

Kinetics and mechanism of the reversible formation of the binuclear species between pyridine-2-carboxylato(pentaammine)cobalt(III) and cobalt(II) in aqueous solution

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Abstract. The kinetics of formation and dissociation of the binuclear complex of cobalt(II) with pyridine-2-carboxylato(pentaammine) cobalt(III) have been studied in the temperature range 10–25°C and at $I = 0.3 \text{ mol dm}^{-3}$ (ClO_4^-). The formation of $(\text{NH}_3)_5\text{CoO}_2\text{CC}_5\text{H}_4\text{NCo}^{4+}$ in the pH range 2.35–3.20 involves the reaction of $\text{Co}(\text{OH})_2^{2+}$ with the protonated (pyridine-N) and the deprotonated forms of the complex. The rate and activation parameters for the formation reaction are consistent with an I_d mechanism. The binuclear species undergoes dissociation to yield the parent cobalt(III) substrate and cobalt(II) via spontaneous and acid-catalysed paths. The rate data at 20°C for the spontaneous dissociation of the binuclear complex and of mono(pyridine-2-carboxylato) cobalt(II) are comparable indicating the chelating nature of the binuclear species.

Keywords. Kinetics; binuclear species; coordinated picolinate; cobalt(II).

1. Introduction

The kinetics of complex formation between Ni(II) and a variety of ligands already coordinated to cobalt(III) have been investigated earlier (Dash and Acharya 1991; Das and Dash 1992; Das 1993; Dash *et al* 1993). However, the formation of the analogous binuclear species with cobalt(II) have been studied only sparsely (Acharya 1993). In an earlier paper, we have reported the kinetics of formation and dissociation of the binuclear complex between Ni(II) and pyridine-2-carboxylato(pentaammine) cobalt(III) (Das and Dash 1993) where the rate of chelation could be isolated from that of the initial monodentate binuclear species under the reaction conditions studied. The present work reports the kinetics of formation and dissociation of the binuclear species formed between cobalt(II) and the above cobalt(III) complex to compare the mechanistic aspects of the complexation behaviour of the two added bivalent metal ions.

2. Experimental

Pyridine-2-carboxylato(pentaammine) cobalt(III) perchlorate was prepared by the literature method (Gould and Taube 1964) and its purity checked by cobalt analysis and UV-visible spectral data.

The stock solution of cobalt(II) perchlorate was prepared by digesting AR grade

cobalt(II) carbonate with HClO_4 and the Co(II) estimated by complexometry (Vogel 1962). Chloroacetic acid–acetate buffer and NaClO_4 were used to adjust pH and ionic strength, respectively. All other chemicals used were of AR grade. All solutions were prepared in double-distilled water.

The pH measurements were made with an Elico digital pH meter, model LI 120, using a combination electrode model CL 51. The reference electrode was filled with 2.0 mol dm^{-3} NaCl instead of KCl and the meter was calibrated using NBS buffers. The concentrations of $[\text{H}^+]$ ($= a_{\text{H}}/f_{\text{H}^+}$) were calculated from the pH data using calculated values of the f_{H^+} by the Davies Equation (Davies 1938). The UV-visible spectra were recorded on a JASCO 7800 UV-visible spectrophotometer. Analysis of the rate data and calculation of activation parameters were made using appropriate least-squares programs adapted to an Apple PC.

2.1 Kinetics

The kinetics of formation of the binuclear complex was determined in the range of pH 2.35–3.20 and of temperature 10–25°C, $[\text{Co}^{2+}] = (1-5) \times 10^{-2}$, $[\text{complex}] = 2 \times 10^{-3}$, and $I = 0.3 \text{ mol dm}^{-3}$, using a computerised SF 51 Hi-Tech (UK) stopped flow spectrophotometer. The formation (absorbance increased with time) and dissociation (absorbance decreased with time) of the binuclear species were followed at 300 nm. For the dissociation reaction, the preformed binuclear species (pH = 6.0) was acidified and the kinetics of its decay was followed. All other kinetic details have been described in our earlier work (Das and Dash 1992). The pseudo-first-order rate constant for any run was taken to be the average from seven determinations and the error quoted is standard deviation. There was no effect of buffer on the reaction as rate constants were unaffected when the buffer strength was varied ($[\text{ClCH}_2\text{COOH}] = 0.017$ to $0.042 \text{ mol dm}^{-3}$ and $[\text{ClCH}_2\text{COO}^-] = 0.003$ to $0.0078 \text{ mol dm}^{-3}$) keeping pH and metal ion concentration constant.

