

Ce(IV) - Induced Electron Transfer in Pentaammine Cobalt (III) Complexes of α -Amino Acids in Micellar Medium

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Abstract: A micellar catalysed oxidation of pentaamminecobalt(III) complexes of α - amino acids by Ce(IV) in acidic medium yielding nearly 40% of Co(II), 40% of HCHO and about 60% of glyoxalatocobalt(III) complex are ultimate products. The unbound amino acids yield about 40% of HCHO and 60% of glyoxalic acid in presence of micelles. The effect of variation of sulphuric acid concentration is not substantial. The decrease in UV-Visible absorbance at $\lambda = 502$ nm for Co(III) complex corresponds to nearly 40% of the initial absorbance. In spite of the stoichiometry of Ce(IV) to unbound ligand is 2.0:1.0, the ratio of Ce(IV) to cobalt(III) complex is 1.5:1.0 accounting for about 40% reduction at the cobalt(III) centre. The kinetic and stoichiometric results have been accounted. A suitable mechanism consistent with the experimental findings has been proposed by involving a radical cation intermediate.

Key words: Pentaamminecobalt(III) complexes • Induced electron transfer reaction • Micelles • Triol • Complex formation

INTRODUCTION

The electron transfer in pentaamminecobalt (III) complexes of α - amino acids with Ce(IV) has been already reported [1-7]. The extent of Ce(IV) oxidation of pentaamminecobalt (III) complexes of α - amino acids with NaLS and CTAB micelles as important to study the rate of decomposition of the complexes. Since micellar catalysis is an area of tremendous interest due to its occurrence in reactions important to Both biochemical, biotechnological and industrial processes. It as the diagnostic tool to find out the Fraction proceeding by synchronous cleavages of N-H and C-C bonds in micellar medium [8-12].

RESULTS AND DISCUSSION

Table 1 summarizes the kinetic data for the Ce(IV) oxidation of free α - amino acids with IN H_2SO_4 at $30 \pm 0.2^\circ C$ in micellar medium. Though the reaction exhibits first - order dependance on Ce(IV), kinetic saturation has been observed with respect to substrate concentration, suggesting a complex formation between Ce(IV) and α - amino acids i.e., stabilization of the Cobalt-substrate complexes in the micelles.

Assuming 1:1 complex involving Ce(IV) and α - amino acids the following rate law has been deduced for this reaction.

$$\frac{\text{rate}}{\text{Ce(IV)}} = k_{\text{obs}} = \frac{k_{\text{limit}} [\alpha - \text{amino acid}]}{K^{-1} + [\alpha - \text{amino acid}]}$$

Where k_{limit} is the limiting specific rate observed at higher $[\alpha - \text{amino acid}] / [\text{Ce(IV)}]$ ratios and K is the formation constant for the Ce(IV) - α - amino acid complex.

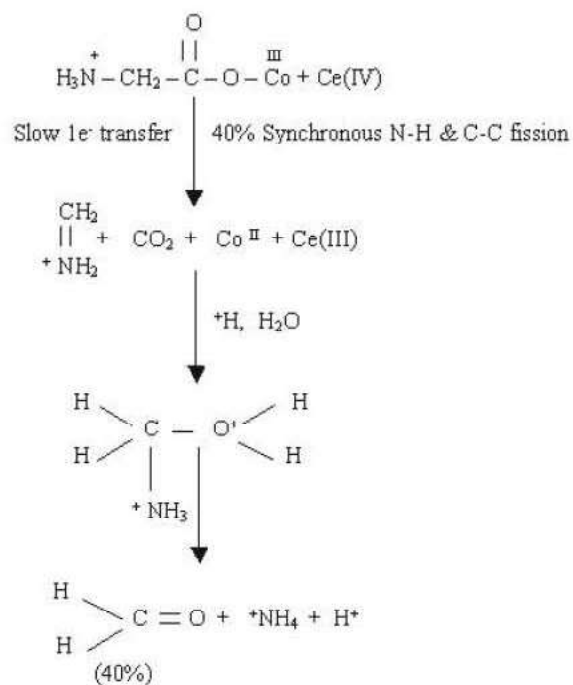
Hence, from the plot of $1/k_{\text{obs}}$ Vs $1 / [\alpha - \text{amino acid}]$ the slope and intercept can be evaluated.

