

Hyperfine interactions in the intramolecular antiferromagnet (Fe salen Cl)₂*

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(Received 9 May 1973)

Magnetic hyperfine interactions in (Fe salen Cl)₂ have been studied using the Mössbauer effect in external magnetic fields up to 80 kOe and for $4.2 \leq T \leq 80^\circ\text{K}$. The low-temperature results are adequately described by a simple intramolecular exchange model with $J = 7.0 \text{ cm}^{-1}$ and a hyperfine interaction constant of -180 kOe per unit spin. At higher temperature the effective field approximation breaks down. Data for (Fe salen)₂O are also briefly reported.

I. INTRODUCTION

There is a large class of transition metal ion complexes in which two or more of the metal ions cluster relatively close to each other but the clusters are relatively well isolated from each other. These polynuclear complexes have been extensively studied over the last few years.^{1,2} Apart from the fact that certain biologically important enzymes contain polynuclear complexes of iron,^{3,4} these systems allow the study of the interactions between transition metal ions in finite surroundings because in many instances, the ions in the cluster interact strongly with each other and the interaction between clusters can be neglected.

The primary technique for studying magnetic interactions in these clusters is to measure the magnetic susceptibility as a function of temperature from which, in principle, it is possible to obtain values of the intramolecular exchange and the moments of the ions in the cluster.¹ Another important technique could be to study the hyperfine interactions in the ions in the cluster, using the Mössbauer effect in the case of iron complexes, although this has been done in relatively few cases. However, one important application has been to the elucidation of the electronic structure of the two Fe-S ferredoxins.⁵⁻⁷ Mössbauer measurements in other binuclear iron compounds have been reported^{8,9} but, except for the proteins, no observations of magnetic hyperfine interactions have been made except to note their absence as proof of the singlet ground state nature of the molecule.^{9,10} If the simple ground exchange model traditionally used to interpret the susceptibility measurements is correct, then magnetic field and temperature-dependent hyperfine interactions should be observed, especially in systems where the electronic interaction with the applied magnetic field becomes comparable to the intramolecular exchange energy.

In this paper we report a study using the Mössbauer effect of the binuclear complex (Fe salen Cl)₂ where salen is *N, N'*-ethylenebis(salicyldiminato) in which we studied the magnetic hyperfine interactions as a function of temperature and magnetic field up to 80 kOe. The structure of this material is known from x-ray diffraction measurements¹¹ and its magnetic susceptibility has been determined over a wide range of temperature.^{8,12} As we show below, the hyperfine interactions we observe are consistent with the simple exchange model, and we obtain a value for the exchange constant which is consistent with the value obtained from susceptibility measurements. We also obtain a value of the hyperfine interaction constant which provides a unique corroboration of the model of two high spin Fe³⁺ ions coupled antiferromagnetically. We also report measurements in (Fe salen)₂O for which the value of J is much larger. In Sec. II below, we outline the exchange model and the hyperfine interaction theory; in Sec. III we present the experimental results.

II. EXCHANGE IN BINUCLEAR SYSTEMS

As several authors^{1,2} have shown, the interactions in polynuclear complexes can be simply described in terms of the classical exchange Hamiltonian,

$$\mathcal{H}_{\text{ex}} = -2 \sum_{ij} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j, \quad (1)$$

where the sum is taken over all interacting pairs in the cluster. In the simplest case of two interacting ions, the energy levels are simply

$$E(S) = -JS(S+1), \quad (2)$$

where \mathbf{S}_1 and \mathbf{S}_2 are the angular momenta of the two coupled paramagnetic ions and $\mathbf{S} = \mathbf{S}_1 + \mathbf{S}_2$. If $\mathbf{S}_1 = \mathbf{S}_2$ and the interaction is antiferromagnetic ($J < 0$), the ground state will have $S = 0$, i. e., will be a singlet

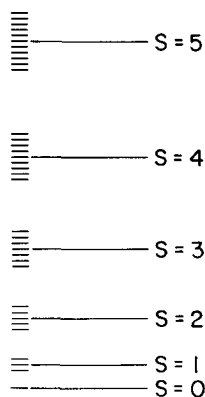


FIG. 1. Energy level diagram for two $S = \frac{5}{2}$ ions coupled with $J < 0$.

state and the material will be nonmagnetic at low temperature (Fig. 1). At higher temperatures the excited states with $S \neq 0$ will be populated and the magnetic moment per transition metal ion will increase until all the states are occupied. Measurement of the magnetic susceptibility as a function of temperature can in principle yield a value of J and this has been done in numerous cases (e.g., see Refs. 1 and 2).