2.2 Acid dissociation constant (K_{NH}) of $(\text{NH}_3)_5\text{CoO}_2\text{CC}_5\text{H}_4\text{NH}^{3+}$

The pH titration of an aqueous solution of the title complex indicated only one inflexion point in the pH range 2.5 to 6.5. The values of the N-protonated complex (protonation occurring at the free pyridine-N) were found to be 4.17 ± 0.12 , 4.15 ± 0.04 and 4.10 ± 0.11 at 15, 20 and 25°C ($I = 0.3 \text{ mol dm}^{-3}$), respectively. These may be compared with the reported value of $pK_{\text{NH}} = 3.98 \pm 0.05$ at 30°C, $I = 0.3 \text{ mol dm}^{-3}$ (Dash *et al* 1981).

3. Results and discussion

3.1 Formation of $(\text{NH}_3)_5\text{CoO}_2\text{CC}_5\text{H}_4\text{NCo}^{4+}$

The pseudo-first order rate constants (k_{obs}) for the reversible formation of the binuclear species at $2.35 \leq \text{pH} \leq 3.18$, $0.01 \leq [\text{Co}^{2+}]_{\text{T}} \leq 0.05 \text{ mol dm}^{-3}$ ($[\text{complex}]_{\text{T}} = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$) and $10.0 \leq t^\circ\text{C} \leq 25.0$ are collected in table 1. It is evident from figure 1 that k_{obs} values at a given pH increase linearly with $[\text{Co(II)}]_{\text{T}}$; the slopes and intercepts of such plots are identified as the overall rates of formation (k_f) and

Table 1. Rate data for the formation of the binuclear complex between cobalt(II) and pyridine-2-carboxylato(pentaammine)cobalt(III)^a.

