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ESR Spectra of Copper Complexes of Cellulose

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Synopsis

The ESR spectra of complexes of fibrous cotton cellulose and cupriammonia dihydroxide or cupriethylene diamine dihydroxide under various experimental conditions were determined. The spectra of both complexes with cotton cellulose were almost identical at −100 and 25°C. The spectrum of the complex of cupriethylene diamine dihydroxide with cellulose was stable to temperatures as high as 100°C. The sum of the linewidths of the hyperfine components of the spectra for each complex was about 180 gauss. Cotton fibers were combed and aligned with their axes (lengths) parallel to the magnetic field ($B_{||}$); after formation of either of the complexes with cellulose a minumum of hyperfine structure of components centered at $H_{||}$ was observed. A maximum of hyperfine structure of these components was observed when the complexed fibers were aligned with their axes perpendicular to the magnetic field ($B_{\perp}$). The opposite was true of components centered at $H_{\perp}$. For a complex of cupriethylene diamine dihydroxide and cellulose at 25°C. and at high pH the $g_{||}$ was 2.2127 and the $g_{\perp}$ was 2.0476. It was suggested that the alignment of most of the complex was its axis of symmetry at a maximum angle to the axes of the cotton fiber, when the axes of the fibers were in the parallel alignment with the magnetic field. At high pH these observations were even more marked. When ramie was used with cupriethylene diamine dihydroxide at high pH, the contribution of components centered at $H_{||}$ to the spectra was zero. Spectra for the copper compounds alone and complexed with cellobiose are also reported.

INTRODUCTION

Rivkind[1–3] has reported the paramagnetic resonance (ESR) spectra of cupriethylene diamine dihydroxide, cupriammonia dihydroxide, and other copper complexes in solution. He reported that changes in viscosity of the solution and the size of the complex ion affected both the resolution of the spectra and the linewidths of the hyperfine components. McGarvey[4,5] studied the electron paramagnetic resonance absorption of copper acetylacetonate in a single crystal and also in solution. In solution the solvents had a marked influence on the g factors, which was attributed to the formation of weak complexes between the solute and solvent. By assuming that the copper ions in solution were present in a microcrystal

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formed from the solvent molecules or complexing groups he explained the linewidths of the hyperfine components of the spectra. Wilson and Kivelson[6] investigated the anisotropic and spin-rotational effects in copper complexes dissolved in organic solvents. Aasa and his associates[7,8] reported the existence of copper–fructose complexes in solution on the basis of an analysis of ESR spectra.

Cupriammonia dihydroxide (CAM) and cupriethylene diamine dihydroxide (CED) have been used as solvents for cotton cellulose in the determination of intrinsic viscosity for the calculation of molecular weight. It has been suggested that cellulose complexes with these copper-containing compounds yield colloidally dispersible products.[9] Neither the nature of the chemical bonds involved in the proposed complexes nor the extent of definition of the proposed complexes has been experimentally shown. Data, based on electron spin resonance (ESR) spectroscopy, on the effects of experimental conditions on the complexes are presented in this report. The concentration of the copper-containing compounds and the pH, temperature, and orientation of the complexed cellulosic fibers in the magnetic field were varied. The ESR spectra of the complexes were interpreted to estimate the degree of molecular orientation in the fibers and to indicate the nature of the chemical bonds involved in these copper complexes of cotton cellulose.

EXPERIMENTAL

Preparation of Samples

Cotton cellulose of the Deltapine variety was purified by extraction with hot ethanol followed by boiling in dilute sodium hydroxide solution, precautions being taken to minimize air oxidation. The sodium hydroxide was removed by washing the cellulose with distilled water, then soured with dilute acetic acid, neutralized with dilute ammonium hydroxide, and again washed with distilled water.[10] The purified cellulose was allowed to condition at 21°C. and 65% R.H., resulting in a product with a moisture content of about 7%. The viscosity-average molecular weight of the purified cellulose was about 700,000. Cellulose II was prepared from purified cotton or from purified ramie by mercerization in the usual manner: immersing the fibers in sodium hydroxide (18%) for 10 min. at 25°C. and then washing the fibers free from sodium hydroxide.

Solutions of CED (1.0*M*) and CAM (0.236*M*) were obtained from commercial chemical suppliers. The solutions were diluted to the desired molarity with distilled water. However, when dilution was greater than fourfold, the solution of CAM was diluted by a solution of ammonium hydroxide of the desired molarity, to minimize decomposition of the complex and precipitation of $Cu(OH)_2$. Other chemicals used were reagent grade.

Methods

The ESR spectra of the complexes were determined in a Varian 4502-15 EPR spectrometer system. The system was equipped with a dual-sample cavity, a rotating cavity, and a variable-temperature accessory allowing operation from about −185 to 300°C. To minimize the effects of absorption of microwave power by the solvents, particularly water, when quartz sample tubes (3 mm. inside diameter) were used, the samples were frozen and the spectra usually determined at −100°C. When the spectra were determined at 25°C., capillary sample tubes (1.6 mm. inside diameter) were used to minimize the volume of solvent in the sensitive area of the resonant cavity.

