

Kinetics and mechanism of complex formation between (histidinato)-pentaamminecobalt(III) and Ni(II) in aqueous medium

Anadi C Dash*, Rabindra K Nanda & Rita Das

Department of Chemistry, Utkal University, Bhubaneswar 751 004, India

Received 20 June 1991; accepted 30 August 1991

The kinetics of reversible formation of binuclear complex between histidinatopentaamminecobalt(III) and Ni(II) has been investigated at 20-40°C, $I = 0.3 \text{ mol dm}^{-3}$, $[\text{Ni(II)}] = 0.01\text{-}0.05 \text{ mol dm}^{-3}$ and $p\text{H} = 5.65$ to 6.84. The formation of the binuclear species occurs via $[\text{H}^+]$ independent and $[\text{H}^+]^{-1}$ dependent paths, the latter arising out of protonation preequilibrium of the pendant amine function of the histidine moiety bound to cobalt(III) by the carboxylate group. The dissociation of the binuclear species is $p\text{H}$ independent in the range studied. The rate and activation parameters for the formation and dissociation of the binuclear species are reported. The rate limiting step in the formation of the binuclear species is the rate of water dissociation from $\text{Ni}(\text{OH}_2)_6^{2+}$. The results are consistent with chelation of Ni(II) by the tertiary nitrogen and primary amine group of histidine moiety.

The kinetics of reversible complex formation between cobalt(III) complex of the type $(\text{NH}_3)_5\text{CoL}^{n+}$ (where $L = \text{oxalate}^1, \text{picolinate}^2$) and Ni^{2+} have been reported. The kinetics and equilibria of complex formation between Ni(II) and N-methylimidazole, 3-methylhistidine and histidine have been studied by Letter and Jordan^{3,4}, who reported that only the neutral form of 3-methylhistidine and neutral form of histidine react with Ni(II). The limited number of studies on the binuclear complexes stated above prompted us to undertake a study of the title reaction, which involves interaction between multiply charged species of the same charge type. It was hoped that the present study would shed light on the importance of the electrostatic interaction effects on the kinetics and mechanism of the formation and dissociation of the binuclear complex of Ni(II) with histidinatopentaamminecobalt(III).

Materials and Methods

The histidinatopentaamminecobalt(III) perchlorate $[(\text{NH}_3)_5\text{CoLH}_2](\text{ClO}_4)_4$, ($L = \text{histidinate}$) was prepared by the method of Hawkins *et al.*⁵. The purity of the sample was checked by analysis of cobalt and UV-visible spectral data, λ_{max} , nm (ϵ , $\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$): 344(81.6), 500(68.4); literature values λ_{max} , nm (ϵ , $\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$): 350(53.8), 501(66.9)⁵.

Solution of Ni(II) chloride (BDH) was prepared and was estimated for Ni^{2+} by complexometric titration using Na_2EDTA^6 . Lutidine and perchloric acid (both AR grade) were used for adjusting $p\text{H}$. Ionic strength was adjusted using sodium perchlor-

ate prepared from sodium carbonate (AR) and HClO_4 (AR). Solutions were prepared from doubly distilled water, the second distillation being made from alkaline KMnO_4 in an all glass distillation still.

The $p\text{H}$ measurements were made by a digital $p\text{H}$ meter, Elico model LI 120, equipped with a combination electrode model CL 51. The $p\text{H}$ meter was standardised against NBS buffers of $p\text{H} = 4.01, 6.86$ and 9.20. The $p\text{H}$ titration of the complex showed two neutralisation points indicating the doubly protonated form of the complex, $(\text{NH}_3)_5\text{Co}(\text{HistH}_2)^{4+}$ (I). A JASCO model 7800 UV-visible spectrophotometer was used to record the spectra.

