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ESR STUDIES OF ELECTRON IRRADIATED $K_3Ir^{III}(CN)_6$ IN KCl SINGLE CRYSTALSI - LIGAND HYPERFINE STRUCTURE IN $Ir^{II}(CN)_6$ SPECIES*

N.V.Vugman, R.P.A.Muniz and J.Danon
 CENTRO BRASILEIRO DE PESQUISAS FÍSICAS
 Rio de Janeiro, Brazil

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INTRODUCTION

Divalent iridium has been reported to occur in some complexes but their existence has not been unequivocally established⁽¹⁾. The EPR spectrum of Ir(IV), a d^5 low spin system, has been investigated⁽²⁾ ⁽³⁾ but to our knowledge no work in Ir(II) has been reported up to this date.

Danon et al.⁽⁴⁾,⁽⁵⁾ succeeded in producing paramagnetic species of d^7 configuration irradiating with electrons diamagnetic d^6 low spin complexes. Following this line we have studied⁽⁶⁾ reduced $K_3Rh(CN)_6$ in a KCl lattice and now we have irradiated $K_3Ir(CN)_6$, an octahedral complex of Ir(III), with a ground-state configuration t_{2g}^6 , expecting that under favorable conditions, reduction effects be produced by electron trapping as reported in Refs. 4,5 and 6.

Instead of using $K_3Ir(CN)_6$ single crystals, which have two non-equivalent positions per unit cell and are not easy to obtain, the Ir(III) complex was diluted in a KCl lattice, as has been done⁽⁶⁾ for $K_3Rh(CN)_6$. The KCl cubic lattice has appropriate symmetry and spacing to accommodate the $Ir(CN)_6^{3-}$ ion which enters substitutionally in the lattice replacing a $|KCl_6|^{5-}$ group. Two positive ion vacancies must be formed in order to keep

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the neutrality. Very conveniently the V_k centers which are formed when alkali halides are irradiated disappear at room temperature. F-centers are not observed by us.

EXPERIMENTAL

The single crystals were grown by slow evaporation from saturated aqueous solution of KCl to which $K_3Ir(CN)_6$ was added in molar proportion of 0.5%. They were of about 2-mm edge and the best ones were chosen by visual inspection.

Irradiation was performed both at room temperature and $77^\circ K$. The samples irradiated at $77^\circ K$ were brought to room temperature in order to eliminate the undesired signal from V_k centers. All samples were irradiated for 20 sec with 2-MeV electrons at a current of $5\mu A$.

The spectra were obtained with a Varian 4500 X-band spectrometer all at liquid-nitrogen temperature. Q-band measurements were performed to obtain angular variation and to check on the coherence of the species assignments.

For examination in the spectrometer the crystals were mounted on a cold-finger cryostat for ESR in such a way that they could be rotated around one of the principal axes. When any of the other two axes of the crystal is parallel to the applied magnetic field, one obtains, in one

scanning, the three principal features of the spectrum. This propiciates a check on the symmetry of the species under study. The spectra could be observed at room temperature, being better resolved however, at liquid nitrogen temperature. The fitting of the ligand hyperfine spectra has been done with a Varian Spectro-System Data 620-I, with a program which treats the spectrum only in first order, neglecting quadrupole interactions, assuming a gaussian line shape.

RESULTS

The spectra observed in the irradiated samples reveal the presence of two paramagnetic species (Fig.1) which we label A and B. Species A has orthorhombic symmetry with $g_z=1.9665$, $g_x=2.2110$ and $g_y=2.2026$. Angular variation studies show that these g -values have their principal axes oriented along the crystalline axes of KCl and follow the familiar $\cos^2 \theta$ law. Species B is isotropic with $g \approx 2.006$. All species form either when the crystals are irradiated at room temperature and 77°K but the signal corresponding to species B is strongly enhanced when the irradiation is performed at room temperature. This work is mainly concerned with species A. The satellite lines which flank the spectrum assigned to species A seem to be due to dipolar interaction.

