

Preparation and Characterization of Hydroxamic Acid Derivative and Its Metal Complexes Derived from Cellulose

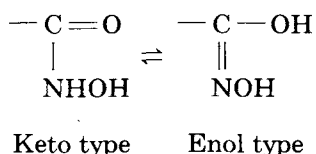
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Synopsis

Cellulose-hydroxamic acid derivatives, which were reported as a novel cellulose derivative were prepared from dialdehyde celluloses obtained by periodate oxidation of cellulose, and certain properties of unusual cellulose derivative containing hydroxamic acid groups and of various metal complexes formed with heavy metal ions were characterized in this investigation.

INTRODUCTION

Hydroxamic acids are originally used for quantitative confirmation of esters, acidic amides, and acidic anhydrides because the metal complexes formed by the action with multivalent metal ion such as Fe^{3+} give characteristic reddish violet color like red wine. Hydroxamic acids are regarded as a kind of replaced derivative of the nitrogen-bound hydrogen in the hydroxylamine molecule, and are expressed as a general formula $\text{R}-\text{CO}-\text{NHOH}$ ($\text{R} = \text{alkyl or allyl}$), having the tautomerism of keto and enol types.¹



This study is aimed to investigate some properties of cellulose derivative containing hydroxamic acid groups introduced in modified cellulose molecule and of its various metal complexes formed with heavy metal ions. We have had much interest in elucidating whether cellulose-hydroxamic acid derivative* has a selective ability to take up or to adsorb heavy metal ions, and also what properties are expected from the metal complexes. For the preparation of hydroxamic acid derivative from cellulose, two procedures are designed here as shown in Figure 1. Procedure (1) has not been previously reported, but procedure (2) has been reported as a novel cellulose derivative by Gal'braikh and Rogovin², and they described that the product formed stable metal complexes with Cu^{2+} or Fe^{3+} .³ Thus, in this study, the preparation by procedure (2) was adapted and followed. The oxidative products of dialdehyde celluloses obtained by per-

* This cellulose derivative is mentioned below as CHA product in this paper.

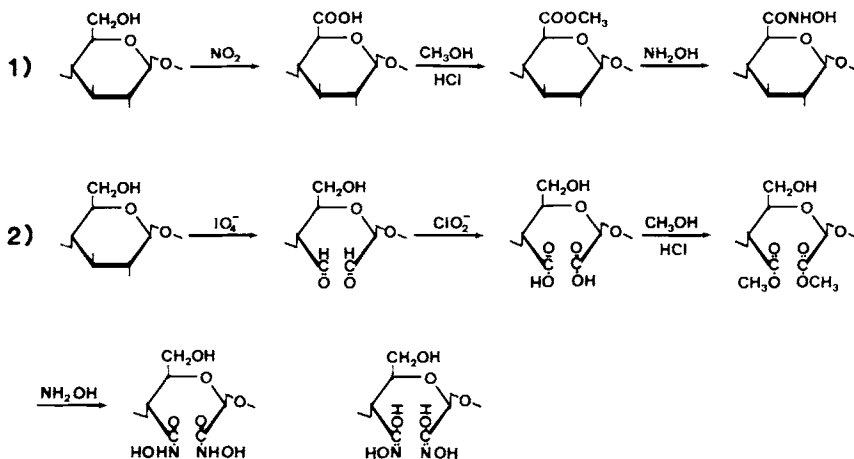


Fig. 1. A scheme for the preparation of hydroxamic acid derivatives from cellulose.

iodate oxidation of cellulose, so called 2,3-dicarboxy celluloses, were used as the starting materials, and the desired CHA products were prepared according to our improved procedure. In this preparation, the following problems were addressed and resolved according to the author's procedure: (1) preparation of dicarboxy cellulose methyl ester, (2) conversion of the methyl ester into the hydroxamic acid derivative, (3) separation of CHA products.

The chemical aspects of hydroxamic acids were first reviewed by Yale¹ and introduced as a compound having specific properties. In addition to specific reactivity of hydroxamic acids, the formation of complexes with metal ions and the use as a kind of scavenger of heavy metal ions were so far investigated. As for certain properties of higher polymer containing hydroxamic acid groups, hydroxamic acid copper-chelate prepared from methyl polyacrylate was investigated in detail by Hatano et al. and characterized.⁴ A series of their reports were the first to describe certain properties of hydroxamic acid metal-chelate from synthetic high polymer. Afterwards, the hydroxamic acids were also pointed out to have the specific property of combining with heavy metal ions other than Cu^{2+} .⁵ In particular, much interest has been directed in having powerful adsorption toward uranium ion (UO_2^{2+}). As a result, organic adsorbents for uranium by using the composite materials containing hydroxamic acid groups have led to development.⁶ On the other hand, the study from reactivity of hydroxamic acids has brought to development of hydroxamic acid derivatives in a new pesticide.⁷ Recently, it has been also pointed out that higher polymer containing hydroxamic acid groups has catalytic activity in certain hydrolytic reaction.⁸ Thus, reaction based on hydroxamic acid groups would be of interest from the viewpoint of conversion to functional polymers.