For the determination of the effects of orientation on the complexed fibrous celluloses in the magnetic field on their ESR spectra the fibers were combed, so that their axes (lengths) were mutually parallel. After treatment of these fibers with the complex ion solution of desired molarity the fibers were drawn into a piece of polyethylene tubing (about 0.8 mm. inside diameter). This sample was cut in a plane perpendicular to the length of the fibers, to give a cylindrical sample about 1–2 mm. in length. This cylindrical sample was attached at a right angle to a piece of quartz tubing and inserted into the most sensitive area of the resonant cavity of the spectrometer. The magnet was rotated around the cavity to give orientations of the fibers varying from parallel to the magnetic field ($B_{||}$) to perpendicular to the magnetic field ($B_{\perp}$). The ESR spectra of the complexed fibrous celluloses were determined at different orientations of the fibers in the magnetic field.

Diphenyl picryl hydrazyl (DPPH) in benzene was used as a standard of reference with a calculated g value of 2.00354. In determinations of g values and linewidths the reference sample and the unknown sample were observed simultaneously with one sample in each of the dual-sample cavities. Their ESR spectra were drawn on a dual-channel recorder on an expanded scale: 1000 gauss per 25 or 50 in. The ESR spectra shown in the figures are photographs of actual recordings made by the spectrometer system; for this purpose a reduced scale in gauss per inch was used.

RESULTS

The ESR spectrum of CED (0.125M) in aqueous solution is shown in Figure 1. The four hyperfine components due to interaction with the copper nuclear spin of $^3/_2$ are resolved ($g_{\text{center}} = 2.1000$). The linewidths of the two outer components ($M = \pm^3/_2$) are equal. Those of the two inner components ($M = \pm^1/_2$) are also equal. At higher concentrations the hyperfine structure smeared out, and with a 0.5M solution a single resonance line with $g = 2.0870$ resulted.

CED (0.125M) adsorbed on cotton cellulose at 25°C. gave an asymmetric spectrum (Fig. 2). At a lower concentration of CED (0.0005M) the spectrum was different, as shown in Figure 3. If the excess CED was re-

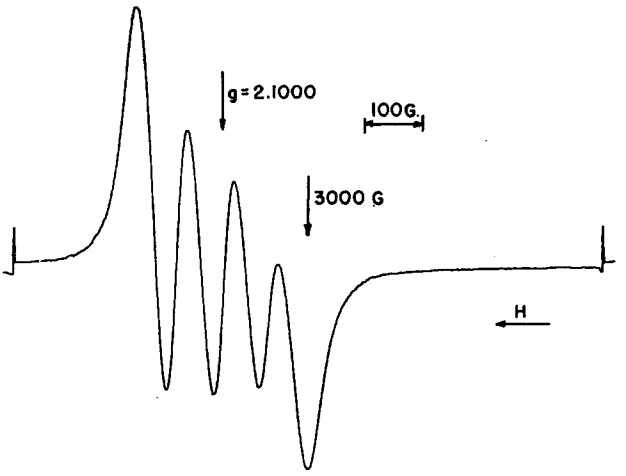

Fig. 1. ESR spectrum of CED (0.125*M*) at 25°C.

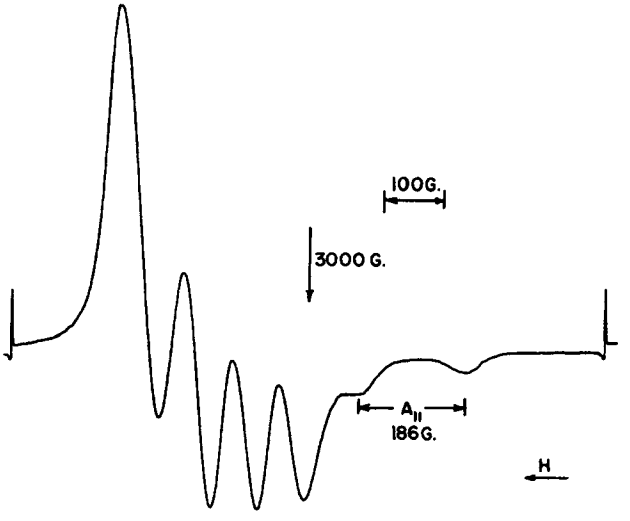

Fig. 2. ESR spectrum of CED (0.125*M*) adsorbed on cotton cellulose at 25°C.

moved by washing in the first case, in which 0.125*M* CED was used, then a spectrum very similar to that observed in Figure 3 was obtained. The difference between the two spectra appeared to be due to CED, which was not complexed with the cotton cellulose. This accounted for the four hyperfine components observed in Figure 2 at higher magnetic fields. At −100°C. CED (0.0005*M*) absorbed on cotton gave the same spectrum as at 25°C. The CED(0.125*M*)/cellulose observed at −100°C. gave a spectrum different from that obtained at 25°C. The four hyperfine lines due to CED not complexed with cellulose would be reduced at −100°C. to a single line. This would account for the observed differences in the

spectra at 25 and −100°C. (see Fig. 4). The spectrum of CED(0.0005*M*)/cellulose did not change on an increase in the temperature of observation to as high as 100°C.

The addition of cellobiose (0.1*M*) to aqueous solutions of CED at 25°C. resulted in an increase in the linewidths of the four hyperfine components

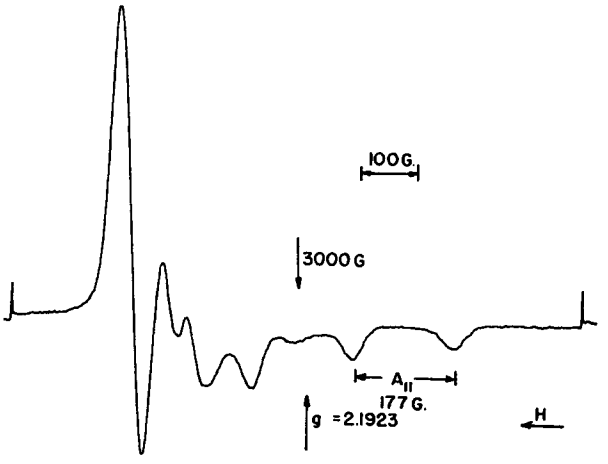

Fig. 3. ESR spectrum of CED (0.0005*M*) adsorbed on cotton cellulose at 25°C.