The perpendicular part of the spectrum ($g=g_x$ or $g=g_y$) consists mainly of two sets of four triplets. Each set is attributed to the interaction with one of the two isotopes of iridium. Iridium occurs in the form of two

stable isotopes, ^{191}Ir and ^{193}Ir , both having nuclear spin $I=3/2$, magnetic moments⁽⁷⁾ of $+(0.1453 \pm 0.0006)\beta_N$ and $+(0.1583 \pm 0.0006)\beta_N$, natural abundances of 38.5% and 61.5%, respectively. The triplets are due to the interaction of the unpaired electron with a ^{14}N which has a nuclear spin $I=1$ and a magnetic moment of $+0.40358\beta_N$. To confirm this assignment we synthesized a $\text{K}_3\text{Ir}(\text{CN})_6$ sample with 95% ^{15}N which has a nuclear spin $I=1/2$ and a nuclear magnetic moment of $-0.28304\beta_N$. The ESR spectrum of $\text{K}_3\text{Ir}(\text{C}^{15}\text{N})_6$ in KCl, irradiated under the same conditions, is almost equal to the spectra of irradiated $\text{K}_3\text{Ir}(\text{C}^{14}\text{N})_6$ in KCl, with the only difference that the triplets become doublets (Fig.2) with a splitting which is 1.403 times the former splitting, as expected for this isotopic substitution⁽⁸⁾. This result strongly suggests that one cyanide of the complex is not equivalent to the others. This cyanide is an axial cyanide since it defines the principal symmetry axis of the complex.

In the parallel feature of the spectrum the iridium quartet is further split by a super-hyperfine structure which is attributed to the interaction of the unpaired electron with the nitrogens of the ligands. This super-hyperfine structure is better resolved in the samples with ^{15}N and can be fairly well accounted for if we assume four equivalent cyanides and one non-equivalent (Fig.3). Obviously these four equivalent cyanides must be the equatorial ones. The spectra are almost first order since there is no quadrupolar interaction with ^{15}N , a spin 1/2 nucleus. The ligand spin Hamiltonian for this case, neglecting nuclear Zeeman coupling, can be written in the following way:

$$\mathcal{H} = \sum_{i=1}^4 \tilde{S} \cdot \tilde{A}^{eq} \cdot \tilde{I}_i + \tilde{S} \cdot \tilde{A}^{ax} \cdot \tilde{I}_5$$

The summation extends to the four equatorial ^{15}N nuclei and I_5 is the nuclear spin of the axial ^{15}N .

The agreement with the experimental data is much better in this case than if we assume five equivalent nitrogens and one non-equivalent or if we assume four equivalent nitrogens, one non-equivalent and the sixth also non-equivalent. This result indicates strongly that species A is a penta and not an hexacoordinated species.

The hyperfine tensor of the axial cyanide has axial symmetry about the C_4 axis of the complex. The A_x and A_y values of the hyperfine tensor of the equatorial cyanides can only be estimated because of the precision of our measurement. This tensor is referred to a local cyanide coordinate system with x along Ir-C-N and seems to have axial symmetry about the y axis, located perpendicular to the equatorial plane. The best $A_x=A_z$ values seems to be $0.26 \times 10^{-4} \text{ cm}^{-1}$, without dipolar corrections.

The values of the ligand hyperfine parameters corrected for dipolar interactions, and the ligand orbital spin densities are given in Table I. The tensor of dipolar interaction has axial symmetry about Ir-C-N and has a value $A_d=0.06 \times 10^{-4} \text{ cm}^{-1}$, supposing a point dipole model⁽⁹⁾ with $\frac{3A}{r^3}$ for the Ir-N distance. The sign of the parameters are chosen in analogy with reference 10.

DISCUSSION

g values

Since the difference between the g_x and g_y values is very small, we can assume an axial symmetry with $g_{\perp} = \frac{g_x^2 + g_y^2}{2}^{1/2} = 2.2068$ and $g_{\parallel} = g_z$.

The symmetry group of the molecule is then C_{4v} and the g values fit the following equations⁽¹¹⁾:

$$g_{\parallel} = 2.0023 \cos 2\gamma + 2\kappa \cdot \text{sen}^2 \gamma$$

$$g_{\perp} = 2.0023 \cos^2 \gamma + \sqrt{6} \kappa \text{sen} 2\gamma$$

with the orbital reduction factor $\kappa = 0.438$ and $\gamma = 6.12^\circ$.

