

## Electron Spin Resonance Studies of Interactions of Ammonia, Copper, and Cupriammonia with Cellulose

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### Synopsis

The electron spin resonance spectra (ESR) of complexes of copper with fibrous cotton cellulose under various experimental conditions were determined. Cupric ions dissolved in solutions of strong bases, such as concentrated ammonium hydroxide, sodium hydroxide, and potassium hydroxide, formed complexes with fibrous cotton cellulose. These complexes had paramagnetic resonance properties and generated characteristic ESR spectra. Cupric ions dissolved in solutions of highly ionized neutral salts, such as sodium chloride, formed complexes with cellulose. These complexes also generated the same characteristic ESR spectra as the complexes formed in solutions of strong base. The reaction between cupric ions and cellulose was evidently very rapid and reversible. When the concentration of ammonia was decreased in, or ammonia was removed from, the cupric ion-ammonium hydroxide-cellulose complexes, the paramagnetic resonance properties of the complex were decreased or lost. Similar results were received when potassium hydroxide was removed from the complexes. The compositions of the complexes evidently are variable, that is, under different experimental conditions the relative intensities of the lines of the ESR spectra of the complexes varied, although the hyperfine splittings of the lines were constant. It was concluded that reactions of cupric ions to form complexes with adjacent hydroxyl groups on the cellulose molecule depended on an optimum spatial arrangement of the hydroxyl groups, that is, distance between the groups. Evidently, wetting of cotton cellulosic fibers with solutions of strong bases or neutral salt allowed rotation about the C<sub>2</sub>-C<sub>3</sub> bond to yield this optimum arrangement. When the base or salt was removed, rotation occurred to give less favorable positions of the hydroxyl groups for complexing with cupric ions.

### INTRODUCTION

There is renewed interest in the interactions of ammonia with cellulose.<sup>1-6</sup> Under anhydrous conditions, liquid ammonia reacts reversibly with cotton cellulose lattice type I to yield cellulose lattice type III that on contact with water reverts to cellulose I.<sup>3</sup> The interactions of cupric ions in strong ammonium hydroxide solutions with hydroxyl groups of glycol-type compounds to form complexes has been reported extensively.<sup>7</sup> Based on conductivity measurements, Reeves<sup>7</sup> suggested that complex formation between cupric ions in strong ammonium hydroxide solutions and adjacent hydroxyl groups was critically dependent on distance between

hydroxyl groups. Distance between hydroxyl groups on adjacent carbon atoms is dependent on angles between the groups. That is, complex formation occurred most readily at true cis position ( $0^\circ$  angle) and at  $60^\circ$  angle, and did not occur at  $120^\circ$  or  $180^\circ$  angles. Spurlin<sup>8</sup> and, more recently, Jayme<sup>9</sup> have reviewed the preparation and properties of copper complexes and metal-amine complexes with cellulose.

The electron spin resonance (ESR) spectra of traces of copper in purified cotton cellulose after reaction of cotton with solutions of sodium hydroxide were recorded.<sup>10,11</sup> Complexes of cupriethylenediamine with cellobiose and cellulose generated similar ESR spectra.<sup>12,13</sup> The ESR spectrum of a well-defined copper-fructose complex that contained sodium nitrate was recorded at  $-196^\circ\text{C}$  by Aasa et al.<sup>14</sup>

We have extended this work to record the effects of strong bases and salts on hyperfine splittings of ESR spectra of complexes of copper with fibrous cotton cellulose. The reversible nature of the complexes was demonstrated.

## EXPERIMENTAL

### Preparation of Samples

Cotton cellulose of the Deltapine variety was purified as previously described.<sup>13</sup> The purified cellulose was allowed to condition at  $21^\circ\text{C}$  and 65% R.H. to yield a product with a moisture content of about 7% and a viscosity-average molecular weight of about 700,000.

Solutions of cupriammonia (0.24*M*) were obtained from commercial sources and were diluted with distilled water and concentrated ammonium hydroxide to the desired molarity. Other chemicals used were reagent grade.