Since the ground state is a singlet state, the magnetic hyperfine interaction will also vanish in the limit $T \rightarrow 0K$ and $H_0 \rightarrow 0$, where H_0 is an externally applied magnetic field. In a finite external field at finite temperature, the total field at the nucleus H_n is given by

$$\mathbf{H}_n = \mathbf{H}_0 + \mathbf{H}_{\text{hf}}, \quad (3)$$

where H_{hf} is the contribution from the magnetic hyperfine interaction.

The calculation of the magnetic hyperfine interaction is straightforward. The Hamiltonian for each ion in the complex is

$$\mathcal{H} = a\mathbf{I}_i \cdot \mathbf{S}_i \quad (4)$$

where a is a constant. This can be recast in terms of the total spin S ,

$$\mathcal{H} = A\mathbf{I}_i \cdot \mathbf{S}, \quad (5)$$

where, for dimers with equivalent ions,

$$A = \frac{1}{2}a. \quad (6)$$

The effective hyperfine field is then

$$H_{\text{hf}} = (A/g_n\mu_n) \langle S \rangle \quad (7)$$

and assuming an isotropic interaction and an electronic relaxation time, which is fast compared to the Larmor precession time,

Thus in this simple case of two identical ions in the cluster and assuming $g = 2$, the hyperfine interaction for all fields and temperatures is characterized by only two constants, $A/g_n\mu_n$ and J , and thus the determination of H_{hf} as a function of H_0 and T allows the determination of those quantities. The magnitude of $A/g_n\mu_n$ is related to the electronic structure of the transition metal ion; in the case of Fe^{3+} it is primarily due to core polarization.¹³

III. EXPERIMENTAL

Stoichiometric amounts of N, N' -disalicylidene ethylenediamine (Schiff base ligand) were reacted with anhydrous ferric chloride in ethanol and the complex was obtained by slow evaporation at 10°C after treatment with anhydrous ether. The crystals are purple needles with a melting point of 256°C .

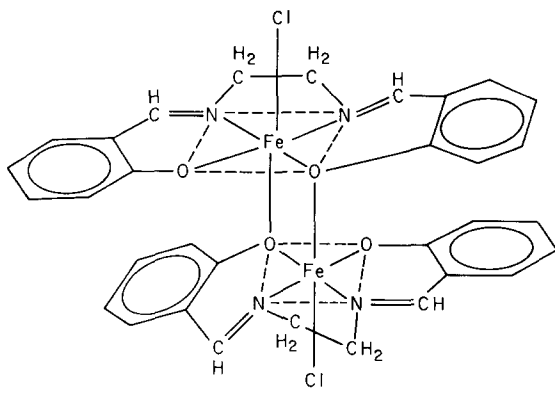
The structure of $(\text{Fe salen Cl})_2$, where salen is N, N' -ethylenebis(salicyldiminato), has been determined by x-ray analysis¹¹ and has two iron ions bridged by a pair of oxygen atoms (see Fig. 2). The $\text{Fe}^{3+}-\text{O}-\text{Fe}^{3+}$ bond angle is close to 90° and the two iron sites are equivalent. Magnetic susceptibility measurements have been reported by Gerloch *et al.*¹² and by Reiff *et al.*,⁸ who obtain $J \sim -7.5 \text{ cm}^{-1}$ and $S_1 = S_2 = \frac{5}{2}$.

The Mössbauer spectra were obtained with a conventional constant acceleration spectrometer. The magnetic fields were generated in a Nb_3Sn superconducting magnet operating in the persistent mode. Temperature stability was better than 0.05°K , and a 100Ω calibrated carbon resistor was employed as a sensor, primarily because of its insensitivity to magnetic fields at low T . For the spectra taken at 77°K , a Pt thermometer corrected for the applied magnetic field was used.

We would like to note here that correct preparation of the absorber is crucial in these measurements. Because the material crystallizes in the form of thin needles they will preferentially pack with the axis of the needle in the plane of the absorber leading to a partial polarization of the quadrupole interaction with respect to the applied magnetic field, which can give spurious results if the spectra are analyzed assuming a randomly oriented powder. For this reason we ground up the $(\text{Fe salen Cl})_2$ crystals together with sugar to assure random orientation.