[Co ²⁺] mol dm ⁻³	k_{obs} (s ⁻¹)				
<i>10.0 ± 0.1°C</i>					
	(2.35 ± 0.02) ^b	(2.65 ± 0.02)	(2.84 ± 0.01)	(3.00 ± 0.02)	
0.01	13.6 ± 0.4	15.5 ± 0.2	17.5 ± 0.4	19.9 ± 0.8	
0.015	15.4 ± 0.6	—	—	—	
0.02	17.0 ± 1.0	21.5 ± 1.7	26.1 ± 1.2	32.1 ± 1.0	
0.03	20.5 ± 0.5	25.9 ± 0.7	35.3 ± 1.3	44.3 ± 1.3	
0.04	23.9 ± 1.0	32.6 ± 1.0	42.8 ± 1.9	56.3 ± 2.4	
0.05	27.6 ± 1.4	39.9 ± 1.0	52.5 ± 1.3	68.2 ± 1.2	
<i>15.0 ± 0.1°C</i>					
	(2.35 ± 0.02)	(2.65 ± 0.02)	(2.81 ± 0.02)	(2.93 ± 0.01)	
0.01	21.3 ± 1.1	22.8 ± 1.2	25.4 ± 1.7	28.4 ± 1.0	
0.015	25.5 ± 0.9	—	—	—	
0.02	28.8 ± 1.3	31.2 ± 0.8	36.4 ± 1.5	42.3 ± 1.7	
0.03	33.1 ± 1.3	39.4 ± 1.2	47.2 ± 1.1	57.5 ± 1.3	
0.04	40.1 ± 1.6	48.7 ± 0.8	59.6 ± 1.1	72.1 ± 2.0	
0.05	49.9 ± 1.7	57.5 ± 1.3	72.9 ± 1.8	86.6 ± 1.4	
<i>20.0 ± 0.1°C</i>					
	(2.35 ± 0.02)	(2.60 ± 0.02)	(2.87 ± 0.01)	(3.03 ± 0.02)	(3.18 ± 0.02)
0.01	33.1 ± 1.3	38.4 ± 1.2	45.8 ± 1.1	55.1 ± 3.2	66.7 ± 1.2
0.015	36.4 ± 1.9	46.1 ± 2.6	58.1 ± 2.1	70.1 ± 3.2	90.5 ± 1.4
0.02	41.3 ± 1.8	51.8 ± 2.8	70.5 ± 2.4	86.2 ± 2.8	112 ± 4.3
0.03	52.4 ± 2.0	67.5 ± 1.6	95.1 ± 2.2	120 ± 3.4	158 ± 7.0
0.04	61.5 ± 2.5	82.8 ± 2.8	120 ± 4.3	154 ± 3.6	205 ± 6.0
0.05	70.1 ± 1.8	99.9 ± 3.8	144 ± 2.3	189 ± 4.3	248 ± 11.2
<i>25.0 ± 0.1°C</i>					
	(2.35 ± 0.02)	(2.65 ± 0.02)	(2.88 ± 0.01)	(3.01 ± 0.02)	(3.16 ± 0.02)
0.01	44.9 ± 3.5	55.9 ± 2.9	66.5 ± 2.6	79.7 ± 2.4	101 ± 2.2
0.015	55.2 ± 3.7	72.1 ± 2.1	87.5 ± 4.2	109 ± 3.1	137 ± 4.2
0.02	66.4 ± 2.4	81.2 ± 4.8	109 ± 3.1	135 ± 8.0	173 ± 7.7
0.03	82.1 ± 4.0	109 ± 2.2	143 ± 7.9	188 ± 6.6	252 ± 16
0.04	98.0 ± 1.8	136 ± 3.6	191 ± 5.4	245 ± 17.0	331 ± 19
0.05	132 ± 6.2	161 ± 11.7	235 ± 8.6	301 ± 8.0	406 ± 34

^a[complex]_T = 2.0 × 10⁻³, I = 0.30 mol dm⁻³, λ = 300 nm; ^bValues in parentheses are pH (average)

of dissociation (k_r) of the binuclear species, respectively. The increase in k_f values with increase in pH may be attributed to the involvement of both N-protonated and NH-deprotonated forms of the complex. However, the k_r values decrease with increase in pH indicating thereby that the rate of dissociation of binuclear species is acid catalysed. An earlier pH titration study (Dash *et al* 1981) of thermodynamic stabilities indicated that Co(II) is most probably chelated by the pyridine-N and the carboxylato group is bound to the cobalt(III) centre. Also, under the experimental conditions (pH = 2.35 – 3.18), both protonated and deprotonated forms of the complex exist ($pK = 4.10 \pm 0.11$ at 25°C). Hence, considering the above facts the possible reaction steps may be delineated as in scheme 1.

For which k_{obs} takes the form:

$$k_{\text{obs}} = k_f[\text{Co}^{2+}] + k_r, \quad (1)$$

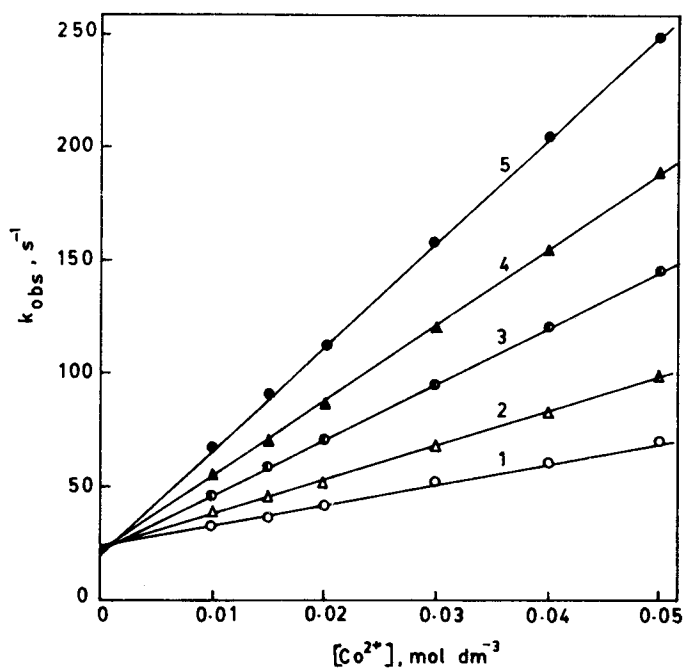
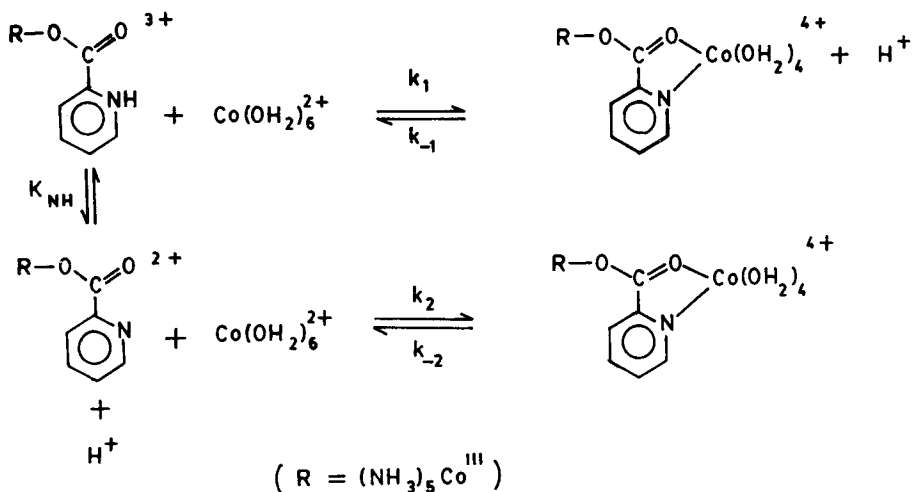


Figure 1. Plots of k_{obs} versus $[\text{Co}^{2+}]$ at 20°C (1-5 at pH-levels 2.35, 2.60, 2.87, 3.03 and 3.18, respectively).



Scheme 1.

where k_f and k_r are given by

$$k_f = (k_1[\text{H}^+] + k_2K_{\text{NH}})/([\text{H}^+] + K_{\text{NH}}), \quad (2)$$

and

$$k_r = k_{-1}[\text{H}^+] + k_{-2} \quad (3)$$

In (2) and (3), k_i and k_{-i} ($i=1$ and 2) are the individual rate constants for the formation and dissociation of the binuclear complex, respectively.

Table 2. Calculated rate and activation parameter data for the formation of $(\text{NH}_3)_5\text{CoO}_2 \cdot \text{CC}_5\text{H}_4\text{NCo}^{4+}$

pH_{av}	$10^{-2}k_f$ ($\text{dm}^3\text{mol}^{-1}\text{s}^{-1}$)	k_1 ($\text{dm}^3\text{mol}^{-1}\text{s}^{-1}$)	$10^{-4}k_2$ ($\text{dm}^3\text{mol}^{-1}\text{s}^{-1}$)	k_r (s^{-1})
$10.0 \pm 0.1^\circ\text{C}$				
2.35	3.45 ± 0.20	77.6 ± 14	2.78 ± 0.07	10.1 ± 0.07
2.65	5.80 ± 0.21			9.6 ± 0.34
2.84	8.71 ± 0.35			8.6 ± 0.23
3.00	12.10 ± 0.38			7.8 ± 0.11
$15.0 \pm 0.1^\circ\text{C}$				
2.35	5.95 ± 0.25	250 ± 34	3.10 ± 0.13	16.1 ± 0.64
2.65	8.68 ± 0.19			13.9 ± 0.31
2.81	11.74 ± 0.35			12.8 ± 0.15
2.93	14.57 ± 0.28			13.7 ± 0.26
$20.0 \pm 0.1^\circ\text{C}$				
2.35	9.44 ± 0.22	336 ± 44	5.98 ± 0.12	23.2 ± 0.72
2.60	14.92 ± 0.27			23.2 ± 0.65
2.87	24.58 ± 0.39			21.2 ± 0.94
3.03	33.51 ± 0.36			20.1 ± 1.01
3.18	46.01 ± 0.44			19.9 ± 0.31
$25.0 \pm 0.1^\circ\text{C}$				
2.35	17.17 ± 0.2	564 ± 68	8.56 ± 0.14	29.9 ± 2.15
2.65	25.96 ± 0.68			31.5 ± 1.70
2.88	41.42 ± 0.69			25.2 ± 1.51
3.01	54.99 ± 0.47			25.2 ± 0.87
3.16	75.37 ± 0.86			24.9 ± 1.13
ΔH^\ddagger (kJ mol^{-1}) = 79.4 ± 7.1^a ; 52.3 ± 5.9^b				
ΔS^\ddagger ($\text{JK}^{-1}\text{mol}^{-1}$) = 74.4 ± 58.6^a ; 24.9 ± 20.1^b				