### Methods

The ESR spectra of interactions of ammonia, copper, and cupriammonia with cotton cellulose were determined in a Varian 4502-15 EPR spectrometer system. The system was equipped with a dual-sample cavity and a variable-temperature accessory. The interactions of anhydrous ammonia in both gaseous and liquid phases with irradiated cotton cellulose were studied as previously described.<sup>2</sup> Interactions of copper and cupriammonia with cellulose were determined at  $25^\circ\text{C}$  on samples of purified cotton fibers that had been soaked in the solutions described in the legends for the figures. Treated samples of cotton fibers were randomly packed into capillary tubes (1.6 mm inside diameter). These small tubes were used to minimize the volume of solvent in the sensitive area of the resonant cavity of the spectrometer, thereby reducing absorption of microwave power.

Diphenyl picryl hydrazyl (DPPH) dissolved in benzene was used as a standard of reference with a calculated *g* value of 2.00354. The *g* values

and linewidths of ESR spectra of the complexes were determined by simultaneously recording the spectra with DPPH in one cavity and a sample of complex in the other cavity.

## RESULTS

Cupriammonia adsorbed on cotton cellulose at 25°C generated the asymmetric ESR spectrum shown in Figure 1A. The spectrum for the cupriammonia-cellulose complex with  $g_{\text{center}} = 2.1176$  was obtained. The ESR spectrum of cupriammonia recorded at 25°C was a broad singlet-type spectrum with indications of four hyperfine components with  $g_{\text{center}} = 2.1137$ .<sup>13</sup> When the concentration of ammonia was reduced in the cupriammonia solution, the ESR spectrum for cupriammonia adsorbed on cellulose at 25°C shown in Figure 1B was obtained. The intensity and hyperfine components of the spectrum (Fig. 1B) were reduced as compared with those of the spectrum for the complex (Fig. 1A).

Copper acetate adsorbed on cotton cellulose at 25°C generated the ESR spectrum shown in Figure 2A. The singlet-type spectrum obtained was typical for cupric ions that are not complexed. Addition of sodium hydroxide solution to obtain copper acetate-sodium hydroxide adsorbed on cellulose at 25°C changed the spectrum to that shown in Figure 2B. The low-field hyperfine splittings are the same as those for cupriammonia-cellulose (Fig. 1A). The spectrum (Fig. 2B) is very similar to that obtained when purified cellulose was treated with sodium hydroxide solutions to yield trace copper-cellulose complexes.<sup>10,11</sup> Solutions of sodium hydroxide did not generate ESR spectra.

The ESR spectrum of the solution of copper sulfate and potassium hydroxide is shown in Figure 3A and is similar to that for cupriethylene-diamine dihydroxide.<sup>13</sup> Copper sulfate-potassium hydroxide adsorbed on cotton cellulose at 25°C generated the ESR spectrum shown in Figure

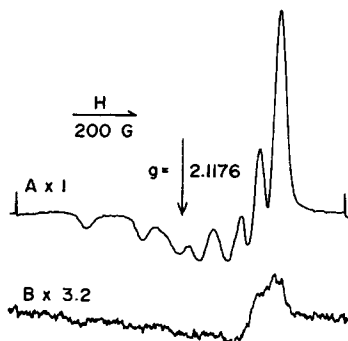


Fig. 1. ESR spectra of cupriammonia adsorbed on cellulose at 25°C. A: Cotton fibers soaked in cupriammonia (0.01M) and concentrated ammonium hydroxide and then padded to remove excess solution. B: Sample A evacuated at about 25 torr and 25°C for 30 min.