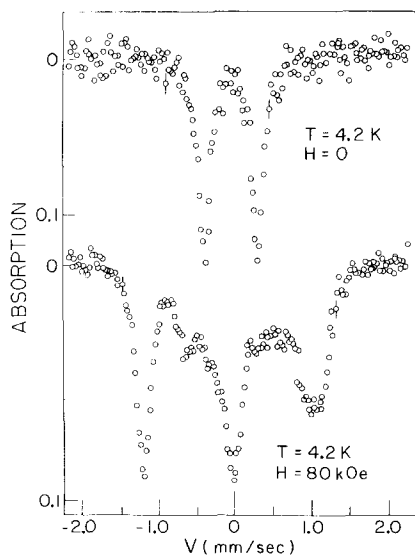
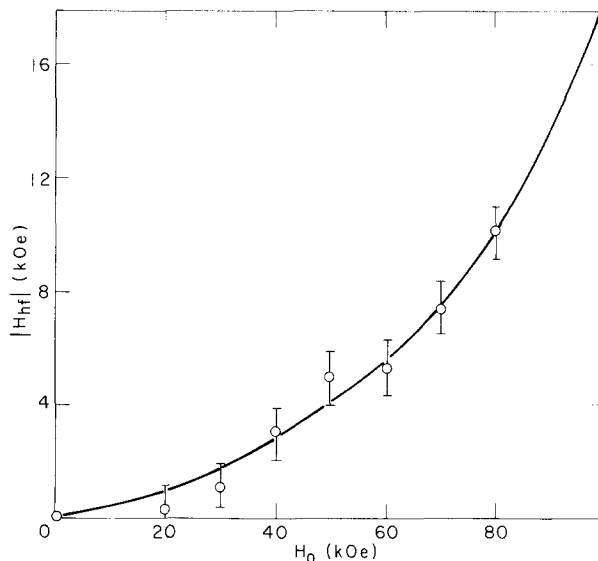
Two low-temperature spectra are shown in Fig. 3. The $H_0 = 0$, $T = 4.2^\circ\text{K}$ spectrum shown in Fig. 3 consists of a single, quadrupole doublet with a

$$H_{\text{hf}}(H_0, T) = \frac{\sum_S \sum_{S_z} (A/g_n\mu_n) S_z \exp\{-[JS(S+1) - g\mu_B H_0 S_z]/kT\}}{\sum_S \sum_{S_z} \exp\{[JS(S+1) - g\mu_B H_0 S_z]/kT\}}. \quad (8)$$

FIG. 2. Structure of $(\text{Fe salen Cl})_2$.

splitting $\Delta E = 1.38$ mm/sec. The spectra in the applied fields are complicated by the fact that the magnetic hyperfine splitting is superposed on the electric quadrupole splitting which, in a powder sample, is randomly oriented with respect to the magnetic field axis. To analyze the results, we compared our spectra with computer-generated spectra using a program due to Singh and Hoy¹⁴ which we modified to generate powder spectra. As the peak positions are quite sensitive to the magnitude of the field at the nucleus H_n , we could determine H_n with good accuracy (± 2 kOe). The $H_0 = 80$ kOe, $T = 4.2$ °K spectrum is shown in Fig. 3; comparison with the spectra computed for $\Delta E_Q = 1.38$ mm/sec yields $H_n = 70$ kOe. Since

$$\mathbf{H}_n = \mathbf{H}_{\text{hf}} + \mathbf{H}_0,$$

FIG. 3. Mössbauer spectra of $(\text{Fe salen Cl})_2$ at 4.2 °K and (a) $H_0 = 0$, (b) $H_0 = 80$ kOe.FIG. 4. H_{hf} in $(\text{Fe salen Cl})_2$ plotted as a function of H_0 for $T = 4.2$ °K.

where \mathbf{H}_{hf} is the effective magnetic field at the nucleus due to the magnetic hyperfine interaction, a measure of \mathbf{H}_n yields \mathbf{H}_{hf} ; in the case at hand we obtain $H_{\text{hf}} = -10$ kOe.

