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Magnetically Perturbed Mössbauer Study of the Products Obtained by Rapid Crystallization of a Schiff Base Iron(III) Dimer[*]

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The Schiff base dimer [Fe(salen)Cl]$_2$ as well as products obtained by its rapid crystallization from nitromethane and pyridine have been studied using ordinary and magnetically perturbed Mössbauer spectra. The spectra were determined form room temperature to 4.2° K and in longitudinal fields up to 26 kilo-Gauss. For the dimer, the principal component of the electric field gradient tensor (V_{zz}) is negative with an intermediate value of asymmetry parameter (η) and internal field equal to applied field. The products resulting from rapid *crystallizations of the dimer show positive V_{zz}, approximate axial symmetry and large internal hyperfine fields in accord with their formulation as essentially* monomeric *in nature. Broad perturbed spectra for these samples confirm the presence of a high degree of magnetic anisotropy. A perculiar temperature dependence of the spectral line widths and peak height ratios indicate sample inhomogenity and contamination by the dimer. The magnetically perturbed spectra agree with the results of previous x-ray investigations which show solvent uncoordinated.*

Introduction

In several recent investigations, detailed magnetic[1,2], x-ray[3] and Mössbauer[4,5,6] studies of the Schiff base complex [Fe(salen)Cl]$_2$ have been made and clearly demonstrate its dimeric nature. That is, this system shows intramolecular antiferromagnetism ($J \approx -7.5$ cm^{-1}) with population of a total spin equal to zero ground state at low temperatures. The material resulting from *slow* crystallization of [Fe(salen)Cl]$_2$ from nitromethane also appears to be dimeric.[7] It was through interesting to see under what conditions a primarily monomeric Fe(salen)Cl · xL species (where L is CH_3NO_2 or C_5H_5N) might result and if magnetically perturbed Mössbauer spectra can be used to demonstrate their monomeric nature as well as the type of coordination.

Experimental

The Mössbauer apparatus, superconducting magnet system and programs for data reduction have been described previously[8]. The complexes studied, Fe(salen)Cl · xC_5H_5N and Fe(salen)Cl · xCH_3NO_2 were prepared by rapid crystallization of the dimer [Fe(salen)Cl]$_2$ by evaporation from hot solvent where the dimer gave analytical data in agreement with its formulation. The resulting materials are rather unstable and tend to lose solvent on standing. Hence, after pulverization, they were cooled in liquid nitrogen prior to determination of their Mössbauer spectra in order to avoid decomposition. All spectral data are with respect to National Bureau of Standards 99.99% iron foil for which the internal field is taken as 330 ±3 kilo-Gauss.[9] The microanalyses were determined by Chemalytic's, Inc., 2330 S. Industrial Park Drive, Tempe, Arizona 85281, U.S.A. Analytical data for the complexes are as follows: [Fe(salen)Cl]$_2$–calc(%) (53.73C, 3.95H, 7.83N) found(%) (53.58C, 3.75H, 7.72N); Fe(salen)Cl . 1/3CH_3NO_2–calc(%) (51.87C, 4,01H, 8.65N) found(%) (52.30C, 3.74H, 8.56N); Fe(salen)Cl·C_5H_5N–calc(%) (57.72C, 4.40H, 9.63N) found(%) (57.38C, 4.44H, 11.18N).

Results

Unperturbed Spectra - The unperturbed Mössbauer spectra of Fe(salen)Cl · xC_5H_5N at room temperature and 4.2°K are shown in Figures 1a and 1b. Very similar unperturbed spectra were obtained with nitromethane and hence, the spectra are not included. The appropriate parameters are however, given in the Ta-

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[**] Present Address.

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Table I. Mössbauer Parameters (mm/sec).

Compound	T(°k)	Quadrupole [a] Splitting (ΔE)	Isomer [a] Shift (δ)	Γ_- [b]	Γ_+	$\frac{\Gamma_-{}^b}{\Gamma_+}$	$\frac{A_-}{A_+}$	$\frac{H_-}{H_+}$
[Fe(salen)Cl]$_2$	4.2	1.36	0.51	0.32	0.33	0.99	1.01	1.02
Fe(salen)Cl . XCH$_3$NO$_2$	300	1.34	0.34	0.43	0.72	0.61	1.07	1.77
	195	1.38	0.39	0.45	0.75	0.59	1.04	1.77
	78	1.41	0.42	0.53	0.90	0.57	0.97	1.73
	4.2	1.34	0.44	0.46	0.39	1.20	1.04	0.85
Fe(salen)Cl . XC$_5$H$_5$N	300	1.51	0.39	0.74	1.02	0.75	1.34	1.82
	78	1.56	0.51	0.79	1.30	0.62	1.10	1.79
	$4.2 < T < 10$	1.59	0.51	0.83	0.79	1.04	1.09	1.05
	4.2	1.53	0.51	0.82	0.69	1.18	1.02	0.87

