

## $\mu$ -Peroxo-bis(bis(diphenylglyoximato)iron(III))의 자기적 성질

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## Magnetic Property of $\mu$ -Peroxo-bis(bis(diphenylglyoximato)iron(III))

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요 약. 팔면체형 철(II)착물  $[\text{Fe}(\text{DPGH})_2(\text{NH}_3)_2]$ 과 산소분자의 반응에서 생성된 산소화생성물,  $[(\text{DPGH})_2\text{FeO}_2\text{Fe}(\text{DPGH})_2]$ 의 자기모멘트를 측정하였다. 산소화 생성물내의 철에 대한 자기모멘트는  $298^\circ\text{K}$ 에서 3.60 B.M (Bohr Magnetron)이며 온도가 내려 감에 따라 감소되어  $4.2^\circ\text{K}$ 에선 1.65 B.M의 값을 보여준다. 이상의 측정결과는 다음과 같이 설명될 수 있다. (1) 산소화생성물내의 두개의 철(III)은 중간스핀상태 ( $S=3/2$ )를 갖는다. (2) 분자내의 두개의 철(III)은 서로 약한 반강자성 짝지음을 일으킨다. 짝지음 상수는  $J=-1\text{cm}^{-1}$  정도이다.

**ABSTRACT.** It was observed that the magnetic moment for iron in  $[(\text{DPGH})_2\text{FeO}_2\text{Fe}(\text{DPGH})_2]$ , the oxygenation product of an octahedral iron(II) complex,  $[\text{Fe}(\text{DPGH})_2(\text{NH}_3)_2]$ , decreases with decreasing temperature from  $\mu=3.60$  B.M (Bohr Magnetron) per iron at  $298^\circ\text{K}$  down to  $\mu=1.65$  B.M per iron at  $4.2^\circ\text{K}$ . This observation may be explained by a weak antiferromagnetic coupling between two iron(III) atoms of intermediate spin state ( $S=3/2$ ) in the molecule with the coupling constant  $J=-1\text{cm}^{-1}$ .

### INTRODUCTION

Magnetic property measurements of a transition metal complex could frequently provide very important, sometimes decisive, information on the oxidation states of the metal and surrounding ligands, and on ligand field splitting. They could also be very helpful for the discussion on the molecular structure of the metal complex.<sup>1</sup>

Magnetic properties have been rather thoroughly studied for iron complexes probably because iron is one of the most abundant transition metals. A study of iron complexes in

biological systems also finds the magnetic properties being very useful for the information on those mentioned above.<sup>2</sup> Significant changes in magnetic properties are usually seen in oxidation of iron(II) to iron(III) complexes. Iron(II) in complexes can be in one of three spin states,  $S=0$ , 1, or 2, while iron(III) in one of  $S=1/2$ ,  $3/2$ , or  $5/2$ . Intermediate spin states,  $S=1$  for iron(II)<sup>3</sup> and  $S=3/2$  for iron(III).<sup>4</sup> have been frequently reported although high-spin and low-spin states are more common for both of iron(II) ( $S=0$  or 2) and iron(III) ( $S=1/2$  or  $5/2$ ).

Antiferromagnetic coupling is one of the

magnetic properties shown by binuclear metal complexes where two paramagnetic metal ions are separated by one or more bridging atoms.<sup>5,6</sup> For the species which show the coupling, the magnetic moment values measured at room temperature, are usually much lower than the theoretical spin-only values at the same temperature. It has been found that ferric dimers with various bridging groups show antiferromagnetic coupling.<sup>5</sup>

Reactions of iron(II) complexes with molecular oxygen yield various products. Of those products, dioxygen iron complexes are of particular interest, since iron plays a key role in oxygen transportation into biological systems. Iron dioxygen complexes may be divided into two groups by their structures: (1) monomeric dioxygen complexes, Fe-O<sub>2</sub>,<sup>7</sup> (2) dimeric dioxygen bridged complexes, Fe-O<sub>2</sub>-Fe.<sup>7,8</sup> Magnetic coupling between two paramagnetic iron atoms can be expected from the group (2) complexes while it is not likely for the group (1) complexes.