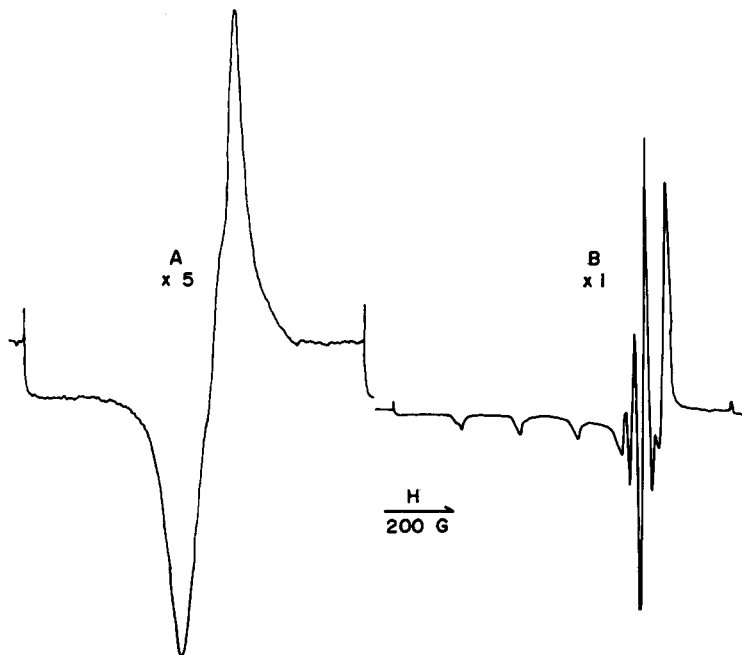


Fig. 2. ESR spectra of copper acetate adsorbed on cellulose at 25°C. A: Cotton fibers soaked in copper acetate (0.3*M*) solution and then padded to remove excess solution. B: Sample A soaked in sodium hydroxide (0.25*M*) solution and then padded to remove excess solution.

3B. The spectrum is similar to that for copper acetate–sodium hydroxide adsorbed on cellulose (Fig. 2B). The hyperfine splittings of the spectra are identical. If a sample of copper sulfate–potassium hydroxide–cellulose was washed with distilled water, the ESR spectrum generated by the product shown in Figure 3C was obtained.

The typical singlet-type spectrum for copper sulfate (1*M*)–sodium chloride (1*M*) is shown in Figure 4A. Copper sulfate–sodium chloride adsorbed on cotton cellulose at 25°C generated the ESR spectrum shown in Figure 4B. The spectrum is similar to spectra for copper acetate–sodium hydroxide–cellulose (Fig. 2B) and copper sulfate–potassium hydroxide–cellulose (Fig. 3B). The intensity of the spectrum for copper–cellulose–salt complex is less than those for copper–cellulose–base complexes. However, the hyperfine splittings of the spectra are similar and almost identical.

Copper borate–zirconyl acetate–sodium hydroxide adsorbed on cotton cellulose at 25°C generated the ESR spectrum shown in Figure 5. The hyperfine splittings of the spectrum are typical for copper–cellulose complexes.

The typical spectrum for cupriethylenediamine–cadmium ethylenetriamine is shown in Figure 6A. Cupriethylenediamine–cadmium ethylenetriamine adsorbed on cellulose at 25°C generated the ESR spectrum shown

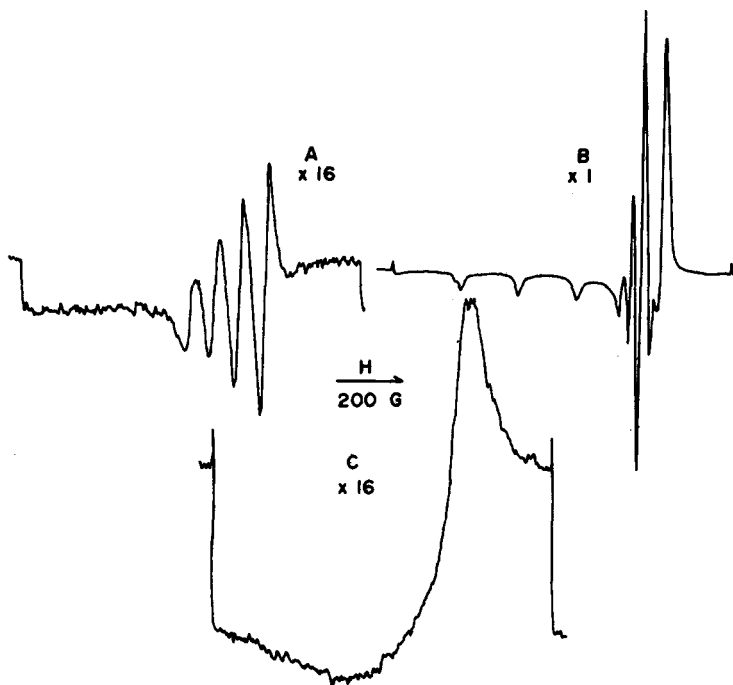


Fig. 3. ESR spectra of copper sulfate-potassium hydroxide adsorbed on cellulose at 25°C. A: Copper sulfate (0.6*M*)-potassium hydroxide (0.2*M*). B: Cotton fibers soaked in solution of sample A and then padded to remove excess solution. C: Sample B washed with distilled water and then padded to remove excess water.