Table 2 lists the formation constants for Ce(IV) - Co complexes of α - amino acid along with the limiting specific rates.

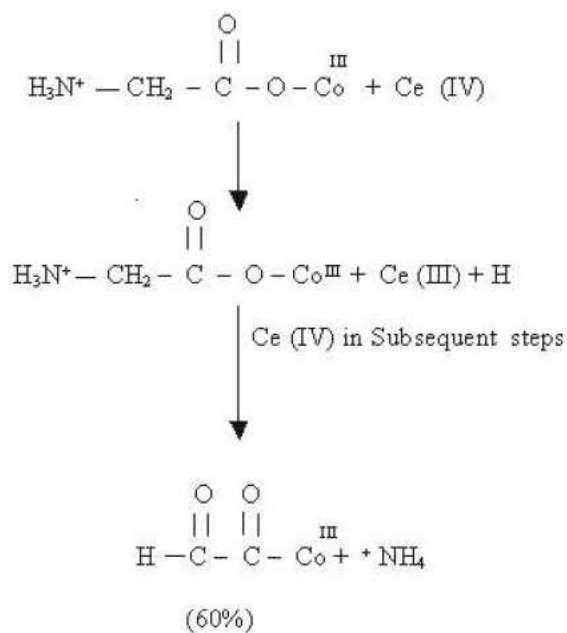
Such complex formation seems to be absent when the carboxyl and it is tied up by Co (III) and the reaction between Ce(IV) and Co (III) complexes of α - amino acids exhibit uncomplicated second order kinetics.

From a comparison of the specific rates for Ce(IV) oxidation of the respective Co(III) complexes and the dimeric Cobalt (III) glycine complex Table 3 and Table 4, one can infer that the oxidation rates of α - amino acids are not significantly affected by complex formation. This may be because the point of attack lies away from the Co (III) centre so that its electrostatic influence is less felt. There is, however a considerable change in the specific rate of Ce(IV) oxidation of the $Co_2^{(III)}$ glycine complex as the two Co (III) centres can exert greater electrostatic influence over the reacting centre. This suggests that Ce(IV) attacks the - NH_2 or - NH centre in the slow step of