[a] The reproducibility of δ and ΔE is ±0.02 mm/sec for the first complex and ±0.04 mm/sec for the latter two. [b] The reproducibility of Γ's is ±0.03 mm/sec for the first complex and for the latter two, ±0.06 mm/sec. Reproducibility of the ratios is $\approx$ 0.1.

ble. In addition, the unperturbed spectrum of [Fe(salen)Cl]$_2$ at 4.2°K is included (Figure 2a) for later comparison. The shape and spectral parameters for [Fe(salen)Cl]$_2$ are in essential agreement with those found in previous investigations.[1,4,5] Isomer shifts and quadrupole splittings are reasonable for sextet iron (III) in highly distorted environments.

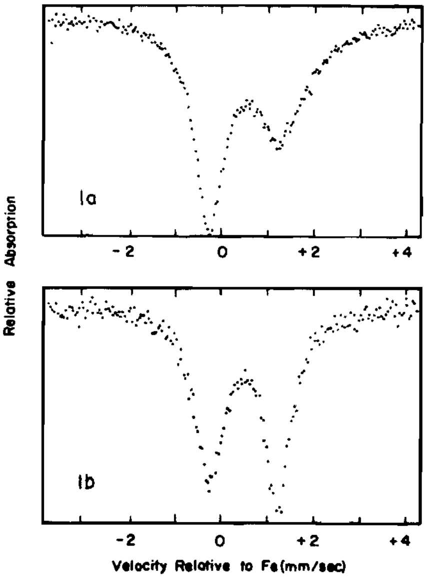

Figure 1a. Mössbauer Spectrum of Fe(salen)Cl · xC$_5$H$_5$N at 300°K. 1b. Mössbauer Spectrum of Fe(salen)Cl · xC$_5$H$_5$N at 4.2°K.

It is clear on inspection of Figure 1 that the peaks of each quadrupole doublet are asymmetric in shape. The same is also found from the material crystallized from nitromethane. The asymmetry is believed due to the superposition of two nearly identical quadrupole doublets, one from monomeric Fe(salen)Cl·xL and the other from [Fe(salen)Cl]$_2$ starting material. Previous[5] work as well as this investigation indicate these two materials have nearly equal isomer shifts and quadrupole splittings and thus, superposition resulting in the observed asymmetric spectra is quite possible. The magnetically perturbed spectra to be discussed subsequently indicate such sample inhomogenity although the principal component appears to be true *monomer*. In any event the effect of such a mixture and spectral superposition on the temperature dependence of peak height and line width ratios is likely to be complex as seen from the Table I. For both the nitromethane and pyridine products line widths of the peaks at negative velocites remain relatively constant as compared to those at positive velocity which undergo an overall large decrease although they curiously have largest values of Γ_+ near 78°K. This latter observation is probably related to the highly inhomogeneous and anisotropic behavior of such materials, as noted in previous x-ray and susceptibility anisotropy studies,[10] as well as contamination by the dimer. Ignoring the anomalous behavior of Γ_+ in the region of 78°K the overall temperature dependence of Γ_+ indicates depopulation of slowly relaxing Kramers doublets ($m_s = \pm 3/2, \pm 5/2$) as observed in

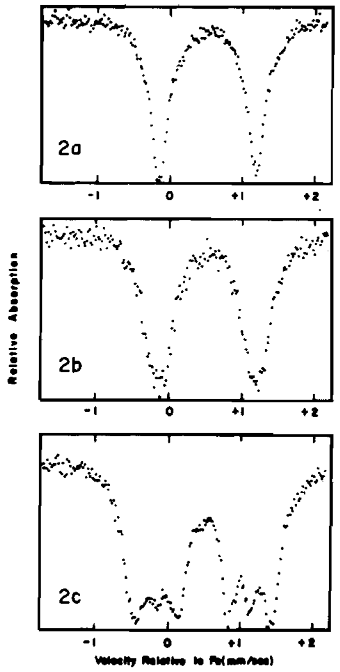

Figure 2a. Mössbauer Spectrum of [Fe(salen)Cl]$_2$ at 4.2°K. 2b. Magnetically Perturbed Mössbauer Spectrum of [Fe(salen)Cl$_2$], $H_{\text{applied}} \approx$ 9 kG. 2c. Magnetically Perturbed Mössbauer Spectrum of [Fe(Salen)Cl]$_2$, $H_{\text{applied}} \approx$ 27 kG.