This report is concerned with comprehensive characterization of properties of CHA product prepared from 2,3-dicarboxy cellulose and of its various metal complexes formed with heavy metal ions. In a previous paper,⁹ we already reported on certain properties of 2,3-dicarboxy cellulose salts combined with various metal ions, which are prepared by mild chlorite oxidation of the dialdehyde cellulose obtained by preiodate oxidation of cellulose. Consequently, the characteristics of the related materials are described in this paper.

EXPERIMENTAL

Preparation of Dialdehyde Celluloses from Cellulose Powder

Dialdehyde celluloses were prepared from commercial cellulose powder (Schleicher & Schüll cellulose powder and Whatman cellulose powder CF-1, 100–200 mesh) according to the method⁹ described previously.

Preparation of 2,3-Dicarboxy Cellulose Na Salt from Dialdehyde Cellulose

Dialdehyde celluloses prepared led to 2,3-dicarboxy cellulose Na salt by oxidation with mild acidified sodium chlorite according to the method⁹ described previously.

Preparation of 2,3-Dicarboxy Celluloses

2,3-Dicarboxy cellulose Na salt prepared was converted to the free form by desalting, and was recovered as described previously.⁹

Methyl Esterification of 2,3-Dicarboxy Cellulose and Conversion to the Hydroxamic Acid Derivative

2,3-Dicarboxy celluloses of free form dried in a vacuum for 48 h at 60°C were mixed with 100 times volumes of 0.06–0.1 N methanolic hydrochloride and stirred at room temperature for 3–5 h. 2,3-Dicarboxy cellulose with more than 80% oxidation ratio was dissolved completely in a medium of methanolic hydrochloride, but that with less than 80% oxidation ratio was sticky on the wall of vessel like a paste without giving a complete solution. The former was neutralized with Amberlite IR 45 (OH⁻), and evaporated to 100 mL volumes. The latter was likewise treated on the soluble fraction after separation by centrifugation. The precipitate separated was suspended in the concentrated solution (100 mL). Both concentrated solutions were separated to three fractions (P-1, P-2, P-3) by fractional precipitation with ethanol.

For the preparation of hydroxamic acid derivative from the methyl ester, the improved procedure of the method¹⁰ described previously by Hurd et al. was applied. The conversion to hydroxamic acid derivative was achieved by allowing to react for 4–5 days at ambient temperature in a hydroxylamine methanol solution adjusted to 9.2–3 with newly prepared sodium ethylate. After evaporation of the solvent, the hydroxamic acid derivative was separated in a yield of more than 80% as sticky, massive solid from the reaction mixture by vigorous shaking in 80% ethanol. Consequently, the inorganic materials and contaminant were removed successfully by this simple procedure. The product was obtained as pale creamy powder by washing with methanol and drying in a vacuum.

Formation of Hydroxamic Acid Metal Complexes and Separation of the Complexes

Hydroxamic acid derivatives prepared were mixed with the aqueous solution containing individual heavy metal ions, and then were stirred at room tem-

perature for 24 h. The mixture was transferred into a cellulose tubing with heavy metal ions, and was dialyzed against distilled water for desalting. The dialyzed solution was evaporated to dryness to give characteristic colored products due to complex formation by introduction of heavy metal ions as shown in a photograph of Figure 2.

Fractionation of the Hydroxamic Acid Co-complex by Using a Cellulose Tubing Film

Hydroxamic acid Co-complex was transferred into a cellulose tubing for dialysis with an exclusion limit of less than M.W. 8000, and was dialyzed against distilled water for 2 days. The fraction of Co-C-1 recovered by evaporation of the dialyzate solution and the dialyzed solution were separated through a cellulose tubing film. The latter was further separated into the fraction of Co-C-2 obtained as precipitate with 3 volumes of ethanol after concentration to 50 mL and the fraction of Co-C-3 recovered by evaporation of the solution after removal of the precipitate. The cobalt contents of each fraction were as follows: Co-C-1; 12.8%, Co-C-2; 15.6%, Co-C-3; 16.6%.