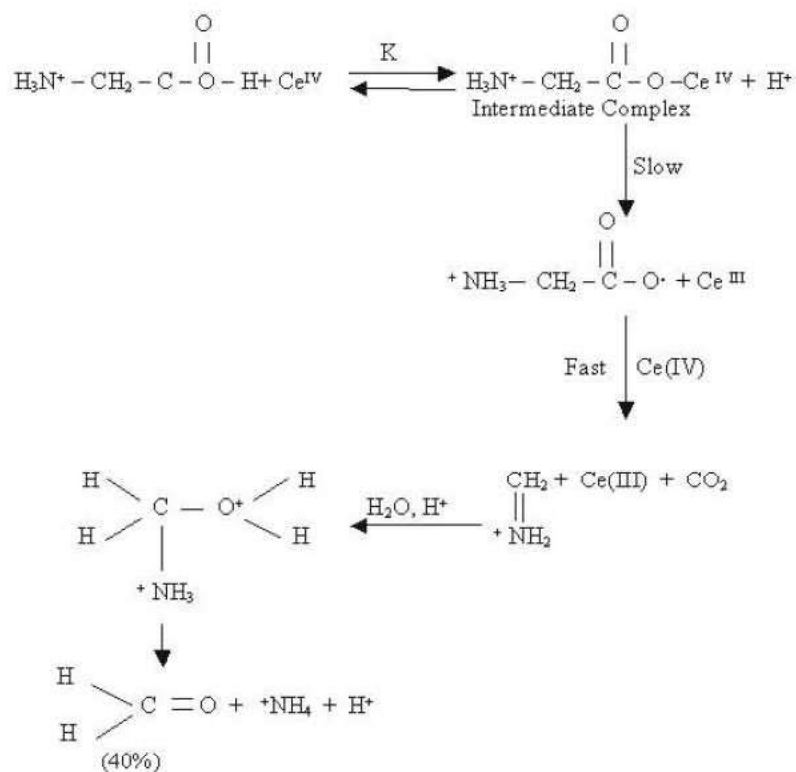
Scheme I

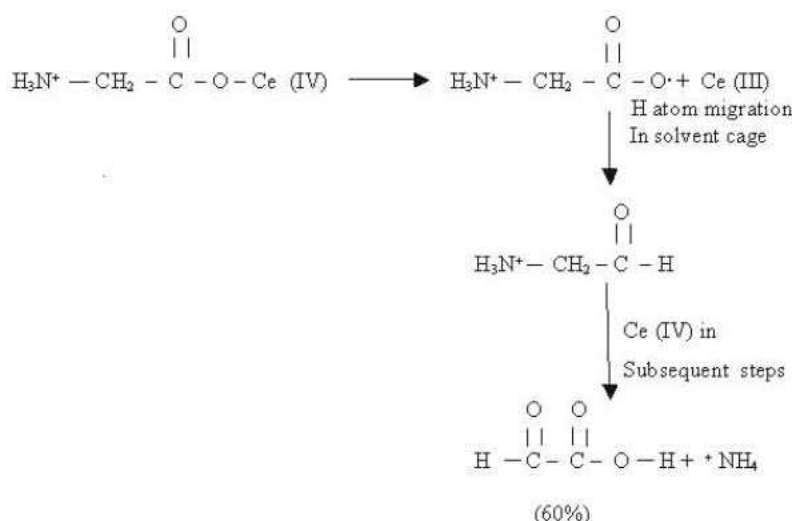


Scheme II



Scheme III



Scheme IVTable 1: First order rate constants for Ce(IV) oxidation of α - amino acids in micelles at $30 \pm 0.2^\circ\text{C}$

Substrate (Unbound)	$10^3[\alpha\text{-amino acids}]$ mol dm^{-3}	$10^3 k_1 \text{ sec}^{-1}$	$10^4 k_{\text{calculated}}$
a) glycine	10	2.6	2.8
	20	2.8	3.0
	30	3.2	3.1
	40	3.5	3.4
	50	4.0	3.9
b) L-alanine	10	1.8	2.0
	20	2.1	2.3
	30	2.5	2.6
	40	3.0	2.9
	50	3.8	3.5
c) N-benzoylalanine	10	17.1	17.4
	20	19.5	19.2
	30	23.0	22.5
	40	25.0	24.5
	50	28.2	28.5
d) N-acetyl glycine	10	16.1	16.5
	20	18.0	18.5
	30	18.9	18.0
	40	19.8	19.2
	50	20.5	20.0
e) N-benzoyl glycine	10	18.7	18.4
	20	20.5	20.0
	30	22.1	22.5
	40	24.0	23.5
	50	26.0	25.0

Ce(IV) ---0.2 M, H₂SO₄---1N, NaLS---0.2 M, Temperature--- $30 \pm 0.2^\circ\text{C}$

the reaction, leading to the formation of a radical $\cdot\text{NH}$ or $\cdot\text{N}$. The reduction in the specific rate of Ce(IV) oxidation of Co (III) complexes of N - Acetyl and N - Benzoyl glycine and N - Benzoyl alanine, compared to that of unbound ligands, points to significant electronic influence of the acyl group and also the electrostatic influence of the Co (III) centre at the seat of attack Viz, the

Table 2: First order rate constants for Ce(IV) oxidation of Co(III) complexes of α - amino acids in micelles at $30 \pm 0.2^\circ\text{C}$

Substrate (Unbound)	$\alpha\text{-amino acids}$ mol dm^{-3}	$10^3 k_1 \text{ sec}^{-1}$	$10^4 k_{\text{calculated}}$
a) glycine	5	2.68	5.36
	10	5.35	5.35
	20	10.72	5.36
	30	15.90	5.30
	40	22.40	5.60
b) L-alanine	5	3.60	7.20
	10	7.38	7.38
	20	14.70	7.35
	30	21.90	7.30
	40	28.93	7.24
c) N-benzoylalanine	5	9.95	19.90
	10	19.08	19.05
	20	38.10	19.05
	30	59.20	19.74
	40	79.40	19.80
d) N-acetyl glycine	5	9.80	19.60
	10	19.50	19.50
	20	39.10	19.50
	30	59.00	19.60
	40	77.90	19.50
e) N-benzoyl glycine	5	20.90	27.94
	10	41.70	31.45
	20	83.10	32.82
	30	124.00	33.56
	40	165.00	34.01

Ce(IV) ---0.2 M, H₂SO₄---1N, NaLS---.2M, Temperature--- $30 \pm 0.2^\circ\text{C}$

NH group. Such an electrostatic influence due to ligation of α - amino acids to the Co (III) centre (in the monomer only) seems to be absent as the amino nitrogen is protonated both in the complex and in the unbound ligand, exerting possibly the same electrostatic influence at the set of attack.