in Figure 6B. The hyperfine splittings of the spectrum indicate the formation of copper-cellulose complex. The presence of cadmium evidently did not affect the hyperfine splittings for the cupriethylenediamine<sup>13</sup> or copper-cellulose complexes.

## DISCUSSION

The interactions of anhydrous ammonia in both liquid and gaseous forms with irradiated cotton cellulose were determined by electron spin resonance spectroscopy.<sup>2</sup> Most of the trapped free radicals in irradiated cellulose were scavenged when cellulose was immersed in anhydrous ammonia (liquid). This indicated that ammonia (liquid) penetrated the highly ordered regions of cellulose. A lower fraction of trapped free radicals in irradiated cellulose was scavenged when cellulose was contacted with anhydrous ammonia (gas) than when the cellulose was contacted with ammonia (liquid). Evidently ammonia (gas) was a weaker swelling agent for cellulose than ammonia (liquid). The effects of ammonia (liquid) on the lattice and degree of order of cotton cellulose have been reported. It was observed that the effects on lattice were reversible under some conditions.<sup>3</sup>

Cupriammonia, a cupric ion-ammonium hydroxide complex, reacts with cellulose to yield a colloiddally dispersible product.<sup>8,9</sup> The cupric ion evidently reacts with adjacent hydroxyl groups on carbons 2 and 3 of the anhydroglucose units of cellulose.<sup>7</sup> Losses of ammonia from the solutions

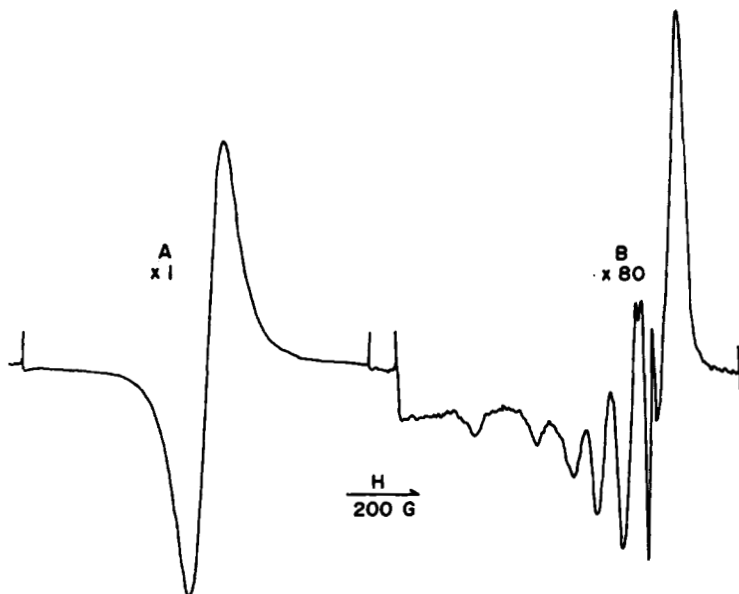


Fig. 4. ESR spectra of copper sulfate-sodium chloride adsorbed on cellulose at 25°C. A: Copper sulfate (1*M*)-sodium chloride (1*M*). B: Cotton fibers soaked in solution of sample A and then padded to remove excess solution.