Kinetics

The kinetics of complexation with Ni(II) was investigated in the temperature range 20-40°C and $I = 0.3 \text{ mol dm}^{-3}$ (NaClO_4). The rate measurement was made at 310 nm using a fully automated HI-TECH (U.K.) SF 51 stopped flow spectrophotometer interfaced by an Apple II GS computer. The reservoir syringes, the flow system and the reaction chamber were thermostated to the desired temperature by circulating water from the thermostatic bath C-85D through the cooler FC 200. The other experimental details were the same as mentioned earlier². The observed pseudo-first order rate constants were calculated by a computer program⁷, which made a least squares fit of absorbance-time data (displayed as voltage output as a function of time) to a single exponential curve applicable for the first order kinetics. The rate data are collected in

Table 1—Rate data for complexation of $[(\text{NH}_3)_5\text{CoLH}_2]^{4+}$ with Ni(II)^a , where L = histidinate

$[\text{Ni(II)}]_{\text{T}}$ (mol dm^{-3})	k_{obs} (s^{-1}) at				
	pH =	20.0 \pm 0.1°C			
		6.78 \pm 0.03	6.60 \pm 0.03	6.14 \pm 0.03	5.68 \pm 0.02
0.01		2.52 \pm 0.20	2.23 \pm 0.04	1.96 \pm 0.07	1.66 \pm 0.05
0.015		3.22 \pm 0.25	3.14 \pm 0.08	2.56 \pm 0.12	2.18 \pm 0.10
0.02		4.12 \pm 0.34	3.94 \pm 0.15	3.18 \pm 0.13	2.65 \pm 0.11
0.03		6.15 \pm 0.12	5.55 \pm 0.14	4.41 \pm 0.08	3.84 \pm 0.08
0.04		8.01 \pm 0.31	7.43 \pm 0.14	5.56 \pm 0.11	4.83 \pm 0.19
0.05		9.90 \pm 0.51	8.77 \pm 0.16	6.95 \pm 0.02	5.85 \pm 0.04
k_{f} ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$)		185.9 \pm 3.7	167.3 \pm 2.8	125.2 \pm 0.5	104.8 \pm 0.9
k_{r} (s^{-1})		0.56 \pm 0.10	0.57 \pm 0.05	0.69 \pm 0.02	0.62 \pm 0.03
		25.0 \pm 0.1°C			
	pH =	6.80 \pm 0.03	6.52 \pm 0.03	6.06 \pm 0.03	5.65 \pm 0.03
0.01		3.15 \pm 0.15	2.63 \pm 0.04	2.21 \pm 0.04	2.02 \pm 0.03
0.015		4.36 \pm 0.12	3.48 \pm 0.07	2.98 \pm 0.05	2.60 \pm 0.04
0.02		5.53 \pm 0.15	4.50 \pm 0.08	3.60 \pm 0.06	3.19 \pm 0.06
0.03		8.11 \pm 0.09	6.35 \pm 0.15	5.01 \pm 0.10	4.33 \pm 0.07
0.04		10.34 \pm 0.15	8.25 \pm 0.08	6.39 \pm 0.27	5.55 \pm 0.09
0.05		12.70 \pm 0.15	10.17 \pm 0.13	7.72 \pm 0.12	6.71 \pm 0.24
k_{f} ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$)		240.0 \pm 3.3	188.0 \pm 1.4	138.0 \pm 1.8	116.9 \pm 0.6
k_{r} (s^{-1})		0.80 \pm 0.09	0.73 \pm 0.03	0.86 \pm 0.04	0.85 \pm 0.01
		30.0 \pm 0.1°C			
	pH =	6.84 \pm 0.03	6.65 \pm 0.02	6.08 \pm 0.03	5.84 \pm 0.02
0.01		5.25 \pm 0.14	4.71 \pm 0.15	3.61 \pm 0.13	3.25 \pm 0.06
0.015		7.51 \pm 0.23	6.57 \pm 0.15	4.85 \pm 0.12	4.55 \pm 0.12
0.02		9.81 \pm 0.24	8.31 \pm 0.37	6.15 \pm 0.13	5.75 \pm 0.15
0.03		14.23 \pm 0.21	11.75 \pm 0.53	8.63 \pm 0.15	8.15 \pm 0.23
0.04		18.31 \pm 0.35	15.31 \pm 0.29	11.17 \pm 0.09	10.51 \pm 0.11
0.05		—	—	13.78 \pm 0.15	12.81 \pm 0.12
k_{f} ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$)		442.3 \pm 5.4	352.7 \pm 2.9	253.3 \pm 1.0	239.8 \pm 1.6
k_{r} (s^{-1})		0.87 \pm 0.11	1.23 \pm 0.06	1.06 \pm 0.03	0.88 \pm 0.04
		40.0 \pm 0.1°C			
	pH =	6.84 \pm 0.02	6.65 \pm 0.02	6.08 \pm 0.03	5.84 \pm 0.02
0.01		10.97 \pm 0.39	9.08 \pm 0.44	7.81 \pm 0.20	7.18 \pm 0.07
0.015		15.09 \pm 0.54	13.14 \pm 0.45	10.65 \pm 0.35	9.73 \pm 0.28
0.02		19.12 \pm 0.84	17.09 \pm 0.49	13.65 \pm 0.42	11.53 \pm 0.54
0.03		28.22 \pm 1.61	23.82 \pm 0.87	18.24 \pm 0.52	16.45 \pm 0.40
0.04		36.76 \pm 1.36	30.97 \pm 0.94	24.09 \pm 0.43	21.83 \pm 0.21
0.05		45.25 \pm 1.76	38.43 \pm 0.38	29.52 \pm 1.38	26.64 \pm 1.30
k_{f} ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$)		856.2 \pm 8.0	726.6 \pm 7.5	539.7 \pm 8.8	485.4 \pm 5.4
k_{r} (s^{-1})		2.33 \pm 0.14	2.13 \pm 0.24	2.47 \pm 0.18	2.32 \pm 0.09