Table 3: Ce(IV) Oxidation of Co(III) complexes of ∞ - amino acids in micelles at 30 \pm 0.2 $^{\circ}$ C

Substrate (bound)	$10^4 k_{\text{limit}}^b$ sec $^{-1}$	K_{am}^{-1}	Correlation coeff. (γ)
Glycine	6.66	6.00	0.99
L-alanine	7.14	4.51	0.97
L-Isoleucine	8.33	8.75	0.98
N-acetyl glycine	37.03	13.50	0.97
N-benzoyl glycine	31.25	7.39	0.99

a) Formation constant, K for Ce(IV) - ∞ - amino acid complexes were calculated as the ratio of intercept or slope from the plot of $1/k_{\text{obs}}$ Vs $1/[\infty$ - amino acids] at 1N H₂SO₄ and 0.2 M NaLS 30 \pm 0.2 $^{\circ}$ C.

b) Rates were calculated from the intercept of the $1/k_{\text{obs}}$ Vs $1/[\infty$ - amino acids] at 1N H₂SO₄ and 0.2 M NaLS

Table 4: Ce(IV) Oxidation of ∞ - amino acids in micelles at 30 \pm 0.2 $^{\circ}$ C

∞ - amino acids	$10^{-2} k_{\text{mol}}^{-1}$ dm $^{-3}$	$10^2 K_{\text{limit}}$ Sec $^{-1}$	Correlation coeff. (γ)
Glycine	0.78	4.4	1.00
L-alanine	0.33	5.0	0.97
N-acetyl glycine	2.90	21.0	0.99
N-benzoyl glycine	2.40	25.0	0.98

a) Formation constant, K for Ce(IV) - ∞ - amino acid complexes were calculated as the ratio of intercept or slope from the plot of $1/k_{\text{obs}}$ Vs $1/[\infty$ - amino acids] at 1N H₂SO₄ and 0.2 M NaLS 30 \pm 0.2 $^{\circ}$ C.

b) Rates were calculated from the intercept of the $1/k_{\text{obs}}$ Vs $1/[\infty$ - amino acids] at 1N H₂SO₄ and 0.2 M NaLS

The stoichiometric results indicate that for one mole of Cobalt (III) complex, about 0.3 mole of Ce(IV) is consumed, whereas with the unbound ligands for one mole of ∞ - amino acid about 0.4 mole of Ce(IV) is consumed. Table 5 and Table 6. The stoichiometric results coupled with kinetic data and product analysis, can be accounted for by the following reaction schemes.

Scheme I proposes that Ce(IV) oxidizes NH center and induces the formation of a radical which in a synchronous step undergoes carbon - carbon bond fission, yielding Co (II). As the amount of HCHO or Co (II) formed is only 40% of $[Co(III)]_{\text{initial}}$. The above reaction probably contribute only 40% of the total reaction. As 1 mole of glycinatocobalt(III) complex consumes 1.5 mol of Ce(IV) yielding nearly 60% of glyoxalatocobalt(III) complex.

Scheme II envisages the formation of nitrogen radical that reacts with Ce(IV) in subsequent steps, yielding ultimately glyoxalatocobalt(III) complex. This probably forms the rest of the reaction (about 60%). In this case the amount of Ce(IV) consumed by one mole of Co (III)

Table 5: Stoichiometric data for Ce(IV) Oxidation of ∞ - amino acids and their corresponding Co(III) complexes in NaLS Medium at 30 \pm 0.2 $^{\circ}$ C