Determination of Co Contents in Metal Complex

The sample (30–40 mg) weighed in a tube was mixed with 10–15 drops of the mixture of conc. H_2SO_4 and conc. HNO_3 (6 : 4, v/v), and was decomposed under heating. The complete dissolved solution was diluted to a constant volume with distilled water, and then cobalt content in the solution was determined by chelatometric titration method.¹¹

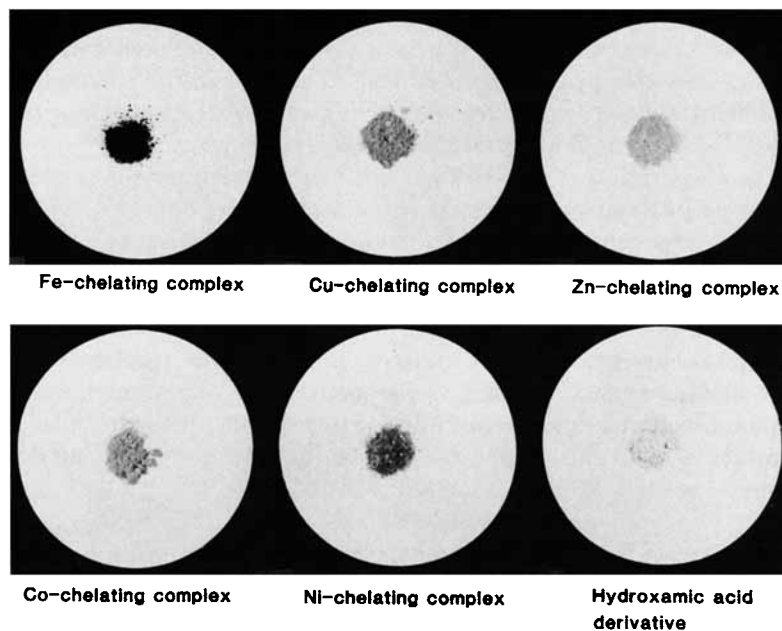


Fig. 2.

TABLE I
Dicarboxy Cellulose Methyl Esters Prepared From Dicarboxy Celluloses (DCC)

DCC used	Amount of DCC (g)	HCl concn. in MeOH (N)	Reaction time (hr)	Yield (g)				Recovery ^a (%)
				P-1	P-2	P-3	Total	
Schleicher & Schüll cellulose								
C-2	5.0	0.06	1.5	0.55	4.06	1.05	5.66	98.6
C-2	5.0	0.06	3.0	0.78	2.94	1.31	5.03	87.7
C-3	5.0	0.1	1.0	0.75	2.70	1.25	4.70	82.0
C-1	5.0	0.08	15.0	2.43	1.45	0.73	4.61	80.5
C-4	5.0	0.09	0.75	0.71	4.17		4.88	85.2
Whatman cellulose								
C-1	5.0	0.1	5.0	3.73	1.26	0.33	5.32	96.0
C-2	5.0	0.08	3.0	3.58	1.53	0.11	5.21	94.0

^a Recovery (%) = $\frac{B}{A} \times 100$. A: Theoretical yield (g), B: Actual yield (g).

Theoretical yield (5.73 g) was applied to DCC Me ester of oxidation ratio 100%. Theoretical yield (5.54 g) was applied to DCC Me ester of oxidation ratio 70%.

Determination of Hydrogen Peroxide

The metal complex (10–20 mg) was added to 0.2 N hydrogen peroxide in 0.1 M phosphate buffer solution (pH 7.0, 100 mL) and the decomposition re-

TABLE II
Analytical Data of Hydroxamic Acid Derivatives Prepared From Dicarboxy Cellulose Methyl Esters

DCC Me ester	Amount of sample (g)	Fraction	Yield		FeCl ₃ reaction	N content (%)		Conversion ^b (%)
			(g)	(%) ^a		Found	Calcd.	
I	5.0	P-1	4.33	85.7	+	12.48	12.61	98.9
		P-3	1.42	—	—	—	—	—
II	5.0	P-1	4.22	83.6	+	12.56	12.61	99.6
		P-3	1.84	—	—	—	—	—
III	5.0	P-1	5.12	102.0	+	5.78	8.83	65.5
		P-3	2.23	—	—	—	—	—
IV	5.0	P-1	4.44	88.4	+	5.38	8.83	60.9
		P-2	1.34	—	±	3.38	—	—
		P-3	2.20	—	—	—	—	—

^a Yield (%) = $\frac{B}{A} \times 100$. A: Theoretical yield (g), B: Actual yield (g).

Theoretical yield (5.05 g) was applied to DCC methyl esters I and II. Theoretical yield (5.02 g) was applied to DCC methyl esters III and IV.

^b Conversion (%) = $\frac{B}{A} \times 100$. A: Theoretical nitrogen content (N calculated) B: Actual nitrogen content (N found).

FeCl₃ reaction (+) indicates that it gives deep red or intense violet color.

I: C-2 prepared from Schleicher & Schüll cellulose. II: C-1 prepared from Whatman cellulose. III: C-4 prepared from Schleicher & Schüll cellulose. IV: C-2 prepared from Whatman cellulose.