These equations have been derived for a d^7 low spin system, with a 2A_1 ground configuration which has an unpaired electron in a d_z^2 orbital, mixed via spin-orbit coupling with a 2E excited configuration. The angle γ , in the formulae above, is such that

$$\text{tg } 2\gamma = -\frac{\sqrt{6} y}{1 - \frac{y}{2}}, \quad \text{where } y = \frac{\lambda}{\Delta},$$

being λ the spin-orbit coupling constant for Ir(II) and Δ the energy

stable isotopes, ^{191}Ir and ^{193}Ir , both having nuclear spin $I=3/2$, magnetic moments⁽⁷⁾ of $+(0.1453 \pm 0.0006)\beta_N$ and $+(0.1583 \pm 0.0006)\beta_N$, natural abundances of 38.5% and 61.5%, respectively. The triplets are due to the interaction of the unpaired electron with a ^{14}N which has a nuclear spin $I=1$ and a magnetic moment of $+0.40358\beta_N$. To confirm this assignment we synthesized a $\text{K}_3\text{Ir}(\text{CN})_6$ sample with 95% ^{15}N which has a nuclear spin $I=1/2$ and a nuclear magnetic moment of $-0.28304\beta_N$. The ESR spectrum of $\text{K}_3\text{Ir}(\text{C}^{15}\text{N})_6$ in KCl, irradiated under the same conditions, is almost equal to the spectra of irradiated $\text{K}_3\text{Ir}(\text{C}^{14}\text{N})_6$ in KCl, with the only difference that the triplets become doublets (Fig.2) with a splitting which is 1.403 times the former splitting, as expected for this isotopic substitution⁽⁸⁾. This result strongly suggests that one cyanide of the complex is not equivalent to the others. This cyanide is an axial cyanide since it defines the principal symmetry axis of the complex.

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$$\mathcal{H} = \sum_{i=1}^4 \tilde{S} \cdot \tilde{A}^{eq} \cdot \tilde{I}_i + \tilde{S} \cdot \tilde{A}^{ax} \cdot \tilde{I}_5$$

It is remarkable that in $[\text{Ir}(\text{CN})_5]^{3-}$ the hyperfine tensor values for the equatorial nitrogens are almost identical to Hayes' values⁽¹⁰⁾ for $[\text{Mo}(\text{CN})_5\text{NO}]^{3-}$ where the bonding with the equatorial cyanides is of π -character. The d_z^2 unpaired electron could only have a π -bonding with the equatorial cyanides in $[\text{Ir}(\text{CN})_5]^{3-}$ if the metal is not on the equatorial plane: in this case there is a non-null overlap between the d_z^2 metal orbital and the π equatorial orbitals. Evidences for this kind of structure has been found⁽¹²⁾ for $[\text{Ni}(\text{CN})_5]^{3-}$, a square pyramidal complex which has the nickel ion located above the equatorial plane the Ni-C-N (equatorial) bonding forming an angle of about 10° with the equatorial plane. This also confirms our pentacoordination assignement.

Obviously, the bonding between the d_z^2 orbital and the axial nitrogen must be a σ bonding. It is also remarkable that the f_p value for the axial nitrogen are very close to that for the equatorial nitrogens, suggesting, in a first glance, that the importance of the σ or π character of the metal-ligand bonding does not influences so much the ligand f_p value. The observed difference between the axial and equatorial cyanides could be due to the fact that the axial cyanide is σ -bonded to the metal.

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TABLE I

LIGAND HYPERFINE PARAMETERS (10^{-4} cm^{-1}) AND ORBITAL
SPIN DENSITIES

	A_x	A_y	A_z	f_s	f_p	
C ^{14}N axial	+ 3.8	+ 3.8	+ 6.2	0.009	0.050	
C ^{14}N equat.	- 0.14	+ 2.31	- 0.32	0.0012	0.053	b, c

a - In coordinate system with z along C_4 axis.

b - The f_p value is calculated assuming $A_z = -0.23 \times 10^{-4} \text{ cm}^{-1}$, the
average value between A_x and A_y .

c - Positive sign combination for A_x , A_y and A_z leads to f_s and f_p
values of 0.0019 and 0.042, respectively.

CAPTIONS TO THE FIGURES

FIG. 1: Spectrum of single crystals of KCl with 0.5% $K_3Ir(CN)_6$, irradiated at $77^\circ K$, recorded at $77^\circ K$, Q-band, taken with the magnetic field parallel to one of the crystalline main axes. To the left the g_x and g_y features of species A and B. The g_z features are superimposed on the extreme right. Species C is isotopic.

FIG. 2: Isotopic substitution experiment showing the interaction with the axial cyanide. This spectrum is part of the $g = g_x$ spectrum of species A. The double lines are due to iridium isotopes.

a) Samples with 99% ^{14}N

b) Samples with 95% ^{15}N

FIG. 3: Ligand hyperfine interaction in the $g = g_z$ spectrum of species A.

a) Reconstitution made assuming interaction with four equivalent ^{15}N and one non-equivalent. The lines are a weighted sum for the two iridium isotopes. The line width is assumed to be 1.7 gauss.

b) Recorded spectrum at $77^\circ K$, showing the first line of the iridium quartet.