$10^2 [Compound]_{\text{initial}}$ mol dm $^{-3}$	$10^2 [Ce(IV)]_{\text{initial}}$ mol dm $^{-3}$	$\Delta [Ce(IV)] / [Co(III)]_{\text{initial}}$	$10^3 [Co(II)]$ mM (%) mol dm $^{-3}$	$10^3 [HCHO]^d$ mM (%) mol dm $^{-3}$	10^3 Glyoxalic acid mM (%) mol dm $^{-3}$
Glycine 1.00	5.00	2.00a	-	3.90(39.2)	5.90(59)
1.00	10.00	2.10 a	-	3.80(38)	6.20(62)
N-acetyl glycine 1.00	5.00	-	-	3.70(37)	6.30(63)
∞ -alanine 1.00	5.00	2.10a	-	-	-
(NH ₃) ₃ Co ^{III} - L ²⁺ L=		2.10a			
L=glycine 1.00	4.90	3.60(36)	3.50(35)f	-	-
L= glycine 0.26	4.90	1.40a	0.09(35)	0.09(35)f	-
L=N-acetyl					
Glycine 1.00	5.00	1.40a	3.40(34)	3.50(35)	-
L= ∞ - alanine 1.00	5.00	1.50a	3.50(35)	-	-
L= ∞ -alanine 0.25	5.00	1.60a	0.09(35)	-	-
Co ^{III} (gly)c 1.00	5.00	-	-	3.60(36)	-

a) Formation constant, K for Ce(IV)- ∞ - amino acid complexes were calculated as the ratio of intercept or slope from the plot of $1/k_{\text{obs}}$ Vs $1/[\infty$ - amino acids] at 1N H₂SO₄ and 0.2 M NaLS 30 \pm 0.2 $^{\circ}$ C.

b) The limiting specific rates were calculated from the intercept of the $1/k_{\text{obs}}$ Vs $1/[\infty$ - amino acids] at 1N H₂SO₄ and 0.2 M NaLS.

Table 6: Stoichiometric data for Ce(IV) Oxidation of ∞ - amino acids and their corresponding Co(III) complexes in CTAB Medium at 30 \pm 0.2 $^{\circ}$ C

$10^2 [Compound]_{\text{initial}}$ mol dm $^{-3}$	$10^2 [Ce(IV)]_{\text{initial}}$ mol dm $^{-3}$	$\Delta [Ce(IV)] / [Co(III)]_{\text{initial}}$	$10^3 [Co(II)]$ mM (%) mol dm $^{-3}$	$10^3 [HCHO]^d$ mM (%) mol dm $^{-3}$	10^3 Glyoxalic acid mM (%) mol dm $^{-3}$
Glycine 1.00	5.00	2.10a	-	3.95(39.5)	5.99(60)
1.00	10.00	2.15a	-	3.90(39)	6.30(63)
N-acetyl glycine 1.00	5.00	-	-	6.50(65)	-
∞ -alanine 1.00	5.00	-	-	3.85(39)	-
(NH ₃) ₃ Co ^{III} - L ²⁺ L=		2.20a		-	
L=glycine 1.00	4.90	1.60a	3.80(38)	3.60(36)f	-
L= glycine 0.26	4.90	1.50a	0.09(35)	0.09(35)f	-
L=N-acetyl					
Glycine 1.00	1.60 a	3.50(35)	3.60(36)	-	-
L= ∞ - alanine 1.00	5.00	1.60a	3.60(36)	-	-
L= ∞ -alanine 0.25	5.00	1.70a	0.08(35)	-	-
Co ^{III} (gly)c 1.00	5.00	1.50a	-	3.80(38)	-

a) Formation constant, K for Ce(IV)- ∞ - amino acid complexes were calculated as the ratio of intercept or slope from the plot of $1/k_{\text{obs}}$ Vs $1/[\infty$ - amino acids] at 1N H₂SO₄ and 0.2 M CTAB 30 \pm 0.2 $^{\circ}$ C.

b) The limiting specific rates were calculated from the intercept of the $1/k_{\text{obs}}$ Vs $1/[\infty$ - amino acids] at 1N H₂SO₄ and 0.2 M CTAB

should be around 0.4 mole, which is in agreement with the observed stoichiometric results. In the case of unbound glycine and N -acetyl glycine in presence of micelles the consumption of Ce(IV) is around 0.4 mol, the yield of HCHO is about 40% and that of glyoxalic acid is about 60%. In the case of the Co (III) glycinato complex, the other product is the Co (III) glyoxalato complex.

Scheme III and IV, electron transfer possibly occurs within the precursor or intermediate complex and our kinetic data evidence the formation of such a binuclear complex with fairly high association constant K, between Ce(IV) and α - amino acid possibly due to the ligation of Ce(IV) to free carboxyl end (which is absent in a Co(III)-complex).