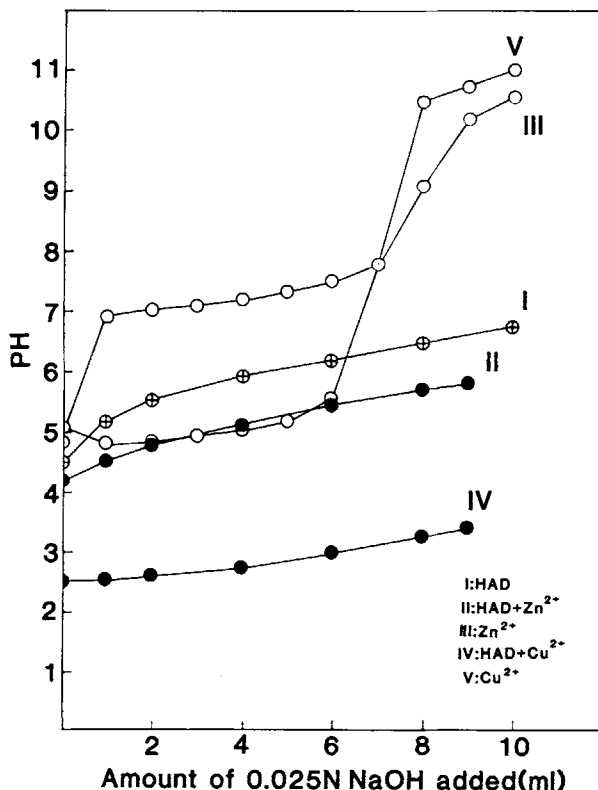


Fig. 3. PH titration curves of hydroxamic acid derivative prepared from dialdehyde cellulose and its metal chelating complexes. HAD stands for a reaction medium of only hydroxamic acid derivative. HAD + Zn²⁺, HAD + Cu²⁺ stand for a reaction medium containing of a mixture of hydroxamic acid derivative and metal ion. Zn²⁺, Cu²⁺ stand for a reaction medium of only metal ion.

action of hydrogen peroxide was followed at fixed temperature during the fixed reaction times. The amounts of hydrogen peroxide remaining in the reaction medium were determined every decided time by the usual oxidation-reduction titrimetric method with standard 0.02 N potassium permanganate solution. The amounts of hydrogen peroxide (mg) were calculated from the following relation:

$$0.02 \text{ N KMnO}_4 \text{ 1 mL} = 0.360 \text{ mg H}_2\text{O}_2$$

RESULTS AND DISCUSSION

Formation of 2,3-Dicarboxy Cellulose Methyl Ester and Hydroxamic Acid Derivative

The yields of 2,3-dicarboxy cellulose methyl esters prepared are shown in Table I. The products were obtained in recovery of more than 80%. The formation of hydroxamic acid derivatives from the methyl esters was confirmed

TABLE III
Amounts of Each Metal Ion Taken Up From Aqueous Mixture Solution
Containing Two Kinds of Equimolar Metal Ions

Metal ions mixed	PH ^a	PH ^b	Amounts of metal ions ^c (mmole/g)	
Cu ²⁺ + Fe ³⁺	1.90	1.69	Fe ³⁺	3.81
			Cu ²⁺	0.12
Cu ²⁺ + Ca ²⁺	5.22	4.89	Cu ²⁺	4.17
			Ca ²⁺	0
Cu ²⁺ + Ag ⁺	4.27	2.37	Cu ²⁺	2.60
			Ag ⁺	2.13
Cu ²⁺ + Mn ²⁺	4.35	2.32	Cu ²⁺	2.29
			Mn ²⁺	0.10
Cu ²⁺ + Zn ²⁺	3.96	2.43	Cu ²⁺	2.38
			Zn ²⁺	0.30
Cu ²⁺ + Ni ²⁺	4.42	2.37	Cu ²⁺	2.02
			Ni ²⁺	0.04
Cu ²⁺ + Cr ³⁺	2.76	2.27	Cu ²⁺	1.79
			Cr ³⁺	0.09

^a PH before addition of sample.

^b PH after addition of sample.

^c Amounts of metal ions taken up into hydroxamic acid derivatives from cellulose. Determined by chelatometric titration method.

by analyses of nitrogen contents introduced in the products and by the characteristic reddish violet coloration with ferric chloride. The analytical data of the hydroxamic acid derivatives prepared from the methyl esters are shown in Table II.

