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MÖSSBAUER AND ESR STUDIES IN LOW SYMMETRY IRON COMPLEXES (*)

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Résumé. — Quelques complexes de transport de fer naturels ainsi que quelques modèles de complexes minéraux ont fourni des résultats Mössbauer et RPE qui sont bien expliqués par un hamiltonien de spin électronique de symétrie rhomboïdale et non de symétrie trigonale comme le suggèrent les déterminations structurelles par rayons X. Un terme d'ordre 4 est important dans le lissage des résultats expérimentaux de RPE et de spectroscopie Mössbauer. Les paramètres de l'hamiltonien de spin sont déterminés à partir des données expérimentales pour la mycobactine P, l'entérobactine et quelques hydroxamates minéraux.

Abstract. — Some naturally occurring iron transport complexes and some inorganic model complexes have given Mössbauer and ESR results which are well explained by a spin Hamiltonian model for the electronic state with rhombic symmetry, and not the trigonal symmetry suggested by X-ray structure determinations. A fourth order term is important in fitting the experimental ESR and ME results. The spin Hamiltonian parameters are determined from the experimental data for mycobactin P, enterobactin and some inorganic hydroxamates.

1. Introduction. — Several high spin ferric complexes have been found recently [1-5] to exhibit an unusual isotropic ESR signal at $g = 4.3$. To a large extent, these iron complexes are of biological origin and have many similar properties. The iron is usually bound by three bidentate ligands in which two oxygen atoms are the actual near neighbors contributed by each ligand. The local molecular arrangement is that of a three bladed propeller which may or may not have a three fold symmetry axis as shown in figure 1. In each of these complex ions there is an extremely high affinity for ferric iron with a binding constant of about $10^{16}$, but a much weaker attraction for ferrous iron. The great affinity for ferric iron is used by these naturally occurring complexes in the accumulation of iron for the living organism. The iron binding complexes which occur naturally include the ferrichromes, the ferrioxamines, the mycobactins and the transferrins. These molecules have different compositions corresponding to the different organisms, but in each case the ferric ion experiences a low symmetry environment.

We have done Mössbauer experiments on these complexes and on some inorganic model complexes, using the paramagnetic hyperfine structure (PHS) in the spectra to obtain information about the electronic state of the iron. This is complementary to the information resulting from ESR measurements.

Mycobactin P is a growth factor for mycobacterium Phlei and several other mycobacteria and has been extensively studied by Snow [6] and Ratledge [7]. Enterobactin is similarly a growth factor for several enteric bacteria such as E. coli and has been studied by Neilands and coworkers [8], and by O'Brien et al. [3].

Many of these iron complexing agents such as ferrichrome A [9] and deferoxamine [10] have the iron bound by three hydroxamic acid residues. Thus it is appropriate to study some of the inorganic hydroxamate complexes to facilitate an understanding of the natural compounds.

2. Sample preparation and experimental details. — The sample of iron free mycobactin P($C_{47}H_{72}O_{10}N_{4}Fe$) with molecular weight of 922, was the gift of Dr. G. A. Snow. Isotopically enriched ($^{57}$Fe) iron in the form of...
of a methanol solution of $^{57}$FeCl₃ was added to a chloroform solution of iron free mycobactin P. An excess of mycobactin P was used to ensure total chelation of the available iron. Mycobactin P is slightly soluble in methanol and this solution was frozen into a glass and used as a Mössbauer absorber. Powder samples of mycobactin P were prepared by simply evaporating the methanol from the sample.

Chemically pure benzhydroxamic acid and nicotinyl hydroxamic acid were obtained from various commercial suppliers. In each case, an excess of the hydroxamic acid was dissolved in methanol and added to a methanol solution of $^{57}$FeCl₃ forming deep purple solutions. These were frozen in liquid nitrogen where the methanol forms a glass and used as Mössbauer absorbers. The frozen solutions proved to give better resolved paramagnetic hyperfine structure (PHS) in the Mössbauer spectrum since the paramagnetic centers were well separated eliminating the spin-spin relaxation effects in the spectrum in contrast to the powder absorbers.