a) $[\text{complex}]_{\text{T}} = 2.0 \times 10^{-3}$, $I = 0.3 \text{ mol dm}^{-3}$, $\lambda = 310 \text{ nm}$.

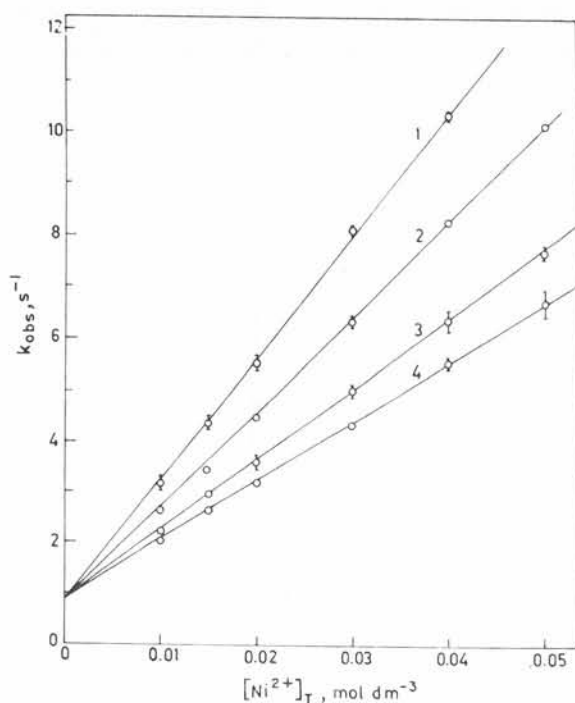


Fig. 1— k_{obs} (s^{-1}) versus $[\text{Ni}^{2+}]_{\text{T}}$ plot at 25°C ($\text{pH} = 6.80 \pm 0.03$ (1), 6.52 ± 0.03 (2), 6.06 ± 0.03 (3), 5.65 ± 0.03 (4))

Table 1. Each value of k_{obs} reported is the mean from at least seven determinations and its error quoted is the standard deviation.

Results and Discussion

The observed pseudo-first order rate constants presented in Table 1 satisfy Eq. (1),

$$k_{\text{obs}} = a[\text{Ni}^{2+}]_{\text{T}} + b \quad \dots (1)$$

at a given acidity. The k_{obs} versus $[\text{Ni}^{2+}]_{\text{T}}$ plots at different acidities were linear, gradients of which decreased with decreasing pH (Fig. 1). Noteworthy is the fact that the intercept ($=b$) of such plots which is ascribed to the dissociation rate constant of the product binuclear complex, is acid-independent indicating that H^+ does not participate in the rate limiting step for the dissociation of Ni^{2+} from the binuclear species, $(\text{NH}_3)_5\text{CoLNi}^{4+}$. The $[\text{H}^+]$ dependence of the slope ($=a$) of such plots must arise due to the protonation pre-equilibrium of the cobalt(III) complex. However, a general scheme consistent with the observed rate data for the formation/dissociation of the binuclear complex may be delineated as in Scheme 1, for which k_{obs} takes the form,