Examination for the Formation of Chelating Complexes by Using pH Titration Curves

In order to confirm the formation of chelating complexes by mixing CHA product and metal ion, pH titration curves were made from the changes of pH values of the products against the amounts of titration with 0.025 N sodium hydroxide solution according to the procedure¹² described previously. Consequently, pH titration curves as shown in Figure 3 were obtained on Cu²⁺ and Zn²⁺. The result indicated a lowering of pH value in the mixture of metal ions and CHA product, in comparison with the case of the changes of pH values of only metal ions and CHA product itself. From observation of a marked drop of pH values in the case of the mixture of Cu²⁺ and CHA product, formation of much more stable complex than that with Zn²⁺ was predicted. The mixture of CHA product and metal ion was found to give no precipitate of hydroxides on the addition of alkali solution as observed in the case of only metal ion. As for other heavy metal ions such as Fe³⁺, Co²⁺, Ni²⁺ formation of chelating complex was observed similarly.

Metal Ions Taken Up by Cellulose Hydroxamic Acid Derivative (CHA Product) from Aqueous Mixture System Containing Two Kinds of Metal Ions

CHA products were mixed with aqueous solution containing two kinds of equimolar Cu²⁺ and another metal ion, and were stirred for 24 h at room tem-

perature. After then, the amounts of metal ion remaining in the aqueous solution were determined by chelatometric titration method¹¹ after separation by centrifugation. From difference between above measurement value and blank value containing only metal ion, amounts of metal ion taken up by the CHA product were obtained as shown in Table III. From this Table, the following properties of CHA product prepared were characterized: (1) In the mixture system of Cu^{2+} and Fe^{3+} , CHA product has higher ability to combine preferentially with Fe^{3+} than with Cu^{2+} . (2) In the mixture system of Cu^{2+} and another metal ions, CHA product has higher ability to combine preferentially with Cu^{2+} than with other metal ions. (3) CHA product has considerable ability to combine with Ag^+ . (4) CHA product has no ability to combine with alkali metal ion or alkaline earth metal ion such as Na^+ , Ca^{2+} .

Thus, it may be concluded that CHA product has selective ability to take up preferentially specific metal ion such as Fe^{3+} or Cu^{2+} .

Catalytic Activity of Metal Complexes in the Decomposition Reaction of Hydrogen Peroxide

Figure 4 shows the decomposition reaction of hydrogen peroxide under the presence of metal complexes formed with various metal ions. The result indicates that metal complexes formed with Cu^{2+} and Co^{2+} , respectively have catalytic activity to accelerate the decomposition reaction of hydrogen peroxide. In particular, Co-complex was found to have higher activity than that of Cu-complex.

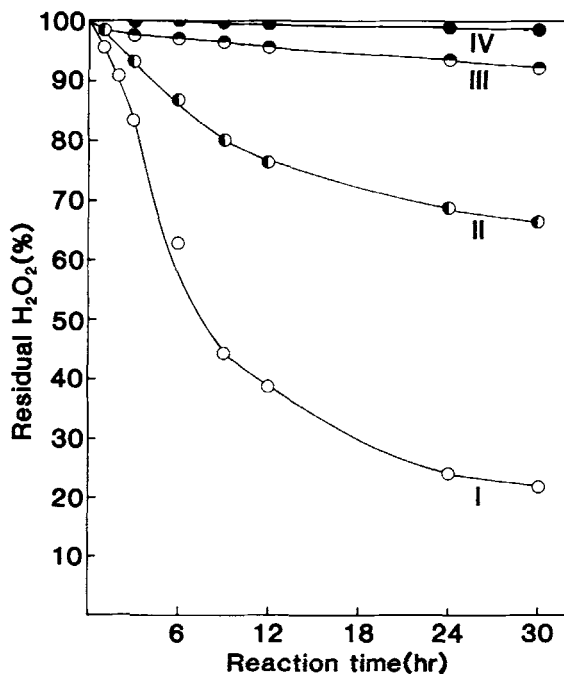


Fig. 4. Decomposition reaction of hydrogen peroxide by use of various hydroxamic acid metal complexes. (I) Co-complex; (II) Cu-complex; (III) Fe-complex; and (IV) N- and Z-complex. Amount of metal complex added: 20 mg, Reaction temp.: 20°C.

However, Fe-complex had very less activity and other Zn and Ni-complexes no activity. Hatano et al.⁴ also reported that hydroxamic acid copper complex of synthetic high polymer revealed similar catalytic activity in the decomposition reaction of hydrogen peroxide. Therefore, the catalytic activity in the decomposition reaction of hydrogen peroxide would be of interest as the reaction based on metal complex containing hydroxamic acid groups. In the decomposition reaction of hydrogen peroxide using Co-complex as shown in Figure 5, the original CHA product had no activity, and cobalt chloride used in the preparation of metal complex was very less active. Consequently, it is assumed that the decomposition reaction of hydrogen peroxide results from the formation of metal complexes. Also, changes of the amounts of addition of metal complex and the reaction temperature have a relation with the activity as would be expected.