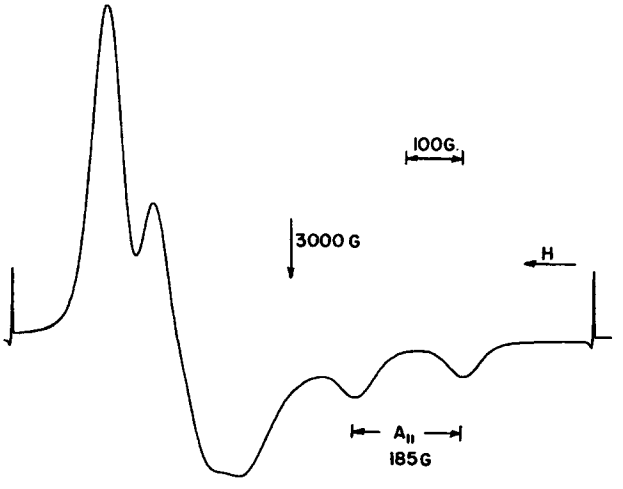

Fig. 4. ESR spectrum of CED (0.125*M*) adsorbed on cotton cellulose at −100°C.

with decreasing magnetic field, as shown in Figure 5, with $g = 2.0989$. At −100°C. a solution of CED(0.0005*M*)/cellobiose(0.1*M*) gave a spectrum very similar to that obtained with CED/cellulose at 25 or −100°C., as shown in Figure 6. With CED (0.125*M*) and the cellobiose (0.1*M*) the high-field structure was smeared out at low temperature, almost the same as with cellulose and CED (0.125*M*).

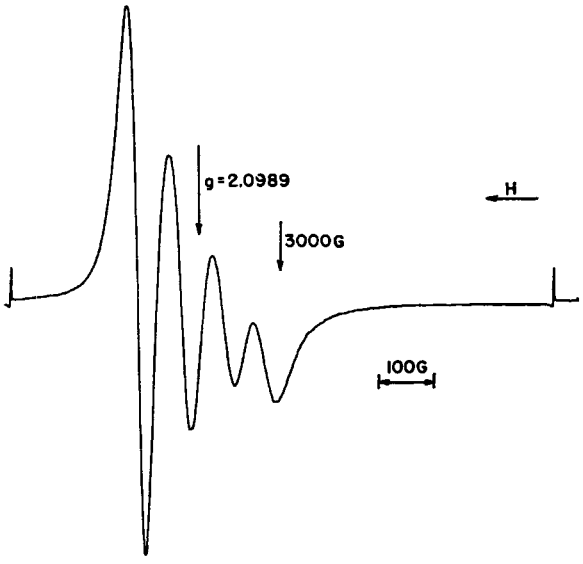

Fig. 5. ESR spectrum of CED (0.125*M*) containing cellobiose (0.1*M*) at 25°C.

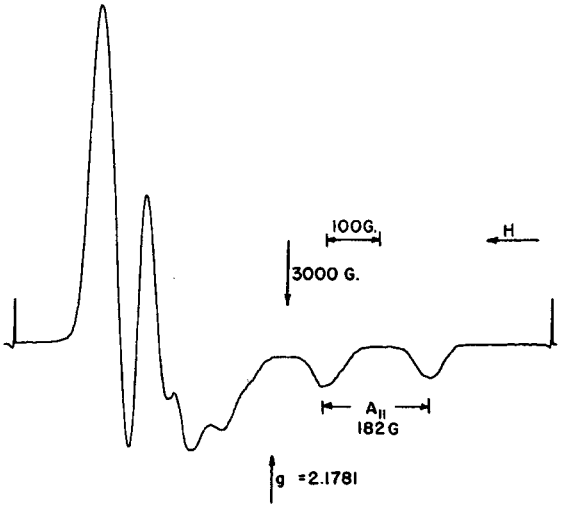

Fig. 6. ESR spectrum of CED (0.0005*M*) containing cellobiose (0.1*M*) at −100°C.

When cellulose (0.075 *g.*) was dissolved in an aqueous solution of CED (30 ml. of 0.5*M*), the spectrum showed partial resolution of the hyperfine components with $g = 2.1002$. A more resolved spectrum on dilution to 0.125*M* CED is shown in Figure 7.

At high pH (7% NaOH added) with CED (0.008*M*) adsorbed on cellulose the hyperfine structure at high magnetic fields was resolved, as shown in Figure 8. The $g_\perp$ and $g_{||}$ values were 2.0476 and 2.2127, respectively; $3A_\perp$ and $A_{||}$ were 68 and 172 gauss, respectively.