Enterobactin (MW 669) was obtained from Professor J. B. Neilands and was combined with $^{57}$FeCl₃ in a methanol solution which was also frozen and used as a Mössbauer absorber. A two-fold excess of enterobactin assures that all the available iron will be complexed.

The Mössbauer data were taken on a constant acceleration spectrometer of the usual design using a multichannel analyzer in time mode operation. The spectrometer was calibrated using an iron foil with zero velocity set at the centroid of the iron foil spectrum.

3. The electronic model. — The $^{57}$S state of the ferric ion in these complexes can be successfully described by the following spin Hamiltonian with $S = 5/2$.

$$\mathcal{H}_e = D[S_x^2 + \lambda(S_y^2 - S_z^2)] + \mu(S_x^4 + S_y^4 + S_z^4)/6 + 2 \beta H \cdot S.$$  

If the electronic state has rhombic symmetry, then the $x, y, z$ axes coincide with the $\xi, \eta, \zeta$ axes. The coordinates $\xi, \eta, \zeta$ are usually identified with the central ion-ligand axes of an octahedral complex. If there is trigonal symmetry in the electronic state, then the $z$-axis is in the $< 111 >$ direction relative to the $\xi, \eta, \zeta$ axes. It is usually expected that the spin Hamiltonian will have the same symmetry and axis system as the molecular coordination of the iron site.

When the electronic relaxation rate is showed to the point at which paramagnetic hyperfine structure can be resolved at low temperature and concentrations, then the features of the magnetically split spectrum can be compared to an electronic model. The Mössbauer data are compared to computer simulations of spectra generated from the full spin Hamiltonian $\mathcal{H} = \mathcal{H}_e + \mathcal{H}_a$, where

$$\mathcal{H}_a = A \cdot S + P[I_x^2 + \lambda(I_z^2 - I_y^2)] - g_\alpha \beta_\alpha H \cdot I.$$  

The simulated Mössbauer spectra depend on five adjustable parameters ($D$, $\lambda$, $\mu$, $A$ and $P$) which determine the position and intensity of each absorption line. It is sometimes possible to determine $P$ independently if the magnetic interaction is washed out due to fast relaxation effects. The magnetic hyperfine interaction $A$ scales the magnetic splitting of the spectrum. The symmetry of the spin Hamiltonian is determined by the zero field splitting parameters $\lambda$ and $\mu$, and these parameters also determine the profile of the Mössbauer spectrum. Since the quadratic part of the zero field splitting and the electric field gradient have the same origin we can constrain them to the same axis system and also constrain the EFG asymmetry parameter by $\eta = 3 \lambda$. The parameter $D$ scales the energy separations of the three Kramers doublets in the absence of an applied field and this can be measured by observing the contributions of each Kramers doublet to the composite spectrum. Each contribution, of course, will be weighted by the appropriate Boltzmann factor.

When frozen solution or powder absorbers are used, it is necessary to simulate the random orientations of the molecular axis relative to the gamma beam and the applied magnetic field. This can be done easily in a step-wise procedure by computing a spectrum for each of many evenly distributed directions of the gamma beam and applied field and then adding the spectra from each direction with equal weights to simulate the random orientations in the absorber. It is this angular averaging which makes it possible to determine the electronic state from the profile of the spectrum.

4. Experimental results and discussion. — Mössbauer experiments were done on a powder sample of $^{57}$Fe complexed to mycobactin P at 4.2 K. Some magnetic hyperfine structure was observed, but the magnetically split resonance lines were quite broad in addition to the broad central line, indicating considerable spin relaxation. When the mycobactin P was dissolved in methanol, the paramagnetic spins were well separated, reducing the spin-spin relaxation and allowing well resolved PHS to be observed in the Mössbauer spectrum as seen in figure 2. The signal to noise ratio is poor because it was very difficult to dissolve appreciable amounts of mycobactin P in methanol and impossible to dissolve it in anything else except chloroform. The solid curves in figure 2 are computer simulations based on the spin Hamiltonian parameters which originally gave a satisfactory fit with $D = 0.34$ cm$^{-1}$, $\lambda = 0.27$, and $\mu = 0$ in which the quartic term was ignored. However, when an ESR spectrum was generated with these parameters (Fig. 2a) a pronounced splitting is predicted in the ESR spectrum at $g = 4.3$. When the ESR experiment was done (Fig. 3a) on mycobactin P, a narrow unsplit ESR resonance was observed at $g = 4.3$. This contradiction of experimental results on the same sample was
resolved by the inclusion of the fourth order term in the spin Hamiltonian. The set of parameters given in Table I (including $\mu = -0.27$) gives reasonably good agreement with the results of both experiments. The fact that $\lambda = 0.46 > 1/3$ merely implies that the principal axis of distortion is in the $y$-direction and not the $z$-direction [11].