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(10) M. Gerloch and F.E. Mabbs, *J. Chem. Soc. A*, 1598 (1967).

ferric hemin by Wertheim and explained by Blume.[11] Thi implies that the presumed monomer has a *positive* zero field splitting parameter, D and the more rapidly relaxing $m_s = \pm 1/2$ Kramers doublet is being populated at low temperatures. It should be pointed out that the area ratios at 4.2°K are close to unity thus ruling out Karyagin asymmetry or significant residual sample orientation as causes of the peak height and shape asymmetry.

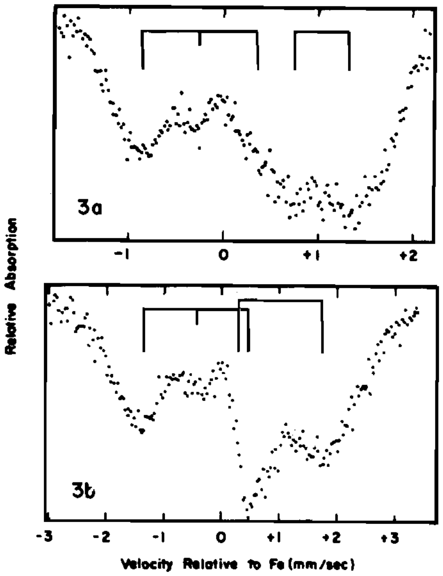

Figure 3a. Magnetically Perturbed Mössbauer Spectrum of Fe(salen)Cl · xCH$_3$NO$_2$, $H_{applied} \approx 5.4$ kG. 3b. Magnetically Perturbed Mössbauer Spectrum of Fe(salen)Cl · xCH$_3$NO$_2$, $H_{applied} = 10$ kG.

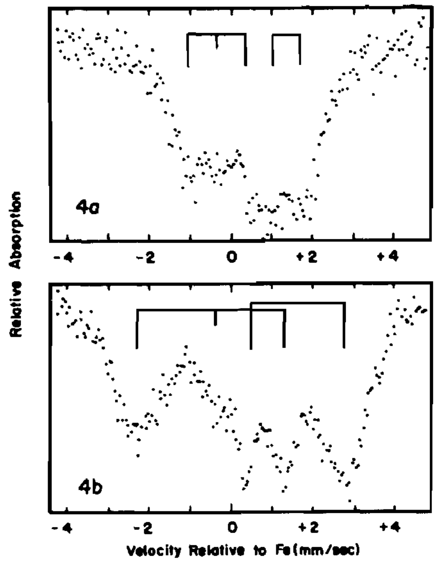

Figure 4a. Magnetically Perturbed Mössbauer Spectrum of Fe(salen)Cl · xC$_5$H$_5$N, $H_{applied} = 4$ kG. 4b. Magnetically Perturbed Mössbauer Spectrum of Fe(salen)Cl · xC$_5$H$_5$N, $H_{applied} = 8.8$ kG.

Perturbed Spectra - The magnetically perturbed spectra will be seen to shed much more light on the nature of the products of crystallization of the dimer. These spectra are shown for the materials obtained from nitromethane (Figure 3) and pyridine (Figures 4 and 5) for various values of applied magnetic field. Several important features of these spectra are to be noted. First of all, there appears to be an apparent triplet at negative velocity and a highly broadened doublet at positive velocity as indicated by the stick diagrams. Further, especially in Fig. 3a and 3b, there is greater initial resolution with increasing field for the absorption intensity at negative velocity as compared to that at positive. In the case of iron-57, the foregoing observations imply the principal component of the electric field gradient tensor positive.[12] The overall shape of the spectra, i.e. a broadened doublet and a triplet with lower intesity central absorption indicates a small asymmetry parameter. The spectrum of Figure 5 is that of a second preparation of Fe(salen)Cl·xC$_5$H$_5$N at slightly larger applied field (4.5 *vs.* 4 kilo-Gauss for Figure 4a) and lower velocity modulus thus resulting in better resolution of the above features.

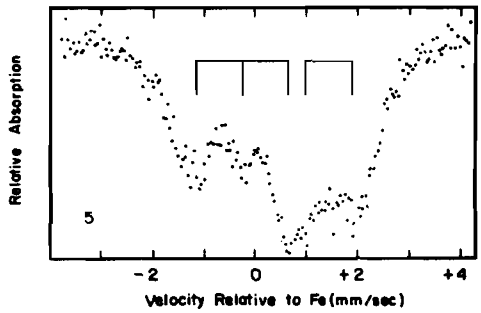

Figure 5. Magnetically Perturbed Mössbauer Spectrum of Fe(salen)Cl · xC$_5$H$_5$N, $H_{applied} = 4.5$ kG.