Values obtained from dependence of temperature on k_1^a and k_2^b , respectively.

The values of k_f and k_r derived from the least squares slopes and intercepts of the plots k_{obs} versus $[\text{Co}^{2+}]$ at specified pH are presented in table 2, as also the rate parameters, k_1 and k_2 , obtained from the slopes and intercepts of plots of $k_f([\text{H}^+] + K_{\text{NH}})$ versus $[\text{H}^+]$ using the values of K_{NH} .

The values of k_1 and k_2 at 20°C are, respectively 2.9×10^4 - and 165-times lower than those of the free pyridine-2-carboxylate ($k_f = 1.0 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, 20°C) (Kowalak *et al* 1969). This difference might arise due to effect of the significant electrostatic repulsion on the outer sphere association constant, K_{OS} , for the diffusion-controlled precursor complex. For example, the value of the outer sphere association constant for (+2) (+1) charge type association, using Fous's equation based on $a = 5 \text{ \AA}$ at 25°C , $I = 0.1 \text{ mol dm}^{-3}$, is found to be $0.07 \text{ dm}^3 \text{ mol}^{-1}$ (Das and Dash 1992). As such still lower values are expected for (+2), (+2) and (+2), (+3) charge type interactions, as in the present case. The values of K_{OS} , 0.05 and $0.005 \text{ dm}^3 \text{ mol}^{-1}$, respectively, for (+2), (+2) and (+2), (+3) charge type association, yield the first-order rate constants, $1.7 \times 10^6 \text{ s}^{-1}$ ($k = k_2/K_{\text{OS}}$) and $1.13 \times 10^5 \text{ s}^{-1}$ ($k' = k_1/K_{\text{OS}}$), respectively. These values are comparable (within a factor of 10) with the water exchange rate constant of $\text{Co}(\text{OH}_2)_6^{2+}$ ($k_{\text{ex}} = (1.1 - 2.4) \times 10^6 \text{ s}^{-1}$ at 25°C (Chmelnick *et al* 1967; Swift and Connick 1962; Hoggard *et al* 1971)). It appears that H_2O dissociation from $\text{Co}(\text{OH}_2)_6^{2+}$ is rate-limiting (I_d mechanism) in the formation of the binuclear species of the title complex. The activation enthalpy and entropy (see table 2)

for the k_2 path are also comparable with those reported for the water exchange reaction of $\text{Co}(\text{OH}_2)_6^{2+}$ $\{\Delta H^\ddagger = 33.6$ to 43.5 kJ mol^{-1} and $\Delta S^\ddagger = -17$ to $+21 \text{ JK}^{-1} \text{ mol}^{-1}\}$ (Margerum *et al* 1978). The slightly higher value of ΔH^\ddagger for the k_1 path is attributed to the involvement of NH-deprotonation in addition to Co-OH₂ dissociation and the relatively higher energy requirement for the corresponding encounter complex formation (+3/+2 charge type association).