Our spectrum is qualitatively similar to the 90 kOe spectrum obtained by Buckley *et al.*,⁹ however, our analysis is different. Since they were primarily interested in showing that the ground state is singlet, they compared their data with spectra computed by Collins and Travis¹⁵ and were able to rule out large hyperfine field contributions, as would be expected, for example, from paramagnetic Fe^{3+} .

In Fig. 4 we plot H_{hf} as a function of H_0 for $T = 4.2$ °K. Figure 5 shows H_{hf} plotted as a function of T for $H_0 = 80$ and $H_0 = 50$ kOe. The solid curves in Figs. 4 and 5 are theoretical for $J = -7.0$ cm⁻¹ and $A/g_n\mu_n = 90$ kOe obtained by a least squares computer fit of Eq. (8) to the data, including all the terms in Eq. (8) up to $S = 5$.

From these results we draw two conclusions: (a) the simple isotropic exchange model seems to work over this range of applied field and temperature in this system; (b) the value of J we obtain is consistent with the value obtained from the susceptibility measurements.

From Eq. (6) we see that the experimental value of -90 kOe for $A/g_n\mu_n$ corresponds to a value of -180 kOe per unit spin in the individual ions. This just corresponds to the projection of the $|S, S_z\rangle$ representation onto the $|S_1, S_2, S_{1z}, S_{2z}\rangle$ representation. In our case, $S_1 = S_2 = \frac{5}{2}$ and $S = 1$. $S_z = +1$ cor-

responds to $\langle S_{1z} \rangle = \langle S_{2z} \rangle = \frac{1}{2}$. The usual value obtained for ionic Fe³⁺ is $-500 \text{ kOe} \div \frac{5}{2} = -200 \text{ kOe}$, in good agreement with the experimental value. The difference may be ascribed to the effects of covalency in reducing the core polarization.

In order to check the internal consistency of our experimental procedure, we compare these results with measurements made in (Fe salen)₂O, which has already been studied using the Mössbauer effect by Reiff¹⁶ and by Buckley *et al.*⁹ Susceptibility measurements¹⁷ in this material are consistent with $g=2.00$, $S=\frac{5}{2}$, and $J=-95 \text{ cm}^{-1}$, more than an order of magnitude larger than in (Fe salen Cl)₂. The $T=4.2 \text{ }^\circ\text{K}$, $H_0=0$, and 80 kOe spectra are shown in Figs. 6(a) and 6(b), respectively. In Fig. 7 we plot H_n vs H_0 at $T=4.2 \text{ }^\circ\text{K}$; the straight line through the data is theoretical [Eq. (8)] for the parameters taken from the susceptibility measurements and assuming $A/g_n\mu_n=100 \text{ kOe}$ and is identical at $T=4.2$ with $H_n=H_0$.

Extension of the calculations based on Eq. (8) for the (Fe salen Cl)₂ to higher temperature shows that H_{hf} should be roughly constant to temperatures above 80 °K and then decreases. However, in spectra taken at 77 °K the lines are broad and diffuse and there is clearly not a unique magnetic field at the nucleus. We interpret this result as a breakdown in the "effective field" approximation represented by Eq. (7). That is, as the electronic relaxation time becomes slower than the nuclear Larmor precession time, the magnetic hyperfine interaction can no longer be represented by an equivalent $\mu \cdot H$ interaction, and we see instead a superposition of hyperfine fields corresponding to the various $|S_z\rangle$ states populated at that temperature.

Buckley *et al.*⁹ have studied the electric quadrupole doublet absorption spectrum of (Fe salen Cl)₂ in zero external field from 4.2 to 300 °K. At

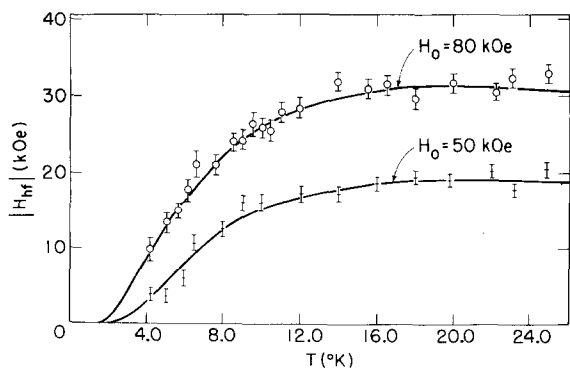


FIG. 5. H_{hf} in (Fe salen Cl)₂ plotted as a function of T for (a) $H_0=80 \text{ kOe}$ and (b) $H_0=50 \text{ kOe}$.