It has been reported that the octahedral iron (II) complexes, [Fe(DPGH)<sub>2</sub>L<sub>2</sub>] ((DPGH)<sub>2</sub>=bis(diphenylglyoximato)bivalent anion, L=NH<sub>3</sub>, pyridine, imidazole), reacts with molecular oxygen to give a  $\mu$ -peroxo ferric dimer [(DPGH)<sub>2</sub>FeO<sub>2</sub>Fe(DPGH)<sub>2</sub>] (see EXPERIMENTAL). Magnetic susceptibility measurement on solid samples of the oxygenation product at room temperature gives  $\mu=3.60$  B. M per iron.<sup>9</sup> The observed magnetic moment is somewhat lower than the theoretical spin-only value ( $\mu=3.87$  B. M per iron) for an intermediate spin state ( $S=3/2$ ) for iron(III). This observation led us to the investigation for temperature dependence of magnetic property of the oxygenation product, [(DPGH)<sub>2</sub>FeO<sub>2</sub>Fe(DPGH)<sub>2</sub>].

## EXPERIMENT

**Physical Measurements.** Magnetic susceptibility measurements (130~298°K) were made on a Cahn-Ventron Model 7600 Faraday Magnetic Balance in our laboratory and in the range of 4.2~270°K at the University of Illinois where Mössbauer spectrum was obtained.<sup>10</sup> Hg[Co(SCN)<sub>4</sub>] ( $\chi_g=16.44 \times 10^6$  cgs unit at 298°K) was used as a standard. Diamagnetic corrections were made using Pascal's constants.<sup>11</sup> Infrared spectra were obtained on a Perkin-Elmer 283 spectrophotometer. Elemental analyses and molecular weight measurements were carried out by Schwartzkopf Microanalytical lab., Woodside, N. Y.

**Preparation.** [Fe(DPGH)<sub>2</sub>L<sub>2</sub>] (L=NH<sub>3</sub>, pyridine, imidazole): prepared by the method described elsewhere.<sup>12</sup> [(DPGH)<sub>2</sub>FeO<sub>2</sub>Fe(DPGH)<sub>2</sub>] was prepared in the following manner. [Fe(DPGH)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>] (0.50g) was stirred in CHCl<sub>3</sub> (150 ml) in air at 25°. The purple suspension turned into a brown-yellow solution in 14 hours. Addition of hexane (250 ml) resulted in precipitation of a brown product which was filtered, washed with CH<sub>3</sub>OH (50 ml) and dried in vacuum (yield, 0.37 g).

*Anal.* Calcd for Fe<sub>2</sub>C<sub>56</sub>H<sub>44</sub>N<sub>8</sub>O<sub>10</sub>: Fe 10.15; C, 61.10; H, 4.04; N, 10.18; MW, 1101. Found: Fe, 10.42; C, 61.45; H, 4.03; N, 10.15; MW, 1117 (measured in CHCl<sub>3</sub>).

The following observations agree with the identity of this compound: (1) infrared spectrum of the compound did not show NH<sub>3</sub> bands, (2) O<sub>2</sub> uptake measurements showed that two moles of [Fe(DPGH)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>] reacts with one mole of O<sub>2</sub>. (3) one mole of this compound reacts with pyridine to give one mole of O<sub>2</sub> and two moles of [Fe(DPGH)<sub>2</sub>(pyridine)<sub>2</sub>], (4) Mössbauer spectrum showed that two irons

in the compound are identical.<sup>10</sup>

## RESULTS AND DISCUSSION

Fig. 1 shows the magnetic moment,  $\mu$ , for iron in  $[(DPGH)_2FeO_2Fe(DPGH)_2]$  in the range of 4.2~298 °K. It is seen that the magnetic moment decreases with decreasing temperature from  $\mu=3.60$  B.M at 298 °K down to  $\mu=1.65$  B.M at 4.2°C per iron. This strongly suggests an antiferromagnetic between two iron atoms in a molecule of the oxygenation product.

Antiferromagnetic coupling between two ferric atoms in a binuclear metal complex has been found for numerous compounds such as  $\mu$ -oxo dimers,<sup>5a, 13</sup>  $\mu$ -hydroxo dimers,<sup>5c, 13a, 14</sup> and others.<sup>5b, 16</sup> The coupling has been observed to occur between two high-spin ( $S=5/2$ ) iron(III)<sup>5a, 5b, 13~15</sup> and between two low-spin ( $S=1/2$ ) iron(III).<sup>5a, 14b</sup> It has not been reported, however, for two iron(III) of intermediate spin ( $S=3/2$ ) although the antiferromagnetic coupling between two transition metal atoms of  $S=3/2$  has been found for dimeric Cr(III)<sup>1</sup> and Mn(IV)<sup>15</sup> complexes, respectively.