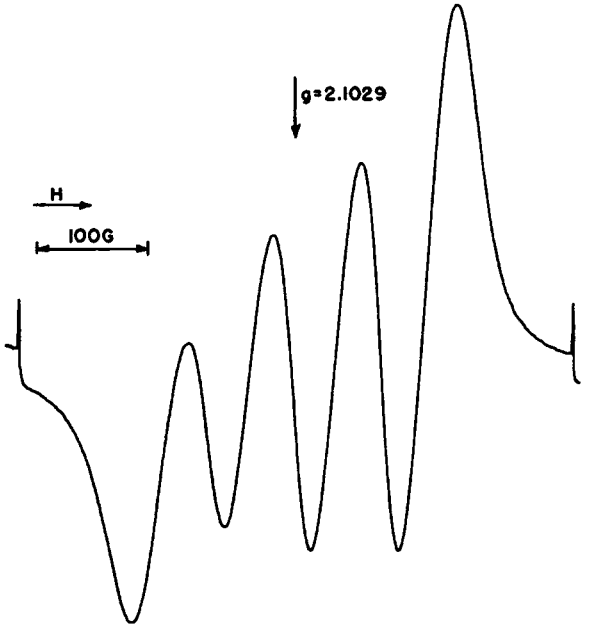

Fig. 7. ESR spectrum of cupriethylene diamine dihydroxide (0.125*M*) containing cotton cellulose (0.25%) at 25°C.

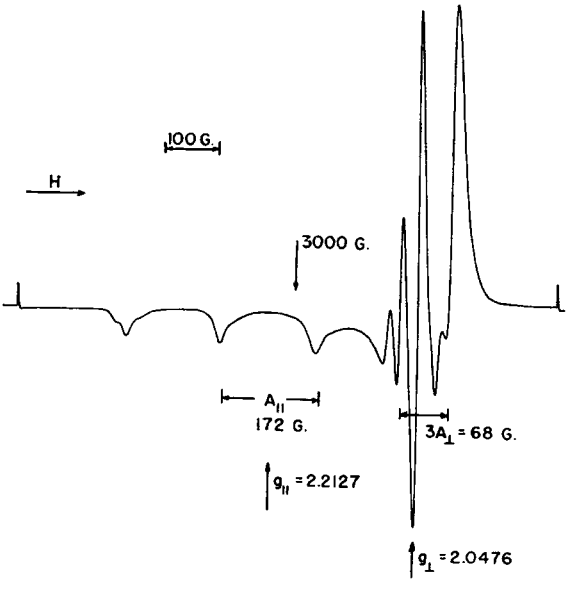

Fig. 8. ESR spectrum of CED (0.008*M*)–NaOH (7%) adsorbed on cotton cellulose at −40°C.

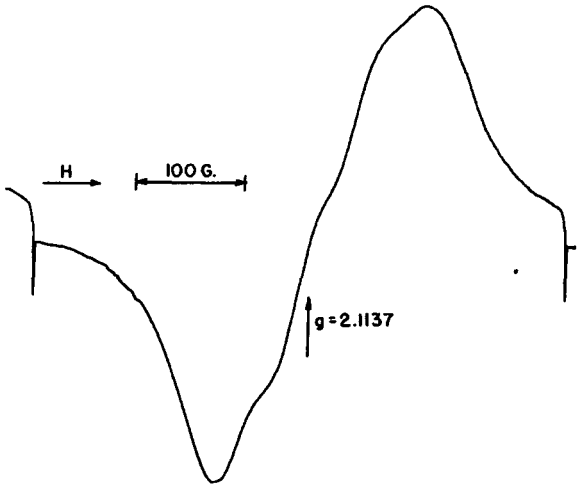

Fig. 9. ESR spectrum of CAM (0.236M) at 25°C.

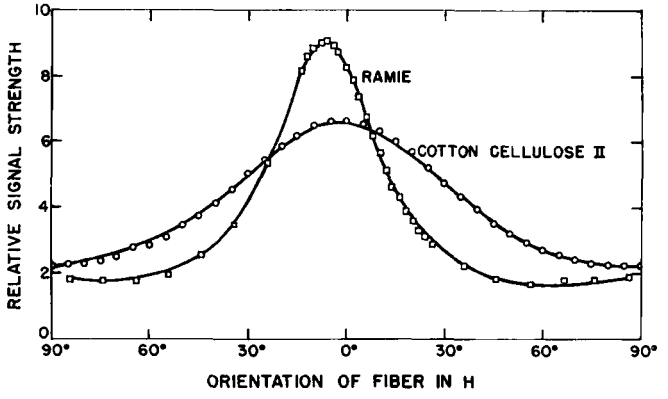

Fig. 10. Effects of orientation of complexed fibers of cotton cellulose II and ramie in magnetic field on the signal strength of hyperfine structure of ESR spectra.

The ESR spectrum of CAM (0.236M) observed at 25°C. gave an indication of four hyperfine components with g = 2.1137; see Figure 9. Variation of experimental conditions with CAM and cellulose or cellobiose, as outlined above for CED, resulted in ESR spectra similar to those obtained from CED and cellulose or cellobiose, as shown in Figures 1–8. When cellulose (0.075 g.) was dissolved in an aqueous solution of CAM (30 ml. of 0.236M), a spectrum with g_{center} = 2.1176 was obtained.