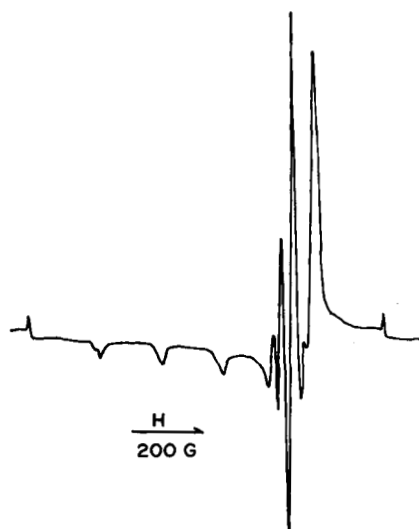


Fig. 5. ESR spectra of copper borate-zirconyl acetate-sodium hydroxide adsorbed on cellulose at 25°C.

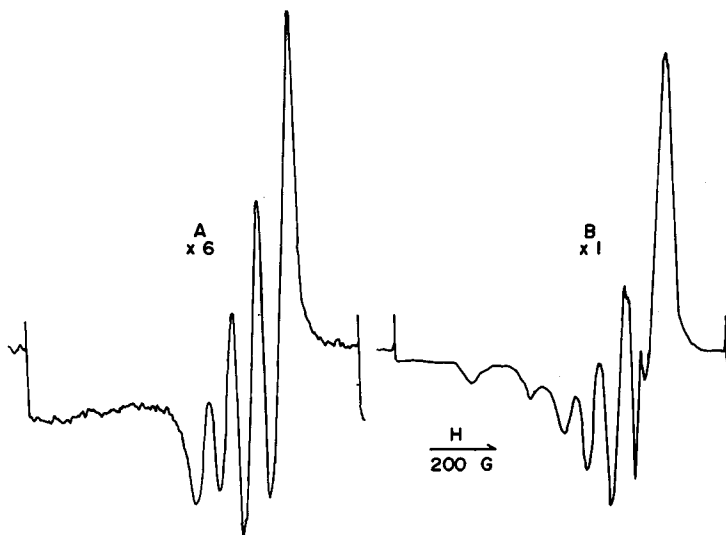


Fig. 6. ESR spectra of cupriethylenediamine-cadmium ethylenetriamine adsorbed on cellulose at 25°C. A: Cupriethylenediamine (0.005*M*)-cadmium ethylenetriamine (0.44*M*). B: Cotton fibers soaked in solution of sample A and then padded to remove excess solution.

cause precipitation of cellulose. We have observed that a complex with paramagnetic properties forms between cupric ions in ammonium hydroxide and cellulose. These properties of the complex are dependent on the concentration of ammonia. Reeves has suggested that a high concentration of strong alkali may bring about reaction between copper and two glycol groups.<sup>7</sup> We have observed that copper salts plus sodium or potassium hydroxide form complexes with cellulose. When the concentration of base is reduced, the paramagnetic properties of the complexes are reduced. Also, copper salts plus other salts form complexes with cellulose that have paramagnetic properties. Complexing of copper with cellulose is likely through the hydroxyl groups on carbons 2 and 3 of the anhydroglucose units of cellulose. The presence of additives, such as bases and salts, may allow rotation about the C<sub>2</sub>-C<sub>3</sub> bond to bring adjacent hydroxyl groups into a spatial relationship, so that they can complex with copper, as suggested by Reeves<sup>7</sup> for glyco-type compounds complexed with copper. Removal of additives may allow rotation of cellulose, so that the distance between hydroxyl groups is too great for them to form a complex with copper.

It is well known that the light fastness of many direct dyes for cotton is improved by an aftertreatment with copper salts. During normal consumer use and laundering, the copper salt may be extracted from the dyed cotton. Similarly, microbial resistance to degradation of cotton may be imparted by incorporation of organic compounds of copper.<sup>8</sup> Experimental conditions for treatment of cotton with copper salts that lead to

complex formation of copper ions with cellulose can be determined by ESR spectroscopy. Further research to determine conditions of after-treatment that minimize the reversibility of complex formation could lead to preparation of cotton textile products with more durable light fastness and microbial resistance.

The sample of cotton treated with copper borate-zirconyl acetate was obtained from Mr. C. J. Conner. Trade names are given as part of the exact experimental conditions. Mention of a trademark or proprietary product does not constitute a guarantee or warranty of the product by the U.S. Department of Agriculture and does not imply its approval to the exclusion of other products that may also be suitable.

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