Antiferromagnetic coupling has been usually found for two paramagnetic metal ions separated by one bridging atom and explained by the mechanism of super-exchange *via* bridging

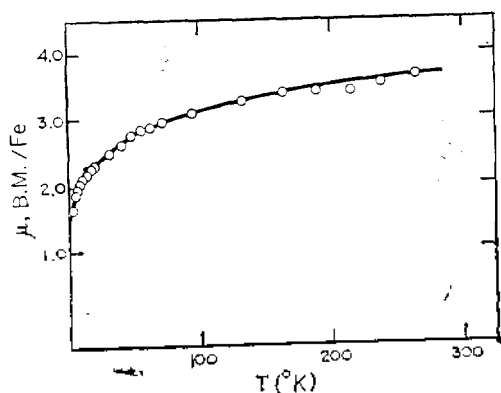


Fig. 1. A plot of magnetic moment,  $\mu$ , of iron in  $[(DPGH)_2FeO_2Fe(DPGH)_2]$  versus absolute temperature.

atom. The coupling has been also found to occur between two metal ions separated two or more atoms,<sup>6</sup> although such a coupling is usually very weak, as expected from the super-exchange *via* intervening atoms. For such weakly antiferromagnetic substances, Neel's point has frequently not been seen.

Fig. 2 shows a plot of magnetic susceptibility of iron in  $[(DPGH)_2FeO_2Fe(DPGH)_2]$  versus absolute temperature. No Nee's point is evident, which suggests that any magnetic exchange present is very weak. This observation rules out the presence of two high-spin ( $S=5/2$ ) iron(III) atoms in  $[(DPGH)_2FeO_2Fe(DPGH)_2]$  since the magnetic moment of high-spin iron(III) with very weak antiferromagnetic

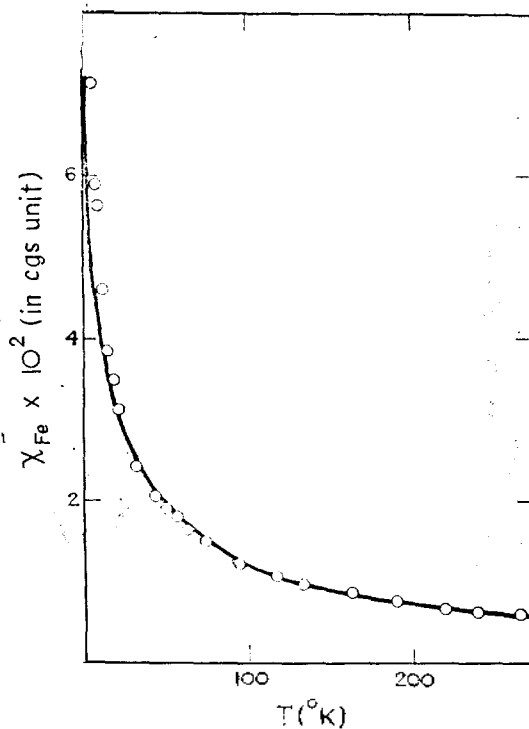


Fig. 2. Temperature dependence of magnetic susceptibility of iron in  $[(DPGH)_2FeO_2Fe(DPGH)_2]$ . The experimental data are shown as circles and the best fit for antiferromagnetic coupling is displayed as the solid line (see text).

coupling should be close to 5.92 B. M (theoretical spin-only value for  $S=5/2$ ) at room temperature. Therefore, the only probable spin state of iron(III) in  $[(DPGH)_2FeO_2Fe(DPGH)_2]$  appears to be intermediate,  $S=3/2$ .