3.2 Dissociation of the binuclear complex, $(\text{NH}_3)_5\text{CoO}_2\text{CC}_5\text{H}_4\text{NCo}^{4+}$

The rate data for the acid catalysed dissociation of binuclear complex, $(\text{NH}_3)_5\text{CoO}_2\text{CC}_5\text{H}_4\text{NCo}^{4+}$ in the range of temperature 10–20°C, $[\text{H}^+] = (0.95 - 24.7) \times 10^{-2} \text{ mol dm}^{-3}$ ($I = 0.3 \text{ mol dm}^{-3}$) are shown in table 3. The observed rate constants were corrected by the rate constant for the formation reaction utilising the values of k_1 , k_2 and K_{NH} . The corrected pseudo-first-order rate constants for the dissociation (i.e., $k_r = k_{\text{obs}} - k_f[\text{Co}^{2+}]$) compare satisfactorily with the values of k_r under comparable acidity obtained from the formation study (see table 2). Values of k_r given in table 3 exhibit strong acid-dependence. Hence, the major path of dissociation of Co^{2+} from $(\text{NH}_3)_5\text{CoO}_2\text{CC}_5\text{H}_4\text{NCo}^{4+}$ is the acid-catalysed path (i.e., the k_{-1} path). Evidence of protonation of the binuclear species in related systems (Dash and Nanda 1973, 1974), even at high acid concentrations ($[\text{H}^+] \leq 1.0 \text{ mol dm}^{-3}$), is lacking. The observed acid dependence, therefore, can be reconciled with the participation of both the protonated and deprotonated forms of the cobalt(III) substrate in the formation of binuclear species; thus supporting the proposed mechanism (scheme 1).

The intercepts and slopes of the linear plots (see figure 2) of k_r vs $[\text{H}^+]$ yield the rate constants for the spontaneous dissociation (k_{-2}) and acid-catalysed dissociation (k_{-1}) of the binuclear species, respectively. A rate comparison for the spontaneous

Table 3. Rate data for the dissociation of the binuclear complex between cobalt(II) and pyridine-2-carboxylato(pentaammine)cobalt(III)^a.

$10^2[\text{H}^+]$ (mol dm^{-3})	10.0 ± 0.1°		15.0 ± 0.1°		20.0 ± 0.1°		25.0 ± 0.1°C	
	k_{obs} (s^{-1})	k_r^b (s^{-1})	k_{obs} (s^{-1})	k_r^b (s^{-1})	k_{obs} (s^{-1})	k_r^b (s^{-1})	k_{obs} (s^{-1})	k_r^b (s^{-1})
0.95	16.1 ± 0.5	11.1	25.3 ± 2.0	16.0	36.5 ± 0.8	21.0	56.6 ± 1.0	31.2
1.90	17.3 ± 0.5	14.0	26.3 ± 1.2	19.1	36.1 ± 1.6	25.0	54.5 ± 1.4	36.1
2.85	19.8 ± 0.6	17.1	27.7 ± 1.0	21.2	38.6 ± 1.5	28.9	57.5 ± 1.8	41.7
3.80	21.5 ± 0.7	19.1	—	—	40.9 ± 2.2	32.0	61.0 ± 2.1	46.2
5.71	26.1 ± 1.0	24.0	34.3 ± 2.8	28.6	49.1 ± 2.1	40.9	69.9 ± 3.1	56.3
7.62	30.2 ± 0.7	28.2	41.6 ± 2.7	36.1	56.2 ± 2.2	48.4	78.1 ± 3.8	65.0
9.50	36.0 ± 0.7	34.1	46.5 ± 2.5	41.1	62.2 ± 3.0	54.6	87.4 ± 3.3	74.7
15.20	46.8 ± 1.1	45.0	63.2 ± 2.0	57.9	82.8 ± 2.6	75.5	113 ± 6.2	101
20.00	60.7 ± 2.5	59.0	77.2 ± 4.5	72.0	101 ± 4.2	94.0	140 ± 6.2	128
24.70	72.7 ± 3.8	71.0	88.1 ± 4.0	83.1	120 ± 6.6	112.5	164 ± 5.0	152
k_{-1} (dm^3 $\text{mol}^{-1} \text{s}^{-1}$)	247 ± 4		288 ± 4		377 ± 5		504 ± 5	
k_{-2} (s^{-1})	9.50 ± 0.45		13.4 ± 0.5		19.3 ± 0.3		26.7 ± 0.5	
ΔH^\ddagger (kJ mol^{-1})	= 32.7 ± 3.2 ^c ; 46.2 ± 1.0 ^d							
ΔS^\ddagger ($\text{JK}^{-1} \text{mol}^{-1}$)	= -83.6 ± 11.2 ^c ; -62.8 ± 2.3 ^d							