Three Co-complexes (Co-C-1, Co-C-2, Co-C-3) differing in molecular weight distribution were fractionated through a cellulose tubing film cut off less than M.W. 8000. The cobalt contents in the fractionated fractions were 12.8%, 15.6%, 16.6% in high order of molecular weight. As shown in Figure 6, Co-complex of Co-C-1 fraction revealed the highest catalytic activity in the decomposition reaction of hydrogen peroxide, although it had the highest molecular weight and the additional lowest cobalt content among three Co-complexes. This finding suggests that the catalytic activity may be caused by the formation of chelating metal complex of higher molecular weight.

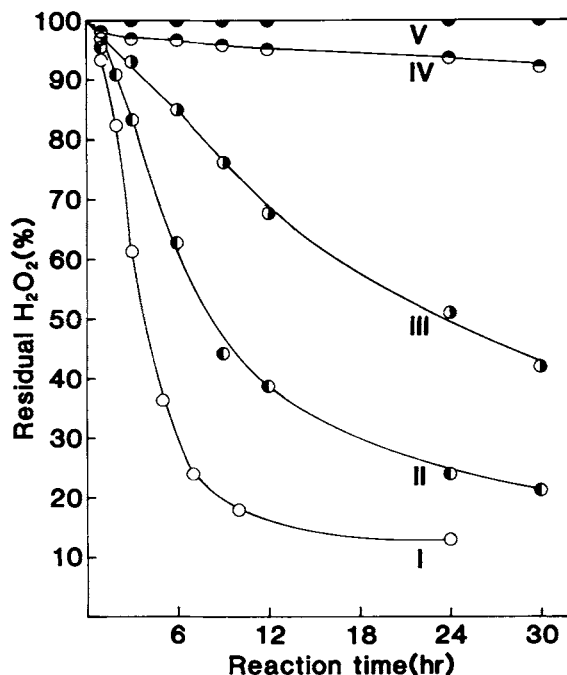


Fig. 5. Decomposition reaction of hydrogen peroxide by use of cobalt complex. (I) Amount of complex added (mg): 20; reaction temp.: 25°C. (II) 20; 20°C. (III) 10; 20°C. (IV) $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ 50 mg; 20°C. (V) HAD product 30 mg; 20°C.

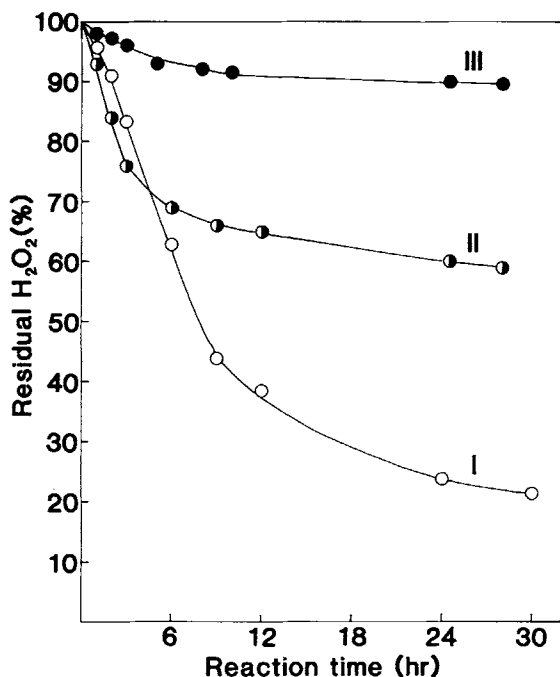


Fig. 6. Decomposition reaction of hydrogen peroxide by use of cobalt complexes with different molecular weight distribution. (I) Cobalt complex (Co-C-1) recovered from the dialyzed solution after dialysis through a cellotubing (cut off less than M.W. 8000) Co content: 12.8%. (II) Cobalt complex (Co-C-2) precipitated by addition of three volumes of EtOH from the dialyzed solution after dialysis Co content: 15.1%. (III) Residue (Co-C-3) obtained by evaporation after removal of fraction (Co-C-2) Co content: 16.6%. Amount of sample added: 20 mg, Reaction temp.: 20°C.

Infrared Spectra of the Products and Structure of Metal Complex

Figure 7 shows the typical IR absorption spectra of 2,3-dicarboxy cellulose Na salt, 2,3-dicarboxy cellulose methyl ester, and hydroxamic acid derivative prepared, respectively. In 2,3-dicarboxy cellulose methyl ester, the absorption¹³ of ester carbonyl groups is observed near 1750 cm^{-1} . Furthermore, for the hydroxamic acid derivative obtained from the methyl ester, the absorption¹³ of amide type carbonyl groups is observed to be near 1680 cm^{-1} . As shown in Figure 8, for the metal complexes formed by introduction of various metal ions, the absorption is observed near 1600 cm^{-1} (shifted to lower wavelength). That means that the formation of chelating complex of the CHA product weakens the double bonding property of carbonyl groups owing to the co-ordinate bond between oxygen atoms of carbonyl groups and metal ions.¹³

Thus, hydroxamic acid metal complexes prepared from 2,3-dicarboxy celluloses, as shown in Figure 9, are considered to contribute to stabilization by such a structure as constituted from the co-ordinate bonding of metal ions formed through the intermolecular and intramolecular linkage in molecular chains. Although the metal complex is shown in both types of keto form (A) and enol form (B), the products formed by introduction of metal ions generally give stable, colored complex without treatment with acid.