For a binuclear molecule with identical metal ions of  $S=3/2$ , the theoretical susceptibility may be calculated by the following equation.<sup>17</sup>

$$\chi = \frac{3K}{(T-\theta)} \left( \frac{14+5x^6+x^{10}}{7+5x^6+3x^{10}+X^{12}} \right) + N_a$$

where  $\chi$ =magnetic susceptibility,  $K=N_g^2\beta^2/3k=0.1251g^2$ ;  $N$ =Avogadro's number;  $g$ ="g" factor, the ratio of magnetic moment to orbital angular momentum;  $\beta$ =Bohr Magneton;  $k$ =Boltzman constant;  $x=\exp(J/KT)$ ;  $J$ =coupling constant;  $T$ =temperature ( $^{\circ}K$ );  $\theta$ =Weiss constant;  $N_a$ =small diamagnetism and also temperature independent paramagnetic contribution to susceptibility.

With no magnetic coupling ( $J=0$ ), substitutions of  $J=0$ ,  $N_a=0$  and  $g=2$  into the above equation give  $\chi=1.8765/T$  and  $\mu=3.87$  B. M at  $298^{\circ}K$ , the spin-only value for  $S=3/2$ .

The best fit of our experimental susceptibility data into the equation can be obtained with  $N_a=0$ ,  $g=1.97$ ,  $\theta=47^{\circ}$  and  $J=-cm^{-1}$  as shown in Fig. 2. A very weak antiferromagnetic coupling with  $J=-1cm^{-1}$  may be explained by the difficulty of super-exchange *via* two bridging oxygen atoms of a non-linear peroxo unit  $(\diagup O \diagdown O \diagup)^{2-}$ . The  $g=1.97$  value is close to the value ( $g=1.99$ ) found in the EPR spectrum of the oxygenation product.<sup>10</sup> The  $\theta=47^{\circ}$  can also be obtained by extrapolation of the plot,  $1/\chi$  versus temperature as shown in Fig. 3.

For some binuclear OH-bridged Cr(III) complexes with  $S=3/2$ , it has been found that the deviation of experimental data from the theoretical values is significant especially at lower temperatures although good agreement is ob-

tained at high temperatures.<sup>18</sup> To explain this deviation, the biquadratic exchange term (higher order in spin coupling) has been introduced,<sup>19</sup> resulting in satisfactory agreement with experimental data. We have not attempted to fit out data into the equation derived with the biquadratic term, since our data are reasonably good in agreement with the above equation.

In order to explain the observed magnetic data which are in between the values for high spin ( $\mu=5.92$  B. M per iron) and low spin ( $\mu=1.73$  B. M per iron) iron(III), a thermal equilibrium between the spin states (high spin low spin) has been proposed.<sup>8b, 18-20</sup> Analogous thermal equilibrium has been suggested to interpret the magnetic data for iron(II).<sup>21</sup> Some of these suggestions were supported by Mössbauer spectral data.<sup>8b, 21</sup> Our observed magnetic data at various temperatures may not be explained by a thermal equilibrium between the spin states of high- and low spin, since the lowest observed value ( $\mu=1.65$  B. M per iron at  $4.2^{\circ}K$ ) is somewhat over than the

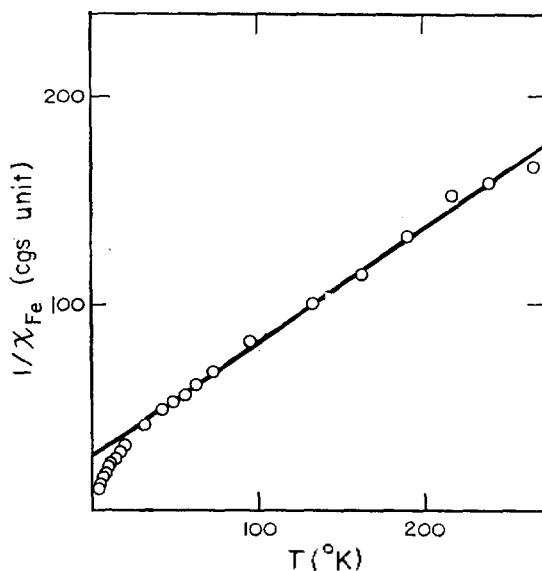


Fig. 3. A plot of  $1/\chi_{Fe}$  of  $[(DPGH)_2FeO_2Fe(DPGH)_2]$  versus temperature.

theoretical spin-only value for low spin iron (III). The observed magnetic moments for low spin iron(III) are usually close to 2.0 B.M.

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