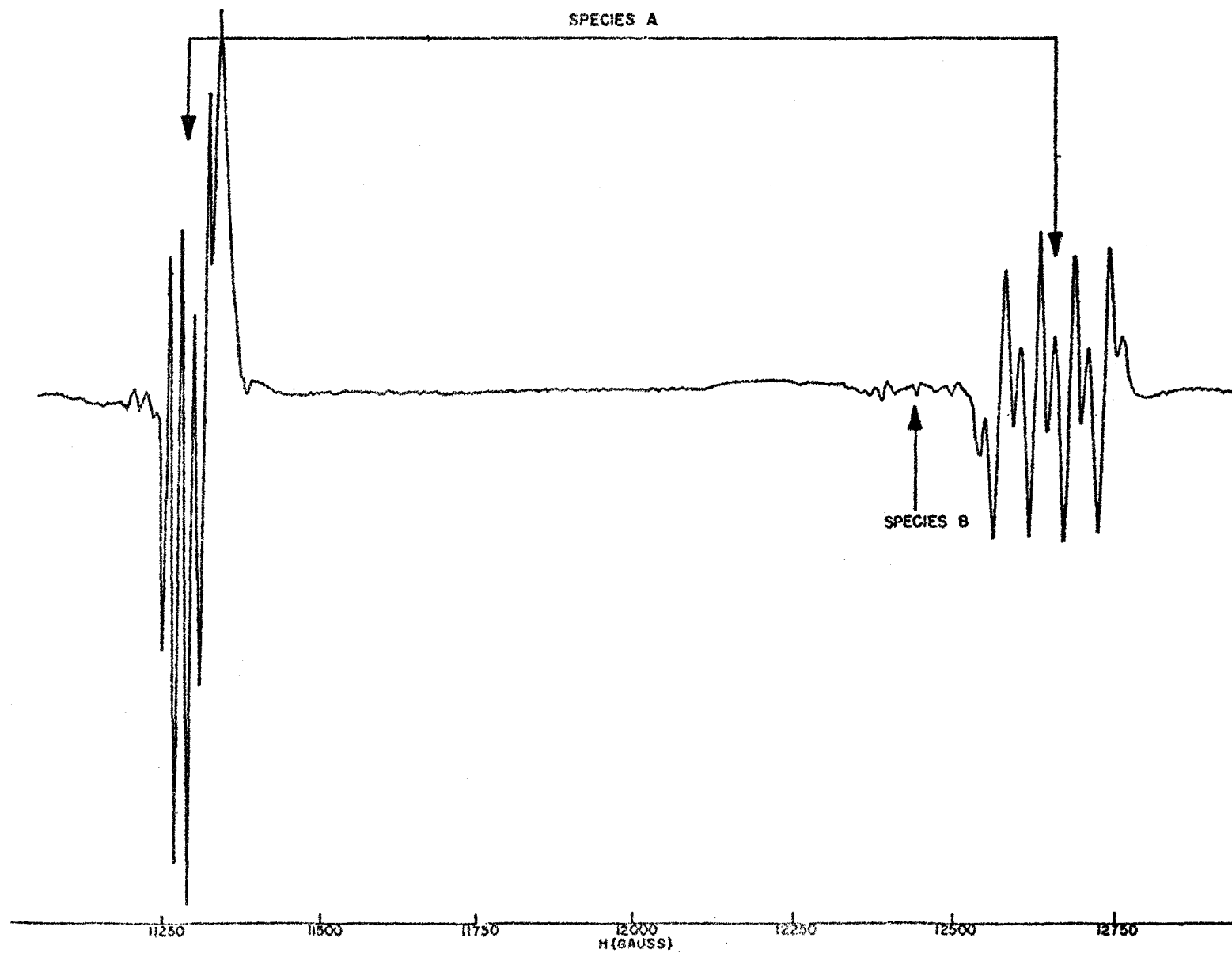


FIG. 1

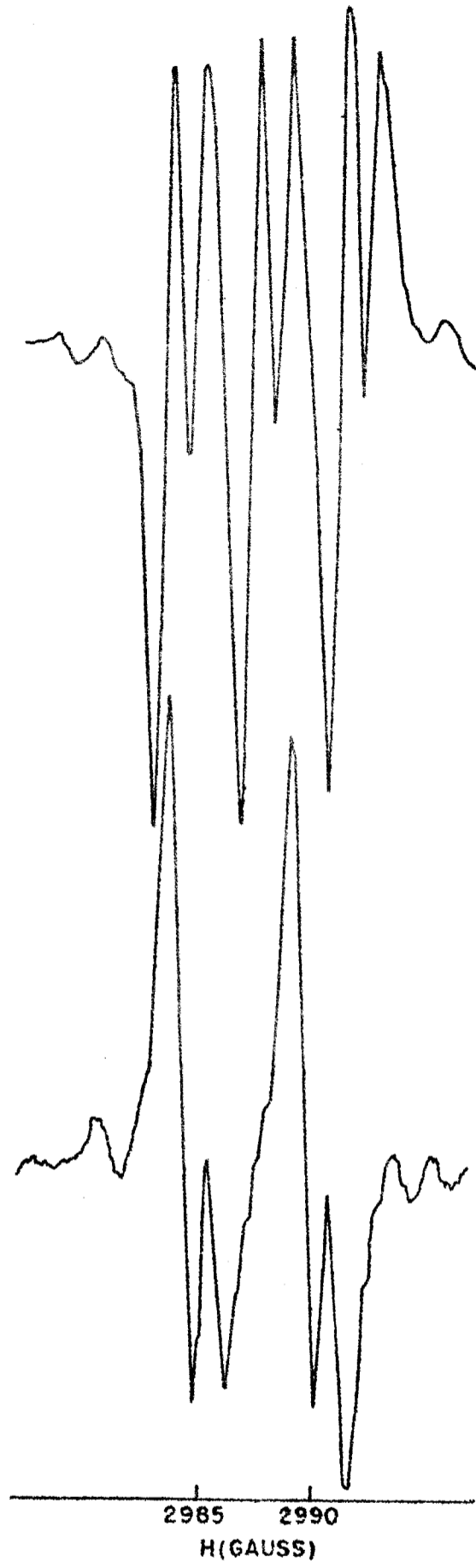