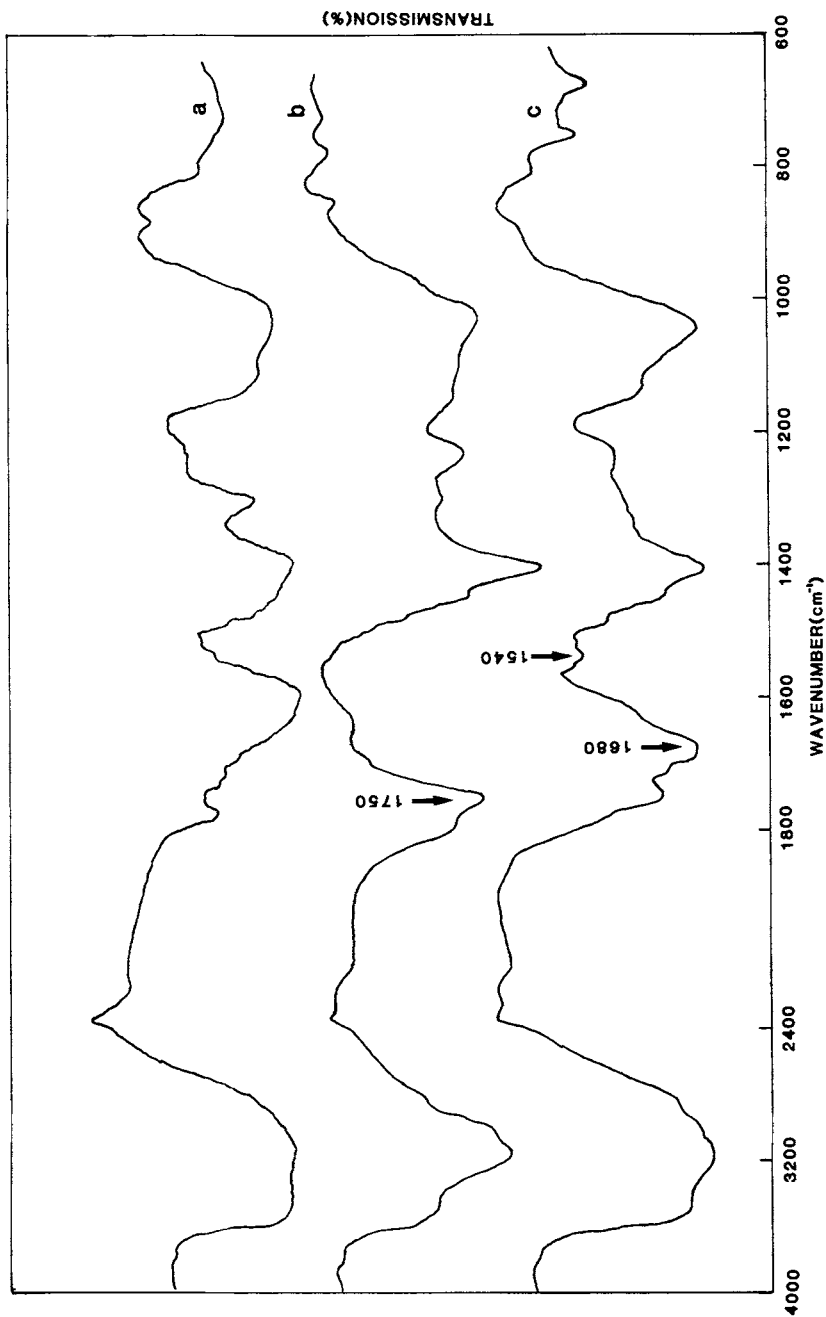


Fig. 7. Infrared spectra of 2,3-dicarboxy cellulose Na salt, 2,3-dicarboxy cellulose methyl ester and hydroxamic acid derivative prepared, respectively. (a) 2,3-dicarboxy cellulose Na salt; (b) 2,3-dicarboxy cellulose methyl ester; and (c) hydroxamic acid derivative.