The effects of rotating the magnetic field around complexed cellulosic fibers, which had been combed and aligned as described under Methods, on the relative signal strength of the major peak of their ESR spectra are shown in Figure 10. When the fibers, both ramie and cotton cellulose II, were parallel to the magnetic field ($B_{||}$), a maximum in signal strength of

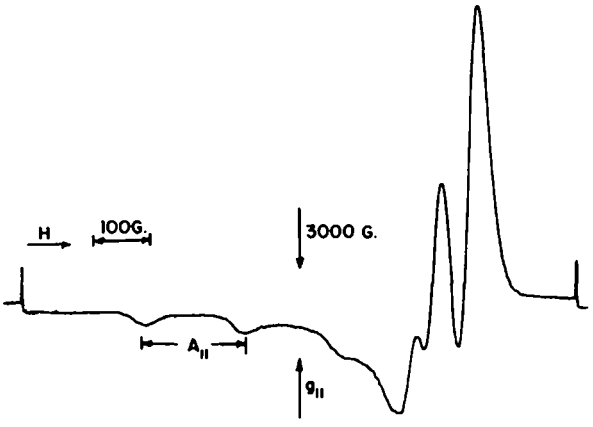

Fig. 11. ESR spectrum of CED (0.008*M*) adsorbed on cotton cellulose fibers oriented $B_{||}$ at −40°C.

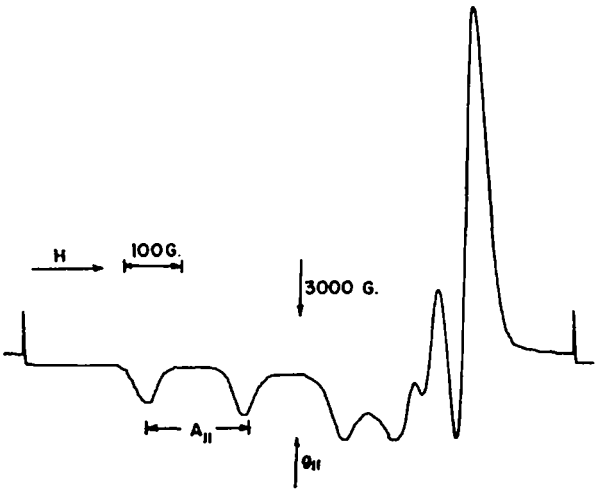

Fig. 12. ESR spectrum of CED (0.008*M*) adsorbed on cotton cellulose fibers oriented $B_{\perp}$ at −40°C.

components centered at a field $H_{\perp}$ was obtained. The strength of the signal decreased to a minimum when the fibers were oriented perpendicular to the magnetic field ($B_{\perp}$). The change in the signal strength, when ramie was used, was more rapid, as the orientation of the fibers was changed from $B_{||}$ to $B_{\perp}$, than when cotton cellulose II was used. When cotton cellulose I was used, a variation in signal strength with fiber orientation in the magnetic field similar to that for cellulose II was obtained but was not as marked.

The effects of the orientation in the magnetic field of fibers of cotton cellulose I, complexed with CED (0.008*M*) and with CED (0.008*M*) plus NaOH, on their ESR spectra are shown in Figures 11–14. The effects of

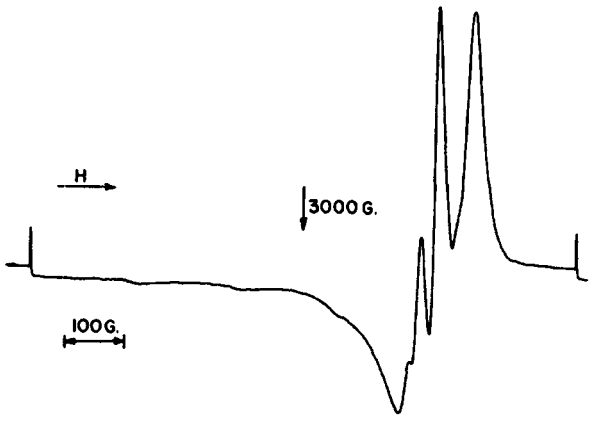

Fig. 13. ESR spectrum of CED (0.008M)-NaOH (7%) adsorbed on cotton cellulose fibers oriented at $B_{||}$ at −40°C.

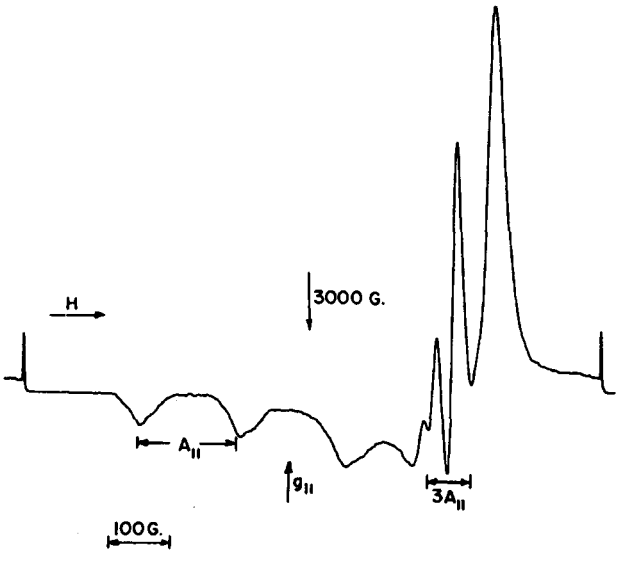

Fig. 14. ESR spectrum of CED (0.008M)-NaOH (7%) adsorbed on cotton cellulose fibers oriented at $B_{\perp}$ at −40°C.

orientation of the fibers in the magnetic field on the hyperfine structure of their spectra were greater for the CED–NaOH–cellulose complex than for the CED–cellulose complex. When ramie was the fiber used, the hyperfine structure at low magnetic fields (centered at $H_{||}$) disappeared completely when the fibers were parallel to the magnetic field, as shown in Figure 15. The ESR spectrum of ramie oriented perpendicularly to the magnetic field is shown in Figure 16.