^a $[\text{complex}]_T = 2.0 \times 10^{-3}$, $[\text{Co}^{2+}]_T = 0.020$ and $I = 0.30 \text{ mol dm}^{-3}$; ^b $k_r = k_{\text{obs}} - \{(k_1[\text{H}^+] + k_2K_{\text{NH}})/([\text{H}^+] + K_{\text{NH}})\}[\text{Co}^{2+}]$; results evaluated from dependence of temperature on k_{-1} ^c and k_{-2} ^d, respectively.

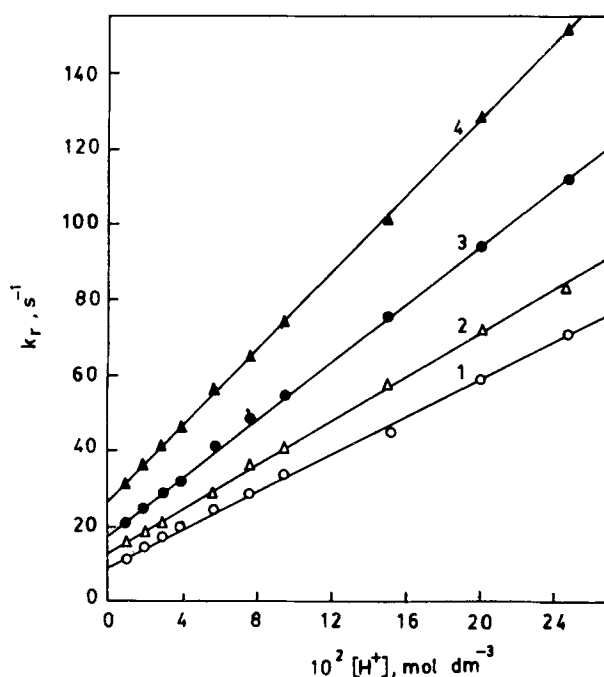


Figure 2. Plots for k_r versus $[H^+]$ (1–4 at temperature = 10, 15, 20 and 25°C, respectively).

dissociation path (k_{-2}) shows that the binuclear species, $(\text{NH}_3)_5\text{CoCC}_5\text{H}_4\text{NCo}^{4+}$, is kinetically ~ 19 and 57 times more stable than mono (imidazole)-cobalt(II) (507 s^{-1} at 25°C) (Steinfeld and Hammes 1962) and mono(ammino)cobalt(II) (1100 s^{-1} at 20°) (Rorabacher 1966), respectively. Its thermodynamic stability is, however, comparable to that of mono(pyridine-2-carboxylato)cobalt(II) (20 s^{-1} at 20°C) (Kowalak *et al* 1969) despite the fact that interionic repulsion between the two positively charged centres, Co(III) and Co(II), of the binuclear species under consideration act in favour of dissociation. This is contrary to the expectation that the Co^{2+} is bound to the pyridine-2-carboxylato moiety through the pyridine-N in unidentate fashion. Hence, it is quite likely that the binuclear species exists in equilibrium with the monobonded \rightleftharpoons chelate form and the equilibrium is favourably displaced towards the chelate form. The activation enthalpy and entropy for the dissociation of the binuclear species are also shown in table 3. The large negative value of ΔS^\ddagger is indicative of the higher degree of solvation of the transition state as compared to the initial state and is in keeping with the dissociative mechanism when the solvated ion (Co^{2+}) is displaced from the binuclear complex.

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