All of the perturbed spectra are highly broadened. This effect is most likely related to the magnetic anisotropy observed in these materials by Gerloch and Mabbs.[10] It is significant that these authors attribute the anisotropy to a five coordinate as opposed to a six coordinate product for, as will be seen, the perturbed spectra of this work are also most consitsent with the five coordinate product. All samples were ground to some extent so as to make them as «isotropic» as possible. However, these materials cannot be highly pulverized as this results in decomposition. Thus the problems of magnetic anisotropy and residual sample orientation cannot be completely avoided. Some of the broadening may also be attributed to the presence of small amounts of the true dimer.

The magnetically perturbed spectra of the dimer are shown in Figures 2b and 2c. An external field of 9 kilo-Gauss just broadens the symmetric unperturbed spectrum of Figure 2a. It is useful to compare the spectra of Figures 3b and 4b to that observed at a comparable aplied field for the dimer (Figure 2b).

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(11) M. Blume, *Phys. Rev. Letters*, *18*, 305 (1967).

(12) R.L. Collins and J.C. Travis, *Mössbauer Effect Methodology*, *3*, 123 (1967).

The significant differences in these spectra will be seen consistent with the formulation of the solvated materials as primarily *monomeric*. For the dimer, increasing the magnetic field results in resolution to a well-defined, narrow lined triplet at positive velocity and a broader triplet at negative. These observations correspond to V_{zz} negative and an intermediate value of η. Since completing this investigation, the author has learned that Buckley, et al.[13] have also determined magnetically perturbed Mössbauer spectra of the dimer and at even larger external fields $\approx$ 90 kilo-Gauss. Their results agree with those found here, i.e. V_{zz} is negative.

Some final points of importance to later discussion are related to the magnitudes of observed effective fields vs applied. The average effective field may be conveniently estimated from the triplet splittings of the perturbed spectra.[12] In this manner, for $[Fe(salen)Cl]_2$ it is found that the applied and observed effective fields are nearly equal i.e. 27 kilo-Gauss applied vs 23 kilo-Gauss observed. Further, the ratio of the triplet splitting patterns (Figure 2c) is unity. Both of these observations are expected for a material behaving as an isotropic diamagnet at low temperature. The intramolecular antiferomagnetic coupling of the dimer would result in jiust this kind of behavior at 4.2°K at which a total spin equal to zero ground state would be almost exclusively populated . On the other hand, in the case of the materials resulting from the crystallizations larger hyperfine fields are observed in all cases and from the application of relatively small fields. For example in the case of $Fe(salen)Cl \cdot xC_5H_5N$ Figure 5, $H_{applied} = 4.5$ kilo-Gauss, $H_{effective} \approx 72$ kilo-Gauss; Figure 4b, $H_{appled} = 8.8$ kilo-Gauss, $H_{effective} \approx 140$ kilo-Gauss.

Discussion

Two simple possibilities are apparent for the coordination of a monomeric Fe(salen)Cl obtained by crystallization from CH_3NO_2 or C_5H_5N. One is distorted octahedral monomer, i.e. Fe(salen)Cl with solvent occupying the remaining axial coordination position. The other is a true five coordinate species with coordination completed by the two imine nitrogens and two anionic oxygens of the Schiff base and an axial chlorine. In the case of high spin iron(III), the sign of V_{zz} will depend primarily on ligand charge distribution as opposed to valence shell orbital occupation important to low spin iron(III). Thus in the latter five coordinate system, the approximate plane of strong sigma bonding provided by the ligand $salen^{2-}$ relative to a single axial Fe–Cl bond is expected to result in V_{zz} *positive*. This is the observation of the present study.

The formation of the hexacoordinate dimer $Fe(salen)Cl_2$ involves rather weak axial coordination through an Fe(salen)Cl group sharing one of its oxygens with the other group and *vice versa*. The weakness of this axial coordination in the dimer is suggested by the long bridge Fe–O bonds ($\approx$2.18 Å) versus 1.90 and 1.98 Å for the in plane Fe–O bonds.[3] Even so, the sign of V_{zz} changes from positive in Fe(salen)Cl. CH_3NO_2 and $Fe(salen)Cl \cdot xC_5H_5N$ to negative in $[Fe(salen)Cl]_2$. In view of this, one might also expect V_{zz} negative for a six coordinate monomer with significant axial coordination by a basic solvent such as pyridine. It thus appears that the solvated materials of this investigation are five coordinate monomers with this species favored under conditions of *rapid* crystallization of the dimer. The fact that the products are monomeric is further supported by the following considerations. Such monomers would be expected to show loss of magnetic exchange as indicated by previous susceptibility studies.[10] In relation to the present study, in the five coordinate monomers such loss of exchange should result in perturbed spectra significantly different from those of the true dimer. In particular, large internal hyperfine fields will be observed in the former and internal fields nearly equal to the applied in the latter. This is seen to be the case by comparison of the perturbed spectra. In conclusion it is seen that perturbed Mössbauer spectra are a useful and simple probe in the determination of the presence or absence of dimerization in iron(III) complexes.

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