The g values and linewidths of the hyperfine components, determined from the ESR spectra for aqueous solutions of cupriethylene diamine

dihydroxide and cupriammonia dihydroxide complexes, are summarized in Tables I and II. The linewidths of these components derived from ESR spectra for copper complexes of fibrous cellulose and cellobiose (0.1M) are summarized in Table III. The effects of orientation in the magnetic field

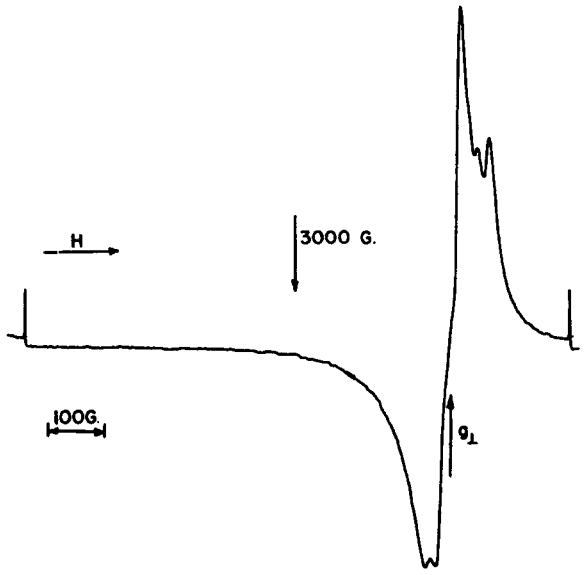

Fig. 15. ESR spectrum of CED (0.001M)–NaOH (7%) on mercerized ramie fibers oriented at $B_{||}$ at 25°C.

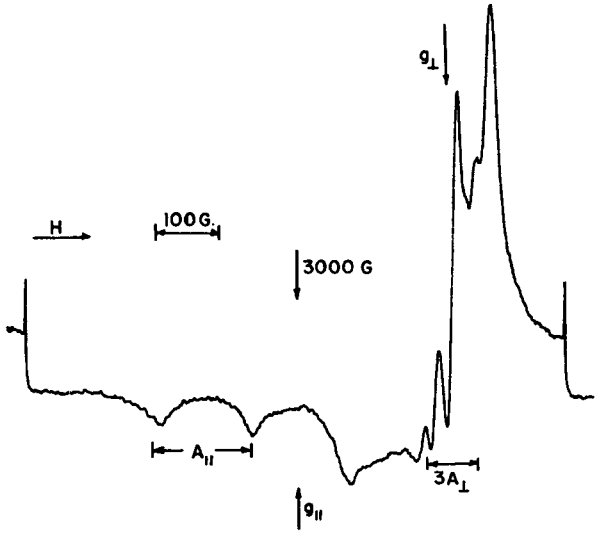

Fig. 16. ESR spectrum of CED (0.001M)–NaOH (7%) on mercerized ramie fibers oriented at $B_\perp$ at 25°C.

TABLE I
g Values Derived from ESR Spectra of Copper Complexes in Solution at 25°C.

Sample	Cu concn., M	g_{center}	g_1	g_2	g_3	g_4
CED	0.125	2.1000	2.0269	2.0770	2.1240	2.1712
CED	0.25	2.1014	2.0286	2.0767	2.1230	2.1680
CED	0.5	2.0967	—	—	—	—
CAM	0.059	2.1142	2.0484	2.0931	2.1362	2.1750
CAM	0.236	2.1137	—	—	—	—
CED/cellulose[a]	0.5	2.1002	—	—	—	—
CAM/cellulose[a]	0.236	2.1176	—	—	—	—
CED/cellobiose[b]	0.125	2.0989	2.0289	2.0769	2.1219	2.1704

[a] 0.25% cellulose in solution.
[b] 0.1M cellobiose.

of copper complexes of fibrous cellulose on g values derived from ESR spectra are summarized in Table IV.

DISCUSSION

The copper complexes used, CED and CAM at concentrations of 0.5M and 0.236M, respectively, showed little resolution of the hyperfine components of their ESR spectra. Dilution of these complexes gave four hyperfine components due to interaction with copper nuclear spin $^3/_2$. The outer components (corresponding to $M \pm {}^3/_2$) were equal in linewidth; the inner components (corresponding to $M \pm {}^1/_2$) were also equal. As shown in Table II, the spectra of CAM had a narrower linewidth of hyperfine components than those of CED. The linewidths showed some dependence on concentration. The addition of cellobiose (0.1M) to aqueous CED (0.125M) caused the hyperfine components to decrease in linewidth with increasing external magnetic field.

For CED (0.0005M) in contact with cellulose at 25°C. the spectrum of the complex, owing to the highly viscous medium and the rotational interaction's being at a minimum, consisted of, possibly, two sets of components, one set centered at $H_{||}$ and the other at $H_{\perp}$. If these two sets were sufficiently well separated, $g_{||}$, $g_{\perp}$, $A_{||}$, and $A_{\perp}$ could be determined directly from the spectra. Three of the hyperfine components contributing to those centered at $H_{||}$ could be observed, as shown in Figure 3. The hyperfine structure at $H_{\perp}$ was not completely resolved. From the spectrum $g_{||}$ and $A_{||}$ were calculated to be 2.1923 and 176–178 gauss. CED solution frozen at −100°C. gave only a single resonance line of 136 gauss. Solutions of this complex (0.0005M), containing cellobiose (0.1M) frozen at −100°C., gave spectra very similar to that of CED in contact with cellulose at 25°C.