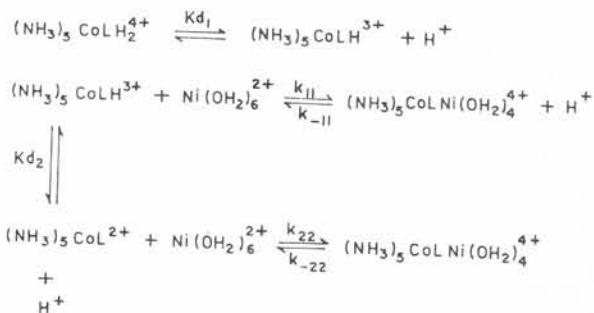
$$k_{\text{obs}} = k_{\text{f}}[\text{Ni}^{2+}]_{\text{T}} + k_{\text{r}} \quad \dots (2)$$

where

$$k_{\text{f}} = \frac{k_{11} + (k_{22} K_{\text{d}_2})/[\text{H}^+]}{(1 + [\text{H}^+]/K_{\text{d}_1} + K_{\text{d}_2}/[\text{H}^+])} \quad \dots (3)$$

Table 2—Calculated rate and activation parameters for the complexation of $[(\text{NH}_3)_5\text{CoLH}_2]^{4+}$ with $\text{Ni}(\text{II})$

Temp. ($\pm 0.1^\circ\text{C}$)	$10^7 k_{22}$ K_{d_2} (s^{-1})	k_{11} (dm^3 $\text{mol}^{-1} \text{s}^{-1}$)	k_{-22} (s^{-1})
20.0	166.3 ± 24.6	100.6 ± 3.8	0.61 ± 0.05
25.0	231.7 ± 15.6	107.2 ± 2.6	0.81 ± 0.05
30.0	312.3 ± 12.5	216.4 ± 2.4	1.01 ± 0.15
40.0	598.5 ± 29.9	452.0 ± 11.2	2.31 ± 0.12
ΔH^\ddagger (kJ mol^{-1})		62.9 ± 11.5	49.8 ± 2.9
ΔS^\ddagger ($\text{JK}^{-1} \text{mol}^{-1}$)		6.6 ± 37.9	-79.5 ± 9.6



(L = Histidinate)
SCHEME-1

and

$$k_{\text{r}} = k_{-11}[\text{H}^+] + k_{-22} \quad \dots (4)$$

The values of $\text{p}K_{\text{d}_1}$ and $\text{p}K_{\text{d}_2}$ reported earlier⁵ are 4.6 ± 0.005 and 7.9 ± 0.01 at 20°C . Hence the denominator of Eq. (3) will essentially reduce to 1 in the pH range 5.65–6.84, so that Eq. (3) reduces to Eq. (5). Also Eq. (4) reduces to Eq. (6), as k_{r} is independent of pH in the range studied (i.e. $k_{-11}[\text{H}^+] \ll k_{-22}$).

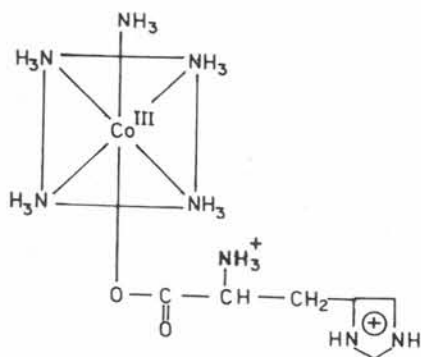
$$k_{\text{f}} = k_{11} + (k_{22} K_{\text{d}_2})/[\text{H}^+] \quad \dots (5)$$

$$k_{\text{r}} = k_{-22} \quad \dots (6)$$

Values of k_{11} and $k_{22} K_{\text{d}_2}$ calculated from the slopes of k_{f} versus $1/[\text{H}^+]$ plots are given in Table 2, along with the values of k_{-22} . The activation parameter data based on the temperature dependence of k_{11} and k_{-22} are also given in Table 2.