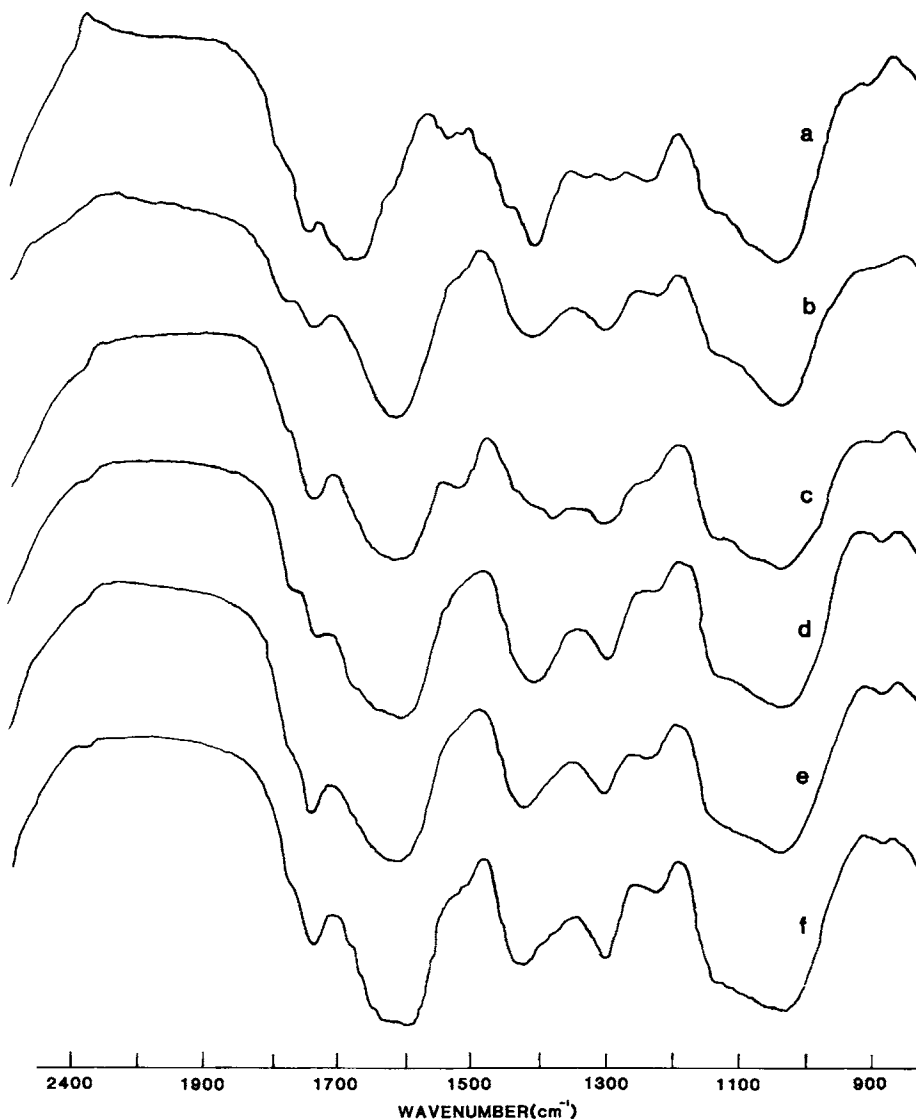


Fig. 8. Infrared spectra of hydroxamic acid derivative and its metal complexes. (a) original hydroxamic acid derivative; (b) Cu-complex; (c) Fe-complex; (d) Zn-complex; (e) Co-complex; and (f) Ni-complex.

CONCLUSION

Mild oxidation with acidified sodium chlorite of dialdehyde cellulose obtained by periodate oxidation of cellulose gives 2,3-dicarboxy cellulose Na salt, which leads to the free form by desalting. 2,3-dicarboxy cellulose affords the methyl ester by treatment at room temperature under the presence of large amounts of anhydrous methanol containing 0.06-0.1 N hydrogen chloride without causing appreciable degradation by methanolysis. The methyl ester derivative is con-

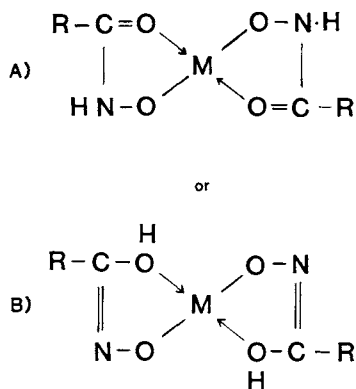


Fig. 9. Formation of metal complex of hydroxamic acid derivative.

verted into the corresponding hydroxamic acid derivative by the action of hydroxylamine methanol solution adjusted to pH 9.2–3 with newly prepared sodium ethylate.

From examination of certain properties concerning hydroxamic acid derivative thus prepared, it may be concluded that (1) the cellulose-hydroxamic acid derivative easily forms metal complexes with various metal ions, (2) CHA has selective ability to take up preferentially specific metal ions such as Fe^{3+} or Cu^{2+} , (3) CHA complexes formed with metal ions such as Co^{2+} or Cu^{2+} have catalytic activity for the decomposition reaction of hydrogen peroxide.

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