In the study of paramagnetic resonance absorption of copper phthalocyanine in solutions of low and high viscosity at 25°C. Roberts and Koski[11,12] calculated $g_0 = 2.097$ in the former and $g_{||} = 2.169$ and $g_{\perp} =$

TABLE II
Linewidths of Hyperfine Components of ESR Spectra of Cupriethylene Diamine Dihydroxide and Cupriammonia Dihydroxide Complexes in Solution

Sample	Cu concn., *M*	Temp. obsvd., °C.	Linewidths of hyperfine components, gauss: Nuclear magnetic quantum number $-3/2$	$-1/2$	$+1/2$	$+3/2$	Overall linewidth, gauss
CED	0.125	25	46.2	40.9	40.2	45.7	231
CED	0.125	−100	—	—	—	—	136
CED	0.25	25	48.2	39.9	40.4	46.7	238
CED	0.5	25	—	—	—	—	133
CAM	0.059	25	44.3	36.3	36.3	44.8	213
CAM	0.236	25	—	—	—	—	199
CED/cellulose[a]	0.5	25	47.0	54.2	52.0	48.3	258
CAM/cellulose[a]	0.236	25	—	—	—	—	200
CED/cellobiose[b]	0.125	25	34.7	38.7	41.2	44.5	228

[a] 0.25% cellulose in solution.
[b] 0.1*M* cellobiose.

TABLE III
Linewidths of Hyperfine Components of ESR Spectra of Copper Complexes of Fibrous Cellulose and Cellobiose (0.1*M*)

Sample	Cu concn., *M*	Temp. obsvd., °C.	Linewidth, gauss $A_{\|\|}$	Linewidth, gauss $A_{\perp}$	Overall linewidth, gauss
CED/cellulose	0.0005	25	176–8	—	—
CED/cellulose	0.125[a]	25	176–8	—	—
CED/cellulose	0.125	25	186–7	—	—
CAM/cellulose	0.118[a]	25	171–4	—	—
CED/cellulose	0.0005	−100	180–3	—	615
CED–NaOH/cellulose	0.001	25	171–2	23	—
CED/cellobiose	0.0005	−100	194–6	—	617
CED/cellobiose	0.125	−100	188	—	—

[a] After treatment washed with distilled water to remove excess CED or CAM.

TABLE IV
g Values Calculated from the ESR Spectra of Copper Complexes of Fibrous Cellulose

Sample	Cu concn., *M*	Temp. obsvd., °C.	$g_{\|\|}$	$g_{\perp}$
CED/cellulose	0.0005	25	2.1923	—
CED/cellulose	0.0005	−100	2.2003	—
CED/cellulose	0.125	−100	2.2003	—
CED–NaOH/cellulose	0.001	25	2.2127	2.0476
CED–NaOH/cellulose	0.001	−40	2.127	2.0476
CAM/cellulose	0.118	25	2.1973	—

2.061 in the latter. In the highly viscous solution the $g_{||}$, $g_{\perp}$, $A_{||}$, and $A_{\perp}$ values could all be calculated from the observed spectrum. The g_0 value was related to $g_{||}$ and $g_{\perp}$ as follows:

$$g_0 = {}^1/_3(g_{||} + 2g_{\perp}) \quad (1)$$

The ESR spectra of copper–fructose solutions at 25°C., frozen at −196°C., gave *g* values and hyperfine linewidths which would also be related.[7,8] In these cases, and also as Wilson and Kivelson[6] observed in studying copper acetyl acetonate in dilute solutions of organic solvents, the small hyperfine splitting at high magnetic fields ($H_{\perp}$ components) was resolved. In our case, although there was evidence of contributions from two sets of components, the structure at high magnetic fields was smeared out. For aqueous solutions of CED at 25°C. a fairly symmetrical spectrum was observed, although the intensity of the hyperfine components did increase with increasing magnetic field. The spectrum observed for CED in which cellulose was dissolved was similar to that for CED. At

$-100°C$. both gave a single resonance line. A more asymmetrical spectrum was observed for aqueous CED solution only when a solute, such as cellobiose, was present in excess. At $-100°C$. this led to observation of spectra in which two sets of components could be present, which were very similar to that of CED in contact with cellulose at 25°C. The CED complex ion (which normally did not give any structure in a frozen state) may be further complexing weakly with the cellulose or cellobiose. This led to anisotropic effects, such as in the case of copper–fructose at $-196°C$., in which the copper was directly coordinated with the fructose molecule.[7,8] The solute molecules in our case would only be able to approach the copper nucleus along the Z axis at right angles to the plane of the complex and thus interact weakly. The aqueous CED solution ($0.0005M$) in which cellobiose ($0.1M$) had been dissolved gave a g value of 2.1019 at 25°C. At $-100°C$. a $g_{||}$ value of 2.1781 could be calculated directly from the spectrum. If we consider the first case as moderately viscous and the second case as highly viscous, then by eq. (1) the value $g_{\perp} = 2.0638$ can be estimated. The moderately viscous solution of CED ($0.125M$) in which cellobiose ($0.1M$) was dissolved gave a spectrum with $g = 2.0989$ at 25°C. The highly viscuos state of CED ($0.0005M$) in contact with cellulose at 25°C. gave $g_{||} = 2.1923$, and a $g_{\perp}$ value of 2.0522 could be estimated.