FIG. 2

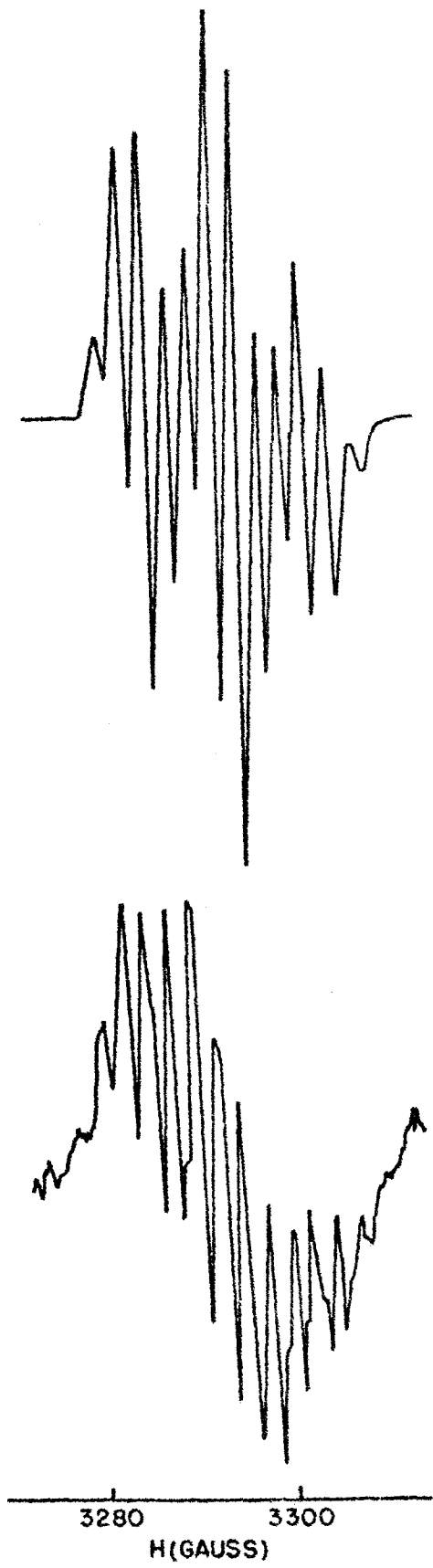


FIG. 3