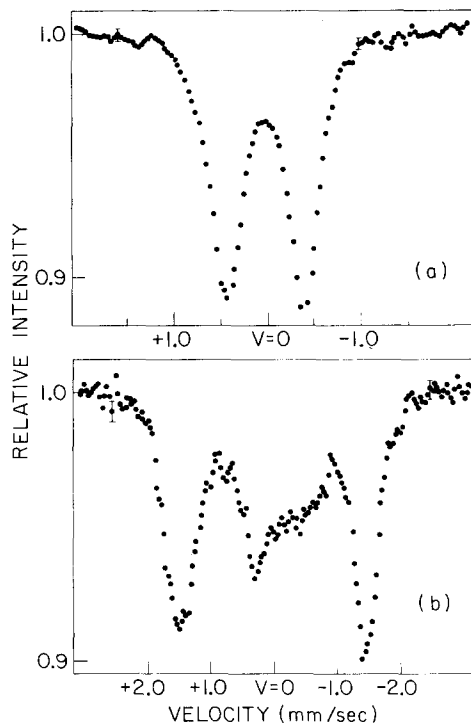


FIG. 6. Mössbauer spectra of (Fe salen)₂O at 4.2 °K and (a) $H_0=0$, (b) $H_0=80 \text{ kOe}$.

4.2 °K the two lines are symmetric but at T increases one peak broadens appreciably and at 300 °K there are significant differences in the total absorption intensity of the two peaks. They ascribe the intensity difference at 300 °K to a Goldanski-

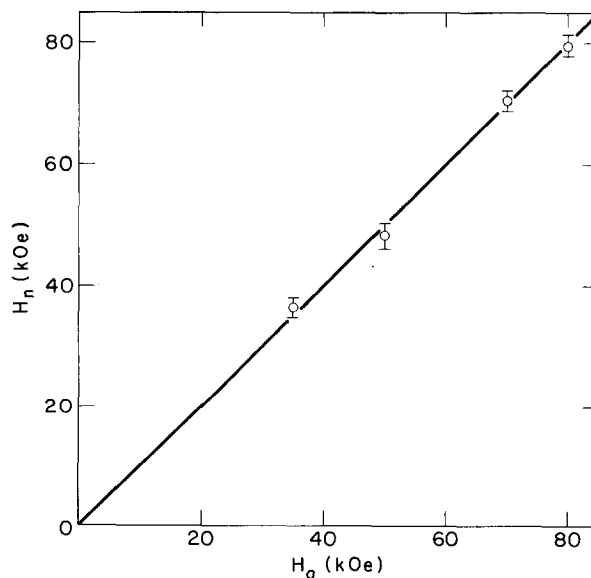


FIG. 7. H_n in (Fe salen)₂O plotted as a function of H_0 .

Karyagin effect and the peak broadening to relaxation effects. At 4.2°K only the $S=0$ state is populated and there is no hyperfine field. At higher T , various states become populated and slow relaxation of the spins leads to a magnetic hyperfine broadening of the electron quadrupole spectrum. Thus the data in zero field and in magnetic fields are consistent with each other, that is, both show effects of a decreasing electronic spin relaxation rate as the temperature increases. Buckley *et al.*⁹ suggest that this decreasing rate is the result of the population of the higher S states. If the clusters relax via intercluster exchange interactions, then the probability of finding neighboring clusters with appropriate spin values for the exchange to take place and conserve spin momentum decreases with increasing T .

CONCLUSION

We have shown that the magnetic field and temperature-dependent magnetic hyperfine interactions in $(\text{Fe salen Cl})_2$ are consistent with a simple exchange model with antiferromagnetic exchange interactions. At higher temperatures (77°K and above) the effective field approximation breaks down because of increasing electronic spin relaxation time. Because of the nature of the powder spectra, we were not able to investigate possible magnetic anisotropy or fine structure splitting in the electronic spectrum. We expect that measurements with single crystals will be very valuable in this regard.

ACKNOWLEDGMENTS

We would like to thank Dr. H. H. Wickman, Dr. W. M. Reiff, and Dr. S. Foner for useful discussions. We are also grateful to Dr. G. Hoy for

making his computer program available to us and for help and advice in making modifications.

- *Work supported in part by the Research Corporation and Grant No. 1014 from the Massachusetts Heart Association.
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