In the absence of internal oxidant, cobalt(III) in the cerium(IV) oxidation of α - amino acids and in presence of micelles, the consumption of cerium(IV) should be more by 40% as both the schemes involve the oxidant cerium(IV) Only. This is in keeping with the observed stoichiometric data viz., 1 mole of α - amino acid requires nearly 2 moles of Ce(IV). In the micellar phase 40% induced electron transfer is observed whereas only 20% reduction at Co(III) centre takes in the absence of micelles.. A plot of specific rate constant versus micelles(detergent) concentration is sigmoidal one. The catalytic effect is more pronounced in presence of NaLS and CTAB. Hence the rate of reaction is increased by the addition of both NaLS and CTAB.

Thus the present study on Ce(IV) induced electron transfer in cobalt(III) bound and unbound α - amino acids in presence of micelles, presents evidence for dualistic mechanistic pathways available for the reaction one preferring N-H and C-C fissions to the extent of 40% whereas, the other proceeding by -N-H- and α - C-H- fissions forming about 60% of total reaction.

Sethuram *et al.* [13] consider the breaking of the N - H bond in a fast step. Still such an amino acid radical formation has been involved in the Ag+ [14] catalysed $S_2O_8^{2-}$ oxidation of α - amino acids.

Experimental: Ammonium cerium (IV) nitrate, (BDH, AnalaR Grade) (Anal: Calculated for $(NH_4)_2 Ce(NO_3)_6$: Ce 25.5 found (Ignition of CeO_2) Ce, 25.5) α - amino acids employed as ligands, Sodium lauryl sulphate (NaLS) and Cetyl Trimethyl Ammonium Bromide(CTAB) Aldrich Products) were used as obtained.

N - acetyl and N - benzoyl glycine and N - benzoyl alanine were prepared by following the procedure of Vogel [15]. The $(NH_3)_5 Co$ (III) complexes of glycine, α - alanine, N - acetyl and N - benzoyl glycine and N - benzoyl alanine were prepared as their perchlorates by the method of Fan [16]. The tris (μ - hydroxo) complex

$(NH_3)_3 Co (OH)_3 (Co (NH_3)_3 (ClO_4)_3$ (triol) has been prepared by the procedure of Siebert and Co workers [17,18].

The reaction between Ce(IV) and Co III complexes was carried out at $30^\circ C \pm 0.2^\circ C$ in presence of micelles in a thermostated bath. The concentrations of unreacted Ce(IV) were determined both iodometrically and spectrophotometrically at 400 nm. The disappearance of Co (III) was followed spectrophotometrically by following the decrease in absorbance at 502 nm (for the monomeric Co (III) complex) and at 520 nm (for the dimeric Co (III) complex). The specific rates estimated from the optical density measurements agree with the values from the volumetric procedure with $\pm 7\%$. Curiously, the change in absorbance observed at 502 nm or 520 nm for the Co (III) complexes of glycine corresponds to very nearly 20% of the initial concentration of Co (III) in absence of micelles, while the change in optical density at 400 nm for Ce(IV) corresponds to 40% of $[Co (III)]_{initial}$ in presence of micelles. Ionic strength was maintained by the addition of suitable quantities of H_2SO_4 and Na_2SO_4 .

Co (II) was estimated after the completion of reaction, by diluting the reaction mixture 10 - fold with concentrated HCl, allowing evolution of chlorine to cease and then measuring the absorbance at 692 nm [19]. ($\epsilon = 560$). The amount of Co (II) estimated in all these cases corresponds to nearly 40% of $[Co (II)]_{initial}$.

After 48h, the product was extracted with ether and analysed iodoimetrically for the amount of HCHO formed in the case of the [glycinato] and [N - acetyl glycinato] Cobalt (III) complexes, the dimeric Co (III) complex and unbound glycine. The yield of HCHO in all these cases is nearly 40% $[Co (III)]_{initial}$ [20] Table 5 and Table 6.

After neutralization of the reaction mixture with sodium bicarbonate, the pH of the aqueous layer was adjusted to about 6.5 and the aqueous layer was separated by filtration in the case of both free ligands and corresponding complexes. On evaporation of water under reduced pressure, the product separated and the percentage yield was calculated. Though the yield of glyoxalic acid was nearly quantitative, the estimation of glyoxalic acid complex was less nearly quantitative, the estimation of glyoxalic acid complex was less nearly quantitative. In both the cases the IR spectra of the product agreed with that of authentic samples of glyoxalic acid or the [glyoxalato] cobalt (III) complex.

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