for aqueous solutions of [Fe(OH) EDTA]<sup>2-</sup>. Therefore, the dimer contribution is very small as expected because of the reduced magnetic moment and the loss of the first coordination sphere contribution. The relaxation rates are proportional to the square of the magnetic moment. Thus, the contributions of the dimer should be decreased by a factor of 9.6 on this basis alone. Estimating the remaining outer sphere contribution using this factor and the result that the dimer comprises 70% of the composition yields an estimate of 0.3 s<sup>-1</sup> mM<sup>-1</sup> if one assumes that the electron relaxation rates in the dimer remain unchanged from those in the monomer. However, that the contribution from the dimer is only of the order of the experimental error suggests that in addition to the change in the magnetic moment, the electron spin relaxation time in the dimer is also significantly shorter than in the monomer.

The dimerization reaction may defeat the efficiency of the electron-nuclear spin relaxation as anticipated. However, it is clear that several factors, including changes in the magnetic moment because of antiferromagnetic coupling and changes in the electron spin relaxation rates, may act in concert to defeat efficient electron-induced nuclear spin relaxation.

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