It is of interest to note that the dissociation rate constant of the binuclear species is pH -independent. Similar observation was made in the study of the acid catalysed dissociation of the binuclear complex of Ni^{2+} with picolinatopentaamminecobalt(III)². This suggests that both the nitrogen centres in histidinatopentaamminecobalt(III), susceptible to protonation, are used up in binding Ni^{2+} . Furthermore, the

small values of the dissociation rate constant, despite the expected appreciable electrostatic repulsion between the like charge centres ($2+/2+$) suggests that Ni^{2+} is chelated in the binuclear complex by the tertiary N- of imidazole and the primary amine function in the alkyl side chain (see Structure I). Substantial entropy loss in the dissociation of the binuclear complex to $\text{Ni}(\text{OH}_2)_6^{2+}$ and the cobalt(III) substrate, as reflected in the large negative value of ΔS^\ddagger for the process, is in keeping with the expect-



(I)

ed solvation demands at least at Ni^{2+} centre when it parts with the chelating ligand moiety. The activation enthalpy for the dissociation reaction is also substantial (see Table 2), which suggests that the Ni-N bond dissociation might be rate controlling⁸.

At 25°C the values of k_{22} turns out to be $1.84 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, which is 17 times higher than that of k_{11} . Since k_{11} and k_{22} paths involve species $(\text{NH}_3)_5\text{CoLH}^{3+}$ and $(\text{NH}_3)_5\text{CoL}^{2+}$ respectively the observed order of reactivity is consistent with the rate influencing effect of the electrostatic repulsion between Ni^{2+} and the cobalt(III) substrate which acts against the precursor encounter complex formation between the reactants. This is also further

clarified when we compare the values of k_{11} and k_{22} with the rate constants for the reaction of $\text{Ni}(\text{OH}_2)_6^{2+}$ with histidine (neutral form) ($k = 2.2 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$), mono cation of histidine methyl ester ($k = 6.0 \times 10^2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$), and neutral histidine methyl ester ($k = 2.6 \times 10^3 \text{ mol}^{-1} \text{ s}^{-1}$) (at 23.7°C, $I = 0.1 \text{ mol dm}^{-3} (\text{KNO}_3)^3$). The rate and activation parameters for the water exchange reaction of $\text{Ni}(\text{OH}_2)_6^{2+}$ are $k_{\text{ex}} (25^\circ\text{C}) \approx 3 \times 10^4 \text{ s}^{-1}$, $\Delta H^\ddagger = 45$ to 51 kJ mol^{-1} and $\Delta S^\ddagger = +2.5$ to $+15 \text{ JK}^{-1}$ (refs 9, 10). The activation enthalpy and entropy data for the k_{11} path suggest that water dissociation from Ni^{2+} centre of the encounter complex is rate limiting in the formation of the binuclear species.

Acknowledgement

Our thanks are due to the Department of Science and Technology, Govt. of India for generous funding to purchase stopped flow spectrophotometer and JASCO UV-visible spectrophotometer. R D is thankful for award of a junior research fellowship.

References

- 1 Dash A C, Nanda R K & Acharya A, *Indian J Chem*, 30A (1991) 769.
- 2 Dash A C, Nanda R K & Das N (unpublished results).
- 3 Letter J E (Jr) & Jordan R B, *Inorg Chem*, 10 (1971) 2692.
- 4 Letter J E (Jr) & Jordan R B, *Inorg Chem*, 13 (1974) 1152.
- 5 Hawkins C J & Lawson P J, *Inorg Chem*, 9 (1970) 6.
- 6 Vogel A I, *A text book of quantitative inorganic analysis* (ELBS and Longmans Green, London) (1962) 435.
- 7 The computer program was made available to us by M/S HI-TECH SCIENTIFIC LTD, Brunel Road, Salisbury, England SP2 7PU, UK.
- 8 Margerum D W, Caley G R, Weatherburn D C & Pagenkopf G K, in *Coordination chemistry*, ACS MONOGRAPH 174, edited by A E Martell (Plenum, New York) (1978) vol. 2.
- 9 Swift J J & Connick R E, *J chem Phys*, 37 (1962) 307.
- 10 Ref. 8, pp-5.