When cellulose was treated with CED solution containing an excess of hydroxyl ion produced by the addition of NaOH, the small linewidth of the hyperfine structure at high magnetic fields was resolved (see Fig. 8). There was sufficient separation of the low-field and high-field components to calculate $g_{||} = 2.2127$, $g_{\perp} = 2.0476$, $A_{||} = 171$–172 gauss, and $A_{\perp} = 23$ gauss, directly from the observed spectrum. CED–NaOH observed at $-100°C$. showed a similar spectrum, but there was not as marked a separation of the two sets of components. At high pH, therefore, the spectrum obtained for CED absorbed on cellulose at 25 or $-40°C$. was almost identical with that observed in copper–fructose solution at $-196°C$.[7,8]

The presence of NaOH increased the accessibility of the cellulose to the copper-complex ions. In this process it appeared that the high-field structure was more resolved because of a decrease in linewidth. This could be due to a greater interaction with the copper nucleus by replacement of an ethylene diamine group by the hydroxyl ion. Moreover, the copper nucleus may be directly attached to the cellulose molecule.

When cotton cellulose fibers treated with CED were aligned initially parallel to the external magnetic field ($B_{||}$), there was a maximum contribution of the components centered at $H_{\perp}$. If the magnetic field was rotated until the fibers were perpendicular across the field ($B_{\perp}$), then a minimum contribution of these components was observed. The opposite case was true of components centered at $H_{||}$. If we consider the complex with an axis of symmetry of its crystalline field at some orientation θ to the applied magnetic field H, then

$$g = (g_{||}^2 \cos^2 \theta + g_{\perp}^2 \sin^2 \theta)^{1/2} \qquad (2)$$

and, since $H = h\nu/gB$, then

$$H = (h\nu/B)(g_{||}^2 \cos^2 \theta + g_{\perp}^2 \sin^2 \theta)^{-1/2} \quad (3)$$

where H is the field for the absorption of energy at a given value of θ. It can be seen from eq. (3) that, when θ has a maximum value, we obtain a maximum contribution from components centered at $H_{\perp}$. This occurred when the fiber axes were aligned perpendicular to the magnetic field, as shown in Figure 12. Similarly, when θ had a minimum value, there was a minimum contribution from these components, as shown in Figure 10. When CED was absorbed on cellulose at high pH, the effect was even more marked.

When ramie was used instead of cotton cellulose, the hyperfine structure with fibers aligned parallel to the field showed no contribution of components centered at $H_{||}$. To give maximum swelling, the fibers were treated with 18% NaOH and then with CED(0.001M)–NaOH(7%). As shown in Figure 10, the sharpness of the intensity/rotation peak was greater for ramie than for cotton cellulose II. This showed an apparent increase in the alignment of the complex. When cotton cellulose I or II was used with no excess NaOH, then the differences in spectra due to the perpendicular and parallel orientations of the fibers in the magnetic field were not well defined. The increased differences in spectra due to orientations of the fibers in H was obtained on treatment of the fibers with NaOH. Mercerized ramie showed the greatest difference between the intensities of the components centered at $H_{\perp}$ in the parallel and perpendicular positions of the fiber axes to the magnetic field. In the parallel alignment, since no contribution from components centered at $H_{||}$ was shown, then θ, the angle of orientation of the axis of symmetry of the copper complex, was very close to 90°, as calculated by eq. (3). We see only the complex with axes of symmetry perpendicular to the fiber axes contributing to the spectrum. Rotation of the magnetic field until it was perpendicular to the fiber axes gave a spectrum with both sets of components. Rotation about the fiber axes in the latter position showed no change with intensity of the two sets of components. These changes in spectra with orientation of the complexed fibers in the magnetic field gave a measure of the degree of molecular orientation in the fibers of cotton cellulose I and II and ramie.

Trade names are given as part of the exact experimental conditions and not as an endorsement of the products over those of other manufacturers.

References

1. A. I. Rivkind, *Dokl. Akad. Nauk S.S.S.R.*, **135**, 365 (1960).
2. A. I. Rivkind, *Russian J. Phys. Chem.* (translated), **35**, 1031 (1961).
3. A. I. Rivkind, *Zh. Fiz. Khim.*, **35**, 2099 (1961).
4. B. R. McGarvey, *J. Phys. Chem.*, **60**, 71 (1956).
5. B. R. McGarvey, *J. Phys. Chem.*, **61**, 1232 (1957).
6. R. Wilson and D. Kivelson, *J. Chem. Phys.*, **44**, 4445 (1966).
7. R. Aasa, B. Malmstrom, P. Saltmann, and T. Vanngard, *Biochem. Biophys. Acta*, **88**, 430 (1964).

8. R. Aasa, R. Pettersson, and T. Vanngard, *Nature*, **190**, 258 (1964).
9. H. M. Spurlin, in *Cellulose and Cellulose Derivatives*, (High Polymers, Vol. V), Part 2, E. Ott, H. M. Spurlin, and M. W. Grafflin, Eds., Interscience, New York–London, 1954, p. 874.
10. J. H. Kettering and C. M. Conrad, *Ind. Eng. Chem., Anal. Ed.*, **14**, 432 (1942).
11. E. M. Roberts and W. S. Koski, *J. Am. Chem. Soc.*, **82**, 3006 (1960).
12. E. M. Roberts and W. S. Koski, *J. Am. Chem. Soc.*, **83**, 1865 (1961).

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