Mössbauer experiments were then done on the benzohydroxamate complex of ferric iron in a frozen methanol solution. In this case the complex was quite soluble in methanol so that the optimum amount of $^{57}\text{Fe}$ could be placed in the absorber and therefore the experimental data are of much better quality as seen in Figure 4. The spectra are qualitatively similar to the mycobactin P spectra and give confidence to the electronic model used to simulate the spectrum. Experiments on the ferric nicotinyl hydroxamate exhibit the same spectral profile that characterizes these electronic states with less than axial symmetry.

Other experiments on $^{57}\text{Fe}$ complexed to enterobactin show unusually sharp resonance lines at liquid helium temperatures and these data are well represented by a calculation (the solid line in Fig. 5). Good agreement between calculation and experiment is achieved only when the fourth order term with coefficient $\mu$ is considered.

In each of the cases considered above, the Mössbauer and ESR data can be represented only by an electronic model with rhombic symmetry, whereas X-ray and other techniques have indicated the iron to be in a site of trigonal symmetry. It is probable that the electrons are more sensitive to small departures from highly symmetric ligand fields.
In trigonal symmetry, one would have $\lambda = 0$ and $z$ in the $<111>$ direction relative to $\zeta, \eta, \zeta$. There is no way to obtain an isotropic $g = 4.3$ from this spin Hamiltonian under these circumstances. Nevertheless, Zalkin et al. [12] have done the X-ray structure of ferrichrome A which indicates trigonal symmetry while Wickman et al. [13] observe an isotropic $g = 4.3$, and Mössbauer data [14] which favors rhombic symmetry. Similarly, enterobactin is thought to have trigonal symmetry from NMR studies [8], but ESR results [3] with $g = 4.3$ and Mössbauer experiments for enterobactin (Fig. 5) also favor the model with rhombic symmetry. Finally, there have been X-ray studies of the benzohydroxamate complex of Fe$^{3+}$ which again show trigonal symmetry [15], but again the Mössbauer experiment (Fig. 4) indicates rhombic symmetry in the electronic state. The spin Hamiltonian parameters found from Mössbauer experiments for these and other ferric complexes are given in Table I. Not all entries in this table were analyzed with the consideration of the fourth order term, but it is safe to say that none of those listed gives evidence for trigonal symmetry. It is probable that a non-negligible $\mu$ will be found in those complexes where it was previously ignored. When the $g = 30/7$ resonance was explained by the «rhombic» spin Hamiltonian ($\lambda = 1/3$), the fourth order term was neglected ($\mu = 0$). If $\mu = 0$, it doesn’t matter whether the principle distortion axis is in the $<111>$ (trigonal) or $<001>$ (rhombic) direction. However, it can be easily shown that the condition of $\lambda = 1/3$ and $\mu = 0$ is a special case of the more general relation $\mu = 0.75 (1 - 3 \lambda)$ which guarantees that there will be an isotropic $g = 30/7$ if the rhombic spin Hamiltonian is used. In trigonal symmetry ($\lambda = 0$), the demand of an isotropic $g$ in one of the Kramers doublets leads to the relation ship that $\mu = -9$ and $g = 10/3$ in contradiction to the experimental ESR results. Likewise the calculated Mössbauer spectra for trigonal symmetry ($\lambda = 0$; $\mu \neq 0$) show marked differences from the rhombic model and from experiment, even when the same parameters ($D, \lambda$ and $\mu$) are used.

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